A STUDY OF SOME STIBONIUM AND OTHER YLIDES

being a Thesis

presented by

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to the

UNIVERSITY OF ST. ANDREWS

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

St. Andrews April, 1987

TO MUM, DAD AND
DAVE

DECLARATIONS

I was admitted to the Faculty of Science of the University of St. Andrews under Ordinance General No. 12 on the 1st October, 1983, and as a candidate for the degree of Ph.D. on the 13th February, 1985.

Signed ....

Date ....12th May 1987....................

I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate to the Degree of Ph.D.

Supervisors... ....

Date ....12 May 87....

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

Signed ....

Date........12th May 1987..................

ACKNOWLEDGEMENTS

I would like to thank Dr. D. Lloyd and Dr. C. Glidewell for proposing this research topic and for their advice, interest and encouragement during the last three years.

I am very grateful for the help of members of the technical staff of this department, in particular Mrs. M. Smith (N.M.R. Spectra), Mrs. S. Smith and Miss C. Jack (C,H, N Microanalyses) and Mr. C. Miller (Mass Spectra).

I am indebted to Professor George Ferguson, University of Guelph, Canada, for the many x-ray structure analyses he has carried out with such great interest and enthusiasm, and also to Professor H. Lumbroso, Université Pierre et Marie Curie, Paris, for the dipole-moment measurements presented in this thesis.

My sincere thanks also go to Mrs. Janice Pay who typed this thesis.

Finally, I gratefully acknowledge a Research studentship from the S.E.R.C.

PUBLICATIONS

(i) Preparation and Variable Temperature N.m.r. Spectra of a Cyclopentadienylidenepyran and a Cyclopentadienylidenedihydropyridine.
D. Lloyd and S. Metcalfe, *J. Chem. Research (S)*, (1983), 292.

(ii) Some Stable Stibonium Ylides. The Use of bis(hexafluoroacetylacetonato)Copper(II) as a Homogeneous Catalyst in the Conversion of Diazo-compounds into Ylides.
C. Glidewell, D. Lloyd and S. Metcalfe, *Tetrahedron*, (1986), **42**, 3887.

(iii) Crystal and Molecular Structure of Triphenylstibonium Bis(phenylsulphonyl)methylide Hemi(chlorobenzene) Solvate.
G. Ferguson, C. Glidewell, D. Lloyd, S. Metcalfe and B. L. Ruhl, *J. Chem. Research (S)*, (1987), 32.

(iv) The Structure of Dimeric Triphenylstibine Oxide.
G. Ferguson, C. Glidewell, B. Kaitner, D. Lloyd and S. Metcalfe, *Acta Cryst.*, in press.

(v) The Effect of the Counter-ion on the Structures of Tetraphenylantimony (V)/Stibonium Compounds: Crystal and Molecular Structures of Tetraphenylantimony (V) Bromide, Perchlorate and Tetraphenylborate.
G. Ferguson, C. Glidewell, D. Lloyd and S. Metcalfe, *J. Chem. Soc., Perkin Trans.II*, submitted.

(vi) A Comparison of Stibonium with Arsonium (and other) Ylides.
G. Ferguson, C. Glidewell, B. Kaitner, D. Lloyd, H. Lumbroso and S. Metcalfe, *J. Chem. Soc.*,

(vi) (continued)
Perkin Trans.II, in preparation.

(vii) A Gentle Method for the Preparation of Ylides, including Arsonium, Stibonium, Bismuthonium, Sulphonium, Telluronium and Thiouronium Ylides.
C. Glidewell, D. Lloyd and S. Metcalfe, *Synthesis,* in preparation.

SUMMARY

INTRODUCTION

A study of the general history of ylides is made, with particular reference to ylides of arsenic, antimony and bismuth.

SECTION 1: Cu(II) Complexes as Catalysts in the Preparation of Ylides

The introduction and development of the use of Cu(II) complexes as catalysts in the production of ylides with a variety of heteroatoms by decomposition of diazo-compounds, or iodonium ylides, in the presence of carbene acceptors is discussed, including mechanism of action. In particular the uses of acetylacetonato Cu(II) and hexafluoroacetylacetonato Cu(II) [$Cu(hfa)_2$] are examined, with examples which illustrate the superiority of the latter, and discussion of the factors which contribute to this.

SECTION 2: Copper-bronze as a Catalyst in the Preparation of Ylides

The brief investigation into the effect of ultrasonic waves on the copper-bronze catalysed preparation of triphenylarsonium 2,3,4-triphenylcyclopentadienylide is discussed.

SECTION 3: Preparation of Some Stibonium Ylides

The preparation of diazo-compounds and their reaction with Ph_3Sb in the presence of $Cu(hfa)_2$ to yield stibonium

ylides was investigated. Analogous reactions using rhodium acetate instead of $Cu(hfa)_2$ did not yield ylides; instead $[Rhac_2]_2(SbPh_3)_2$ appeared to form which inhibited further reaction.

The reaction of Ph_3SbCl_2 with a variety of active methylene compounds in the presence of base in some cases did yield ylide. However, contamination of the ylides with side-products occurred and yields were poorer than from the diazo method.

Attempts to prepare stibonium ylides *via* the "salt-method" or by decomposition of an iodonium ylide in the presence of Ph_3Sb were unsuccessful.

SECTION 4: Properties of Stibonium Ylides

The physical and spectroscopic properties of stibonium ylides are described. IR, UV and mass spectral data are given, and, in some cases, dipole moments have been determined, together with the dipole moments of the analogous arsonium ylides for comparison. High-field ^{13}C n.m.r. spectra of several of the ylides have been obtained, again with the spectra of the corresponding arsonium ylides. For the first time, resonances for the ylidic carbons, which have very long relaxation times, have been observed and recorded.

All the spectroscopic data would seem to indicate little difference in the degree of dipolar character on going from arsonium to stibonium ylides.

SECTION 5: X-ray Structures

The x-ray structures of triphenylstibonium bis(phenylsulphonyl)methylide and triphenylstibonium 4,4-dimethyl-2,6-dioxocyclohexylide have been determined along with the structures of their arsonium analogues. The results reveal the presence of electrostatic interaction between the heteroatoms (As or Sb) and an oxygen atom of one of the α-substituents. This interaction is greater in the stibonium ylides affording them more covalent character than their arsonium counterparts.

For reference purposes, x-ray structures of a number of antimony compounds, Ph_4SbX, ($X = Ph_4B$, Br, ClO_4) have been obtained, and also that of triphenylstibine oxide.

SECTION 6: Reactions of Stibonium Ylides

Attempts to prepare perchlorate salts of the ylides were unsuccessful: either hydrolysis of the ylide ensued, or $(Ph_3Sb\text{-}O\text{-}SbPh_3)(ClO_4)_2$ was formed, presumably *via* hydrolysis of the desired perchlorate salts. The preparation of the picrate salt of triphenylstibonium diacetylmethylide was more successful, although the salt was again unstable.

The new stibonium ylides were found to be unreactive in Wittig reactions.

SECTION 7: Bismuthonium Ylides

Spectroscopic evidence was obtained for the existence of triphenylbismuthonium bis(phenylsulphonyl)methylide and triphenylbismuthonium 2,6-dioxocyclohexylide, formed by the $Cu(hfa)_2$ catalysed decomposition of diazo bis(phenylsulphonyl)-methane and 2-diazocyclohexane-1,3-dione respectively in the presence of Ph_3Bi. Triphenylbismuthonium 2,6-dioxocyclohexylide was unreactive towards 2,4-dinitrobenzaldehyde.

SECTION 8: Iodonium Ylides

Some investigation into the preparation of novel cyclic iodonium ylides was carried out, but this topic was discontinued in favour of the study of stibonium ylides.

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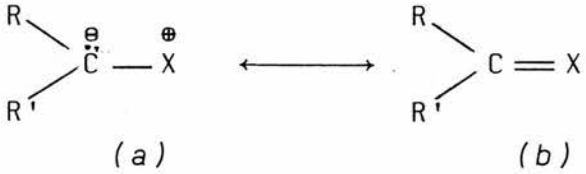
INTRODUCTION

PART I

INTRODUCTION

1. YLIDES

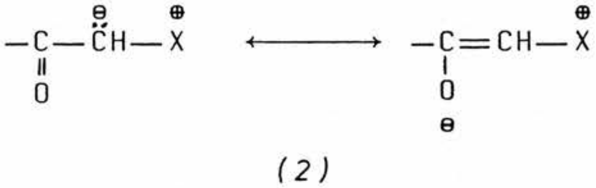
An ylide is a species in which a carbanion is attached directly to a heteroatom carrying an appreciable amount of positive charge[1] *(1a)*. In resonance terms such a structure may be only one contributor to the overall structure of the ylide molecule.



(a) *(b)*

(1)

For example, an ylide may also have an enolate structure *(2)* in which the negative charge of the carbanion is delocalised by the carbonyl group resulting in greater overall stability. Other electron accepting groups such as cyano-, nitro- and sulphonyl-, can provide similar stabilisation. The importance



$$-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{\ddot{C}}H-\overset{\oplus}{X} \longleftrightarrow -\underset{\underset{\underset{\ominus}{O}}{|}}{C}=CH-\overset{\oplus}{X}$$

(2)

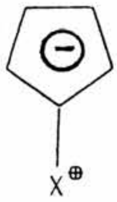
of the covalent structure *(1b)* is largely dependent on the nature of X.

It is possible to isolate some ylides as stable crystalline species. This stability is directly due to delocalisation of the non-bonded electrons of the carbanion. (It is rarely possible to isolate normal carbanions due to their extreme sensitivity to oxygen and moisture.) There are a number of ways in which this stability can be achieved:-

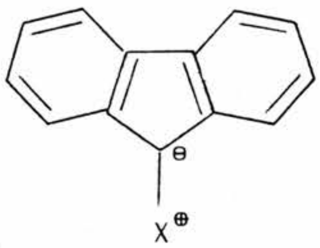
(i) the carbanionic substituents, R and R' *(1)*, may contain electron withdrawing groups such as carbonyl-, cyano-, nitro-, sulphonyl-, *etc.*, or

(ii) the carbanion may be part of cyclopentadiene *(3)*, fluorene *(4)* or indene *(5)* rings which have stable 6π electron systems, or

(iii) stabilisation by the heteroatom X *(1)* itself.



(3)



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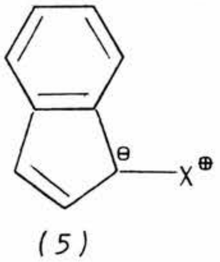
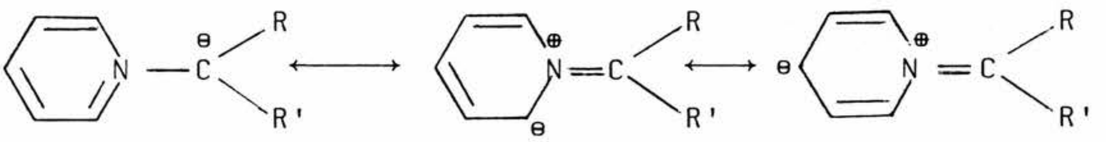


(5)

In order for the heteroatom to stabilise an adjacent carbanion, it must possess vacant orbitals of low energy which can overlap effectively with the filled 2p orbital of the carbanion to give some degree of covalency [*cf.* *(1b)*] *i.e.* it must be capable of expanding its valence shell to accommodate 10 electrons.

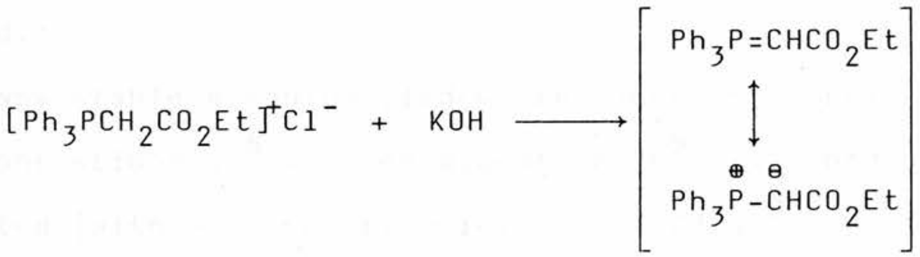
Most time has been devoted to studying the role of Group V elements in ylide chemistry, and to a lesser extent, those of Group VI. The first row element of Group V, nitrogen, cannot provide stabilisation in ylides by valence shell expansion since the next vacant orbital, the 3s, is of too high an energy to interact with the 2p orbital of the carbanion. In addition the orbital symmetry is unfavourable for good overlap if the carbanion is planar. Despite this, however, nitrogen ylides do exist, but are generally thermally unstable and very nucleophilic. In ammonium ylides it is assumed that the only stabilisation occurs through electrostatic interaction between the opposite charges and so ammonium ylides are less stable than those ylides whose heteronium group can participate in π-bonding. Pyridinium ylides *(6)* are more stable, since in addition to electrostatic interaction, a greater degree of stability can be achieved through a resonance interaction with the pyridinium ring. Some evidence for this comes from an x-ray study by Bugg[2] *et al* which showed that the C–N ylide bond was shorter than that expected for a $C_{sp^2}-N_{sp^2}$ single bond.



(6)

Although no oxygen ylides have been isolated, there is spectroscopic evidence for their existence[3] at low temperatures, and also as reaction intermediates.

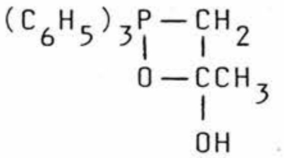
The next elements in Groups V and VI, phosphorus and sulphur, have vacant orbitals whose energy and symmetry are compatible with those of the carbanionic 2p orbital and hence are more suitable for effective overlap. As a result, ylides of sulphur and phosphorus (especially) are very common and have been studied extensively. Indeed the very first ylide to have been prepared was the phosphonium ylide[4] *(7)* by Michaelis and Gimborn in 1894, although at the time they proposed a different structure for the compound. They obtained the ylide by treatment of an aqueous solution of (ethoxycarbonylmethyl)triphenylphosphonium chloride with cold potassium hydroxide solution.



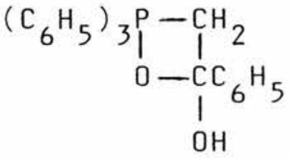
$$[Ph_3PCH_2CO_2Et]^+Cl^- + KOH \longrightarrow \left[\begin{array}{c} Ph_3P{=}CHCO_2Et \\ \updownarrow \\ Ph_3\overset{\oplus}{P}{-}\overset{\ominus}{C}HCO_2Et \end{array}\right]$$

(7)

In 1899 Michaelis and Kohler reported[5] the preparation of two "phosphonium betaines" *(8)* and *(9)* which subsequently have been shown to be ylides[6] *(10)* and *(11)*. It was quite by chance rather than design that Michaelis chose phosphonium salts which produced stable, isolable ylides.



(8)



(9)

$(C_6H_5)_3P{=}CHCOCH_3$

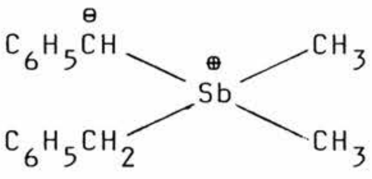
(10)

$(C_6H_5)_3P{=}CHCOC_6H_5$

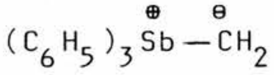
(11)

Proceeding down Group V, arsenic and antimony would also be expected to provide similar stabilisation through pπ-dπ bonding despite the fact that the d orbitals become more diffuse going down the group. It has been suggested[7], however, that in ylides, the positive charge present on the heteroatom could cause sufficient contraction of the d orbitals for such overlap to become feasible. There is little evidence that bismuth can expand its valence shell (most bismuth compounds are trivalent), but it was hoped that under favourable conditions ylides of bismuth might be formed.

Many stable arsonium ylides are known, but until now only one stibonium[8] and one bismuthonium[9] ylide had been isolated (although the stibonium ylides *(12)*[10] and *(13)*[11] have been reported in solution).



(12)



$(C_6H_5)_3\overset{\oplus}{Sb}-\overset{\ominus}{C}H_2$

(13)

The diminishing ability of heteroatoms to be involved in π-bonding on going down the group evidently leads to a decreased contribution from the covalent canonical form *(1b)* of the ylide and hence to decreased stability. In addition, on going from phosphorus to arsenic to antimony the length of the carbon-heteroatom bond increases (1.87, 1.98 and 2.18 Å),[12] while the electronegativity of the heteroatom decreases (2.1, 2.0 and 1.9)[13]. Both these factors should increase the trend towards lower stability. Although this was found to be generally the case, it was of great interest that an x-ray structure[14] of the new stibonium ylide[15] *(14)* revealed that the ylidic C–Sb bond has considerably more covalent character than was expected (see later for more detailed discussion).

$$(PhSO_2)_2C{=}SbPh_3 \longleftrightarrow (PhSO_2)_2\overset{-}{C}{-}\overset{+}{Sb}Ph_3$$

(14)

The Group VI neighbours of arsenic and antimony, selenium and tellurium, also form ylides, although relatively little study has been done on the latter.

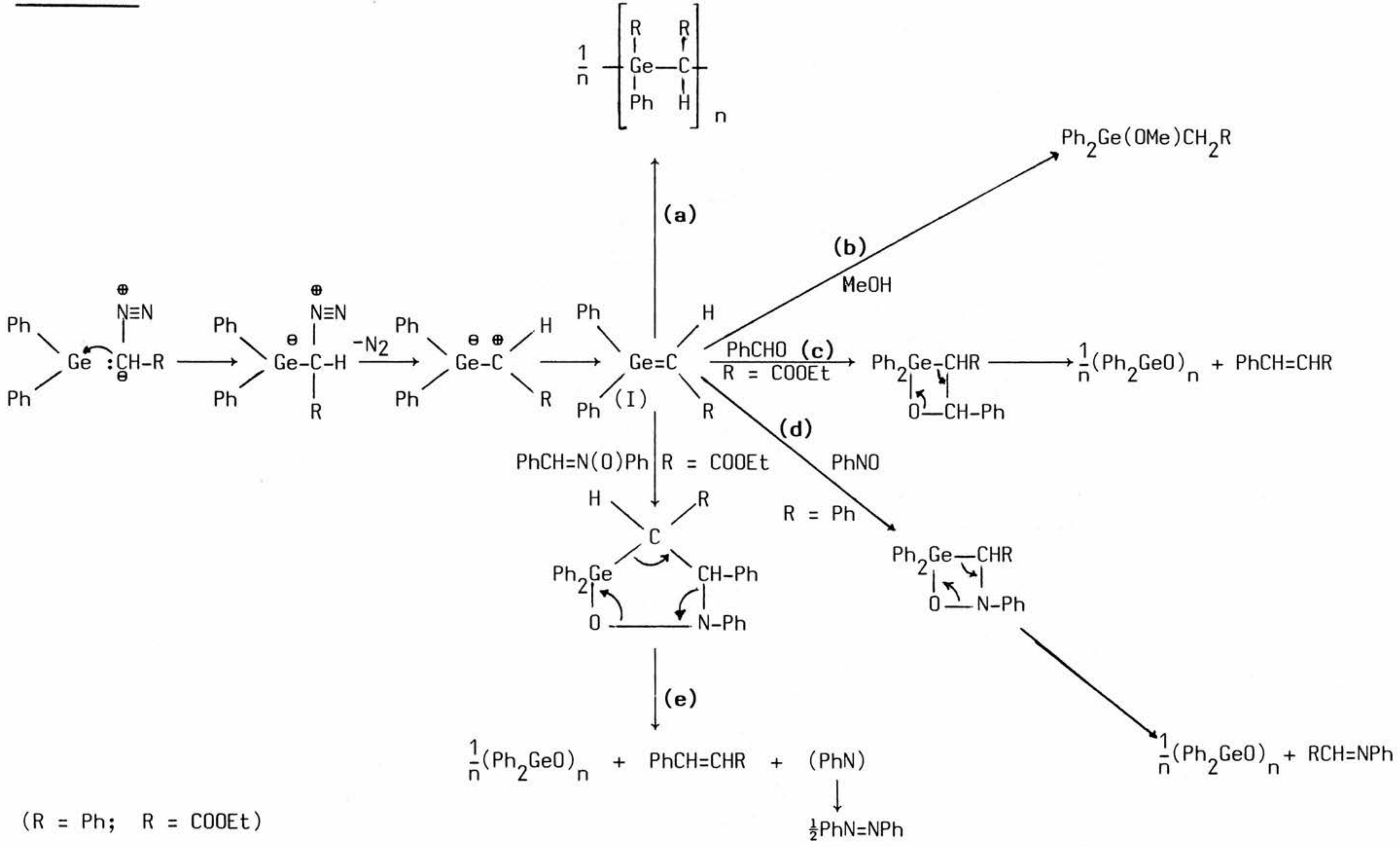
Moving on to Group VII of the Periodic Table, it is found that numerous ylides of iodine[16a-g] have been reported and also some ylides of bromine and chlorine[16e,17]. Indeed iodonium ylides have been used to prepare ylides containing other heteroatoms (see later). It has further been suggested that even xenonium ylides[18] could be prepared but, as yet, no attempts have been made to do so.

Very recent work in the Chemistry Department of the University of St. Andrews by Dr. K. Lumbard has involved the attempted synthesis of ylides of tin and germanium[19], the Group IV neighbours of arsenic and antimony. In an investigation of the reactions of germylenes (Ph_2Ge, PhGeCl, F_2Ge)

with diazo-compounds ($PhCHN_2$, $EtOOCCHN_2$), Rivière *et al*[20] reported evidence for the formation of intermediates containing germanium-carbon double bonds (*i.e.* germanium ylides or germenes). The reaction is believed to proceed by initial nucleophilic attack on the germylene by the diazo-compound. The adduct thus formed loses nitrogen to give the transient germene. Evidence for the formation of such a species was obtained by the isolation and identification of the products of the reaction with various trapping reagents. Scheme 1 shows the reactions of the germene intermediate (I) formed from diphenyl germanium and diazo-compound. (It is to be assumed that other dipolar canonical forms exist for the structure of this germene which are not drawn out here.) In the absence of any trapping reagent, (I) simply polycondenses to form oligomers (route a). Methanol was found to add across the double bond of (I) resulting in the corresponding alkoxygermane (route b). (I) was also found to undergo Wittig type reactions with aldehydes to give alkenes and germoxanes although in low yield (route c) and with nitrosobenzene to give imines and germoxanes (route d). A cycloaddition reaction of (I) to α-diphenylnitrone was also found to take place with the formation of germoxanes and the corresponding alkene and azo-compound, again in low yield (route e). Therefore, although (I) was never isolated by the French workers, there seems little doubt as to its existence.

If one were to attempt to isolate such germenes it

SCHEME 1^{20}



(R = Ph; R = COOEt)

seemed necessary to provide them with as much stabilisation as possible. In order to do this both electron-donor and electron-acceptor groups would be needed as shown in *(15)*.

$(\varepsilon\text{-donor})_2X{=}C(\varepsilon\text{-acceptor})_2$

Donor = $[(Me_3Si)_2N]-$

Acceptor = $-SO_2Ar$

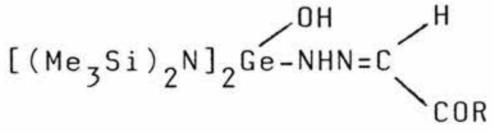
$-COR$

X = Sn, Ge

(15)

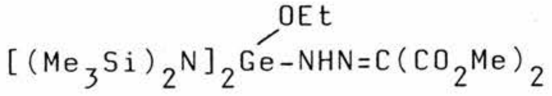
With this in mind, Dr. Lumbard investigated the reactions of diazo-compounds containing sulphonyl or carbonyl groups with the germylene, $[(Me_3Si)_2N]_2Ge$. These reactions all showed evidence for an initial coupling reaction between diazo-compound and germylene to give adducts of the type $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}CXY$ (where X and Y are electron-acceptor groups). Although these compounds did not survive the chromatographic work-up procedures, it was evident from the compounds which were isolated that they had indeed been intermediates.

It was found that the germanium-nitrogen double bond being formed was susceptible to addition reactions. Thus water or ethanol was found to add across the bond or even a further molecule of diazo-compound giving molecules of the type *(16)*, *(17)* and *(18)*.



$[(Me_3Si)_2N]_2Ge(OH){-}NHN{=}C(H)(COR)$

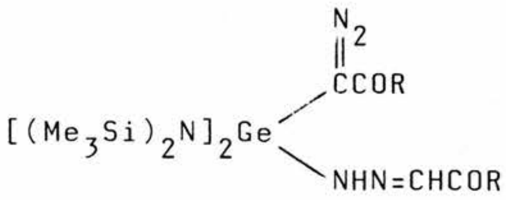
(16)



$[(Me_3Si)_2N]_2Ge(OEt){-}NHN{=}C(CO_2Me)_2$

(17)

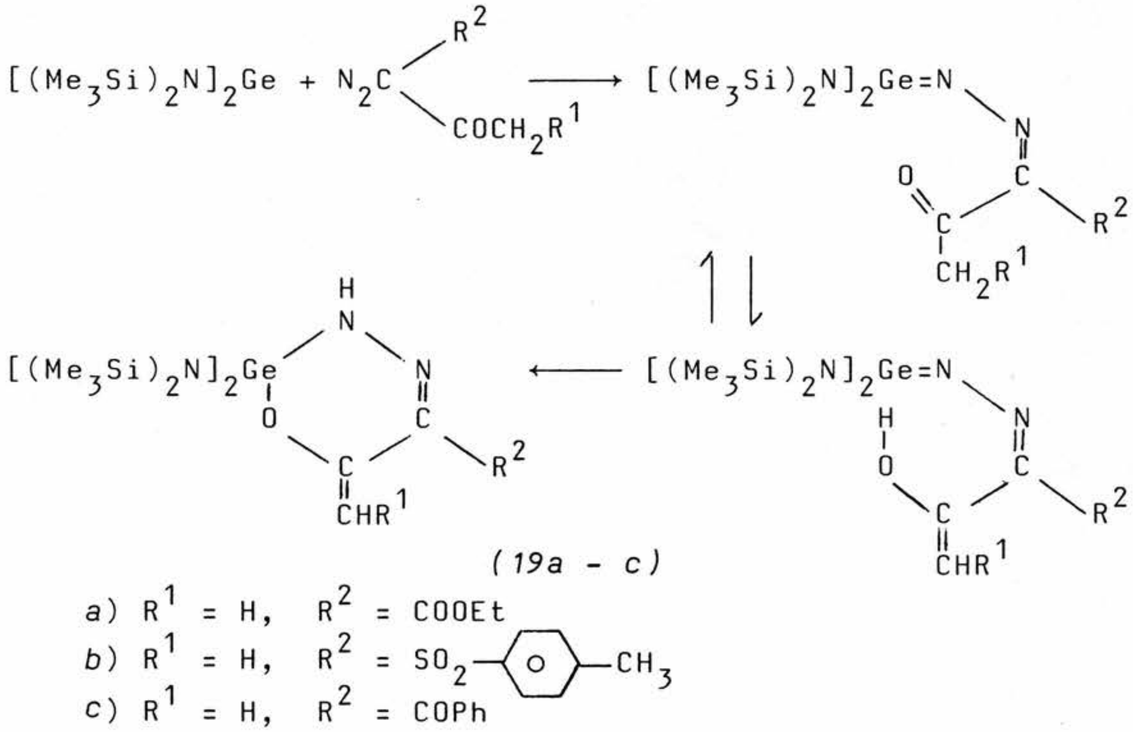
(R = OEt or Ph)



(18)

R = OEt, Ph

Further evidence for the germanium-nitrogen double bond came from experiments using disubstituted diazo-compounds carrying an enolisable carbonyl group. In these cases the cyclic compounds (19) were isolated, presumably *via* the reaction route shown.



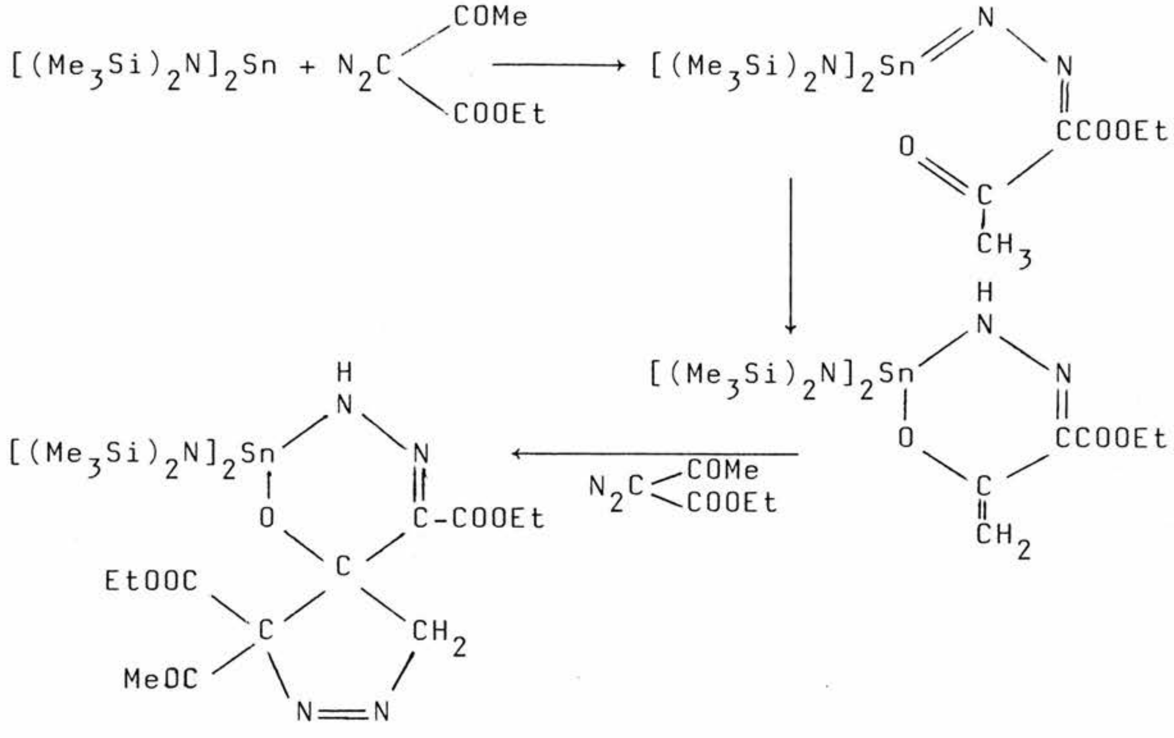
(19a - c)

a) $R^1 = H$, $R^2 = COOEt$

b) $R^1 = H$, $R^2 = SO_2-C_6H_4-CH_3$

c) $R^1 = H$, $R^2 = COPh$

When similar reactions were carried out using the corresponding stannylene, yet another type of compound was obtained (20).



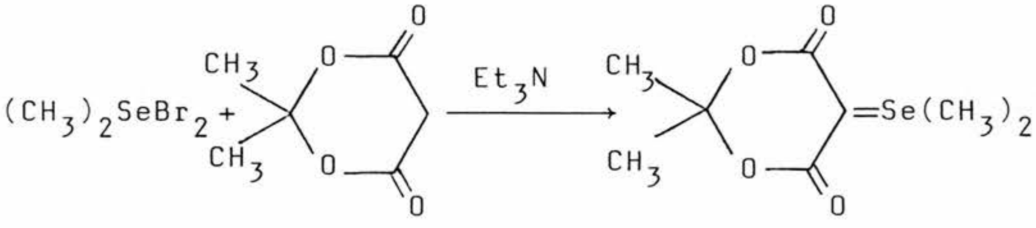
(20)

Therefore in attempting to isolate compounds containing germanium-carbon double bonds which are stabilised by both electron-donor and electron-acceptor groups, the course of the reaction has been altered in favour of the formation of germanium-nitrogen double bonds.

2. PREPARATION OF YLIDES

The method by which the first phosphonium ylide *(7)* was prepared is called the "salt method" and is the most common procedure for the preparation of ylides generally. It involves the synthesis of a suitable heteronium salt which has an acidic proton on one of the substituent groups. Treatment of such a salt with an appropriate base removes this proton to give the ylide.

A second method makes use of dihalogeno-compounds which, in the presence of base, may react with compounds containing a reactive methylene group to give ylides. For example, Reaction 1[21].



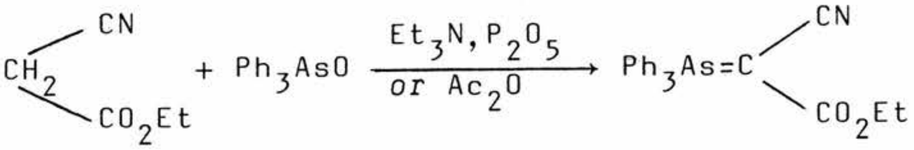
Reaction 1

This method has been used to prepare selenonium[21], telluronium[22], phosphonium[23] and arsonium[23] ylides and, as described in this thesis, in some cases for stibonium ylides.

A third method which has been used to prepare sulphonium[24], arsonium[25] and iodonium[16d] ylides also makes use of compounds containing reactive methylene groups. Treatment of the methylene compound with a sulphoxide, an arsine oxide or an iodoso compound in the presence of a suitable condensing reagent (P_2O_5 or acetic anhydride), yields respectively a sulphonium, arsonium or iodonium ylide (Reactions 2, 3, 4).

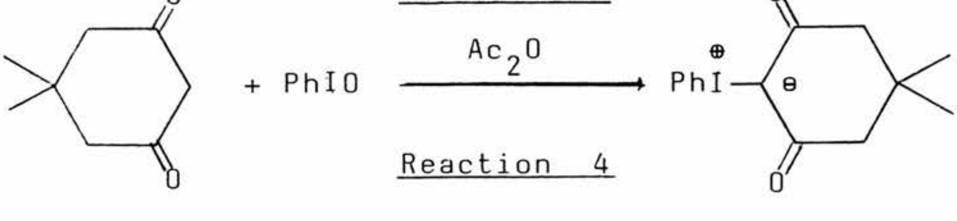
$$(PhSO_2)_2CH_2 + Me_2SO \xrightarrow{Ac_2O} Me_2S{=}C(SO_2Ph)_2$$

Reaction 2



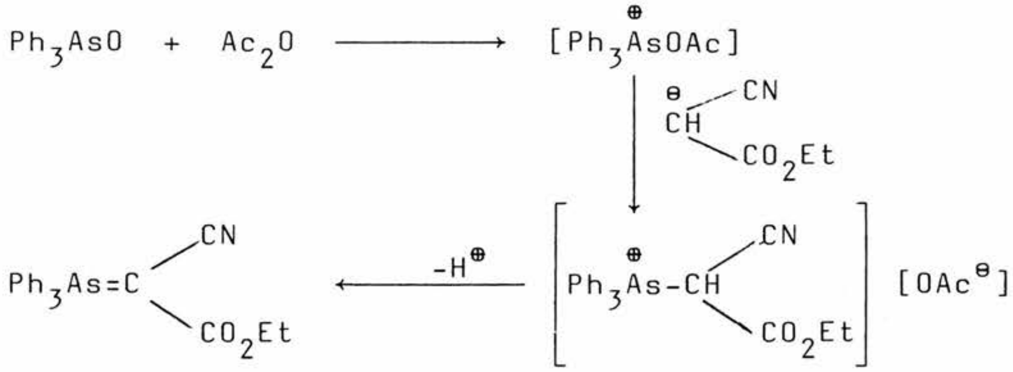
$$CH_2(CN)(CO_2Et) + Ph_3AsO \xrightarrow[or\ Ac_2O]{Et_3N,\ P_2O_5} Ph_3As{=}C(CN)(CO_2Et)$$

Reaction 3



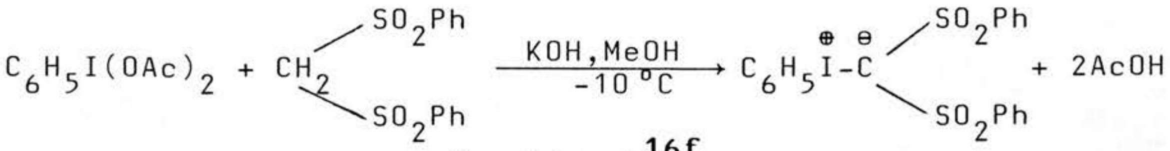
Reaction 4

The mechanism involves the initial formation of an acetoxy or phosphorylated heteronium cation which then reacts with a carbanion to form a heteronium salt (Scheme 2). In the example shown cyano and carbethoxy electron-withdrawing groups make the salt acidic and it is then easily deprotonated by triethylamine or acetic anhydride to give the ylide.



Scheme 2

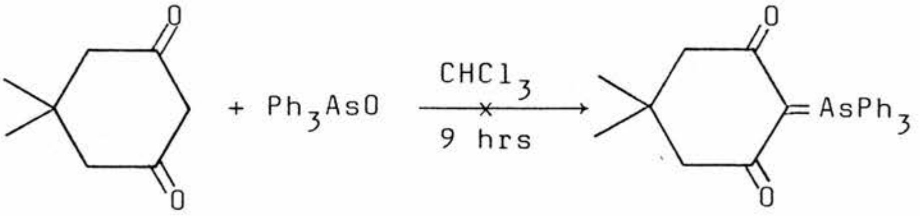
In a reaction analogous to this, phenyliodonium ylides[16b,c,f] can be prepared from (diacetoxyiodo)benzene and reactive methylene compounds in the presence of base (Reaction 5)



Reaction 5[16f]

Selenonium[26] and telluronium[27] ylides can also be made from selenoxides and telluroxides and a variety of active methylene compounds. No condensing agent is necessary and the reaction simply proceeds in chloroform at ambient temperature or under reflux.

Since arsenic is the Group V neighbour of tellurium and might be expected to have similar properties, this simple reaction was attempted in the preparation of an arsonium ylide (Reaction 6).



Reaction 6

However, no ylide was obtained even after nine hours in refluxing chloroform.

Finally we come to reactions involving diazo-compounds which have been used successfully to produce ylides containing a wide range of heteroatoms. They are themselves a type of di-nitrogen ylide being typically nucleophilic and often thermally unstable. They are useful because when they decompose they provide a source of carbenes which can react with suitable carbene acceptors to yield ylides.

Carbenes are neutral, bivalent carbon intermediates in which a carbon atom has two covalent bonds to other groups and two non-bonding orbitals containing two electrons between them. If these electrons are spin-paired the carbene is in a singlet state (the total spin, $S = 0$ and the multiplicity $= 2S + 1$). If, however, their spins are parallel, $S = 1$ and the carbene is in a triplet state. Carbenes are found to undergo several characteristic reaction types:-

i) insertion reactions into C-H bonds

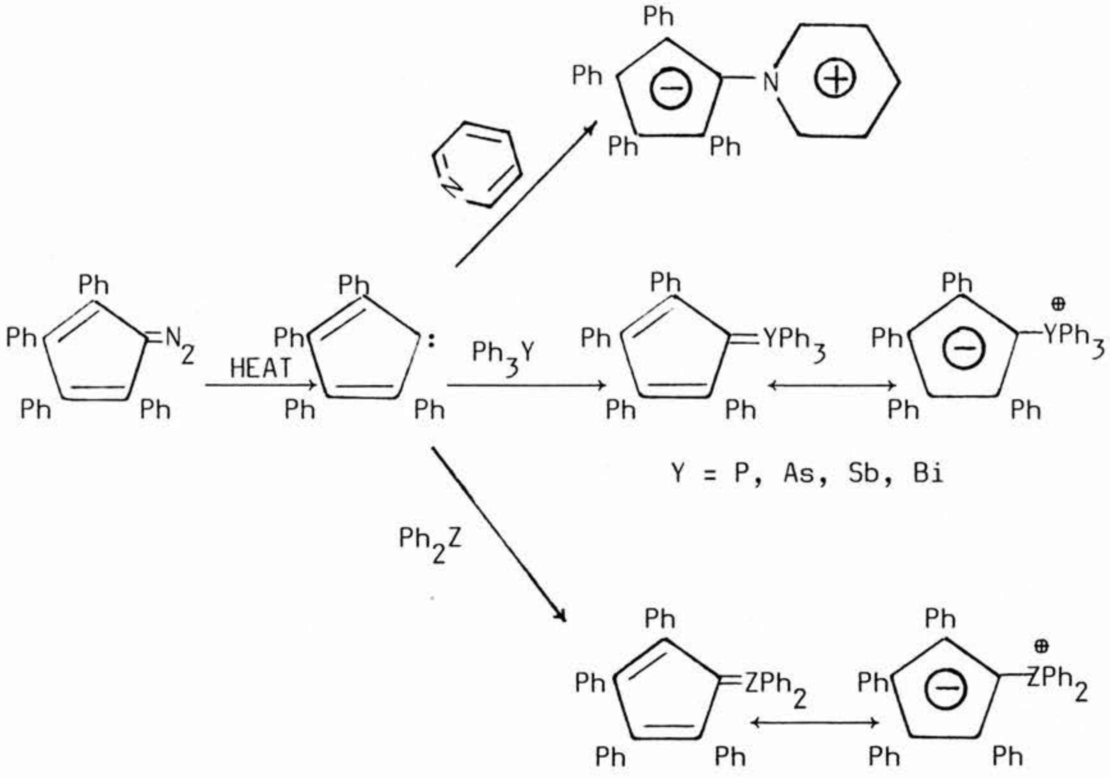
ii) addition reactions to multiple bonds or carbene acceptors, and

iii) rearrangement reactions.

Speaking generally, singlet carbenes react in a concerted fashion and are therefore stereospecific in their action. On the other hand, because of their diradical structure, triplet carbenes generally react in a two-step mechanism and are non-stereospecific.

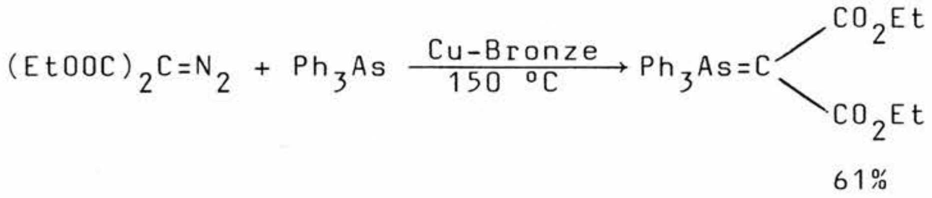
So many factors influence the nature of the ground state of a carbene that it is impossible to generalise and state which type of compound produces singlet carbenes and which type produces triplet carbenes - each case should be examined separately. It is sometimes possible to detect triplet carbenes by the use of E.S.R. spectroscopy, or to determine the multiplicity of a carbene intermediate by looking at the stereochemistry of the products of the reaction with carbene traps. However, neither method is guaranteed to give infallible results.

The photolysis or thermolysis of diazo-compounds is perhaps the most general route to carbenes. Those formed by photolysis are high energy species which often react indiscriminately. Thermal decomposition of diazo-compounds provides less energetic carbenes but, if the diazo-compound is thermally quite stable, high reaction temperatures may be needed. This is the situation shown in Scheme 3 which illustrates one of the earliest methods of producing ylides by the decomposition of diazo-2,3,4,5-tetraphenylcyclopentadiene requiring temperatures of around 130 °C. A thermogravimetric study[28] of the decomposition of this diazo-compound in the presence of PPh_3, $AsPh_3$, $SbPh_3$ and $BiPh_3$ showed that in each case quantitative loss of nitrogen occurred at 124 °C. Since the same weight loss step occurs with each set of reactants, it can be concluded that a common course of reaction is involved in each case, *i.e.* the formation of the carbene tetraphenylcyclopentadienylidene. This method provided the first ylides of antimony[8], bismuth[9], selenium[29] and tellurium[30] to be isolated. (Scheme 3)



Scheme 3

It was later found that such reactions could be catalysed by the addition of copper turnings or copper-bronze to the melt. For example, attempts to prepare triphenylarsonium bis(ethoxycarbonyl)methylide from diethyl diazomalonate and triphenylarsine in a melt failed, but succeeded in a 61% yield when copper-bronze was present in the melt.[25] (Reaction 7)

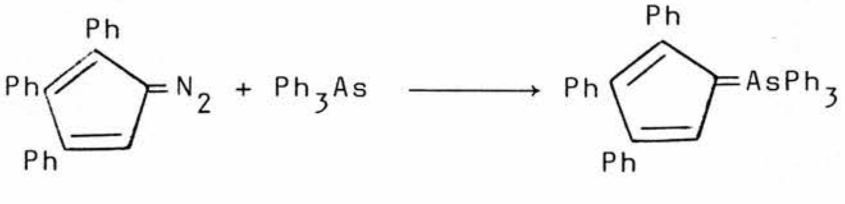


$$(EtOOC)_2C{=}N_2 + Ph_3As \xrightarrow[150\ ^\circ C]{Cu\text{-}Bronze} Ph_3As{=}C(CO_2Et)_2 \quad 61\%$$

Reaction 7

This ylide could not be prepared by the "arsine oxide" method.

Taking this a stage further, it was found that copper-bronze also acted as a catalyst in solution. For example reaction of diazo-2,3,4-triphenylcyclopentadiene with triphenylarsine in the presence of copper-bronze in refluxing benzene gave a 55% yield of ylide[31] (Reaction 8). In the absence of catalyst and solvent a temperature of 150 °C was required for reaction to occur and the yield was only about 10%.[31]



Reaction 8

A further improvement occurred when copper-bronze was replaced by soluble copper salt catalysts,[32] commonly bis(acetylacetonato)Cu(II) and, as described in this thesis, bis(hexafluoroacetylacetonato)Cu(II) (see later). It is through the use of this latter copper catalyst that a number of new stibonium and bismuthonium ylides have been prepared.

Since the presence of such copper catalysts effectively lowers the decomposition temperature of the diazo-compounds resulting in much cleaner reactions with improved yields of the desired products, it is doubtful whether free carbenes are involved in these reactions. Carbene-copper complexes seem much more likely and would be more selective in their reaction.

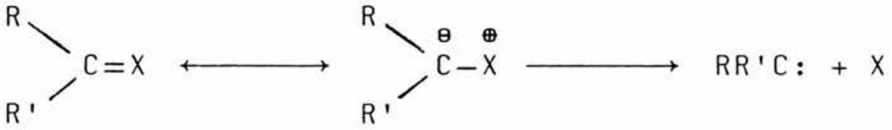
3. PROPERTIES OF YLIDES

The relative contributions of the covalent and dipolar canonical forms to the structure of an ylide determine its stability and hence its properties. In general, as the polarity of the carbon-heteroatom bond becomes greater, the stability of the ylide decreases and reactivity increases.

In some cases more specific information on carbon-heteroatom bonds in ylides is available from X-ray studies, dipole moment measurements and pK_a values. The usual spectroscopic techniques (UV, IR and NMR spectroscopy and Mass spectrometry) are also invaluable in assessing the polarity of ylides. These features and the types of reactions ylides undergo will be examined in turn.

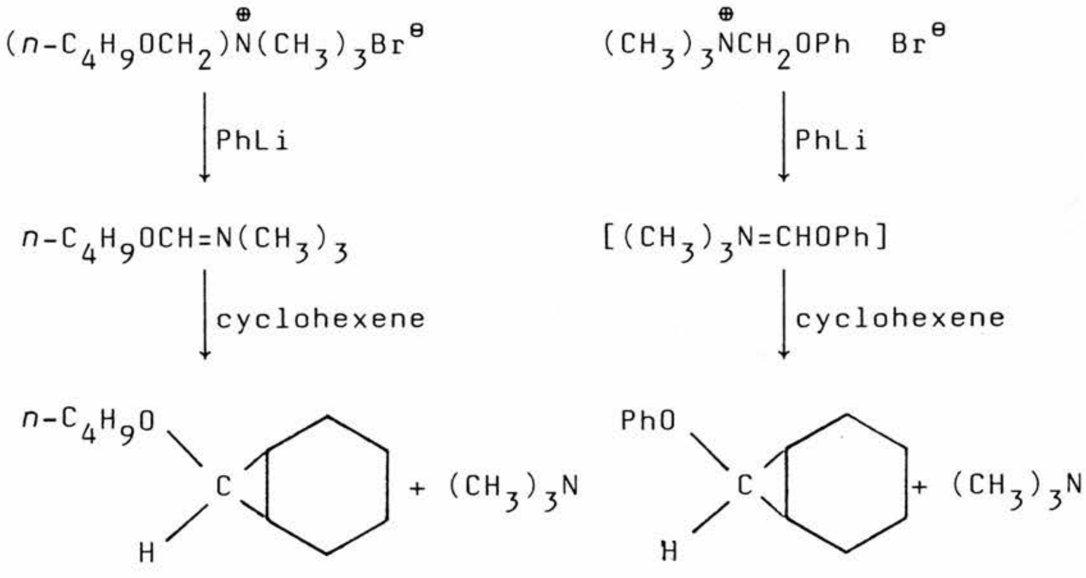
i) *STABILITY*

From experiment it appears that less stable ylides may decompose by a reaction which can be considered the reverse reaction of that shown in Scheme 3 in which ylides are formed by decomposition of diazo-compounds, *i.e.* the ylide decomposes to give a carbene and a neutral molecule (Reaction 9).



Reaction 9

Ammonium ylides are particularly unstable and decompose readily. For example, Wittig and Krauss[33] found that when n-butoxymethyltrimethylammonium bromide and trimethyl-(phenoxymethyl)ammonium bromide were treated with organolithium reagents in the presence of cyclohexene they were able to isolate 7-(n-butoxy)norcarane *(21)* (15%) and 7-phenoxynorcarane *(22)* (48%) respectively (Scheme 4). This was considered to be due to the formation of n-butoxymethylene and phenoxymethylene as intermediates.

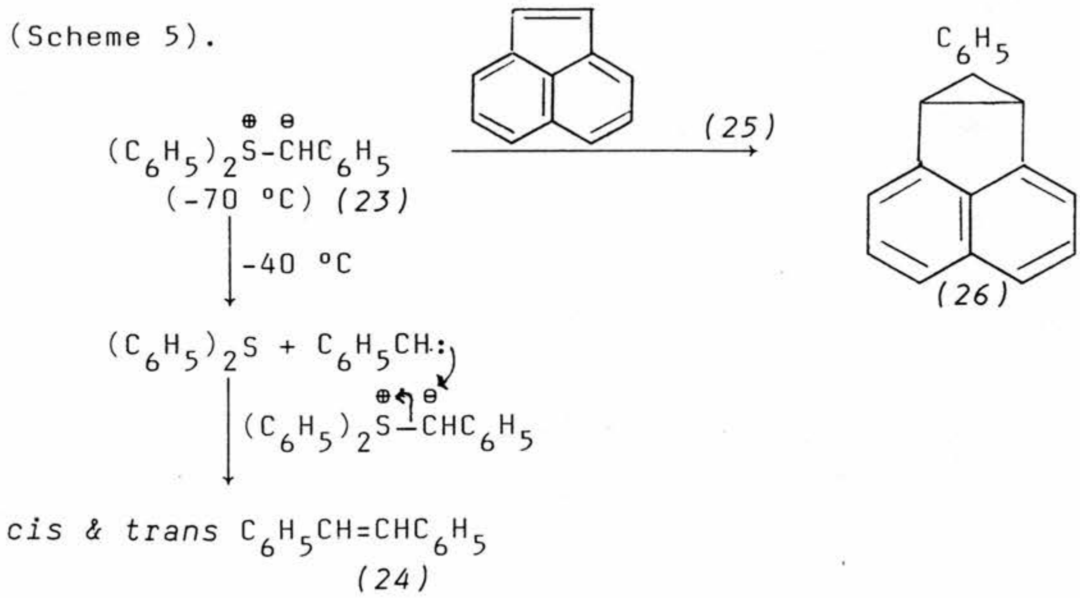


(21) *(22)*

Scheme 4

In general thermal instability has not proved a problem with either phosphonium or arsonium ylides, but it was thought to be a rational explanation for the failure of the "diazo melt" method as a general method of preparation of stibonium ylides.[34]

Ylides of Group VI elements appear to be less stable than those of Group V and it has been suggested that the less stable sulphonium ylides also decompose in this way to carbenoid intermediates and sulphides. Johnson *et al*[35] discovered that benzylidenediphenylsulphurane *(23)* was stable in solution at -70 °C under nitrogen but when the temperature was raised to -40 °C the yellow colour of the ylide disappeared. From this resulting solution they were able to isolate a mixture of *cis*- and *trans*-stilbene *(24)* in 78% yield. Formation of the ylide in the presence of an equivalent of acenaphthylene *(25)* led to the isolation of the cyclopropane adduct *(26)* in 43% yield and with no trace of stilbenes (which suggests that their precursor was trapped) (Scheme 5).

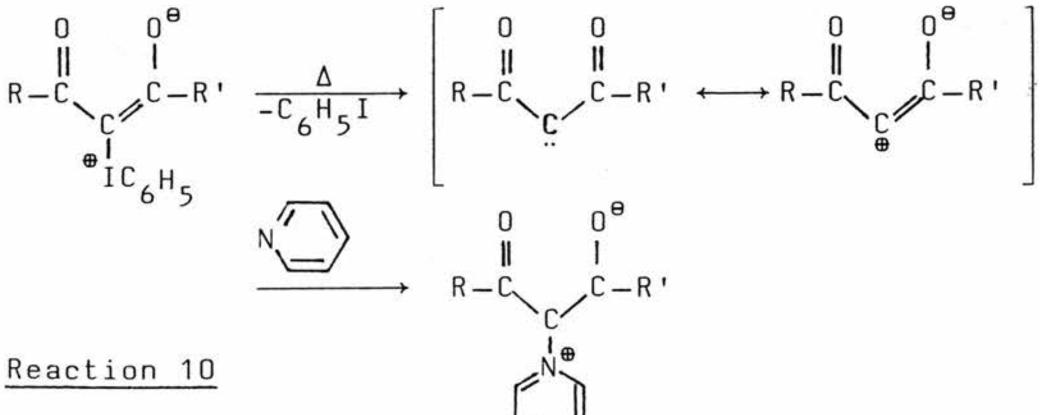


Scheme 5

There is no experimental work on the decomposition pathways of selenonium and telluronium ylides but stability does appear to decrease on going from ylides of selenium to the corresponding ylides of tellurium.

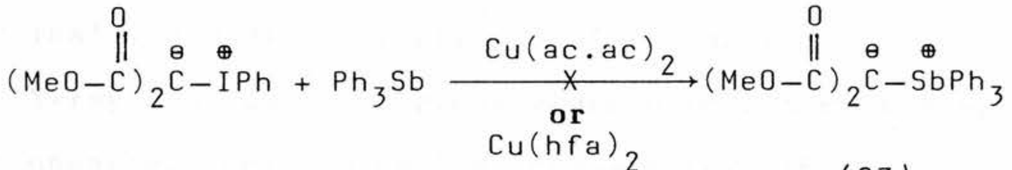
The series of tetraphenylcyclopentadienylides shown in Scheme 3 illustrates well the relative stabilities of Group V and VI ylides. It has been found[36] that the ylides of phosphorus and arsenic are completely stable in air as are those of sulphur and selenium if protected from sunlight which causes some surface decomposition. The pyridinium and stibonium ylides are stable in the solid state but decompose slowly in solution, whereas the ylides of tellurium and bismuth decompose slowly in the solid state and more quickly in solution.

The decomposition of iodonium ylides is also considered to proceed *via* carbene intermediates and this has been utilised as a synthetic route to ylides containing other heteroatoms. For example it has been found[37] that iodonium ylides of β-carbonyl compounds undergo decomposition in the presence of pyridine to give the corresponding pyridinium ylide (Reaction 10).



Reaction 10

It is interesting to note that decomposition of these iodonium ylides is facilitated by the presence of copper salts, particularly bis(acetylacetonato)Cu(II). For example the yield of pyridinium ylide in Reaction 10 (R = R' = OC_2H_5) rose almost twofold from 48% to 80% when bis(acetylacetonato)Cu(II) was present in the reaction mixture.[38] This method has been extended to the preparation of sulphonium, thiouronium[39], selenonium, phosphonium and arsonium[40, 16c] ylides. Attempts to prepare a stibonium ylide *(27)* in this way failed even in the presence of bis(hexafluoroacetylacetonato)Cu(II).



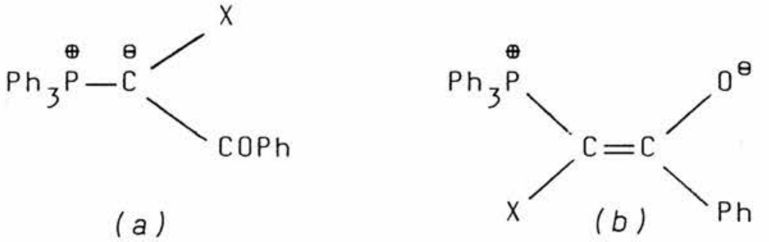
$$(\mathrm{MeO{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_2\overset{\ominus}{\mathrm{C}}{-}\overset{\oplus}{\mathrm{I}}\mathrm{Ph} + \mathrm{Ph_3Sb} \underset{\substack{\mathbf{or}\\ \mathrm{Cu(hfa)_2}}}{\overset{\mathrm{Cu(ac.ac)_2}}{\xrightarrow{\quad\times\quad}}} (\mathrm{MeO{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_2\overset{\ominus}{\mathrm{C}}{-}\overset{\oplus}{\mathrm{Sb}}\mathrm{Ph_3}$$

(27)

ii) *X-RAY STUDIES*

X-ray studies can give valuable information about the nature of bonding in ylides and provide good evidence for the presence of π-bonding. They may also allow one to estimate population densities for the various canonical forms which contribute to the overall structure of the ylide.

X-ray data on ylides of phosphorus, sulphur, selenium, arsenic and antimony have shown that in all cases the ylidic carbon-heteroatom bond length lies somewhere in the region between a double and a single bond. For example, Stephens[41] has reported the results of the structure determination of the phosphonium ylides *(28)*. The ylide P-C bond lengths when X = I or Cl are, respectively, 1.71 Å and 1.74 Å.

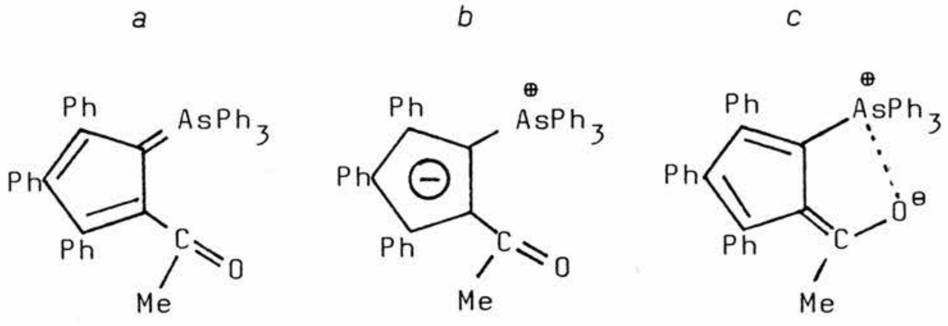


X = I, Cl

(28)

This is intermediate in length between a single P-C bond (1.87 Å) and a double P=C bond (1.67 Å). In all, the results show that structure *(28b)*, in which the oxygen of the carbonyl group is orientated in a *cis* position to the phosphonium group, contributes appreciably to the overall structure of the molecule. Such interaction would be both sterically and electrostatically favourable.

X-ray studies[42] of triphenylarsonium 2-acetyl-3,4,5--triphenylcyclopentadienylide suggest that three major canonical forms contribute to the structure of the molecule, *viz. (29a, b, c)*. With reference to tables of standard



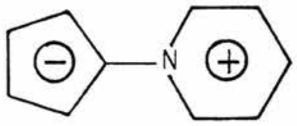
(29)

bond lengths, it was estimated that in order to account for the bond-length distribution in and around the cyclopentadiene ring, structures *(29a, b and c)* would need to contribute respectively 30 - 35%, 20 - 30% and 40 - 45% to the ground state of the molecule.

As mentioned earlier, x-ray study^{14} of the new stibonium ylide *(14)* has shown the ylidic C-Sb bond to have more covalent character than expected and this is explained by interaction between antimony and oxygen similar to that between arsenic and oxygen as just described.

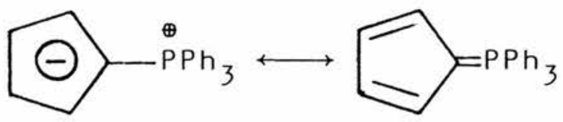
iii) *DIPOLE MOMENTS*

Dipole moment measurements are also useful in assessing the degree of covalency present in ylides. For example the dipole moment of the completely dipolar pyridinium ylide *(30)* is 13.5 D^{43} (in S.I. units, D ≡ 3.3356×10^{-30} C m), which reflects the absence of π-bonding. The dipole moment of the phosphonium ylide *(31)*, however, is 7.0 D^{44} and this is assumed to mean that there is approximately equal contribution to the structure from each of the resonance forms (*a* and *b*).



μ = 13.5 D

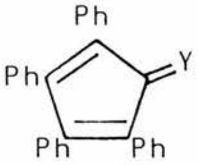
(30)



a *b*

(31)

The dipole moments of the series of tetraphenylcyclopentadienylides *(32a - d)* have been determined.^{45}



(32)

a, Y = PPh_3

b, Y = $AsPh_3$

c, Y = $SbPh_3$

d, Y = SPh_2

e, Y = $SePh_2$

f, Y = $TePh_2$

g, Y = 

h, Y = $BiPh_3$

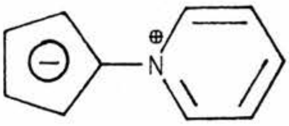
The dipole moments for *(32)* Y = SPh_2, PPh_3, $AsPh_3$ and $SbPh_3$ are 6.69, 7.75, 8.32 and 2.2 D respectively. With the exception of the stibonium ylide which has an anomalously low dipole moment, the dipole moments increase as the ability of the heteroatom to become involved in π-bonding decreases. This is as expected, but as yet there is no good explanation for the remarkably low dipole moment exhibited by the stibonium ylide. The dipole moments of several new stibonium ylides have recently been determined.[46] They are also lower than expected but in these cases intramolecular association of the antimony with neighbouring oxygens can account for this. (See later for more detailed discussion.)

iv) BASICITY

Many ylides form salts on treatment with acids, *i.e.* they are basic. One would expect the trend of increasing dipole moment in a series such as *(32)* to be paralleled by an increase in basicity. The basicity of an ylide is dependent on the amount of negative charge present on the carbanionic carbon. This in turn is determined by the nature of the carbanionic substituents R and R' *(1)* and also by the substituents on the heteroatom. Thus for any given ylide, electron-withdrawing substituents on the ylidic-

-carbon reduce its electron density and hence its basicity. For electron-donating substituents the converse is true. On going from electron-donating to electron-withdrawing substituents on the heteroatom, there is also a decrease in the basicity of the ylide. Electron-withdrawing substituents increase the amount of positive charge on the heteroatom which leads to a greater degree of π-bonding in the ylidic bond and therefore lower basicity.

A study of the acid dissociation constants (pK_a values) of the perchlorate salts of the series of ylides *(32a - c)* has been carried out spectroscopically in 95% ethanol solution.[36] The pK_a values for the phosphonium and arsonium salts were found to be 5.3 and 7.6 respectively. An accurate value for the stibonium perchlorate could not be obtained due to its rapid decomposition in ethanol. However, approximate measurements suggested that it was greater than that of the arsonium perchlorate. Neither diphenylsulphonium- nor diphenylselenonium-tetraphenylcyclopentadienylides formed salts with 70% perchloric acid which shows that they are very weak bases and presumably have pK_a values less than 5.3. Therefore the order of decreasing basicity in the series is Sb > As > P > Se ≈ S as one would expect from dipole moment measurements (Sb is the exception), and consideration of the anticipated charge distribution on the molecule. Since nitrogen cannot participate in π-bonding in ylides, nitrogen ylides are extremely basic. For example the pK_a of the conjugate acid of *(33)* is reported to be 10.0.[47]



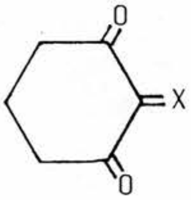
(33)

4. SPECTRA OF YLIDES

i) *INFRARED SPECTROSCOPY*

Information relating to the polarity of ylides can also be obtained from infrared, ultraviolet and nuclear magnetic resonance spectroscopy. In ylides whose carbanionic substituents, R and R', *(1)* contain functional groups which are active in the infrared, the position of absorption of these groups can give a good guide to the degree of dipolar character present in the molecule. In ylides whose substituents, R and R', contain stabilising electron-withdrawing groups, the stretching frequencies associated with these groups are found to be uniformly low due to delocalisation of negative charge into these groups. Table 1 shows the stretching frequencies associated with the carbonyl and sulphonyl groups in two series of ylides. (The usual range for carbonyl absorption is about 1850 - 1650 cm^{-1} and for sulphonyl 1350 - 1310 cm^{-1} and 1160 - 1120 cm^{-1}.)

It may be noted that, in general, the stretching frequencies become steadily lower on going from ylides of phosphorus down Group V to ylides of bismuth. This trend is consistent with the corresponding expected increase in polarity of the ylidic bond on going down the group.

INFRARED			
		$(PhSO_2)_2C=Y$	
X	nujol ν max cm^{-1}	*Y*	nujol ν max cm^{-1}
		PPh_3	1310,1130[48]
$AsPh_3$	1595,1572sh,1540	$AsPh_3$	1292,1122[25]
$SbPh_3$	1595,1570sh,1512	$SbPh_3$	1280, 1112
$BiPh_3$	broad absorption[a] 1500 → 1370	$BiPh_3$	1278, 1118

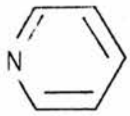
[a] Hexachlorobuta-1,3-diene was used to make a mull since nujol absorbs in this region.

Table 1

ii) *ULTRAVIOLET SPECTROSCOPY*

The trend of increasing dipolar character in a series of ylides is also observable from their ultraviolet spectra. In general, as ylides become more polar, their absorption maxima shift to longer wavelengths. Again some comparative work has been done on the series of tetraphenylcyclopentadienylides[36] *(32a - h)*. The results are shown in Table 2.

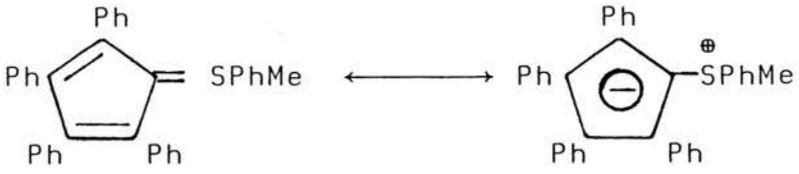
Table 2

Ylide *(32)*	Y	λ_{max} (nm)	Solvent
a	PPh_3	288	EtOH
b	$AsPh_3$	291	EtOH
c	$SbPh_3$	349	$CHCl_3$
d	SPh_2	292(sh328)	PhH
e	$SePh_2$	294(sh347)	EtOH
f	$TePh_2$	335(sh280); [347(sh280)]	MeOH; [PhH]
g		538; [595]	EtOH; [PhH]
h	$BiPh_3$	525; [596]	EtOH; [PhH]

It is interesting that the wavelengths of the absorption maxima of the pyridinium ylide and the bismuthonium ylide are almost identical and are also solvent dependent. These two ylides are dark blue-purple in colour whereas the others are yellow. These factors suggest that the pyridinium and bismuthonium ylides must have electronic structures which are very similar to each other but different from the rest. As mentioned before one major difference in pyridinium ylides is that they cannot exist in a covalent form. These results above suggest that this is also true for the bismuthonium ylide presumably because the 6d-orbitals of the bismuth are too diffuse to overlap effectively with the orbitals of the cyclopentadiene ring. There is a similar colour change on going from the pentaphenyl derivatives of phosphorus, arsenic and antimony to pentaphenylbismuth - the former are either colourless or yellow, whereas the latter is deep violet. With the exception of the diphenyltelluronium ylide which shows a small solvent shift, the position of absorption of the other ylides is independent of solvent.

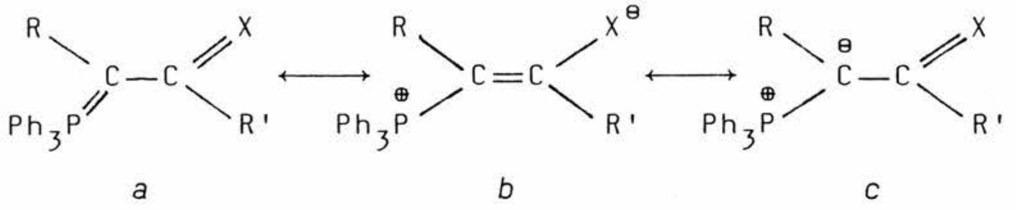
iii) *NMR SPECTROSCOPY*

Both ^{1}H n.m.r. and ^{13}C n.m.r. spectroscopy can be very useful in showing the extent and location of charge in ylides. For example a comparison of the ^{1}H n.m.r. spectrum of methylphenylsulphonium tetraphenylcyclopentadienylide *(34)* with that of methylphenylsulphide shows a shift downfield of 0.43p.p.m. (δ 2.33 to 2.76) for the methyl protons of the ylide.[49] This may be due to the deshielding effect of the positively charged sulphur in the dipolar canonical form.



(34)

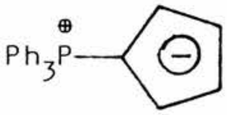
^{13}C n.m.r. spectroscopy, especially, gives valuable information on charge distribution in ylides. In a study of the ^{13}C n.m.r. spectra of some phosphonium ylides, Gray[50] has reported the chemical shifts and ^{13}C - ^{31}P nuclear spin couplings of a series of ylides of the type $Ph_3PC(R)CO_2R'$. Ylides of this type may be expected to have a structure made up of the general resonance forms *(35a - c)*.



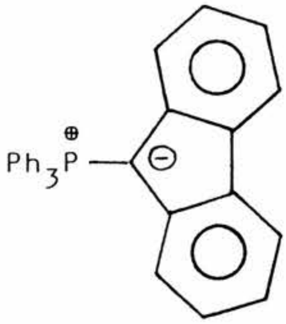
(35)

The data obtained show high shieldings for the ylidic carbon and hence *(35c)* appears to represent the best bonding description of these ylides.

Gray[50] also looked at the ^{13}C spectra of triphenylphosphonium cyclopentadienylide and fluorenylide. From the results obtained, he concluded that the structures of the ylides were best represented by *(36)* and *(37)* *i.e.* the anionic negative charge is localised on the ylidic carbon in the fluorenylide but is delocalised throughout the ring in the cyclopentadienylide.



(36)

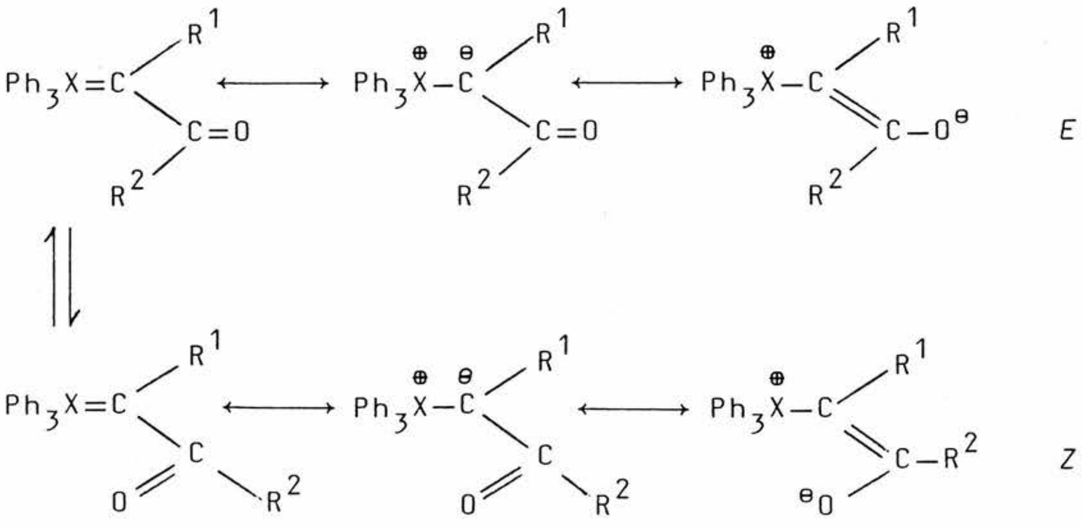


(37)

Until now no data on the ^{13}C spectra of arsonium ylides have been reported. Indeed in attempts to obtain spectra it was found that no signal for the ylidic carbon could be observed[34]. However, with the use of the Brüker WH-360 n.m.r. spectrometer at the University of Edinburgh the ^{13}C spectra of a series of arsonium ylides (together with ^{13}C

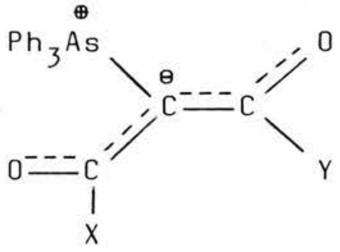
spectra of their analogous stibonium ylides) have been obtained. The spectra all show small signals for the ylidic carbons. The chemical shifts of these carbons show considerable shielding which is relatively greater in the arsonium ylides than in the stibonium ylides. Here again is more evidence for the greater degree of covalency in the stibonium ylides than expected, which complements the X-ray[14] and dipole moment data[46] also obtained.

Variable temperature ^{1}H n.m.r. spectroscopy can also be used to investigate the possible existence of geometric isomers in an ylide. Much study has been done on carbonyl substituted ylides which may exist in either *cis (Z)* or *trans (E)* forms as shown in Scheme 6. Such isomerism arises from delocalisation of negative charge from the ylidic carbon into the carbonyl group which results in partial double bond character in the α-β C-C bond and hence the enolate forms.



Scheme 6

Variable temperature studies on phosphonium[51], arsonium[52] amd sulphonium[53] ylides have shown that such isomerism does exist and have provided values for the energy barriers to interconversion of the isomers. The results showed that the *cis* forms *(Z)* predominated over the *trans* forms *(E)*. Variable temperature studies were also carried out on ylides carrying two electron-withdrawing substituents[25] which could each exist in either a *Z* or *E* conformation. No evidence for the presence of geometric isomers was found and it was therefore concluded that the ylides prefer to exist with both groups in *cisoid* configurations, *e.g.* *(38)*



(38)

This form would be energetically favourable since it allows interaction between the positively charged arsenic and the negative carbonyl oxygen atoms.

iv) MASS SPECTROSCOPY

Mass spectroscopy can give information on the stability of the carbon-heteroatom bond in ylides. Stable ylides often show molecular ion peaks and may break down in a manner similar to the thermal decomposition of ylides discussed earlier. This is indeed true of arsonium ylides which fragment at the ylidic bond and then show breakdown of the arsonium moiety.[25] Almost all of the new stibonium ylides show molecular ion peaks and follow a fragmentation pattern akin to that of arsonium ylides. No molecular ion peaks were found in the spectra of the bismuthonium ylides.

5. REACTIONS OF YLIDES

i) *General*

Reactions of ylides can be divided into two basic types:

(a) those reactions which are typical of carbanions,

and

(b) those reactions in which both the carbanionic and the heteroatom moieties participate.

The ease with which an ylide may be attacked by nucleophiles or electrophiles is related to the polarity of the carbon--heteroatom bond. Like carbanions, some ylides are sensitive to oxygen and moisture and therefore to hydrolysis. An ylide may be hydrolysed simply on exposure to water while others require long heating in the presence of hydroxide. In the series *(32a - f and h)* it was found that the ylides of phosphorus, arsenic, sulphur and selenium were unaffected by treatment for 18 hours in refluxing ethanolic potassium hydroxide.[36] Ylides of antimony, bismuth and tellurium, however, were readily decomposed by alkali. Indeed attempts to recrystallise the stibonium ylide from ethanol led to its complete conversion to triphenylantimony oxide and tetraphenylcyclopentadiene. Likewise the stibonium ylides described in this thesis decompose rapidly when in contact with protic solvents.

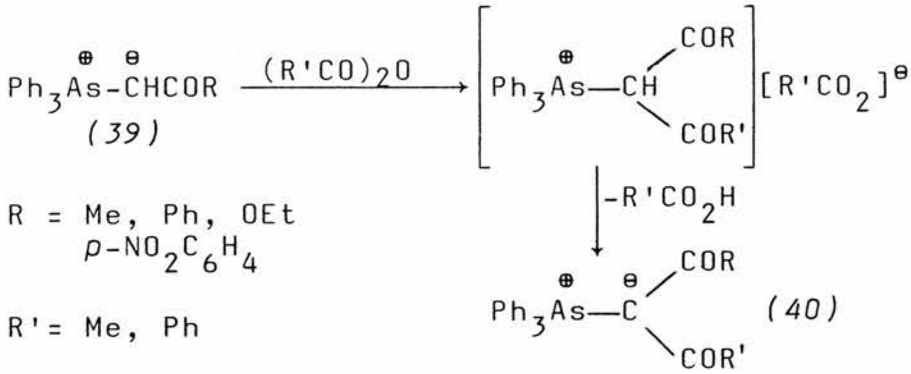
Hydrolysis of phosphonium ylides appears to take place by the formation initially of a heteronium hydroxide which then decomposes to give a phosphine oxide. Reaction 11 shows the first reported example of the hydrolysis of an ylide.[54] The group which is ejected from the hydroxide seems to be

$$Ph_3P{=}CHMe \xrightarrow{H_2O} [Ph_3P{-}CH_2Me]^+OH^- \longrightarrow PhH + Ph_2EtPO$$

<u>Reaction 11</u>

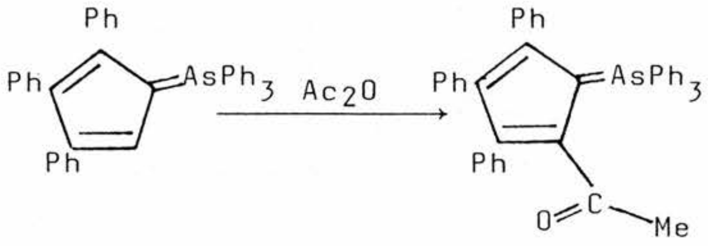
the one which is most capable of forming a stable carbanion. Presumably hydrolysis of other ylides proceeds in a similar fashion.

Providing an ylide is sufficiently dipolar, other electrophiles may attack at the carbanionic centre. For example monoketoylides *(39)* can be acylated with carboxylic anhydrides according to Reaction 12.[25]



<u>Reaction 12</u>

Also treatment of triphenylarsonium acetonylide with phenyl isocyanate gave the ylide[25] *(40)*, R = Me, R' =-NHPh. If the negative charge on the ylidic carbon is delocalised onto other parts of the molecule, reaction may ensue at an atom not directly attached to the heteroatom[55] (Reaction 13).

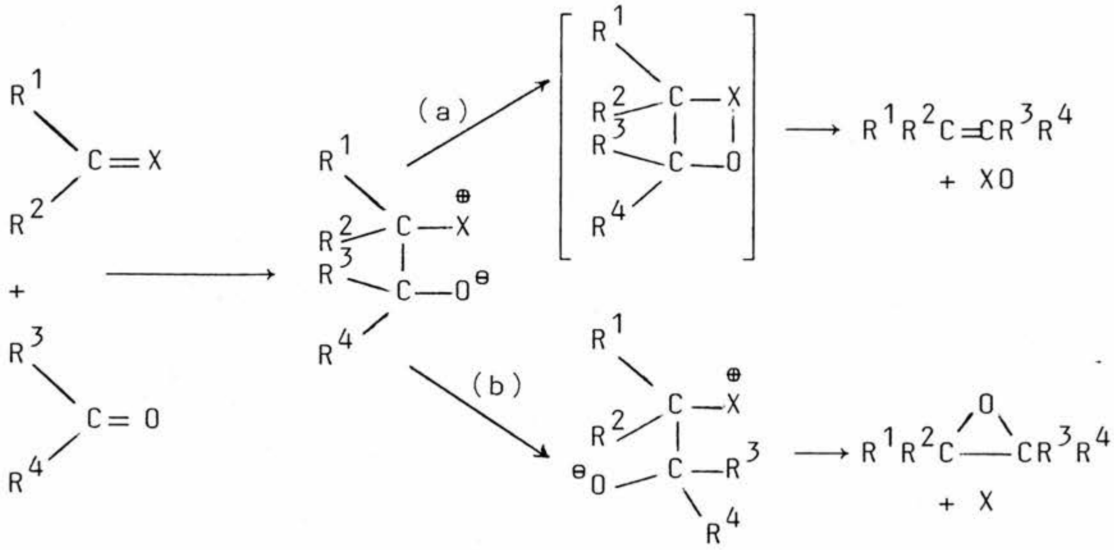


Reaction 13

For this reason one must take care when choosing a condensing reagent for the preparation of ylides by the "oxide" method. If acylation of the ylide is possible then triethylamine and phosphorus pentoxide are more suitable reagents than acetic anhydride.

The second type of reaction in which ylides participate (where both carbanion and heteroatom play a part) is of much greater synthetic importance. This type of reaction, named after the man who in the 1950s developed it, is the Wittig Reaction: it involves a condensation-elimination reaction between an ylide and an aldehyde or ketone. The reaction is thought to proceed *via* the formation of a betaine intermediate which may decompose to give products (Scheme 7).

The ability of an ylide to participate in such a reaction depends largely on the nucleophilicity of the ylidic carbon, *i.e.* on how much negative charge is localised there. In the first place this is determined by the degree of



Scheme 7

dipolar character in the ylide which depends on the nature of the heteroatom. One must then consider the nature of the substituents on the ylide. Electron-withdrawing substituents on the ylidic carbon reduce the nucleophilicity of the ylide by reducing the electron-density on this carbon. In extreme cases, as in the new stibonium ylides, the ylidic conformation is such that the heteroatom is already virtually 5-coordinate (*cf.* the cyclic betaine) due to electrostatic interaction with an oxygen atom of the α substituents. Electron-withdrawing substituents on the heteroatom also reduce the nucleophilicity of the ylide since, by reducing electron density on the heteroatom they increase its ability to participate in π-bonding. Conversely electron--donating substituents on the ylidic carbon or on the heteroatom increase the nucleophilicity of the ylide for exactly the opposite reasons. Finally the nature of the carbonyl compound also affects the reactivity of an ylide towards it in a Wittig reaction (see later). The pathways taken by ylides of various heteroatoms will now be examined.

ii) *PHOSPHONIUM YLIDES IN WITTIG REACTIONS*

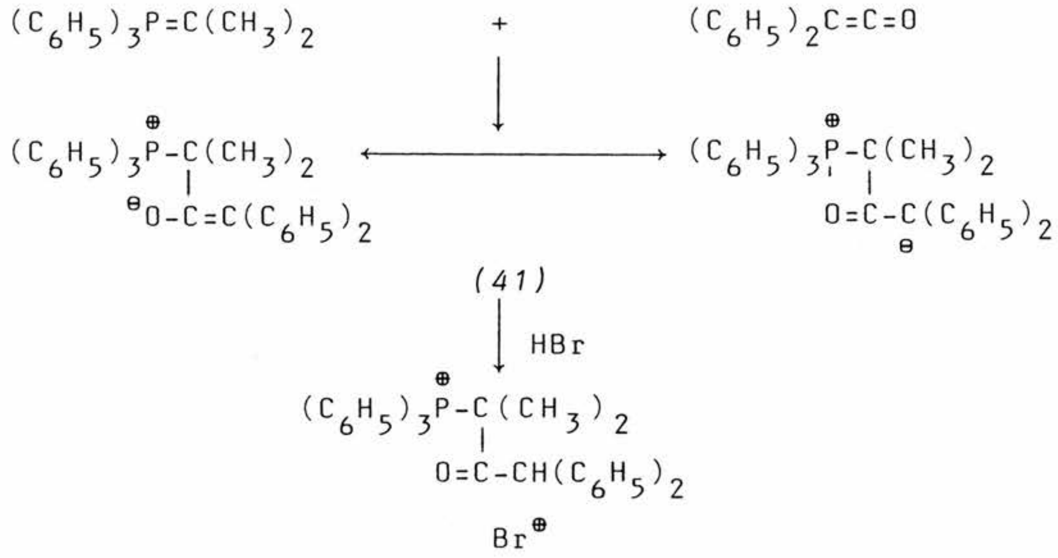
It has been found that phosphonium ylides yield alkenes in Wittig reactions, *i.e.* after betaine formation, path (a) in Scheme 7 is the preferred course. The driving force along this route appears to be formation of the highly stable triphenylphosphine oxide. (The P=O bond of Ph_3PO has a bond dissociation energy of 128 kcal mol^{-1}.[1])

The mechanism shown in Scheme 7 was proposed by Wittig and Geissler[56] to account for the products of the reaction between triphenylphosphonium methylide and benzophenone (Reaction 14).

Reaction 14

This mechanism was consistent with a previous observation by Wittig and Rieber[57] that reaction of trimethylphosphonium methylide with benzophenone led to the isolation of a hydroxyphosphonium salt, after treatment of the reaction mixture with mineral acid (obviously formed by protonation of a betaine intermediate).

To investigate the structure of a betaine intermediate (*viz*. open-chain or cyclic) the dipole moment[58] and ^{31}P n.m.r. spectrum of *(41)* were obtained.



(41)

(42)

Reaction 15

The dipole moment of the betaine was reported as 4.34 D, which the authors suggested to be too low for that expected for a betaine in which there was no interaction between phosphorus and oxygen atoms. From this and ^{31}P n.m.r. chemical shift data, it was concluded that the cyclic form does contribute appreciably to the overall structure of the betaine. Treatment of the betaine with HBr gave the conjugate acid *(42)*.

While investigations into the mechanism of the Wittig reaction were taking place, it was discovered that there was a difference between the mechanistic pathway of stabilised ylides (those which could be isolated and used in a subsequent experiment) and that of non-stabilised ylides (those which could not be isolated). Figure 1 shows the Wittig Reaction Energy Profiles[1] for stabilised *(A)* and non-stabilised *(B)* ylides.

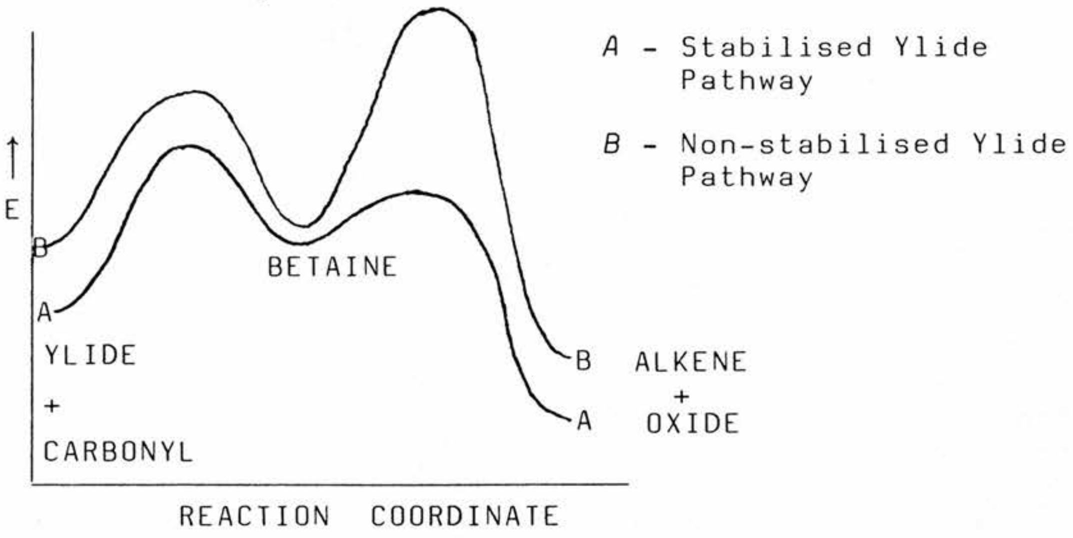
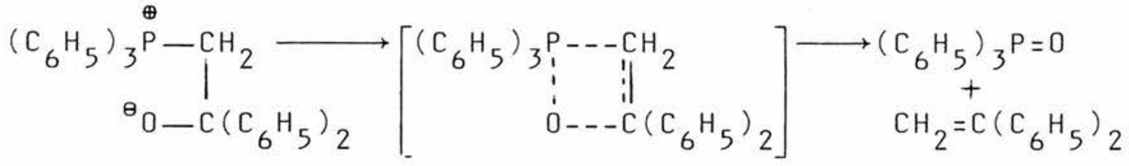


Figure 1

Studies on triphenyl- and tri-n-butylphosphonium ethoxycarbonylmethylides[59] with substituted benzaldehydes suggested that stabilised ylides react with carbonyl compounds in a slow reversible first step (betaine formation) which is followed by rapid decomposition to alkene and phosphine oxide. The reaction was found to be second order overall (first order in each of aldehyde and ylide) and the rate of production of alkene was equal to the rate of consumption of ylide. Added to this, the rate of the reaction was found to increase as the polarity of the solvent used increased - all of which complements the proposed formation of a polar betaine in the rate-determining step.

Studies[60,68] of the reaction of the non-stabilised ylide, triphenylphosphonium methylide, with benzaldehyde led to the isolation of a betaine intermediate (as in the reaction of the same ylide with benzophenone above). When the isolated betaine was heated at low temperatures, it decomposed to benzaldehyde and ylide. When it was heated to a much higher temperature, however, decomposition to alkene and phosphine oxide ensued. This suggests that for non-stabilised ylides the slow rate-determining step is the decomposition of betaine to products.

As mentioned earlier, it is also necessary to consider the role of the carbonyl compound in these reactions. With stabilised ylides, where betaine formation is the slow step, the important feature to consider is nucleophilic attack by the ylidic carbon on the carbonyl carbon. Thus the greater the electrophilicity of the carbonyl carbon the more receptive it is to attack by the ylide. In agreement with this, Johnson and La Count[61] found that aldehydes were more reactive than ketones with triphenylphosphonium fluorenylide, and that the reactivity of para-substituted benzaldehydes decreased in the order: $NO_2 > Cl > H > OCH_3 > N(CH_3)_2$. In reactions with non-stabilised ylides where betaine decomposition is the slow step, ketones are generally more reactive than aldehydes. For example Wittig[62] *et al* reported that triphenylphosphonium methylide reacted faster with benzophenone than with benzaldehyde. This, they suggested, was due to the stabilising effect of the two phenyl rings on the incipient double bond of the transition state between betaine and products (Reaction 16).



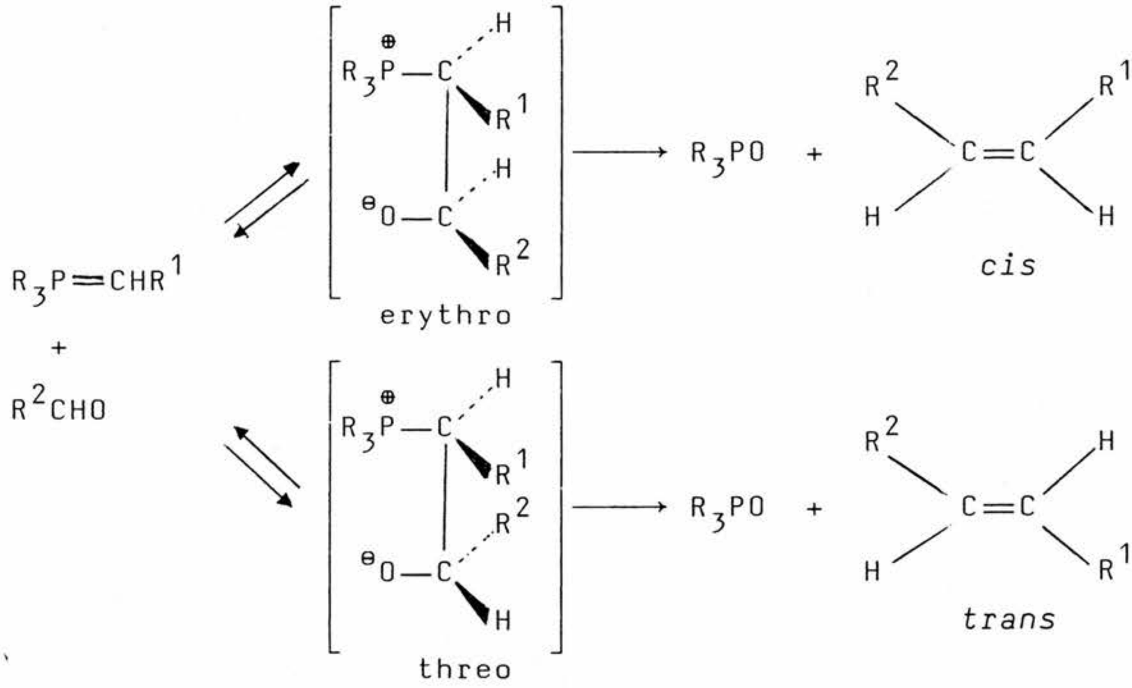
$$(C_6H_5)_3\overset{\oplus}{P}-CH_2 \;/\; {}^{\ominus}O-C(C_6H_5)_2 \longrightarrow \left[(C_6H_5)_3P\cdots CH_2 \;/\; O\cdots C(C_6H_5)_2\right] \longrightarrow (C_6H_5)_3P{=}O + CH_2{=}C(C_6H_5)_2$$

Reaction 16

It has been found that while the nature of the substituents on the phosphorus affects the nucleophilicity of an ylide and hence the formation of betaine from stabilised ylides, with non-stabilised ylides it is the betaine decomposition step which is affected. In the latter case where betaine decomposition is the slow step, the presence of electron-donating substituents on the phosphorus increases the electron density on the phosphorus making subsequent nucleophilic attack by the oxyanion of the betaine to form products more difficult. This allows a build-up of betaine which may then be isolated. With stabilised ylides, the betaine decomposition step is so rapid that the betaine cannot be isolated and so the nature of the substituents on phosphorus has little effect on the decomposition.

To summarise, changes in the structure of stabilised ylides affect the betaine formation step which depends on the nucleophilicity of the ylide and the electrophilicity of the carbonyl group. In contrast, changes in the structure of non-stabilised ylides affect the betaine decomposition step which depends on the ease of transfer of the oxyanion to phosphorus and also on the stability of the alkenic product.

The Wittig reaction of phosphonium ylides with aldehydes or ketones can give rise to *cis* or *trans* alkenes, although not surprisingly the more stable *trans* alkene is usually the dominant isomer. Formation of the *cis* and *trans* alkenes is thought to arise *via* the intermediacy of erythro- and threo-betaines respectively (Scheme 8).



Scheme 8

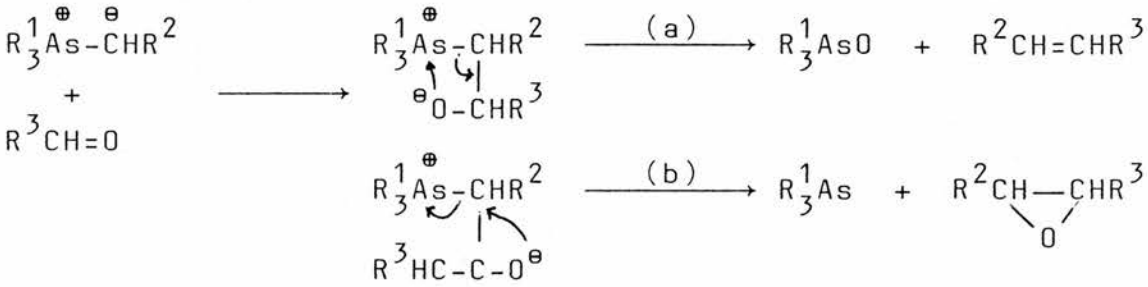
Obviously the threo-betaine is sterically more favourable than the erythro-betaine since the large groups, R^1 and R^2, are not eclipsed and, in addition, can provide stabilisation in the transition state for alkene formation through conjugation with the incipient double-bond. Such conjugation should be more difficult in the transition state of the erythro-betaine since R^1 and R^2 can not become coplanar with the double bond being formed. This, however, is a greatly simplified view of the reaction and many other factors can influence which isomer is dominant. For example, temperature, polarity of solvent and even the presence of excess reagent can all affect the ratio of *cis/trans* isomer obtained.

iii) *SULPHONIUM YLIDES IN WITTIG REACTIONS*

In complete contrast to phosphonium ylides, ylides of sulphur yield exclusively epoxides[63] in Wittig reactions, *i.e.* after betaine formation path (b) (Scheme 7) is the preferred course. The driving force along path (a) is diminished because the S=O bond is much weaker than the P=O bond. Therefore nucleophilic substitution of the heteroatom by the oxygen to give the epoxide takes place preferentially. Added to this, the heteronium sulphide moiety is a good leaving group which also favours this pathway. Selenonium ylides, too, yield only epoxides in Wittig reactions.

iv) *ARSONIUM YLIDES IN WITTIG REACTIONS*

The bond strength of the As=O bond is intermediate in value between the P=O and S=O bond strengths, and the arsonium moiety can also be a good leaving group. Therefore, in Wittig reactions arsonium ylides can yield alkenes or epoxides, or a mixture of both.[64] In general it has been found that stabilised arsonium ylides give alkenes[36,65] in Wittig reactions, whereas non-stabilised ylides give either epoxides[66] or rearrangement products thereof. Scheme 9 shows the reaction pathways of an arsonium ylide with a carbonyl compound.



Scheme 9

In the formation of alkene *via* path (a), electrons are displaced away from the arsenic and so the reaction ought to be favoured by electron-donating substituents on the arsenic and/or an electron-withdrawing group, R^2. In the formation of epoxide *via* path (b), electrons are displaced towards arsenic and this reaction should therefore be favoured by electron-withdrawing substituents on arsenic.

A study of the influence of different heteroatom substituents on the reactions of a series of arsonium ylides, $X_2Y\overset{+}{A}s\text{-}\overset{-}{C}HPh$, with benzaldehyde has been carried out by Gosney *et al*[64(b)]. The ylides were generated *in situ* by the action of *n*-butyllithium on the corresponding hydrobromide, $X_2Y\overset{+}{A}s\text{-}CH_2PhBr^-$. The results are shown in Table 3.

As can be seen, electron-donating substituents on the arsenic lead to almost exclusive alkene formation in (j). At the other extreme, X = Y = C_6H_5 in (a), there is almost

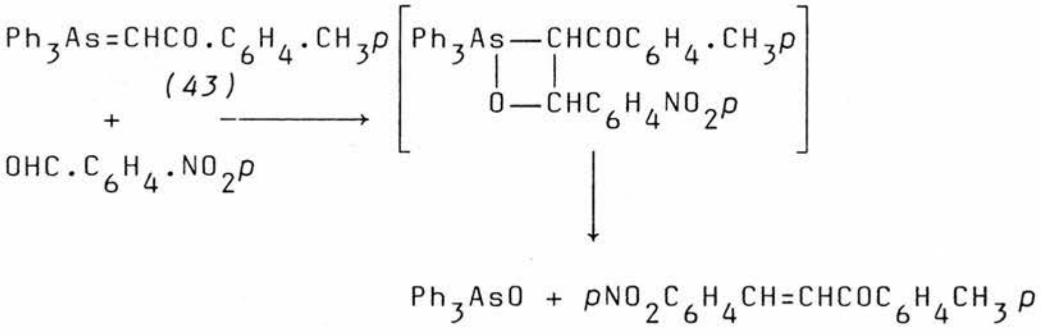
$X_2Y\overset{+}{A}s\text{-}CH_2PhBr^-$			Yields (%)	
	X	Y	*cis+trans* epoxide	*cis+trans* alkene
(a)	C_6H_5	C_6H_5	79	7
(b)	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	66	10
(c)	C_6H_5	*p*-$(CH_3)_2NC_6H_4$	65	11
(d)	*p*-$(CH_3)_2NC_6H_4$	C_6H_5	57	15
(e)	*p*-$(CH_3)_2NC_6H_4$	*p*-$CH_3OC_6H_4$	33	12
(f)	*p*-$(CH_3)_2NC_6H_4$	*p*-$(CH_3)_2NC_6H_4$	24	25
(g)	C_6H_5	C_2H_5	47	27
(h)	C_2H_5	C_6H_5	13	62
(i)	*n*-C_3H_7	C_6H_5	18	70
(j)	C_2H_5	C_2H_5	1	87

Table 3[64(b)]

exclusive epoxide formation. In effect, therefore, as the electron-donating capacity of the substituents, X and Y, increases, the ratio of alkene/epoxide produced increases. Thus it is possible to control the reaction pathway to some extent by the nature of the arsonium substituents.

The effect of the carbanionic substituents on the reactions of a series of stabilised arsonium ylides, $R_3As=CHCOX$, with *p*-nitrobenzaldehyde has also been studied.[67] The results showed that as the basicity of the ylide increased so its reactivity towards the aldehyde increased. This correlates well with results from studies of analogous phosphonium ylides.[68]

Another outcome from this work was that the ylide *(43)* reacted faster in benzene than in more polar solvents such as DMF and DMSO. This is inconsistent with the formation of a betaine intermediate, and the author has instead suggested that a concerted mechanism may occur between ylide and aldehyde with a neutral pentacovalent cyclic transition state, Reaction 17.

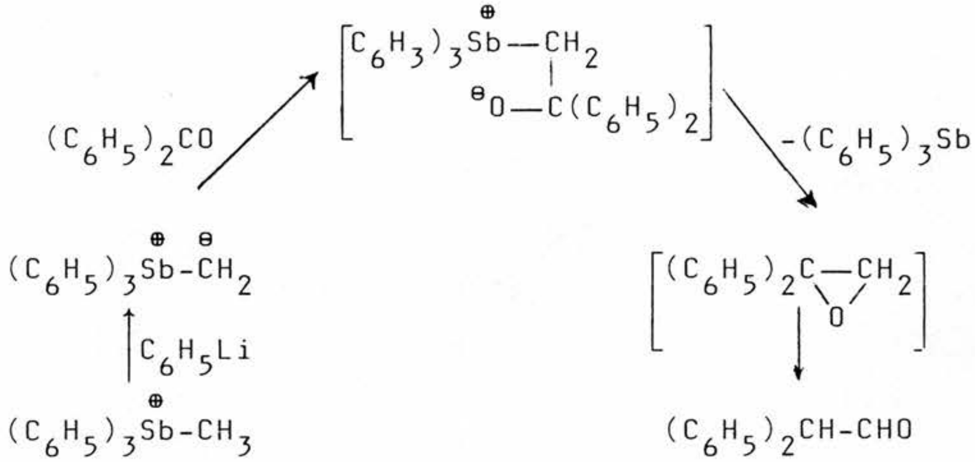


Reaction 17

It should be noted, however, that for epoxide formation to occur in a reaction, a betaine intermediate must be involved.

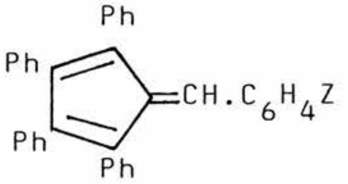
v) *STIBONIUM YLIDES IN WITTIG REACTIONS*

There are only two reported reactions of stibonium ylides with carbonyl compounds. The first of these is the reaction of triphenylstibonium methylide (generated in solution) with benzophenone. The reaction produced triphenyl stibine and diphenylacetaldehyde which the authors[11] suggested was formed by rearrangement of an intermediate epoxide (Scheme 10).



Scheme 10

The second reaction is that of triphenylstibonium tetraphenylcyclopentadienylide *(32c)* with benzaldehyde and *p*-nitrobenzaldehyde.[36] In both cases the fulvene *(44)* was obtained and no epoxide *(45)*. The yield of fulvene more than doubled in the reaction with the more reactive *p*-nitrobenzaldehyde.



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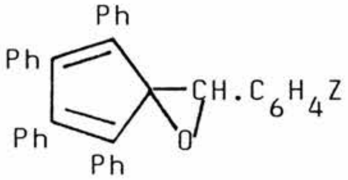
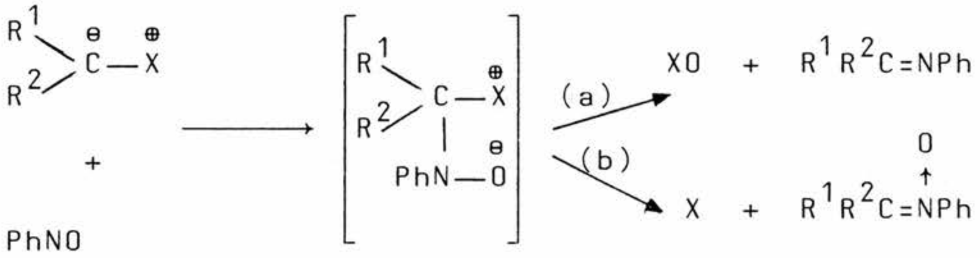


(45)

$Z = H$, or $p\text{-}NO_2$

None of the new stibonium ylides described in this thesis was found to react in Wittig reactions. This is perhaps surprising since reactivity tends to increase going down Group V due to the increasing contribution from the dipolar canonical form. However, charge delocalisation in these new stibonium ylides is probably sufficiently great to cause the electron density on the ylidic carbon to be too low for nucleophilic attack on the aldehyde to occur. The reaction may also be inhibited by intramolecular oxygen-antimony interaction (see later).

In a reaction analogous to the Wittig reaction, ylides may react with nitrosobenzene, presumably *via* a similar mechanism, to give anils or anil oxides (Scheme 11).



Scheme 11

As with aldehydes, phosphonium ylides generally give the anil (path a), sulphonium ylides the anil oxide (path b) and arsonium ylides can give either product. Reaction of triphenylstibonium tetraphenylcyclopentadienylide with nitrosobenzene gave the anil oxide.[36] Again none of the new stibonium ylides were found to react with nitrosobenzene.

PART II

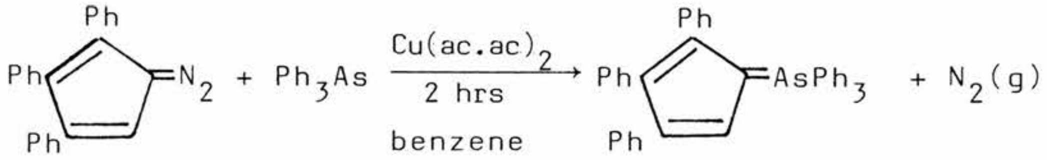
DISCUSSION

PART II

DISCUSSION

1. COPPER II COMPLEXES AS CATALYSTS IN THE PREPARATION OF YLIDES

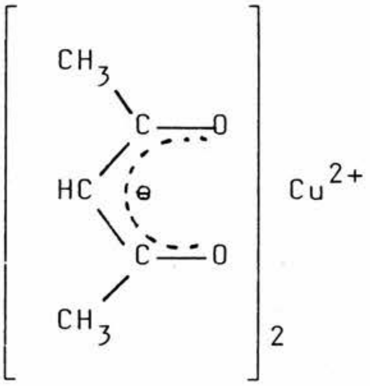
As mentioned earlier, certain Cu(II) complexes (most commonly of β-diketones) have been used as catalysts in the production of ylides by decomposition of diazo-compounds or iodonium ylides in the presence of carbene acceptors. Bis(acetylacetonato)copper(II) [Cu(ac.ac)$_2$] especially has been used most successfully in the preparation of arsonium ylides[32], *e.g.* Reaction 18.



Reaction 18

The use of Cu(ac.ac)$_2$ as a catalyst allowed reactions such as (18), which had previously required melt conditions at temperatures above the decomposition temperature of the diazo-compounds (about 150 °C), to be carried out in homogeneous solution and at much lower temperatures - a distinct advantage if the ylide is at all labile to heat. On going from melt to solution, the yield in Reaction 18 increased from 10% to 85%. Under melt conditions, reaction has been shown to involve the decomposition of the diazo-compound to provide a carbene which is immediately trapped by the Ph_3As. It has been suggested that these copper catalysts work by forming a complex with the diazo-compound and carbene acceptor, holding them in a favourable orientation for reaction between them to occur. There is probably an equilibrium situation between the free reactants and the complex adduct and, if conditions are favourable, reaction proceeds to give products.

Tetra co-ordinate derivatives of copper usually have square-planar configurations and a complex thus formed would have an octahedral configuration in which reacting molecules could occupy adjacent sites - a necessary requirement for reaction to proceed. Evidence supporting this mechanism comes from experiments in which Reaction 18 was repeated using a series of different copper catalysts.[32] Compounds *(46)* and *(47)* were found to be effective as catalysts, but compounds *(48)*, *(49)* and *(50)*, in which the ligands occupy coplanar sites around the copper, were not - presumably because incoming molecules would be forced to complex at opposite sides of the copper, too far apart to react with one another. In these cases diazo-compound was recovered unchanged. The fact that these reactions proceed at lower temperatures when $Cu(ac.ac)_2$ is present in the reaction mixture, complements the proposed mechanism of complex formation between $Cu(ac.ac)_2$ and diazo-compound. Diazo-compound is recovered unchanged in those reactions where no ylide is produced which further suggests that both



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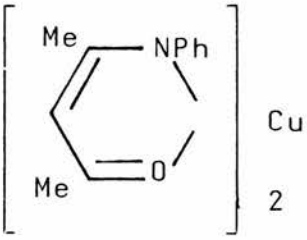

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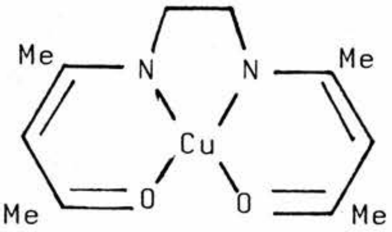

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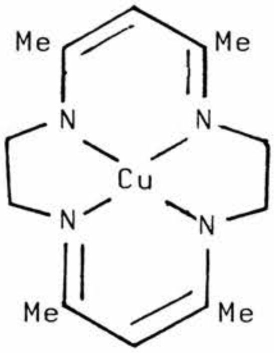

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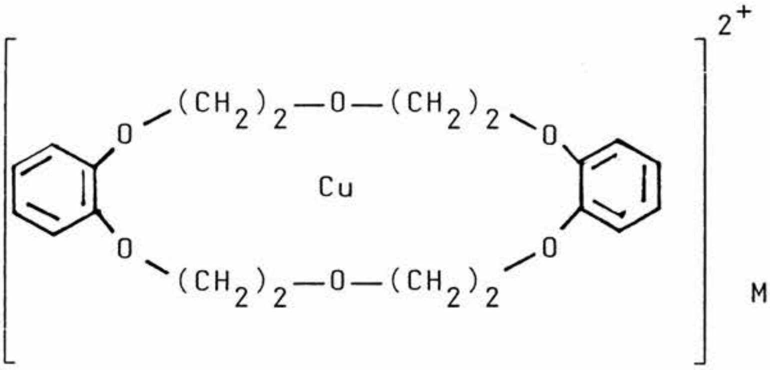

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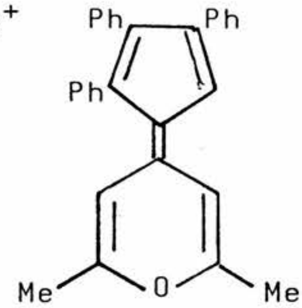
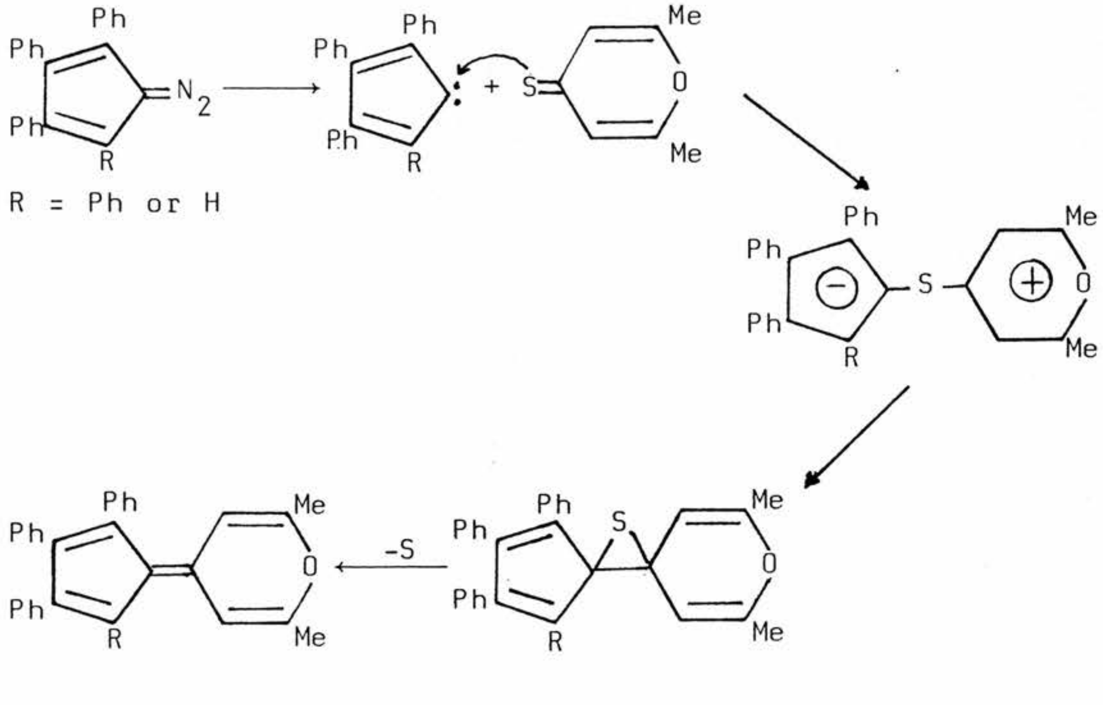


(51)

diazo-compound and Ph_3As are involved in complex formation with the copper. Co, Ni, Pt, Zn and vanadyl acetylacetone complexes have also been tried as catalysts[32] but in no case was ylide formed. The mechanism of reaction is clearly not so simple, since other factors influence its action. For example, there appears to be a minimum quantity of catalyst required for each reaction and also a minimum reaction temperature.

Some work by the author involved the synthesis of the cyclopentadienylidenepyran *(51)* from diazo-2,3,4-triphenylcyclopentadiene and 2,6-dimethyl-4H-pyran-4-thione.[69] Thermogravimetric studies[28] of this reaction suggest that a cyclopentadienylidene carbene intermediate is involved (see Reaction 19).



Reaction 19

Since Reaction 19 appears, in effect, very similar to Reaction 18, it was thought worthwhile to find out if $Cu(ac.ac)_2$ would catalyse this reaction also. Normal reaction conditions of refluxing mesitylene gave only a 10.5% yield of *(51)*. However, no increase in yield occurred when $Cu(ac.ac)_2$ was present although a lower boiling solvent (toluene) could now be used. The reason for this may be attributed to the poor nucleophilicity of sulphur in the pyranthione. To improve the interaction between copper and sulphur it seemed necessary to make the copper more electron deficient. This was achieved by preparing bis(hexafluoroacetylacetonato)Cu II $[Cu(hfa)_2]$[70] with six strongly electron attracting fluorines. When $Cu(hfa)_2$ was used as a catalyst, a 34.5% yield (after recrystallisation) of *(51)* was obtained and the reaction could now be carried out in refluxing benzene. This result complements further the proposed reaction mechanism.

Following the success of $Cu(hfa)_2$ as a catalyst in Reaction 19, it was decided to investigate its possible use in the production of ylides (ultimately those of Sb and Bi) from diazo-compounds. In order to find the optimum conditions for its use, Reaction 18 was repeated in a variety of solvents and at several temperatures using $Cu(hfa)_2$ as catalyst. In each case the molar ratio of diazo-compound to triphenylarsine to catalyst was 1 : 2 : 0.04. The results can be seen in Table 4.

The most successful solvent used in the reaction was

Solvent	Reaction Temp.(°C)	Reaction Time (hrs)	Yield (%)	m.p. Ylide* (°C)
MeOH	64	2	0	
MeOH	64	7.5	0	
EtOH	78.5	2	5	200 - 206
THF	64	2	23.5	204 - 208
Benzene	80	2	77.5	198 - 202
Benzene	50	16	45	209 - 212
Benzene	50	48	68	210 - 214
Benzene	r.t.	312	31	208 - 212

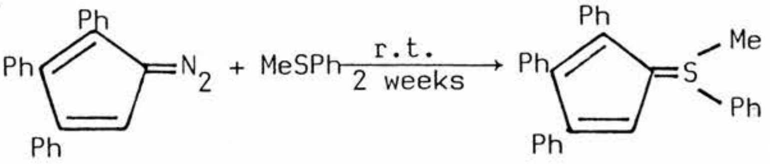
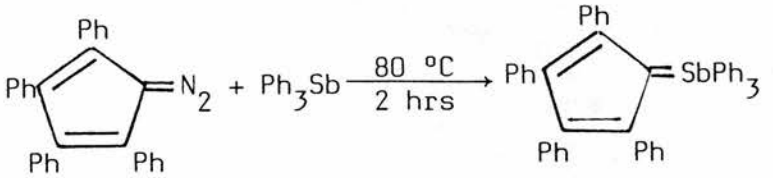
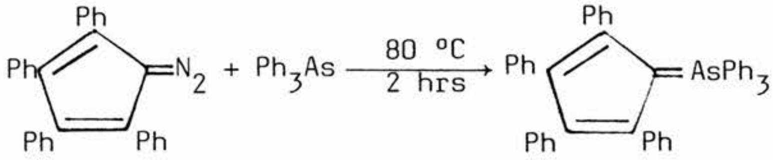
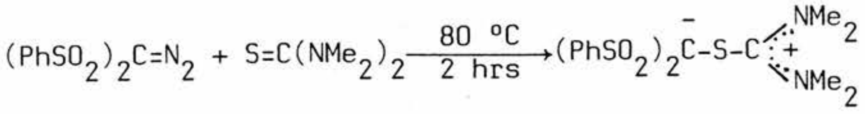
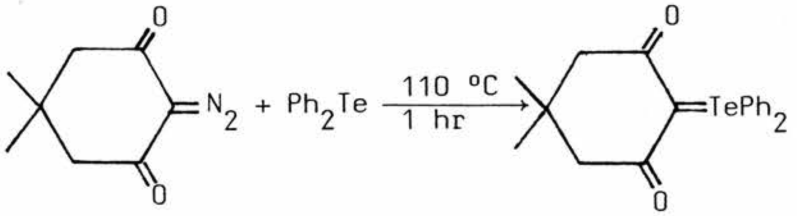
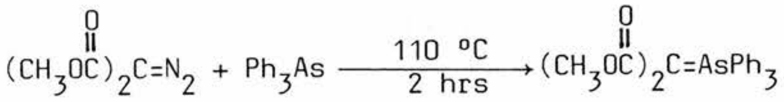
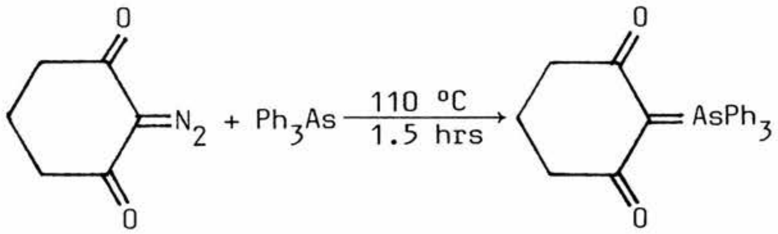
*In each case ylide was recrystallised from benzene/light petrol (40 - 60°) (lit.[31] 198 - 200 °C)

Table 4

benzene since even at room temperature (albeit for two weeks) a 31% yield of ylide was obtained. This is probably due to the greater solubility of the reactants in benzene (solubility increased on going from methanol to ethanol to THF to benzene) and also, in the case of the alcohols, competition for catalyst sites may occur from lone pairs of electrons on the oxygens. Thus the catalyst would become flooded with solvent and little reaction could take place.

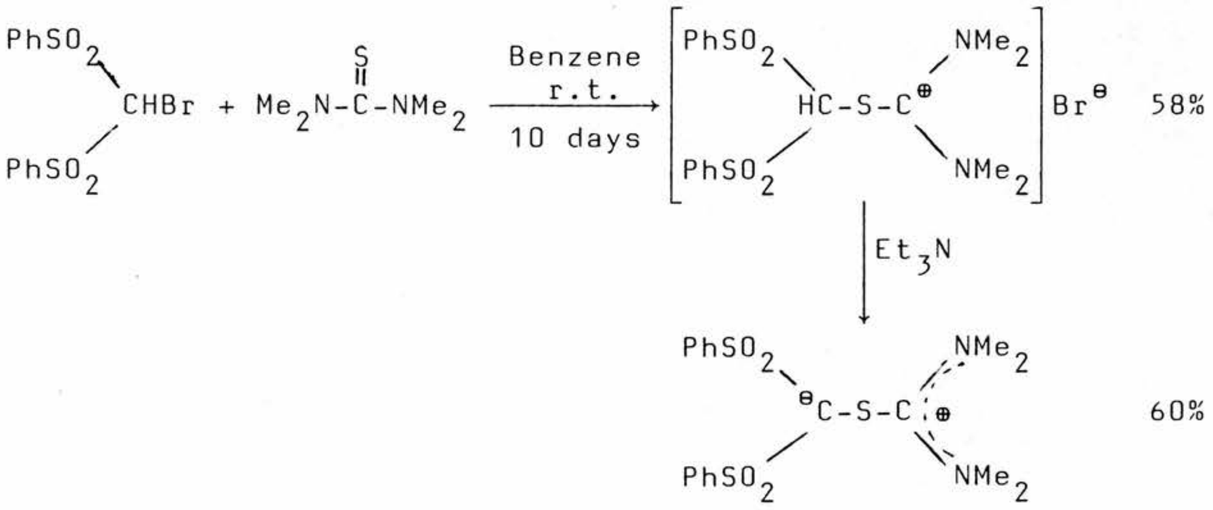
It soon became apparent that $Cu(hfa)_2$ was an excellent catalyst for the production of a wide variety of ylides and that it could indeed provide us with a new synthetic route to ylides of Sb and Bi (see later). Table 5 contains some

Table 5

Reaction		Yield %
(i)		31
(ii)		32
(iii)		66
(iv)	 $(PhSO_2)_2C=N_2 + S=C(NMe_2)_2 \xrightarrow[2\ hrs]{80\ ^{\circ}C} (PhSO_2)_2\overset{-}{C}\text{-}S\text{-}C^{+}(NMe_2)_2$	65
(v)		23
(vi)	 $(CH_3O\overset{\overset{O}{\parallel}}{C})_2C=N_2 + Ph_3As \xrightarrow[2\ hrs]{110\ ^{\circ}C} (CH_3O\overset{\overset{O}{\parallel}}{C})_2C=AsPh_3$	62
(vii)	$(p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2)_2C=N_2 + Ph_3As \xrightarrow[5.5\ hrs]{80\ ^{\circ}C} (p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2)_2C=AsPh_3$	69
(viii)		20
(ix)	$(PhSO_2)_2C=N_2 + Ph_3Sb \xrightarrow[2\ hrs]{80\ ^{\circ}C} (PhSO_2)_2C=SbPh_3$	78

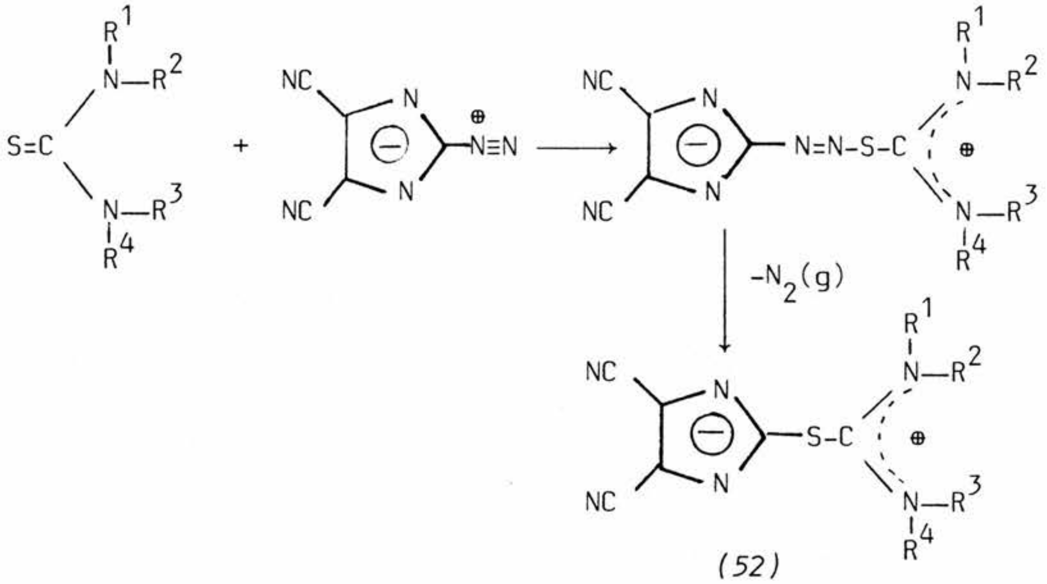
reactions it was found to catalyse.

The thiouronium ylide in (iv) had previously been made by treatment of N,N,N',N'-tetramethyl-S-bis(phenylsulphonyl)methylthiouronium bromide with triethylamine[71] in an overall yield of about 35% (see Scheme 12).



Scheme 12

The use of $Cu(hfa)_2$ provides us with a much more efficient route to this ylide. The only other examples of thiouronium ylides from diazo-compounds have been made by Gronski and Hartke[39,72]. Ylides of the type *(52)* (see Reaction 20) can be prepared by simply mixing the reactants at temperatures ranging from room temperature to that of refluxing acetonitrile (81.6 °C). Yields are at best about 57% and reaction times may be long.



(52)

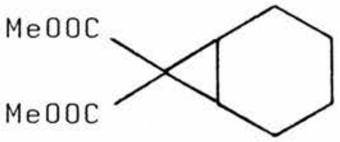
Reaction 20

The tellurium ylide (v) is the only example known which has been prepared by the copper catalysed decomposition of a diazo-compound in solution.

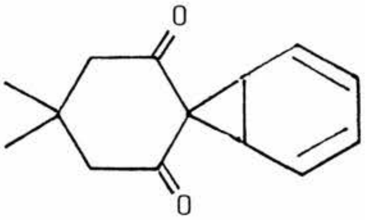
To compare the action of $Cu(hfa)_2$ with $Cu(ac.ac)_2$, Reaction (ix) was repeated using $Cu(ac.ac)_2$ as catalyst. In this case a yield of only 47% of ylide was obtained under identical reaction conditions, although this increased to 73% if heating was continued for 5 hours.

When dimethyl diazomalonate was heated with $Cu(hfa)_2$ in refluxing toluene containing cyclohexene, a low (8%) yield of the bicyclic ester *(53)* was obtained. When cyclohexene was used as solvent, the yield of *(53)* rose to 26.5%. None of *(53)* was formed in the absence of $Cu(hfa)_2$ which means that $Cu(hfa)_2$ must also play a role in these reactions. The low yields of *(53)* obtained are probably an indication of the poorer co-ordination of cyclohexene with copper.

When a solution of diazodimedone in benzene containing $Cu(hfa)_2$ was heated, a small amount of an adduct, $m/e = 210$, was obtained along with unreacted diazodimedone. This was assumed to be compound *(54)*. In all of these reactions no evidence was found for the existence of dimer formed by two carbenes reacting together.



(53)



(54)

Since this work with $Cu(hfa)_2$ began, an interesting paper[73] has appeared concerning the effects of electron--withdrawing groups on the Lewis Acidity of Cu II complexes. Thermodynamic data are reported for the formation in benzene solution of addition compounds of certain Cu II keto-enolate complexes with some heterocyclic bases. It was found that the introduction of electron-withdrawing substituents such as carbethoxy or fluorine into the copper complexes resulted in much increased stabilities of the adduct, largely due to entropy factors. It can be seen from Table 6 that relative to the simplest member of the series, $Cu(ac.ac)_2$, replacement of H by methyl makes the enthalpy of adduct formation less negative without much change in the adduct stability (due to compensating changes in $\Delta S°$). Replacement of methyl by fluorine also leads to more negative enthalpy values for

Table 6[73]

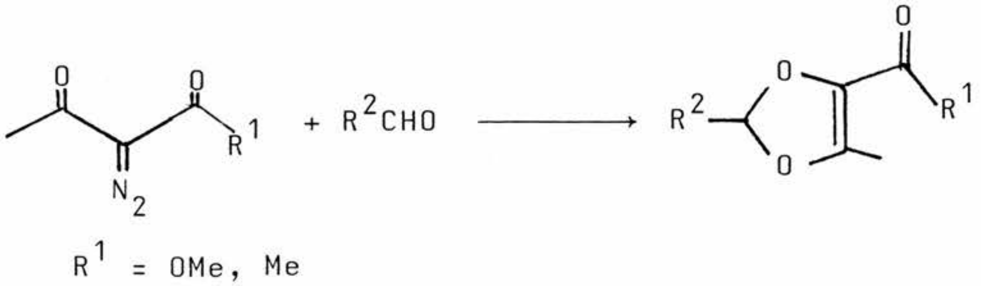
Thermodynamic Data for Formation of 1:1 Adducts of 4-Methylpyridine with Cu(RCOCHCOR')$_2$ in Benzene Solution at 30 °C ($\Delta H°$, $\Delta G°$ in kJ mol^{-1}, ΔS in JK^{-1} mol^{-1})

R	R'	K	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$
CH_3	CH_3	5.4 ± 0.3	30.4 ± 0.8	4.25 ± 0.15	86 ± 3
CMe_3	CH_3	5.9 ± 0.1	23.0 ± 1.0	4 47 ± 0.04	61 ± 5
CMe_3	CMe_3	5.7 ± 0.7	19.0 ± 0.5	4.38 ± 0.33	48 ± 3
CMe_3	CHF_2	260 ± 4	25.4 ± 0.8	14.01 ± 0.04	38 ± 3
CMe_3	CF_3	1994 ± 220	26.8 ± 1.1	19.14 ± 0.30	25 ± 5
CMe_3	C_2F_5	2672 ± 347	30.3 ± 0.8	19.88 ± 0.35	34 ± 4
CMe_3	C_3F_7	3234 ± 278	31.6 ± 0.8	20.36 ± 0.25	37 ± 4

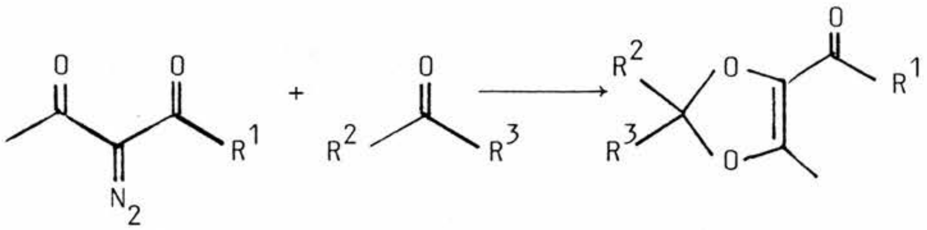
adduct formation but, because ΔS° remains virtually unchanged, values for the stabilities of the adduct are greatly increased. The enthalpy changes are presumably due to changes in the inductive properties of the ligands. The fact that ΔS° values are similar for $-C(CH_3)_3$ and $-CF_3$ substituted compounds is probably due to the methyl group being isoelectronic with fluorine and of comparable size. Hydrogen is much smaller than either, and so, when formation of the adduct occurs, solvent displacement will be similar for methyl and fluoro substituted compounds but much less for the hydrogen substituted compounds.

It is perhaps reasonable to assume that if we were to proceed to $Cu(hfa)_2$, a still greater increase in adduct stability would occur. It is therefore easy to see why $Cu(hfa)_2$ is so superior as a catalyst over $Cu(ac.ac)_2$.

Another quite recent paper[74] reports the use of $Cu(ac.ac)_2$, $Cu(hfa)_2$ and related Cu II β-ketoenolate complexes as catalysts in the preparation of polysubstituted dioxoles. These complexes were found to catalyse the cycloaddition of diazocarbonyl compounds to aldehydes and ketones (see Reactions 21 and 22).



Reaction 21



R^1 = OMe, Me

Reaction 22

This novel cycloaddition provides us with another example of the value of these Cu II complexes in syntheses involving decomposition of diazo-compounds.

2. COPPER-BRONZE AS A CATALYST IN THE PREPARATION OF YLIDES

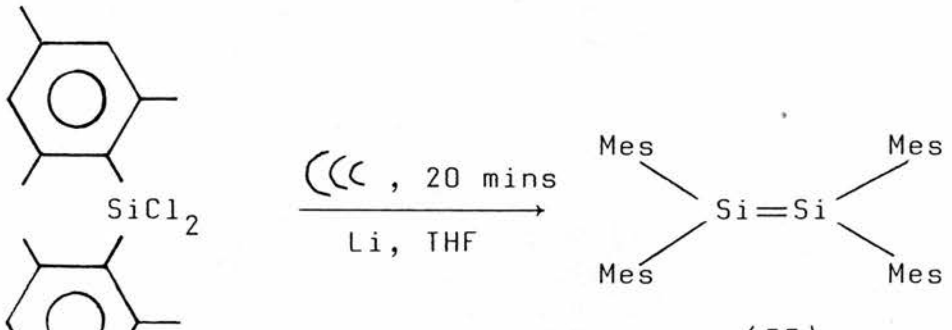
As mentioned in the introduction, copper-bronze has also been used as a catalyst in the preparation of ylides from diazo-compounds[31]. A paper[75] on the use of ultrasonic waves as a means of enhancing the rate of certain heterogeneous reactions led to some additional work on the use of copper-bronze as a catalyst. Boudjouk *et al*[75] reported that the Wurtz-type coupling of organic halides, RX (R = alkyl, aryl, benzyl and benzoyl; X = Cl, Br and I), and organometallic chlorides, R_3MCl (R = alkyl, aryl; M = Si, Sn) using lithium wire at room temperature, proceeded at a convenient rate only in the presence of sonic waves. Also sonically accelerated couplings of silicon and tin halides were discussed. For example, the reaction of lithium with some simple dichlorosilanes gives high yields of cyclopolysilanes (Reaction 23).

$$R_2SiCl_2 \xrightarrow[Li]{(((} (R_2Si)_n \qquad 70 - 95\%$$

$R = Me, n = 6$
$R = Ph, n = 4$

Reaction 23

Compound *(55)*, containing a Si-Si double bond, can also be prepared rapidly with the aid of sonic waves (Reaction 24). The Si-Si double bond is stabilised by the four mesityl groups.



(55)

Dimesityldichlorosilane

Tetramesityldisilene
(~ 90% crude)

Reaction 24

It was thought possible that this rate enhancement may be due to the ultrasonic waves simply cleaning the surface of the lithium wire. It was decided to find out whether ultrasonic waves had any effect on reactions catalysed by copper-bronze. Reaction 18 was therefore repeated in duplicate with copper-bronze replacing $Cu(ac.ac)_2$ as a catalyst. One reaction flask was heated in an ultrasonic water bath, the other by conventional means. In both cases no reaction took place and starting material was recovered. Since copper-bronze contains about 2% grease and copper oxide it was thought that it may be necessary to activate it before use. This was done by treatment with iodine in acetone and then concentrated hydrochloric acid[76], and the reactions repeated. This time a 58% yield of ylide was obtained under standard conditions and a 40% yield of ylide from the reaction with the ultrasonic heating device - the reverse result of that expected. To verify the results the reactions were repeated but again no ylide was obtained although freshly prepared copper-bronze had been used. It was thought that perhaps the ultrasonic waves were causing some decomposition of the ylide, and so a sample of triphenylarsonium 2,3,4-triphenylcyclopentadienylide was heated in refluxing benzene in the ultrasonic bath for two hours. Quantitative recovery of the ylide with no depression of melting-point showed that no decomposition had taken place.

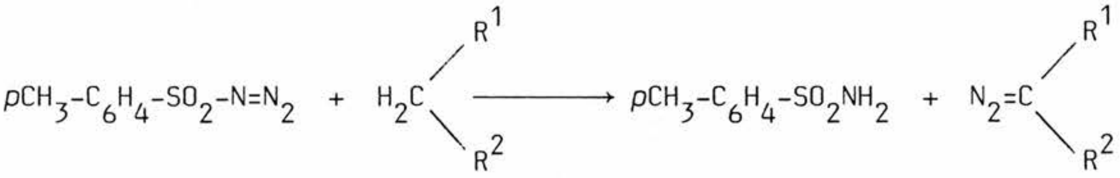
No real benefit was thus gained by using ultrasonic waves, and the inconsistent results obtained in reactions involving copper-bronze demonstrate the superiority of soluble copper catalysts over their heterogeneous counterparts.

3. PREPARATION OF SOME STIBONIUM YLIDES

Since the preliminary investigations into the potential of $Cu(hfa)_2$ as a catalyst in the preparation of ylides led to the isolation of the stibonium ylide *(14)* in good yield, it seemed imperative then to investigate its action with other diazo-compounds. A number of diazo-compounds were therefore prepared containing stabilising electron-accepting groups such as sulphonyl, keto and ester functions. These compounds were all prepared using standard literature procedures.

i) *PREPARATION OF DIAZO-COMPOUNDS*

A wide range of diazo-compounds can be made by the direct reaction of compounds containing active methylene groups with *p*-tosylazide and a suitable base.[77] The reaction involves replacement of the two hydrogen atoms of the active methylene group by the diazo group of the *p*-tosylazide to give a diazo-compound and *p*-toluenesulphonamide (Reaction 25).

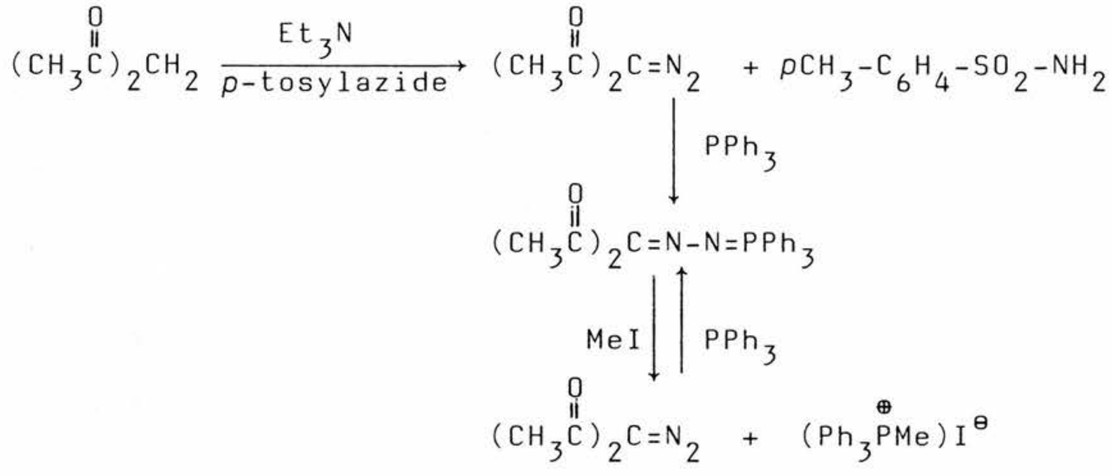


$$p\mathrm{CH_3{-}C_6H_4{-}SO_2{-}N{=}N_2} + \mathrm{H_2C}(\mathrm{R^1})(\mathrm{R^2}) \longrightarrow p\mathrm{CH_3{-}C_6H_4{-}SO_2NH_2} + \mathrm{N_2{=}C}(\mathrm{R^1})(\mathrm{R^2})$$

Reaction 25

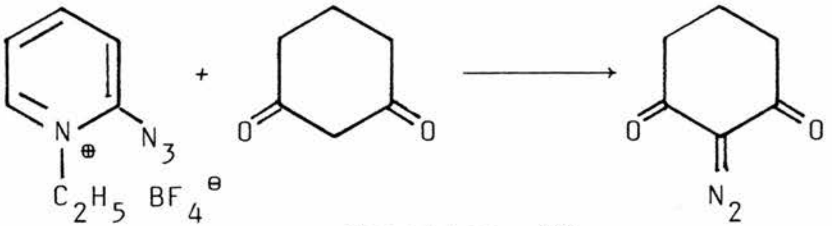
The *p*-toluenesulphonamide formed is extracted as a salt by treatment of the methylene chloride phase with aqueous KOH. The desired diazo-compound remains in the methylene chloride fraction, and is obtained by evaporation of solvent. Diazo derivatives of cyclopentadienes, cyclohexadienes, 1,3-dicarbonyl-, 1,3-disulphonyl- and 1,3-ketosulphonyl- compounds, ketones, carbonic acid esters and β-iminoketones can all be prepared in this way and, indeed, this was the method employed for the preparation of the diazo-compounds *(58)* - *(68)*.

In the preparation of diacetyldiazomethane *(57)*, this method presents a problem since the diazo-compound is soluble in water. In this case a phosphinazine[78] is prepared which on treatment with methyliodide gives methyltriphenyliodide (solid) and diacetyldiazomethane (Scheme 13).



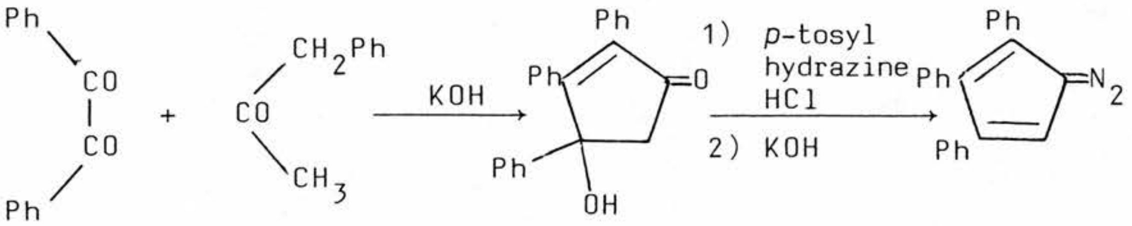
Scheme 13[78]

In the preparation of 2-diazocyclohexane-1,3-dione *(69)*, the above method using *p*-tosylazide and base was not reliable, often giving poor yields. Another method using an azidinium salt was therefore used (Reaction 26). This method was reported to have been successful in the preparation of 2-diazo-5,5-dimethylcyclohexane-1,3-dione[79], and was indeed found to be more reliable in this particular case.



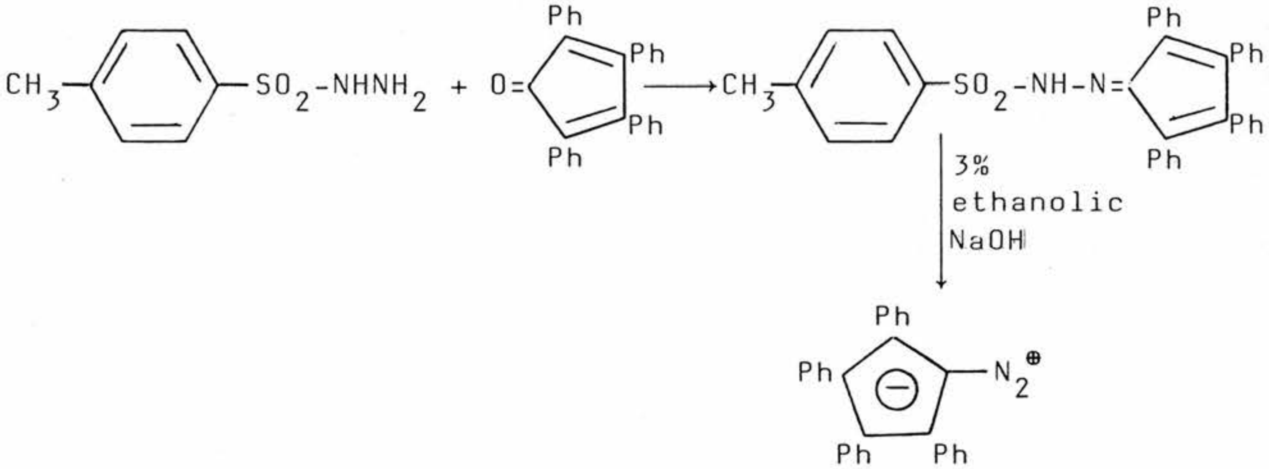
Reaction 26

2,3,4-Triphenyldiazocyclopentadiene *(56)*, was prepared according to Reaction 27[80].



Reaction 27

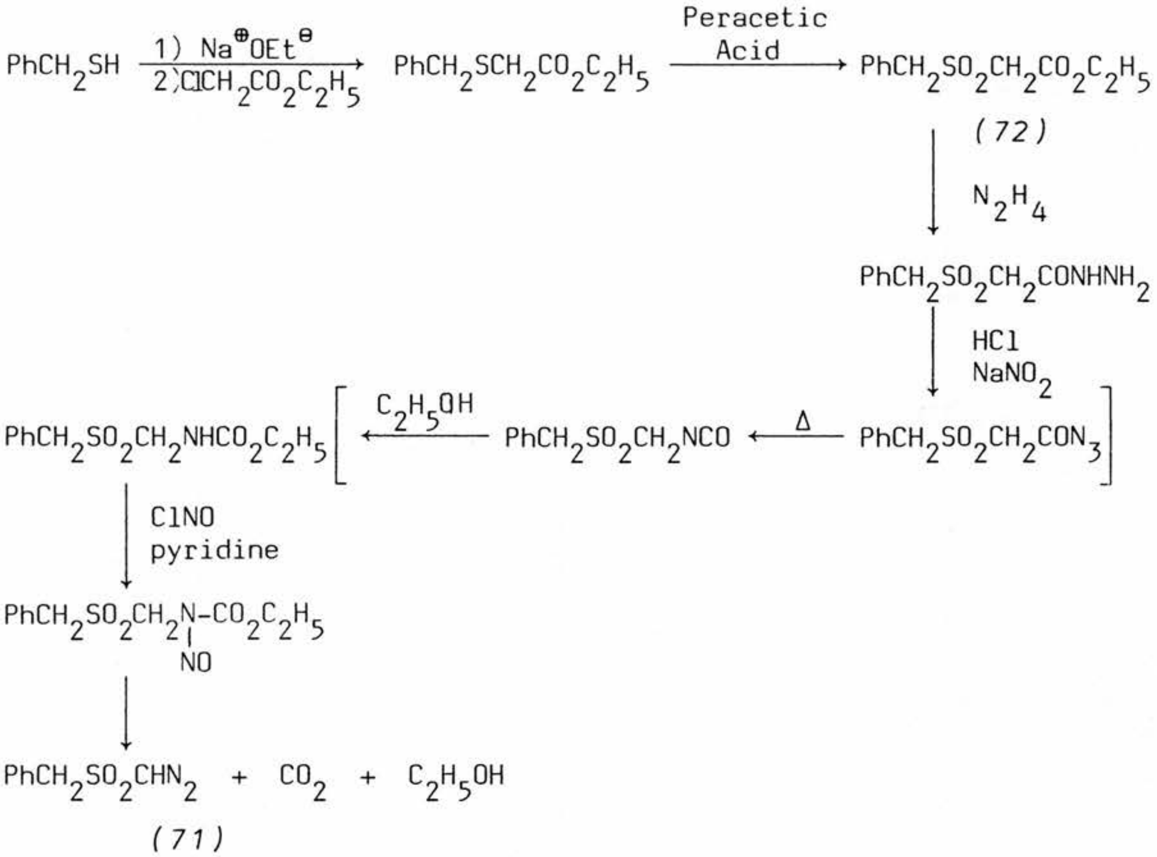
Attempts to prepare tetraphenyldiazocyclopentadiene by the literature method[81] (Reaction 28) proved unsuccessful and the starting material, tetracyclone, was always recovered.



Reaction 28

Attempts to reduce tetracyclone to tetraphenylcyclopentadiene which could then be treated with *p*-tosylazide and base to give the diazo-compound were also unsuccessful. Two literature methods[82,83] were followed but in neither case could the results be reproduced. However, a small amount of diene existed from previous work on this subject which gave enough diazo-compound (from treatment with *p*-tosylazide and base[84]) to attempt the necessary reactions.

Benzylsulphonyldiazomethane *(71)* was prepared as shown in Scheme 14.[85]



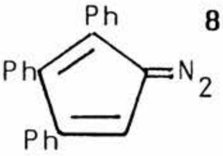
Scheme 14

The last step of the reaction scheme involves stirring a solution of the nitroso compound with neutral alumina in the absence of light for about two days.[86] The diazo-compound obtained is of high purity and is reasonably stable if excluded from light. Attempts to prepare a diazo-compound from the intermediate, ethyl benzylsulphonylacetate, *(72)* by treatment with sodium hydroxide and *p*-tosylazide led to hydrolysis of the ester function giving $PhCH_2SO_2CH_2CO_2^{\ominus}Na^{\oplus}$.

Attempts to prepare the diazo-compound from benzylphenylsulphone were also unsuccessful since even ethanolic potassium hydroxide appeared to have no effect on this methylene compound.

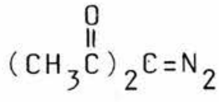
ii) *REACTION OF DIAZO-COMPOUNDS WITH TRIPHENYLSTIBINE*

The reactions of the diazo-compounds with Ph_3Sb in the presence of $Cu(hfa)_2$ were investigated and the results can be found in Table 7. The reactions were carried out under nitrogen using dry solvents with a 2 : 1 : 0.04 molar ratio of Ph_3Sb : diazo-compound : $Cu(hfa)_2$. Most of the reactions were carried out in refluxing benzene although occasionally a reaction required a higher temperature and refluxing toluene was used. With the monosubstituted diazo-compounds, *(67)*, *(70)* and *(71)*, reactions proceeded at room temperature. Reaction times varied from a few minutes to twenty-four hours and the course of the reactions could be monitored by infrared spectroscopy. Diazo-compounds show intense $-N_2$ stretching frequencies at about 2100 cm^{-1} and so a reaction can be seen to be complete when no diazo peak remains in the infrared spectrum of a sample of the reaction mixture. When the reaction is complete, in most cases removal of solvent and trituration of the residue with ether, petrol or hexane yields ylide. Triphenylstibonium 4,4-dimethyl-2,6-dioxocyclohexylide was obtained from the residue by chromatography on alumina. The ylides are susceptible to hydrolysis to triphenylstibine oxide and the corresponding methylene compound, and so extreme care had to be taken to



80

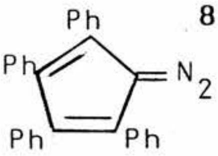
(56)



$\mathrm{(CH_3\overset{O}{\overset{\|}{C}})_2C{=}N_2}$

78

(57)



84

(58)

87

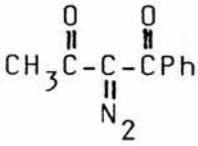
$\mathrm{(PhSO_2)_2C{=}N_2}$

(59)

88

$\mathrm{(\mathit{p}\text{-}CH_3C_6H_4SO_2)_2C{=}N_2}$

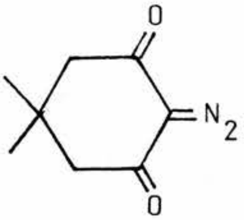
(60)



$\mathrm{CH_3\overset{O}{\overset{\|}{C}}\text{-}\underset{N_2}{\underset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}Ph}$

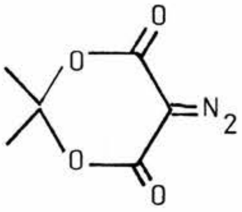
78

(61)



89

(62)



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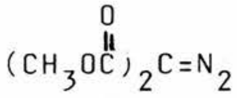
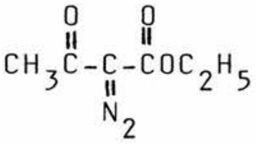
(63)



$\mathrm{(CH_3O\overset{O}{\overset{\|}{C}})_2C{=}N_2}$

78

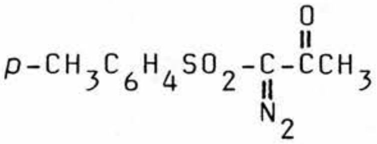
(64)



$\mathrm{CH_3\overset{O}{\overset{\|}{C}}\text{-}\underset{N_2}{\underset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}OC_2H_5}$

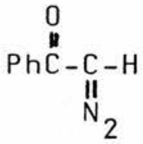
78

(65)



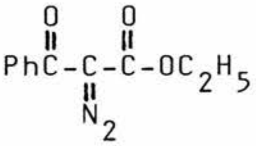
$\mathrm{\mathit{p}\text{-}CH_3C_6H_4SO_2\text{-}\underset{N_2}{\underset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}CH_3}$

(66)



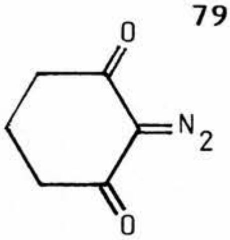
$\mathrm{Ph\overset{O}{\overset{\|}{C}}\text{-}\underset{N_2}{\underset{\|}{C}}\text{-}H}$

(67)



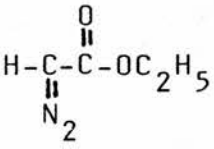
$\mathrm{Ph\overset{O}{\overset{\|}{C}}\text{-}\underset{N_2}{\underset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_2H_5}$

(68)



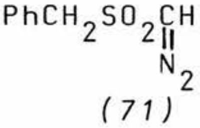
79

(69)



$\mathrm{H\text{-}\underset{N_2}{\underset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_2H_5}$

(70)

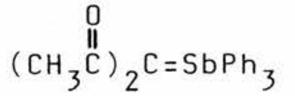
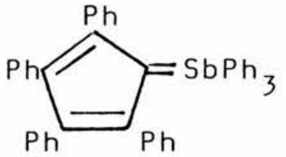
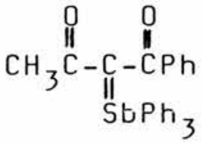
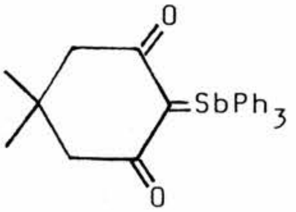
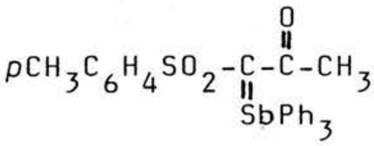


$\mathrm{PhCH_2SO_2\underset{N_2}{\underset{\|}{C}}H}$

85,86

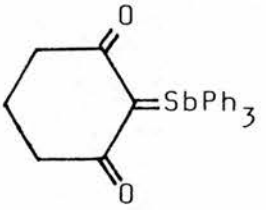
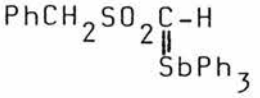
(71)

Table 7

Diazo-compound	Ylide	Reaction time (h)	Reaction Tempera-ure (°C)	Yield %
(57)	 $(CH_3\overset{O}{\overset{\|}{C}})_2C{=}SbPh_3$ *(73)*	1	80	59
(58)	 *(74)*	2	80	>32
(59)	$(PhSO_2)_2C{=}SbPh_3$ *(14)*	2	80	78
(60)	$(pCH_3C_6H_4SO_2)_2C{=}SbPh_3$ *(75)*	6	80	77
(61)	 $CH_3\overset{O}{\overset{\|}{C}}-\underset{\underset{SbPh_3}{\|}}{C}-\overset{O}{\overset{\|}{C}}Ph$ *(76)*	1	80	46
(62)	 *(77)*	2	110	40
(63)	-	1	110	0
(64)	-	2	110	0
(65)	-	2	80	0
(66)	 $pCH_3C_6H_4SO_2-\underset{\underset{SbPh_3}{\|}}{C}-\overset{O}{\overset{\|}{C}}-CH_3$ *(78)*	2	80	38
(67)	-	24	20	0
(68)	-	2	80	0

(69)/

Table 7 (cont'd)

Diazo-Compound	Ylide		Reaction time (h)	Reaction Temperature (°C)	Yield %
(69)		*(79)*	1.5	80	58
(70)	-		24	20	0
(71)	 $\mathrm{PhCH_2SO_2\underset{\underset{SbPh_3}{\|}}{C}-H}$	*(80)*	0.25	20	58

exclude them from moisture, particularly during recrystallisations.

Triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide *(74)* was previously prepared in a melt at 150 °C in 87% yield.[8] It was found that Cu(hfa)$_2$ would catalyse the formation of this ylide in refluxing benzene. However, the ylide, on precipitation from the reaction mixture, formed a suspension which proved impossible to filter off completely, and this is reflected in the apparently much lower yield obtained by this method.

Diazo-compounds *(59)*[87] and *(60)*[88] provided the best yields of stibonium ylides although it is interesting to note that *(60)* required a heating period three times as long as that of *(59)* to obtain a comparable yield of ylide.

After two hours in refluxing benzene with Ph_3Sb and $Cu(hfa)_2$, the decomposition of diazo-compound *(62)*[89] was not complete but the reaction mixture had gone very dark in colour. Heating was therefore discontinued, and evaporation of solvent gave a brown tar which gave no solid on trituration with ether, petrol or hexane. The infrared spectrum, however, showed carbonyl absorption which may have been due to the presence of ylide. The residue was therefore purified by chromatography on alumina giving a 15% yield of triphenylstibonium 4,4-dimethyl-2,6-dioxocyclohexylide. In this case it was thought better perhaps to use a higher reaction temperature over a shorter period of time to effect the complete decomposition of diazo-compound. When refluxing toluene was used, a 40% yield of ylide was obtained although the reaction mixture still produced a brown tar which had to be purified by chromatography on alumina.

Diazo-compound *(57)*[78] gave the corresponding ylide which appeared to be contaminated with triphenylstibine oxide. An analytical sample was obtained only after several recrystallisations. The same problem arose with ylide produced from acetylbenzoyldiazomethane.[78] A black tar was obtained from the reaction mixture which only after persistent trituration with a mixture of ether and hexane gave triphenylstibonium acetylbenzoylmethylide, again contaminated with triphenylstibine oxide. Recrystallisation did not remove this impurity nor recrystallisation with charcoal.

Attempts to purify this ylide by chromatography on alumina led to its decomposition.

Reaction of benzylsulphonyldiazomethane with Ph_3Sb in the presence of $Cu(hfa)_2$ led to the isolation of solid which from spectral evidence appears to be triphenylstibonium benzylsulphonylmethylide. Again, however, attempts to purify this compound were unsuccessful. This diazo-compound was visibly more reactive than the others, since on addition of $Cu(hfa)_2$ to a solution of diazo-compound and Ph_3Sb, evolution of nitrogen was observed almost immediately, and was complete within a few minutes.

The reaction of *p*-tosylacetyldiazomethane *(66)* was looked at only briefly, but again spectral evidence suggests that the product of reaction was triphenylstibonium *p*-tosylacetylmethylide.

In the reaction of the diazo derivative of Meldrum's acid[89] *(63)* with Ph_3Sb, it was found that after two hours in refluxing benzene, little decomposition of the diazo-compound had occurred. This was also true after heating for a further three hours with fresh catalyst. The reaction was therefore repeated in refluxing toluene but after one hour the reaction mixture was virtually black and so heating was discontinued. As the solution cooled, unchanged diazo-compound precipitated and this was filtered off. Evaporation of solvent from the filtrate gave a black tar which gave no solid on trituration with ether, petrol or hexane, but which from an infrared spectrum still contained diazo-compound.

Similarly dimethyl diazomalonate[78] *(64)* was still present in the reaction mixture after two hours under reflux in benzene with Ph_3Sb and $Cu(hfa)_2$. A small amount of triphenylstibine oxide was isolated from the reaction mixture, however. Since triphenylarsonium bis(methoxycarbonyl)methylide is a known compound[16c], the reaction of *(64)* with Ph_3As and $Cu(hfa)_2$ was investigated to determine the temperature needed for this reaction to ensue. After five hours under reflux in benzene, a yield of only 16% of arsonium ylide was obtained and unchanged diazo-compound was still present. However, refluxing in toluene for two hours led to complete decomposition of the diazo-compound and the yield of ylide was now 62%. The reaction of *(64)* with Ph_3Sb and $Cu(hfa)_2$ was therefore repeated in refluxing toluene. Under these conditions the diazo-compound did indeed decompose, but there was no evidence for the presence of any ylide, and again only triphenylstibine oxide was isolated.

No ylide was isolated from the reaction of either of the diazo-compounds *(65)*[78] and *(68)* with Ph_3Sb and $Cu(hfa)_2$. In each case, however, some triphenylstibine oxide was obtained from the reaction mixtures. Presumably in these reactions where triphenylstibine oxide is isolated, some ylide has indeed formed but has then decomposed under the reaction conditions.

From these results, it appears that two strongly electron-

-withdrawing groups are needed on the ylidic carbon to provide sufficient stabilisation to enable these stibonium ylides to be isolated [with the exception of *(80)*]. Sulphonyl groups appear to be best able to do this, which is probably why triphenylstibonium benzylsulphonylmethylide could be isolated. Keto functions also provide good stabilisation in these ylides by delocalisation of negative charge, but ester functions are not powerful enough in this respect, and no stibonium ylides containing ester functions were isolated.

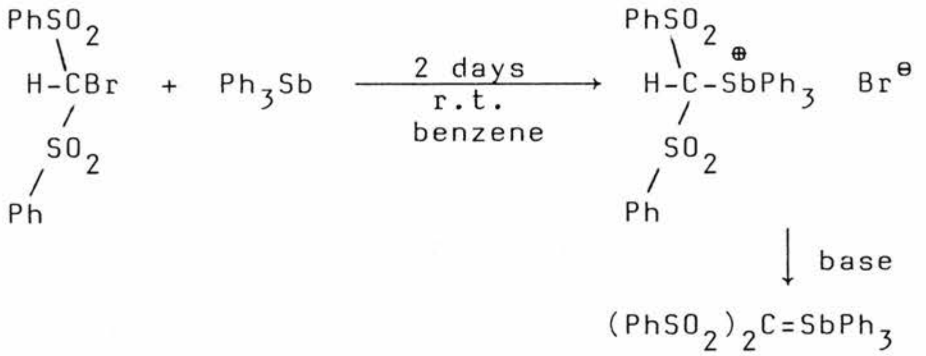
The precise structure of triphenylstibine oxide which is obtained from hydrolysis of these ylides, has eluded researchers for many years due to the inability to obtain single crystals on which x-ray analysis could be carried out. Reports[90] on the compound present conflicting data, and it seems that the structure may depend on how the oxide is formed. Suggestions have been made that the oxide may have a polymeric structure, but this has never been proven conclusively.

However, during recrystallisation of a sample of triphenylstibonium bis(tolyl-*p*-sulphonyl)methylide from methylene chloride and hexane, large crystals were obtained which from their infrared spectrum and C,H microanalysis, appeared to be triphenylstibine oxide. Moisture must have been present in the solvent which caused decomposition of the ylide. An x-ray structure determination was carried out[106] on this oxide, the results of which will be discussed later.

Although this method of producing stibonium ylides from diazo-compounds proved very successful, other possible methods were also investigated.

iii) *ATTEMPTED PREPARATION OF A STIBONIUM YLIDE BY THE "SALT METHOD"*

As already mentioned, the "salt method" is probably the most common procedure for the preparation of ylides generally. It seemed necessary, therefore, to investigate its feasibility in the preparation of a stibonium ylide. After the successful preparation of the stable triphenylstibonium bis(phenylsulphonyl)methylide in high yield by the diazo method, an attempt was made to prepare this same ylide by the sequence of reactions shown below (Scheme 15)

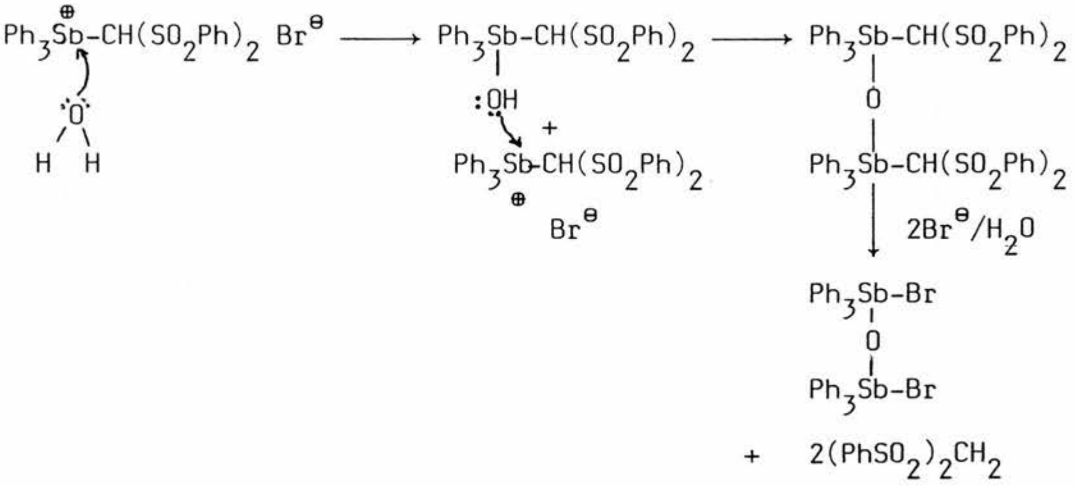


Scheme 15

The reactants, bis(phenylsulphonyl)bromomethane[91] and triphenylstibine, were dissolved in benzene and left at room temperature. After two days large colourless crystals had appeared which were filtered off, washed with benzene and ether and dried, m.p. 248 - 250 °C. This compound, however, exhibited no sulphonyl absorption in the infrared.

Its spectrum, in fact, is very similar to that of triphenylstibine oxide but with additional absorption between 760 and 772 cm^{-1}. Although the identity of this compound was uncertain at the time, it was later assigned as oxybis(triphenylantimony)dibromide, $(Ph_3Sb\text{-}O\text{-}SbPh_3)Br_2$, a non-ionic species containing 5-coordinate antimony. C,H Microanalysis is consistent with this formula as are literature data[92] on melting point (252 - 253 °C) and infrared absorptions. The infrared absorption at 760 - 772 cm^{-1} has been suggested to be due to the Sb-O-Sb group.

For this compound to have formed, some moisture must have been present in the reaction mixture. A plausible mechanism for its formation, involving attack of initially formed bromide salt by water, is shown in Scheme 16.

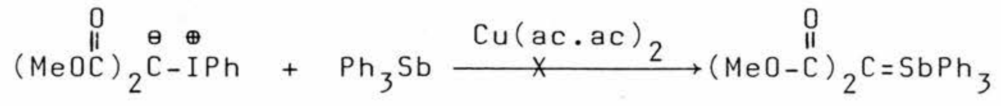


Scheme 16

iv) *THE ATTEMPTED PREPARATION OF A STIBONIUM YLIDE FROM AN IODONIUM YLIDE*

The catalytic decomposition of iodonium ylides by

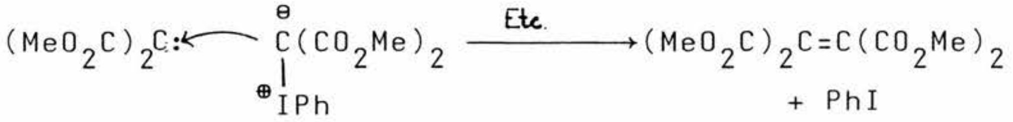
$Cu(ac.ac)_2$ in the presence of carbene acceptors has been used to prepare ylides containing a wide range of heteroatoms.[39,40,16c] Reaction 29 has been attempted previously[16c] but after two hours in refluxing benzene gave unchanged Ph_3Sb.



$$(MeO\overset{O}{\overset{\|}{C}})_2\overset{\ominus}{C}-\overset{\oplus}{I}Ph + Ph_3Sb \xrightarrow[\times]{Cu(ac.ac)_2} (MeO-\overset{O}{\overset{\|}{C}})_2C=SbPh_3$$

Reaction 29

Since $Cu(hfa)_2$ was found to be superior as a catalyst to $Cu(ac.ac)_2$, and since none of this particular ylide had been isolated from the reaction of dimethyl diazomalonate with Ph_3Sb, Reaction 29 was repeated with the replacement of $Cu(ac.ac)_2$ by $Cu(hfa)_2$. After two hours under reflux in benzene, solvent was removed from the reaction mixture and trituration of the residue with solvent ether gave a small amount of triphenylstibine oxide. Chromatography of the remaining residue gave unchanged Ph_3Sb, and also 1,1,2,2-tetrakis(methoxycarbonyl)ethene in 33% yield. This dimer is formed by decomposition of the iodonium ylide to a carbene-type intermediate which then attacks a second molecule of iodonium ylide as shown in Reaction 30. It is unlikely that this dimer is formed by two "carbenes" meeting in solution since their concentration will always be very low.



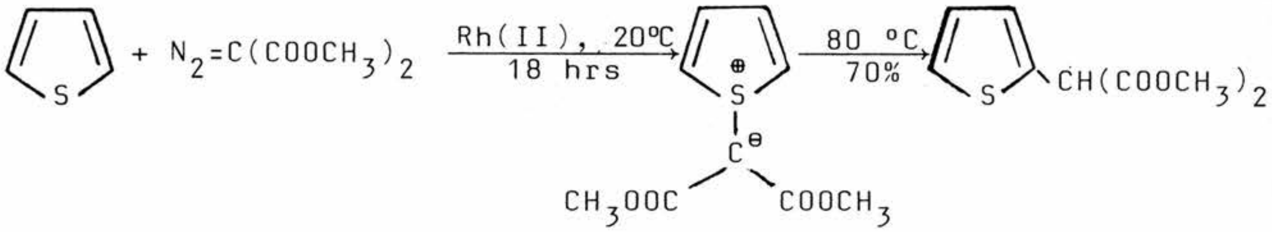
$$(MeO_2C)_2C\!: \leftarrow \underset{\oplus IPh}{\overset{\ominus}{C}}(CO_2Me)_2 \xrightarrow{Etc.} (MeO_2C)_2C=C(CO_2Me)_2 + PhI$$

Reaction 30

Because of the high percentage of dimer formed in this reaction further investigation with other iodonium ylides was not pursued.

v) *ATTEMPTED PREPARATION OF STIBONIUM YLIDES BY THE RHODIUM ACETATE CATALYSED DECOMPOSITION OF DIAZO-COMPOUNDS*

Rhodium acetate has been used to catalyse reactions involving the decomposition of diazo-compounds under mild conditions. For example Reaction 31 proceeds at 20 °C over 18 hours giving a 95% yield of thiophenium ylide *(81)*.[93]

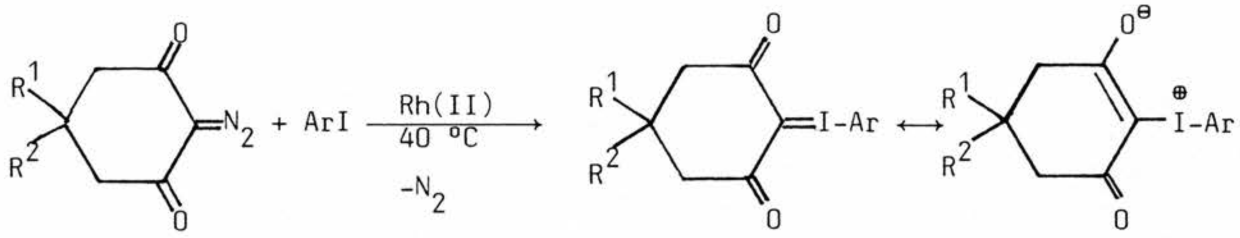


(81) *(82)*

Reaction 31

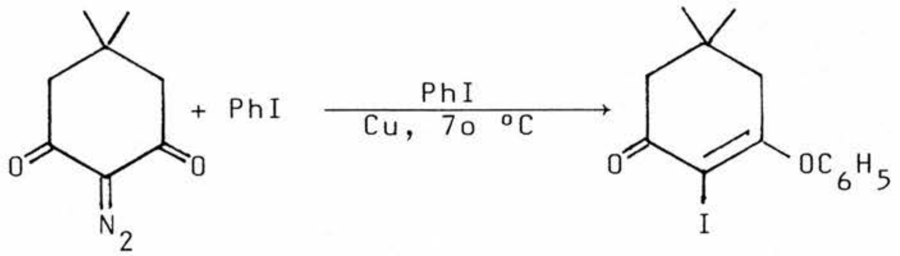
When the ylide is heated at about 80 °C it rearranges to dimethyl thiophene-2-malonate *(82)* by an intramolecular mechanism.[94] *(82)* is obtained directly by conducting the initial reaction with rhodium acetate at 80 °C, or by the use of conventional copper catalysts.

Rhodium acetate has also been used to catalyse the preparation of iodonium ylides.[16g] For example, diazo-compounds of β-diketones have been found to react with iodoaryl compounds giving good yields of iodonium ylides, *e.g.* Reaction 32.



Reaction 32

The iodo-compounds served also as solvents in these reactions. It was reported that traditional copper catalysts such as copper-bronze, $Cu(ac.ac)_2$ and $CuCl_2$ required higher temperatures and longer reaction times which resulted in rearrangement of the initially formed iodonium ylide. Thus diazodimedone and iodobenzene gave *(83)*.



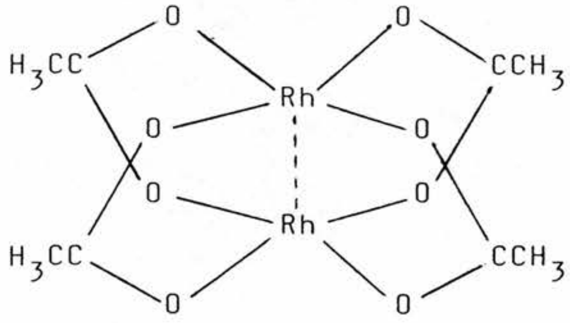
(83)

The reaction of diazodimedone with iodobenzene in the presence of $Cu(hfa)_2$ was investigated following the conditions used for the rhodium acetate catalysed reaction. However, no iodonium ylide was obtained in this case.

The wide use of rhodium acetate as a catalyst in reactions involving decomposition of diazo-compounds, encouraged a study of its use in the preparation of stibonium ylides. Rhodium acetate was therefore prepared from rhodium trichloride according to the method of Rempel *et al*[95], and its role in the reactions of diazo-bis(phenylsulphonyl)methane and diacetyldiazomethane with Ph_3Sb investigated.

It was found that rhodium acetate did indeed catalyse the decomposition of the diazo-compounds in solution, even at room temperature. However, when both diazo-compound and Ph_3Sb were present in solution, no evolution of nitrogen was observed and the reaction mixtures became red in colour.

The structure of rhodium acetate is that of a binuclear dimer (84) (cf. cupric acetate). It forms stable adducts of the type $Rh_2ac._4L_2$[96] which, with π-bonding ligands such as PPh_3, are typically red in colour. Hence the red colour observed in these solutions is probably due to the presence of $Rh_2ac._4(Ph_3Sb)_2$.



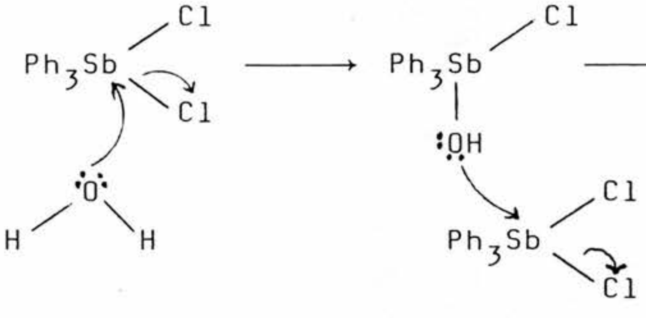
(84)

The mechanism of action of rhodium acetate in reactions such as 31 and 32 is not known, but since its two vacant co-ordination sites are at opposite sides of the molecule, it is obviously different from that of $Cu(hfa)_2$ where reacting species can co-ordinate at *cis* sites.

vi) *REACTIONS OF ACTIVE METHYLENE COMPOUNDS WITH TRIPHENYLANTIMONY DICHLORIDE*

Many phosphonium and arsonium ylides can be prepared by the reaction of active methylene compounds with Ph_3PCl_2 and Ph_3AsCl_2 in the presence of base. The procedure of Horner and Oediger[23] for the preparation of these ylides of phosphorus and arsenic from the corresponding triphenyldichlorides was followed in attempts to prepare stibonium ylides from a variety of active methylene compounds and Ph_3SbCl_2. The reaction procedure involves heating the reactants under reflux in a small volume of dry benzene for ten to twenty minutes with triethylamine. On cooling the reaction mixture, triethylamine hydrochloride should precipitate and can be filtered off leaving ylide in solution. In the preparation of some phosphonium and arsonium ylides, ylide precipitated with the $Et_3N.HCl$. In these cases the hydrochloride was removed by washing with cold methanol or water.

All of the reactions attempted involving Ph_3SbCl_2, produced a compound whose infrared spectrum looked very similar to that of triphenylstibine oxide but with additional absorption between 760 and 770 cm^{-1}. Its melting-point was also close to that of the oxide. The mass spectrum showed signals which could correspond to fragments containing C, H, O and Sb, and also fragments containing C, H, Cl and Sb, but was not consistent with the spectra of either triphenylstibine oxide or triphenylantimony dichloride, or indeed that expected from a mixture of both. It later became apparent that the infrared spectrum of this compound was very like that of the solid obtained from the reaction of $(PhSO_2)_2CHBr$ with Ph_3Sb. This observation, coupled with the fact that both solids were isolated from reactions involving halogenated compounds, suggested that the structures of these compounds might be related. Literature study[92] led to the assignment of these compounds as oxybis(triphenylantimony)dibromide for the solid from the reaction of $(PhSO_2)_2CHBr$ and Ph_3Sb as previously mentioned, and oxybis-(triphenylantimony)dichloride for the solid from the reactions of Ph_3SbCl_2. Again, as in the formation of $(Ph_3SbBr)_2O$, the presence of moisture in the reaction mixtures has presumably led to the production of $(Ph_3SbCl)_2O$. Scheme 17 shows a possible mechanism for its formation.



Scheme 17

(a) Reaction of Ph_3SbCl_2 with Acetylacetone

Reactions as described above gave a precipitation of white solid which was filtered off and found to be a mixture of triethylamine hydrochloride and $(Ph_3Sb\text{-}O\text{-}SbPh_3)Cl_2$. Evaporation of solvent from the filtrate and addition of ether to the residue gave triphenylstibonium diacetylmethylide (53%) of melting-point 166 - 170 °C (melting-point of pure ylide is 186°). The infrared spectrum showed that the ylide was contaminated with $(Ph_3Sb\text{-}O\text{-}SbPh_3)Cl_2$.

(b) Reaction of Ph_3SbCl_2 with Benzoylacetone

Again in this reaction a mixture of $Et_3N.HCl$ and $(Ph_3Sb\text{-}O\text{-}SbPh_3)Cl_2$ was collected. Both of these compounds were also found to be present in the ylide fraction which was obtained as in (a). Their removal was attempted by washing the ylide mixture quickly with ice-cold methanol and then with ether. This succeeded in removing the hydrochloride but not the dichloride. The resulting impure triphenylstibonium acetylbenzoylmethylide had melting-point 168 - 182 °C and comprised a yield of 27%.

(c) Reaction of Ph_3SbCl_2 with Cyclohexane-1,3-dione

Reaction as in (a) and (b) gave a mixture of $Et_3N.HCl$ and $(Ph_3Sb\text{-}O\text{-}SbPh_3)Cl_2$ which was removed by filtration. From the filtrate triphenylstibonium 2,6-dioxocyclohexylide, contaminated with $(Ph_3Sb\text{-}O\text{-}SbPh_3)Cl_2$, was obtained of melting-point 156 - 182 °C. In an attempt to remove the dichloride, the mixture was dissolved in dry methylene chloride and filtered through a bed of neutral alumina on hyflo. Removal of solvent from the filtrate gave ylide which appeared to be free of the dichloride. However, only a small amount of ylide was recovered. To try to remedy this, the reaction was repeated and the solution of ylide and dichloride in methylene chloride was simply stirred with a small amount of neutral alumina, which was then filtered off through hyflo. This was equally successful in removing the dichloride, and did not cause such loss of ylide. The melting-point of the ylide thus obtained was 168 - 170 °C (melting-point of pure ylide is 169 - 172 °C). The yield, however, was only 20% compared to 58% by the diazo method.

The reactions of Ph_3SbCl_2 with dimedone, dimethylmalonate or bis(phenylsulphonyl)methane gave no ylide, but in each case $Et_3N.HCl$ and/or $(Ph_3Sb\text{-}O\text{-}SbPh_3)Cl_2$ were obtained.

Therefore, although ylides can be produced by this method, the reaction is evidently not so generally applicable as the diazo method. In addition, contamination with $(Ph_3Sb\text{-}O\text{-}SbPh_3)Cl_2$ is a problem, and the yields of ylide obtained are also lower.

4. PROPERTIES OF STIBONIUM YLIDES

i) *GENERAL*

The new stibonium ylides are all colourless solids which are stable indefinitely if kept in a dry atmosphere. They appear to be very basic and in protic solvents are hydrolysed to triphenylstibine oxide and the corresponding methylene compound. For example, when a sample of triphenylstibonium bis(phenylsulphonyl)methylide *(14)* was heated under reflux in wet ethanol for five minutes and then cooled (Reaction 33), white solid precipitated which was filtered off and found to be bis(phenylsulphonyl)methane (87%). Removal of ethanol from the filtrate gave a white residue containing triphenylstibine oxide. The mechanism of hydrolysis was discussed previously.

$$\underset{(14)}{(PhSO_2)_2C{=}SbPh_3} \longrightarrow (PhSO_2)_2CH_2 + Ph_3SbO$$

Reaction 33

A further experiment illustrated the protonation of triphenylstibonium 2,6-dioxocyclohexylide by trifluoroacetic acid. Since attempts to prepare and isolate salts from these stibonium ylides often resulted in their decomposition, this reaction was looked at by ^1H n.m.r. spectroscopy. ^1H n.m.r. spectra of this ylide were obtained before and after the addition of trifluoroacetic acid. The spectrum of the sample containing the acid showed a broadening of the signals for the six aliphatic protons of the cyclohexanedione ring and, in addition, a new signal at δ 7.96 corresponding to one proton. This provides good evidence for protonation of the ylide by this acid, although it is not clear whether it is protonation of the ylidic carbon, or of an oxygen atom of the α-substituents.

The new ylides have been found to be reasonably stable to moderate heating: for example, when a solution of $(PhSO_2)_2C{=}SbPh_3$ was heated under reflux in dry benzene for several hours, it caused no decomposition. However, care was necessary during recrystallisation of this ylide from chlorobenzene (b.p. = 132 °C), where prolonged heating resulted in some decomposition.

The ylides are very polar and are thus insoluble in solvents such as ether or alkanes. They are reasonably soluble in chlorinated solvents such as dichloromethane and chlorobenzene and also in benzene and ethyl acetate, ylides *(14)* and *(75)* being the least soluble. Chloroform was avoided as a solvent since it was suspected of causing some decomposition of the ylides. In powdered form the ylides possess much static and stick to glass surfaces and spatulas. This is presumably a consequence of their high polarity.

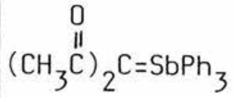
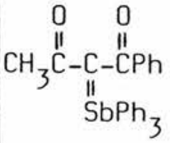
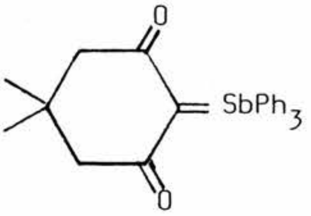
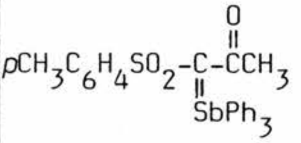
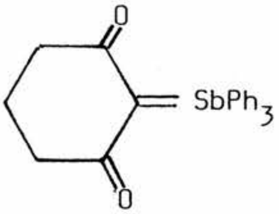
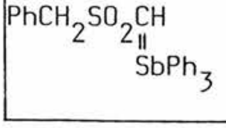
With careful recrystallisation, and after several attempts, good sized crystals of ylides *(14)* and *(77)* were obtained which were examined by x-ray crystallography (see later).

ii) *INFRARED SPECTRA OF YLIDES*

Table 8 shows the absorption frequencies of the functional groups of ylides *(14)*, *(73)* and *(75)* - *(80)*; where possible values for the corresponding arsonium and phosphonium ylides are also shown.[25] As can be seen, the stretching frequencies of the functional groups, sulphonyl and carbonyl, are uniformly low due to delocalisation of negative charge into these groups from the ylidic carbon. In general, the frequencies become steadily lower on going from phosphonium to arsonium to stibonium ylides. This is consistent with the corresponding expected increase in the degree of delocalisation of negative charge in these ylides.

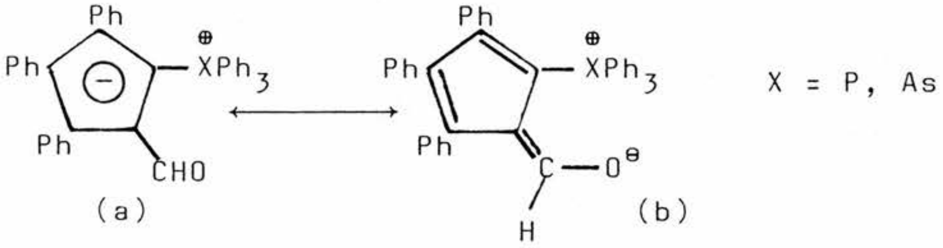
Although ylide *(78)* contains a carbonyl group, no carbonyl absorption is seen in the infrared spectrum. Such a situation

Table 8

Ylide	nujol ν_{max} cm^{-1}	nujol[a] ν_{max} cm^{-1}	nujol[b] ν_{max} cm^{-1}
 $(CH_3C(=O))_2C{=}SbPh_3$	1570, 1505	1580, 1510	1580, 1545
$(PhSO_2)_2C{=}SbPh_3$	1280, 1112	1292, 1122	1310, 1130
$(pCH_3C_6H_4SO_2)_2C{=}SbPh_3$	1280, 1112	1292, 1120	
 $CH_3C(=O){-}C(=SbPh_3){-}C(=O)Ph$	1580, 1555, 1495	1578, 1555, 1515	1560, 1530
	1585, 1505	1605, 1545	
 $pCH_3C_6H_4SO_2{-}C(=SbPh_3){-}C(=O)CH_3$	1334, 1130[c]		
	1595, 1570sh, 1512	1595, 1572sh, 1540	
 $PhCH_2SO_2CH{=}SbPh_3$	1302, 1115		

a Values for the corresponding arsonium ylides.[25]
b Values for the corresponding phosphonium ylides.[25]
c No carbonyl absorption observed.

was reported for ylides *(85)* whose infrared spectra showed no normal carbonyl absorption.[49] This was suggested to be due to a large contribution to the structure of the ylides from form (b) in which there is the possibility of intramolecular association between phosphorus or arsenic and the oxygen of the formyl group. A similar situation may exist in the stibonium ylide *(78)*.



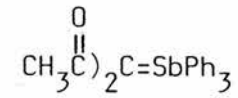
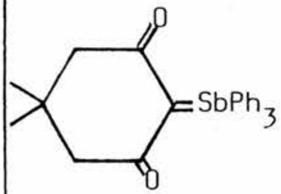
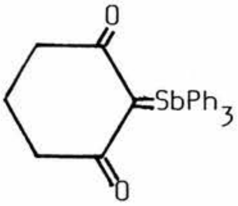
(85)

iii) *ULTRAVIOLET SPECTRA OF YLIDES*

Table 9 shows the UV data obtained on methanolic solutions of pure samples of the ylides *(14)*, *(73)*, *(77)* and *(79)*. Triphenylstibonium bis(tolyl-*p*-sulphonyl)methylide *(75)* was so insoluble in methanol that no spectrum could be obtained. After some time in methanol, the ylide appeared to have dissolved but in fact was found to have decomposed to triphenylstibine oxide and bis(tolyl-*p*-sulphonyl)methane - presumably a hydrolysis reaction due to the presence of water in the methanol. Because of the ease of hydrolysis of these ylides, the methanolic solutions of the other ylides were made up, and spectra recorded, as quickly as possible.

All spectra of the stibonium ylides contain a broad band in the region 240 - 325 nm associated with intramolecular

Table 9

Ylide	MeOH λ_{max} nm (log ε)	MeOH * λ_{max} nm (log ε)
 $CH_3\overset{O}{\overset{\|}{C}})_2C=SbPh_3$	271(3.96), 221(4.48)	275(4.20), 216(4.41)
$(PhSO_2)_2C=SbPh_3$	263(3.61), 218(4.46)	285(3.77), 265(4.03), 217(4.54)
	266(4.30), 224(4.42)	265(4.30), 213(4.40)
	264(4.25), 220(4.45)	262(4.06), 209(4.30)

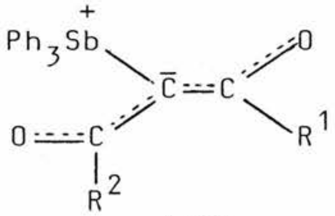
$^*\lambda_{max}$ of corresponding arsonium ylides where known.[25]

charge transfer. As can be seen the λ_{max} of the stibonium and arsonium ylides are very similar which may suggest that there is little difference in the polarities of the $\overset{+}{Sb}-\overset{-}{C}$ and $\overset{+}{As}-\overset{-}{C}$ bonds.

Solid state UV spectra of ylide *(75)* and the analogous arsonium ylide were recorded. The spectra are virtually identical with λ_{max} values at 297 and 300 nm respectively, which again implies a similarity in the polarities of the two ylidic bonds.

iv) *NMR SPECTRA OF YLIDES*

The ^1H n.m.r. spectra of these stibonium ylides are very similar to those of the analogous arsonium ylides[25] in that there is no evidence for the existence of more than one structural isomer at normal working temperatures. As with the arsonium ylides, the most likely conformation for the substituents on the ylidic carbon is with both in cisoid configurations which can allow favourable electrostatic interaction between the antimony and neighbouring oxygens *(86)*.



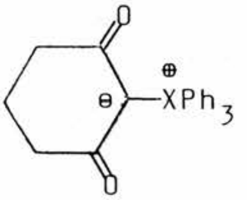
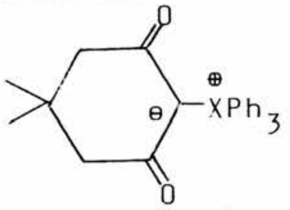
(86)

^{13}C N.m.r. spectra of a number of these stibonium ylides and also those of their arsonium analogues have been obtained with the use of the Brüker WH-360 n.m.r. spectrometer in the Chemistry Department of the University of Edinburgh. With the use of this equipment, it has been possible for the first time to observe signals in the spectra corresponding to the ylidic carbons. ^{13}C spectra obtained previously of arsonium ylides showed no signal for the ylidic carbon[34] due to its long relaxation time.

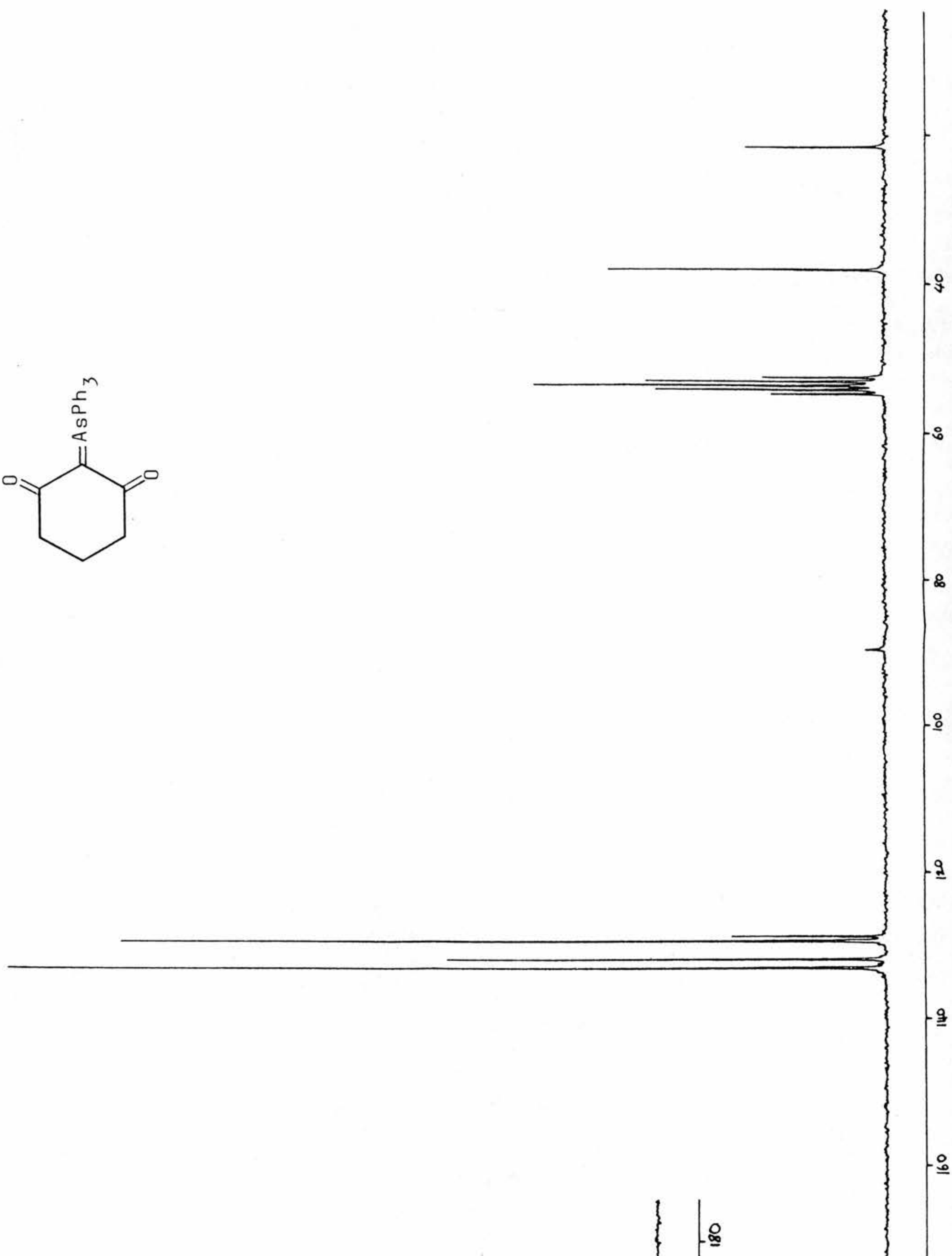
Since evidence was accumulating to suggest that these new stibonium ylides have more covalent character than was expected, spectra of three pairs of analogous arsonium and stibonium ylides were obtained in order to compare the positions of the resonances of the ylidic carbons in each case. Table 10 gives the frequencies corresponding to these ylidic carbons and the actual spectra can be seen on pages 94 - 99. The triphenylarsonium 2,6-dioxocyclohexylide had not been made previously, but was prepared by the diazo method and characterised in the usual way.

Table 10

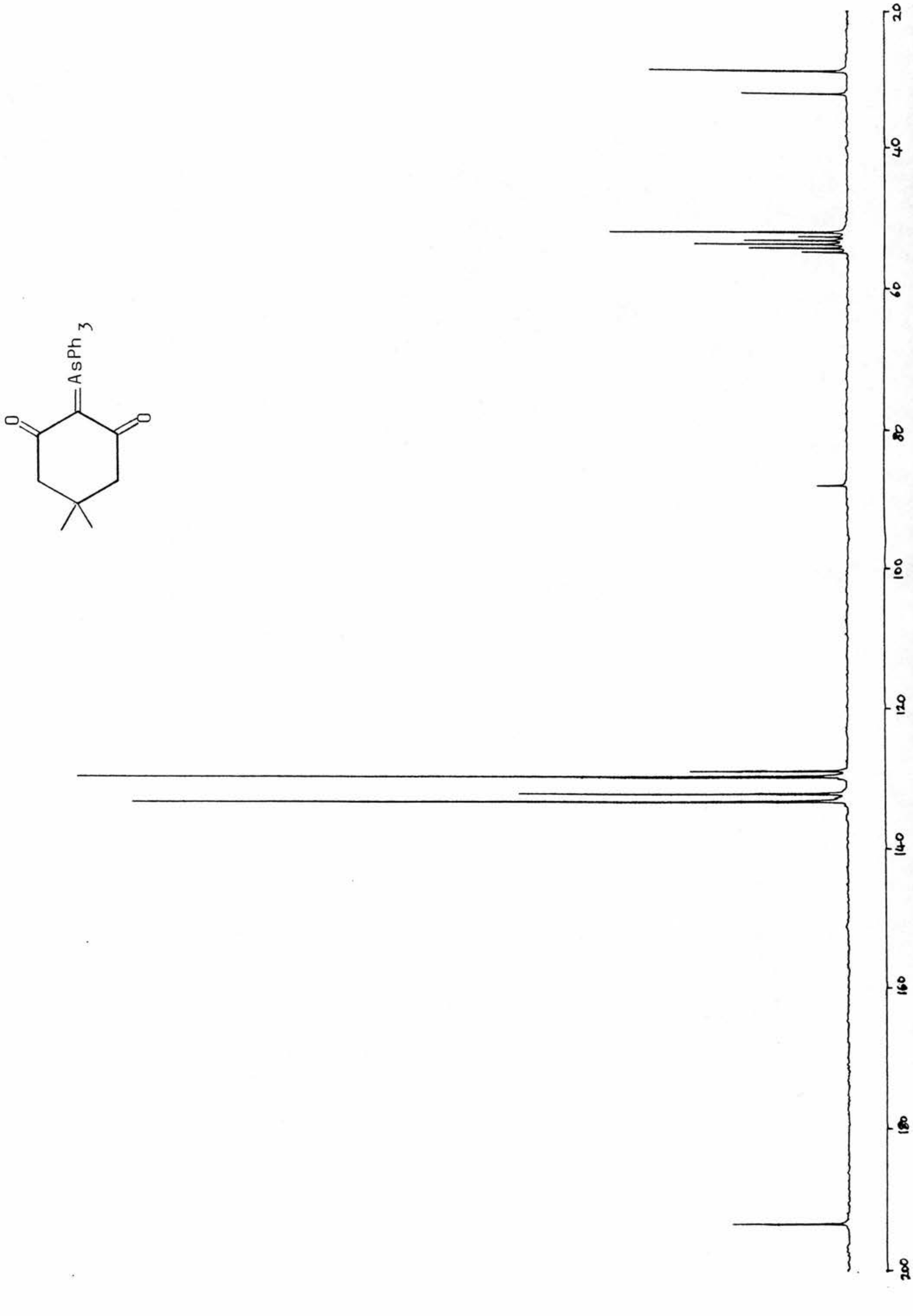
^{13}C n.m.r. Resonances for the Ylidic Carbons of some Arsonium and Stibonium Ylides

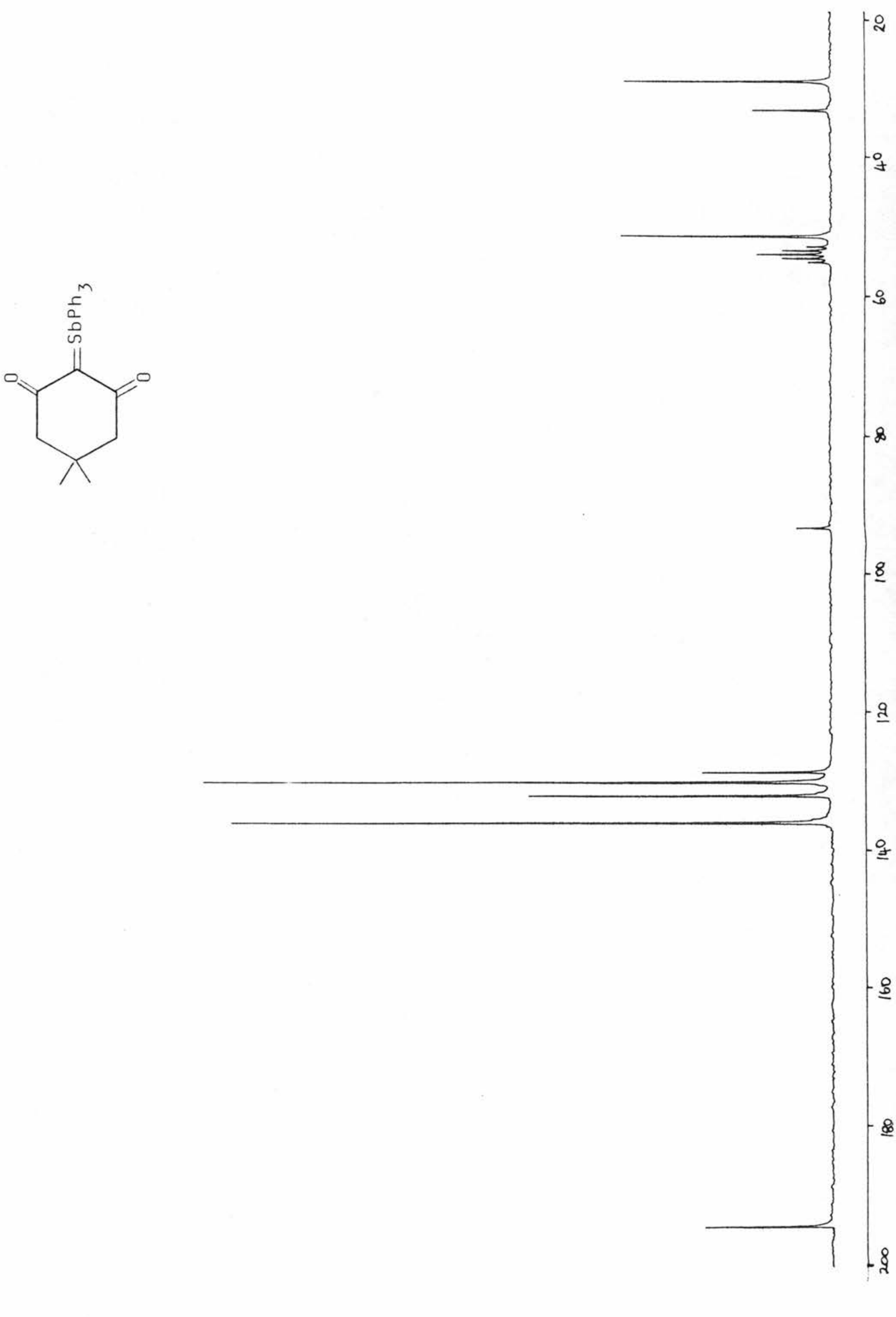
X			$(PhSO_2)_2\overset{\ominus}{C}-\overset{\oplus}{X}Ph_3$
As	δ 89.61	δ 87.90	δ 69.84
Sb	δ 95.08	δ 93.21	δ 70.48 δ 74.65

There is a slight ambiguity about the spectrum of $(PhSO_2)_2C{=}SbPh_3$. This ylide appears to have a particularly low intensity quaternary carbon, and there is also a detectable level of impurity in the sample. Consequently two peaks appear in the region of expected absorption of the ylidic carbon. In the other pairs of ylides the change in shift for the ylidic carbon on going from X = As to X = Sb is approximately 5 p.p.m. This suggests that the peak at

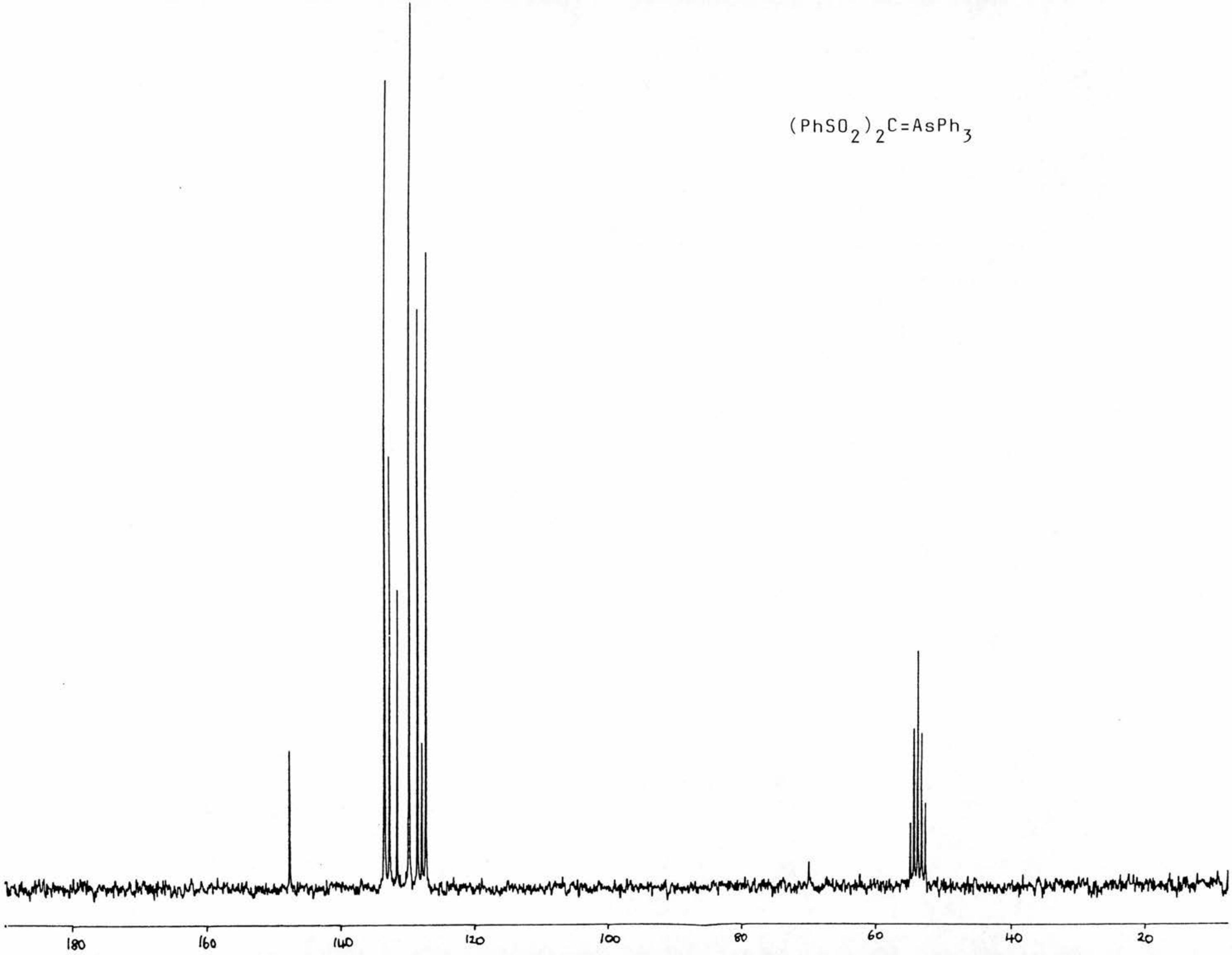

AsPh$_3$
O
O
40
60
80
100
120
140
160
180
180
200

SbPh3
20
40
60
80
100
120
140
160
180
200

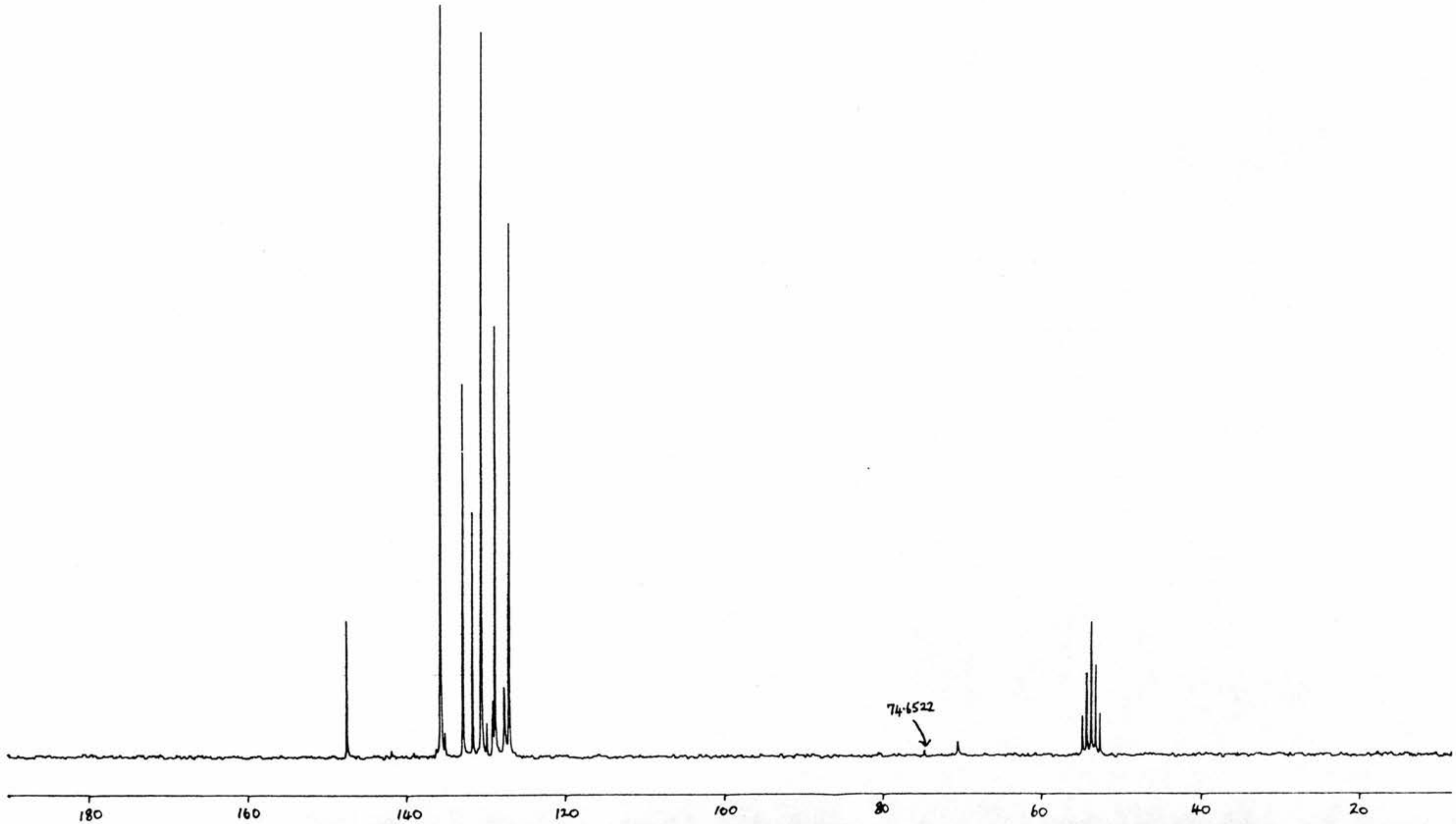

AsPh3
O
O
20
40
60
80
100
120
140
160
180
200


SbPh$_3$
20
40
60
80
100
120
140
160
180
200

(PhSO$_2$)$_2$C=AsPh$_3$



$(PhSO_2)_2C=SbPh_3$



δ 74.65 is probably the one due to the ylidic carbon.

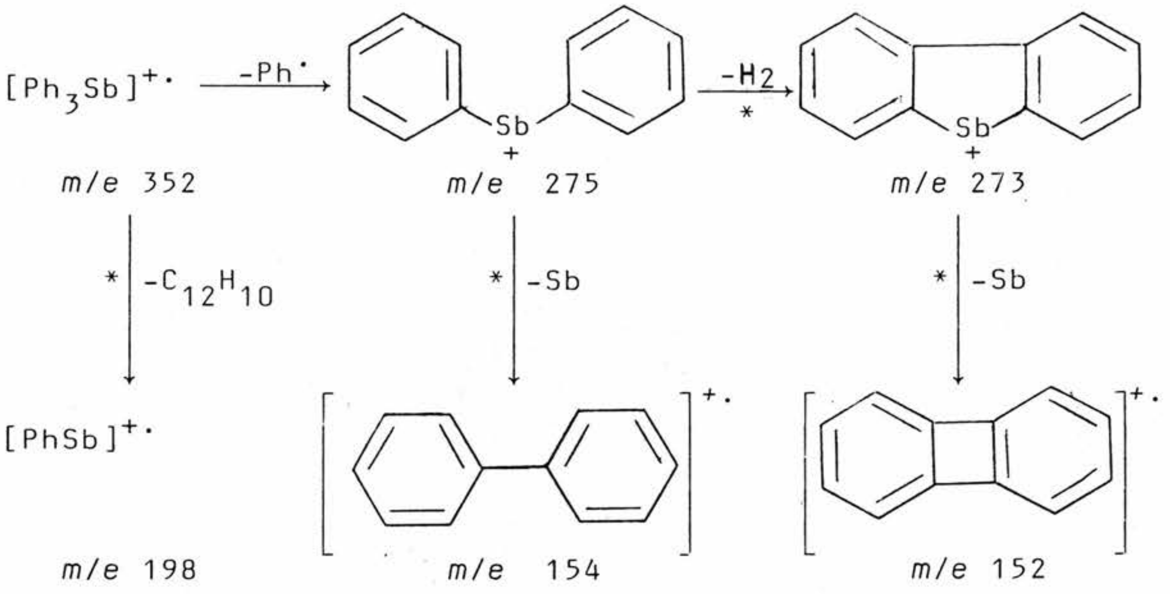
In the spectra of each pair, the chemical shifts of the ylidic carbons show considerable shielding which is relatively greater in the arsonium ylides than in the corresponding stibonium ylides. This may suggest that there is a greater degree of negative charge localised on the arsonium ylidic carbons than on the stibonium ylidic carbons, *i.e.* the arsonium ylides are relatively more polar. This is contrary to the long-held assumption that the ylides should become more polar on going from As to Sb because of less effective interaction between the carbanionic 2p orbital and the d orbital of the heteroatom. Again, however, such results can be explained by contributions to the structures of the stibonium ylides from conformations in which there is significant Sb-O electrostatic interactions.

v) *MASS SPECTRA OF YLIDES*

Evidently there was no information already available on the mass spectra of stibonium ylides, and indeed, it was only relatively recently that a study was carried out on the decomposition of arsonium ylides in the mass spectrometer.[25] It has been found that the mass spectra of these new stibonium ylides resemble closely the mass spectra of their arsonium analogues. With the exception of ylides *(75)*, *(78)* and *(80)*, molecular ion peaks are observed for each of the new stibonium ylides and in the cases of *(73)* and *(76)*, (M + 1) peaks. The existence of two isotopes of antimony, ^{121}Sb and

^{123}Sb, (natural abundance 57.3 and 42.7% respectively) gives a characteristic doublet pattern in the mass spectra for ions containing one antimony atom.

Fragmentation of arsonium ylides involves cleavage of the $\overset{\oplus}{As}-\overset{\ominus}{C}$ bond with subsequent breakdown of the arsonium moiety.[25] Fragmentation of the stibonium ylides also follows this pattern with cleavage of the $\overset{\oplus}{Sb}-\overset{\ominus}{C}$ bond followed by breakdown of $[Ph_3Sb]^{+\cdot}$ in a manner analogous to the breakdown of $[Ph_3As]^{+\cdot}$ (Scheme 18).



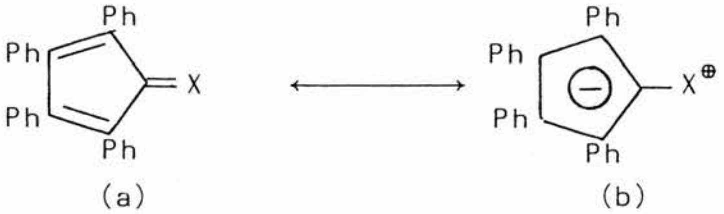
Scheme 18

In some cases *(14)*, *(73)* and *(77)*, the molecular ion peaks are more intense than those due to $[Ph_3Sb]^{+\cdot}$ which at first seemed surprising in view of the expected relative weakness of the ylidic bond. However, the ylides may well be stabilised by intramolecular interaction between the positively charged antimony and the negatively charged oxygen atoms of the α-substituents. Indeed crystallographic evidence for this in ylides *(14)* and *(77)* was later found.

Ions arising from the loss of characteristic groups from the carbanionic portions of the molecules are also observable in the spectra of all of the ylides. Loss of a phenyl group from the molecular ion also seems to be a characteristic feature of these ylides. The mass spectra of ylides *(75)* and *(79)* are illustrated on page 103 with corresponding data in Table 11, page 104.

vi) *DIPOLE MOMENTS*

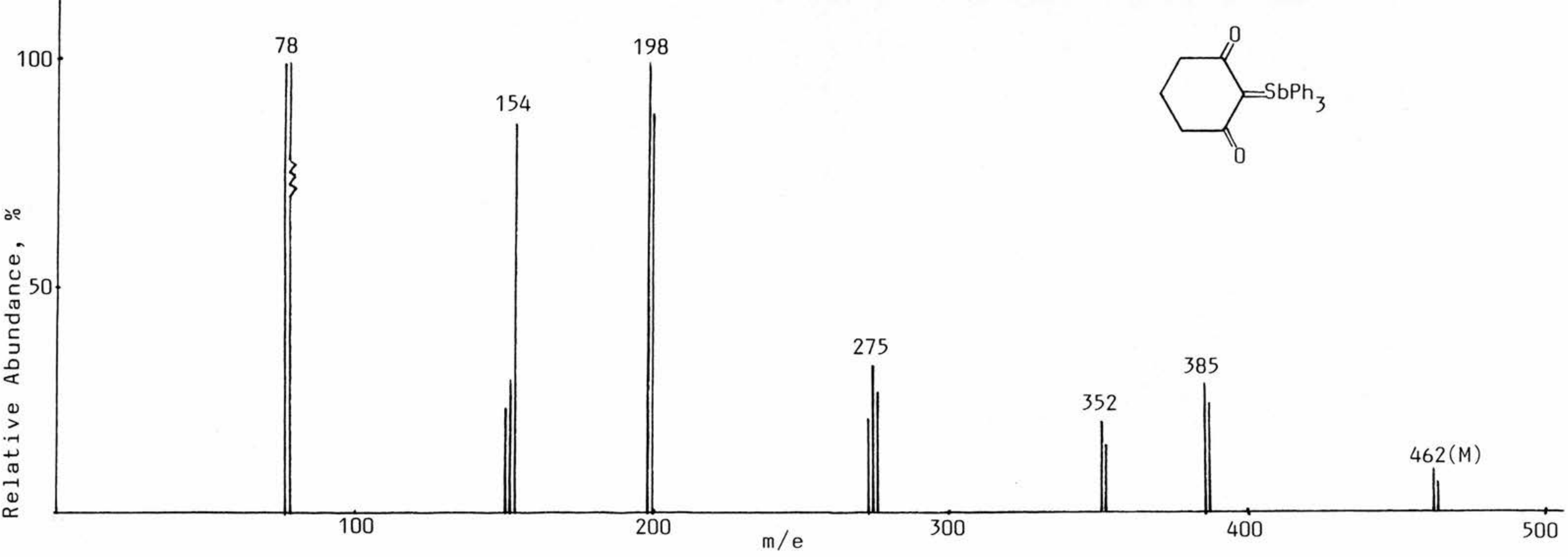
The dipole moments of the series of ylides *(87)* have been determined by Lumbroso.[45]



(87)

(X = SPh_2, PPh_3, $AsPh_3$, $SbPh_3$)

The results reported show that the dipole moments, and hence contribution to the structures of the ylides from *(87b)* increase in the order Sb < S < P < As (μ = 2.2, 6.69, 7.75, 8.32 D respectively). This is the expected trend with the exception of the stibonium ylide which has an anomalously low dipole moment. Uv spectra and pK_a measurements[36] indicate that contribution to the structure of the ylides from the dipolar canonical form increases in the order S << P < As < Sb. No explanation has been reported for this odd result but the


Relative Abundance, %
100
50
78
154
198
275
352
385
462(M)
SbPh$_3$
O
O
100
200
300
400
500
m/e

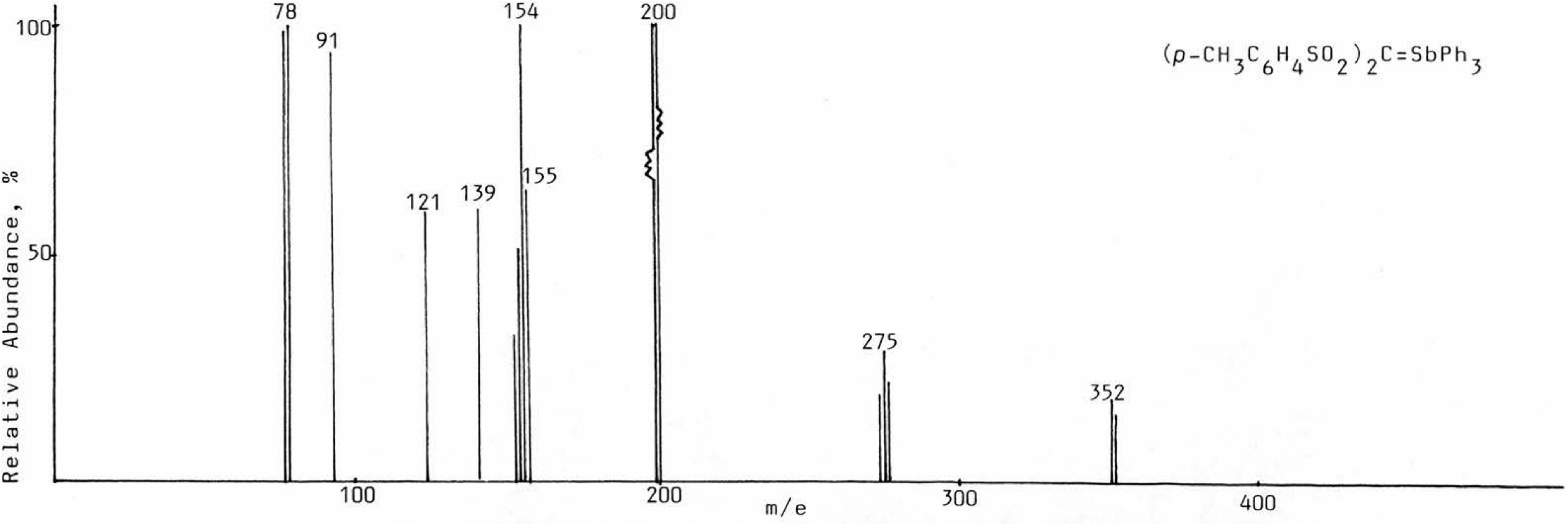
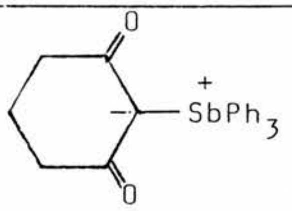
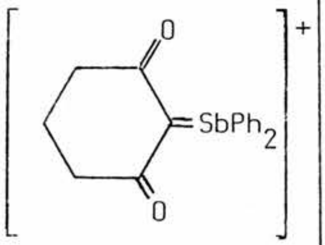
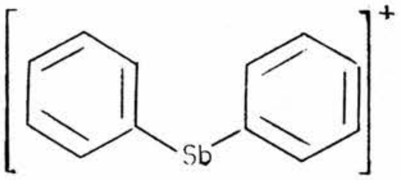
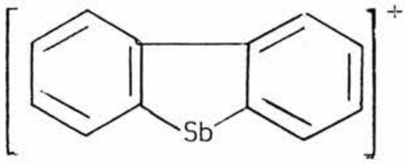
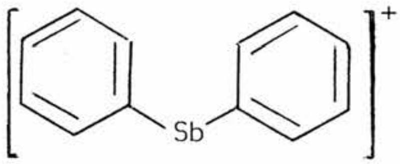
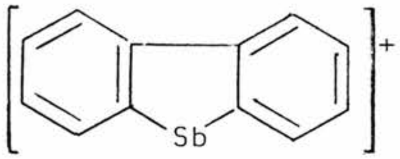
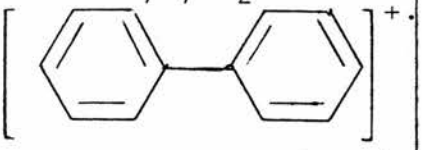
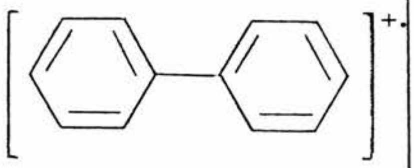
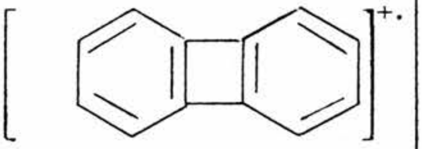
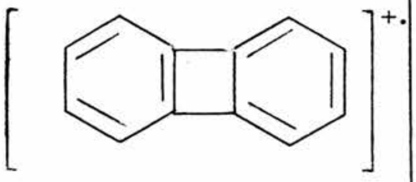

Relative Abundance, %
100
50
78
91
121
139
154
155
200
275
352
$(p\text{-}CH_3C_6H_4SO_2)_2C{=}SbPh_3$
100
200
300
400
m/e

Table 11

		$(p\text{-}CH_3C_6H_4SO_2)_2\overset{-}{C}\text{-}\overset{+}{Sb}Ph_3$	
$^m/_e$	corresponding fragment	$^m/_e$	corresponding fragment
462 464	M^+	352 354	$[Ph_3Sb]^{+\cdot}$
385 387		275 277	
352 354	$[Ph_3Sb]^{+\cdot}$	273 275	
275 277		198 200	$[PhSb]^{+\cdot}$
273 275		155	$[C_7H_7SO_2]^+$
198 100	$[PhSb]^{+\cdot}$	154	
154		152	
152		139	$[C_7H_7SO]^+$
78	$[C_6H_6]^{+\cdot}$	121	$[C_7H_7S]^+$
		91	$[C_7H_7]^{+\cdot}$
		78	$[C_6H_6]^{+\cdot}$

authors[45] compared it to that obtained for tri(*p*-tolyl)-stibine oxide which was also found to have a very low dipole moment. However, in view of the recent findings on the structure of triphenylstibine oxide, and hence most probably the tri(*p*-tolyl)stibine oxide, this low dipole moment is not unreasonable.

With the isolation of these new stibonium ylides, it was possible to carry out more dipole moment measurements. The dipole moments of triphenylstibonium 2,6-dioxocyclohexylide and triphenylstibonium bis(phenylsulphonyl)methylide have thus been determined and, for comparative purposes, the dipole moments of their arsonium analogues.[46] The results obtained are shown in Table 12.

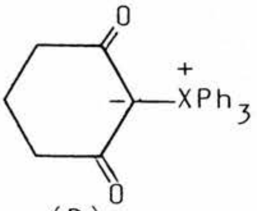
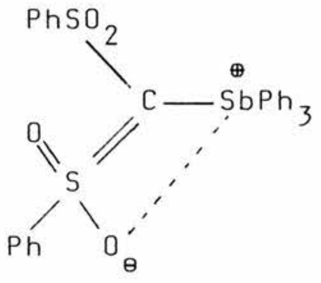
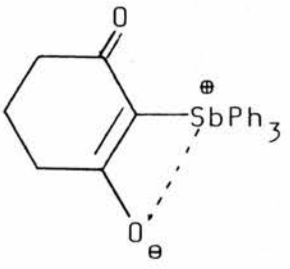
X	$(PhSO_2)_2\overset{-}{C}-\overset{+}{X}Ph_3$ μ(D)	 μ(D)
As	7.96	3.62
Sb	7.85	3.78

Table 12

As can be seen, there is virtually no change in the dipole moments on going from X = As to X = Sb. Although these results are not as dramatic as those in the series *(87)*, they are certainly contrary to what might be expected from consideration of the relative abilities of arsenic and antimony to participate in π-bonding. However, the lower than expected dipole moments of these stibonium ylides can again be explained by contributions to the structures from the resonance forms *(88)* and *(89)* where there is electrostatic interaction between the positively charged antimony and the negatively charged oxygen atoms of the α-substitutents.



(88)



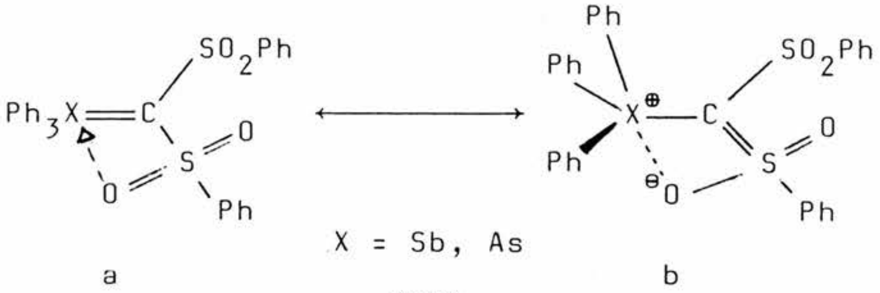
(89)

Although such interaction is also possible in the arsonium ylides, it has been found to be appreciably stronger, and therefore of greater significance, in the stibonium ylides. (See next section.)

5. X-RAY STRUCTURES

(a) *TRIPHENYLSTIBONIUM BIS(PHENYLSULPHONYL)METHYLIDE*

The isolation of suitable crystals of triphenylstibonium bis(phenylsulphonyl)methylide *(14)* enabled the first x-ray crystallographic investigation of a stibonium ylide to be carried out;[14] the crystals contained chlorobenzene of solvation, but there was no evidence for close contacts between the chlorobenzene and the ylide molecules. The results provide evidence for the interaction between antimony and oxygen which has been proposed as an explanation for the unexpected results discussed in previous sections. The x-ray analysis has shown that the structure and conformation of this ylide are as shown in *(90a and b)*.



(90)

Evidence to support this is as follows. (See also figure 2a which shows all significant bond lengths and angles, and page 110.)

i) The C-Sb ylide bond is relatively short [2.042 (3) Å] indicating appreciable double-bond character. This value lies between the sums of the covalent radii of singly-bonded and doubly-bonded carbon and antimony (2.18, 1.975 Å)[13], but is significantly nearer to the value for a double bond than is the case for the corresponding bond in arsonium ylides.[97]

ii) The ylidic carbon has a near trigonal planar configuration.

iii) One S-O bond is noticeably longer [1.454(3) Å] than the other three [1.436(3), 1.435(3), 1.433(3) Å].

iv) The bond angle Sb-C-S(1) [112.0(2)°] is much smaller than the bond angle Sb-C-S(2) [123.9(2)°], and also, the bond angle C-S(1)-O(11) [103.3(2)°] is smaller than the other C-S-O angles [107.9(2), 108.9(2) and 113.4(2)°]. These angles can only be explained by the presence of some attractive force between Sb and O(11) which pulls O(11) towards the antimony atom.

(v) The ylidic carbon-sulphur bond is short for a single bond.[98]

(vi) The configuration of the antimony atom lies between that of a tetrahedral atom and a trigonal bipyramid, as commonly found in pentacoordinate antimony compounds[99], thus resembling pentaphenylantimony.[100] The apical positions are occupied by O(11) and by one of the phenyl groups, which is attached to antimony by a longer bond [2.124(4) Å] than are the other two phenyl groups [2.099(3) and 2.100(3) Å]. This could explain the loss of a phenyl group from the molecular ion of the ylide in the mass spectrum: since one antimony--phenyl bond is longer than the other two, it is presumably also weaker.

(vii) The distance apart of O(11) and the antimony atom is 2.844(3) Å, about 0.5 Å less than the sum of the van der Waals' radii[101], whereas the distance between O(21) and the antimony atom is 3.447(3) Å.

(viii) The antimony-phenyl bonds are shorter than those previously recorded.[99,100,102] This may be due to the effect of the positive charge on the antimony atom. However, no dimensional information for comparative purposes was available at this point concerning tetraphenylstibonium cations. This was later resolved when the x-ray structures of a series of compounds of general formula, Ph_4SbX were obtained[103a] - see sections 5d, e and f.

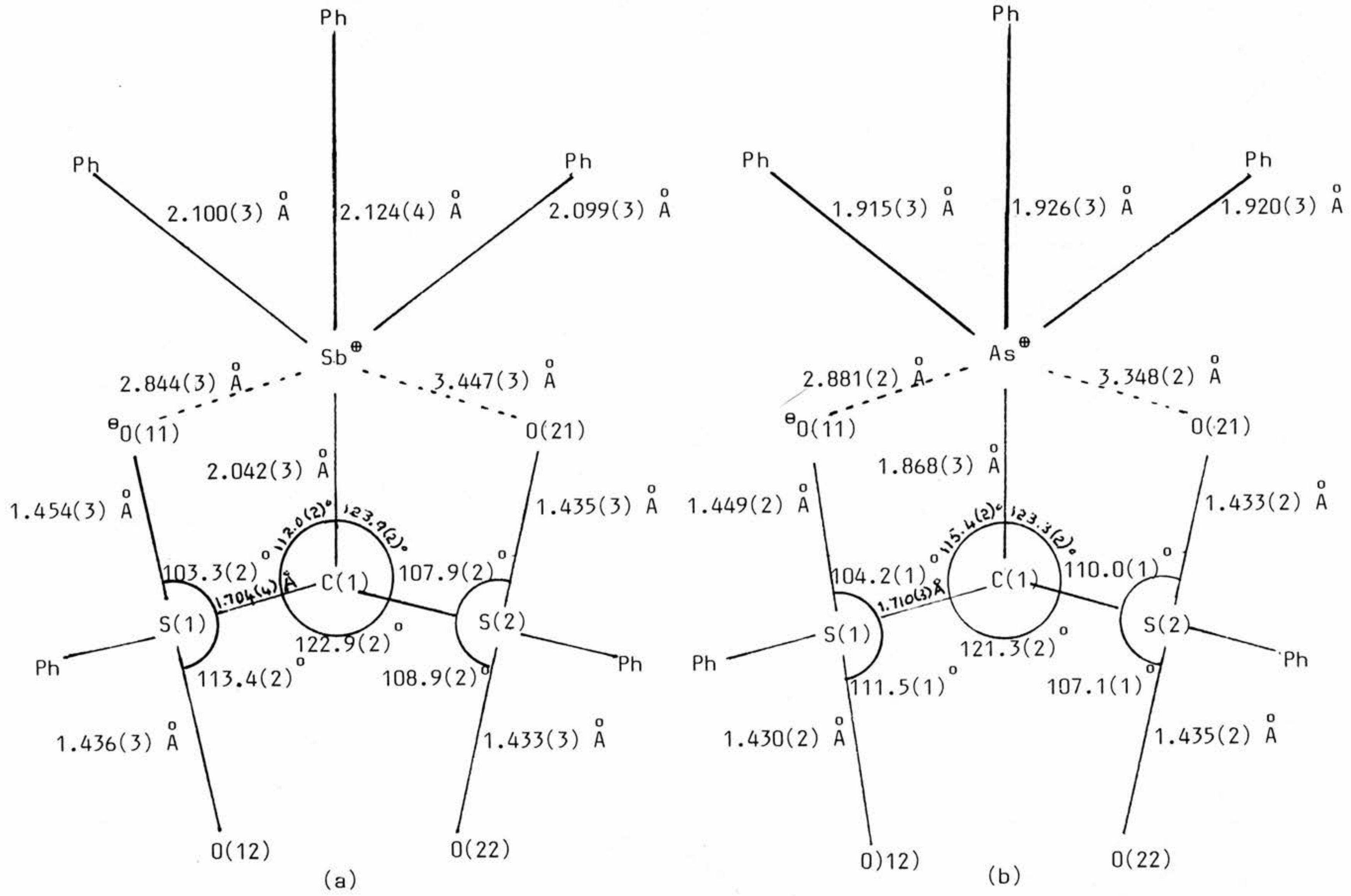
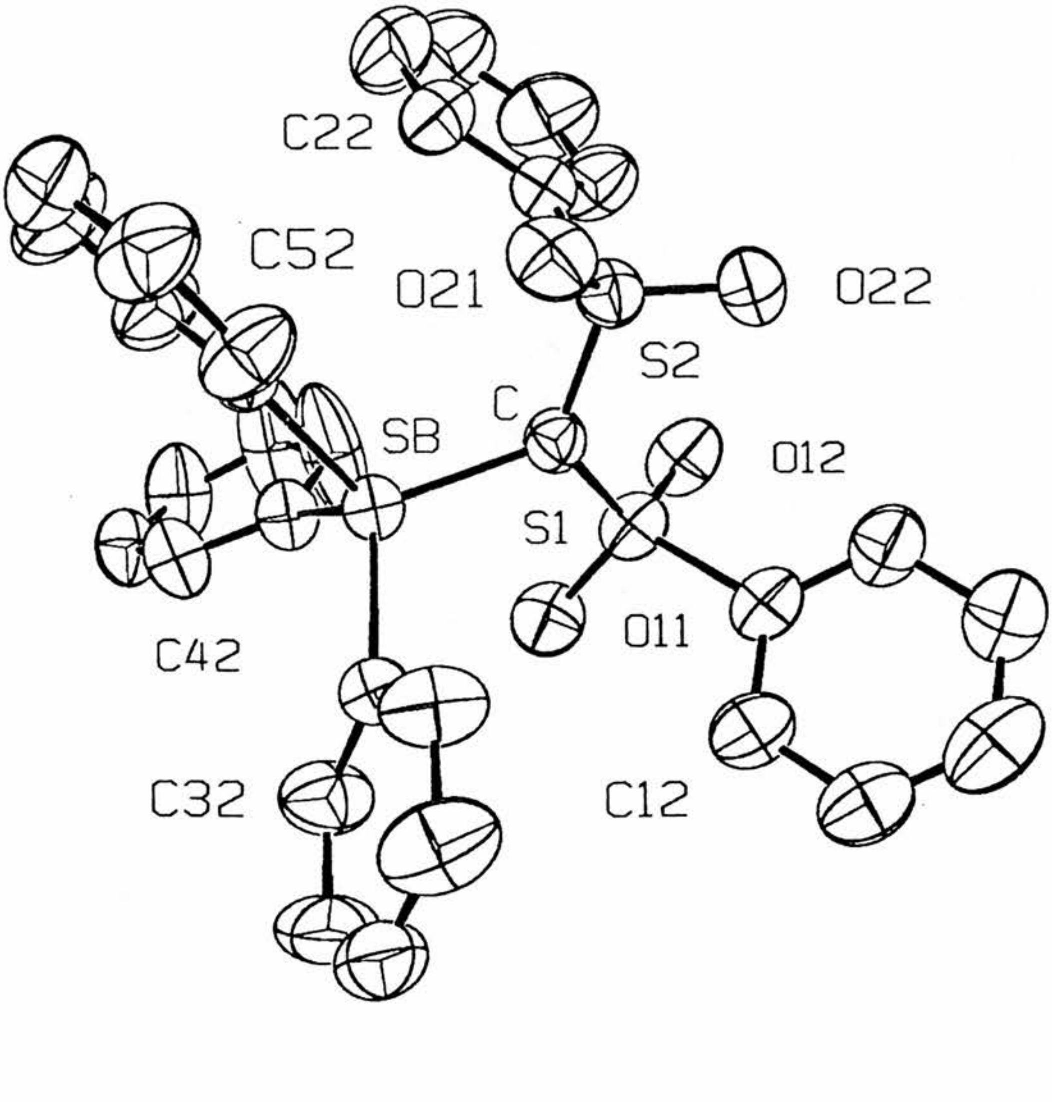
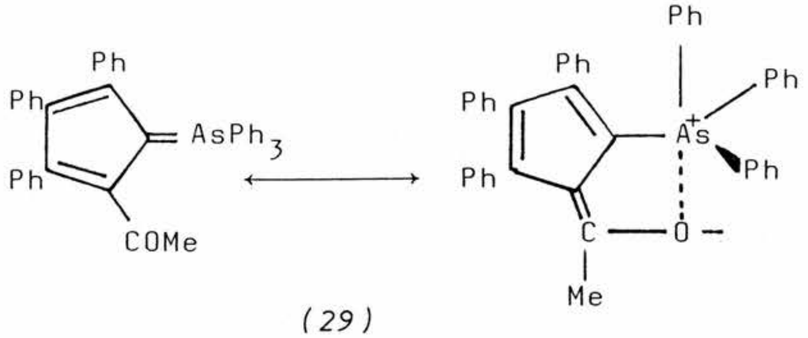

Ph
Ph
Ph
2.100(3) Å
2.124(4) Å
2.099(3) Å
Sb⊕
2.844(3) Å
3.447(3) Å
⊖O(11)
O(21)
2.042(3) Å
1.454(3) Å
1.435(3) Å
112.0(2)°
123.9(2)°
103.3(2)°
1.704(4) Å
C(1)
107.9(2)°
S(1)
S(2)
Ph
Ph
122.9(2)°
113.4(2)°
108.9(2)°
1.436(3) Å
1.433(3) Å
O(12)
O(22)
(a)
Ph
Ph
Ph
1.915(3) Å
1.926(3) Å
1.920(3) Å
As⊕
2.881(2) Å
3.348(2) Å
⊖O(11)
O(21)
1.868(3) Å
1.449(2) Å
1.433(2) Å
115.4(2)°
123.3(2)°
104.2(1)°
1.710(3) Å
C(1)
110.0(1)°
S(1)
S(2)
Ph
Ph
121.3(2)°
111.5(1)°
107.1(1)°
1.430(2) Å
1.435(2) Å
O)12)
O(22)
(b)

Figure 2


C22
C52
O21
O22
S2
C
SB
O12
S1
O11
C42
C32
C12

These results show that the metal-atom coordination in this ylide is very similar to that found in triphenylarsonium 2-acetyl-3,4,5-triphenylcyclopentadienylide where there is also such interaction between arsenic and oxygen *(29)*, and the apical phenyl group is again attached to the arsenic atom by a longer bond than are the other two phenyl groups.[42]

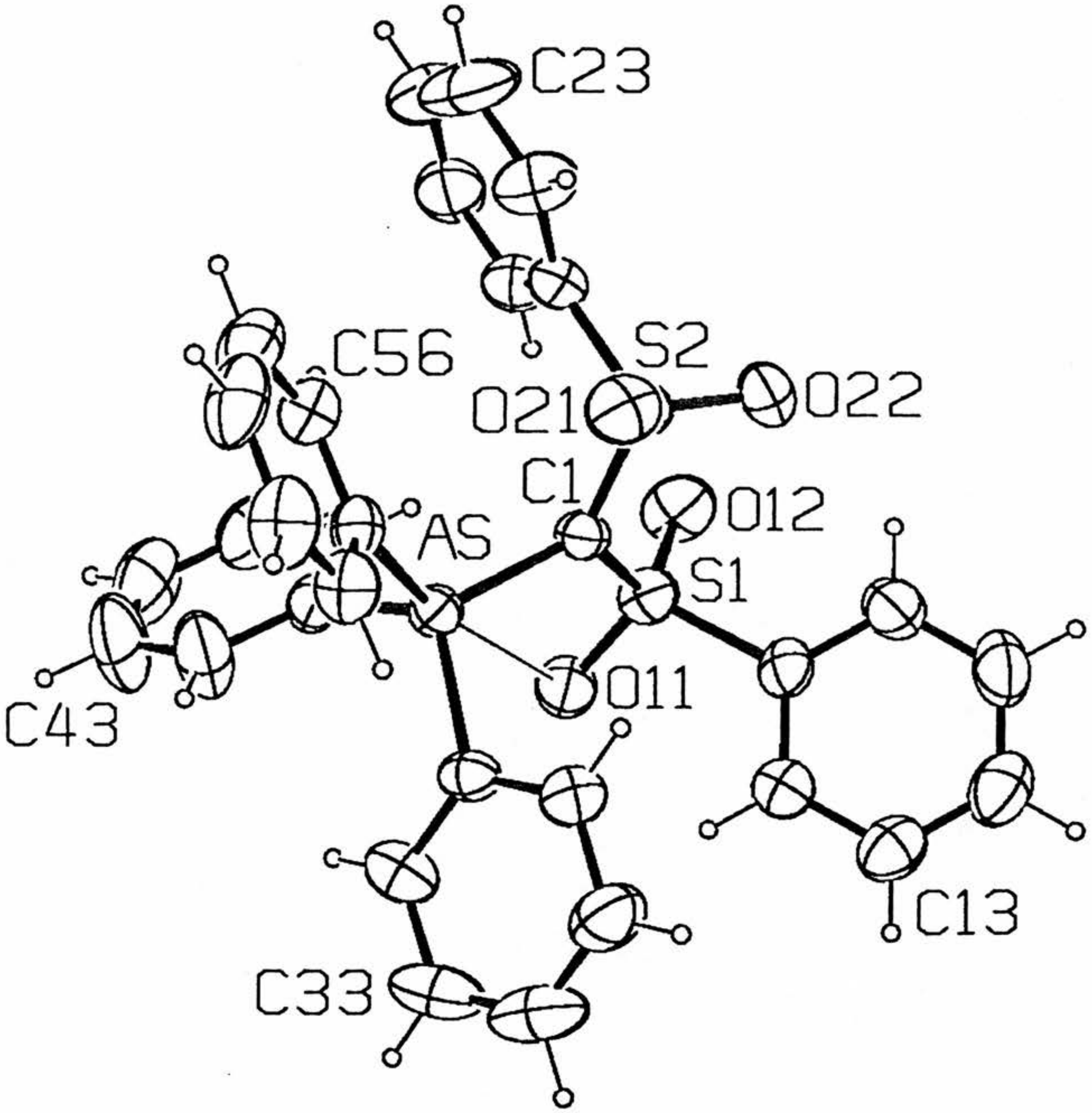


(29)

However, the ylidic bond of the stibonium ylide *(14)* would appear to have relatively more double-bond character than that of *(29)*.

(b) TRIPHENYLARSONIUM BIS(PHENYLSULPHONYL)METHYLIDE

To enable a fairer comparison of the relative heteroatom--oxygen interactions to be made (Sb-O *vis-a-vis* As-O), an x-ray structure determination of triphenylarsonium bis(phenylsulphonyl)methylide was also obtained. The results show that the structure and conformation of this ylide are very similar to those of the stibonium ylide *(14)*, [see *(90a and b)*], and reveal that the interaction between arsenic and oxygen is weaker than that between antimony and oxygen. Indeed the As-O distance is longer than the Sb-O distance by 0.04 Å (See Figure 2b which shows all significant bond lengths and angles,

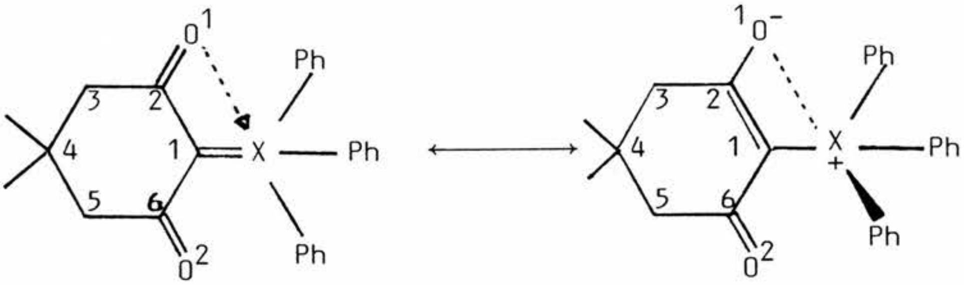

C23
C56
S2
O21
O22
C1
O12
AS
S1
O11
C43
C13
C33

and also page 112 for perspective view of ylide.)

One further point of interest to note is that *(90b)* resembles closely the transition state of an intramolecular Wittig-type reaction. This will be found to be of significance when considering the reactions of these ylides.

(c) *TRIPHENYLSTIBONIUM- AND TRIPHENYLARSONIUM 4,4-DIMETHYL-2,6-DIOXOCYCLOHEXYLIDES*

To provide another direct comparison of the heteroatom--oxygen interaction on going from arsonium to stibonium ylides, the structures of the title compounds were determined by x-ray crystallography.[103b] The structure and conformation of these ylides are shown in *(91a and b)* where once more there is interaction between the heteroatom and one of the α-oxygen atoms.



X = As, Sb

(91)

Evidence for such structures is of a similar nature to that listed for triphenylstibonium and triphenylarsonium bis(phenylsulphonyl)methylides. (See also figures 3a and b which again show all significant bond lengths and angles.)

(i) The X-C ylidic bond lengths indicate significant double bond character which is greater for X = Sb.

(ii) The bond angles $X-C_1-C_2$ are appreciably smaller than the bond angles $X-C_1-C_6$, and, to a lesser degree, the bond angles $O_1-C_2-C_1$ are smaller than the bond angles $O_2-C_6-C_1$. Again this is more pronounced in the stibonium ylide, and is indicative of some interaction which pulls O_1 towards the heteroatom and which does so more strongly for X = Sb.

(iii) The C_1-C_2 bond is short for a single bond and, in the stibonium ylide, is significantly shorter than the C_1-C_6 bond. $[\delta(C_1-C_2)/(C_1-C_6)] = 0.019$ and 0.067 Å for X = As and X = Sb respectively.

(iv) In the stibonium ylide, one phenyl group is attached to antimony by a longer bond than are the other two.

(v) The distance apart of the oxygen atom, O_1, and the heteroatom is much less than the $X-O_2$ distance, and indeed, as in the bis(phenylsulphonyl)methylides, the $Sb-O_1$ distance is shorter even than the corresponding $As-O_1$ distance.

In the stibonium ylide, the cyclohexane ring has a distorted boat conformation with some atoms disordered over two sites with a 2/3 : 1/3 ratio: if the carbon atoms 1 - 4 are considered to form a plane, then C_5 and C_6 are continually moving from one side of this plane to the other. The best fit of the x-ray data to a complex physical phenomenon provides two structures, corresponding to the two energy minima, and hence two independent sets of bond lengths. This phenomenon is evidently due to the very strong Sb-O

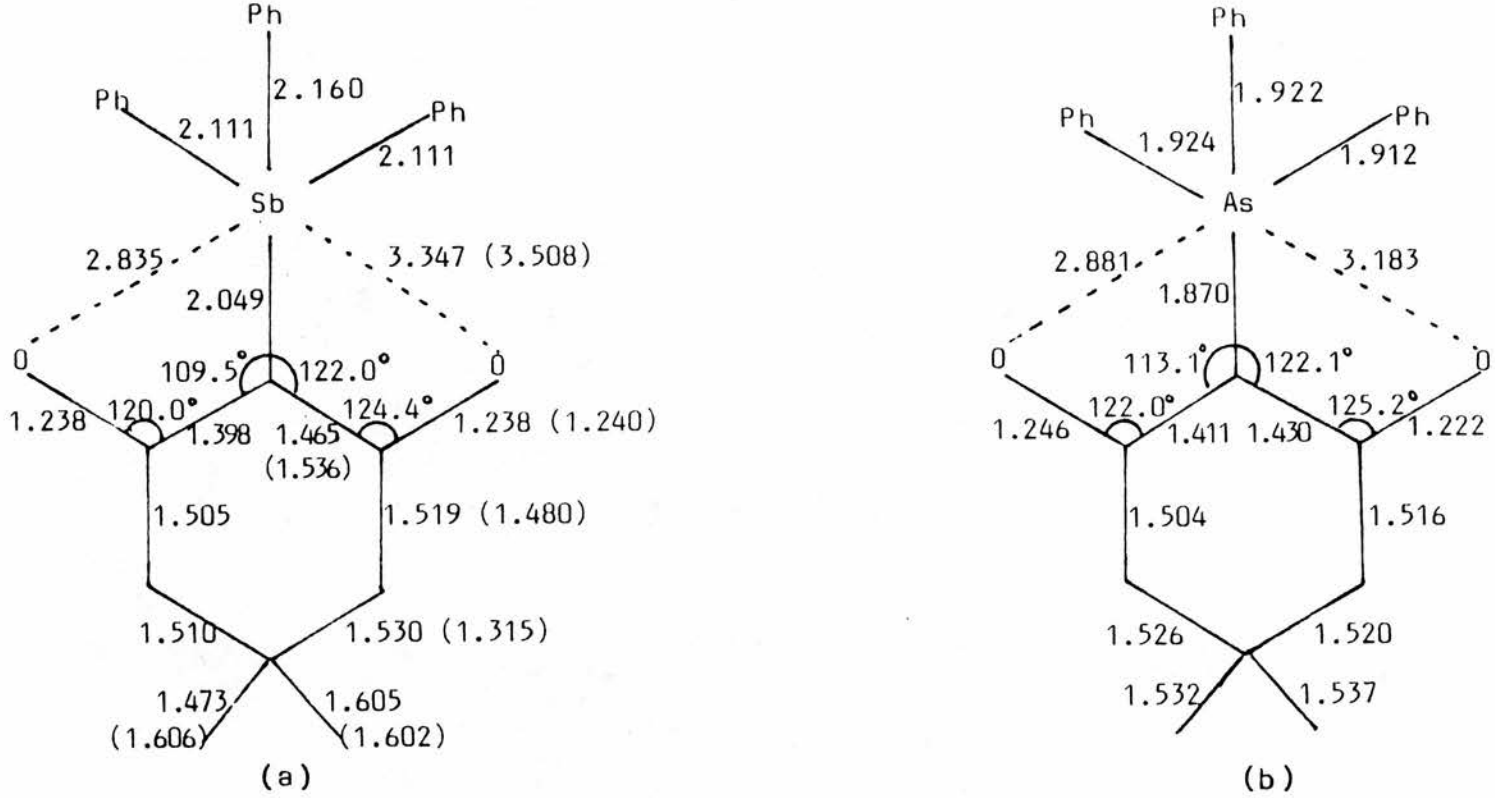


Figure 3

Bond lengths in Å

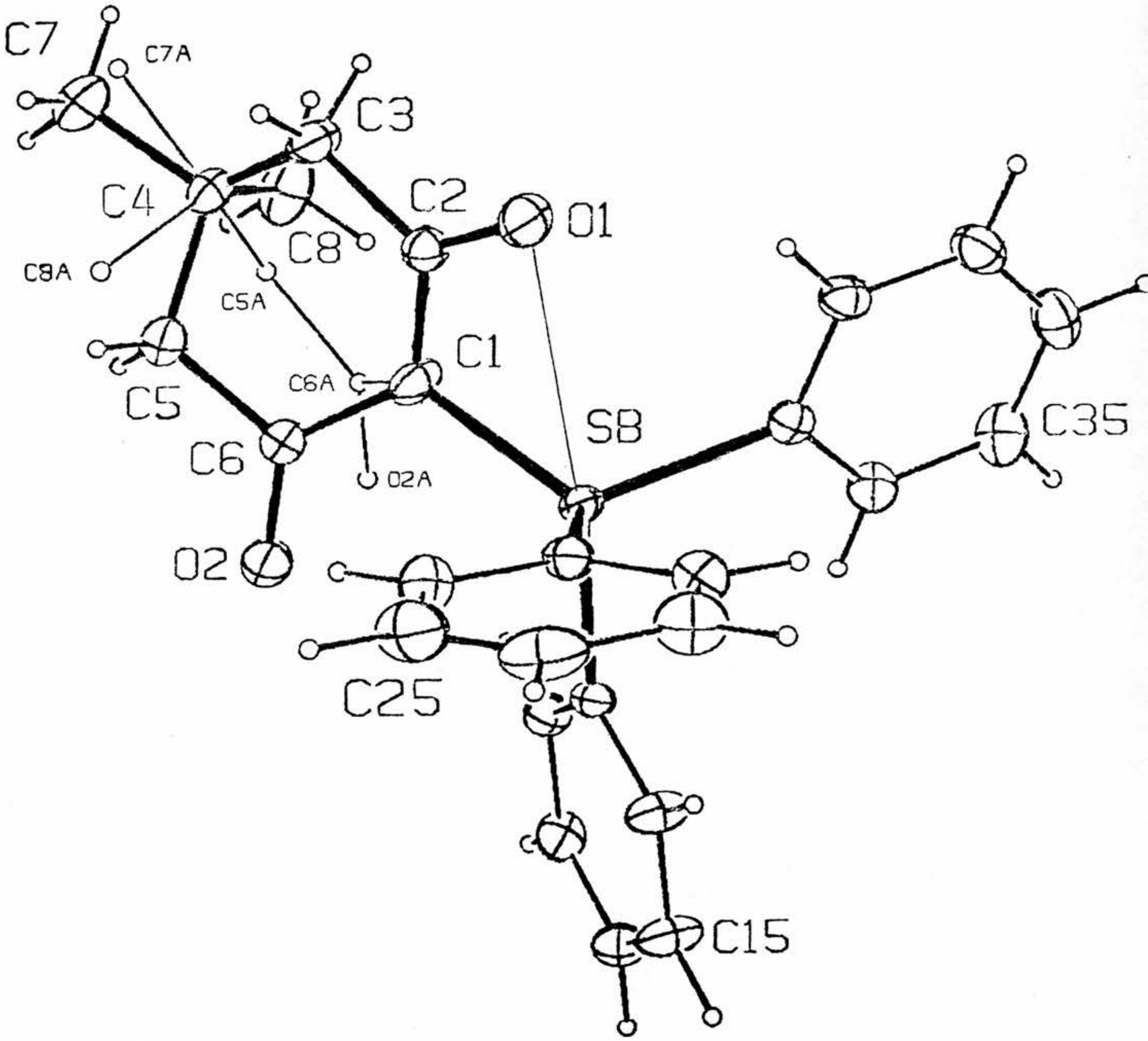
interaction present in the molecule, which must hold C_1-C_4 of the ring fairly rigidly allowing C_5 and C_6 to flap backwards and forwards (see page 117 for perspective view of this ylide).

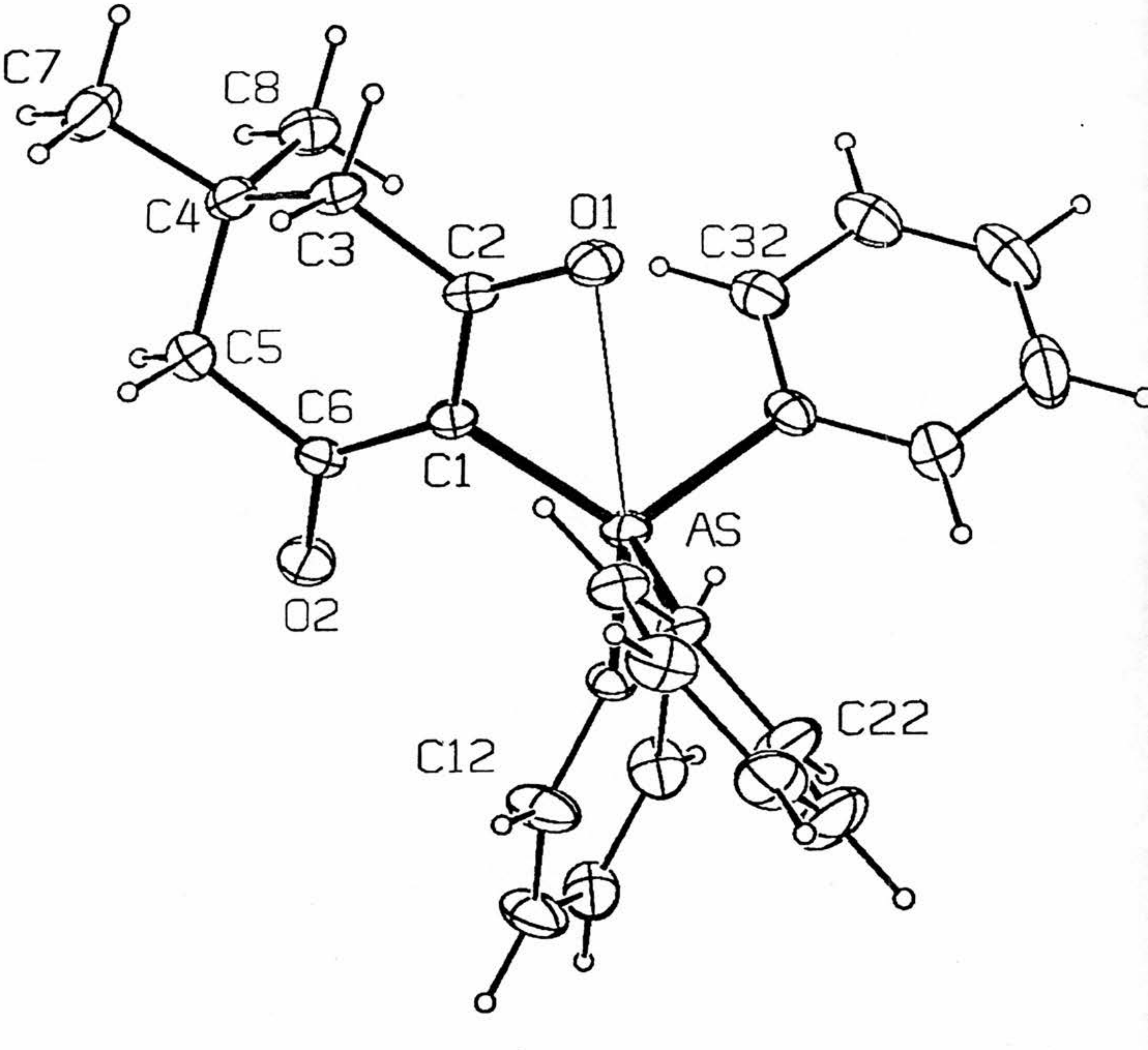
There is no such distortion in the arsonium ylide since the As-O interaction is much weaker. Consequently the cyclohexane ring of this ylide has an envelope conformation (see page 118).

(d) *TETRAPHENYLSTIBONIUM TETRAPHENYLBORATE*

Having established the ylidic Sb-C bond lengths in triphenylstibonium bis(phenylsulphonyl)methylide and triphenylstibonium 4,4-dimethyl-2,6-dioxocyclohexylide, and found that they are significantly shorter than the corresponding Sb-phenyl bond lengths, it was necessary to obtain dimensional information on an unperturbed tetrahedral Ph_4Sb^+ cation for comparison.

A sample of Ph_4SbBPh_4[104] was therefore prepared (*via* Ph_4SbBr[105], Reaction 34), and an x-ray structure analysis carried out. The results,[103a] however, show that the crystals contain two types of disorder, 1) distributional disorder of the boron and antimony between the tetrahedral ions, and 2) disorder in the orientation of these ions, so that each ion has eight part-weight phenyl rings. In effect, no useful data could be obtained from such a structure.


C7
C7A
C3
C4
C2
O1
C8A
C8
C5A
C1
C5
C6A
SB
C35
C6
O2A
O2
C25
C15


C7
C8
C4
C3
C2
O1
C32
C5
C6
C1
AS
O2
C22
C12

$$\begin{tikzcd}
Ph_3Sb + AlCl_3 \arrow[r] & {[Ph_3SbAlCl_3]} \arrow[r, "PhBr"] & {[Ph_4Sb^+][AlCl_3{}^-Br]} \arrow[r, "KBr"] & Ph_4SbBr \arrow[d, "NaBPh_4"] \\
 & & & {[Ph_4Sb^+][BPh_4{}^-]}
\end{tikzcd}$$

Reaction 34

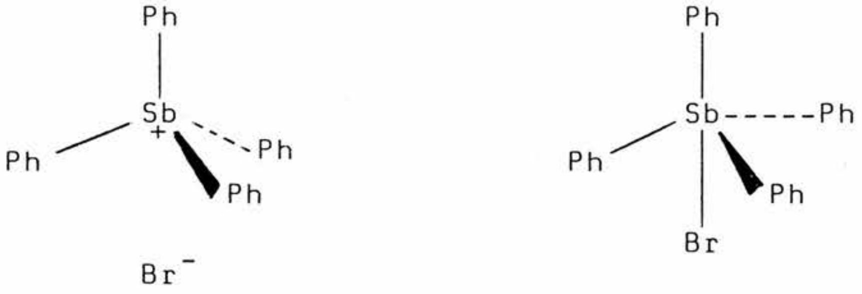
X-ray structure analyses of crystals of Ph_4SbBr and Ph_4SbClO_4 (prepared by treatment of Ph_4SbBr with sodium perchlorate) were then obtained in the hope that they would provide the desired dimensional information.

(e) *TETRAPHENYLANTIMONY(V) BROMIDE*

The results of this analysis show that the bromo-compound consists of isolated trigonal bipyramidal molecules with the bromine atom occupying an apical site just as oxygen occupies an apical site in Ph_4SbOH[102b] and Ph_4SbOMe.[102a] The apical Sb-C distance (2.151 Å) is longer than the equatorial Sb-C distances (mean value 2.102 Å) again as found in Ph_4SbOH and Ph_4SbOMe, and also in $(Ph_3SbO)_2$[106,107] and trigonal bipyramidal Ph_5Sb.[108]

Although these Sb-C distances are typical, the Sb-Br distance (2.965 Å) is significantly longer than the values found in $SbBr_3$[109] (2.490 Å), $Ph_2SbBrCl_2$[110] (2.446 Å) and Ph_2SbBr_3[110] (equatorial 2.478, apical 2.557 and 2.673 Å), but a good deal less than the sum of the van der Waals' radii[101] (about 4.0 Å).

The mean C_{eq}-Sb-C_{ax} angle is 95.8° which indicates a distortion of the Ph_4Sb- portion of the molecule away from a regular trigonal bipyramid towards a tetrahedron. This, in conjunction with the long Sb-Br bond length would suggest that the structure of Ph_4SbBr is intermediate between a salt and a stiborane (as represented by *92a* and *b* respectively) but with a greater contribution from the latter. See also page 122.



(a) *(b)*

(92)

This result complements some unpublished work carried out in the Chemistry Department at St. Andrews University by Dr. G. Harris and Dr. A. Khan. This work involved an investigation into the conductivities of the series of compounds Ph_4SbX, X = F, Cl, Br, I. It was found that Ph_4SbF and Ph_4SbCl were very poor conductors of electricity, Ph_4SbBr was a moderate conductor and Ph_4SbI was an excellent conductor. It was thus concluded that Ph_4SbF and Ph_4SbCl have molecular structures and that Ph_4SbI is ionic. It was predicted that Ph_4SbBr would have a structure neither wholly covalent nor wholly ionic, and this has been shown to be the case.

(f) *TETRAPHENYLANTIMONY(V) PERCHLORATE*

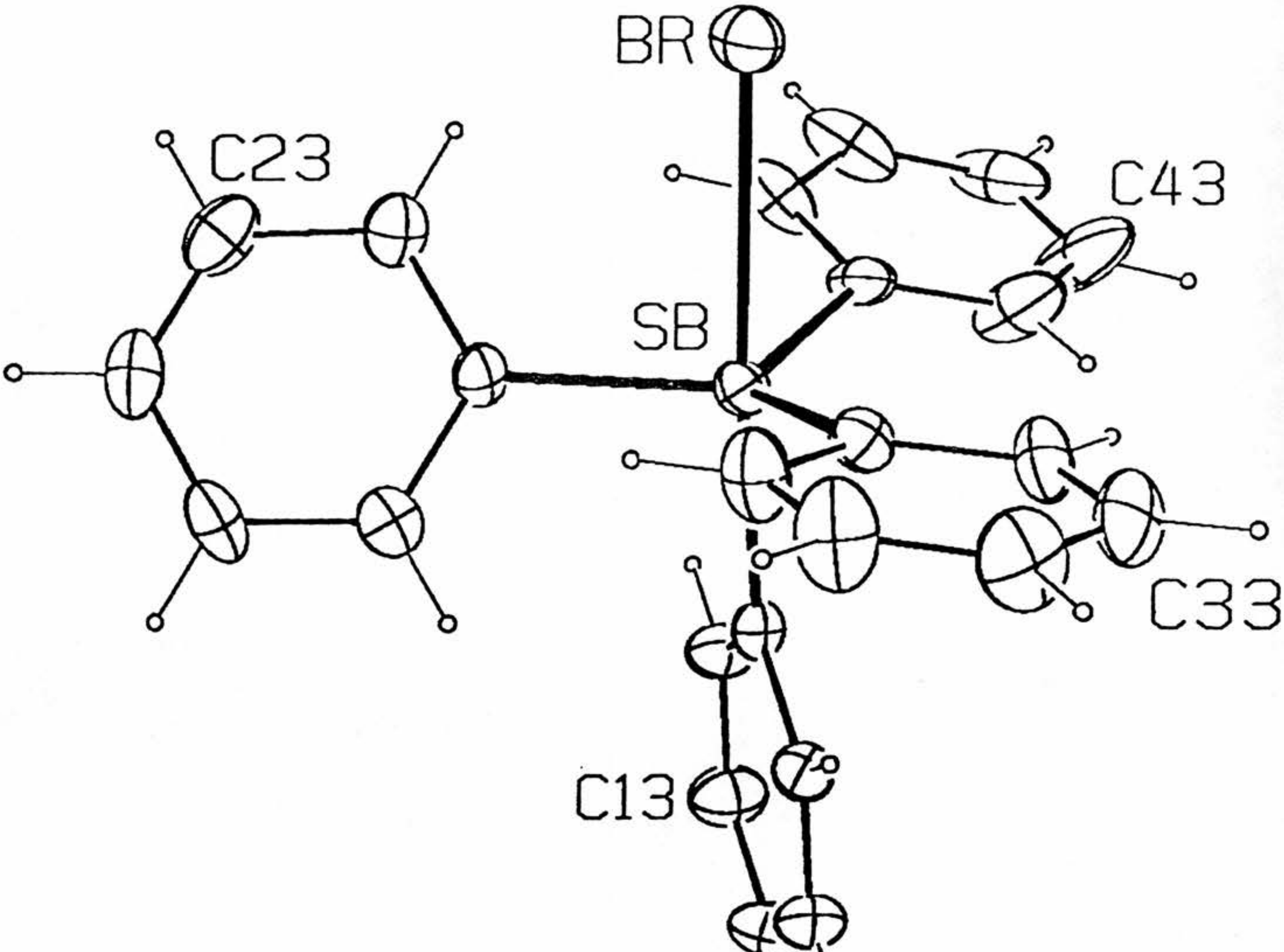
The results of this x-ray analysis show that Ph_4SbClO_4 is a completely ionic salt with regular tetrahedral Ph_4Sb^+ cations (C-Sb-C bond angles are 109.44°) and tetrahedral ClO_4^- anions. The unique Sb-C bond length is 2.095(2) Å which is only slightly shorter than the corresponding Sb-C bond lengths of the Ph_3Sb^+- portions of the stibonium ylides (2.099 - 2.160 Å), but significantly longer than the Sb-C ylidic distances. This confirms the importance of the covalent canonical forms *(90a)* and *(91a)*, X = Sb. As would be expected, the Sb-C distances in 5-coordinate Sb species are longer than 2.095 Å *e.g.* Ph_4SbOH,**[102b]** Ph_4SbOME,**[102a]** Ph_5Sb.**[108]** See page 123 for perspective view of the Ph_4Sb^+ cations, and page 124 which illustrates the packing arrangement of Ph_4Sb^+ cations and ClO_4^- anions.

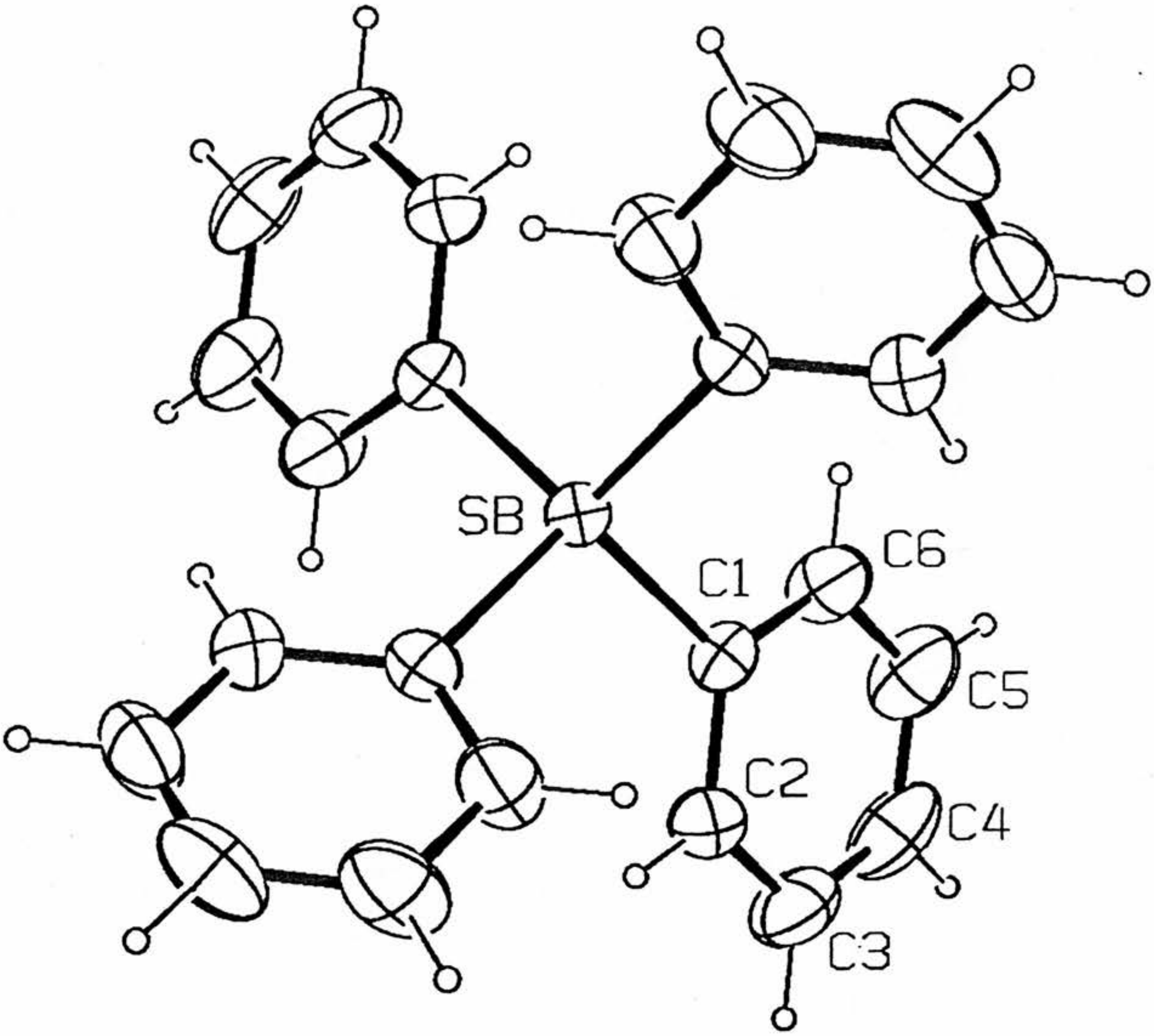
In conclusion, several important results have emerged from these x-ray studies. They can be summarised as follows:

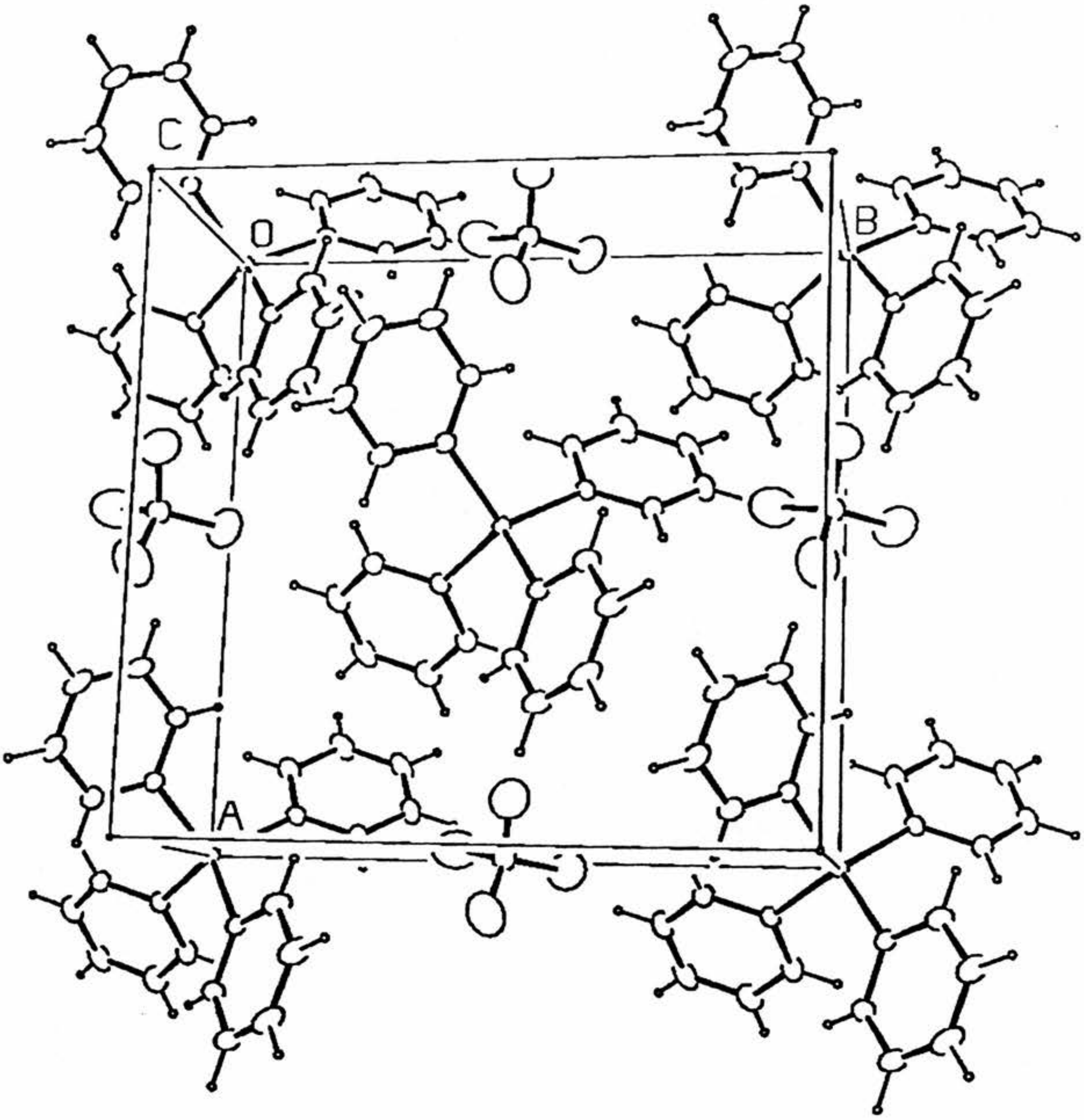
(1) The stibonium ylides have relatively more covalent character than their arsonium analogues.

(2) There appears to be an unexpectedly strong affinity between antimony and oxygen. This is exemplified by the ready decomposition of these ylides to triphenylstibine oxide, and by the isolation from reaction mixtures of compounds of the type $(Ph_3Sb\text{-}O\text{-}SbPh_3)X_2$

(3) There is a close resemblance between the structures of these ylides and the transition states of intramolecular


BR
C23
C43
SB
C33
C13


SB
C1
C6
C5
C2
C4
C3


C
O
B
A

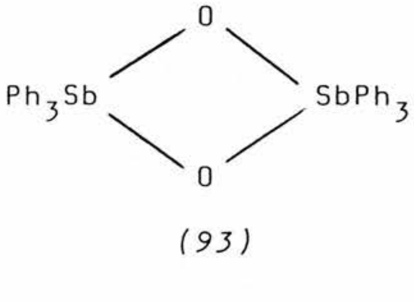
Wittig-type reactions, which will be found to have an important effect on their reactivity (see later).

(g) *TRIPHENYLSTIBINE OXIDE*

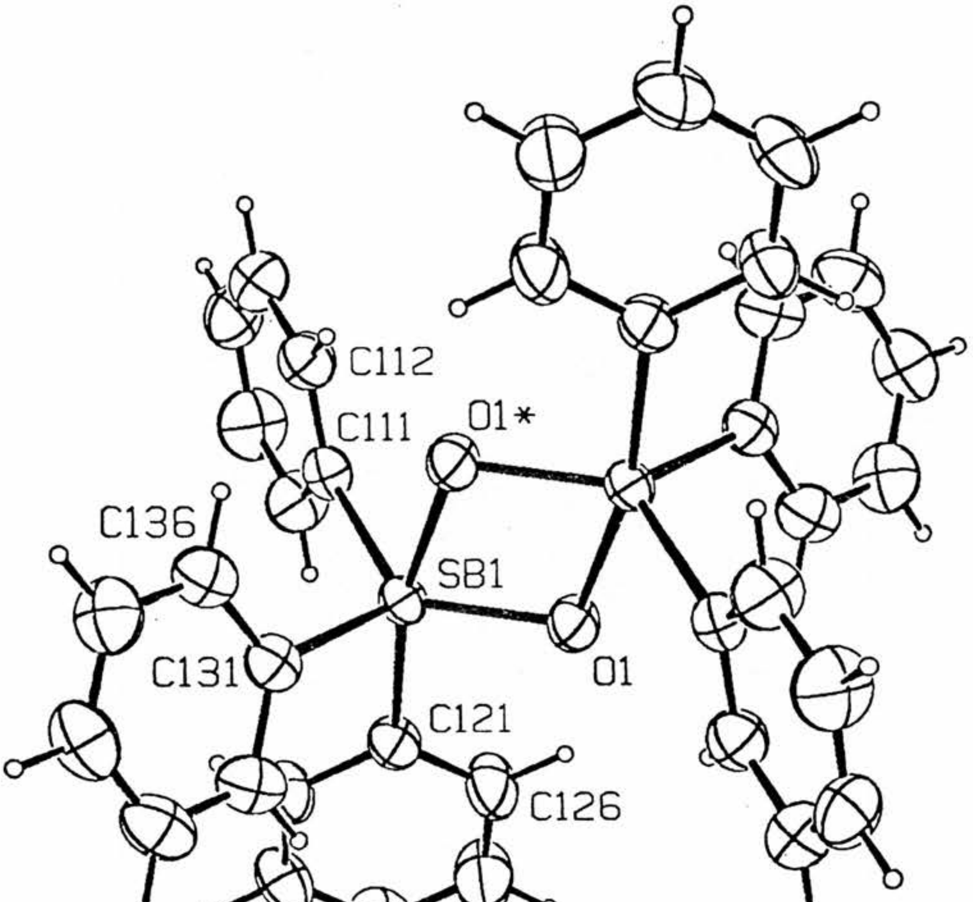
Until recently there had been much uncertainty about the structures of compounds described as triphenylstibine oxide,[90] since the inability to obtain single crystals of the compounds meant that no conclusive structural evidence could be acquired by x-ray crystallography.

However, during a recrystallisation of triphenylstibonium bis(tolyl-*p*-sulphonyl)methylide from methylene chloride and hexane, hydrolysis of the ylide ensued and large crystals of a product were obtained whose elemental analysis, and spectra, showed it to be a triphenylstibine oxide.

These crystals were therefore analysed by x-ray crystallography.[106] However, just after the results of this analysis were obtained, a paper by Bordner *et al*[107] was published characterising, by x-ray crystallography, the structure of a triphenylstibine oxide, obtained from the thermal decomposition of Ph_4SbOH. The results reported in this thesis correspond with those of Bordner and reveal the structure of the oxide to be that of a centrosymmetric dimer, *(93)* and page 126.



(93)


C112
C111
O1*
C136
SB1
C131
O1
C121
C126

Each Sb atom exhibits regular trigonal bipyramidal coordination by three carbon and two oxygen atoms. The ring oxygens occupy one apical and one equatorial site. For Sb(1) (see page 126), the apical atoms are C(121) and $O(1)^*$ and the equatorial atoms are C(111), C(131) and O(1). Of the three Sb-C distances, the apical Sb(1)-C(121) distance is significantly longer [2.161(2) Å] than the other two [2.134(2) and 2.129(2) Å]; likewise the apical $Sb(1)-O(1)^*$ distance [2.075(2) Å] is significantly longer than the equatorial Sb-O(1) distance [1.934(2) Å].

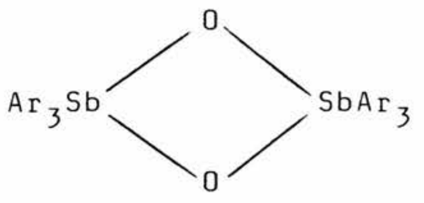
This dimeric structure found for triphenylstibine oxide is very different from that of triphenylstibine sulphide[111] which is monomeric containing near-tetrahedral antimony. The structure also accounts for the low dipole moment of the oxide (estimated as 1.65 - 1.95 D) compared with the sulphide (5.45 D).[45] It is interesting to note the differences in structure between the triaryl oxides of phosphorus, arsenic and antimony. These can be depicted most simply by *(94)*, *(95)* and *(96)* respectively,

$Ar_3P=O$

(94)

$Ar_3\overset{+}{A}s-\bar{O}$

(95)



(96)

6. REACTIONS OF STIBONIUM YLIDES

(i) *THE ATTEMPTED PREPARATION OF PERCHLORATE SALTS*

The basic nature of these ylides would suggest that they ought to form salts with suitable acids. Triphenylstibonium tetraphenylcyclopentadienylide has been found to form the corresponding perchlorate salt on treatment with perchloric acid.[36] However, this salt was found to decompose readily during recrystallisation from ethanol if left in solution for too long. With this in mind, attempts were made to prepare perchlorate salts from a number of these new stibonium ylides. The results are as follows:

(a) Treatment of triphenylstibonium bis(tolyl-*p*-sulphonyl)-methylide with perchloric acid led to hydrolysis of the ylide, and bis(tolyl-*p*-sulphonyl)methane was isolated in 76% yield.

(b) The reaction of triphenylstibonium bis(phenylsulphonyl)-methylide with perchloric acid produced a compound whose IR spectrum contained perchlorate absorptions, but no sulphonyl absorptions.

(c) Reaction of triphenylstibonium diacetylmethylide with perchloric acid produced the same compound as in (b).

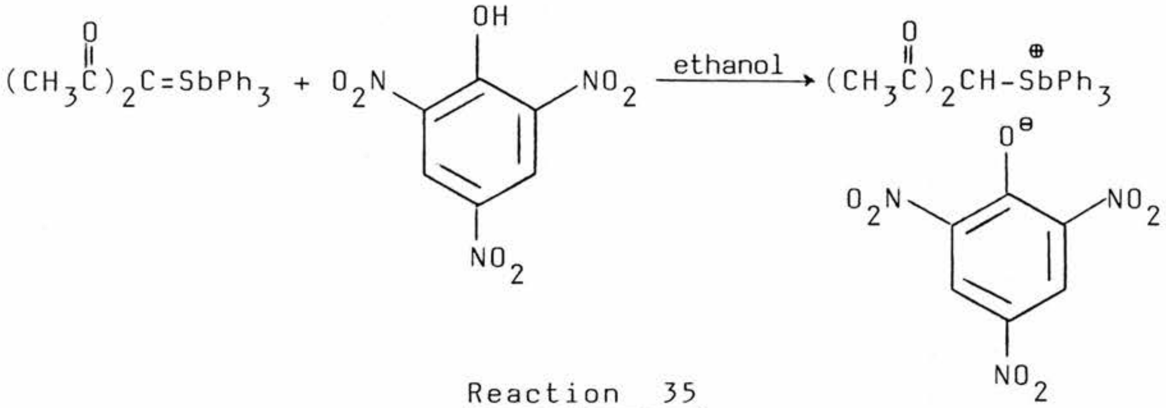
Initially this compound from (b) and (c) was thought possibly to be $Ph_3Sb^+OHClO_4^-$. Compounds of the type $Ph_3SbOH.Y$ show -OH absorption in the IR in the region where nujol absorbs, and is observable only with special mulling agents. It was not suprising, therefore, that no usual -OH absorption was seen in the IR, although broad, weak absorption at about 3300 cm^{-1} did seem to indicate the presence of hydroxyl groups. However, while surveying the literature for information on such a species, a possible alternative for the identity of this compound was found, *viz*. oxybis(triphenylantimony)diperchlorate, $(Ph_3Sb\text{-}O\text{-}SbPh_3)(ClO_4)_2$. Literature data on this compound by Doak *et al*[92] correspond with that of the compound obtained from the ylides. It is suggested[92] that this diperchlorate is an ionic species because the IR perchlorate absorptions match closely those of metallic, ionic perchlorate salts.

However, an x-ray crystallographic study[112] of $(Ph_3SbN_3)_2O$ and $(Ph_3BiClO_4)_2O$ reveals that these compounds are in fact non-ionic, containing metal-oxygen-metal bridges with trigonal bipyramidal configurations at the metal atoms. The authors of this work re-investigated the IR spectra of hydrated and anhydrous forms of $(Ph_3SbClO_4)_2O$ and concluded that the spectral data reported by Doak are more appropriate to a hydrated form of this compound. If this were the case, it would explain the observance of broad weak bands at 3300 cm^{-1} in the spectra of the products obtained from the stibonium ylides. Comparison of the IR data for the anhydrous forms of $(Ph_3SbClO_4)_2O$ and $(Ph_3BiClO_4)_2O$ led to the conclusion that the two compounds have similar structures.[112] $(Ph_3BiClO_4)_2O$ was found to be asymmetric with a Bi-O-Bi bond angle of 142.4(7)°. The two independent halves of the molecule adopt slightly distorted trigonal bipyramidal configurations with a bridging oxygen at one vertex and a perchlorate oxygen at the other.

A whole series of compounds of the type $(Ph_3Sb\text{-}O\text{-}SbPh_3)X_2$[92]

exists (*e.g.* X = Cl, Br, NO_3, ClO_4, SO_4), and it was while investigating the identity of the solid isolated from the reactions of the ylides with perchloric acid, that the identities of previously obtained compounds, namely the oxybis(triphenylstibonium)dichloride and -dibromide already mentioned, were realised.

(ii) *ATTEMPTED PREPARATION OF THE PICRATE SALT OF TRIPHENYLSTIBONIUM DIACETYLMETHYLIDE*

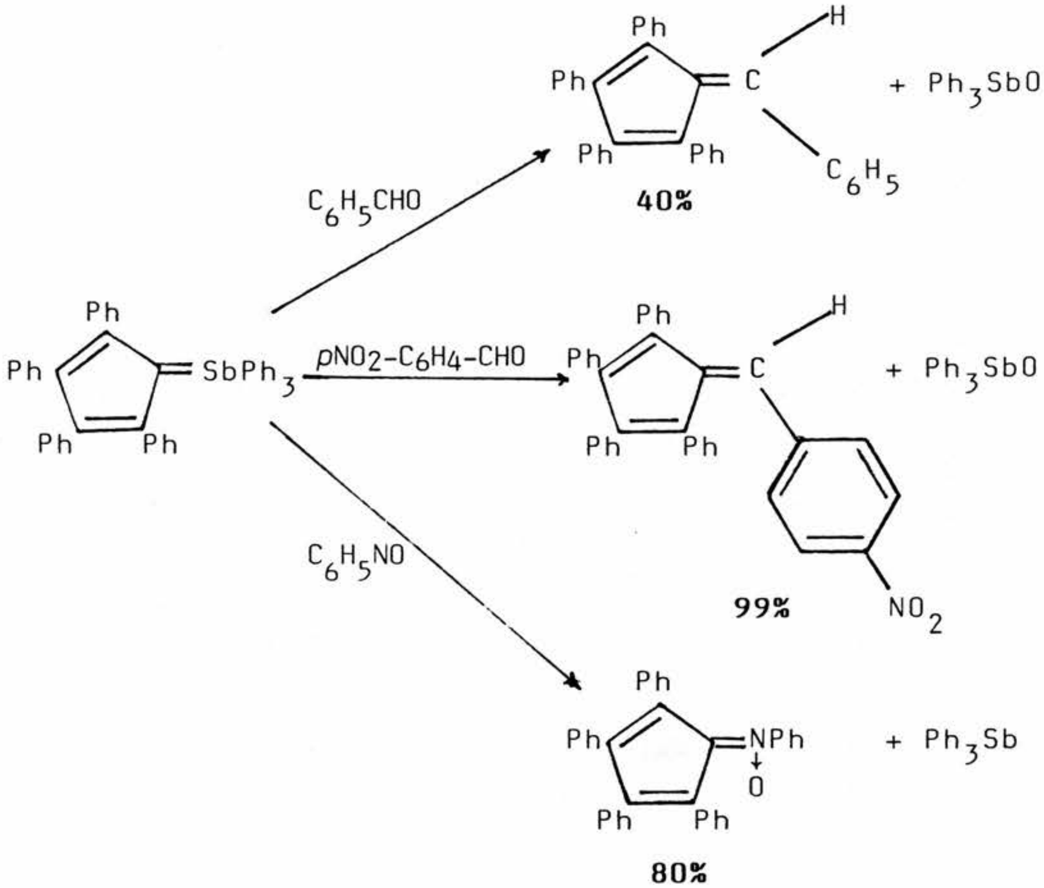


Reaction 35

Reaction of ylide with picric acid in ethanol (reaction 35) gave pale yellow solid which showed nitro and carbonyl absorption in the IR spectrum. The position of the carbonyl absorption was at a higher wavenumber (1600, 1570 cm^{-1}) than that in the spectrum of the ylide (1570, 1505 cm^{-1}) as would be expected since the acetyl groups no longer form part of a carbanionic moiety. It was found that decomposition of the salt occurred as shown by a gradual darkening of its surface. C, N, H Microanalysis of a sample recrystallised from ethanol was low in C and H, and high in N, for $C_{29}H_{24}N_3O_9Sb$.

(iii) *THE WITTIG REACTION OF STIBONIUM YLIDES*

Triphenylstibonium tetraphenylcyclopentadienylide was found to react with benzaldehyde, *p*-nitrobenzaldehyde and nitrosobenzene as shown in Scheme 19.[36]



Scheme 19

It is interesting that this ylide gave alkenes and not epoxides in these reactions, since the only other reported reaction of a stibonium ylide with a carbonyl compound, namely that of $Ph_3Sb{=}CH_2$ with benzophenone, gave Ph_3Sb and diphenylacetaldehyde, which the authors suggested was formed by rearrangement of an intermediate epoxide.[11]

These results, however, may reflect similarities between stabilised arsonium and stibonium ylides, and non-stabilised arsonium and stibonium ylides since, in general, stabilised arsonium ylides have been found to yield alkenes[36,65] in Wittig reactions, whereas non-stabilised arsonium ylides yield epoxides[66] or rearrangement products therof.

The reactions of the new stibonium ylides *(14)*, *(73)*, *(75)*, *(76)*, *(77)*, *(79)* and *(80)* with 2,4-dinitrobenzaldehyde have been investigated and also the reactions of *(75)* with *p*-nitrobenzaldehyde and with nitrosobenzene. However, in no case was there evidence for any type of reaction other than, in some cases, simple hydrolysis of the ylide. Even the mono-stabilised triphenylstibonium benzylsulphonylmethylide was unreactive towards 2,4-dinitrobenzaldehyde.

The arsonium analogues of *(14)*, *(73)*, *(76)* and *(77)*, have previously been reported to be unreactive towards 2,4-dinitrobenzaldehyde.[25] However, since the reactivity of an ylide in a Wittig reaction depends on the localisation of sufficient negative charge on the ylidic carbon, it was initially expected that these stibonium ylides would be more reactive because of the expected increase in dipolar character on going from arsonium to stibonium ylides. Evidently these simple assumptions are invalid: ^{13}C n.m.r. spectra indicate that a greater degree of negative charge is localised on the arsonium ylidic carbons than on the stibonium ylidic carbons, and x-ray analyses reveal that it is in fact the arsonium ylides which have more dipolar character. In view of these results, it is therefore not surprising that the stibonium ylides are no more reactive than their arsonium analogues. In addition, as mentioned earlier, the structures of the stibonium ylides which were determined, already resemble closely the transition states of intramolecular Wittig reactions.

The combination of these factors presumably accounts for the low reactivity of these stibonium ylides in Wittig reactions, even with highly activated substrates.

7. BISMUTHONIUM YLIDES

The stability of an ylide is influenced by the amount of pπ-dπ overlap between the ylidic carbon and the heteroatom. Thus bismuthonium ylides would be expected to be much less stable than ylides of other Group V elements (P, As, Sb) since the 6d orbitals of bismuth are probably too large and diffuse to overlap effectively with the 2p orbital of the ylidic carbon. This was indeed found to be the case in the only example of a bismuthonium ylide which has been reported, *viz*. triphenylbismuthonium 2,3,4,5-tetraphenylcyclopentadienylide, formed by the thermal decomposition of diazo-2,3,4,5-tetraphenylcyclopentadiene in the presence of triphenylbismuth.[9] This ylide was found to be reasonably stable as a solid, but decomposed rapidly in solution or by the action of acid or alkali.

The instability of this ylide and its UV spectral properties, indicated that it was very different from the analogous phosphonium, arsonium and stibonium ylides, but very similar to pyridinium 2,3,4,5-tetraphenylcyclopentadienylide, in which no pπ-dπ overlap is possible. For example, the pyridinium and bismuthonium ylides are intensely blue in colour and show solvatochromism, whereas the other ylides are yellow and do not show this effect. Thus it seems that in these ylides, bismuth behaves very much like nitrogen, the first member of Group V, rather than like antimony which is immediately above it in the group, *i.e.* as expected, bismuth cannot readily expand its valence shell.

Having successfully prepared and isolated new, stable stibonium ylides by the $Cu(hfa)_2$ catalysed decomposition of diazo-compounds in the presence of triphenylantimony, attempts were then made to prepare several bismuthonium ylides by the same method. Thus the reactions of diazo-bis-(phenylsulphonyl)methane, diazo-bis(tolyl-*p*-sulphonyl)methane and 2-diazocyclohexane-1,3-dione with triphenylbismuth in the presence of $Cu(hfa)_2$ were investigated.

From the reaction of diazo-bis(tolyl-*p*-sulphonyl)methane with Ph_3Bi, a small amount of solid was obtained whose IR spectrum looked very similar in pattern to that of the triphenylstibonium bis(tolyl-*p*-sulphonyl)methylide. However, a ^1H n.m.r. spectrum of this solid suggested that it was in fact bis(tolyl-*p*-sulphonyl)methane.

The reaction of diazo-bis(phenylsulphonyl)methane with Ph_3Bi gave a small amount of solid whose IR spectrum again looked similar in pattern to that of the analogous stibonium ylide. In this case the ^1H n.m.r. spectrum contained resonances for aromatic protons only, centred at δ 7.6. This suggests that the solid may well be triphenylbismuthonium bis(phenylsulphonyl)methylide (22%). The mass spectrum, although containing no molecular ion peak, shows peaks at m/e ratios which correspond to fragments in which the ylidic bond is still intact. Peaks corresponding to ions formed from the breakdown of both $[Ph_3Bi]^{\dot{+}}$ and the carbanionic moiety are also evident. The ylide is khaki-coloured and fairly insoluble in common solvents. Attempts to purify it by recrystallisation were unsuccessful and an analytical sample was not obtained. It decomposed slowly in the solid state to bis(phenylsulphonyl)methane.

The reaction of 2-diazocyclohexane-1,3-dione with Ph_3Bi was also investigated. When the reactants were heated under reflux in benzene for 1.25 hours, khaki-coloured solid was obtained which, from spectral evidence, appeared to be triphenylbismuthonium 2,6-dioxocyclohexylide (28%). When the reactants were heated under reflux for 2.5 hours, the yield increased to 42%. This ylide was extremely insoluble in all common solvents and could not be recrystallised. However, a ^1H n.m.r. spectrum was obtained of a sample in d^5-pyridine. This spectrum resembled closely the spectra of the analogous arsonium and stibonium ylides, with integral ratios of the correct order. The IR spectrum showed no normal carbonyl absorption, but the nujol absorptions at around 1400 cm^{-1} were extremely broad. The carbonyl absorptions would be expected to be at lower wave-numbers than in the analogous stibonium ylide (1500 and 1585 cm^{-1}), and so it is possible that they appear as low as 1400 cm^{-1}. An IR spectrum of the ylide was therefore obtained using hexachlorobuta-1,3-diene as a mulling agent which has no absorptions in this region. This spectrum shows clearly a broad intense absorption centred at 1440 cm^{-1}.

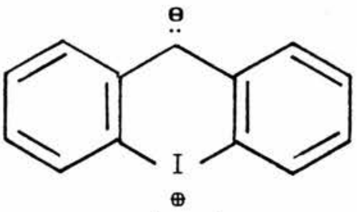
The mass spectrum of this ylide contains no molecular ion peak, but shows peaks at m/e ratios corresponding to fragments from the breakdown of $[Ph_3Bi]^{+\cdot}$ and also from the carbanionic moiety. This ylide appears to be reasonably stable, remaining unchanged even after several months. Its reaction with 2,4-dinitrobenzaldehyde was investigated but even after 6 hours under reflux in benzene, no change was detected.

Considering the structures of the stibonium ylides, where there is interaction between the antimony atom and the oxygen atoms of the α-substituents, it is possible that there is similar such interaction in this bismuthonium ylide. This factor, combined with the probable deficiency of negative charge on the ylidic carbon, as indicated by the low carbonyl absorptions in the infrared, may well account for the lack of reactivity shown by this ylide towards 2,4-dinitrobenzaldehyde.

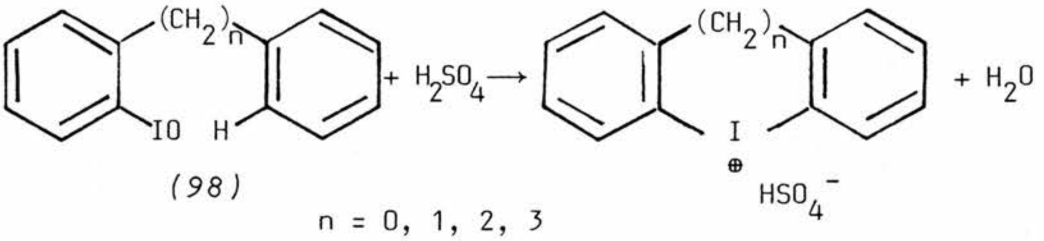
An attempt to prepare triphenylbismuthonium diacetylmethylide by the reaction of triphenylbismuth dichloride with acetylacetone in the presence of triethylamine was unsuccessful, resulting in the formation of a black intractable tar.

8. IODONIUM YLIDES

Interest in the iodonium ylide *(97)* stemmed from a review on organic polyvalent compounds.[113] In this review the ring closure of a series of iodoso compounds *(98)* was discussed (Reaction 37).



(97)

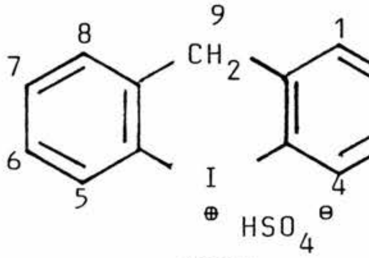


(98)

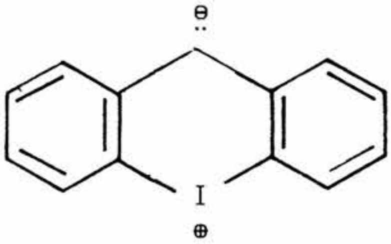
n = 0, 1, 2, 3

Reaction 37

Most interesting is the case where n = 1, since this would give compound *(99)* with an acidic proton on carbon 9. It was hoped that by removal of this proton from *(99)*, the novel ylide *(100)* could be formed and isolated.

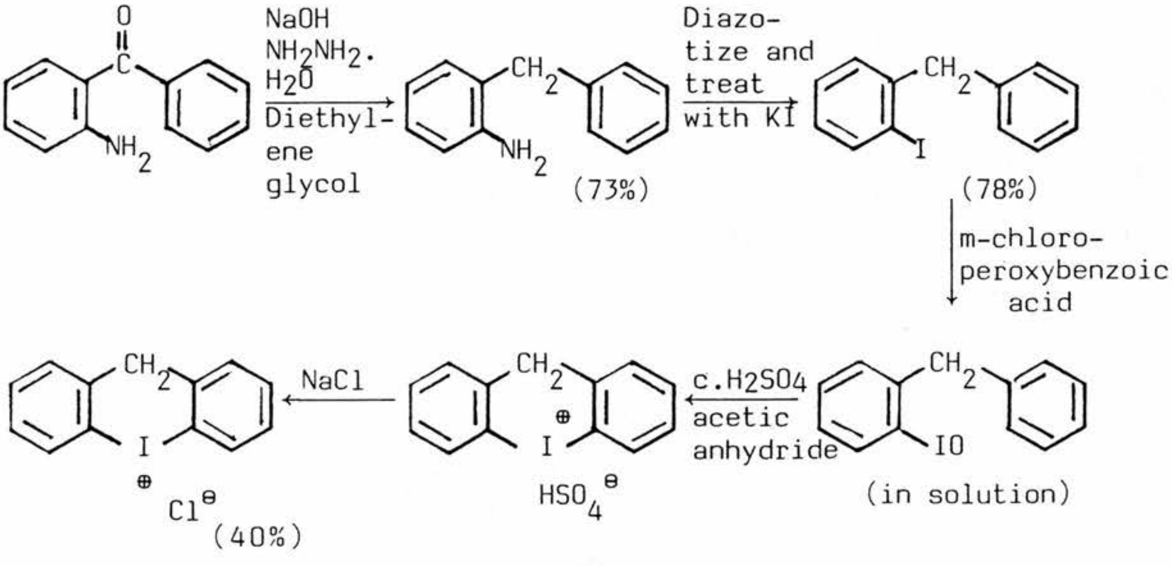


(99)



(100)

The salt *(101)* was therefore prepared according to the set of reactions in Scheme 20.[114,115]

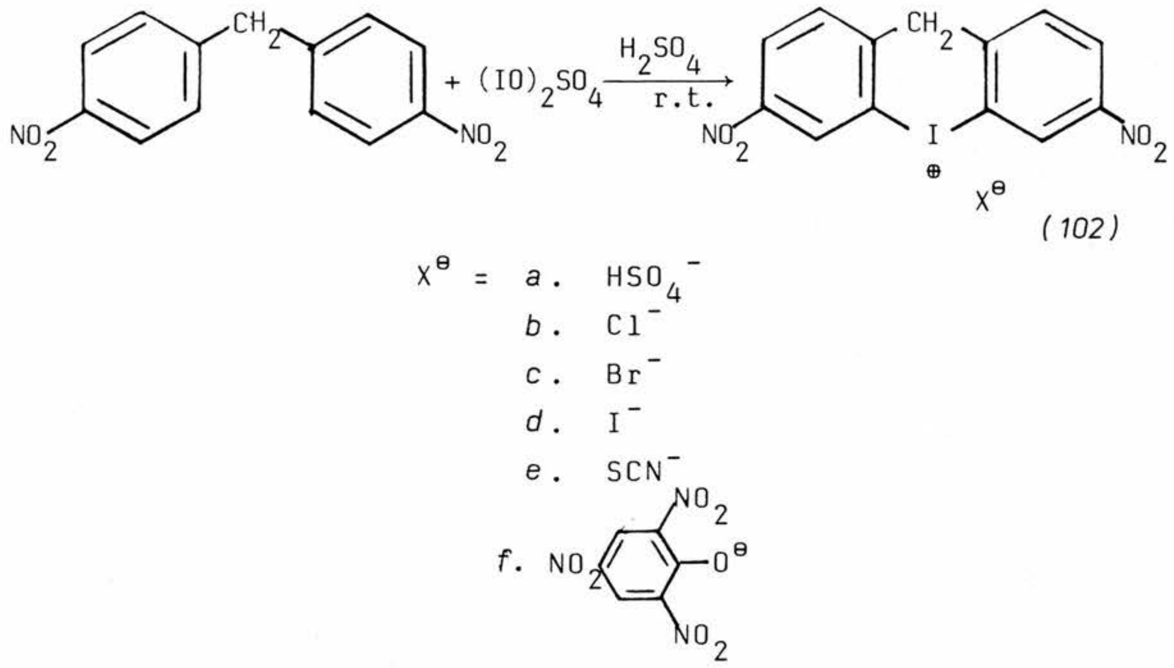


(101)

Scheme 20

A ^1H n.m.r. spectrum of *(101)* in DMSO showed a singlet at δ 4.35 for the methylene protons and a multiplet at δ 7.9 for the eight aromatic protons. Addition of D_2O to the sample caused no change in the spectrum suggesting that the methylene protons are not particularly acidic. A solution of sodium dimsyl was prepared by addition of sodium metal to deuterated DMSO and a spectrum of *(101)* in this solution was obtained. The resonances appeared to have moved upfield slightly to δ 4.125 and δ 7.55 respectively indicating that some ylide may have formed.

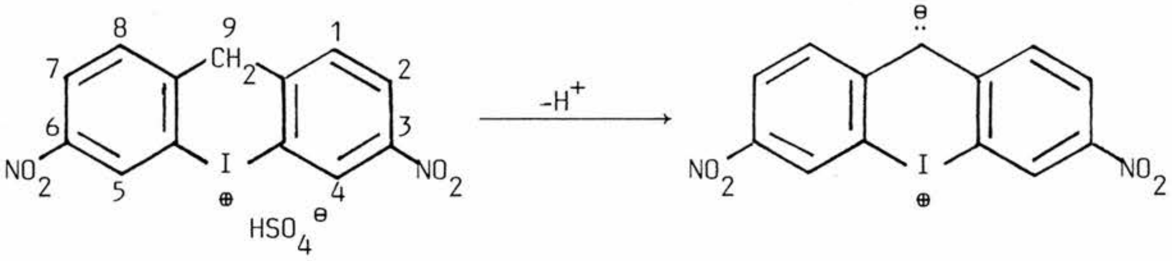
At this point, a publication[116] from *Acta Chimica Sinica* was obtained which gave details on the preparation of the series of iodonium salts *(102)*,(Scheme 21).



Scheme 21

The Chinese workers had prepared the iodonium bisulphate *(102a)* by treatment of 4,4'-dinitrodiphenylmethane with iodosylsulphate. The bisulphate could be converted into the chloride *(102b)*, bromide *(102c)*, iodide *(102d)*, thiocyanate *(102e)*, and picrate *(102f)* by treating a solution of it in formic acid with sodium chloride, sodium bromide, potassium iodide, potassium thiocyanate, or picric acid respectively. With the white bisulphate *(102a)*, an interesting colour change was observed on treatment with sodium hydroxide solution. If a little powdered bisulphate *(102a)* was shaken with 2 ml of 10% NaOH solution and 3 ml of pyridine at room temperature, a bluish-green colour gradually developed in the organic layer while the solid slowly disappeared. On acidifying the solution it became brownish-

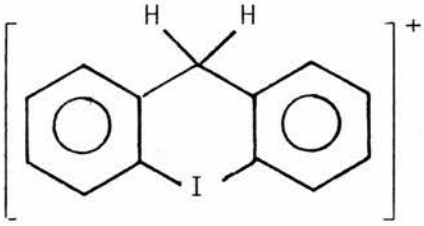
-yellow in colour but the blue-green colour returned on addition of alkali. The blue-green colour of the pyridine solution was stable for two weeks, but the workers made no attempt to isolate the species responsible for it. It was thought very possible that the colour was due to compound *(103)* formed by the removal of a proton from carbon 9 of the bisulphate (Reaction 38).



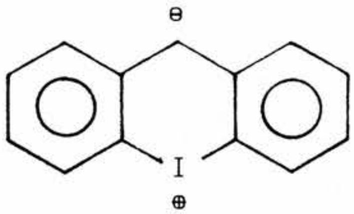
(102a) *(103)*

Reaction 38

It was considered that the methylene protons of *(102a)* would be more acidic than those of compound *(99)* because of the electron-withdrawing effect of the nitro groups, and consequently, the nitro groups might help to stabilise *(103)*. The bisulphate was therefore prepared by treatment of 4,4'-dinitrodiphenylmethane with iodine, sodium iodate and concentrated sulphuric acid at room temperature (yield 65%). A sample of 2,2',4,4'-tetranitrodiphenylmethane (with two more stabilising nitro groups) was also treated in this way but no ring closure took place even after four weeks at room temperature. The iodonium bisulphate *(102a)* displayed the colour change mentioned in the Chinese publication, and isolation of this blue-green species was to be attempted. However, theoretical calculations[117] carried out on the species of interest, *(104)* and *(105)*, gave some interesting results (see pages 142 and 143 for bond orders and bond lengths.

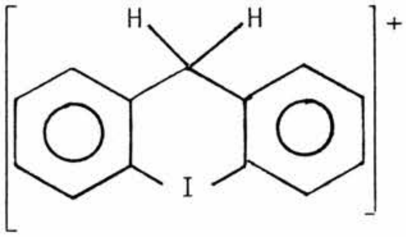


(104)



(105)

These results basically show that, structurally, species *(104)* and *(105)* can best be represented by *(106)* and *(107)* respectively. In the cation *(106)*, the two outer rings are like benzene having delocalised 6π electron systems. In the neutral molecule *(107)*, however, there are localised double bonds in the outer rings and, in the centre ring, a 6π pentadienide-type system. The distribution of charge in the centre ring is shown in *(108)*.



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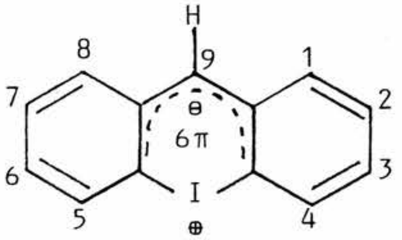
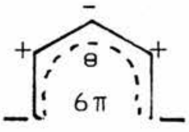


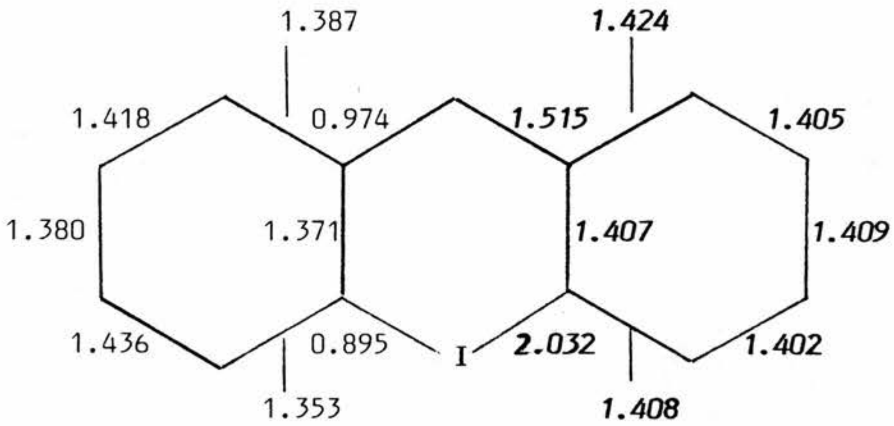
(107)



(108)

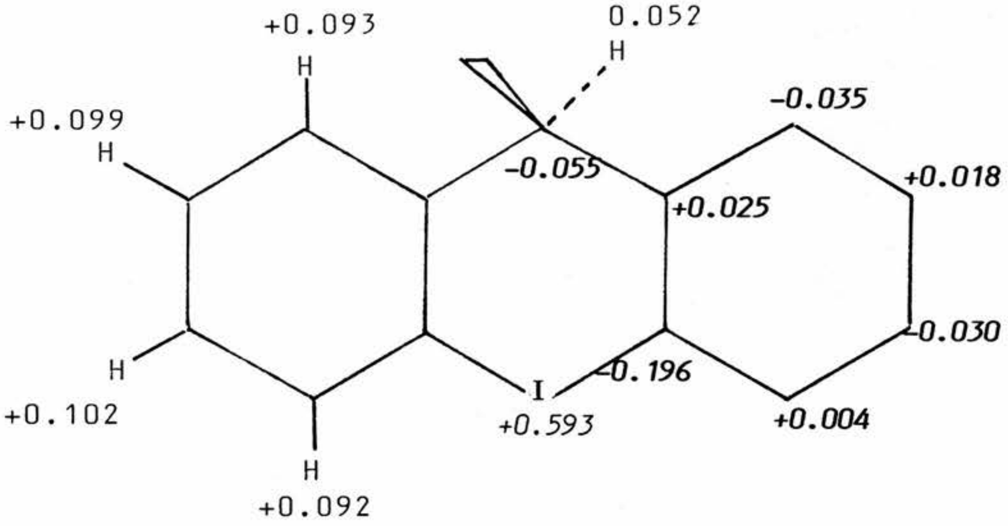
Therefore, the presence of electron-withdrawing nitro groups on the outer rings will do little to stabilise the neutral molecule, but, the presence of a nitro group on carbon 9 might have a marked effect.

Results for the cation *(104)* :



Bond orders are in normal print

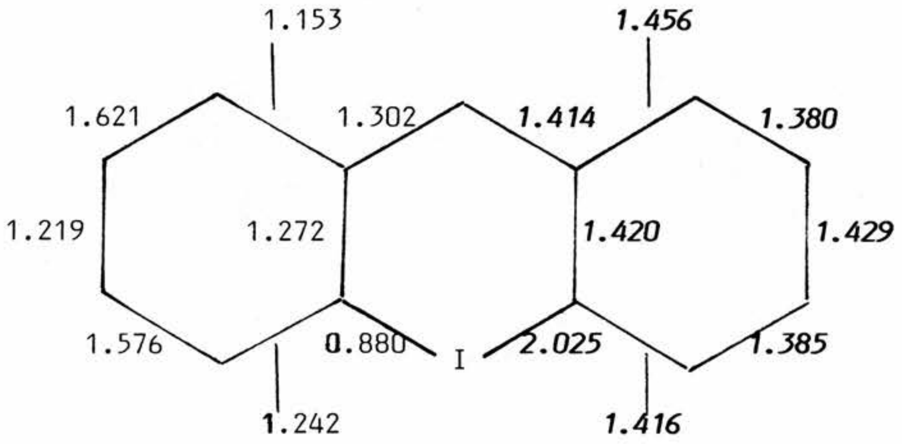
Bond lengths (Å) are in italics



Charges at H are in normal print

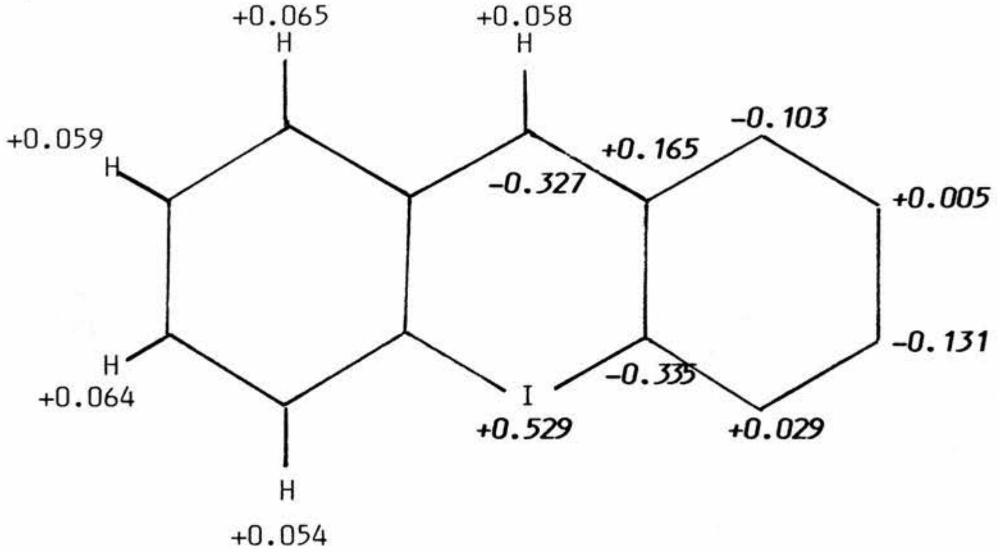
Charges at C, I are in italics

Results for the neutral molecule *(105)* :



Bond orders are in normal print

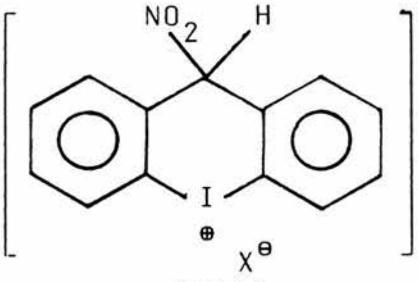
Bond lengths (Å) are in italics



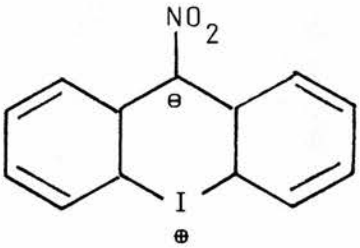
Charges at H are in normal print

Charges at C,I are in italics.

Feuer and Friedman have reported[118] the preparation of diphenylnitromethane from diphenylmethane. It might thus be possible to prepare 2-iodo-diphenylnitromethane and then use the ring closure method discussed here to prepare compound *(109)*, and subsequently the novel iodonium ylide *(110)*.



(109)



(110)

However, no more work was carried out on this topic.

PART III

EXPERIMENTAL

PART III

EXPERIMENTAL

1. MATERIALS AND APPARATUS

^1H N.m.r. spectra were carried out on a Brücker WP-80 Spectrometer operating at 80 MHz and also on a Varian EM 360 Spectrometer operating at 60 MHz.

Chemical shifts (δ) are given in p.p.m. relative to tetramethylsilane as internal standard.

^{13}C N.m.r. spectra were carried out on a Brücker WH-360 Spectrometer at the University of Edinburgh operating at 50 MHz. Chemical shifts (δ) are given in p.p.m. relative to the solvent (CD_2Cl_2).

IR Spectra were obtained with a Perkin-Elmer 1310 Infrared Spectrophotometer

UV Spectra were measured with a Unicam SP 800 instrument.

Solid state UV spectra were measured with an edt Research OAs 400 Optoacoustic Spectrometer by Dr. J. Toynbee.

Mass spectra were carried out by Mr. C. Millar and microanalyses by Mrs. S. Smith and Miss C. Jack, St. Andrews University.

Column chromatography was carried out on silica gel Grade M60, or aluminium oxide 90. Neutral aluminium oxide activity grade 1 was also used.

Light petroleum had boiling-point 40 - 60°.

Solvents used in the preparation of ylides were dried and redistilled, and the reactions were carried out under nitrogen.

Diazo-compounds were prepared according to standard literature procedures (see text for references). Ethyl diazoacetate was bought from Aldrich Chemical Company and diazo-compounds *(66), (67) and (68)* were prepared by Dr. K. W. Lumbard, St. Andrews University.

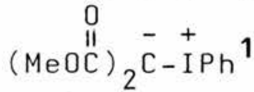
Rhodium trichloride used in the preparation of rhodium acetate was a gift from Dr. I. Gosney, Edinburgh University.

The following compounds were prepared according to standard literature procedures:

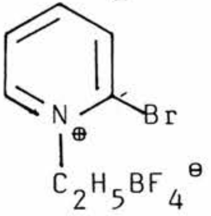
i) *p*-tosyl azide[119]

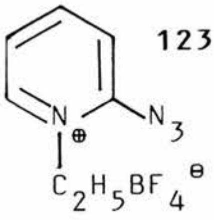
ii) $(PhS)_2CH_2$[120] and $(PhSO_2)_2CH_2$[91]

iii) $(p\text{-}CH_3C_6H_4S)_2CH_2$ and $(p\text{-}CH_3C_6H_4SO_2)_2CH_2$[121]

iv) 

$(\mathrm{MeO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_2\overset{-}{\mathrm{C}}-\overset{+}{\mathrm{I}}\mathrm{Ph}$[122]

v) 

and 

[123]

vi) 2,4-dinitrobenzaldehyde[124]

2. REACTIONS OF 2,3,4-TRIPHENYLDIAZOCYCLOPENTADIENE

(i) *TRIPHENYLARSINE*

The reactions of diazo-compound (0.5 g; 1.56 mmol),

Ph_3As (0.95 g; 3.12 mmol) and $Cu(hfa)_2$ (0.03 g) in a variety of solvents at several temperatures and with varying reaction times were carried out. The results are shown in Table 4, page 55. Triphenylarsonium 2,3,4-triphenylcyclopentadienylide was obtained from the reaction mixtures by evaporation of solvent and trituration of the residue with solvent ether. Recrystallisation was from benzene/light petrol.

This reaction was repeated in duplicate in refluxing dry benzene for 2 hours using copper-bronze (0.12 g) as a catalyst instead of $Cu(hfa)_2$. One reaction flask was heated by conventional means (a), the other in an ultrasonic water-bath (b). Work-up as above gave no ylide in either case.

Repeat experiments using activated copper-bronze[76] gave 58% yield of ylide from (a) and 40% yield of ylide from (b).

ii) *METHYLPHENYLSULPHIDE*

Diazo-compound (0.5 g; 1.56 mmol), methylphenylsulphide (0.39 g; 3.12 mmol), and $Cu(hfa)_2$ (0.03 g) were dissolved in dry benzene (30 ml) and kept at room-temperature for two weeks. Work-up as in (i) gave methylphenylsulphonium 2,3,4-triphenylcyclopentadienylide (0.20 g; 31%) as cream-coloured solid, m.p. 140 °C decomp. (lit. 125 - 138 °C)[31].

iii) *DIPHENYLSULPHIDE*

Diazo-compound (0.5 g; 1.56 mmol), diphenylsulphide (0.58 g; 3.12 mmol) and $Cu(hfa)_2$ (0.03 g) were heated under reflux in dry benzene (30 ml) for two hours. Work-up as (i) gave unchanged diazo-compound.

3. REACTIONS OF 2,3,4,5-TETRAPHENYLDIAZOCYCLOPENTADIENE

i) *TRIPHENYLARSINE*

Diazo-compound (0.17 g; 0.43 mmol), Ph_3As (0.26 g; 0.86 mmol), and $Cu(hfa)_2$ (0.01 g) were heated under reflux in dry benzene (20 ml) for two hours. Evaporation of solvent and trituration of residue with solvent ether gave triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (0.19 g; 66%) as pale yellow solid, m.p. 204 - 206 °C (lit.[125] 228 - 230 °C). Recrystallisation of a sample from nitromethane gave yellow crystals, m.p. 238 - 240 °C.

ii) *TRIPHENYLSTIBINE*

Diazo-compound (0.17 g; 0.43 mmol), Ph_3Sb (0.30 g; 0.86 mmol) and $Cu(hfa)_2$ (0.01 g) were heated under reflux in dry benzene (20 ml) for two hours. Work-up as in (i) gave a suspension of triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide which could not be filtered off completely. 0.1 g Ylide was collected (32%), m.p. 210 °C (decomp.) (lit.[8] 196 - 198 °C). A 2.14×10^{-5} molar solution in CCl_4 gave a UV spectrum with λ_{max} = 345 nm and ε = 41589 (lit.[8] λ_{max} = 349 nm and ε = 41500).

4. REACTIONS OF DIAZO-COMPOUNDS WITH TRIPHENYLSTIBINE IN THE PRESENCE OF $Cu(hfa)_2$

i) *DIAZO-BIS(PHENYLSULPHONYL)METHANE (59)*

Diazo-compound (0.40 g; 1.24 mmol), Ph_3Sb (0.87 g; 2.48 mmol) and $Cu(hfa)_2$ (0.025 g) were heated under reflux in dry benzene (30 ml) for two hours. Evaporation of solvent and trituration of the residue with solvent ether gave triphenylstibonium bis(phenylsulphonyl)methylide (0.62 g; 78%). A sample recrystallised from chlorobenzene as chunky colourless crystals of m.p. 196 - 198 °C. (Found: C, 57.84; H, 3.88. $C_{31}H_{25}O_4S_2Sb$ requires C, 57.51; H, 3.89%.)

ii) *DIAZO-BIS(TOLYL-p-SULPHONYL)METHANE* (60)

Diazo-compound (2.10 g; 6 mmol), Ph_3Sb (4.24 g; 12 mmol) and $Cu(hfa)_2$ (0.14 g) were heated under reflux in dry benzene (100 ml) for 6 hours. Work-up as in (i) gave triphenyl stibonium bis(tolyl-*p*-sulphonyl)methylide (3.10 g; 77%). A sample recrystallised from benzene/light petrol had m.p. = 192° decomp. (Found: C, 58.84; H, 4.36. $C_{33}H_{29}O_4S_2Sb$ requires C, 58.68; H, 4.33%.)

iii) *2-DIAZO-5,5-DIMETHYLCYCLOHEXANE-1,3-DIONE* (62)

Diazo-compound (0.50 g; 3 mmol), Ph_3Sb (2.12 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry toluene (50 ml) for two hours. Removal of solvent gave a brown tar which could not be induced to crystallise by trituration with solvent ether, light-petrol or hexane. The tar was therefore applied to an alumina column and elution initially with light-petrol gave unchanged Ph_3Sb (1.11 g). Further elution with methylene chloride gave a sticky solid which, when washed with ether, gave triphenylstibonium 4,4-dimethyl--2,6-dioxocyclohexylide (0.59 g; 40%). A sample recrystallised from ethylacetate had melting point = 162 - 164 °C. (Found: C, 63.60; H, 5.05. $C_{26}H_{25}O_2Sb$ requires C, 63.57; H, 5.13%.)

iv) *DIACETYLDIAZOMETHANE (57)*

Diazo-compound (0.38 g; 3 mmol), Ph_3Sb (2.12 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry benzene (50 ml) for one hour. Evaporation of solvent and trituration of the residue with solvent ether gave bis(acetylacetonato)Cu(II) which was removed by filtration. Evaporation of ether from the filtrate and trituration of the residue with light-petrol gave triphenylstibonium diacetylmethylide (0.80 g; 59%) as cream-coloured solid. A sample recrystallised several times from benzene had m.p. 186 °C decomp. (Found: C, 61.79; H, 4.80; *m/e* = 451.0650. $C_{23}H_{21}O_2Sb$ requires C, 61.23; H, 4.69; $(M + 1)^+$ = 451.0656, for ^{121}Sb.)

v) *ACETYLBENZOYLDIAZOMETHANE (61)*

Diazo-compound (0.56 g; 3 mmol), Ph_3Sb (2.12 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry benzene (50 ml) for one hour. Evaporation of solvent and trituration of the residue with solvent ether/hexane gave triphenylstibonium acetylbenzoylmethylide (0.70 g; 46%) of m.p. 148 - 150 °C. The ylide, however, appeared to be contaminated with triphenylstibine oxide and could not be purified satisfactorily. (Found: *m/e* = 513.0817; $C_{28}H_{23}O_2Sb$ requires $(M + 1)^+$ = 513.0813, for ^{121}Sb.)

vi) *2-DIAZOCYCLOHEXANE-1,3-DIONE (69)*

Diazo-compound (0.41 g; 3 mmol), Ph_3Sb (2.12 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry benzene

(50 ml) for 1.5 hours. Work-up as in (i) gave triphenylstibonium 2,6-dioxocyclohexylide (0.80 g; 58%) as cream-coloured solid. A sample recrystallised from ethyl acetate, with charcoal, had m.p. 169 - 172 °C. (Found: C, 62.34; H, 4.56. $C_{24}H_{21}O_2Sb$ requires C, 62.24; H, 4.57%.)

vii) ACETYL-*p*-TOSYLDIAZOMETHANE *(66)*

Diazo-compound (0.35 g; 1.50 mmol), Ph_3Sb (1.06 g; 3 mmol) and $Cu(hfa)_2$ (0.035 g) were heated under reflux in dry benzene (25 ml) for two hours. Work-up as in (i) gave triphenylstibonium acetyl-*p*-tosylmethylide (0.32 g; 38%) of m.p. 170 °C decomp. Attempted recrystallisation from methylene chloride/hexane with charcoal, led to some decomposition to triphenylstibine oxide. (Found: *m/e* = 497.0867; $C_{27}H_{25}O_3SSb$ requires $(M - 65)^+$ = 497.0864, for ^{121}Sb).

viii) BENZYLSULPHONYLDIAZOMETHANE *(71)*

Diazo-compound (0.19 g; 1 mmol), Ph_3Sb (0.70 g; 2 mmol) and $Cu(hfa)_2$ (0.02 g) were dissolved in dry benzene (20 ml). Immediately nitrogen evolution started and was complete after a few minutes. An IR spectrum of the reaction mixture showed that all the diazo-compound had decomposed and so solvent was evaporated and trituration of the residue with solvent ether gave triphenylstibonium benzylsulphonylmethylide (0.30 g; 58%) as cream-coloured solid, m.p. 168 - 170 °C. Attempts to purify the ylide by recrystallisation from methylene chloride/hexane or benzene/

hexane were unsuccessful. (Found: *m/e* = 444.0148; $C_{26}H_{23}SO_2Sb$ requires $(M - 76)^+$ = 444.0142, for ^{121}Sb.)

ix) *DIMETHYL DIAZOMALONATE (64)*

Diazo-compound (0.47 g; 3 mmol), Ph_3Sb (2.12 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry benzene (50 ml) for two hours. Evaporation of solvent gave a yellow oil containing unchanged diazo-compound. Addition of solvent ether to this oil gave triphenylstibine oxide (0.1 g). This reaction was repeated in refluxing toluene for two hours. Work-up as in (i) gave triphenylstibine oxide (0.3 g).

x) *5-DIAZO-2,2-DIMETHYL-1,3-DIOXANE-4,6-DIONE (63)*

Diazo-compound (0.51 g; 3 mmol), Ph_3Sb (2.12 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry benzene (50 ml) for five hours. An IR spectrum of the reaction mixture after this time still showed the presence of unchanged diazo-compound. The reaction was therefore repeated in refluxing toluene. After one hour under reflux, the reaction mixture was almost black in colour and so heating was stopped. As the reaction mixture cooled, unchanged diazo-compound precipitated and was filtered off (0.1 g). Evaporation of solvent from the filtrate gave a black tar which still contained diazo-compound, but could not be induced to crystallise by trituration with solvent ether.

xi) *ETHYL DIAZOACETOACETATE (65)*

Diazo-compound (0.46 g; 3 mmol), Ph_3Sb (2.12 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry benzene

(50 ml) for two hours. Work-up as in (i) gave triphenylstibine oxide (0.64 g).

xii) *ETHYL DIAZOBENZOYLACETATE (68)*

Diazo-compound (0.65 g; 3 mmol), Ph_3Sb (2.12 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry benzene (50 ml) for two hours. Evaporation of solvent and trituration of the residue with light petrol gave triphenylstibine oxide (0.4 g).

xiii) *BENZOYLDIAZOMETHANE (67)*

Diazo-compound (0.1 g; 0.68 mmol), Ph_3Sb (0.48 g; 1.36 mmol) and $Cu(hfa)_2$ (0.015 g) were dissolved in dry benzene (15 ml) and left at room-temperature for 24 hours. Work-up as in (i) gave triphenylstibine oxide (0.06 g).

xiv) *ETHYL DIAZOACETATE (70)*

Diazo-compound (0.17 g; 1.5 mmol), Ph_3Sb (1.06 g; 3 mmol) and $Cu(hfa)_2$ (0.035 g) were dissolved in dry benzene (25 ml) and left at room-temperature for 24 hours. Work-up as in (i) gave triphenylstibine oxide (0.18 g).

5. REACTIONS OF DIAZO-COMPOUNDS WITH TRIPHENYLARSINE IN THE PRESENCE OF $Cu(hfa)_2$

i) *DIAZO-BIS(PHENYLSULPHONYL)METHANE*

Diazo-compound (0.40 g; 1.24 mmol), Ph_3As (0.70 g, 2.28 mmol) and $Cu(hfa)_2$ (0.025 g) were heated under reflux in dry benzene (25 ml) for two hours. Evaporation of solvent and trituration of the residue with ether gave triphenylarsonium bis(phenylsulphonyl)methylide (0.43 g, 58%) of m.p. 240 - 250 °C. Recrystallisation from chlorobenzene gave colourless crystals of m.p. 248 - 250 °C (lit.[23] 252 - 254 °C).

ii) *DIMETHYL DIAZOMALONATE*

Diazo-compound (0.47 g; 3 mmol), Ph_3As (1.83 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry benzene (50 ml) for 5 hours. Work-up as in (i) gave triphenylarsonium bis(methoxycarbonyl)methylide (0.21 g; 16%). However, an IR spectrum of the ether filtrate showed that unchanged diazo-compound was still present. The reaction was therefore repeated in refluxing toluene. After 2 hours under reflux, decomposition of diazo-compound was complete as shown by an IR spectrum of the reaction mixture. Work-up as in (i) gave ylide (0.80 g; 62%) of m.p. 178 - 181 °C (lit.[16c] 186 - 188 °C).

iii) *2-DIAZO-CYCLOHEXANE-1,3-DIONE*

Diazo-compound (0.41 g, 3 mmol), Ph_3As (1.84 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry benzene (50 ml) for four hours, after which time little decomposition of diazo-compound had taken place. The reaction was therefore repeated in refluxing toluene. After 1.5 hours under reflux, solvent was evaporated giving an oily yellow/brown residue which could not be induced to crystallise by trituration with solvent ether, light petrol or hexane. However, an IR spectrum of this residue indicated that ylide was present. The residue was therefore dissolved in dry methylene chloride (50 ml) and the solution stirred with just enough neutral alumina to remove the brown colour. The alumina was then filtered off and evaporation of solvent from the filtrate gave a pale yellow oil which on trituration with solvent ether/hexane gave triphenylarsonium 2,6-dioxocyclohexylide (0.25 g, 20%) as a white solid. Recrystallisation twice from methylene chloride/hexane gave pure ylide, m.p. 162 - 164 °C. (Found: C, 69.83; H, 5.12. $C_{24}H_{21}O_2As$ requires C, 69.24; H, 5.08%.)

6. <u>REACTIONS OF DIAZO-COMPOUNDS WITH TRIPHENYLBISMUTH IN THE PRESENCE OF Cu(hfa)$_2$</u>

i) *DIAZO-BIS(TOLYL-p-SULPHONYL)METHANE*

Diazo-compound (0.54 g, 1.55 mmol), triphenylbismuth (1.36 g; 3.10 mmol) and Cu(hfa)$_2$ (0.04 g) were heated under reflux in dry benzene (25 ml) for 2 hours. Evaporation of solvent and trituration of the residue with solvent ether gave bis(tolyl-*p*-sulphonyl)methane (0.2 g).

ii) *DIAZO-BIS(PHENYLSULPHONYL)METHANE*

Diazo-compound (0.5 g; 1.55 mmol), triphenylbismuth (1.36 g; 3.10 mmol) and Cu(hfa)$_2$ (0.04 g) were heated under reflux in dry benzene (25 ml) for 2 hours. Work-up as in (i) gave 0.25 g of khaki-coloured solid, m.p. 107 - 109 °C. IR and UV spectra and ^{1}H n.m.r. suggest that this solid may be triphenylbismuthonium bis(phenylsulphonyl)methylide (22%).

iii) *2-DIAZOCYCLOHEXANE-1,3-DIONE*

Diazo-compound (0.2 g; 1.5 mmol), triphenylbismuth (1.32 g; 3 mmol) and Cu(hfa)$_2$ (0.04 g) were heated under reflux in dry benzene (25 ml) for 1.25 hours. Work-up as in (i) gave triphenylbismuthonium 2,6-dioxocyclohexylide (0.22 g, 28%) as khaki-coloured solid, m.p. 224 - 228 °C. When the reaction time was increased to 2.5 hours, the yield of ylide increased to 42%

7. REACTIONS OF TRIPHENYLANTIMONYDICHLORIDE WITH ACTIVE METHYLENE COMPOUNDS

i) *ACETYLACETONE*

Ph_3SbCl_2 (1.06 g; 2.5 mmol) was dissolved in dry benzene (7 ml). A solution of acetylacetone (0.25 g; 2.5 mmol) and triethylamine (0.61 g; 6 mmol) in dry benzene (5 ml) was added and the mixture heated under reflux for 20 minutes. The reaction mixture was then cooled and filtered, giving triethylamine hydrochloride and oxybis(triphenylstibonium)dichloride (0.60 g). Evaporation of solvent from the filtrate and addition of solvent ether to the residue gave triphenylstibonium diacetylmethylide (0.6 g; 53%) of m.p. 166 - 170 °C (lit.[15] 186 °C decomp.). An IR spectrum showed that the ylide was contaminated with oxybis(triphenylstibonium)dichloride.

ii) *BENZOYLACETONE*

Ph_3SbCl_2 (1.06 g; 2.5 mmol) was dissolved in dry benzene (7 ml), and a solution of benzoylacetone (0.41 g; 2.5 mmol) and triethylamine (0.61 g; 6 mmol) in dry benzene (5 ml) was added. The mixture was heated under reflux for 20 minutes and then cooled and filtered. This gave a mixture of triethylamine hydrochloride and oxybis(triphenylstibonium)dichloride (0.45 g). Evaporation of solvent from the filtrate and trituration of the residue with solvent ether gave triphenylstibonium acetylbenzoylmethylide contaminated with triethylamine hydrochloride and oxybis(triphenylstibonium)dichloride (0.52 g). In order to remove these impurities, the solid was washed quickly with ice-cold methanol and then with ether. This succeeded in removing the triethylamine hydrochloride, but not the dichloride. The remaining crude ylide weighed 0.34 g, comprising a yield of 27%, m.p. 168 - 182 °C.

iii) *CYCLOHEXANE-1,3-DIONE*

Ph_3SbCl_2 (1.06 g; 2.5 mmol) was dissolved in dry benzene (7 ml) and a solution of cyclohexane-1,3-dione (0.28 g; 2.5 mmol) and triethylamine (0.61 g; 6 mmol) in dry benzene (5 ml) was added. The mixture was heated under reflux for 20 minutes, cooled and filtered. This gave a mixture of triethylamine hydrochloride and oxybis(triphenylstibonium)-dichloride (0.57 g). Evaporation of solvent from the filtrate and trituration of the residue with solvent ether gave triphenylstibonium 2,6-dioxocyclohexylide contaminated with oxybis(triphenylstibonium)dichloride (0.23 g), m.p. 156 - 182 °C. To try to remove the dichloride, the solid was dissolved in dry methylene chloride and filtered quickly through a layer of neutral alumina supported on hyflo super--cel. Evaporation of solvent from the filtrate and trituration of the residue with solvent ether gave ylide (0.05 g), m.p. 168 - 170 °C (lit.[15] 169 - 172 °C).

The reaction was repeated and again a mixture of ylide and oxybis(triphenylstibonium)dichloride was obtained. This time the solid was dissolved in methylene chloride and simply stirred briefly with a small amount of neutral alumina which was then filtered off. Evaporation of solvent from the filtrate and trituration of the residue with solvent ether gave ylide, m.p. 167 - 169 °C, with little loss of material.

iv) *DIMEDONE*

Ph_3SbCl_2 (1.06 g; 2.5 mmol) was dissolved in dry benzene (7 ml) and a solution of dimedone (0.35 g; 2.5 mmol) and triethylamine (0.61 g; 6 mmol) in dry benzene (5 ml) was added. The mixture was heated under reflux for 20 minutes, cooled and filtered, giving a mixture of triethylamine hydrochloride and oxybis(triphenylstibonium)dichloride (0.6 g). Evaporation of solvent from the filtrate and trituration of the residue with solvent ether/hexane with simultaneous cooling, gave more oxybis(triphenylstibonium)-dichloride (0.3 g).

v) *DIMETHYL MALONATE*

Ph_3SbCl_2 (1.06 g; 2.5 mmol) was dissolved in dry benzene (7 ml) and a solution of dimethyl malonate (0.33 g; 2.5 mmol) and triethylamine (0.61 g; 6 mmol) in dry benzene (5 ml) was added. The mixture was heated under reflux for 20 minutes, cooled and filtered, giving a mixture of triethylamine hydrochloride and oxybis(triphenylstibonium)-

dichloride (0.53 g). Evaporation of solvent from the filtrate and trituration of the residue with solvent ether gave more oxybis(triphenylstibonium)dichloride.

vi) *BIS(PHENYLSULPHONYL)METHANE*

Ph_3SbCl_2 (1.06 g; 2.5 mmol) was dissolved in dry benzene (7 ml) and a solution of bis(phenylsulphonyl)methane (0.74 g; 2.5 mmol) and triethylamine (0.61 g; 6 mmol) in dry benzene (5 ml) was added. The mixture was heated under reflux for 20 minutes, cooled and filtered, giving triethylamine hydrochloride and unchanged bis(phenylsulphonyl)methane.

8. REACTION OF TRIPHENYLBISMUTH DICHLORIDE WITH ACETYLACETONE

Ph_3BiCl_2 (0.51 g; 1 mmol) was dissolved in dry benzene (3 ml) and a solution of acetylacetone (0.1 g; 1 mmol) and triethylamine (0.24 g; 2.4 mmol) in dry benzene (2 ml) was added. This caused the mixture to go brown in colour. However, the mixture was heated under reflux for five minutes and then solvent evaporated. This gave a black tar which could not be induced to crystallise.

9. MISCELLANEOUS REACTIONS

i) *REACTION OF DIAZO-BIS(PHENYLSULPHONYL)METHANE WITH Ph_3Sb IN THE PRESENCE OF $Cu(Ac.Ac)_2$*

Diazo-compound (0.48 g; 1.5 mmol), Ph_3Sb (1.06 g; 3 mmol) and $Cu(ac.ac)_2$ (0.02 g) were heated under reflux in dry benzene (25 ml) for two hours. Evaporation of solvent and trituration of the residue with solvent ether, gave triphenylstibonium bis(phenylsulphonyl)methylide (0.45 g, 47%). When the reaction time was increased to 5 hours, a 73% yield of ylide was obtained.

ii) *REACTION OF DIMETHYL DIAZOMALONATE WITH CYCLOHEXENE*

a) Diazo-compound (0.47 g; 3 mmol), cyclohexene (0.49 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry toluene (50 ml) for two hours. Evaporation of solvent gave a brown oil which was extracted several times with hot petrol. As the combined petrol fractions cooled, white solid precipitated which was filtered off, dried and found to be the bicyclic ester[32] *(53)* (0.05 g; 8%).

b) Reaction was repeated as in (a) but simply using the cyclohexene as solvent with no toluene present. Work-up as in (a) gave a 26.5% yield of *(53)*.

When reactions (a) and (b) were repeated with no catalyst present, no bicyclic ester was obtained.

iii) *PREPARATION OF N,N,N',N'-TETRAMETHYLTHIOURONIUM BIS-(PHENYLSULPHONYL)METHYLIDE*

Diazo-bis(phenylsulphonyl)methane (0.50 g; 1.55 mmol), tetramethylthiourea (0.41 g; 3.10 mmol) and $Cu(hfa)_2$ (0.04 g) were heated under reflux in dry benzene (30 ml) for two hours. Evaporation of solvent gave ylide as pale orange solid, which when washed with methanol, became cream-coloured (0.43 g; 65%) with m.p. 171 - 174 °C (lit.[71] 170 - 173 °C).

iv) *REACTION OF DIAZODIMEDONE WITH IODOBENZENE IN THE PRESENCE OF $Cu(hfa)_2$*

Diazo-compound (0.33 g; 2 mmol) and $Cu(hfa)_2$ (0.05 g) were heated in iodobenzene (4.0 g; 19.6 mmol) at about 55 °C for 30 minutes. However, no iodonium ylide precipitated on cooling of the reaction mixture as occurs when ylide has formed.[16g]

v) *REACTION OF DIAZODIMEDONE AND $Cu(hfa)_2$ IN REFLUXING BENZENE*

Diazo-compound (0.25 g; 1.50 mmol) and $Cu(hfa)_2$ (0.035 g) were heated under reflux in dry benzene for two hours. Removal of solvent and trituration of the residue with solvent ether/hexane, gave unchanged diazo-compound (0.2 g). Evaporation of solvent from the filtrate and further trituration of the residue with hexane, gave 0.05 g of silver-grey solid with carbonyl absorption in the IR at 1545 cm^{-1}. *M/e* = 210 suggested that the solid was compound *(54)* in the text, formed by the addition of dimedone carbene to benzene.

vi) *PREPARATION OF DIPHENYLTELLURONIUM 4,4-DIMETHYL-2,6--DIOXOCYCLOHEXYLIDE*

Diazodimedone (0.17 g; 1 mmol), Ph_2Te (0.56 g; 2 mmol) and $Cu(hfa)_2$ (0.025 g) were heated under reflux in dry benzene (20 ml) for two hours. An IR spectrum of the reaction mixture, however, still contained a large diazo-peak. Solvent was evaporated, therefore, and replaced by dry toluene. Fresh catalyst was added and the mixture heated under reflux for a further hour. Evaporation of solvent gave a brown oil which on trituration with solvent ether/hexane gave ylide (0.1 g; 23%) as cream-coloured solid, m.p. 154 - 158 °C (lit.[27] 162 - 163 °C).

vii) *REACTION OF PHENYLIODONIUM BIS(METHOXYCARBONYL)METHYLIDE WITH Ph_3Sb*

Iodonium ylide (1.00 g; 3 mmol), Ph_3Sb (2.12 g; 6 mmol) and $Cu(hfa)_2$ (0.07 g) were heated under reflux in dry benzene (50 ml) for two hours. Evaporation of solvent and trituration of the residue with solvent ether gave triphenylstibine oxide, 0.18 g, m.p. 208 °C decomp. (lit.[107] 220 - 221 °C). Solvent was evaporated from the filtrate and the residue applied to a silica column made up with light petrol. Elution with petrol gave Ph_3Sb (1.29 g), m.p. 48 - 50 °C. Further elution with 5% methanol in ethyl acetate gave 1,1,2,2-tetrakis(methoxycarbonyl)ethene (0.13 g; 33%) of m.p. 110 - 115 °C (lit.[16c] 123 - 125 °C). Elution with methanol gave trace amounts of a dirty brown oil which was not characterised.

viii) *REACTION OF TRIPHENYLARSINE OXIDE WITH DIMEDONE*

Triphenylarsine oxide (0.32; 1 mmol) and dimedone (0.42 g; 3 mmol) were heated under reflux in chloroform for nine hours. Evaporation of solvent gave solid, which from the IR spectrum and t.l.c., was shown to be a mixture of unchanged reactants.

ix) *THERMAL STABILITY OF TRIPHENYLSTIBONIUM BIS(PHENYLSULPHONYL)METHYLIDE*

Ylide (0.5 g; 0.77 mmol) was heated under reflux in dry benzene (25 ml) for two hours. Removal of solvent gave unchanged ylide whose ultraviolet spectrum was identical to that of the pure ylide with identical ε values (within ±0.05), indicating that no decomposition had occurred.

x) *STABILITY OF TRIPHENYLARSONIUM 2,3,4-TRIPHENYLCYCLOPENTADIENYLIDE*

Ylide (0.5 g; 0.84 mmol), m.p. 208 - 212 °C, was heated under reflux in dry benzene (30 ml) in an ultrasonic water-bath for two hours. Evaporation of solvent gave unchanged ylide with no depression of melting-point, indicating that no decomposition of ylide is caused by ultrasonic waves, or indeed by heating at this temperature.

xi) *ATTEMPTED PREPARATION OF ETHYL (BENZYLSULPHONYL)DIAZOACETATE*

Ethyl benzylsulphonylacetate (2.04 g; 8.5 mmol) was dissolved in 60% ethanol (15 ml) containing sodium hydroxide (0.34 g; 8.5 mmol) and the solution cooled to 0 °C. *p*-Tosyl azide (1.66 g; 8.5 mmol) in ethanol (2 ml) was then added in one portion and the mixture stirred for 15 minutes. White solid formed and was filtered off. This solid was soluble in water and a ^{1}H n.m.r. spectrum showed that the ethyl group was no longer present. This suggested that the compound was sodium benzylsulphonylacetate formed by hydrolysis of the ester function in the starting material.

xii) *ATTEMPTED PREPARATION OF α-DIAZOBENZYLPHENYLSULPHONE*

To a cold solution (-5 °C) of *p*-tosylazide (7.38 g;

37.5 mmol) in ethanol (10 ml) was added benzylphenylsulphone (2.9 g; 2.5 mmol) in 60% ethanol (25 ml) containing potassium hydroxide (0.7 g; 12.5 mmol). The mixture was stirred for 20 minutes, but no reaction occurred and unchanged benzylphenylsulphone was recovered.

10. REACTIONS OF DIAZO-COMPOUNDS WITH Ph_3Sb IN THE PRESENCE OF RHODIUM ACETATE DIMER

i) *DIAZO BIS(PHENYLSULPHONYL)METHANE*

Diazo-compound (0.1 g, 0.3 mmol) and Ph_3Sb (0.21 g; 0.6 mmol) were dissolved in dry benzene (10 ml) and a pinch of $[Rh(ac)_2]_2$ was added. This caused the solution to become red in colour, presumably due to the formation of $Rh_2(ac)_4(SbPh_3)_2$. No further reaction appeared to have taken place even after heating the solution under reflux for two hours.

ii) *DIACETYLDIAZOMETHANE*

Diazo-compound (0.38 g; 3 mmol), Ph_3Sb (2.12 g; 6 mmol) and $[Rh(ac)_2]_2$ (0.01 g) were dissolved in dry benzene (50 ml), again giving a red solution of $Rh_2(ac)_4(SbPh_3)_2$. As in (i) no decomposition of diazo-compound occurred.

11. ETHANOLYSIS OF TRIPHENYLSTIBONIUM BIS(PHENYLSULPHONYL)-METHYLIDE

A solution of ylide (0.2 g; 0.31 mmol) in ethanol (10 ml) was heated under reflux for 5 minutes. On cooling bis(phenylsulphonyl)methane precipitated and was filtered off (0.07 g; 76%). Solvent was evaporated from the filtrate and the residue boiled with water (10 ml) for several minutes and then decanted while hot. On cooling, more bis(phenylsulphonyl)methane precipitated (0.01 g). The white residue which had been boiled with water was found to be triphenylstibine oxide, m.p. 200 °C decomp.

12. ATTEMPTED PREPARATION OF TRIPHENYL[(BISPHENYLSULPHONYL)-METHYL]STIBONIUM BROMIDE

Bromobis(phenylsulphonyl)methane (0.5 g; 1.33 mmol) and Ph_3Sb (0.47 g; 1.33 mmol) were stirred in benzene (40 ml) until a clear solution was obtained. After two days at room temperature, colourless crystals had appeared which were filtered off and washed with benzene and then solvent ether, 0.44 g, m.p. 248 - 250 °C. This solid was not the expected stibonium bromide, however, but oxybis(triphenylstibonium)-dibromide (75%). (Found: C, 49.66; H, 3.44; $C_{36}H_{30}Br_2OSb_2$ requires C, 49.03; H, 3.43%.)

13. PREPARATION OF PICRATE SALT OF TRIPHENYLSTIBONIUM DIACETYLMETHYLIDE

Ylide (0.2 g; 0.44 mmol) and picric acid (0.1 g; 0.44 mmol) were each dissolved in the minimum of hot ethanol and the two solutions combined. On cooling, pale yellow picrate salt precipitated and was filtered off and washed with a little cold ethanol (0.21 g; 70%). A sample recrystallised from ethanol had m.p. 190 °C decomp. Gradual surface decomposition of the salt was observed. (Found: C, 49.38; H, 2.96; N, 7.036. $C_{29}H_{24}N_3O_9Sb$ requires

C, 51.20; H, 3.55; N, 6.18%.)

14. ATTEMPTED PREPARATIONS OF PERCHLORATE SALTS OF STIBONIUM YLIDES

i) *TRIPHENYLSTIBONIUM BIS(TOLYL-p-SULPHONYL)METHYLIDE*

Perchloric acid (0.05 ml of 70 - 73%) was added to a suspension of ylide (0.165 g; 0.24 mmol) in ethanol (0.5 ml). The ylide dissolved, and then solvent ether (5 ml) was added to the solution. This caused white solid to precipitate which was filtered off and found to be bis(tolyl-*p*-sulphonyl)methane (0.06 g; 76%), m.p. 130 °C (lit.[121] 135 °C).

ii) *TRIPHENYLSTIBONIUM BIS(PHENYLSULPHONYL)METHYLIDE*

Perchloric acid (0.1 ml 70 - 73%) was added to a suspension of ylide (0.31 g; 0.5 mmol) in ethanol (1 ml). The ylide dissolved and then solvent ether (10 ml) was added to the solution. White solid precipitated which was filtered off and found to be oxybis(triphenylstibonium)-diperchlorate (0.21 g; 91%), m.p. 305 - 307 °C (lit.[92] >300 °C).

iii) *TRIPHENYLSTIBONIUM DIACETYLMETHYLIDE*

Perchloric acid (0.1 ml, 70 - 73%) was added to a suspension of ylide (0.22 g; 0.5 mmol) in ethanol (1 ml). The ylide dissolved, and then solvent ether (10 ml) was added to the solution. White solid precipitated which was filtered off and found to be, as in (ii), oxybis(triphenylstibonium)diperchlorate (0.2 g; 87%), m.p. 307 - 308 °C (lit.[92] >300 °C).

15. ATTEMPTED WITTIG REACTIONS OF STIBONIUM YLIDES WITH 2,4-DINITROBENZALDEHYDE

i) *TRIPHENYLSTIBONIUM BIS(TOLYL-p-SULPHONYL)METHYLIDE*

Ylide (0.67 g; 1 mmol) and 2,4-dinitrobenzaldehyde (0.20 g; 1 mmol) were heated under reflux in dry benzene (30 ml) for 6.5 hours. Evaporation of solvent and trituration of the residue with solvent ether gave unchanged ylide (0.53 g), which was filtered off. Evaporation of solvent from the filtrate and trituration of the residue with light petrol gave 0.24 g solid which by t.l.c. and the IR spectrum appeared to be a mixture of bis(tolyl-*p*--sulphonyl)methane and 2,4-dinitrobenzaldehyde.

Repeat experiment with heating for 28 hours and work-up as above, gave 0.47 g unchanged ylide and 0.3 g of a mixture of bis(tolyl-*p*-sulphonyl)methane and 2,4-dinitrobenzaldehyde.

ii) *TRIPHENYLSTIBONIUM 2,6-DIOXOCYCLOHEXYLIDE*

Ylide (0.36 g; 0.78 mmol) and 2,4-dinitrobenzaldehyde (0.16 g; 0.78 mmol) were heated under reflux in dry benzene (25 ml) for five hours. Evaporation of solvent and trituration of the residue with solvent ether gave unchanged ylide (0.33 g).

iii) *TRIPHENYLSTIBONIUM BIS(PHENYLSULPHONYL)METHYLIDE*

Ylide (0.65 g; 1 mmol) and 2,4-dinitrobenzaldehyde (0.2 g; 1 mmol) were heated under reflux in dry toluene (30 ml) for 8 hours. As the mixture cooled, unchanged ylide crystallised and was filtered off (0.4 g). Solvent was evaporated from the filtrate, and a t.l.c. of the residue indicated the presence of unchanged ylide and aldehyde only.

iv) *TRIPHENYLSTIBONIUM 4,4-DIMETHYL-2,6-DIOXOCYCLOHEXYLIDE*

Ylide (0.20 g; 0.41 mmol) and 2,4-dinitrobenzaldehyde (0.08 g; 0.41 mmol) were heated under reflux in dry benzene (20 ml) for 7 hours. Evaporation of solvent and trituration of the residue with solvent ether gave unchanged ylide (0.1 g). A t.l.c. of the ether filtrate showed that no reaction appeared to have taken place. Application of the filtrate to a short alumina column and elution with solvent ether, gave quantitative recovery of 2,4-dinitrobenzaldehyde, m.p. 66 - 70 °C (lit.[124] 69 - 71 °C).

v) *TRIPHENYLSTIBONIUM DIACETYLMETHYLIDE*

Ylide (0.45 g; 1 mmol) and 2,4-dinitrobenzaldehyde (0.2 g; 1 mmol) were heated under reflux in dry benzene (30 ml) for 7 hours. Evaporation of solvent and trituration of the residue with light petrol gave unchanged ylide (0.42 g).

vi) *TRIPHENYLSTIBONIUM ACETYLBENZOYLMETHYLIDE*

Ylide (0.35 g; 0.68 mmol) and 2,4-dinitrobenzaldehyde (0.14 g; 0.68 mmol) were heated under reflux in dry benzene (25 ml) for 4.5 hours. Evaporation of solvent and trituration of the residue with solvent ether gave unchanged ylide (0.12 g). A t.l.c. of the ether filtrate showed the presence of a compound other than aldehyde or ylide. Application of the filtrate to a silica column and elution with ethyl acetate/light petrol (1 : 9) gave benzoyl acetone (0.04 g). Further elution gave quantitative recovery of the aldehyde.

vii) *TRIPHENYLSTIBONIUM BENZYLSULPHONYLMETHYLIDE*

Ylide (0.10 g; 0.2 mmol) and 2,4-dinitrobenzaldehyde (0.04 g; 0.2 mmol) were heated under reflux in dry benzene (10 ml) for 6 hours. Evaporation of solvent gave a mixture of ylide and aldehyde as shown by t.l.c. and an IR spectrum.

16. ATTEMPTED WITTIG REACTION OF TRIPHENYLSTIBONIUM BIS(TOLYL-*p*-SULPHONYL)METHYLIDE WITH *p*-NITROBENZALDEHYDE

Ylide (0.57 g, 0.8 mmol) and *p*-nitrobenzaldehyde (0.13 g; 0.8 mmol) were heated under reflux in dry benzene (30 ml) for 7 hours. Evaporation of solvent gave a sticky residue which on trituration with solvent ether gave bis(tolyl-*p*--sulphonyl)methane, (0.34 g; 85%) from decomposition of ylide.

17. ATTEMPTED WITTIG REACTION OF TRIPHENYLSTIBONIUM BIS(TOLYL-*p*-SULPHONYL)METHYLIDE WITH NITROSOBENZENE

Ylide (0.67 g; 1 mmol) and nitrosobenzene (0.11 g; 1 mmol) were heated under reflux in dry benzene (30 ml) for 7 hours. Evaporation of solvent and trituration of the residue with solvent ether gave unchanged ylide (0.47 g). Concentration of the ether filtrate gave more solid which was filtered off and found to be bis(tolyl-*p*-sulphonyl)-methane (0.06 g).

18. ATTEMPTED WITTIG REACTION OF TRIPHENYLBISMUTHONIUM 2,6-DIOXOCYCLOHEXYLIDE

Ylide (0.14 g, 0.3 mmol) and 2,4-dinitrobenzaldehyde (0.06 g; 0.3 mmol) were heated under reflux in dry benzene (10 ml) for 6 hours. Evaporation of solvent gave slightly sticky solid which was shown by t.l.c. and an IR spectrum to be a mixture of unchanged ylide and aldehyde.

19. SPECTRA

(a) *^{1}H n.m.r. SPECTRA*

i) *Triphenylstibonium bis(tolyl-p-sulphonyl)methylide (75)*

δ ($CDCl_3$) 2.38 s (6H), 7.10 - 8.00 m (23H)

ii) *Triphenylstibonium bis(phenylsulphonyl)methylide (14)*

δ (CD_2Cl_2) 7.25 - 7.75 m

iii) *Triphenylstibonium 2,6-dioxocyclohexylide (79)*

δ (CD_2Cl_2) 2.05 (quintet) (2H), 2.43 t (4H),
7.48 m (9H), 7.70 m (6H)

iv) *Triphenylstibonium 2,6-dioxocyclohexylide + Trifluoroacetic Acid*

δ (CD_2Cl_2) 1.73 - 2.60 m (6H), 7.27 - 7.80 m (15H),
7.96 (1H)

v) *Triphenylstibonium diacetylmethylide (73)*

δ (CD_2Cl_2) 1.85 s (6H), 7.40 - 7.75 m (15H)

vi) *Triphenylstibonium 4,4-dimethyl-2,6-dioxocyclohexylide (77)*

δ ($CDCl_3$) 1.175 s (6H), 2.425 s (4H), 7.625 m (9H),
7.860 m (6H)

vii) *Triphenylstibonium acetyl-p-tosylmethylide (78)*

δ ($CDCl_3$) 2.40 s (3H), 2.47 s (3H), 7.30 - 7.67 m (19H)

viii) *Triphenylstibonium benzylsulphonylmethylide (80)*

δ (CD_2Cl_2) 4.54 s (2H), 5.17 s (1H), 7.12 - 7.83 m (20H)

ix) *Triphenylarsonium 2,6-dioxocyclohexylide*

δ ($CDCl_3$) 2.03 (quintet) (2H), 2.43 t (4H), 7.37 - 7.70 m (15H)

x) *Triphenylbismuthonium 2,6-dioxocyclohexylide*

δ (d^5-pyridine) 1.82 (quintet) (2H), 2.45 t (4H), 7.13 - 7.68 m (11H), 8.27 - 8.45 m (4H)

xi) *Triphenylbismuthonium bis(phenylsulphonyl)methylide*

δ (CD_2Cl_2) 7.00 - 8.20 m

xii) *Triphenylstibine Oxide Dimer*

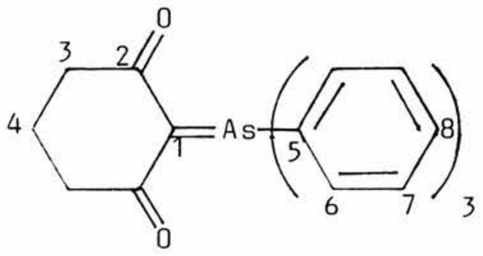
δ (CD_2Cl_2) 7.17 - 7.85 m

xiii) *Oxybis(triphenylstibonium)diperchlorate*

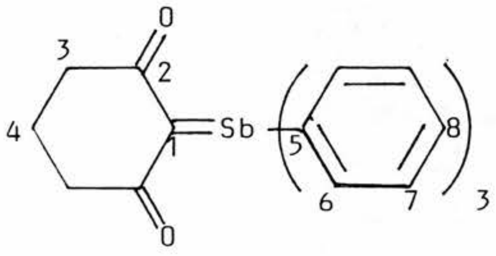
δ (CD_3OD) 7.72 - 8.20 m

s = singlet, t = triplet, m = multiplet

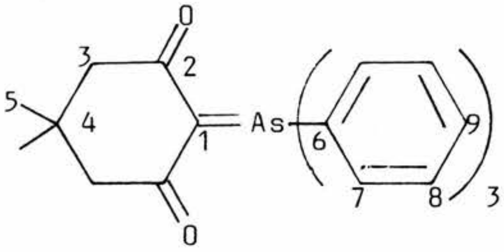
(b) ^{13}C N.M.R. SPECTRA



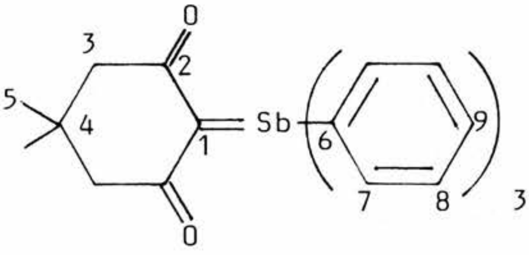
Carbon	δ/p.p.m.
4	21.5270
3	38.0756
1	89.6140
5	128.7106
7	129.3416
8	131.8461
6	133.0302
2	194.1771



Carbon	δ/p.p.m.
4	22.2318
3	37.1591
1	95.0819
5	128.5046
7	129.8508
8	131.7949
6	135.8075
2	195.2101



Carbon	δ/p.p.m.
5	28.8510
4	32.0672
3	52.0385
1	87.9065
6	128.6654
8	129.4456
9	131.9578
7	133.0817
2	193.3715



Carbon	δ/p.p.m.
5	28.9151
4	33.1049
3	51.3074
1	93.2167
6	128.4920
8	129.9888
9	131.9454
7	135.8664
2	194.3278

$(PhSO_2)_2C^1{=}AsPh_3$

Carbon	δ/p.p.m.
1	69.8476
Aromatic	127.1030
	127.7236
	128.3723
	129.6620
	131.4933
	132.6571
	133.3887
	147.4915

$(PhSO_2)_2C^1{=}SbPh_3$

Carbon	δ/p.p.m.
1	70.4855
Aromatic	126.8839
	127.4820
	128.6523
	130.3907
	131.5506
	132.7892
	135.6198
	147.4729

(c) *I R SPECTRA*

i) *Triphenylbismuthonium bis(phenylsulphonyl)methylide*

$\nu(SO_2)/cm^{-1}$ (nujol mull) 1278, 1118

ii) *Triphenylbismuthonium 2,6-dioxocyclohexylide*

$\nu(C{=}O)/cm^{-1}$ (hexachloro-buta-1,3-diene mull) broad band centred at 1440.

(d) *U V SPECTRA*

i) *Triphenylbismuthonium bis(phenylsulphonyl)methylide*

$\lambda_{max.}$ MeOH 211 (log ε = 4.42), 258 (log ε = 3.90), 264 (log ε = 3.87), 272 (log ε = 3.80).

ii) *Triphenylbismuthonium 2,6-dioxocyclohexylide*

$\lambda_{max.}$ MeOH 267 (log ε = 4.02)

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