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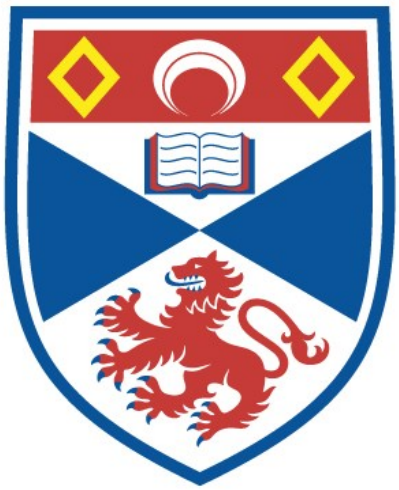

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SYNTHETIC APPLICATIONS OF FLASH VACUUM PYROLYSIS OVER MAGNESIUM

by

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Thesis presented for the degree of

DOCTOR OF PHILOSOPHY

University of St Andrews September 1990

Dedication

To mummy

Declaration

I Adebayo Ojo Oyewale hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any other degree of professional qualification.

Signed Date 16th Sept. 1990

I was admitted to the Faculty of Science of the University of St. Andrews under Ordinance General No. 12 on October 1st 1987 and as a candidate for the degree of Ph.D. on October 1st 1988.

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Lecture Courses

The following is a statement of the courses attended during the period of research; Organic Research Seminars (3 years attendance); Industrial Organic Chemistry (8 lectures) and Fatty Acids and Lipids (2 days), Professor F.D. Gunstone; Asymmetric Synthesis(8 lectures), Naturally Occuring Organo-sulphur Compounds (3 lectures) and Heavy-atom Multiply Bonded Compounds (3 lectures), all Dr R.A. Aitken; Free Radical Chemistry(8 lectures), Dr J.C. Walton; Homogeneous Catalysis (8 lectures) and Semi-conductor Growth Technology (3 lectures), Professor D.J. Cole-Hamilton; Materials Science(3 days), ICI Research ; Pharmaceutical Chemistry(8 lectures), Dr A.R. Butler and Dr R.A. Aitken; NMR Spectroscopy (8 lectures) and Advanced NMR Spectroscopy (3 lectures), Dr R.K. Mackie; Alicyclic Chemistry(8 lectures), Dr F.G. Riddell; and Naphthalenes, Anthracenes and Other Polycyclic Compounds(3 lectures), Dr D.M.G. Lloyd.

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Finally, thanks are also due to B.P. International for the financial support.

ABSTRACT

The thermal reaction over activated magnesium of some 120 organic substrates has been investigated under flash vacuum pyrolysis(FVP) conditions. The activation was achieved by freshly resublimed Grignard grade magnesium onto glass wool at 700°C under vacuum. Magnesium prepared in this form showed an effective dehalogenating activity on a wide range of organic halides. FVP of simple aliphatic halides like 2-chloro-2,3-dimethylbutane and 2,3-dichloro-2,3-dimethylbutane, resulted in dehydrohalogenation to give the corresponding monoenes and dienes. The dehydrobromination of neopentyl bromide over magnesium gave a mixture of 2-methyl-2-butene and 2-methyl-1-butene, a product mixture that cannot be accounted for by either radical or carbene chemistry.

A similar process was observed with terminal dihalides to give dienes, however with increased chain length a dehalogenation process involving hydrogen transfer predominates to give monoenes. The debromination of 1,3-dibromopropane over magnesium led to cyclopropane. Dehydrohalogenation was similarly observed with cyclic dihalides, haloalkenes and haloalkynes and for substrates of adequate chain length, dehalogenation of the haloalkenes or haloalkynes was followed by cyclisation on to the unsaturated end of the molecule to give cyclic products. Germinal dihalides underwent dehalogenative homocoupling to give symmetrical dienes except for 1,1-dichloropropane and 2,2-dichloropropane where simple dehydrochlorination was observed to give the chloroalkenes.

FVP of benzylic- and benzylidene- halides over magnesium led to dehalogenative homocoupling to give bibenzyls and stilbenes respectively. Various substituted bibenzyls and stilbenes were prepared in moderate to high yields. The amount of magnesium surface available for reaction and

a comparative study of the thermal reaction of zinc, calcium and magnesium with benzyl chloride was carried out. On pyrolysis of *o*-halobenzyl halides and *o*-halobenzylidene halides in the presence of excess magnesium, the loss of both side chain and ring halogens led to coupling and cyclisation to 9,10-dihydrophenanthrene and phenanthrene respectively. The ease of ring dehalogenation decreases from iodine to bromine and chlorine, with fluorine virtually unreactive. Attempts to prepare symmetrical disubstituted phenanthrenes from substituted *o* -halobenzylidene chlorides met with only limited success. Under the pyrolytic conditions, benzotrichloride was converted to α,α'-dichlorostilbene, α,α,α',α'-tetrachlorobibenzyl and diphenylacetylene, the yield of the last two products being dependent on the reaction conditions.

The thermal dehalogenation of α,α'-dihalo-*o*-xylenes over magnesium gave benzocyclobutene. The same process afforded fluorinated benzocyclobutenes and benzodicyclobutene in good yields. The debromination of α,α,α',α'-tetrabromo-*m*-xylene over magnesium led to pyrene.

For haloalkylbenzenes, the basic reaction on pyrolysis over magnesium was dehydrohalogenation to arylalkenes, but this was sometimes accompanied by bond isomerisation and rearrangement. In the case of 1-chloro-4-phenylbutane, an additional process of cyclisation on to the phenyl ring to give tetrahydronaphthalene was observed. The thermal reaction of 3-chloropropiophenone and 2-bromoacetophenone over magnesium led not only to dehalogenation products but also to deoxygenated products. 2-Bromoethyl phenyl ether mainly underwent dehalogenation and fragmentation to phenol.

The dehalogenation of chlorobenzene and 1,2-dihalobenzenes was also achieved on pyrolysis over magnesium. Although the main product

obtained from the latter was triphenylene, the involvement of benzyne as an intermediate is in doubt.

The dehalogenation of long chain acid chloride over magnesium, was accompanied by fragmentation to give a mixture of alkenes and alkanes.

The magnesium-induced 1,6-dehalogenation of α,α'-halogenated *p*-xylenes in the gas phase led to *p*-xylylenes, which polymerised. α,α'-Dichloro-*p*-xylene gave poly(*p*-xylylene) and poly(α-chloro-*p*-xylyene); while α,α,α',α'-tetrachloro-*p*-xylene and α,α,α',α'-tetrabromo-*p*-xylene gave poly(α,α'-dichloro-*p*-xylylene) and poly(α,α'-dibromo-*p*-xylyene) respectively. Also prepared were poly(α,α,α',α'-tetrachloro-*p*-xylylene) and poly(α,α,α',α'-tetrafluoro-*p*-xylylene) from the corresponding hexahalo-*p*-xylene. Thermal stability measurements and the solid state ^{13}C NMR, including molecular weight estimation were carried out on the polymers.

Some of the processes observed with aryl compounds on pyrolysis over magnesium were extented to halogenated thiophene compounds, especially for the preparation of 1,2-dithienylethenes and derivatives. Attempts to prepare benzodithiophenes from halo-dichloromethyl-thiophenes gave halogenated products and isomeric benzodithiophenes. The isomeric benzodithiophenes obtained and the likely route to them was investigated. Attempts to generated 2,3-thiophyne by dehalogenation of mono- and di-halothiophenes were inconclusive. The thermal reaction of a series of epoxides in the presence or absence of magnesium was investigated. The main process in the absence of magnesium, was rearrangement to carbonyl compounds, while in the presence of magnesium, deoxygenation and dehydration reactions were observed in addition to the thermal rearrangement.

CONTENTS

EXPERIMENTAL

Page No

INTRODUCTION

A. Pyrolytic extrusion and elimination reactions

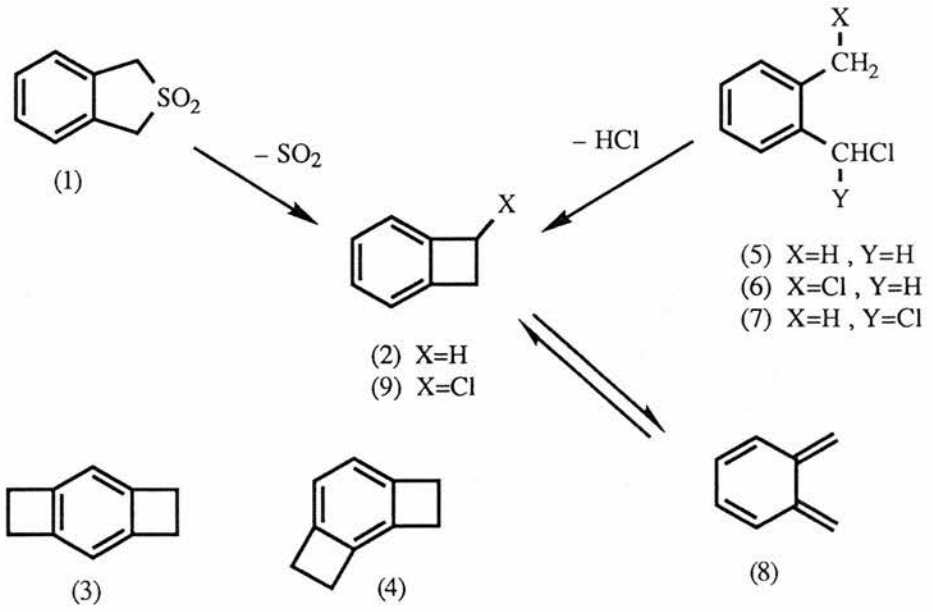
High temperature reactions date back to the beginning of experimental chemistry. To the alchemists and first chemists, destructive distillation of mineral and organic material was one of the few preparative techniques available. Thus fire was a favourite tool of the alchemist and virtually all known materials were subjected to pyrolytic reactions, like dry distillations of wood, bones and oils and this was a major source of new compounds. The large contribution of pyrolytic experiments to the development of organic chemistry was reviewed in a classic monograph "The pyrolysis of carbon compounds" written by Hurd[1] in 1929. This book, reviewed all the pyrolytic processes that had been examined critically at the time, the processes ranging from the decomposition of solids at their melting point to the decomposition of gases at 1100°C.

Traditional pyrolysis reactions usually involve prolonged exposure times at high temperature, and often give rise to low yields or tarry residues, especially when the reaction is carried out in the molten phase. However, over the years subtle techniques have evolved which allow pyrolytic reactions to have a broader range of synthetic application. Thus reactions can be performed conveniently in the gas phase with short contact times at relatively high temperatures and under low-pressure conditions. Brown[2] in a recent monograph reviewed flash vacuum pyrolysis, describing the apparatus and methods available, as well as conditions for effective transformation and maximum yield, devoid of the sledgehammer approach of classical pyrolysis.

However, despite the long history of pyrolysis and the introduction of new techniques, relatively few reactions have become standard procedures in organic synthesis. The most common of these is fragmentation which involves extrusion of very stable small molecules

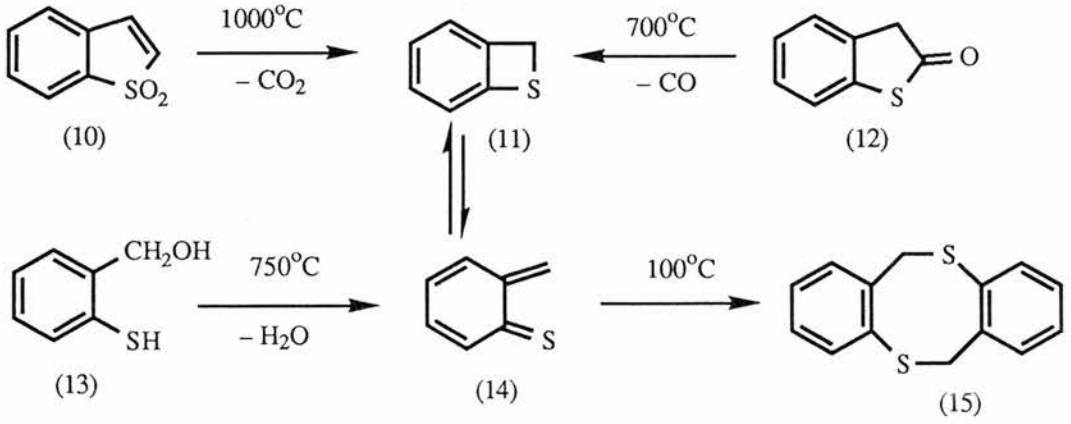
such as nitrogen, carbon monoxide, carbon dioxide, hydrogen halides, sulphur monoxide, sulphur dioxide, ethylene, acetylene, acetone and even elements like sulphur[3], tellurium[4] and arsenic.[5]

The modern technique of flash vacuum pyrolysis, with its unique conditions of low pressure and short contact time, has made possible the synthesis of highly strained small ring systems via extrusion or elimination reactions, which are otherwise inaccessible through other methods. Cava[6] first made benzocyclobutene(**2**) by extruding sulphur dioxide from 1,3-dihydroisothianaphthene-2,2-dioxide(**1**) on pyrolysis over a nichrome wire heated to 770°C. A double version of this approach has been successful in providing the benzodicyclobutenes(**3**)[7] and (**4**)[8]; however the extension of this reaction to the preparation of tricyclobutabenzene has so far been unsuccessful[9]. A more general route to benzocyclobutenes is 1,4-elimination of hydrogen chloride from a-chloro-*o*-xylenes on pyrolysis at 600-700°C; thus 2-methylbenzyl chloride(**5**) gave benzocyclobutene(**2**) in 70% yield on pyrolysis at 630°C[10]. Similarly, 1-chlorobenzocyclobutene(**9**) was prepared from α,α'-dichloro-*o*-xylene(**6**) at 720°C[11] and from 2-methylbenzylidene chloride(**7**) at 700°C[12].

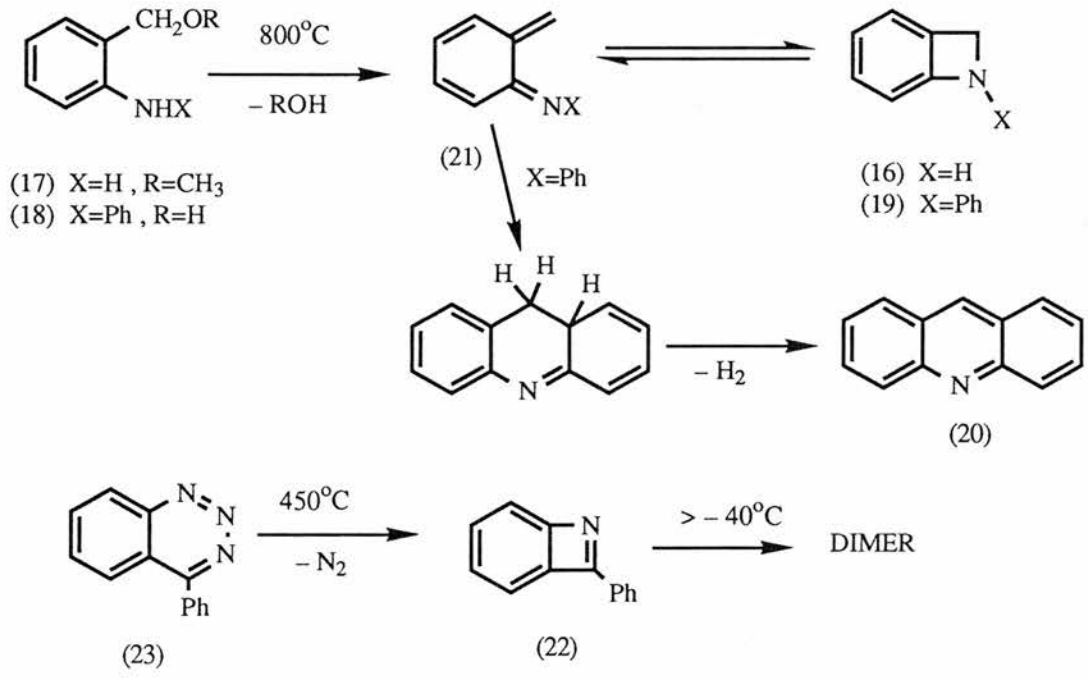


The synthesis of various aryl- substituted benzocyclobutenes[13] has been achieved using this pyrolytic method. Benzocyclobutenes and their analogues open up to their quinonoid[14] form :*o*-xylylenes(**8**), which are highly reactive dienes in Diels-Alder reactions[14]. They are frequently used in natural product synthesis[15] and are key intermediates in the preparation of [2n]-cyclophanes[13,16] pyridinophanes[17] and tropoquinophanes[18].

Unsaturated four-membered heterocycles which are rare, have also been accessed through pyrolytic extrusion reactions. Benzo[b]thiophene-1,1-dioxide(**10**) loses carbon dioxide at 1000°C[19] to give benzothiete(**11**) in 45% yield, and an improved yield of 80% was obtained from benzo[b]thiophene-2(3H)-one(**12**) at 700°C and 0.05mmHg with extrusion of carbon monoxide[20]. Gas phase pyrolysis of 2-hydroxy-methylthiophenol(**13**) at 750°C and 0.01mmHg readily gives (**11**), presumably via the initial loss of water to give *o*-thioquinonemethide(**14**) which, by valence tautomerisation gives (**11**). The valence tautomerisation occurs much more readily with the sulphur analogue (**11**) than in the parent benzocyclobutene(**2**) and this was proved by the easy reaction of benzo[b]thiete(**11**) with boiling cyclohexene to give the Diels-Alder adduct[13], presumably via (**14**). Heating (**11**) in the absence of a dienophile results in dimerisation to (**15**), in close analogy to the behaviour of benzocyclobutene[21].

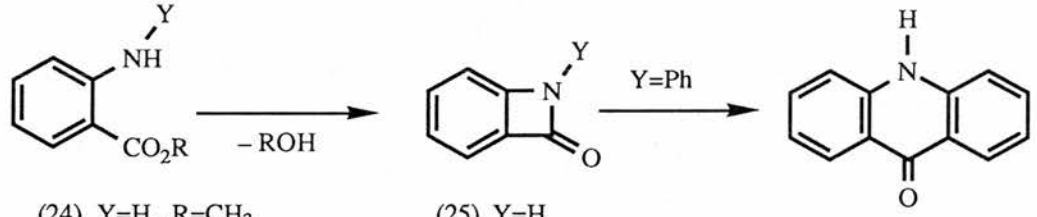


Benzoazetine(**16**) was postulated as a possible intermediate in the pyrolysis of 2-aminobenzyl methyl ether(**17**) at 800°C and 0.03mmHg in a stream of thiophenol[22]. Similar gas phase pyrolysis of N-phenyl-2-(hydroxymethyl)aniline(**18**) failed to give the expected N-phenyl-benzo[b]azetine(**19**); instead acridine(**20**) was the product. Apparently, the intermediate *o*-quinonemethide imine(**21**) undergoes intramolecular cyclisation, followed by an irreversible thermal dehydrogenation to acridine[13]. Rees and coworkers[23] obtained 2-phenylbenzazete(**22**) in about 64% yield by extruding a molecule of nitrogen from 4-phenyl-1,2,3-benzotriazine(**23**) at 450°C and 10^{-3}mmHg. The benzazete was stable up to –40°C but dimerises on warming.



Extrusion reactions have also been employed in the synthesis of lactones, thiolactones and lactams. Thus methylanthranilate (**24**) lost methanol at 800°C to give β-lactam(**25**)[22], while N-phenylanthranilic acid(**26**) lost a molecule of water to give N-phenyl-β-lactam(**27**), which readily undergoes intramolecular cyclisation of the *o*-quinonoid form

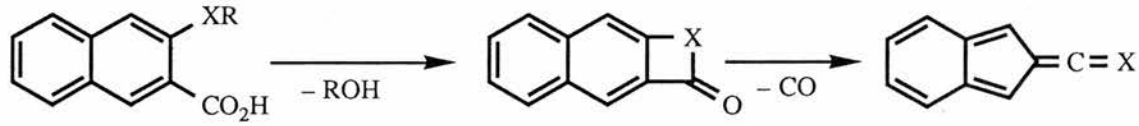
followed by tautomerisation to acridone(**28**)[13]. Due to their instability, benzo-b-thiolactones have been observed only in a low temperature matrix[24] and in the gas phase using photoelectron spectroscopy[25]; however Wentrup *et al*[26] isolated the first stable β-thiolactone, namely naphtho[2,3-b]thiet-2-one(**30**) from the pyrolytic extrusion of water from 3-mercapto-2-naphthoic acid(**29**). They also reported the synthesis of naphtho[2,3-b]azet-2(1H)-one(**32**) from the corresponding amino-carboxylic acid(**31**) and naphtho[2,3-b]oxetone(**34**) from the carboxylic acid-ester(**33**). However, with most of the lactones, thiolactones and lactams, the pyrolysis condition may also cause decarbonylation leading to the formation of compound(**35**).



(24) Y=H , R=CH_3
(26) Y=Ph , R=H

(25) Y=H
(27) Y=Ph

(28)



(29) X=S , R=H
(31) X=NH , R=H
(33) X=O , R=$COCH_3$

(30) X=S
(32) X=NH
(34) X=O

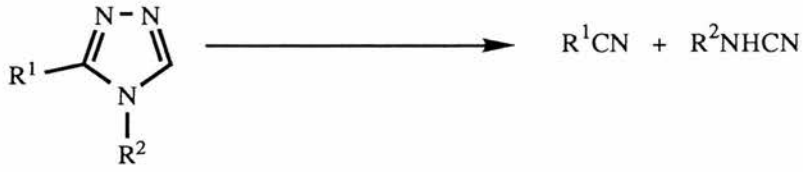
(35)

In extrusion reactions, it can sometimes be difficult to predict which fragment will be lost from a given molecule and in some cases the observed processes for two apparently similar structures are different. For example 1-phenyl-1,2,4-triazoles undergo a 1,5-phenyl shift at high temperatures of 650-800°C and the intermediates then lose nitrogen to give, ultimately, isoindoles. Thus 1,3,5-triphenyl-1,2,4-triazole(**36**) gave 1,3-diphenylisoindole(**37**), the diphenyl-1,2,4-triazole(**38**) gave

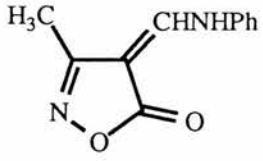
1-phenylisoindole(**39**) and the 1-phenyl compound(**40**) gave isoindole(**41**). However, 3-phenyl-(**42**) and 4-phenyl-1,2,4-triazole(**43**) behaved differently in that nitrogen was not lost as N_2, but products of ring opening and cleavage were formed instead[27]. Wentrup also observed different processes in isoxazolone(**44**) which lost CO_2 and acetonitrile at 650°C[28] while the isomeric oxazolone(**45**) lost only CO to give N-acetylketenimine[28].

(36) $R^1=R^2=R^3=Ph$
(38) $R^1=R^3=Ph$, $R^2=H$
(40) $R^1=Ph$, $R^2=R^3=H$

(37) $R^2=R^3=Ph$
(39) $R^3=Ph$, $R^2=H$
(41) $R^2=R^3=H$



(42) $R^1=H$, $R^2=Ph$
(43) $R^1=Ph$, $R^2=H$



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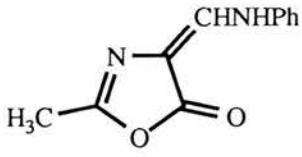

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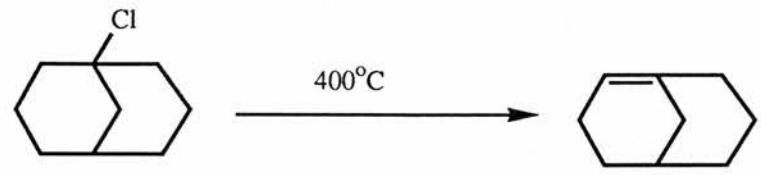
Thermal dehalogenation or dehydrohalogenation, like other extrusion reactions, has been extensively studied since the recognition of pyrolysis as an experimental technique. Hurd[1] in his monograph, reviewed the pyrolysis of various halogen compounds up to the year 1929. This ranges from simple alkyl halides, like methyl chloride and ethyl bromide to dihalogen compounds like ethylene dichloride and dibromopropane. In general, the process observed was simple

dehydrohalogenation to the alkenes, some of which recombine with the eliminated hydrogen halide to give the starting material or its isomer. However for compounds containing three or more halogens, thermal dehalogenation or dehydrohalogenation often led to the formation of unsaturated coupled compounds. Thus both carbon tetrachloride and chloroform gave tetrachloroethylene as the main product on pyrolysis at between 1000-1400°C. Similar processes occur with aromatic compounds, those with halogen in the side chain and with adjacent hydrogen, readily lose HX to give the alkene, while compounds like benzyl- or benzal chloride undergo dehalogenative coupling to stilbenes when passed over a red hot wire. Alicyclic halogen derivatives simply eliminate HX to give cyclic alkenes; thus *cis*-1,2-dibromocyclohexene gave cyclohexadiene while dihydronapthalene was prepared from β-chlorotetralin.

Subsequent interest in β-elimination of hydrogen halides from organic halides has been kinetic rather than preparative in nature. Academic interest in the pyrolysis of alkyl halides was kindled in 1949 by a series of papers by Barton *et al*[29] and who based on their studies proposed a radical chain processes for alkyl halide decomposition in the gas phase. Apart from the kinetic studies, the synthetic potential of thermal dehalogenation or dehydrohalogenation has been used in the preparation of important products, especially cyclophanes[13,16,17,18] and benzocyclobutenes, which are a source of *o*-xylylenes important intermediates in natural product[15] and carbohydrate synthesis[30]. It has also been applied in the generation of reactive intermediates, cyclisation and coupling reactions as well as in the synthesis of highly strained molecules, like the *anti*-Bredt alkenes (**46**), and (**47**) or (**48**).[31] Short reviews are presented in the following sections on various methods of effecting dehalogenation thermally and in solution.



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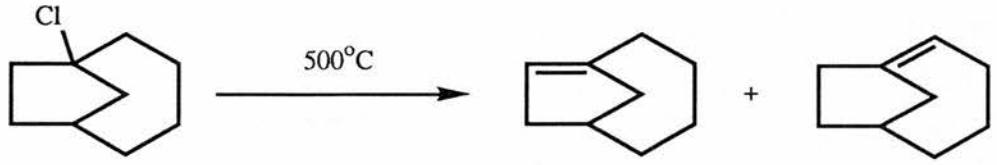

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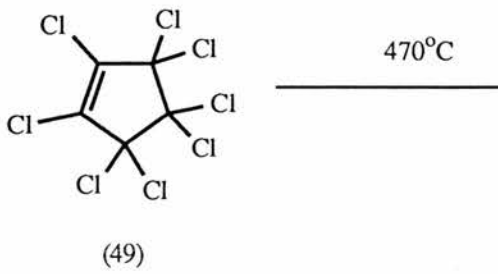
B. Thermal reaction of halocompounds

1. Simple thermal dehalogenation

(a) Perhalogenated compounds

Since the classical pyrolysis of various halogenated compounds reviewed by Hurd[1] in his monograph, there has been a growing interest in exploring the synthetic potential of thermal dehalogenation. Thus in the late forties and early fifties, series of papers were published on the pyrolysis of perhalogenated compounds. Krynitsky *et al*[33] found that both tetrachloroethylene and hexachloro-1,3-butadiene were stable up to 550°C, whereas hexachloropropene and octachloro-1,3-pentadienes fragment at 400-500°C to give mixtures of carbon tetrachloride, tetrachloroethylene, hexachloroethane and other chlorinated compounds. Roedig[34] observed that some perchlorinated alkanes or alkenes fragment on distillation at temperatures of between 200-280°C; thus perchlorobutane disproportionates to hexachloroethane and tetrachloroethylene, while perchlorobut-1-ene gave only tetrachloroethylene. However 1H-nonachlorobutane lost a molecule of HCl in addition to fragmentation to give tetrachloroethylene. Although these processes were of little synthetic value, owing to the mixture of products obtained, kinetic aspects of the reactions were fully studied.

Perchlorocyclopentene(**49**) readily lost a molecule of chlorine on pyrolysis at 470°C in a stream of carbon tetrachloride, to give (**50**)[35] and the perchlorofulvalene(**52**) was prepared by thermal dechlorination of (**51**)[36]. Beck *et al*[37] observed aromatic ring participation in the intermediate formed when 2,3,4,5,6,7,8-heptachloro-1-naphthyl isocyanide dichloride(**53**) was dechlorinated at 400°C to produce perchloro-5-azaacenaphthylene(**54**) in good yield. This illustrates the use of thermal dehalogenation in aromatisation and cyclisation reactions.



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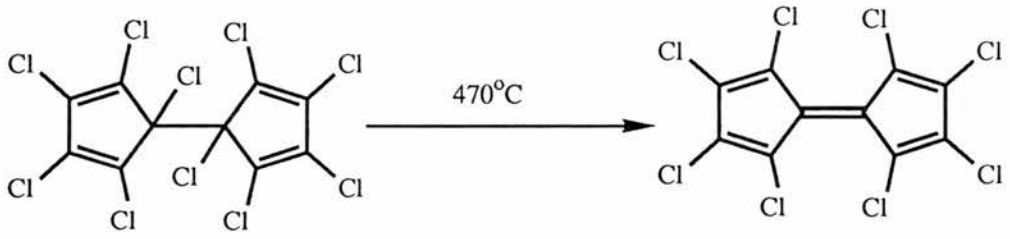

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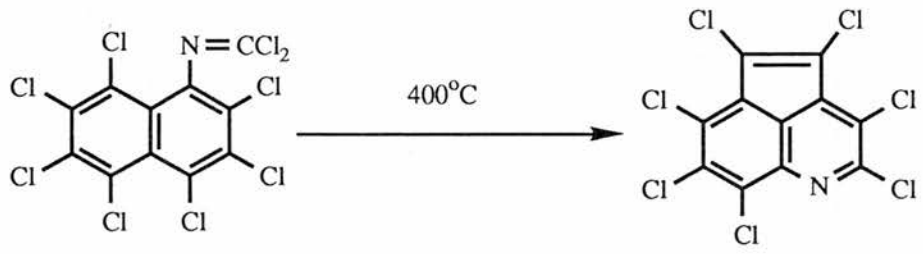

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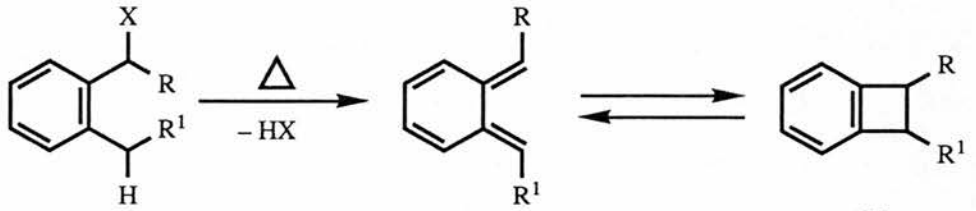
(b) Formation of benzocyclobutenes

The thermal β-elimination of hydrogen halides from organohalogen compounds usually occurs with low regio- and stereo-selectivity and is therefore of minor synthetic use[32]. An exception is the

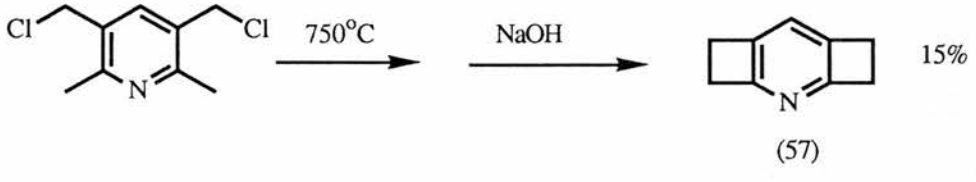
specific 1,4-elimination of hydrogen halides from 2-alkylbenzyl halides(**55**) to form benzocyclobutenes(**56**). Benzocyclobutene(**2**) was obtained by Maccoll *et al*[10] from 2-methylbenzyl chloride(**5**) in 70% yield and the chloro derivative from the corresponding dichloro



(55) (56)

compound(**6**) in a yield of 53%. Grignard reaction allows the transformation of (**9**) into various benzocyclobutenes in good yields (e.g. (**56**), R = COOH, R' = H (72%) or R = CHO, R' = H (74%)[38], which are of interest as synthetic building blocks.

This approach has also been applied to heteroaromatic systems with the preparation of [2,3:5,6]dicyclobutapyridine(**57**)[39]. Boekelheide *et al*[40] synthesised various substituted cyclobutapyridines(**58**), which



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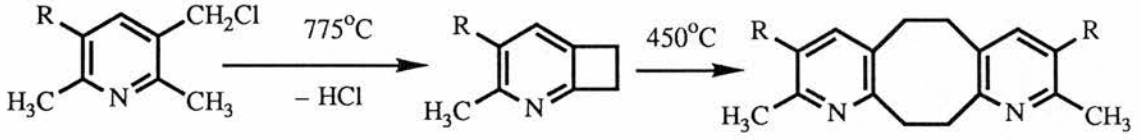
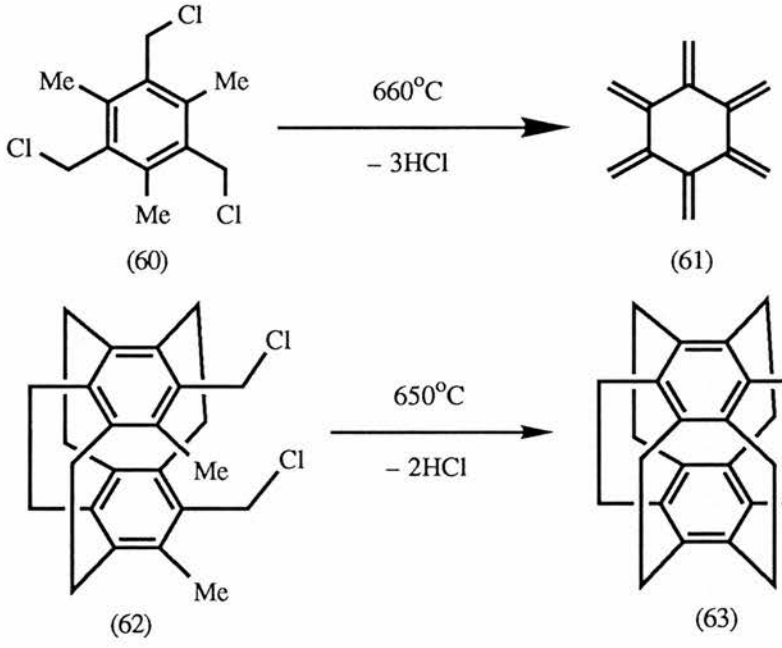


(58) (59)

when heated to 450°C in the absence of a trapping agent dimerise to (**59**). The synthesis of benzocyclobutenone was similarly achieved by hydrogen chloride elimination from 2-methylbenzoyl chloride, whereby the *o*-quinoid ketene was assumed to be the initial product[41].

A remarkable application of such 1,4-elimination reported by Schiess *et al*[38] and by Boekelheide *et al*[42] was the synthesis of hexaradialene (**61**) from commercially available (**60**) by triple hydrogen chloride elimination at 660 °C. The chemical behaviour and spectroscopic evidence demonstrated that (**61**) exists exclusively in the tris-*o*-quinoid form and in spite of the presence of a cyclic 6p-electron system, no specific aromatic character was evident. These studies have been extended to the synthesis of naphtharadialene by Hart *et al*[43]. The long-sought [2.2.2.2.2.2.](1,2,3,4,5,6)cyclophane(**63**) ("superphane") was first made in 40% yield by double hydrogen chloride elimination from compound(**62**)[44], further illustrating the synthetic value of this methodology.

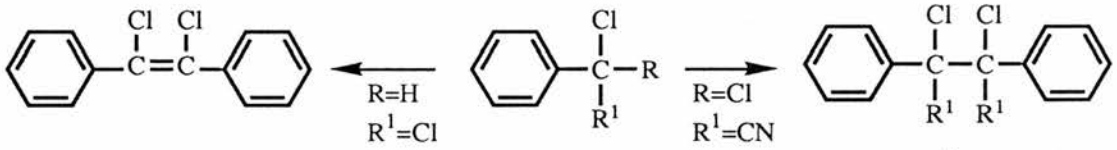


(c) Dehalogenative coupling

Thermal dehalogenative coupling reactions date back to the classical coupling of chloroform and carbon tetrachloride. Hurd in his monograph reviewed these coupling reactions; for example anthracene was first synthesised[45] by heating benzyl chloride for several hours with about two

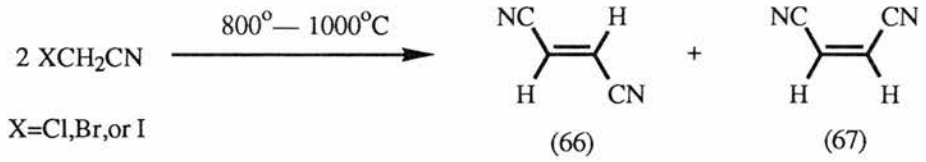
volumes of water at 190-215°C, while the distillation of benzyl chloride through a tube filled with pumice or chalk at a temperature of 400-600°C gave about 25% of stilbene[46]. Tetraphenylethylene was prepared[47] by heating diphenylmethylbromide at 250-300°C. Similarly, when benzal chloride and benzotrichloride are passed through a red hot tube, *Z*- and *E*- α,α'-dichlorostilbene(**64**) and α,α,α',α'-tetrachlorobibenzyl(**65**) are obtained respectively[48]. Ever since this early observation of dehalogenative coupling reactions, their synthetic potential has been explored by various research workers.

A major draw back to these thermal dehalogenative couplings is low yield and, over the years attempts have been made to improve the yield by carrying out the dehalogenative coupling of various organic halides in the presence of metals or transition metal complexes. Examples



(64) (69) (65) R^1=Cl (68) R^1=CN

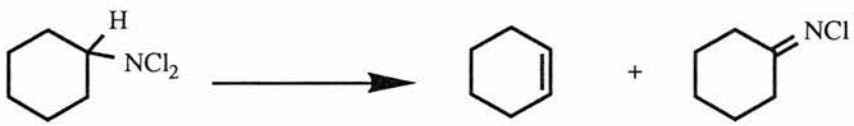
of this work are discussed in the later sections. However despite this drawback, Hashimoto and coworkers[49] found that the pyrolysis of monohalogenoacetonitriles at 800-1000°C under reduced pressure resulted in a novel pyrolytic coupling reaction to yield fumaro-(**66**) and maleonitrile(**67**) in 50-60% yields. Earlier attempts to prepare these compounds in the liquid phase proved rather difficult and proceeded in low yields[49]. Recently, Wiersum[50] reported the isolation of previously unknown 2,3-dichlorodiphenylsuccinonitriles(**68**) from a recycle pyrolysis of α,α-dichlorobenzyl cyanide(**69**) at 500°C.



(66) (67)

(d) Generation of reactive intermediates

There has been a growing interest in the formation of multiple bonds between heteroatoms by thermal elimination of hydrogen chloride. Some of the multiply bonded compounds are only accessible through this method because of their high reactivity and instability. Roberts *et al*[51] discovered that N,N-dichloroamines at a gas chromatography inlet temperature of 240°C, readily b-eliminate the elements of HCl and NCl to form alkenes or dehydrochlorinate leading to the chloroimine(**70**). Pure thioformaldehyde(**72**) was obtained for photoelectron spectroscopic studies from the pyrolysis of methane sulphenyl chloride(**71**) at 575°C[52]. Pyrolysis of methane sulphinyl chloride(**73**) at 600°C similarly gave sulphine(**74**)[53] which is analogous to the generation of ketene from acetyl choride[54].

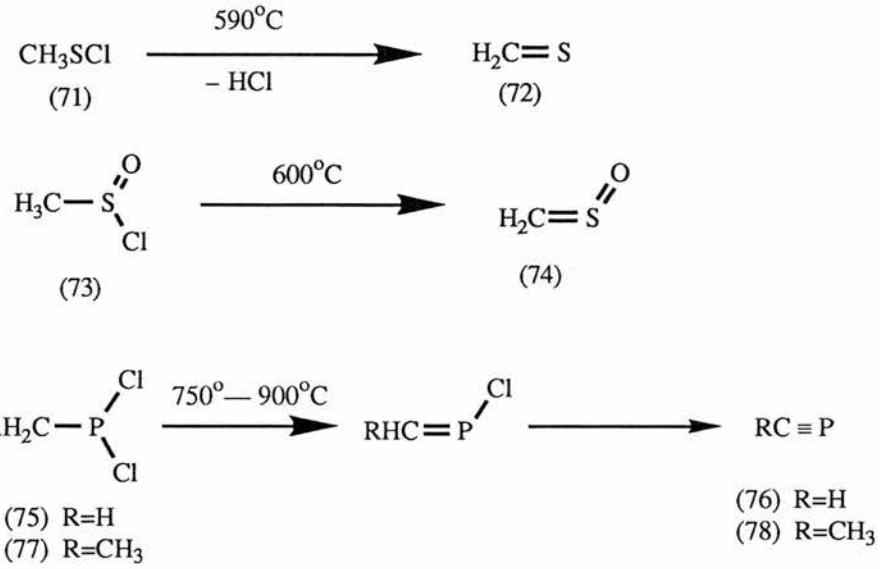


48% 52%

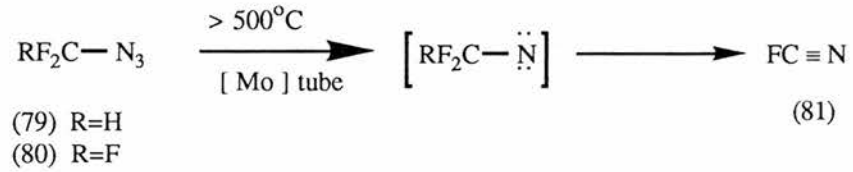
(70)

The generation and characterisation of carbon-phosphorus multiple bonds, especially those of low coordinate tervalent phosphorus is of current interest. The formation and microwave spectroscopic detection of phosphaethyne(**76**) was first reported from the pyrolysis of the dichlorophosphine(**75**)[55]. However recently Denis *et al*[56] reported the isolation and full characterisation by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy of the phosphaalkynes(**76**) and (**78**) from pyrolysis of (**75**) and (**77**);

compound (**78**) can be kept for three days in solution at room temperature without significant decomposition.



A novel method of handling highly explosive fluorinated compounds for the thermal generation of fluoroacetylenes, has recently been developed by Bock and coworkers[57]. Thus the potentially explosive compounds(**79**)[58] and (**80**)[59] were thermally decomposed in a controlled

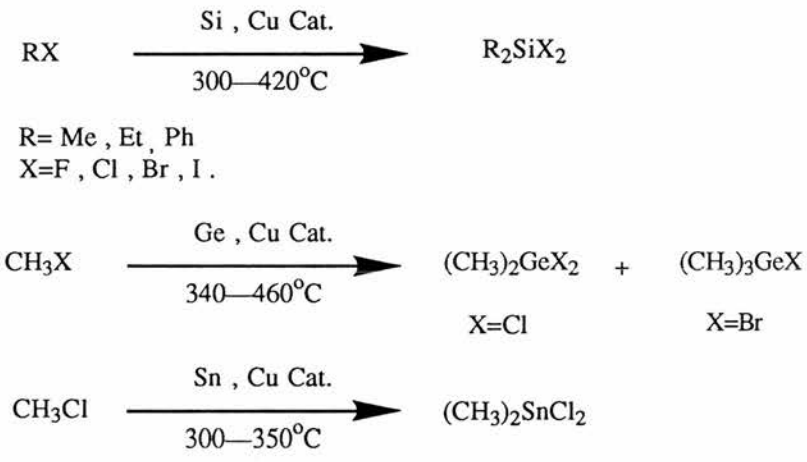


way by using a flow system in a molybdenum tube furnace under reduced pressure, to give pure cyanogen fluoride(**81**). The reaction was presumed to go via the intermediate nitrene (F_2RCN:) formed by loss of nitrogen from the azide, followed by dehydrofluorination or defluorination.

2. Reaction of organohalides over solid reagents

(a) Pyrolytic formation of organometallic compounds

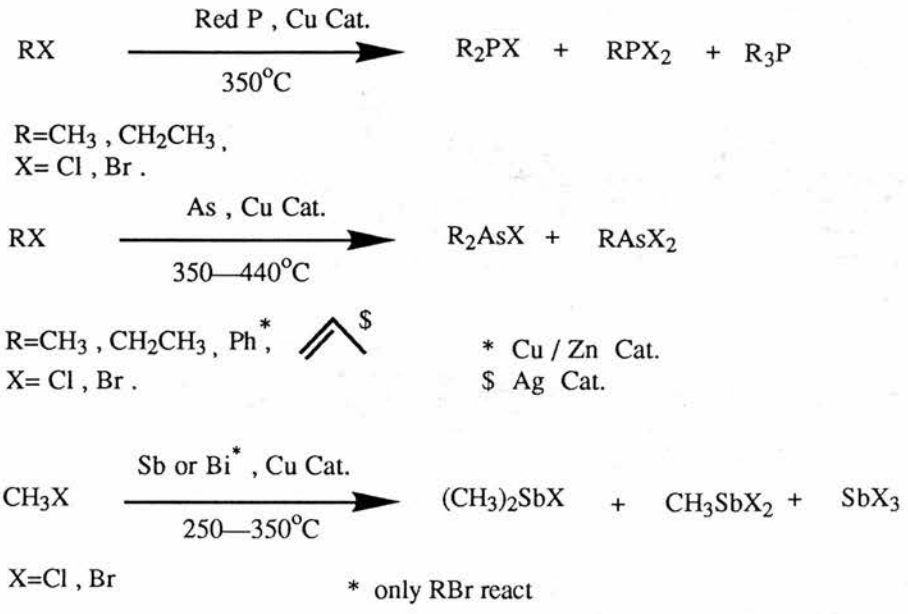
The pyrolysis of hydrocarbon halides over elements has been employed for the direct synthesis of various organometallic compounds. The general procedure is to pulverise "metallic" elements, mixed in the desired proportion of catalyst (if any), and then to support the powder on convolutions of glass wool or on masses of asbestos within the glass tube.



Scheme 1

The tube is heated in an electric furnace to the desired temperature with a stream of hydrogen flowing through it and then the hydrogen is shut off and a slow stream of the desired hydrocarbon halide is passed through the tube[60]. The action of methyl chloride upon elemental silicon[61], germanium[62] and tin[63] usually in the presence of copper as catalyst, produces organometallic chlorides of the type $(CH_3)_aMCl_{4-a}$, where M represents the group 14 element used (*Scheme 1*). Other hydrocarbon halides show related reactions and suitable conditions vary with the halide employed but usually the temperature varies from 350- 460°C.

Maier[64] prepared organophosphorus compounds directly from red phosphorus. Thus methyl chloride reacts with phosphorus in the presence



Scheme 2

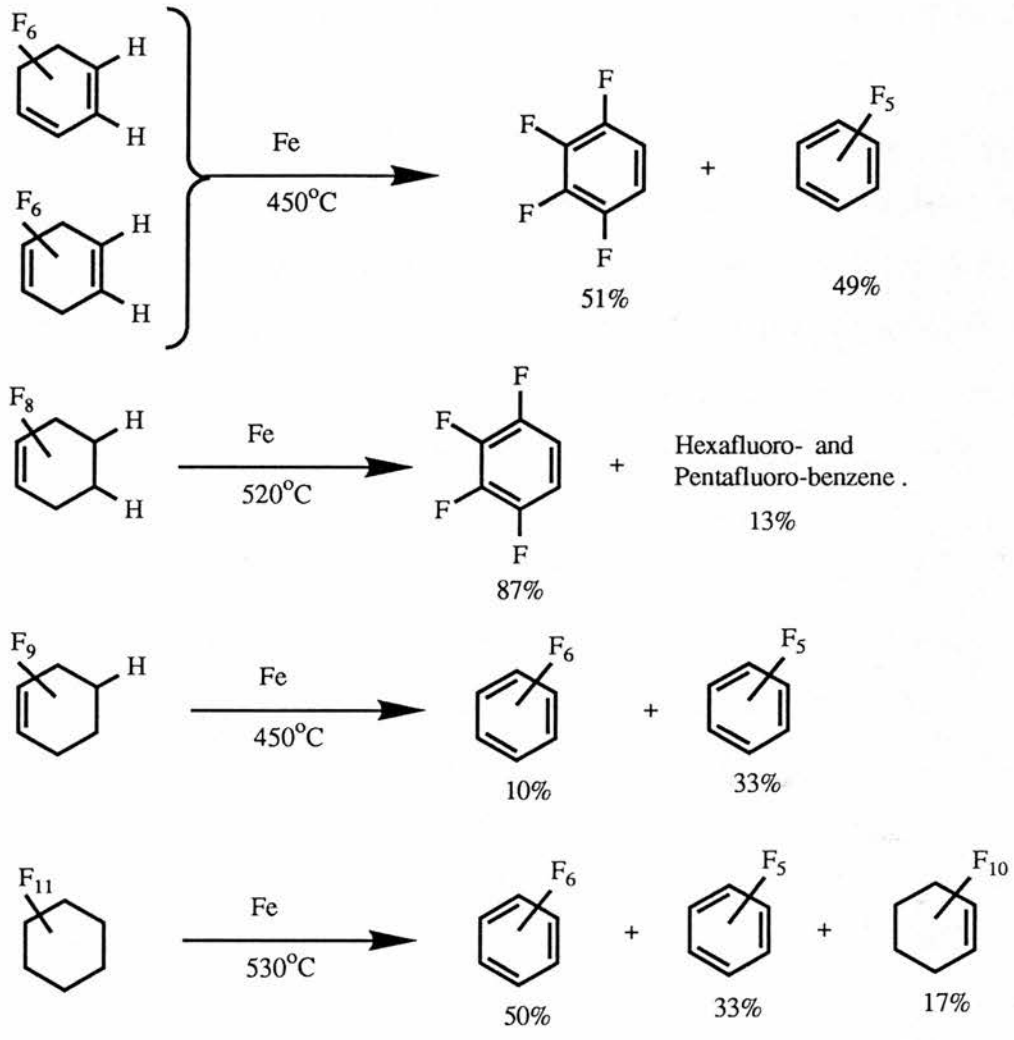
of catalytic copper at 340-360°C to give good yields of dichloromethylphosphine, chlorodimethylphosphine and trimethylphosphine. Methyl bromide at 350°C gave excellent yields of trimethylphosphine (97%) with 2% bromodimethylphosphine, while ethyl bromide yielded about 95% dibromoethylphosphine and 4% bromodiethylphosphine (*Scheme 2*). Similarly both organoarsenic and organoantimony compounds have been prepared by pyrolytic reaction of hydrocarbon halides with elemental arsenic and antimony respectively. Methyl chloride with powdered arsenic at 350-370°C gave 80% dichloromethylarsine and 20% chlorodimethylarsine, while ethyl bromide gave a low yield of ethyldichloroarsine. Halides of unsaturated hydrocarbons, such as vinyl bromide and vinyl chloride react at 400-440°C, with a mixture of arsenic, copper and zinc to give vinyldihaloarsines, divinylhaloarsines and arsenic trihalides

(*Scheme 2*)[60]. At 500°C bromobenzene reacts with arsenic in the presence of silver as a catalyst to give phenyldibromoarsine[60].

Antimony reacts with methyl chloride at 360°C in the presence of copper to form 10% dimethylchloroantimonide, 58% methyldichloro-antimonide and 32% trichloroantimonide and with methyl bromide at 350°C to yield 38% dimethylbromoantimonide, 40% methyldibromo-antimonide and 22% tribromoantimonide[60]. In the reaction of bismuth with methyl chloride, no methylbismuth chlorides were isolated, however methyl bromide at 250°C gave a low yield of methylbismuth dibromide[60]. In summary, the reaction of lower alkyl and arylhalides with silicon is a rather general reaction, but becomes less general with germanium and almost specific for methyl chloride with tin. Similarly for group 15 elements, the reaction is more general for arsenic than for antimony or bismuth. The hydrocarbon bromides gave better yields than do the corresponding chlorides[60].

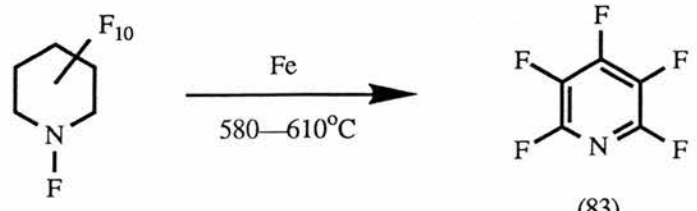
(b) Dehalogenation over solid metals

Gas phase dehalogenation of various halogenated substrates has been achieved by pyrolysis over heated solid metals. Tatlow *et al*[65] pioneered a general method for the preparation of perfluoro-aromatic compounds by the defluorination of alicyclic fluorocarbons. The method consists of passing the compound to be defluorinated in the vapour phase, in a stream of nitrogen over a heated metal, usually iron or nickel gauze, packed into a tubular vessel[65]. This method was used to prepare hexa-, penta- and tetra- fluorobenzenes from the appropriate polyfluoro-cyclohexanes, -cyclohexenes and -cyclohexadienes by reaction over heated iron gauze at 400-555°C (*Scheme 3*)[66]. When nickel packing was tried, erratic results were obtained.

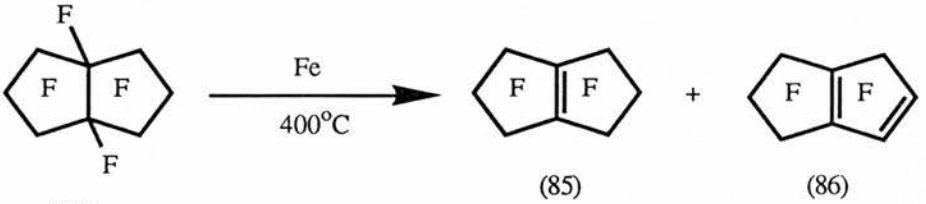


Scheme 3

Pentafluoropyridine(**83**) was prepared by defluorination of undecafluoropiperidine(**82**) on a clean iron surface at 580-610°C and 1mmHg, with a short contact time of ~1 sec.[67]. The authors attributed the ease of aromatisation at such contact time to the N-F bond facilitating defluorination. The defluorination of alicyclic fluorocarbons usually requires long contact times, and while octafluorotoluene was formed in 25% yield from perfluoro(methylcyclohexane) at 500°C and atmospheric pressure with a long contact time, no defluorination was observed with iron at 700°C for 1 sec. at 1mmHg.

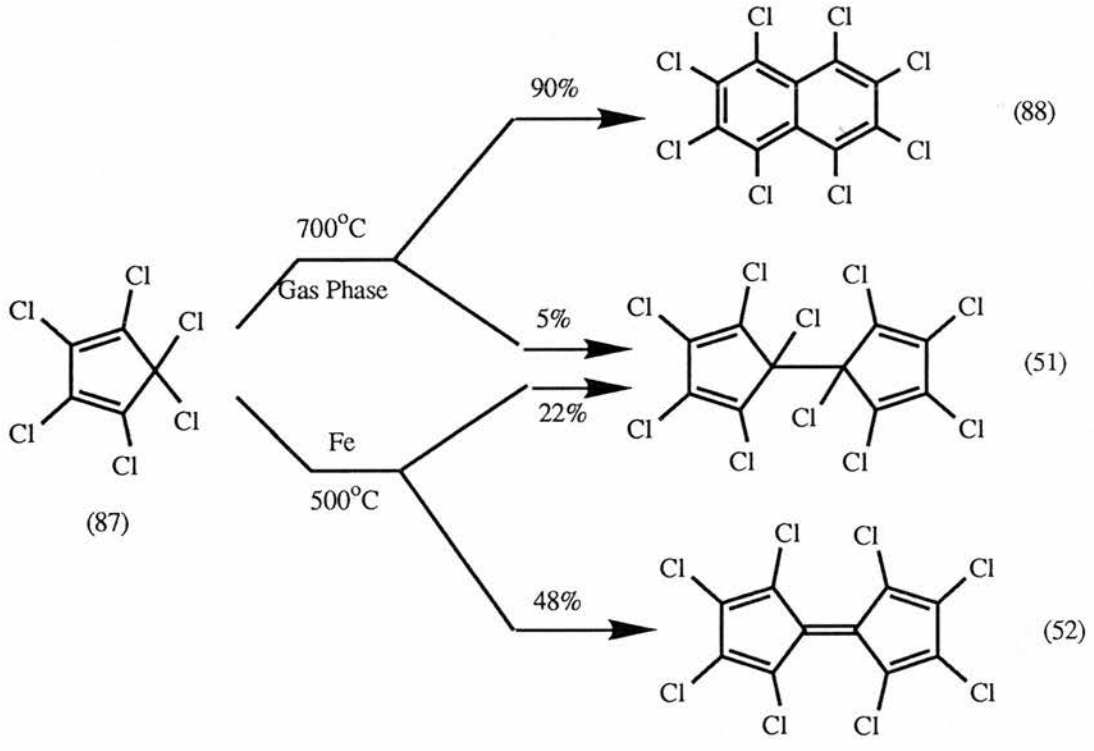


(82) (83)



(84) (85) (86)

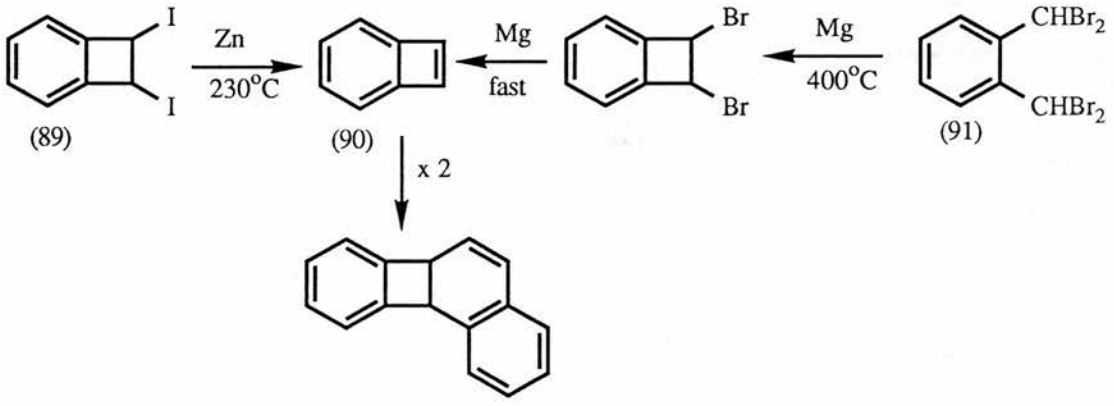
Similarly, the perfluorobicyclic compound(**84**) was defluorinated over iron at 400°C, to give a mixture of the perfluorobicyclooctene(**85**)



and perfluorobicyclooctadiene(**86**)[68]. Dehalogenative coupling was the observed process when hexachlorocyclopentadiene(**87**) was passed over iron at 500°C to give 48% of the perchlorofulvalene(**52**) and 22% of bis(pentachlorocyclopentadienyl) (**51**). However, pyrolysis of compound

(**87**) in the absence of iron at 700°C gave 90% octachloronaphthalene(**88**) and 5% of (**51**)[69].

Nickel has been used as an alternative to iron in the conversion of perfluorocyclohexane to hexafluoro- and pentafluoro-benzene (*Scheme 3*)[65], and in the preparation of pentafluoropyridine(**83**) from undecafluoropiperidine at 560°C[70]. When perfluoroperhydro-indane, -fluorene, -phenanthrene,-anthracene or -pyrene were passed over nickel turnings at 490°C, various defluorinated products were obtained[71]. More recent work on the pyrolysis over solid metals has been for the generation of highly reactive intermediates. The direct spectroscopic observation of benzocyclobutadiene(**90**) was first made when *cis*-1,2-diiodobenzo-cyclobutene(**89**) was vapourised over zinc powder at 230°C[72]. A more

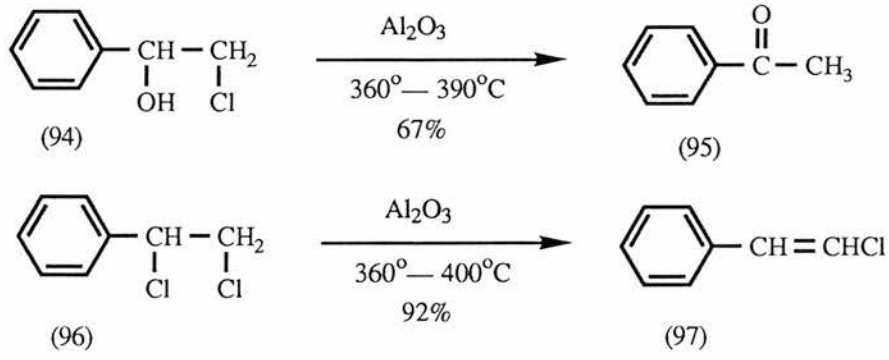


convenient route to (**90**) is from the commercially available α,α,α',α'-tetrabromo-*o*-xylene(**91**), which was debrominated at 440-470°C over sublimed magnesium[73]. Dehalogenation over silver has been used for the preparation of phosphorus compounds with low

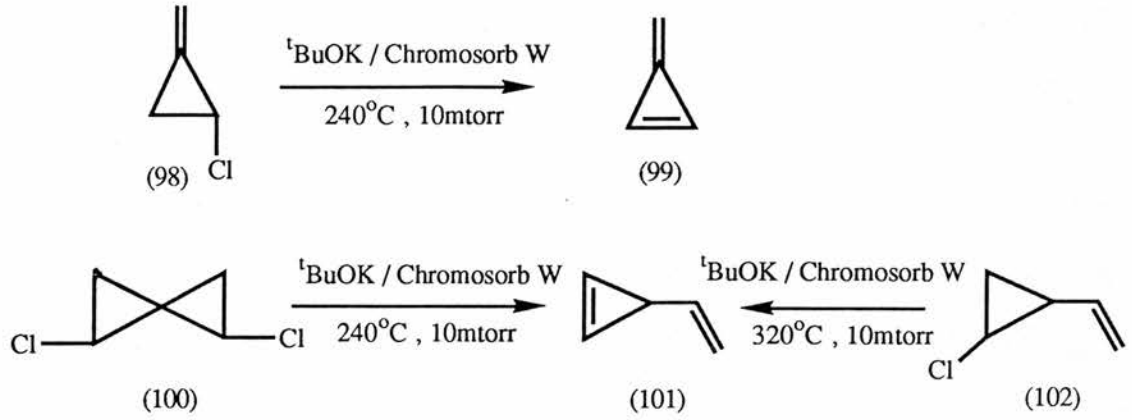
coordination number. Thus both phosphorus oxymonochloride(**92**) and phosphorus thiomonochloride(**93**) were obtained in the gas phase dechlorination of the corresponding trichlorides with silver turnings at temperatures above 800°C[74].

(c) Dehydrohalogenation over solid bases

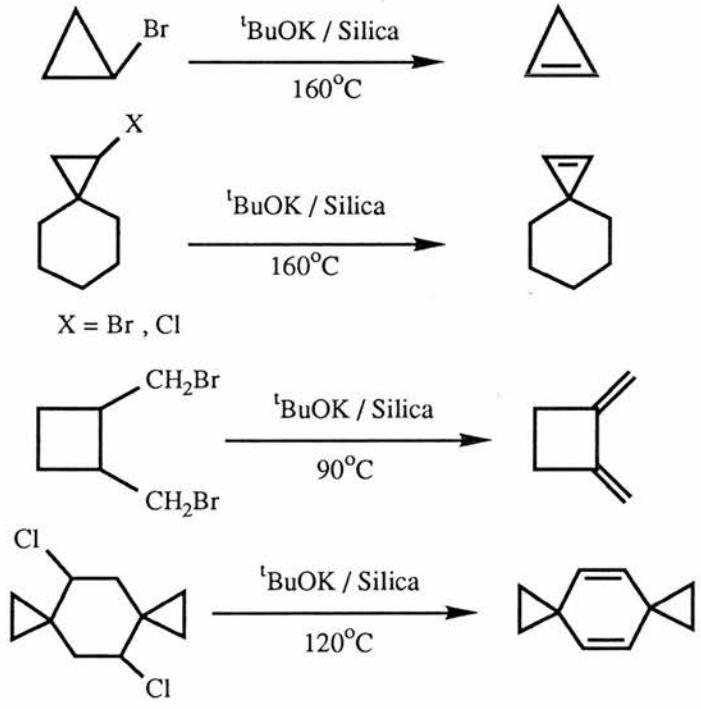
When halocompounds are vapourised over solid bases under flash vacuum conditions, the bases induce dehydrohalogenation as well as scavenging the released hydrogen halide, thereby preventing recombination. When vapour phase dehydrohalogenation reactions over basic catalysts such as alumina were investigated by Emerson *et al*[75], it was found that styrene chlorohydrin(**94**) at 360-390°C lost hydrogen chloride and tautomerised to acetophenone(**95**). Under the same conditions styrene dichloride(**96**) gave an almost quantitative yield of β-chlorostyrene(**97**).



However, recent interest in this area has been for the synthesis of highly strained molecules and reactive intermediates. Potassium *t*-butoxide adsorbed on chromosorb*W* was used to generate methylenecyclopropene(**99**) from 2-chloromethylenecyclopropane(**98**) and 3-vinylcyclopropene(**101**) from either 2,4-dichlorospiropentane (**100**) or 1-chloro-2-vinylcyclopropane(**102**)[76].



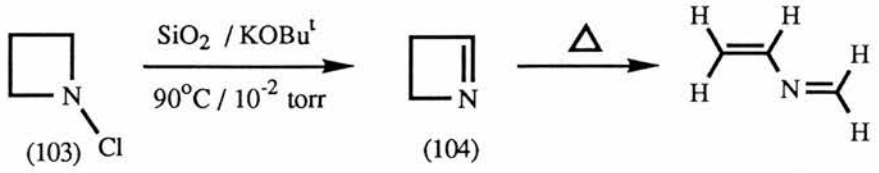
Similar highly strained cycloalkenes were obtained by Denis and coworkers[77], by vapour phase dehydrohalogenation of halocycloalkanes over potassium *t*-butoxide supported on silica (*Scheme 4*).



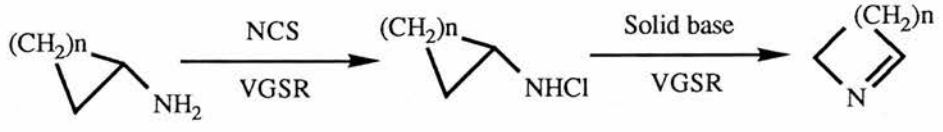
Scheme 4

Denis *et al*[78] developed a method of vacuum gas-phase/solid-phase reactions (VGSR), for the synthesis of reactive species. The method is a one-pot multistep sequence carried out in a single vacuum line : N-chlorination of primary amines on solid N-chlorosuccinimide was

followed by the a-elimination reaction of the resulting N-chloroamines over solid potassium *t*-butoxide, to generate reactive imines. Although,

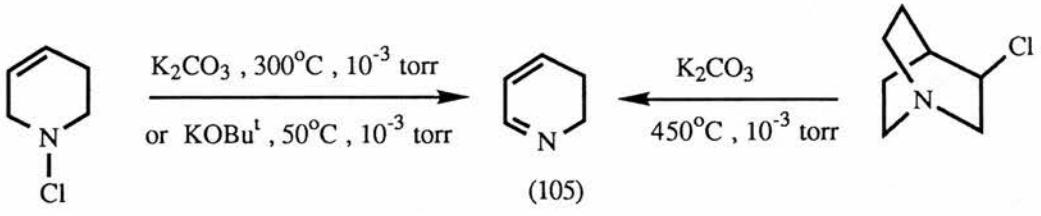


2-phenyl-1-azetine can be obtained by base promoted 1,2-elimination of HCl from 2-phenyl-N-chloroazetidine, the parent compound was too unstable to be isolated under similar conditions[79]. Using the VGSR apparatus, dehydrochlorination of N-chloroazetidine(**103**) led to 1-azetine(**104**) at 90°C with a yield of 98% and purity of 95%[80].



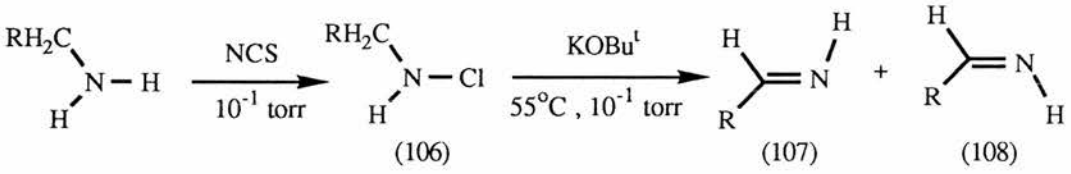
Scheme 5

Various other cyclic imines have also been prepared using this methodology (*Scheme5*)[81] and of particular synthetic interest was the preparation and characterisation of 2,3-dihydropyridine(**105**), which is of importance in biological systems as compounds of this type have been postulated as intermediates in the biosynthesis of alkaloids[82].



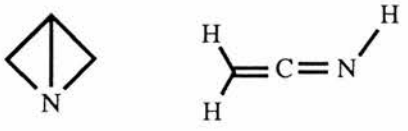
The generation and characterisation of highly reactive aldimines (**107**) and (**108**) have also been made possible by the VGSR technique.

Although the products are usually obtained as a mixture of isomers, some stereoselectivity was observed, the main product in all cases being the *E*-isomer (**107**). 1-Azabicyclo[1.1.0]butane(**109**) was the main product in the elimination of HCl from (**106**, R = $CH{=}CH_2$)[78]. The metastable isomers of acetonitrile, vinylideneamine(**110**)[83] and the new molecule prop-2-ynylideneamine(**111**)[84] have both been synthesised using the VGSR technique. Mechanistic study by isotopic labelling showed that a-elimination was the main (if not the only) pathway for most of these transformations, although no intramolecular cyclisation *via* C-H insertion was observed.

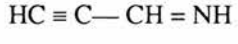


(106) (107) (108)

R = Me, R = Et, R = ^{n}Pr, R = —$CH{=}CH_2$,
R = —$CH_2CH{=}CH_2$, R = —$(CH_2)_2CH{=}CH_2$.



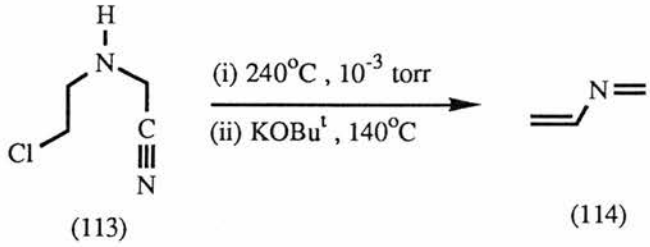
(109) (110)



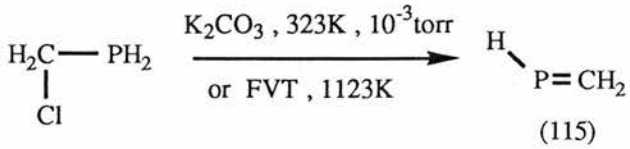
(111)

(112)

The VGSR technique has also been applied to non N-chlorinated substrates. Thus, gas phase dehydrochlorination of β-chloroethylazide over solid KOBu^t affords vinyl azide which was directly thermolysed to give 2H-azirine(**112**), another isomer of acetonitrile[83]. 2-Azabutadiene (**114**) was similarly prepared by thermolysis of (**113**), followed by removal of HCN and HCl elimination on KOBu^t at 140°C[85]. Methylidene phosphine(**115**) was obtained by HCl elimination from chloromethylphosphine by K_2CO_3[86].



(113) (114)



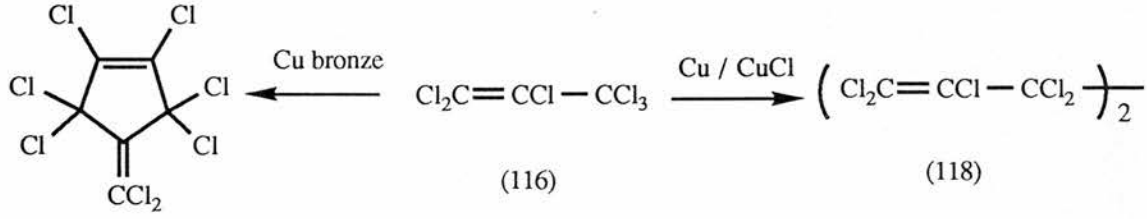
(115)

C. Dehalogenation in solution

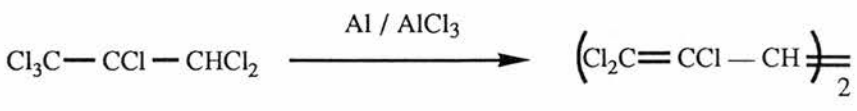
1. Aliphatic halides

(a) Coupling reactions

Ever since the discovery in 1855, that when sodium reacts with alkyl halides it leads to the coupling of two alkyl groups (Wurtz coupling), there has been a growing interest in effecting such reactions with less reactive metals. Thus, copper bronze was found to dehalogenate perchloropropene(**116**), with loss of two molecules of chlorine to give the coupled cyclised product (**117**)[87], while copper in the presence of a catalytic amount of copper(1)chloride gave only the coupled product, perchlorohexa-1,5-diene(**118**)[88]. Similar reactions have been achieved using aluminium turnings with a catalytic amount of aluminium trichloride. Thus 1H-heptachloropropane(**119**) gave 3,4-di-H-hexachlorohexa-1,3,5-triene(**120**)[89].

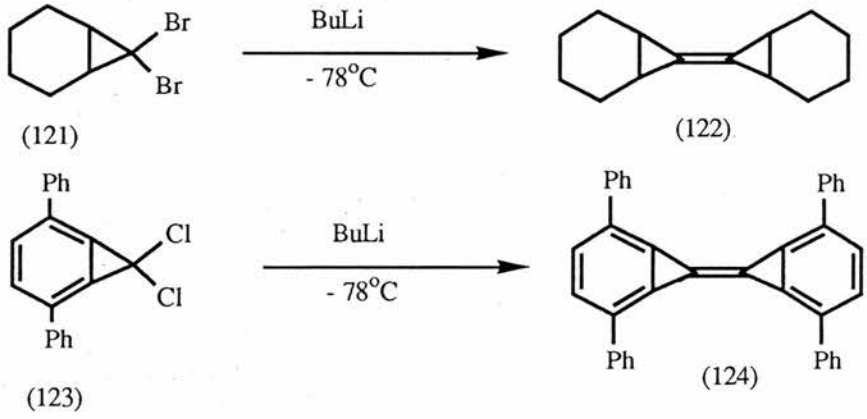


(117) (116) (118)



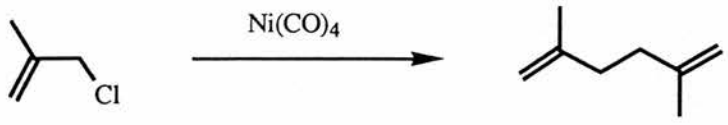
(119) (120)

Roedig[89] reported similar dehalogenative coupling of various perchlorinated compounds using the aluminium/aluminium trichloride reagent. Recently, coupling of alkyl halides was achieved in good yields with lithium metal under sonication while only trace amounts of products (<5%) were observed in the absence of ultrasound[90]. When 7,7-dibromobicyclo[4.1.0]heptane(**121**) was treated with *n*-butyl lithium, the dehalogenated coupled compound(**122**) was isolated[91] and very recently the fascinating hydrocarbon(**124**) was similarly obtained from (**123**)[92]. Both reactions are believed to involve the intermediacy of the cyclopropylidene.

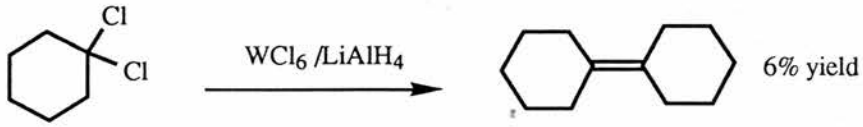


Owing to the difficulty of the Wurtz reaction[90] and the mixtures of products often obtained when other metals are used[89], there has been a growing interest in the use of transition metal complexes for dehalogenative coupling of organic halides. Nickel carbonyl [$Ni(CO)_4$][93] and titanium trichloride or titanium tetrachloride/$LiAlH_4$ reagent[97] were used to couple various alkyl halides. Thus β-methylallyl chloride(**125**) gave 2,5-dimethyl-1,5-hexadiene(**126**) in good yields. Dehalogenative coupling of alkyl-, allyl- and vinyl- halides with titanocene[94] and chromium trichloride/$LiAlH_4$[95] have also been reported. Olah *et al* prepared various alkenes *via* dehalogenation of *vic*-dihaloalkanes with the

$TiCl_3$ or $TiCl_4/LiAlH_4$[97] and $VCl_3/LiAlH_4$[98] reagents. Thus, 1,2-dibromo-cyclohexane, -cycloheptane and -cyclooctane, gave high yields of cyclohexene, cycloheptene and cyclooctene respectively. There



(125) (126)

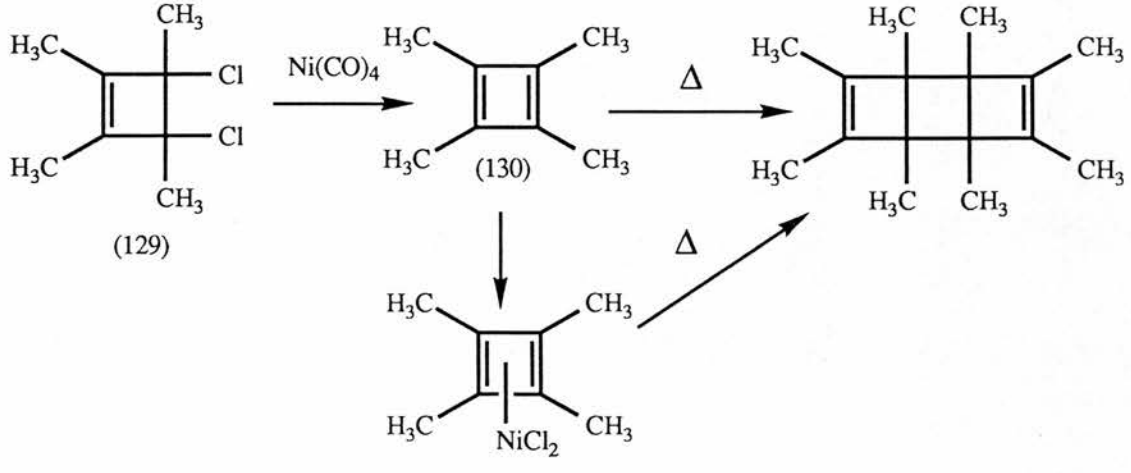


(127) (128)

are no reports on dehalogenative coupling of *gem*-dihaloalkanes with transition metal complexes though the benzylidene halides are known to couple to the stilbene[96,97]. An attempt to couple 1,1-dichlorocyclohexane (**127**) with the $WCl_6/LiAlH_4$ reagent[99], only gave a 6% yield of the coupled product (**128**).

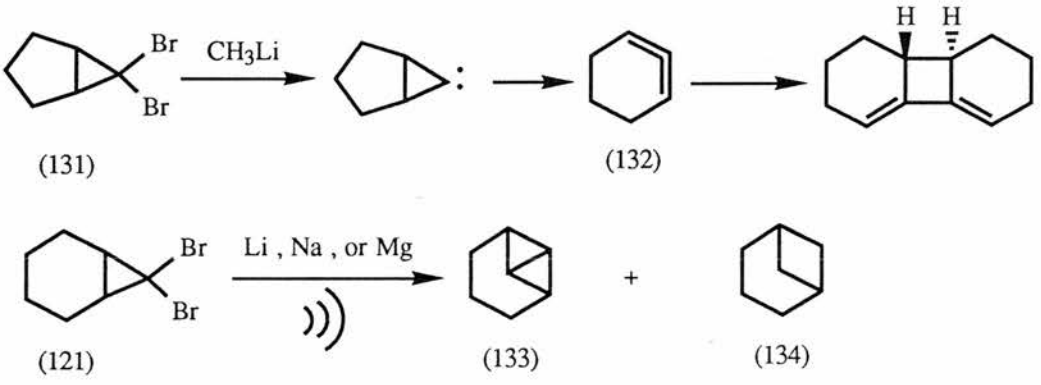
(b) Formation of highly strained ring systems

Dehalogenation is a major route to highly strained ring compounds. The *anti*-aromatic cyclobutadiene(**130**) was prepared by dehalogenation of dichlorocyclobutene(**129**) with lithium amalgam[100], nickel carbonyl[$Ni(CO)_4$][101], iron carbonyl[$Fe_2(CO)_9$][102] and antimony pentafluoride[103].

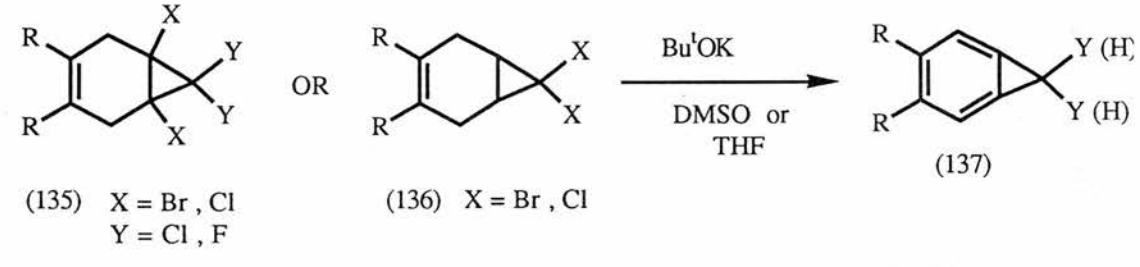


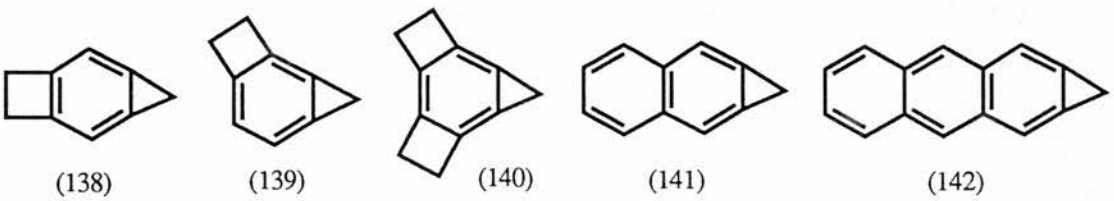
(129) (130)

When 6,6-dibromobicyclo[3.1.0]hexane (**131**) was debrominated with methyl lithium, the bicyclic carbene generated ring expanded to cyclohexa-1,2-diene (**132**), which reacted further to give its dimer and tetramer[104]. In the reaction of 7,7-dibromobicyclo[4.1.0]heptane (**121**) with lithium, sodium and magnesium under ultrasonic irradiation, the main product isolated was the tricyclic compound (**133**) formed by carbene insertion[105]. With magnesium/anthracene in THF both (**133**) and (**134**) were observed, in addition to other non-carbenoid products[106].

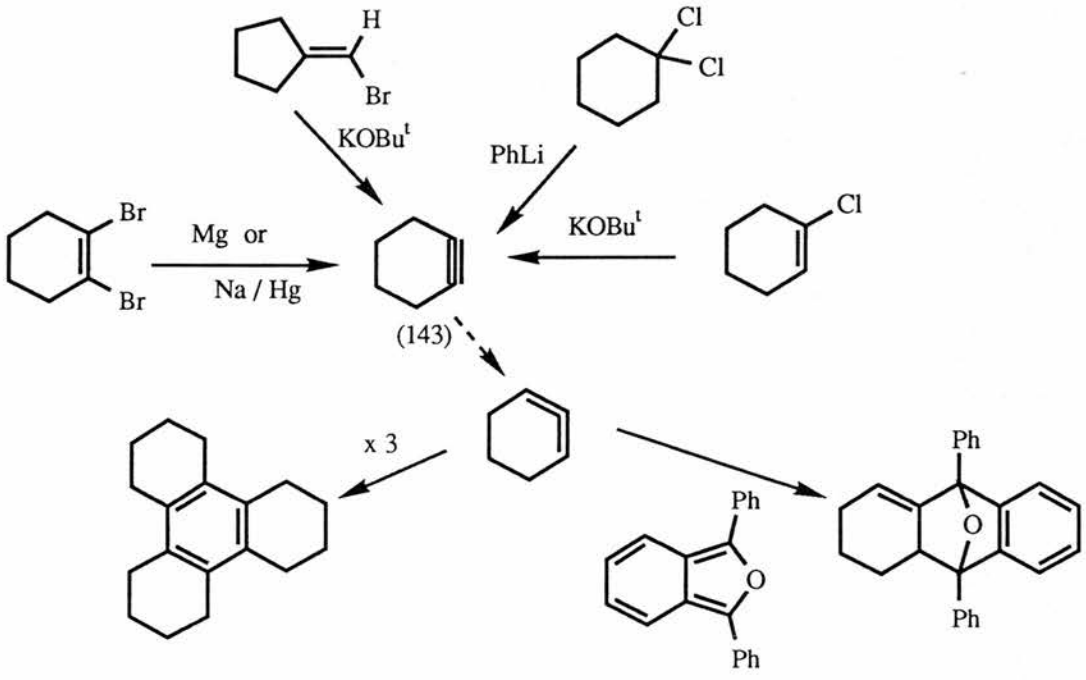


However, when halogenated bicyclo[4.1.0]heptane derivatives such as (**135**) and (**136**) are dehalogenated with potassium *t*-butoxide in THF or DMSO, the products obtained are bicyclo[4.1.0]hepta-1,3,5-triene derivatives(**137**). This route has been exploited for the synthesis of various cyclopropaarenes(**138-142**)[107].



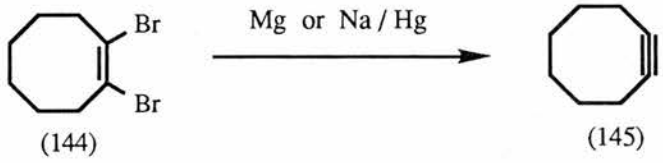


Cyclic alkynes are also accessible through the dehalogenation reaction. Thus, cyclohexyne(**143**) was generated by dehalogenation of



Scheme 6

1,2-dibromocyclohex-1-ene with metal amalgams, or dehydrohalogenation of 1,1-dichlorocyclohexane with phenyl lithium, and 1-chlorocyclohexene or bromomethylenecyclopentane with potassium *t* -butoxide (*Scheme 6*)[108]. Similarly, cyclooctyne (**145**) was prepared by dehalogenation of 1,2-dibromocyclooct-1-ene (**144**), with magnesium- or sodium amalgam[108].



(144) (145)

2. Benzylic halides

(a) Dehalogenative coupling with metals or transition metal complexes

The dehalogenative coupling of benzylic halides to bibenzyls has been achieved with several metals and transition metal complexes. Benzyl chloride(**146**) and its substituted derivatives were converted to bibenzyls(**148**) in low to moderate yields with magnesium in refluxing ether[109], sodium in boiling xylene[110] and iron under reflux with water[111]. Powdered tin in refluxing toluene was used to couple chlorodiphenylmethane to give 1,1,2,2-tetraphenylethane; while α-chloroethylbenzene(**147**) gave 2,3-diphenylbutane(**149**)[112]. Improved yields of coupled products from benzyl halides were reported

(146) R=H
(147) R=CH_3

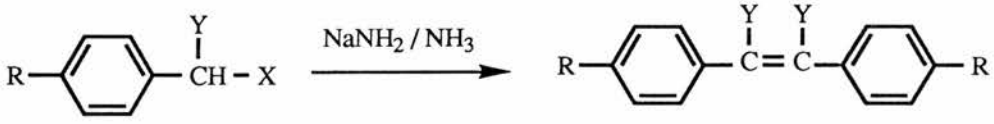
(148) R=H
(149) R=CH_3

using activated nickel[113]. Using sonication, activated copper and nickel were reported to give excellent yields of bibenzyls from various substituted benzylic halides[114]. Transition metal complexes which have been used to couple benzylic halides include $TiCl_3$ or $TiCl_4/LiAlH_4$[97], $VCl_3/LiAlH_4$[98] and $W(CO)_6$ or $WCl_6/LiAlH_4$[99].

(b) Dehalogenative coupling with bases

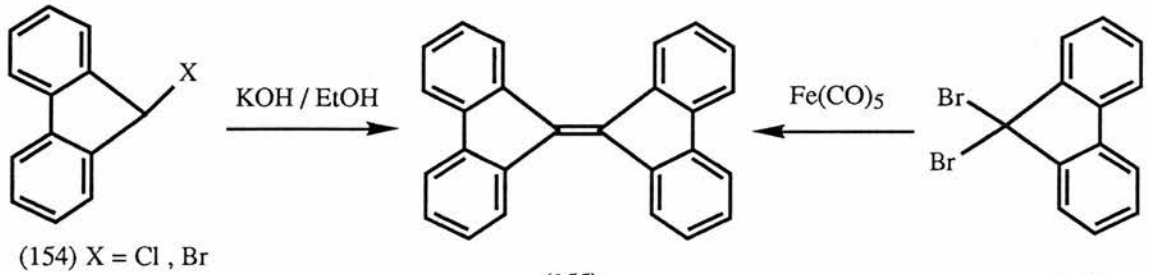
When benzylic halides are treated with bases, dehydrohalogenative coupling to stilbenes is often observed. Metal amides like lithium-, sodium-, and potassium amide[115] are the commonest bases used although metal alkoxides gave similar reactions[116]. Thus 4,4'-dinitrostilbene(**151**) was prepared from 4-nitrobenzyl chloride(**150**) with potassium

hydroxide in alcohol[116] and 3,4-bis(*p*-methoxyphenyl)hex-3-ene(**153**) from 1-bromo-1-(*p*-methoxy-phenyl)propane(**152**) with sodamide in



(150) Y=H , R=NO_2 , X=Cl
(152) Y=CH_2CH_3 , R=OCH_3 , X=Br

(151) Y=H , R=NO_2
(153) Y=CH_2CH_3 , R=OCH_3



(154) X = Cl , Br

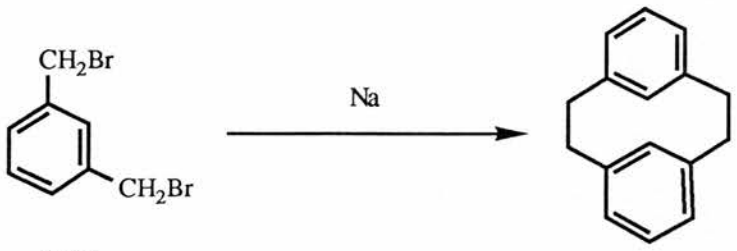
(155)

(170)

liquid ammonia[115]. Bases such as sodium iodide[117] and the anion of dimethylsulphoxide[118] have also been employed for the coupling reaction. The alkali amide and alkoxide reactions were used for the synthesis of 9,9-bifluorenylidene(**155**) from 9-halo-fluorenes(**154**); and 1,1,2,2-tetra-phenylethene from halodiphenylmethanes[119].

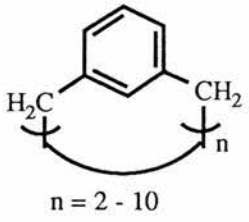
(c) Cyclophanes

In recent years there has been growing interest in the chemistry of cyclophanes, *i.e* molecules in which two or more aromatic nuclei are joined by two or more saturated carbon chains. The first synthesis of a cyclophane was by Pellegrin[121], who prepared [2.2]metacyclophane(**157**) by the Wurtz coupling of *m*-xylylene dibromide(**156**) in 1899. The Wurtz coupling was also used for the synthesis of [2.2]paracyclophane[122] and [2.2]orthocyclophane[123] from 1,2-bis(*p*-bromomethylphenyl)ethane and *o*-xylylene dibromide respectively.



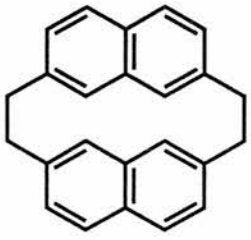
(156) (157)

Larger ring sized metacyclophanes(**158**) were prepared by dehalogenation using sodium with a catalytic amount of sodium iodide and bromobenzene in anhydrous ether or THF[124]. The naphthyl-analogue(**159**) of the metacyclophane was similarly prepared[124].



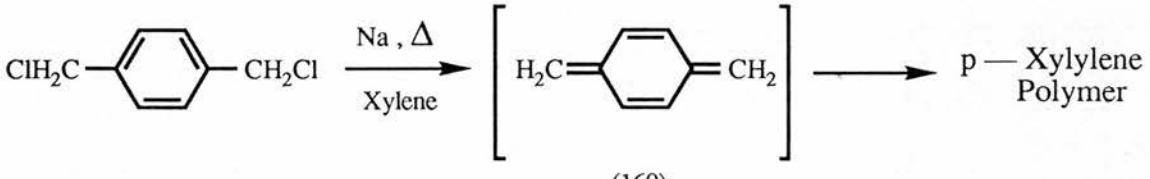
n = 2 - 10

(158)



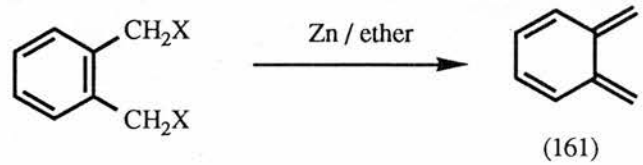
(159)

Of particular interest are *p*-xylylene(**160**) and *o*-xylylene(**161**); the former in polymer synthesis and the latter as a highly reactive diene in Diels-Alder reactions. Thus, the polymer of *p*-xylylene was obtained when *p*-xylylene dichloride was treated with sodium in refluxing xylene[110]. The same polymer was obtained from *p*-xylylene dibromide with sodium or lithium and a catalytic amount of tetraphenylethylene in THF[125].



(160)

Apart from sodium[123], other reagents have been used for the generation of *o*-xylylene from *o*-xylylene dihalides some of which are zinc metal[126], sodium iodide in DMF[127], and a copper(0)-isonitrile complex[128]. The sodium iodide method was employed for the synthesis of α,α'-diphenyl-*o*-xylylene(**162**)[127], as well as the thiophene(**163**)[129] and indole(**164**)[130] analogues, which were trapped with various dienes.



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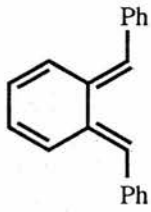

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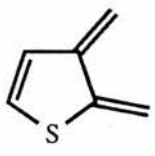

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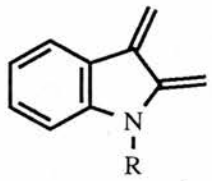
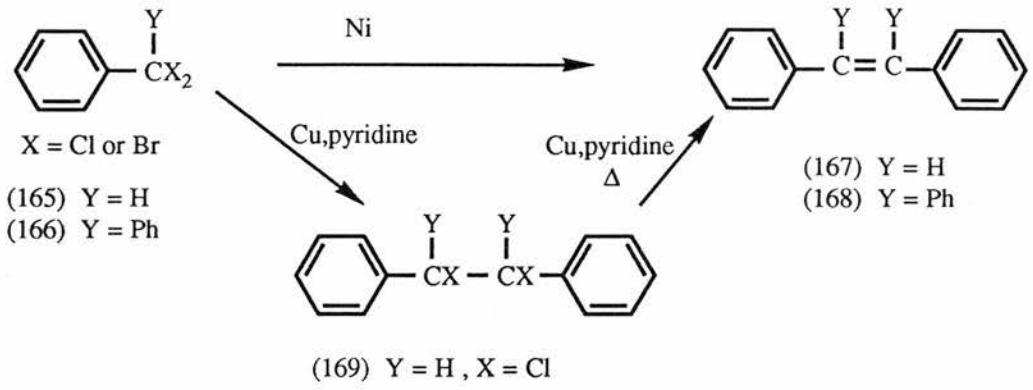


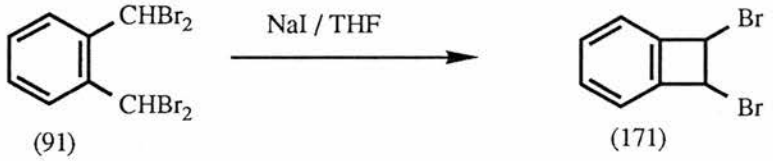
(164)

3. Benzylidene halides

Dehalogenative coupling of benzylidene halides by metals is of importance for the formation of carbon-carbon bonds. Metals such as tin[120], iron[111], sodium[45] and activated nickel[113] induce coupling of benzylidene halides(**165**) to give stilbene derivatives(**167**). Metal complexes such as $TiCl_3$ or $TiCl_4/LiAlH_4$[97], $VCl_3/LiAlH_4$[98], $W(CO)_6$ or $WCl_6/LiAlH_4$[99] and $(Me_2SiCl)_2$ with catalytic $Pd(PPh_3)_4$[131] have also been employed for the conversion of benzylidene halides to stilbenes. However, when benzylidene chloride was treated with copper in pyridine[132] or trialkylphosphite-copper(1)chloride[133], only the partially dehalogenated α,α'-dichlorobibenzyl(**169**) was isolated as the major product. Further dehalogenation of (**169**) to (**167**) was however achieved with copper in boiling pyridine.

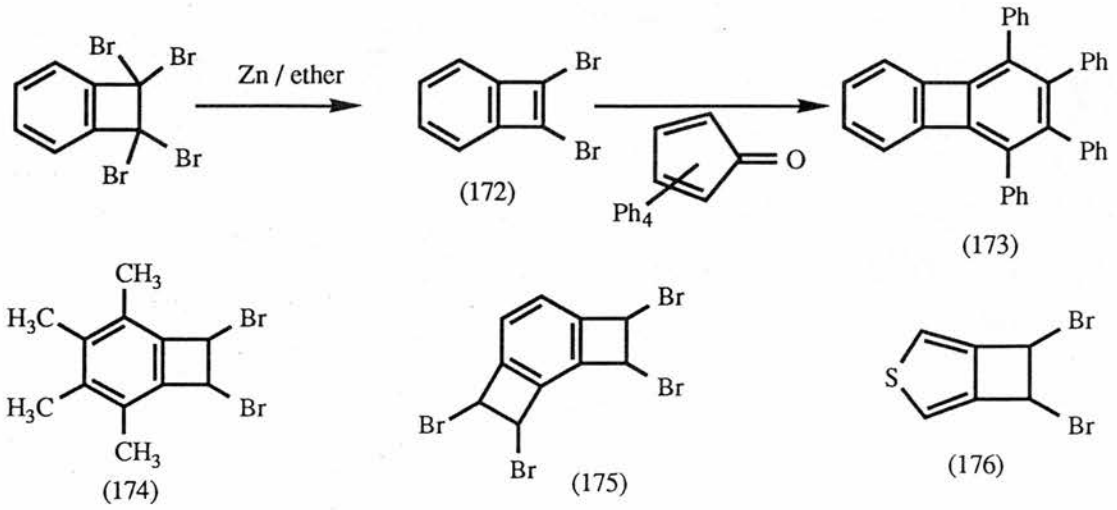


Similarly, various dihalodiarylmethanes(**166**) were dehalogenatively coupled to tetraarylethylenes(**168**) using copper[134], copper bronze[135], zinc, mercury, silver[136] and sodium iodide[139], as well as metal complexes such as $Fe(CO)_5$ or $HgFe(CO)_4$[137] and $Na(CO)_4$ or $Co_4(CO)_{10}$[138]. 9,9-Bifluorenylidene(**155**) was prepared in excellent yield, from 9,9-dibromofluorene(**170**) with iron pentacarbonyl.



The main route to α,α'-dihalobenzocyclobutenes is by dehalogenation of *gem*-dihalocompounds. Thus both sodium iodide[139] and a copper(0)-isonitrile complex[128] gave α,α'-dibromobenzocyclobutene(**171**) upon reaction with α,α,α',α'-tetrabromo-*o*-xylene(**91**). The sodium iodide method is the most widely used and has been used for the synthesis of the dibromocyclobutene derivatives (**174**)[140], (**175**)[140] and (**176**)[141]. Shepherd *et al*[142] prepared the dibromobenzocyclobutadiene(**172**) by the debromination of tetrabromobenzocyclobutene with zinc. The formation of (**172**), which is a highly reactive molecule, was confirmed by trapping with 2,3,4,5-tetra-

phenylcyclopenta-2,4-dienone to give 1,2,3,4-tetraphenyl-biphenylene(**173**).

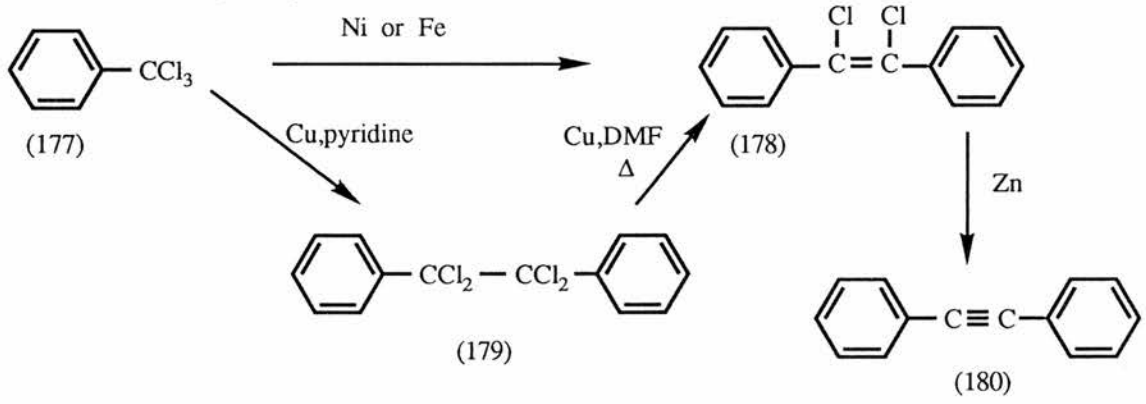


4. Benzotrihalides or Benzylidyne halides

The reductive coupling of benzylidyne trihalides(**177**) has been studied extensively and previous work employed metals such as iron powder in hot water,[111] copper in pyridine[132], sodium in liquid ammonia[115] and zinc dust in DMF[143]. Active metal agents in low-oxidation states such as zero-valent titanium[95], nickel[113], cobalt[138] and iron[144] compounds or slurries have also been used, as well as copper(I)[145], titanium(II)[95], vanadium(II)[146], iron(II)[144], cobalt(I), and cobalt(II) species[138]. Other reagents that have been employed for the dehalogenative coupling reaction include, triphenylphosphine[133], trialkylphosphites[133] and hexamethyldisilane[131].

The end product of the dehalogenative coupling of benzylidyne trichloride, with most of the reagents was 1,2-dichloro-1,2-diphenyl-ethene(α,α'-dichorostilbene)(**178**), however the intermediacy of 1,2-diphenyl-1,1,2,2-tetrachloroethane(**179**) was postulated and in some cases the intermediate isolated. With sodium in liquid ammonia, copper in pyridine, trialkylphosphite, ferrous chloride and vanadium compounds,

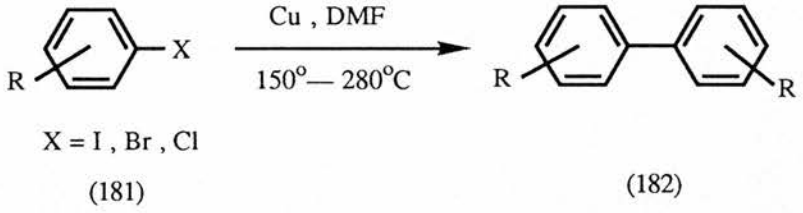
the major product isolated was compound (**179**). In a comparative study[143] on the reaction of zinc, copper and iron with benzotrichloride, it was observed that only zinc led to complete dehalogenation to diphenylacetylene(**180**), while with copper at 65°C only (**179**) was isolated, however it was readily converted to (**178**) at 140°C in DMF. On the other hand, with iron powder in boiling aqueous suspension, only (**179**) was isolated after an hour, but after 24 hours, it was quantitatively converted to (**178**).



5. Arylhalides

(a) Synthesis of biaryls

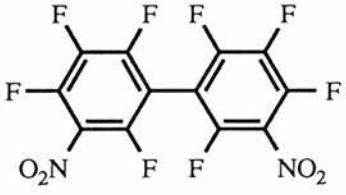
One of the common routes to biaryls(**182**) is the Ullmann synthesis. It involves the condensation of two molecules of aryl halide (**181**) in the presence of finely divided copper in DMF in the temperature range of 150°C to 280°C, to form a new aryl-aryl bond. The reaction is



suitable for the preparation of symmetrical and unsymmetrical biaryls and works best with aryl iodides, with reactivity decreasing greatly from iodine, to bromine to chlorine. Aryl fluorides are generally

unreactive[147]. The yield varies with substituents on the ring: electronegative groups such as nitro and esters, particularly at the ortho position are strongly activating on the arylhalide. Substituents such as amino, hydroxy and free carboxylic acid groups, which provide an alternative reaction path, inhibit the aryl coupling. Many of the reactions have important applications in synthesis and have been a subject of recent review[147]. Compounds (**183**), (**184**), (**185**) and (**186**) are selected examples of novel compounds synthesised by the Ullmann coupling[147].

However, due to the drastic conditions required for the Ullmann synthesis and the fact that good yields are only obtained with aryliodides, the use of other metals and variation in reaction conditions has been explored. Recently, coupling of various arylhalides has been achieved with magnesium[148], activated nickel[90], nickel complexes[149], lithium[90] and activated copper[90,114]. Sonication gave greatly improved yields with lithium, activated copper and nickel.



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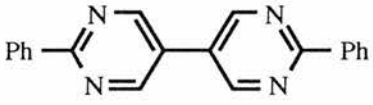

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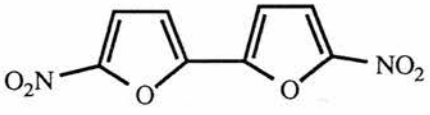

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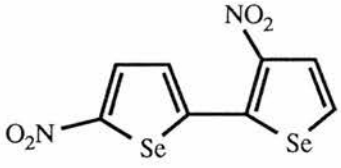
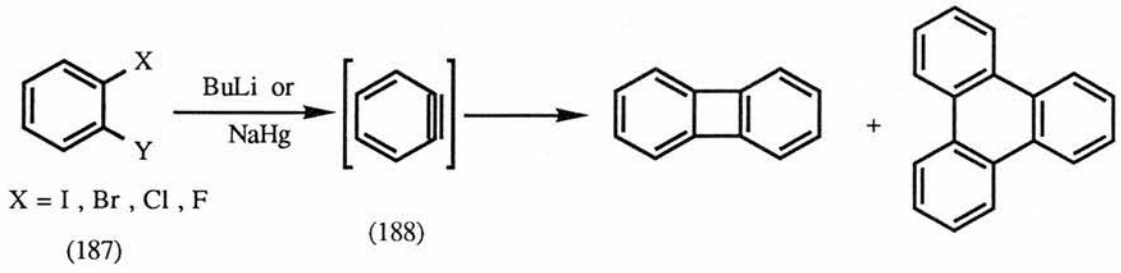


(186)

(b) Generation of benzyne

Simultaneous dehalogenation of 1,2-dihalobenzenes(**187**) is one of the routes to benzyne(**188**). Several reagents has been used to effect such a reaction and this includes butyl lithium,[150] lithium- or sodium amalgam,[151] magnesium[152] and copper[147]. Simple photolysis[153] of

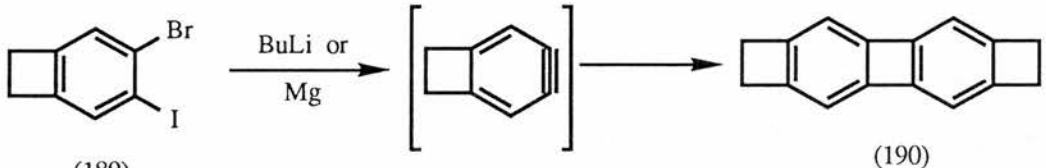
1,2-diiodobenzene led to the loss of a molecule of iodine, generating benzyne. Dehydrohalogenation of mono-haloaryl compounds(**181**) with bases such as sodium-, lithium- or potassium amide[154], sodium ethoxide[155] and phenyl- or butyl lithium[156], also generates arynes.



X = I , Br , Cl , F

(187) (188)

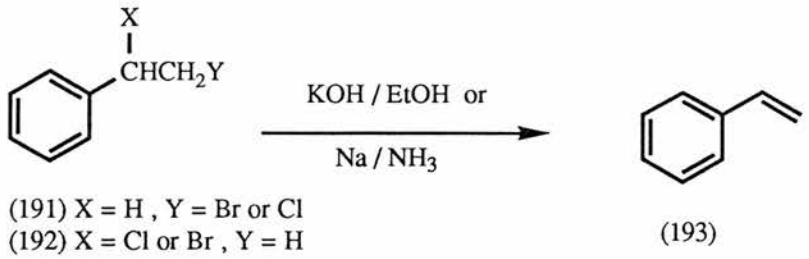
Benzyne is a highly reactive and transient species, and its existance can be confirmed by trapping with dienophiles or from its dimer or trimer products. Thus Vollhardt *et al*[150] prepared 2,3:6,7-dicyclobutabiphenylene(**190**) by butyl lithium or magnesium induced dehalogenation of (**189**).



(189) (190)

6. Arylalkylhalides or Haloalkylbenzenes

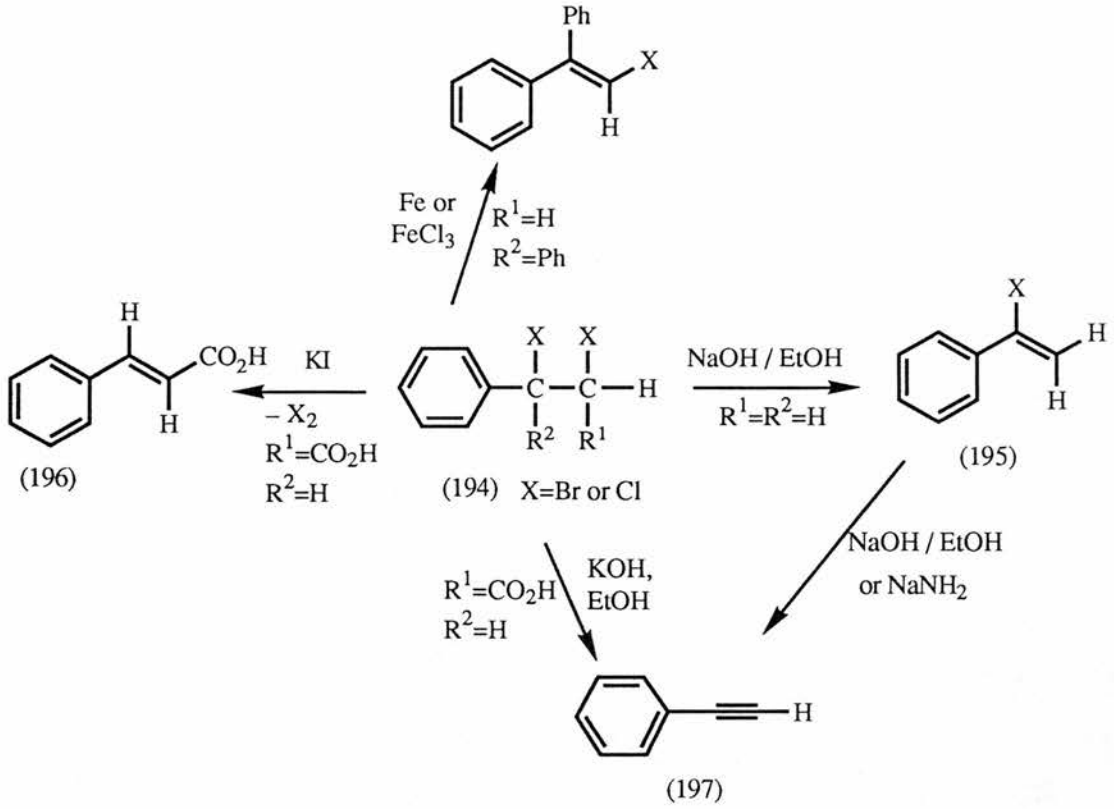
Arylalkylhalides preferentially undergo unimolecular dehydrohalogenation reactions with bases rather than dehydrohalogenative bimolecular coupling. Thus both 1-halo-(**191**) and 2-haloethylbenzenes(**192**) gave styrene(**193**) on treatment with alcoholic KOH[157] and sodamide[115] respectively.



(191) X = H , Y = Br or Cl
(192) X = Cl or Br , Y = H

(193)

Similarly 1,2-dihaloethylaryl compounds(**194**) are converted to the corresponding 1-halostyrenes(**195**) with alcoholic alkali[75] and freshly reduced iron[158]. However, the halostyrenes can be further dehydrohalogenated to the acetylene(**197**) with alcoholic alkali[159] or sodamide[159]. Potassium iodide[159,160] on the other hand, dehalogenates rather than dehydrohalogenates 1,2-dihaloethylaryl compounds(**194**) to give compound (**196**).



(196)

(194) X=Br or Cl

(195)

(197)

D. Programme of Research

Despite the extensive use of flash vacuum pyrolysis (FVP) in recent years for the study of thermolysis reactions most work has involved unimolecular reactions and there have only been isolated reports of pyrolysis over solid reagents. The previous work on pyrolysis over solid metals has mainly been for the generation of reactive intermediates, thus both zinc[72] and magnesium[73] have been used for the generation of benzocyclobutadiene(**90**). Recently, the trivalent phosphorus intermediates, phosphorus oxymonochloride and phosphorus thiomonochloride, were prepared by thermal dehalogenation of the corresponding trichlorides over silver[74], and dichloroketene was generated from trichloroacetylchloride when thermolysed over zinc[161].

The aim of the present work was to investigate the reactions of various organic substrates over solid metals under FVP conditions, with a view to preparing isolable products as opposed to the generation of reactive intermediates. The metal of choice for this project was magnesium, mainly because of its well established reactivity with organic halides in solution, and the aim was to investigate the corresponding reactions in the gas phase. It was envisaged that during the course of these investigations, the reactivity of other metals like zinc, aluminium and calcium would provide an interesting comparison to the observed processes with magnesium. In the long term, it was hoped that the investigation of the reaction of both halogenated and non-halogenated organic substrates over solid metals under FVP conditions, could open a whole new area of organic chemistry which has hardly been touched.

Preliminary work[162] had shown that the preparation of the metal was critical and best reactivity and high surface area was obtained near the metals melting point. Although this work was not aimed at studying

reactive intermediates, the prospect of generating radicals, carbenes, carbynes or metal-bound species, was recognised and products isolated might give an insight to the process(es) involved and lead to the discovery of interesting new chemical transformations.

EXPERIMENTAL

A Symbols and Abbreviations

mmol	millimoles
M	mol dm^{-3}
h,min	hours, minutes
GC-MS	gas chromatography-mass spectrometry
GC	gas liquid chromatography
TLC	thin layer chromatography
NMR	nuclear magnetic resonance
δ	chemical shift
J	spin-spin coupling constant
s,d,t,q,m	singlet, doublet, triplet, quartet, multiplet
M.S.	mass spectroscopy
m/z	mass to charge ratio
M^+	mass of molecular ion
FVP	flash vacuum pyrolysis
m.p.	melting point
b.p.	boiling point
THF	tetrahydrofuran
DMF	dimethylformamide
NBS	N-bromosuccinimide
NCS	N-chlorosuccinimide
C.T.	contact time

B. Instrumentation and General Techniques

1. NMR Spectroscopy

a. ^{1}H NMR

Routine spectra were obtained at 60 MHz on a Varian EM-360 spectrometer. Spectra of new compounds were obtained at 80 MHz on a Bruker WP 80 and high resolution spectra were obtained at 300 MHz on a Bruker AM-300 spectrometer both operated by Mrs M Smith.

b. ^{13}C NMR

All spectra were obtained at 75 MHz on a Bruker AM-300 spectrometer operated by Mrs M Smith.

c. ^{19}F NMR

Spectra were obtained at 75 MHz on a Bruker WP 80 spectrometer operated by Mrs M Smith.

All spectra were obtained from solutions in deuteriochloroform, unless otherwise indicated and chemical shifts of ^{1}H and ^{13}C NMR are expressed in parts per million to high frequency of tetramethylsilane while ^{19}F is expressed in parts per million to high frequency of fluorotrichloromethane.

d. Solid State ^{13}C NMR

Spectra were obtained at 500 MHz on a Bruker MSL 500 spectrometer operated by Dr F.G. Riddell

2. Thermogravimetric Analysis

Thermogravimetric studies were carried out on a Perkin-Elmer 7 Series thermal analysis system at a temperature range of 30-900°C –

courtesy of BP Research Centre, Sunbury, and on a Stanton-Redcroft thermogravimetric balance operated by Mrs S Smith.

3. Photochemical Reactions

The lamps used were 125W and 400W medium pressure water cooled mercury lamps supplied by Applied Photophysics Ltd, London. Large scale reactions were carried out by inserting the quartz or pyrex reactor well in a vessel containing the reaction mixture. Small scale reactions could be performed by attaching a quartz tube containing the reaction mixture to the side of the reactor well.

4. Gas Liquid Chromatography

A Pye Unicam 4500 chromatograph with a flame ionisation detector was used with nitrogen as carrier gas and a 2m x 4.5mm glass column. The chromatograph was attached to a Spectraphysics SP 4290 integrator. The columns used were 10% neopentylglycolsuccinate (NPGS) and 3% silicone (dimethyl, OV101) both on chromosorb W (80-100 mesh).

5. Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry studies were carried out on a Hewlett-Packard 5890A gas chromatograph coupled to a Finnigan Incos mass spectrometer with computerised data processing and library search operated by Mr C Miller and the author.

6. Mass Spectrometry

Mass spectra and accurate mass measurements were obtained on a Finnigan Incos mass spectrometer operated by Mr C Miller. For spectra of compounds containing chlorine and bromine only the peaks due to ^{35}Cl and ^{79}Br are listed.

7. Elemental Analysis

Microanalysis for carbon, hydrogen and nitrogen were carried out on a Carlo-Erba 1106 elemental analyser operated by Mrs S Smith.

8. Melting Points

Routine melting points were determined using an Electrothermal melting point apparatus while melting points of new compounds were determined on a Reichert hot-stage microscope.

9. Infrared Spectroscopy

Spectra were obtained on a Perkin-Elmer 1420 ratio recording spectrophotometer. Solids were run as nujol mulls and liquids as thin films, both on sodium chloride plates. Spectra were calibrated with the polystyrene peak at 1603 cm^{-1}.

10. Thin Layer Chromatography

This was carried out using 0.2mm layers of silica (Merck, Kieselgel $60F_{254}$) on aluminium sheets. The components were observed under ultraviolet light.

11. Preparative Thin Layer Chromatography

This was carried out using 1.0mm layers of silica (Merck, Kieselgel 60-80 mesh), containing 0.5% Woelm fluorescent green indicator, on glass plates. After locating the components with ultraviolet light, the bands were scraped off and the products removed from the support by soaking in dichloromethane for 3h.

12. Flash Chromatography

This was carried out using Fisons silica gel for chromatography (60-120 mesh).

13. Drying and Evaporation of Organic Solutions

Organic solutions were dried by standing over anhydrous magnesium sulphate and were evaporated under reduced pressure on a rotary evaporator.

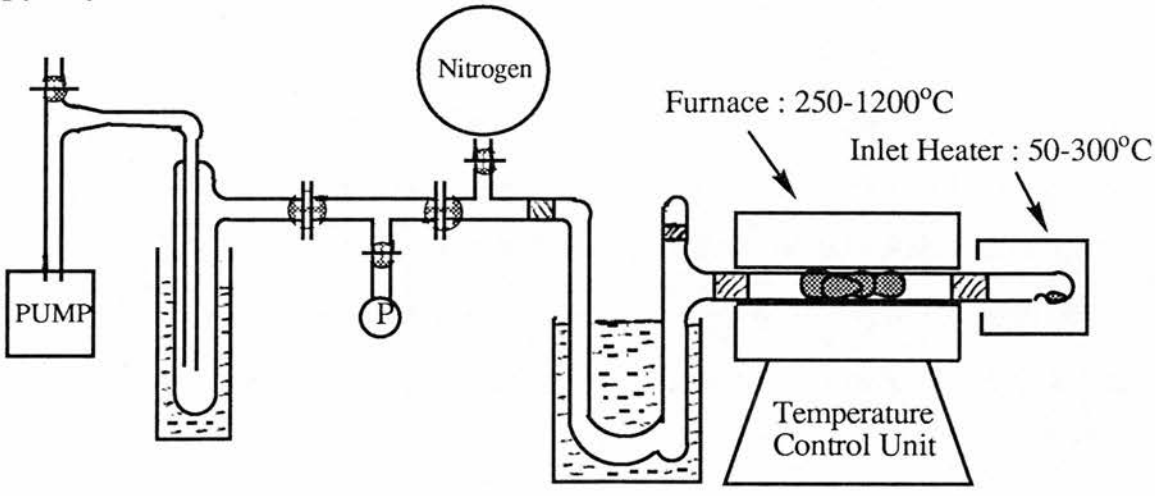
14. Drying and Purification of Solvents

Commercially available solvents were used without further purification unless otherwise indicated. Where pure acetone or carbon tetrachloride were required the commerical Analytical Reagent (A.R) grade solvents were used. Dry absolute ethanol was prepared by heating under reflux with Grignard grade magnesium turnings and iodine for 3h then distilling onto molecular sieves. Dry ether and dry toluene were prepared by the addition of sodium wire. Extra dry tetrahydrofuran was prepared by preliminary drying with sodium wire and then distilling from potassium benzophenone ketyl. Dry N,N-dimethylformamide was prepared by heating under reflux with calcium hydride under a nitrogen atmosphere for 2h then distilling onto molecular sieves. "Petroleum ether" refers to light petroleum, the redistilled 40-60°C boiling fraction being used for chromatography.

15. Flash Vacuum Pyrolysis

The apparatus used was based on the design of W.D. Crow, Australian National University. A similar set up is illustrated in a recent monograph by Brown.[2]

The essential features of the apparatus are shown below. The sample was volatilised from a horizontal inlet tube, heated via an external heat source (unless otherwise indicated) through a 30 x 2.5cm silica tube. Grignard grade magnesium turnings were placed in the middle of the silica tube between two loosely packed 10cm plugs of glass wool. The tube was heated under vacuum to 700°C by a Carbolite Eurotherm Tube Furnace MTF-12/38A, the temperature being measured by a Pt/Pt-13% Rh thermocouple situated at the centre of the furnace. The temperature was then reduced to the pyrolysis temperature, usually 600 or 650°C and after filling the system with nitrogen, the stopper taken off the tube and replaced by the inlet tube. The non-volatile products were collected at the furnace exit and the volatile products collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 10^{-1}-10^{-3}mmHg by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured on a Pirani gauge situated between the trap and the pump. Under these conditions the contact time in the hot zone was estimated to be in the range 1-10ms. For very volatile substrates the adequate contact with magnesium required for complete reaction was achieved either by controlling the pressure through a N_2 gas leak or external freezing of the substrate in a vertical inlet tube during the pyrolysis.



The pyrolyses conditions are quoted as follows: "(weight of material volatilised, furnace temperature, average pressure during the pyrolysis, inlet temperature, weight of magnesium)".

Pyrolysis were generally carried out using 200mg - 2g of material. After the pyrolysis the system was isolated from the pump and filled with nitrogen gas. The products were then dissolved out of the trap in deuteriochloroform (for volatile products) or dichloromethane (for solids, followed by evaporation) and analysed by NMR and GC-MS. Yields were estimated by adding a known amount of benzene, cyclohexane, dichloromethane or 1,2-dichloroethane and comparing the NMR signals; and/or by GC integration of the relative area of each peak.

C. Preparation and Fvp of Aliphatic Halides

1. Haloalkanes

(a) Fvp of neopentyl bromide (1-bromo-2,2-dimethyl-propane)

Fvp of the title compound (1.32g, 600°C, 7.6 x 10^{-1}mmHg, inlet-room temperature, 1.5g magnesium) gave a colourless liquid as product. The product consisted of 2-methylbut-1-ene(33%);δ_H 1.05(3H, t, J 9Hz), 1.7(3H, s), 2.05(2H ,q ,J 9Hz) and 4.65(2H, broad s); δ_C 12.3(C-4), 22.5(C-5), 30.6(C-3), 108.4(C-1) and 147.0(C-2) and 2-methylbut-2-ene (43%); δ_H 1.55(3H, d, J 4Hz), 1.65(3H, s), 1.7(3H, s) and 5.15(1H, q, J 9Hz); δ_C 13.4(C-4),17.3(C-5), 25.6(C-1), 118.5(C-3) and 131.3(C-2). A trace amount of 2-methylpropene; δ_C 24.1($2CH_3$), 110.5(C-1) and 141.6(C-2) was also evident.

(b) Preparation and Fvp of 2-chloro-2,3-dimethylbutane

(i) Preparation of 2-chloro-2,3-dimethylbutane

This was prepared by the method of Whitmore *et al*[163] Pinacolyl alcohol (3,3-dimethylbutan-2-ol, 10.0g, 0.1mol) was added to concentrated hydrochloric acid saturated with HCl gas at –10°C. The tube was sealed and the solution shaken occasionally at room temperature. After a few hours an upper layer separated out and this was allowed to accumulate for 3 days. The upper layer was separated and taken up with ether, washed with concentrated hydrochloric acid and twice with water. The organic layer was dried, concentrated and kugelrohr distillation gave 2-chloro-2,3-dimethylbutane(5.9g, 50%) as a larchrymatory liquid, b.p. 40°C/20mmHg(lit.[163] 116-117.5°C); δ_H 1.0 (6H, d, J 3Hz), 1.5 (6H, s) and 1.5-1.9 (1H, m). The reaction involved a methyl migration to give the more stable tertiary carbonium ion.

(ii) Fvp of 2-chloro-2,3-dimethylbutane

Fvp of the title compound (0.52g, 600°C, 4.2 x 10^{-1}mmHg, inlet - ice-cooled vertical inlet tube, 1.0g magnesium) gave a liquid product. The ^{1}H NMR and GC-MS showed that it consisted of two major compounds namely 2,3-dimethylbut-2-ene(52.3%); δ_H 1.68(s) and 2,3-dimethylbut-1-ene(23.7%); δ_H 1.05(6H, d, J 3Hz), 1.75(3H, m), 2.1-2.5(1H, m) and 4.75(2H,m). Another batch run under the same conditions at 500°C gave 46.3% of 2,3-dimethylbut-2-ene and 37.3% of 2,3-dimethylbut-1-ene.

(c) Preparation and Fvp of 2,3-dichloro-2,3-dimethylbutane

(i) Preparation of 2,3-dichloro-2,3-dimethylbutane

This was prepared from pinacol (2,3-dimethylbutane-2,3-diol). Pinacol (12.0g, 0.1mol) was added to concentrated hydrochloric acid saturated with HCl gas at –10 °C. Work up as in b(i) and kugelrohr distillation gave 2,3-dichloro-2,3-dimethylbutane(10.1g, 64.0%) as a solid, b.p. 80°C/20mmHg(lit.[164] b.p. 136-146°C); δ_H 1.7(s).

(ii) Fvp of 2,3-dichloro-2,3-dimethylbutane

Fvp of the title compound (0.16g, 600°C, 7.0 x 10^{-1}mmHg, inlet - room temperture, 1.0g magnesium) gave a colourless liquid. The ^{1}H NMR of the product showed only 2,3-dimethylbuta-1,3-diene (84.0%); δ_H 1.9(6H, s), 4.95(2H, s) and 5.05(2H, s).

(iii) Fvp of pinacol (2,3-dimethylbutane-2,3-diol)

Fvp of pinacol (0.44g, 600°C, 5.2 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave a liquid, which consisted mainly of acetone(67.2%); δ_H 2.15(s), with small amounts of 2,3-dimethyl-buta-1,3-diene(7.9%); δ_H 1.9(6H, s), 4.95(2H, s) and 5.05(2H, s), 2,3-dimethylbut-2-ene(2.5%); δ_H 1.65(s), 2,3-dimethylbut-1-ene(10.2%); δ_H 1.1(6H, d), 1.6(3H, s), 1.7(1H, m) and 4.8(2H, m) and pinacolone (3,3-dimethylbutan-2-one, 7.0%); δ_H 1.15(9H, s) and 2.1(3H, s). Repeat

pyrolysis under the same conditions at a higher temperature of 700°C, gave only acetone(83.4%) with traces of the other products mentioned above.

Repeat pyrolysis without magnesium (0.56g, 600°C, 3.6 x 10^{-1}mmHg, inlet - room temperature) gave a solid, which was mainly the starting material. Repeat pyrolysis under the same conditions at a higher temperature of 700°C and without magnesium gave a mixture of acetone(20.4%), 2,3-dimethylbutadiene(20.4%), and pinacolone (19.9%), with small amounts of 2,3-dimethylbut-1-ene, 2,3-dimethyl-but-2-ene and starting material.

(d) Fvp of 1,3-dibromopropane

Fvp of the title compound (0.69g, 600°C, 7.0 x 10^{-1}mmHg, inlet - ice-cooled vertical inlet tube, 1.0g magnesium) gave a gaseous product which was trapped with $CDCl_3$. The NMR of the product gave δ_H 0.28(s) and δ_C 3.0; which is indicative of cyclopropane(60.0%). A trace amount of propene gas; δ_H 1.8(3H, d of t, J 3,1Hz), 4.9-5.2(2H, m) and 5.7-6.2(1H, m); δ_C 19.3(C-3), 115.6(C-1) and 133.8(C-2) was also observed.

(e) Fvp of 1,2-dibromopropane

Fvp of 1,2-dibromopropane (0.62g, 600°C, 6.0 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave a gaseous product which was trapped with $CDCl_3$. The ^1H NMR showed that the product consisted mainly of propene(76.6%); δ_H 1.8(3H, d of t, J 3,1Hz), 4.9-5.2(2H, m), and 5.7-6.2(1H, m); with a small amount of 2-bromopropene(11.7%); δ_H 2.2(3H, m) and 5-1-5.2(2H, m).

(f) Fvp of 1,4-dichlorobutane

Fvp of the title compound (0.31g, 600°C, 8.0 x 10^{-1}mmHg, inlet - ice-cooled vertical inlet tube, 1.0g magnesium) gave a liquid with gaseous components, which was trapped with $CDCl_3$. The ^1H NMR of the

product was rather complex but the ^{13}C NMR showed that it consisted of buta-1,3-diene; δ_C 117.6(C-1,C-4) and 137.8(C-2,C-3), but-1-ene; δ_C 13.8(C-4), 26.8(C-3), 113.2(C-1) and 140.6(C-2), but-2-ene; δ_C 17.9(C-1,C-4), and 126.0(C-2,C-3) and cyclobutane; δ_C 22.8. However, the GC-MS of the product indicated the presence of small amounts of various dimeric C_8H_{14} - dienes and - cyclopropyl compounds. The yields were buta-1,3-diene(24.3%), but-1-ene(10.8%), but-2-ene (4.1%) and cyclobutane(2.2%).

(g) Fvp of 1,3-dichlorobutane

Fvp of the title compound (0.64g, 600°C, 8.0 x 10^{-1}mmHg, inlet - ice-cooled vertical inlet tube, 1.0g magnesium) gave a liquid with gaseous components, which was trapped with $CDCl_3$. Both ^1H and ^{13}C NMR were complex, however the main product was clearly buta-1,3-diene; δ_H 5.0-5.2(4H, m) and 6.25 - 6.6(2H, m); δ_C 117.5(C-1,C-4) and 137.9 (C-2,C-4), with small amounts of but-2-ene; δ_C 17.9(C-1,C-4) and 125.0(C-2,C-3) and but-1-ene. However the GC-MS of the product showed it to also contain various dimeric C_8H_{14} - dienes and - cyclopropyl compounds. Determination of yield was rather difficult, but it was estimated that the yield of 1,3-butadiene was about 38.0%.

(h) Fvp of 1,5-dibromopentane

Fvp of the title compound (0.46g, 600°C, 6.4 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave a liquid as product. Both ^1H NMR and GC-MS showed that the product consisted of pent-1-ene (29.4%); δ_H 0.95(3H, t, J 5Hz), 1.5(2H, sextet), 2.1(2H, q), 4.9-5.2 (2H, t of m) and 5.75-6.25(1H, m); m/z 70, penta-1,3-diene(17.7%); δ_H 1.75(3H, d of m, J 3Hz), 4.9-5.2(2H, t of m) and 5.75-6.25(3H, m); m/z 68; and cyclopentane(5.6%); δ_H 1.55(s); m/z 70; with traces of pent-2-ene and penta-1,4-diene. Most of the compounds were further

confirmed with authentic samples, using GC (OV101, 50°C). Repeat pyrolysis under the same conditions but at a temperature of 700°C, gave the same mixture of compounds namely pent-1-ene(23.2%), penta-1,3-diene (18.0%) and cyclopentane(7.2%) with traces of pent-2-ene and penta-1,4-diene; while at 500°C the mixture consisted of pent-1-ene (30.7%), penta-1,3-diene(22.3%), cyclopentane(8.6%), with traces of pent-2-ene and penta-1,4-diene.

(i) Fvp of 1,4-dibromopentane

Fvp of the title compound (0.38g, 600°C, 8.0 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave a liquid as product. Both ^{1}H NMR and GC-MS showed that the product consisted mainly of penta-1,3-diene(46.6%); δ_H 1.75(3H, d of m, J 3Hz), 4.9-5.2(3H, m), and 6.0-6.7(2H, m); m/z 68, a mixture of pent-1-ene and pent-2-ene (18.2%-total) and penta-1,4-diene(6.0%); δ_H 2.75-2.95(2H, m), 4.9-5.3(4H, m) and 5.9-6.5(2H, m). The three major compounds, penta-1,3-diene, pent-1-ene and pent-2-ene were further confirmed with authentic samples using the GC (OV101, 50°C).

(j) Fvp of 1,6-dibromohexane

Fvp of the title compound (1.22g, 600°C, 7.0 x 10^{-1}mmHg, inlet - 60-65°C, 1.2g magnesium) gave a colourless liquid as product. Both ^{1}H NMR and GC-MS showed that the main product was hex-1-ene (72.5%); δ_H 0.9(3H, m), 1.3-1.5(4H, m), 2.1(2H, m), 4.9-5.2(2H, t of m) and 5.7-6.5(1H, m); m/z 84; with small amounts of cyclohexane; δ_H 1.5 and butenes. GC (OV101, 52°C) comparison with authentic samples confirmed both hex-1-ene and cyclohexane.

(k) Fvp of 1,8-dibromooctane

Fvp of the title compound (1.14g, 600°C, 7.8 x 10^{-1}mmHg, inlet - 72-76°C, 1.5g magnesium) gave a liquid product. The ^{1}H NMR was rather complex, however the GC-MS showed that the product consisted of

oct-1-ene(20.4%), hex-1-ene(16.3%), octa-1,7-diene(2.5%), octane (2.1%), cyclooctane(trace) and an unidentified compound with m/z 112 (12.0%) - ethylcyclohexane? All the compounds were confirmed with authentic samples, using the GC (OV101, 52°C). The GC-MS also showed trace amounts of fragmentation products like butenes and butadiene. Yield was determined from GC integration of the relative area of each peak.

2. Haloalkenes

(a) Fvp of 4-bromobut-1-ene

Fvp of the title compound (0.51g, 600°C, 8.0 x 10^{-1}mmHg, inlet - ice-cooled vertical inlet tube, 1.0g magnesium) gave a liquid with gaseous components which was trapped with $CDCl_3$. The ^1H NMR showed peaks mainly in the unsaturated region, indicating that the major product was buta-1,3-diene(58.4%); δ_H 5.0-5.2(4H, m) and 6.25-6.6(2H,m). Other products evident on the ^1H NMR were but-2-ene(10.9%); δ_H 1.7(6H, m) and 5.35(2H, m); and but-1-ene(10.0%); δ_H 1.0(3H, t, J 6Hz), 2.10(2H, m), 5.25-5.6(2H, m), and 6.3-6.7(1H, m). The products were confirmed on the GC-MS, which also showed small peaks corresponding to various C_8H_{14}-diene and -cyclopropyl compounds.

(b) Fvp of 5-bromopent-1-ene

Fvp of the title compound (0.79g, 600°C, 7.6 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave a liquid product with gaseous components, which was trapped with $CDCl_3$. The ^1H NMR and GC-MS showed that the major product was hexa-1,5-diene(53.0%); δ_H 2.15 (4H, m), 4.9-5.1(4H, t of m) and 5.8(2H, m); m/z 82; with small amounts of cyclopentene(8.1%); δ_H 1.8(2H, quintet, J 8Hz), 2.3(4H, t, J 8Hz) and 5.7 (2H, s); m/z 68; and an unidentified compound with m/z 110(6.2%) - (2-propenyl)cyclopentane (?) Both hexa-1,5-diene and cyclopentene were further confirmed with authentic samples, using GC (OV101, 52°C).

(c) Fvp of 6-bromohex-1-ene

Fvp of the title compound (0.17g, 600°C, 7.8 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave a liquid product. The ^{1}H NMR and GC-MS showed that the product consisted mainly of cyclohexene(50.2%); δ_H 1.7(4H, m), 2.05(4H, m) and 5.8(2H, m); m/z 82; three isomers of hexadienes; 1,3-isomer δ_H 1.0(3H, t, C-6), 1,4-isomer δ_H 2.8(2H, m, C-3), 1,5-isomer δ_H 2.15(4H, m, C-3 and C-4) with a combined yield of 22.4%; and methylcyclopentene(4.0%). The major products, cyclohexene and hexa-1,5-diene were further confirmed with authentic samples using the GC (OV101, 52°C).

3. Germinal dihaloalkanes

(a) Fvp of 2,2-dichloropropane

Fvp of the title compound (0.35g, 600°C, 5.6 x 10^{-1}mmHg, inlet - ice-cooled vertical inlet tube, 1.0g magnesium) gave a colourless liquid. The product was found to consist mainly of 2-chloropropene(74.0%); δ_H 2.1-2.2(3H, m) and 5.1-5.2(2H, m); δ_C 26.1(C-3), 112.7(C-1) and 138.8(C-2); m/z 76; with trace amounts of allene; δ_H 4.75(s) and δ_C 73.8(C-1,C-3) and 212.9(C-2) and 2,3-dichloro-2,3-dimethylbutane. A repeat run under the same conditions but with a pressure of 1.0mmHg gave the same mixture of compounds as products namely 2-chloropropene (74.0%), allene(2.4%) and 2,3-dichloro-2,3-dimethylbutane(5.6%).

(b) Preparation and Fvp 1,1-dichloropropane

(i) Preparation of 1,1-dichloropropane

This was prepared from propionaldehyde (10.0g, 0.17mol) and phosphorus pentachloride (35.8g, 0.17mol) in dichloromethane stirred overnight at room temperature. The mixture was poured into water and the organic layer washed with sodium hydrogen carbonate solution, sodium bisulphite solution and water; dried and evaporated. Kugelrohr distillation gave 1,1-dichloropropane (polymerises during distillation) as a

liquid,b.p. 50°C/20mmHg(lit.[165] 88.3 °C); δ_H 1.1(3H, t), 2.0(2H, m) and 5.9(1H, d of t). However, the ^{13}C NMR showed the presence of other compounds in addition to the expected 1,1-dichloropropane, so a commercial sample was used for pyrolysis.

(ii) Fvp of 1,1-dichloropropane

Fvp of the title compound (0.64g, 600°C, 5.8 x 10^{-1}mmHg, inlet - ice-cooled vertical inlet tube, 1.6g magnesium) gave a liquid product. The NMR and GC-MS indicated the presence of the *E* and *Z*-isomers of 1-chloroprop-1-ene(*E*, 27.5%); δ_H 1.8(3H, d, J 2Hz), 5.8-6.3(2H, m); δ_C 16.1(C-3), 117.6(C-2) and 128.8(C-1); m/z 76; and 1-chloroprop-1-ene (*Z*, 49.8%); δ_H 1.7(3H, d, J 2Hz), 5.8-6.3(2H, m); δ_C 12.6(C-3), 119.2(C-2) and 126.3(C-1); m/z 76. Also present were small amounts of 3-chloropropene; δ_C 45.2(C-3), 117.5(C-1) and 134.3(C-2); m/z 76, hexa-1,5-diene; δ_C 33.5(C-3, C-4), 114.8(C-1, C-6) and 138.3(C-2, C-5), 2-chloropropene; δ_C 27.5(C-3), 113.5(C-1) and 141.0(C-2), 1,2-dichloropropane; δ_C 22.5(C-3), 49.6(C-1) and 56.0(C-2); m/z 112; and the starting material; δ_C 10.3(C-3), 37.2(C-2) and 75.1(C-1); m/z 112.

(c) Preparation and Fvp of 1,1-dichlorobutane

(i) Preparation of 1,1-dichlorobutane

This was prepared from butyraldehyde (10.0g, 0.14mol) and phosphorus pentachloride (28.8g, 0.14mol) in dichloromethane, stirred at room temperature overnight. The mixture was poured into water, and the organic layer washed with sodium hydrogen carbonate solution, sodium bisulphite solution and water; dried and evaporated. Kugelrohr distillation gave 1,1-dichlorobutane(5.4g, 30.7%, polymerises during distillation), b.p. 50°C/20mmHg(lit.[165] 114-115°C); δ_H 1.0(3H, t, J 3Hz), 1.6(2H, m), 2.0(2H, m) and 5.95(1H, t, J 3Hz); and δ_C 13.4 (C-4), 18.2(C-3), 40.9(C-2) and 93.5(C-1).

(ii) Fvp of 1,1-dichlorobutane

Fvp of the title compound (0.35g, 600°C, 3.6 x 10^{-1}mmHg, inlet - room temperature, 1.5g magnesium) gave a liquid product. The ^{1}H NMR of the product was simple but the integral was not very informative, δ_H 1.0(t, J 3Hz), 2.15(quintet of m), 4.6(m), 5.2(m) and 6.25 (m), however the ^{13}C NMR showed that it consisted of compounds suspected to be the 3 isomers of octa-3,5-diene - δ_C *E,E*-isomer 14.3(C-1,C-8), 17.6(C-2,C-7), 110.5(C-3,C-6) and 142.6(C-4,C-5), *Z,Z*-isomer 14.9 (C-1,C-8), 17.5(C-2,C-7), 111.3(C-3,C-6) and 142.9(C-4,C-5); and *E,Z*-isomer 14.3, 14.8(C-1,C-8), 20.8(C-2,C-7), 110.1, 111.8(C-3,C-6) and 141.2, 144.0(C-4,C-5).

The GC-MS of the products showed 3 peaks, however only one peak gave a m/z of 110(M^+,28%), 95(20), 81(97), 67(100), 53(47) and 41(48), corresponding to a C_8H_{14} compound. The other 2 peaks gave identical mass spectra fragmentation pattern with m/z 126(M^+,18%), 111(8), 97(5), 81(3), 69(8), 57(40), 55(100) and 39(28), corresponding to a C_9H_{18} compound. The weight of the product was 0.12g, corresponding to a yield of 79.2% assuming the products were octadienes. The main products were the *E,E*- and *E,Z*-isomers, with only a small amount of the *Z,Z*-isomer, based on ^{13}C peak intensity of equivalent carbons.

(d) Preparation and Fvp of 1,1-dichloropentane

(i) Preparation of 1,1-dichloropentane

This was prepared from valeraldehyde (pentanal, 10.0g, 0.12mol) and thionyl chloride (13.8g, 0.12mol) with a catalytic amount of DMF; in dichloromethane. The mixture was heated under reflux for 1h, cooled and evaporated. Kugelrohr distillation gave 1,1-dichloropentane (9.5g, 58.0%) as a light yellow liquid, b.p. 60°C/20mmHg(lit.[166] 139.4-140.2°C); δ_H 0.85(3H, t, J 3Hz), 1.35(4H, m), 1.9(2H, m) and 5.75

(1H, t, J 3Hz); and δ_C 13.5(C-5), 21.8(C-4), 26.6(C-3), 38.4(C-2) and 93.2(C-1).

(ii) Fvp of 1,1-dichloropentane

Fvp of the title compound (0.85g, 600°C, 1.9 x 10^{-1}mmHg, inlet - room temperature, 1.5g magnesium) gave a liquid product. The ^{1}H NMR was not very informative, δ_H 0.9(t of m), 1.3(m), 2.0(m), 4.4(m), 5.0(m) and 6.1(d of m), however the ^{13}C NMR showed that it consisted of compounds suspected to be the 3 isomers of deca-4,6-diene, δ_C *E,E*-isomer 13.4(C-1,C-10), 22.6(C-2,C-9), 25.9(C-3,C-8), 108.1(C-4,C-7) and 142.9(C-5,C-6), *Z,Z*-isomer 13.3(C-1,C-10), 22.0 (C-2,C-9), 35.8(C-3,C-8), 108.9(C-4,C-7) and 143.3(C-5,C-6) and *E,Z*-isomer 13.2, 13.3(C-1,C-10), 23.2, 23.3(C-2,C-9), 25.9, 29.4 (C-3,C-8), 107.7, 109.4(C-4,C-7) and 141.5, 144.3(C-5,C-6). Also present was a very small amount of pent-1-yne, δ_C 13.0(C-5), 20.2 (C-4), 21.8(C-3), 68.0(C-1) and 84.0(C-2).

The GC-MS of the products showed 3 peaks, each with an m/z of 154, corresponding to a $C_{11}H_{22}$ compound. The peaks showed a similar mass fragmentation pattern, m/z 154(M^+,13%), 125(24), 83(18), 69(27), 57(48), 41(100) and 27(22). The weight of the product was 0.32g, corresponding to a yield of 76.2% assuming the products were decadienes. The main products were the *E,E*- and *EZ*-isomers, with only a small amount of the *Z,Z*-isomer, based on ^{13}C peak intensity of equivalent carbons and GC traces.

(e) Preparation and Fvp of 1,1-dichlorohexane

(i) Preparation of 1,1-dichlorohexane

This was prepared from hexan-1-al(10.0g, 0.1mol) and thionyl chloride(12.0g, 0.1mol), with catalytic amounts of DMF. The mixture was kept under reflux for 1h, cooled and evaporated. Kugelrohr distillation gave 1,1-dichlorohexane(12.5g, 80.4%) as a light yellow

liquid, b.p. 65°C/20mmHg(lit.[167] 62-62.5°C/20mmHg); δ_H 0.85 (3H, t, J 3Hz), 1.3(4H, m) 1.4(2H, m), 1.9(2H, m) and 5.75 (1H, t, J 3Hz); and δ_C 12.9(C-6), 21.5(C-5), 23.5(C-4), 30.2(C-3), 38.0(C-2) and 92.6(C-1).

(ii) Fvp of 1,1-dichlorohexane

Fvp of the title compound (0.57g, 600°C, 8.0 x 10^{-2}mmHg, inlet - room temperature, 1.5g magnesium) gave a liquid product. The ^{1}H NMR was not very informative, δ_H 0.9(m), 1.3(m), 1.6-2.1(m), 4.4(m), 5.0(m) and 5.7-6.2(m), however the ^{13}C NMR showed that it consisted of compounds suspected to be the 3 isomers of dodeca-5,7-diene, δ_C *E,E*-isomer 13.8(C-1,C-12), 22.3(C-2,C-11), 23.7(C-3,C-10), 31.8(C-4,C-9), 108.7(C-5,C-8) and 143.0 (C-6,C-7), *Z,Z*-isomer 14.0(C-1,C-12), 22.5(C-5,C-11), 31.3(C-3,C-10), 32.5 (C-4,C-9), 109.5(C-5,C-8) and 143.3(C-6,C-7) and *E,Z*-isomer 13.8 (C-1,C-12), 22.1(C-2,C-11), 27.1(C-3,C-10), 31.9, 32.6(C-4,C-9), 108.2, 109.9(C-5,C-8) and 141.5, 144.4(C-6,C-7). Also present was a very small amount of hex-1-yne.

The GC-MS of the products showed 3 peaks, each with a m/z of 182, corresponding to a $C_{13}H_{26}$ compound. The peaks showed a similar mass fragmentation pattern, m/z 182(M^+,18%), 139(20), 97(20), 82(60), 67(29), 55(100) and 41(48). The weight of the product was 0.21g, corresponding to a yield of 68.1% assuming the products were dodecadienes. The main products were the *E,E*- and *E,Z*-isomer, with only a small amount of the *Z,Z*-isomer, based on ^{13}C peak intensity of equivalent carbons and GC traces.

Pyrolysis of the title compound in the absence of magnesium gave mainly unchanged starting material.

4. Fvp of haloalkynes

(a) 6-Chlorohex-1-yne

Fvp of the title compound (0.47g, 600°C, 5.0 x 10^{-1}mmHg inlet - ice-cooled vertical inlet tube, 1.5g magnesium) gave a liquid. The NMR and GC-MS indicated that the product consisted mainly of 3-methylenecyclopentene(28.3%); δ_H 2.25(4H, m), 4.85(2H, m, vinyl CH_2) and 6.25(2H, broad m); δc 29.1(C-5), 32.4(C-4), 102.3(vinyl CH_2), 128.5(C-1), 139.2(C-2) and 155.0(C-3); m/z 80; and 4-methylene-cyclopentene(22.4%); δ_H 2.55(4H, m), 4.9(2H, m, vinyl CH_2), and 5.75(2H, m); δ_C 33.2(C-3,C-5), 104.8(vinyl CH_2), 134.8(C-1,C-3) and 153.2(C-4); m/z 80. There were also small amounts of cyclohexane; δ_C 22.9(C-4,C-5), 25.4(C-3,C-6), and 127.3(C-1,C-2), cyclo-hexa-1,3-diene; δ_C 22.3(C-5,C-6), 124.5(C-1,C-4) and 126.3(C-2,C-3) and benzene.

(b) 7-chlorohept-1-yne

Fvp of the title compound (0.60g, 600°C, 6.0 x 10^{-1}mmHg, inlet-ice-cooled vertical inlet tube, 1.5g magnesium) gave a liquid product. The ^{1}H NMR of the product was rather complex, however the ^{13}C NMR indicated a major product suspected to be 3-methylenecyclohexene; δ_C 26.4(C-5), 28.4(C-6), 35.5(C-4), 106.6(vinyl CH_2), 128.4(C-1), 132.5(C-2) and 150.1(C-3); ^{1}H NMR showed a doublet at 4.55 (vinyl CH_2). Additional signals suspected to be due to small amounts of 4-methylenecyclohexene; δ_C 27.0(C-6), 29.2(C-3), 32.3(C-5), 110.4(vinyl CH_2), 129.6, 130.3(C-1,C-2) and 143.4(C-4), was also observed. There were numerous small signals on the ^{13}C NMR, which are unassigned. The GC-MS showed two C_7H_{10} and two C_7H_{12} compounds with small amounts of other C_4, C_5 and C_6 compounds. Due to the complex nature of the ^{1}H NMR, it was impossible to determine the yield of the suspected products. Repeat pyrolysis at 500°C under the same conditions gave

mainly the starting materials, in addition to some of the products suspected for the pyrolysis at 600°C.

(c) 8-chlorooct-1-yne

Fvp of the title compound (0.53g, 600°C, 6.0 x 10^{-1}mmHg, inlet-room temperature, 1.5g magnesium) gave a liquid product. The ^{1}H and ^{13}C NMR of the product was complex and peak assignment was impossible. The GC-MS showed a mixture of various compounds ranging from C_4 to C_8 hydrocarbons. Repeat pyrolysis at 500°C under the same conditions gave mainly unreacted starting material, with a complex mixture of unidentified compounds.

5. Vicinal cyclic halides

(a) Preparation and Fvp of 1,2-dibromocyclohexane

(i) Preparation of 1,2-dibromocyclohexane

1,2-Dibromocyclohexane was prepared by direct bromination of cyclohexene[168]. Cyclohexane (10g, 0.12mol) in carbon tetrachloride (150ml) was cooled to –5°C with a salt/ice bath and while effectively stirring, 20g(0.13mol) of bromine in carbon tetrachloride was added dropwise over 2h. The mixture was then allowed to warm up to room temperature and stirred for a further 1h and evaporated. The residual liquid was distilled twice to give the desired dibromocyclohexane(17.3g, 58.6%) as a colourless liquid, b.p. 120°C/20mmHg(lit.[169] 116°C/ 29mmHg). The product was confirmed with the disappearance of the alkene peaks at δ_H 5.6 which was replaced with a peak at δ_H 4.5(m). The product darkens on standing.

(ii) Fvp of 1,2-dibromocyclohexane

Fvp of the title compound (0.82g, 600°C, 9.0 x 10^{-1}mmHg, inlet - 60-65°C, 1.0g magnesium) gave a colourless liquid. The ^{1}H NMR showed peaks identical to those of benzene; δ_H 7.4(s),

cyclohexa-1,3-diene; δ_H 2.15(4H, m) and 5.9(4H,m) and cyclohexene; δ_H 1.65(4H, m), 2.0(4H, m) and 5.75(2H, m). The three compounds were further confirmed with the GC-MS and with authentic samples using the GC (OV101, 52°C). The yields were benzene(28.0%), cyclohexa-1,3-diene(34.8%) and cyclohexene(30.0%).

Repeat pyrolysis of dibromocyclohexane through a tube packed with only glass wool i.e. no magnesium gave a dark liquid which continuously evolved hydrogen bromide gas (tested with aqueous ammonia). The ^{1}H NMR showed only a peak δ_H 7.4(s) corresponding to benzene, this was confirmed on the GC (OV101, 52°C) with an authentic sample. The yield was 78.1%.

(b) Preparation and Fvp of 1,2-dichlorocyclooctane

(i) Preparation of 1,2-dichlorocyclooctane

This was prepared by the method of Ghelfi *et al*[170]. To a stirred suspension of manganese dioxide (7.0g, 75mmol) in a solution of cyclooctene (5.5g, 50mmol) in 50ml THF, trimethylchlorosilane (32.7g, 300mmol) was slowly added. The reaction was initially exothermic but the temperature was maintained at about 40°C with a waterbath. After the addition was completed, the mixture was heated at about 60°C for 1h. The dark purple solution gradually turned colourless. On cooling the mixture was poured into water and extracted with petroleum ether (40/60), and the organic layer dried, evaporated and kugelrohr distillation gave 1,2-dichlorocyclooctane (9.7g, 84%) as a colourless liquid, b.p. 150°C/20mmHg(lit.[170] 105-119°C/10mmHg). The product was confirmed by the ^{1}H NMR which showed the disappearance of the alkene peak which was replaced with a peak at δ_H 4.2(m).

(ii) Fvp of 1,2-dichlorocyclooctane

Fvp of the title compound (0.62g, 600°C, 8.0 x 10^{-1}mmHg, inlet - 60-65°C, 1.0g magnesium) gave a liquid whose ^{1}H NMR spectrum was

rather complex. GC-MS of the product was also complex consisting of compounds with m/z108 (C_8H_{12}, 7 isomers), m/z 110(C_8H_{14}), m/z 106 (C_8H_{10}), m/z 96(C_7H_{12}) and traces of benzene, toluene and cyclohexadiene. Repeating the pyrolysis at a lower temperature of 500°C gave a liquid product whose ^1H NMR and GC-MS were better than from previous experiment but still complex. Products obtained were cyclooctene(28.4%), compound with m/z 110(4.5%), and compounds with m/z 108(5-isomers with combined yield of 35.3%); with traces of other compounds. In both experiments no halogenated products were observed.

Repeating the pyrolysis at 600°C without magnesium (tube packed with only glass wool) gave a bright yellow liquid which darkened on exposure to air, with vigorous evolution of HCl gas (test with NH_3 (aq)). The products obtained were cycloocta-1,3-diene(28.4%), m/z 108; chlorocyclohexene(16.0%), m/z 116; 1-chlorocyclooct-1-ene and 3-chlorocyclooct-1-ene(29.0%, total), m/z 144; with traces of benzene, toluene and compounds with m/z 108. When the pyrolysis was carried out at 500°C without magnesium, the product were cycloocta-1,3-diene (25.7%), m/z 108; and four compounds with the same m/z as chlorocyclooctene(m/z 114, combined yield of 55.5%); with only a trace of chlorocyclohexene. Identification and yield of all products was based on GC-MS evidence only.

D. Preparation and Fvp of Benzylic halides

1. Fvp of benzyl halides

(a) Fvp of benzyl chloride over magnesium

Fvp of the title compound (1.0g, 600°C, 1.0 x 10^{-1}mmHg, inlet-room temperature, 1.0g magnesium) gave a product which consisted of two fractions, a liquid part down the cold trap and a solid part at the furnace exit. The liquid was carefully removed with a pipette using $CDCl_3$, while the solid was dissolved out with dichloromethane and the solvent evaporated. The ^1H NMR showed that the liquid was toluene(16.1%); δ_H 2.25(3H, s) and 7.1(5H, s), while the solid was mainly bibenzyl. However GC-MS showed that the solid also contained small amounts of stilbene(3.8%); m/z 180 and diphenylmethane(5.8%); m/z 168. All products were further confirmed with authetic samples using the GC(NPGS, 170°C). Recrystallisation of the solid from ethanol gave pure bibenzyl(58.1%), m.p. 52.5-53.0°C(lit.[171] 52°C); δ_H 2.95 (2H, s) and 7.35(5H, s); δ_C 37.9(CH_2), 125.9(C-4), 128.3(2C), 128.4(2C) and 141.8(C-1); m/z 182.

(b) Fvp of benzyl bromide over magnesium

Fvp of the title compound (1.0g, 600°C, 2.0 x 10^{-1}mmHg, inlet-room temperature, 1.0g magnesium) gave a product which consisted of two fractions, a liquid and a solid. The ^1H NMR indicated that the liquid fraction was toluene(20.5%), while the solid fraction consisted of bibenzyl(68.7%), stilbene(2.5%) and diphenylmethane(1.1%). All compounds were further confirmed with authentic samples using the GC(NPGS, 170°C). Pure bibenzyl, m.p. 53-53.5°C, was obtained by recrystallisation of the solid product from methanol.

(c) Determination of available magnesium using excess benzyl chloride

Fvp of benzyl chloride (3.1g, 600°C, 4.2 x 10^{-1}mmHg, inlet-room temperature, 1.0g magnesium) gave a mixture of solid and liquid as product. The ^{1}H NMR integration indicated a 37.4%(1.16g) recovery of starting material. Therefore the amount of reacted benzyl chloride was 15.3mmol(1.9/126.5). Assuming 1 mole of magnesium reacts with 2 moles of benzyl chloride, for 1g of Mg(41.1 mmol) therefore, the percentage of magnesium available for reaction is about 20%(15.3/82.2).

(d) Fvp of benzyl chloride over calcium

Fvp of the title compound (0.70g, 800°C, 1.8 x 10^{-1}mmHg, inlet-room temperature, 4.0g calcium) gave a liquid product. The ^{1}H NMR and GC-MS showed that the product consisted of only toluene(42.9%); δ_H 2.3(3H, s), and 7.25(5H, s); m/z 92 and benzene(11.4%); δ_H 7.4 (s); m/z 78.

(e) Fvp of benzyl chloride over zinc

Fvp of the title compound (0,60g, 400°C, 6.4 x 10^{-1}mmHg, inlet-room temperature, 5.0g zinc) gave a liquid product. The ^{1}H and GC-MS showed that it consisted of only toluene(32.0%); δ_H 2.3(3H, s) and 7.25(5H, s); m/z 92, bibenzyl(7.3%); δ_H 2.9(4H, s) and 7.3(10H, s); m/z 182 and diphenylmethane(5.0%); δ_H 3.95(2H, s) and 7.3(10H, s); m/z168.

2. Substituted benzylic halides

(a) α-Haloxylenes

(i) Fvp of α-bromo-*o*-xylene(2-methylbenzyl bromide)

Fvp of the title compound (1.0g, 600°C, 1.5 x 10^{-1}mmHg, inlet - 60-65°C, 1.0g magnesium) gave a product which consisted of two fractions, a liquid and a solid. The ^{1}H NMR and GC(NPGS, 80°C)

analysis showed that the liquid consisted of *o*-xylene(19.7%); δ_H 2.1 (6H, s) and 6.9(4H, s) and small amount of benzocyclobutene(2.9%); δ_H 3.0(4H, s) and 6.85(4H, s). The ^1H NMR and GC-MS of the solid fraction showed that it contained 1,2-di(*o*-tolyl)ethane (2,2'-dimethylbibenzyl, 69.5%) and 2,2'-dimethylstilbene(1.3%). Recrystallisation from methanol gave pure 1,2-di(*o*-tolyl)ethane, m.p. 66-67°C(lit.[172] 65°C); δ_H 2.3(6H, s), 2.9(4H, s) and 7.25(8H, s); δ_C 19.3(CH_3), 34.1(CH_2), 126.0 and 126.1(C-4, C-5), 128.8 and 130.2 (C-3,C-6), 135.9(C-2), and 140.1(C-1); m/z 210.

(ii) Fvp of α-chloro-*p*-xylene(4-methylbenzyl chloride)

Fvp of the title compound (1.0g, 600°C, 6.0 x 10^{-1} mmHg, inlet-room temperature, 1.0g magnesium) gave a faint yellow solid as product. The ^1H NMR and GC-MS showed that the product consisted of *p*-xylene (23.0%); δ_H 2.2(6H, s) and 6.9(4H, s); m/z 106(confirmed with authentic sample using the GC - NPGS, 80°C); and 1,2-di(*p*-tolyl)ethane (4,4'-dimethylbibenzyl, 60.0%) with small amounts of 4,4'-dimethylstilbene(1.7%); m/z 208. Recrystallisation of the solid product from methanol gave a crystalline faint yellow solid, which was pure 1,2-di(*p*-tolyl)ethane, m.p. 81-83°C(lit.[173] 82°C); δ_H 2.35(6H, s), 2.9(4H, s) and 7.2(8H, s); δ_C 21.0(CH_3), 37.6(CH_2), 128.3(C-2,C-6), 129.0(C-3,C-5), 135.3(C-4) and 138.8(C-1); m/z 210.

(b) Preparation and Fvp of 4-methoxybenzyl chloride

(i) Preparation of 4-methoxybenzyl chloride

The title compound was prepared from 4-methoxybenzyl alcohol and thionyl chloride. To a solution of the alcohol (9.0g, 65mmol) in dichloromethane, thionyl chloride (5ml, 8.15g, 68.5mmol) in dichloromethane was slowly added through a dropping funnel. Instant reaction was observed. After the addition, the mixture was heated under reflux on a waterbath for about 1h. On cooling it was poured into

ice-water and the organic layer separated, dried and evaporated. Kugelrohr distillation gave 4-methoxybenzyl chloride(7.82g, 76.6%) as a colourless liquid, b.p. 90°C/0.5mmHg(lit.[174] 116-120°C); δ_H 3.7(3H, s), 4.5(2H, s), 6.8 and 7.1(4H, AB pattern, J 4Hz).

(ii) Fvp of 4-methoxybenzyl chloride

Fvp of the title compound (0.42g, 600°C, 3.6 x 10^{-2}mmHg, inlet-room temperature, 0.5g magnesium) gave a product, which consited of a liquid and a solid fraction. The ^{1}H NMR and GC-MS of the liquid fraction showed that it contained mainly 4-methylanisole; δ_H 2.1(3H, s), 3.65(3H, s) and 6.7-7.4(4H, m); m/z 122, 4-ethylanisole; δ_H 1.15(3H, t, J 5Hz), 2.55(2H, q, J 4Hz), 3.6(3H, s) and 6.7-7.4(4H, m); m/z 136, *p*-cresol; m/z 108, toluene; m/z 92 and anisole; m/z 108. It was impossible to determine the yield of these compounds as both GC traces and ^{1}H NMR peaks overlapped with each other. The solid fraction was mainly insoluble polymer flakes, but the dichloromethane soluble part gave a green solid. The ^{1}H NMR and GC-MS of the soluble solid fraction showed that it contained mainly 4,4'-dimethoxybibenzyl(14.3%); δ_H 2.9 (4H, s), 3.7(6H, s) and 6.75 and 7.05(8H, AB pattern, J 4Hz); m/z 242, with small amounts of *p*-cresol(1.4%); m/z 108, bis(4-methoxy-phenyl)methane(1.1%), 4,4'-dimethoxystilbene(0.7%) and other components(<0.5%). Yield of each compound was determined by GC integration.

(c) Halo-benzyl halides

(i) Fvp of 2-fluorobenzyl chloride

Fvp of the title compound (0.34g, 600°C, 2.0 x 10^{-2}mmHg, inlet-ice cooled vertical inlet tube, 0.5g magnesium) gave a product which consisted of two fractions, a solid and a liquid. The ^{1}H NMR and GC-MS of the liquid showed that it consisted of toluene(5.3%); δ_H 2.3(3H, s), and

7.2(5H, s); m/z 92 and 2-fluorotoluene(7.4%); δ_H 2.25(3H, d, J 2Hz) and 7.1(4H, m); m/z 110. The solid product contained mainly 2,2'-difluorobibenzyl(73.1%), with small amount of 9,10-dihydrophenanthrene (4.6%); m/z 180. Recrystallisation of the solid from ethanol gave pure 2,2'-difluorobibenzyl, m.p. 39-40°C(lit.[175] 40-41°C); δ_H 3.0(4H, s) and 7.0-7.4(8H, m); δ_C 29.7(CH_2), 115.2(C-3, d, J 22Hz), 123.9(d, J 3Hz), 127.8(d, J 8Hz), 128.3(C-1, d, J 12Hz), 130.7(d, J 5Hz) and 161.2 (C-2, d, J 245Hz); δ_F –90.6(d, J 11Hz); m/z 218.

Variations in the pressure (ie contact time) gave varied product composition and yield - see table 1.

(ii) Fvp of 2-fluorobenzyl bromide

Fvp of the title compound (0.38g, 600°C, 4.0 x 10^{-2}mmHg, inlet - cooled vertical inlet tube, 0.5g magnesium) gave two fractions, a liquid and a solid. The ^{1}H NMR and GC(NPGS, 170°C) of the liquid showed the presence of toluene(3.6%) and 2-fluorotoluene(11.0%); while the solid consisted of 2,2'-difluorobibenzyl(79.8%) and 9,10-dihydrophenanthrene (3.0%). Variations in the product composition and yield were observed with change in pressure - see Table 1. Recrystallisation of the solid product from ethanol gave pure 2,2'-difluorobibenzyl, m.p. 40°C(lit.[175] 40-41°C).

(iii) Fvp of 3-fluorobenzyl chloride

Fvp of the title compound (0.28g, 600°C, 1.1mmHg, inlet - ice cooled vertical inlet tube, 0.5g magnesium) gave two fractions, a liquid and a semi-solid. The ^{1}H NMR and GC-MS of the liquid showed the presence of only 3-fluorotoluene(19.1%); δ_H 2.25(3H,s) and 6.8-7.2 (4H,m); m/z 110, while the solid consisted of 3,3'-difluorobibenzyl (59.0%), bibenzyl(5%); m/z 182, and 3,3'-difluorostilbene(1.7%); m/z 216. Variations in the product composition and yield were observed with change in pressure see Table 1. Attempted recrystallisation from

ethanol gave a low melting solid which did not crystallise out properly, however the spectra of the waxy-solid obtained showed that it was pure 3,3'-difluorobibenzyl, m.p. 32-34°C(lit.[175] 32-33°C); δ_H 2.9(4H, s), and 6.8-7.5(8H, m); δ_C 37.2(CH_2), 112.9(d, J 21Hz), 115.3(d, J 21Hz), 124.1(d, J 2Hz), 129.8(d, J 8Hz), 143.8(C-1, d, J 7Hz) and 162.9 (C-3, d, J 245Hz); δ_F –86.6(t, J 7Hz); m/z 218.

(iv) Fvp of 3-fluorobenzyl bromide

Fvp of the title compound gave similar products to 3-fluorobenzyl chloride, which are 3-fluorotoluene(12.1%), 3,3'- difluorobibenzyl (67.0%), 3,3'-difluorostilbene(4.9%), bibenzyl(2.9%) and 3-fluoro-bibenzyl(2.3%). Similar variations in product composition and yield were also observed with change in pressure - see Table 1.

(v) Fvp of 4-fluorobenzyl chloride

Fvp of the title compound (0.39g, 600°C, 7.0 x 10^{-2}mmHg, inlet - ice cooled vertical inlet tube, 0.5g magnesium) gave two fractions, a liquid and a solid. The ^{1}H NMR and GC-MS of the products showed the presence of toluene(6.0%) and 4-fluorotoluene(5.1%); δ_H 2.5(3H, s) and 6.7-7.2(4H, m); m/z 110 in the liquid fraction; and 4,4'-difluorobibenzyl (63.3%), 4-fluorobibenzyl(4.8%); m/z 200, and bibenzyl(2.1%); m/z 182, in the solid fraction. Variation in the product composition and yield was observed with change in pressure - see Table 1. Recrystallisation of the solid from ethanol gave pure 4,4'-difluorobibenzyl, m.p. 92-93°C (lit.[175] 90°C); δ_H 2.9(4H, s) and 7.0-7.25(8H, m); δ_C 37.1(CH_2), 115.0, (C-2, C-6, d, J 5Hz); 129.8(C-3, C-5, d, J 8Hz), 137.0(C-1) and 161.4 (C-4, d, J 244Hz); δ_F –92.1(t, J 19Hz); m/z 218.

(vi) Fvp of 4-fluorobenzyl bromide

Fvp of the title compound gave a similar product to 4-fluorobenzyl chloride, which are 4,4'-difluorobibenzyl(73.4%), 4-fluorobibenzyl (6.1%), bibenzyl(1.2%) 4-fluorotoluene(11.5%) and toluene(4.9%).

Similar variations in the product composition and yield were also observed with change in pressure - see table 1.

(vii) Fvp of 2-chlorobenzyl chloride

Fvp of the title compound (0.39g, 600°C, 4.0 x 10^{-1}mmHg, inlet-room temperature, 0.5g magnesium) gave two fractions, a liquid and a solid. The ^{1}H NMR and GC-MS of the liquid showed the presence of mainly 2-chlorotoluene(17.5%); δ_H 2.3(3H, s), and 7.0-7.3(4H, m); m/z 126; with a small amount of toluene(1.8%). The solid product consisted mainly of 2,2'-dichlorobibenzyl(66.1%). Variations in the product composition and yield were observed with change in pressure - see table 1. Recrystallisation of the solid from ethanol gave pure 2,2'-dichlorobibenzyl, m.p. 61-62°C(lit.[176] 62°C); δ_H 3.1(4H, s) and 7.2-7.6(8H, m); δ_C 33.7(CH_2), 126.7, 127.5, 129.5, 130.6, 134.0 (C-2) and 139.0 (C-1); m/z 251.

(viii) Fvp of 4-chlorobenzyl chloride

Fvp of the title compound (1.0g, 600°C, 1.8 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave two fractions, a liquid and a solid. The ^{1}H NMR and GC-MS of the liquid showed the presence of toluene(3.9%), and 4-chlorotoluene(5.5%) while the solid consisted of 4,4'-dichlorobibenzyl(37.0%), bibenzyl(6.2%), stilbene(5.6%), 4-chloro-bibenzyl(3.9%) and 4,4'-dichlorostilbene(1.1%). Variations in the product composition and yield were observed with change in pressure - see Table 1. Recrystallisation from ethanol gave pure 4,4'-dichlorobibenzyl, m.p. 100-101°C(lit.[177] 100°C); δ_H.2.9(4H, s), 7.0(4H, AB pattern, J 4Hz) and 7.2(4H, AB pattern, J 4Hz); δ_C 37.0(CH_2), 128.5(2C), 128.9(C-1), 129.8(2C) and 139.6(C-4); m/z 251.

(ix) Fvp of 2-bromobenzyl bromide

Fvp of the title compound (0.41g, 600°C, 2.0 x 10^{-3}mmHg, inlet - room temperature, 0.5g magnesium) gave two fractions, a liquid and a solid. The ^{1}H NMR and GC-MS of the liquid showed the presence of 2-bromotoluene(24.0%); δ_H 2.3(3H,s) and 7.0-7.4(4H,m); m/z 171 and toluene(2.5%). The solid product consisted of 2,2'-dibromobibenzyl (51.1%), phenanthrene(6.3%), 9,10-dihydrophenanthrene(2.3%) and bibenzyl(3.3%); the presence of the last three was further confirmed with authentic samples using the GC(OV101, 200°C). Variations in the pressure (ie contact time) gave varied product composition and yield - see Table 1. Recrystallisation of the solid product from ethanol gave a grey solid, which was pure 2,2'-dibromobibenzyl, m.p. 84-86°C(lit.[178] 83-84°C); δ_H 3.1(4H, s), 7.3(6H, m) and 7.7(2H, d of m); δ_C 36.4(CH_2), 124.5(C-2), 127.4, 127.8, 130.6, 132.8 and 140.5(C-1); m/z 340.

(x) Fvp of 4-bromobenzyl bromide

Fvp of the title compound (0.31g, 600°C, 8.0 x 10^{-3}mmHg, inlet - room temperature, 0.5g magnesium), gave two fractions, a liquid and a solid. The ^{1}H NMR and GC-MS of the liquid consisted mainly of 4-bromotoluene(28.1%); δ_H 2.3(3H, s) and 6.8-7.2(4H, m); m/z 171 and a small amount of toluene. The solid product consisted mainly of 4,4'-dibromobibenzyl(43.1%). Variations in the pressure (ie contact time) gave varied product composition and yield - see Table 1. Recrystallisation of the solid product from ethanol gave white solid of 4,4'-dibromobibenzyl, m.p. 117-118°C(lit.[179] 114°C); δ_H 2.9(4H, s), 7.1(4H, m) and 7.5(4H, m) and 7.5(4H, m); δ_C 37.2(CH_2), 119.8(C-4), 130.2(2C), 131.4(2C) and 140.1(C-1); m/z 340.

(xi) Fvp of 2-Iodobenzyl chloride

Fvp of the title compound (0.35g, 600°C, 6.0 x 10^{-1}mmHg, inlet - room temperature, 0.5g magnesium) gave two solid fractions, one down

the cold trap and the other at the furnace exit. The ^1H NMR and GC (OV101, 200°C) - comparison with authentic sample, of the former showed that it contained 9,10-dihydrophenanthrene and phenanthrene with only a trace amount of 2-iodotoluene; while the second solid fraction consisted manily of 2,2'-diiodobibenzyl, 9.10-dihydrophenanthrene and phenanthrene. The presence of the latter two were confirmed with authentic samples on the GC. The yield of products based on GC integrals are 2,2'-diiodobibenzyl(40.2%), 9,10-dihydrophenanthrene (30.7%); δ_H 2.8 (4H, s) and 7.0-7.5 (8H, m); m/z 180, phenanthrene (12.4%); m/z 178, bibenzyl(4.1%), monoiodostilbene(2.6%) and trace of 2-iodotoluene. Variations in the product composition and yield were observed with change in pressure - see Table 1. Pure 2,2'-diiodobibenzyl was obtained by recrystallisation of the second solid from ethanol, m.p. 102-103°C(lit.[180] 101.5-102°C); δ_H 3.05(4H, s), 6.9-7.15(2H, m), 7.25-7.45(4H, m) and 7.9-8.1(2H, d of m); δ_C 41.8(CH_2), 101.2 (C-2) 128.5, 128.9, 130.3, 140.0 and 144.2; m/z 434.

(d) Preparation and Fvp of 2,3,4,5,6-pentafluorobenzyl chloride

(i) Preparation of 2,3,4,5,6-pentafluorobenzyl chloride

To a solution of 2,3,4,5,6-pentafluorobenzyl alcohol (8.3g, 42mmol) in ether, a catalytic amount of DMF and thionyl chloride (5 ml, 8.15 g, 68.5mmol) was slowly added with effective stirring. The solution was then heated for 1h on a waterbath. On cooling it was poured into ice-water and the organic layer separated, dried and evaporated. Kugelrohr distillation of the residue gave 2,3,4,5,6-pentafluorobenzyl chloride (79.9%) as a colourless liquid, b.p. 50°C/1.0mmHg(lit.[181] 156-157°C); δ_H 4.5 (broad s); m/z 217.

(ii) Fvp of 2,3,4,5,6-pentafluorobenzyl chloride

Fvp of the title compound (0.44g, 600°C, 6.0mmHg - with N_2 gas leak, inlet-room temperature, 0.5g magnesium) gave two fractions of products, a liquid and a white solid. The NMR of the liquid showed only 2,3,4,5,6-pentafluorotoluene(22.8%); δ_H 2.2-2.3(m) while the solid product was 2,2',3,3',4,4',5,5',6,6'-decafluorobibenzyl(34.8%), m.p. 109-110°C(lit.[181] 107-108°C); δ_H 3.10(broad s); δ_C 22.5(CH_2), the other peaks were complex because of fluorine coupling; δ_F –117.7(m), –129.2(m) and –135.5(m); m/z 362.

(e) Fvp of halodiphenylmethanes (benzhydryl halides)

(i) Fvp of chlorodiphenylmethane(benzhydryl chloride)

Fvp of the title compound (0.40g, 600°C, 4 x 10^{-3}mmHg, inlet-room temperature, 0.5g magnesium) gave two solid fractions, one in the cold trap and the other in the inlet heater. The solid in the cold trap was a mixture of diphenylmethane; δ_H 3.95(2H, s) and 6.95-7.0(10H, s); δ_C 41.9, 126.0, 128.4, 128.9, and 141.0; m/z 168, and 1,1,2,2-tetraphenylethane; while the second solid was mainly 1,1,2,2-tetraphenylethane. The GC-MS confirmed the products and the yield was diphenylmethane(19.5%) and 1,1,2,2-tetraphenylethane (70.8%). Pure 1,1,2,2-tetraphenylethane was obtained by recrystallisation of the second fraction from ethanol, m.p. 214°C (lit.[182] 213°C); δ_H 4.8(1H, s) and 7.0-7.3(10H, m); δ_C 55.3, 124.8, 127.1, 127.5 and 142.4; m/z 334.

(ii) Fvp of bromodiphenylmethane (benzhydryl bromide)

Fvp of the title compound (difficult to volatilise) gave the same product mixture as chlorodiphenylmethane, namely diphenylmethane (18.5%) and 1,1,2,2-tetraphenylethane(61.0%).

3. α,α'-Dihaloxylenes

(a) Fvp of α,α'-dichloro-*o*-xylene

Fvp of α,α'-dichloro-*o*-xylene (0.6g, 600°C, 7.5 x 10^{-1}mmHg, inlet - 60-65°C, 1.5g magnesium) gave a liquid as the major product, with a small amount of semi-solid. The ^{1}H NMR and GC-MS of the liquid showed that it consisted of bicyclo[4.2.0]octa-1,3,5-triene (benzocyclobutene, 72.6%); δ_H 3.15(4H, s) and 7.0-7.25(4H, m); m/z 106, *o*-xylene (15.3%); δ_H 2.2(6H, s) and 7.0-7.25(4H, m); m/z 106 and a trace of toluene. The small amount of semi-solid consisted of a complex mixture of dimeric products like dimethylbibenzyl, dimethylstilbene and 1,2,5,6-dibenzocyclooctadiene.

(b) Fvp of α,α'-dichloro-*p*-xylene

Fvp of the title compound (1.05g, 600°C, 6.4 x 10^{-1}mmHg, inlet-room temperature, 1.2g magnesium) gave a yellow polymer, which was insoluble in conventional solvents. Microanalysis of the polymer gave C, 66.9; H, 5.9. C_8H_7Cl requires C, 69.3; H, 5.1% - indicative of poly(α-chloro-*p*-xylylene). Based on the microanalysis result, the yield of the polymer was 61.2%(0.51 g). Thermal analysis on the material showed that it was stable in N_2 atmosphere up to 360°C and in air up to 300°C, after which there was a gradual weight loss to between 550- 600°C at which it decomposed. The degradation point in N_2(360°C) was sharp while in air(300°C) it was gradual.

Repeat pyrolysis under different conditions (0.72g, 600°C, 2.8 x 10^{-2}mmHg, inlet-room temperature, 2.0g magnesium) gave a white brittle polymer, which was also insoluble in conventional solids. Microanalysis of the material gave C, 90.0; H, 7.8. C_8H_8 requires C, 92.3; H, 7.7%. Based on the microanalysis result, the yield of the polymer material was 71.6%(0.31g). Solid state ^{13}C NMR of the material, δ_C 39.9(CH_2), 129.3(C-2,C-3,C-5,C-6), 139.7 and 141.4

(C-1,C-4) - indicative of poly(*p*-xylylene). Using a small CH_3(δ_C 21.1) end group measurement, the polymer was estimated to consist of 21 units, giving an approximate molecular weight of 2184. Thermogravimetric analysis showed that the polymer was stable up to 520°C in nitrogen and 480°C in air; there was no weight loss in nitrogen up to 520°C while in air a steady loss of about 40% weight was observed between 300500°C.

(c) Preparation and Fvp of α,α'-dibromo-4-fluoro-*o*-xylene

(i) Preparation of 4-fluoro-*o*-xylene

4-Amino-*o*-xylene (60.0g, 0.5mol) was dissolved in concentrated hydrochloric acid (126ml) and water (126ml) in a beaker fitted with a mechanical stirrer. While stirring, it was cooled to 0 - 5°C with a salt/ice bath and a solution of sodium nitrite (38.0g, 0.56mol) in water (150ml) was slowly added, keeping the temperature below 5 °C. The diazotisation was completed after 5 mins (turned KI-starch paper to instant blue). To the diazonium solution was slowly added a chilled solution of sodium tetrafluoroborate (76.0g, 0.7mol) in water (150ml) while stirring and keeping the temperature at about 5°C. After 10 min, the xylene diazonium fluoroborate salt was filtered with suction on a Buchner funnel, drained well and washed with 50ml ice water, 40ml methanol and 50ml of ether; the solid was sucked free of liquid after each washing. The salt was spread on a filter paper and allowed to dry out in a desiccator overnight.

Half of the xylene diazonium fluoroborate salt was taken in a round bottom flask connected to a condenser attached to two ice-cooled two-necked receiver flask, with the last flask connected to an inverted funnel (via a rubber tubing) immersed in a 10% sodium hydroxide solution in a beaker. The salt was slowly decomposed by heating with a flame and cautious heating was continued from time to time as was

necessary to keep the reaction going. When the decomposition was completed, the flask was heated strongly to drive off any remaining fluoroxylene. The second half was similarly decomposed and the combined distillate from the receiver flasks was washed thrice with a 10% solution of sodium hydroxide (to remove any HF) and twice with saturated sodium chloride solution.[183]. The residue was taken up in ether, washed twice with water, and the organic layer dried, evaporated and Kugelrohr distillation gave 4-fluoro-*o*-xylene(34.5g, 56.1%) as a colourless liquid, b.p. 60 °C/20mmHg(lit.[184] 143-144 °C/730mmHg); δ_H 2.1(6H, broad s) and 6.6-7.1(3H, m); δ_C 18.8, 19.7, 112.4 (d, J 21Hz), 116.4(d, J 21Hz), 130.85(d ,J 8Hz), 132.1(d, J 3Hz), 138.7 (d, J 7Hz) and 161.6(d, J 242Hz); m/z 124.

(ii) Preparation of α,α'-dibromo-4-fluoro-*o*-xylene

To 4-fluoro-*o*-xylene (6.2g, 50mmol) in carbon tetrachloride was slowly added bromine (17.0g, 110mmol) in carbon tetrachloride. While adding the bromine, the mixture was photolysed with a 125W mercury lamp under reflux at 110°C, for about 4h[186]. On cooling, the solvent was evaporated and Kugelrohr distillation gave α,α'-dibromo-4-fluoro-*o*-xylene(10.8g, 76.6%) as a colourless lachrymatory liquid (solidified on standing), m.p. 61 °C(lit.[186] 60°C); δ_H 4.6(2H, s), 4.65(2H, s), 7.0 (2H, m) and 7.3(1H, m); δ_C 29.0, 29.2, 116.2(d, J 21Hz), 117.8 (d, J 23Hz), 132.3(d, J 3Hz), 132.8(d, J 9Hz), 138.8(d, J 8Hz) and 162.4 (d, J 250Hz); m/z 282.

(iii) Fvp of α,α'-dibromo-4-fluoro-*o*-xylene

Fvp of the compound (1.27g, 600°C, 2.0 x 10^{-2}mmHg, inlet - 60°-65°C, 1.6g magnesium) gave a colourless liquid which consisted of 4-fluorobenzocyclobutene(79.7%) and 4-fluoro-*o*-xylene(8.1%). Kugelrohr distillation gave pure 4-fluorobenzocyclobutene, b.p. 60°C/ 20 mmHg(lit.[187] 153-154 °C/760mmHg); δ_H 2.95(4H, s), 6.6

(1H, d of d) and 6.75(2H, m); δ_C 28.9, 29.0(d, J 2Hz), 110.5 (d, J 22Hz), 114.2(d, J 23Hz), 124.1(d, J 9Hz), 140.8(d, J 3Hz), 147.0 (d, J 7Hz) and 163.0(d, J 243Hz); m/z 122.

(d) Preparation and Fvp of α,α'-dibromo-3-fluoro-*o*-xylene

(i) Preparation of 3-fluoro-*o*-xylene

This was prepared[183] as for 4-fluoro-*o*-xylene, from 3-amino-*o*-xylene(60.0g) to give the xylene diazonium fluoroborate salt. The salt could not be dried overnight as it readily decomposed: instead it was thoroughly dried by suction immediately after preparation and decomposed as for 4-fluoro-*o*-xylene. Kugelrohr distillation gave 3-fluoro-*o*-xylene(28.7g, 46.7%) as a colourless liquid, b.p. 60 °C/ 20 mmHg(lit.[186] 60 °C/26mmHg); δ_H 2.1(3H, d, J 2Hz), 2.15(3H, s) and 6.8-7.1(3H, m); δ_C 10.6(d, J 6Hz), 19.5(d, J 3Hz), 112.7(d,J 23Hz), 123.6 (d, J 16Hz), 125.3(d, J 2Hz), 126.5(d, J 9Hz), 139.2(d, J 4Hz) and 161.7 (d, J 242.7Hz); m/z 124.

(ii) Preparation of α,α'-dibromo-3-fluoro-*o*-xylene

This was prepared as for α,α'-dibromo-4-fluoro-*o*-xylene, by photolysis of 3-fluoro-*o*-xylene(6.2g, 50mmol) and bromine(17.0g; 110mmol) in carbon tetrachloride at 110°C.[185] Work up and kugelrohr distillation gave α,α'-dibromo-3-fluoro-*o*-xylene(11.9g, 84.4%) as a colourless lachrymatory liquid (solidified on standing), m.p. 41-42°C (lit.[188] 41-42.5°C); δ_H 4.75(2H, s), 4.8(2H, d, J 2Hz), and 7.0-7.5 (3H, m); δ_C 21.0(d, J 7Hz), 28.9(d, J 3Hz), 116.2(d, J 22Hz), 125.0 (d, J 15Hz), 127.1(d, J 3Hz), 131.1(d, J 10Hz), 139.3 and 161.7 (d, J 250Hz); m/z 282.

(iii) Fvp of α,α'-dibromo-3-fluoro-*o*-xylene

Fvp of the title compound (1.04g, 600°C, 2.0 x 10^{-1}mmHg, inlet - 60-65°C, 1.5g magnesium) gave a liquid product, which consisted of 3-fluorobenzocyclobutene(76.6%) and 3-fluoro-*o*-xylene(8.4%).

Kugelrohr distillation gave pure 3-fluorobenzocyclobutene, b.p. 60°C/ 20mmHg(lit.[186] 74°C/100mmHg); δ_H 3.0(4H, broad), 6.75(2H, m) and 7.05(1H, m); δ_C 27.1, 30.0, 113.7(d, J 21Hz), 119.1(d, J 4Hz), 129.2 (d, J 6Hz), 129.7(d, J 16Hz), 148.8(d, J 10Hz) and 156.3(d, J 255Hz); m/z 122.

(e) Fvp of 1,2,4,5-tetrakis(bromomethyl)benzene

Fvp of the title compound (0.57g, 600°C, 1.2 x 10^{-2}mmHg, inlet - 130°-135°C, 2.0g magnesium) gave a white solid in the cold trap. The ^{1}H NMR and GC-MS indicated that the product consisted mainly of tricyclo[6.2.0.0.^{3,6}]deca-1,3,7-triene(1,2,4,5-benzodicyclobutene, 46.6%); δ_H 3.2(8H,s) and 6.9(2H, s); δ_C 29.5($4CH_2$), 117.4(2C) and 143.5(4C); m/z 130, with a trace amount of 1,2,4,5-tetramethylbenzene as the only byproduct.

(f) Preparation and Fvp of α,α',2,3,5,6-hexabromo-*p*-xylene

(i) Preparation of α,α',2,3,5,6-hexabromo-*p*-xylene

2,3,5,6-Tetrabromo-*p*-xylene (5.0g, 11.8mmol) and bromine (4.0g, 25.0mmol) in carbon tetrachloride were photolysed (uv lamp, 400W) for 4h under reflux(130-140 °C). On cooling, the solid precipitate was filtered off and was found to be insoluble in conventional solvents. Microanalysis gave C, 16.8; H, 0.6. $C_8H_4Br_6$ requires C, 16.6; H, 0.7%. The solid state ^{13}C NMR gave δ_C 45.0($2CH_2$), 125.0(4C) and 145.0(2C), no peak for CH_3. The product was further confirmed as α,α',2,3,5,6-hexabromo-*p*-xylene(6.6g, 98.0%) by the mass spectrum: m/z 579(8%,M^+), 500(83), 419(100), 338(15), 259(18), 179(5) and 98(8), and has a melting point of 271°C (Lit.[189] 268-269°C). Attempted bromination with NBS/benzoyl peroxide gave a mixture of products and starting material.

(ii) Fvp of α,α',2,3,5,6-hexabromo-*p*-xylene

Fvp of the title compound (0.67g, 600°C, ~ 10^{-3}mmHg, inlet - 130-135 °C, 1.6g magnesium) gave nothing in the cold-trap, however there was a polymer material and solid in the inlet tube. Microanalysis and the melting point of the solid, indicated that it was just recovered starting material (0.32g, 47.8%). Microanalysis of the polymer gave C, 17.3; H, 1.7%. $C_8H_3Br_5$ requires C, 19.3; H, 0.6% and $C_8H_4Br_4$ requires C, 22.9; H, 1.0%.

Repeat pyrolysis at 650°C through an empty tube (i.e. no magnesium, no glasswool) gave a white solid, with red elemental bromine down the cold trap. Microanalysis of the solid gave C, 19.4; H, 1.0; $C_8H_4Br_4$ requires C, 22.9; H, 1.0%; and $C_8H_3Br_5$ requires C, 19.3%; H, 0.6%. The yield based on the analysis result was 69.0%. The solid state ^{13}C NMR gave δ_C 45.0, 130.0, and 145.0.

E. Preparation and Fvp of Haloalkylbenzenes

1. Fvp of bromoethylbenzenes

(a) 2-Bromoethylbenzene

Fvp of 2-bromoethylbenzene (0.43g, 600°C, 2.0 x 10^{-2}mmHg, inlet - room temperature, 0.5g magnesium) gave a colourless liquid as the major product, with a small amount of solid. The ^{1}H NMR and GC-MS showed that the liquid consisted mainly of styrene(69.7%); δ_H 5.1(1H, d of d, J 5,1Hz), 5.6(1H, d of d, J 9,1Hz), 6.6 - 6.7 (1H, q, J 8Hz) and 7.0-7.5(5H, m); m/z 104, ethylbenzene(14.3%); δ_H 1.15(3H, t, J 4Hz), 2.5(2H, q, J 4Hz) and 7.0-7.5(5H, m); m/z 106 and toluene(5.2%). The GC-MS analysis of the solid product showed that it consisted of traces of various dimeric products of dehalogenated starting material. The same product mixture was obtained at most pyrolytic conditions, however at a pressure of about ~ 10^{-3}mmHg a rather unexpected isomerisation of 2-bromoethylbenzene to 1-bromoethylbenzene - δ_H 1.95(3H, d, J 3Hz), 5.1(1H, q, J 2Hz); δ_C 26.7, 49.5; was observed. However, attempt to repeat this isomerisation failed. Pyrolysis of the starting material in a tube packed with only glasswool without magnesium gave only unchanged starting material.

(b) 1-Bromoethylbenzene

Fvp of 1-bromoethylbenzene (0.39g, 600°C, 2.0 x 10^{-1}mmHg, inlet - room temperature, 0.5g magnesium) gave a colourless liquid, whose ^{1}H NMR and GC-MS showed that it contained only styrene(80.2%) and ethylbenzene(18.8%). The same product mixture was obtained under varied pyrolytic conditions.

2. Preparation and Fvp of phenylpropylhalides

(a) Fvp of 1-bromo-3-phenylpropane

Fvp of the title compound (0.41g, 600°C, 4.0 x 10^{-1}mmHg, inlet - room temperature, 0.5g magnesium) gave a colourless liquid. The ^{1}H NMR, GC-MS and GC (OV101, 100°C - comparison with authentic samples) showed that the product consisted of β-methylstyrene(*Z*-and*E*-, 15.0% and 40.9%); δ_H 1.8(3H, d, J 3Hz), 6.3-6.5(2H, m) and 7.0-7.3 (5H, m); m/z 118, allylbenzene(3-phenylprop-1-ene, 20.5%); δ_H 3.3 (2H, broad d, J 3Hz), 4.9-5.2(3H, m), and 7.0-7.3(5H, m); m/z 118, toluene(6.1%); m/z 92, styrene(4.6%); m/z 104, bibenzyl(3.7%); m/z 182, and a trace of ethylbenzene.

(b) Fvp of 1-chloro-3-phenylpropane

Fvp of the title compound gave the same product mixture as 1-bromo-3-phenylpropane, which are β-methylstyrene(*Z*-and *E*-,19.7 and 45.1%), allylbenzene(3-phenylprop-1-ene, 25.8%), bibenzyl(1.8%), ethylbenzene(1.4%) and a trace of toluene.

(c) Preparation and Fvp of 1-bromo-2-phenylpropane and control pyrolysis of isomeric phenylpropenes

(i) Preparation of 1-bromo-2-phenylpropane

To a solution of α-methylstyrene(35g, 0.30mol) in THF(50ml) cooled on an ice-bath, 1.0M borane in THF(15ml, 0.15mol) was gradually added by means of a syringe *via* a rubberseptum[190]. The solution was stirred for 1h and water (50ml) was added dropwise to destroy excess hydride. The mixture was then heated on a water bath (45°C) and aqueous 3M sodium hydroxide (120ml) added, followed by a dropwise addition of 30% hydrogen peroxide (60ml). The mixture was allowed to cool to room temperature and extracted with ether. The aqueous layer was saturated with solid sodium chloride and extracted twice with ether. The combined ether extract was washed twice with

aqueous sodium chloride, dried and evaporated. Kulgelrohr distillation gave 2-phenylpropan-1-ol(31.8g, 78.9%) as a thick colourless oil, b.p. 140°C/20mmHg(lit.[191] 114°C/14mmHg).

To the alcohol(6.3g, 46.3mmol) cooled in an ice-bath, phosphorus tribromide (4.2g, 15.5mmol) was added dropwise and the mixture stirred overnight.[173] It was then heated on a waterbath for 1h, cooled, poured into ice-water and extracted with ether. The organic layer was dried, evaporated and Kugelrohr distillation gave 1-bromo-2-phenyl-propane (6.4g, 69.6%); b.p. 100°C/20mmHg(lit.[191] 106-108°C/18mmHg); δ_H 1.5 (3H, d, J 3Hz) 3.0-3.7(3H, m) and 7.3(5H, s).

(ii) Fvp of 1-bromo-2-phenylpropane

Fvp of the title compound (0.42g, 600°C, 4.0 x 10^{-1}mmHg, inlet - room temperature, 0.5g magnesium) gave a colourless liquid. The ^{1}H NMR, GC-MS and GC(OV101, 100°C - comparison with authentic samples) showed that the product consisted of α-methylstyrene(13.5%); δ_H 2.15(3H, m), 5.3-5.9(1H, t of d), 6.6-7.0(1H, q) and 7.2-7.7(5H, m); m/z 118, β-methylstyrene(*E*-and *Z*-59.3%); δ_H 1.75-1.85(3H, d, J 3Hz), 6.3-6.5(2H, m) and 7.0-7.3(5H, m); m/z 118, allylbenzene (3-phenylprop-1-ene, 18.2%); δ_H 3.2-3.4(2H, broad d, J 3Hz), 4.9-5.2(3H, m) and 7.0-7.3(5H, m); m/z 118 and traces of styrene and toluene.

(iii) Control Fvp of trans β-methylstyrene, α-methylstyrene and allylbenzene

Each of the title compounds was pyrolysed separately under the normal conditions (i.e. with magnesium) at 600°C. α-Methylstyrene gave unchanged starting material; β-methylstyrene gave allylbenzene(14%) and the starting β-methylstyrene(86%); and allylbenzene gave β-methylstyrene(86%) and the starting allylbenzene(14%). The figures quoted are percentage composition rather than percentage yield.

3. Fvp of 1-chloro-4-phenylbutane

Fvp of the title compound (0.36g, 600°C, 2.0 x 10^{-1}mmHg, inlet - room temperature, 0.5g magnesium) gave a colourless liquid. The ^{1}H NMR and GC-MS of the product showed that it consisted of 1,2,3,4-tetrahydronaphthalene(35.5%); δ_H 1.6-1.8(4H, m), 2.5-2.8 (4H, m) and 7.0-7.4(4H, m); m/z 132, 3-isomers of phenylbutenes and phenylbutane, with a combined yield of 53.8% - based on GC integration of the peaks. Trace amounts of styrene, toluene and bibenzyl, were also observed on the GC-MS. A repeat pyrolysis at a longer contact time (~1.0mmHg) gave the same mixture of compounds as above, except that the yield of styrene was greatly increased to about 20.0%.

4. (a) Fvp of 2-bromoethyl phenyl ether

Fvp of the title compound (0.43g, 600°C, 7.5 x 10^{-1}mmHg, inlet - 60-65°C, 0.5g magnesium) gave a dark liquid with strong phenolic odour. The ^{1}H NMR and GC-MS showed that the product consisted of phenol (36.1%); δ_H 5.5(1H, s, -OH) and 6.8-7.2(5H, m), 1,1-diphenoxyethane (12.6%); δ_H 1.6(3H, d, J 3Hz), 5.8(1H, q, J 3Hz) and 6.8-7.2(10H, m); m/z 214 - confirmed with authentic sample, acetaldehyde(4.6%); δ_H 2.0 (3H, d, J 1Hz) and 9.6(1H, q, J 1Hz) and a compound suspected to be 2,3-diphenoxybutane(9%); δ_H 2.1(6H, d, J 3Hz), 6.3(2H, q, J 3Hz), and 6.8-7.2(10H, m). Biphenyl(trace) was also found to be present on the GC-MS. Repeat pyrolysis at a longer contact time (~15mmHg) gave mainly phenol(57.0%) with small amounts of the other products.

(b) Preparation and Fvp of 1,1-diphenoxyethane

(i) Preparation of 1,1-diphenoxyethane[193]

A mixture of β-bromophenetole(2-bromoethyl phenyl ether, 35.0g, 0.17mol) and finely powdered potassium hydroxide(45.0g) was heated under reflux on an oil bath for 3h. The system was then set up for

distillation and phenyl vinyl ether was collected at 154-155°C (lit.[192] b.p. 155-156°C). The ^{1}H NMR confirmed the product as phenyl vinyl ether; δ_H 4.5(1H, d of d, J 3,1Hz), 4.8(1H,d of d, J 7,1Hz), 6.5 - 6.7(1H, q, J 3Hz) and 7.0-7.5(5H, m).

To the phenyl vinyl ether (5.0g, 41.7mmol) was added phenol (4.0g, 42.5mmol) and chloranil(tetrachloro-*p*-benzoquinone, 4.5g); and the mixture heated under reflux for 15h in THF. The mixture was allowed to cool, solvent evaporated and the residue taken up with ether. The solid chloranil was filtered off and the ether layer washed with 1M sodium hydroxide (5 x 100ml) and water (3 x 100ml). The ether layer was dried and evaporated. Distillation gave two fractions, unreacted phenyl vinyl ether (45°C/20mmHg) and 1,1-diphenoxyethane, b.p. 150°C/0.1mmHg(lit.[193] 152-153°C/0.1mmHg); δ_H 1.6(3H, d, J 3Hz), 5.8(1H, q, J 3Hz) and 6.8-7.2(10H, m); m/z 214.

(ii) Fvp of 1,1-diphenoxyethane

Fvp of the title compound (0.29g, 600°C, 1.0 x 10^{-2}mmHg, inlet - room temperature, 0.5g magnesium) gave a liquid. The ^{1}H NMR showed that the liquid consisted of phenol; δ_H 6.8(1H, s, -OH) and 6.8-7.5 (5H, m), phenyl vinyl ether; δ_H 4.5(1H,d of d, J 3,1Hz), 4.8 (1H, d of d, J 7,1Hz), 6.5 - 6.7(1H, q, J 3Hz) and 7.0-7.5(5H, m), benzaldehyde; δ_H 6.8-7.9(5H, m) and 9.85(1H, s), toluene; δ_H 2.35 (3H, s) and 6.8-7.5(5H, m) and small amount of starting material.

(iii) Fvp of Phenyl vinyl ether

Fvp of the title compound over magnesium gave unchanged starting material.

5. Fvp of α-bromoacetophenone

Fvp of the title compound (0.37g, 600°C, 1.4 x 10^{-2}mmHg, inlet-room temperature, 0.5g magnesium) gave a light yellow liquid. The

NMR and GC-MS of product showed that it consisted of acetophenone (41.6%); δ_H 2.6(3H, s) and 7.0-8.0(5H, m); δ_C 26.5(CH_3), 128.3 (C-3,C-5), 128.5(C-2,C-6), 132.1(C-4), 137.1(C-1) and 198.0(C=0); m/z 120, phenylacetylene(ethynylbenzene, 30.6%); δ_H 3.1(1H, s) and 7.0-8.0(5H, m); δ_C 77.3(≡C-H), 83.6(Ph-C≡), 122.1(C-1), 128.3 (C-3,C-5), 128.8(C-4) and 133.0(C-2,C-6); m/z 102 and styrene(6.4%).

6. Fvp of β-Chloropropiophenone

Fvp of the title compound (0.30g, 600°C, 3.0 x 10^{-3}mmHg, inlet-room temperature, 0.5g magnesium) gave a yellow oil. The NMR and GC-MS of the product showed that it consisted of acrylophenone(63.6%); δ_H 5.85(1H, d of d, J 5,1Hz), 6.4(1H, d of d, J 9,2Hz), 7.1 - 7.15 (1H, q, J 6Hz) and 7.3-8.0(5H, m); δ_C 128.5(2C), 128.6(2C), 130.0, 132.3, 133.0, 137.2 and 190.8; m/z 132, propiophenone(10.0%); δ_H 1.1 (3H, t, J 2Hz), 2.9-3.0(2H, q, J 2Hz), 7.3-8.0(5H, m); m/z 134, Indan-1-one(11.2%); δ_H 2.55(2H, m), 3.05(2H, m), and 7.3-8.0(4H, m); m/z 132 and 1-phenylprop-1-yne(5.0%); δ_H 1.95(3H, s) and 7.3-8.0 (5H, m); m/z 116, with traces of styrene, phenylacetylene and acetophenone.

F. Preparation and Fvp of Benzylidene Halides

1. General procedure for preparation of benzylidene halides

These are readily prepared by direct halogenation of a well stirred dichloromethane solution of the corresponding benzaldehydes using either $SOCl_2$, PCl_5 or $SOBr_2$ at room temperature or heated under reflux with a waterbath. In some cases, when thionyl chloride is used, complete chlorination is only achieved in the presence of a catalytic amount of DMF. The products are generally washed with water to remove excess halogenating agent and washed free of unreacted aldehyde with sodium bisulphite, dried and distilled or recrystallised. In some cases the work-up has to be done with care as the benzylidene halides were easily hydrolysed back to the aldehydes, but once obtained pure they are quite stable, at least for a few days. Full details for the individual cases are given below.

2. Preparation and Fvp of benzylidene chloride

(a) Preparation of benzylidene chloride

This was prepared from benzaldehyde(10.7g, 0.1mol) and thionyl chloride(12g, 0.1mol); heated under reflux for 2h.and extracted with ether. Kugelrohr distillation gave benzylidene chloride(14.1g, 87.1%) as a colourless liquid, b.p. 85°C/10mmHg(lit.[194] 89-90°C/10mmHg); δ_H 6.8(1H, s) and 7.5(5H, m).

(b) Fvp of benzylidene chloride

Fvp of the title compound (0.51g, 600°C, 6.8 x 10^{-1}mmHg, inlet-room temperature, 1.0g magnesium) gave two fractions, a liquid and a solid. The NMR and the GC-MS of the liquid fraction showed that it consisted of mainly toluene(11.8%); δ_H 2.3(3H, s) and 7.1-7.3(5H, m) and small amounts of benzene(6.0%) and styrene(1.1%), while the solid

fraction consisted of stilbene(*Z*-and *E*-,49.4%); m/z 180 and bibenzyl (20.2%); m/z 182, with traces of phenanthrene and diphenylmethane. Pure stilbene was obtained by recrystallisation of the solid from ethanol, m.p. 120-122°C(lit.[195] 124°C); δ_H 7.1(2H, s) and 7.2-7.5(10H, m); δ_C 126.4(C-2,C-6), 127.5(C-4), 128.5(C-3,C-5,C-7), and 137.2(C-1); m/z 180. All compounds were further confirmed with authentic samples using the GC (NPGS, 190°C).

3. Preparation and Fvp of α,α-dichloroxylenes

(a) Preparation and Fvp of α,α-dichloro-*o*-xylene

(i) Preparation of α,α-dichloro-*o*-xylene

This was prepared from *o*-tolualdehyde(12g, 0.1mol) and thionyl chloride(13.0g, 0.1mol); heated under reflux for 2h and extracted with ether. Kugelrohr distillation gave α,α-dichloro-*o*-xylene(15.0g, 86.0%) as a colourless liquid,b.p. 60°C/1.0mmHg(lit.[196] 125°C); δ_H 2.45(3H, s), 7.0(1H, s) and 7.2-8.0(4H, m); m/z 174.

(ii) Fvp of α,α-dichloro-*o*-xylene

Fvp of the title compound (0.83g, 600°C, 7.0 x 10^{-1}mmHg, inlet-room temperature, 1.5g magnesium) gave two fractions, a liquid and a solid. The ^{1}H NMR and GC-MS of the liquid fraction showed the presence of *o*-xylene(13.3%); δ_H 2.2(6H, s) and 7.0-7.3(4H, m); m/z 106, benzocyclobutene(17.2%); δ_H 3.15(4H, s) and 7.0-7.3(4H, s); m/z 104, toluene(6.8%); m/z 92 and traces of 2-methylstyrene and 2-methylethylbenzene. The solid fraction consisted of 2,2'-dimethylstilbene(*Z*-:*E*-,5.1% and 30.9%); δ_H 2.45(5H, s) and 7.1-7.5 (10H, m); m/z 208, 2,2'-dimethylbibenzyl(9.7%); δ_H 2.35(6H, s), 2.9 (4H, s) and 7.1-7.5(8H, m); m/z 210 and a compound with m/z 194 (1.4%) - suspected to be 2-methylstilbene. The yield was determined by GC integration of the peaks.

(b) Preparation and Fvp of α,α-dichloro-*m*-xylene

(i) Preparation of α,α-dichloro-*m*-xylene

This was prepared from *m*-tolualdehyde(12g, 0.1mol) and thionyl chloride(13.0g, 0.1mol) in dichloromethane(80ml); heated under reflux for 2h with a waterbath. Kugelrohr distillation gave α,α-dichloro-*m*-xylene(15.6g, 89.0%) as a colourless liquid, b.p. 130°C/20mmHg(lit.[197] 110-111°C/15mmHg); δ_H 1.4(3H, s), 6.6 (1H, s) and 7.0-7.4(4H, m); m/z 174.

(ii) Fvp of α,α-dichloro-*m*-xylene

Fvp of the title compound (0.84g, 600°C, 7.0 x 10^{-1}mmHg, inlet-room temperature, 1.2 g magnesium) gave two fractions, a liquid and a solid. The NMR and GC-MS of the liquid fraction showed the presence of mainly *m*-xylene(11.4%); δ_H 2.3-2.4(6H, s) and 7.0-7.3(4H, m); m/z 106, toluene(5.0%) and 3-methylstyrene(trace). The solid fraction consisted of 3,3'-dimethylstilbene(48.3%); δ_H 2.4(6H, s), 7.2(2H, s) and 7.1-7.4(8H, m); δ_C 21.4(CH_3), 123.7, 127.2, 128.3 ,128.5, 128.6, 137.4 and 138.1; m/z 208 and 3,3'-dimethylbibenzyl(12.2%); δ_H 2.3(6H, s), 2.9 (4H, s), and 7.1-7.4(8H, m); δ_C 21.4(CH_3), 38.0(CH_2), 126.6, 128.0, 128.2, 129.2, 137.8 and 141.9; m/z 210.

c. Preparation of Fvp of α,α-dichloro-*p*-xylene

(i) Preparation of α,α-dichloro-*p*-xylene

This was prepared from *p*-tolualdehyde(12g, 0.1mol) and thionyl chloride(13g, 0.1mol); heated under reflux for 2h on a waterbath and extracted with ether. Kugelrohr distillation of the solid residue, gave a white crystalline solid confirmed as α,α-dichloro-*p*-xylene(12.4g, 71%); b.p. 130°C/20mmHg(lit.[198] 105°C/18mmHg); δ_H 2.4(3H, s), 6.8(1H, s), 7.3 and 7.5(4H, AB pattern, J 4Hz); m/z 174.

(ii) Fvp of α,α-dichloro-*p*-xylene

Fvp of the title compound (0.51g, 600°C, 7.0 x 10^{-1}mmHg, inlet-55-58°C, 1.2g magnesium) gave two fractions, a liquid and a solid. The ^{1}H NMR and GC-MS of the liquid fraction showed the presence of *p*-xylene(5.5%); δ_H 2.35(6H, s) and 7.2(4H, s), with trace amounts of toluene and 4-methylstyrene. The solid fraction consisted of 4,4'-dimethylbibenzyl(20.7%); δ_H 2.5(6H, s), 3.0(4H, s), and 7.2-7.6 (8H, m) and 4,4'-dimethylstilbene(*Z*-:*E*-,6.8% and 56.3%); recrystallisation from ethanol gave pure 4,4'-dimethylstilbene, m.p. 183-184°C(lit.[199] 181.7°C); δ_H 2.35(6H, s), 7.0(2H, s), 7.15 and 7.4 (8H, AB pattern, J 4Hz); δ_C 21.2(CH_3), 126.3(2C), 127.6, 129.3(2C), 134.7 and 137.2; m/z 208.

4. Preparation and Fvp of methoxybenzylidene chlorides

(a) Preparation and Fvp of *o*-methoxybenzylidene chloride

(i) Preparation for *o*-methoxybenzylidene chloride

This was prepared from *o*-anisaldehyde(6.6g, 50mmol) and phosphorus pentachloride(10.5g, 50mmol) in dichloromethane; stirred at room temperature for 1h. Excess PCl_5 was removed by filtration. Evaporation and Kugelrohr distillation gave *o*-methoxybenzylidene chloride(8.5g, 91.0%) as a colourless liquid, b.p. 100°C/1.0mmHg (lit.[200] 231°C); δ_H 3.70(3H, s), 6.70(1H, d), 6.95(1H, m), 7.25(2H, m), and 7.80(1H, d); δ_C 55.5, 66.5, 110.7, 121.0, 127.9, 128.4, 131.2 and 154.3. Although the product readily hydrolyses it can be stored in the freezer for a few days.

(ii) Fvp of *o*-methoxybenzylidene chloride

Fvp of the title compound (0.71g, 600°C, 4.0 x 10^{-1}mmHg, inlet - 60-65°C, 1.5g magnesium) gave as the main product a colourless liquid,

with a small amount of thick oil. The NMR and GC-MS showed that the liquid consisted of toluene(61.4%); δ_H 2.2(3H, s) and 7.4(5H, s); m/z 92., xylene(7.5%), benzocyclobutene(3.8%) plus trace amounts of benzene and ethylbenzene. The small amount of thick oil consisted of a mixture of methylbibenzyl(m/z 196), dimethylbibenzyl(m/z 210), bibenzyl(m/z 182), 1,1-methylenebis(methylbenzene) (m/z 196), plus other hydrocarbons m/z 192($C_{15}H_{12}$ - methylphenanthrene?), m/z 194($C_{15}H_{14}$ - methylstilbene?) and stilbene. No attempt was made to determine the yield of these components.

(b) Preparation and Fvp of *p*-methoxybenzylidene chloride

(i) Preparation of *p*-methoxybenzylidene chloride

This was prepared from *p*-anisaldehyde(13.4g, 98mmol) and thionyl chloride(13.0g, 109mmol) in toluene[201]; heated under reflux for 2h with an oil bath. The solvent and excess thionyl chloride was evaporated and kugelrohr distillation of the solid residue gave *p*-methoxybenzylidene chloride(14.4 g, 76.6%),b.p. 100°C/1.0mmHg(lit.[202] 134°C/14mmHg); δ_H 3.75(3H, s), 6.65(1H, s), 6.9 and 7.4(4H, AB pattern, J 5Hz). The product was unstable and readily hydrolyses to regenerate the anisaldehyde but can be stored for a long period in the freezer.

(ii) Fvp of *p*-methoxybenzylidene chloride

Fvp of the title compound(1.0 g, 600°C, 7.8 x 10^{-1}mmHg, inlet - 72-76°C, 1.3g magnesium) gave two fractions of product, a liquid and a solid. The ^{1}H NMR and GC-MS of the liquid showed that it consisted of *p*-methoxystyrene(18.2%); δ_H 3.75(3H, s), 5.1(1H, d of d, J 4,1Hz), 5.6 (1H, d of d, J 8,1Hz), 6.6 - 6.65(1H, q, J 6Hz) and 7.2-7.5(5H, m); m/z 134, styrene(6.1%); δ_H 5.1(1H, d of d, J 5,1Hz), 5.6 (1H, d of d, J 9,1Hz), 6.6 - 6.7(1H, q, J 8Hz) and 7.2-7.5(5H,m); m/z 104, ethylbenzene; δ_H 1.25(3H, t, J 2Hz), 2.65(2H,q,J 2Hz) and

7.2-7.5(5H, m); m/z 106, toluene(5.6%), anisole(3.6%) and benzene (trace). The solid consisted mainly of stilbene(*Z*-and *E*-,19.2%); m/z 180, 4-methoxystilbene(3.0%); m/z 210 and a trace of methylstilbene. The yield and characterisation of the solid product was mostly based on the GC-MS evidence.

5. Preparation and Fvp of 1-dichloromethyl-2-methoxynaphthalene

(i) Preparation of 1-dichloromethyl-2-methoxy-naphthalene

The title compound was prepared from 2-methoxy-1-naphthaldehyde (4.7g, 25mmol) and phosphorus pentachloride(6.25g, 30mmol) in dichloromethane; stirred at room temperature for 1h. The residue after the solvent was evaporated, was a greenish yellow solid, which on an attempted recrystallisation from ethanol, gave an insoluble white solid. The white solid was found to be pure 1-dichloromethyl-2-methoxy-naphthalene[194](4.2g, 69.5%); δ_H 3.9(3H, s), 7.15(1H,d, J 5Hz), 7.4 (1H, m), 7.6(1H,m), 7.85(3H, m) and 8.8(1H, s); δ_C 56.7, 64.6, 112.2, 124.1, 125.0, 126.9, 128.8, 129.7, 130.6, 132.8, 137.6 and 152.3.

(ii) Fvp of 1-dichloromethyl-2-methoxynaphthalene

Fvp of the title compound (0.53g, 600°C, 5.0 x 10^{-1}mmHg, inlet - 85-90°C, 1.5g magnesium) gave a liquid product. The NMR and GC-MS showed that it consisted of 1-methylnaphthalene(51.0%); δ_H 2.65(3H, s), 7.3(2H, quintet, J 5Hz), 7.45(2H, m), 7.7(1H, d, J 5Hz), 7.8(1H, d, J 5Hz), and 7.95(1H, d, J 5Hz); δ_C 19.3(CH_3), 124.1(C-8), 125.5(C-7), 125.7 (C-3), 125.8(C-6), 126.3(C-4), 127.8(C-5), 128.5(C-2), 132.6(C-9), 133.5(C-10), and 134.2(C-1); m/z 142, 1,2-dimethylnaphthalene(10.1%); δ_H 2.45(3H, s), 2.55(3H, s), 7.5-8.1(6H, m); δ_C 14.5(CH_3 -1), 21.0 (CH_3 -2); m/z 156 and small amounts of 2,3-dihydronaphtho[2,1-b]furan;

δ_C 25.8, 105.5, 112.4, 123.5, 124.4, 125.1, 125.5, 126.2, 127.8, 128.7 and 144.1; m/z 168, ethylnaphthalene(m/z 156) and 2-methylnaphthalene.

6. Preparation and Fvp of halobenzylidene halides

(a) Preparation and Fvp 2-chlorobenzylidene chloride

(i) Preparation of 2-chlorobenzylidene chloride

This was prepared from 2-chlorobenzaldehyde(25g, 0.18mol) and phosphorus pentachloride(41.6g, 0.20mol) in dichloromethane; heated under reflux for 2h on a water bath. Kugelrohr distillation gave 2-chlorobenzylidene chloride(29.4g, 84.5%) as a colourless liquid, b.p. 120°C/1.0mmHg(lit.[202] 227-230°C); δ_H 7.0(1H, s), 7.0-7.3(3H, m) and 7.6-7.8(1H, m).

(ii) Fvp of 2-chlorobenzylidene chloride

Fvp of the title compound (0.90g, 600°C, 6.2 x 10^{-1}mmHg, inlet - 60-65°C, 1.5g magnesium) gave two fractions, a liquid and a solid. The ^{1}H NMR and GC-MS of the liquid fraction showed that it consisted of 2-chlorotoluene(2.0%), toluene(1.6%), chlorobenzene(1.0%) and small amount of 2-chlorobenzylchloride. The solid consisted of α,2,2'-trichlorostilbene(*Z*-:*E*-,8.2% and 40.8%); m/z 282, 2,2-dichlorostilbene(7.6%); m/z 248, phenanthrene(6.4%) and traces of other compounds. The yield and characterisation of products was based mainly on the GC-MS, in combination with the ^{1}H NMR.

Repeat pyrolysis at higher magnesium to substrate ratio (0.51g of S.M., 600°C, 6.4 x 10^{-1}mmHg, inlet - 60-65°C, 2.0g magnesium) gave as the liquid fraction, toluene(2.3%), benzene(3.7%) and trace of 2-chlorotoluene; while the solid fraction consist of phenanthrene(47.2%), stilbene(3%) and dihydrophenanthrene(1%). All the three products in the solid fraction were further confirmed with authentic samples on the GC (OV101, 200 °C). The yield was determined from GC integration.

(b) Preparation and Fvp of 4-chlorobenzylidene chloride

(i) Preparation of 4-chlorobenzylidene chloride

This was prepared from 4-chlorobenzaldehyde(28.1g, 0.2mol) and phosphorus pentachloride(41.6g, 0.2mol) in dichloromethane; heated under reflux for 2h on a waterbath. Kugelrohr distillation gave 4-chlorobenzylidene chloride(30.1g, 77%) as a colourless liquid, b.p. 120°C/1.0mmHg(lit.[203] 127-132/22mmHg); δ_H 6.8(1H, s) and 7.2-7.7(4H, m).

(ii) Fvp of 4-chlorobenzylidene chloride

Fvp of title compound (0.66g, 600°C, 5.2 x 10^{-1}mmHg, inlet - 60-65°C, 1.3g magnesium) gave two fractions, a liquid and a solid. The ^{1}H NMR and GC-MS of the liquid fraction showed that it consisted of chlorobenzene(2.0%), benzene(1.8%), 4-chlorotoluene(1.1%) and toluene (1.5%). The solid fraction consisted of α,4,4'-trichlorostilbene(*Z-:E-* 1:1, 20.1%); m/z 282, 4,4'-dichlorostilbene(*Z-:E-* 1:2, 22.7%); m/z 248, monochlorostilbene(4.8%), with small amounts of monochlorobibenzyl and dichlorobibenzyl. Recrystallisation of the solid fraction from ethanol gave 4,4'-dichlorostilbene, m.p. 177-178°C(lit.[204] 176°C); δ_H 7.2(1H, s) and 7.5-7.6(4H, m); δ_C 127.7(2C), 128.0, 128.9(2C), 133.5 and 135.5. The yield was based on GC integration.

(c) Preparation and Fvp of 2-chloro-6-fluorobenzylidene chloride

(i) Preparation of 2-chloro-6-fluorobenzylidene chloride

The title compound was prepared from 2-chloro-6-fluorobenzaldehyde(5.0g, 31.5mmol) and phosphorus pentachloride(6.6g, 31.7mmol) in dichloromethane; stirred at room temperature for 2h. Kugelrohr distillation gave 2-chloro-6-fluorobenzylidene chloride(5.8g, 86.5%) as a colourless liquid, b.p. 100 °C/1.0mmHg(lit.[205] 95°C/

16mmHg); δ_H 6.9-7.4(m); with a singlet at 7.2 ppm equivalent to the -$CHCl_2$ proton and the aldehyde -CHO proton peak has disappeared.

(ii) Fvp of 2-chloro-6-fluorobenzylidene chloride

Fvp of the title compound (0.51g, 600°C, 1.0 x 10^{-1}mmHg, inlet - room temperature, 0.5g magnesium) gave a white solid as product. The NMR and GC-MS showed that the product consisted of 2-chloro-6-fluorotoluene(2.1%); δ_H 2.3(CH_3, d, J 2Hz); m/z 144, 2-chloro-6-fluorobenzylchloride(6.7%); δ_H 4.8(CH_2Cl, d, J 2Hz); m/z 179, 2,2'-dichloro-6,6'-difluorostilbene(*Z*-:*E*-,9.5 and 47.5%), trichlorodifluorostilbene(4.0%); m/z 320 and tetrachlorodifluorostilbene (5.0% two isomers). Preparative TLC using petroleum ether as solvent gave pure *E*-2,2'-dichloro-6,6'-difluorostilbene; m.p. 106-107°C; (Found: C,54.8; H,2.3. $C_{14}H_8Cl_2F_2$ requires C,58.9; H,2.8%); υ_{max} 3080, 1720, 1605, 1575, 1250, 1215, 1160, 980, 900, 780 and 730 cm^{-1}; δ_H 7.0-7.3 (6H, m) and 7.5(2H, s); δ_C 114.8(C-5, d, J 23Hz), 124.2(C-1, d, J 14Hz), 125.7(C-3, d, J 3Hz), 126.8(C-4, d, J 13Hz), 128.7(C-7, d, J 10Hz), 134.8 (C-2, d, J 5Hz) and 161.1(C-6, d, J 253Hz); m/z 284(M^+, 28%), 248(5), 214(100), 194(15), 154(8), 124(24) and 106(42); δ_F ($CFCl_3$) –83.6 (d of d, J 77.7, 7.4Hz).

Repeat pyrolysis (0.65g, 650°C, 1.8 x 10^{-1}mmHg, inlet - 60°-65°C, 1.8g magnesium) gave a solid product. The ^1H NMR spectrum was not informative, but ^{13}C and GC-MS showed that it contained mainly *Z*-:*E*-2,2'-dichloro-6,6'-difluorostilbene(13.5% and 35.0%), with small amount of 1,2-bis(2-chloro-6-fluorophenyl)ethyne(6.7%); δ_C 90(–C≡), m/z 282. The spectral data for the *E*- isomer were as given above, while for the *Z*-isomer; δ_C 113.8(C-5, d, J 21Hz), 114,3(C-1, d, J 22Hz), 125.0 (C-3, d, J 3Hz)), 126.6(C-4, d, J 18Hz), 130.2(C-7, d, J 10Hz), 130.8 (C-2, d, J 9Hz) and 163.2(C-6, d, J 255Hz); m/z 284(M^+,35%), 249(5), 214(100), 194(23), 154(12), 124(20) and 106(45).

(d) Preparation and Fvp of 2-chloro-5-nitrobenzylidene chloride

(i) Preparation of 2-chloro-5-nitrobenzylidene chloride

This was prepared from 2-chloro-5-nitrobenzaldehyde(2.5g, 13.5mmol) and phosphorus pentachloride(2.8g, 13.5mmol) in dichloromethane; heated under reflux for 2h on a waterbath. Kugelrohr distillation(170°C/5.0mmHg) gave a thick colourless oil, which solidifies on standing to a white solid and this was confirmed as 2-chloro-5-nitrobenzylidene chloride; m.p. 31-32°C; (Found: C,35.6; H,1.6; N,7.6. $C_7H_4Cl_3NO_2$ requires C,35.0; H,1.7; N,5.8%); δ_H 6.9 (1H, s), 7.45(1H, d, J 5Hz), 8.15(1H, d of d, J 5,3Hz) and 8.8 (1H, d, J 2Hz); δ_C 66.6, 124.2, 125.5, 130.9, 137.5, 139.3 and 147.2; m/z 239(35%,M^+), 204(100), 158(50), 123(96), 97(40) and 73(70). The product is moisture sensitive.

(ii) Fvp of 2-chloro-5-nitrobenzylidene chloride

Fvp of the title compound (0.36g, 600°C, 1.5 x 10^{-1}mmHg, inlet - 60-65°C, 1.0g magnesium) gave an intractable product. The ^1H NMR was not informative, however the GC-MS showed that it consisted of the mainly chlorophenathrene; m/z 212, and starting material, in addition to other products. Attempted separation by preparative TLC, using petroleum ether as solvent, was unsuccessful. Repeat pyrolysis gave similar intractable products.

(e) Preparation and Fvp of 6-chloro-3,4-methylenedioxy-benzylidene chloride

(i) Preparation of 6-chloro-3,4-methylenedioxybenzylidene chloride

This was prepared from 6-chloro-3,4-methylenedioxybenzaldehyde (2.3g, 12.5mmol) and phosphorus pentachloride(2.6g, 12.5mmol) or thionyl chloride with catalytic DMF, in dichloromethane; stirred under

reflux on a waterbath for 2h. Kugelrohr distillation (150°C/0.1mmHg) gave a colourless liquid which solidified on standing to give a white solid and this was confirmed as 6-chloro-3,4-methylenedioxybenzylidene chloride; m.p. 43-44°C; (Found: C,39.3; H,1.9. $C_8H_5Cl_3O_2$ requires C,40.1; H,2.1%); δ_H 6.0(2H, s), 6.8(1H, s), 7.1(1H, s) and 7.3(1H, s); δ_C 68.2, 102.4, 108.0, 109.0, 123.2, 130.9, 147.5 and 149.4; m/z 238 (50%,M^+), 203(100), 173(5), 147(18), 133(8), 111(28), and 74(33).

(ii) Fvp of 6-chloro-3,4-methylenedioxybenzylidene chloride

Fvp of the title compound (0.35g, 600°C, 1.0 x 10^{-1}mmHg, inlet - 130-135°C, 1.0g magnesium) gave a solid product(50.2 mg). The solid consisted mainly of 1,2-bis(6-chloro-3,4-methylenedioxyphenyl)ethene; m/z 336(M^+,100%, $^{35}Cl_2$), 271(10), 266(98), 243(42), 209(20), 168(18), 150(40), 122(32) and 75(43), with small amounts of phenanthrene; m/z 178, stilbene; m/z 180 and a compound suspected to be methylphenanthrene; m/z 192.

Repeated pyrolysis at higher magnesium to substrate ratio and at higher temperatures (650- 700°C) gave only very low yields of mainly phenanthrene, with small amounts of bibenzyl and two compounds suspected to be methylphenanthrene (m/z 192) and methylanthracene (m/z 192).

(f) Preparation and Fvp of 2-bromo-4,5-dimethylbenzylidene chloride

(i) Preparation of 5-bromo-4-amino-*o*-xylene[206]

This was prepared from 4-amino-*o*-xylene which was first acetylated with acetic anhydride to 4-acetamido-*o*-xylene. The acetamido-*o*-xylene(40g, 0.25mol) was dissolved in the minimum amount of glacial acetic acid, and bromine(45g, 0.28mol) in glacial acetic acid was added gradually at 0°C. A yellow precipitate was obtained. The solvent was

evaporated and the precipitate taken up with ether. The ether layer was washed twice with water, dried and evaporated to give a yellow crystalline solid of bromoacetamido-*o*-xylene, which was hydrolysed with 50% aqueous sulphuric acid by refluxing for 1h, to give 5-bromo-4-amino-*o*-xylene(30g, 61%); δ_H 2.1(6H, s), 3.7(2H, s), 6.5(1H, s) and 7.1 (1H, s).

(ii) Preparation of 2-bromo-4,5-dimethylbenzaldehyde

This was modelled after the method used for the preparation of 2-bromo-4-methylbenzaldehyde[207]. 5-bromo-4-amino-*o*-xylene(10g, 50mmol) was diazotised at –5° to +5 °C, with sodium nitrite(3.5g) and concentrated HCl(10ml) and the diazonium salt was neutralised with hydrated sodium acetate. A 10% solution of formaldoxime was prepared by refluxing paraformaldehyde(2.8g, 93mmol) and hydroxylamine hydrochloride(6.5g, 93mmol) in water until a clear solution was obtained and hydrated sodium acetate (13g, 95mmol) was added and reflux for a further 30min.

To the formaldoxime solution was added hydrated $CuSO_4$(1.3g), sodium sulphite(0.2g) and a solution of sodium acetate(16g in 50ml H_2O); the mixture was maintained at 10-15°C by means of a cold water bath. While stirring, the diazonium solution was siphoned under slight N_2 pressure slowly into the formaldoxime solution (care - pasty mass that prevents stirring if too much is added at a time). The mixture was heated under reflux for 2h, 100ml concentrated HCl added and heating continued for another 2h and then it was saturated with NaCl. It was then extracted with ether and the organic layer washed with saturated NaCl solution and aqueous 10% sodium bicarbonate solutions, evaporated and aqueous 40% sodium metabisulphate solution (previously heated to 60°C) was added and stirred overnight.

The solid addition product obtained was washed with ether and suspended in H_2O(100ml) and conc.H_2SO_4(20ml) was slowly added with cooling; and then heated under relux for 2h. On cooling, it was extracted with ether, washed thrice with saturated NaCl solution, dried and evaporated. The solid mass obtained was recrystallised from ethanol to give a faint yellow solid confirmed as 2-bromo-4,5-dimethylbenzaldehyde (5.3 g, 50%); m.p. 64-65°C; (Found: C,51.3; H,4.4. C_9H_9BrO requires C,50.7; H,4.3%); υ_{max} 3050(ArC-H), 1690(C=O), 1595(ArC-C), 1250, 1180, 1140, 1035(Ar-Br), 975, 915, and 865 cm^{-1}; δ_H 2.3(3H, s), 2.35 (3H, s), 7.5(1H, s), 7.8(1H, s) and 10.4(1H, s); δ_C 19.1, 19.9, 124.1, 130.3, 131.1, 134.4, 136.8, 145.7 and 191.5; m/z 213(M^+,95%), 211(100), 185(16), 132(11), 103(61) and 77(64).

The use of 4,5-dibromo-*o*-xylene[207], butyl lithium and DMF at −70°C was later found to be a more convenient route to 2-bromo-4,5-dimethylbenzaldehyde, with a higher yield.

(iii) Preparation of 2-bromo-4,5-dimethylbenzylidene chloride

This was prepared from 2-bromo-4,5-dimethylbenzaldehyde(1.5g, 7mmol) and thionyl chloride(1.5g, 12.6mmol) in dichloromethane; heated under reflux with a waterbath for 2h. Kugelrohr distillation gave a colourless liquid, confirmed as 2-bromo-4,5-dimethylbenzylidene chloride; b.p. 100°C/5.0 x 10^{-2}mmHg; (Found: C, 40.6; H, 3.2. $C_9H_9BrCl_2$ requires C, 40.3, H, 3.4%); δ_H 2.3(6H, d), 7.25(1H, s), 7.45 (1H, s), and 7.9(1H, s); δ_C 19.3, 19.4, 70.7, 117.2, 129.7 133.1, 136.3, 137.3, and 140.7; m/z 268(M^+,10%), 233(100), 152(8), 115(57), 89(14), and 75(17).

(iv) Fvp of 2-bromo-4,5-dimethylbenzylidene chloride

Fvp of the title compound (0.52g, 600°C, 7.4 x 10^{-2}mmHg, inlet - 85-90°C, 1.5g magnesium) gave two fractions of product. The NMR and GC-MS showed the product consisted mainly of *Z*-and *E*-

2,2'-dibromo-4,4',5,5'-tetramethylstilbene; δ_C 19.3, 19.4, 127.7, 128.7, 133.6, 134.1, 134.2, 136.1 and 138.2; m/z 394 and *Z*-and *E*-α-chloro-2,2'-dibromo-4,4',5,5'-tetramethylstilbene; m/z 428, with small amounts of various halogenated compounds. The ^{1}H NMR was not very informative and it was rather difficult to determine the yield.

Repeat pyrolysis (0.96g, 600°C, 8.0 x 10^{-2}mmHg, inlet - 85-90°C, 2.5g magnesium) gave two fractions, a liquid and a solid. The NMR and GC-MS of the liquid fraction showed that it consisted of 1,2,4-trimethylbenzene(11.9%); δ_C 19.2, 19.7, 20.9, 126.4, 129.6, 130.5, 133.3, 135.2 and 136.3; m/z 134 and *o*-xylene(6.4%); δ_C 19.7($2CH_3$), 125.8(C-3,C-6), 129.8(C-4,C-5) and 136.5(C-1,C-2); m/z 120, with traces of dimethylstyrene and dimethylethylbenzene. The solid fraction consisted of three isomers of tetramethylphenanthrene(12.2, 16.2, 3.4%); m/z 234 and 3,3',4,4'-tetramethylstilbene(*Z*-:*E*-,1.4% and 13.2%); m/z 236. Both the ^{1}H and ^{13}C NMR were rather complex, therefore yield and product identification was mainly based on the GC-MS evidence.

7. Preparation and Fvp of α,α,α',α'-tetrahaloxylenes

(a) Preparation and Fvp of α,α,α',α'-tetrachloro-*p*-xylene

(i) Preparation of α,α,α',α'-tetrachloro-*p*-xylene

This was prepared from terephthaldicarboxaldehyde(5.0g, 37.3mmol) and phosphorus pentachloride(16.0g, 77.0mmol) in dichloromethane, stirred at room temperature for 2h. Excess PCl_5 was destroyed by adding water, the organic layer dried and solvent removed, to give a crystalline solid which was recrystallised from petroleum ether to give α,α,α',α'-tetrachloro-*p*-xylene(8.1g, 90.0%); m.p. 93-95°C (lit.[208] 92-94°C); δ_H 6.7(2H, s) and 7.6(4H, s); m/z 244.

(ii) Fvp of α,α,α',α'-tetrachloro-*p*-xylene

Fvp of the title compound (2.2g, 600°C, 8.0 x 10^{-1}mmHg, inlet - 95-100°C, 2.0g magnesium) gave as main product a polymer material coated in the cold trap, with trace of a liquid which consisted of *p*-xylene (1.1%), toluene(0.6%) and benzene(0.8%). As the polymer was insoluble in conventional solvents, it was simply peeled off from the cold trap. Microanalysis of the material gave, C, 59.6; H, 3.4. $(C_8H_6Cl_2)_n$ requires C, 55.5; H, 3.5% - indicative of poly(α,α'-dichloro-*p*-xylylene). Based on the microanalysis result, the yield of the polymer was 76.9%(1.20g). The solid state ^{13}C NMR gave δ_C 66.7(CHCl), 128.3 (4 aromatic C) and 140.1(2 quaternary aromatic C). Thermal analysis showed that the material starts degrading at a temperature as low as 50°C in both N_2 and air atmosphere but the material finally decomposed at about 400°C under N_2 and 600°C in air. The material gave a sharp isotherm at about 50°C in both air and N_2.

(b) Preparation and Fvp of α,α,α',α'-tetrabromo-*p*-xylene

(i) Preparation of α,α,α',α'-tetrabromo-*p*-xylene

This was prepared from terephthaldicarboxaldehyde(2.0g, 14.9mmol) and thionyl bromide(6.2g, 29.8mmol)[209] heated under reflux at 100-120°C for 3h. On cooling, the residual gaseous fumes were removed with a stream of N_2 gas and the solid residue taken up with hot chloroform. Cooling on an ice-bath gave fine solid precipitate of α,α,α',α'-tetrabromo-*p*-xylene(3.8g, 60.6%); m.p. 169-170°C (lit.[209] 169°C); δ_H (CD_3COCD_3); 7.2(2H, s) and 7.7(4H, s); m/z 422.

(ii) Fvp of α,α,α',α'-tetrabromo-*p*-xylene

Fvp of the title compound (0.98g, 600°C, 1.5 x 10^{-2}mmHg, inlet - 150-160°C, 2.0g magnesium) gave a faint yellow polymeric material as the only product, which was worked up as in 7(a). Microanalysis of the material gave C, 40.9; H, 2.0. $(C_8H_6Br_2)_n$ requires C, 36.7; H, 2.3% -

indicative of poly(α,α'-dibromo-*p*-xylylene). The yield of polymer material was 25%(0.15 g) based on the microanalysis result. The solid state ^{13}C NMR gave δ_C 62.3(CHBr), 128.9(4 aromatic C) and 139.9 (2 quaternary aromatic C). Thermal analysis on the material showed that it was stable in N_2 and in air atmosphere up to 200°C after which there was a gradual weight loss to between 500- 800°C at which it decomposed.

(c) Preparation and Fvp of α,α,α',α'-tetrachloro-*o*-xylene

(i) Preparation of α,α,α',α'-tetrachloro-*o*-xylene

This was prepared from phthalic dicarboxaldehyde(2.0g, 15.0mmol) and thionyl chloride(5.0g, 42mmol) in dichloromethane, heated under reflux at 100-120°C for 2h. The black solid mass obtained, after the solvent was removed, was rather difficult to recrystallise and continously fumed in air, although the ^1H NMR showed the absence of the aldehyde (-CHO) proton peak and the presence of $-CHCl_2$ peak at δ_H 7.2. A commercial sample was however used for the pyrolysis.

(ii) Fvp of α,α,α',α'-tetrachloro-*o*-xylene

Fvp of the title compound (1.1g, 600°C, 8.0 x 10^{-2}mmHg, inlet - 85-90°C, 1.5g magnesium) gave a faint yellow liquid and a solid. The NMR and GC-MS showed that the two fractions consisted of the same mixture of compounds namely 7,8-dichlorobicyclo[4.2.0]octa-1,3,5-triene[210] (*cis* and *trans*,49.7%), *cis*-isomer; δ_H 5.6(2H, s) and 7.3(4H, m); δ_C 68.1(C-7,C-8), 123.0(C-2,C-5), 131.0(C-3,C-4) and 138.2(C-1,C-6), *trans*-isomer; δ_H 5.2(2H, s) and 7.3(4H, m); δ_C 62.2(C-7, C-8), 122.9 (C-2,C-5), 131.3(C-3,C-4) and 141.3(C-1,C-6); m/z 173 and 7,7,8-trichlorobicyclo[4.2.0]octa-1,3,5-triene[211](17.9%); δ_H 5.7(1H, s) and 7.2-7.5(4H, m); δ_C 60.7, 71.2, 128.2, 128.5, 130.4, 132.0, 143.1, and 145.8; m/z 208. There were also small amounts of 7-chlorobicyclo[4.2.0]octa-1,3,5-triene and bicyclo[4.2.0]octa-1,3,5-triene.

Repeat pyrolysis at higher magnesium to substrate ratio (1.0g of s.m, 600°C, 1.2 x 10^{-2}mmHg, inlet - 85-90°C, 2.8g magnesium) gave only a yellow solid product which consisted of 7,8-dichloro-bicyclo[4.2.0]octa-1,3,5-triene(14.8%) and benzocyclobutadiene dimer[73] (45%); δ_C 43.2, 43.7, 120.7, 121.5, 120.9, 125.9, 126.7, 127.6(2C), 127.7(2C), 133.1, 134.7, 148.5 and 149.0; m/z 204, with only trace amounts of the trichlorobicyclo[4.2.0]octa-1,3,5-triene. The yield was determined from the GC integral.

(d) Fvp of α,α,α',α'-tetrachloro-*m*-xylene

Fvp of the title compound (0.69g, 600°C, 9.0 x 10^{-2}mmHg, inlet - 85-90°C, 2.0g magnesium) gave a light yellow solid. The NMR showed that it consisted mainly of pyrene(21.3%); δ_H 8.1-8.2(m). GC-MS showed that the product consisted of pyrene(21.3%), 3,3'-dimethyl-stilbene(*Z*-:*E*-,4.3% and 11.9%), 3,3'-dimethylbibenzyl(10.0%), methylbibenzyl(3.7%), methylstilbene(2.3%) and dihydropyrene(0.8%). Repeat pyrolysis (0.96g, 600°C, 4.2 x 10^{-2}mmHg, inlet - 150- 160°C, 1.7g magnesium) showed only two products - pyrene(54.4%); δ_H 8.1-8.2(m); δ_C 124.9(4C-2,2C-5), 125.8(2C-1), 127.4(4C-4) and 131.1(4C-3); m/z 202 and 3,3'-dimethylstilbene(4.6%).

G. Fvp of Benzotrihalides(Benzylidyne Halides)

1. Fvp of benzotrichloride

Fvp of the title compound (0.43g, 600°C, 2.6 x 10^{-1}mmHg, inlet - room temperature, 0.8g magnesium) gave mainly a yellow solid with a trace of liquid. The liquid fraction was mainly traces of benzylidene chloride and starting material. The NMR and GC-MS of the solid fraction showed that it consisted of α,α,α',α'-tetrachlorobibenzyl (21.6%); δ_C 126.6(2C), 128.2(2C), 129.0, 129.1 and 137.5; m/z 320, α,α'-dichlorostilbene(*Z*-:*E*-22.5% and 19.4%); m/z 249; and diphenylacetylene(12.0%); m/z 178.

Repeat pyrolysis at longer contact time (1mmHg) gave a yellow solid, which consisted of α,α,α',α'-tetrachlorobibenzyl(8.4%), α,α'-dichlorostilbene(*Z*-:*E*-21.0% and 20.0%); δ_C 128.2(128.2,2C), 129.0(128.5), 129.1(129.7,2C), 130.7(129.8) and 137.5(137.1) - value of the other isomer in brackets and diphenylacetylene(30.0%); δ_C 89.4, 123.2, 128.1(2C), 128.3, 131.6(2C). The yield was determined from GC integration.

2. Fvp of benzotrifluoride

Fvp of the title compound (0.39g, 600°C, 40mmHg - N_2 leak, inlet - ice-cooled vertical inlet tube, 0.5g magnesium) gave mainly a liquid fraction, with a small amount of solid. The GC-MS indicated the liquid fraction was mainly recovered starting material. While the solid contained various fluorinated compounds, the major ones include - α,α,α',α'-tetrafluorobibenzyl; m/z 254, bis(trifluoromethyl)biphenyl; m/z 290, α,α'-difluorostilbene; m/z 216, α-fluorostilbene; m/z 198, fluorophenanthrene; m/z 196, diphenylacetylene; m/z 178, α,α,α'-trifluorobibenzyl; m/z 236 and small amounts of various unidentified compounds. Product identification was based entirely on

GC-MS evidence. No attempt was made to determine the yield of the products, as most of the starting material was unreacted.

3. Fvp of *p*-(bromomethyl)benzotrifluoride

Fvp of the title compound (0.81g, 600°C, 8.0 x 10^{-2}mmHg, inlet - room temperature, 1.2g magnesium) gave a solid and a polymer material as products. The ^{1}H NMR and GC-MS of the solid showed that it was mainly recovered starting material(30.0%), with a small amount of 4,4'-bis(trifluoromethyl)bibenzyl(4.3%); δ_H 2.9(4H, s) and 7.1-7.4 (8H, m); m/z 318, 4-trifluoromethyltoluene(7.8%); δ_H 2.3(3H, s) and 7.1-7.4(4H, m); m/z 160, and α-bromo-α',α'-difluoro-*p*-xylene(trace); m/z 219. Microanalysis of the polymer gave C, 64.1; H, 4.3; $C_8H_6F_2$ requires C, 68.6; H, 4.3% - indicative of poly(α,α-difluoro-*p*-xylylene). Based on the microanalysis result the yield of the polymer was 12.6% (42.1 mg). Solid state ^{13}C NMR of the material showed - δ_C 36.8 (CH_2, broad), 79.3(CF_2, broad), 120.2(C-2,C-3,C-5,C-6,broad), 160.7 (C-1,C-4,broad) and based on small end group (CH_3,δ_C 13.0) analysis it was estimated to have a molecular weight of 990(ie a heptamer).

Thermogravimetric analysis of the polymer showed that it was stable in air up to 500°C but undergoes a steady weight loss from about 100°C. Similar analysis in N_2 showed a double isotherm at 100°C and 550°C, but also underwent a steady weight loss from about 100°C.

4. Fvp of *o*-(chloromethyl)benzotrifluoride

Fvp of the title compound (0.38g, 600°C, 6.6 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave two fractions, a liquid and a solid. The ^{1}H NMR and GC-MS showed the liquid consisted of the starting material, in addition to numerous other compounds, some of which are toluene; m/z 92, 2-trifluoromethyltoluene; m/z 160,

2,2,2-trifluoro-1-(trifluoromethyl)ethylbenzene or its isomer; m/z 228, phenylacetylene; m/z 102, benzocyclobutene; m/z 104, 2,2-difluoro-ethenylbenzene; m/z 140, trifluoromethylstyrene; m/z 172 and various fluorinated and chlorinated compounds. The solid fraction consisted mainly of 2,2'-trifluoromethylbibenzyl; m/z 318 and 2,2'-trifluoro-methylstyrene, with numerous other compounds. Due to the complex nature of both the ^{1}H NMR spectrum and GC-MS, it was impossible to determine the yield of products. Product identification was entirely based on the GC-MS evidence.

5. Fvp of 1,4-bis(trichloromethyl)benzene

Fvp of the title compound (1.54g, 600°C, 4.4 x 10^{-2}mmHg, inlet - 130-135°C, 2.0g magnesium) gave a white polymer, which was insoluble in conventional solvents. Microanalysis of the polymer gave C, 38.6; H, 1.2. $(C_8H_4Cl_4)_n$ requires C, 39.7; H, 1.7%. Based on the microanalysis result, the yield of the polymer material was 1.16g(94.0%). Solid state ^{13}C NMR of the material; δ_C 97.8($2CCl_2$), 131.7(C-2,C-3,C-5,C-6) and 140.4(C-1,C-4) - indicative of poly(α,α,α',α'-tetrachloro-*p*-xylene). Using a $CHCl_2$ end group analysis, the polymer was estimated to consist of 10 units, giving an approximate molecular weight of 2420. Thermal analysis of the polymer in air showed a double isotherm at 300°C and 390°C; and a gradual weight loss was observed from 300°C to 540°C. In a N_2 atmosphere, a single isotherm was observed at 360°C, after which a gradual weight loss continued to 650°C.

6. Fvp of 1,4-bis(trifluoromethyl)benzene

Fvp of the title compound (1.49g, 600°C, 2.0mmHg, inlet - ice-cooled vertical inlet tube, 1.5g magnesium) gave two fractions, a

white polymer and a liquid, as product. The ^{1}H NMR and GC-MS showed that the liquid consisted mainly of the starting material and numerous fluorinated compounds. The polymer was insoluble in conventional solvents. Microanalysis of the material gave C, 54.6; H, 2.2. $(C_8H_4F_4)_n$ requires C, 54.6; H, 2.3% - indicative of poly(α,α,α',α'-tetrafluoro-*p*-xylylene). Based on the microanalysis result, the yield of polymer was 0.40g(32.7%) - uncorrected for recovered starting material. Solid state ^{13}C NMR of the material was not obtained, because the material was electrostatic and therefore could not be obtained in a form suitable for measurement. Thermogravimetric analysis indicated that the polymer was stable up to 620°C in nitrogen and 570°C in air; there was however a gradual weight loss of about 25% between 50-500°C, in both air and nitrogen.

H. Fvp of Mono- and Di-haloBenzenes

1. Fvp of chlorobenzene

Fvp of chlorobenzene (0.63g, 700°C, 15.0mmHg - N_2 leak, 1.0g magnesium) gave two fractions, a liquid and a solid. The liquid fraction was found to be benzene(60.3%); δ_H 7.25(s); m/z 78, while the solid was biphenyl(28.2%); δ_H 7.3-7.5(m); m/z 154. Both products were further confirmed by comparison with authentic samples on the GC (OV101, 150°C).

2. Fvp of 1,2-dichlorobenzene

Fvp of the title compound (1.38g, 600°C, 6.8 x 10^{-1}mmHg, inlet - room temperature, 2.0g magnesium) gave three fractions, a liquid, a solid in the cold trap and a solid at the furnace exit. The NMR and GC-MS indicated that the liquid product was mainly the starting material and benzene(12.6%), while the solid in the cold trap was mainly biphenyl(2.6%) with trace amounts of biphenylene. The solid at the furnace exit consisted mainly of triphenylene(6.5%) with small amounts of biphenyl and terphenyl.

Repeat pyrolysis at 700°C under the same conditions gave a similar product mixture to above. The product mixture was kugelrohr distilled (100 °C/20 mm Hg) leaving behind the solid product(0.11g, about 11.0%). The solid consisted of triphenylene(80% composition); δ_H 7.65 (6H, m) and 8.65(6H, m); δ_C 123.4(6C), 127.3(6C) and 129.9(6C); m/z 228, biphenyl(12% composition); δ_H 7.3-7.6(m); δ_C 127.3(6C), 128.8(4C) and 141.2(2C); m/z 154 and biphenylene(8% composition); δ_H 6.6(4H, m) and 6.7(4H, m); δ_C 117.4(4C), 128.3(4C) and 151.5(4C); m/z 152. All products were further confirmed with authentic samples on the GC (OV101, 250°C).

3. Fvp of 1,2-dibromobenzene

Fvp of the title compound (2.0g, 600°C, 8.0 x 10^{-1}mmHg, inlet 60-65°C, 2.0g magnesium) gave a liquid and a solid product. The NMR and GC-MS analysis indicated that the liquid product was mainly unreacted starting material with small amounts of benzene and bromobenzene. The solid fraction(73.0mg, 11.0% - corrected for recovered starting material) consisted mainly of triphenylene; m/z 228, with small amounts of biphenyl; m/z 154 and biphenylene; m/z 152.

Repeat pyrolysis at 700°C under the same conditions gave a liquid and a solid product. The liquid product was only benzene(18.0%); δ_H 7.3(s); while the solid product consisted of triphenylene(12.9%), biphenyl(4.3%) and biphenylene(1.0%). The ^1H and ^{13}C NMR values for triphenylene, biphenyl and biphenylene, were the same as in section 2.and all products were further confirmed with authentic samples on the GC (OV101, 250°C).

4. Fvp of 1-bromo-2-chlorobenzene

Fvp of the title compound (1.07g, 600°C, 1.0 x 10^{-1}mmHg, inlet - room temperature, 1.5g magnesium) gave three fractions, a liquid, solid in cold trap and a solid at furnace exit. The ^1H NMR indicated that the liquid product consisted of the starting material and benzene; while the solid in the cold trap consisted of biphenyl(5.7%); δ_H 7.35(2H, m), 7.45 (4H, m) and 7.6(4H, m) and biphenylene(1.1%); δ_H 6.65(4H, m) and 6.75 (4H, m); with traces of benzene. The solid at the furnace exit was triphenylene(10.8%); δ_H 7.65(6H, m) and 8.65(6H, m). All products were further confirmed with authentic samples on the GC (OV101; 250°C).

5. Preparation and Fvp of 3,4-dibromo-*o*-xylene

(i) Preparation of 3,4-dibromo-*o*-xylene[206]

This was prepared from 5-bromo-4-amino-*o*-xylene[206]. 5-Bromo-4-amino-*o*-xylene(10.0g, 50mmol) was dissolved in 48% hydrobromic acid(80 ml) and water(300ml) at –5 to +5°C, the mixture was then diazotised with 10% solution of sodium nitrite. The diazonium solution was siphoned under slight N_2 pressure, into a solution of cuprous bromide(100g) in conc. hydrobromic acid(270ml) and H_2O(100ml) kept at 90°C. The solution was extracted with ether, dried and solvent evaporated to give a solid mass. Recrystallisation from ethanol gave 4,5-dibromo-*o*-xylene(10.4g, 78.8%) as a light yellow plates, m.p. 88 °C(lit.[206] 88 °C); δ_H 2.2(6H, s) and 7.5(2H, s); δ_C 19.7, 121.7, 134.8 and 138.2.

(ii) Fvp of 3,4-dibromo-*o*-xylene

Fvp of the title compound (1.12g, 600°C, 4.0 x 10^{-2}mmHg, inlet - 85-90°C, 3.0g magnesium) gave mainly a liquid product, with small amount of yellow solid. The ^{1}H NMR showed that the liquid product was *o*-xylene(77.1%); δ_H 2.3(6H, s) and 7.1(4H, s), while the GC-MS showed that the solid was tetramethylbiphenyl(7.0%); m/z 210. Repeat pyrolysis at 700°C gave the same mixture of products.

6. Fvp of 4-bromo-5-fluoro-*o*-xylene[211]

Fvp of the title compound (0.31g, 600°C, 6.0 x 10^{-2}mmHg, inlet - 60-65°C, 1.5g magnesium) gave mainly a liquid product with small amount of solid. The ^{1}H NMR and GC-MS indicated that the liquid was mainly 4-fluoro-*o*-xylene(75.3%); δ_H 2.25(6H, s) and 7.2(3H, s); m/z 124 and small amounts of 4-bromo-*o*-xylene; m/z 184. The solid fraction was unreacted starting material. Repeat pyrolysis at 700°C gave the same mixture of product.

I. Preparation and Fvp of Halogenated Thiophenes

1. Preparation and Fvp of 2-thiophenemethylbromide (2-bromomethylthiophene)

(i) Preparation of 2-bromomethylthiophene

This was prepared from 2-thiophenemethanol(6.8g, 60mmol) and phosphorus tribromide(5.4g, 20mmol) in dichloromethane; heated under reflux for 2h. The mixture was poured into water and the organic layer separated, washed twice with water and the sodium bicarbonate solution, dried and evaporated. Kugelrohr distillation gave 2-bromomethyl-thiophene as a colourless liquid, b.p. 120°C/0.1mmHg(lit.[212] 80-82 °C/ 15mmHg), which was rather unstable and readily polymerises on standing. The product was used immediately after preparation.

(ii) Fvp of 2-bromomethylthiophene

Fvp of the title compound (0.14g, 600°C, 1.0mmHg, inlet - room temperature, 1.0g magnesium) gave two fractions, a liquid and a solid. The ^1H NMR and GC-MS of the liquid fraction showed that it was 2-methylthiophene(14.6%); δ_H 2.5(3H, s) and 6.6-7.2(3H, m); m/z 98, while the solid fraction consisted of 1,2-di(2-thienyl)ethane(25.0%); δ_H 3.1(4H, s) and 6.7-7.2(6H, m); m/z 194, dithienylmethane(6.0%); δ_H 4.2(2H, d, J 2Hz) and 6.7-7.2(6H, m); m/z 180, 5-methyl-2,2'-bithiophene (3.0%); m/z 180 and trace amounts of thiophene and 1,2-di(2-thienyl)ethene.

2. Preparation and Fvp of dichloromethylthiophenes

(a) Preparation and Fvp of 2-dichloromethylthiophene

(i) Preparation of 2-dichloromethylthiophene

This was prepared from 2-thiophenecarboxaldehyde(22.8g, 0.2mol) and phosphorus pentachloride (42.0g, 0.2mol); stirred at room temperature for 1h. The mixture was poured into ice water and extracted

with ether, the organic layer was washed (twice) quickly with water, dried and evaporated. Kugelrohr distillation gave a colourless liquid, which darkened on standing and was moisture sensitive. The product was confirmed as 2-dichloromethylthiophene(23.4g, 70%); b.p. 90°C/ 4mmHg(lit.[213].87°C/7mmHg); δ_H 6.9(1H, m), 6.95(1H, s), 7.2(1H, m) and 7.35(1H, d of d, J 2,1Hz); δ_C 66.6, 126.4, 126.5 127.8 and 143.7; m/z 167.

(ii) Fvp of 2-dichloromethylthiophene

Fvp of the title compound (0.61g, 600°C, 2.0 x 10^{-1}mmHg, inlet - room temperature, 1.5g magnesium) gave two fractions, a liquid and a solid. The NMR and GC-MS showed that the solid fraction consisted mainly of 1,2-di(2-thienyl)ethene[214](*Z*-:*E*-,3.6% and 39.2%), *E*-isomer δ_H 7.1(m); δ_C 120.4, 123.2, 124.9, 126.6 and 141.3; m/z 192, with benzo[1,2-b:4,3-b']dithiophene(6.3%, confirmed with synthesised authentic sample); m/z 190, 1-chloro-1,2-di(2-thienyl)ethene(3.6%); m/z 226 and 1,2-di(2-thienyl)ethane(1.5%), while the liquid product consisted of a complex mixture of compounds, including 2-methylthiophene.

(b) Preparation and Fvp of 3-dichloromethylthiophene

(i) Preparation of 3-dichloromethylthiophene

This was prepared from 3-thiophenecarboxaldehyde(5.0g, 45.0mmol) and phosphorus pentachloride(9.5g, 45.7mmol), stirred overnight in dichloromethane. Work up and kugelrohr distillation gave a colourless liquid, which darkened on standing. The product was confirmed as 3-dichloromethylthiophene(5.9g, 79.2%); b.p. 90°C/ 4mmHg. Due to the air-sensitive nature of the product, microanalysis was rather difficult and was reflected in the result - (Found: C, 41.0; H, 2.4. $C_5H_4Cl_2S$ requires C, 36.0; H, 2.4%); δ_H 6.85(1H, s), 7.3

(1H, s), 7.35(1H, s) and 7.45(1H, m); δ_C 66.8, 123.4, 125.6, 127.2 and 140.8 .

(ii) Fvp of 3-dichloromethylthiophene

Fvp of the title compound (0.61g, 600°C, 2.5 x 10^{-1}mmHg, inlet - room temperature, 1.5g magnesium) gave two fractions, a liquid and a solid. The NMR and GC-MS showed that the liquid consisted mainly of 3-methylthiophene(5.0%) with small amounts of thiophene and 3-vinylthiophene; while the solid consisted mainly of 1,2-di(3-thienyl)ethene[214](*Z*-:*E*-,7.1% and 26.7%), *E*-isomer δ_H 7.05 (2H, s) and 7.4(6H, m); δ_C 121.9, 122.9, 124.7, 126.1 and 140.0; m/z 192 and benzo[2,1-b:3,4-b']dithiophene(8.0%); m/z 190, 1-chloro-1,2-di(3-thienyl)ethene(8.8%, two isomers); m/z 226 and 1,2-di(3-thienyl)ethane(2.6%).

(c) Preparation and Fvp of 3-methyl-2-dichloromethyl-thiophene

(i) Preparation of 3-methyl-2-dichloromethylthiophene

To 3-methyl-2-thiophenecarboxaldehyde(2.9g, 23mmol) in dichloromethane, was added phosphorus pentachloride(5.0g, 23mmol) with stirring. After stirring at room temperature for 1h, the mixture was washed (twice) with water, dried and evaporated. Kugelrohr distillation gave 3-methyl-2-dichloromethylthiophene(3.3g, 77.6%) as a colourless liquid; b.p. 100°C/4mmHg. Due to the air-sensitive nature of the product, microanalysis was rather difficult and was reflected in the result (Found: C, 12.95; H, 3.5. $C_6H_6Cl_2S$ requires C, 39.8; H, 3.3%); δ_H 2.2 (3H, s), 6.7(1H, d, J 4Hz), 6.9(1H, s) and 7.15(1H, d, J 4Hz); δ_C 13.7, 65.7, 126.0, 130.0, 135.7 and 137.4; m/z 180(53%,M^+), 165(10), 144(82), 125(60), 109(100), 97(35), 65(40) and 45(58).

(ii) Fvp of 3-methyl-2-dichloromethylthiophene

Fvp of the title compound (0.83g, 600°C, 3.6 x 10^{-1}mmHg, inlet - room temperature, 1.5g magnesium) gave a thick liquid. The NMR and GC-MS showed that it consisted of 1,2-bis(3-methyl-2-thienyl)ethene (*Z*-:*E*-,16.0% and 23.4%), *E*-isomer; δ_H 2.25(6H, s), 6.75(2H, d, J 3Hz), 6.95(2H, s) and 7.0(2H, d, J 3Hz); δ_C 13.9, 119.4, 122.4, 130.8, 135.2 and 136.4; m/z 220, with 1,2-bis(3-methyl-2-thienyl)ethyne(4.7%); m/z 218, 4,5,9,10-tetrahydrocycloocta[1,2-b:6,5-b']dithiophene(4.0%); m/z 220, methylthiophene(1.9%), 2,3-dimethylthiophene(3.2%) and 3-isomers of compounds m/z 188(4.5%). The yield was determined from GC integrals.

(d) Preparation and Fvp of 5-methyl-2-dichloromethyl-thiophene

(i) Preparation of 5-methyl-2-dichloromethylthiophene

This was prepared as for 3-methyl-2-dichloromethylthiophene above, from 5-methyl-2-thiophenecarboxaldehyde(2.9g, 23mmol) and phosphorus pentachloride(5.0g, 23mmol). Kugelrohr distillation gave 5-methyl-2-dichloromethylthiophene(3.4g, 80%) as a faint yellow liquid; b.p. 90°C/4mmHg. Due to the air-sensitive nature of the product, micro analysis was rather difficult and was reflected in the result; (Found C, 40.6; H, 3.4. $C_6H_6Cl_2S$ requires C, 39.8; H, 3.3%); δ_H 2.45(3H, s), 6.65 (1H, d, J 2Hz), 6.95(1H, s) and 7.05(1H, d, J 2Hz); δ_C 15.9, 67.5, 125.0, 127.1, 141.9 and 143.6; m/z 180(62%,M^+), 165(8), 145(100), 125(35), 109(80), 95(30), 69(50) and 45(65).

(ii) Fvp of 5-methyl-2-dichloromethylthiophene

Fvp of the title compound (0.86g, 600°C, 4.0 x 10^{-1}mmHg, inlet - room temperature, 1.5g magnesium) gave a solid product and a polymeric material. The solid product was 1,2-bis(5-methyl-2-thienyl)ethene(39.4%); m.p. 94-96°C(Lit.[214] 92-93°C); δ_H 2.45(6H, s),

6.6(2H, d, J 3Hz), 6.75(2H, d, J 3Hz), and 6.85(2H, s); δ_C 16.2, 121.3, 126.4, 126.5, 139.5 and 141.2; m/z 220. No analysis was carried out on the polymer material as it was insoluble in any conventional solvents, however it is assumed that the polymer was formed *via* the *p*-xylylene analogue of the thiophene involving the 2- and 5- positions.

3. (a) Fvp of 2-bromothiophene

Fvp of 2-bromothiophene (0.93g, 600°C, 3.6 x 10^{-1}mmHg, inlet - ice cooled vertical inlet tube, 2.0g magnesium) gave a yellowish liquid (0.43g), which was found to consist mainly of the starting material with a trace of thiophene. Some insoluble polymer flakes were observed at the furnace exit.

(b) Fvp of 3-bromothiophene

Fvp of 3-bromothiophene (0.90g, 600°C, 5.8 x 10^{-1}mmHg, inlet - ice cooled vertical inlet tube, 1.5g magnesium) gave a liquid (0.45g) which was found to be unreacted starting material. Some insoluble polymer flakes were observed at the furnace exit.

(c) Preparation and Fvp of 2,3-dibromothiophene

(i) Preparation of 2,3-dibromothiophene[215]

This was prepared from 3-bromothiophene(20g, 0.12mol) and N-bromosuccinimide(22g, 0.12mol) in 1:1(v/v) chloroform/acetic acid (150ml). The mixture was heated under reflux for 1h, with stirring and on cooling, poured into ice water. The organic layer was washed with water, 0.5M sodium hydroxide and water until neutral; dried and evaporated. Kugelrohr distillation gave a colourless liquid which was confirmed as 2,3-dibromothiophene(14.0g, 82.0%); b.p. 70°C/4mmHg (lit.[216] b.p. 80°C/10mmHg); δ_H 6.8(1H, d, J 3Hz) and 7.2(1H, d, J 3Hz).

(ii) Fvp of 2,3-dibromothiophene

Fvp of the title compound (0.97g, 600°C, 5.8 x 10^{-1}mmHg, inlet - room temperature, 1.5g magnesium) gave a liquid (0.38g) and an insoluble polymer flake. The liquid was found to be the unreacted starting material. Repeat pyrolysis at 700°C gave the starting material, bromothiophene and some thiophene.

4. Preparation and Fvp of 3-bromo-2-chloromethylthiophene

(i) Preparation of 3-bromo-2-chloromethylthiophene

2,3-Dibromothiophene was converted to 3-bromo-2-thiophene-carboxaldehyde according to the method of Gronowitz.[215] The aldehyde (7.5g, 39mmol) was reduced to the alcohol, with sodium borohydride (0.8g, 21mmol) in absolute ethanol at 60°C. On cooling the solvent was evaporated and the white solid mass obtained was treated with water and acidified with 5M HCl; extracted with ether and the organic layer washed with sodium carbonate solution and water. The organic layer was dried, evaporated and the crude liquid was confirmed with ^{1}H NMR to be 3-bromo-2-thienylmethanol. The crude alcohol(7.0g, 36mmol) was converted to the chloride, with triethylamine(3.7g, 37mmol) and thionyl chloride(4.5g, 38mmol) in dichloromethane at 50°C. Work up and kugelrohr distillation gave a lachrymatory oil which was confirmed as 3-bromo-2-chloromethylthiophene; b.p. 150°C/20mmHg (lit.[217] 106-108°C/12mmHg); δ_H 4.7(2H, s), 6.9(1H, d, J 3Hz) and 7.3 (1H, d, J 3Hz).

(ii) Fvp of 3-bromo-2-chloromethylthiophene

Fvp of the title compound (0.82g, 600°C, 9.0 x 10^{-1}mmHg, inlet - 60-65°C, 1.5g magnesium) gave a solid product (0.043g). The ^{1}H NMR was rather complex. The GC-MS showed that the product consisted mainly of 1,2-di(2-thienyl)ethene(2 isomers); m/z 192,

dihydrobenzodithiophene; m/z 192, benzodithiophene(2-isomers); m/z 190 and naphthalene; m/z 128, with traces of methylbromothiophene, indene, benzothiophene and an unidentified compound with m/z 130. Due to the low yield of the total product, no attempt was made to determine the yield of individual compounds. Product identification was solely based on GC-MS evidence.

5. Preparation and Fvp of halo-dichloromethylthiophenes

(a) Preparation and Fvp of 3-bromo-2-dichloromethyl-thiophene

(i) Preparation of 3-bromo-2-thiophenecarboxaldehyde

2,3-Dibromothiophene(21.6g, 90mmol) was converted to 3-bromo-2-thiophenecarboxaldehyde[215] with 2.5M solution of *n* butyl lithium(36ml, 90mmol) and N,N-dimethylformamide(6.6g, 90mmol) in anhydrous ether at –70 °C. The dibromothiophene and butyl lithium solution was siphoned under N_2 pressure into the DMF solution; and the mixture stirred overnight. Work up and kugelrohr distillation gave a colourless liquid, which was confirmed as 3-bromo-2-thiophene-carboxaldehyde(12.2g, 71.5%); 55°C/0.1mmHg(lit.[215] 114-116°C/ 12mmHg); δ_H 7.1(1H, d, J 2Hz), 7.8(1H, d of d, J 2, 1Hz) and 9.9 (1H, d, J 1Hz).

(ii) Preparation of 3-bromo-2-dichloromethylthiophene

To the aldehyde(3.0g, 15.7mmol), prepared above in dichloromethane, was slowly added phosphorus pentachloride(3.5g, 16.8mmol); and the mixture was heated under reflux for 1h. Work up and kugelrohr distillation gave a colourless liquid, which was confirmed as 3-bromo-2-dichloromethylthiophene(3.5g, 90.1%); b.p. 60°C/ 0.1mmHg; δ_H 6.95(1H, d, J 2Hz), 7.1(1H, s) and 7.45(1H, d, J 2Hz); δ_C 65.2, 109.7, 127.7, 129.3 and 138.8; m/z 246(10%,M^+), 211(80), 165(4), 130(8), 95(12), 81(12), 69(12) and 45(100).

(iii) Fvp of 3-bromo-2-dichloromethylthiophene

Fvp of the title compound (1.1g, 600 °C, 6.0 x 10^{-2}mmHg, inlet - 30-40°C, 1.6g magnesium) gave a solid product. The ^{1}H NMR was rather complex. The GC-MS and ^{13}C NMR showed that the product consisted of 1,2-bis(3-bromo-2-thienyl)ethene(*Z*-:*E*-3.9% and 24.8%), *E*-isomer; δ_C 111.5, 121.3, 124.5, 130.9 and 136.5 (confirmed with prepared sample); m/z 350 and chloro-1-(3-bromo-2-thienyl)-2-(2'-thienyl)ethene(12.8%); δ_C 115.3, 123.4, 123.6, 127.1, 127.8, 129.9, 130.2, 130.8, 132.0, and 136.4; m/z 306. Other compounds present include chloro-1,2-di(2-thienyl)ethene(6.1%); m/z 224, 1,2-bis(3-bromo-2-thienyl)ethyne(3.4%); δ_C 88.3(–C≡); m/z 348, with trace amounts of chloro-1,2-bis(3-bromo-2-thienyl)ethene(two isomers) and benzodithiophene(one isomer).

Repeat pyrolysis under the same conditions but at a temperature of 650°C, gave a product which consisted of 1,2-bis(3-bromo-2-thienyl)ethene(*Z*-:*E*-1.7% and 6.9%), chloro-1,2-di(2-thienyl)ethene (5.7%), chloro-1-(3-bromo-2-thienyl)-2-(2'-thienyl)ethene(4.7%) and three isomers of benzodithiophenes(3.5%, 2.6%, 4.9%); m/z 190. Trace amounts of 1,2-bis(3-bromo-2-thienyl)ethyne and 1-(3-bromo-2-thienyl)-2-(2-thienyl)ethene(two isomers) were also observed. Similar pyrolysis at 700°C gave the three isomers of benzodithiophene namely benzo[1,2-b:4,3-b']dithiophene(8.3%); δ_C 118.7, 121.9, 126.5, 134.6 and 136.4; m/z 190, benzo[1,2-b:3,4-b']dithiophene(4.6%); δ_C 118.9, 120.1, 121.6, 124.2, 124.7, 127.0, 133.6, 134.4, 136.2 and 136.8; m/z 190 and benzo[2,1-b:3,4-b']dithiophene(7.6%); δ_C 116.8, 122.9, 127.1, 136.8 and 137.5; m/z 190. The benzodithiophenes were confirmed with ^{13}C NMR values and GC trace of prepared samples. The yield was determined from GC integrals and consistituted about 86% of the total product. The other compounds present are chloro-1,2-di(2-thienyl)ethene(4.2%), with

traces of naphthalene(m/z 128), benzothiophene(m/z 134), phenylthiophene(m/z 160) and 1,2-bis(3-bromo-2-thienyl)ethene (m/z 350).

(b) Preparation and Fvp of 2-chloro-3-dichloromethylthiophene

(i) Preparation of 2-Chloro-3-thiophene-carboxaldehyde[218]

3-Bromothiophene(21.0g, 0.13mol) was converted to 2-chloro-3-bromothiophene with N-chlorosuccinimide(17.0g, 0.13mol) in a 1:1 mixture of chloroform and acetic acid(150 ml) which was heated under reflux for 1h. The NMR confirmed the product as 2-chloro-3-bromo-thiophene; δ_H 6.8(1H, d, J 3Hz), and 6.95 (1H, d, J 3Hz). To the 2-chloro-3-bromothiophene(14.0g, 70.8mmol) in anhydrous ether, a 2.5M solution of *n* butyl lithium(29.0ml, 70.8mmol) was added at –70°C and after about 15min, a solution N,N-dimethylformamide(5.2g, 70.8mmol) in anhydrous ether was added rapidly while stirring. Work-up and kugelrohr distillation gave a colourless liquid, which was confirmed as 2-chloro-3-thiophene-carboxaldehyde(6.2g, 60%); b.p. 60°C/0.1mmHg(lit.[218] 60-62°C/ 0.1mmHg); δ_H 7.1(1H, d, J 3Hz), 7.25(1H, d, J 3Hz), and 9.95(1H, s).

(ii) Preparation of 2-chloro-3-dichloromethylthiophene

To the aldehyde(3.0g, 20.5 mmol), prepared in dichloromethane, was slowly added phosphorus pentachloride(4.5g, 21.6mmol) and the mixture was heated under reflux for 1h. Work-up and Kugelrohr distillation gave a colourless liquid, which was confirmed as 2-chloro-3-dichloromethylthiophene(2.8g, 72.5%); b.p. 55°C/0.1mmHg; δ_H 6.95(1H, s), 7.25(1H, d, J 3Hz) and 7.45(1H, d, J 3Hz); δ_C 62.7, 123.2, 124.9, 125.6 and 136.1; m/z 201(10%,M^+), 165 (100), 131 (4), 103 (5), 95 (10), 79 (22), 69 (16) and 45 (42).

(iii) Fvp of 2-chloro-3-dichloromethylthiophene

Fvp of the title compound (0.70g, 600°C, 3.5 x 10^{-2}mmHg, inlet - 30-40°C, 1.7g magnesium) gave a solid product. GC-MS showed that it consisted mainly of 1,2-bis(2-chloro-3-thienyl)ethene(*Z-:E-*,5.4% and 16.8%); m/z 260, and chloro-1,2-bis(2-chloro-3-thienyl)ethene (*Z-:E-*4.7% and 10.1%); m/z 296. Also present are small amounts of chloro-1,2-di(3-thienyl)ethene(*Z-:E-*0.5% and 2.3%); m/z 226, 1,2-di(2-chloro-3-thienyl)ethyne; m/z 258, benzodithiophene(1,2-b:3,4-b' and 2,1-b:2,4-b' isomers, 1.2% each); m/z 190 and 1,2-di(3-thienyl)-ethene; m/z 192. The yield and product identification was based entirely on the GC-MS, except for the benzodithiophenes which were confirmed with prepared samples.

Repeat pyrolysis under similar conditions at 650°C gve a product, which consisted mainly of 1,2-bis(2-chloro-3-thienyl)ethene(18.0%), benzo[1,2-b:3,4-b']dithiophene(3.2%) and benzo[2,1-b:3,4-b']dithiophene (1.1%). There were also traces (<0.5%) of benzothiophene; m/z 134, phenylthiophene; m/z 160, 1,2-dithienylethene; m/z 192, chloro-1,2-dithienylethene; m/z 226 and 1,2-bis(2-chloro-3-thienyl)ethyne; m/z 258. Pyrolysis at 700°C gave the same mixture of compounds namely 1,2-bis(2-Chloro-3-thienyl)ethene(*Z-:E-*,1.4% and 9.5%), 1,2-bis(2-chloro-3-thienyl)ethyne(5.8%), chloro-1,2-bis(2-chloro-3-thienyl)ethene (two isomers, 0.6% and 2.6%), benzo[1,2-b:3,4-b']dithiophene(3.4%), benzo[2,1-b:3,4-b']dithiophene(1.5%) and 1,2-di(3-thienyl)ethene (trace).

(c) Preparation and Fvp of 3-bromo-4-dichloromethylthiophene

(i) Preparation of 3-bromo-4-thiophene-carboxyaldehyde[219]

Tetrabromothiophene(30g, 75mmol) and zinc dust(30g) in acetic acid(15ml) and water(50ml) was heated under reflux for 1h. The apparatus was then set up for distillation with a Dean and Stark trap and

the mixture was rapidly distilled with the aqueous layer continously returned to the flask until no organic layer distilled over with the water. The organic layer was taken up with ether, washed with water, dried and evaporated. Kugelrohr distillation gave 3,4-dibromothiophene(11.2g, 61.7%); b.p. 60°C/0.1mmHg(lit.[219] 94-95°C/12mmHg; δ_H 7.2(s).

A solution of 3,4-dibromothiophene(11.0g, 45mmol) and 2.5M butyl lithium(18ml, 45mmol) in anhydrous ether at –70°C, was siphoned under N_2 pressure into a solution of N,N-dimethylformamide(3.5g, 45mmol) in anhydrous ether; and stirred overnight. Work up and Kugelrohr distillation gave 3-bromo-4-thiophenecarboxaldehyde (6.0g, 70.4%); b.p. 60°C/0.1mmHg(lit.[217] 108-111°C/11mmHg); δ_H 7.4(1H, d, J 4Hz), 8.2(1H, d, J 4Hz), and 9.9(1H, s); δ_C 110.8, 125.2, 135.0, 137.1, and 184.3.

(ii) Preparation of 3-bromo-4-dichloromethylthiophene

To the aldehyde(2.2g, 11.5mmol) prepared above in dichloromethane, was slowly added phosphorus pentachloride(3.0g, 14.4mmol) and the mixture heated under reflux for 1h. Work up and Kugelrohr distillation gave a colourless liquid, which was confirmed as 3-bromo-4-dichloromethylthiophene(2.02, 71.4%); b.p. 100°C/0.1mmHg; (Found: C, 25.1; H, 1.2. $C_5H_3BrCl_2S$ requires C, 24.4; H, 1.2%); δ_H 6.7 (1H, s), 7.25(1H, d, J 4Hz), and 7.7(1H, d, J 4Hz); δ_C 65.5, 108.7, 124.4, 126.4 and 139.8; m/z 246(18%,M^+), 211(95), 165(2). 130(21), 105(6), 95(23), 69(15) and 45(100).

(iii) Fvp of 3-bromo-4-dichloromethylthiophene

Fvp of the title compound (0.94g, 600°C, 8.5 x 10^{-2}mmHg, inlet - 60-65°C, 1.7g magnesium) gave a solid product. GC-MS showed that it consisted of 1,2-bis(4-bromo-3-thienyl)ethene(*Z-:E-*,4.1% and 17.8%); m/z 350, 1,2-bis(4-bromo-3-thienyl)ethyne(7.3%); m/z 348 and a trace amount of an isomer of benzodithiophene(0.4%). The yield and

product identification was based entirely on GC-MS evidence. Repeat pyrolysis at 650°C, and 700°C gave insoluble polymer flakes and small amounts of solid. GC-MS showed that the solid consisted of similar mixtures of compounds to those obtained at 600°C, but the yield was much lower.

6. Preparation of authentic samples of Benzodithiophenes

(a) Preparation of Benzo[1,2-b:4,3-b']dithiophene[217]

3-Bromothiophene was converted to 3-bromo-2-thiophene-carboxaldehyde as in 5(a). One half of the aldehyde was reduced to the alcohol with sodium borohydride and then converted to 3-bromo-2-chloromethylthiophene as in 4. To a solution of 3-bromo-2-chloro-methylthiophene(7.0g, 33.0mmol) in benzene, was added a solution of triphenylphosphine (9.0g, 34.0mmol) in benzene; and the mixture heated under reflux for 2days. On cooling, the white precipitate was filtered, washed with ether and dried by suction. NMR confirmed the product as (3-bromo-2-thienylmethyl)triphenylphosphonium chloride. To a suspension of the phosphonium salt(11.4g, 24.0mmol) in anhydrous DMF under N_2, 2.0g of freshly prepared sodium ethoxide (from sodium metal and ethanol) in DMF, was added and the mixture stirred for 30mins. 3-bromo-2-thiophenecarboxaldehyde(4.5g, 24.0mmol) in DMF was then added and stirred for 2h. Work-up gave an oil which was passed down a flash chromatography column (SiO_2, hexane) and the liquid obtained after solvent evaporation was left standing overnight. A small amount of yellow crystalline solid, found to be *E*-1,2-bis(3-bromo-2-thienyl)-ethene[217]; δ_H 7.1(2H, d, J 4Hz), 7.25(2H, s) and 7.3(2H, d, J 4Hz); δ_C 111.5, 121.3, 124.5, 130.9, and 136.5; m/z 350, was observed, while the *Z*-isomer remained as a liquid; δ_H 6.7(2H, s), 6.9(2H, d, J 3Hz) and 7.1 (2H, d, J 3Hz).

To *Z*-1,2-bis(3-bromo-2-thienyl)ethene(5.0g, 14.0mmol) in anhydrous ether, was added a 2.5M solution of butyl lithium(12.5ml, 30.0mmol) at –70°C under N_2 followed after 10min by anhydrous cupric chloride(4.0g, 30.0mmol) in one portion. The mixture was stirred at -70°C for 2h and overnight at room temperature. Work up gave a solid product, which on recrystallisation(70% aq.ethanol) gave a light green solid, which was cofirmed as benzo[1,2-b:4,3-b']dithiophene; m.p. 118°C(lit.[217] 117°C); δ_H 7.65(2H, d, J 3Hz), 7.80(2H, d, J 3Hz) and 7.90 (2H, s); δ_C 118.7, 121.9, 126.4, 134.6 and 136.4; m/z 190; .

(b) Preparation of benzo[1,2-b:3,4-b']dithiophene[220]

(2-Thienylmethyl)triphenylphosphonium bromide was prepared from 2-bromomethylthiophene and triphenylphosphine. To a suspension of the phosphonium salt(10.0g, 22.0mmol) in THF, under N_2, was added 2.5M solution of butyl lithium(9.0ml, 23.0mmol) and stirred for 30 min, after which 3-thiophenecarboxaldehyde(2.0g, 18mmol) in THF was slowly added. The mixture was left stirring overnight, after which it was heated under reflux for 2h and work up gave a yellow solid with some oily liquid. Kugelrohr distillation(160°C/0.5mmHg) gave a white solid, leaving behind triphenylphosphine oxide. The white solid was found to be a mixture of *Z*-and *E*-isomers of 1-(2'-thienyl)-2-(3'-thienyl)ethene (2.8g, 82.0%); m/z 192.

The mixture of *Z*- and *E*-1-(2'-thienyl)-2-(3'-thienyl)ethene(2.0g, 10.0mmol) was dissolved in toluene(500ml) and iodine(0.13g, 5% mole equivalent) was added. The mixture was photolysed at room temperature for 8h; after which the solvent was evaporated leaving an oily residue, which was extracted with ether. Kugelrohr distillation(140°C/ 0.5mmHg) of the residue gave a mixture of the desired product with iodine. A second distillation (100°C/0.5mmHg) sublimed the iodine leaving the product in the kugelrohr bulb in the furnace, the temperature

was then increased to 140°C and the product sublimed into a clean bulb. The solid obtained was confirmed as benzo[1,2-b:3,4-b']dithiophene (0.82g, 41.0%); m.p. 41°C(lit.[217] 40-41°C); δ_H 7.15 and 7.2 (2H, AB pattern, J 2Hz), 7.3(2H, d, J 4Hz), 7.4(2H, d, J 4Hz), 7.55 (2H, d, J 5Hz), and 7.65(2H, d, J 2Hz); δ_C 118.6, 119.8, 121.3, 123.8, 124.3, 126.8, 133.3, 134.1, 135.9, and 136.5; m/z 190.

Attempts to prepare benzo[1,2-b:3,4-b']dithiophene by cyclisation of 1-(3-bromo-2-thienyl)-2-(2'-bromo-3'-thienyl)ethene with cupric chloride[217] were unsuccessful. The 1-(3-bromo-2-thienyl)-2-(2'-bromo-3'-thienyl)ethene was prepared by coupling 2-bromo-3-thiophene-carboxaldehyde(see 6c) and 3-bromo-2-thienylmethyl)triphenyl-phosphonium chloride as in 6(a). Spectral data for 1-(3-bromo-2-thienyl)-2-(2'-bromo-3'-thienyl)ethene; δ_H 6.95(2H, m), 7.2(2H, m), and 7.35(2H, m); δ_C 111.2 and 112.0(2C-Br), 121.8, 122.4, 124.3, 124.6, 126.3, 130.9, 136.8, and 137.6; m/z 350.

(c) Attempted preparation of benzo[2,1-b:3,4-b']-dithiophene

3-Thiophenecarboxaldehyde(25.2g, 0.23mol) and triethylortho-formate(50.0g) in absolute alcohol(240ml), with concentrated hydrochloric acid (5 drops) was heated under reflux for 6h. On cooling, the mixture was poured into water and extracted twice with ether. The organic layer was dried, concentrated and kugelrohr distilled to give the diethylacetal of 3-thiophenecarboxaldehyde[221](34.0g, 81.3%); δ_H 1.2 (6H, t), 3.5(4H, q), 5.5(1H, s) and 7.2(3H, m). To the diethylacetal (21.5g, 0.12mol) in anhydrous ether (150ml), cooled to –45°C (cyclohexanone/solid CO_2) under N_2, was added dropwise 2.5M butyl lithium(47.0ml, 0.12mol). After addition the mixture was stirred for 30 mins at –45°C, and then siphoned under slight N_2 pressure into a solution of bromine(12.0g, 75mmol) in anhydous ether(500ml) at –70°C.

The mixture was stirred for 2h at –70°C and then allowed to warm to room temperature, after which it was added to ice water, acidified with dilute HCl and extracted with ether. The organic phase was neutralised with aqueous sodium bicarbonate, dried and kugelrohr distilled to give diethylacetal of 2-bromo-3-thiophenecarboxaldehyde. This was hydrolysed with boiling ethanol(85ml) and concentrated HCl(6ml) for 30min and then extracted with ether. The organic layer was washed with aqueous sodium bicarbonate, dried and Kugelrohr distillation gave 2-bromo-3-thiophenecarboxaldehyde[222](8.4g, 37.8%); b.p. 100°C/ 1.0mmHg; δ_H 7.3(2H, s) and 9.8(1H, s).

The aldehyde(4.0g, 20.8mmol) was reduced to the alcohol with sodium borohydride(0.5g, 13.2mmol) in ethanol to give 2-bromo-3-thienylmethanol(2.8g, 69.3%); δ_H 4.2(1H, s), 4.3(2H, s), 6.9 (1H, d, J 4Hz) and 7.1(1H, d, J 4Hz). The alcohol was converted to the chloride with thionyl chloride and triethylamine in dichloromethane at 50°C. To the crude 2-bromo-3-chloromethylthiophene in toluene was added a solution of triphenylphosphine(4.0g, 15.0mmol) in toluene and the mixture heated under reflux and under N_2 for 2days. The white solid obtained on cooling was filtered and washed with ether to give (2-bromo-3-thienylmethyl)triphenylphosphonium chloride[217] (5.9g, 86.8%) - identified from the characteristic phosphonium salt peak on the ^{1}H NMR; δ_H 5.5(2H, d, J 7Hz).

The phosphonium salt was coupled with 2-bromo-3-thiophen-carboxaldehyde as in 6(a), to give 1,2-bis(2-bromo-3-thienyl)ethene[217]; δ_H 7.1(2H, s) and 7.4(4H, s); δ_C 111.7, 122.7, 124.6, 126.2 and 137.9; m/z 350. Attempts to cyclise this compound with butyl lithium and anhydrous cupric chloride[217], as in 6(a) was unsuccessful, rather a tarry material was obtained during work-up or in some cases a mixture of

1,2-di(3-thienyl)ethene, monobromodithienylethene and starting material was recovered.

(d) Attempted preparation of benzo[1,2-b:5,4-b']-dithiophene[223]

3-Bromo-2-chloromethylthiophene was prepared as in 4. The chloride(4.0g, 18.9mmol) in carbon disulphide(50ml) was added to a stirred solution of thiophene(3.2g, 38.0mmol) and stannic chloride (0.5g, 1.9mmol) in carbon disulphide(100ml) at 0°C. The mixture was stirred for 4h, then poured into ice water and 2M HCl and shaken vigorously. The mixture was extracted with ether (twice) and washed with saturated sodium bicarbonate solution and with water (tarry material was evident during the work-up), then dried and evaporated. The ^1H NMR of the crude liquid showed that it contained a mixture of compounds, but careful kugelrohr distillation gave 3-bromo-2-(2-thienylmethyl)thiophene(very low yield); b.p. 150°C/ 10^{-2}mmHg(lit.[223] 95-97 °C/0.05mmHg); δ_H 4.1(2H, s) and 6.7-7.0 (5H, m). Due to the low yield of the 3-bromo-2-(2-thienylmethyl)-thiophene and difficult route to the precursor the synthesis of benzo[1,2-b:5,4-b']dithiophene was not pursued any further.

(e) Attempted coupling of 3-thiophenecarboxaldehyde to give 1,2-di(3-thienyl)ethene

The reaction was modelled along the McMurry method[224] for coupling carbonyl compounds. To a slurry of titanium(III)chloride (13.8g, 89.4mmol) in dry THF under N_2, was added lithium aluminium hydride(1.7g, 44.7mmol); a deep black slurry resulted and while stirring, 3-thiophenecarboxaldehyde (5.0g, 41.0mmol) in THF was slowly added. The mixture was heated under reflux for 4h under N_2. On cooling it was filtered to remove titanium residues and washed with ether. The organic layer was then washed (twice) with water, dried and evaporated to give a

light greenish solid, which was found to be 1,2-di(3-thienyl)ethane-1,2-diol(two isomers) and not the expected 1,2-di(3-thienyl)ethene. Spectral data for 1,2-di(3-thienyl)ethane-1,2-diol (3.5g, 70.0%; two isomers ± and *meso*-18:82); m.p. 140-142°C (lit.[218] 138°C); Found: C, 53.6; H, 4.2. $C_{10}H_{10}O_2S_2$ requires C, 53.1; H, 4.45%; δ_H (CD_3COCD_3) 4.55(2H, broad s, OH peak), 4.8(2H, s), 6.9 (2H, q, J 3,2Hz), 7.05(2H, d, J 2Hz) and 7.25(2H,dd, J 3,2Hz); δ_C 75.2, 122.5, 125.4, 127.5 and 144.1; m/z 209(1%), 191(2), 179(2), 147(1), 113(75), 97(6) and 85(100).

7. Fvp of prepared benzodithiophenes and dibromodithienyl-ethenes

(a) Fvp of benzo[1,2-b:4,3-b']dithiophene

Fvp of the title compound (650°C, 5.8 x 10^{-2}mmHg, inlet - 85-90°C, 1.5g magnesium) gave unchanged starting material.

(b) Fvp of benzo[1,2-b:3,4-b']dithiophene

Fvp of the title compound (650°C, 4.0 x 10^{-2}mmHg, inlet 85-90°C, 1.5g magnesium) gave unchanged starting material.

(c) Fvp of 1,2-bis(3-bromo-2-thienyl)ethene

Fvp of the title compound (650°C, 2 x 10^{-2}mmHg, inlet - 130-135°C, 1.5g magnesium) gave a product which consisted of benzo[1,2-b:3,4-b']dithiophene, benzo[1,2-b:4,3-b']dithiophene and benzo[2,1-b:3,4-b'] dithiophene, in a percentage composition of 29, 69, and 2% respectively. The first two compounds were confirmed from GC traces of prepared samples, while the last compound was inferred on the basis of a similar GC peak obtained from the product of pyrolysis of 3-bromo-2-dichloromethylthiophene (see 5a).

(d) Fvp of 1-(3-bromo-2-thienyl)-2-(2'-bromo-3'-thienyl)ethene

Fvp of the title compound (650°C, 4.0 x 10^{-2}mmHg, inlet - 130-135°C, 1.5g magnesium) gave a product which consisted mainly of benzo[1,2-b:3,4-b']dithiophene(92.5% composition) with benzo[1,2-b:4,3-b']dithiophene(2.8% composition), benzo[2,1-b:3,4-b']dithiophene(trace) and an identified isomer of benzodithiophene(4.7% composition).

(e) Fvp of 1,2-bis(2-bromo-3-thienyl)ethene

Fvp of the title compound (650°C, 5.0 x 10^{-2}mmHg, inlet - 130-135°C, 1.5g magnesium), led to decomposition in the inlet tube, without any isolable product coming through the furnace. Repeat pyrolysis gave the same result and because only a limited amount of the starting material was available, the experiment was abandoned.

8. Preparation and Fvp of 3-chlorobenzo[b]thiophene-2-carbonyl-chloride

(i) Preparation of 3-chlorobenzo[b]thiophene-2-carbonyl-chloride and its ethyl ester[225]

To cinnamic acid(8.0g, 0.1mol), was slowly added excess thionyl chloride(20ml) and the mixture heated under reflux for 2h, after which pyridine(2.0g, 20mmol) in thionyl chloride(15ml) was added. The heating was continued overnight. On cooling a yellow solid mass was obtained and excess thionyl chloride evaporated. The residue was dissolved in dichloromethane and elemental sulphur filtered off, the solvent was evaporated and the solid recrystallised from hexane to give a light yellow solid, which was confirmed as 3-chlorobenzo[b]thiophene-2-carbonylchloride; m.p. 113-114°C(lit.[225] 113.5-114.5); υ_{max} 3060, 1760, 1600, 1310, 1250, 1170(d), 1100(d), 1070, 950, 900 and 670-760(m);

δ_H 7.5-8.2(m); δ_C 123.4,125.3, 126.9, 130.2, 130.4, 131.3, 137.7, 141.0 and 158.8.

The acid chloride was converted to its ethyl ester with hot ethanol, to give a yellowish solid, which was confirmed as ethyl 3-chlorobenzo[b]thiophene-2-carboxylate; m.p. 69°C(lit.[225] 69-69.5°C); υ_{max} 3025, 1715, 1515, 1310, 1250, 1090, 1060, 1020, 940 and 750; δ_H 1.4(3H, t), 4.5(2H, q), 7.5-7.7(2H, m) and 7.8-8.2(2H, m); δ_C 14.9, 62.4, 123.3, 124.3, 126.0, 126.6, 127.8, 128.7, 137.6, 139.1 and 161.9.

(ii) Fvp of 3-chlorobenzo[b]thiophene-2-carbonylchloride

Fvp of the title compound (0.60g, 600°C, 8.0 x 10^{-2}mmHg, inlet - 110-115°C, 1.5g magnesium) gave a solid product. GC-MS showed that it consisted mainly of 3-chlorobenzo[b]thiophene(25.4%); m/z 168 and benzo[b]thiophene(14.9%); m/z 134. A rerun under similar conditions gave a mixture of 3-chlorobenzo[b]thiophene(27.4%); δ_H 7.2-7.4(3H, m), and 7.7-7.9(2H, m); δ_C 120.7, 121.7, 122.8, 123.5, 124.8, 125.2, 136.0 and 138.3; m/z 168, benzo[b]thiophene(5.2%); δ_C 122.4, 123.8, 124.0, 124.1, 124.5, 126.2, 139.5 and 139.6; m/z 134, phenylacetylene(3.6%); δ_H 3.0(≡CH); δ_C 77.1(≡CH), 83.6(Ph-C≡); m/z 102 and indene(2.5%); δ_H 3.3(CH_2, s) 6.5(1H, m), 6.8(1H, m); δ_C 39.0(CH_2); m/z 116. The yield was determined from GC integrals.

J. Preparation and Fvp of Long Chain Aliphatic Acid Chlorides

1. General procedure for preparation of the acid chlorides[226]

These are readily prepared by direct chlorination of the corresponding acid with thionyl chloride,and heated under reflux for 1 or 2h in dichloromethane. The solvent is then removed and the residue kugelrohr distilled to give the desired acid chloride.

2. Fvp of octanoyl chloride

Fvp of octanoyl chloride(0.59g, 600°C, 5.0 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave a liquid product, which consisted of hex-1-ene(37.0%), octane(24.2%) and oct-1-ene(9.0%), with small amounts of hept-1-ene, heptane and hexane - see Table 2. Product identification and yield was based on the GC-MS.

3. Fvp of decanoyl chloride

Fvp of decanoyl chloride(0.55g, 600°C, 3.4 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave a liquid product, which consisted of dec-1-ene(15.2%), nonane(24.4%), non-1-ene(10.8%), oct-1-ene(10.9%), hept-1-ene(14.8%) and dec-1-yne(6.1%), with small amounts of decane, octane and heptane - see Table 2. Product identification and yield was based on the GC-MS.

4. Fvp of lauroyl chloride (dodecanoyl chloride)

Fvp of lauroyl chloride(0.48g, 600°C, 5.0 x 10^{-1}mmHg, inlet - 85-90°C, 1.0g magnesium) gave a liquid product, which consisted of non-1-ene(21.6%), oct-1-ene(13.1%), dodec-1-yne(12.3%), dodec-1-ene (9.2%), dec-1-ene(9.0%), undec-1-ene(7.8%) and undecane(7.3%), with

small amounts of decane, nonane, octane - see Table 2. Product identification and yield was based on the GC-MS.

5. Fvp of myristoyl chloride (tetradecanoyl chloride)

Fvp of myristoyl chloride(0.50g, 600°C, 2.9 x 10^{-1}mmHg, inlet - 95-100°C, 1.0g magnesium) gave a liquid product, which consisted of tridecane(16.0%), undec-1-ene(14.3%), tetradec-1-ene(10.2%), dec-1-ene (10.2%), tetradec-1-yne(7.7%) and dodec-1-ene(6.3%), with small amounts of tridec-1-ene, oct-1-ene, hept-1-ene and non-1-ene - see Table 2. Lower temperatures of 500°C and 450°C gave similar product mixtures - see Table 2. Product identification and yield was based on the GC-MS.

6. Fvp of palmitoyl chloride (hexadecanoyl chloride)

Fvp of palmitoyl chloride(0.48g, 600°C, 4.0 x 10^{-1}mmHg, inlet - 130-135°C, 1.0g magnesium) gave a liquid product which consisted of tridec-1-ene(9.4%), pentadecane(8.7%), dodec-1-ene(8.7%), undec-1-ene (8.1%), dec-1-ene(7.6%), non-1-ene(6.1%) and hexadec-1-yne(6.1%), with small amounts of other products - see Table 2. Product identification and yield was based on the GC-MS.

7. Fvp of tridec-1-ene

Fvp of tridec-1-ene(0.39g, 600°C, 6.4 x 10^{-1}mmHg, inlet - 60-65°C, 1.0g magnesium) gave a liquid product which was mainly the starting material with only traces of other products.

(K). Preparation and Fvp of Epoxides

1. Preparation and Fvp of tetramethylethylene oxide

(i) Preparation of tetramethylethylene oxide[227]

To a solution of tetramethylethylene(2,3-dimethylbut-2-ene, 5.0g, 60.0mmol) in dichloromethane, was added anhydrous sodium carbonate (15.0g) and the mixture cooled on an ice bath. While stirring , a solution of 33% peracetic acid(15.0g, 65.0mmol) was added dropwise and the mixture allowed to warm to room temperature and stirred for a further 3h. The mixture was poured into water and the lower organic layer separated, dried and evaporated. Kugelrohr distillation gave a colourless liquid, which was confirmed as tetramethylethylene oxide(4.8g, 80.0%); b.p. 90°C(lit.[227] 90.5-91°C); δ_H 1.3(s) [cf with starting material δ_H 1.65].

(ii) Fvp of tetramethylethylene oxide

Fvp of the title compound (0.21g, 600°C, 6.8 x 10^{-1}mmHg, inlet - ice cooled vertical inlet tube, 1.0g magnesium) gave a liquid product. The GC-MS and NMR showed that it consisted mainly of 2,3-dimethylbutadiene(76.4%); δ_H 1.9(6H, s), 4.95(2H, s) and 5.05 (2H, s); δ_C 20.6($2CH_3$), 113.1(C-2,C-3) and 143.6(C-1,C-4); m/z 82, with small amounts of pinacolone(3,3-dimethylbutan-2-one, 5.3%); δ_H 1.15 (9H, s) and 2.1(3H, s); δ_C 24.6(CH_3), 26.5($3CH_3$), 44.4(C-3), and 212.4 (C-2) and tetramethylethylene(2.3%); δ_H 1.65(s); δ_C 20.4($4CH_3$), and 123.4(C-2,C-3).

Repeat pyrolysis <u>without</u> magnesium; (0.24g, 600°C, 7.0 x 10^{-1}mmHg, inlet - ice cooled vertical inlet tube) gave a liquid product which consisted mainly of the starting epoxide(61.2%) and pinacolone(12.8%) plus two minor compounds with the same molecular mass(m/z 100) as the starting material.

2. Fvp of cyclopentene oxide

Fvp of the title compound (0.44g, 600°C, 4.6 x 10^{-1}mmHg, inlet - ice cooled vertical inlet tube, 1.0g magnesium) gave a liquid product. The ^{1}H NMR showed that it was unreacted starting material. The same result was obtained when the pyrolysis was repeated at longer contact time (N_2 leak).

3. Preparation and Fvp cyclohexene oxide (7-oxabicyclo[4.1.0]-heptane)

(i) Preparation of cyclohexene oxide

The method employed was the same as for tetramethylethylene oxide[227]. Prepared from cyclohexene(5.0g, 61.0mmol), anhydrous sodium carbonate(15.0g), and 33% peracetic acid(15.0g, 65.0mmol). Kugelrohr distillation gave pure cyclohexene oxide(2.5g, 42.0%); b.p. 130°C/760mmHg(lit.[228] b.p. 131.5°C); δ_H 1.3(4H, m), 1.8(4H, m) and 3.0(2H, broad s).

(ii) Fvp of cyclohexene oxide

Fvp of the title compound (0.48g, 600°C, 6.2 x 10^{-1}mmHg, inlet - ice cooled vertical inlet tube, 1.0g magnesium) gave yellow liquid. The NMR and GC-MS of the product showed that it consisted of cyclohex-1,3-diene(25.4%); δ_H 2.2(4H, m) and 5.9(4H, m); m/z 80, benzene(7.9%); m/z 78, cyclopentanecarboxaldehyde(10.2%); δ_H 1-2 (9H, m) and 9.75(1H, d, J 2Hz); m/z 98, cyclohexanone(35.3%); δ_H 1.8 (6H, m) and 2.2(4H, m); m/z 98 and a small amount of phenol.

Repeat pyrolysis without magnesium (0.33g, 600°C, 8.0 x 10^{-1}mmHg, inlet - icc-cooled vertical inlet tube) gave mainly the starting epoxide(95%) with only traces of cyclohexadiene, cyclohexene and cyclopentanecarboxaldehyde.

4. (a) Fvp of cyclooctene oxide (9-oxabicyclo[6.1.0]nonane)

Fvp of the title compound (0.34g, 600°C, 9.0 x 10^{-1}mmHg, inlet-room temperature, 1.0g magnesium) gave a liquid product. The ^{1}H NMR and GC-MS showed that it consisted mainly of two products, octa-1,7-diene(17.7%); δ_H 1.3-2.5(4H, m), 4.9-5.2(4H,m) and 5.7-6.2 (2H, m); m/z 110 and cyclooctene(26.4%); δ_H 1.3-2.5(10H, m) and 5.7-6.0(2H,m); m/z 110. In addition to these two products, small amounts (<3% each) of 12 compounds with m/z ranging from 106-110, were also observed on the GC-MS.

Repeat pyrolysis without magnesium (0.51g, 600°C, 8.0 x 10^{-1}mmHg, inlet-room temperature) gave a product which consisted of only rearranged isomers of the starting material, namely cyclooctanone (70.9%); δ_H 1.3-2.2(10H, m) and 2.3-2.5(4H, m); m/z 126, and cycloheptanecarboxaldehyde(14.0%); δ_H 1.3-2.2(13H, m), and 9.8 (1H, d, J 1Hz); m/z 126.

(b) Fvp of cyclooctene

Fvp of cylooctene(0.47g, 600°C, 9.0 x 10^{-1}mmHg, inlet - ice cooled vertical inlet tube, 1.0g magnesium) gave a liquid, which consisted of 1,7-octadiene(32.2%); δ_H 1.3-1.6(4H, m), 2.0-2.3(4H, m), 5.1(4H, t of m) and 5.8-6.0(2H, m) and the starting material(47.4%), with cyclooctane(7.0%) and vinyl cyclohexane(trace). Repeat pyrolysis without magnesium gave a liquid which also consisted of 1,7-octadiene and the starting material in a percent composition of 21% and 79% respectively.

5. Fvp of Styrene oxide (1,2-epoxyethylbenzene)

Fvp of the title compound (0.48g, 600°C, 8.0 x 10^{-1}mmHg, inlet-room temperature, 1.0g magnesium) gave a liquid product. The NMR and GC-MS of the product indicated that it consisted of

phenylacetaldehyde(26.4%); δ_H 3.6(2H, d, J 1Hz), 7.2-7.6(5H, m) and 9.8 (1H, t, J 2Hz); m/z 120, styrene(23.8%); δ_H 5.1(1H,dd, J 5,1Hz), 5.6 (1H,dd, J 9,1Hz), 6.6 - 6.7(1H,q, J 8Hz) and 7.2-7.5(5H, m); m/z 104, phenylacetylene(ethynylbenzene, 11.9%); δ_H 3.05(1H, s) and 7.2-7.6(5H, m); m/z 102, toluene(15.9%); δ_H 2.3(3H, s) and 7.2(5H, s); m/z 92, bibenzyl(4.2%) and acetophenone(1.0%).

Repeat pyrolysis without magnesium (0.27g, 600°C, 7.6 x 10^{-1}mmHg, inlet - room temperature), gave a liquid, which consisted of phenylacetaldehyde(60.4%), toluene(20.1%) and bibenzyl(9.4%).

6. Preparation and Fvp of 1,2-epoxy-2-phenylpropane

(i) Preparation of 1,2-epoxy-2-phenylpropane

This was prepared from α-methylstyrene(5.0g, 42.0mmol), anhydrous sodium carbonate(20.0g) and 33% peracetic acid(11.0g, 48mmol). Work up and Kugelrohr distillation gave 1,2-epoxy-2-phenylpropane(4.1 g, 70.1%); b.p. 110°C/20mmHg(lit.[229] 85-88°C/17mmHg); δ_H 1.6(3H, s), 2.1(1H, d, J 4Hz), 2.3(1H, d, J 4Hz) and 7.3(5H, m); δ_C 21.6, 56.4, 56.7, 125.3(2C) 127.4, 128.3(2C) and 141.3, .

(ii) Fvp of 1,2-epoxy-1-phenylpropane

Fvp of the title compound (0.36g, 600°C, 8.0 x 10^{-1}mmHg, inlet - room temperature, 1.0g magnesium) gave two fractions, a liquid and a solid product. The products consisted of 2-phenylpropionaldehyde (31.7%); δ_H 1.4(3H, d, J 4Hz), 3.5(1H, q of d), 7.2-7.5(5H, m) and 9.8 (1H, d, J 1Hz); m/z 134, α-methylstyrene(17.9%); δ_H 2.15(3H, m), 5.1-5.4(2H, d of m) and 7.2-7.5(5H, m); m/z 116, styrene(12.4%); δ_H 5.1(1H, dd, J 5,1Hz), 5.6(1H, dd, J 9,1Hz), 6.6 - 6.7(1H,q, J 8Hz) and 7.2-7.5(5II, m); m/z 104, acetophenone(10.4%); δ_H 2.5(3H, s) and

7.2-8.0(5H, m) and an unidentified compound m/z 132 (methylbenzofuran (?), 9.0%).

Repeat pyrolysis without magnesium (0.39g, 600°C, 7.2 x 10^{-1}mmHg, inlet-room temperature) gave a liquid product which consisted of 2-phenylpropionaldehyde(53.7%), styrene(33.5%) and acetophenone(11.2%).

7. Preparation and Fvp of 1,2-epoxy-1-phenylpropane

(i) Preparation of 1,2-epoxy-1-phenylpropane

This was prepared from β-methylstyrene(5.0g, 42.0mmol), anhydrous sodium carbonate(20.0g) and 33% peracetic acid(11.0g 48.0mmol). Work up and Kugelrohr distillation gave 1,2-epoxy-1-phenyl propane(3.8g, 65.0%); b.p. 110°C/20mmHg(lit.[230] 197-199°C/ 760mmHg); δ_H 1.4(3H, d, J 3Hz), 3.0(1H, m), 3.5(1H, d, J 1Hz) and 7.3 (5H, s); m/z 134; .

(ii) Fvp of 1,2-epoxy-1-phenylpropane

Fvp of the title compound (0.45g, 600°C, 9.0 x 10^{-1}mmHg, inlet-room temperature, 1.0g magnesium) gave mainly a liquid, with a small amount of solid. The NMR and GC-MS showed that the product consisted of 1-phenyl-propan-2-one(23.0%); δ_H 2.15(3H, s), 3.7(2H, s), and 7.1(5H, m); δ_C 29.2(CH_3), 51.0(CH_2), 127.1, 128.7(2C), 129.4(2C), 134.2 and 206.5(C=O); m/z 134, β-methylstyrene(23.6%); δ_H 1.7 (3H, d, J 4Hz), 6.1(2H, m) and 7.1(5H, m); m/z 118, 1-phenylprop-1-yne(5.5%); δ_H 2.15(3H, s) and 7.1(5H, m), 3-phenyl-prop-1-ene(4.0%) and small amounts of bibenzyl, toluene, styrene and ethylbenzene.

Repeat pyrolysis without magnesium under similar condidtions gave 1-phenylpropan-2-one(45.5%), ethylbenzene(12.6%), 2-phenylpropion-

aldehyde(7.6%), bibenzyl(6.3%), starting material(15.1%) and small amounts of styrene and toluene.

8. Preparation and Fvp of stilbene oxide

(i) Preparation of stilbene oxide

Prepared from *E*-stilbene(5.0g, 28.0mmol), anhydrous sodium carbonate(15.0g) and 33% peracetic acid(7.0g, 30.0mmol): Work up gave a mixture of the desired product and the starting material, recrystallisation from ethanol/water(70:30) dissolved the epoxide with most of the starting material insoluble. Filtration and cooling gave pure stilbene oxide(2.2g, 40.7%); m.p. 69°C(lit.[231] 69°C); δ_H 3.9(2H, s), and 7.5 (10H, s); δ_C 62.8(2C), 125.5(4C), 128.3(2C), 128.5(4C) and 137.1(2C); m/z 196.

(ii) Fvp of stilbene oxide

Fvp of the title compound (0.34g, 600°C, 3.0 x 10^{-1}mmHg, inlet - 60-65°C, 1.5g magnesium) gave mainly a solid product with a small amount of liquid. The NMR and GC-MS showed that the solid consisted of stilbene(*Z*-:*E*-,7.4% and 48.7%); δ_H 7.2(2H, s) and 7.3-7.7(10H, m); δ_C 126.5(4C), 127.6(2C), 128.6(4C) and 137.3(2C); m/z 180, with diphenylacetylene(13.5%), diphenylmethane(12.4%), fluorene(2.6%) and α-phenylacetophenone(3.4%). The liquid consisted of toluene(2.0%) and 1,1-diphenylethene(1.1%).

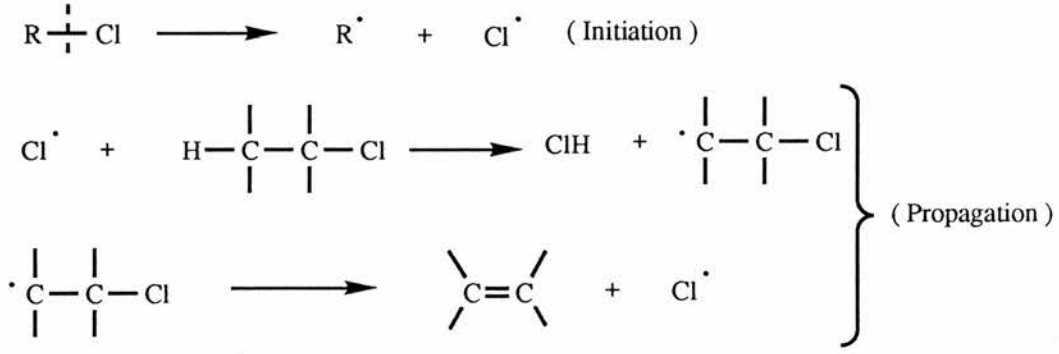
Repeat pyrolysis under similar condition without magnesium gave mainly the starting material(42.7%) with α-phenylacetophenone(14.9%); δ_H 4.25(2H, s) and 7.2-8.0(10H, m); δ_C 59.7(CH_2), 198.4(C=O), 1,1-diphenylethylene oxide(10.7%); δ_H 4.35(2H, s), 7.2-7.5(10H, m); δ_C 45.4(CH_2), 133.1(Ph_2C), diphenylacetaldehyde(8.5%); δ_H 7.2 (1H, d, J 2Hz), 7.2-7.5(10H, m) and 10.05(1H, d, J 2Hz); δ_C 64.0 (Ph_2CH-), 197.5(CHO), with small amounts of diphenylmethane and stilbene.

DISCUSSION

A. Flash Vacuum Pyrolysis of Aliphatic Halides over Magnesium

1. General Background

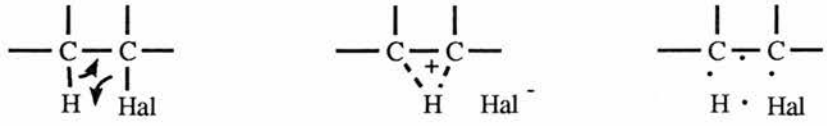
The pyrolytic β-elimination of hydrogen halides from alkyl halides has been of greater interest to kineticists than to preparative chemists because of low conversion and isomerisation arising from recombination of the alkene produced with hydrogen halides. The reaction is mechanistically very complicated, because it may occur by radical or radical chain pathways, by surface-catalysed processes, or by unimolecular decomposition through transition states with some degree of heterolytic character[2]. Unless unsaturated inhibitors are present, some alkyl chlorides and many alkyl bromides and iodides tend to decompose in the gas phase by radical or radical chain processes such as that proposed by Barton and Onyon[232], for the case of alkyl chlorides (*Scheme 7*).



Scheme 7

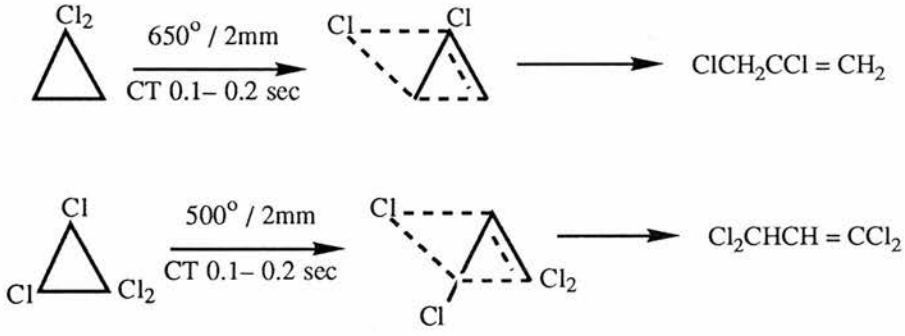
In clean glass or silica reactors rapid surfacc catalysed decomposition is usually the initially observed process, before unimolecular elimination sets in. Unimolecular β-elimination of hydrogen halides in the gas phase was originally considered to be a 4-centre *cis*-elimination (**198**) but Maccoll *et al*[233] favoured a highly polar transition state approaching a tight carbonium ion-halide ion pair (**199**). The advantages and difficulties of such a transition state were highlighted by Smith and

Kelly[234], who prefer the polar semi-ion pair transition state (**200**) proposed by Benson and Bose[235].



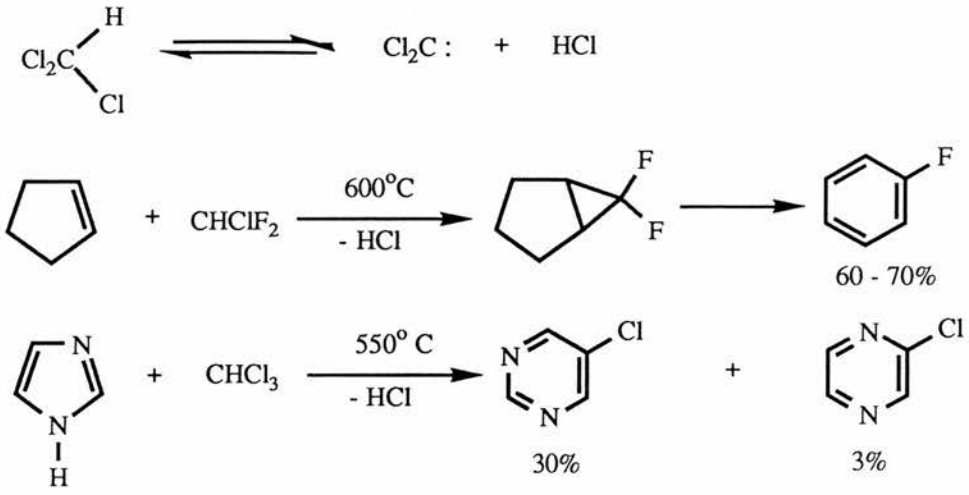
(198) (199) (200)

The thermal rearrangements of alkyl halides in the gas phase are very similar to those which occur in solution *via* ionic or ion-pair intermediates. Fields *et al*[236] reported the isomerisation of a number of chlorocyclopropanes to 3-chloropropenes at 500-650°C and proposed a concerted migration of chlorine (*Scheme 8*).



Scheme 8

Reactions which might be interpreted as involving α-elimination of hydrogen halide to give a carbene are occasionally observed in the pyrolysis of alkyl halides, but such reactions have usually been regarded as having polar and radical character. The formation of carbenes by α-elimination is better established in the case of the haloforms and related compounds, which readily lose hydrogen halide at 400-600°C and the halocarbenes generated have been employed in synthesis[237](*Scheme 9*).



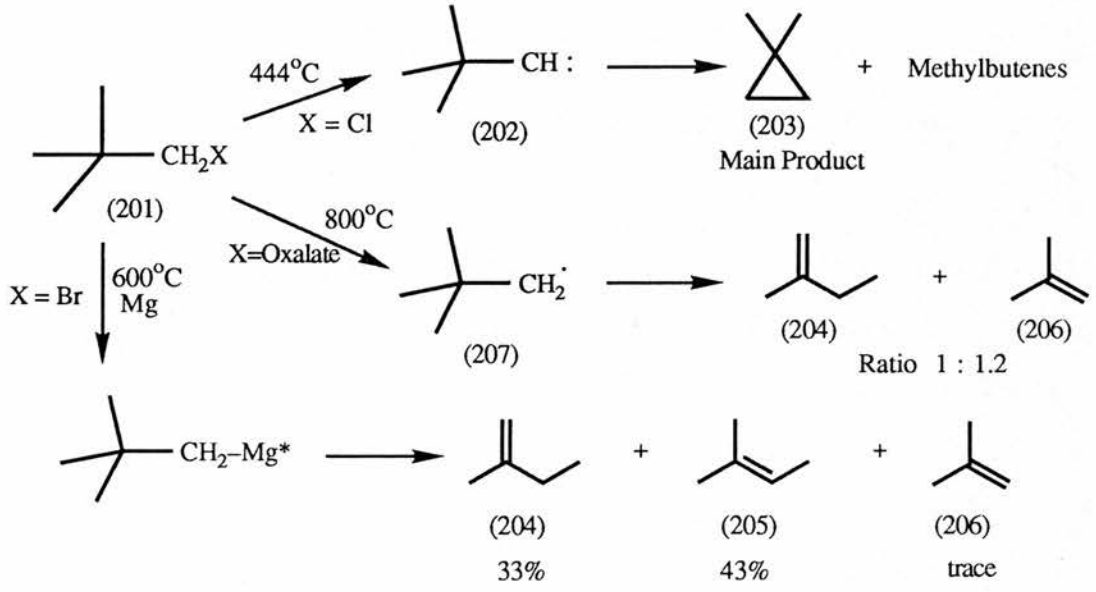
Scheme 9

2. Simple aliphatic halides

In previous studies the α-elimination of hydrogen chloride from neopentyl chloride(**201**) on pyrolysis at 444°C to give *t*-butylcarbene (**202**) was used to account for the formation of 1,1-dimethylcyclopropane (**203**)[238]. This was confirmed by the independent generation of (**202**) from the pyrolysis of the sodium salt of *t*-butylmethylene-N'-*p*-toluene-*p*-sulphonylhydrazine at 800°C, when a mixture of alkenes was obtained, together with 1,1-dimethylcyclopropane[239].

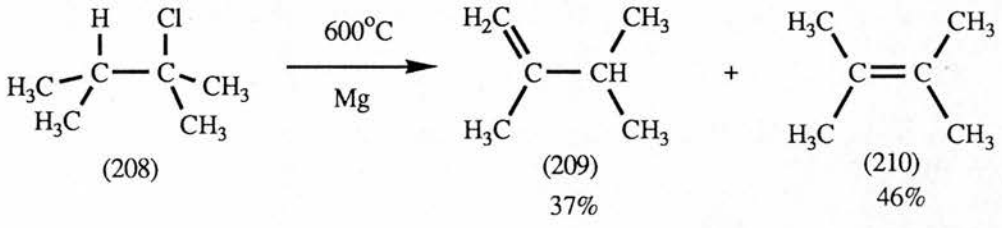
However, when neopentyl bromide was pyrolysed over magnesium at 600°C, it gave virtually a quantitative mixture of 2-methylbut-1-ene (**204**), and its more stable isomer, 2-methylbut-2-ene(**205**), with a trace amount of 2-methylpropene(**206**), but no 1,1-dimethylcyclopropane was observed. This product mixture precludes the carbene pathway as well as the radical route, since neopentyl radical(**207**) generated from bis-neopentyl oxalate at 800°C gave only 2-methylpropene(**206**) and 2-methylbut-1-ene(**204**)[239]. A metal-surface induced elimination process is envisaged to be involved (*Scheme 10*). A recent report[240] on the

thermal reactions of various neopentyl species, has clarified the product mixture obtained from each species.

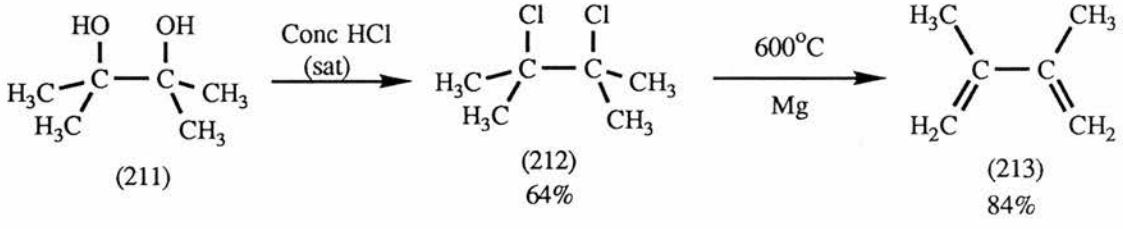


Scheme 10

Pinacolyl alcohol (3,3-dimethylbutan-2-ol) was readily converted to 2-chloro-2,3-dimethylbutane(**208**) with concentrated HCl (saturated). The reaction goes *via* 1,2-methyl rearrangement[163]. Pyrolysis of (**208**) over magnesium led to β-elimination of hydrogen chloride to give 2,3-dimethylbut-1-ene(**209**) and the more stable isomer 2,3-dimethylbut-2-ene(**210**). Thermal isomerisation of (**209**) to (**210**) under the pyrolysis condition may have played a key part in the ratio of the products observed. Similar dehydrohalogenation of (**208**) has been recently reported using DBU[241] and KOH[242].

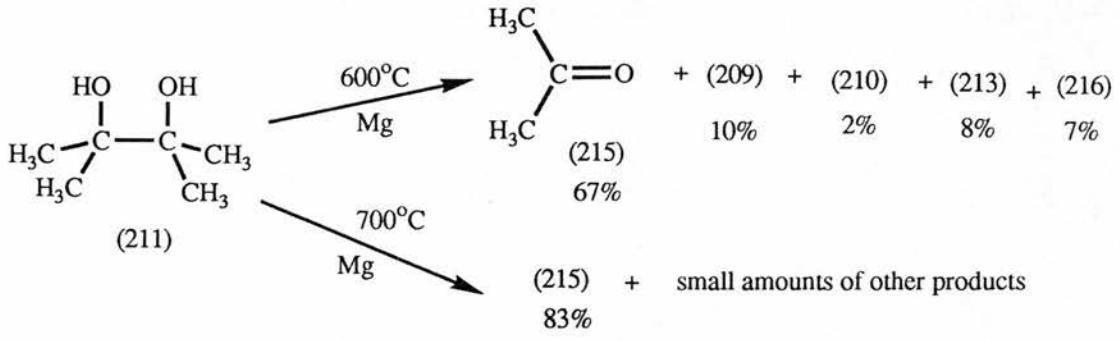


Chlorination of pinacol(**211**) with concentrated HCl saturated with HCl gas gave 2,3-dichloro-2,3-dimethylbutane(**212**). On pyrolysis over magnesium this underwent exclusive β-elimination of two molecules of hydrogen chloride, to give 84% yield of 2,3-dimethylbutadiene(**213**), as the only product. The isolation of only (**213**) tends to suggest a magnesium-induced stepwise dehydrochlorination as opposed to the simultaneous loss of the two chlorine atoms to give the diradical, which should have led to 2,3-dimethylbut-2-ene(**214**), which was not obtained. Such elimination is favoured as the required β-hydrogens are in the immediate vicinity of the leaving chlorine atoms.

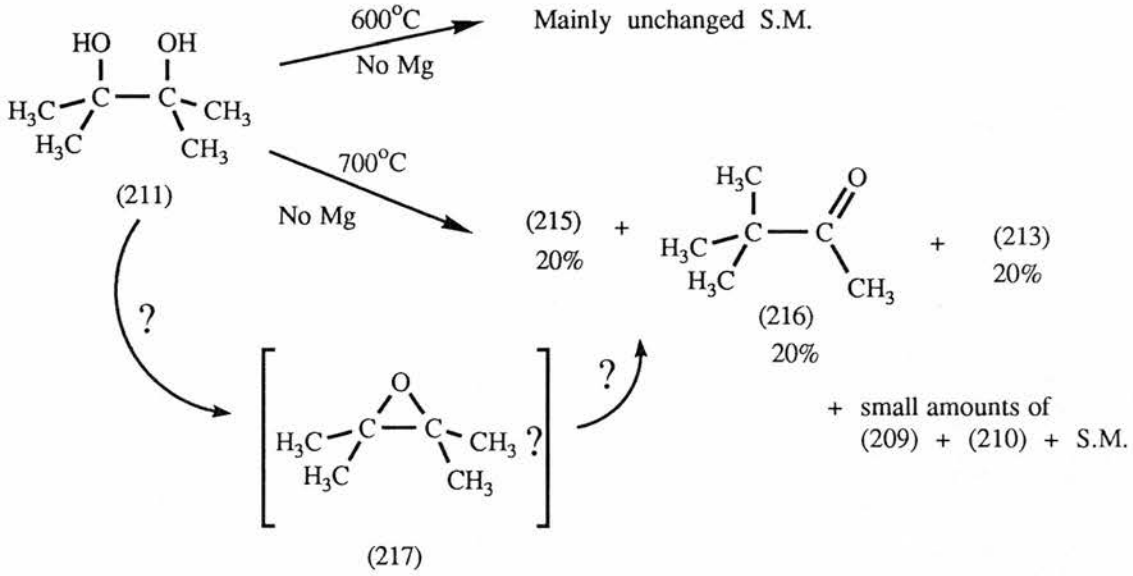


(211) (212) 64% (213) 84%

When pinacol(**211**) itself, was passed over magnesium at 700°C, the main process observed was oxidative cleavage to give an 83% yield of acetone(**215**) as opposed to the expected dehydration to (**213**), which was previously observed with alumina[243] and copper[244]. The other products obtained in small amounts were 2,3-dimethylbut-1-ene(**209**) and 2,3-dimethylbut-2-ene(**210**). The oxidative cleavage was observed to a small extent at 700°C, even without magnesium in addition to dehydration and rearrangement to pinacolone(**216**) and dehydration to 2,3-dimethylbutadiene(**213**). Literature reports on oxidative cleavage of 1,2-diols were achieved with reagents such as periodic acid[245], calcium hypochlorite[246], N-iodosuccinimide[247] and N-bromosuccinimide/ potassium carbonate with a catalytic amount of triphenylbismuth[248]. The reaction was postulated to involve an intermediate alkoxy radical.



The observed enhancement of the oxidative cleavage of pinacol by magnesium in the gas phase, may involve magnesium-oxygen complexation and the C-C fission reaction occurring through an alkoxyl-type radical, but whether the magnesium ends up as magnesium hydride or the hydrogen was lost as hydrogen gas, is unclear. The formation of (**213**) and (**216**) may involve the intermediate epoxide (**217**)-(see later) as they were part of the major products obtained when (**211**) was pyrolysed at 700°C in the absence of magnesium ..

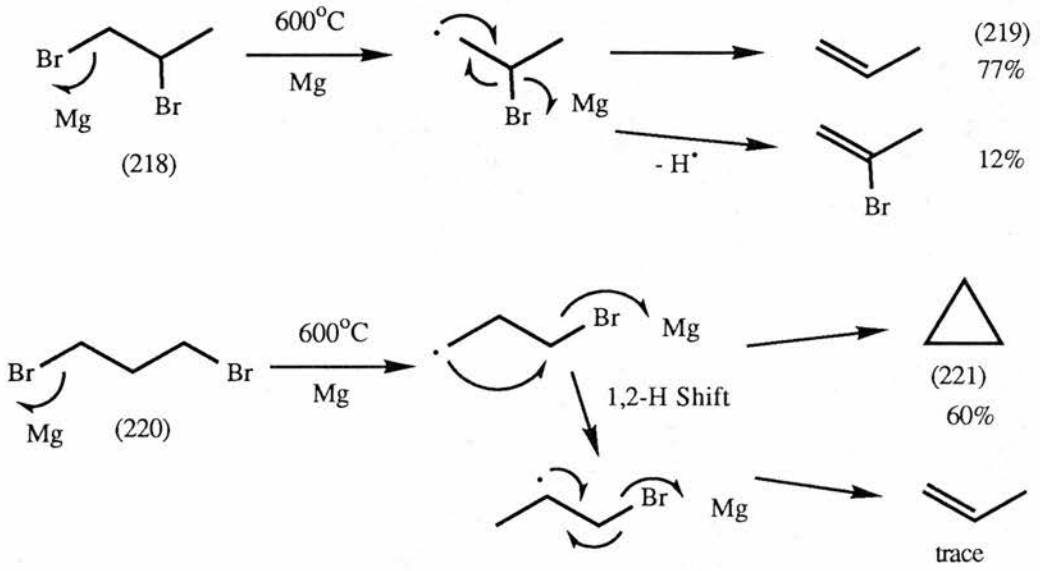


3. Aliphatic dihalo-compounds

(a) Vicinal and Terminal dihalides

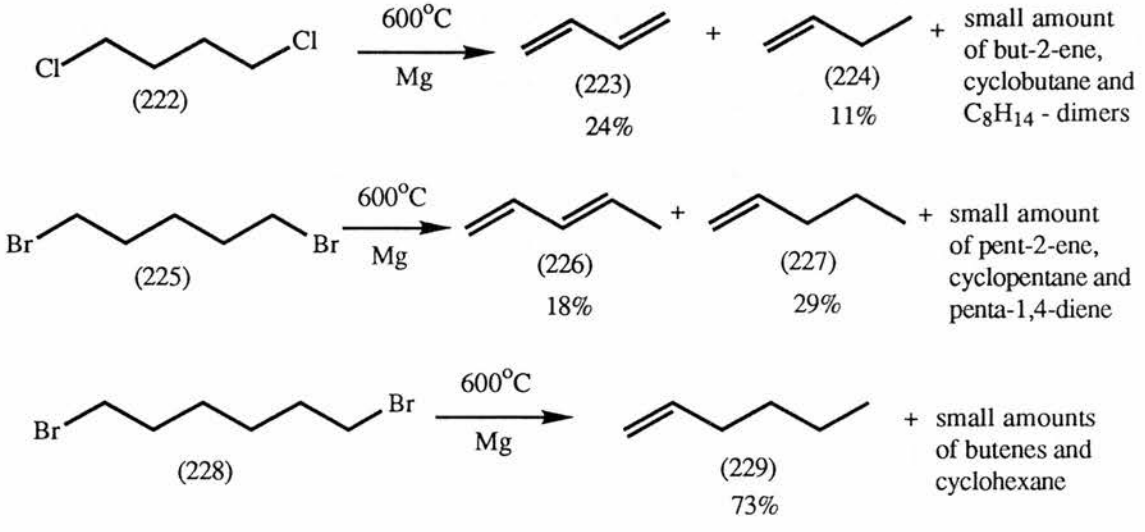
In contrast to dehydrohalogenation, thermal dehalogenation is rare in organic chemistry except when the thermal reaction involves metals (see Introduction). Magnesium played a similar role for most of the

dihalides studied here, thus pyrolysis of 1,2-dibromopropane(**218**) over magnesium gave exclusively propene(**219**), while 1,3-dibromopropane (**220**) gave mainly cyclopropane(**221**), with only traces of propene (**219**). A magnesium induced elimination involving a metal bound species or radicals is envisaged as the process that led to the observed products.

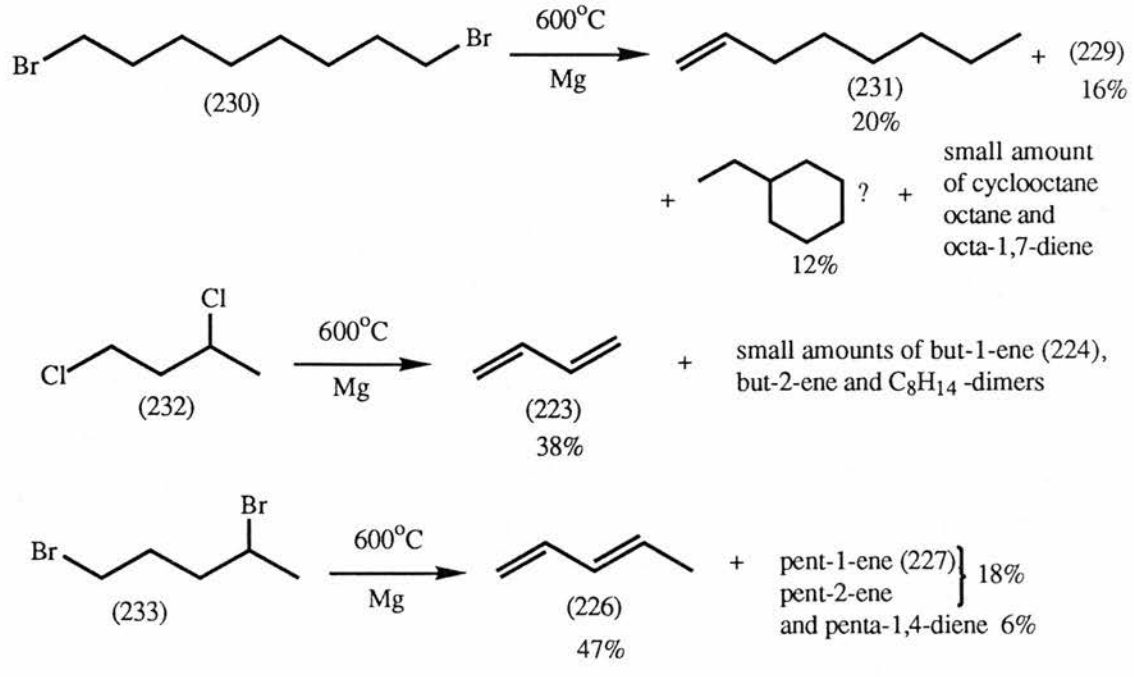


For terminal dihalides, as the chain length increases from C_4 to C_8, the feasibility of the type of elimination shown above diminishes, although small amounts of cyclic products, from cyclobutane to cyclooctane were still observed on pyrolysis. The main product obtained from this series of substrates are those of simple β-elimination of hydrogen halides to give dienes and those formed from a process suspected to involve stepwise dehalogenation followed by intramolecular hydrogen transfer from the carbon adjacent to the one bearing the second halogen and the loss of the second halogen, which may be spontaneous and promoted by a β-radical centre. Thus, 1,4-dichlorobutane(**222**) gave mainly butadiene(**223**) through β-elimination of hydrogen chloride and a mixture of butenes containing mainly but-1-ene(**224**), *via* the stepwise dehalogenation-

hydrogen transfer process. As the chain length increases the latter process predominates. Thus 1,5-dibromopentane(**225**) gave an almost equal mixture of penta-1,3-diene(**226**) and pent-1-ene(**227**), with only traces of other products, while 1,6-dibromohexene(**228**) gave almost exclusively hex-1-ene(**229**)

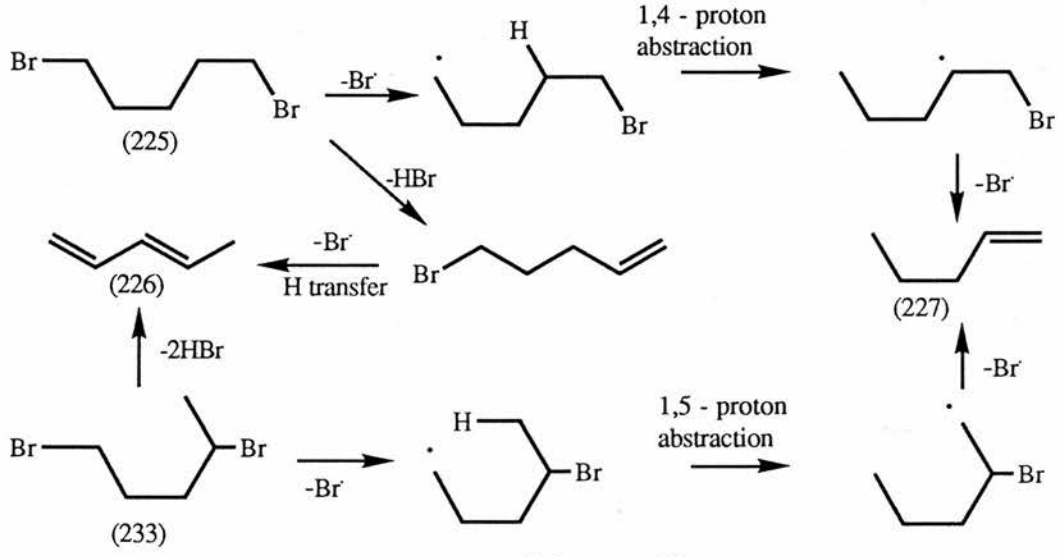


With increasing chain length of the starting dihalide, fragmentation sets in and this was evident in the small amount of butene produced from 1,6-dibromohexane(**228**) while 1,8-dibromooctane(**230**) gave not only oct-1-ene(**231**) but an equal amount of hex-1-ene(**229**). For 1,3-



dichlorobutane(**232**) and 1,4-dibromopentane(**233**) the loss of HX was the favoured process to give mainly the diene, with small amounts of other products. A mechanistic scheme for compound (**233**) is given in *Scheme 11* .

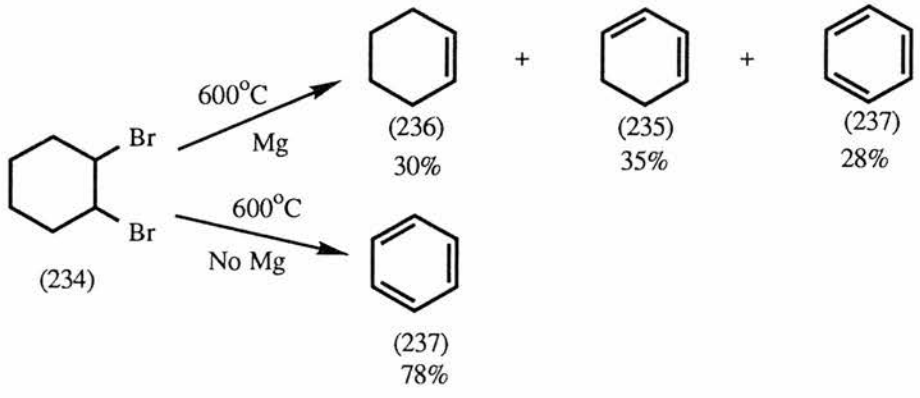
The change in process, from simple β-elimination to step-wise dehalogenation - hydrogen transfer, is indicative of the ease of hydrogen transfer with increased flexibility in the molecular skeleton which favours intramolecular transfer (*Scheme 11*).



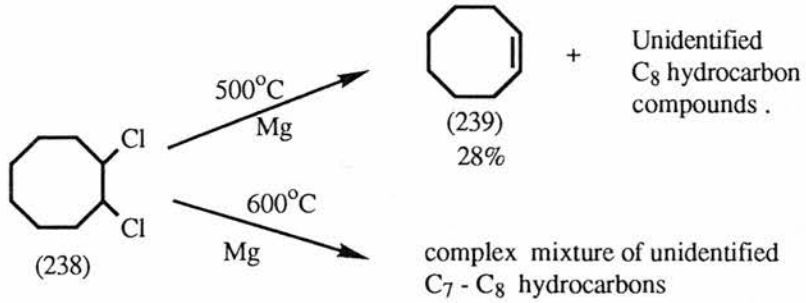
Scheme 11

Challenor and Ingold reported[249] the formation of cyclohexa-1,3-diene(**235**) in about 25% yield by heating *cis*-1,2-dibromocyclohexane (**234**) above its boiling point of 230°C under the pressure of 800mmHg. However, when (**234**) was pyrolysed over magnesium, complete debromination was observed giving a mixture of cyclohex-1,3-diene (**235**), cyclohexene(**236**) and benzene(**237**) but rather surprising was the fact that when (**234**) was passed through a glass wool packed tube (ie no magnesium) at 600°C and 0.5mmHg, the only product isolated in a high yield of 78% was benzene(**237**). This suggests that the already known[249] loss of HBr, was greatly enhanced by high vacuum and larger surface

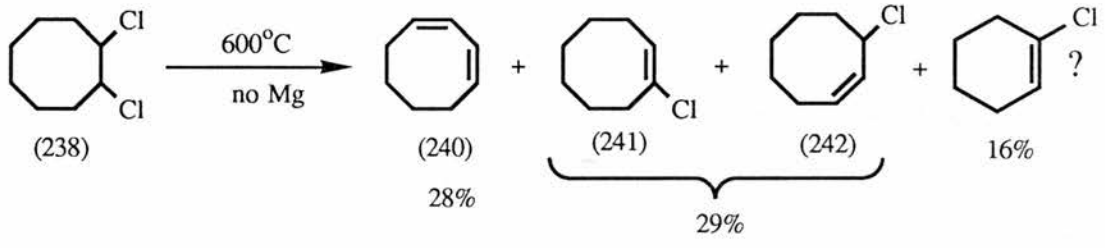
area. The formation of cyclohexa-1,3-diene is therefore believed to be largely a surface induced thermal reaction, with benzene being a secondary product, under the pyrolytic conditions. The only contribution of magnesium seems to be in the formation of cyclohexene, which involves loss of two bromine atoms, either through elimination on the surface of the magnesium or *via* a radical process involving an initial bromine abstraction by the magnesium, followed by spontaneous loss of the second bromine promoted by the β-radical centre.



When 1,2-dichlorocyclooctane(**238**) was pyrolysed over magnesium at 600°C,a complex mixture of hydrocarbon products was obtained. At the lower temperature of 500°C the major product was that of dechlorination to give cyclooctene(**239**). However, the overall reaction was more complex based on the large number of products obtained. The complex nature of the thermal reaction of (**238**) over magnesium was attributed to competing processes occuring, which include thermal



dehydrochlorination, magnesium-induced dechlorination to cyclooctene, which itself is known[250] to thermally ring open to octa-1,7-diene, ring contraction and fragmentation processes. No halogenated product was observed. The thermal reaction of (**238**) when passed through a glass wool packed tube (ie no magnesium) was straightforward dehydrochlorination to give cycloocta-1,3-diene(**240**), and compounds with m/z 144 and one chlorine atom present suspected to be 1-chlorocyclooct-1-ene(**241**) and 3-chlorocyclooct-1-ene(**242**); products of incomplete reaction.

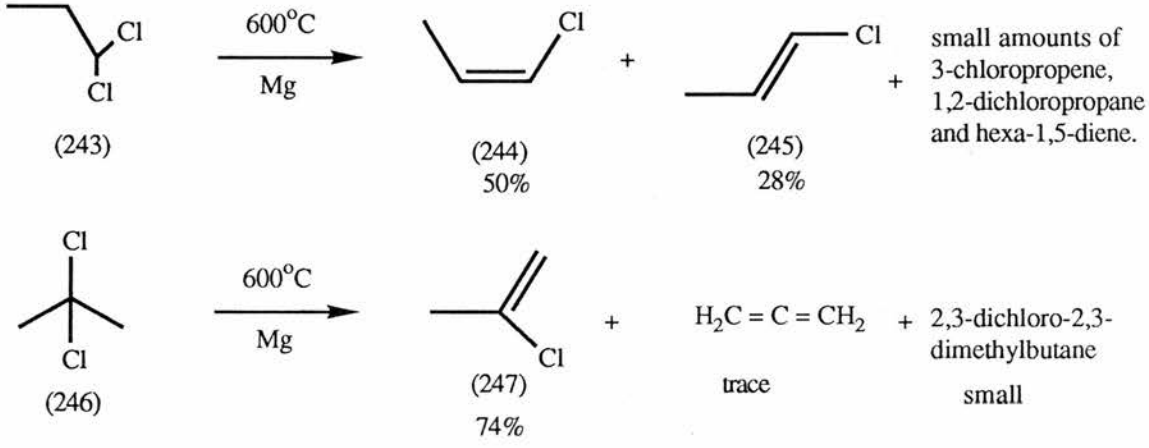


(b) Geminal dihalides

Kinetic studies on the gas phase pyrolysis between 400-460°C of 1,1-dichloropropane(**243**) and 1,1-dichlorobutane(**248**) have been previously reported[251]. The investigation centred around the determination of the equilibrium *Z:E* ratio of the chloroalkene products and the rate constant for the dehydrochlorination reaction, but no quantitative determination of products was carried out. A similar study[252] carried out over a molten salt catalyst (mainly $ZnCl_2$-containing melts) led to the suggestion of an E_1-elimination mechanism in which the carbonium ion, formed by chloride abstraction by the $ZnCl_2$, is absorbed on the surface of the salt, as the reason for the observed predominance of the *Z*-alkene.

When 1,1-dichloropropane(**243**) was pyrolysed over magnesium, β-elimination of a molecule of HCl was the main reaction path, to give

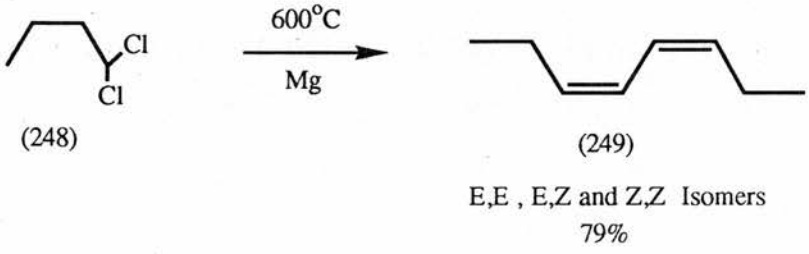
Z:E-1-chloroprop-1-ene(**244,245**) in a ratio of 1.8:1 which was the same ratio reported[252] for pyrolysis over the molten salts. Small amounts of rearrangement products 2-chloroprop-1-ene and 3-chloroprop-1-ene; recombination product 1,2-dichloropropane; and dimeric product hexa-1,5-diene, were also obtained. Similar β-elimination of a molecule of HCl from 2,2-dichloropropane(**246**) when pyrolysed over Mg gave a high yield of 2-chloroprop-1-ene(**247**), with only trace amounts of allene (loss of 2HCl) and the dimeric product 2,3-dichloro-2,3-dimethylbutane.



The higher members of this series of compounds 1,1-dichlorobutane (**248**);1,1-dichloropentane(**250**) and 1,1-dichlorohexane(**253**) were prepared from the corresponding aldehydes by treatment with phosphorus pentachloride. The yields were only moderate as the compounds tend to polymerise during distillation and as they distill over at about the boiling point of phosphorus oxychloride,a by-product of the reaction, repeated distillation was required. Attempts to remove the by-product by washing with water often hydrolysed the product back to the starting aldehyde.

The pyrolysis of compound (**248**) over magnesium, gave a product, which based on the ^{13}C NMR, was believed to consist of the *E,E*-, *Z,Z*- and *E,Z*- isomers of octa-3,5-diene(**249**), although the MS suggested otherwise. Only one of the three peaks of the GC trace gave a molecular

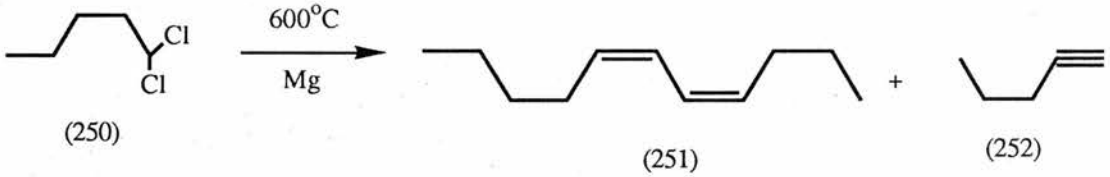
mass of 110, corresponding to the compound (**249**), the other two peaks gave a molecular mass of 126, a CH_4 unit more than (**249**). Since the number of carbon signals on the ^{13}C NMR did not tally with those for an unsymmetrical C_9-diene, the products are assumed to be (**249**) despite the MS information. The yield based on (**249**) was 79%.



(248) (249)

E,E , E,Z and Z,Z Isomers
79%

Similar results were obtained when 1,1-dichloropentane (**250**) and 1,1-dichlorohexane (**253**) were pyrolysed over magnesium. Compound (**250**) gave products suspected to be the *E,E*-, *Z,Z*- and *E,Z*- isomers of deca-4,6-diene(**251**) in a yield of 78%, although the three peaks of the

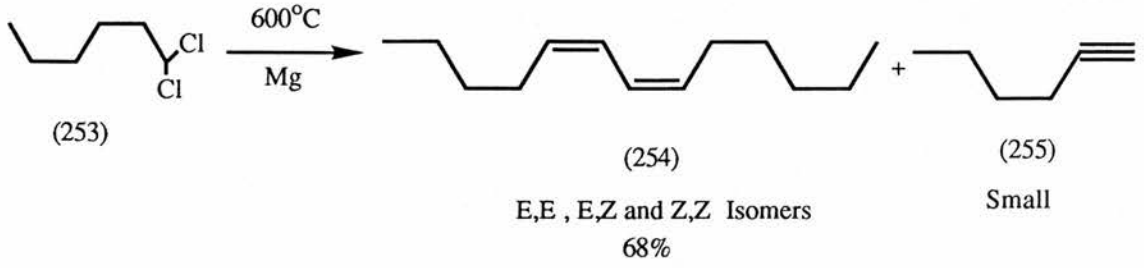


(250) (251) (252)

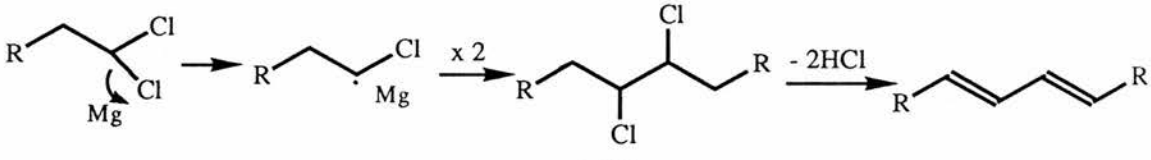
E,E , E,Z and Z,Z Isomers
76%

Small

GC trace also gave a molecular mass of 154, a CH_4 unit more than (**251**). From compound (**253**) were obtained products suspected to be the *E,E*-, *Z,Z*-, and *E,Z*-isomers of dodeca-5,7-diene(**254**) in a yield of 68%, although the three peaks of the GC trace, also gave a molecular mass of 182, a CH_4 unit more than (**254**). The only other products obtained from (**250**) and (**253**) were small amounts of pent-1-yne(**252**) and hex-1-yne (**255**) respectively.



For all the three substrates (**248**), (**250**) and (**253**), the ^{13}C NMR spectra of the products obtained on pyrolysis over magnesium, were quite clean and showed a consistent pattern. The GC traces were also consistant, however the mass spectra always gave a molecular mass a CH_4 unit more than the suspected reductive homocoupled dienes (**249**), (**251**) and (**254**). The mass spectra of the products showed a consistent fragmentation pattern and the first fragment lost from the suspected (**249**) was a methyl group, from (**251**) an ethyl group and from (**254**) a propyl group. In all the three cases examined, the main products were usually the *E,E*- and *E,Z*- isomers, with only a small amount of *Z,Z*-isomer. Despite the discrepancy of the molecular mass on the GC-MS, the route to the suspected products was believed to involve magnesium-induced dehalogenative homocoupling to give the dichloro compound(**256**), followed by β-elimination of two molecules of hydrogen chloride.



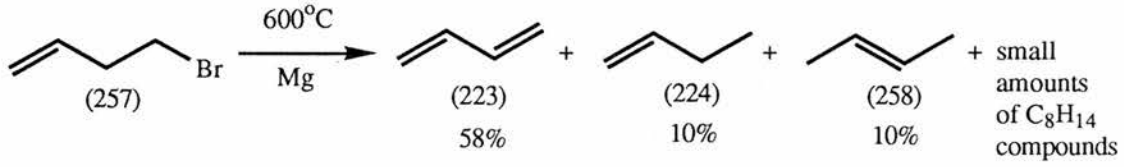
(256)

4. <u>ω-Halo-alkenes and -alkynes</u>

(a) <u>ω-Haloalkenes</u>

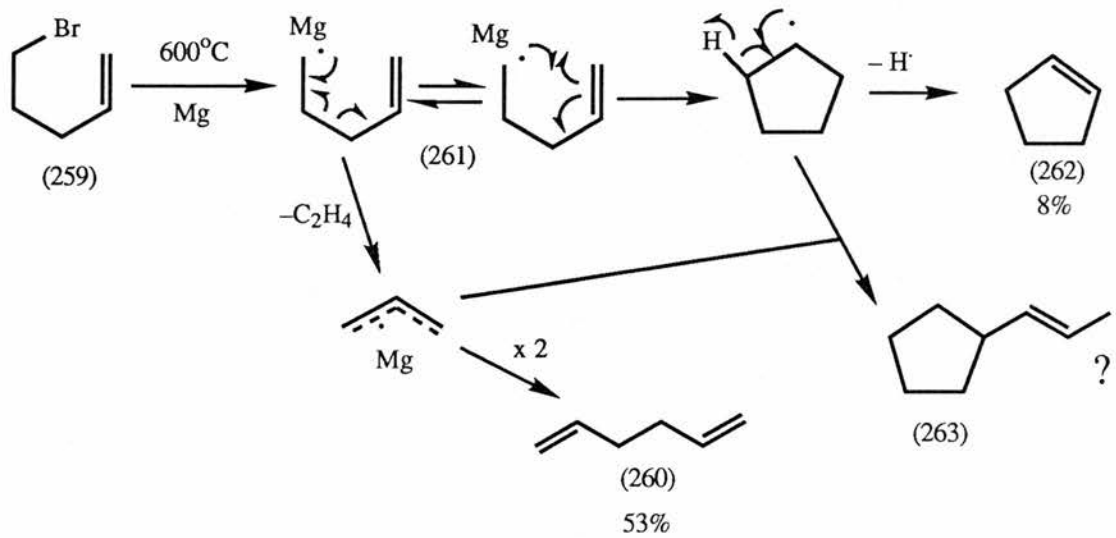
Pyrolysis of the halo-alkenes over magnesium, might be expected to result in loss of halogen to give a radical or radical like centre, which can

either insert into the unsaturated part of the molecule to give cyclic products or simply lose a hydrogen atom to give a diene. In fact, when 4-bromobut-1-ene(**257**) was pyrolysed over magnesium the main process was the loss of hydrogen bromide to give 58% yield of buta-1,3-diene (**223**) presumably *via* an initial magnesium-induced debromination, followed by loss of hydrogen from the β-radical centre. The other products, but-1-ene(**224**) and but-2-ene(**258**) obtained in 10% yield each, tend to support the stepwise nature of the reaction, as the intermediate formed by debromination would pick up hydrogen to give but-1-ene, which can thermally isomerise to the more stable but-2-ene. An alternative process could be isomerisation involving hydrogen transfer prior to either loss or gain of a hydrogen atom.

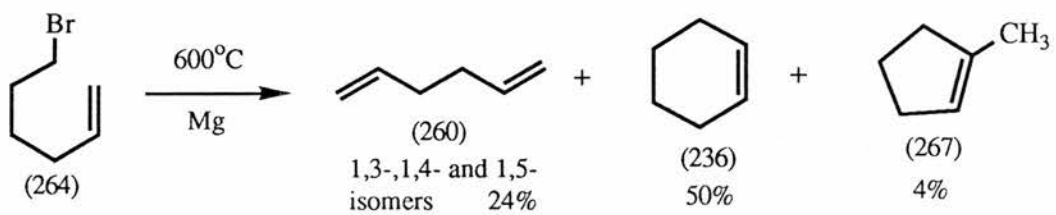


The pyrolytic reaction of 5-bromopent-1-ene(**259**) over magnesium seems to go *via* a different pathway, as the major product obtained in 53% yield, was hexa-1,5-diene(**260**) which is one carbon unit more than the starting material. This tends to suggest the formation of a 4-penten-1-yl species or radical(**261**) which is known[253] to undergo two unimolecular reactions, namely intramolecular addition to form cyclopentyl radical and decomposition into ethylene and allyl radical. These processess led to the formation of cyclopentane, cyclopentene, and propylcyclopentane, among others. Although small amounts of cyclopentene(**262**) and a compound with m/z 110 suspected to be 2-propenylcyclopentane(**263**), were also obtained as products of the pyrolysis over magnesium, the higher yield of (**260**) suggests the predominance of the decomposition process and a possible adsorption of

the allyl radical on to the surface of the magnesium. The proposed mechanism is given below.

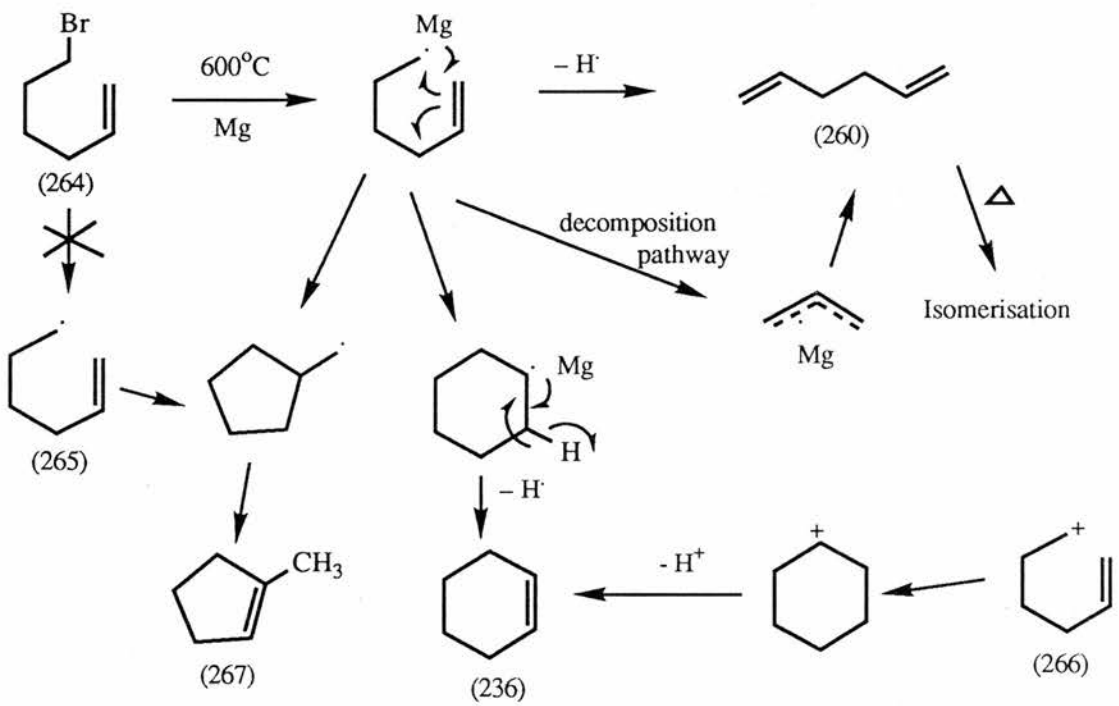


The involvement of gas-phase radicals in these reactions should be confirmed by the generation of 5-hexen-1-yl radicals(**265**) which is known to preferentially cyclise to a five-membered ring[254]. The pyrolysis of 6-bromohex-1-ene(**264**) over magnesium, which should lead to (**265**), gave 50% of cyclohexene(**236**), 22% of three isomers of hexadiene(**260**) and 4% of methylcyclopentene(**267**). Formation of these products precludes a radical intermediate as the main reaction



pathway, rather a metal-bound species was presumed to be involved. This mode of cyclisation to (**236**) is the same as that reported[255] for the 6-hexenyl cation(**266**) in solution. The differing behaviour of (**265**) and (**266**) was attributed to differences in the transition state, with the cation (**266**) preferentially attacking the centre of the double bond where the

electron density is high. A mechanism involving a transition state incorporating the magnesium could account for the formation of cyclohexene(**236**). The higher yield of cyclohexene as compared to the yield of (**262**) from (**259**) may be due to the involvement of a larger and more favourable transition state in the route to (**236**). The hexadienes could arise from the magnesium-induced β-elimination of hydrogen bromide or *via* the decomposition pathway noted earlier with 5-bromopent-1-ene(**259**).

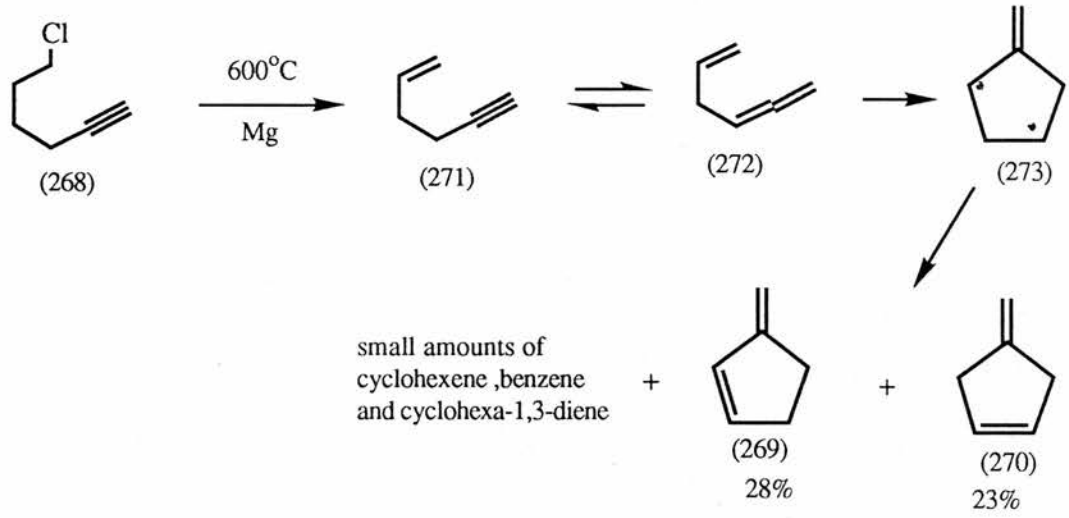


(b) ω-Haloalkynes

Despite the additional energetic increment required to distort the linear acetylenic bond and permit its incorporation into a cyclic transition state, an abundance of evidence indicates that alkynes normally react faster in intramolecular thermal pericyclic reactions than do their alkene counterparts[256]. The fact that alkynes involved in thermal pericyclic reactions, may possess a partial allenic bond character, which is capable

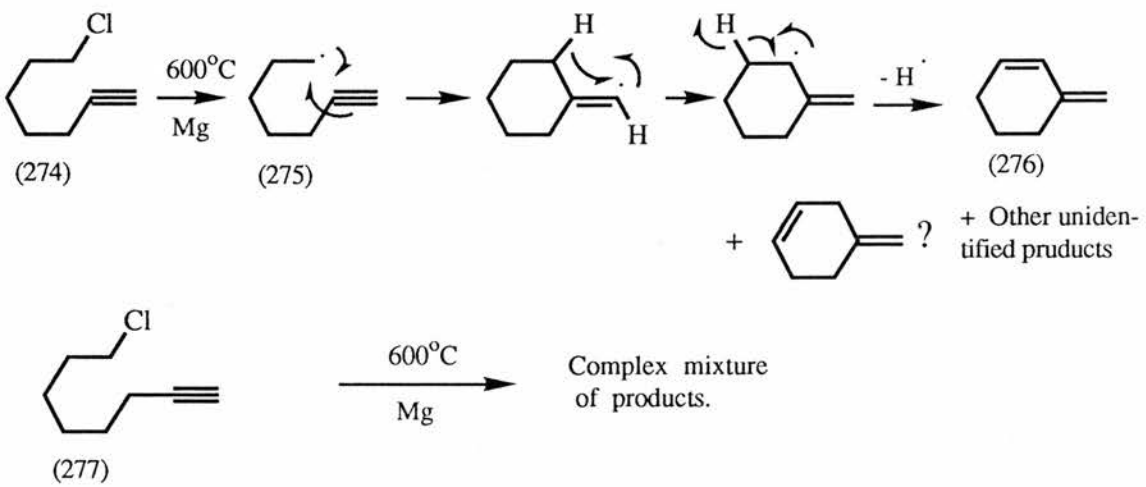
of considerable deformation[257], may account for their observed high reactivity.

When 6-chlorohex-1-yne(**268**) was pyrolysed over magnesium at 600°C, the two major products obtained were 28% of 3-methylenecyclopentene(**269**) and 22% of 4-methylenecyclopentene (**270**); with small amounts of cyclohexene, cyclohexa-1,3-diene, and benzene. The formation of the two major products indicated the likely involvement of a hex-5-en-1-yne species(**271**), which is known to undergo a thermal reversible Cope rearrangement, invoving a [3,3] sigmatropic shift, to it allenic derivative(**272**). At temperatures somewhat higher than those required for the rearrangement, an irreversible cyclisation sets in which leads to a mixture of (**269**) and (**270**), presumably *via* the 1,3-diradical intermediate(**273**)[258]. The minor products are presumably formed through a process similar to that proposed above for the 5-hexen-1-yl species, involving a magnesium-bound cyclic transition state, which may lead to cyclohexa-1,2-diene. Benzene is a secondary product.



Similar pyrolysis of 7-chlorohept-1-yne(**274**) and 8-chlorooct-1-yne (**277**), gave a complex mixture of products, and identification of

individual compounds was impossible. However, for 7-chlorohept-1-yne the major product seems to be 3-methylenecyclohexene(**276**), presumably formed *via* the heptynyl species (**275**) followed by intramolecular cyclisation involving hydrogen shifts. The possibility of alternative cyclisation modes (various transition state size), varied reaction pathways of the assumed diradical intermediate and bond isomerisation (*via* pericyclic rearrangements), may account for the complex nature of the reactions involving both 7-chlorohept-1-yne(**274**) and 8-chlorooct-1-yne(**277**). Repeat pyrolysis at a lower temperature of 500°C failed to show any significant difference in the number of products observed, rather a large amount of unreacted starting material was obtained



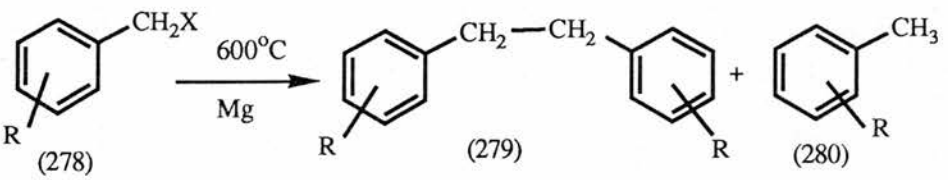
B. Flash vacuum Pyrolysis of Benzylic Halides and α,α'-Dihalo-*o*-Xylenes over magnesium

1. Benzylic halides

Apart from the classical thermal decomposition of benzyl chloride dicussed in the introduction only the thermal reaction of α-halo-*o*-xylene (**5**) has received great attention, because it readily undergoes a 1,4-β-elimination of hydrogen halide, to give *o*-xylylene (**8**), an important intermediate in the synthesis of cyclophanes[16], benzocyclobutenes[13] and in Diels-Alder reactions[14]. This is in contrast to the extensive literature reports on the dehalogenative coupling of benzylic halides in solution using various reagents, some of which was reviewed in the Introduction.

In the gas phase, benzylic halides might be expected to react in a similar manner to that observed in solution, with the likely formation of benzyl radicals on dehalogenation. An alternative reaction might be the α-elimination of hydrogen halide to give carbenes. As carbenes are very reactive species their concentration in solution is always low and therefore carbene coupling is a statistically unlikely process and when formal carbene dimers are isolated, this often involves an attack of the carbene on its precusor. In contrast vapour phase reaction is likely to give dimers even if these are only formed on condensation of the carbene in the cold trap.

On pyrolysis over magnesium at 600°C benzyl chloride or bromide (**278**) gave mainly a mixture of homo coupled product, bibenzyl(**279**) and the reduction product, toluene(**280**). Also obtained were small amounts of stilbene and diphenylmethane. The bromide gave a higher overall yield of the products than the chloride, this may be due to the well known higher reactivity of bromides towards magnesium in solution, especially for Grignard reactions.



(278) (279) (280)

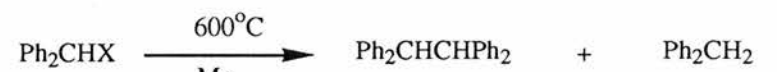
60 — 80% 5 — 20%

X= Br, Cl

R= H , 2- CH_3 , 4- CH_3 , 2- F, 3- F, 4- F, 2- Cl , 4- Cl, 2- Br, 4- Br, 2- I , 2,3,4,5,6- pentafluoro .

\+ Small amounts of Stilbenes and Diphenylmethanes.

Similarly, substituted benzyl halides on pyrolysis over magnesium afforded the corresponding disubstituted bibenzyls(**279**) in good to high yield. The corresponding reduction products, toluenes, were formed as side products in all cases. In addition, small amounts of other products (eg stilbenes) were also produced (see Table 1). Halo-diphenylmethanes (**281**) also underwent a similar reaction to give 1,1,2,2-tetraphenylethane(**282**) and diphenylmethane(**283**). The yields of 60-80% of bibenzyls obtained are comparable to those reported from low oxidation state transition metal reagents, often employed for the homocoupling of benzylic halides in solution. Of particular interest were the results recently reported[113] on the homocoupling of various benzylic halides in solution, using nickel in the metallic state, as both the coupled products bibenzyls and the reduction products, toluenes were obtained.



X=Cl or Br (281) (282) 60-70% (283) 18-20%

In the particular case of 2-methylbenzyl bromide(**284**) this was previously reported[10] to give benzocyclobutene(**2**) on pyrolysis at 700°C. The pyrolysis of (**284**) over magnesium at 600°C gave 70% of 2,2'-dimethylbibenzyl(**285**) and 20% of *o*-xylene(**286**). Only about 3% of the thermal product (**2**) was obtained. The lower operating

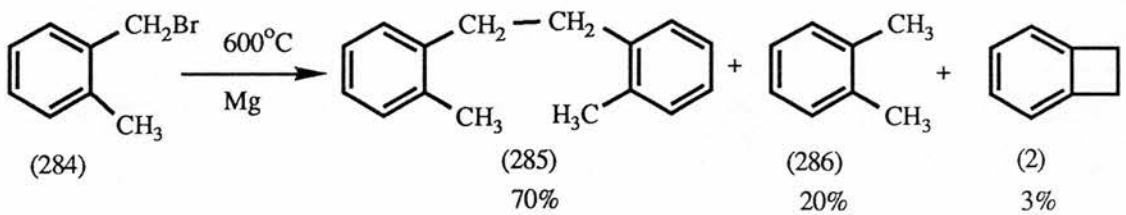
TABLE I

R-$C_6H_4CH_2X$	Temp(°C)	Press(Torr)	Yield % A	B	C	D	E	Others	Total Yield %
R=H, X=Cl	600	1.0×10^{-1}	58.1	16.1	-	-	3.8	Diphenylmethane = 5.8	83.8
R=H, X=Br	600	2.0×10^{-1}	68.7	20.5	-	-	2.5	Diphenylmethane = 1.1	92.7
R=2-CH_3, X=Br	600	1.5×10^{-1}	69.5	19.7	-	-	1.3	Benzocyclobutene = 2.9	93.4
R=4-CH_3, X=Cl	600	6.0×10^{-1}	50.0	23.0	-	-	1.7	Ditolylmethane = 2.5	77.2*
R=2-F, X=Cl	600	1.0×10^{0}	50.0	3.7	3.5	8.8	9.7	Toluene = 3.6	79.3
	600	2.0×10^{-2}	78.2	7.4	4.6	-	-	Toluene = 3.6	93.8*
R=2-F, X=Br	600	1.1×10^{0}	51.3	8.9	10.9	8.1	-	Toluene = 8.3 Stilbene = 8.0	95.5
	600	4.0×10^{-2}	79.8	11.0	3.0	-	-	Toluene = 3.6	97.4*
R=2-Cl, X=Cl	600	6.5×10^{-1}	24.5	14.5	5.5	1.4	-	Toluene = 1.8 Bibenzyl = 0.5	48.2
	600	4.0×10^{-1}	66.1	17.5	-	-	-		83.6*
	600	7.0×10^{-3}	68.5	23.0	-	-	-		91.5*
R=2-Br, X=Br	600	1.0×10^{0}	35.5	22.8	7.0	13.0	-	Toluene = 3.2 Monobromobibenzyl = 3.1	84.6
	600	8.0×10^{-1}	21.6	12.5	21.3	17.3	-	Toluene = 9.7 Bibenzyl = 1.9 Monobromobibenzyl = 1.7	86.0
	600	2.0×10^{-2}	51.1	24.0	2.3	6.3	-	Toluene = 2.5 Bibenzyl = 3.3	89.5
R=3-F, X=Cl	600	1.1×10^{0}	59.0	19.1	-	-	1.7	Bibenzyl = 5.0	
	600	7.6×10^{-2}	48.5	15.3	-	-	-	Bibenzyl = 4.6 Monofluorobibenzyl = 5.0	73.4*
R=3-F, X=Br	600	8.0×10^{-1}	50.9	8.0	-	-	1.7	Bibenzyl = 11.5 Monofluorobibenzyl = 10.1 Stilbene = 4.4	86.6
	600	1.3×10^{-2}	66.9	12.1	-	-	4.9	Bibenzyl = 2.9 Monofluorobibenzyl = 2.3	89.1*
R=4-F, X=Cl	600	1.0×10^{0}	58.1	21.8	-	-	5.2	Bibenzyl = 2.4 Monofluorobibenzyl = 4.3	91.9
	600	7.0×10^{-2}	63.3	5.1	-	-	-	Bibenzyl = 2.1 Monofluorobibenzyl = 4.8 Toluene = 6.0	81.3*
R=4-F, X=Br	600	1.0×10^{0}	73.4	11.5	-	-	-	Bibenzyl = 1.2 Monofluorobibenzyl = 6.1 Toluene = 4.9	97.1
	600	3.5×10^{-2}	53.0	23.3	-	-	-	Bibenzyl = 1.9 Monofluorobibenzyl = 3.4	81.6*
R=4-Cl, X=Cl	600	4.8×10^{0}	10.4	6.3	-	-	-	Bibenzyl = 22.0 Stilbene = 11.8 Toluene = 11.8	62.3
		1.8×10^{-1}	36.9	5.5	-	-	1.1	Bibenzyl = 6.2 Stilbene = 5.6 Toluene = 3.9	59.2
R=4-Br, X=Br	600	1.2×10^{0}	-	-	-	-	-	Bibenzyl = 38.3 Toluene = 13.6 Stilbene = 1.7	53.6
	600	8.0×10^{-3}	43.1	28.1	-	-	-		71.2*
R=2-I, X=Cl	600	2.5×10^{-2}	40.1	10.9	16.2	6.5		Bibenzyl = 10.2 Monoiodostilbene = 6.2	
	600	6.0×10^{-1}	40.2	trace	30.7	12.4		Monoiodobibenzyl = 3.6 Bibenzyl = 4.1 Monoiodostilbene = 2.6	93.7* 90.0

A (R-$C_6H_4CH_2$-)$_2$; B R-$C_6H_4CH_3$; C Dihydrophenanthrene; D Phenanthrene; E (R-C_6H_4CH=)$_2$

* corrected for recovered starting material

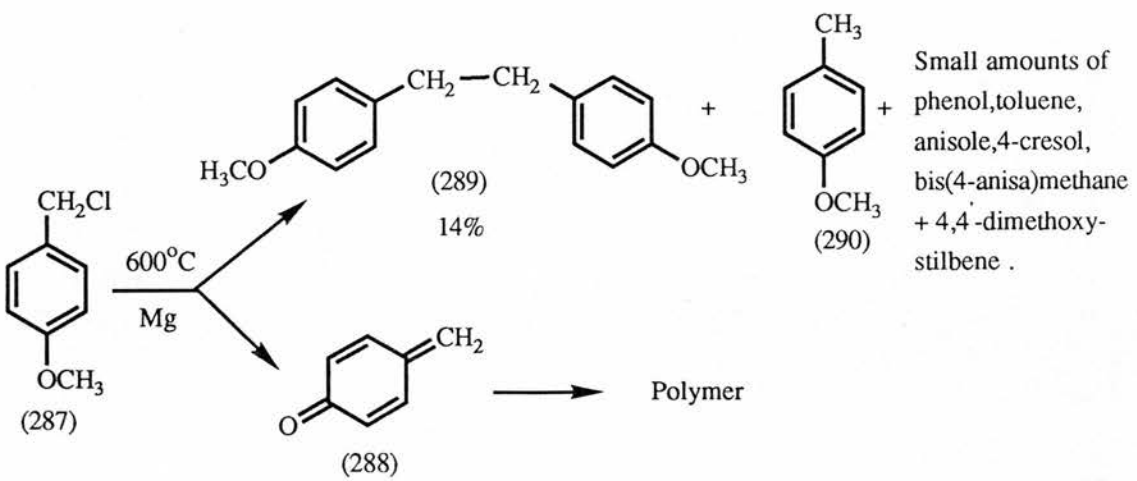
temperature of 600°C used for the pyrolysis over magnesium and the alternative reaction path provided by the magnesium surface, may account for the observed low yield of the thermal product (**2**).



(284) (285) 70% (286) 20% (2) 3%

\+ small amount of dimethylstilbene

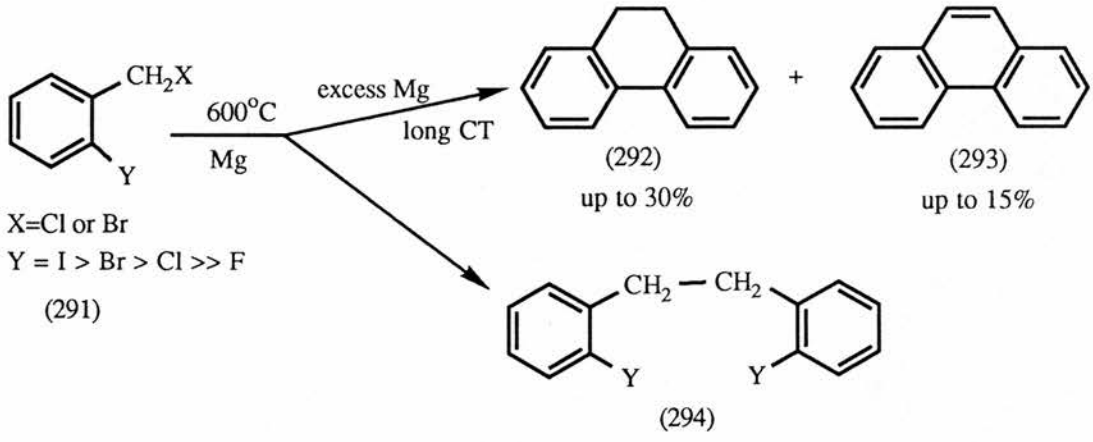
When 4-methoxybenzyl chloride(**287**) was pyrolysed over magnesium, most of the product obtained was intractable polymer flakes, presumably formed from the *p*-quinonemethide(**288**) *via* loss of a chlorine atom and methyl radical. Such loss of a methyl group from aromatic OMe, under thermal conditions is known[259] and the formation of the stabilised intermediate(**288**) might have enhanced the process. Apart from the polymer, the other major product was the expected 4,4'-dimethoxybibenzyl(**289**) in 14% yield, with small amounts of 4-methylanisole, anisole, cresol, phenol, toluene, 4,4'-dimethoxystilbene and bis(4-anisyl)methane, observed on the GC-MS of the pyrolysate.



(287) (288)

In the course of this investigation, particular attention was given to the pyrolytic reaction of halo-substituted benzyl halides as preliminary results showed small amounts of partial ring dehalogenated products. Studies involving variation of pyrolysis conditions, indicated that the amount of ring dehalogenated product obtained was dependent on the available magnesium surface, as well as the substrate contact time over the magnesium (See Table 1). Thus greater magnesium to substrate ratio and longer contact time (poor vacuum) led to higher yields of ring dehalogenated products.

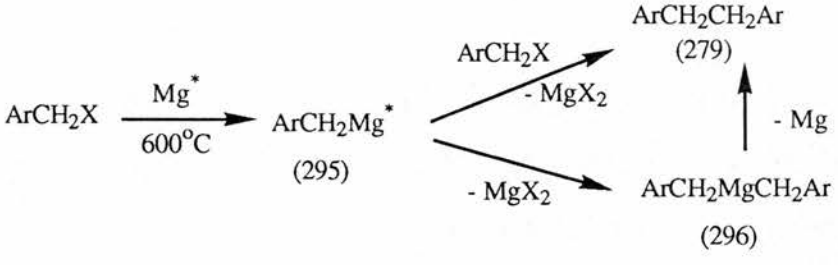
The significance of this observation was that for *o*-halobenzyl halides (**291**) the loss of both the side chain and ring halogens, led not only to dimerisation but also cyclisation to 9,10-dihydrophenanthrene(**292**) and its secondary product, phenanthrene(**293**). The reactivity of the ring halogen was in agreement with the known trend of halogen reactivity, iodine being the most readily removed, followed by bromine



and chlorine, with fluorine virtually unaffected (see Table 1). A yield of up to 30% of (**292**) and 12% of (**293**) was obtained from 2-iodobenzyl chloride with a pressure of 0.6 mm Hg and excess of magnesium. Similar control of pyrolysis conditions was employed to obtain 2,2'-dihalobibenzyls(**294**) with minimal involvement of the ring

dehalogenation process. For 4-halobenzyl halides, ring dehalogenation simply led to unsubstitued bibenzyl(**148**), as one of the reaction products (see Table 1).

Apart from the processes highlighted above, the main pyrolytic reaction of benzylic halides over magnesium was homocoupling to bibenzyls and reduction to toluenes. Pure bibenzyls were often obtained by recrystallisation or preparative TLC of the pyrolysate. The reaction presumably proceeded in a stepwise manner with the likely involvement of the benzyl-magnesium bound species(**295**). The metathesis of the species (**295**) would afford the dibibenzyl-magnesium species(**296**), which could then eliminate the coupled product from its surface. An alternative route could involve direct reaction of the species (**295**) with benzyl halide to give the coupled product (**279**). However, the possibility of a radical mechanism cannot be completely excluded. Both the radical and organometallic intermediates were proposed in the homocoupling reaction of benzylic halides in solution using metallic iron in water[111] and metallic nickel in 1,2-dimethoxyethane[113]. The source of the hydrogen for the reduction product, toluene, is unknown but may be from abstraction from the substrate and in all reactions the glass wool was coated with carbon and tar. The ring dehalogenation is a secondary process, after the homocoupling reaction, when the pyrolysis conditions are suitable.



2. Other studies involving benzyl chloride

(a) Determination of available magnesium surface

The amount of magnesium surface available for pyrolytic reaction was determined by passing a known excess amount of benzyl chloride (**146**) over a known small amount of magnesium. Thus 3.1g benzyl chloride passed over 1.0g magnesium at 600°C, gave 1.2 g unreacted starting material, implying that 1.9g of the starting material has been transformed presumably by the magnesium.

$$1.0 \text{ g of Mg} = \frac{1}{24.3} = 0.0411 \text{ mol}$$

$$\text{Number of moles of reacted starting material} = \frac{1.9}{126.5} = 0.0153 \text{ mol}$$

Assuming the transformation of $Mg \rightarrow MgCl_2$

then 1 mol Mg ≡ 2 mol benzyl chloride

$$\% \text{ Mg available for reaction} = \frac{\text{moles of reacted starting material}}{2 \times \text{moles of magnesium}} \times 100$$

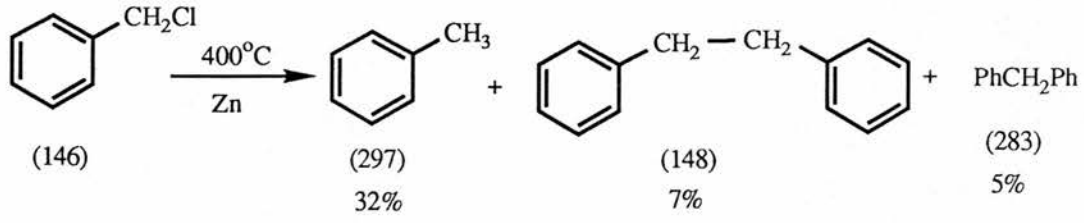
$$= \frac{0.0153}{2 \times 0.0411} \times 100 = 20\%$$

So only about 20% of the magnesium was available for reaction and by taking this result into perspective, complete reaction can be achieved using the appropriate magnesium to substrate ratio. The magnesium employed for this particular experiment was found to be completely reacted, as the usual vigorous reaction was not observed, when the residual content in the furnace tube was plunged into dilute hydrochloric acid.

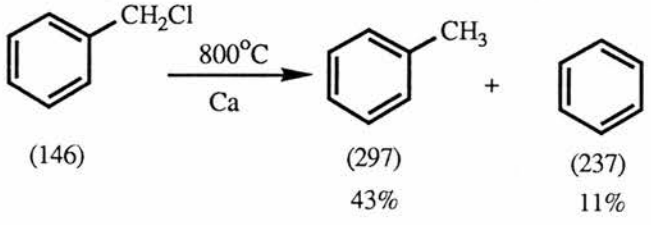
(b) Pyrolysis over zinc and calcium

As a comparison to the observed reaction of benzylic halides over magnesium, benzyl chloride(**146**) was pyrolysed over zinc at 400°C and calcium at 800°C. The choice of reaction temperature was based on the observed high reactivity of magnesium near its melting point, thus the temperatures used were near the metals melting point. The product

obtained over zinc was mainly that of dehalogenative reduction to toluene



(**297**),with only small amounts of the dehalogenative coupled products bibenzyl(**148**) and diphenylmethane(**283**). However, the pyrolysis of (**148**) over calcium gave only (**297**) and benzene(**237**), without any coupled product.



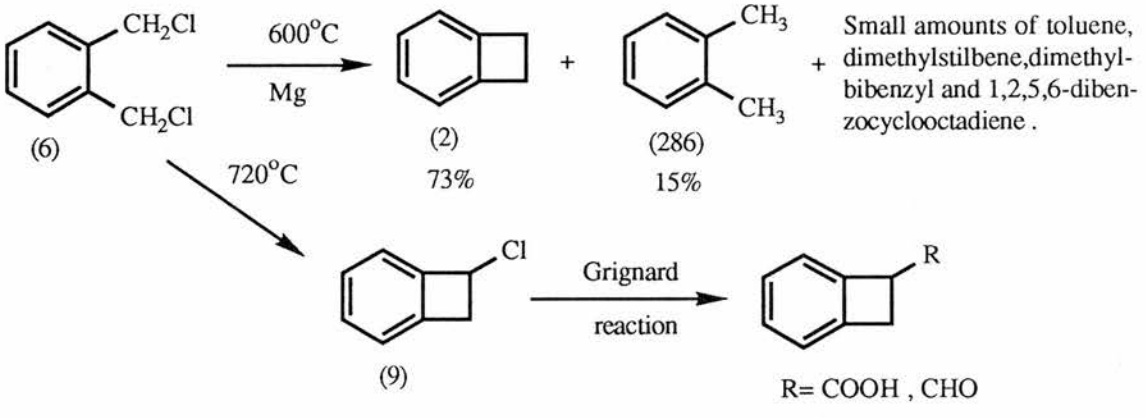
Although the basic reaction of dehalogenation was also observed with zinc and calcium as for magnesium, the nature and composition of products vary from those obtained from magnesium. The formation of mainly toluene from both zinc and calcium, tend to suggest that the species formed on dehalogenation was too short-lived on the metal surface to allow for homocoupling reaction, rather it simply abstracted hydrogen. It may even be a true radical species. The source of the hydrogen is unknown, though the likely sources are from unreacted starting material or decomposition products, as the yield of products was generally low. The higher temperature used for the pyrolysis over calcium,may tend to favour the release of the dehalogenated species from the metal surface as well as the decomposition reaction. This was evident from the fact that

no homocoupled product was obtained and the higher yield of (**146**) as well as the formation of the decomposition product benzene(**237**).

Magnesium is therefore better suited for the dehalogenative homocoupling of benzylic halides, while calcium mainly led to reduction with zinc having an intermediate action.

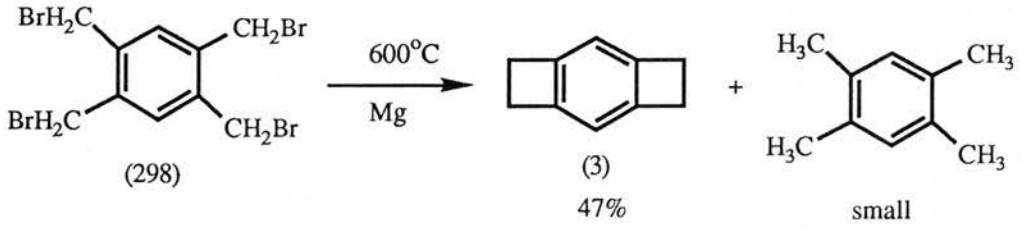
3. α,α'-Dihalo-*o*-xylenes

As mentioned in the Introduction, the thermal route to chlorobenzocyclobutene(**9**) was *via* the 1,4-elimination of hydrogen chloride from α,α'-dichloro-*o*-xylene(**6**)[11] at 720°C. Grignard reaction allows the transformation of (**9**) into various substituted benzocyclobutenes in good yields (e.g., R = COOH,CHO) which are of interest as synthetic building blocks.[38]



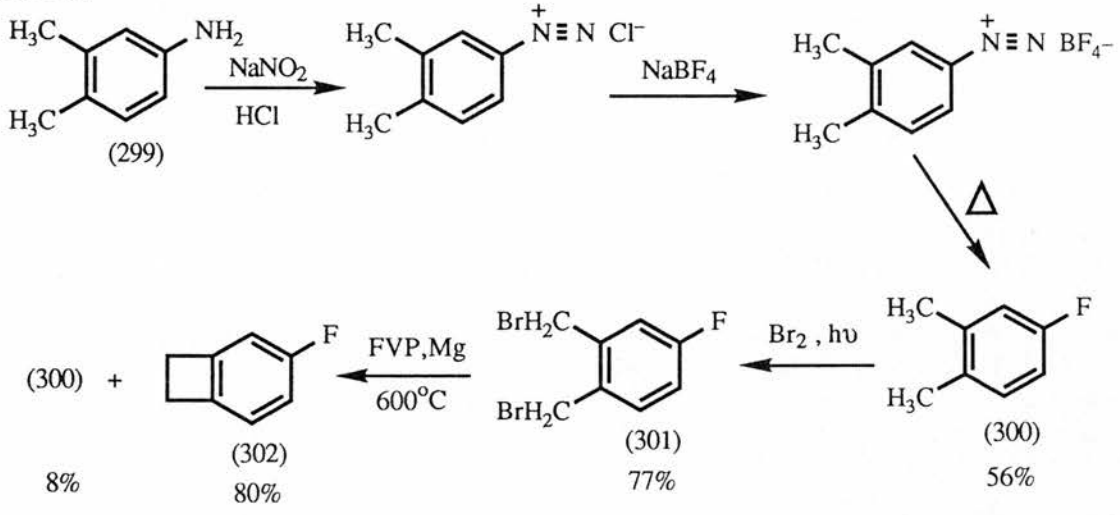
Investigation of the reaction of (**6**) over magnesium at 600°C, showed complete dehalogenation to unsubstituted benzocyclobutene(**2**), rather than the thermal 1,4-elimination of hydrogen chloride. The yield of (**2**) from (**6**) was 73%, with only about 15% of *o*-xylene(**286**) as the major by-product. Similar elimination of two molecules of bromine over magnesium from 1,2,4,5-tetrakis(bromomethyl)benzene(**298**) gave only a 50% yield of 1,2,4,5-benzodicyclobutene(**3**) and a small amount of

1,2,4,5-tetramethylbenzene. The moderate yield was attributed to the difficulty in volatilising (**298**), some of which decomposed in the inlet tube.



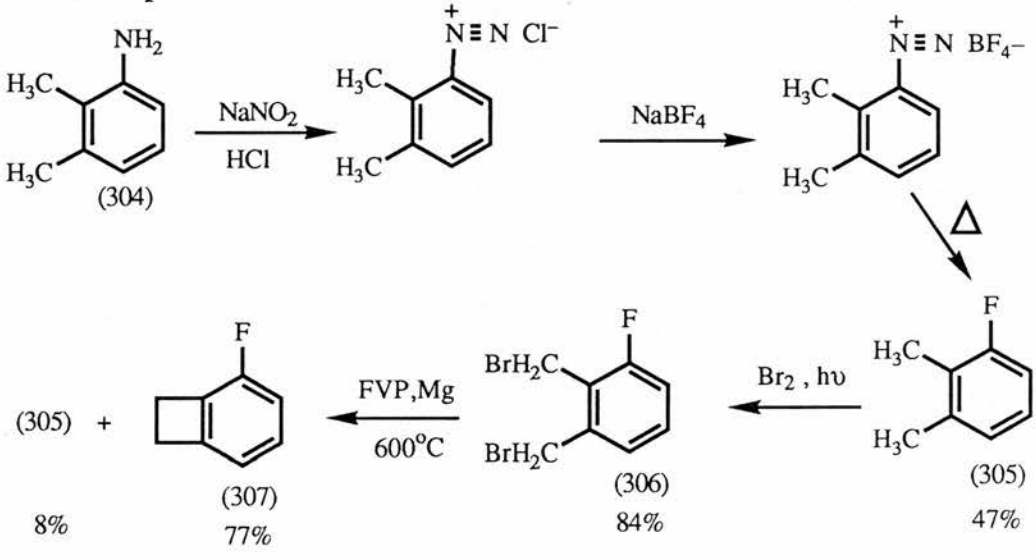
(298) (3) 47% small

As an extension to the above process, the two isomeric fluorobenzocyclobutenes (**302**) and (**307**) were prepared in a three step route from readily available dimethylanilines(**299**) and (**304**), employing the thermal dehalogenation over magnesium as the key step. The anilines (**299**) and (**304**) were diazotised with sodium nitrite and hydrochloric acid, and the diazonium salt converted to its fluoroborate salt with sodium tetrafluoroborate. Thermal decomposition of the salts gave the fluoro-*o*-xylenes(**300**) and (**305**) in reasonable yields. Photochemical bromination of (**300**) and (**305**), with molecular bromine, afforded the α,α'-dibromo-*o*-xylene derivatives(**301**) and (**306**) respectively in high yields.



(299) (300) 56% (301) 77% (302) 80% 8%

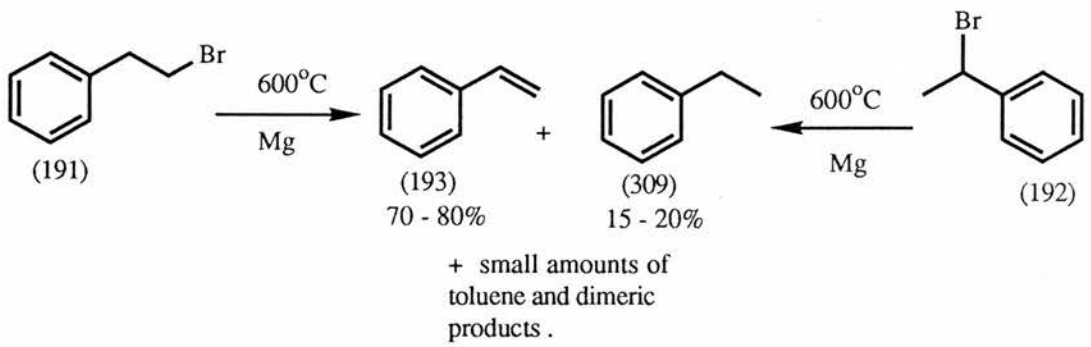
The pyrolysis of (**301**) and (**306**) over magnesium at 600°C gave a 79% yield of 4-fluorobenzocyclobutene(**302**) and a 77% yield of 3-fluorobenzocyclobutene(**307**) respectively. The only side products obtained were the fluoro-*o*-xylenes (**300**) and (**305**) respectively. The magnesium-induced thermal dehalogenation method involves two fewer steps than the only literature method[186] for the synthesis of these fluorobenzocyclobutenes from fluorinated 1,3-dihydro-benzo[b]thiophene-2,2-dioxide.



C. Flash Vacuum Pyrolysis of Haloalkylbenzenes over Magnesium

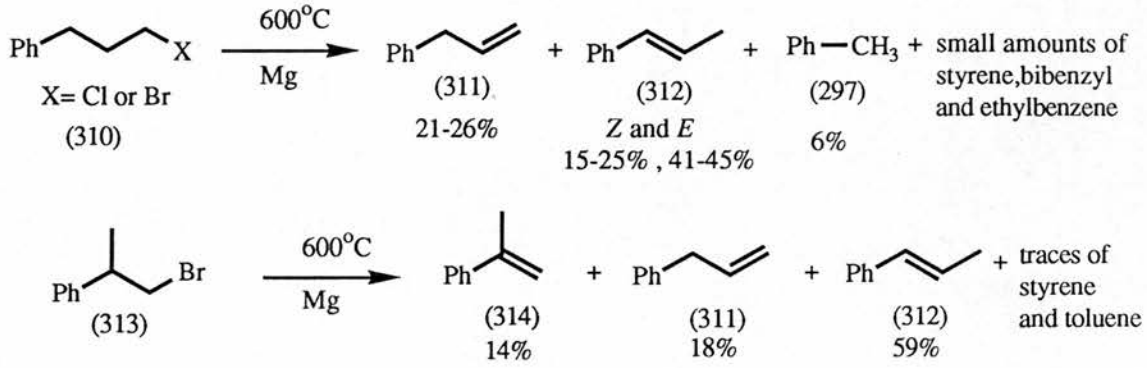
The reactions of haloalkylbenzenes with bases in solution are well known. They preferentially undergo unimolecular dehydrohalogenation as opposed to bimolecular coupling and this reaction has been employed for the preparation of styrenes[115,157] and acetylenes.[159] Similar dehydrohalogenation has also been achieved thermally by passing styrene chlorohydrin(**94**) and styrene dichloride(**96**) over alumina at 360-400°C to give acetophenone(**95**) and β-chlorostyrene(**97**)[75] respectively.

When 2-bromoethylbenzene(**191**) or 1-bromoethylbenzene(**192**) were passed over magnesium at 600°C, dehydrobromination was the main reaction to give a high yield of styrene(**193**). The only major side product was ethylbenzene(**309**) but small amounts of toluene and unidentified dimeric products were also obtained.

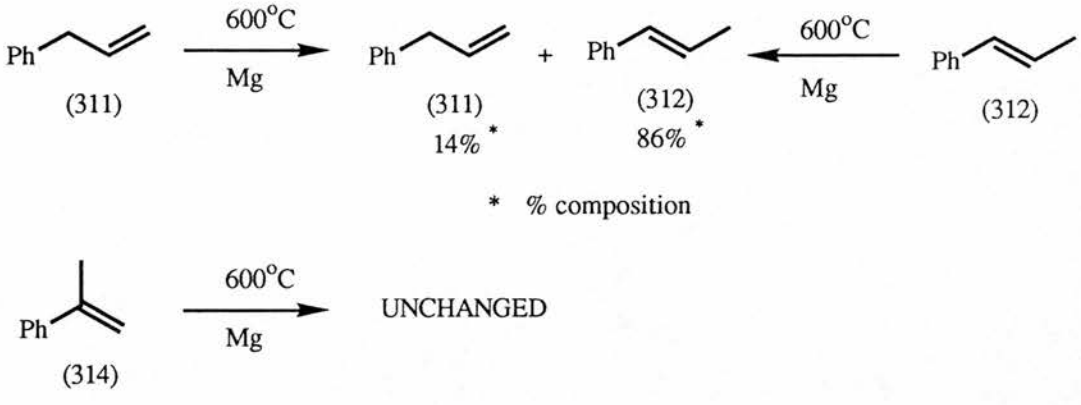


This investigation was extended to longer side chains; thus the pyrolysis of 1-halo-3-phenylpropane(**310**) over magnesium gave mainly allylbenzene(3-phenylprop-1-ene)-(**311**) and *Z,E* β-methylstyrene (1-phenylprop-1-ene)-(**312**). The isomeric 1-bromo-2-phenylpropane (**313**) was prepared by hydroboration of α-methylstyrene (2-phenylprop-1-ene)-(**314**) to 2-phenylpropan-1-ol, which was brominated with phosphorus tribromide. On pyrolysis over magnesium

(**313**) gave a mixture of α-methylstyrene(**314**), allylbenzene(**311**) and β-methylstyrene(**312**).



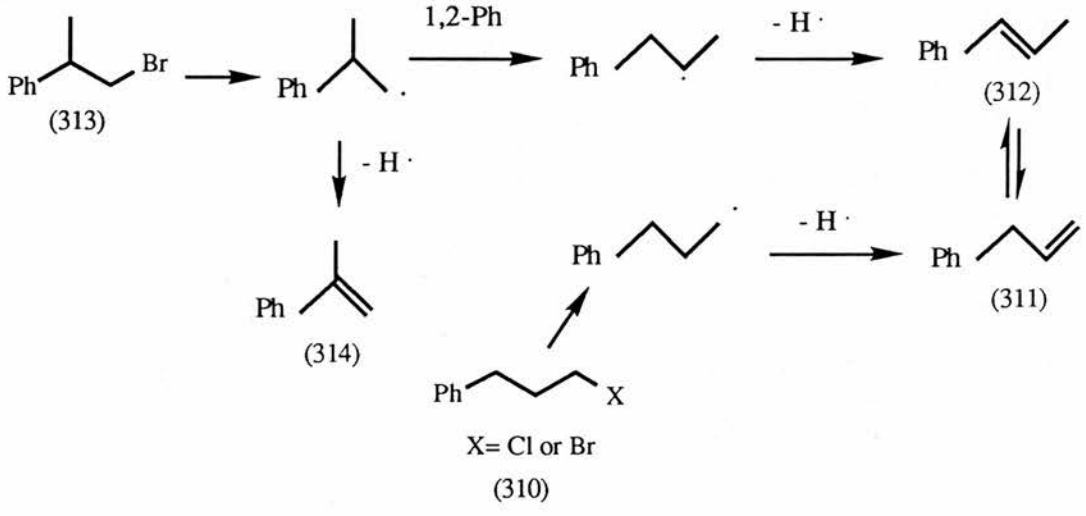
The transformation of (**310**) to (**312**) presumably involved the initial formation of (**311**) *via* β-elimination of hydrogen halide, followed by double bond isomerisation to go into conjugation with the phenyl ring. This interconversion was confirmed by a control pyrolysis of each of (**311**) and (**312**), both of which gave an equilibrium composition of 14% of (**311**) and 86% of (**312**).



The formation of (**314**) from (**313**) was simply a β-elimination of hydrogen bromide while the route to (**311**) and (**312**), must have involved a skeletal rearrangement of the species formed on dehalogenation, as (**314**) itself remained unchanged on control pyrolysis at 600 °C. A 1,2-phenyl migration is proposed in the mechanism given

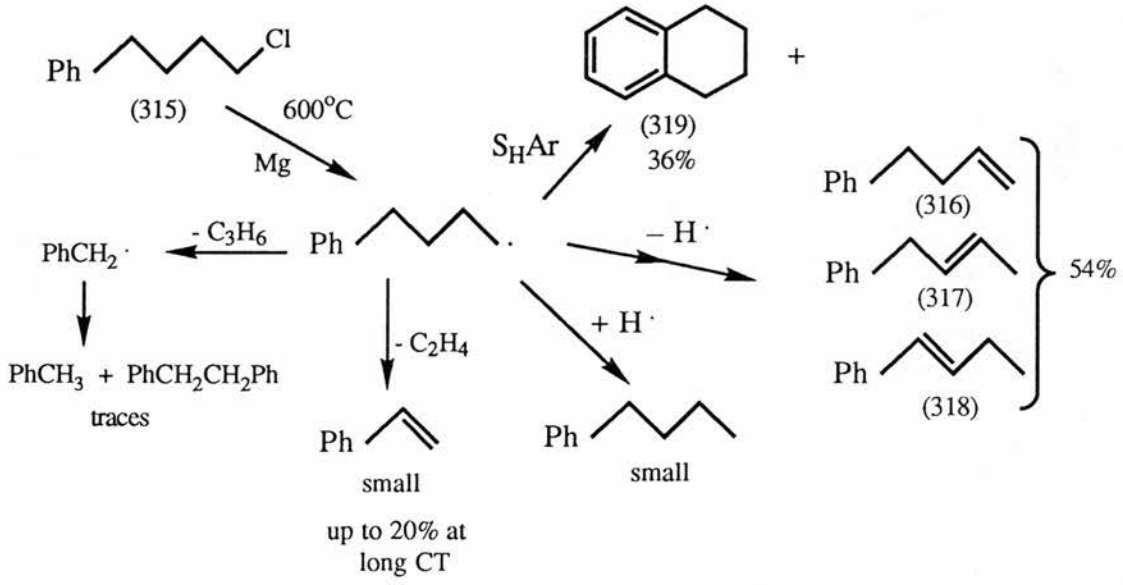
below. A similar process has been previously reported[260] in solution, as the dehydrobromination of (**313**) with Mg and $CoBr_2$ gave, in addition to the expected (**314**), both (**311**) and (**312**) .

Mechanism

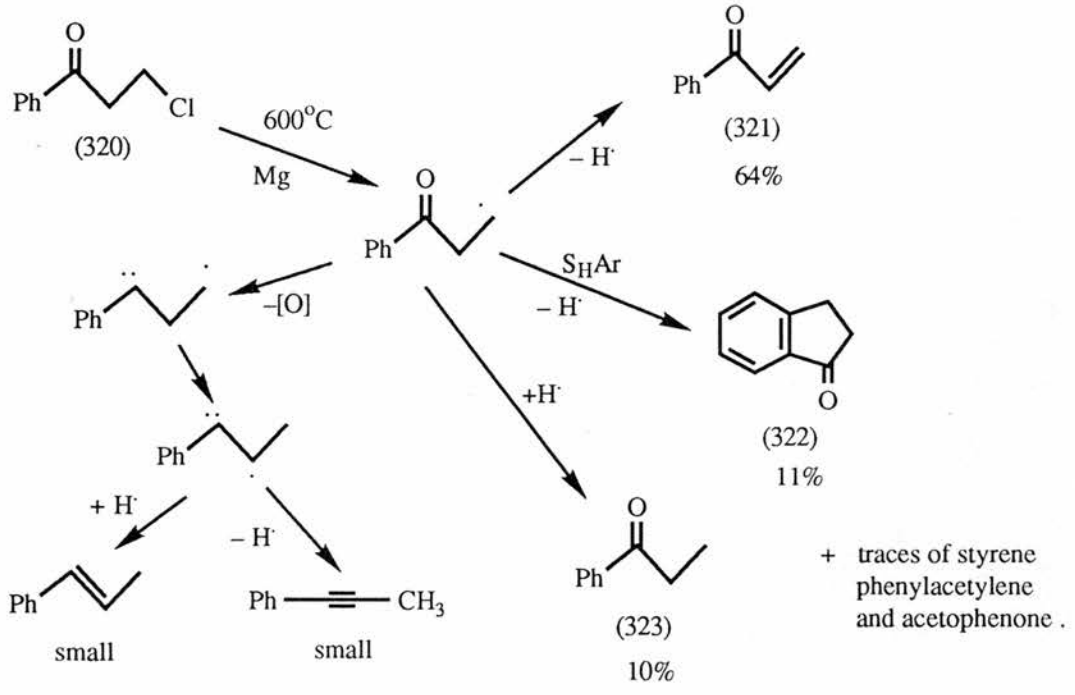


With 1-chloro-4-phenylbutane(**315**), the expected dehydrochlorination to 4-phenylbut-1-ene(**316**) was observed and this was accompanied by double bond isomerisation to give the other isomeric phenylbutenes(**317**) and (**318**). Apart from this process, the only other major product obtained was tetrahydronaphthalene(**319**) which was assumed to have been formed by intramolecular attack of the intermediate formed on dechlorination, on to the phenyl ring. This process is similar to the one earlier observed from the thermal debromination of 6-bromohex-1-ene(**264**), in which the intermediate formed cyclises on to its alkene-tail to give cyclohexene(**236**). The minor products obtained were phenylbutane and styrene(**193**), the latter an obvious decomposition product from the loss of ethylene. This decompostion pathway is similar to the one earlier observed in the thermal reaction of 5-bromopent-1-ene (**259**) over magnesium. An increased yield of up to 20% of the decomposition product (**193**) was obtained, when the pyrolysis was

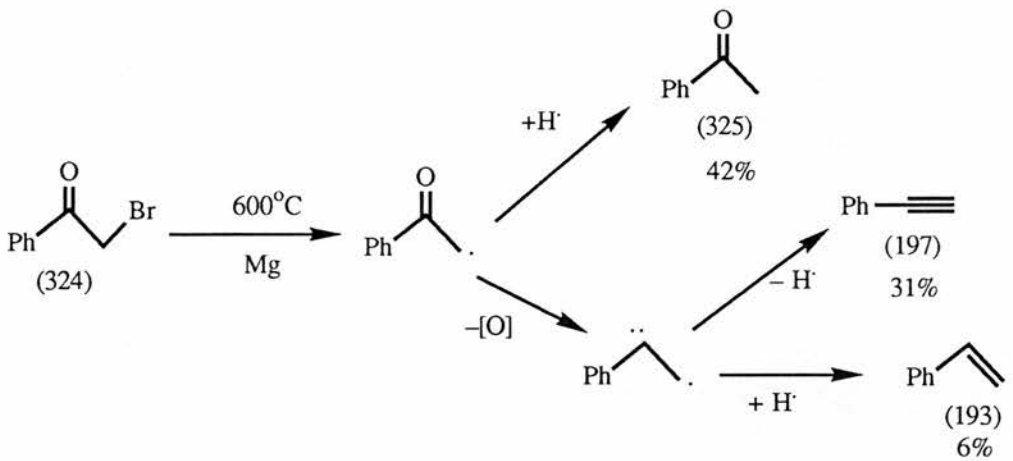
carried out at a longer contact time achieved under a higher pressure of 1.0mmHg.



Similar dehydrochlorination produced acrylophenone(**321**) in 64% yield, from 3-chloropropiophenone(**320**) on pyrolysis over magnesium at 600°C. Also observed was attack on the phenyl ring to give indanone (**322**), similar to the process noted above. The other products obtained were propiophenone(**323**), with small amounts of acetophenone and deoxygenated products 1-phenylprop-1-ene and 1-phenylprop-1-yne.

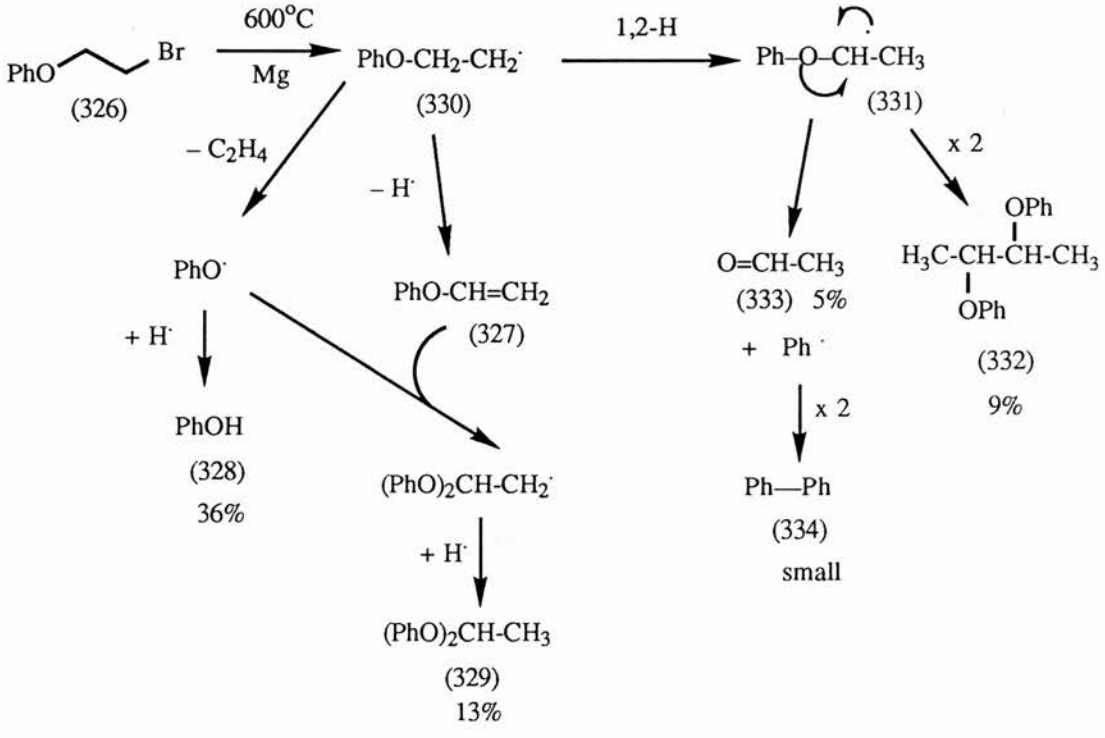


However, when 2-bromoacetophenone(**324**), which has no β-hydrogen, was pyrolysed over magnesium, the major products obtained were acetophenone(**325**) and phenylacetylene(**197**). The higher yield of the deoxygenated product (**197**) from (**324**) when compared to the amount of deoxygenated product from (**320**), may be due to the absence of β-hydrogen to facilitate the elimination of hydrogen halide. Thus, the species formed on dechlorination remains on the metal surface until it can pick up hydrogen to give (**325**), but an alternative route is provided by the deoxygenation process to give stable products. The involvement of the phenacyl radical, $PhCOCH_2^{\bullet}$, is doubtful, as it is known[261] to rearrange and decarbonylate to the benzyl radical at 500°C. The role of the magnesium in the deoxygenation process is not clear. A mechanism proposed for the observed products is given below. Although the intermediate is formally drawn as a carbene radical its real nature on the magnesium surface is unknown.



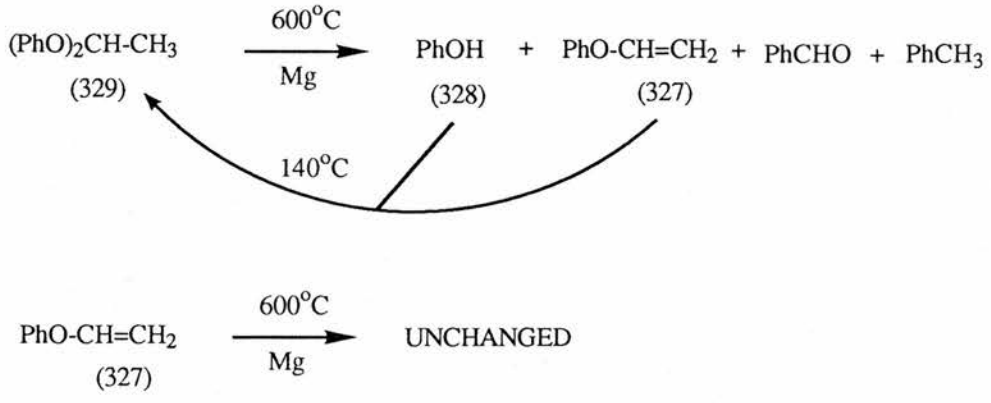
When 2-bromoethyl phenyl ether(**326**) was pyrolysed over magnesium, the expected phenyl vinyl ether(**327**) was not obtained, rather the major products were phenol(**328**), 1,1-diphenoxyethane(**329**) and a compound suspected to be 2,3-diphenoxybutane(**332**) - d_H 2.1(6H, d, J 3Hz), 6.3(2H, q, J 3Hz). Also obtained were small amounts of

acetaldehyde(**333**) and biphenyl(**334**). The formation of phenol clearly emanated from a decomposition process, presumably from the dehalogenated species(**330**) as the independent pyrolysis of (**327**) gave unchanged starting material. A literature report[262] indicated that the thermal decomposition of allyl phenyl ether to phenoxy and propenyl radicals, was achieved only at 950°C.



Although phenyl vinyl ether (**327**) was not one of the products obtained from the pyrolysis over magnesium, it was presumably involved in the formation of (**329**) *via* the attack of a phenoxy-type radical either in the cold trap or the furnace. Compound(**329**) was prepared by literature method[193] and the process involved heating phenol(**328**) together with vinyl phenyl ether(**327**) at 150°C and the phenoxy radical was suggested to be involved. When (**329**) was pyrolysed over magnesium the products obtained were phenol(**328**), phenyl vinyl ether (**327**), benzaldehyde and toluene. This illustrated the interconversion of

(**329**) with (**327**) and (**328**) with temperature change. The formation of acetaldehyde(**333**) and biphenyl(**334**) suggested the involvement of the species(**331**), presumably formed by a 1,2-hydrogen shift from (**330**), which on decomposition led to the two products. The same intermediate species could have led to the compound suspected to be (**332**) on dimerisation. The low yield of (**332**), (**333**) and (**334**) indicated that the rearrangement process does not occur readily.



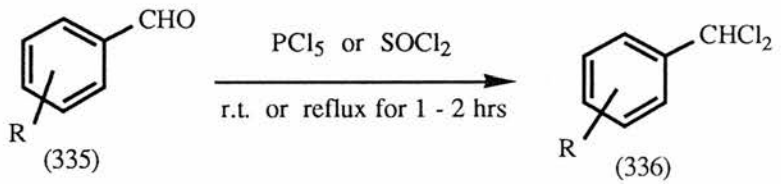
For all the processes observed on pyrolysis of the haloalkylbenzenes over magnesium, the involvement of radical species cannot be entirely ruled out, though the metal-bound species is suspected to be the real intermediate involved.

D. Preparation and Flash Vacuum Pyrolysis of Benzylidene Halides over Magnesium

Following the observed reductive homocoupling of benzylic halides on pyrolysis over magnesium, it was of interest to investigate the behaviour of the analogous benzylidene halides. A similar reaction should lead to dihalobibenzyls or stilbenes, if the magnesium is active enough to effect the removal of all the halogens. The prospect of simultaneous dehalogenation to generate a carbene, an intermediate of great interest, was also recognised.

1. Preparation of benzylidene halides

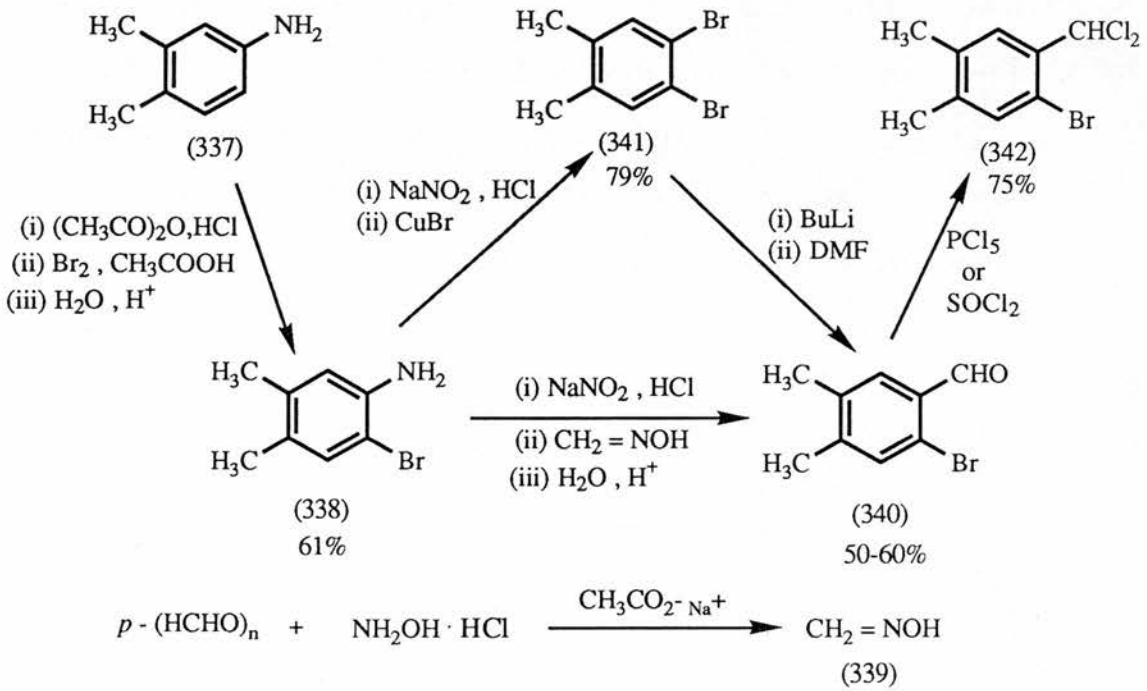
All the substrates used for this investigation were accessed from the corresponding aldehydes by direct halogenation with PCl_5, $SOCl_2$ or $SOBr_2$.



R= H , 2- CH_3 , 3- CH_3 , 4- CH_3 ,
2- OCH_3 , 4- OCH_3 , 2- Cl ,
4- Cl , 6- Cl 2- F, 2- Cl 5- NO_2 ,
6- Cl 4,5- methylenedioxy- .

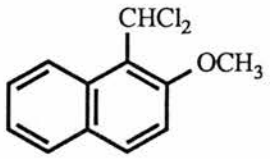
The aldehydes(**335**) were obtained commercially except for the hitherto unknown 2-bromo-4,5-dimethylbenzaldehyde(**340**). Compound (**340**) was prepared from 3,4-dimethylaniline(**337**) by direct bromination, with molecular bromine, of its acetyl derivative to give 2-bromo-3,4-dimethylaniline(**338**) on deprotection. Diazotisation and formylation, with formaldoxime solution(**339**),[207] afforded the aldehyde (**340**) on hydrolysis. An alternative route employed for the synthesis of (**340**), was the diazotisation of(**338**), followed by bromination with

hydrobromic acid and cuprous bromide, to give 1,2-dibromo-3,4-dimethylbenzene(**341**)[206]. Lithium-halogen exchange reaction with one mole equivalent of butyl lithium at –70°C, followed by formylation with DMF, gave (**340**) in a higher overall yield.

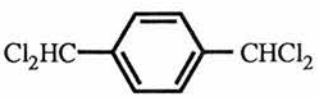


The benzylidene chlorides(**336**) were prepared by either heating the corresponding aldehyde(**335**) with thionyl chloride under reflux or stirring at room temperature with phosphorus pentachloride. Of all the benzylidene chlorides prepared only 2-chloro-5-nitrobenzylidene chloride, 6-chloro-3,4-methylenedioxybenzylidene chloride and 2-bromo-3,4-dimethylbenzylidene chloride(**342**) were hitherto unknown. Similarly prepared were 1-dichloromethyl-2-methoxy-naphthalene(**343**) and α,α,α'α'-tetrachloro-*p*-xylene(**344**). Attempted preparation of α,α,α'α'-tetrachloro-*o*-xylene from the corresponding aldehyde was unsuccessful as the product could not be isolated in pure form, instead a commercial sample was used for the pyrolysis. The overall yields of compounds (**336**) were good to excellent and they are mostly stable at room temperature for at least a few days. Thionyl bromide was used to

prepare α,α,α'α'-tetrabromo-*p*-xylene(**345**) from terephthaldicarboxaldehyde in a moderate yield.



(343)

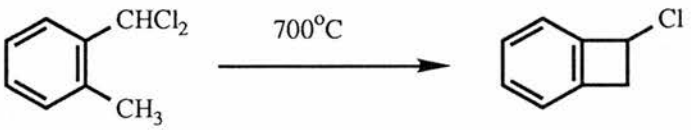


(344)

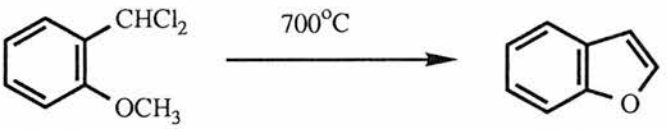
(345)

2. Flash vacuum pyrolysis of benzylidene chlorides

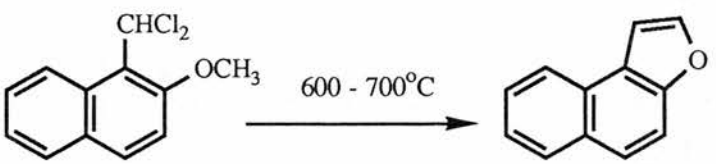
The thermal reaction of benzylidene chlorides has received very little attention and the recent literature report[12] centred around the use of 2-methylbenzylidene chloride(**7**) as an alternative precursor to chlorobenzocyclobutane(**9**) on pyrolysis at 700°C. The furans(**347**) and (**348**) were accessed by pyrolysis of 2-methoxybenzylidene chloride (**346**) and its naphthyl analogue(**343**) respectively, at 600-700°C.[12] This is in contrast to the numerous reports on dehalogenation of benzylidene chloride in solution especially the reductive homocoupling reaction using transition metal complexes.



(7) (9)

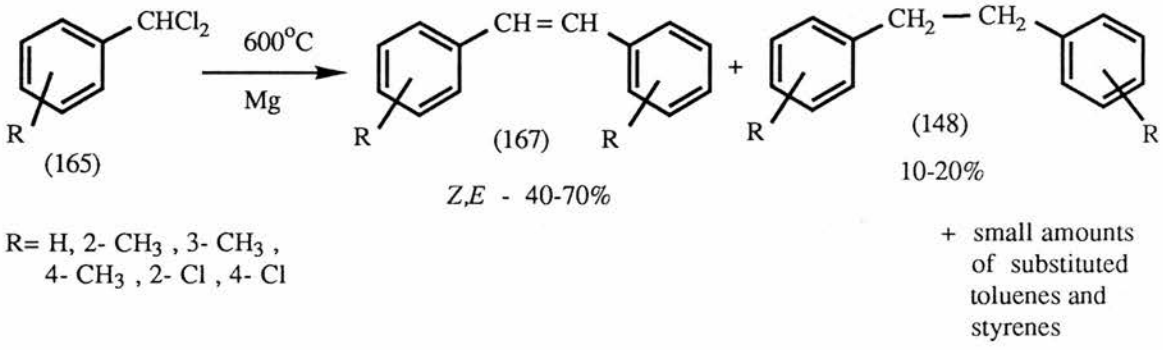


(346) (347)



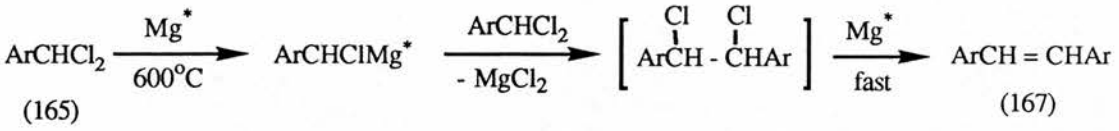
(343) (348)

When the parent member of this series, benzylidene chloride(**165**,R=H) was pyrolysed over magnesium at 600°C, the major products obtained were *Z*-and *E*–stilbene(**167**,R=H) in 50% yield. Other products included bibenzyl(**148**,R=H) and toluene(**297**,R=H), with very small amounts of benzene, phenanthrene and some unidentified compounds. The observed process was extended to the synthesis of various symmetrically disubstituted stilbenes(**167**) in moderate yields of 40-70%. In all cases, the only major by-product was the bibenzyl and, where possible, it was separated by recrystallisation of the pyrolysate to give pure stilbene. The stilbenes generally consisted predominantly of the *E*-isomer with a small amount of the *Z*-isomer.



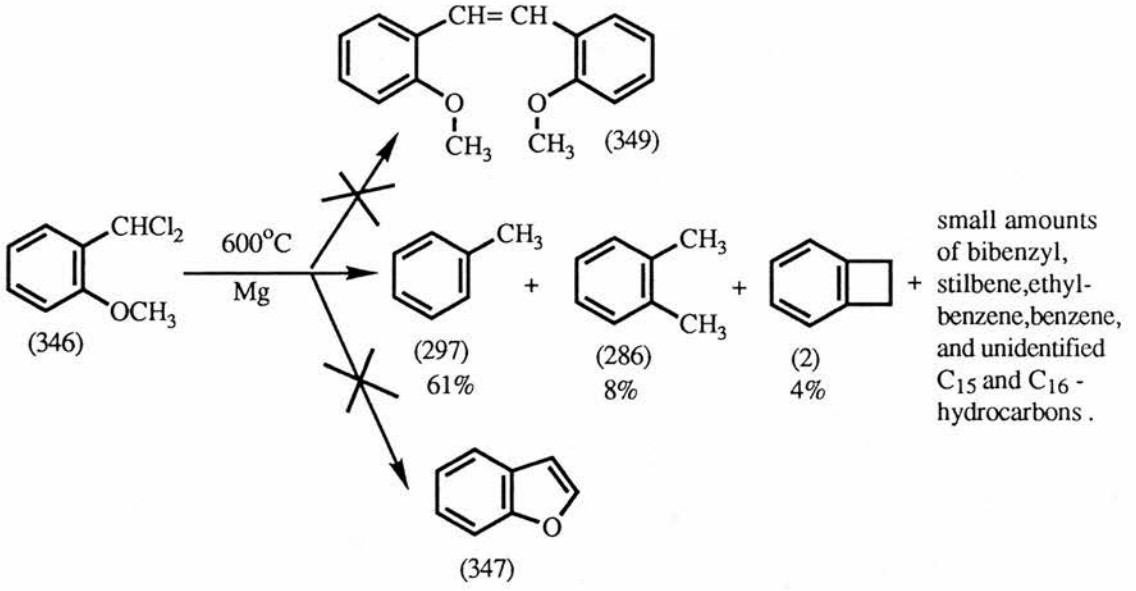
There are two likely mechanistic pathways for this reductive coupling of benzylidene chloride, either *via* a carbene or carbene-magnesium complex intermediate or *via* a step-by-step dehalogenation. In solution, a carbene mechanism was suggested[137] for the iron pentacarbonyl mediated coupling of benzylidene chloride. Later literature reports suggested the carbenoid and carbene-transition metal complex intermediates, based on the trapping of cyclopropane derivatives in the reaction of nickel, iron, cobalt[138] or tungsten[99] complexes with *gem*-dihalides in the presence of alkenes. On the other hand, the step-by-step mechanism was suggested for the reaction of benzylidene

halides with metallic iron[111] or nickel,[113] based on the intermediate products isolated.



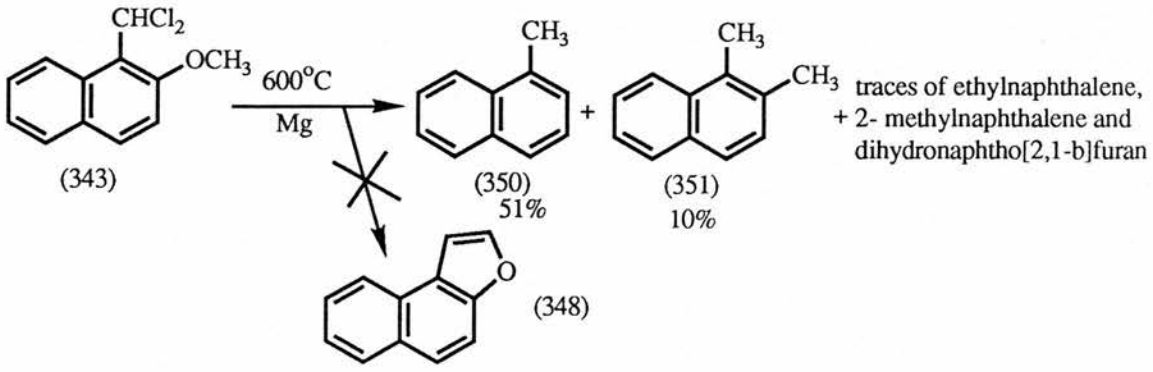
There are no similar studies on the reaction of benzylidene halides in the gas phase. However, based on some intermediate products isolated in the pyrolysis of some benzylic polyhalides (see later section) over magnesium, the step-by-step dehalogenation mechanism was presumed to be involved in the formation of the stilbenes here.

Attempted preparation of 2,2'-dimethoxystilbene(**349**) by pyrolysis of 2-methoxybenzylidene chloride(**346**) over magnesium was



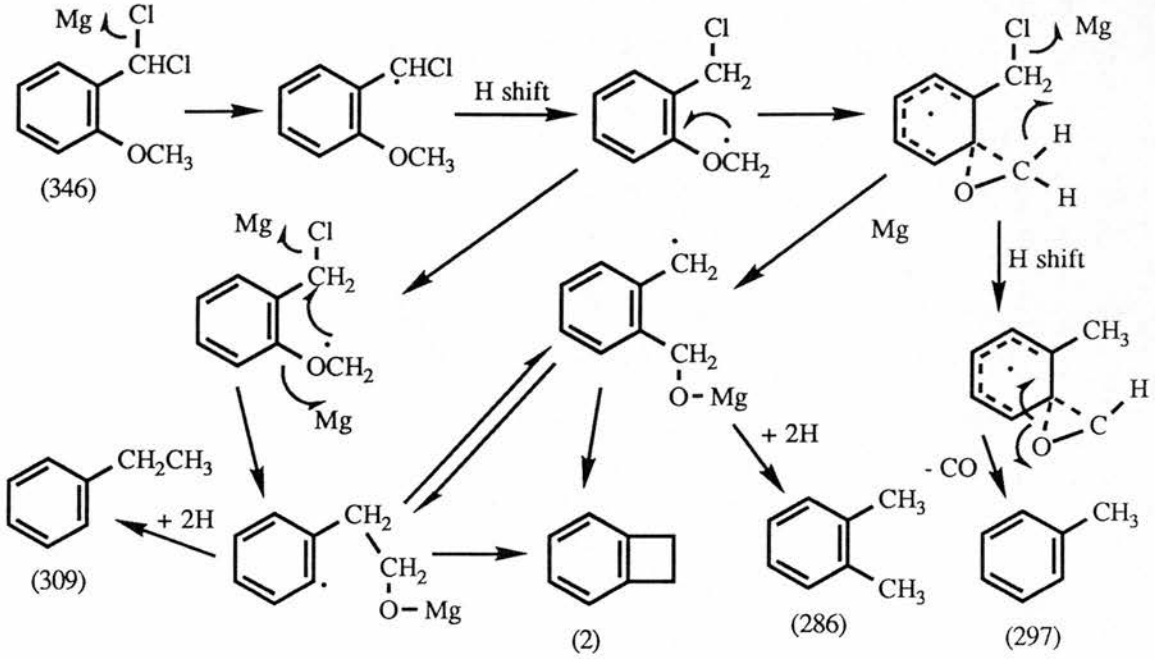
unsuccessful. Instead when (**346**) was pyrolysed the major product obtained was toluene(**297**) in 61% yield. Other products included 8% of *o*-xylene(**286**) and 4% of benzocyclobutene(**2**), with traces of benzene, ethylbenzene, bibenzyl, stilbene and other unidentified C_{15} and C_{16}

hydrocarbon compounds. A similar result was obtained on pyrolysis of 1-dichloromethyl-2-methoxynapthalene(**343**) over magnesium, as the

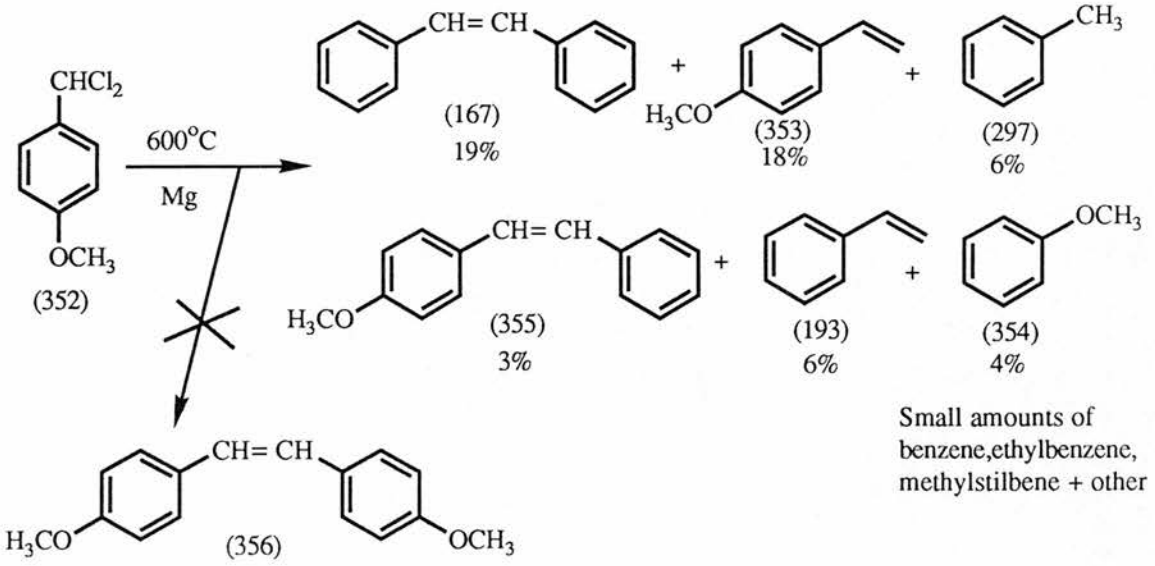


major products were 51% of 1-methylnaphthalene(**350**) and 10% of 1,2-dimethylnapthalene(**351**), with traces of naphthalene, 2-methyl-naphthalene and ethylnaphthalene.

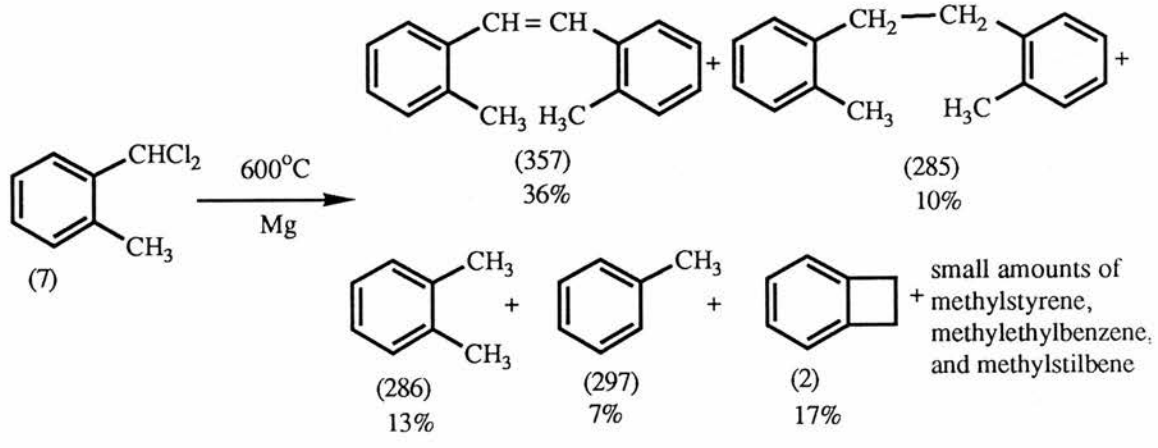
This was a rather surprising result as both (**346**) and (**343**) have been previously reported[12] to give (**347**) and (**348**) respectively on conventional pyrolysis at 700°C. Although the methoxy group is known not to be a thermally stable substituent at very high temperatures or at high temperatures with long contact time, only the methyl radical was lost with oxygen retained for aromatic OMe, at temperatures above 600°C.[259] A mechanism involving H-transfer from the methoxy group on to the adjacent carbon following magnesium-induced dechlorination and subsequent rearrangement, is proposed as the path that led to the observed products. An H-transfer process by ^{2}H labelling has been similarly reported for the 2-methoxybenzyl radical.[263]



When 4-methoxybenzylidene chloride(**352**) was pyrolysed over magnesium, there was almost complete loss of the methoxy group to give 18% unsubstituted stilbene(**167**) and *p*-methoxystilbene(**355**) in less than 5% yield. The other major products obtained were *p*-methoxystyrene (**353**), styrene(**193**), ethylbenzene(**309**), toluene(**297**) and anisole(**354**), with small amounts of benzene and a compound with m/z 194, suspected to be methylstilbene. Although the route to some of the products is unknown, most seem to have emanated from the thermal fragmentation of the expected product, 4,4'-dimethoxystilbene(**356**).

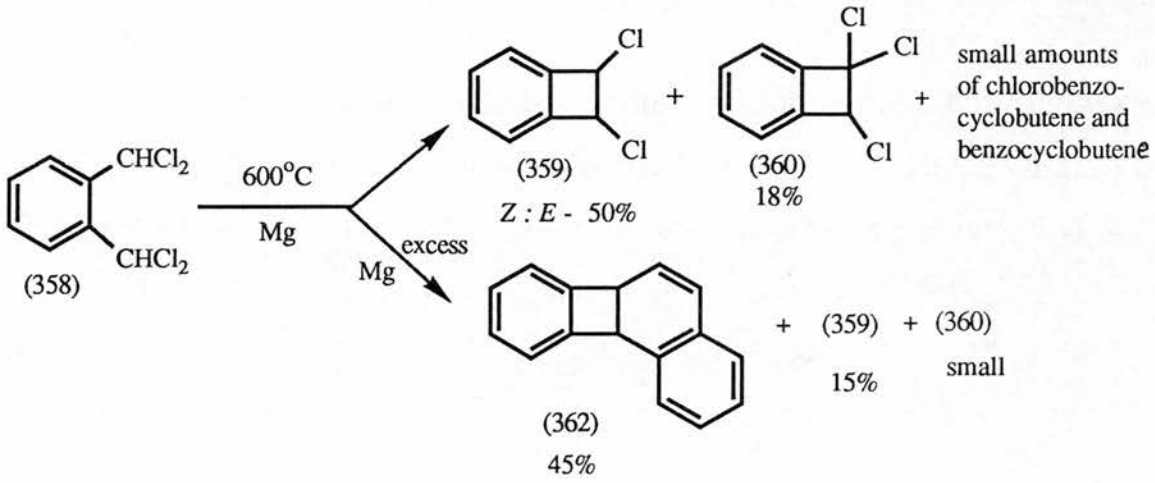


As stated earlier, conventional pyrolysis of 2-methylbenzylidene chloride(**7**) at 700°C, has been reported[12] to give chlorobenzocyclobutene(**9**). However, when (**7**) was pyrolysed over magnesium, the major product obtained was 2,2'-dimethylstilbene(**357**), with 2,2'-dimethylbibenzyl(**285**). In addition to (**357**) and (**285**) were obtained 17% of (**2**), 13% of (**286**) and 7% of (**297**), with small amounts of 2-methylstyrene, 2-methylethylbenzene and methylstilbene. The formation of (**2**) suggested the involvement of an H-transfer process from the methyl group to the adjacent carbon bearing the chlorines, after the magnesium-induced dechlorination. A similar process was postulated[12] to be involved in the formation of (**9**) from (**7**) and has been suggested above to account for the thermal reaction of (**346**) over magnesium.



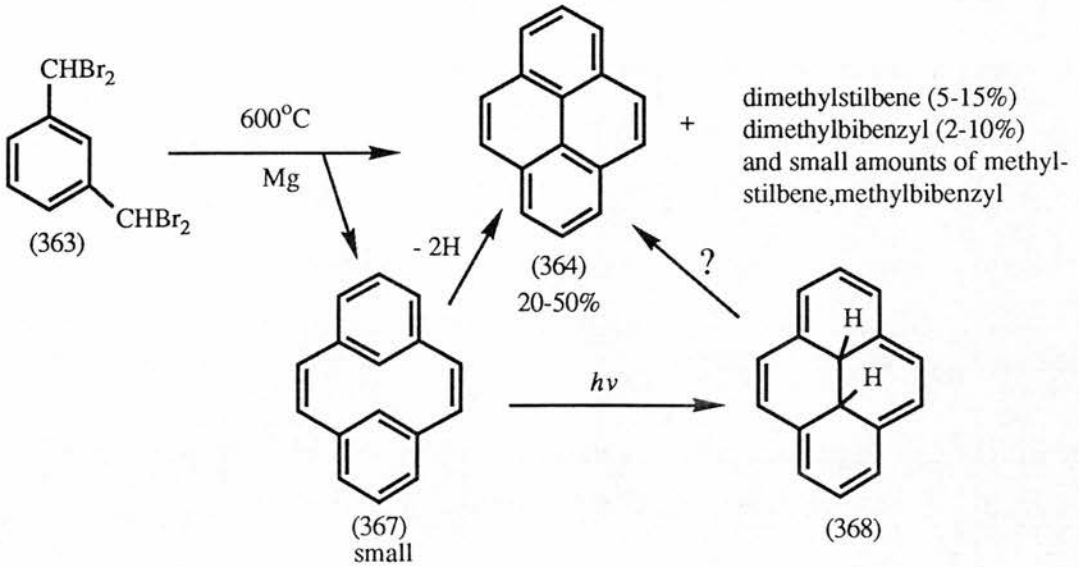
The investigation of the thermal behaviour of halobenzylidene chlorides over magnesium, led to some interesting developments, which will be discussed in the next section. In line with the series of substrates under investigation, the thermal reaction of α,α,α',α'-tetrachloro-*o*-xylene(**358**) and α,α,α',α'-tetrabromo-*m*-xylene(**363**) over magnesium was studied. When (**358**) was pyrolysed over magnesium, the major products were *Z*-and *E*-7,8-dichlorobicyclo[4.2.0]octa-1,3,5-triene(**359**) and 7,7,8-trichlorobicyclo[4.2.0]octa-1,3,5-triene(**360**), with small

amounts of 7-chlorobicyclo[4.2.0]octa-1,3,5-triene(**361**) and



benzocyclobutene(**2**). However, when the pyrolysis was repeated with a large magnesium:substrate ratio, in order to effect complete dechlorination, the major products obtained were 45% of the benzocyclobutadiene dimer(**362**) and 15% of (**359**). The product (**362**) has been previously reported[73] from α,α,α',α'-tetrabromo-*o*-xylene(**91**) on pyrolysis over magnesium.

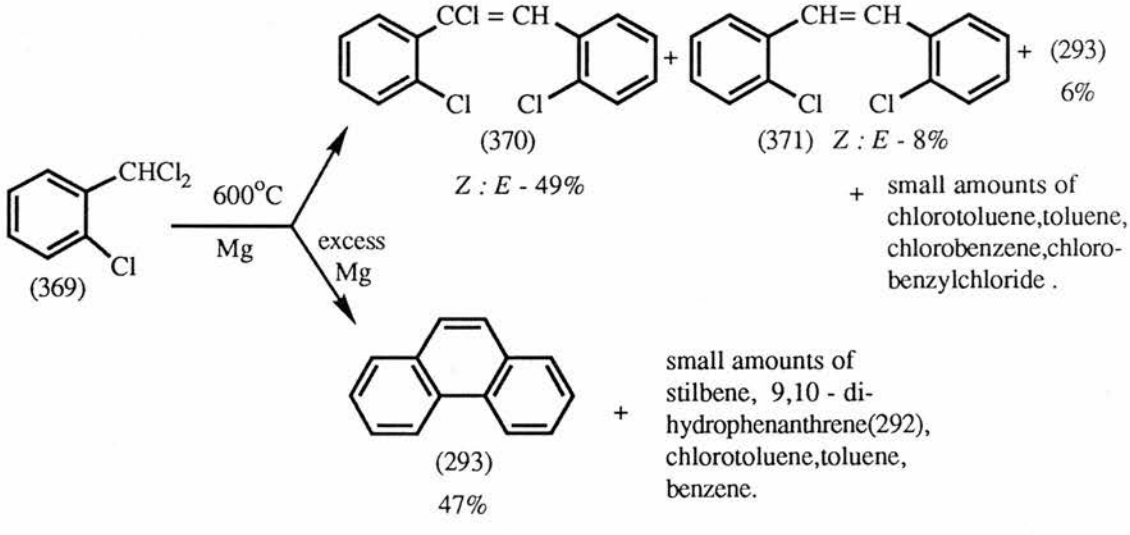
The pyrolysis of (**363**) over magnesium gave mainly pyrene(**364**) in about 22% yield. The other products obtained in small amounts were *Z*-and *E*-3,3'dimethylstilbene(**365**), 3,3'-dimethylbibenzyl(**366**), methylbibenzyl, methylstilbene and [2.2] *m*-cyclophane(**367**). The



formation of (**364**) was believed to go *via* (**367**), followed by bond isomerisation to (**368**) and loss of two hydrogen atoms. Such bond isomerisation has been reported[264] on photolysis of (**367**).

3. The thermal reaction of halobenzylidene chlorides over magnesium

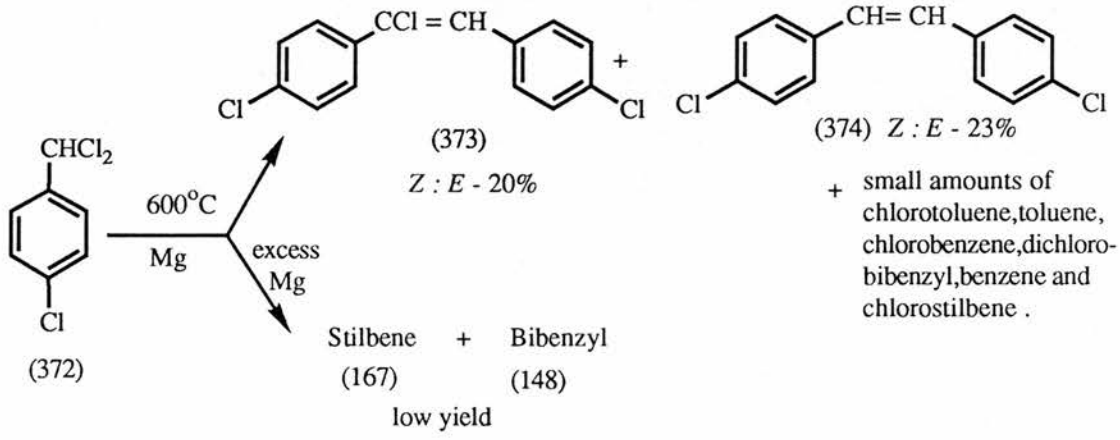
As mentioned in the previous section, the basic thermal reaction of benzylidene chlorides over magnesium, was reductive homocoupling to stilbenes. When 2-chlorobenzylidene chloride(**369**) was pyrolysed the major products obtained were 50% of *Z*-and *E*-α,2,2'-trichlorostilbene (**370**), 8% of *Z*-and *E*-2,2'-dichlorostilbene(**371**) and 6% of phenanthrene(**293**). Also obtained were small amounts of chlorotoluene, chlorobenzene, toluene and chlorobenzyl chloride. As the products



obtained still contained chlorines, especially at the α-position of the main product, a large excess of magnesium was used for a repeat pyrolysis of (**369**). The product obtained was about 50% of phenanthrene(**293**), which is about 90% of the pyrolysate, with small amounts of stilbene (**167**), 9,10-dihydrophenanthrene(**292**), toluene(**297**), benzene(**237**) and chlorotoluene. The formation of (**293**) is similar to the earlier observed

process with (**291**) involving both side-chain and ring dehalogenation to give (**292**).

A similar result was obtained from 4-chlorobenzylidene chloride (**372**), as the product consisted of 20% of *Z*-and*E*-α,4,4'-trichlorostilbene(**373**), 23% of *Z*-and*E*-4,4'-dichlorostilbene(**374**) and

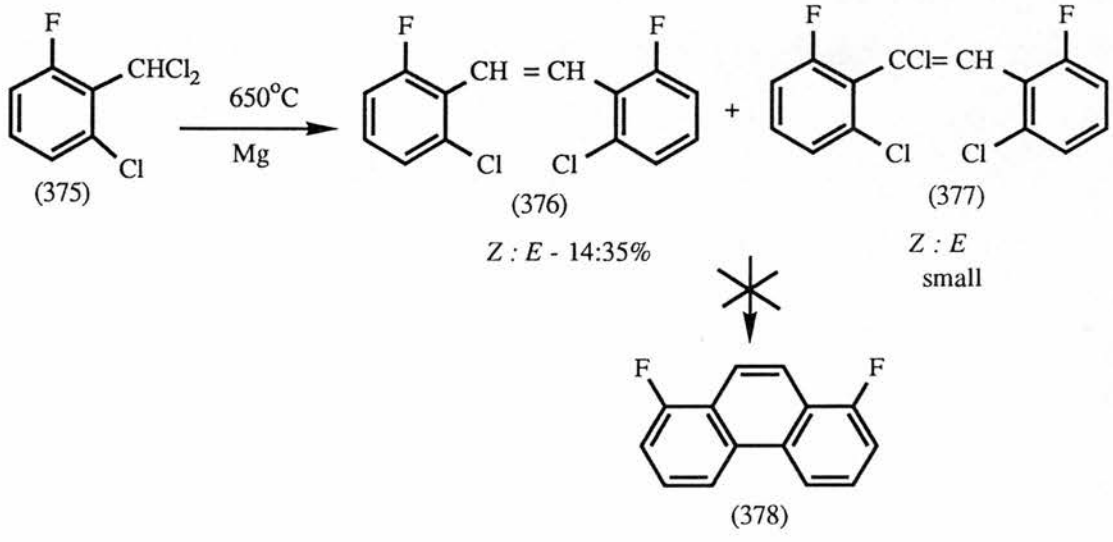


small amounts of monochlorostilbene, dichlorobibenzyl, chlorotoluene, chlorobenzene, toluene and benzene. However, when the pyrolysis of (**372**) was carried out in the presence of excess magnesium, the major products obtained in low yields were the completely dehalogenated compounds stilbene(**167**) and bibenzyl(**148**).

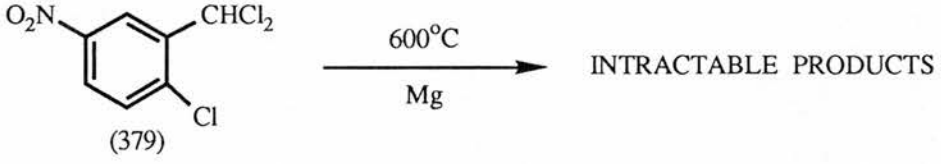
The potential of the observed conversion of (**369**) to phenanthrene (**293**) was recognised, as substituted 2-chlorobenzylidene chlorides might be expected to give symmetrically disubstituted phenanthrenes. The literature methods[265] to these type of compounds is not trivial. Four substrates 2-fluoro-6-chlorobenzylidene chloride(**375**), 2-chloro-5-nitro-benzylidene chloride(**379**), 6-chloro-3,4-methylenedioxybenzylidene chloride(**380**) and 2-bromo-3,4-dimethylbenzylidene chloride(**342**) were prepared for investigation.

Pyrolysis of (**375**) over magnesium gave *Z*-and*E*-2,2'-dichloro-6,6'-difluorostilbene(**376**), and *Z*-and*E*-6,6'-difluoro-α,2,2'-trichloro-stilbene(**377**). Repeat pyrolysis of (**375**) with a large excess of

magnesium failed to give the expected 1,8-difluorophenanthrene(**378**), instead the pyrolysate consisted mainly of (**376**) and the higher temperature of 700°C, led to partial fragmentation of (**375**). Preparative TLC of the pyrolysate gave the pure hitherto unknown 2,2'-dichloro-6,6'-difluorostilbene(**376**).

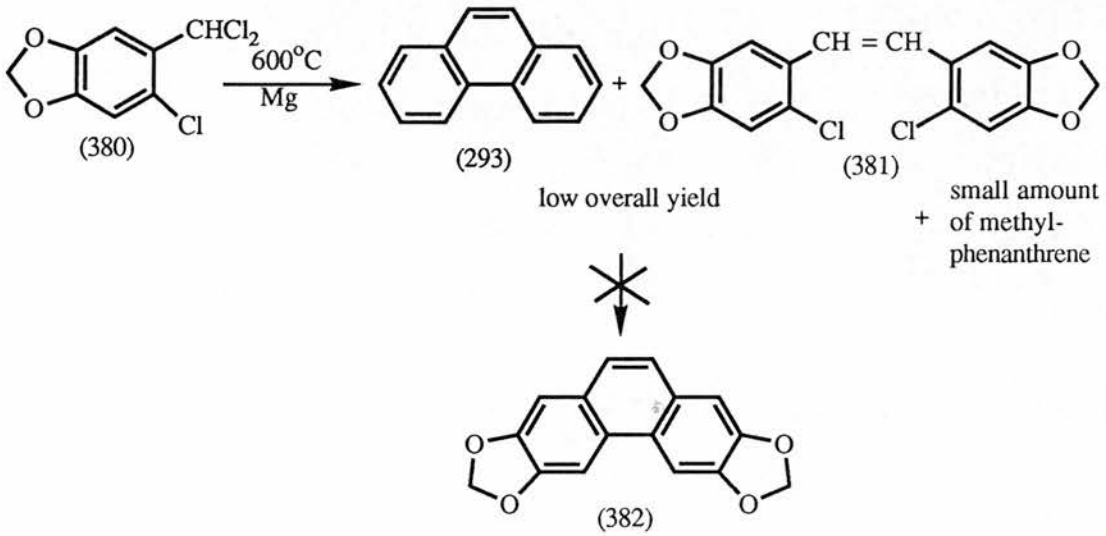


The pyrolysis of (**379**) over magnesium led to intractable products and TLC of the pyrolysate did not give any identifiable compound. This was not surprising as the nitro group is known[266] not to be a thermally stable substituent and the various reactive species it could generate might be responsible for the thermal decomposition of (**379**).

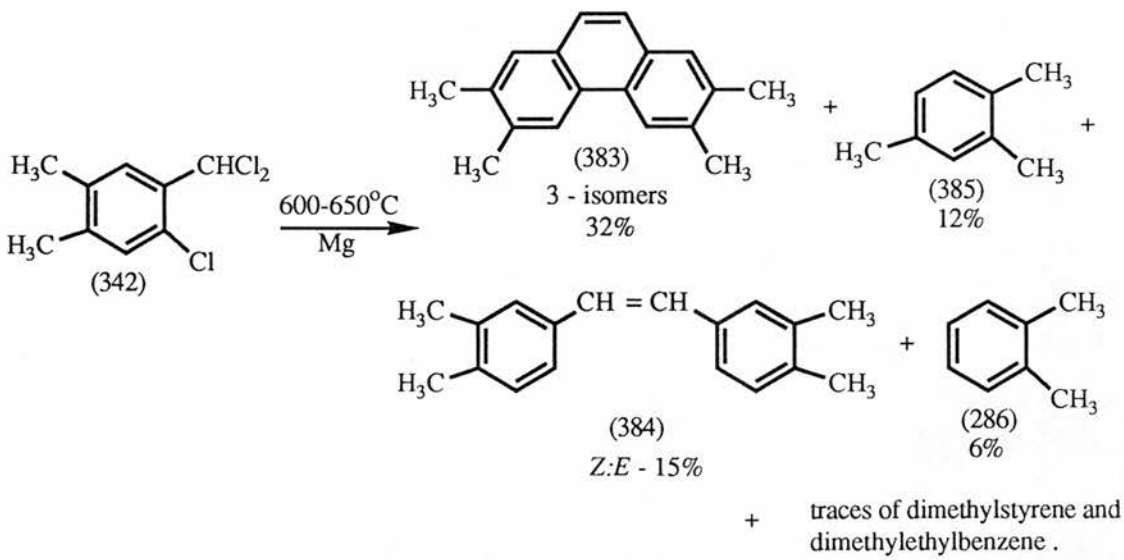


When (**380**) was pyrolysed over magnesium, the major products were unsubstituted phenanthrene(**293**) and 1,2-bis(6-chloro-3,4-methylenedioxyphenyl)ethene(**381**), with small amounts of stilbene and a

compound with m/z 192, suspected to be methylphenanthrene. Repeat pyrolysis of (**380**) with excess magnesium and at a higher temperature of 700 °C, gave mainly (**293**), with small amounts of two compounds with m/z 192, suspected to be methylphenanthrene and methylanthracene, but not the expected phenanthro[2,3-d:6,7-d']bis[1,3]dioxole(**382**).



Pyrolysis of (**342**) over magnesium gave a mixture of various halogenated compounds; however with excess magnesium the product was mainly three compounds with the same molecular mass as the expected 2,3,6,7-tetramethylphenanthrene(**383**) in a combined yield of

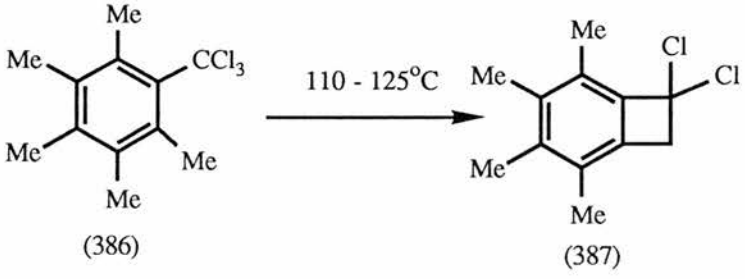


about 32%. The other products obtained were *Z*-and*E*-tetramethyl-stilbene(**384**), 1,2,4-trimethylbenzene(**385**), *o*-xylene (**286**) and trace amounts of dimethylstyrene and dimethylethylbenzene. Clear identification of the compounds was impossible and assignment was mainly based on the molecular mass obtained from the GC-MS.

Although the conversion of (**369**) to phenanthrene(**293**), seemed initially a viable synthetic route to disubstituted phenanthrenes, however the results showed that the presence of substituents on the substrate (**369**) either complicated the reaction as for (**379**) or led to isomeric products as for (**342**). The likely route to the isomeric products will be discussed later with respect to thiophenes(section I).

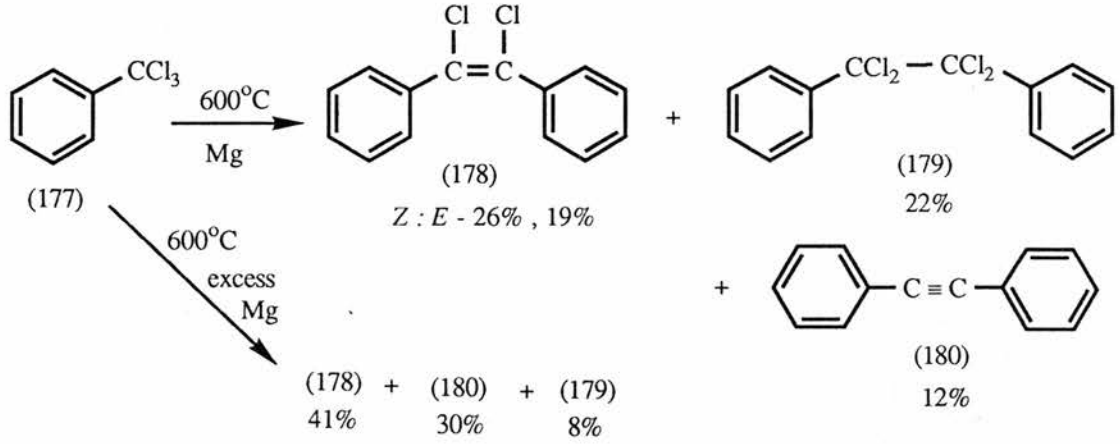
E. Flash Vacuum Pyrolysis of Benzotrihalides over Magnesium

The gas phase reaction of benzotrihalides has hardly received any attention. However, Hart[267] observed that trichloromethyl-pentamethylbenzene(**386**) lost hydrogen chloride on melting at 110-125°C to give the benzocyclobutane derivative(**387**). With the rather interesting results obtained on pyrolysis of benzylic and benzylidene halides over magnesium, an investigation of the reaction of the benzotrihalides would complete the study of these series of compounds.



(386) (387)

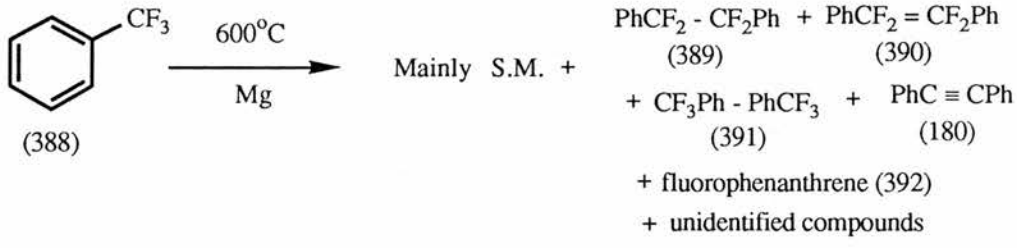
When benzotrichloride(**177**) was pyrolysed over magnesium at 600°C, the product obtained consisted of 42% *Z*-and*E*-α,α'-dichlorostilbene(**178**), 22% of α,α,α',α'-tetrachlorobibenzyl(**179**) and 12% of diphenylacetylene(**180**). However, at longer contact time



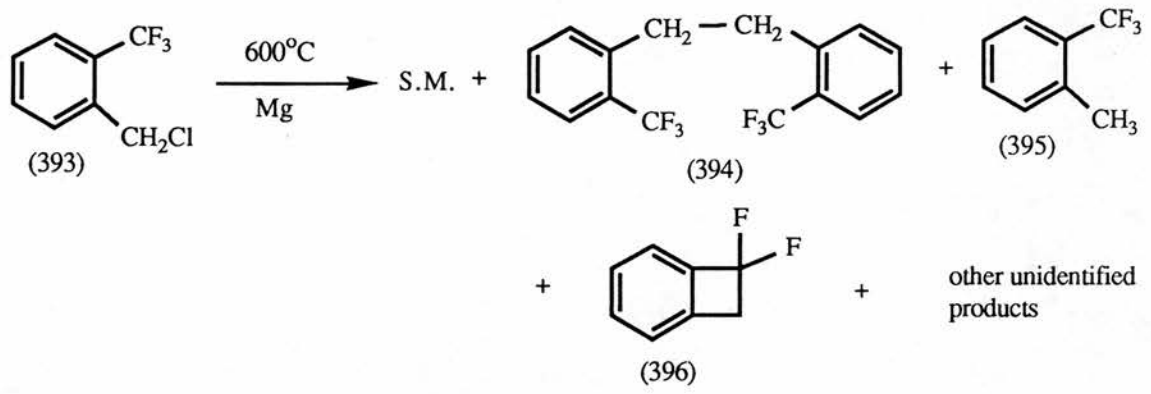
(achieved at a pressure of 1mmHg) the product consisted of 41% of (**178**) and 30% of (**180**), with only 8% of (**179**). This result suggested that

compound (**179**) was an intermediate in the reaction leading to (**178**) and (**180**). The isolation of (**179**) confirmed the step-by-step mechanism proposed earlier for the reductive homocoupling of benzylic and benzylidene halides when pyrolysed over magnesium.

The pyrolysis of benzotrifluoride(**388**) over magnesium failed to give clear cut products, rather a large amount of starting material was recovered. This was assumed to be largely due to the high volatility of (**388**) which resulted in a short contact time and the weak reactivity of fluorine toward the magnesium, which was noted in earlier cases. Some of the compounds observed on the GC-MS of the pyrolysate were α,α,α',α'-tetrafluorobibenzyl(**389**), α,α'-difluorostilbene(**390**), bis(trifluoromethyl)biphenyl(**391**), diphenylacetylene(**180**) and fluorophenanthrene ? (**392**), as well as other unidentified compounds. The yield of products was extremely low, based on the amount of (**388**) recovered.



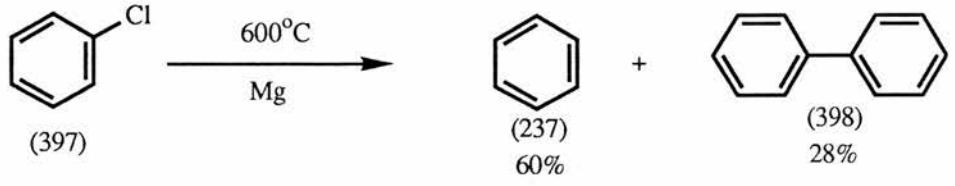
Pyrolysis of 2-trifluoromethylbenzyl chloride(**393**) over magnesium gave a product which consisted of a complex mixture of fluorinated compounds and the starting material. Some of the compounds identified based on their molecular mass, are bis(trifluoromethyl)bibenzyl (**394**), *o*-trifluoromethyltoluene(**395**) and difluorobenzocyclobutane (**396**).



The thermal reaction over magnesium of 4-trifluoromethylbenzyl bromide and other benzotrihalides investigated will be discussed in the section on polymers(section G).

F. Flash Vacuum Pyrolysis of Mono- and Di-Halobenzenes over Magnesium

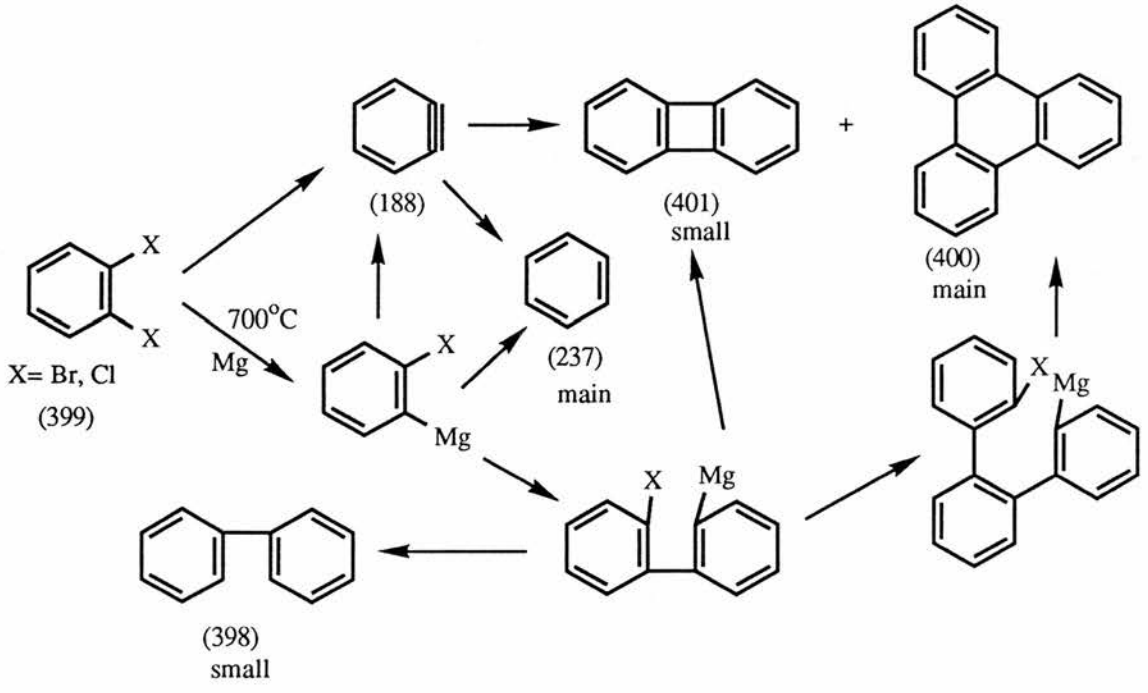
As a result of the aryl ring dehalogenation observed during the pyrolysis over magnesium of some substrates already studied, the thermal reaction of some halobenzenes was investigated. When chlorobenzene (**397**) was passed over magnesium at 600°C, the products isolated were 60% of benzene(**237**) and 28% of biphenyl(**398**). The formation of (**398**) is similar to that observed in solution with metals such as magnesium,[148] nickel[90] and copper[147] where aryl metal complex was postulated as the intermediate involved in the formation of the biaryls. In the gas phase, a similar magnesium-bound phenyl species was envisaged, which preferentially abstracts hydrogen to give (**237**) or couple to give (**398**), a statistically less favoured process. The source of the hydrogen is unknown but suspected to be from any of the starting material, products or decomposed species.



(397) → (237) 60% + (398) 28%

The dehalogenation of 1,2-dihalobenzenes in solution has been used extensively in the chemical literature, for the generation of the reactive intermediate benzyne (**188**). Some of the reagents that have been employed are copper in DMF[147], magnesium in THF[152], butyl lithium in THF[150] and sodium amalgam.[151] Thermal decomposition of 2-halobenzoic acid salts[268] and photochemical deiodination of 1,2-diiodobenzene,[153] has also been used for the generation of (**188**). The generation of (**188**) from 1,2-halobenzenes(**399**) in the gas phase over magnesium was therefore of interest.

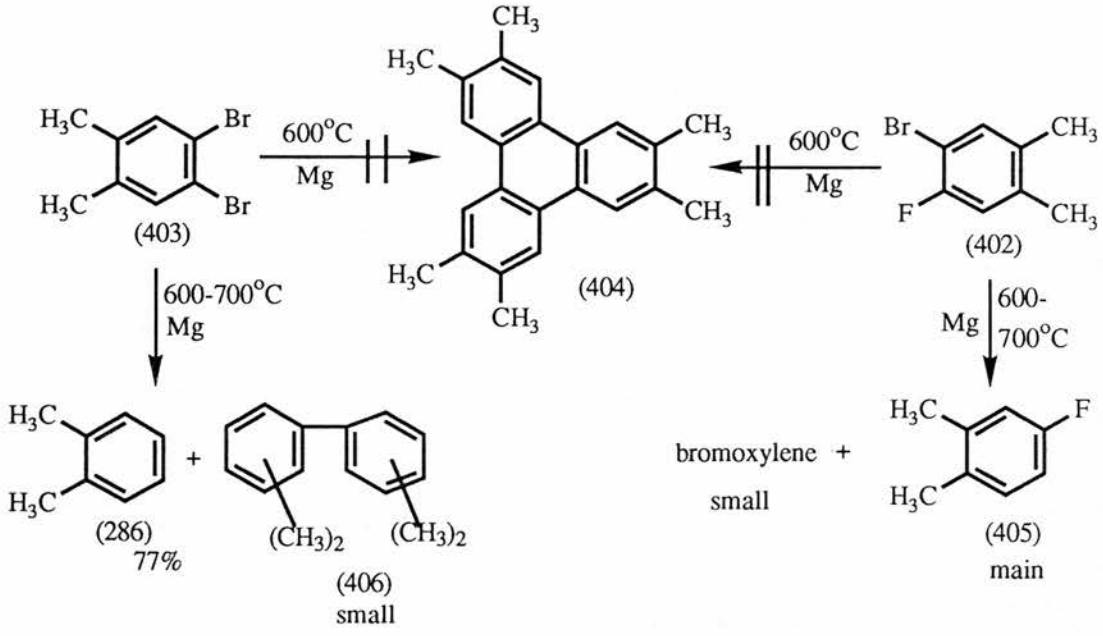
When 1,2-dichlorobenzene, 1,2-dibromobenzene or 1-bromo-2-chlorobenzene was pyrolysed over magnesium at 600°C, the pyrolysate consisted mainly of the starting material. However at 700°C, the liquid fraction of the product consisted mainly of benzene(**237**), with small amounts of mono-halobenzenes. The solid fraction obtained in about 10-20% yield, usually consisted mainly of triphenylene(**400**), with small amounts of biphenyl(**398**) and biphenylene(**401**). In general, bromine is more readily removed than chlorine and the best yield of the coupled products was obtained from 1,2-dibromobenzene.



Compounds (**400**) and (**401**) are the normal products of the benzyne(**188**) intermediate, however the formation of (**398**) in this investigation suggested a step-by-step dehalogenative coupling, akin to the postulated mechanism for the formation of (**400**) and (**401**) from 1,2-dihalobenzenes using lithium amalgam[151] in solution. Although the involvement of (**188**) cannot be entirely ruled out, the stepwise Wurtz-type coupling process on the magnesium surface is preferred as the

route to (**398**), (**400**) and (**401**) and this may account for the low yields observed as the probability of the coupling is statistically low in the gas phase.

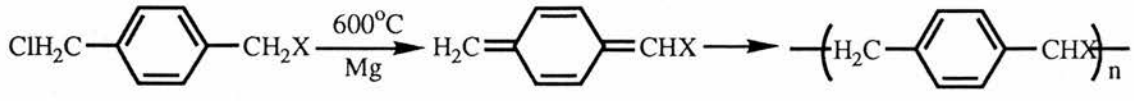
Despite the low yields of the coupled products on dehalogenation of 1,2-dihalobenzenes over magnesium, the solid product consisted mainly of triphenylene(**400**). An attempt to extend this to the preparation of hexamethyltriphenylene(**404**) from either 4-bromo-5-fluoro-*o*-xylene (**402**)[211] or 4,5-dibromo-*o*-xylene(**403**)[206] was unsuccessful, even though dehalogenation did occur on pyrolysis over magnesium. The problem seems to be that the extra methyl groups can act as a source of hydrogen for the benzyne intermediate. The main product from the dibromo compound(**403**) was *o*-xylene(**286**) and for the bromofluoro compound (**402**) most of the fluorine stays attached to the ring to give 4-fluoro-*o*-xylene(**405**). The only coupled product obtained in very low yield from (**403**) was tetramethylbiphenyl(**406**).



G. Polymerisation of α-Halogenated-*p*-Xylenes in the Gas Phase over Magnesium

The first poly-*p*-xylylenes were prepared[269] about a century ago. Since Szwarc's[270] discovery of the formation of *p* -xylylene(**160**) by the pyrolysis of *p*-xylene at 1000°C and 4mmHg, the chemistry of *p*-xylylenes has been more thoroughly investigated and was reviewed[272] in 1958. Gilch and Wheelwright[272] reported the preparation of various *p*-xylylene polymers by treating α-halo-*p*-xylenes with bases in solution. The reaction involved a 1,6-dehydrohalogenation to give xylylene which then polymerises and they found that the more halogens in the α-positions (up to five), the weaker the base necessary for dehalogenation. However, as far as is known, no investigation of the reaction of α-halo-*p*-xylenes in the gas phase has been reported.

As stated earlier in this report, when α-chloro-*p*-xylene(**410**) was pyrolysed over magnesium at 600°C, the product obtained was 4,4'-dimethylbibenzyl(**279**,R=CH_3). However, when α,α'-dichloro-*p*-xylene(**407**) was pyrolysed over magnesium, a white polymer deposit, which was insoluble in common solvents, was obtained in the cold trap. Micro analysis of the material was consistent with poly(*p*-xylylene) (**408**) and this was confirmed with the solid state ^{13}C NMR (Figure 1a). Using the solid state NMR, the end group analysis of terminal CH_3 gave an estimated number monomer units of 21, corresponding to a molecular mass of 2184. The material exhibited remarkable heat stability and showed no weight loss at a temperature up to 450°C in N_2 (Figure 1b) and 300°C in air(Figure 1c).



X = Cl (407) X = H (160) X = Cl (410) X = H (408) 61% X = Cl (409) 72%

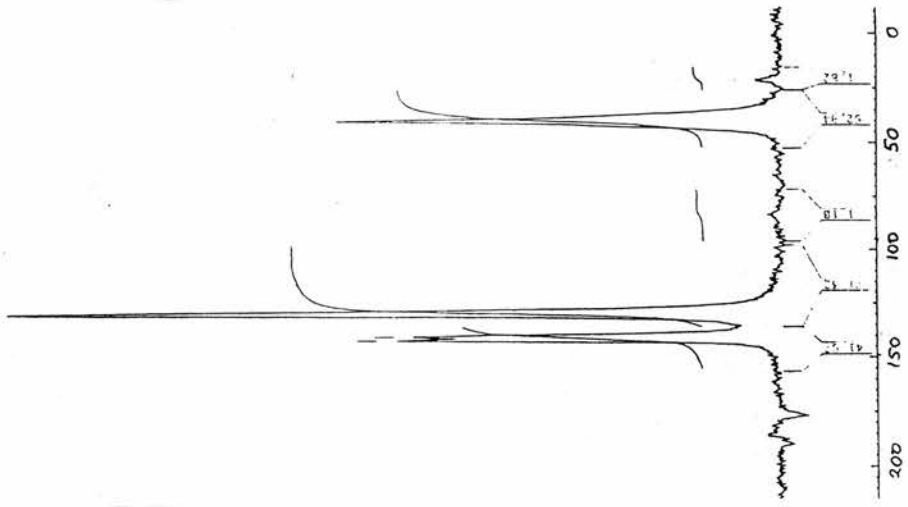


Figure 1a Solid state MAS ^{13}C NMR of polymer (**408**)

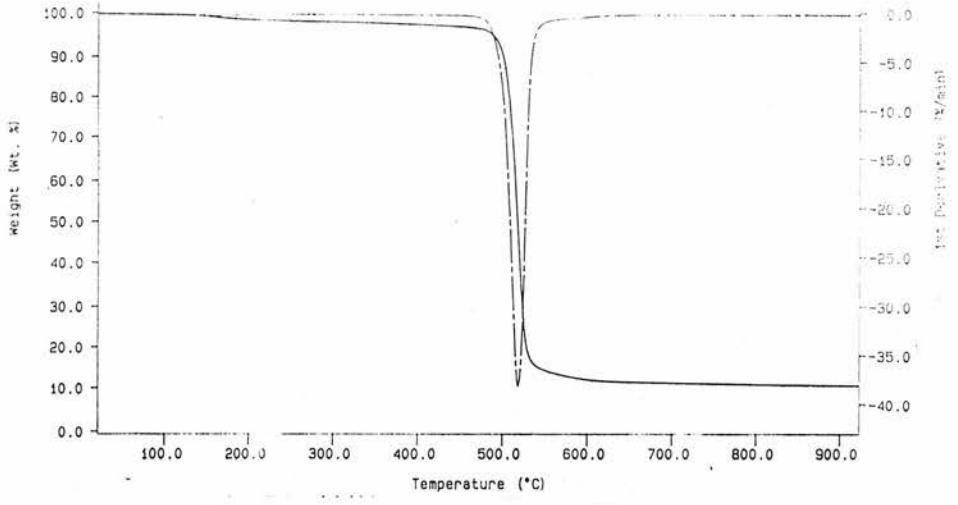


Figure 1b Thermogravimetric analysis of polymer (**408**) in N_2

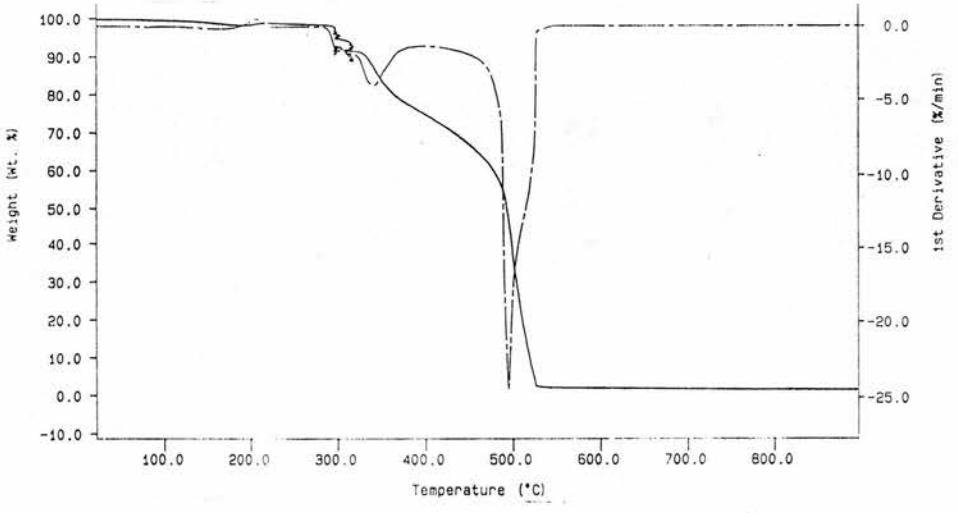
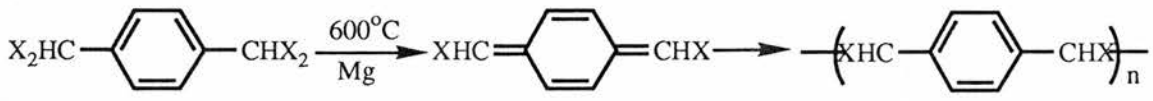


Figure 1c Thermogravimetric analysis of polymer (**408**) in air

However, when (**407**) was pyrolysed over small amount of magnesium, a bright yellow polymer was obtained. The microanalysis was in agreement with the poly(α-chloro-*p*-xylylene) (**409**). Thermal analysis on the material showed similar stability to (**408**) although degradation starts at a lower temperature of 360°C in N_2 atmosphere. At the degration point, a sharp isotherm was obtained under N_2 while a gradual degradation from 300°C to 600°C was observed in air.

The formation of (**408**) involved a 1,6-dechlorination to give *p*-xylylene(**160**), in the presence of large excess of magnesium, while a 1,6-dehydrochlorination process was involved in the formation of (**409**) via the α-chloro-*p*-xylylene(**410**), in the absence of a sufficient amount of magnesium.

As an extension of the study, α,α,α',α'-tetrachloro-*p*-xylene(**334**) and α,α,α',α'-tetrabromo-*p*-xylene(**345**) were prepared from terephthalaldehyde by treatment with phosphorus pentachloride and thionyl bromide respectively. On pyrolysis over magnesium, compound (**344**) gave a polymer material, whose microanalysis and solid state ^{13}C NMR - d_C 66.7(CHCl), 128.3(4 aromatic C) and 140.1(2 quaternary aromatic C) were consistent with poly(α,α'-dichloro-*p*-xylylene) (**411**). The material showed a sharp isotherm at a temperature as low as 40°C in both air and N_2 and this may be due to incorporated monomer units or the loss of hydrogen chloride, although the thermal behaviour of (**412**) does not support the latter assumption. The material finally decomposed at above 400°C.



X = Cl (344)
X = Br (345)

X = Cl (411) 77%
X = Br (412) 25%

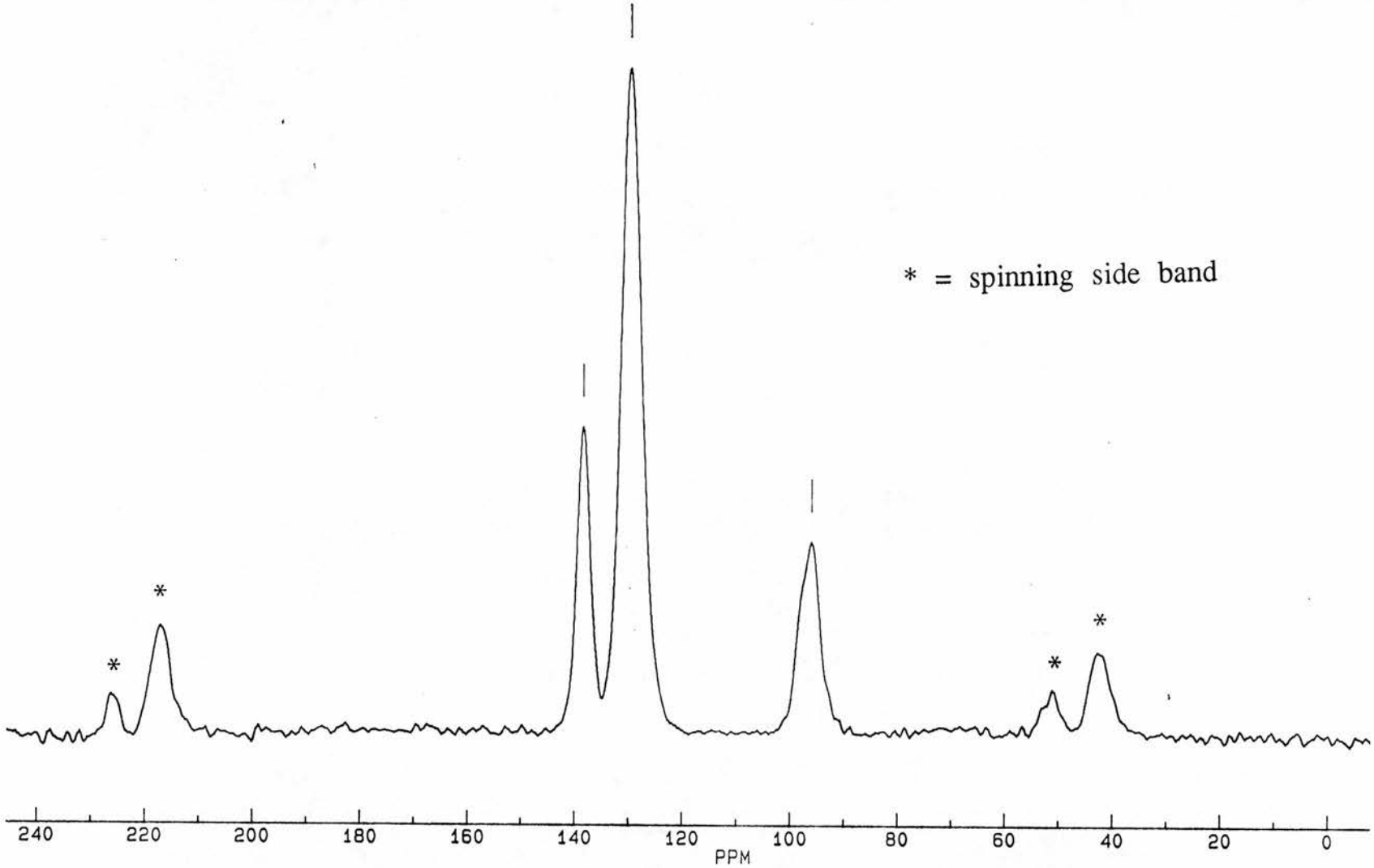
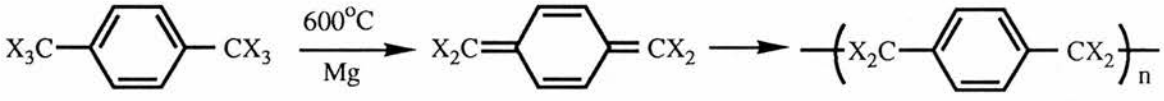


Figure 2 Solid state MAS ^{13}C NMR of polymer (**414**)

Similarly, the pyrolysis of compound (**345**) gave the poly(α,α'-dibromo-*p*-xylylene) (**412**), confirmed by microanalysis and solid state ^{13}C NMR - d_C 62.3(CHBr), 128.9(4 aromatic C) and 139.9 (2 quatenary aromatic C). The polymer material was obtained in a relatively lower yield due to poor volatility of the substrate(**345**), as some of it decomposed in the inlet tube. Compound (**412**) showed no weight loss up to a temperature of 200°C in both air and N_2, during thermal analysis, after which it gradually decomposed over a temperature range of 300-500°C.

When α,α,α,α',α',α'-hexachloro-*p*-xylene(**413**) was passed over magnesium, the poly(α,α,α',α'-tetrachloro-*p*-xylylene) (**414**) was obtained. The microanalysis and solid state ^{13}C NMR (Figure 2) were consistent with (**414**) and the $CHCl_2$ NMR end group analysis indicated 10 monomer units, corresponding to a molecular mass of 2420. The polymer material (**414**) was stable up to between 250-300°C, in both N_2 and air, after which a gradual weight loss was observed until between 550-650°C, when it decomposed. Similarly prepared was poly(α,α,α',α'-tetrafluoro-*p*-xylylene) (**416**) from α,α,α,α',α',a'-hexafluoro-*p*-xylene



X = Cl (413)
X = F (415)

X = Cl (414) 94%
X = F (416) 33%

(**415**), although the yield was quite low. This was attributed to the high volatility of (**415**) which led to a short contact time and low reactivity of fluorine towards magnesium. The solid state ^{13}C NMR was not obtained because the material was electrostatic and was difficult to obtain in a state suitable for measurement and only a broad peak was obtained on the

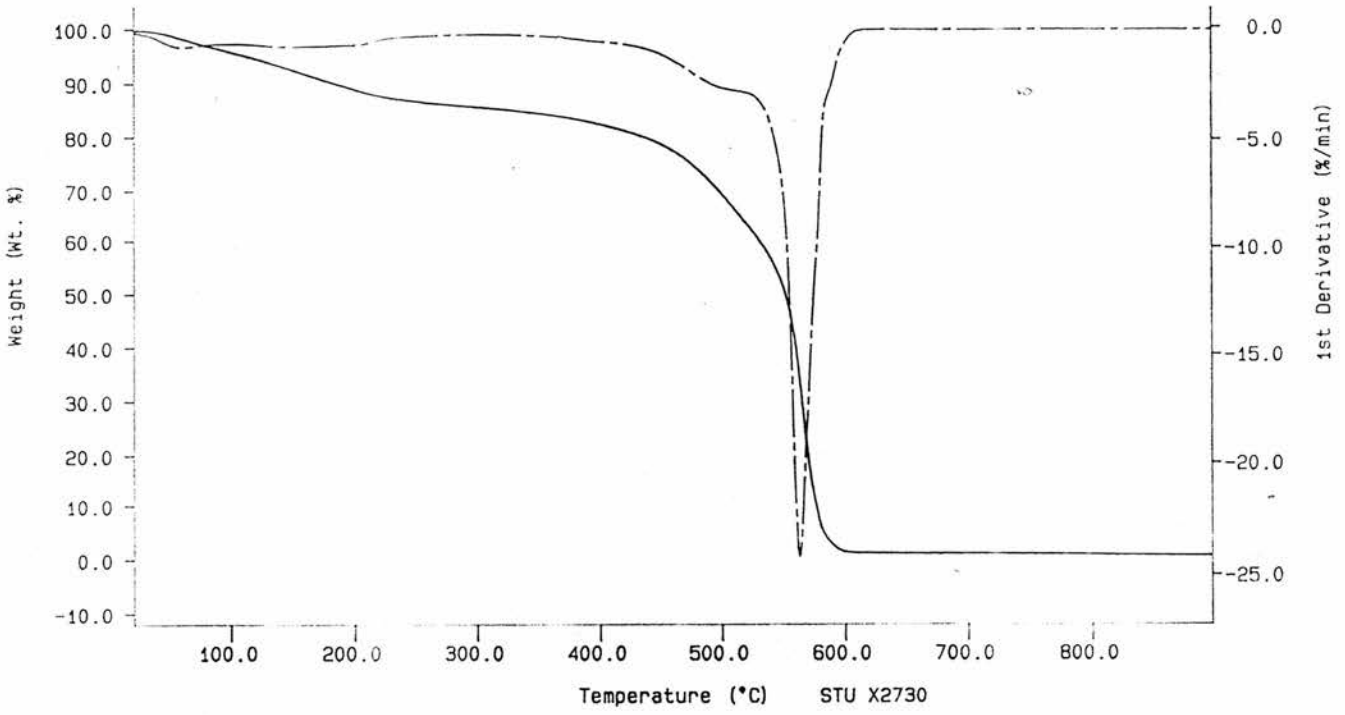


Figure 3a Thermogravimetric analysis of polymer (**416**) in N_2

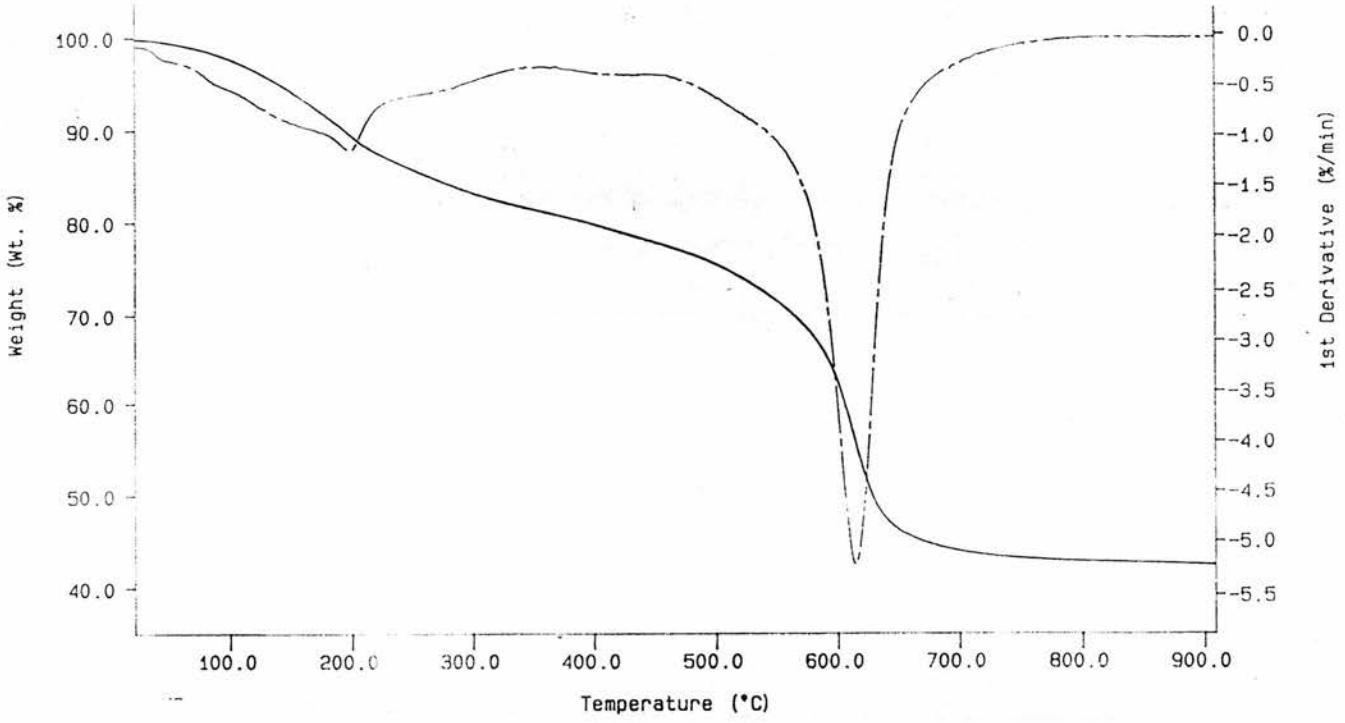
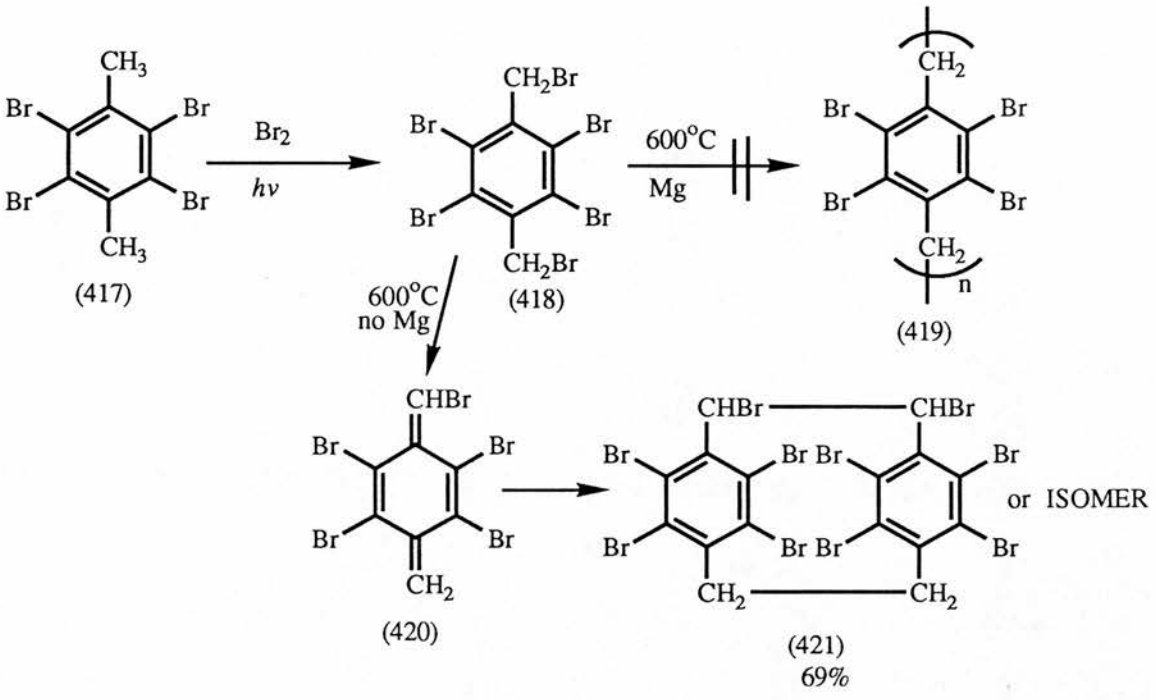


Figure 3b Thermogravimetric analysis of polymer (**416**) in air

spectrum, although this may also be due to F-C coupling. Thermogravimetric analysis of (**416**) showed a gradual weight loss from 100°C but it only decomposed at about 600°C in both N_2(Figure 3a) and air(Figure 3b). This may be due to incorporation of oligomers in the polymeric material.

The bromine content of organic fire retardants incorporated into polymers and other materials is very crucial. The bromine was postulated to act in conjunction with antimony oxide, the synergistic used for most fire retardants, and therefore the effectiveness of a brominated flame retardant is proportional to the percent bromine in the material[273]. Thus extending this method of polymer formation, *via* the *p*-xylylene generated on thermal dehalogenation over magnesium, to ring brominated aryl substrates might be expected to give a polymer with incorporated fire retardancy.

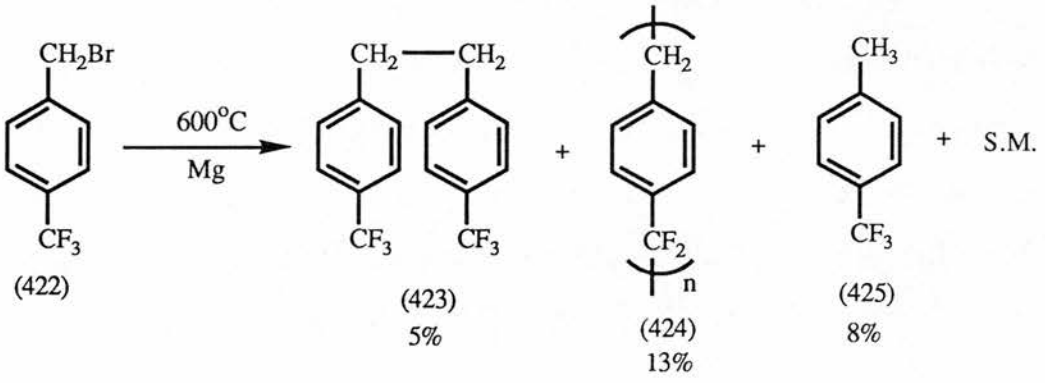
α,α',2,3,5,6,-Hexabromo-*p*-xylene(**418**) was therefore prepared: Photochemical bromination, with molecular bromine, of 2,3,5,6-tetrabromo-*p*-xylene(**417**) gave an almost quantitative yield of



(**418**). However, when (**418**) was pyrolysed over magnesium, most of the material decomposed both in the furnace and inlet tube, as a high temperature was required to sublime the involatile (**418**). The decomposition in the furnace may be due to attack of the magnesium on the ring halogens leading to fragmentable species. So only small amounts of a polymer material and unchanged starting material were obtained in the inlet tube. The microanalysis of the polymer material was different from that expected for poly(2,3,5,6-tetrabromo-*p*-xylylene) (**419**) and its actual nature is unknown. When (**418**) was pyrolysed at 600°C without magnesium, a white solid was obtained. The microanalysis was consistent with pentabromo-*p*-xylylene(**420**) and as the material was not a polymer, it was suspected to be the cyclophane(**421**) formed by thermal 1,6-dehydrobromination and dimerisation.

Attempts to prepare 4,4'-bis(trifluoromethyl)bibenzyl(**423**) by the pyrolysis over magnesium of 4-trifluoromethylbenzyl bromide(**422**) gave not only the expected (**423**) but also a polymer material. The microanalysis of the polymer was as expected for α,α-difluoro-*p*-xylylene (**424**) a product of 1,6-debromofluorination. Although the solid state ^{13}C NMR peaks were broad, it was in agreement with those expected for poly(α,α,-difluoro-*p*-xylylene) (**424**) - d_C 37 (CH_2), 79(CF_2), 120 (4 aromatic carbons) and 161 (2 aromatic quartenary carbons). The end group analysis showed only 7 monomer units corresponding to a molecular mass of 990. On thermogravimetric analysis the material showed a gradual weight loss from 100°C and decomposed at about 500°C in both N_2 and air. The yield of the polymer was only 13% and that of (**423**) was about 5%. In addition to these products were 8% of

4-trifluoromethyltoluene(**425**) and a large amount of unchanged starting



(422)

(423) 5%

(424) 13%

(425) 8%

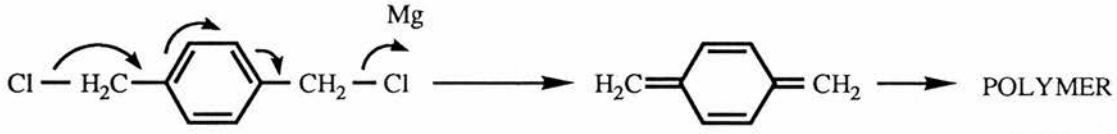
material. This tends to suggest that the substrate's reactivity over magnesium was reduced by the trifluoromethyl group.

For all the α-halogenated-*p*-xylenes studied over magnesium in the gas phase, the basic reaction was 1,6-dehalogenation to give the *p*-xylylene which then polymerised. The yields were from moderate to high except for (**412**) in which the substrate was difficult to volatilise and for (**416**) in which adequate contact time was difficult to achieve due to substrate high volatility coupled with low reactivity of fluorine. Some of the polymer materials exhibited remarkable heat stability and the fact that they are deposited straight from the gas phase could be used for uniform thin film deposition of insulating polymers.

The polymers (**408**), (**409**) and (**414**) had been previously prepared[273] from α-halogenated-*p*-xylenes by base induced 1,6-dehydrohalogenation in solution. The polymers that were prepared in the gas phase showed similar properties to those obtained in solution, although the number of monomer units obtained in the gas phase polymers were more than those reported in solution. The mechanism for the base induced polymerisation was postulated[272] to involve the formation of anions, by base abstraction of a proton from the side-chain carbon. This was followed by the elimination of a chloride ion from the

6-position, to form the relatively stable *p*-xylylenes which in turn polymerised.

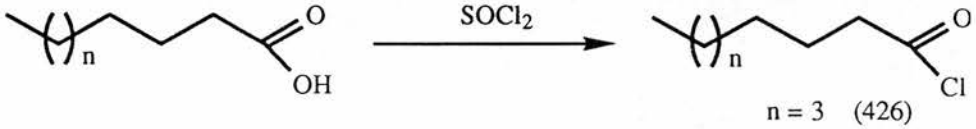
In the gas phase the reaction presumably involves a magnesium induced dehalogenation, followed by bond isomerisation with the elimination of the second halogen, which may be spontaneous or also magnesium induced. The proposed reaction path is exemplified with the substrate (**407**).



(407) (160) (408)

H. Preparation and Flash Vacuum Pyrolysis of Long Chain Acid Chlorides over Magnesium

The acid chlorides used for this investigation were prepared[226] by treating the corresponding carboxylic acid with thionyl chloride. Thus the following acid chlorides were prepared:- octanoyl chloride(**426**), decanoyl chloride(**427**), lauroyl chloride(**428**), myristoyl chloride(**429**) and palmitoyl chloride(**430**). The yields were from moderate to good.



n = 3 (426)
n = 5 (427)
n = 7 (428)
n = 9 (429)
n = 11 (430)

The thermal dehydrohalogenation of acid chlorides with a β-hydrogen is well known[54] to give ketenes. However, at the temperature of 500-600°C required for the generation of the ketenes, decarbonylation and rearrangement occur[54]. It was anticipated that for the series of acid chlorides prepared, pyrolysis over magnesium would result in dehalogenation and subsequent decarbonylation, to give alkenes, one carbon less than the starting acid chloride. The overall process anticipated was to convert the readily accessible even-number long chain acid chlorides to odd-number long chain terminal alkenes, which are not readily accessible.

On pyrolysis of the acid chlorides (**426**) to (**430**) over magnesium, the expected dehalogenation and deoxygenation was observed. However, instead of the expected odd number alkenes, a mixture of odd- and even- number alkenes were obtained, with small amounts of alkanes and in some cases alkynes. Table 2 shows the acid chlorides pyrolysed, the products obtained and their yields. The route to the products is unknown,

TABLE 2

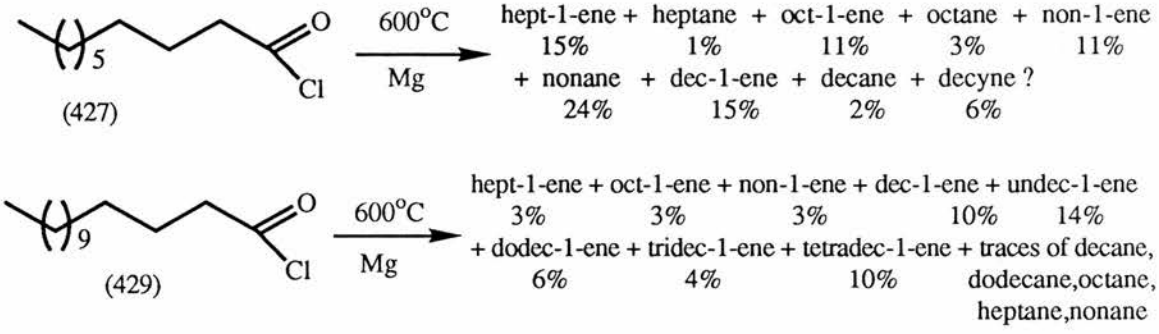
	T°C	YIELD(%) a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t	u	v	Others	Overall Yield
Octanoyl chloride $CH_3(CH_2)_6COCl$	600	37.0	tr	6.8	tr	9.0	24.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		77.0%
Decanoyl chloride $CH_3(CH_2)_8COCl$	600	-	-	14.8	0.9	10.9	3.4	10.8	24.4	15.2	1.7	-	-	-	-	-	-	-	-	-	-	-	-	Decyne? (6.1%)	89.3%
Lauroyl chloride (dodecanoyl chloride) $CH_3(CH_2)_{10}COCl$	600	-	-	-	-	13.1	tr	21.6	1.3	9.0	2.3	7.8	7.3	9.2	-	-	-	-	-	-	-	-	-	Dodecyne (12.3%)	85.0%
Myristoyl chloride	600	-	-	3.0	tr	3.0	tr	2.8	tr	10.2	0.8	14.3	0.5	6.3	1.3	4.3	16.0	10.2	0.4	-	-	-	-	-	73.1%
(tetradecanoyl chloride)	500	-	-	-	-	11.0	tr	11.1	tr	14.7	tr	13.5	tr	5.5	1.5	2.7	10.9	8.5	0.3	-	-	-	-	Tetradecyne (7.7%)	87.4%
$CH_3(CH_2)_{12}COCl$	450	-	-	6.2	1.2	7.0	0.9	7.3	0.1	9.4	1.6	9.9	2.6	8.2	6.0	7.3	16.5	2.4	1.2	-	-	-	-	-	90.0%
Palmitoyl chloride (Hexadeconyl chloride) $CH_3(CH_2)_{14}COCl$	600	-	-	2.8	-	4.2	-	6.1	-	7.6	-	8.1	0.5	8.7	0.7	9.4	1.2	4.9	2.0	3.6	8.7	3.6	0.5	Hexadecyne (6.1%)	82.7%

tr = trace

(a) Hex-1-ene, (b) Hexane, (c) Hept-1-ene, (d) Heptane, (e) Oct-1-ene, (f) Octane, (g) Non-1-ene, (h) Nonane, (i) Dec-1-ene, (j) Decane, (k) Undec-1-ene, (l) Undecane,

(m) Dodec-1-ene, (n) Dodecane, (o) Tridec-1-ene, (p) Tridecane, (q) Tetradec-1-ene, (r) Tetradecane, (s) Pentadec-1-ene, (t) Pentadecane, (u) Hexadec-1-ene, (v) Hexadecane

but a random fragmentation process was envisaged to have occurred after the initial loss of chlorine. No chlorinated or oxygenated products were observed. The deoxygenation process itself may be magnesium-induced or spontaneous after dehalogenation. The type of product mixtures obtained are exemplified below with decanoyl chloride(**427**) and myristoyl chloride(**429**).



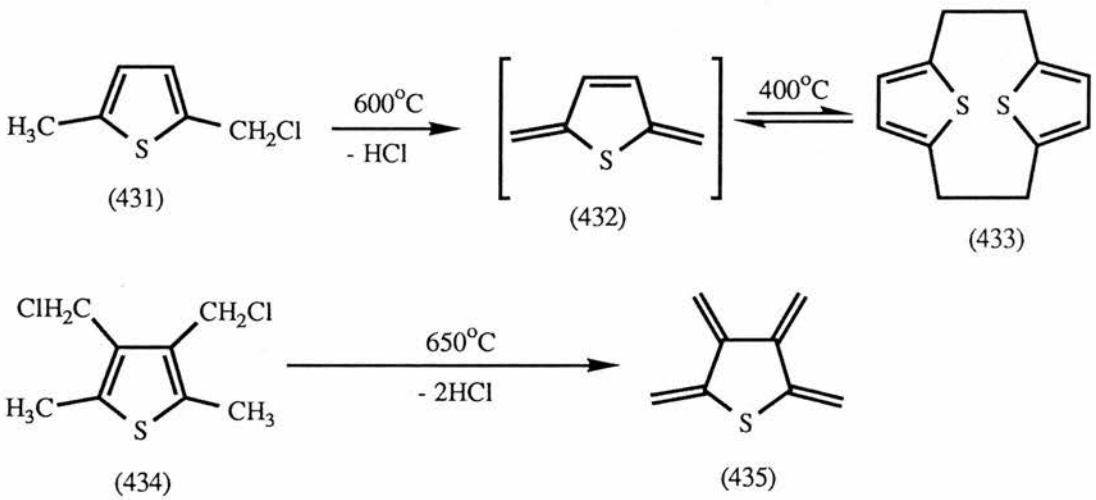
Formation of these product mixtures was initially thought to be temperature dependent and therefore a lower pyrolysis temperature might reduce the fragmentation process. However, the pyrolysis of myristoyl chloride at temperatures of 500°C and 450°C gave the same mixture of products, in about the same ratio. The possibility of the initially formed alkenes thermally fragmenting was ruled out, as the pyrolysis of tridec-1-ene over magnesium gave unchanged starting material.

For all the acid chlorides pyrolysed, the alkane and alkene products obtained are of equal or less carbon atoms than the starting material. This indicated that recombination of fragmented units to give products was unlikely. In most cases the alkenes are the major products with only small amounts of the corresponding alkanes except when the product is one carbon less than the starting material when a reversal of this pattern was observed.

I. Preparation and Flash Vacuum Pyrolysis of Halogenated Thiophenes over Magnesium

1. General background

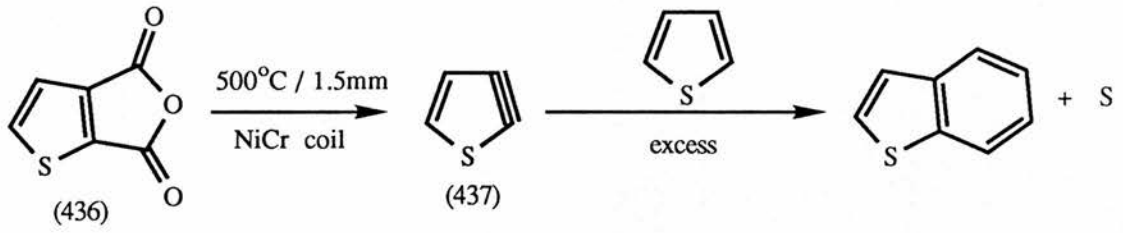
Thiophenes are not as thermally stable as their phenyl analogues. It has previously been reported[274] that pyrolysis of thiophene at 800-850°C led to fragmentation and some of the products isolated were naphthalene, benzothiophene, phenylthiophene and bithienyl. However interesting studies has been carried out on various thiophene compounds by employing lower pyrolysis temperatures. The thiophene analogue(**432**) of *p*-xylylene was generated by elimination of hydrogen chloride from 2-chloromethyl-5-methylthiophene(**431**) on pyrolysis at 600°C[275]. The



intermediate(**432**) was only stable at low temperatures and readily dimerised to (**433**) on warming. It can however be regenerated by pyrolysing (**433**) at 400°C. A double elimination of hydrogen chloride from compound (**434**) at 650°C gave thiophene analogue(**435**) of pentaradialene[275].

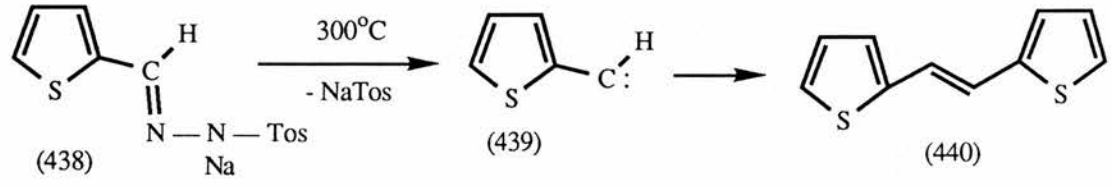
The chemistry of arynes is of great interest in aromatic chemistry. Reinecke and Newson[276] generated the thiophene analogue, 2,3-thiophyne

(**437**) by pyrolysis of thiophene-2,3-dicarboxylic anhydride (**436**) in

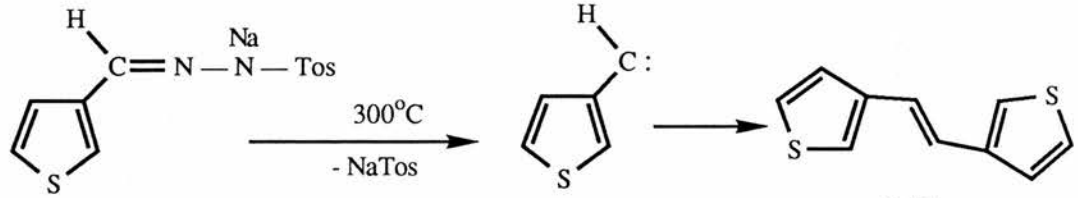


(436) (437)

the presence of thiophene. The major products from attack of (**437**) on thiophene at 500°C were benzothiophene and sulphur. A detailed study on the chemistry of 2- and 3-thienylmethylenes (**439**) and (**442**) in the



(438) (439) (440)



(441) (442) (443)

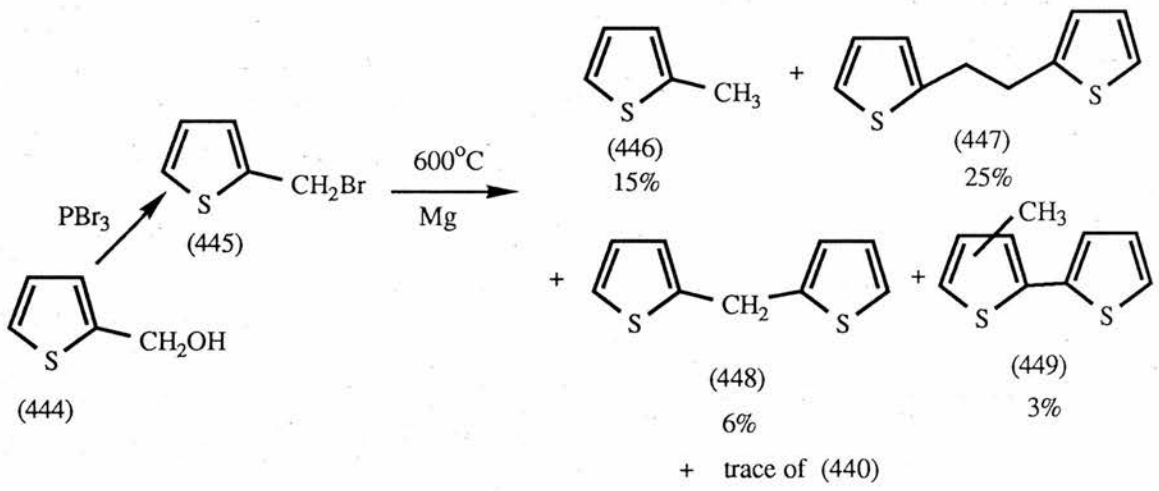
gas phase was recently reported[214]. The species (**439**) and (**442**) were generated by pyrolysis of their corresponding tosylhydrazone sodium salts (**438**) and (**441**). The principal processes of (**439**) and (**442**) at 300°C was dimerisation to give *Z*-and*E*-1,2-di(2-thienyl)ethene(**440**) and *Z*-and*E*-1,2-di(3-thienyl) ethene(**443**) respectively.

It was therefore of interest to investigate the thermal reaction of various halogenated thiophenes over magnesium. The emphasis was on being able to achieve the same interesting transformation on thiophenes as those observed with aliphatic and aromatic compounds on pyrolysis over magnesium. It was hoped that the pyrolysis temperature of 600°C used

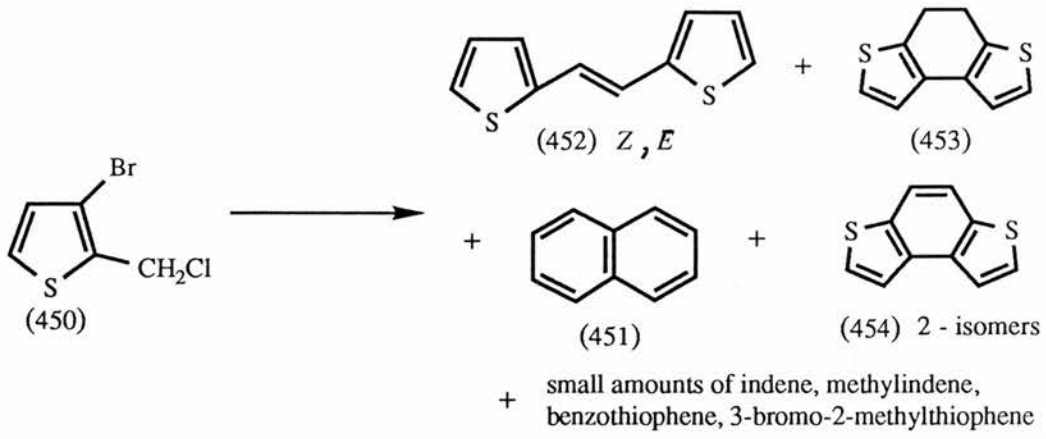
for previous investigation would not lead to significant thermal decomposition

2. Mono-and di-halomethylthiophenes

2-Bromomethylthiophene(**445**) was prepared from 2-thiophenemethanol(**444**) and phosphorus tribromide. Compound (**445**) was unstable and readily polymerised and had to be pyrolysed immediately after preparation. On pyrolysis over magnesium at 600°C, the major products obtained were 2-methylthiophene(**446**) and 1,2-di(2-thienyl)ethane(**447**) with small of amounts di(2-thienyl)methane (**448**) and methyl-2,2'-bithiophene(**449**).

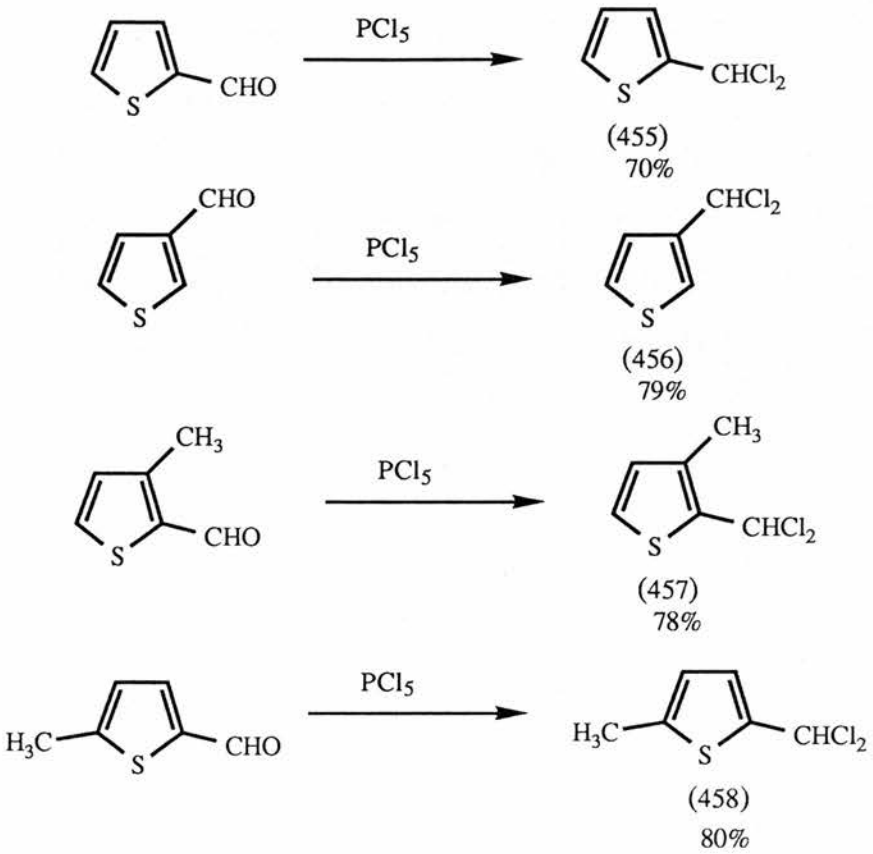


As 3-bromo-2-chloromethylthiophene(**450**) was available from another experiment, its reaction on pyrolysis over magnesium was investigated. The major products obtained were naphthlene(**451**), *Z*-and *E*-1,2-di(2-thienyl)ethene(**452**), dihydrobenzodithiophene(**453**) and two isomers of benzodithiophene(**454**). Also present were small amounts of other compounds and as the overall yield of isolated product was very low, no attempt was made to determine the yields of individual compounds.

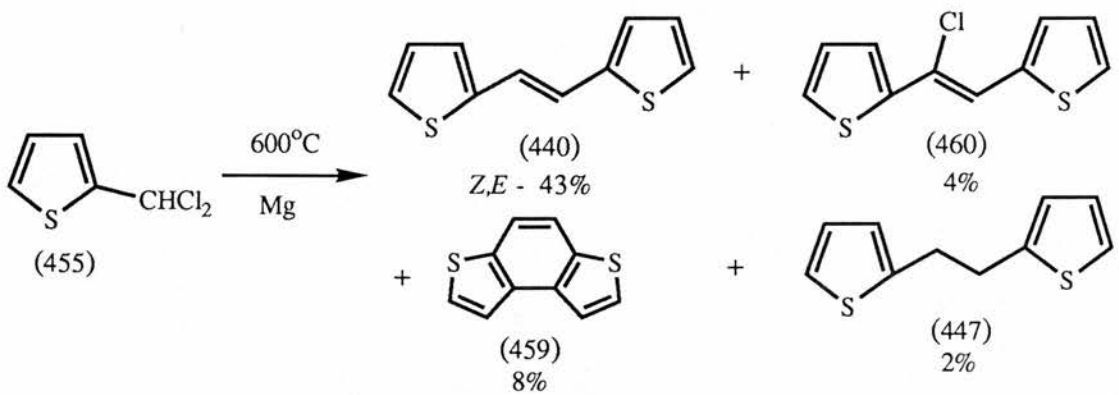


For the two compounds (**445**) and (**450**) examined, the main reactions were dehalogenative homocoupling and reduction, similar to the processes observed with the analogous benzylic halides. However, the overall yield of products from the thiophene compounds were much lower than those obtained from the corresponding benzylic halides. This is not surprising as the lower thermal stability of thiophenes has earlier been highlighted and fragmentation could account for the low yield. The naphthalene, benzothiophene and indenes obtained from (**450**) are obvious products of fragmentation.

As noted earlier, benzylidene chlorides are readily accessible from the corresponding aldehydes by treating with phosphorus pentachloride. As an extension to the investigation on thiophenes the following compounds, 2-dichloromethylthiophene(**455**), 3-dichloromethyl-thiophene(**456**), 2-dichloromethyl-3-methylthiophene(**457**) and 2-dichloromethyl-5-methylthiophene(**458**) were similarly prepared from their corresponding aldehydes. The products are generally unstable as they readily polymerised, however they can be stored for several days in the refrigerator without significant decompostion. The yield of products was generally good.

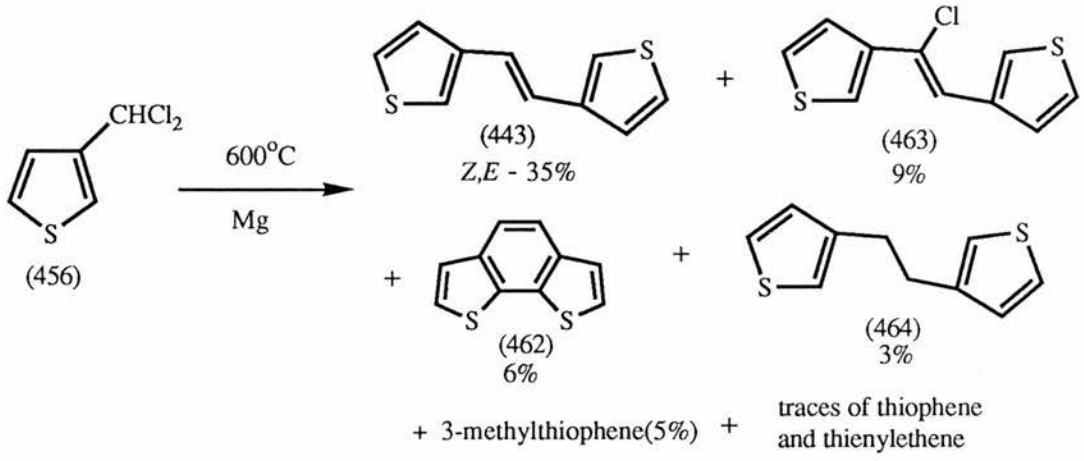


The pyrolysis of (**455**) over magnesium gave about 43% of *Z*-and *E*-1,2-di(2-thienyl)ethene(**440**) with small amounts of benzo[1,2-b:4,3-b']dithiophene(**459**), chloro-1,2-di(2-thienyl)ethene(**460**) and 1,2-di(2-thienyl)ethane(**447**). Also present were trace amounts of 2-methylthiophene and other unidentified compounds.

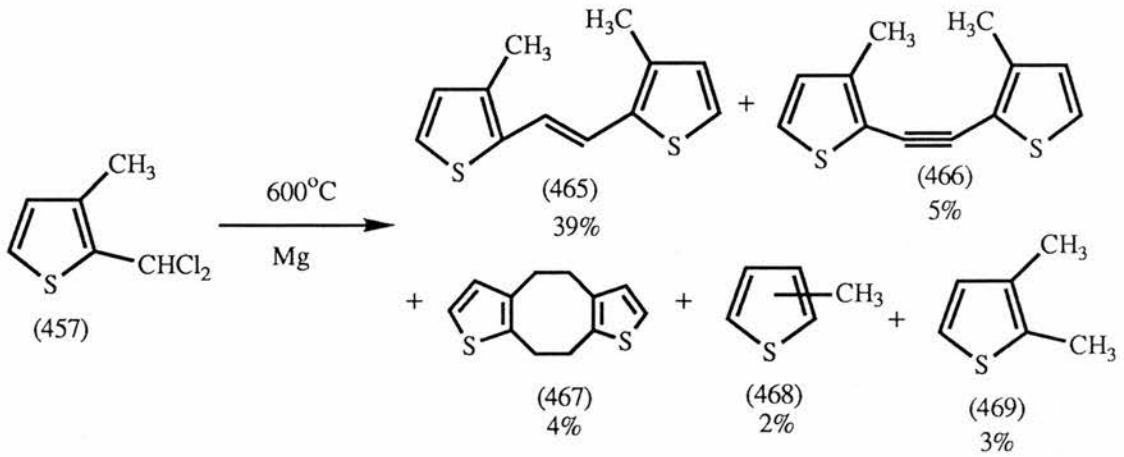


\+ small amounts of methylthiophene and other unidentified compounds .

Similarly, when (**456**) was pyrolysed over magnesium, the products obtained were *Z*-and *E*-1,2-di(3-thienyl)ethene(**461**), benzo[2,1-b:3,4-b']-dithiophene(**462**), chloro-1,2-di(3-thienyl)ethene (**463**), 1,2-di(3-thienyl)ethane(**464**) and 3-methylthiophene, with trace amounts of thiophene and thienylethene.

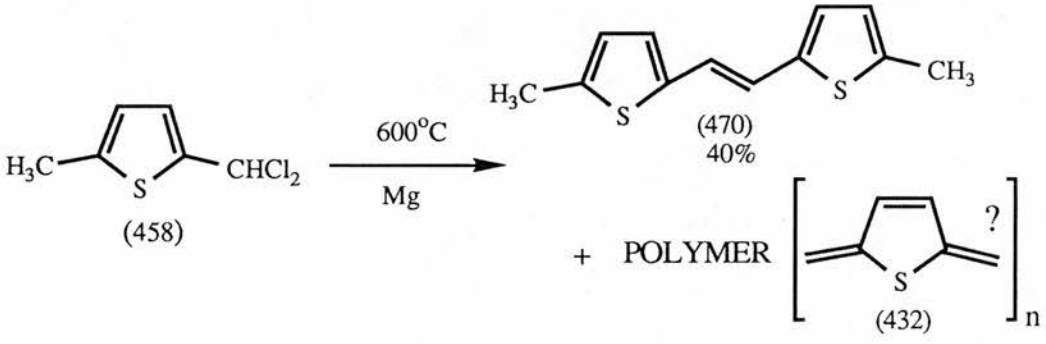


The pyrolysis of (**457**) gave about 40% of *Z*-and*E*-1,2-bis(3-methyl-2-thienyl)ethene(**465**) and small amounts of 1,2-bis(3-methyl-2-thienyl)ethyne(**466**), 4,5,9,10-tetrahydrocycloocta[1,2-b:6,5-b']di-thiophene(**467**), methylthiophene(**468**), 2,3-dimethylthiophene



(**469**) and traces of three unidentified compounds each with m/z of 188. The pyrolysis of (**458**) also gave about 40% of *Z*-and*E*-1,2-bis(5-methyl-

2-thienyl) ethene(**470**) as the main product, and a polymeric material, whose nature was not determined. Thc formation of (**467**) from (**457**) and the polymer from (**458**), indicated the likely involvement of the thiophene analogue of xylyenes(**163**) and (**432**) respectively. The involvement of the intermediate(**163**) has been previously reported[275,279] from α-halo-2,3-dimethylthiophenes on pyrolysis at 750°C and the intermediate(**432**) from α-chloro-2,5-dimethyl-thiophene[275] on pyrolysis at 600°C.



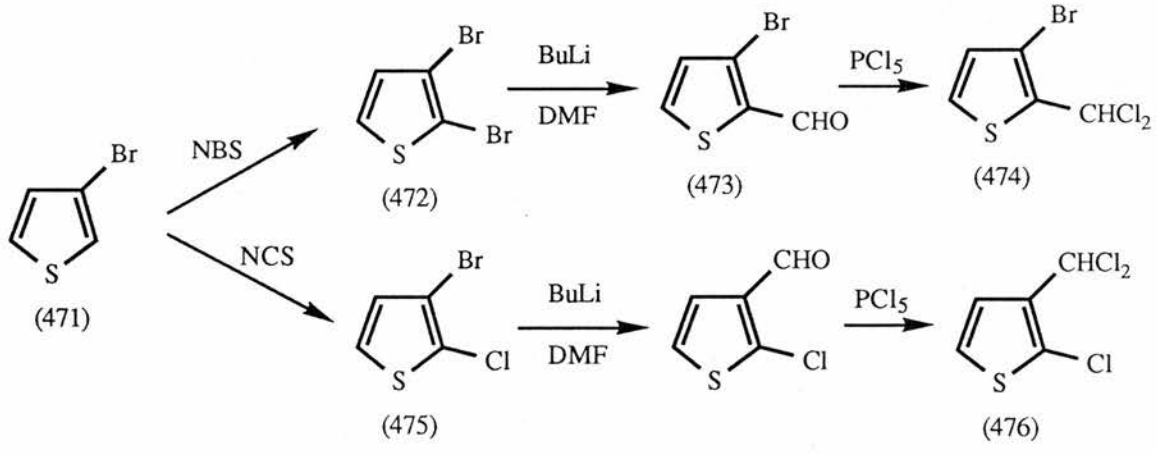
The products obtained from all the dichloromethylthiophenes investigated over magnesium, were mainly homocoupled compounds similar to those obtained from the analogous benzylidene chlorides. The yields were generally lower than those of the corresponding benzylidene chloride.

A step-by-step mechanism was proposed in the previous sections for the observed homocoupling reaction of benzylic, benzylidene and benzylidyne halides when pyrolysed over magnesium. A similar mechanism is believed to be involved in the reactions of the thiophenes. The formation of chloro-2-dithienylethenes (**460**) and (**463**), from (**455**) and (**456**) respectively and 1,2-di(3-methyl-2-thienyl)ethyne(**466**) from (**457**) suggested a dehydrochlorination reaction of the initially formed 1,2-dichloro-1,2-dithienylethane intermediate. This further confirms the stepwise nature of the dehalogenative coupling reaction as opposed to a

possible carbene coupling reaction. The thienyl carbenes have however been previously reported[214] to give the same dithienylethene products as those obtained from the magnesium induced stepwise dehalogenation process.

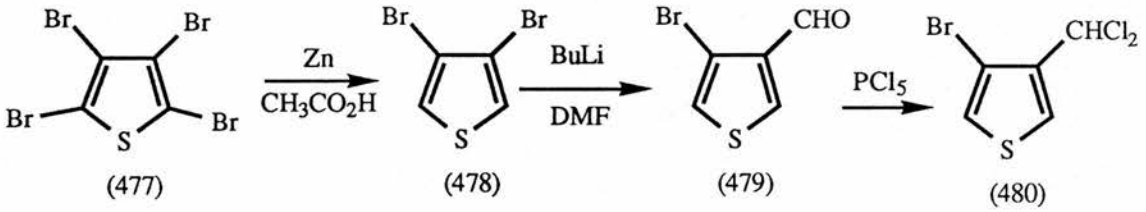
3. Halo-dichloromethylthiophenes and benzodithiophenes

Following the complete dehalogenation of 2-chlorobenzylidene chloride(**369**) observed on pyrolysis over magnesium to give phenanthrene(**293**) *via* homocoupling and cyclisation, similar thiophene substrates might be expected to lead to benzodithiophenes on dehalogenation. Thus 3-bromo-2-dichloromethylthiophene(**474**), was prepared from 3-bromo-2-thiophenecarboxaldehyde(**473**). The aldehyde was synthesised from 3-bromothiophene(**471**) *via* bromination with N-bromosuccinimide to 2,3-dibromothiophene(**472**) and formylation



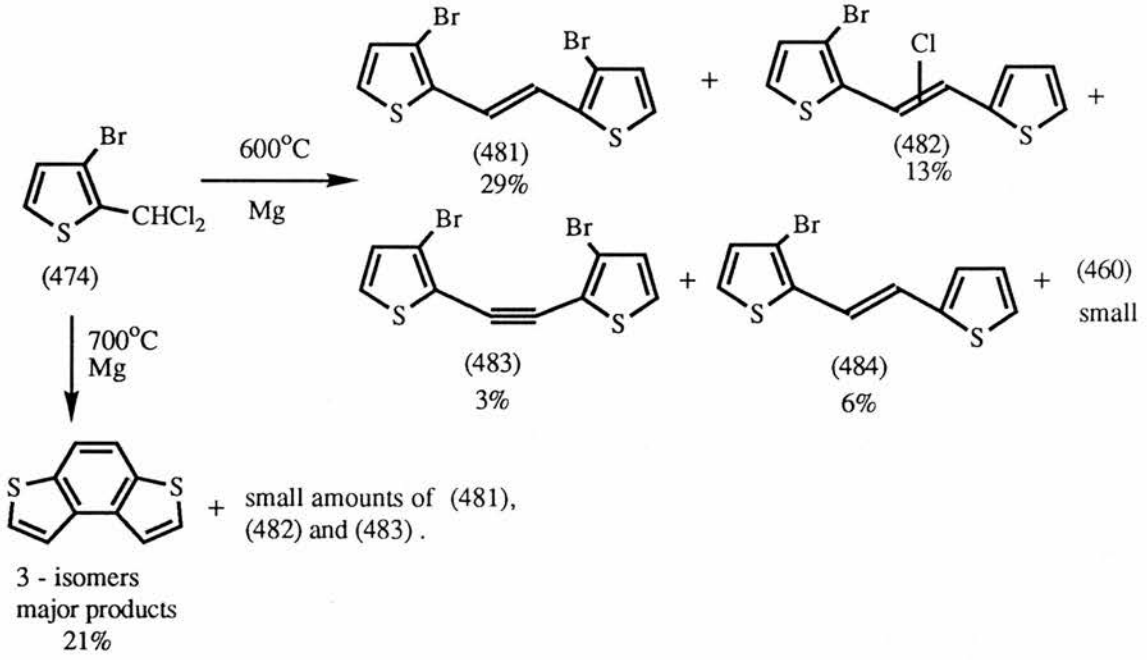
with butyl lithium and DMF. Similarly prepared was 2-chloro-3-dichloromethylthiophene(**476**) from 2-chloro-3-bromo-thiophene(**475**) obtained by chlorination of 3-bromothiophene(**471**) with N-chlorosuccinimide. For the synthesis of 3-bromo-4-dichloro-methylthiophene(**480**), tetrabromothiophene(**477**) was reduced with zinc/acetic acid to 3,4-dibromothiophene(**478**). Formylation of (**478**)

with butyl lithium and DMF gave 3-bromo-4-thiophenecarboxyaldehyde (**479**) which was converted to 3-bromo-4-dichloromethylthiophene(**480**) with phosphorus pentachloride.

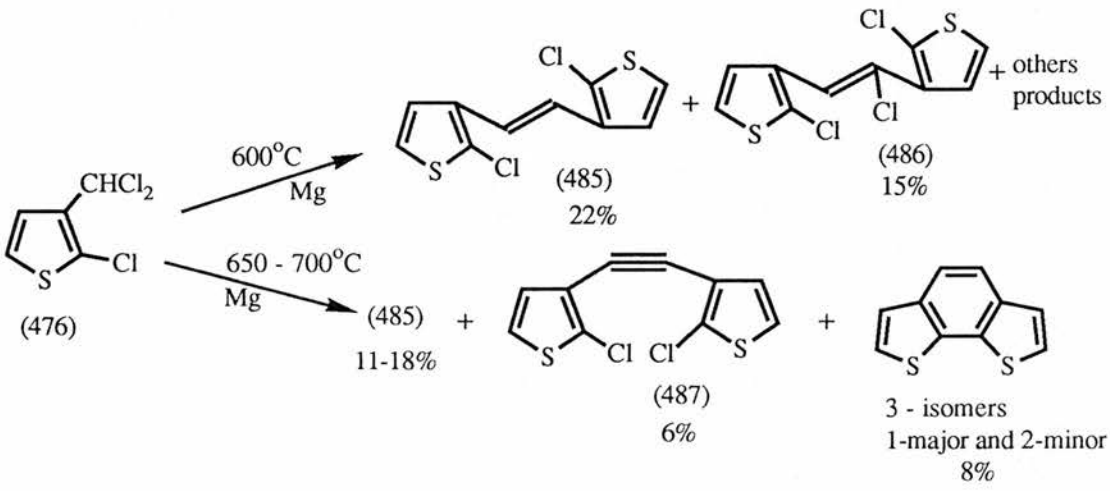


(477) (478) (479) (480)

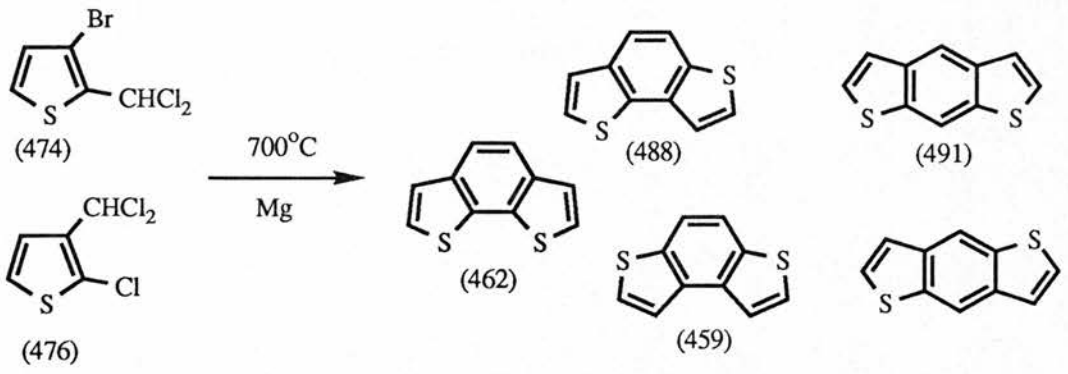
The pyrolysis of (**474**) over magnesium was expected to give benzo[1,2:4,3-b']dithiophene(**459**). However at 600 °C, the major products obtained were *Z*-and*E*-1,2-bis(3-bromo-2-thienyl)ethene(**481**) and chloro-1-(3-bromo-2-thienyl)-2-(2-thienyl)ethene(**482**) with small amounts of 1-chloro-1,2-di(2-thienyl)ethene(**460**), 1,2-di(3-bromo-2-thienyl)ethyne(**483**) and bromo-1,2-di(2-thienyl)ethene(**484**). At 650°C a similar product mixture was obtained in addition to three isomers of benzodithiophene and at 700°C the major products were the three isomers of benzodithiophene.



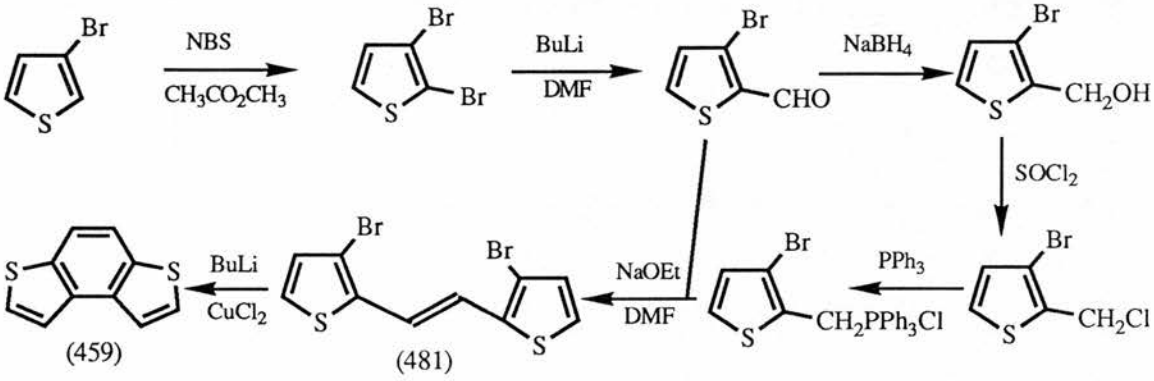
When compound (**476**), which was expected to give benzo[2,1-b:3,4-b']dithiophene(**462**), was pyrolysed at 600°C the products obtained consisted of various chlorinated compounds, the major ones been *Z*-and*E*-1,2-bis(2-chloro-3-thienyl)ethene (**485**) and *Z*-and*E*-1-chloro-1,2-bis(2-chloro-3-thienyl)ethene(**486**). At the temperatures of 650°C and 700°C, the major products were (**485**) and 1,2-bis(2-chloro-3-thienyl)ethyne(**487**), in addition the one major and two minor peaks on the GC-MS with m/z 190 corresponding to benzodithiophenes.



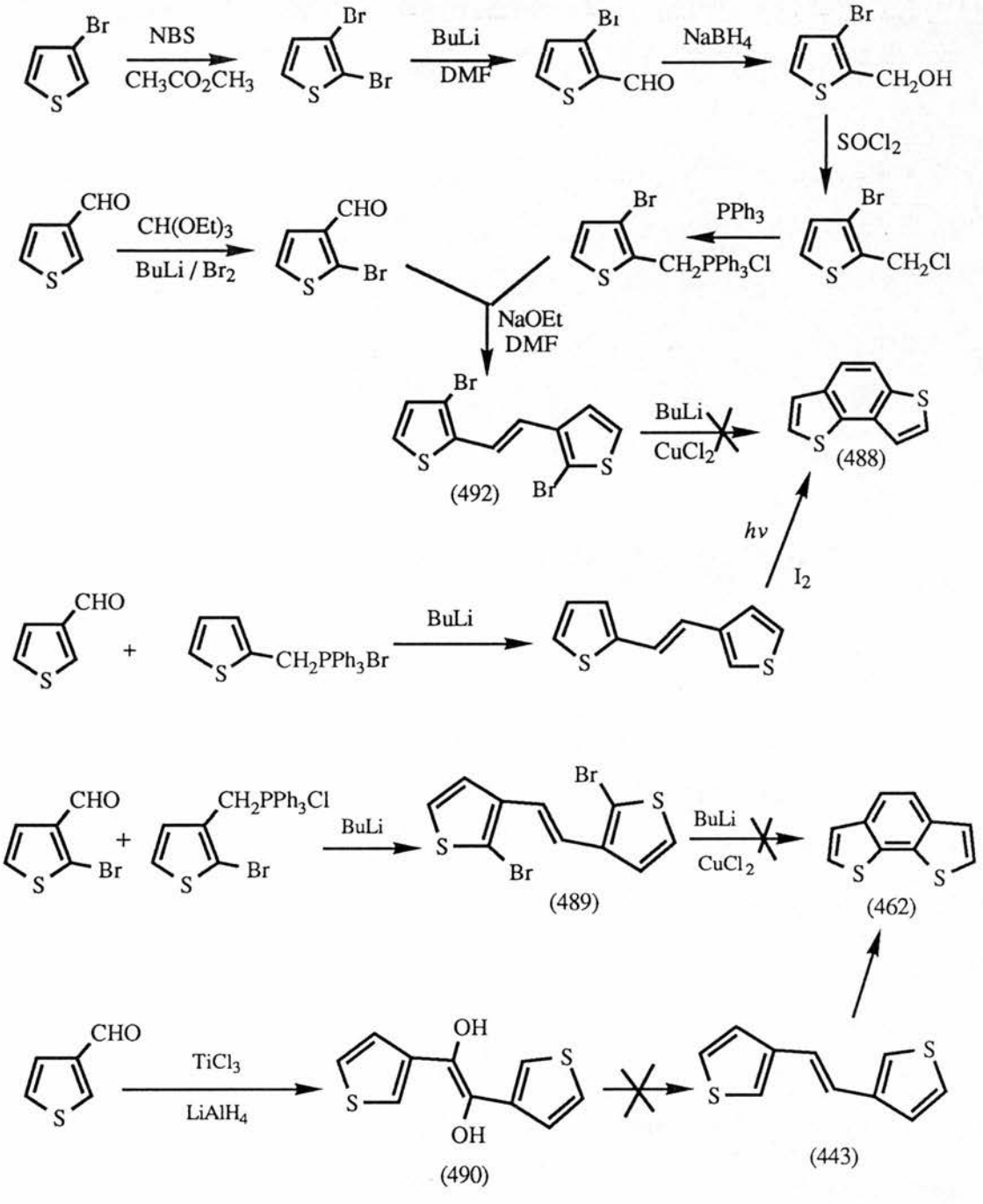
The various halogenated compounds obtained from both (**474**) and (**476**) are clearly homocoupled products of incomplete dehalogenation. The stepwise nature of the dehalogenation process may account for the products (**482**) and (**483**) from substrate (**474**) and products (**486**) and (**487**) from substrate (**476**). The products obtained indicated that the removal of the ring bromine takes place more readily than for chlorine. Although the complex nature of the products obtained and the low overall yield was disappointing, the route to the three isomeric benzodithiophenes from both (**474**) and (**476**) was intriguing as there was no obvious route to these isomeric products.



In an attempt to identify the benzodithiophenes produced on the pyrolysis of both (**474**) and (**476**), the isomers benzo[1.2-b:4,3-b']dithiophenes(**459**) and benzo[1,2-b:3,4-b']dithiophene(**488**) were prepared by literature methods.

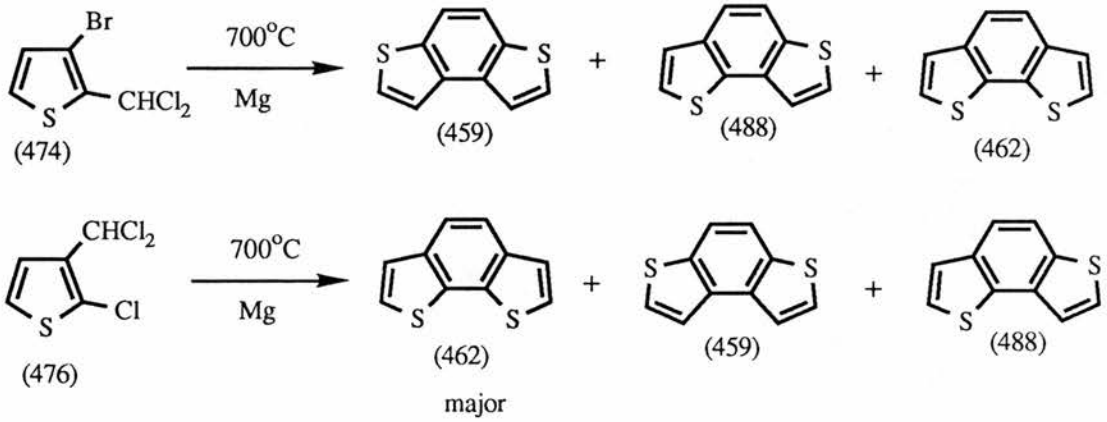


Attempts to prepare benzo[2,1-b:3,4-b']dithiophene(**462**) by butyl lithium and copper(1)chloride cyclisation of 1,2-di-(3-bromo-2-thienyl) ethene (**489**) was unsuccessful. An alternative route attempted, to couple 3-thiophenecarboxaldehyde to 1,2-di(3-thienyl) ethene(**461**) followed by photocyclisation, was also unsuccessful, as the coupling reaction with titanium(III)chloride/$LiAlH_4$ only resulted in 1,2-di(3-thienyl) ethane-1,2-diol(**490**). Similar attempt to prepare benzo[1,2-b:5,4-b']dithiophene (**491**) using a literature method was abandoned because of the very low yield of precursors.



The GC analysis and ^{13}C NMR comparison of the pyrolysates from (**474**) and (**476**), with the prepared samples of (**459**) and (**488**), indicated that the three benzodithiophenes obtained from (**474**) are compounds (**459**), (**488**) and (**462**). While the major benzodithiophene obtained from (**476**) was compound (**462**), with the smaller products

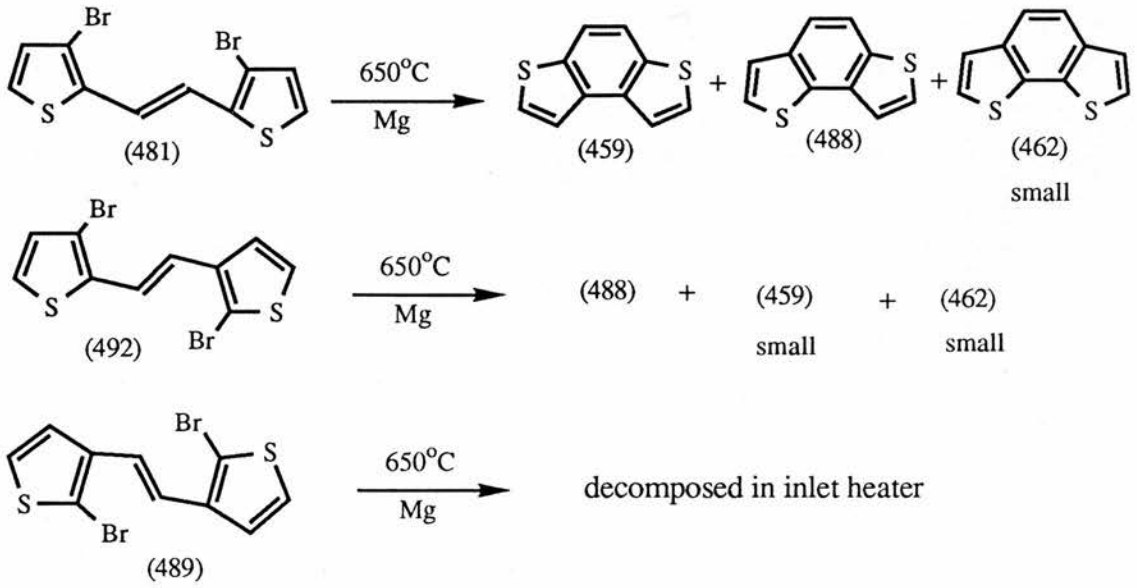
being the isomers (**459**) and (**488**). The route of these isomeric products was puzzling and of mechanistic interest.



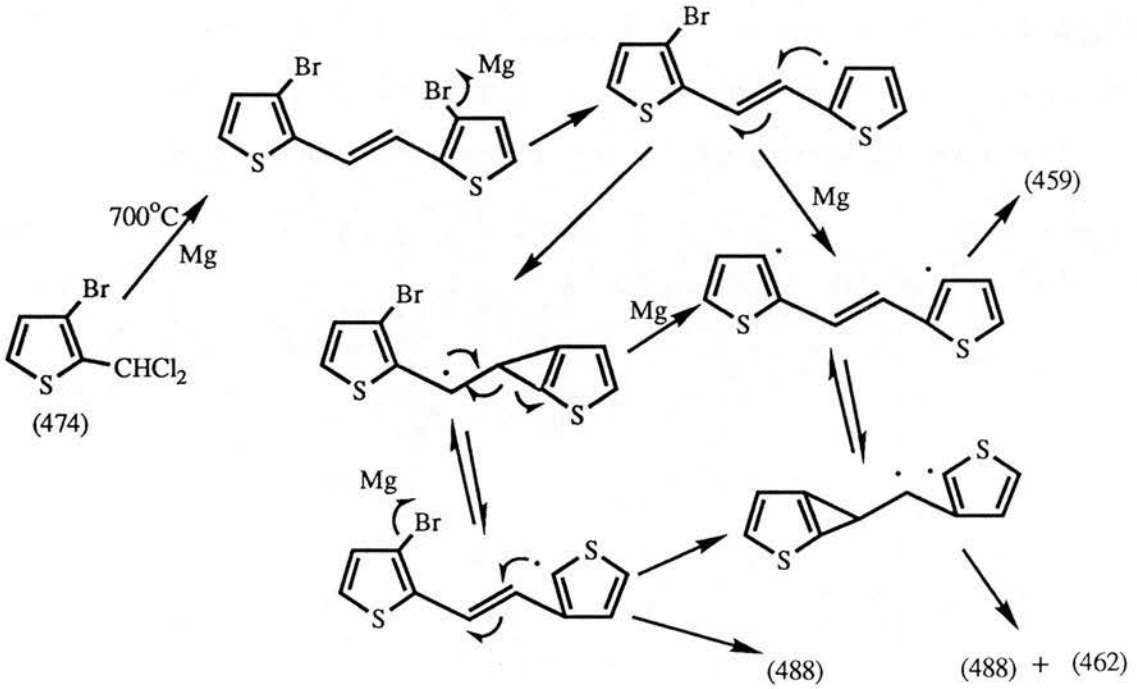
A possible route to these isomers was suspected to be the thermal isomerisation of the expected benzo[1,2-b:4,3-b']dithiophene(**459**) from 3-bromo-2-dichloromethylthiophene(**474**) and benzo[2,1-b:3,4-b'] dithiophene(**462**) from 2-chloro-3-dichloromethylthiophene(**476**), to the other isomers obtained. However this possibility was dismissed as independent pyrolysis of the prepared (**459**) and (**488**) over magnesium gave unchanged starting material.

As part of the mechanistic study 1,2-di(3-bromo-2-thienyl)ethene (**481**) and 1-(3-bromo-2-thienyl)-2-(2'-bromo-3'-thienyl)ethene(**492**) were separately pyrolysed over magnesium. The pyrolysis of (**481**) gave mainly isomers (**459**) and (**488**) with small amounts of (**462**), while (**492**) gave mainly (**488**) with small amounts of (**459**) and (**462**). Unfortunately, an attempt to pyrolyse 1,2-di(2-bromo-3-thienyl)ethene (**489**) was unsuccessful as it decomposed in the inlet tube. However, the

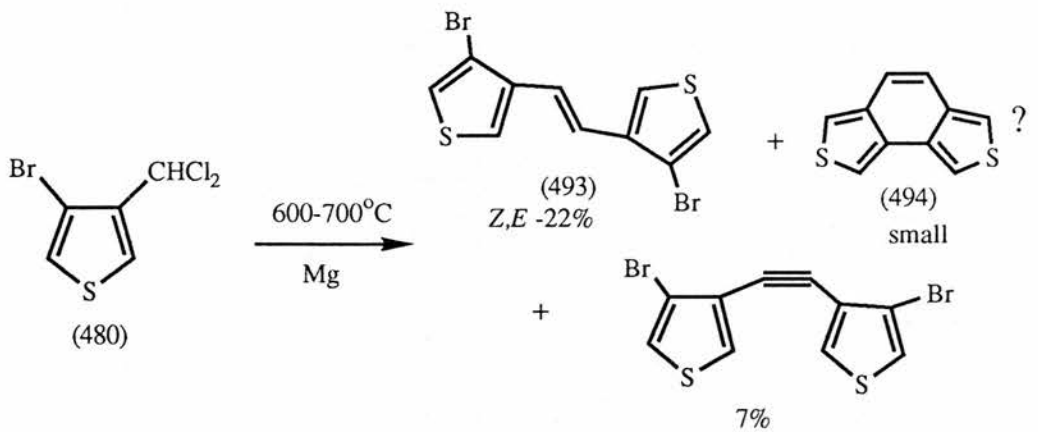
products obtained from this investigation suggested the likely route to the isomeric benzodithiophenes obtained from (**474**) and (**476**).



The reaction is believed to have involved initial coupling of (**474**) and (**476**) in a step-by-step process to give the dihalodithienylethenes (**481**) and (**485**) respectively. This process is similar to that observed for other substrates throughout this investigation. In the presence of magnesium and at adequate temperatures this is followed by a stepwise dehalogenation of (**481**) and (**485**) to generate a radical-like centre, which may add to the adjacent alkene bond. The addition gives rise to a three-membered cyclic intermediate which can ring open either way leading to cross-over between the 2- and 3-positions on the thiophene ring. This process could account for the formation of the isomeric benzodithiophenes and the mechanism proposed is exemplified below with 3-bromo-2-dichloromethyl-thiophene(**474**). A similar process is proposed for the reaction of 2-chloro-3-dichloromethylthiophenes(**476**) as well as for the earlier observed conversion of 2-chlorobenzylidene chloride(**369**) to phenanthrene(**293**).

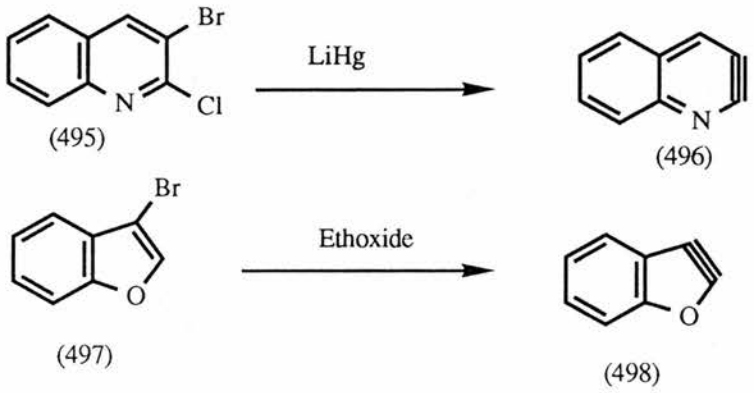


The pyrolysis of 3-bromo-4-dichloromethylthiophene (**480**) over magnesium gave mainly *Z*-and*E*-1,2-bis(4-bromo-3-thienyl) ethene (**493**) at 600°-700°C and only a small amount of a single isomer of benzodithiophene. Based on the studies discussed in the earlier part of this section, the benzodithiophene obtained from (**480**) was definitely not the isomers (**459**), (**462**) and (**488**) but is suspected to be benzo[1,2-c:3,4-c']dithiophene (**494**).



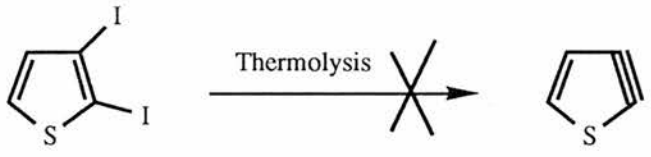
4. Other thiophene compounds

The generation of benzyne(**188**) by dehalogenation of 1,2-dihalobenzenes(**187**) in solution has been well investigated (see Introduction). Some heterocyclic analogues of this reactive intermediate have also been generated in a similar manner, thus 2-chloro-3-bromoquinoline(**495**) was dehalogenated with lithium amalgam to give



(495) (496) (497) (498)

the intermediate(**496**)[277]. The species(**498**) was generated by dehydrobromination of 3-bromo-benzofuran(**497**) with base[155]. However, attempts to generate 2,3-thiophyne(**437**) by thermal deiodination of 2,3-diiodothiophene were unsuccessful[279]. The prospect

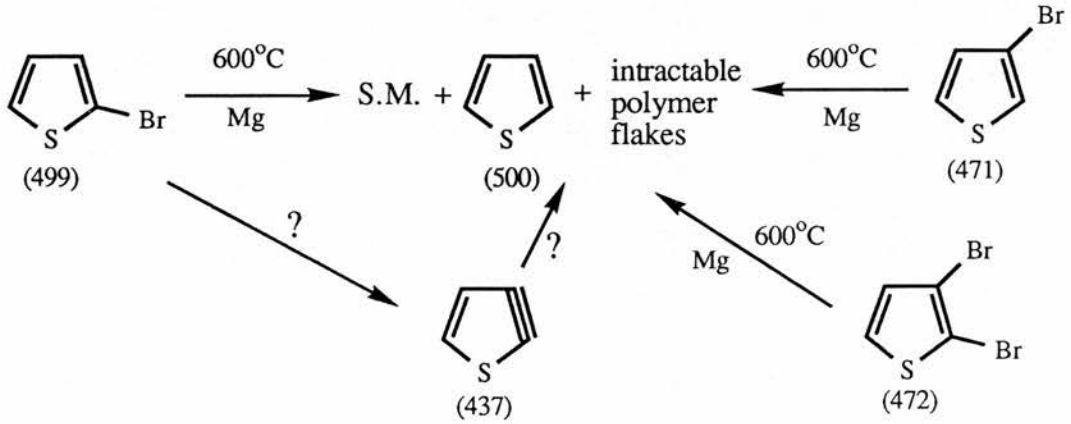


(437)

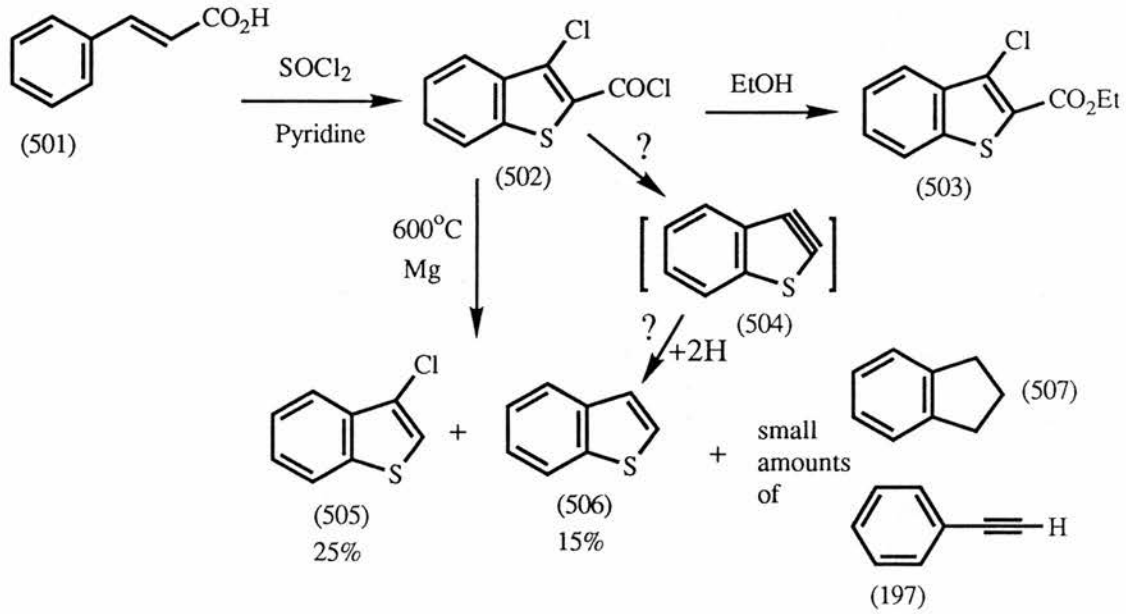
of generating (**437**) and its derivatives by pyrolysis over magnesium was investigated. The species(**437**) if generated was expected to give trithienylene and bithienylene, in a similar manner to benzyne(**188**).

However, the pyrolysis of 2-bromothiophene(**499**) and 3-bromothiophene(**471**) over magnesium at 600-700°C simply give a mixture of starting material, thiophene(**500**) and some intractable polymer flakes. Similarly, the pyrolysis of 2,3-dibromothiophene(**472**)

gave a mixture of starting material, bromothiophenes(**499**) and (**471**), thiophene(**500**) and the intractable polymer flakes. Although the expected trithienylene and bithienylene were not obtained, the route to (**500**) and the polymer flakes might involve the intermediate(**437**).



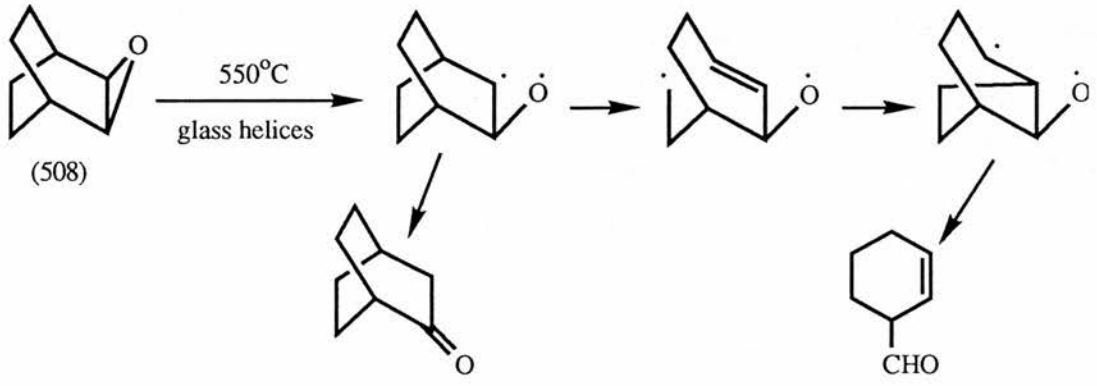
3-Chloro-2-chlorocarbonylbenzo[b]thiophene(**502**) was prepared from cinnamic acid(**501**) and thionyl chloride in the presence of pyridine. Compound(**502**) was converted to its ethyl ester(**503**) for characterisation by treating with hot ethanol. The pyrolysis of (**502**) over magnesium was expected to lead to the elimination of both chlorines



and decarbonylation, thereby generating the species(**504**). However on pyrolysis the major products obtained were 3-chlorobenzothiophene (**505**) and benzothiophene(**506**). Also present were small amounts of phenylacetylene(**197**) and indane(**507**). The formation of (**506**) may involve the intermediate(**504**) which then abstracts two hydrogen atoms to give the product.

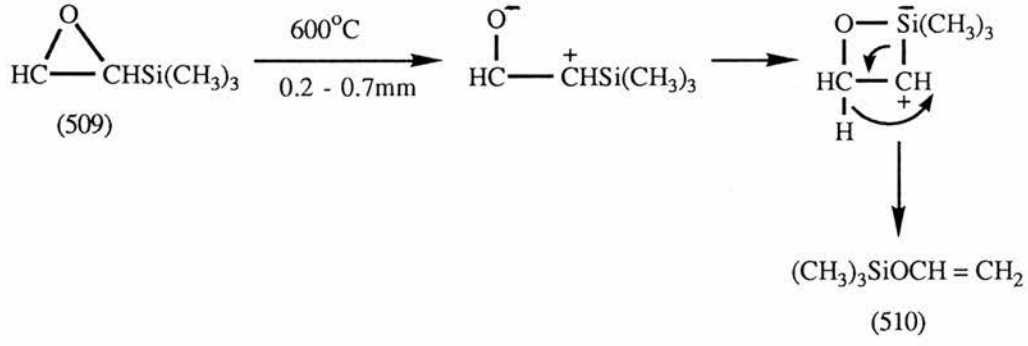
J. Preparation and Flash Vacuum Pyrolysis of Epoxides

Thermal rearrangment of epoxides is well known and has been a subject of a review[280]. Hudrlik *et al* [281] gave a useful short list of references to kinetic and preparative studies of the thermal decomposition of simple epoxides, in which the major reaction is often rearrangement to a carbonyl compound. The results of most gas phase studies suggested the involvement of diradical intermediates and this is typified by the thermal



(508)

rearrangment of norbornene oxide(**508**) reported by Garin[282]. A preparatively useful rearrangement was that of α,β-epoxysilanes(**509**) to



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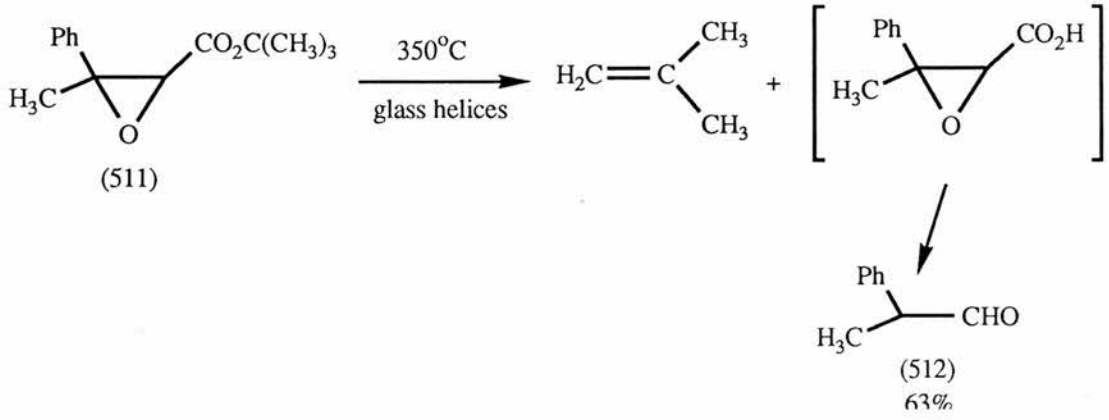


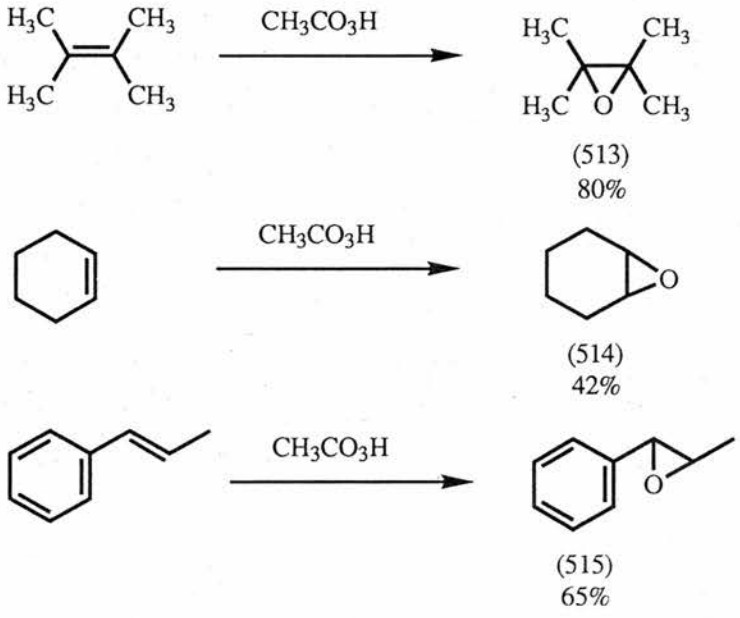
(511) (512)

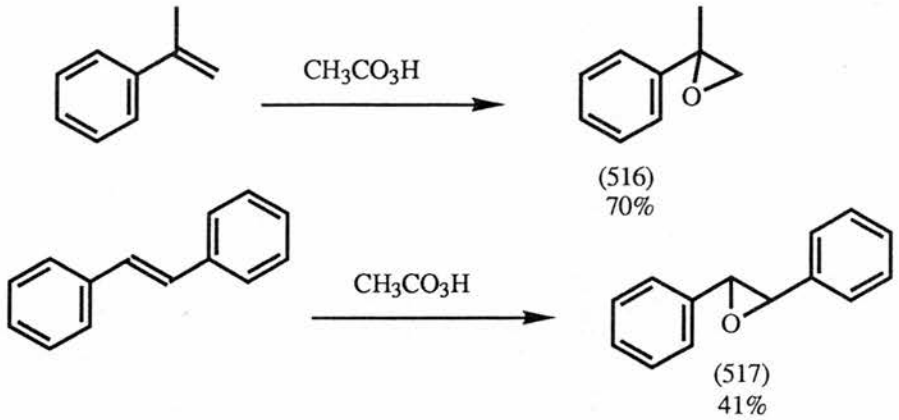
63%

the silyl enol ethers(**510**) in 66-77% yield for a range of such compounds[281]. The pyrolysis and rearrangement of glycide *t*-butyl ester (**511**) to 2-phenylpropanal(**512**) in a high yield is another example of the thermal reaction of epoxides.

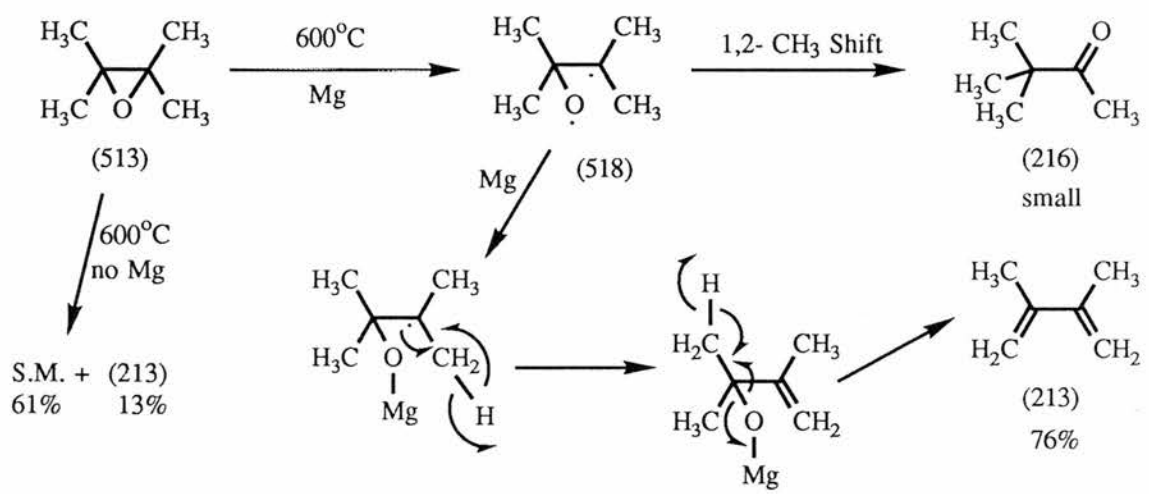
In the course of this investigation of pyrolysis over magnesium, some deoxygenation reactions have been encountered, especially in the observed partial dehydration of pinacol(**211**) to 2,3-dimethylbut-1-ene(**209**) and 2,3-dimethylbut-2-ene(**210**). An epoxide intermediate was proposed as a likely route to the products. In order to investigate the scope of this deoxygenation reaction and as part of the desire to study the thermal reaction over magnesium of substrates other than halogenated ones, a series of epoxides were prepared.

The epoxides used for this investigation were prepared by oxidising the desired C=C double bond using peracetic acid with sodium hydrogen carbonate as scavenger for acetic acid. Thus tetramethylethylene oxide (**513**), cyclohexene oxide(**514**), 1,2-epoxy-1-phenylpropane(**515**), 1,2-epoxy-2-phenylpropane(**516**) and stilbene oxide(**517**) were prepared. The other epoxides used for this investigation are commercial samples.



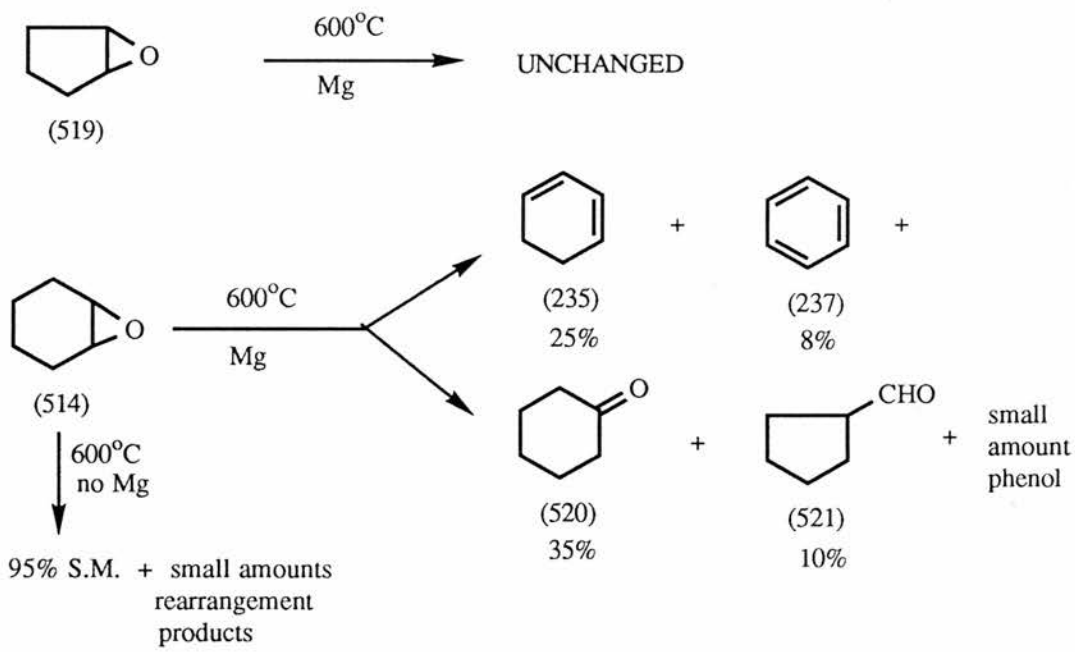


The pyrolysis of tetramethylethylene oxide(**513**) over magnsesium gave a 76% yield of 2,3-dimethybutadiene(**213**) and small amounts of pinacolone(**216**). The conversion of (**513**) to (**213**) was a dehydration process and to ascertain that the reaction was not just thermal, the epoxide (**513**) was pyrolysed under identical conditions without magnesium. About 61% of the starting material was recovered unchanged and the only product obtained was 13% of pinacolone(**216**). This is a product of thermal rearrangement involving a 1,2-methyl shift presumably *via* the diradical(**518**). The diradical may also be involved in the formation of (**213**), with magnesium enhancing the ring opening process as well as



removing the oxygen *via* complexation, thereby providing an alternative reaction path to the 1,2-methyl shift. One of the literature methods to (**213**) involved the dehydration of pinacol(**211**) over alumina[243] or copper[244] at high temperatures and the reaction was postulated to involve the epoxide(**513**) as an intermediate.

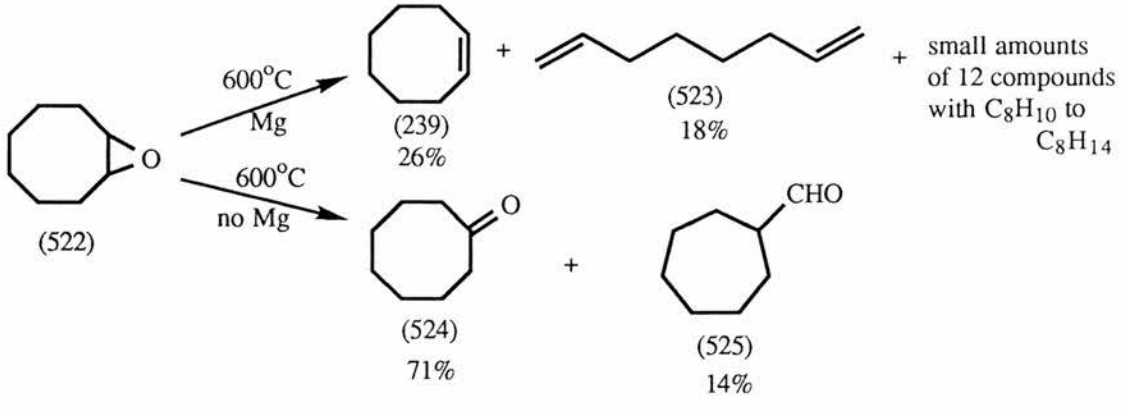
When cyclopentene oxide(**519**) was pyrolysed with or without magnesium only unchanged starting material was recovered. However with cyclohexene oxide(**514**), the pyrolysis over magnesium gave 25% of the dehydration product, cyclohexa-1,3-diene(**235**) and its secondary product, benzene(**237**) in 8% yield. The other products obtained were the rearrangement compounds cyclohexanone(**520**) in 35% and cyclopentane carboxaldehyde(**521**) in 10% yield. The products indicated two competing processes, dehydration and rearrangement, and there was



no evidence to suggest that either process was simply thermal, as the pyrolysis of the epoxide(**514**) without magnesium gave about 95% unchanged starting material with only small amounts of the rearrangment

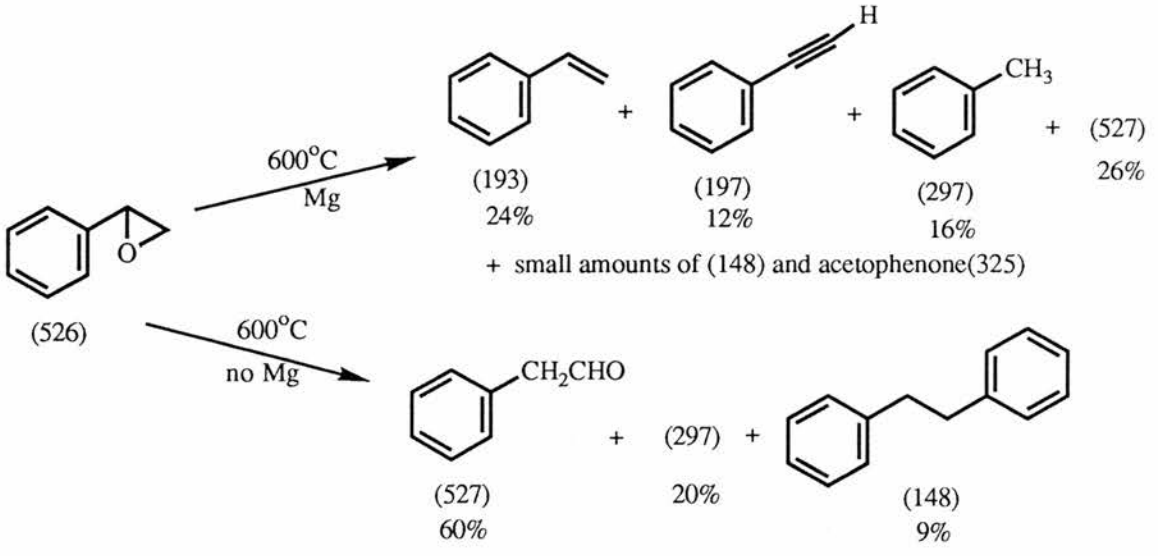
products (**520**) and (**521**). A previous literature report[281] also showed that (**514**) was recovered unchanged at 600°C.

The pyrolysis of cyclooctene oxide(**522**) over magnesium gave a complex mixture of products, of which the main ones were 26% of cyclooctene(**239**) and 18% of octa-1,7-diene(**523**). The other unidentified products were small amounts of 12 compounds with mass corresponding to C_8H_{10} to C_8H_{14} hydrocarbons and are suspected to be products of ring contraction. No oxygenated product was observed. Repeat pyrolysis of the epoxide(**522**) without magnesium gave only products of rearrangement cyclooctanone(**524**) in 71% and cycloheptanecarboxaldehyde(**525**) in 14% yield. The dehydration process observed over magnesium with the other epoxides examined was not evident for (**522**), rather deoxygenation to (**239**) was the main process. The reason for this is not known. The product (**523**) is likely a secondary product of (**239**) as the thermal ring opening of (**239**) to (**523**) has been previously reported[250].

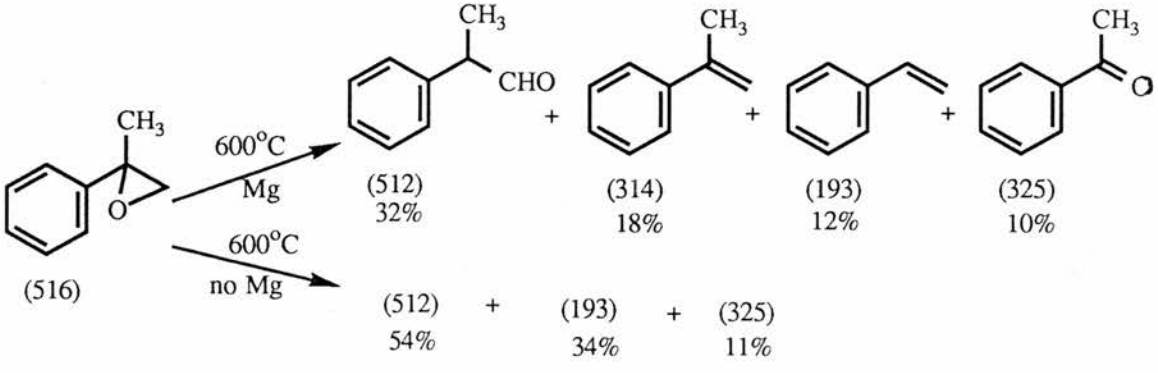


When styrene oxide(**526**) was pyrolysed over magnesium, the products obtained were 24% of styrene(**193**), 12% of phenylacetylene (**197**) and 16% of toluene(**297**). In the absence of magnesium, the products obtained were 60% of phenylacetaldehyde(**527**), 20% of toluene

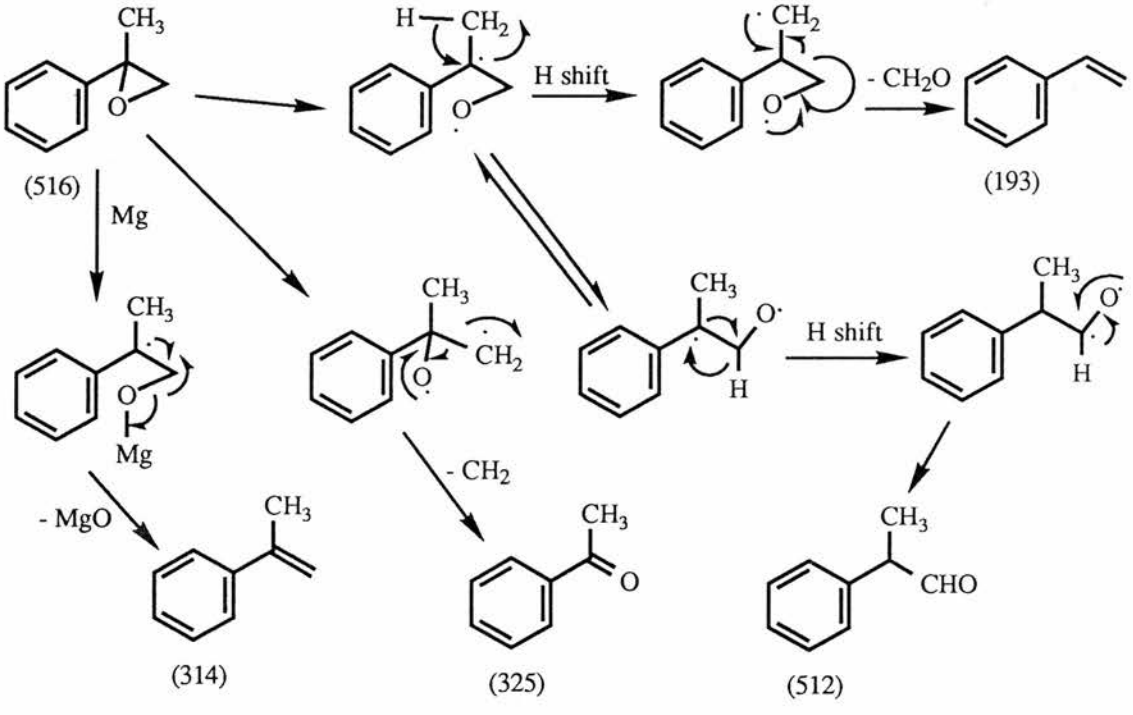
(**297**) and 9% of bibenzyl(**148**). It was obvious that both (**297**) and (**148**) were products of fragmentation and (**527**) was a product of thermal rearrangement involving either 1,2-hydrogen or -phenyl migration. The deoxygenation to (**193**) and dehydration to (**197**) are believed to involve some form of magnesium-oxygen interaction either *via* an oxygen-centred radical or complexation. A previous literature report[283] on the pyrolysis of (**526**) at 500°C mentioned toluene(**297**) as the only product and that the rearrangement product(**527**) was only obtained at 200-300°C. The authors favoured the 1,2-hydrogen migration of the diradical, formed by epoxide ring opening, as the route to (**527**).



The pyrolysis of 1,2-epoxy-2-phenylpropane(**516**) over magnesium gave mainly the rearrangement product 2-phenylpropionaldehyde(**512**)

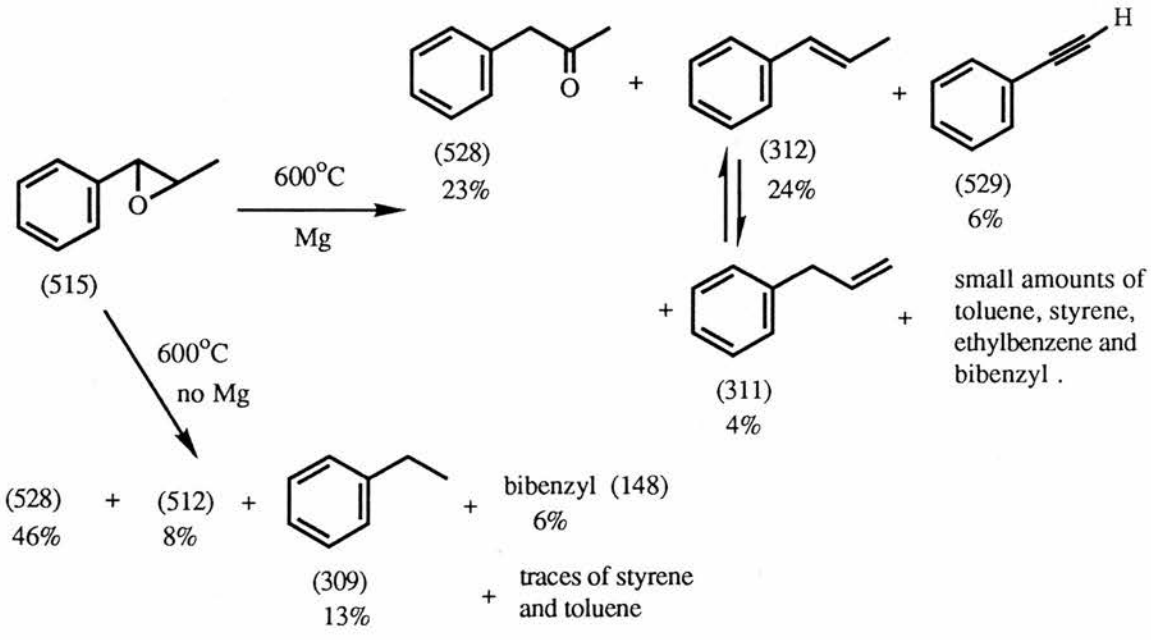


in 32% yield. Also present were 18% of α-methylstyrene(**314**), 13% of styrene(**193**) and 10% of acetophenone(**325**). The products obtained in the absence of magnesium were 54% of 2-phenylpropionaldehyde(**512**), 34% of styrene(**193**) and 11% of acetophenone(**325**). The rearrangement to (**512**) and fragmentation, involving the loss of formaldehyde to (**193**) and the loss of a methylene group to (**325**) are obvious thermal processes and were the predominant reaction paths with or without magnesium. Only α-methylstyrene(**314**) seems to be a magnesium-induced product. Lack of readily accessible hydrogens precludes the dehydration process noted with the other epoxides. A mechanistic route to the product is suggested below.

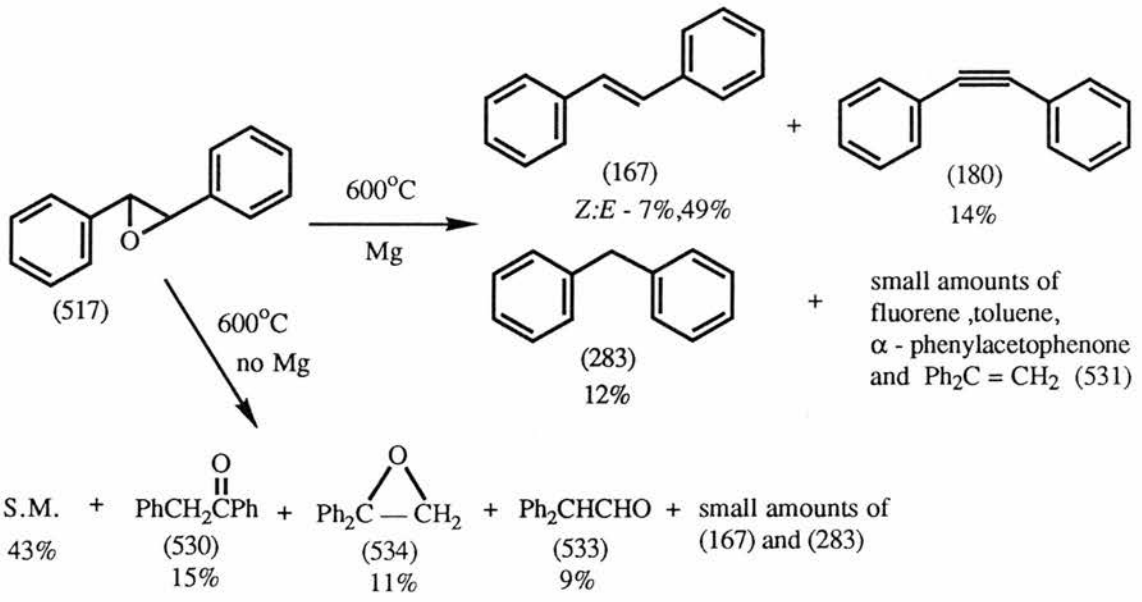


A similar reaction was observed with 1,2-epoxy-1-phenylpropane (**515**). The products obtained when pyrolysed over magnesium were 23% of rearrangement product 1-phenylpropan-2-one (**528**), 24% of β-methylstyrene (**312**) and 4% of 3-phenylprop-1-ene (**311**) both products of deoxygenation. The only other major product was 6% of dehydration product 1-phenylpropyne(**529**). The other products were small amounts

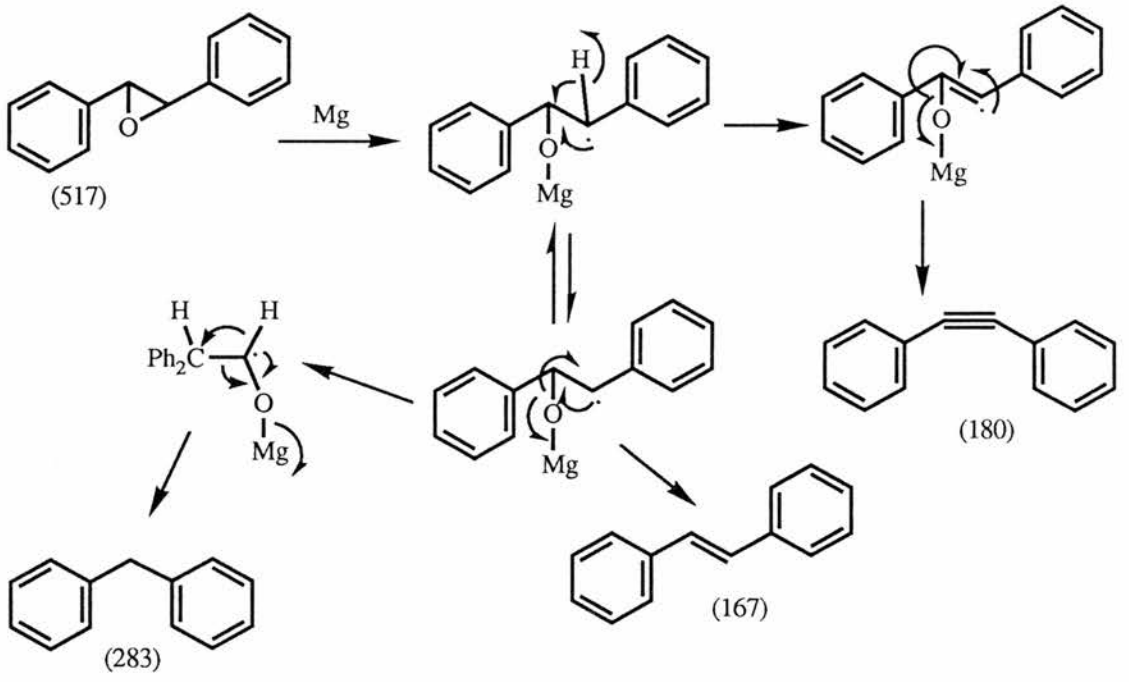
of toluene, styrene, ethylbenzene and bibenzyl. In the absence of magnesium, the products obtained were 46% of 1-phenylpropan-2-one (**528**), 13% of ethylbenzene(**309**), 8% of 2-phenylpropanal(**512**) and 6% of bibenzyl(**148**), with trace amounts of styrene and toluene. The formation of both (**528**) and (**512**) suggested a 1,2-phenyl or 1,2-methyl shift occuring in addition to the earlier proposed 1,2-hydrogen shift. The thermal isomerisation of (**312**) and (**311**) has been confirmed in an earlier experiment during the course of this investigation.



The last epoxide investigated was stilbene oxide(**517**). When (**517**) was pyrolysed over magnesium, the major products were 56% of deoxygenation products, *Z*-and*E*-stilbene(**167**), 14% of dehydration product diphenylacetylene(**180**) and 12% of decarbonylation product, diphenylmethane(**283**). The other products obtained in small amounts were α-phenylacetophenone(**530**), fluorene, toluene(**297**) and 1,1-diphenylethene(**531**). The pyrolysis in the absence of magnesium gave about 43% unchanged starting material, with three rearrangement products α-phenylacetophenone(**530**), 1,1-diphenylethylene oxide(**532**)

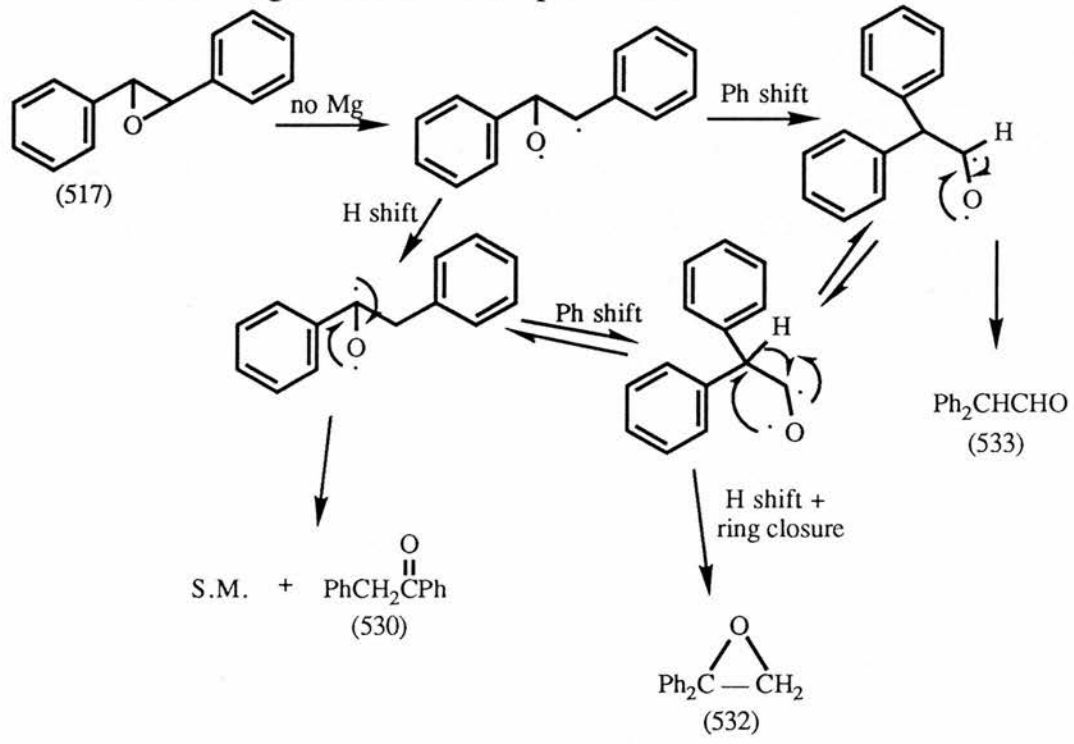


and 1,1-diphenylethanal(**533**) in 15%, 11% and 9% yields respectively. Also present were small amounts of stilbene and diphenylmethane.



The pyrolysis of (**517**) in the presence of magnesium led mainly to the magnesium-induced processes of deoxygenation and dehydration to give (**167**) and (**180**) respectively. The role of magnesium in the formation of (**283**) in unclear, although it was presumably attached in some form to oxygen prior to decarbonylation. In the absence of magnesium, rearrangement gave the carbonyl compounds (**530**) and

(**533**), but the formation of (**532**) suggested the epoxide ring closure after 1,2-hydrogen or -phenyl shift. A mechanism is proposed for both the thermal and magnesium induced processes.



For all the epoxides investigated, the main reaction in the absence of magnesium was the known rearrangement to give the carbonyl compounds presumably *via* the diradical formed on epoxide ring opening. Some thermal fragmentation processes were also observed especially in the cases of (**516**) and (**526**), where elimination of stable small molecules was feasible. In the presence of magnesium, some of the thermal rearrangement products were still obtained but products which can only be directly attributed to the effect of the magnesium were also formed. In the case of (**513**) (**522**) and (**517**), the magnesium induced processes of deoxygenation and/or dehydration predominated. The dehydration process was more pronounced with aliphatic epoxides while the deoxygenation was more evident in epoxides containing aromatic groups. This was attributed to the greater availability of removable hydrogens in the former case than in the latter.

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