SYNTHETIC APPLICATIONS OF FLASH VACUUM PYROLYSIS

by

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Thesis presented for the degree of
MASTER OF PHILOSOPHY

University of St. Andrews January 1994

Dedication

To Tracy.

Declaration

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

Signed ..... Date 6th Jan 1994

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Lecture Courses

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ABSTRACT

The synthesis and flash vacuum pyrolysis (FVP) of a range of γ,δ-unsaturated-β-oxoalkylidenetriphenylphosphoranes has been used to generate conjugated enynes via the pyrolytic extrusion of Ph_3PO. The temperature dependance of this reaction has been studied and it has been established that FVP at 500 °C leads almost exclusively to the *E*-enyne while FVP at 700 °C leads to a mixture of both *E* and *Z* isomers. FVP of the ylides at higher temperatures has been found to initiate cyclisation reactions to form 2-vinylnaphthalenes and related products from 2-methyl cinnamoylalkylidenetriphenylphosphoranes and the mechanism of this reaction has been investigated by a deuterium labelling study. A further secondary thermal process of the ylide bearing 2-methoxyphenyl and cinnamoyl groups leads by a tandem cyclisation to a mixture of isomeric benzofurans.

FVP of a range of simple acetylenic esters has been examined and the fragmentation patterns observed are consistent with formation and intramolecular insertion of vinylidene carbenes.

The application of FVP over magnesium to aldehydes and ketones has been examined and is found to result in deoxygenative coupling in the former case and dehydration to give alkynes in the latter, although low yields and mixtures of products produced mean the process is unlikely to be synthetically useful.

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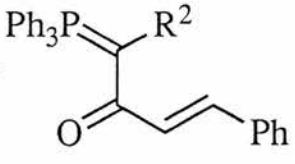
Preparation of 

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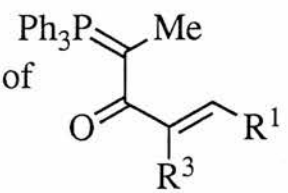
Preparation of 

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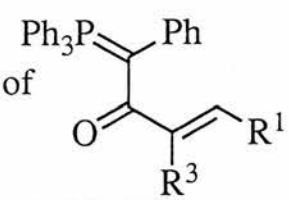
Preparation of 

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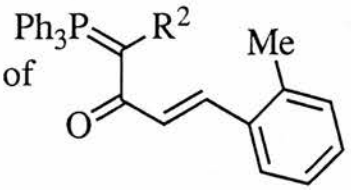
Preparation of 

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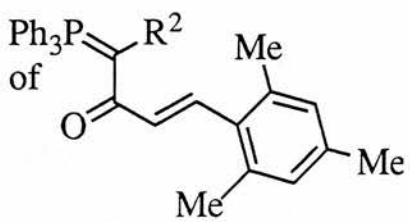
Preparation of 

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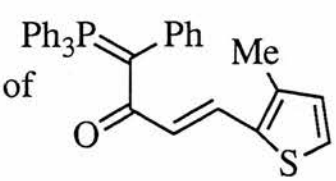
Preparation of 

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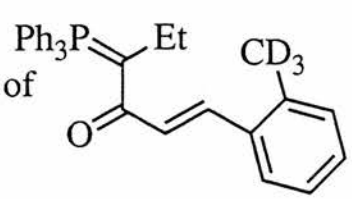
Preparation of 

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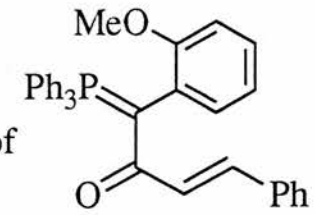
Preparation of 

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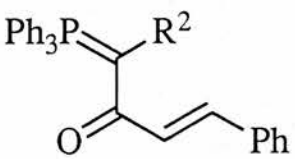
FVP of 

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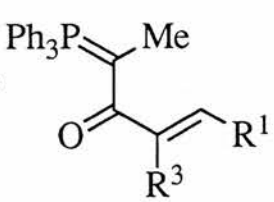
FVP of 

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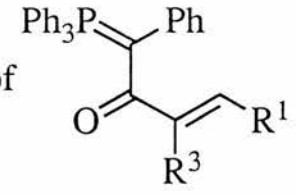
FVP of 

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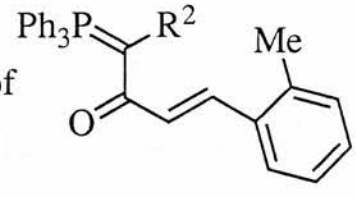
FVP of 

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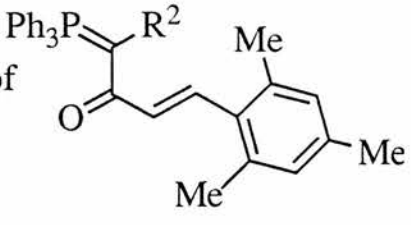
FVP of 

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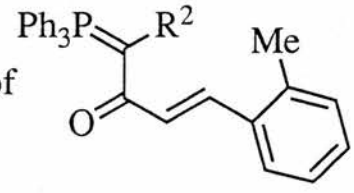
FVP of 

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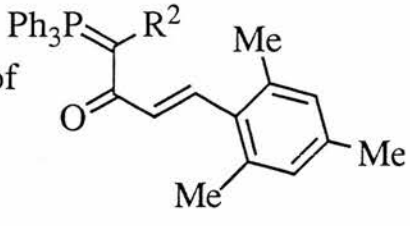
FVP of 

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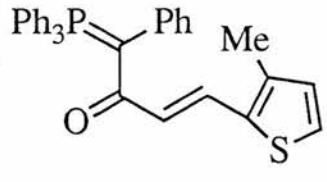
FVP of 

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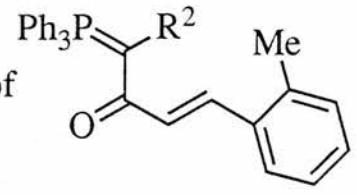
FVP of 

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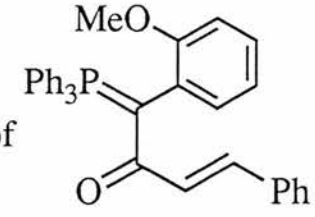
FVP of 

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INTRODUCTION

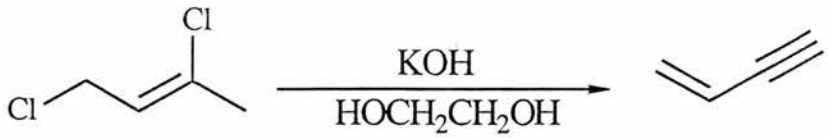
A. Preparation of alkynes and enynes.

In his book 'Chemistry of acetylenes'[1] Viehe gives a comprehensive account of the synthesis and reactions of the carbon-carbon triple bond. For the synthesis of these compounds two reactions are of primary importance, elimination and substitution. With the exception of acetylene and propyne, which are available from carbides, electric arc processes and cracking processes, every alkyne must be generated by an elimination reaction. Subsequent substitution reactions may then be used to further construct the synthetic target. The synthetic target discussed in detail in this account is the conjugated enyne and its many precursors.

Conjugated enynes are components of many natural products and as such are important intermediates in synthesis. The enyne function can be stereoisomeric with respect to the *E* and *Z* isomers and as the activity of many natural products is dependant on a set conformation, a major advantage is found in stereoselective synthesis.

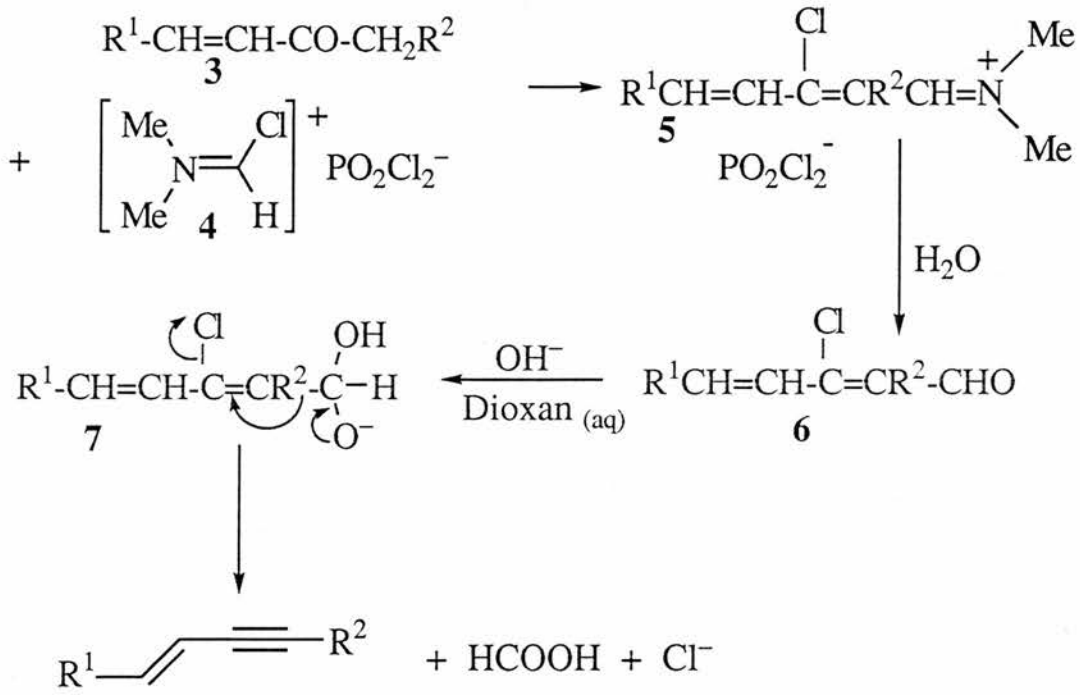
1. Synthesis of conjugated enynes by elimination reactions.

Among the many routes to the acetylenes, the dehydrohalogenative elimination reaction has been found to be the most important in terms of utility and convenience. The reaction is not without some particular drawbacks, among which the most serious is the need for strong bases to accomplish the elimination, an obvious disadvantage where base sensitive groups are present. The route does however afford a valuable synthesis of simple enynes exemplifed by Hennion *et al* 's[2] preparation of vinylacetylene **2** from 1,3-dichlorobut-2-ene **1**.



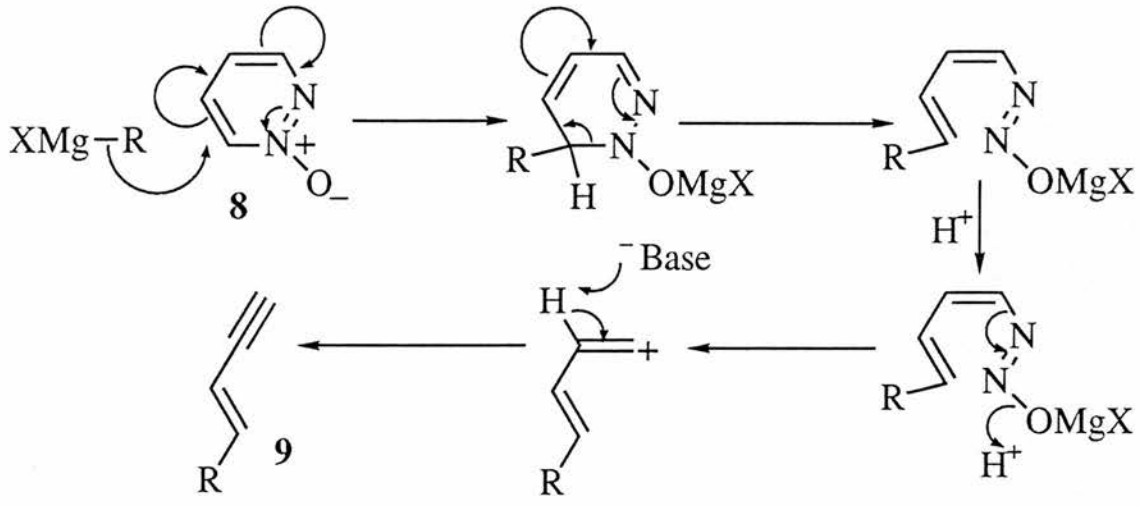
1 **2** 50%

A more versatile route for the formation of terminal acetylenes[3] and enynes involves deformylation of the products formed by the reaction of Vilsmeier reagent with α,β-unsaturated ketones.



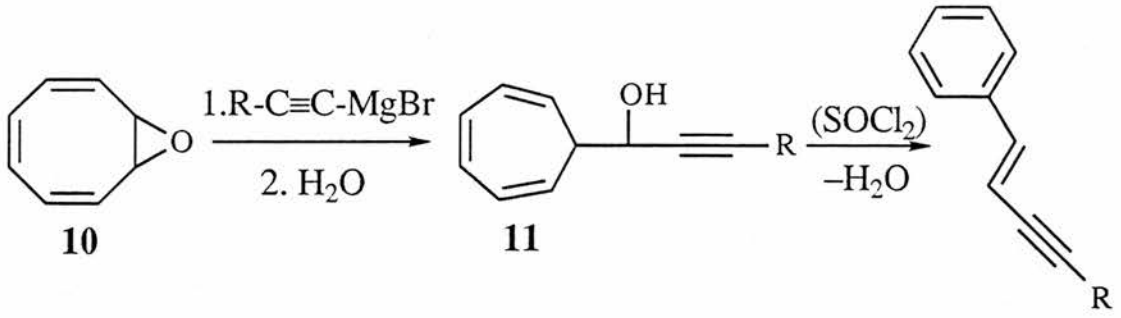
The first step involves the reaction of Vilsmeier reagent[4] **4** with an α,β-unsaturated ketone **3** to give an immonium salt **5** which hydrolyses on addition of water to give the corresponding γ,δ-unsaturated-β-chloroacrolein.**6** It is assumed that the initial step in the deformylation involves an attack on the carbonyl carbon by a hydroxyl anion to give **7** which then breaks apart by the mechanism shown. In many but not all cases the reaction to give alkynes only proceeds where R_2 is hydrogen. In Bodendorf's paper concerning enynes[5] only the terminal products are sought and no examples of attempts to use any R^2 substituent other than H are cited.

A quite elegant route to terminal 1,3-enynes first examined by some Japanese workers[6] and later developed by Pattenden[7] involves the action of a Grignard reagent on pyridazine-1-oxide **8**.



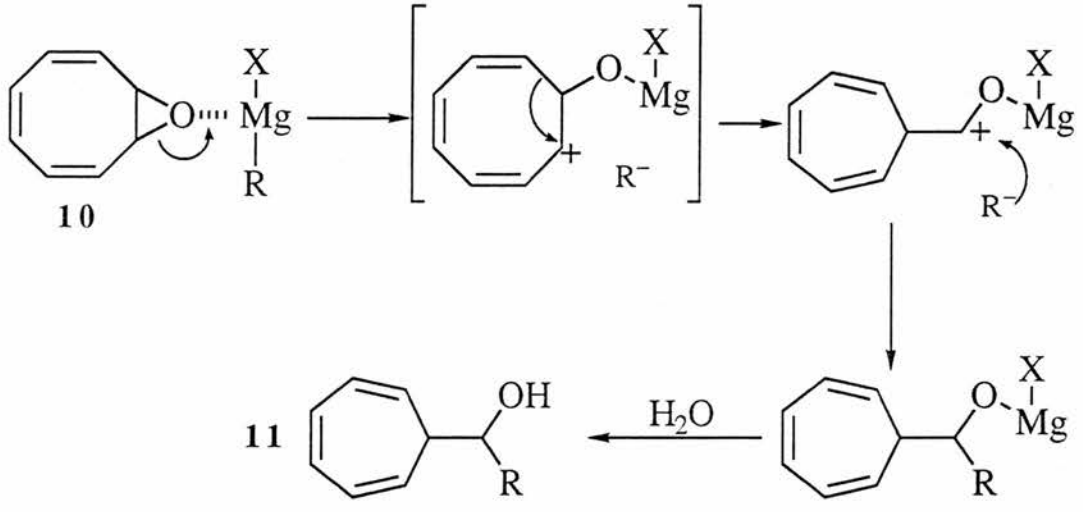
This ring opening reaction gives specifically the *E*-enyne **9** in 52-77% yields for the examples studied. Importantly, the reaction was found to be useful in the formation of enynes from relatively electrophilic Grignard reagents with the more nucleophilic alkyl Grignards leading to the corresponding 1,3-dienes rather than the enyne. A further interesing feature of the reaction is the possibility of constructing further enyne functionalisations by a two step procedure. To illustrate this an *E,E*-dienediyne was prepared by first reacting PhMgBr with **8** to give styrylacetylene **9**, R = Ph. This was then converted to the corresponding Grignard reagent by reaction with ethyl magesium bromide and reacted a second time with **8** to give finally *E,E*-1-phenylocta-1,5-diene-3,7-diyne **9**, R = PhCH=CH-C≡CH in 21% yield.

From a ring fragmentation above we will now consider a ring contraction as a novel route to styrylalkynes. Müller *et. al.*[8] reported a route to these compounds via 7,8-epoxy-1,3,5-cyclooctatriene.



10 **11**

The first step in this rather unusual transformation from **10** to **11** is believed to be due to the magnesium from the Grignard reagent acting as a Lewis acid to catalyse the ring contraction viz:-



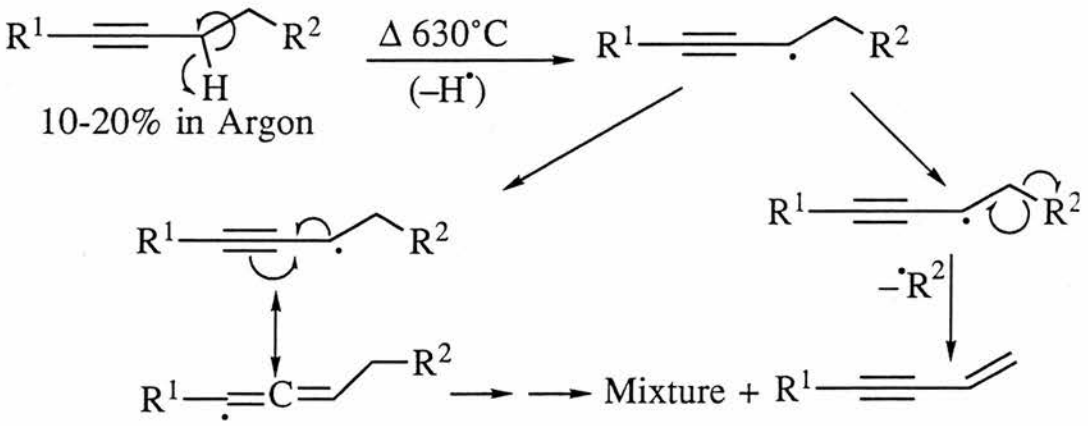
10 **11**

This mechanism is in agreement with the findings of Ganellin and Pettit[9] and Matsuda and Sugishita[10], the latter group confirming the structures of some 2,4,6-cylcoheptatrienyl carbinols prepared by the Grignard reaction.

The styryralkynes are produced by the route shown in overall yields of 39-64% and only in cases where R is alkyl are mixtures of the *E* and *Z* isomers found. For all others cited only the *E* isomer of the products was formed.

Zimmerman *et al* [11] describe an unusual route to conjugated enynes via the high temperature pyrolysis of alkynes. Alkynes of various R^1 and R^2 chain lengths were subjected to high temperatures for short periods of

time in an inert atmosphere and the products studied. The main conclusion found was that the loss of hydrogen radical was more likely to occur on the R group with the greatest number of carbon atoms ie. from R^2 in the following scheme:

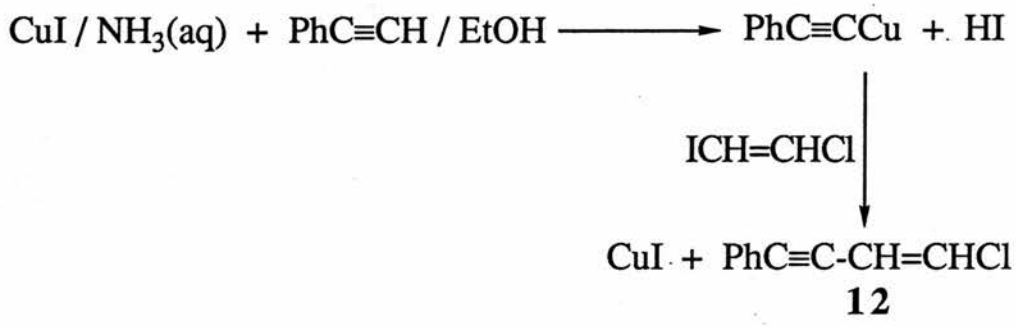


The reaction is of more mechanistic than preparative interest since the yields are low and many side reactions take place as would be expected by this radical route.

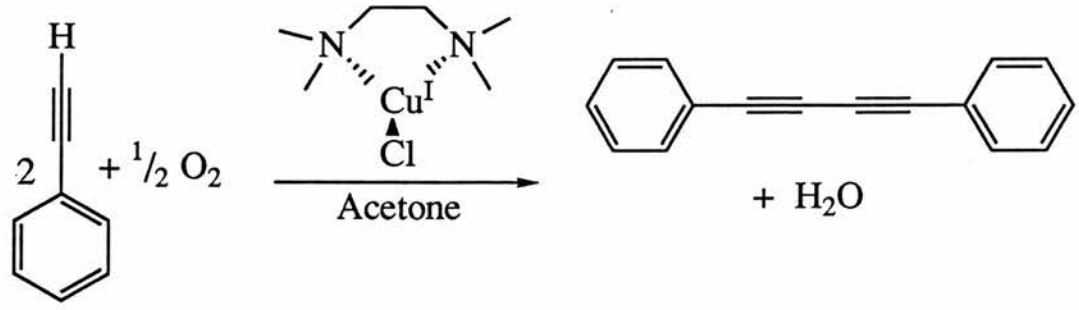
2. Substitution reactions of alkynes as a route to enynes.

One of the most common current methods for the synthesis of diynes and polyynes is an adaptation of the oxidative cross coupling of alkynes first noted by Glaser[12] in 1870. In a review of the area Raphael[13] translates his first account to say that "Oxidation with air of an ammoniacal alcoholic solution of the copper derivative of phenylacetylene resulted in a smooth coupling reaction to yield diphenyldiacetylene." Later accounts[14] report the copper derivative of phenylacetylene to be a canary yellow solid isolable in high yield and claim that this and other such isolable copper acetylides readily react with aryl halides to give diarylacetylenes and with

halo alkenes to give enynes[15]. The following example shows the formation of 1-chloro-4-phenylbut-1-en-3-yne **12**.

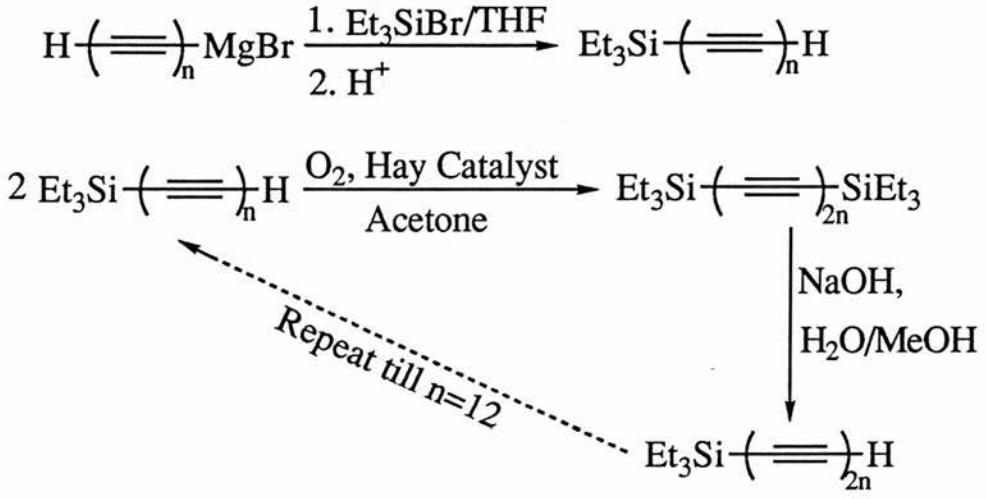


Oxidative coupling was investigated by Eglinton and Galbraith[16] as a route to macrocyclic acetylenic componds. From this study they found that copper (II) acetate in methanol / pyridine solution was an effective oxidative coupling reagent in catalytic quantities, however for general preparative purposes it was more convenient to use an excess of the reagent due to the slow reaction rate. Hay[17,18] studied this type of reaction with a selection of copper based catalysts. He established the stoichiometry of the reaction by measuring the absorbtion of oxygen then further used this parameter to establish the relative rates of the oxidative coupling achieved by three different catalysts. The best one found was copper(I)chloride-N,N,N',N'-tetramethylethylenediamine which, in time, became known as the "Hay catalyst". An example of this reaction is shown below:-



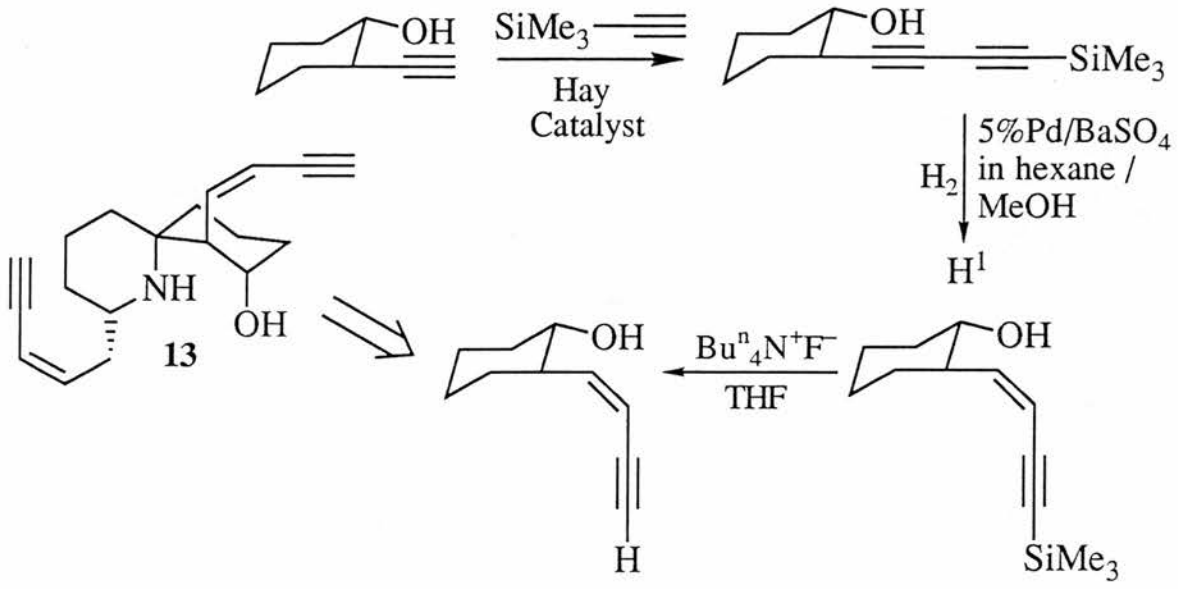
In an attempt to access poly-ynes by oxidative coupling using Hay's catalyst and acetylene[19] the reaction products were found to be polymeric

species as a result of uncontrolled chain growth. The best way to avoid this is to apply an easily removable protecting group to one end of the alkyne undergoing coupling. Walton[20] *et al.* successfully obtained a dodecayne using a stepwise synthesis detailed below. The silyl protecting groups employed stopped the uncontrolled chain growth leading to respectable yields of well defined products for each step. On top of this a single silyl group could be removed by a partial cleavage reaction using very dilute base and an excess of the disilylacetylene.



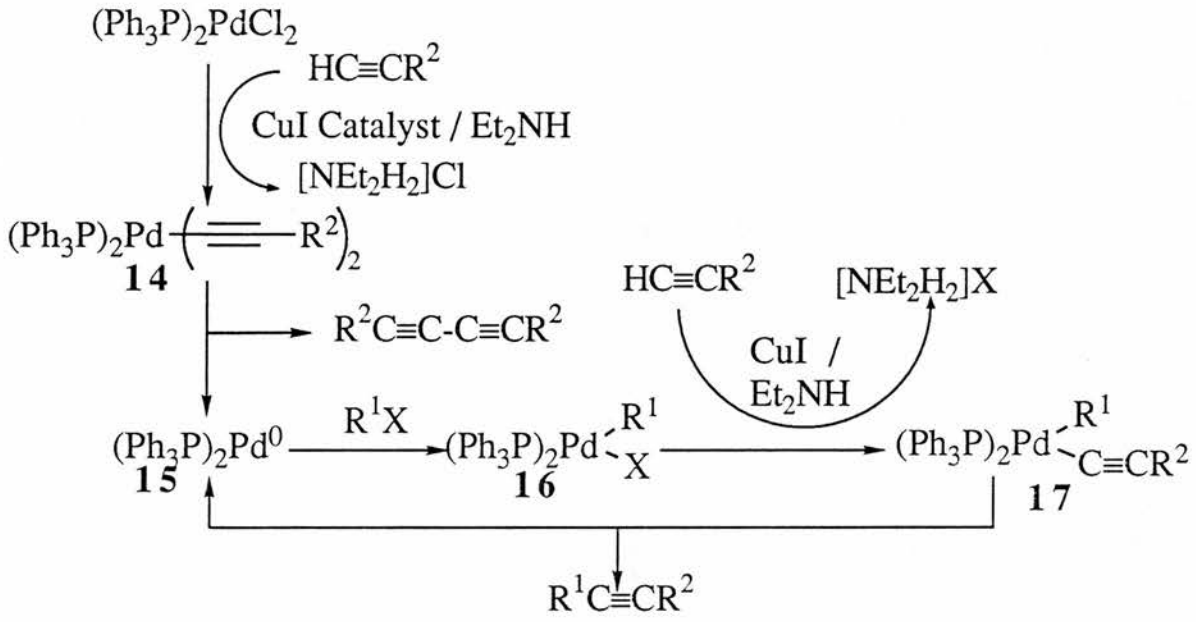
An important consquence of the use of silyl protecting groups is that they block hydrogenation reactions at the α,β-alkyne bond. This effect ensures that hydrogenation of a subsequent conjugated alkyne bond on the chain will result in the enyne of a configuration determined by the hydrogenation catalyst employed. This route was successfully followed by Raphael[21] in pursuit of a stereoselective synthesis of terminal *Z*-enynes as a precursor to the natural product histrionicotoxin **13**. Starting from trans-2-ethynylcyclohexanol, oxidative coupling with trimethylsilylacetylene using Hay's catalyst gave the trimethylsilylbutadiynylcyclohexanol. Hydrogenation of this compound over 5% Pd on $BaSO_4$ containing

quinoline gave the silylated *Z* -enyne in 65% yield with 15% unreacted starting material as the only other identifiable component.



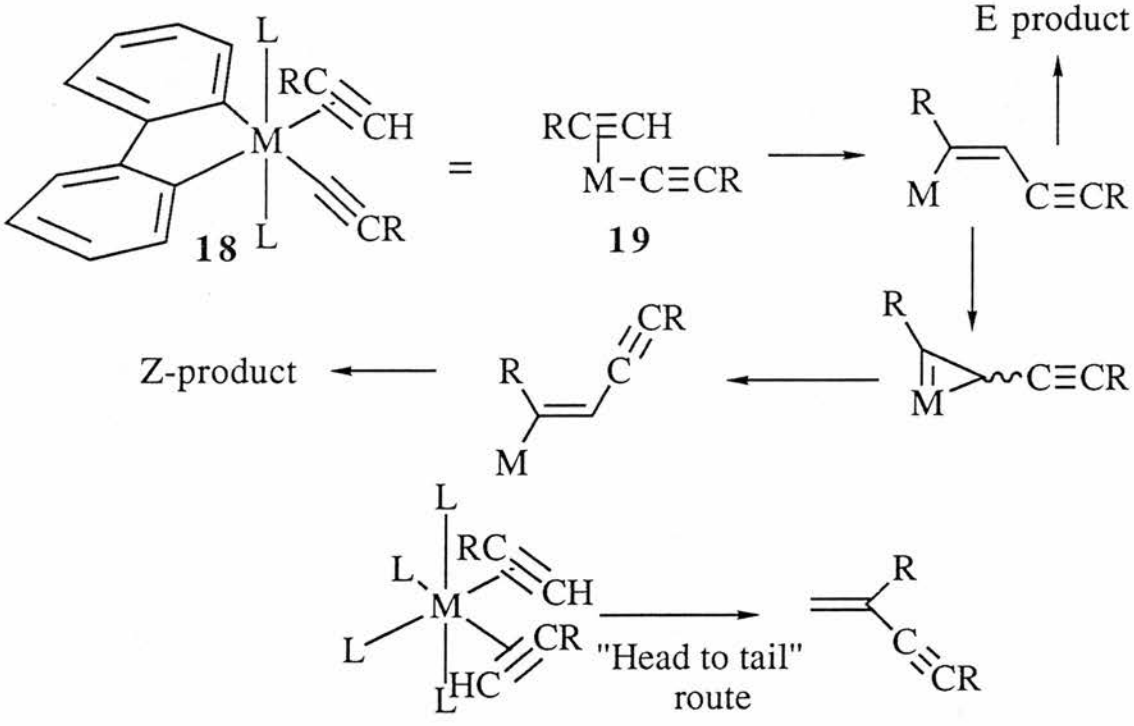
The technique of oxidative coupling has been developed with the introduction of many new catalysts and systems involving co-catalysts. These reactions can be very complex and in many cases[22,23,24] the conditions are carefully tuned to give the best results from particular catalyst systems. One very versatile system which contains the key elements of most of these reactions is described by Sonogashira.[25] This deals with the general case of catalytic substitutions of acetylenic hydrogen with bromoalkanes, iodoarenes and bromopyridines. Generally the complete reactions can be achieved by stirring for 3 to 6 hours at room temperature a mixture of terminal acetylene and organohalide with cuprous iodide co-catalyst in the presence of a catalytic quantity of bis(triphenyphosphine)palladium dichloride. The yields are good to excellent and a tentative mechanism has been put forward involving initial formation of bis(triphenyphosphine)dialkynylpalladium (II) **14** which gives a catalytic species bis(triphenyphosphine)palladium(0) **15** through a reductive elimination of 1,4-diphenylbutadiyne. Subsequent oxidative

addition of aryl or vinyl halide followed by an alkynylation of the adduct **16** to give an aryl or vinyl-alkynyl derivative of palladium **17** which easily regenerates the original bis(triphenyphosphine)palladium(0) by reductive elimination of the substitution product.

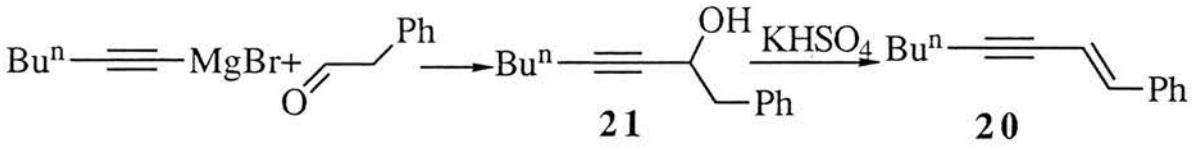


Sonogashira noted the retention of configuration of the haloalkynes used to produce enynes by this method and later adaptation of the conditions[26] resulted in improved product yields, especially on coupling to *Z*-alkenes which originally gave the most disappointing yields. Other catalysts such as iridium biphenyl-2,2'-diyl tris-trimethylphosphine chloride[27] have been shown to give stereoselective head to head alkyne dimerisation according to the reaction conditions and the steric bulk of the substrate alkynes. Such action is of great interest as this shows potential to build specific stereochemistry on dimerisation. The careful design of catalyst allows for end on metal coordinaton of one alkyne and a side on metal-alkyne π system bond to the other. The coupling effect and the configuration of the catalyst **18** are believed to be as shown. This configuration **19** should lead to the "head to head" dimerisation observed

in the products while other catalysts[28] supporting two metal-alkyne π system bonds commonly give "head to tail" dimers. Stereoselectivity is believed to be controlled by the relative coordination of the PMe_3 ligand to the metal which in turn is controlled by concentration of this ligand and the silver fluoroborate co-catalyst. The PMe_3 coordination is believed to suppress the formation of the intermediate vinyl complex leading to an excess of the *E*-enyne while adding a great excess of silver fluoroborate to suppress PMe_3 coordination can lead to exclusive formation of the *Z* -isomer.

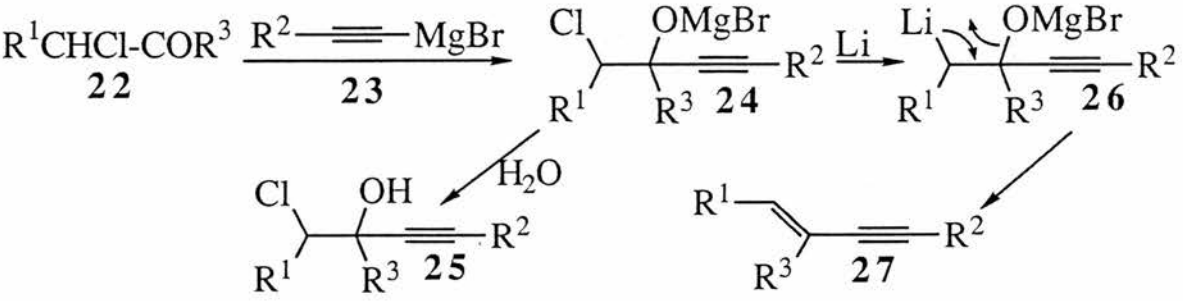


Other methods for the preparation of conjugated enynes have been developed from more conventional organic chemistry. In a typical example in the course of the synthesis of a model for agropyrene, 1-phenylocten-3-yne **20** was formed via 1-phenyloct-3-yne-2-ol **21** generated by the Grignard synthesis[29].



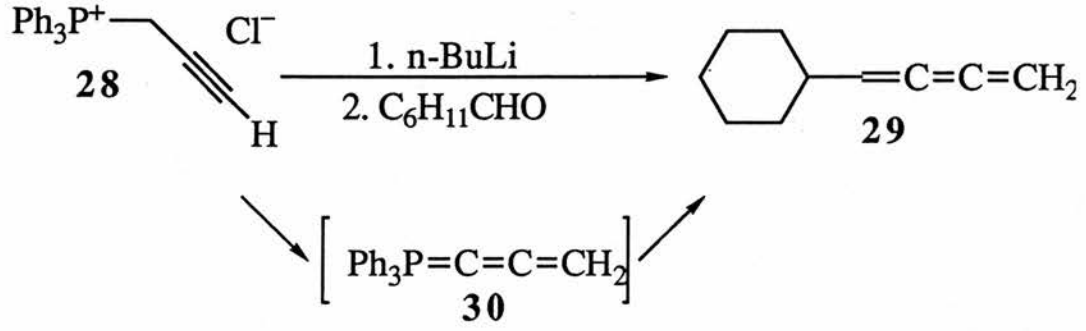
The configuration of this and other enynes prepared were unspecified in this account. More recent and more compex Grignard procedures have been shown to yield mixtures of *E* and *Z* enynes, a good example being the versatile synthesis reported by Barluenga *et. al.* in 1985.[30] Here an α-chloroaldehyde or ketone is reacted with an acetylenic Grignard reagent **23** to give the intermediate **24** which may be characterised by hydrolysis to the corresponding chlorohydrin **25**. Reaction of **24** with lithium powder should yield the unstable β-substituted organolithium compound **26** which undergoes spontaneous β-elimination to form the enyne **27**.

In practice the reaction must be carried out at –78 °C to avoid interaction between the lithium powder and the observed products. However, at such a low temperature the chlorine-lithium exchange is unsatisfactory or does not occur to any extent. Resulting yields on switching to lithium naphthalide or in some cases lithium-1-dimethylaminonaphthalide were in the order of 50-80% at this low temperature but at greatly increased cost to the procedure.

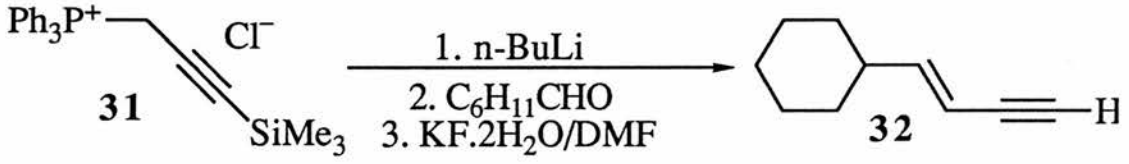


Corey[31] investigated the Wittig reaction as a means of alkene formation for stereoselective synthesis of enynes. Earlier work[32] had

uncovered that only conjugated aldehydes were suitable substrates for Wittig condensation with the propargylidene triphenyphosphorane derived from **28**, the reagent of choice for enyne synthesis. Unconjugated aldehydes were found to give unstable cumulenes **29** possibly via isomerisation of **28** to **30**.

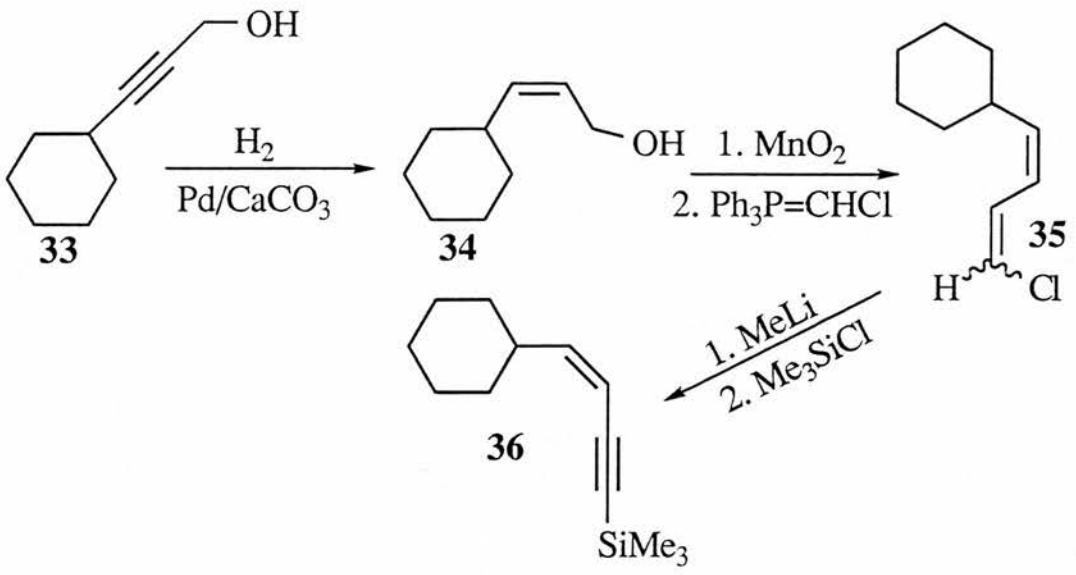


To avoid this side reaction the terminal trimethylsilyl propargylic phosphonium salt **31** was prepared with the intention of stabilising the ylide.

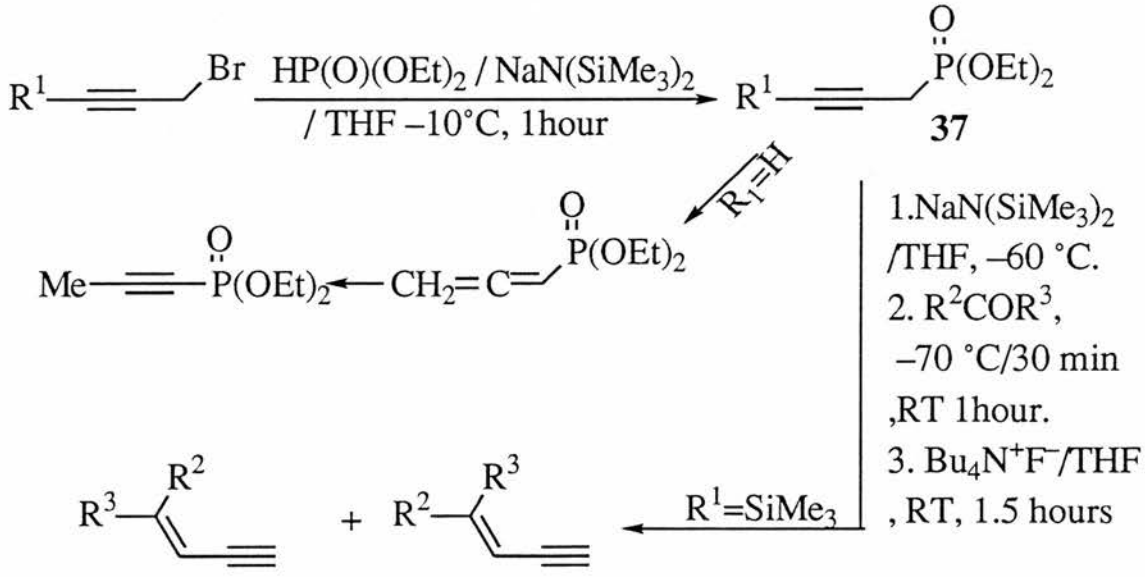


Reaction as before with cyclohexane carbaldehyde yielded the desired *E* enyne **32** (E/Z >10:1) from which the TMS protecting group could be quantitatively removed on addition of an excess of potassium fluoride dihydrate in DMF.

A more complex procedure is described to obtain the *Z* enyne. Here propargylic alcohol **33** was reduced to the *Z* allylic alcohol **34** in 98% yield. Oxidation gave the sensitive conjugated *Z* adehyde which was immediately treated with chloromethylenetriphenylphosphorane to give the chlorodiene **35** as a mixture of *E* and *Z* isomers. This in turn was treated with methyl lithium in THF to effect dehydrohalogenation then quenched after 12 hours with trimethylsilyl chloride to give the *Z* enyne **36** in 57% overall yield.



Further work on the Wittig synthesis by Wright *et. al.*[33] lead to the application of the Horner-Wadsworth-Emmons variant[34]. Here diethyl (3-trimethylsilyl-2-propynyl) phosphonate **37** was prepared as a reagent to construct a variety of terminal enynes from aromatic aldehydes and aromatic and aliphatic ketones. Again, isomerisation results upon use of the unsilylated ylide, in this case to give the 1-propynylphosphonate, but the derivatised ylide gives good yields of the enynes.

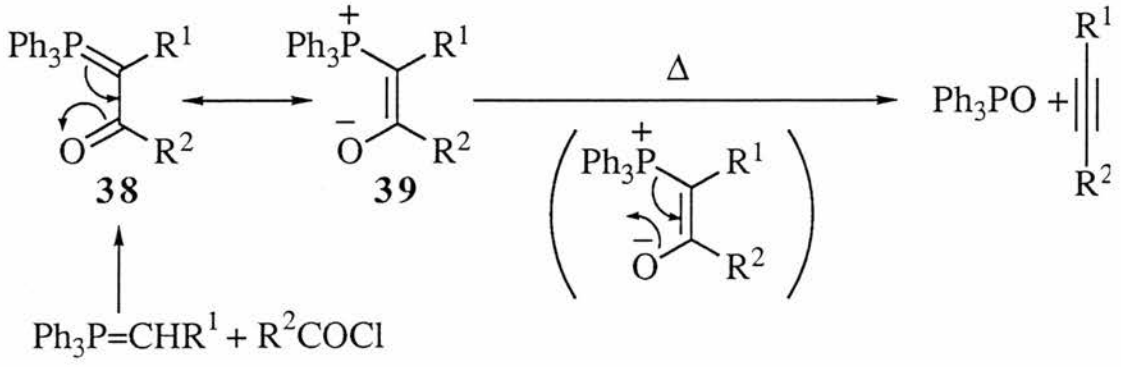


3. Preparation and pyrolysis of β-Oxoalkylidenetriphenylphosphoranes as a route to alkynes and enynes.

Traditional pyrolysis reactions usually involve prolonged exposure times to high temperatures often giving rise to low yields or tarry residues. The development of Flash Vacuum Pyrolysis is one solution to finding a more subtle technique and here reactions are carried out in the gas phase at very low pressures and high temperatures. This gives rise to very short exposure times reducing side reactions and resulting in cleaner products.

In his monograph, Brown[35] gives a thorough examination of the scope of pyrolytic experiments and the methods used. For this work the more important processes involve the generation of transient and highly reactive molecules. These are conveniently generated by the high temperature fragmentation / extrusion from the parent to yield very stable molecules such as N_2, C_2H_4, CO_2, SO_2 and most importantly Ph_3PO.

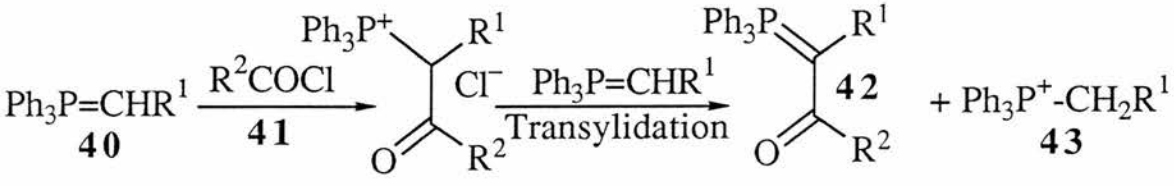
The extrusion of phosphine oxide from β-oxoalkylidenetriphenylphosphoranes **38** via conventional pyrolysis has long been known as a route to alkynes, the first recorded example being that of Trippett and Walker's preparation of diphenylacetylene in 1959.[36]



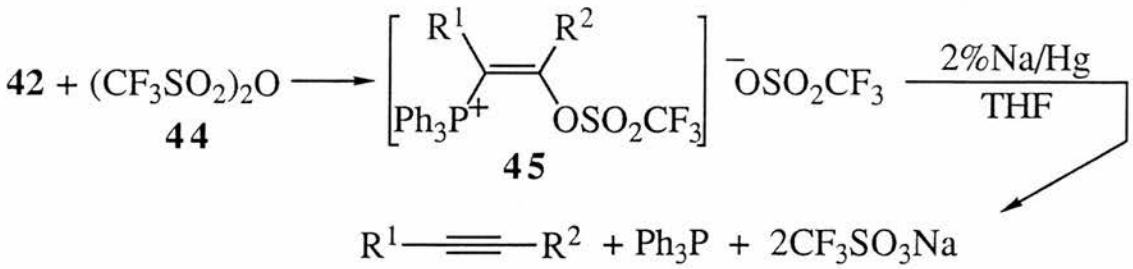
In this instance α-benzoylbenzylidenetriphenylphosphorane **38** (R^1 and R^2 = Ph) was heated to 300 °C for 30 minutes at one atmosphere to yield phosphine oxide and the acetylene quantitatively. This method was also reported by Märkl[37] as providing a good general synthesis of acetylenic esters for $R^1 = CO_2Me$.

Further work by Trippett and Walker[38] revealed that the reaction works best when at least one substituant is an electron withdrawing group (CO_2Et or CN) or otherwise capable of stabilising the phosphonium enolate **39** eg. a phenyl group. On attempting pyrolysis where both substituents were alkyl groups very low yields of the desired acetylenes were observed and strong allenic absorbtions were found in the infrared spectra of the products.

More recently Bestmann[39] described an indirect method to produce aliphatic alkynes from the oxoylides in cases which were unsuccessful using Trippett's pyrolysis method. The preparation of the oxoylides involves treatment of ylides **40** with acid chlorides **41** in a transylidation reaction[40] to give the acyl ylide **42** together with an equivalent of the phosphonium salt **43**.

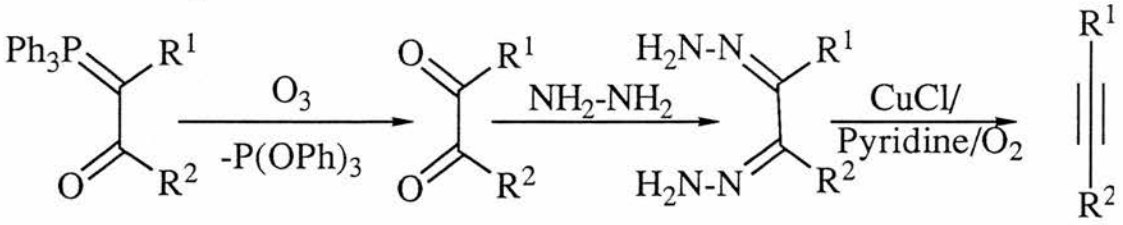


For conversion of **42** to the alkyne Bestmann's synthesis relies on the action of trifluoromethanesulphonic anhydride **44** to provide triflates **45**. These are then reduced by sodium amalgam to release the alkyne, triphenylphosphine and sodium triflate.



Although the above synthesis involves an extra step compared to the pyrolytic extrusion of triphenylphosphine oxide and uses expensive trifluoromethanesulphonic anhydride, this may be recovered by regeneration from the sodium salt and the triphenylphosphine may also be extracted and reused. The extra step reduces the overall yield to only ≈20-40% in the examples cited and no attempts to produce a terminal alkyne using this method were reported.

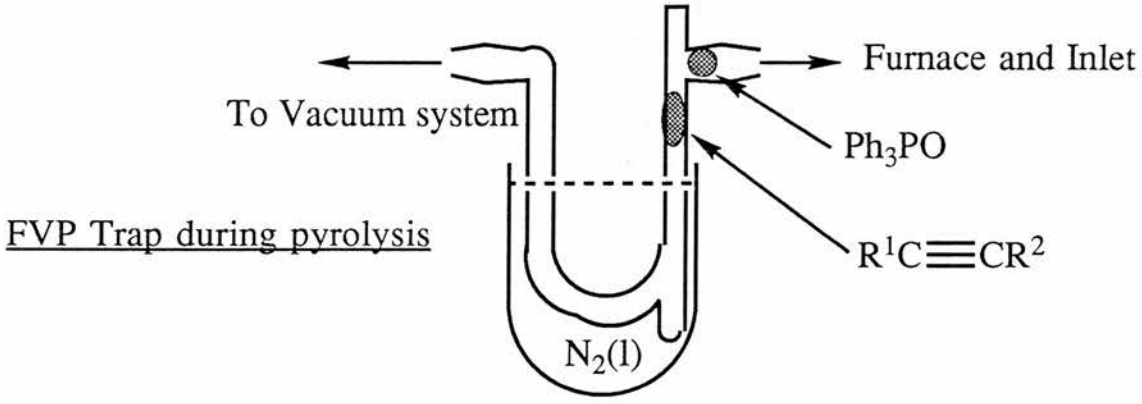
In a variant of the above method acetylenes have been generated via 1,2-diketones.[41] Here the acyl ylides are oxidised with the adduct of ozone to triphenyl phosphite to give the 1,2-diketones which are subsequently converted into the bis-hydazones. Oxidation with O_2/CuCl in pyridine yields the acetylenes.



The above synthesis served as a useful source of alkyl acetylenes however the two extra steps required (particularly the conversion to the diketone with yields of around 60%) compared to the pyrolysis route limited the yields obtained.

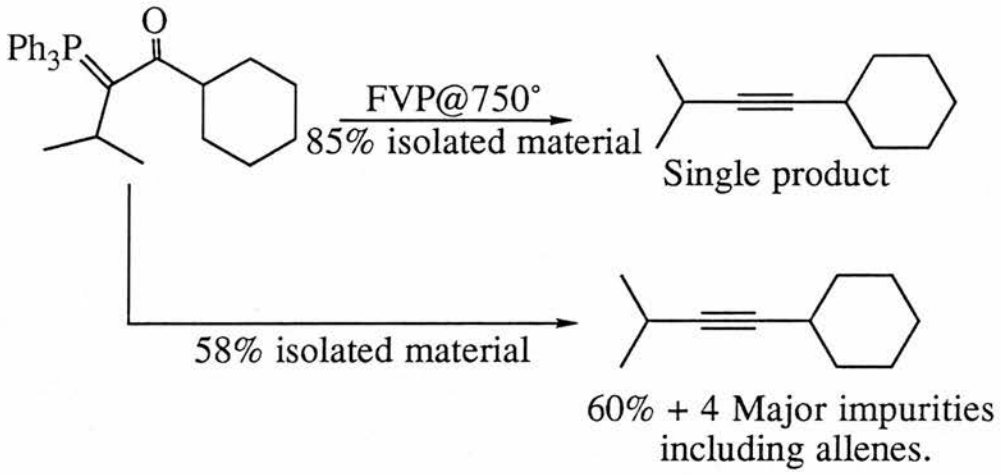
The first general synthesis of alkynes by triphenylphosphine oxide extrusion from β-oxoalkylidinetriphenylphosphoranes was reported from this laboratory in 1985.[42] It was found that flash vacuum pyrolysis of the acylated ylides described by Bestmann resulted in clean conversion to the

corresponding alkynes in good yield. Many examples of terminal alkynes (R^1=H) previously unavailable via pyrolysis were obtained in good yield and a further advantage lay in the collection of the products in the pyrolysis trap naturally separated from the phosphine oxide because of their greater volatility. This effect is illustrated below:-

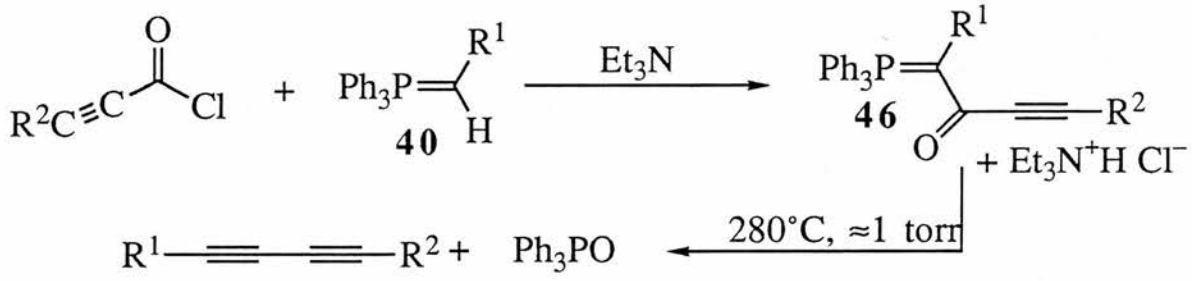


The pyrolyses were run at a pressure of 10^{-2} torr and a temperature of 750 °C. This high temperature was found to be necessary for complete conversion but the contact time in the hot zone at this low pressure was sufficiently short to afford a mild pyrolysis with no allenic by-products. Only one side reaction was observed occurring in cases where R^2 was a cyclobutyl group. The ring strain was relieved by extrusion of ethene to yield the vinyl alkyne in good yield at 750 °C with increasing proportions of the desired cyclobutyl alkyne found on reduction of the temperature. At 600°C a greater proportion of the cyclobutyl alkyne to the vinyl was found but this was amongst much unchanged starting material.

In a control experiment a β-oxoalkylidenetriphenylphosphorane with R^1=Pr^i and R^2=cyclohexyl was subjected to the FVP conditions and a reduced pressure distillation. The different results are illustrated:-



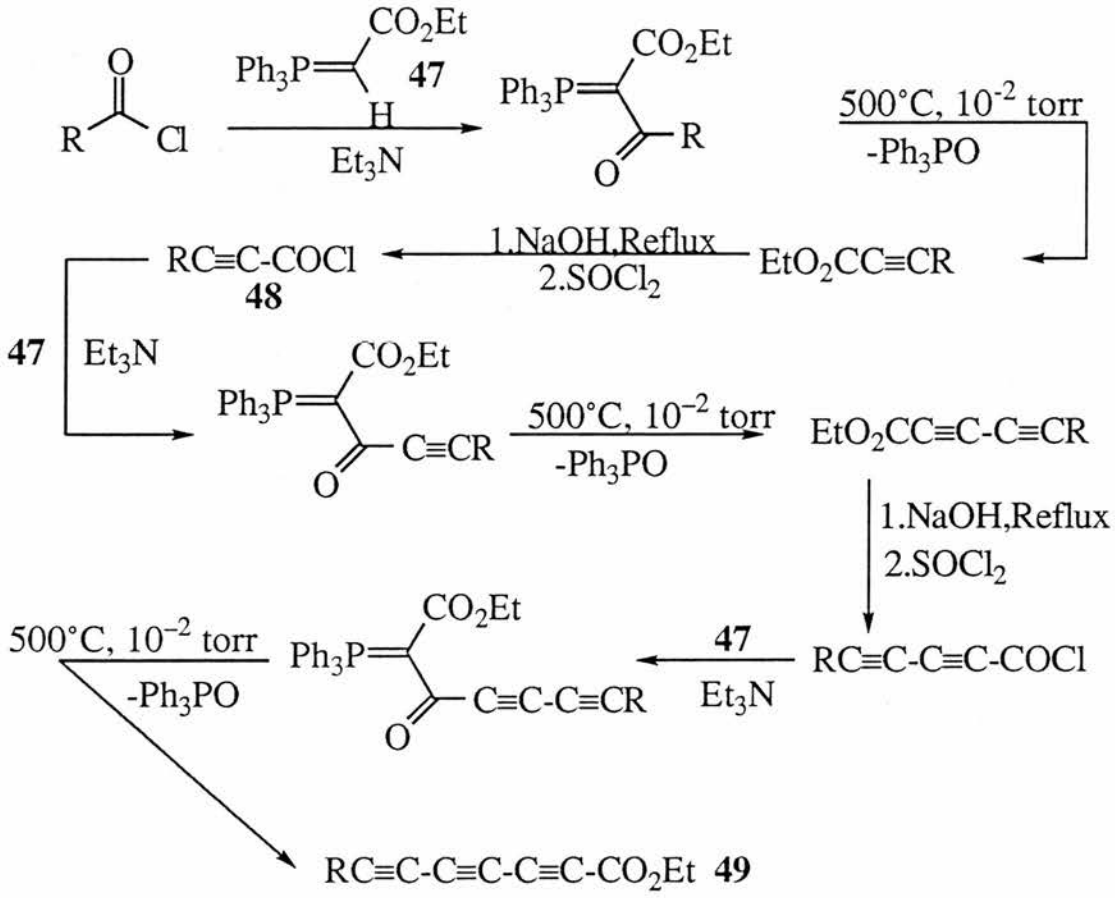
In an early investigation Trippett[43] used conventional pyrolysis in the synthesis of some diacetylenes. The study was limited to the pyrolysis of β-oxoalkylidenetriphenylphosphoranes with R^1= Ph, CN or CO_2Et to lend stability to the phosphonium enolate and in this case where the initial phosphorane **40** is less basic, one equivalent of triethylamine was used rather than a second equivalent of **40** to give the starting materials **46** for pyrolysis.



R^1	R^2	% Yield
CN	Ph	30
Ph	Ph	24
EtO_2C	Bu^n	16
EtO_2C	Ph	9

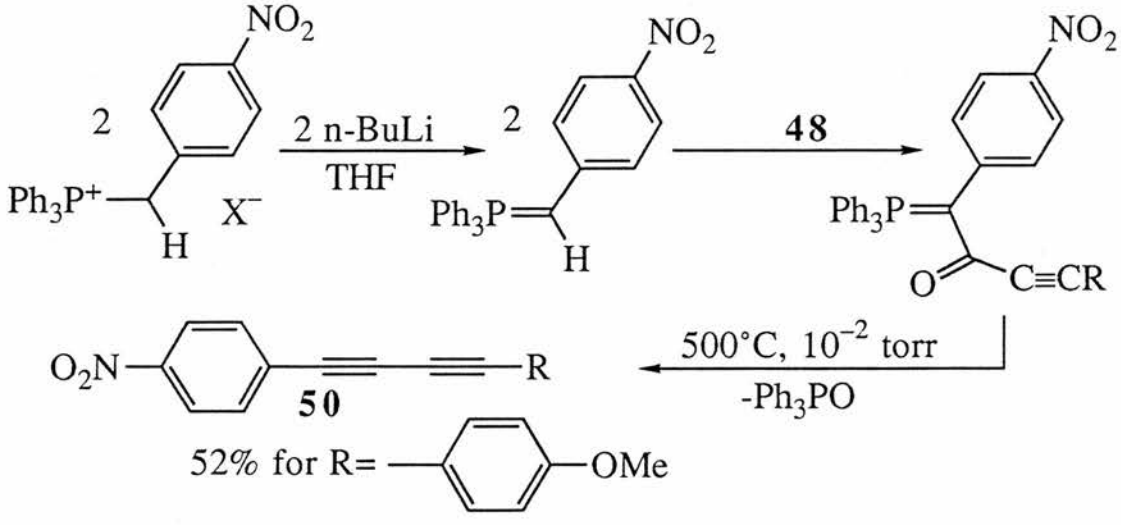
As shown the technique was successful in the formation of a range of diacetylenes but in moderate to poor yield.

In 1990 a report from this laboratory[44] described FVP of acetylenic ylides **46** (R^1= CO_2Et) to give diacetylenic esters in improved yield on pyrolysis at 500 °C at 10^{-1} to 10^{-2} torr. As a direct comparison 1-ethoxycarbonyl-2-oxo-4-phenylbut-3-yn-1-ylidenetriphenylphosphorane was prepared and pyrolysed to yield the ethyl 5-phenylpenta-2,4-diynoate in 88% yield. More importantly pyrolysis of the same starting material at 750°C and 10^{-1} torr gave 1-phenylbuta-1,3-diyne in 18% yield. This was presumed to be due to the fragmentation of the ethoxycarbonyl group into equivalents of ethene and CO_2. Many examples were cited to give a general two step conversion of acid chlorides to terminal alkynes and diynes and the convenience of the synthesis is enhanced by the commercial availability of the stable ethoxycarbonylmethylenetriphenylphosphorane **47** used as starting material.



Development of this synthesis led to a stepwise construction of conjugated diacetylenic and triacetylenic esters.[45] An acetylenic ester, $R(C{\equiv}C)_nCO_2Et$, may be converted to the acid by base hydrolysis then refluxed with thionyl chloride to produce the acid chloride ready for subsequent reaction with a further equivalent of **47**. Following pyrolysis this procedure may be repeated building up the alkyne chain.

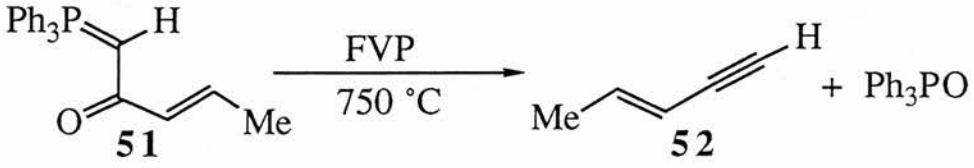
This route was found to be effective in the formation of diynes and in one case a triyne **49** (R = p-Me-C_6H_4). Typical overall yields for the diynes were in the order of 20-30% with the triyne precursor exceptionally good at this stage with a 62% yield. The overall yield of the triyne was a poor 19% and this reflects the sensitiviy of the polyynes which makes three conjugated alkyne bonds an upper limit for this synthesis. A versatile feature of the synthesis is the ability to produce a variety of unsymmetrical diynes by changing **47** for another ylide and undertaking an acylation reaction with **48**.



Some of the unsymmetrical diynes such as **50** produced by this method may be of interest in non linear optics as potential second harmonic generators as in this field 4-methoxy-4-nitrotolan,[46] an easily accessible alkyne, has been found to display excellent S.H.G. potential due to its large

transition moments. The variety of diynes accessible may provide materials with enhanced S.H.G. performance from the greater degree of inherent conjugation.

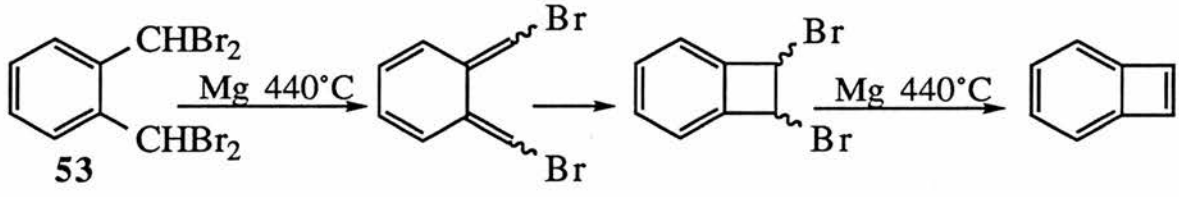
The success of alkyne formation on pyrolytic extrusion of triphenylphosphine oxide has also been applied to the production of a few conjugated enynes. Thus, for example, the original paper from this laboratory[42] included FVP of **51** to give pent-2-ene-4-yne **52** in 59% isolated yield.



51 **52**

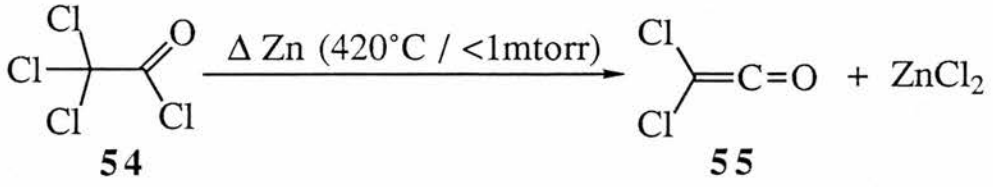
B. Flash Vacuum Pyrolysis over solid reagents.

FVP over solid reagents is an underexploited field which promises to offer many synthetic possibilities both in the generation of reactive intermediates and as a general preparative method. The technique normally uses a metal reagent which is heated under vacuum either in the form of finely divided powder or sublimed over some support in the vacuum system. By these methods zinc[47], silver[48] and magnesium have been found to offer dehalogenative activity resulting in reactive intermediates which rearrange to unstable compounds. A good example is given by Koenig et al.[49] in the preparation of benzocyclobutadiene. This is achieved by FVP over magnesium of α,α,α',α'-tetrabromo-*o*-xylene **53** through the following process:-



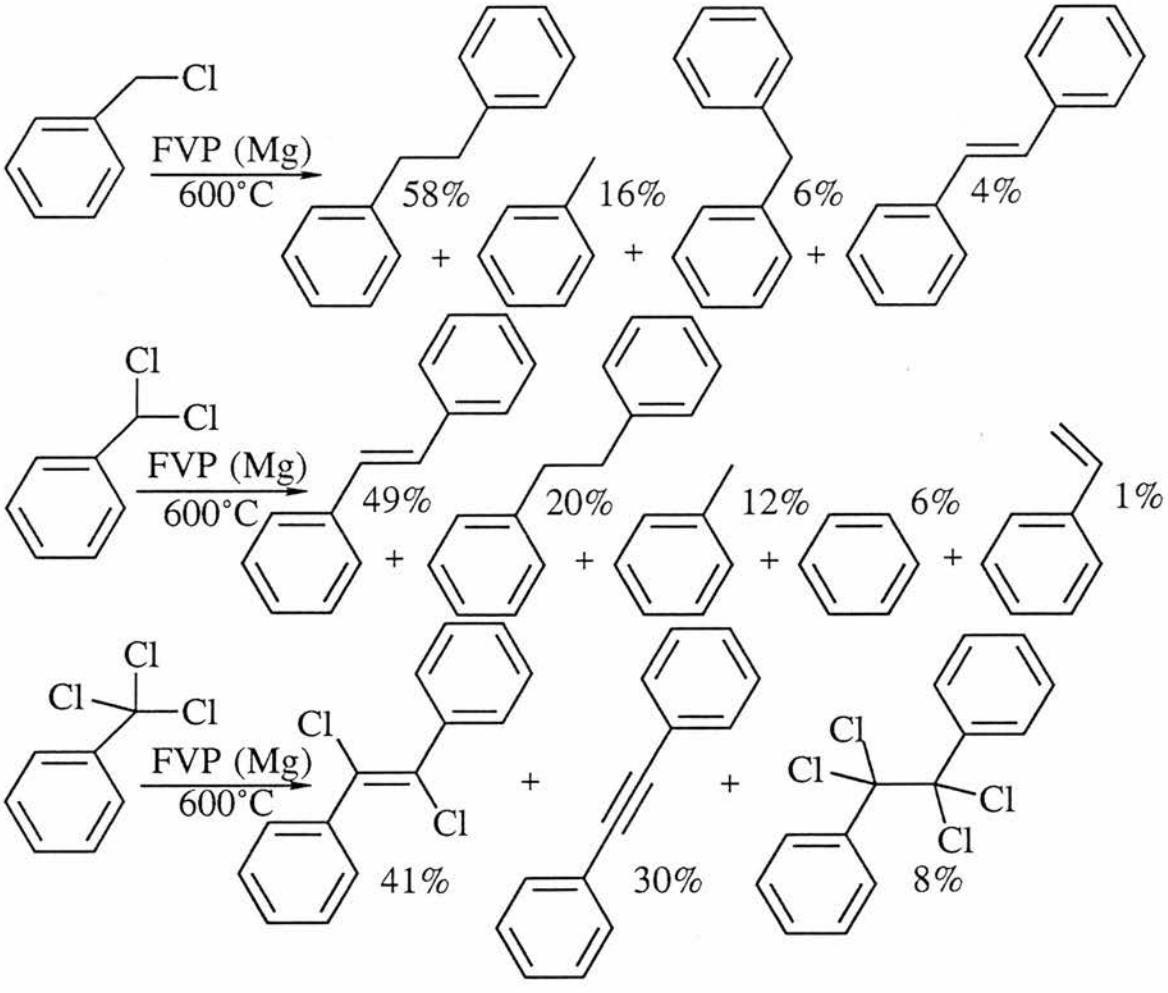
Benzocyclobutadiene is a very reactive species which otherwise could not be directly observed. Its convienient preparation in the vacuum system allowed direct spectroscopic observation which would be extremely difficult by any other means.

A further example of the generation and spectroscopic detection of an unstable species by pyrolysis over zinc is given by Hargittai *et al* [50] in their study of dichloroketene. The dichloroketene **55** is produced in a high vacuum environment on the entrance to an electron diffraction instrument. This is achieved by releasing trichloroacetyl chloride **54** into a heated tube containing zinc metal connected to the sample nozzle of the instrument. **54** reacts with the zinc in a dehalogenation reaction to supply **55** directly to the diffraction chamber.



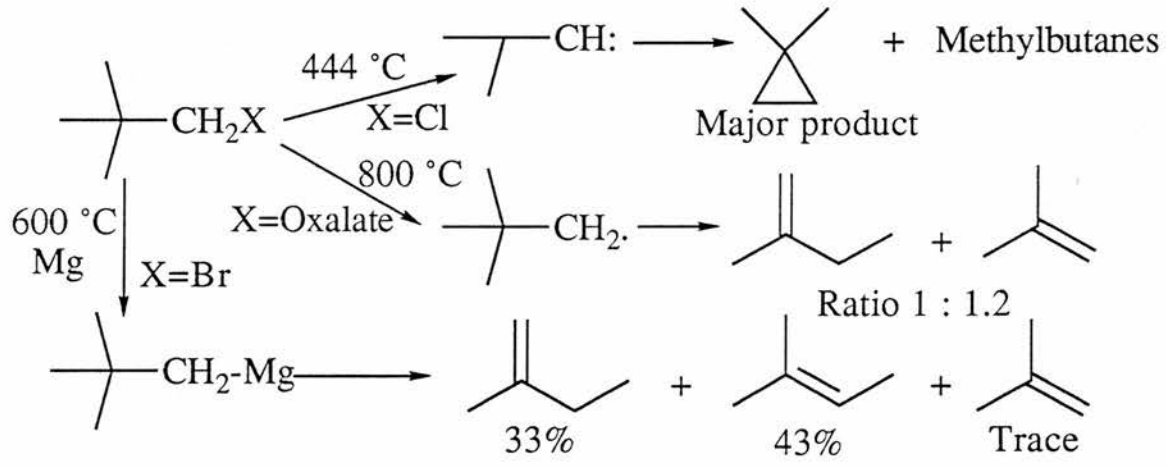
54 **55**

In an extensive study of the synthetic applications of flash vacuum pyrolysis over magnesium, Oyewale[51] investigated the pyrolytic behaviour of some 120 organic compounds using the technique. One of the most common observations was the formation of dimerised products as a result of the dehalogenation reactions. This is clearly demonstrated in the following examples of the pyrolysis of benzylic halides.

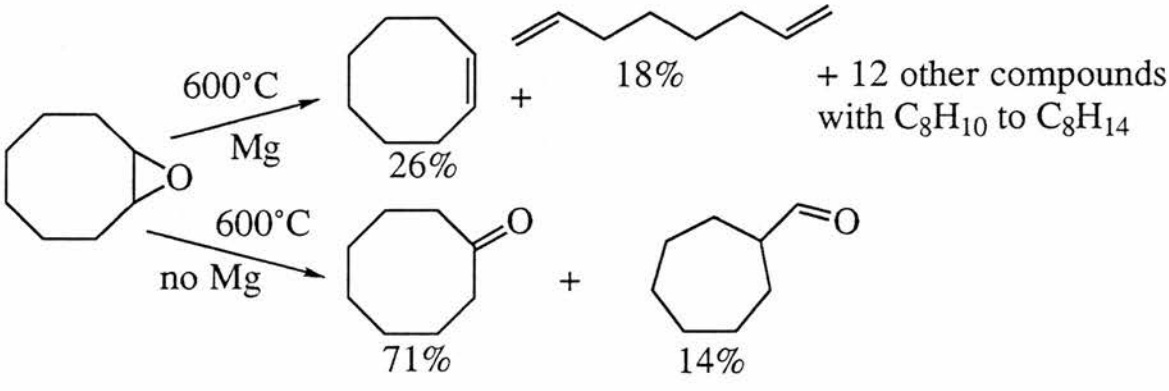


Since almost all of the observed products result from dimerisation, two possible important processes are bimolecular reaction in the gas phase

or the cold trap or active coupling on the magnesium surface. The surface coupling hypothesis is most likely since most FVP reactions involve unimolecular processes due to the low pressures employed. Evidence for such coupling is provided by the unusual products found from the pyrolysis of neopentyl bromide over magnesium. In this case the products observed were mainly 2-methylbut-1-ene and 2-methylbut-2-ene. Such a mixture is not observed from either a carbene[52] or radical[53] pathway but may be explained as having occurred through a metal surface elimination process as shown below.

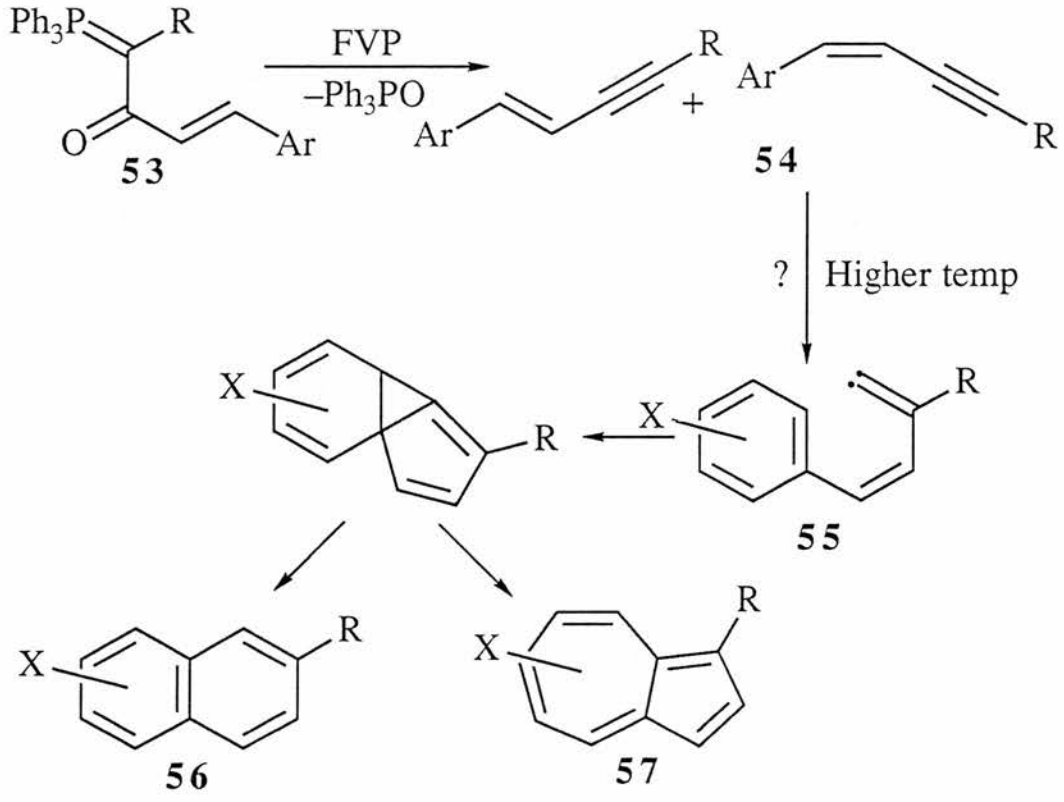


Along with organic halides the action of magnesium on some epoxides was studied and this led to the discovery that the magnesium also possessed some deoxygenative activity as illustrated with cyclooctene oxide.



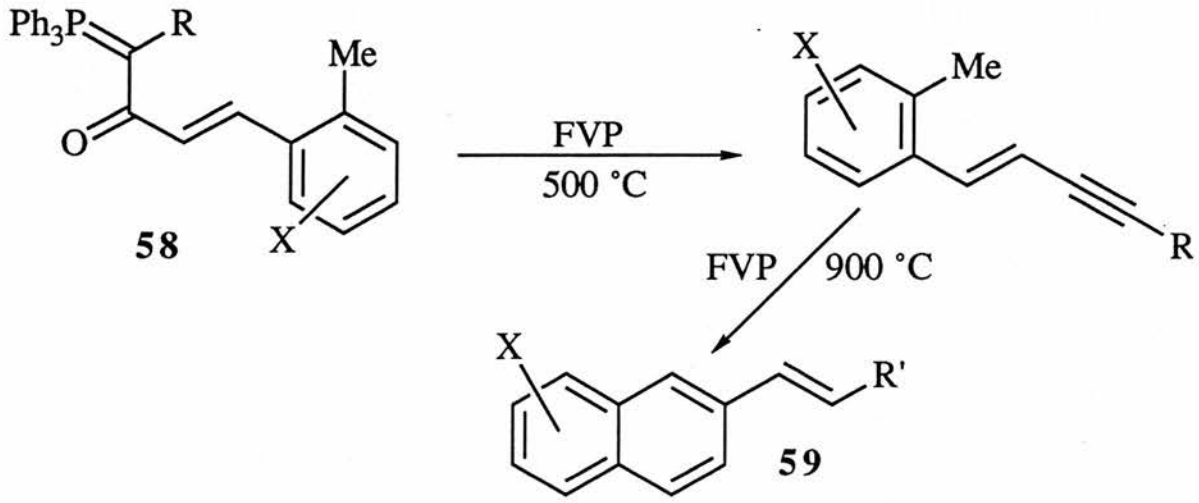
C Programme of Research

The main objective of the present work was to examine in detail the pyrolysis of a range of γ,δ-unsaturated-β-oxoalkylidine triphenylphosphoranes **53**. In a previous preliminary study in this laboratory,[54] Boeters had prepared a wide range of ylides **53** but their pyrolysis had only been attempted in a few cases. As already mentioned pent-2-en-4-yne **52** was obtained from FVP of **51** in 59% yield. It was expected that **53** would likewise provide access to a wide range of conjugated enynes **54** and it was of particular interest to see whether control of the *E* / *Z* ratio of the products could be achieved by adjusting the pyrolysis temperature.

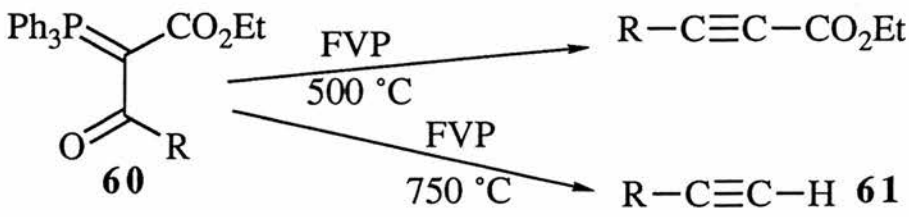


It was originally expected that the enynes might undergo further reaction on increasing the furnace temperature by rearrangement to styrylvinylidene **55** which could then add as shown and provide useful syntheses of substituted naphthalenes **56** and azulenes **57**. However the

preliminary work on this had proved disappointing but did lead to the discovery of an unexpected new reaction - the formation of vinylnaphthalenes **59** on pyrolysis of ylides **58** in which the aryl group contained an o-methyl substituent. The mechanism of this novel transformation was to be examined in detail.



A second area involves the unexpected loss of the whole ethoxycarbonyl group observed on increasing the temperature of pyrolysis of ylides **60** from 500 °C to 750 °C to give terminal alkynes **61**.[44]



The mechanism of this apparently novel process was unclear and it was hoped that pyrolysis of a range of different acetylenic esters might help to clarify the mechanism.

Finally, it has been mentioned that pyrolysis over magnesium was previously found to give useful and sometimes unexpected products from a wide range of halogenated substrates.[51] In that study, epoxides were also examined and some deoxygenation was observed. It was now planned to examine a range of carbonyl compounds in this system for the first time in the hope that deoxygenation might afford a gas phase equivalent to the McMurray reaction.

EXPERIMENTAL

A Symbols and Abbreviations

mmol	millimoles
M	mol dm^{-3}
h,min	hours, minutes
GCMS	gas chromatography-mass spectrometry
TLC	thin layer chromatography
NMR	nuclear magnetic resonance
δ	chemical shift
J	spin-spin coupling constant
4ry	quaternary
br, s, d, t, q, m	broad, singlet, doublet, triplet, quartet, multiplet
ν_{max}	infra-red absorbtion frequency
λ_{max}	ultraviolet / visible absorbtion frequency
MS	mass spectrometry
m/z	mass to charge ratio
M^+	mass of molecular ion
FVP	flash vacuum pyrolysis
mp	melting point
bp	boiling point
ether	diethyl ether
THF	tetrahydrofuran

B Instrumentation and General Techniques

1 N.M.R. 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 WP80 or at 200 MHz on a Varian Gemini 200. High resolution spectra were obtained at 300 MHz on a Bruker AM-300 spectrometer operated by Mrs M Smith.

b ^{13}C NMR

Spectra were obtained at 75 MHz on a Bruker AM-300 spectrometer operated by Mrs M Smith and at 50 MHz on a Varian Gemini 200.

c ^{31}P NMR

Spectra were obtained at 32 MHz on a Varian CFT-20 and a Bruker WP-80 or at 121 MHz on a Bruker AM-300 spectrometer operated by Mrs M Smith.

d ^{2}H NMR

Spectra were obtained at 46 MHz on a Bruker AM-300 spectrometer operated by Mrs M Smith.

All spectra were obtained from solutions in deuteriochloroform except where indicated otherwise and chemical shifts are expressed in parts per million to high frequency of tetramethylsilane.

2 Infrared Spectroscopy

Spectra were obtained on a Perkin-Elmer 1420 ratio recording spectrophotometer or on a Perkin-Elmer 1710 fourier transform spectrophotometer. Solution spectra were run in methylene chloride or deuteriochloroform using matched sodium chloride cells of path length 0.1mm. Spectra were calibrated with the polystyrene peak at 1603 cm^{-1}.

3 Mass Spectrometry

Accurate mass measurements were obtained on an A.E.I. M.S.-902 instrument and mass spectra obtained on a Finnigan Incos 50 mass spectrometer, both operated by Mr C Millar.

4 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. Mass spectra obtained were matched against the mass spectra of authentic samples.

5 Elemental Analysis

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

6 Melting points

Melting points, both routine and for new compounds were determined on a Reichert hot-stage microscope. All melting points are uncorrected.

7 Thin Layer Chromatography

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

8 Preparative Thin Layer Chromatography

This was carried out using 1.0 mm 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 methylene chloride for 30min.

9 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.

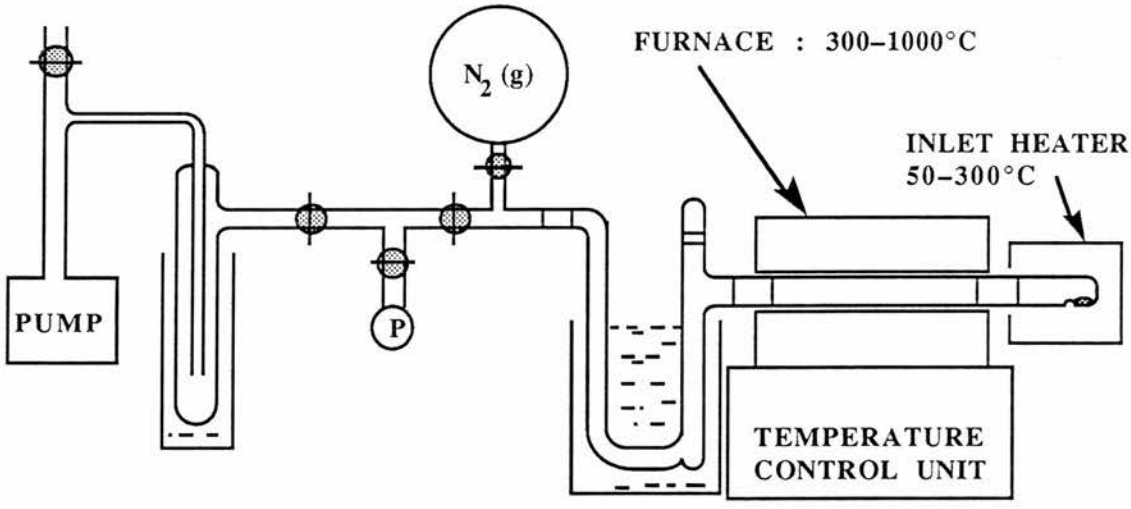
10 Drying and Purification of Solvents

Commercially available solvents were used without further purification unless otherwise indicated. Dry ethyl acetate was prepared by storing over molecular sieves. Dry toluene was prepared by the addition of sodium wire. Extra dry THF was prepared by preliminary drying with sodium wire and then distilling from potassium benzophenone ketyl. Dry dichloromethane was distilled from phosphorus pentoxide and stored over molecular sieves. Triethylamine was dried by heating under reflux with potassium hydroxide for 2 h then distilling onto molecular sieves. A commercial solution of n-butyl lithium in hexanes was used. Where necessary, the strength of this solution was checked by titration with diphenylacetic acid under nitrogen.

11 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.[35] The essential features of the apparatus are shown below. The

sample was volatilised from a horizontal inlet tube, heated via an external heat source, through a 30 x 2.5 cm silica tube. This was heated at temperatures in the range of 300–1000 °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 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^{-2} to 10^{-3} Torr 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 1–10 ms.

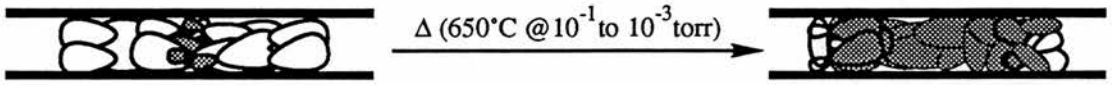


The pyrolysis conditions are quoted thus: "(weight of material volatilised, furnace temperature, pressure during the pyrolysis, inlet temperature)".

12 Flash Vacuum Pyrolysis over Magnesium

Further considerations to those above must be taken into account when a solid reagent such as magnesium is used and these are related to the effective surface area of the reagent and the handling of what is a highly

air and moisture sensitive material at the operational temperature. For this purpose a standard quantity of magnesium (about 1.5 g) was used for almost all pyrolyses and the sample mass was generally kept down to a scale that ensured at least a 10 fold molar excess of magnesium to oxygen or halogen. This quantity of Grignard grade magnesium was sandwiched into the centre of the pyrolysis tube with glass wool then heated under vacuum (10^{-1} - 10^{-3} Torr) to 650 °C for 15 minutes. Under these conditions the magnesium sublimed over the glass wool to form a very large active surface area ready for the pyrolysis reaction.



Mg turnings sandwiched by glass wool

Resublimed magnesium available for gas phase reaction at 600°C

Once the magnesium was sublimed, the furnace temperature was reduced to the pyrolysis temperature. For almost all of the experiments run this was set to 600 °C. The apparatus was then purged with nitrogen and a stopper at the inlet end was replaced with the sample tube. The system was then re-evacuated and a liquid nitrogen filled Dewar placed around the U-shaped trap.

Depending upon the volatility of the sample, an inlet heater was used to slowly drive the sample into the gas phase whereupon the resultant vapours passed through the pyrolysis tube where they underwent reaction. The products were collected in order of increasing volatility down the trap.

13 Pyrolysate collection.

The pyrolyses were judged to be complete when only relatively involatile residues remained in the inlet tube after prolonged heating.

The pyrolysate was observed in either crystalline or liquid form between the trap inlet and the exit from the Dewar of liquid nitrogen. The

Dewar was removed and the system purged with nitrogen gas. The bulb on top of the trap was removed and any highly volatile products found at the bottom of the trap could be quickly dissolved in a suitable solvent such as deuterated chloroform to preserve them at room temperature for analysis by NMR.

Less volatile products that remain solid at room temperature appeared in bands down the trap in order of their relative volatilities. These were conveniently separated by individually washing them down with solvent and collecting the solutions by pipette. The individual yields of these components were estimated by either weight after evaporation of the solvent or by ^1H nmr integration on addition of a known quantity of a suitable solvent from CH_2Cl_2 (δ_H 5.3), $MeNO_2$ (δ_H 4.3) or $(CH_2Cl)_2$ (δ_H 3.7); the choice being dependant on obtaining a clean baseline on the ^1H spectra of the product in a region to suit the solvent

The least volatile products were found at the furnace exit. These were removed firstly by replacing the bulb to the top of the trap then separating the trap from the pyrolysis tube. Retention of a slow nitrogen flow at this stage served to reduce the risk of aerial oxidation of the hot products and aided cooling to room temperature when the products were dissolved out with solvent as before or in some cases scraped out directly to a sample vial and weighed.

C Preparation of Ylides

1 Preparation of starting materials

a Preparation of (Methoxycarbonylmethyl)triphenylphosphonium chloride

This compound and the other required phosphonium salts were prepared by a modification of the method of Michaelis and Gimborn[55] . An example is given below.

Triphenylphosphine (65.5 g, 250 mmol) was stirred in dry toluene (300 ml) while methyl chloroacetate (26.1 g, 240 mmol) was slowly added. The solution was heated under reflux for 2.5 h and left to cool overnight. The precipitated product was then filtered off and the liquors retained to provide a second crop of the precipitate. This were washed thoroughly with petroleum ether and dried to give (methoxycarbonylmethyl)triphenylphosphonium chloride (69.2 g, 78%) as colourless crystals, m.p. 226.5-228 °C (lit.,[56] 227 °C).

b Preparation of Methoxycarbonylmethylenetriphenylphosphorane **99**

(Methoxycarbonylmethyl)triphenylphosphonium chloride (9.26 g, 25 mmol) was dissolved in water (100 ml) and stirred briskly for 10 min before filtering off any remaining solids. NaOH (1.00 g, 25 mmol) in water (2 ml) was added dropwise with brisk stirring continuing 30 min after the addition. The supernatant liquid was poured off and the sticky solid remaining was dissolved in CH_2Cl_2. The solution was washed with water then dried and evaporated to yield methoxycarbonylmethylenetriphenylphosphorane (6.7 g, 83%), m.p.168-170 °C (lit.,[57] 169-169.5 °C) as a light yellow solid.

c Preparation of 2-methylcinnamic acid **86**

This compound was prepared by the method of Young.[58] Finely divided sodium metal (0.76 g, 33 mmol) was stirred in ethyl acetate (60 ml) over an ice / salt bath. o-Tolualdehyde (3.98 g, 33 mmol) was added and the mixture stirred for 3 h to yield a dull green suspension. Glacial acetic acid was added dropwise with stirring until a bright yellow colouration was observed then water (70 ml) was added and the mixture stirred for 20 min. The organic layer was separated and washed with a sodium carbonate solution (10 g / 75 ml water) then dried and evaporated to give ethyl 2-methylcinnamate (5.43 g, 87%) as a dull yellow oil. NaOH solution (25 ml, 2 M) was added to the ester and the solution heated under reflux for 2.5 h. The resulting mixture was extracted with ether which was discarded. Conc. HCl (10 ml) was added dropwise to the aqueous layer with brisk stirring resulting in a bright yellow precipitate which was taken up in CH_2Cl_2. Drying and evaporation gave 2-methylcinnamic acid (3.25 g, 69%) as bright yellow / orange crystals which were used directly to obtain the acid chloride.

d Preparation of 2,4,6-trimethylcinnamic acid **87**

Using the same procedure as above, mesitaldehyde (5 g, 33 mmol) was added to the Na metal in ethyl acetate. The identical work up produced ethyl 2,4,6-trimethylcinnamate (6.7 g, 93%) which was hydrolysed to provide 2,4,6-trimethylcinnamic acid (7.3 g crude) as yellow crystals which were used directly to obtain the acid chloride.

e Preparation of 2-trideuteriomethylcinnamic acid **167**

i 4,4-dimethyl-2-(2-trideuteriomethylphenyl)-2-oxazoline.

This compound was prepared by modification of the method of Gschwend.[59] A solution of 4,4-dimethyl-2-phenyl-2-oxazoline **166** (1.58

g, 9 mmol) was stirred under nitrogen in dry THF (60 ml) over an isopropanol / liquid nitrogen bath until the solution cooled to –70 °C. A solution of n-butyl lithium in hexanes (4.5 ml of 2M solution, 9 mmol) was added slowly via syringe at this temperature which was maintained for 5 min after the addition then the flask was removed from the bath for 1 h to attain room temperature. The flask was then cooled again to –70°C and d_3-methyl iodide (1.40 g, 9.66 mmol) was added via syringe. The flask was left to stir under nitrogen and allowed to warm to room temperature overnight. The contents were then poured into saturated aqueous ammonium chloride (100 ml) and extracted with ether (3 x 100 ml) which was dried and evaporated to yield the crude product as a yellow oil. Kugelrohr distillation (85°C / 0.1 Torr) gave 4,4-dimethyl-2-(2-trideuteriomethylphenyl)-2-oxazoline **167** (2.17 g, 68%) contaminated by some unmethylated oxazoline; δ_H 7.78-7.72 (1H, m), 7.45-7.15 (3H, m), 4.04 (2H, s) and 1.38 (6H, s); δ_D 2.52 (3D, s); δ_C 162.8 (C-2), 131.2, 131.0, 130.4, 129.8, 128.3, 125.5, 78.6 (C-5), 67.8 (C-4) and 28.5 (2C).

ii. Preparation of 2-trideuteriomethylbenzaldehyde **169**

The following reactions are based on the methods of Meyers *et al.* [60] A solution of 4,4-dimethyl-2-(2-trideuteriomethylphenyl)-2-oxazoline **167** (2.17 g, 7.7 mmol) in dry THF (100 ml) was stirred while liquid ammonia (300 ml) was carefully added and the mixture allowed to settle with stirring before adding lithium metal (0.32 g, 45 mmol) in small pieces. The solution was allowed to stir for 1 h then water (10 ml) was added dropwise and the solution left to stir overnight. The mixture was partitioned between water and ether and the ether extract separated, dried and evaporated to yield the crude amino alcohol**168** (2.49 g) as a yellow oil; δ_H 7.36-7.03 (4H, m), 3.61 (2H, s), 3.28 (2H, s) and 1.1 (6H, s); δ_D 2.34 (3D, s).

The crude amino alcohol was stirred in methylene chloride (100 ml) with the addition of N-chlorosuccinimide (1.73 g, 9 mmol) for 1 h. Alumina (75 g) was then added and the suspension left to stir vigorously overnight. The alumina was filtered off and washed thoroughly with methylene chloride (200 ml) and the combined filtrate was evaporated down to 5 ml and dropped onto a sinter funnel (8 cm) covered with a slurry of silica and methylene chloride. Methylene chloride (500 ml) was run through the sinter funnel under gravity and the solution was dried ($MgSO_4$) and evaporated to yield a yellow oil. Kugelrohr distillation (140 °C / 50 mTorr) gave 2-trideuteriomethylbenzaldehyde **169** in a mixture with benzaldehyde (0.40 g) in a ratio 73 / 27 (by ^1H NMR) corresponding to a yield of 0.292 g, 31%); δ_H 10.25 (1H, s), and 7.82-7.20 (4H, m); δ_D 2.65 (3D, s).

iii. Preparation of 2-trideuteriomethylcinnamic acid

This compound was prepared by the method of Young as described for the unlabelled compound. Sodium metal (0.09 g, 4 mmol) was stirred in dry ethyl acetate below 0 °C. The mixture of 2-trideuteriomethylbenzaldehyde and benzaldehyde from (ii) (0.40 g, 3.4 mmol) was added and the procedure described before followed to provide a crude product which was kugelrohr distilled (120 °C / 50 mTorr) to yield ethyl 2–trideuteriocinnamate as a mixture with ethyl cinnamate (0.36 g, 56%). Subsequent base hydrolysis provided the expected acid; δ_H (60 MHz) 10.12 (1H, s), 8.12 (1H, half AB pattern, *J* 16), 7.75-7.1 (4H, m) and 7.20 (1H, half AB pattern, *J* 16) which was used directly to obtain the acid chloride.

f Preparation of Cinnamoyl Chloride **62**

Cinnamic acid (3.3 g, 25 mmol) was heated under reflux with thionyl chloride (20 ml) for 2 h. The excess thionyl chloride was evaporated off and the remaining oil was Kugelrohr distilled (100 °C / 1 Torr) to give cinnamoyl chloride (84%) as a light yellow oil.

g 2-methylcinnamoyl chloride **88**

Using the same procedure as above 2-methylcinnamic acid (3.25 g, 20.1 mmol) was converted to 2-methylcinnamoyl chloride (3.20 g, 89%) as a light yellow oil (b.p. 200 °C, 10 Torr).

h 2,4,6-trimethylcinnamoyl chloride **89**

Using the same procedure as above 2,4,6-trimethylcinnamic acid (5.83 g, 30.7 mmol) was converted to 2,4,6-trimethylcinnamoyl chloride (4.15g, 65%) as colourless crystals.

i 2-trideuteriomethylcinnamoyl chloride

Using the same procedure as above 2-trideuteriomethylcinnamic acid (0.36 g, 2.1 mmol) was converted to 2-trideuteriomethylcinnamoyl chloride (0.22 g, 1.2 mmol, 57%) as a light yellow oil (b.p. 160 °C / 300 mTorr).

2 Preparation of alkylidenetriphenylphosphoranes and acylation to β-oxoalkylidenetriphenylphosphoranes

These compounds were prepared by modification of the method of Bestmann.[40] The appropriate alkyltriphenylphosphonium halide (25 mmol) was suspended in dry THF (150 ml) and stirred under a nitrogen atmosphere. n-Butyl lithium solution in hexane (11.2 ml of 2.5 M sol^{n}, 28 mmol) was added via syringe and the mixture was left to stir for 30 minutes. Over this time the deep orange / red colouration of the alkylidenetriphenylphosphorane developed. The appropriate acid chloride (12.5 mmol) was dissolved in dry THF (5 ml) and slowly added via syringe to the stirred solution. The mixture was then left to stir for 3 h then poured into water (100 ml) and extracted with ether. After drying and evaporation the product was recrystallised from ethyl acetate with the rate of crystallisation enhanced by the addition of ether (2 ml) to give the corresponding β–oxoalkylidenetriphenylphosphorane.

(α-Cinnamoylmethylene)triphenylphosphorane **63.** Reaction as above gave yellow crystals (43%), m.p. 157-160 °C (lit.,[61] non-crystalline) (Found: M$^+$, 406.1495. $C_{28}H_{23}OP$ requires M$^+$, 406.1486); ν_{max} /cm^{-1} 1634, 1517, 1330, 1103, 973, 885, 760, 729 and 690; δ_H 7.8–7.2 (21H, m), 6.93 (1H, half AB pattern, *J* 18) and 4.05 (1H, d, *J* 24); δ_P +15.6; *m/z* 406 (M$^+$, 100%), 405 (55), 378 (21), 377(20), 363 (7), 353 (5), 329 (6), 303 (70), 275 (58), 262 (60), 202 (12), 185 (15) and 183 (65).

(α-Cinnamoylethylidene)triphenylphosphorane **64.** Reaction as above gave yellow crystals (49%), m.p. 205–206 °C (lit.,[40] 205–208 °C); ν_{max} /cm^{-1} 1630, 1438, 1167, 1103, 982, 908, 847, 738 and 690; δ_H 7.8–7.2 (22H, m)

and 1.82 (3H, d, *J* 16); δ_P +15.6; *m/z* 420 (M^+, 7%), 278 (50), 277 (100), 262 (80), 201 (30), 183 (50), 152 (20) and 131 (30).

(α-Cinnamoyl-1-propylidene)triphenylphosphorane **65.** Reaction as above gave yellow prisms (60%), m.p. 211-213 °C (Found: C, 83.2; H, 6.3. $C_{30}H_{27}OP$ requires C, 82.9; H, 6.3%); ν_{max} /cm^{-1} 1631, 1495, 1165, 1101, 975, 921, 860, 763, 729 and 691; δ_H 7.7–7.25 (22H, m), 2.17 (2H, d of q, *J* 22, 7) and 0.96 (3H, t, *J* 7); δ_P +18.0; *m/z* 434 (M^+, 64%), 419 (99), 357 (11), 343 (7), 331 (6), 315 (2), 302 (14), 287 (22), 279 (9) and 262 (100).

(α-Cinnamoyl-1-butylidene)triphenylphosphorane **66.** Reaction as above gave yellow needles (49%), m.p. 187-189.5 °C (lit.,[62] 204–207 °C); ν_{max} /cm^{-1} 1632, 1501, 1438, 1164, 1106, 1082, 975, 720 and 692; δ_H 7.75–7.2 (22H, m), 2.2–1.95 (2H, m), 1.32 (2H, sextet, *J* 7) and 0.70 (3H, t, *J* 7); δ_P +17.8; *m/z* 448 (M^+, 12%), 420 (20), 419 (100), 278 (40), 277 (80), 262 (60), 201 (10), 183 (40) and 131 (25).

(α-Cinnamoyl-2-methyl-1-propylidene)triphenylphosphorane **67**. Reaction as above gave yellow crystals (53%), m.p. 219-220 °C (Found: C, 83.2; H, 6.6. $C_{31}H_{29}OP$ requires C, 83.0; H, 6.5%); ν_{max} /cm^{-1} 1626, 1430, 1181, 1103, 1073, 977, 748, 697 and 686; δ_H 7.7–7.25 (22H, m), 2.10 (1H, d of septets, *J* 25, 7) and 1.30 (6H, d, *J* 7); δ_P +16.2; *m/z* 448 (M^+, 15%), 435 (15), 434 (45), 279 (26), 277 (56), 262 (100), 201 (15), 183 (58) and 131 (58).

(α-Cinnamoyl-1-pentylidene)triphenylphosphorane **68.** Reaction as above gave yellow needles (66%), m.p. 179–180 °C (Found: C, 83.4; H, 6.8. $C_{32}H_{31}OP$ requires C, 83.1; H, 6.8%); ν_{max} /cm^{-1} 1634, 1157, 1097, 968, 852, 746, 721 and 690; δ_H 7.7–7.25 (22H, m), 2.10 (2H, d of t, *J* 22, 7),

1.29 (2H, m), 1.10 (2H, sextet, *J* 7) and 0.96 (3H, t, *J* 7); δ_P +18.0; *m/z* 462 (M^+, 15%), 434 (11), 420 (30), 419 (100), 289 (5), 287 (6), 277 (48), 201 (13) and 183 (36)

(α-Cinnamoyl-α-phenylmethylene)triphenylphosphorane **69.** Reaction as above gave yellow crystals (66%), m.p. 228-230 °C (Found: C, 84.9; H, 5.7. $C_{34}H_{27}OP$ requires C, 84.6; H, 5.6%); ν_{max} /cm^{-1} 1640, 1580, 1490, 1430, 1205, 1100, 970, 750 and 690; δ_H 7.75–7.1 (21H, m), 7.02 (5H, s) and 6.93 (1H, half AB pattern, *J* 16); δ_P +15.95; *m/z* 482 (M^+, 100%), 481 (34), 454 (3), 405 (5), 379 (13), 363 (3), 351 (8), 303 (7), 278 (10), 277 (22), 262 (60), 204 (65) and 183 (28).

(α-Cinnamoyl-α-4-nitrophenylmethylene)triphenylphosphorane **70.** .Reaction as above gave yellow crystals (37%), m.p. 266-267 °C (Found: C, 77.1; H, 4.9; N, 2.6. $C_{34}H_{26}NO_3P$ requires C, 77.4; H, 5.0; N, 2.7); ν_{max} /cm^{-1} 1623, 1570, 1475, 1360, 1097 and 975; δ_H 7.85 and 7.05 (4H AB pattern, *J* 8), 7.7-7.2 (21H, m) and 6.90 (1H, half AB pattern, *J* 16); δ_P +15.9; *m/z* 527 (M^+, 1.5%), 293 (2), 279 (23), 278 (70), 277 (100), 263 (15), 262 (50), 250 (19), 249 (50), 202 (75), 201 (60), 199 (40) and 183 (50).

(α-Cinnamoyl-α-2-thienylmethylene)triphenylphosphorane **71.** Reaction as above gave yellow crystals (46%), m.p. 196-199 °C (Found: M^+, 488.1401. $C_{32}H_{25}OPS$ requires M^+, 488.1364); ν_{max} /cm^{-1} (CH_2Cl_2)1624, 1570, 1490, 1426, 1365, 1338, 1212, 1187, 1164, 1100, 972, 900 and 832; δ_H 7.75–7.10 (22H, m), 6.97 (1H, m), 6.72 (1H, m) and 6.52 (1H, m); δ_P +16.6; *m/z* 488 (M^+, 50%), 438 (3), 408 (9), 308 (11), 277 (12), 263 (10), 262 (40), 210 (100) and 183 (35).

(α-2-Chlorocinnamoylethylidene)triphenylphosphorane **72.** Reaction as above gave yellow crystals (51%), m.p. 185-186 °C (Found: C, 76.5; H, 5.3. $C_{29}H_{24}ClOP$ requires C, 76.6; H, 5.3); ν_{max} /cm^{-1} 1620, 1470, 1370, 1150, 1100, 1038, 970 and 845 ; δ_H 7.75–7.3 (16H, m), 7.25-7.05 (5H,m) and 1.82 (3H, d, *J* 16); δ_P +18.0; *m/z* 456,(^{37}-Cl-M$^+$, 12%), 45 (15), 454 (^{35}Cl-M$^+$, 35), 453 (12), 419 (12), 405 (5), 391 (9), 377 (4), 343 (3), 317 (15), 289 (22), 278 (28), 277 (72), 263 (48), 262 (100), 201 (36) and 183 (95).

(α-(α-Methyl(cinnamoyl)ethylidene)triphenylphosphorane **73.** Reaction as above gave yellow crystals (63%), m.p. 120-122 °C (Found: C, 83.2; H, 6.3. $C_{30}H_{27}OP$ requires C, 82.9; H, 6.3%); ν_{max} /cm^{-1} 1485, 1438, 1369, 1179, 1135, 11.7, 998, 962, 845, 753, 711 and 695; δ_H 7.77–7.16 (20H, m), 6.74 (1H, s), 2.16 (3H, s), and 1.78 (3H, d, *J* 16);δ_P +17.8;*m/z* 434 (M$^+$, 2%), 317 (1), 279 (2), 277 (7), 262 (33), 201 (7), 183 (25), 162 (20), 145 (66), 117 (100) and 91 (60).

(α-4-Methylcinnamoyl-α-phenylmethylene)triphenylphosphorane **77.** Reaction as above gave yellow crystals (66%), m.p. 236–237 °C (Found: C, 84.9; H, 6.0. $C_{35}H_{29}OP$ requires C, 84.7; H, 5.9%); ν_{max} /cm^{-1} 1622, 1474, 1360, 1187, 1100 and 952; δ_H 7.75–7.15 (20H, m), 7.03 (5H, m), 6.87 (1H, half AB pattern, *J* 16) and 2.28 (3H, s); δ_P +15.6; *m/z* 496 (M$^+$, 85%), 495 (50), 379 (10), 303 (8), 294 (8), 277 (21), 266 (17), 263 (27), 262 (100), 261 (12), 218 (70) and 183 (60).

(α-4-Chlorocinnamoyl-α-phenylmethylene)triphenylphosphorane **78.** Reaction as above gave yellow crystals (66%), m.p.245-246 °C (Found: ^{35}Cl-M$^+$, 516.1396. $C_{34}H_{26}ClOP$ requires ^{35}Cl-M$^+$, 516.1410); ν_{max} /cm^{-1} ($CDCl_3$) 1623, 1590, 1486, 1423, 1400, 1364, 1260, 1210, 1183, 1100, 974

and 818; δ_H 7.7–7.15 (20H, m), 7.02 (5H m) and 6.83 (1H, half AB pattern, *J* 16); δ_P +16.05; *m/z* 518 (^{37}Cl–M$^+$, 23%), 517 (32), 516 (^{35}Cl–M$^+$, 64), 515 (32), 277 (45), 263 (23), 262 (100), 238 (30), 203 (30) and 183 (50).

(α-2-Chlorocinnamoyl-α-phenylmethylene)triphenylphosphorane **79.** Reaction as above gave yellow crystals (74%), m.p. 241-243 °C (Found: C, 78.8; H, 5.1. $C_{34}H_{26}ClOP$ requires C, 79.0; H, 5.1); ν_{max} /cm^{-1} 1620, 1587, 1474, 1360, 1184, 1100, 1030, 972, and 950; δ_H 7.7–7.2 (19H, m), 6.98 (5H, s) 7.05-6.95 (1H, m) and 6.87 (1H, half AB pattern, *J* 16); δ_P +16.1; *m/z* 518 (^{37}-Cl-M$^+$, 22%), 517 (30), 516 (^{35}Cl-M$^+$, 65), 515 (36), 482 (24), 481 (60), 379 (14), 351 (6), 278 (18), 277 (50),263 (22), 262 (100), 238 (16), 203 (30) and 183 (60).

(α-2-Nitrocinnamoyl-α-phenylmethylene)triphenylphosphorane **80.** Reaction as above gave orange crystals (60%), m.p. 253-254 °C (Found: C, 77.7; H, 4.9; N, 2.6. $C_{34}H_{26}NO_3P$ requires C, 77.4; H, 5.0; N, 2.7); ν_{max} /cm^{-1} 1600, 1566, 1480, 1342, 1098, 970 and 948; δ_H 7.85-7.2 (20H, m), 6.98 (5H, s) and 6.82 (1H, half AB pattern, *J* 15); δ_P +16.4; *m/z* 527 (M$^+$, 80%), 510 (3), 495 (2), 481 (10), 408 (6), 392 (5), 391 (5), 380 (25), 379 (100), 352 (30), 351 (50), 277 (28), 262 (50), 201 (25) and 183 (65).

(α-3,4-Methylenedioxycinnamoyl-α-phenylmethylene)triphenyl phosphorane **81**. Reaction as above gave yellow crystals (81%), m.p. 220-222 °C (Found: M$^+$, 526.1765. $C_{30}H_{27}OP$ requires M$^+$, 526.1698); ν_{max} /cm^{-1} (CH_2Cl_2) 1621, 1600, 1485, 1430, 1372, 1338, 1228, 1204, 1180, 1100, 1037, 997, 976, 952, 930, 850 and 807; δ_H 7.7–7.2 (16H, m), 6.98 (5H,s), 6.85-6.6 (4H, m) and 5.84 (2H, s); δ_P +15.7; *m/z* 526 (M$^+$, 97%),

525 (58), 405 (5), 379 (12), 351 (7), 303 (5), 278, (34), 277 (81), 264 (25), 263 (25), 262 (100), 248 (50) and 183 (60).

(α-3-(2-Furyl)propenoyl-α-phenylmethylene)triphenylphosphorane **82.** Reaction as above gave yellow crystals (55%), m.p. 254-256 °C (Found: C, 81.6; H, 5.4. $C_{32}H_{25}O_2P$ requires C, 81.3; H, 5.3%); ν_{max} /cm^{-1}(CH_2Cl_2) 1625, 1492, 1430, 1362, 1217, 1178, 1100, 1010, 972, 950 and 812; δ_H 7.75–7.15 (17H, m), 7.03 (5H, m) 6.82 (1H, half AB Pattern*J* 16) and 6.36 (2H, m); δ_P +15.9; *m/z* 472 (M^+, 72%), 443 (3), 418 (2), 415 (2), 389 (3), 379 (8), 351 (5), 278 (9), 277 (21), 263 (20), 262 (100), 201 (15), 194 (65) and 183 (40).

(α-3-(2-Thienyl)propenoyl-α-phenylmethylene)triphenylphosphorane **83.** Reaction as above gave orange crystals (77%), m.p. 241–243 °C (Found: C, 78.25; H, 5.1. $C_{32}H_{25}OPS$ requires C, 78.7; H, 5.2%); ν_{max} /cm^{-1} 1615, 1590, 1475, 1370, 1098 and 952; δ_H 7.7–7.3 (16H, m), 7.1–6.85 (3H, m), 7.00 (5H, m) and 6.72 (1H, half AB pattern, *J* 15); δ_P +15.8; *m/z* 488 (M^+, 30%), 487 (20), 278 (40), 277 (80), 263 (30), 262 (100), 207 (30), 201 (15), 199 (15) and 183 (70).

(α-3-(5-Methyl-2-thienyl)propenoyl-α-phenylmethylene)triphenyl phosphorane **84** Reaction as above gave yellow crystals (58%), m.p. 138-140 °C (Found: C, 78.5; H, 5.3. $C_{33}H_{27}OPS$ requires C, 78.9; H, 5.4%); ν_{max} /cm^{-1} (CH_2Cl_2) 1621, 1488, 1365, 1320, 1220, 1205, 1170,1100, 1040, and 950; δ_H 7.75–7.3 (16H, m), 7.02 (5H,s), 6.85 (1H, half AB pattern, *J* 3), 6.60 (1H, half AB pattern, *J* 16), 6.56 (1H, half AB pattern of q, *J* 3,1) and 2.37 (3H, d, *J* 1); δ_P +15.7; *m/z* 502 (M^+, 57%), 501 (24), 474 (2), 379 (7), 351 (3), 303 (5), 279, (5), 278 (6), 277 (15), 263 (27), 262 (100), 224 (60), 201 (9), 185 (11), 184 (12) and 183 (56).

(α-(α-Methylcinnamoyl)α-phenylmethylene)triphenylphosphorane **85.** Reaction as above gave yellow crystals (48%), m.p. 115-116 °C (Found: C, 84.4; H, 6.0. $C_{35}H_{29}OP$ requires C, 84.6; H, 5.9%); ν_{max} /cm^{-1} 1590, 1467, 1363, 1122, 1100, 1068, 1026, 997 and 968; δ_H 7.80–6.85 (25H, m), 6.70 (1H, q, ^4J 2) and 1.87 (3H, d, ^4J 2); δ_P +14.7;*m/z* 496 (M^+, 32%), 495 (36), 419 (2), 405 (2), 380, (6), 379 (22),. 351 (11), 303 (36), 275 (10), 263 (24), 262 (100) and 183 (60).

(α-2-Methylcinnamoylethylidene)triphenylphosphorane **90**. Reaction as above gave yellow crystals (41%), m.p. 170-172 °C (Found: M^+, 434.1750. $C_{30}H_{27}OP$ requires M^+, 434.1800); ν_{max} /cm^{-1} (CH_2Cl_2) 1618, 1487, 1430, 1377, 1162, 1100, 1050, 970, 912 and 846; δ_H 7.90–7.10 (21H, m), 2.42 (3H, s) and 1.83 (3H, d, *J* 16); δ_P +18.0; *m/z* 434 (M^+, 24%), 289 (5), 277 (19), 262 (100), 183 (35), 145 (13), 135 (13) and 108 (13).

(α-2-Methylcinnamoyl-1-propylidene)triphenylphosphorane **91.** Reaction as above gave yellow needles (38%), m.p.169-171.5 °C (Found: C, 83.1; H, 6.6. $C_{31}H_{29}OP$ requires C, 83.0; H, 6.5%); ν_{max} /cm^{-1} 1627, 1436, 1162, 1104, 968, 918, 753, 720 and 690; δ_H 7.84–7.10 (21H, m), 2.42 (3H, s) 2.21 (2H, d of q, *J* 22, 7), 0.98 (3H, t, *J* 7), ; δ_P +17.7; *m/z* 448 (M^+, 22), 433 (78), 371 (3), 55 (4), 331 (6), 303 (10), 287 (14), 277 (41), 262 (100), 201 (20), 183 (90), 145 (50), 115 (38) and 108 (75).

(α-2-Methylcinnamoyl-2-methyl-1-propylidene)triphenylphosphorane **92.** Reaction as above gave yellow crystals (54%), m.p. 208-210 °C (Found: C, 83.0; H, 6.8. $C_{32}H_{31}OP$ requires C, 83.1; H, 6.8%); ν_{max} /cm^{-1} 1631, 1438, 1402, 1340, 1181, 1103, 1073, 971, 940, 896, 764, 730 and 693; δ_H 7.70–7.08 (21H, m), 2.38(3H,s), 2.12 (1H, d of septets, *J* 25, 7) and 1.32 (6H, d,

J 7); δ_P +16.0; *m/z* 462 (M^+, 18%), 447 (52), 385 (3), 303 (5), 277 (42), 262 (54), 218 (22), 201 (16), 183 (29) 145 (100), 116 (67) and 131 (58).

(α-2-Methylcinnamoyl-α-phenylmethylene)triphenylphosphorane **93**. Reaction as above gave yellow crystals (66%), m.p. 259–260 °C (Found: C, 84.5; H, 5.7. $C_{35}H_{29}OP$ requires C, 84.7; H, 5.9%); ν_{max} /cm^{-1} 1625, 1497, 1434, 1262, 1219, 1198, 1102, 972, 760, 715, 700 and 687; δ_H 7.8–7.3 (20H, m), 7.0 (5H, s), 6.90 (1H, half AB pattern, *J* 16) and 2.33 (3H, s); δ_P +15.7; *m/z* 496 (M^+, 50%), 481 (4), 403 (17), 379 (16), 351 (12), 277 (83), 262 (70), 218 (19), 201 (100), 183 (47), 165 (22), 145 (61), 115 (41) and 180 (22).

(α-2-Methylcinnamoyl-α-methoxycarbonylmethylene)triphenyl phosphorane **100.** Methoxycarbonylmethylenetriphenylphosphorane **99** (1.67 g, 5 mmol) was dissolved in dry toluene (30 ml) and stired for 20 min then 2-methyl cinnamoyl chloride **88** (0.90 g, 5 mmol) in dry toluene (5 ml) was added dropwise The mixture was stirred for 2 h at 40 °C then washed with water (100 ml). The solution was then dried and evaporated to give yellow crystals of the title ylid (1.83 g, 77%), m.p. 210-211.5 °C (Found: M^+, 478.1687. $C_{31}H_{27}O_3P$ requires M^+, 478.1698); ν_{max} /cm^{-1} 2945, 1735, 1664, 1573, 1530, 1333, 1106, 764, 720 and 688; δ_H 8.13 (1H, half AB pattern, *J* 16), 7.8-7.35 (17H, m) 7.20-7.06 (3H, m), 3.18 (3H, s) and 2.36 (3H, s); δ_P +18.9; *m/z* (20 eV) 478 (M^+, 43%), 463 (40), 450 (37), 417 (9), 385 (13), 361 (9), 333 (10), 301 (6), 277 (100), 262 (26), 172 (16), 159 (41) and 157 (45).

(α-2,4,6-Trimethylcinnamoylethylidene)triphenylphosphorane **94**. Reaction as above gave yellow crystals (36%), m.p. 215-218 °C (Found: C, 82.5; H, 6.7; M^+,462.2135. $C_{32}H_{31}OP$ requires C, 83.1; H, 6.8%;

M+,462.2113); ν_{max} /cm^{-1} (CH_2Cl_2) 1621, 1605, 1487, 1430, 1370, 1160, 1100, 1042, 980, 908, 850 and 819; δ_H 7.85–7.25 (16H, m), 6.95 (1H, d , half AB pattern, *J* 16), 6.89 (2H, s), 2.39 (6H, s), 2.26 (3H, s), and 1.76 (3H, d, *J* 16); δ_P +18.1; *m/z* 462 (M+,83 %), 447 (10), 385 (11), 369(18), 342 (8), 317 (33), 289 (94), 262 (100), 217 (18), 201 (22), 183(86), and 108 (65).

(α-2,4,6-Trimethylcinnamoyl-1-propylidene)triphenylphosphorane **95**. Reaction as above gave yellow crystals (58%), m.p. 174-176 °C (Found: C, 83.4; H, 7.25. $C_{33}H_{33}OP$ requires C, 83.2; H, 7.0%); ν_{max} /cm^{-1} 3055, 1701, 1482, 1439, 1163, 1106, 998, 988, 750 and 693; δ_H 7.8–7.3 (16H, m), 7.0–6.75 (3H, m), 2.37 (6H, s), 2.25 (3H, s), 2.3–1.8 (2H, m) and 0.91 (3H, t, *J* 7); δ_P +18.0; *m/z* 476 (M+,46 %), 461 (98), 399 (8), 331(16), 317 (11), 303 (31), 287 (34), 277 (11), 262 (100), 201 (19), 183 (73), 153 (19), 119 (14) and 108 (48).

(α-2,4,6-Trimethylcinnamoyl-2-methyl-1-propylidene)triphenyl phosphorane **96**. Reaction as above gave yellow crystals (62%), m.p. 192–194 °C (Found: C, 83.1; H, 7.2. $C_{34}H_{35}OP$ requires C, 83.2; H, 7.2%); ν_{max} /cm^{-1} 1634, 1489, 1332, 1386, 1102, 1074, 978, 869, 843, 722, 695 and 689; δ_H 7.75–7.3 (16H, m), 6.90 (1H, half AB pattern, *J* 16), 6.85 (2H, s), 2.37 (6H, s), 2.25 (3H, s), 2.3–1.7 (1H, m) and 1.24 (6H, d, *J* 7); δ_P +16.0; *m/z* 490 (M+, 40%),475 (100), 461 (9), 413 (13), 397 (7), 357 (8), 345 (7), 303 (22), 287 (11), 279 (10), 262 (28), 231 (18) 201 (25), 183 (23), 167 (41) and 108 (31).

(α-2,4,6-Trimethylcinnamoyl-α-phenylmethylene)triphenylphosphorane **97**. Reaction as above gave pale yellow crystals (40%), m.p. 199–201 °C (Found: C, 84.5; H, 6.5. $C_{37}H_{33}OP$ requires C, 84.7; H, 6.3%); ν_{max} /cm^{-1}

1653, 1506, 1436, 1365, 1212, 1101, 986, 951, 856, 840, 755, 709 and 693; δ_H 7.9–7.3 (16H, m), 7.0 (5H, m), 6.79 (2H, s), 6.50 (1H, half AB pattern, *J* 16) and 2.23 (9H, s); δ_P +15.95; *m/z* 524 (M^+, 60%), 509 (5), 431 (13), 405 (6), 379 (13), 351 (18), 303 (8), 277 (60), 262 (100), 231 (11), 215 (8), 201 (20), 183 (48), 173 (15), 165 (14) and 108 (20).

(α-3-(3-Methyl-2-thienyl)propenoyl-α-phenylmethylene)triphenyl phosphorane. **141.** Reaction as above gave yellow crystals (57%), m.p. 235-238 °C (Found: C, 78.6; H, 5.15. $C_{33}H_{27}OPS$ requires C, 78.9; H, 5.4%); ν_{max} /cm^{-1} (CH_2Cl_2) 1610, 1590, 1475, 1430, 1352 1200, 1100, 1070, 1036,1000, 956, 852 and 830; δ_H 7.75–7.3 (16H, m), 7.02 (5H, s), 6.98 (1H, half AB pattern, *J* 3), 6.73 (1H, half AB pattern, *J* 16), 6.60 (1H, half AB pattern of q, *J* 16) and 2,22(3H, s); δ_P +15.8 *m/z* 502 (M^+, 60%), 501 (25), 409 (2), 379 (7), 379 (8), 351 (7), 303, (4), 278 (16), 277 (45), 263 (20), 262 (100), 240 (18), 224 (60), 201 (14), 185 (12), 184 (10) and 183 (50).

(α-2-Trideuteriomethylcinnamoyl-1-propylidene)triphenylphosphorane
165. Reaction as above gave a viscous yellow oil which solidified on trituration (0.64 g crude). Recrystallisation from ethyl acetate aided by addition of a single small crystal of (α-2-methylcinnamoyl-1-propylidene)triphenyl phosphorane gave small dull yellow crystals (0.23 g) which were recrystallised again by dissolving in dry methylene chloride (0.5 ml) and ethyl acetate (1 ml) solution, boiling off the methylene chloride and seeding the ethyl acetate to give large bright yellow crystals of (α-2-trideuteriomethylcinnamoyl-1-propylidene)triphenylphosphorane (0.22g, 41%), m.p. 169–171°C ; δ_H 7.80–7.10 (21H, m), 2.19 (2H, d of q, *J* 22, 7) and 0.96 (3H, t, *J* 7); δ_D 2.39 and δ_P 17.8 [comparable to (α-2-methylcinnamoyl-1-propylidene)triphenylphosphorane above]

(α-Cinnamoyl-α-2-methoxyphenylmethylene)triphenylphosphorane **98.** Reaction as above gave orange crystals (31%), m.p. 203-204 °C (Found: C, 81.4; H, 5.7; M^+, 512.1868. $C_{35}H_{26}NOP$ requires C, 82.0; H, 5.7%; M^+, 521.1905); ν_{max} /cm^{-1} ($CHCl_3$) 3058, 2960, 1630, 1590, 1573, 1496, 1478, 1435, 1372, 1240, 1105, 1048, 1028, 980, 954 and 692; δ_H 7.75-7.05 (23H, m), 7.0-6.7 (2H, m),6.42 (1H, half AB pattern, *J* 8) and 3.24 (3H, s); δ_P +15.1; *m/z* 512 (M^+, 7%), 481 (54), 409 (3), 368 (13), 351 (5), 337 (6), 303 (9), 277 (8), 263 (18), 262 (48) and 183 (100).

D Low temperature FVP of the β-oxoalkylidenetriphenyl phosphoranes.

1. (α-Cinnamoylmethylene)triphenylphosphorane **63**

FVP of the title compound (106 mg, 700 °C, 2 mTorr, inlet 100 °C) gave *1-phenylbut-1-en-3-yne* **104** [lit.,[63] δ_H 7.2 (5H, m), 6.90 (1H, d *J* 18), 6.00 (1H, d of d,^3J 18, ^4J 3) and 2.91 (1H, d, ^4J 3). Configuration unspecified.] as a yellow oil (8%); composed of:-

E-1-Phenylbut-1-en-3-yne **104a** (58%); δ_H 7.92-7.22 (5H, m), 7.06 (1H, d *J* 16), 6.15 (1H, d of d,^3J 16, ^4J 2) and 3.06 (1H, d, ^4J 2); δ_C 143.1 (C-1), 135.8, 128.9, 128.7, 126.3, 106.9 (C-2), 84.1 (C-3), and 79.3 (C-4)

Z-1-Phenylbut-1-en-3-yne **104b** (42%); δ_H 7.92-7.22 (5H, m), 6.72 (1H, d *J* 12), 5.70 (1H, d of d,^3J 12, ^4J 2) and 3.37 (1H, d, ^4J 2); δ_C assignment uncertain. IR + MS not obtained due to polymerisation.

2. (α-Cinnamoylethylidene)triphenylphosphorane **64**

FVP of the title compound (100 mg, 700 °C, 40 mTorr, inlet 200 °C) gave *1-phenylpent-1-en-3-yne* **105** as a yellow oil (53%) (Found: M^+, 142.0786. $C_{11}H_{10}$ requires M^+, 142.0783); ν_{max} /cm^{-1} 3010, 2905, 2840, 2280, 2190,

1600, 1180, 1110 and 950 [lit.,[64] ν_{max} /cm^{-1} 2230, 2190 and 953]; *m/z* 142 (M$^+$, 75%), 141 (100), 128 (8), 115 (70), 86 (47), 84 (77), 73 (48) and 63 (18). Composed of:-

E-1-Phenylpent-1-en-3-yne **105a** (57%); δ_H 7.95–7.15 (5H, m), 6.87 (1H, half AB pattern, *J* 16), 6.15 (1H, half AB pattern of q, ^3J 16, ^5J 2) and 2.02 (3H, d, ^5J 2) [lit.,[64] δ_H 7.95–7.70 (1H, m), 7.45-7.0 (4H, m), 5.4-7.0 (2H, m, ^3J 16, ^5J 2.5) and 1.94 (3H, m, ^5J 2.5)]; δ_C 140.1 (C-1), 136.5, 128.6, 128.2, 126.0, 108.8 (C-2), 88.3 (C-3), 78.9 (C-4) and 4.5 (C-5).

Z-1-Phenylpent-1-en-3-yne **105b** (43%); δ_H 7.95–7.15 (5H, m), 6.58 (1H, d, half AB pattern, *J* 12), 5.70 (1H, half AB pattern of q, ^3J 12, ^5J 2) and 2.09 (3H, d, ^5J 2) [lit.,[65] δ_H 7.95–7.70 (1H, m), 7.45-7.0 (4H, m), 5.4-7.0 (2H, m, ^3J 13, ^5J 2.5) and 1.94 (3H, m, ^5J 2.5)]; δ_C 142.0 (C-1), 136.6, 128.4, 128.3, 126.0, 108.1 (C-2), 93.2 (C-3), 78.3 (C-4) and 4.8 (C-5).

3. (α-Cinnamoyl-1-propylidene)triphenylphosphorane **65**

FVP of the title compound (104 mg, 700 °C, 40 mTorr, inlet 140 °C) gave *1-phenylhex-1-en-3-yne* **106** as a yellow oil (33%) (Found: M$^+$, 156.0931. $C_{12}H_{12}$ requires M$^+$, 156.0939); ν_{max} /cm^{-1} 2905, 2195, 1660, 1600, 1312, 1164, 1092, 1050 and 950; *m/z* 156 (M$^+$, 68%), 141 (100), 128 (33), 115 (77), 102 (8), 99 (10), 77 (15) and 63 (22). Composed of:-

E-1-Phenylhex-1-en-3-yne **106a** (56%); δ_H 7.90–7.20 (5H, m), 6.89 (1H, half AB pattern, *J* 16), 6.18 (1H, half AB pattern of t, ^3J 16, ^5J 2), 2.54-2.32 (2H, m) and 1.21 (3H, t, *J* 8); δ_C 140.0 (C-1), 136.5, 128.6, 128.1, 126.0, 108.8 (C-2), 94.2 (C-3), 79.0 (C-4), 13.9 (C-6) and 13.3 (C-5).

Z-1-Phenylhex-1-en-3-yne **106b** (44%); δ_H 7.90–7.20 (5H, m), 6.58 (1H, half AB pattern, *J* 12), 5.72 (1H, half AB pattern of t, ^3J 12, ^5J 2), 2.54-2.32 (2H, m) and 1.21 (3H, t, *J* 8); δ_C 137.3 (C-1), 136.7, 128.4, 128.2, 126.0, 108.1 (C-2), 98.9 (C-3), 78.6 (C-4), 13.7 (C-6) and 13.6 (C-5).

4. (α-Cinnamoyl-1-butylidene)triphenylphosphorane **66**

FVP of the title compound (270 mg, 500 °C, 10 mTorr, inlet 170 °C) gave *E-1-phenylhept-1-en-3-yne* **107a** as a yellow oil (42%); δ_H 7.92–7.14 (5H, m), 6.88 (1H, half AB pattern, *J* 16), 6.17 (1H, half AB pattern of t, ^3J 16, ^5J 2), 2.48-2.25 (2H, m), 1.70-1.50 (2H, m) and 1.02 (3H, t, *J* 8).

FVP of the title compound (96 mg, 700 °C, 52 mTorr, inlet 150 °C) gave *1-phenylhept-1-en-3-yne* **107** as a yellow oil (21%) (Found: M+, 170.1089. $C_{13}H_{14}$ requires M+, 170.1096); ν_{max} /cm^{-1} 2900, 2840, 2290, 2200, 1590, 1165, 1065, 950 and 805; *m/z* 170 (M+, 52%), 155 (25), 141 (98), 139 (28), 128 (28), 115 (100), 102 (10), 91 (19), 89 (13), 77 (15), 63 (29) and 61 (25). Composed of:-

E-1-Phenylhept-1-en-3-yne **107a** (53%); δ_H 7.92–7.14 (5H, m), 6.88 (1H, half AB pattern, *J* 16), 6.17 (1H, half AB pattern of t, ^3J 16, ^5J 2), 2.48-2.25 (2H, m), 1.70-1.50 (2H, m) and 1.02 (3H, t, *J* 8); δ_C 140.0 (C-1), 136.5, 128.6, 128.2, 126.0, 108.9 (C-2), 92.9 (C-3), 79.9 (C-4), 22.2 (C-6), 21.6 (C-5) and 13.6 (C-7).

Z-1-Phenylhept-1-en-3-yne **107b** (47%); δ_H 7.92–7.14 (5H, m), 6.55 (1H, half AB pattern, *J* 12), 5.70 (1H, half AB pattern of t, ^3J 12, ^5J 2), 2.48-2.25 (2H, m), 1.70-1.50 (2H, m) and 1.02 (3H, t, *J* 8); δ_C 137.2 (C-1), 136.7 128.4, 128.2, 126.0, 108.2 (C-2), 98.0 (C-3), 79.4 (C-4), 21.9 (C-6), 22.0 (C-5) and 13.6 (C-7).

5. (α-Cinnamoyl-2-methyl-1-propylidene)triphenylphosphorane **67**

FVP of the title compound (107 mg, 700 °C, 30 mTorr, inlet 160 °C) gave *5-methyl-1-phenylhex-1-en-3-yne* **108** as a yellow oil (67%) (Found: M+, 170.1103. $C_{13}H_{14}$ requires M+, 170.1096); ν_{max} /cm^{-1} 2950, 2905, 2860, 2200, 1590, 1310, 1050, 950 and 900 ; *m/z* 170 (M+, 23%), 155 (62), 141 (33), 128 (63), 115 (74), 102 (17), 91 (21), and 27 (100). Composed of:-

E-5-methyl-1-phenylhex-1-en-3-yne **108a** (56%); δ_H 7.90–7.20 (5H, m), 6.78 (1H, half AB pattern *J* 16), 6.08 (1H, half AB pattern of d, ^3J 16, ^5J 2), 2.82-2.25 (1H, m), and 1.12 (6H, d, *J* 8); δ_C 139.9 (C-1), 136.6, 128.6, 128.0, 126.0, 108.8 (C-2), 98.3 (C-3), 78.8 (C-4) 23.0 (2C, C-6) and 21.3 (C-5).

Z-5-methyl-1-phenylhex-1-en-3-yne **108b** (48%); δ_H 7.90–7.2 (5H, m), 6.47 (1H, half AB pattern *J* 12), 5.60 (1H, half AB pattern of d, ^3J 12, ^5J 2), 2.82-2.55 (1H, m), and 1.14 (6H, d, *J* 8); δ_C 137.3 (C-1), 136.7, 128.5, 128.1, 126.0, 108.2 (C-2), 102.8 (C-3), 78.4 (C-4), 22.6 (2C, C-6) and 21.5 (C-5).

6. <u>(α-Cinnamoyl-1-pentylidene)triphenylphosphorane **68**</u>

FVP of the title compound (178 mg, 500 °C, 9 mTorr, inlet 140 °C) gave *E-1-phenyloct-1-en-3-yne* **109a** as a yellow oil (58%); δ_H 7.92–7.15 (5H, m), 6.87 (1H, half AB pattern, *J* 16), 6.17 (1H, half AB pattern of t, ^3J 16, ^5J 2), 2.55-2.31 (2H, m), 1.68-1.20 (4H, m) and 0.95 (3H, t, *J* 7).

FVP of the title compound (101 mg, 700 °C, 25 mTorr, inlet 150 °C) gave *1-phenyloct-1-en-3-yne* **109** as a yellow oil (25%), ν_{max} /cm^{-1} 2955, 2920, 2845, 2310, 2200, 1605, 1100, 1055 and 952, [lit.,[65] (*E*-isomer),2190 and 960]; *m/z* 184 (M^+, 23%), 155 (62), 141 (33), 128 (63), 115 (74), 102 (17), 91 (21), and 27 (100). Composed of:-

E-1-Phenyloct-1-en-3-yne **109a** (50%); δ_H 7.92–7.15 (5H, m), 6.87 (1H, d, half AB pattern *J* 16), 6.17 (1H, half AB pattern of t, ^3J 16, ^5J 2), 2.55-2.31 (2H, m), 1.68-1.20 (4H,m) and 0.95 (3H, t, *J* 7) [lit.,[65] δ_H (CCl_4) 7.12 (5H, m), 6.70 (1H, d, *J* 16), 5.99 (1H, d of t, ^3J 16, ^5J 2), 2.45-2.13 (2H, m), 1.70-1.1 (4H, m) and 0.88 (3H, t, *J* 7)]; δ_C 139.9 (C-1), 136.5, 128.6, 128.1, 126.0, 108.9 (C-2), 93.0 (C-3), 79.7 (C-4) 30.9 (C-6), 22.0 (C-7), 19.3 (C-5) and 13.6 (C-8).

Z-1-Phenyloct-1-en-3-yne **109b** (50%);δ_H 7.92–7.15 (5H, m), 6.48 (1H, d, half AB pattern *J* 12), 5.65 (1H, half AB pattern of t, ^3J 12, ^5J 2), 2.55-2.31 (2H, m), 1.68-1.20 (4H, m) and 0.95 (3H, t, *J* 7); δ_C 137.2 (C-1), 136.7, 128.4, 128.2, 126.0, 108.2 (C-2), 97.8 (C-3), 79.2 (C-4) 30.6 (C-6), 22.0 (C-7), 19.6 (C-5) and 13.6 (C-8).

7. (α-Cinnamoyl-α-phenylmethylene)triphenylphosphorane **69**

FVP of the title compound (107 mg, 700 °C, 25 mTorr, inlet 210 °C) gave *1,4-Diphenylbut-1-en-3-yne* as a yellow oil **110** (99%); ν_{max} /cm^{-1} 3005, 2190, 1588, 1476, 1242, 948 and 802 [lit.,[64] ν_{max} /cm^{-1} 953]; *m/z* 204 (M$^+$, 73%), 127 (12), 103 (22), 91 (21), 77 (6) and 27 (100). Composed of:-

E-1,4-Diphenylbut-1-en-3-yne **110a** (57%); δ_H 7.75–7.20 (10H, m), 7.06 and 6.40 (2H, AB pattern, *J* 16), [lit.,[64] δ_H 7.55–7.10 (10H, m), 7.03 and 6.27 (2H, AB pattern, *J* 16)]; δ_C 141.3 (C-1), 136.3, 131.5, 128.8, 128.7, 128.4, 128.2, 126.3, 123.4, 108.1 (C-2), 91.7 (C-3) and 88.9 (C-4).

Z-1,4-Diphenylbut-1-en-3-yne **110b** (43%); δ_H 7.75–7.20 (10H, m), 6.72 and 5.93 (2H, AB pattern *J* 12); δ_C 138.7 (C-1), 136.5, 131.4, 128.7, 128.6, 128.3, 128.2, 126.3, 123.5, 107.4 (C-2), 95.8 (C-3) and 88.2 (C-4).

8. (α-Cinnamoyl-α-4-nitrophenylmethylene)triphenylphosphorane **70**

FVP of the title compound (100 mg, 500 °C, 14 mTorr, inlet 120 °C) gave *E-4-(4-nitrophenyl)-1-phenylbut-1-en-3-yne* **111** as a yellow oil (16%) (Found: M$^+$, 249.0779 $C_{16}H_{11}NO_2$ requires M$^+$, 249.0790); ν_{max} /cm^{-1} 2924, 2190, 1588, 1517, 1339, 1107, 850 and 747; δ_H 8.26–8.16 (2H, m), 7.66–7.55 (2H, m), 7.52–7.25 (5H, m) and 7.13 and 6.40 (2H, AB pattern, *J* 16); δ_C 146.8, 143.4 (C-1), 135.8, 132.1, 129.7, 128.4, 126.5, 123.7, 128.4, 107.1 (C-2), 94.4 (C-3) and 89.8 (C-4); *m/z* 249(M$^+$, 48%), 219

(24), 202 (64), 189 (14), 176 (5), 150 (8), 105 (9) , 86 (60), 84 (100) and 109 (10).

9. (α-Cinnamoyl-α-2-thienylmethylene)triphenylphosphorane **71**

FVP of the title compound (200 mg, 500 °C, 17 mTorr, inlet 140 °C) gave *E-1-phenyl-4-(2-thienyl)but-1-en-3-yne* **112** as a yellow oil (66%) (Found: M+, 210.0497. $C_{14}H_{10}S$ requires M+, 210.0503); ν_{max} /cm^{-1} 3020, 2960, 2280, 1600, 1240, 1050, 950 and 890; δ_H 7.55–6.90 (9H, m) and 6.35 (1H, half AB pattern, ^3J 16); δ_C 141.2 (C-1), 136.2 , 131.7, 128.74, 128.70, 127.3, 127.1, 126.3, 123.5, 107.7 (C-2), 92.8 (C-3) and 84.9 (C-4); *m/z* 210 (M+, 49%), 165 (25), 152 (7), 139 (7), 84 (100), 77 (9) and 63 (13).

10. (α-2-Chlorocinnamoylethylidene)triphenylphosphorane **72**

FVP of the title compound (100 mg in 1.5 ml CH_2Cl_2, 900 °C, CH_2Cl_2 spray 100 mTorr, inlet 300 x 0.2mm bore steel tube) gave *1-(2-chlorophenyl)pent-1-en-3-yne* as a minor component mixed with starting material. δ_H 6.12 (1H, half AB pattern of q, ^3J 16,^5J 2) **113a** [*E*-isomer] and 5.80 (1H, half AB pattern of q, ^3J 12,^5J 2) **113b** [*Z*-isomer].

11. (α-(α-Methylcinnamoyl)ethylidene)triphenylphosphorane **73**

FVP of the title compound (280 mg, 500 °C, 17 mTorr, inlet 130 °C) gave *E-2-methyl-1-phenylpent-1-en-3-yne* **114** as a yellow oil (67%) (Found: M+, 156.0945. $C_{12}H_{12}$ requires M+, 156.0939); ν_{max} /cm^{-1} 2960, 2905, 2285, 2215, 1690, 1592, 1241 and 903; δ_H 7.45–7.19 (5H, m), 6.80 (1H, s), 2.07 (3H, s) and 2.03 (3H, s); δ_C 137.0, 134.6 (C-1), 128.9, 128.2, 126.9, 120.5 (C-2), 84.8 (C-3), 83.5 (C-4), 19.4 and 4.3 (C-5); *m/z* 156 (M+, 72%), 155 (27), 141 (100), 128 (21), 115 (48), 105 (9), 91 (19), 84 (10), 77 (23), 63 (21) and 51 (26).

12. (α-4-Methylcinnamoyl-α-phenylmethylene)triphenylphosphorane **77**

FVP of the title compound (1.51g, 480 °C, 12 mTorr, inlet 130 °C) gave *1-(4-methylphenyl)-4-phenylbut-1-en-3-yne* **115** as a light yellow solid (82%) (Found: M+, 218.1080. $C_{17}H_{14}$ requires M+, 218.1096); ν_{max} /cm^{-1} 3005, 2950, 2900, 2180, 1585, 1478, 1110, 950 and 793; δ_H 7.52–7.08 (9H, m), 7.01 (1H, d, *J* 16), 6.34 (1H, d, *J* 16) and 2.34 (3H, s); δ_C 141.3 (C-1), 138.7, 133.6, 131.5, 129.4, 128.3, 128.0, 126.2, 123.5, 107.0 (C-2), 91.4 (C-3), 89.1 (C-4) and 21.3 ; *m/z* 218 (M+, 100%), 217 (45), 203 (56), 189 (9), 178 (3), 165 (47), 141 (5), 126 (5), 119 (7), 115 (11), 105 (15) and 91 (16).

13. (α-4-Chlorocinnamoyl-α-phenylmethylene)triphenylphosphorane **78**

FVP of the title compound (160 mg, 500 °C, 15 mTorr, inlet 180 °C) gave *E-1-(4-chlorophenyl)-4-phenylbut-1-en-3-yne* **116** as a yellow oil (39%) (Found: M+, 238.0551. $C_{16}H_{11}{}^{35}Cl$ requires M+, 238.0547) ; ν_{max} /cm^{-1} 3020, 2965, 2910, 2295, 2195, 1590, 1478, 1004 and 950; δ_H 7.72–7.22 (9H, m), 6.97 (1H, half AB pattern, ^3J 16) and 6.55 (1H, half AB pattern, ^3J 16) ; δ_C 139.8 (C-1), 134.8, 134.3, 131.5, 128.9, 128.34, 128.30, 127.4, 123.2, 108.8 (C-2), 92.3 (C-3) and 88.5 (C-4). *m/z* 238 (^{35}Cl–M+, 17%), 216 (20), 202 (100), 126 (9), 101 (21), 77 (19) and 63 (17).

14. (α-2-Chlorocinnamoyl-α-phenylmethylene)triphenylphosphorane **79**

FVP of the title compound (160 mg, 500 °C, 16 mTorr, inlet 160 °C) gave *E-1-(2-chlorophenyl)-4-phenylbut-1-en-3-yne* **117** as a yellow oil (58%) (Found: M+, 238.0545. $C_{16}H_{11}{}^{35}Cl$ requires M+, 238.0547) ; ν_{max} /cm^{-1} 3020, 2965, 2910, 2290, 2185, 1600, 1243 and 948; δ_H 7.61–7.16 (10H, m) and 6.39 (1H, half AB pattern, ^3J 16) ; δ_C 137.0 (C-1), 134.3, 133.2, 131.6, 130.0, 129.5, 128.4, 128.4, 126.9, 126.1, 123.1, 110.7 (C-2), 92.6 (C-3)

and 88.6 (C-4). *m/z* 238 (^{35}Cl–M$^+$, 23%), 202 (100), 126 (4), 101 (21), 88 (8), 75 (9), 63 (11) and 51 (13).

15. (α-2-Nitrocinnamoyl-α-phenylmethylene)triphenylphosphorane **80**

FVP of the title compound (120 mg, 500 °C, 13 mTorr, inlet 130 °C) gave *E-1-(2-nitrophenyl)-4-phenylbut-1-en-3-yne* **118** as a light brown oil (19%) (Found: M$^+$, 249.0782. $C_{16}H_{11}NO_2$ requires M$^+$, 249.0790); ν_{max} /cm^{-1} 3063, 2955, 2922, 2853, 2242, 2196, 1603, 1508, 1343, 1259 and 805; δ_H 8.08–7.92 (1H, m), 7.68–7.22 (9H, m), 6.39 (1H, half AB pattern, ^3J 16); δ_C 147.5, 135.7, 133.2 (C-1), 132.6, 131.7, 128.9, 128.7, 128.4, 127.8, 124.8, 122.8, 113.6 (C-2), 83.6 (C-3) and 88.1 (C-4) *m/z* 249(M$^+$, 31%), 232 (9), 217 (18), 202 (36), 189 (19), 175 (14), 165 (15), 128 (50), 114 (31), 105 (100), 92 (52) and 77 (64).

16. (α-3,4-Methylenedioxycinnamoyl-α-phenylmethylene)triphenyl phosphorane **81**

FVP of the title compound (200 mg, 500 °C, 15 mTorr, inlet 190 °C) gave *E-1-(3,4-methylenedioxyphenyl)-4-phenylbut-1-en-3-yne* **119** as a yellow oil (58%) (Found: M$^+$, 248.0829. $C_{17}H_{12}O_2$ requires M$^+$, 248.0834); ν_{max} /cm^{-1} 2870, 2760, 2240, 2180, 1695, 1465, 1025 and 900; δ_H 7.50–7.12 (5H, m), 7.0–6.71 (4H, m), 6.19 (1H, half AB pattern, *J* 16) and 5.95 (2H, s) ; δ_C 148.2 (2C), 140.9 (C-1), 131.4 , 130.8, 128.3, 128.1, 123.5, 121.7, 108.4 (C-2), 106.1, 105.1, 101.3, 91.3 (C-3) and 89.0 (C-4); *m/z* 248 (M$^+$, 82%), 218 (11), 189 (100), 163 (15), 150 (5), 139 (8), 121 (8) and 109 (10).

17. (α-3-(2-furyl)propenoyl-α-phenylmethylene)triphenylphosphorane **82**

FVP of the title compound (160 mg, 500 °C, 14 mTorr, inlet 140 °C) gave *E-4-(2-furyl)-1-phenylbut-1-en-3-yne* **120.** as a yellow oil (55%) (Found:

M+, 194.0735. $C_{14}H_{10}O$ requires M+, 194.0729); ν_{max} /cm^{-1} 3010, 2240, 2180, 1588, 1478, 1008, 940 and 893; δ_H 7.45–7.20 (6H, m), 6.79 (1H, half AB pattern, *J* 16) and 6.44-6.23 (3H, m); δ_C 152.2, 143.0 (C-1), 131.4, 128.3, 128.2, 128.1, 123.4, 111.9, 110.1, 106.1 (C-2), 92.4 (C-3) and 88.9 (C-4); *m/z* 194 (52%), 166 (14), 165 (100), 155 (11), 141 (31), 139 (24), 128 (13), 115 (42), 91 (25), 86 (50), 84 (73) and 77 (13).

18. (α-3-(2-thienyl)propenoyl-α-phenylmethylene)triphenylphosphorane **83**

FVP of the title compound (184 mg, 500 °C, 30 mTorr, inlet 170 °C) gave *E-4-phenyl-1-(2-thienyl)but-1-en-3-yne* **121** as a yellow oil (47%) (Found: M+, 210.0497. $C_{14}H_{10}S$ requires M+, 210.0503); ν_{max} /cm^{-1}3020, 2970, 2285, 2240, 1586, 1478, 1010 and 900; δ_H 7.50–6.93 (9H, m) and 6.19 (1H, half AB pattern, ^3J 16); δ_C 141.5, 134.0 (C-1), 131.4, 128.3, 128.2, 127.8, 127.1, 125.5, 123.3, 107.3 (C-2), 92.1 (C-3) and 88.7 (C-4); *m/z* 210 (M+, 57%), 184 (100), 165 (32), 152 (18), 139 (26), 105 (32) and 84 (63).

19. (α-3-(5-methyl-2-thienyl)propenoyl-α-phenylmethylene)triphenyl phosphorane **84**

FVP of the title compound (190 mg, 500 °C, 10 mTorr, inlet 150 °C) gave *E-1-phenyl-4-(5-methyl-2-thienyl)but-1-en-3-yne* **122** as a yellow oil (34%) (Found: M+, 224.0675. $C_{15}H_{12}S$ requires M+, 244.0660); ν_{max} /cm^{-1} 3050, 2980, 2918, 2227, 1590, 1472, 1436, 1260, 1118, and 797; δ_H 7.72–7.25 (5H, m), 7.40 (1H, half AB pattern, ^3J 16), 6.83 (1H, half AB pattern, ^3J 9), 6.64 (1H, half AB pattern, ^3J 9), 6.50 (1H, half AB pattern, ^3J 16) and 2.47 (3H, s); δ_C 140.7, 139.5, 134.4 (C-1), 131.4, 128.3, 128.0, 127.5, 126.0, 123.5, 105.8 (C-2), 91.7 (C-3), 88.9 (C-4) and 15.6; *m/z*

224 (M^+, 100%), 223 (70), 224 (15), 208 (11), 198 (13), 189 (16), 178 (9), 165 (16), 151 (7), 105 (26), 77 (15) and 51 (14).

20. (α-(α-methylcinnamoyl)-α-phenylmethylene)triphenylphosphorane **85**

FVP of the title compound (158 mg, 500 °C, 15 mTorr, inlet 140 °C) gave *E-1,4-diphenyl-2-methylbut-1-en-3-yne* **123** as a yellow oil (55%) (Found: M^+, 218.1100. $C_{17}H_{14}$ requires M^+, 218.1092); ν_{max} /cm^{-1} 3005, 2905, 2195, 1948, 1591, 1478, 1063 and 912; δ_H 7.51–7.19 (10H, m), 6.94 (1H, q, ^4J 1) and 2.16 (3H, d, ^4J 1); δ_C 136.8, 136.1 (C-1), 131.5, 129.0, 128.3, 128.3, 128.0, 127.2, 123.4, 119.8 (C-2), 93.2 (C-3), 88.4 (C-4) and 19.3; *m/z* 218 (M^+, 100%), 202 (88), 189 (13), 139 (8), 115 (18), 101 (10), 89 (11), 77 (18) and 63 (17).

21. (α-2-Methylcinnamoylethylidene)triphenylphosphorane **90**

FVP of the title compound (95 mg, 500 °C, 12 mTorr, inlet 200 °C) gave *E-1-(2-methylphenyl)pent-1-en-3-yne* **124** as a yellow oil (15%) (Found: M^+, 156.0941. $C_{12}H_{12}$ requires M^+, 156.0939); ν_{max} /cm^{-1} 3000, 2905, 2840, 2300, 1565, 1335, 1180 and 1110; δ_H 7.75–7.02 (5H, m), 6.03 (1H, half AB pattern of q, ^3J 16, ^5J 2), 2.32 (3H, s), 2.00 (3H, d, ^5J 2); δ_C 137.9 (C-1), 137.9, 135.5, 130.4, 128.2, 126.1, 124.8, 109.7 (C-2), 87.9 (C-3) 79.2 (C-4), 19.8 and 4.5 (C-5); *m/z* 156 (M^+, 78%), 141 (100), 128 (34), 115 (81), 91 (19), 77 (19), 63 (30) and 51 (30).

22. (α-2-Methylcinnamoyl-1-propylidene)triphenylphosphorane **91**

FVP of the title compound (200 mg, 500 °C, 16 mTorr, inlet 140 °C) gave *E-1-(2-methylphenyl)hex-1-en-3-yne* **125** as a yellow oil (77%) (Found: M^+, 170.1103. $C_{13}H_{14}$ requires M^+, 170.1092); ν_{max} /cm^{-1} 2900, 2230, 1780, 1680, 1595, 1469, 1338, 1309 and 947; δ_H 7.50–7.05 (5H, m), 6.06 (1H, dt, ^3J 16, ^5J 2), 2.47-2.29 (5H, m) and 1.20 (3H, t, ^3J 8); δ_C

137.8,(2C)(C-1) 135.5, 130.4 , 128.1, 126.1, 124.8, 109.8 (C-2), 93.8 (C-3), 79.4 (C-4), 19.8, 13.9 (C-6) and 13.3 (C-5); *m/z* 170 (M^+, 77%), 155 (100), 141 (52), 128 (51), 115 (47), 84 (32) and 77 (21).

23. (α-2-Methylcinnamoyl-2-methyl-1-propylidene)triphenylphosphorane **92**

FVP of the title compound (200 mg, 500 °C, 40 mTorr, inlet 120 °C) gave *E-1-(2-methylphenyl)-5-methylhex-1-en-3-yne* **126** as a yellow oil (75%) (Found: M^+, 184.1258. $C_{14}H_{16}$ requires M^+, 184.1252); ν_{max} /cm^{-1} 2900, 2300, 1680, 1596, 1314, 955, 853 and 816; δ_H 7.47–7.05 (5H, m), 6.08 (1H, half AB pattern of d, ^3J 16, ^5J 2), 2.75 (1H, septet of d, J 7, ^5J 2), 2.36 (3H, s), 1.23 (6H, d, ^3J 7); δ_C 137.7 (C-1), 137.7, 135.5, 130.4, 128.1, 126.1, 124.8, 109.8 (C-2), 97.9 (C-3) 79.2 (C-4),.23.0 (C-6), 21.3 (C-5) and 19.8; *m/z* 184 (M^+, 100%), 169 (89), 154 (78), 128 (64), 115 (40), and 77 (24).

24. (α-2-Methylcinnamoyl-α-phenylmethylene)triphenylphosphorane **93**

FVP of the title compound (116 mg, 500 °C, 22 mTorr, inlet 160 °C) gave *E-1-(2-methylphenyl)-4-phenylbut-1-en-3-yne* **127** as a yellow oil (65%) (Found: M^+, 218.1093. $C_{17}H_{14}$ requires M^+, 218.1092); ν_{max} /cm^{-1} 2900, 2840, 2295, 1590, 1092, 1060, 948 and 800; δ_H 7.56–7.16 (10H, m), 6.31 (1H, d, J 16) and 2.40 (3H, s); δ_C 139.0 (C-1), 137.0, 135.8, 131.5, 130.6, 128.3, 128.2, 126.1, 124.8, 123.5, 109.1 (C-2), 91.3 (C-3), 89.2 (C-4) and 19.8; *m/z* 218 (M^+, 100%), 197 (37), 182 (48), 169 (65), 156 (43), 141 (27) and 128 (19).

25. (α-2-Methylcinnamoyl-α-methoxycarbonylmethylene)triphenyl phosphorane **100**

FVP of the title compound (410 mg, 500 °C, 25 mTorr, inlet 210 °C) gave *E-4-methoxycarbonyl-1-(2-methylphenyl)but-1-en-3-yne* **128** as a light yellow oil (92%) (Found: M+, 200.0870. $C_{13}H_{12}O_2$ requires M+, 200.0837); ν_{max} /cm^{-1} 2951, 2208, 1710, 1597, 1484, 1478, 1255, 1111, 1089 and 749; δ_H 7.60–7.42 (2H, m), 7.30–7.13 (3H, m), 6.13 (1H, half AB pattern, ^3J 16), 3.83 (3H, s) and 2.38 (3H, s); δ_C 154.5, 145.6 (C-1), 136.6, 134.0, 130.8, 129.9, 126.4, 125.3, 105.5 (C-2), 86.6 (C-3), 81.7 (C-4), 52.7 and 19.7 ; *m/z* (20 eV), 200 (M+, 25%), 185 (4), 182 (3), 169 (17), 155 (13), 141 (100), 129 (18), 115 (30), 91 (10), 77 (8) and 63 (12).

26. (α-2,4,6-Trimethylcinnamoylethylidene)triphenylphosphorane **94**

FVP of the title compound (103 mg, 500 °C, 26 mTorr, inlet 150 °C) gave *E-1-(2,4,6-trimethylphenyl)pent-1-en-3-yne* **129** as a yellow oil (48%) (Found: M+, 184.1248 . $C_{14}H_{16}$ requires M+, 184.1257); ν_{max} /cm^{-1} 2900, 2840, 2205, 1600, 1430, 1028, 955 and 856; δ_H 7.00–6.80 (3H, m), 5.68 (1H, half AB pattern of q,^3J 16, ^5J 2), 2.26 (6H, s), 2.25 (3H, s) and 2.01 (3H, d, ^5J 2); δ_C 138.6, (C-1), 136.8, 136.0 133.0, 128.9, 113.9 (C-2), 87.4 (C-3) 79.1 (C-4), 20.4 (3C) and 4.0 (C-5); *m/z* 184 (M+, 74%), 182 (15), 170 (37), 169 (100), 167 (24), 156 (21), 155 (31), 154 (29), 153 (34), 152 (27), 141 (56), 128 (29), 115 (42) and 91 (22).

27. (α-2,4,6-Trimethylcinnamoyl-1-propylidene)triphenylphosphorane **95**

FVP of the title compound (80 mg, 500 °C, 20 mTorr, inlet 140 °C) gave *E-1-(2,4,6-trimethylphenyl)hex-1-en-3-yne* **130** as a yellow oil (45%) (Found: M+, 198.1412. $C_{15}H_{18}$ requires M+, 198.1404) ; ν_{max} /cm^{-1} 2900, 2205, 1600, 1460, 1310, 1055, 952 and 852; δ_H 6.97–6.78 (3H, m), 5.67 (1H, d of t, ^3J 16, ^5J 2), 2.48–2.11 (11H, m) and 1.23 (3H, t, ^3J 7); δ_C 138.4

(C-1), 136.8, 136.0, 133.1, 128.8, 113.9 (C-2), 93.1 (C-3), 79.0 (C-4), 21.0, 20.9, 13.9 (C-6) and 13.3 (C-5); *m/z* 198 (M^+, 98%), 183 (40), 169 (100), 154 (41), 141 (49), 128 (31) and 115 (30).

28. (α-2,4,6-Trimethylcinnamoyl-2-methyl-1-propylidene)triphenyl phosphorane **96**

FVP of the title compound (90 mg, 500 °C, 4 mTorr, inlet 120 °C) gave *E-5-methyl-1-(2,4,6-trimethylphenyl)hex-1-en-3-yne* **131** as a yellow oil (70%) (Found: M^+, 212.1561. $C_{16}H_{20}$ requires M^+, 212.1560); ν_{max} /cm^{-1} 2905, 2850, 2200, 1600, 1450, 1310, 955 and 900; δ_H 7.00–6.85 (3H, m), 5.72 (1H, d of d, ^3J 16, ^5J 2), 2.76 (1H, septet of d, ^3J 7, ^5J 2), 2.32 (6H, s), 2.30 (3H, s) and 1.26 (6H, d, ^3J 7); δ_C 138.3 (C-1), 136.7, 136.0, 133.2, 128.8 , 113.9 (C-2), 97.1 (C-3), 78.8 (C-4), 23.0 (C-6), 21.3 (C-5) and 21.0 (3C); *m/z* 212 (M^+, 100%), 197 (41), 182 (55), 169 (84), 156 (58), 141 (55), 128 (40) and 115 (39).

29. (α-2,4,6-Trimethylcinnamoyl-α-phenylmethylene)triphenyl phosphorane **97**

FVP of the title compound (100 mg, 500 °C, 44 mTorr, inlet 140 °C) gave *E-4-phenyl-1-(2,4,6-trimethylphenyl)but-1-en-3-yne* **132** as a yellow oil (19%) (Found: M^+, 246.1416. $C_{19}H_{18}$ requires M^+, 246.1401) ; ν_{max} /cm^{-1} 2900, 2840, 2290, 1600, 1243, 1063, 956 and 802; δ_H 7.76–7.25 (5H, m), 7.10 (1H, half AB pattern, ^3J 16), 6.89 (2H, s), 5.97 (1H, half AB pattern, ^3J 16), 2.35 (6H, s) and 2.29 (3H, s); δ_C 139.9 (C-1), 137.1, 136.2, 132.9, 131.5 , 128.9, 128.3, 128.1, 123.4, 113.2 (C-2), 90.7 (C-3), 88.2 (C-4), 21.1 and 21.0; *m/z* 246 (M^+, 100%), 231 (67), 215 (75), 182 (19), 169 (36), 152 (23), 128 (32) and 115 (38).

30. Identification of the Byproduct in pyrolysis of an old sample of ylide **90**

FVP of (α-2-methylcinnamoylethylidene)triphenylphosphorane **90** (196 mg, 500 °C, 213 mTorr, inlet 160 °C) gave colourless crystals of triphenylphosphine oxide and an oil composed of *E-1-(2-methylphenyl)pent-1-en-3-yne* **124** (10%) [spectra as in 9. above] and an almost equivalent quantity of an unknown compound; δ_H 7.84 (1H, half AB pattern *J* 16), 7.54 (1H, dd, *J* 7, 1), 7.5–7.02 (3H by integration), 6.68 (1H, half AB pattern *J* 16), 2.64 (2H, q, *J* 7), 2.38 (3H, s) 1.13 (3H, t, *J* 7); δ_C 200.7, 139.5, 137.8, 133.4, 130.0, 126.9, 126.3, 126.2, 34.3, 19.7 and 8.2. The appearance of a carbonyl signal in the ^{13}C spectrum and the vinyl and ethyl protons in the ^{1}H spectrum led to the conclusion that the unknown was the hydrolysis product of the phosphorane, 1-(2-methylphenyl)pent-1-en-3-one .

An authentic sample of this material was produced by the method of Heilbron *et al*[66] as follows. o-Tolualdehyde (9.0 g, 75 mmol), NaOH (1 ml of 2M soln , 2 mmol) and butan-2-one (11.00 g, 150 mmol) were stirred in 50% aqueous ethanol (100 ml) for 48 hours. The resultant muddy brown mixture was poured into water (50 ml) and extracted with ether. The ethereal solution was dried, evaporated and distilled to give 1-(2-methylphenyl)pent-1-en-3-one (3.96 g, 30%); bp. 160 °C / 26 Torr (lit.,[67] 157 °C / 25 Torr) ^{1}H and ^{13}C NMR identical to the compound above.

E. High temperature flash vacuum pyrolysis of the β-oxoalkylidenetriphenylphosphoranes.

1. (α-2-Methylcinnamoylethylidene)triphenylphosphorane **90**

FVP of the title compound (109 mg, 900 °C, 26 mTorr, inlet 140 °C) gave a mixture of triphenylphosphine oxide [δ_H 7.74–7.37 (15H, m); δ_C 132.4 (d, $^1J_{CP}$ 104), 132.1 (d, $^2J_{CP}$ 10), 132.0 and 128.5 (d, $^3J_{CP}$ 12)] and 2-vinylnaphthalene **133** (7%) indicated by δ_H 6.91 (1H, dd, *J* 18,11), 5.86 (1H, dd, *J* 18,1) and 5.33 (1H, dd, *J* 11,1).

2. (α-2-Methylcinnamoyl-1-propylidene)triphenylphosphorane **91**

FVP of the title compound (101 mg, 900 °C, 15 mTorr, inlet 140 °C) gave colourless crystals of triphenylphosphine oxide as above and an oil composed mainly of 2-vinylnaphthalene **133** (23%); δ_H as above. GC-MS of the oil showed it to contain 2-vinylnaphthalene **133** (75%) [*m/z* 154 (M^+, 100%), 128 (29)], indene (15%) [*m/z* 116 (M^+,84%), 115 (100)], naphthalene (8%) [*m/z* 128 (M^+, 100%), 102 (15)] and traces of toluene [*m/z* 92 (M^+, 51%), 91 (100)], ethylbenzene [*m/z* 106 (M^+, 38%), 91 (100)], 2-methylstyrene [*m/z* 118 (M^+, 57%), 117 (15)] and 2-propenylnaphthalene **134** [*m/z* 168 (M^+, 100%), 153 (58)].

In an attempt to reduce the number of components from the pyrolysis and isolate the 2-vinylnaphthalene for ^{13}C spectroscopy the pyrolysis was repeated at a slightly lower temperature and the products separated on preparative TLC. Repeat pyrolysis (180 mg, 850 °C, 14 mTorr, Inlet 140 °C) followed by preparative TLC thus gave pure 2-vinylnaphthalene **133** (14 mg, 23%); δ_H 7.9–7.15 (7H, m), 6.91 (1H, dd, *J* 18,11), 5.86 (1H, dd, *J* 18,1) and 5.33 (1H, dd, *J* 11,1); δ_C 136.9 (C-1'), 135.0 (C-2), 133.5 (C-8a), 133.1 (C-4a), 128.1 (C-4), 128.0 (C-8), 127.7 (C-5), 126.4 (C-1), 126.2 (C-7), 125.9 (C-6), 123.2 (C-3) and 114.2 (C-

2'). [lit.,[67] δ_C 136.9 (C-1'), 134.9 (C-2), 133.5 (C8a), 133.1 (C-4a), 128.1 (C-4), 128.0 (C-8), 127.6 (C-5), 126.4 (C-1), 126.2 (C-7), 125.8 (C-6), 123.1 (C-3) and 114.1 (C-2)].

3. (α-2-Trideuteriomethylcinnamoyl-1-propylidene)triphenylphosphorane **165**

FVP of the title compound (180 mg, 850 °C, 40 mTorr, inlet 140 °C) and subsequent isolation by preparative TLC gave 1,1'-dideuterio-2-vinylnaphthalene **170**(13 mg, 21%); δ_H 7.9–7.15 (6H, m), 5.86 (1H, s) and 5.33 (1H, s); δ_D (41 MHz) 7.62 (1D, s) and 6.95 (1D, s); [lit.,[67] δ_H 7.65 (H-1) and 6.80 (H-1')]; δ_C (75MHz) 136.9 (C-1') very weak, 134.9 (C-2), 133.5 (C-8a), 133.2 (C-4a), 128.1 (C-4), 128.0 (C-8), 127.7 (C-5), C-1 signal not present, 126.2 (C-7), 125.9 (C-6), 123.2 (C-3) and 114.0 (C-2').

4. (α-2-Methylcinnamoyl-2-methyl-1-propylidene)triphenylphosphorane **92**

FVP of the title compound (175 mg, 900 °C, 60 mTorr, inlet 130 °C) gave triphenylphosphine oxide identified as above and a colourless oil composed of 2-vinylnaphthalene **133** (17%); δ_H as above and 2-propenylnaphthalene (7%); δ_H 7.9–7.3 (7H, m), 6.75–5.75 (2H, m) and 2.0–1.85 (3H, m). GC-MS showed the presence of 2-vinylnaphthalene **133** [*m/z* 154 (M^+, 100%), 153 (58%)], 2-propenylnaphthalene **134** [*m/z* 168 (M^+, 100%), 128 (29)] and traces of indene [*m/z* 116 (M^+, 84%), 115 (100)], naphthalene [*m/z* 128 (M^+, 100%), 102 (15)] and toluene [*m/z* 92 (M^+, 51%), 91 (100)].

5. (α-2-Methylcinnamoyl-α-phenylmethylene)triphenylphosphorane **93**

FVP of the title compound (17 mg, 900 °C, 40 mTorr, inlet 160 °C) gave a solid at the furnace exit. A fraction taken by dissolving out the crystals near the neck of the trap was shown by TLC to contain a mixture of

triphenylphosphine oxide and 2-benzylnaphthalene **134** (both verified by TLC with authentic samples) and a further unknown hydrocarbon. ^{1}H NMR showed the presence of 2-benzylnaphthalene **137** (25%); δ_H 7.85–7.6 (4H, m), 7.5–7.25 (3H, m), 7.25 (5H, s) and 4.14 (2H, s) together with evidence for benzo[c]fluorene **138** (9%); δ_H 8.72 (1H, dd, *J* 8, 2), 8.34 (1H, dd, *J* 7, 2), 7.9–7.2 (8H, m) and 3.96 (2H, s) [lit.,[68] 8.69 (1H, dd, *J* 8, 1), 8.31 (1H, dd, *J* 8, 1), 7.86–7.10 (8H, m) and 3.87 (2H, s)].

6. (α-2,4,6-Trimethylcinnamoylethylidene)triphenylphosphorane **94**

FVP of the title compound (100 mg, 900 °C, 32 mTorr, inlet 140 °C) gave a solid at the furnace exit shown by TLC to be triphenylphosphine oxide and a colourless oil found to be mainly 5,7-dimethyl-2-vinylnaphthalene **135** (22%); δ_H 7.95–7.8 (1H, m), 7.7–7.1 (4H, m), 6.88 (1H, dd, *J* 18, 10), 5.83 (1H, dd, *J* 18, 1), 5.30 (1H, dd, *J* 10, 1) 2.60 (3H, s) and 2.42 (3H, s)

7. (α-2,4,6-Trimethylcinnamoyl-1-propylidene)triphenylphosphorane **95**

FVP of the title compound (99 mg, 900 °C, 42 mTorr, inlet 120 °C) gave a solid at the furnace exit shown by TLC to be triphenylphosphine oxide and a colourless oil found to be clean 5,7-dimethyl-2-vinylnaphthalene **135** (22%); δ_H as above; δ_C 137.0, 135.5, 134.0, 133.9, 129.1, 128.5, 128.3, 126.3, 125.4, 124.2, 122.1, 113.8, 21.6 and 19.2

8. (α-2,4,6-Trimethylcinnamoyl-2-methyl-1-propylidene)triphenyl phosphorane **96**

FVP of the title compound (130 mg, 900 °C, 28 mTorr, inlet 130 °C) gave a solid at the furnace exit shown by TLC to be triphenylphosphine oxide and a colourless oil found to be a mixture of *E*- and *Z*-5,7-dimethyl-2-propenylnaphthalene **136** (6%); δ_H 7.9–7.7 (1H, m), 7.65–7.3 (3H, m),

7.05 (1H, m), 6.75–5.75 (2H, m), 2.59 (3H, s), 2.42 (3H, s) and 2.0-1.85 (3H, m) and 5,7-dimethyl-2-vinylnaphthalene **135** (14%); δ_H as above.

9. (α-2,4,6-Trimethylcinnamoyl-α-phenylmethylene)triphenyl phosphorane **97**

FVP of the title compound (114 mg, 900 °C, 30 mTorr, inlet 100 °C) gave a solid at the furnace exit. A fraction taken by dissolving out the crystals near the neck of the trap was shown by TLC to contain triphenylphosphine oxide and two unknown hydrocarbons. ^{1}H NMR showed the presence of 2-benzyl-5,7-dimethylnaphthalene **139** (16%); δ_H 7.9–6.8 (10H, m), 4.12 (2H, s), 2.62 (3H, s) and 2.44 (3H, s) together with evidence for 8,10-dimethylbenzo[c]fluorene **140** (13%) δ_H 8.5–8.4 (2H, m), 8.2–7.1 (6H, m), 3.96 (2H, s), 2.71 (3H, s) and 2.63 (3H, s).

10. (α-3-(3-methyl-2-thienyl)propenoyl-α-phenylmethylene)triphenyl phosphorane **141**

FVP of the title compound (200 mg, 850 °C, 40 mTorr, inlet 60 °C) gave a solid at the furnace exit. A fraction taken by dissolving out the crystals near the neck of the trap was shown by TLC to contain a mixture of triphenylphosphine oxide and two unknown components. Preparative TLC failed to separate the unknowns and the mixture was isolated as a colourless oil (30 mg) which consisted by GC-MS of **142** (60%); *m/z* 226 (M^+, 16%), 225 (83), 224 (66), 222 (24), 208 (8), 189 (14), 178 (16), 147 (100), 121 (12), 111 (46), 89 (54), 86 (18), 77 (19), 69 (20) and 63 (40) and **143** (40%); *m/z* 224 (M^+, 20%), 223 (100), 222 (83), 222 (24), 189 (28), 176 (17),163 (5), 150 (7), 111 (48), 89 (54), 98 (20), 88 (16) 76 (7) and 63 (7); ^{1}H NMR for the mixture gave a complex aromatic region and two singlets; δ_H 8.13–7.1 (m), 4.07 (s) and 3.99 (s) with the ratio of the singlets 60:40 indicating that they are due to the separate components found by GC-

MS. Making the assumption that the products are formed similarly to those of 9. above then the products are 5-benzylbenzothiophene **142** (20%) and 6H-fluoreno[3,4-b]thiophene **143** (13%).

11. (α-2-Methylcinnamoyl-α-methoxycarbonylmethylene)triphenyl phosphorane **100**

FVP of the title compound (200 mg, 830 °C, 14 mTorr, Inlet 160 °C) gave a solid at the furnace exit which was shown by TLC to be triphenylphosphine oxide and a yellow oil (49 mg) that turned to a dark red colour on exposure to air which contained triphenylphosphine oxide and further components by ^{1}H NMR. The spectrum was identical to that below save for the presence of triphenylphosphine oxide.

Pyrolysis of 4-methoxycarbonyl-1-(2-methylphenyl)but-1-en-3-yne **128** (70 mg, 830 °C, 90 mTorr, inlet 60 °C), obtained from low temperature pyrolysis of the above, gave a yellow oil (61 mg) that turned to a dark red colour on exposure to air . Analysis by GC-MS showed the presence of 2-methylnaphthalene (21%) [*m/z* 142 (M^+, 96%), 141 (100)], 2-ethylnaphthalene (58%) [*m/z* 156 (M^+,37%), 141 (100)] and 2-vinylnaphthalene **133** (7%) [*m/z* 154 (M^+, 100%), 153 (66)] in the ratio 3:8:1. ^{1}H NMR of the mixture gave a multiplet (δ_H 7.89–7.1) incorporating signals from all components plus additional signals as follows; 2-methylnaphthalene δ_H 2.48 (3H, s), 2-ethylnaphthalene δ_H 2.79 (2H, q, J 8) and 1.31 (3H, t, J 8), and 2-vinylnaphthalene **133** δ_H 6.91 (1H, dd, *J* 18,11), 5.86 (1H, dd, *J* 18,1) and 5.33 (1H, dd, *J* 11,1). The spectrum also showed evidence of a small quantity of methanol; δ_H 3.47 (3H, s) and 3.42 (1H, s) and a trace of an unidentified component δ_H 4.78 (s) and 4.73 (s).

12. (α-Cinnamoyl-α-2-methoxyphenylmethylene)triphenylphosphorane **98**

FVP of the title compound (210 mg, 830 °C, 19 mTorr, inlet 120 °C) gave a solid at the furnace exit which was shown by TLC to be triphenylphosphine oxide and a red liquid which contained of triphenylphosphine oxide and further components by ^{1}H NMR. Preparative TLC gave a red oil (56 mg) which was characterised by GC-MS to be two isomers of benzonaphthofuran. benzo[b]naphtho[2,1d]furan **145** (14%); *m/z* 219 (M^+ +1, 17%), 218 (M^+, 100), 202 (2), 190 (5), 189 (38), 188 (10), 187 (11), 163 (10), 150 (3), 139 (4), 109 (60), 95 (64), 94 (27), 82 (30), 74 (7) and 63 (12); benzo[b]naphtho[1,2d]furan **144** (44%); *m/z* 219 (M^+ +1, 17%), 218 (M^+, 100), 203 (1), 190 (6), 189 (42), 188 (11), 187 (12), 163 (11), 150 (3), 139 (4), 109 (40), 98 (3), 94 (94) 82 (34), 74 (7) and 63 (12).[lit.,[69] benzo[b]naphtho[1,2-d]furan; *m/z* 220 (4), 219 (36), 218 (M^+, 100%), 190 (313), 189 (58), 164 (4) and 163 (13)].

The major isomer **144** has the greatest contribution to δ_H 8.58 (1H, d, *J* 8), 8.32 (1H, m), 8.0–7.81 (2H, m), 7.78–7.59 (2H, m) and 7.58–7.33 (4H, m); δ_C 155.6 (4ry), 154.2 (4ry), 129.08, 128.45, 127.04, 125.76, 124.28, 123.30, 123.04, 121.81, 112.56 and 111.72 and many other smaller peaks of uncertain assignment [lit.,[69] benzo[b]naphtho[1,2-d]furan δ_C 155.8 (4ry) and 154.2 (4ry); lit.,[70] benzo[b]naphtho[1,2-d]furan δ_C(D.E.P.T) 129.08, 128.43, 127.02, 125.74, 124.26, 123.33, 123.03, 121.81, 112.58 and 111.75]; Evidence for the minor isomer is found from δ_H 8.39 (1H, d, *J* 8) and a similar small signal from 7.33-7.15 (m).

UV-Vis For mixture obtained λ_{max} (μm) 240.1, 252.0, 260.6, 281.1, 310.4, 324.4, 333.3 and 339.8 [lit.,[71] benzo[b]naphtho[1,2-d]furan; λ_{max} (μm) 240, 252, 280, 316 and 339. benzo[b]naphtho[2,1-d]furan; λ_{max} (μm) 260, 295, 324, 334 and 340. benzo[b]naphtho[2,3-d]furan; λ_{max} (μm) 262, 271, 283, 319 and 358].

F. High temperature flash vacuum pyrolysis of acetylenic esters.

1. Methyl phenylpropiolate **181**

FVP of the title compound (140 mg, 780 °C, 34 mTorr, inlet RT) gave a light yellow liquid found by ^{1}H NMR to consist of phenylacetylene **183** (37%); δ_H 7.67-7.25 (5H, m) and 3.07 (1H, s); δ_C 132.2, 128.5, 128.3, 122.1, 83.6 and 77.2, unchanged methyl phenylpropiolate **181** (13%); δ_H 7.67–7.25 (5H, m) and 3.86 (3H, s), and styrene (4%); δ_H 7.67-7.25 (5H, m), 6.68 (1H, m), 5.73 (1H, dd, *J* 20,1) and 5.23 (1H, dd, *J* 12,1).

2. Preparation and pyrolysis of ethyl methyl acetylenedicarboxylate **184**

The starting material was prepared by pyrolysis of the requisite ylide 4-ethyl-1-methyl-2-oxo-3-triphenylphosphoranylidenebutanedioate prepared by Hérion in this laboratory.[72] FVP of this (1.10 g, 500 °C, 22 mTorr, inlet 120 °C) gave ethyl methyl acetylenedicarboxylate **184** as a colourless oil (346 mg, 88%); δ_H 4.29 (2H, q, *J* 7), 3.48 (3H, s) and 1.33 (3H, t, *J* 7); δ_C 152.3, 151.7, 75.0, 74.2, 63.1, 53.5 and 13.9.

Pyrolysis of **184** (42 mg, 760 °C, 140 mTorr, inlet RT) gave a colourless liquid composed of acrolein (45%); δ_H 9.62–9.58 (1H, m) and 6.55–6.32 (3H, m), and traces of methyl propiolate **185**; δ_H 3.71 (3H, s,) and 2.89 (1H, s) and acetaldehyde; δ_H 9.79 (1H, q, *J* 0.5) and 2.21 (3H, d, *J* 0.5). The presence of ethene in the pyrolysate was supported by a later ^{1}H spectrum showing a diminished intergral for a signal at δ_H 5.41 (s)

3. Pyrolysis of methyl propiolate **185**

FVP of the title compound (120 mg, 830 °C, 380 mTorr, inlet cooled with solid CO_2/MeOH) gave a small quantity of a volatile colourless liquid much

of which was lost in the vacuum system. The liquid was dissolved in $CDCl_3$ and found to consist of acrolein (15%); δ_H 9.62–9.58 (1H, m) and 6.55–6.32 (3H, m); δ_C 194.5, 138.5, 137.9, unchanged methyl propiolate **185** (trace); δ_H 3.71 (3H, s,), and 2.89 (1H, s), and formaldehyde (trace); δ_H 9.73 (1H, s) and 5.02-4.88 (m) [authentic formaldehyde polymerised in $CDCl_3$ to give δ_H 5.08-4.86 (m)]. The presence of ethene in the pyrolysate was supported by a later ^1H spectrum showing a diminished intergral for a signal at δ_H 5.41 (s).

4. Pyrolysis of dimethyl acetylenedicarboxylate

FVP of the title compound (90 mg, 830 °C, 400 mTorr, Inlet 70 °C) gave a small quantity of a volatile colourless liquid which was dissolved out in $CDCl_3$ and found to consist of acrolein (68%); δ_H 9.62-9.58 (1H, m) and 6.55–6.32 (3H, m); δ_C 194.5, 138.5 and 137.8; formaldehyde, monomer (trace); δ_H 9.73 (1H, s) and a large multiplet for formaldehyde polymer; δ_H as above. The presence of ethene in the pyrolysate was supported by a later ^1H spectrum showing a diminished intergral for a signal at δ_H 5.41 (s).

G Pyrolysis of oxygen functionalised compounds over magnesium.

1. FVP of benzaldehyde

FVP of the title compound (530 mg, 600 °C, 350 mTorr, inlet RT, 1.52 g Mg) gave two fractions, white crystals and a viscous yellow liquid. The whole was dissolved out and analysed by GC-MS. The products consisted of unchanged benzaldehyde (46%) [*m/z* 106 (M^+, 37%), 51 (100)], diphenylmethane (6%) [*m/z* 168 (M^+, 91%), 167 (100)], 1,2-diphenylethane (11%) [*m/z* 182 (M^+, 7%), 91 (100)], 1,2-diphenylethene (8%) [*m/z* 180 (M^+, 92%), 179 (100)] and diphenylacetylene (6%) [*m/z* 178 (M^+, 100%), 76 (46)].

FVP of the title compound (510 mg, 700 °C, 300 mTorr, inlet RT, 1.54 g Mg) gave two fractions, white crystals and a light yellow oil. The whole was dissolved out and analysed by GC-MS. The products consisted of benzene (5%) [*m/z* 78 (M^+, 100%), 49 (52)], toluene (9%) [*m/z* 92 (M^+, 33%), 91 (100)], diphenylmethane (2%) [*m/z* 168 (M^+, 90%), 167 (100)], 1,2-diphenylethane (2%) [*m/z* 182 (M^+, 8%), 91 (100)], 1,2-diphenylethene (4%) [*m/z* 180 (M^+, 92%), 179 (100)] and diphenylacetylene (2%) [*m/z* 178 (M^+, 100%), 76 (46)].

2. FVP of o-tolualdehyde

FVP of the title compound (450 mg, 600 °C, 220 mTorr, inlet RT, 1.51 g Mg) gave three fractions, viscous oil droplets,white crystals and a light transparent oil. The whole was dissolved out and analysed by GC-MS. The products consisted of unchanged o-tolualdehyde (19%) [*m/z* 120 (M^+, 33%), 91 (52)], di-o-toluylmethane **194** (2%) [*m/z* 210 (M^+, 7%), 105 (100)], 1,2-di-o-toluylethene **195** (1%) [*m/z* 208 (M^+, 57%), 115

(100)], 1,2-di-o-toluylacetylene **196** (1%) [*m/z* 206 (M^+, 90%), 89 (100)] and trace amounts of eight further components.

3. FVP of benzyl alcohol

FVP of the title compound (410 mg, 700 °C, 410 mTorr, inlet RT, 1.51 g Mg) gave two fractions, white crystals and a yellow liquid. The whole was dissolved out and analysed by GC-MS. The products consisted of benzene (7%) [*m/z* 78 (M^+, 100%), 49 (28)], toluene (11%) [*m/z* 92 (M^+, 28%), 91 (100)], diphenylmethane (2%) [*m/z* 168 (M^+, 90%), 167 (100)], 1,2-diphenylethane (1%) [*m/z* 182 (M^+, 9%), 91 (100)], 1,2-diphenylethene (2%) [*m/z* 180 (M^+, 92%), 179 (100)] and diphenylacetylene (trace) [*m/z* 178 (M^+, 100%), 76 (22)].

4. FVP of acetophenone

FVP of the title compound (300 mg, 650 °C, 510 mTorr, inlet RT, 1.50 g Mg) gave a yellow liquid. The whole was dissolved out and analysed by GC-MS. The products consisted of benzene (4%) [*m/z* 78 (M^+, 100%), 49 (40)], phenylacetylene (29%) [*m/z* 102 (M^+, 98%), 50 (100)], and unchanged acetophenone (5%) [*m/z* 120 (M^+, 20%), 77 (100)]; δ_H for the mixture:- 7.58–7.23 (m), 3.10 (1H, s) (phenylacetylene) and 2.59 (3H, s) (acetophenone).

Preparative FVP of acetophenone

FVP of the title compound (1.22g, 650 °C, 550 mTorr, inlet RT, 1.50 g Mg) gave a yellow liquid. The whole was dissolved out and analysed by ^1H NMR. The products consisted of phenylacetylene; δ_H 3.10 (1H, s) (4%), and acetophenone; δ_H 2.59 (3H, s,) (55%),.

Intermediate pressure pyrolysis of acetophenone

FVP of the title compound (880 mg, 600 °C, 1800mTorr (N_2 leak), inlet RT, 1.54 g Mg) gave a light yellow liquid. The whole was dissolved

out and analysed by GC-MS. The products consisted of phenylacetylene (4%) [*m/z* 102 (M^+, 98%), 50 (100)], benzaldehyde (8%) [*m/z* 106 (M^+, 48%), (100)] and unchanged acetophenone (16%) [*m/z* 120 (M^+, 18%), 77 (100)].

5. FVP of propiophenone

FVP of the title compound (530 mg, 600 °C, 500 mTorr, inlet 30 °C, 1.52 g Mg) gave a light yellow oil. The whole was dissolved out and analysed by GC-MS. The products consisted of benzene (1%) [*m/z* 78 (M^+, 100%), 49 (52)], toluene (2%) [*m/z* 92 (M^+, 33%), 91 (100)], styrene (3%) [*m/z* 104 (M^+, 100%), 78 (80)], 1-phenylpropene (10%) [*m/z* 118 (M^+, 70%), 117 (100), 91 (60)], indane (1%) [*m/z* 118 (M^+, 62%), 117 (100)], indene (7%) [*m/z* 116 (M^+, 52%), 115 (100)] and 1-phenylpropyne (21%) [*m/z* 116 (M^+, 50%), 115 (100)],

6. FVP of benzophenone

FVP of the title compound (450 mg, 600 °C, 220 mTorr, inlet RT, 1.51 g Mg) gave three fractions, white crystals, a yellow solid and a light transparent oil. The whole was dissolved out and analysed by GC-MS. The products consisted of unchanged benzophenone (34%) [*m/z* 182 (M^+, 19%), 77 (100)], diphenylmethane (12%) [*m/z* 168 (M^+, 84%), 167 (100)], fluorene (2%) [*m/z* 166 (M^+, 100%), 82 (39)], 1,2-diphenylethene (1%) [*m/z* 180 (M^+, 100%), 89 (50)] and traces of 1,2-diphenylethane [*m/z* 182 (M^+, 30%), 167 (100)] and tetraphenylethene [*m/z* 332 (M^+, 55%), 126 (100)]

7. FVP of cyclohexanone

FVP of the title compound (470 mg, 650 °C, 650 mTorr, inlet RT, 1.57 g Mg) gave a colourless liquid. This was dissolved out and analysed by GC-MS. The product was simply unchanged cyclohexanone (64%) [*m/z* 98 (M^+, 15%), 27 (100)].

8. FVP of 2-acetylthiophene

FVP of the title compound (765 mg, 650 °C, 490 mTorr, inlet RT, 1.51 g Mg) gave an intractable orange polymer like material on exposure of the pyrolysate to air approaching room temperature. The pyrolysis was repeated (630 mg, 650 °C, 400 mTorr, inlet RT, 1.50 g Mg) and a small quantity (about 3mg) of a colourless liquid among the orange solid was isolated by adding $CDCl_3$ the trap. ^1H NMR of the liquid showed it to be mainly 2-ethenylthiophene; δ_H 7.54–6.96 (3H, m), 6.95–6.74 (1H, m), 5.60 (1H, half AB pattern of d, *J* 16, 2) and 5.17 (1H, half AB pattern of d, *J* 12, 2).

9. FVP of 2-propionylthiophene

FVP of the title compound (765 mg, 650 °C, 490 mTorr, inlet RT, 1.49 g Mg) gave two fractions, a brown / orange oil and a yellow solid. The products which remained liquid (162mg) were drawn out and analysed by GC-MS. The remaining material polymerised rapidly on standing in $CDCl_3$. The liquid products consisted of thiophene (1%) [*m/z* 84 (M^+, 79%), 45 (100)], an unidentified C_7H_{10} hydrocarbon (3%) [*m/z* 94 (M^+, 19%), 91 (10), 79 (100), 77 (77), 65 (19), 53 (17), 51 (25), 39 (73) and 27 (52)], toluene (3%) [*m/z* 92 (M^+, 40%), 91 (100)], 2-ethenylthiophene (2%) [*m/z* 110 (M^+, 63%), 39 (100)] 2-ethynylthiophene (7%) [*m/z* 108 (M^+, 100%), 69 (52)] 2-prop-1-enylthiophene (10%) [*m/z*

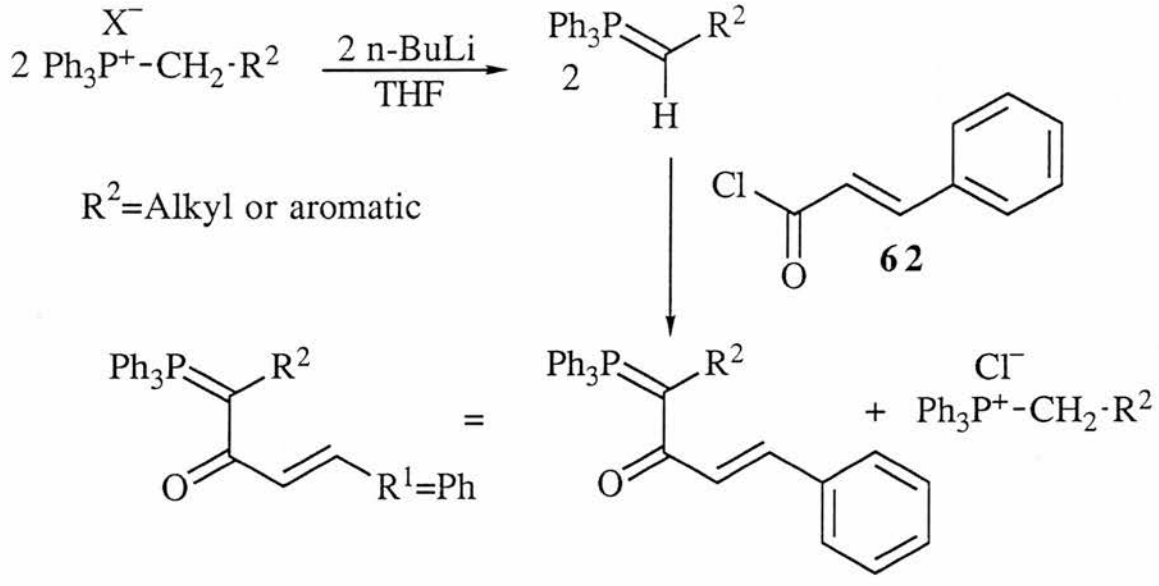
124 (M^+, 51%), 45 (100)] and 2-prop-1-ynylthiophene (4%) [*m/z* 122 (M^+, 96%), 121 (100)].

DISCUSSION

A Preparation of the γ,δ-Unsaturated-β-oxoalkylidenetriphenyl phosphoranes

Many of the following syntheses were done by Boeters[54] in the course of earlier work in this laboratory. In the course of the present work all of the compounds listed in the experimental section have been either freshly prepared by the author or are from old stock but fully characterised for the first time. Where such old stock has been used the compound number will be followed with an asterisk *.

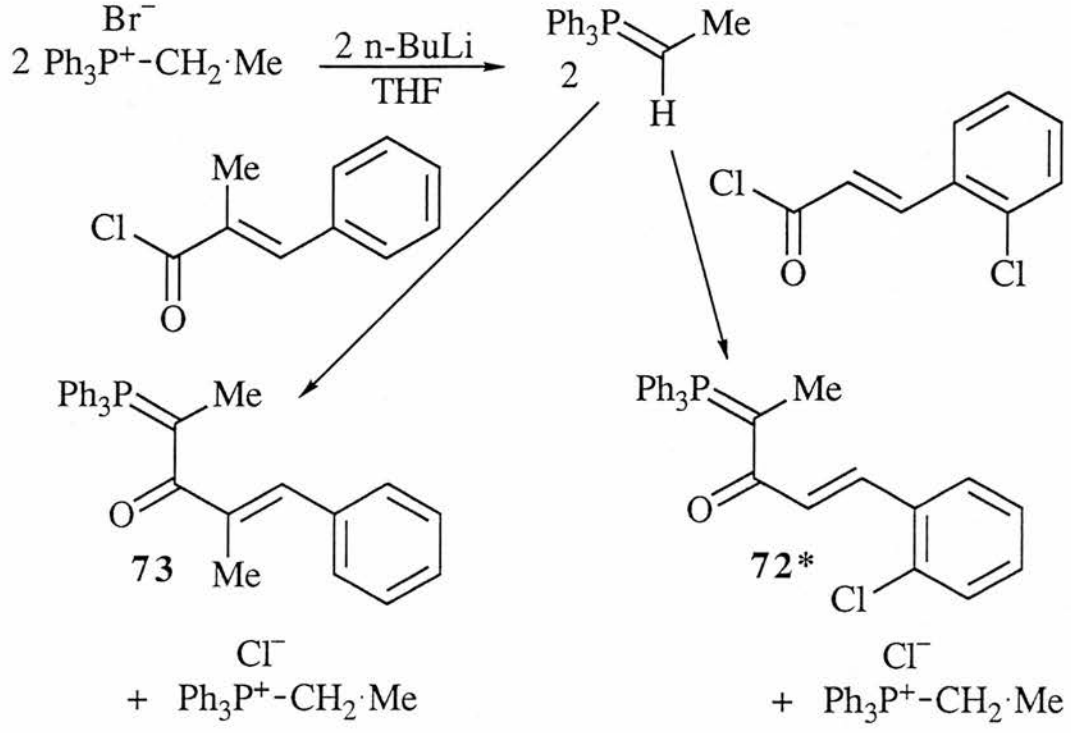
The preparation of the γ,δ-unsaturated-β-oxoalkylidenetriphenyl phosphoranes was achieved by modification of the method of Bestmann[40] as illustrated below.



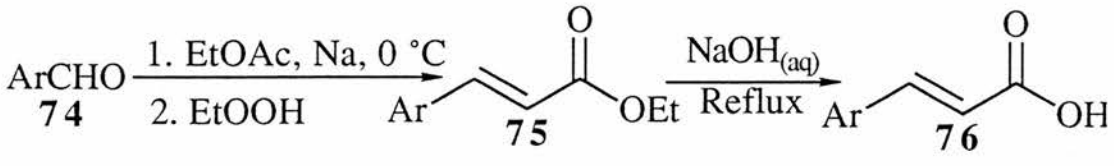
63	R^2=H	**66**	R^2=Pr^n	**69**	R^2=Ph
64	R^2=Me	**67**	R^2=Pr^i	**70***	R^2=4-Nitrophenyl
65	R^2=Et	**68**	R^2=Bu^n	**71***	R^2=2-Thienyl

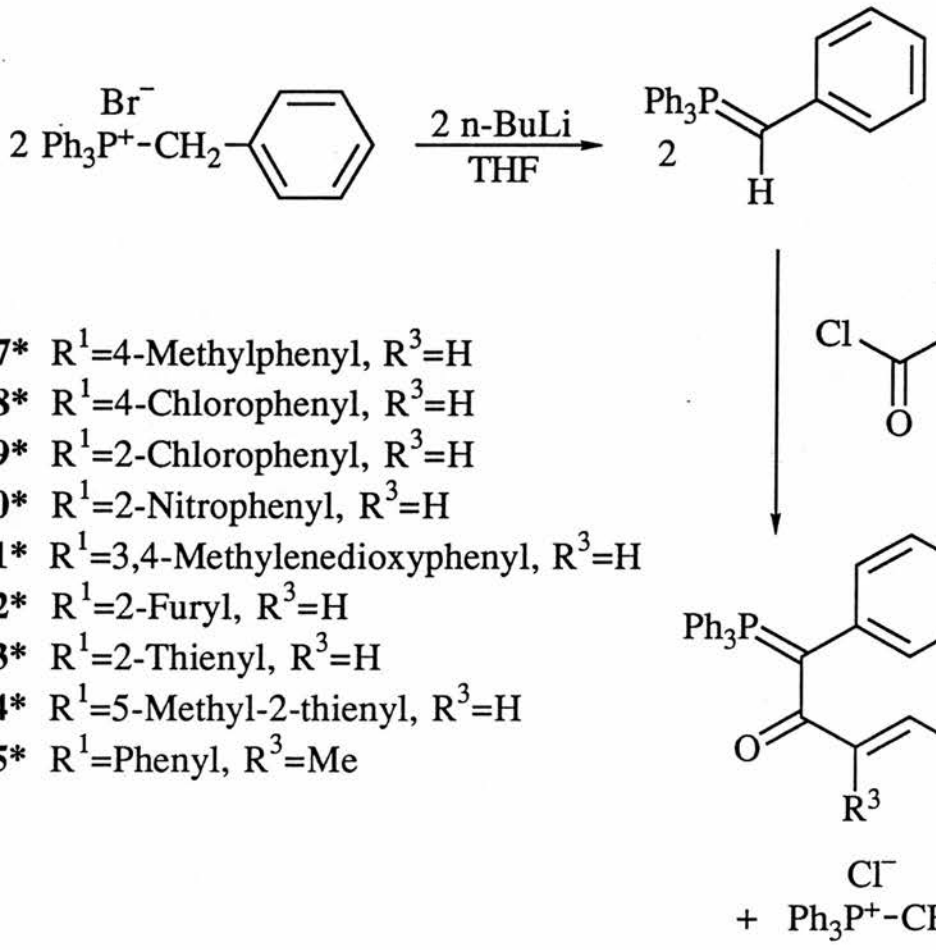
The reaction was accomplished by using two equivalents of a precursor ylide generated from the action of n-butyl lithium on a phosphonium salt, with one equivalent of cinnamoyl chloride.

In the further examples illustrated below, 2 equivalents of ethyl triphenylphosphonium bromide were converted to the ethylidenetriphenylphosphorane followed by addition of the requisite acid chloride generated from the appropriate commercially available acid.



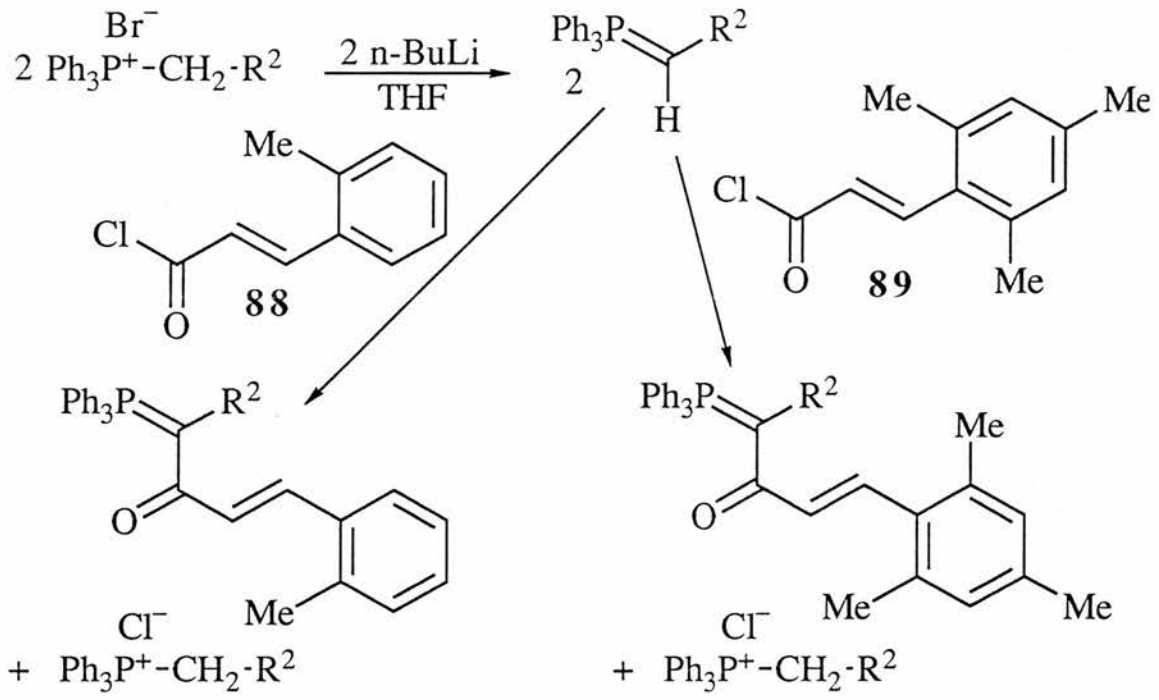
Similarly the benzylidene equivalents of those above and others were prepared as shown overleaf. Here two equivalents of benzyl triphenylphosphonium bromide were converted to the benzylidenetriphenylphosphorane followed by addition of the requisite acid chloride generated from the appropriate commercially available acid. Where the required acids **76** were not readily available they were prepared from the appropriate aldehyde **74** by the method of Young[58] by firstly generating the ester **75** and subsequent base hydrolysis.





77* R^1=4-Methylphenyl, R^3=H
78* R^1=4-Chlorophenyl, R^3=H
79* R^1=2-Chlorophenyl, R^3=H
80* R^1=2-Nitrophenyl, R^3=H
81* R^1=3,4-Methylenedioxyphenyl, R^3=H
82* R^1=2-Furyl, R^3=H
83* R^1=2-Thienyl, R^3=H
84* R^1=5-Methyl-2-thienyl, R^3=H
85* R^1=Phenyl, R^3=Me

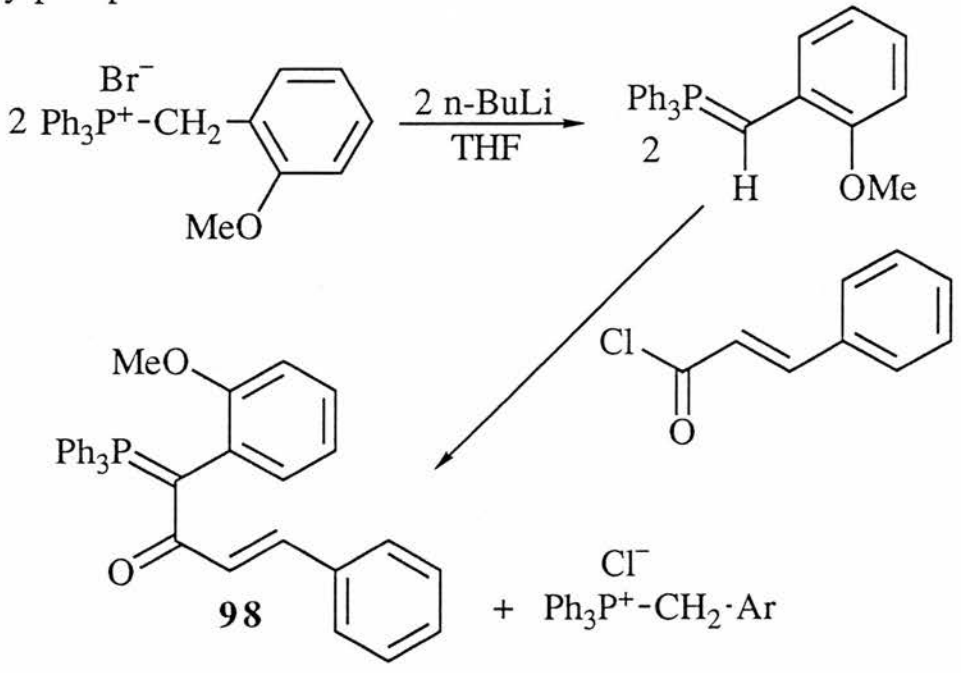
As indicated in the Programme of Research the γ,δ-unsaturated-β-oxoalkylidenetriphenylphosphoranes with o-methyl substituents are of special interest and are treated separately. These compounds were synthesised similarly to those above using starting materials derived from Young's method[58] such that 2-methylbenzaldehyde **74** (Ar=2-methylphenyl) gave 2-methylcinnamic acid **86** (**76**, Ar=2-methylphenyl) and by the same method 2,4,6-trimethylbenzaldehyde yielded 2,4,6-trimethylcinnamic acid **87** (**76**, Ar=2,4,6-trimethylphenyl). Subsequent conversion to the acid chlorides **88** and **89** allowed the synthesis of the requisite ylides as shown.



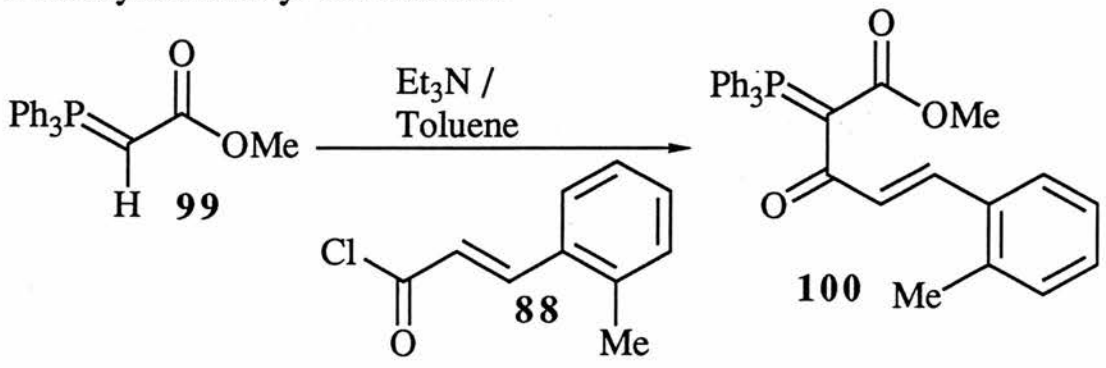
90 R^2=Me
91 R^2=Et
92 R^2=Pr^i
93 R^2=Ph

94 R^2=Me
95 R^2=Et
96 R^2=Pr^i
97 R^2=Ph

One further contribution to this study was made by earlier work by Burns[73] in the synthesis of (α-cinnamoyl-α-2-methoxyphenylmethylene) triphenylphosphorane **98** as illustrated below.



Having obtained many examples of alkyl and aromatic β-oxo ylides, another preparation was required to synthesize an ylide with an ester function. Using the method of Trippett,[43] (α-2-methylcinnamoyl-α-methoxycarbonylmethylene)triphenylphosphorane **100** was produced from the reaction of methoxycarbonylmethylenetriphenylphosphorane **99** with 2-methylcinnamoyl chloride **88.**



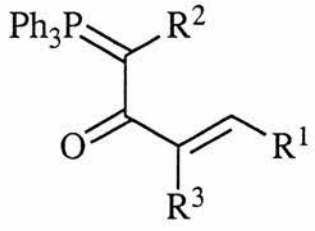
A major advantage found in the above synthesis in comparison to that for the earlier γ,δ-unsaturated-β-oxoalkylidenetriphenylphosphoranes lies in the lower basicity and greater stability of **100.** This allows the use of triethylamine as a base rather than the more expensive requirement of a second equivalent of the phosphorane for the acylation to take place.

The yield of the ylides was variable with the poorest found for those with the smallest alkyl groups as R^2. The majority of the ylides with aromatic R^2 groups were formed in good yield. This is found to reflect the contribution to stability of the phosphonium enolate of an aromatic R^2 which was predicted by Trippett and Walker[38] to give a compound that should easily lose phosphine oxide on pyrolysis to give the corresponding alkyne. In the case of **100** the electron withdrawing effect of the methoxycarbonyl group is clearly demonstrated to give good stabilisation of the phosphonium enolate as shown with the yield of the ylide and to be seen later in the yield of the corresponding enyne on pyrolysis.

The ^{31}P NMR spectra of the products were found to be a good primary indicator for the formation of the ylides since in all cases the

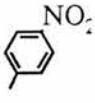
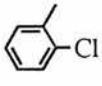
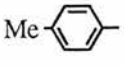
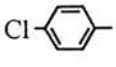
spectrum indicated a signal between δ_P+14-18 when the correct products were formed with all common impurities such as the precursor phosphonium salt and other by-products such as triphenylphosphine oxide giving rise to signals well outside of this region.

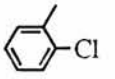
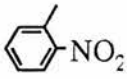
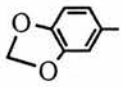
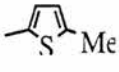
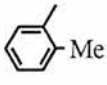
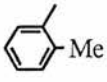
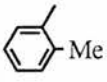
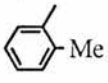
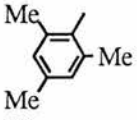
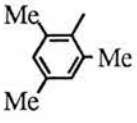
The yields of ylides **101** prepared are summarised in Table 1 together with their ^{31}P NMR shifts.

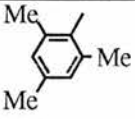
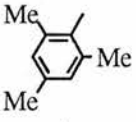
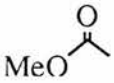
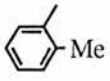


101

Table 1. Preparation of Ylides **101** and pyrolysis to give enynes **102**

No.	R^2	R^1	R^3	%Yield of **101**	δp	%Yield of **102** (Pyrolysis at 500°C unless indicated)	*E* / *Z* ratio at stated temperature
63	H		H	33	+15.6	8 (700)	58 / 42
64	Me		H	47	+15.6	53 (700)	57 / 43
65	Et		H	60	+18.0	33 (700)	56 / 44
66	Pr^n		H	43	+16.2	42 21 (700)	90+ / Trace 53 / 47
67	Pr^i		H	53	+16.2	67 (700)	56 / 48
68	Bu^n		H	66	+18.0	58 25 (700)	90+ / Trace 50 / 50
69			H	66	+16.0	99 (700)	57 / 43
70			H	37	+15.9	16	Trace *Z*
71			H	46	+16.6	66	Trace *Z*
72	Me		H	51	+18.0	Mainly decomp.	Trace [E] found
73	Me		Me	63	+17.1	67	Trace *Z*
77			H	66	+15.6	82 (480)	Trace *Z*
78			H	66	+16.1	39	Trace *Z*

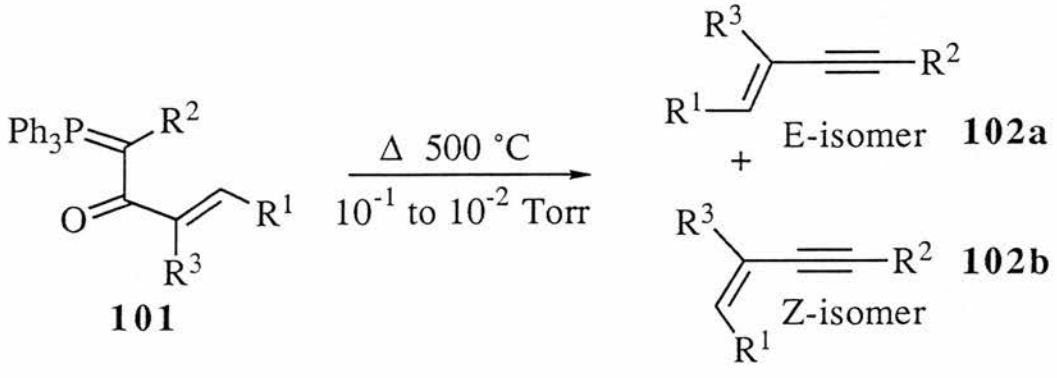
No.	R^2	R^1	R^3	%Yield of **101**	δp	%Yield of **102** (Pyrolysis at 500°C unless indicated)	*E* / *Z* ratio at stated temperature
79			H	74	+16.1	58	Trace *Z*
80			H	60	+16.4	42 19	Trace *Z*
81			H	81	+15.7	58	Trace *Z*
82			H	55	+16.0	55	Trace *Z*
83			H	77	+15.8	47	Trace *Z*
84			H	58	+15.7	34	Trace *Z*
85			Me	48	+14.7	55	Trace *Z*
90	Me		H	41	+18.0	15	Trace *Z*
91	Et		H	38	+17.7	77	Trace *Z*
92	Pr^i		H	54	+16.1	75	Trace *Z*
93			H	66	+15.7	65	Trace *Z*
94	Me		H	36	+18.1	48	Trace *Z*
95	Et		H	58	+18.0	45	Trace *Z*

No.	R^2	R^1	R^3	%Yield of **101**	δp	%Yield of **102** (Pyrolysis at 500°C unless indicated)	*E* / *Z* ratio at stated temperature
96	Pr^i		H	62	+16.0	70	Trace *Z*
97			H	40	+16.0	19	80 / 20
100			H	77	+18.9	92	Trace *Z*

B Low Temperature Flash Vacuum Pyrolysis of the γ,δ-Unsaturated-β-oxoalkylidene triphenylphosphoranes **101**

Flash Vacuum Pyrolysis of the title compounds at 500 °C generally gave the corresponding conjugated enynes in good to moderate yield. As a general synthesis of these compounds this approach was found to be competitive with the various methods investigated in the introduction both in terms of convenience and economics.

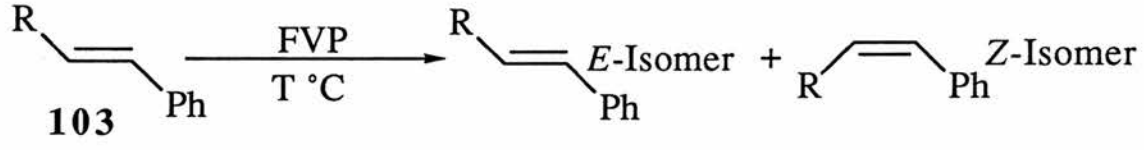
The results of low temperature pyrolysis of the ylides **101** at 500 °C and in some cases 700 °C are summarised in Table 1.



An important factor in the synthesis of enynes by this route is the stability of the ylides on heating under vacuum. The relatively unsucesssful pyrolysis of (α-cinnamoylmethylene)triphenylphosphorane **63** is believed to be partly due to the non-crystalline nature of the ylide. Much of the mass of this ylide decomposes without sublimation in the FVP inlet leading to the poor 8% yield of the 1-phenylbut-1-en-3-yne **104**. In the pyrolysis of (α-2-chlorocinnamoylethylidene)triphenylphosphorane **72** this ylide, although crystalline, also decomposed in the inlet. In order to overcome this problem an attempt was made to mimic the solution spray FVP used successfully by Diederich *et al*[86] to allow pyrolysis of poorly volatile and thermally unstable precursors. Diederich introduced a fine spray of dilute benzene solutions of the starting materials into a pyrolysis tube packed with quartz rings. The spray was diffuse and dilute enough to ensure fast transfer of the starting material into the gas phase in the hot zone without decomposition. The simplified version used here to obtain 1-(2-chlorophenyl)pent-1-en-3-yne **113** from the corresponding ylide **72** consisted of an identical set up to that discussed in the experimental section save that the inlet tube was replaced with a septum through which a fine cannula was passed to draw in a methylene chloride solution of the ylide at a slow rate. This simple setup was successful in providing a partial transformation of the starting material into what is believed to be the enyne by the ^{1}H NMR spectrum of the pyrolysate. Interestingly the bulk of the ylide did not react even at 900 °C. This is believed to be due to the faster transfer time through the hot zone accelerated by the fast expansion of the methylene chloride as it enters the pyrolysis tube making the pyrolysis extremely mild even at this temperature.

The pyrolysis experiments have shown that the major products from FVP of the ylides **101** at 500 °C are the *E*-1,3-enynes **102a** with traces of the corresponding *Z*-1,3-enynes **102b** found in all cases, their presence

detected through the appearance of small signals on the ^1H NMR spectra corresponding to the *Z*-isomers' alkenyl protons with a smaller coupling constant than that found for the *E*-isomer. This is unusual when it is considered that the precursor ylides have been characterised as being purely *E*-isomers and leads to the conclusion that the *E-Z* isomerisation is due to the pyrolysis technique. The effect is even more pronounced on pyrolysis at 700 °C especially in the case of the formation of 1-phenyloct-1-en-3-yne from **68** where the product is a 50 / 50 mixture of the *E* and *Z* isomers. This behaviour has previously been noted by Hickson and McNab[87] in a study of the FVP of alkenes **103** at various temperatures. All the alkenes examined exhibited very little or no E / Z isomerisation on FVP at 500 °C but on pyrolysis at 600 °C the effect became pronounced with measurable isomerisation occurring in all cases studied as indicated in the examples below.



103

	% *Z* at T °C (data from ref. 75)			
R	600 °C	700 °C	800 °C	900 °C
Ph	9	15	16	17
CH_2OH	2	5	23	29
CN	1	14	33	38

One of the major factors involved in the increase in isomerisation as a function of temperature is the degree of steric strain across the alkene bond whish is increased on isomerisation from *E* to *Z*. The largest R group (phenyl) therefore should be expected to undergo the least isomerisation and it has been shown to do so with the increase with repect to temperature flattening out at about 800 °C. For the smaller R groups

this strain is less pronounced and in the case of R=CN the greatest degree of isomerisation is seen producing 38% of the *Z*-isomer at 900 °C. Temperatures of this magnitude start to decompose the alkenes so the study was not pursued at higher temperatures.

The similar isomerisation seen here with the enynes **102** is more pronounced probably due to the carbon-carbon triple bond α to the alkene. The bond is sterically undemanding and could be described as a spacing group between the R^1 and R^2 groups lowering the energy difference between the two isomers and hence promoting the formation of the *Z*-isomer as the activation energy of the transformation is approached. Similarly the activation energy for the isomerisation seems to be lower for the enynes than for the least sterically hindered alkenes

In Table 3 the ^{13}C NMR spectra of all of the pyrolysis products are tabulated displaying the correlations found which led to positive identification of each carbon atom. Where sufficient *Z* isomer was found in order to clearly diffrentiate between the *E* and *Z* isomers of the enynes on the ^{13}C spectra the relevant ^{13}C spectrum of both isomers is tabulated. The numbering system used is illustrated below.

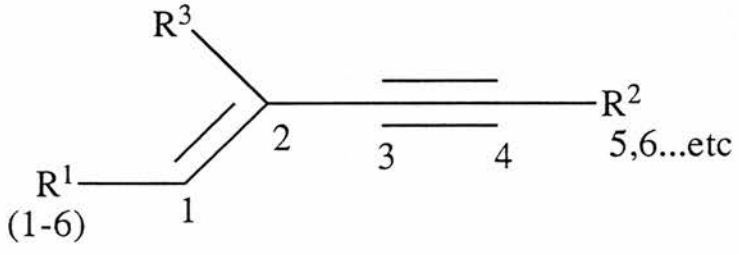


Table 3. ^{13}C NMR spectra of Enynes **102** from FVP of Ylides **101**

Enyne no.	R^2	R^1	E/Z	R^1 Signals						Enyne signals				R^2 Signals				Aromatic substituents		R^3
				C-1	C-2	C-3	C-4	C-5	C-6	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	2-Me	4-Me	Methyl
104	H	Phenyl	E	135.8	126.3	128.7	128.9			143.1	106.9	84.1	79.3							
105a	Methyl	Phenyl	E	136.5	126.0	128.6	128.2			140.1	108.8	88.3	78.9	4.5						
105b			Z	136.6	126.0	128.4	128.3			137.3	108.1	93.2	78.3	4.8						
106a	Ethyl	Phenyl	E	136.5	126.0	128.6	128.1			140.0	108.8	94.2	79.0	13.3	13.9					
106b			Z	136.7	126.0	128.4	128.2			137.3	108.1	98.9	78.6	13.6	13.7					
107a	n-Propyl	Phenyl	E	136.5	126.0	128.6	128.1			140.0	108.9	92.9	79.9	21.6	22.2	13.6				
107b			Z	136.7	126.0	128.4	128.2			137.2	108.2	98.0	79.4	21.9	22.0	13.6				
108a	i-Propyl	Phenyl	E	136.6	126.0	128.6	128.0			139.9	180.8	98.3	78.8	21.3	23.0					
108b			Z	136.7	126.0	128.5	128.1			137.3	108.2	102.8	78.4	21.5	22.6					
109a	n-Butyl	Phenyl	E	136.5	126.0	128.6	128.1			139.9	108.9	93.0	79.7	19.3	30.9	22.0	13.6			
109b			Z	136.7	126.0	128.4	128.2			137.2	108.2	97.8	79.2	19.6	30.6	22.0	13.6			
110a	Phenyl	Phenyl	E	136.3	126.3	128.4	128.2			141.3	108.1	91.7	88.9	123.4	131.5	128.7	128.2			
110b			Z	136.5	126.3	128.6	128.3			138.7	107.4	95.8	88.2	123.5	131.4	128.7	128.2			
111	4-Nitro phenyl	Phenyl	E	135.8	126.5	128.9	129.3			143.4	107.1	94.4	89.8	123.9	132.1	128.4	146.8			
112	2-Thienyl	Phenyl	E	136.2	126.3	128.7	128.7			141.2	107.7	92.8	84.9	123.5	131.7†	128.7†	127.3†			

Enyne no.	R^2	R^1	E/Z	R^1 Signals						Enyne signals				R^2 Signals				Aromatic substituents		R^3
				C-1	C-2	C-3	C-4	C-5	C-6	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	2-Me	4-Me	Methyl
114	Methyl	Phenyl	E	137.0	128.2	128.9	126.9			134.6	120.5	84.8	83.5	4.3						19.4
115	Phenyl	4-Methyl phenyl	E	133.6	126.2	129.4	138.7			141.3	107.0	91.4	89.1	123.5	131.5	128.3	128.1		21.3	
116	Phenyl	4-Chlorophenyl	E	134.8	127.4	128.9	134.3			139.8	108.8	92.3	88.5	123.2	131.5	128.3	128.3			
117	Phenyl	2-Chlorophenyl	E	134.3	132.2	130.0	129.5	126.0	127.0	137.0	110.7	92.6	88.6	123.1	131.6	128.4	128.4			
118	Phenyl	2-Nitrophenyl	E	132.6	147.5	124.8	128.9	135.7	128.7	133.2	113.6	83.6	88.1	122.8	131.7	128.4	127.8			
119	Phenyl	3,4-Methylenedioxy phenyl	E	130.9	105.1	148.2	148.2	106.1	121.7	140.9	108.4	91.3	89.0	123.5	131.4	128.3	128.1			101.3‡
120	Phenyl	2-Furyl	E	152.2	111.9†	110.1†	128.1			143.0	106.1	92.4	88.9	123.4	131.4	128.3	128.2			
121	Phenyl	2-Thienyl	E	141.5	127.8†	127.1†	125.5†			134.0	107.3	92.1	88.7	123.3	131.4	128.3	128.2			
122	Phenyl	5-Methyl-2-thienyl	E	140.7	126.0	127.7	139.5			134.4	105.8	91.7	89.0	123.5	131.4	128.3	128.0		15.7	
123	Phenyl	Phenyl	E	136.8	128.3	129.0	127.2			136.1	119.8	93.2	88.4	123.4	131.5	128.3	128.0			19.3

Enyne no.	R^2	R^1	E/Z	R^1 Signals						Enyne signals				R^2 Signals				Aromatic substituents		R^3
				C-1	C-2	C-3	C-4	C-5	C-6	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	2-Me	4-Me	Methyl
124	Methyl	2-Methylphenyl	E	137.9	135.5	130.4	128.2	124.8	126.1	137.9	109.7	87.9	79.2	4.5				19.8		
125	Ethyl	2-Methylphenyl	E	137.8	135.5	130.4	128.1	124.8	126.1	137.8	109.8	97.9	79.3	13.3	13.9			19.8		
126	i-Propyl	2-Methylphenyl	E	137.7	135.5	130.4	128.1	124.8	126.1	137.7	109.8	97.9	79.2	21.3	23.0			19.8		
127	Phenyl	2-Methylphenyl	E	137.0	135.8	130.6	128.2	124.8	126.1	139.0	109.1	91.3	89.2	123.5	131.5	128.3	128.2	19.8		
128	Methoxy carbonyl	2-Methylphenyl	E	136.6	134.0	130.8	129.9	125.3	126.4	145.6	105.5	86.6	81.7	154.5		52.7		19.7		
129	Methyl	2,4,6-Trimethyl Ph.	E	136.8	136.0	128.9	133.0			138.6	113.8	87.4	79.1	4.0				20.4	20.4	
130	Ethyl	2,4,6-Trimethyl Ph.	E	136.8	136.0	128.8	133.1			138.4	113.9	93.0	79.0	13.3	13.9			21.0	20.9	
131	i-Propyl	2,4,6-Trimethyl Ph.	E	136.7	136.1	128.8	133.2			138.3	113.9	97.1	78.8	21.3	23.0			21.0	21.0	
132	Phenyl	2,4,6-Trimethyl Ph.	E	137.1	136.1	129.0	133.5			139.9	113.2	90.7	88.8	123.4	131.5	128.3	128.1	21.1	12.0	

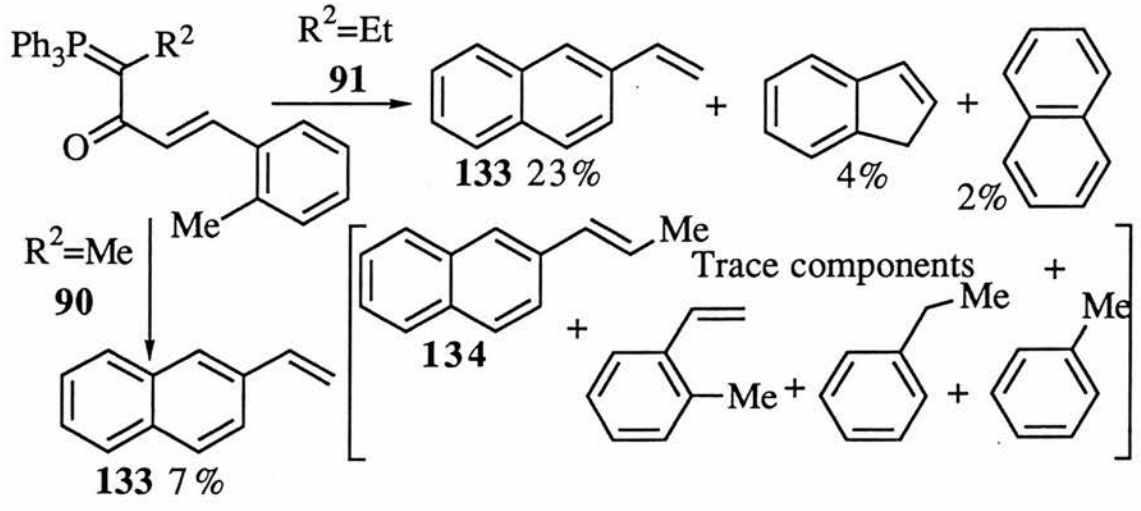
† Assignment uncertain and may be reversed.
‡ OCH_2O of methylenedioxyphenyl

C High temperature Flash Vacuum Pyrolysis of the γ,δ-unsaturated-β-oxoalkylidenetriphenylphosphoranes

1. Introduction and Results

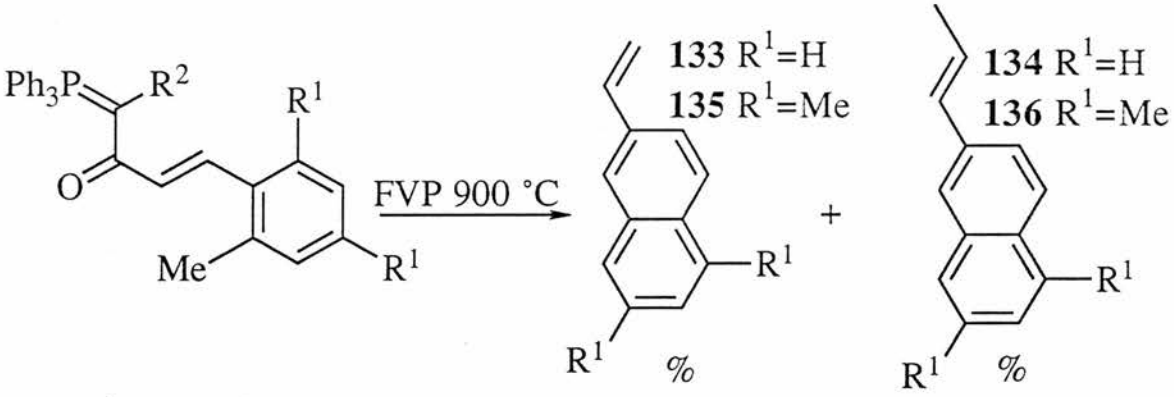
As outlined in the programme of research, preliminary work on the high temperature FVP of ylides to form enynes in which the aryl group contains an o-methyl substituent had been found to generate vinyl naphthalenes.[74]

High temperature FVP of a range of suitably substituted γ,δ-unsaturated-β-oxoalkylidenetriphenylphosphoranes was run and the pyrolysates analysed. The simplest example, (α-2-methycinnamoylethylidine)triphenylphosphorane **90** was found to provide 2-vinylnaphthalene **133** in 7% yield on pyrolysis at 900 °C with the remaining material being lost to a combination of residues remaining in the inlet and breakdown products such as involatile soot and possibly volatile gases which escaped before analysis. The greatest part of the loss was found to be due to the decomposition of the ylide in the inlet and this was supported by pyrolysis of the more thermally stable (α-2-methycinnamoyl-1-propylidene)triphenylphosphorane **91** giving a 23% yield of 2-vinylnaphthalene in a mixture of 7 components.



A subsequent pyrolysis of **91** at a lower temperature of 850 °C followed by preparative TLC of the pyrolysate yielded clean 2-vinylnaphthalene **133** (23%) thus showing that the cyclisation reaction may be achieved at slightly lower temperatures with the possible benefit of decreased decomposition of the starting material leading to increased yields. This experiment allowed the recording of the ^{13}C NMR spectrum of the 2-vinylnaphthalene and unambiguous comparison to the literature assignments.

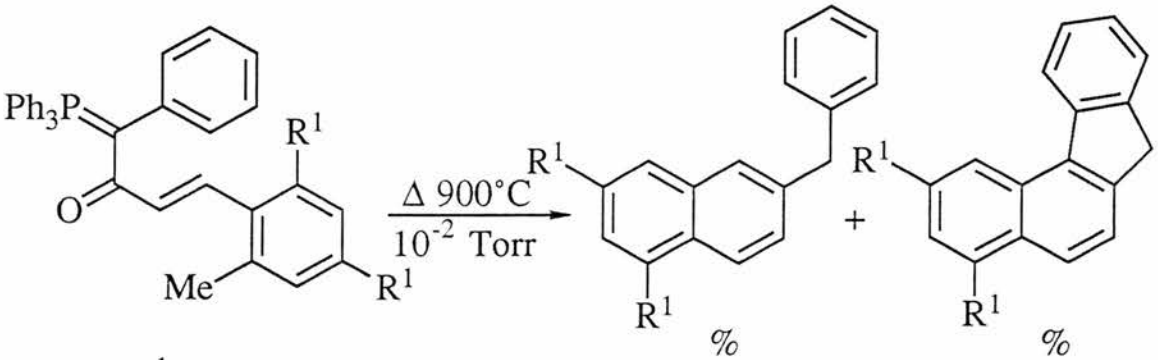
Further pyrolyses including the FVP of the α-2,4,6-trimethycinnamoyl variants (R^2=Me, Et, Pr^n) of the above led to similar products and the results of all the pyrolyses at 900 °C are illustrated below.



	%	%
90 R^2=Me, R^1=H	7	0
91 R^2=Et, R^1=H	23	Trace
92 R^2=Pr^i, R^1=H	17	7
94 R^2=Me, R^1=Me	22	0
95 R^2=Et, R^1=Me	22	0
96 R^2=Pr^i, R^1=Me	14	6

Where R^2 is an isopropyl group the loss of a methyl radical from this chain is believed to form the 2-propenylnapthalene products. Further radical fragmentation of the propenyl side chain is a likely route to the 2-vinylnaphthalenes.

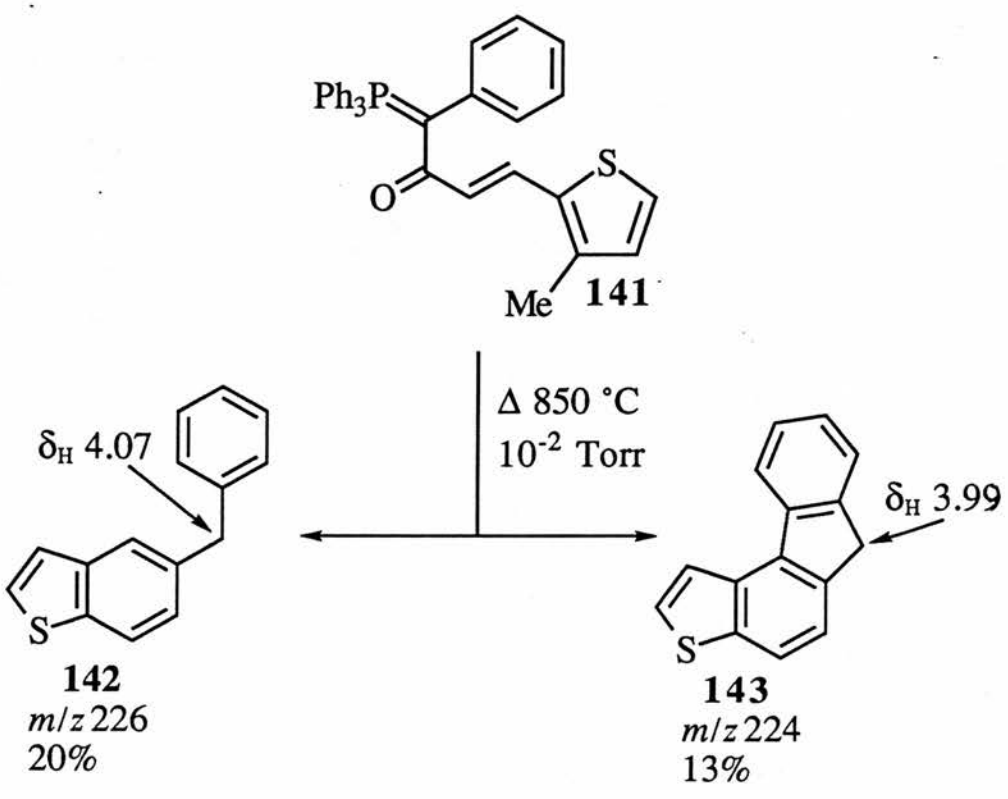
FVP of (α-2-methycinnamoyl-α-phenylmethylene)triphenyl phosphorane **93** at 900 °C gave two products, 2-benzylnaphthalene **137** (25%) and benzo[c]fluorene **138** (9%). The apparent lack of any other products from further fragmentation is probably due in part to the stability of the intermediate benzyl radical. The low yield may be due to the formation of large involatile aromatic hydrocarbons formed as radical addition products of the slightly longer lived intermediates. The trimethylcinnamoyl analogue **97** bevaved similarly giving **139** and **140** as shown



		%		%
93 R^1=H	**137**	25	**138**	9
97 R^1=Me	**139**	16	**140**	13

A further example of this type of tandem cyclisation may be seen on the pyrolysis of (α-3-(3-methyl-2-thienyl)propenoyl-α-phenylmethylene triphenylphosphorane **141**. In this case 3-methyl-2-thienyl may be regarded as a close analogue to the 2-methylphenyl, having the o-methyl required for the second cyclisation. FVP at 900 °C gave an oil which, by GCMS was composed of two products in a ratio of 3:2. The most abundant component had a molecular mass of 226 and the smaller a mass of 224. The same ratio was found for two singlet peaks on the ^{1}H NMR spectrum at δ_H 4.07 and 3.99 indicating that they were due to each of the separate components. These two signals relate well to the 2H singlets found for 2-benzylnaphthalene δ_H 4.14 and benzo[c]fluorene δ_H 3.96 and combined with

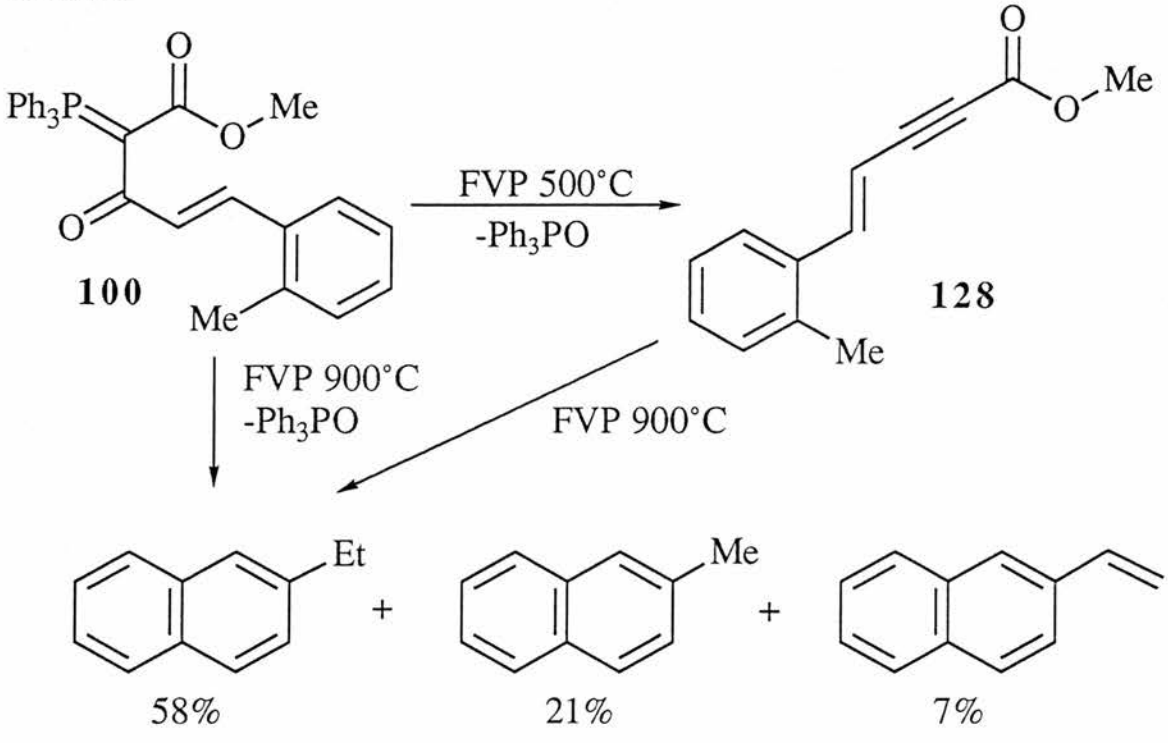
the molecular masses the evidence points towards the formation of 5-benzylbenzothiophene **142** and 6H-fluoreno[3,4-b]thiophene **143**.



In the pyrolyses run above it is seen that the outcome of the transformation depends upon the composition of the R^2 group. Where R^2 is alkyl some fragmentation of this group results which is seen from the loss of either hydrogen atoms or perhaps methyl radicals. Where R^2 is aromatic this group either stays complete or is involved in a second or "tandem" cyclisation. In an attempt to look further into the behavior of the enyne function under high temperature FVP another R^2 function was sought which would be less likely to fragment than the alkyl group and distinct from the aromatic group. Previous work[44] had shown the ease of synthesis of acetylenic esters by a similar low temperature FVP reaction. At high temperature the ethyl esters were believed to lose the stable fragments CO_2 and ethylene but pyrolysis of methyl esters was not expected to result in such easy fragmentation of the ester group. It was

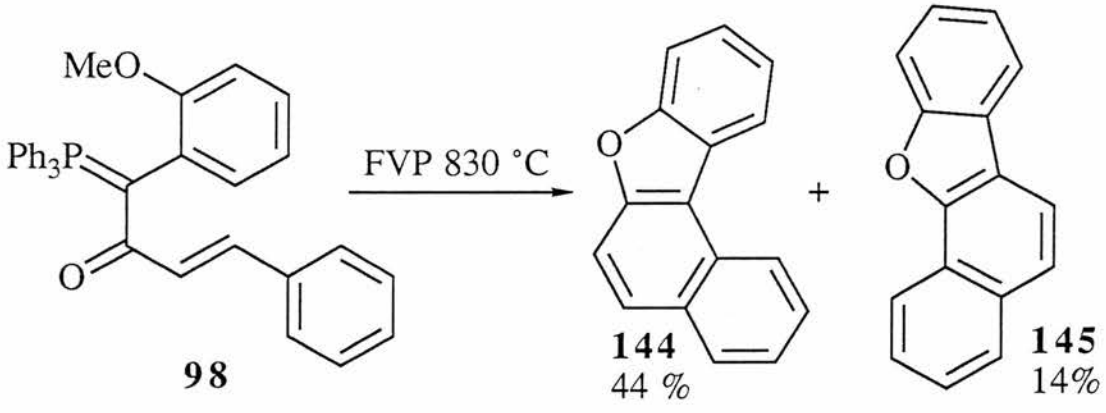
thus decided that using the methoxycarbonyl group as R^2 could help probe the mechanism of the observed cyclisations.

FVP of (α-2-methylcinnamoyl-α-methoxycarbonylmethylene) triphenylphosphorane **100** at 830 °C and FVP of its low temperature pyrolysis product 4-methoxycarbonyl-1-(2-methylphenyl)-but-1-en-3-yne **128** both gave rise to an unexpected mixture of naphthalenes detailed as follows:-



Again a cyclisation to the 2-substituted naphthalene is observed but the predominant product is the ethyl substituted naphthalene rather than the vinyl. Since the same result is seen from both the ylide **100** and the enyne **128** this clearly demonstrates that the pyrolytic extrusion of Ph_3PO from the ylide is the first step in such reactions and plays no part in the following rearrangements of the enynes. The pyrolysis of this methyl ester functionalised enyne involves an interesting process that seems unrelated to the alkyl and aromatic group cyclisations. Although failing with the original aim of investigating the mechanism of the latter cyclisations the experiment has uncovered a potential high yielding synthesis of further substituted 2-ethylnaphthalenes.

The last example of high temperature pyrolysis of ylides investigated was the FVP of (α-cinnamoyl-α-2-methoxyphenylmethylene) triphenylphosphorane **98**. This compound differed distinctly from the rest in that the o-methyl substituent on R^1 was absent. A 2-methoxyphenyl group as R^2 was investigated as a possible source of a methyl radical leaving group which could trigger further cyclisation. The results of the pyrolysis indeed indicate the loss of this radical and appropriate cyclisation to form two isomers of benzonaphthofuran. Study of the ^{13}C NMR spectra showed the major product to be benzo[b]naphtho[1,2-d]furan **144** and UV-VIS studies point towards a mixture of this isomer and benzo[b]naphtho[2,1-d]furan **145.**



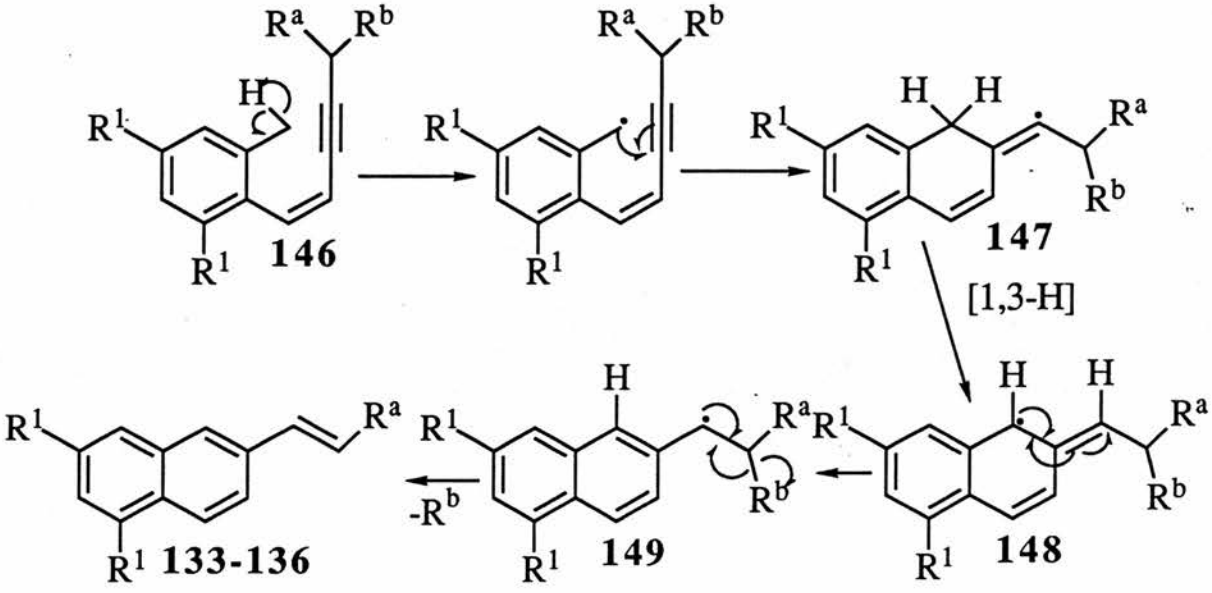
98

144
44 %

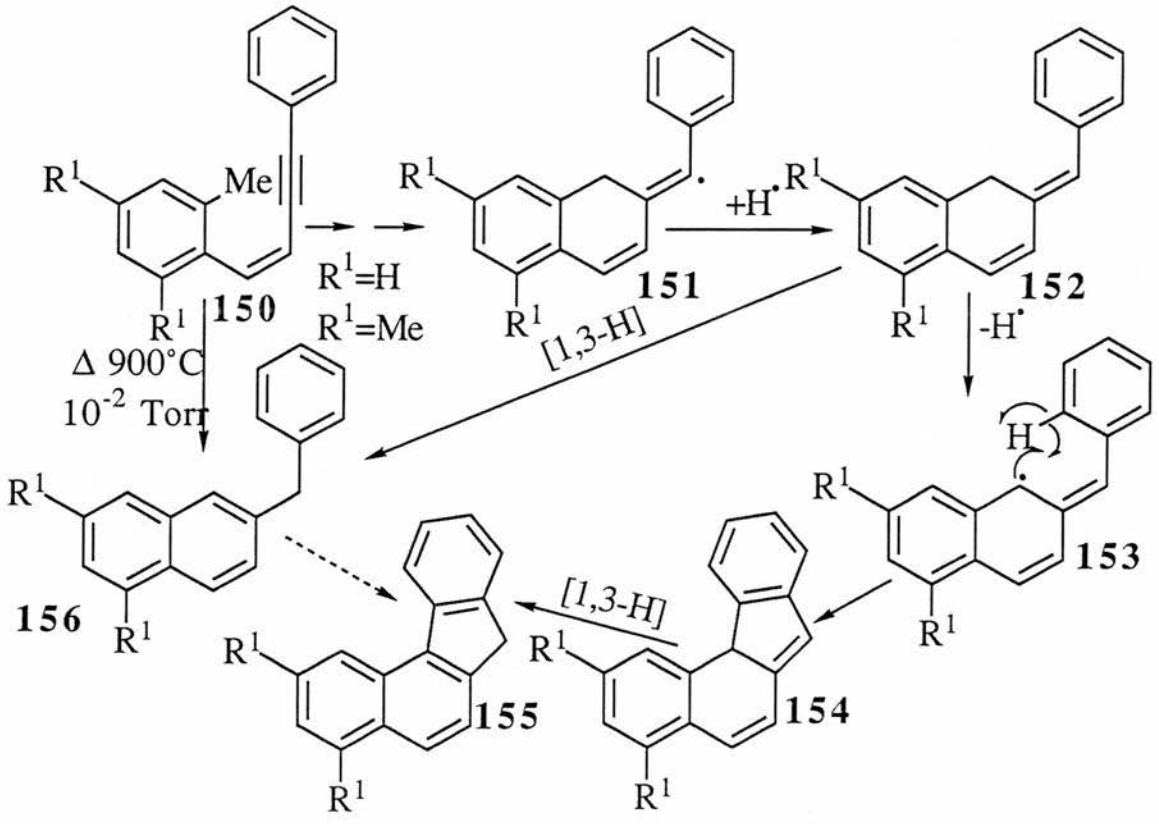
145
14%

2. <u>Mechanistic study into the cyclisation reaction to form vinylnaphthalenes and related products.</u>

From the previous study[74] the cyclisation reaction was originally believed to go via a radical route initiated by the high temperture removal of a benzylic hydrogen atom, this being supported by various reports of the generation of such radicals under similar conditions.[75,76] Starting from the enyne **145** loss of a benzylic hydrogen atom leads to cyclisation **146**. A 1,3-H shift driven by aromatisation from **148** to **149** followed by the loss of a radical leaving group leads to the 2-vinylnaphthalene products **133-136**.



A slightly different route is taken where R^a and R^b are replaced by a phenyl group **150**. The cyclisation to generate the naphthalene skeleton occurs as before but now there is obviously no leaving group for the final stage available and so pyrolysis did not result in a vinyl product but instead yielded small amounts of 2-benzylnaphthalene and benzo[c]fluorene (**155**, **156** R^1=H). To check for the possible formation of **155** from **156** the 2-benzylnaphthalene was synthesised and subsequent pyrolysis lead to a conversion to benzo[c]fluorene but only to the extent of 7% so this route could not account for the product mixture. The route below was proposed for the transformation.

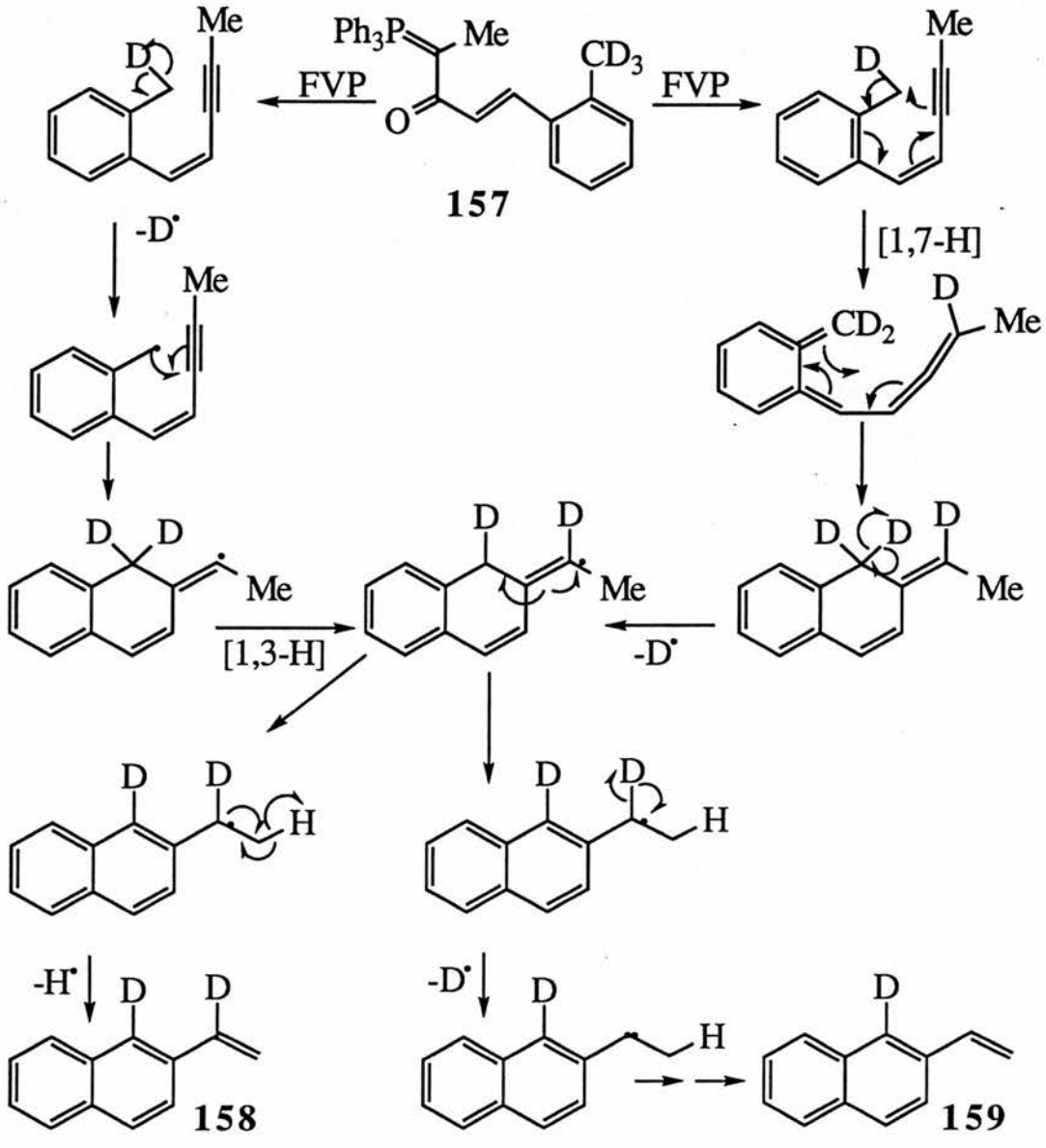


The conversion of **150** to **151** occurs by the same steps as found in for the alkyl variant **146** to **147** above. This is followed by abstraction of a hydrogen atom to give **152** which can then do two things; a 1,3-H shift will lead directly to the benzylnaphthalene or thermal loss of a benzylic hydrogen atom will lead in three stages to the benzo[c]fluorene.

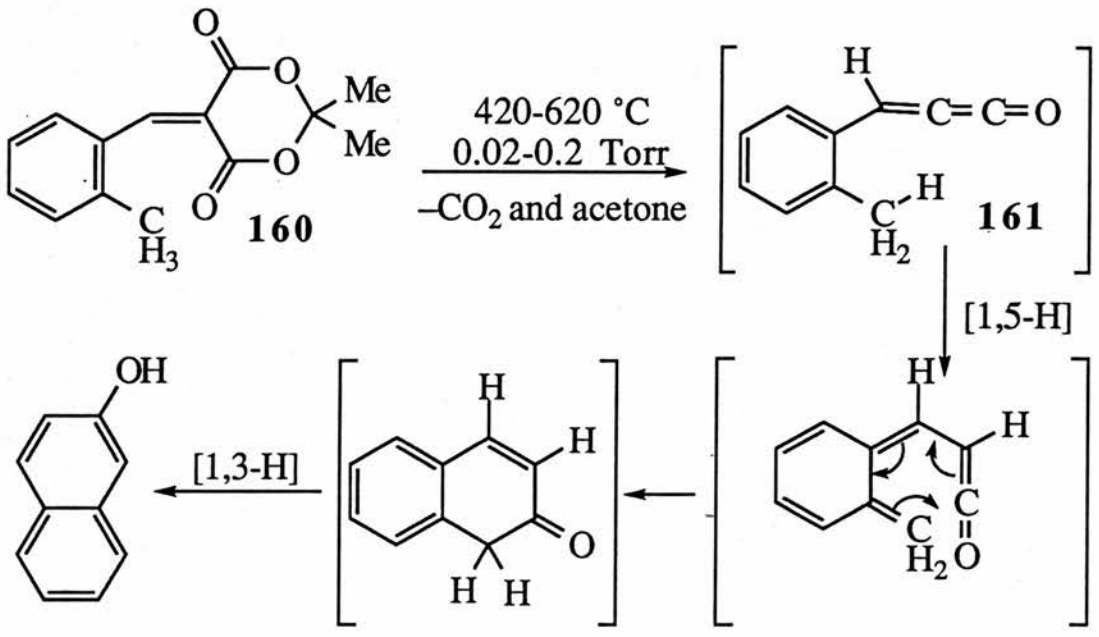
Although these reactions give low product yields in a difficult to separate mixture of hydrocarbons they are interesting because pyrolysis can lead to new products such as 5,7-dimethyl-2-vinylnaphthalene **135** (from **94** or **95**) which are difficult to achieve by any other route and also offers the possibility of the synthesis of many other novel substituted vinylnaphthalenes, benzofluorenes and heterocyclic relatives such as the 5-benzylbenzothiophene **142** and 6H-fluoreno[3,4-b]thiophene **143** found from this work.

In a preliminary study in this laboratory[78] the mechanism of the cyclisation reaction to form the vinylnaphthalenes was probed by a

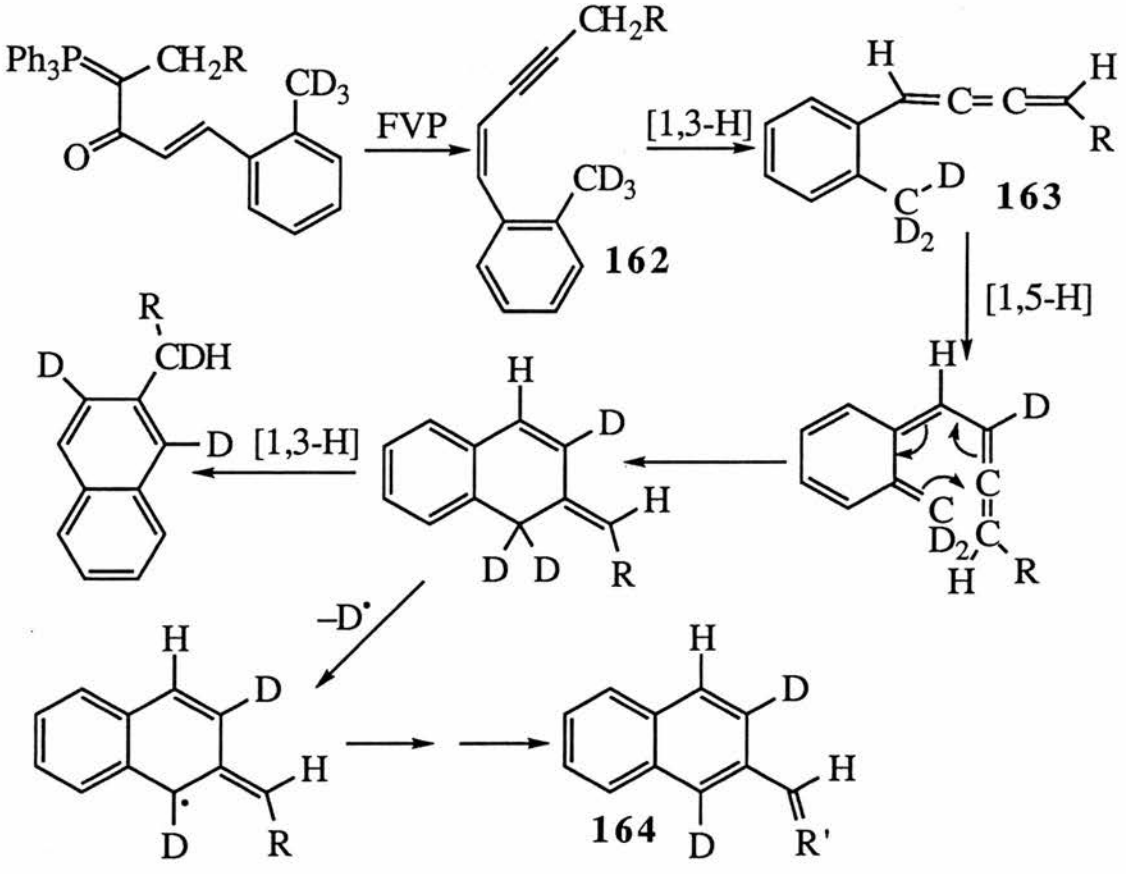
deuterium labelling experiment. This involved the synthesis and FVP of (α-2-trideuteriomethylcinnamoylethylidene)triphenylphosphorane **157** and a study by ^{1}H and ^{2}H NMR of the pyrolysate to attempt to determine the presence of and positions of the deuterium atoms in the expected 2-vinylnaphthalene product. The study was inconclusive largely because of the small quantity of the deuteriated ylide yielded by the synthesis and the low yield of 2-vinylnaphthalene obtained by the pyrolysis of this compound. The original aim of the experiment was to enable differentiation between the scheme discussed earlier in this section involving the cyclisation being triggered by loss of benzylic hydrogen or an alternative starting with a [1,7] hydrogen shift. Both of these would give **158** while another mechanism where the [1,3-H] shift was followed by loss of the second benzylic proton to form a carbene which would give **159**. The possibility of a [1,7] hydrogen shift initiating the cyclisation cannot be discounted as both mechanisms would lead to the same products from the labelled ylide.



The current work was aimed at obtaining a conclusive result on this and also excluding another mechanism proposed by Brown[79] originally to explain the formation of 2-naphthol from the pyrolysis of 2,2-dimethyl-5-(2'-methylbenzylidene)-1,3-dioxan-4,6-dione **160**.

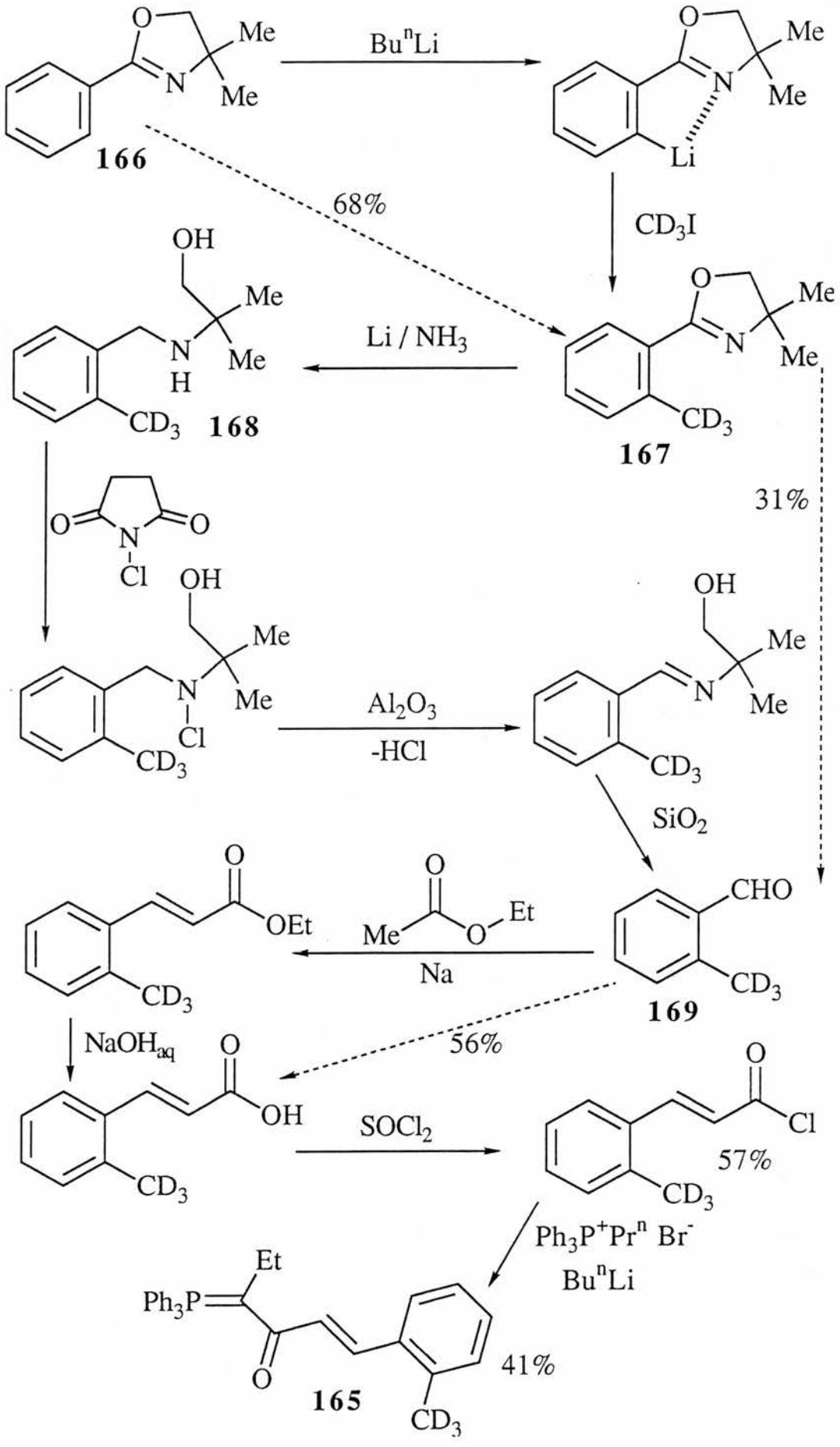


The mechanism relies on the formation of the intermediate 2-methylbenzylideneketene **161** which is analogous to the butatriene **163** which could be formed from enynes **162** as shown. This may be tested by deuterium labelling

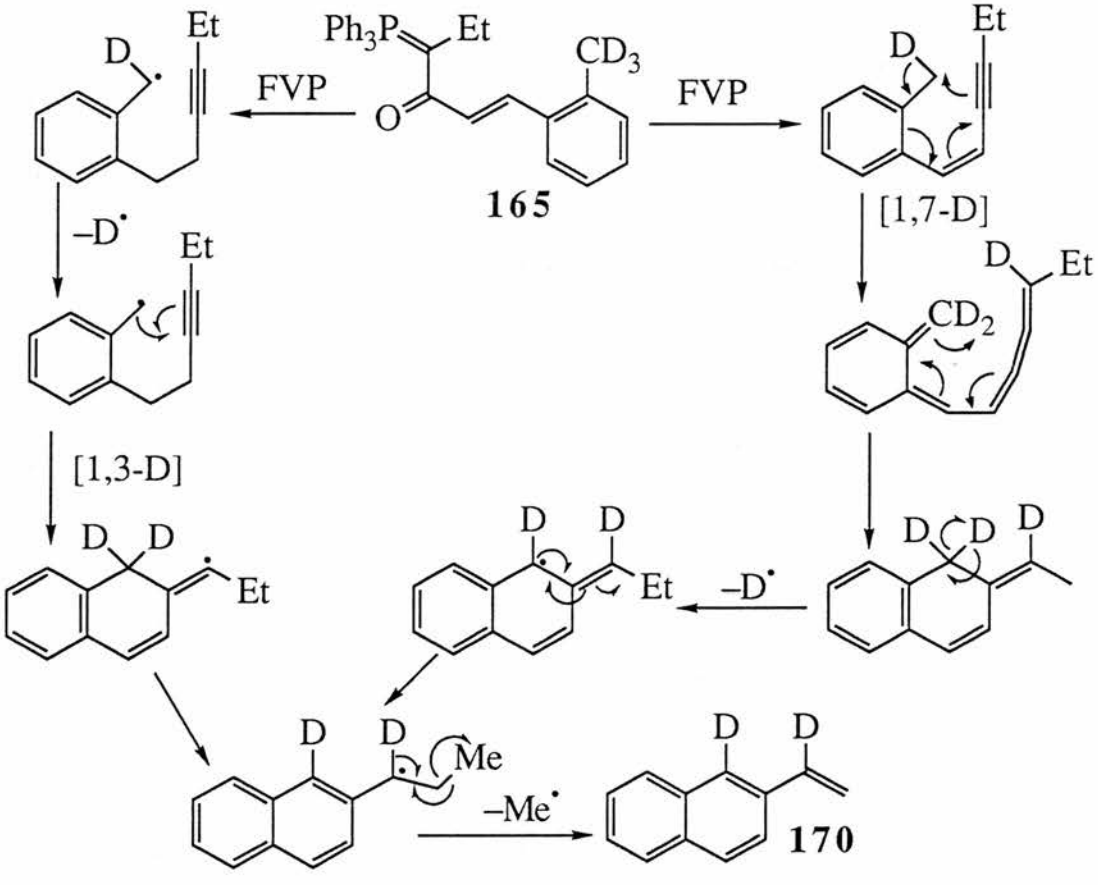


Following on the experience of the synthesis and pyrolytic behavior of the many examples of suitable ylides a new labelling experiment was devised to probe the mechanism of the cyclisation. This involved the synthesis and pyrolysis of (α-2-trideuteriomethylcinnamoyl-1-propylidine) triphenylphosphorane **165**. Since the pyrolysis of the unlabelled ylide gave the highest yield of 2-vinylnaphthalene which was easily isolated to allow unambiguous ^{13}C NMR spectrum assignment, the ^{13}C spectrum of the labelled ylide's pyrolysate was expected to yield further diagnostic data for the reaction mechanism. The synthesis of the labelled ylide was devised to give a workable quantity of material from as little expensive deuteriated starting materials as possible and was successful in providing a sufficient quantity of the ylide from only 1.4 g of d_3-methyl iodide.

The preparation of **165** began by o-lithiation of the oxazoline **166** followed by addtion of the d_3-methyl iodide to give 4,4-dimethyl-2-(2-trideuteriomethylphenyl)-2-oxazoline **167**. Reductive cleavage of this oxazoline with lithium in liquid ammonia yields the amino alcohol **168**. Using Meyers[60] procedure N-chlorination of the amino alcohol was achieved by the addition of N-chlorosuccinimide in methylene chloride. This was followed by HCl elimination by alumina to give the corresponding imine which was hydrolysed on a simple silica column to give 2-trideuteriomethylbenzaldehyde **169**. The remaining steps towards the ylide are as discussed earlier for the undeuteriated compound **91.**


Me
Me
O
N
166
Bu^{n}Li
Li
68%
CD$_3$I
OH
Me
N
H
Me
CD$_3$
168
Li / NH$_3$
167
31%
O
N
Cl
O
Al$_2$O$_3$
-HCl
SiO$_2$
OEt
Et
Na
CHO
169
NaOH$_{aq}$
56%
SOCl$_2$
Cl
57%
Ph$_3$P$^+$Pr^n Br$^-$
Bu^{n}Li
Ph$_3$P
41%
165

Pyrolysis of the deuteriated ylide **165** and subsequent isolation of the 2-vinylnaphthalene product by preparative TLC allowed study of the position of the deuterium atoms by ^{1}H, ^{2}H and ^{13}C spectroscopy. Comparison of the spectra with those of the authentic undeuteriated compound and the literature assignments revealed the product to be exclusively 1,1'-dideuterio-2-vinylnaphthalene **170**. This result is consistent with either the benzyl radical or [1,7-H] shift mechanisms as shown below and definitely rules out the mechanisms involving a carbene to give **159** and a [1,5-H] shift to give **164**.



The initial step of the reaction may be either radical or concerted. This situation is not easily resolved even though radical processes such as the loss of benzylic hydrogen are well documented, since the radical route must at some stage involve a 1,3-H shift. Although this is thermally

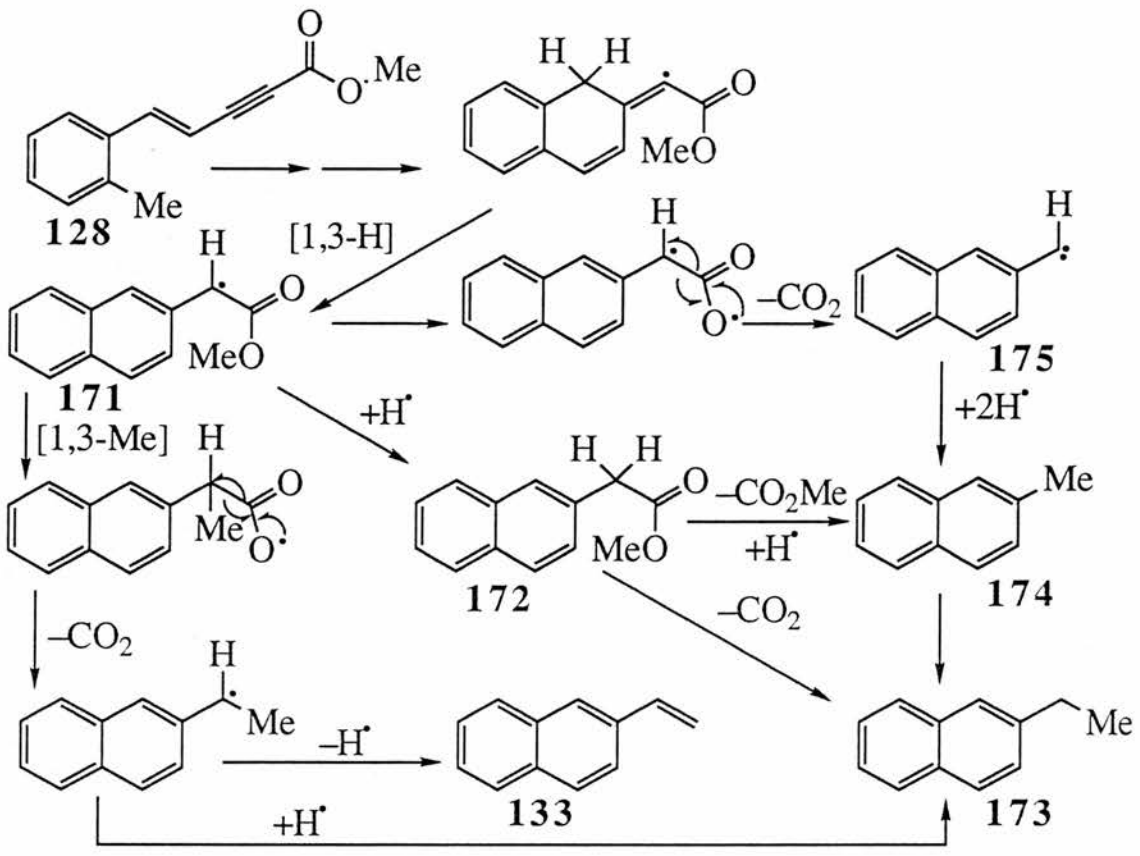
disfavoured it is a feasible route under FVP conditions and in this case is assisted by formation of the stable naphthalene system.

3. Mechanistic study of the cyclisation reaction of 4-methoxycarbonyl-1-(2-methylphenyl)but-1-en-3-yne**128**

An equally interesting mechanism is at play in the pyrolytic conversion of 4-methoxycarbonyl-1-(2-methylphenyl)but-1-en-3-yne **128** into 2-ethylnaphthalene. This was an unexpected result since it is difficult to propose a mechanism where CO_2 is lost and the methyl migrates conventionally for this case. If a methyl migration is the route taken then it would most obviously be a 1,3-shift which is at best an unlikely process.

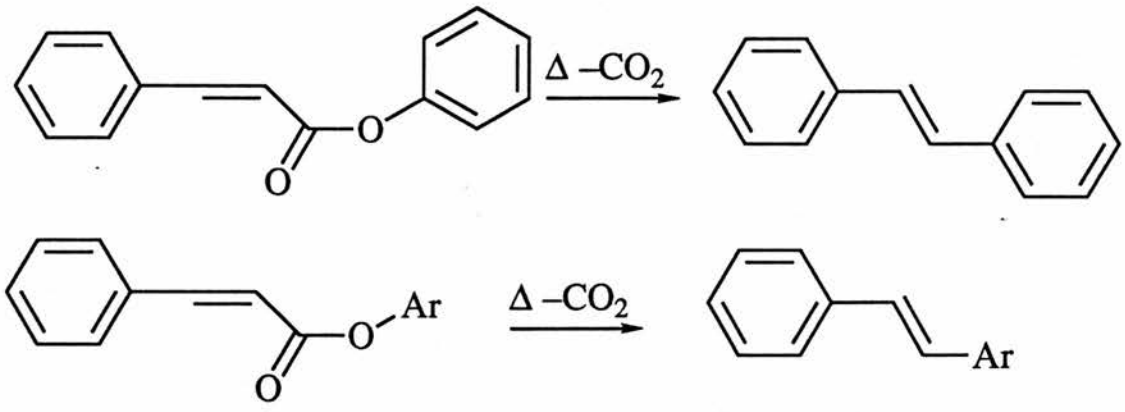
Some alternative mechanisms may be postulated for the transformation using clues from the other species present in the pyrolysate. Assuming the cyclisation reaction of the enyne **128** to form the 2-substituted naphthalenes would follow the same route as that for the ylides (**90-96**) then the benzyl radical **171** would be formed and further reactions of this would produce the final products. For example capture of a hydrogen atom to give **172** followed by loss of CO_2 would give 2-ethylnaphthalene **173** while loss of methoxycarbonyl radical and capture of a hydrogen atom would give 2-methylnaphthalene **174**. Coming back to the 1,3-Me shift hypothesis and taking the process a little further this may be used to account for all the major products if it is regarded as an inefficient process. If the shift is successful then the major product 2-ethylnaphthalene **173** is formed. If the methyl radical is lost in the process as a result of a relaxation of the transition state then the 2-methylnaphthalene **174** product may be formed via a carbene **175**. The minor product, 2-vinylnaphthalene **133**, may be the result of the loss of a hydrogen atom from the methyl group on consolidation of the benzyl

radical as has been seen before for the formation of the 2-vinylnaphthalenes from the ylides (**90-96**).



The above mechanism is entirely speculative and does not account for the formation of the small quantity of methanol produced, however since only a trace is observed this may be due to an insignificant side reaction. Many further connotations are possible that are not described, for example the possible capture of methyl radical by the many larger species of parent radical and this process may be important in the formation of the 2-ethylnaphthalene.

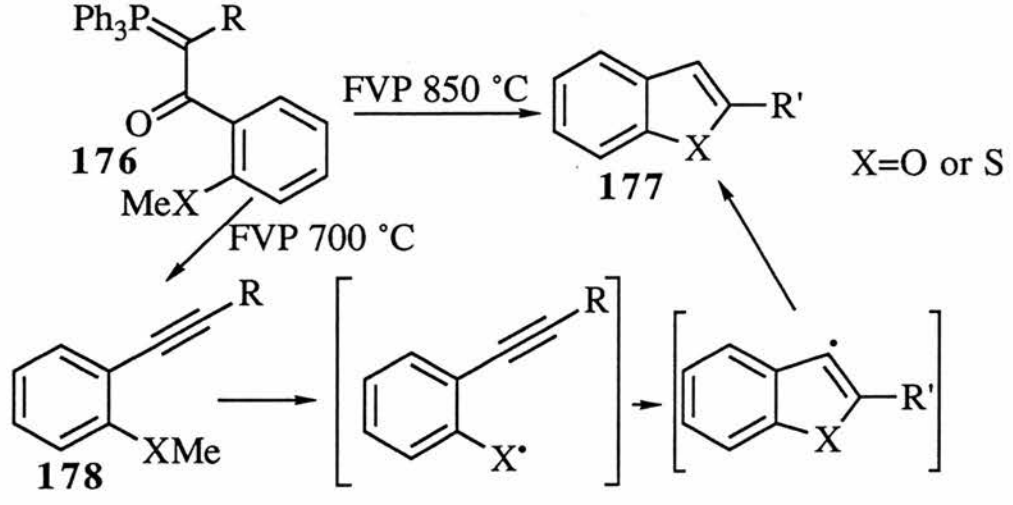
Some interesting examples of the pyrolysis of esters appear in Hurd's book[80]. In particular Anschütz[81,82] found that slow distillation of phenyl cinnamate.at atmospheric pressure produces stilbene and carbon dioxide. This was found to be a general reaction for aryl cinnamates.



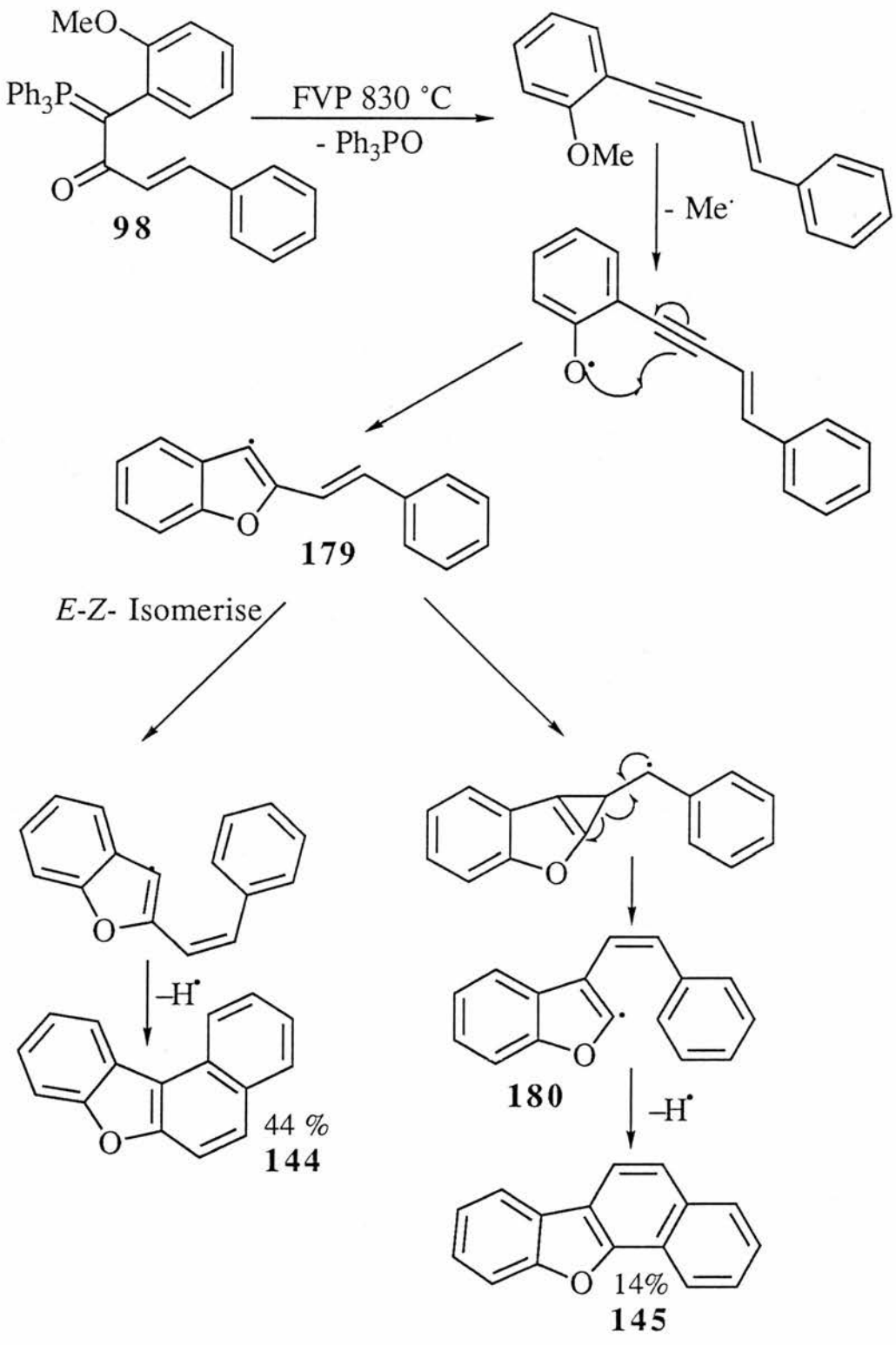
For the pyrolysis of **128** perhaps this extrusion of carbon dioxide and subsequent consolidation is being seen for the alkyl equivalent.

4. Tandem cyclisation of a 2-methoxyphenyl enyne

The FVP of (α-cinnamoyl-α-2-methoxyphenylmethylene) triphenylphosphorane **98** was run with the aim of furthering an earlier investigation in this laboratory[77] which focused upon the demethylation of (2-methoxyphenyl) and (2-methylthiophenyl) ylides **176** by high temperature FVP to produce 2-substituted benzofurans and benzothiophenes. The synthesis of the alkyne **178** is achieved by the pyrolytic extrusion of Ph_3PO from the corresponding ylide **176** and the benzofurans and benzothiophenes are formed directly on pyrolysis at 850 °C.



In the case of (α-cinnamoyl-α-2-methoxyphenylmethylene) triphenylphosphorane **98** the pyrolysis resulted in the formation of two isomers of benzonaphthofuran believed to be benzo[b]naphtho[1,2-d]furan **144** and benzo[b]naphtho[2,1-d]furan **145**. A mechanism was devised which can very elegantly account for these products and relies on the formation of the benzofuryl radical **179** as a key intermediate. Rather than consolidation by picking up a hydrogen atom the larger radical may take two routes at this stage, either undergoing *E*-*Z*-isomerisation to find the correct geometry for cyclisation into the benzo[b]naphtho[1,2-d]furan or radical attack of the styryl double bond to give the cyclopropenyl-benzyl radical intermediate. The opening of the cyclopropenyl ring may take place in the opposite sense resulting in a 1,2-styryl shift to give the isomeric 3-styryl-2-benzofuryl radical **180** which upon cyclisation gives rise to the minor product benzo[b]naphtho[2,1-d]furan.



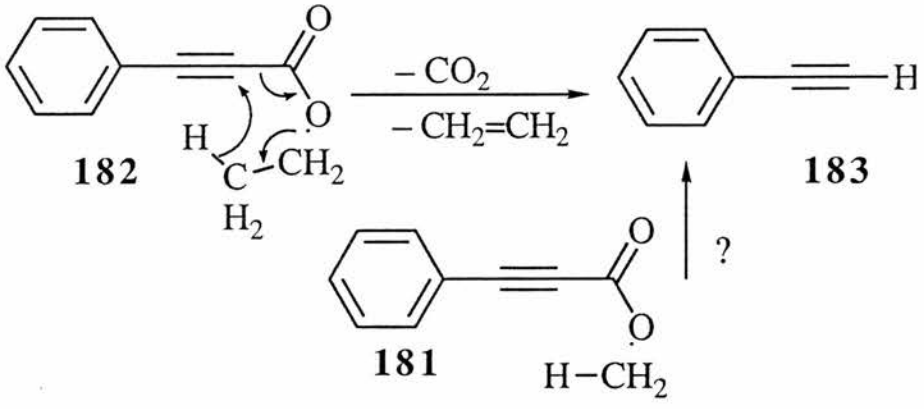
This mechanism is supported by two important features. It does not allow for the formation of benzo[b]naphtho[2,3-d]furan and this isomer is not observed in the mixture and also the minor product is the one resulting from the additional rearrangement process prior to cyclisation.

D High temperature flash vacuum pyrolysis of acetylenic esters

1. Introduction and Results

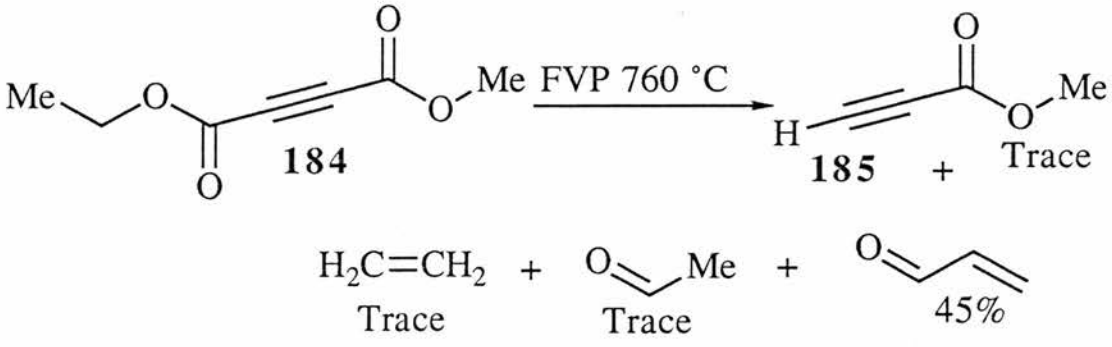
Previous work in this laboratory[44] has shown that FVP of acetylenic ethyl esters at 750 °C produces the corresponding terminal alkynes by the loss of the ethoxycarbonyl group. Following this and the unexpected transformation of 4-methoxycarbonyl-1-(2-methylphenyl)-but-1-en-3-yne **128** into 2-ethylnaphthalene on high temperature FVP a study of the pyrolysis of acetylenic methyl esters was run to look for other transformations which might throw some light on the mechanism of these reactions. Methyl phenylpropiolate **181** was the first ester to be investigated since the earlier work had shown that ethyl phenylpropiolate **182** produced phenylacetylene **183** on FVP so a direct comparison of the two ester functions was possible.

FVP of methyl phenylpropiolate **181** at 780 °C gave a 37% conversion to phenylacetylene **183** as a mixture with unchanged starting material and a small quantity of styrene (4%). This compares favourably with the literature[44] where pyrolysis of ethyl phenyl propiolate **182** at 750 °C gave a 48% yield of phenylacetylene. The methyl ester thus seemed to behave in much the same fashion as the ethyl ester but while the ethyl ester was presumed to be lost as CO_2 and ethene, no such route was available for the former.



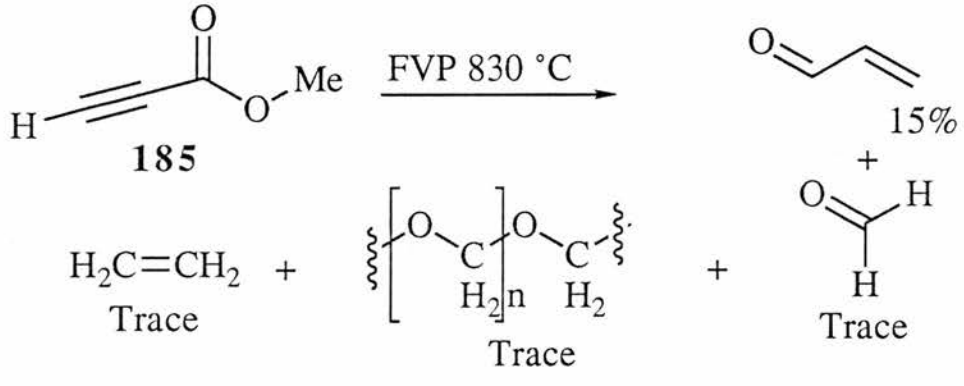
The loss of the ethoxycarbonyl group may be easily represented as going through an electrocyclic double elimination rather like a Cope rearrangement to form the stable fragments ethene and CO_2. The same mechanism applied to the methoxycarbonyl group would require the loss of methylene which is such a reactive species that it may not be regarded as a likely leaving group.

The lower yield of phenylacetylene produced by the methyl ester and the remaining starting material after the pyrolysis is significant especially since this pyrolysis was run at a temperature 30 °C higher than that of the ethyl ester. This indicated that the ethoxycarbonyl group was lost more easily than the methoxycarbonyl hinting that they may leave by different mechanisms. To support this hypothesis ethyl methyl acetylenedicarboxylate **184** was prepared[72] and subjected to FVP at 760 °C. Provided that the ethoxycarbonyl group leaves more easily than the methoxycarbonyl then some methyl propiolate **185** should be expected in the pyrolysate and there should be an absence of the alternative ethyl propiolate. This was found to be the case however, the largest component in the pyrolysate was found to be acrolein - an entirely unexpected product.



The discovery of the volatile ethene in the pyrolysate by a rapidly diminishing ^1H NMR signal lends immediate support to the proposed fragmentation of the ethoxycarbonyl group to this gas and CO_2 which is more difficult to detect. Considering the loss of the ethoxycarbonyl group as an efficient process the next obvious investigation was the pyrolysis of

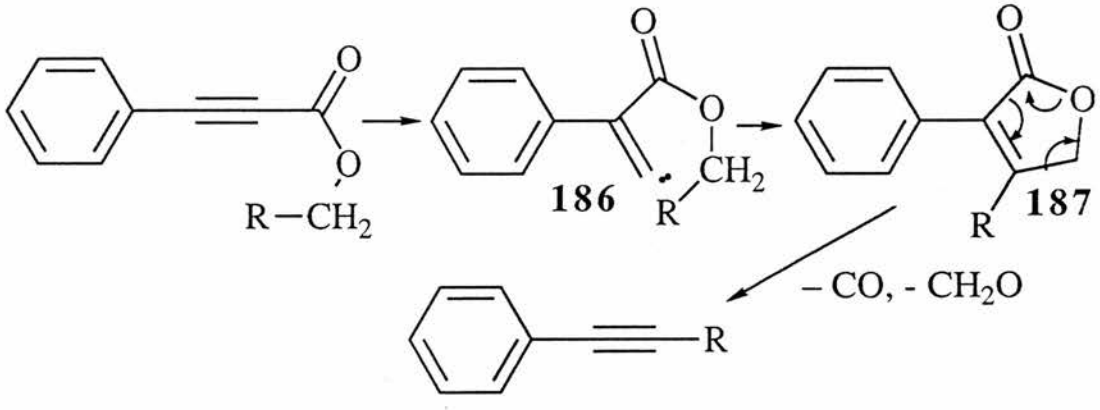
methyl propiolate **185** to see if this molecule was responsible for the formation of the acrolein. FVP of methyl propiolate proved difficult due to the volatility of the material which tended to distill through the vacuum system as the FVP apparatus was pumping down. To compensate for this the sample tube was kept cold and a higher than normal furnace temperature of 830 °C was applied to ensure reaction of the fast moving volatile vapours. The pyrolysate collected again contained acrolein as the major product and traces of unreacted methyl propiolate, formaldehyde monomer and polymer and evidence of ethene.



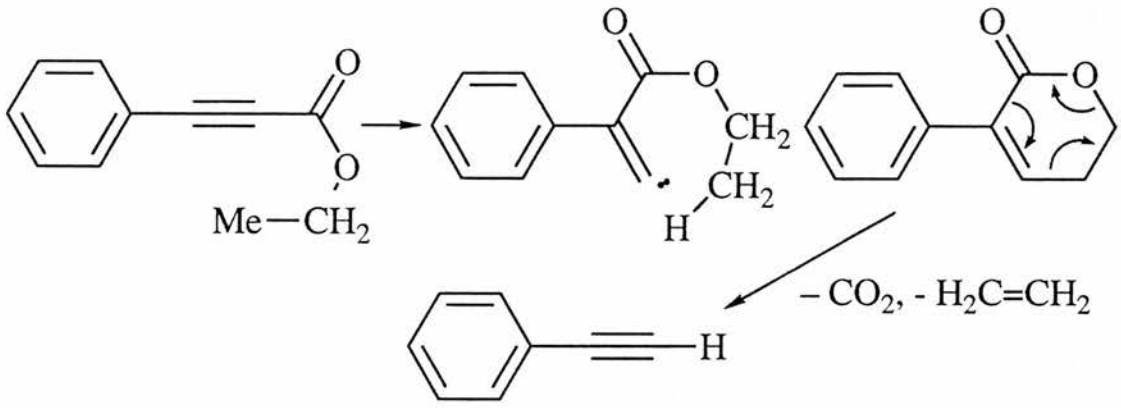
Having apparently traced the source of the formation of acrolein to the methyl propiolate, it was then thought interesting to determine whether formation of acrolein could also take place in other acetylenic methyl esters. This was done by performing the FVP of dimethylacetylenedicarboxylate (at 830 °C) to test for the formation of products similar to those of the ethyl methyl analogue. The products were acrolein (68%), formaldehyde polymer and traces of formaldehyde monomer and ethene.

2. Mechanistic interpretation of the loss of ethoxycarbonyl and rearrangements of methoxycarbonyl on FVP of acetylenic esters.

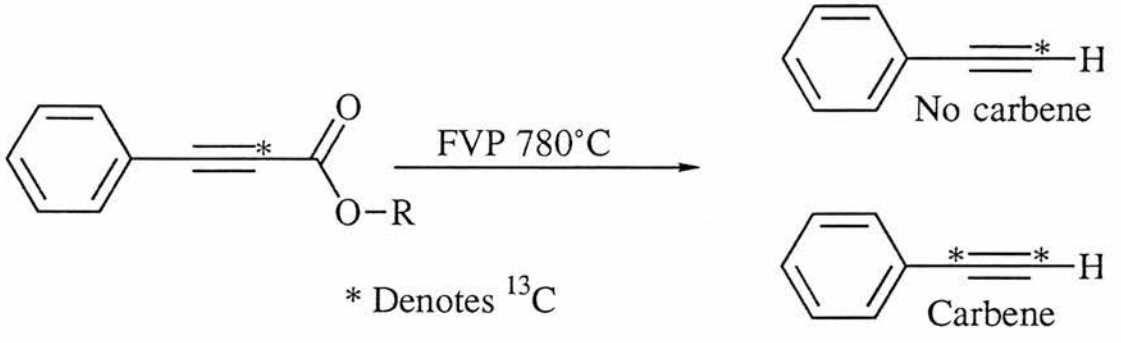
In the pyrolysis of methyl phenylpropiolate the loss of the methoxycarbonyl group may be accounted for by 1,2-migration of either the phenyl or ester group to form vinylidene carbene **186** and subsequent insertion to form a five membered ring intermediate **187** followed by loss of CO and formaldehyde as shown. This may account for the transformation seen except for the absence of formaldehyde in the pyrolysate. This is however a minor point as the formaldehyde was later discovered from subsequent pyrolyses to polymerise rapidly on contact with air during collection of the pyrolysate from the trap. In the later experiments care was taken to dissolve out all the pyrolysate from the trap as quickly as possible to avoid loss so in this case the formaldehyde may have polymerised to an insoluble state before analysis and remained undetected.



For the case of methyl phenylpropiolate (R=H) the mechanism gives the terminal alkyne but for any other ester this would result in a substituted phenylacetylene. For example ethyl phenylpropiolate (R=Me) would give phenylpropyne so some alternative mechanism must be used for the loss of the ethoxycarbonyl group. This may go by the electrocyclic elimination proposed earlier or perhaps more likely by a six membered ring intermediate formed by carbene insertion as above.

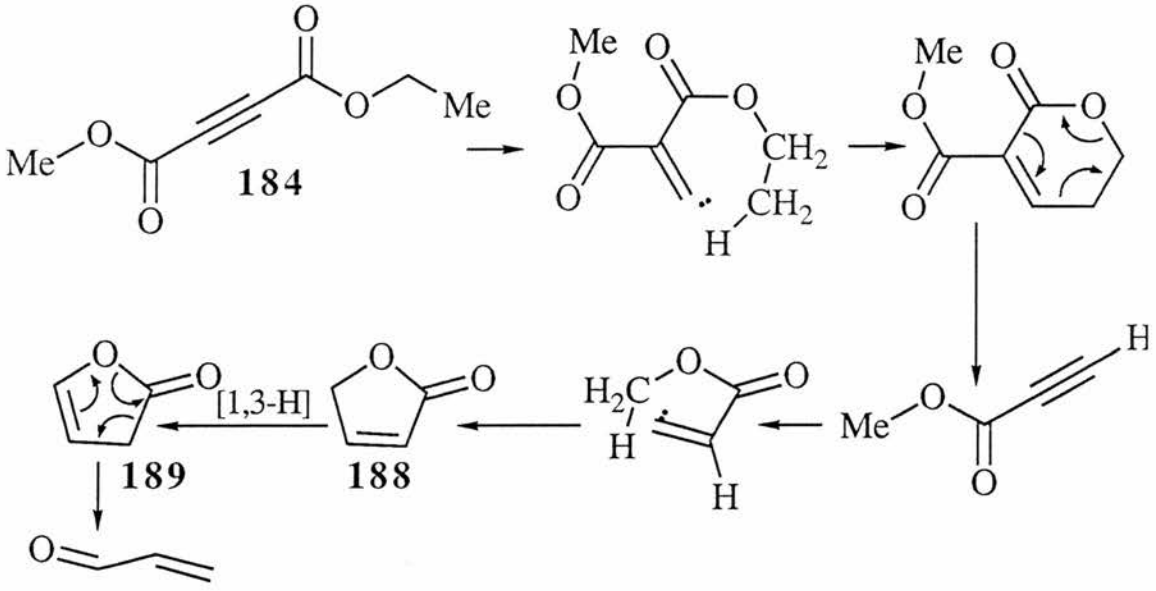


This mechanism is indistinguishable from the electrocyclic elimination since exactly the same products are formed. Evidence in support of this mechanism could possibly be obtained by ^{13}C labelling of one of the acetylenic carbons. On pyrolysis, formation of the carbene by phenyl migration would cause scrambling of the labeled site and ^{13}C spectroscopy would show an increased signal for the originally unlabeled acetylenic carbon. However if the carbene is formed entirely by migration of the ester group both routes would give the same product and no useful information would be gained.

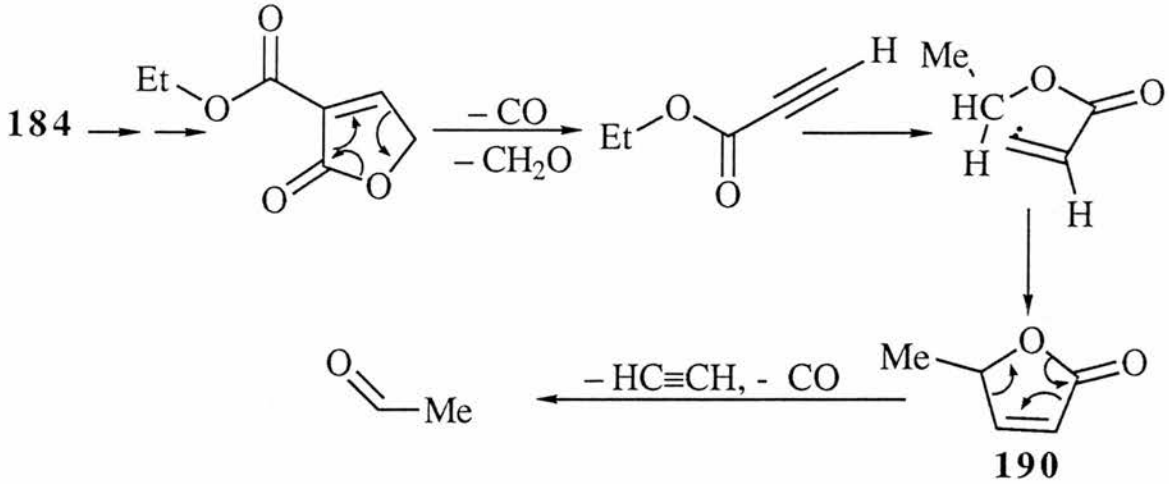


In the FVP of ethyl methyl acetylenedicarboxylate **184** the ethoxycarbonyl group was found to be completely disproportionated. Some methyl propiolate was found and the major product was acrolein. The loss of ethoxycarbonyl thus seems to be the first step in the reaction and a secondary process is evidently providing the acrolein which was assumed to be formed from the methyl propiolate. FVP of authentic

methyl propiolate was found to provide acrolein supporting this asssumption and so the the overall mechanism may be accounted for by the following mechanism. Firstly the ethoxycarbonyl group is lost as CO_2 and ethylene following an intramolecular carbene insertion. This forms the methyl propiolate and here again the acetylene rearranges to a carbene and undergoes insertion into the methyl C-H bond to form the 2,5-dihydrofuran-2-one intermediate **188**. A 1,3-H shift gives 2,3-dihydrofuran-2-one **189** which readily fragments with the loss of carbon monoxide to give acrolein.

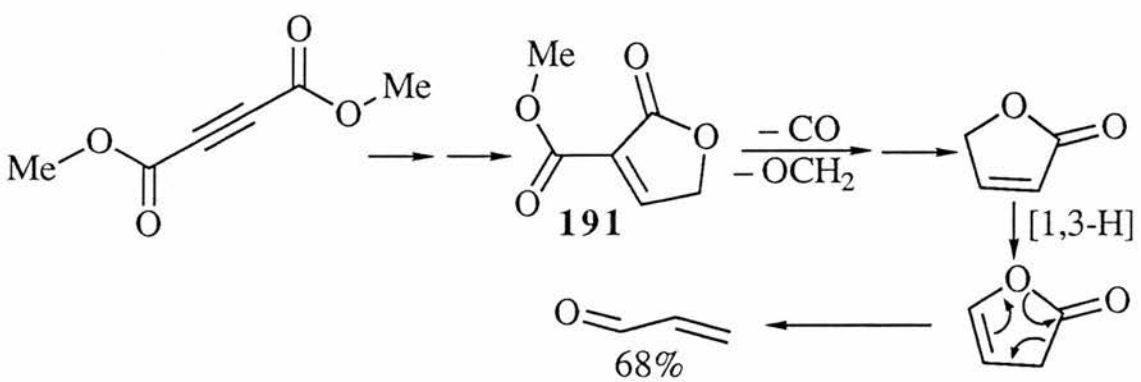


This mechanism does not account for the formaldehyde or acetaldehyde which were both seen in the prolysate but these may be accounted for by a side reaction which is essentially a reversal of the above mechanism where the carbene inserts to the methyl ester as the first step to generate formaldehyde, CO and ethyl propiolate.

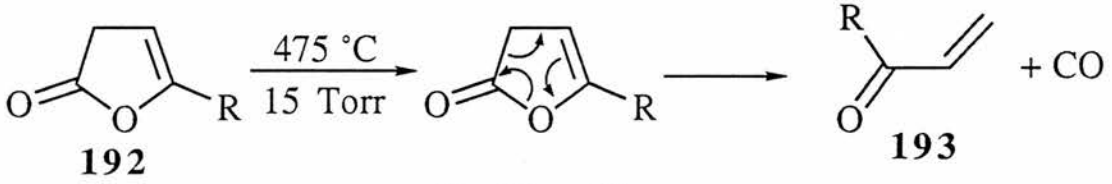


The ethyl propiolate may then form 5-methyl-2,5-dihydrofuranone **190** which fragments by losing CO and acetylene to give acetaldehyde. The corresponding reaction of **188** likewise provides a source of formaldehyde.

The 5-methyl-2,5-dihydrofuranone **190** is apparently stabilised against the 1,3-H shift seen for the unsubstituted analogue since no methyl vinyl ketone was observed. Such stabilisation may also be observed with the methyl ester function in the same position and this may be used to account for the products observed on FVP of dimethyl acetylenedicarboxylate. Here the first step involves the formation of the carbene and subsequent insertion to give the 3-methoxycarbonyl-2,5-dihydrofuran-2-one **191**. Loss of CO and formaldehyde then yields methyl propiolate which again undergoes insertion leading to the unsubstituted dihydrofuranones which finally give acrolein.



The rearrangements discussed above are closely related to the gas phase thermolysis of 2(3H)-furanones investigated by Skorianetz and Ohloff.[83] They found that pyrolysis at 450 °C of 5-methyl and 5-phenyl-2,3-dihydrofuranones **192** gave the corresponding vinylketones **193** in high yield with the evolution of CO.



192 **193**

R= Ph or Me

Presumably this reaction would also be seen where substituents are present on other sites of the dihydrofuranone ring leading to the rearrangements discussed in this work.

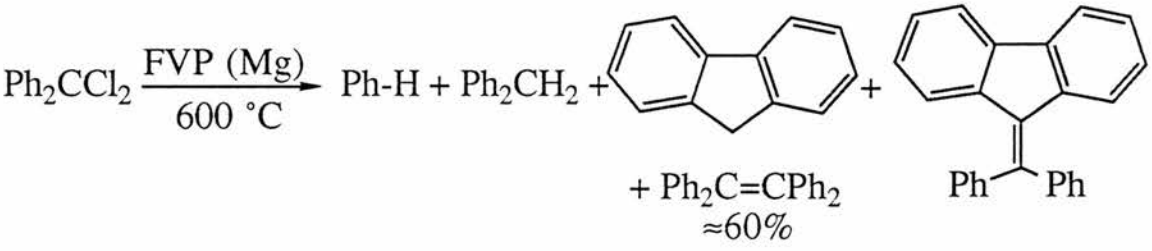
E Pyrolysis of oxygen functionalised compounds over magnesium.

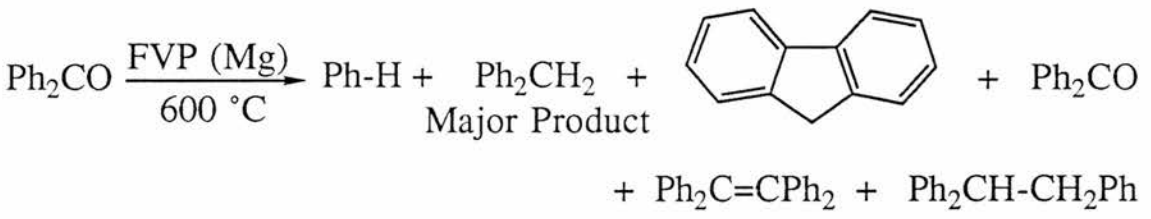
1. Introduction.

As outlined in the Introduction an extensive study by Oyewale[51] investigated the behaviour of organic compounds on FVP over magnesium. The technique proved to be efficient in the dehalogenation and dehydrohalogenation of a wide range of organic halides and also showed potential in deoxygenation of some epoxides.

A subsequent study[84] investigating the dehalogenative effects of FVP over magnesium on the heavier group 14 halides found an anomalous result in the pyrolysis of diphenyldichloromethane. A great deal of benzophenone was present in the products due to partial hydrolysis of the

starting material. When clean diphenyldichloromethane was used the pyrolysis products differed less than expected although it was discovered that the degree of hydrolysis of the original diphenyldichloromethane was substantial. With the aim of finding which products were due solely to the benzophenone this material was pyrolysed under the same conditions and the products from both reactions are shown below.





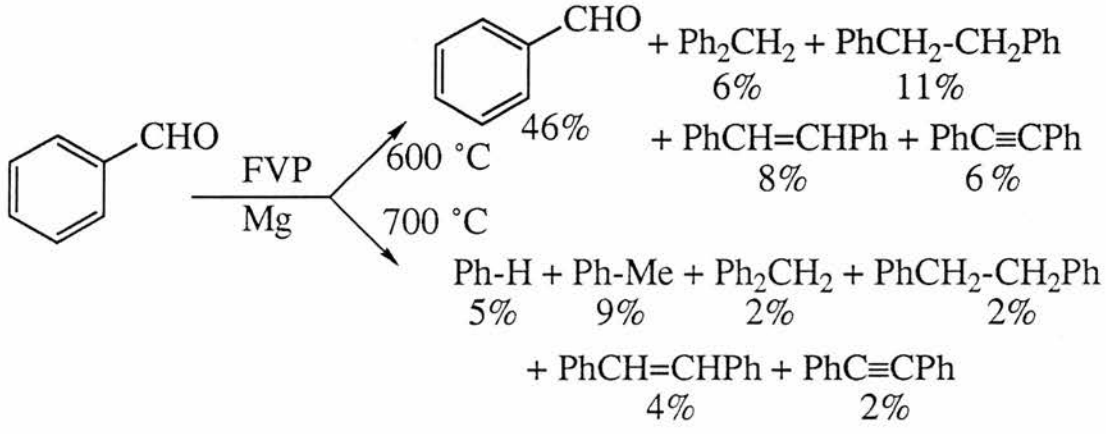
In both cases the components of the pyrolysate were identified by GCMS and no accurate quantitation was attempted. The ratios of peak integration on the chromatogram were sufficient to conclude that FVP over magnesium is effective in deoxygenation of this ketone giving different products possibly by a different mode of action to that of the analogous vicinal dichloride.

For the present work, FVP over magnesium of aromatic aldehydes, alchohols and ketones was run to investigate the possible deoxygenative effect of the technique on these substrates. It was hoped that the deoxygenation of these molecule on pyrolysis may provide the coupled products found on pyrolysis of their halide analogues that are detailed in the Introduction and that this coupling might provide a gas phase

magnesium induced variant of McMurray's titanium induced carbonyl-coupling reactions[85]

2. FVP over magnesium of aromatic aldehydes and alcohols.

Pyrolysis of benzaldehyde **C** over magnesium at 600 °C resulted mainly in unchanged starting material and a mixture of coupled products. In an attempt to increase the deoxygenative activity of the Mg the pyrolysis was repeated at 700 °C and the difference in the products investigated.

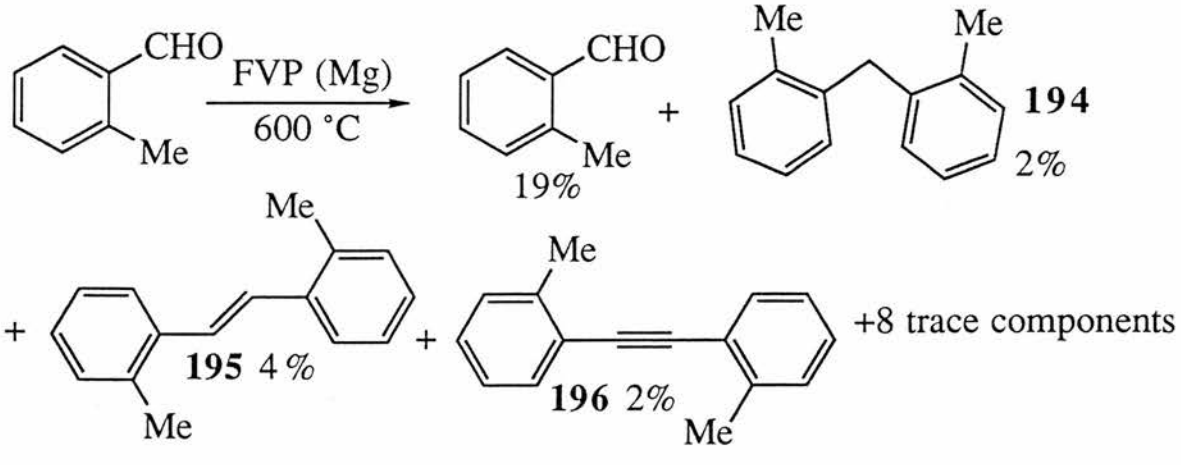


From the results of these pyrolyses it is clearly seen that the magnesium exhibits deoxygenative activity towards benzaldehyde and that this activity is temperature dependant with the activity increasing with temperature. A further observation is that much of the initial mass of the starting material is lost with the greatest loss occurring on pyrolysis at 700 °C. This is comparable with the findings of previous work[51,84] where varying degrees of loss of analogous organic halides were presumed to occur by degradation of the material over the magnesium surface to create surface bound species and stable fragments such as benzene. On pyrolysis of benzaldehyde at 700 °C both benzene and toluene may be assumed to have been formed by this route and their presence should also account for the unexpected appearance of diphenylmethane from pyrolysis at both

temperatures which may be formed by combination of phenyl or benzyl radicals either in the gas phase or on the metal surface.

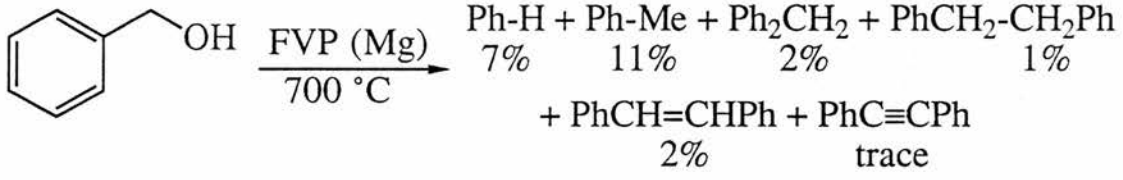
Both pyrolyses resulted in the production of varying quantities of the coupled products 1,2-diphenylethane, 1,2-diphenylethene, and diphenylacetylene. This shows that coupling of carbonyls can be achieved by FVP over magnesium but the nature of the coupling reaction is unclear. It may occur either as part of a metal bound process or, as the variety of products suggests, from the abstraction of oxygen by the metal and subsequent recomination of the resulting radical or carbene intermediates either in the gas phase or in the cold trap.

Pyrolysis of a further simple aromatic aldehyde, o-tolualdehyde was run to look for the formation of similar coupled products that would be labelled with the 2-methyl motif. The results of the pyrolysis indicate that the 2-methylated products **194**,**195** and **196** are formed but in lower yields with many other side products. These other products were formed in trace quantities and their identities not firmly established, however the mass spectra of these components indicated that they were likely to be fused products formed probably as a consequence of the loss of benzylic hydrogen from the 2-methyl substituents.



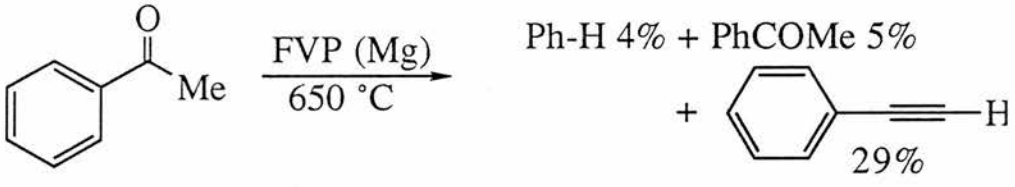
Pyrolysis of benzyl alcohol at 700 °C gave the same products as the analogous aldehyde but in different proportions. The benzene and toluene

products are favoured over the coupled products. This indicates that the alcohol may lose OH to the magnesium more easily than the loss of oxygen from the aldehyde and may spend less time on the Mg surface with a corresponding drop in the probability of metal induced coupling.



3. <u>FVP over magnesium of aromatic ketones.</u>

FVP over magnesium of the simplest aromatic ketone, acetophenone gave a mixture of 3 components;- benzene, unchanged acetophenone and, the main product, phenylacetylene.

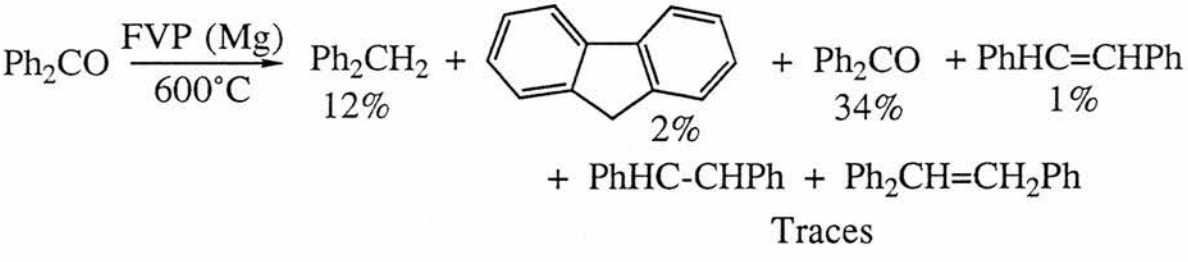


The magnesium appears to have a different mode of action on the ketone distinct from the deoxygenation seen for the aldehyde. The reaction is effectively a dehydration of the ketone to give the acetylene with no evidence of long lived metal bound species which could give rise to coupled products. This is a very interesting process as the one step conversion of the ketone results in a significant yield of the much more valuble acetylene. For this reason the pyrolysis was repeated on a small preparative scale to investigate the possibility of generating viable quantities of phenylacetylene from this process. The result was a disappointing 4% yield of phenylacetylene from 1.22 g of acetophenone pyrolysed over 1.5 g of magnesium. This shows that the magnesium either does not operate catalytically or that it is rapidly poisoned by the ketone. A further attempt

at increasing the yield of the acetylene was run by increasing the pyrolysis pressure by means of a nitrogen gas leak to try to increase the contact time of the ketone over the magnesium. This again gave a 4% yield of phenylacetylene and also produced an 8% yield of benzaldehyde showing that the process is pressure dependant.

Pyrolysis of propiophenone over magnesium gave a 21% yield of 1-phenylpropyne along with 1-phenylpropene (10%), indene (7%), styrene (3%) indane (1%) and small quantities of benzene and toluene. The products indicate that for the greatest part of the reacted material a similar dehydration reaction to that seen on the pyrolysis of acetophenone has occurred, this time resulting in the formation of the 1-phenylpropyne and again no coupled products were observed.

The FVP over Mg of benzophenone was run to allow quantitation of the products observed from earlier work. The resulting pyrolysate showed a different mixture of products to that observed before.



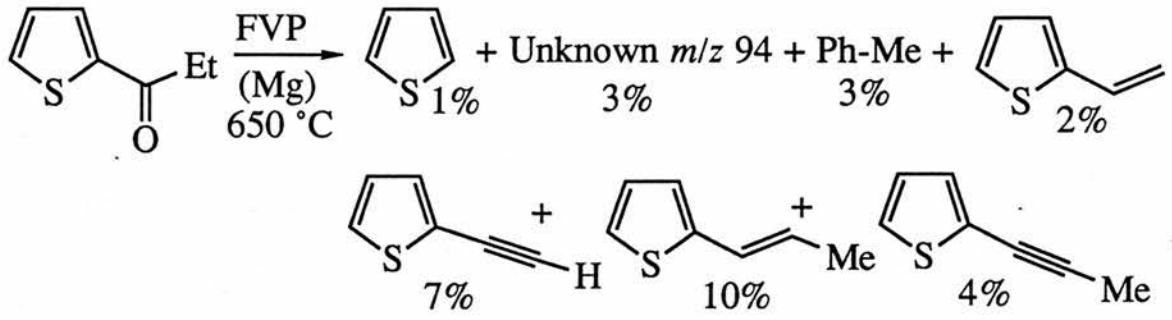
This change in the mixture of products is believed to be due to the change in the quantity of the ketone used as the starting material since in this case more was used than in the previous work[85]. As discussed already the magnesium seems to be poisoned by the passage of the organic material resulting in a change in activity and this may lead to different results on pyrolysis of different quantities of the same compound. The appearence of fluorene is believed to be due to a radical cyclisation reaction effectively fusing the two phenyl groups of the benzophenone which has also

undergone deoxygenation. The trace of tetraphenylethene is probably due to a coupling reaction that has not been seen with the simpler aromatic ketones. This leads to the suggestion that it may be formed by the coupling of diphenylcarbene produced by deoxygenation of benzophenone. The alkyl analogues of the carbene would not be so stable and may have too short a lifetime to form such coupled products.

So far only the benzylic carbonyls have been investigated for deoxygenation. The following examples were run for a comparative study. Pyrolysis of cyclohexanone over Mg resulted in recovery of 64% of unchanged cyclohexanone. The magnesium seems to be inactive towards this compound save for the unknown fate of the missing material.

Since some success was found in the generation of alkynes from the dehydrogenation of acetophenone and propiophenone their thienyl analogues were pyrolysed to look for similar activity. Pyrolysis over Mg of 2-acetylthiophene resulted in the formation of an orange intractable polymer on exposure of the pyrolysate to air. In a repeat experiment the pyrolysate was immediately dissolved in deuteriochloroform as soon as the trap was opened and the ^{1}H NMR spectrum of the material indicated that the pyrolysate was mainly composed of 2-ethynylthiophene. For this compound the dehydration reaction was successful and resulted in the expected alkyne which rapidly polymerised on contact with moist air.

Pyrolysis of 2-propionylthiophene again resulted mainly in insoluble polymeric material. Extraction of this material with deuteriochloroform provided a complex mixture illustrated overleaf.



Again the expected acetylene has been formed but in this case the 2-(prop-1-ynyl)thiophene has been generated in only 4% yield in competition with other processes which have given larger quantities of 2-(prop-1-enyl)thiophene and 2-ethynylthiophene. Both of the latter products may be accounted for by radical processes occurring on or after the deoxygenation or dehydration steps. The mechanism behind these transformations remains unclear and none more so than the appearance of the toluene and unknown component which is believed to be a C_7H_{10} hydrocarbon. The appearance of these two products could be due to another unprecedented reaction involving the desulphurisation of the heterocycle but this cannot be proven without further studies.

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