SOME REACTIONS OF ARSENIC YLIDS.

A Thesis submitted to the
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by

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The experimental work described
in this thesis has been carried out by
the author in the Department of Chemistry
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The work has not been presented, and
is not being concurrently presented for
any other degree.

M. A. Walker
M. A. Walker.
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I gratefully dedicate this thesis to my husband, Brian, for his constant encouragement.
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SUMMARY.

The preparation and reactions of arsonium ylids have been reviewed.

A critical comparison of phosphorus and arsenic has been made in an attempt to correlate the bonding and chemistry of their ylids.

A study of the reaction of alkylidenearsoranes with carbonyl compounds has been carried out and has led to some understanding of the factors which control the formation of olefins or epoxides.

An investigation of the experimental conditions necessary for the preparation of arsonium ylids was made in an endeavour to prepare the unreported \( \lambda \)-alkyl-\( \beta \)-ketoarsonium ylids.

The course of the reaction of both alkylidenearsoranes and \( \beta \)-ketoalkylidenearsoranes with various functional groups has been investigated.
INTRODUCTION.

The first organoarsenic compound was probably prepared by Cadet de Glassicourt in 1760. He heated arsenic trioxide with potassium acetate and obtained two immiscible liquids, the heavier of which was spontaneously inflammable and became known as 'Cadet's fuming liquid'. It was later shown to be tetramethyldiarsine ("cacodyl"). Since then many thousands of organoarsenic compounds have been prepared, but little has been published on arsonium ylids.

The term 'ylid' refers to the class of polar compounds which have an heteroatom attached to a carbanion, represented by the general formula (1).

\[
\begin{array}{c}
\oplus \quad \odot \\
M - C < \\
\end{array}
\]

(1)

This description includes systems in which the heteroatom carries less than the full positive charge (2)

\[
\begin{array}{c}
\oplus \quad \begin{array}{c}
\oplus \\
\oplus \\
\odot \\
\end{array} \\
\odot - M - C < \\
\end{array}
\]

(2)

and also molecules in which an important contributing resonance structure meets the definition (3).

\[
\begin{array}{c}
\oplus \quad \odot \\
M - C - C - \longleftrightarrow \\
\oplus \quad \odot \\
M - C - C -
\end{array}
\]

(3)
Ylids were so named by Wittig\(^{(1)}\) in 1940. The term was derived by use of the ending –yl to imply open valence (i.e. alkyl) and the ending –id to imply anionicity, (i.e. acetylid) both on a carbon atom.

This class of compounds was investigated first by Staudinger and Meyer\(^{(2)}\) and also by Coffman and Marvel\(^{(3)}\). The subsequent discovery by Wittig\(^{(4)}\), that phosphonium ylids undergo reaction with carbonyl compounds to give olefins, signalled the beginning of tremendous activity in organophosphorus chemistry. The great success of this work stimulated further research into ylids containing other heteroatoms of the same group and in fact into any system containing similar structural features i.e. any heteroatom group which is capable of providing adequate stabilisation for a carbanion should form an ylid.

Arsenic, like phosphorus, is a Group V element, and therefore the electronic configurations are similar in the outer shell, each having two paired electrons in an s-orbital and three unpaired electrons in p-orbitals.

\[
P \quad [\text{Ne}] \quad 3s^2 \quad 3p^3
\]

\[
\text{As} \quad [\text{Ar}] \quad 3d^{10} \quad 4s^2 \quad 4p^3
\]

It is not surprising, then, that arsonium ylids have been prepared and reacted. Johnson\(^{(5)}\) has reviewed all relevant publications up to 1966, which are now presented together with more up to date information.
Preparation of Arsonium Ylids.

The most widely applicable method for the preparation of arsonium ylids (5) has been by the reaction of quaternary arsonium halides (4) with a suitable base. (the 'Salt Method').

\[
\begin{align*}
\oplus \text{As} & \quad \text{C} & \quad \text{R}_1^{\text{H}} & \quad \text{Base} \\
& \quad \text{H} & \quad \text{R}_2^{\text{H}} & \\
\end{align*}
\]

Since the arsonium salt (4) is ultimately converted to ylid, it must carry at least one primary or secondary alkyl group linked to arsenic. This method depends on the availability of the arsonium halides, which are prepared by treating an arsine (6) with an alkyl halide.

\[
\begin{align*}
\text{As} & \quad + \quad \text{C} & \quad \text{R}_1^{\text{H}} & \quad \text{R}_2^{\text{H}} & \quad \text{X} \\
& \quad \text{H} & \quad & & \\
\end{align*}
\]

The reaction between alkyl halides and trialkylarsines to produce alkyl arsonium salts has been known for over one hundred years\(^6\). In general alkyl bromides or iodides interact easily with trialkylarsines, but, as more negative groups, i.e. phenyl, are substituted on the arsine, the reaction becomes more difficult. There have been very few attempts to evaluate the factors effecting arsonium salt formation.\(^7\) \(^8\)
Although aryl halides do not normally undergo reaction with arsines, Chatt and Mann\(^{(9)}\) found that bromobenzene and triphenylarsine gave tetraphenylarsonium bromide in the presence of aluminium trichloride. The reaction probably proceeds by addition of the aryl halide to an initially formed 1:1 complex (7)\(^{(10)}\).

\[
(C_6H_5)_3As + AlCl_3 \rightarrow (C_6H_5)_3As.AlCl_3
\]

This method has been used to prepare compounds of the type

\[
Ar Ar' Ar'' Ar''' As^+ X^- (11)
\]

A similar type of complex (8) probably forms when triphenylarsine reacts with methyl iodide in the presence of mercuric iodide\(^{(12)}\).

\[
[(C_6H_5)_3As]_2.Hgl_2 + CH_2I \rightarrow [(C_6H_5)_3As.CH_2]_2[Hgl_4] (8)
\]

In spite of the vast number of arsonium salts prepared, very few alkylidenearsoranes have been reported.

The preparation of methylenetriphenylarsorane (10) has been reported, but no attempts have been made to isolate the ylid. Several groups, Henry and Wittig\(^{(13)}\), Grim and Seyferth,\(^{(14)}\) and Seyferth and Cohen\(^{(15)}\) prepared a solution of this ylid by treating an ethereal slurry of methyltriphenylarsonium iodide (9) with phenyl-lithium.
A volatile arsonium ylid, trimethylsilylmethylenetrimer-
methylarsorane (12) has, however, been isolated(16). It
was distilled from a reacting mixture of the corresponding
arsonium chloride (11) and butyl-lithium in ether.

\[
\text{(CH}_3\text{)}_3\text{As-CH}_2\text{-Si(CH}_3\text{)}_3\text{Cl} \quad \text{+BuLi} \rightarrow \quad \text{(CH}_3\text{)}_3\text{As-CH-Si(CH}_3\text{)}_3\text{+LiCl+BuH}
\]

(11) (12)

The arsonium chloride was prepared by the reaction of
trimethylarsine with chloromethyltrimethylsilane for four
days at 100°C in a sealed ampoule. Confirmation of the
existence of the ylid (12) was obtained by reaction with
methyl iodide and hydrogen halides to give the corresponding
arsonium salts. Miller(16) postulates that the properties
of this ylid depend to some extent on the presence of σ-bonding
from carbon to silicon and suggests the following canonical
forms (13).

\[
\text{(CH}_3\text{)}_3\text{As-CH-Si(CH}_3\text{)}_3 \leftrightarrow \quad \text{(CH}_3\text{)}_3\text{As-CH-Si(CH}_3\text{)}_3 \leftrightarrow \quad \text{(CH}_3\text{)}_3\text{As-CH-Si(CH}_3\text{)}_3
\]

(a) (b) (c)

(13)

This idea is also suggested by Schmidbaur(17) for the analogous
phosphorus ylids, in which the ylid function in trialkylalkylidene-
phosphoranes is considered to be stabilized by silyl residues
and destabilised by alkyl residues. However, comparing the
thermal stability of the analogous nitrogen ylids, that have
a transitory existence, in the order $P > As >> N$, it seems to indicate that the 'onium atom' is more important in determining the properties than is the trimethylsilyll group.

The reaction of (12) with trimethylsilanol (14) leads to a "desilylation" of the ylid with the formation of hexamethyldisiloxane (15) and methylenetrimethylarsorane (16) (18).

$$\begin{align*}
(\text{CH}_3)_3\text{As}-\text{CH-Si(CH}_3)_3 + (\text{CH}_3)_3\text{SiOH} & \rightarrow (\text{CH}_3)_3\text{SiOSi(CH}_3)_3 + (\text{CH}_3)_3\text{As-CH}_2 \\
(12) & \quad (14) \quad (15) \quad (16)
\end{align*}$$

The driving force for this reaction is the formation of the siloxane linkage.

This is the first reported instance (1968) of the basic member of the arsenic ylid series. It is interesting to note that it is thermally unstable above $38^\circ C$, yielding, amongst other products, trimethylarsine and ethylene.

Unsubstituted and substituted benzylidenetriphenylarsoranes (17) have also been prepared in solution by the salt method (19) (20) (21)

$$\begin{align*}
\text{As} & \quad \text{CH} \quad \text{Ar} \\
(17)
\end{align*}$$

Wittig and Laib (22) and Johnson (23) have both prepared fluorenylidenearsoranes (18). The former group alkylated trimethylarsine with 9-bromofluorene and obtained a yellow ethereal solution of the ylid (18a) by treatment with phenyl-lithium.

$$\begin{align*}
18a & = (\text{CH}_3)_3 \\
18b & = (\text{C}_6\text{H}_5)_3 \\
18c & = (\text{C}_6\text{H}_5\text{CH}_2)(\text{CH}_3)_2
\end{align*}$$
Johnson, however, found that the aryl analogue (18b) could be prepared from the salt simply by reaction with aqueous sodium hydroxide. Fluorenylidetriphenylarsorane (18b) separated as yellow plates and, although satisfactory analysis figures were not obtained, its identity was substantiated by subsequent reaction. With dilute acid the ylid formed its salt and with base the ylid reacted to give fluorene and triphenylarsine oxide.

Wittig and Laib (22) also prepared benzylfluorenylidenedimethylarsorane (18c) in an attempt to observe a Stephens rearrangement, but found the ylid perfectly stable undergoing normal reactions. However when they attempted to prepare solutions of benzyl(benzylidene)dimethylarsorane (20) only its transient existence was observed.

Dropwise addition of phenyl-lithium to an ethereal solution of the corresponding salt (19) produced a short-lived yellow colour, subsequent reaction then occurring. Quenching the reaction with concentrated acid produced dibenzyl (24), with water produced stilbene (23) and with methyl iodide produced trimethyl(1,2-diphenylethyl)arsonium iodide (22).
The first step in the reaction was considered by Wittig and Laib to be a Stephens rearrangement. This is the only one known for arsenic. The initial observation of such a rearrangement was made by Stephens and his co-workers in 1928, when treating benzyldimethylphenacylammonium bromide with aqueous hydroxide. The product obtained was (1-benzoyl-2-phenyl)ethyldimethylamine.

Later it was shown that a variety of groups would undergo migration including benzyl, phenacyl, allyl and propargyl, and that a variety of bases would catalyze the reaction.
Subsequently the rearrangement has been demonstrated to be intramolecular and also concerted,\(^{(27)}\) since the migrating group retains its asymmetry during the course of the rearrangement.

Thus the carbanion of the arsonium ylid attacks the migrating group to give the arsine \((21)\). It is evident that this arsine would then quaternize to yield the observed salt \((22)\). The formation of stilbene, in the presence of excess phenyl-lithium, is a little harder to visualise. No other products were isolated, although the authors put forward the following postulate.

\[
\begin{align*}
\text{CH}_3\text{As} & \xrightarrow{\text{CH}-\text{C}_6\text{H}_5} \text{CH}_3\text{As} \xrightarrow{\text{C}_6\text{H}_5\text{Li}} \text{CH}_3\text{As} \xrightarrow{\text{C}_6\text{H}_5} \text{CH}_3\text{As} \xrightarrow{\text{Li}^+} \text{CH}_3\text{As} \xrightarrow{\text{C}_6\text{H}_5} \text{CH}_3\text{As} \xrightarrow{\text{Li}^+} \\
\text{C}_6\text{H}_5 & \xrightarrow{\text{As} \xrightarrow{\text{CH}-\text{C}_6\text{H}_5} \text{C}_6\text{H}_5} \xrightarrow{\text{As} \xrightarrow{\text{CH}-\text{C}_6\text{H}_5} \text{Li}^+} \text{C}_6\text{H}_5 & \xrightarrow{\text{CH}_3 \xrightarrow{\text{CH}_2-\text{C}_6\text{H}_5} \text{CH}_3} \text{CH}_3 & \xrightarrow{\text{CH}_2-\text{C}_6\text{H}_5} \text{CH}_3
\end{align*}
\]

In view of observations made during the course of my own experiments, it seems reasonable that the route to biphenyl may have been simple nucleophilic displacement reaction at the arsenic.
10.

β-Ketoalkyldenearsoranes have also been prepared by the salt method. The very first report of an arsonium ylid was in fact the preparation of phenacylidenetriphenylarsorane (28) by Michaelis(28) in 1902. Michaelis found that phenacyl bromide and triphenylarsine formed a salt which, on treatment with sodium hydroxide, gave a new substance, formulated by him as (27)

\[
(C_6H_5)_3As + C_6H_5COCH_2Br \rightarrow (C_6H_5)_3As - CH_2 - COC_6H_5Br
\]

Kröhnke(29) repeated the experimental and obtained the same product, but formulated the substance as an arsonium ylid (28).

\[
(C_6H_5)_3As \rightarrow CH - CO - C_6H_5
\]

(28)

More recently several analogous β-keto arsonium ylids have been prepared by Nesmeyanov et al.(30) Experimentally they found that two types of reaction conditions could be successfully employed for preparing these ylids from their salts.

(a) By treatment of the salt with sodium amide in liquid ammonia at -78°C for twenty minutes, which gave the solid ylid on work up, or

(b) By treatment of a concentrated ethanolic solution with
an equivalent of sodium methyleate in methanol at room temperature.

One of the most convenient methods of preparation for phosphorus ylids, i.e. by passing ammonia into a chloroform solution of the salt, was mainly unsuccessful when applied to arsenic ylids.

It is noticeable that no (-alkyl)acylidenearsoranes (29) have been prepared.

\[
\begin{align*}
(C_6H_5)_3\text{As} & \quad \text{O} \quad \text{O} \\
& \quad \text{C} \quad \text{CO} \quad \text{R}^1 \\
& \quad \text{R}
\end{align*}
\]

\[(29)\]

β-Ketocyclidenearsoranes have also been prepared by a second general route, i.e. by the reaction of dihalotriarylarsonsoranes (30) with compounds containing active methylene groups.

\[
\begin{align*}
R_1 & \quad \text{X} \\
R_2 & \quad \text{As} \\
R_3 & \quad \text{X}
\end{align*}
\]

\[(30)\]

Horner and Oediger (31) allowed dichlorotriphenylarsorane (31) to react with a number of active methylene compounds, at 80°C, in the presence of triethylamine to afford the stabilized arsenium ylids (32).

\[
\begin{align*}
(C_6H_5)_3\text{As} \quad \text{Cl}_2 & \quad \text{CH}_2 \\
& \quad \text{X} \\
& \quad \text{Y}
\end{align*}
\]

\[(31)\]

\[
\begin{align*}
\left(\frac{C_2H_5}{3}\right)\text{As} & \quad \text{O} \quad \text{O} \\
& \quad \text{C} \quad \text{X} \\
& \quad \text{Y}
\end{align*}
\]

\[(32)\]
One remaining route for the preparation of arsonium ylids has been observed. This was involved in the preparation of a cyclopentadienyldenearsorane. The first attempted preparation of this type of ylid was made by Nesmeyanov and his co-workers using the 'salt-method'. A good yield of cyclopentadienyltriphenylarsorane bromide (35) was obtained by treating triphenylarsine oxide (33) with cyclopentadienylmagnesium bromide (34).

\[
\text{(33)} \quad \text{(34)} \quad \text{(35)}
\]

However, the action of base on the salt (35) did not result in the formation of ylid. The authors either recovered the salt unchanged or it was hydrolysed. This result was unexpected, as they remark, since the analogous phosphorus compound (32) is very stable.

Lloyd and Singer were more successful and succeeded in isolating tetraphenylcyclopentadienyldenetriphenylarsorane (36).
This was achieved by heating, at its melting point, diazotetraphenylcyclopentadiene in the presence of triphenylarsine. The authors suggest that the arsonium ylid (36) results from reaction of a carbene with the lone pair on the arsine. However, evidence for the presence of carbene is not given so it may well be a reaction promoted by the presence of triphenylarsine.

Properties of Arsonium Ylids.

Ylids are unique substances in many ways. They are polar molecules as indicated by dipole measurements yet they exhibit solubility behaviour characteristic of covalent compounds. Although very little is known about the chemical and physical properties of arsonium ylids, of those isolated all behaved in the expected manner by dissolving in benzene or chloroform and by being insoluble in water and/or ethanol. However, they will dissolve in dilute aqueous acid showing they are basic and that they undergo the reverse reaction used in their formation from arsonium salts. Thus Wittig and Laib (22) isolated the expected salt (37) after treatment.
of fluorenylidene(trimethyl)arsorane (18a) with hydrogen bromide and potassium iodide.

Fluorenylidene(tribenzyl)arsorane (18b) could be stored at room temperature for some months before it began to lose colour (hydrolyse) but the \( \beta \)-keto arsoranes (30) decomposed more rapidly during storage. All of the arsonium ylids mentioned here are termed 'stable', which is meant to infer that they can be handled in the atmosphere. 'Reactive' ylids are taken as those which must be handled under nitrogen since they are very reactive to water or oxygen. Stability, then, refers in this context to chemical stability and not to any inherent thermodynamic stability. Indeed of those ylids reported it appeared that arsonium ylids were not thermally sensitive, unlike sulphonium ylids, many of which decompose spontaneously to 'carbenoid' intermediates and sulphide. However later work in this thesis shows that thermal instability may be a problem.

The Reactions of Arsonium Ylids.

The reported reactions that arsonium ylids undergo are
few in number. In general they have been found to be more reactive than their phosphorus analogues as will be demonstrated. Since arsonium ylids are essentially a special form of carbanion they should partake in many of the reactions such as alkylation, acylation, Michael additions, characteristic of nucleophiles.

This has been demonstrated with methylenetriphenylarsorane (10), which displaced bromide ion in trimethylbromosilane (38) to form the trimethylsilylmethylenetriphenylquaternary bromide (39) and also formed a 1:1 adduct (40) with boron trifluoride.

\[
\begin{align*}
\text{(C}_6\text{H}_5\text{)}_3\text{As} - \text{CH}_2 + (\text{CH}_3)_3\text{Si Br} & \rightarrow (\text{C}_6\text{H}_5\text{)}_3\text{As} - \text{CH}_2 - \text{Si(Ch}_3\text{)}_3\text{Br} \\
(10) & \quad (38) & \quad (39)
\end{align*}
\]

These reactions show close similarities to those of methylene-triphenylphosphorane.

Phenacylidenetriphenylarsorane (28) also behaved typically giving the expected products (41) and (42) with bromine and sulphur trioxide.
The sulphobetaine (42) was prepared by sulphonation in dioxane using a technique developed by Nesmeyanov (33) and was a crystalline solid, m.p. 246°C.

It would appear that arsonium ylids are subject to hydrolysis, but the conditions required to effect cleavage of an (As-C) bond vary widely with the structure of the ylid. Thus stable ylids remain unchanged in the presence of water, while the reactive ylid, methylenetriphenylarsorane (10) formed rapidly the quaternary arsonium hydroxide. This could be trapped by addition of picric acid resulting in the precipitation of the arsonium picrate. (15) This is in contrast to the phosphonium ylid which rapidly decomposes to hydrocarbon and phosphine oxide.

Fluorenylidetriphenylarsorane (18b) and phenacylidene-triphenylarsorane (28) both require base to bring about hydrolysis, but the products are those to be expected by analogy with phosphorus. No evidence for a mechanism has been presented for arsonium ylids, but the hydrolysis probably proceeds via a pentacovalent intermediate (5) (43).
The most stable carbanion is ejected and for the cases in question these would be fluorenylidene and phenacylidene respectively, giving fluorene and acetophenone, the isolated products.

Most of the reactions of arsonium ylids studied have been concerned with their behaviour towards carbonyl compounds to compare them with phosphonium ylids, i.e. a Wittig reaction. This type of ylid reaction is unique in that both the heteroatom and the carbanion are involved mechanistically during the reaction. The first published report of one such reaction for arsenic was made by Wittig and Laib when they treated benzophenone with fluorenylidene trimethylarsorane (18a). The reaction appeared disappointing in that the product isolated (9-fluorenyldiphenylcarbinol (45)) was simply the result of carbanion addition.
However, the authors used a one mole excess of phenyl-lithium in their reaction mixture and it is feasible that this may have caused a different mechanism. Later work shows that this reaction is odd man out and Johnson\(^{(5)}\) suggests that a reinvestigation is called for. Some of the work, however, published in this thesis suggests organo-lithium attack at the 'onium atom, which is exactly that preferred by Wittig and Laib to explain the products.

\[
\begin{align*}
\text{HgO} & \quad \xrightarrow{\text{C}_6\text{H}_2\text{Li}} \quad \text{C}_6\text{H}_5\text{Li} \quad \xrightarrow{(\text{CH}_3)_2\text{As}} \quad \text{(CH}_3)_2\text{As-C}_6\text{H}_5 \\
\text{H}_2\text{O} & \quad \xrightarrow{\text{H}_2\text{O}} \quad (\text{CH}_3)_3\text{As C}_6\text{H}_5 + \quad (\text{C}_6\text{H}_5)_2\text{C}^{\theta} \text{OH}
\end{align*}
\]

Both trimethylphenylarsonium iodide (44) and the alcohol (45) were identified. However the last stage, hydrolytic cleavage, seems rather surprising.

Johnson\(^{(23)}\) later published the reaction of fluorenylidene-triphenylarsorane with a number of carbonyl compounds and showed that a normal Wittig reaction took place giving the expected olefin (46) and triphenylarsine oxide.
His results are shown in Table (I).

Table (I)

The Reaction of Fluorenylidetriphenylarsorane
with Substituted Benzaldehydes.

<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>Yield of Olefin (46)</th>
<th>Yield of Arsine Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>$C_6H_5$</td>
<td>74</td>
<td>37</td>
</tr>
<tr>
<td>H</td>
<td>$pNO_2-C_6H_4$</td>
<td>92</td>
<td>26</td>
</tr>
<tr>
<td>H</td>
<td>$pCl-C_6H_4$</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>H</td>
<td>$pCH_3O-C_6H_4$</td>
<td>89</td>
<td>65</td>
</tr>
<tr>
<td>H</td>
<td>$p(CH_3)_2N-C_6H_4$</td>
<td>97</td>
<td>51</td>
</tr>
<tr>
<td>H</td>
<td>$CH_3$</td>
<td>91</td>
<td>78</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$C_6H_5$</td>
<td>$C_6H_5$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The arsorane, undergoing reaction equally well with all substituted benzaldehydes, was non-specific. Also no evidence for any simple carbanionic additions was found.
At about the same time as this publication appeared, Henry and Wittig\textsuperscript{(13)} reported the reaction of methylene-triphenylarsorane with benzophenone. Four products were obtained: triphenylarsine, diphenylacetaldehyde (48), triphenylarsine oxide and diphenylethylene (49). The former and latter pair were each formed in equimolar amounts. The authors suggested that, after the initial formation of the ylid from its salt, reaction with benzophenone produced an intermediate (47). This could either rearrange to give arsine oxide and olefin or by some other route rearrange to give arsine and an epoxide ring, which rearranged to give the observed aldehyde.

\[
\begin{align*}
(C_6H_5)_3\text{As}-CH_3 & \xrightarrow{\Theta} C_6H_2Li \quad (C_6H_5)_3\text{As}-CH_2 \xrightarrow{\Theta \Theta} (C_6H_5)_2CO \quad [C_6H_5)_3\text{As}-CH_2 \xrightarrow{\Theta} O-C -(C_6H_5)_2 \\
(C_6H_5)_2CHCHO & \xleftarrow{\Theta \Theta} (C_6H_5)_2C\text{-CH}_2 + (C_6H_5)_2\text{As} \\
(C_6H_5)_3\text{As}-0 & \xrightarrow{\Theta \Theta} (C_6H_5)_2C\text{-CH}_2
\end{align*}
\]

The major portion of the intermediate (47), or betaine as it is now called, decomposed to triphenylarsine and the corresponding product. It is worth noticing that Wittig...
worked this reaction up by column chromatography after hydrolysis with 6N hydrochloric acid, and that epoxides are known to rearrange under acid conditions.\(^{(35)}\)

Evidence that epoxides are, in fact, primary products was supplied by Johnson and Martin.\(^{(19)}\) They allowed benzylidene triphenylarsorane (50) to react with p-nitrobenzaldehyde in ether and subsequent chromatography yielded triphenylarsine, 4-nitrostilbene epoxide (51), triphenylarsine oxide and 4-nitrostilbene (52).

\[
\begin{align*}
(C_6H_5)_3As-CHC_6H_5 + O_2N &\rightarrow (C_6H_5)_3As+C_6H_5CH-CH=\overset{\text{CHO}}{\text{O}} \quad (51) \\
(C_6H_5)_3As-O+C_6H_5-CH=CH-\overset{\text{NO}_2}{\text{CH}} &\rightarrow (C_6H_5)\_3As-0+C_6H_5-CH-CH-\overset{\text{NO}_2}{\text{CH}} \quad (52)
\end{align*}
\]

Obviously arsonium ylids can react with carbonyl compounds to give two possible products, either olefins or epoxides. Discussion of this will be dealt with in the following pages of thesis.

Huang\(^{(36)}\) caused carbomethoxymethylene triphenylarsorane (53) to react with various carbonyl compounds and obtained \(\alpha,\beta\)-unsaturated esters (54),

\[
\begin{align*}
(C_6H_5)_3As-CH-COOMe+H^1\overset{R}{\text{C}=\overset{R}{\text{C}}=0} &\rightarrow (C_6H_5)_3As-O+H^1\overset{R}{\text{C}=}\overset{R}{\text{C}}=\overset{R}{\text{C}}=\overset{R}{\text{C}}=\overset{R}{\text{C}}\text{OOMe} \\
(53) &\quad (54)
\end{align*}
\]
and Nesmeyanov\(^{(30)}\) treated phenacylidenetriphenylarsoranes (28) with carbonyls to give \(4,\beta\)-unsaturated ketones (55).

\[
\begin{align*}
\text{(C}_6\text{H}_5\text{)}_3\text{As} - \text{CH} - \text{CO} - \text{C}_6\text{H}_5 + \text{R}_1\text{C}=\text{O} & \rightarrow (\text{C}_6\text{H}_5\text{)}_3\text{As} - \text{O} + \text{R}_1\text{C} = \text{CH} - \text{CH} - \text{CO} - \text{C}_6\text{H}_5
\end{align*}
\]

(55)

This concludes the survey of the literature of arsonium ylids in this thesis.
Group Properties.

The predictable properties of organoarsenic chemistry in relation to phosphorus and other Group V elements are exemplified by consideration of group properties (Table II).

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>P</th>
<th>As</th>
<th>Sb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic Structure</td>
<td>He</td>
<td>Ne</td>
<td>Ar</td>
<td>Kr</td>
<td>Xe</td>
</tr>
<tr>
<td>2s^2p^3</td>
<td>3s^2p^3</td>
<td>3d^10s^2p^3</td>
<td>4d^10s^2p^3</td>
<td>4f^14s^2p^3</td>
<td></td>
</tr>
<tr>
<td>Sum of 1st 3 I.P</td>
<td>91.6</td>
<td>60.4</td>
<td>58.0</td>
<td>52.3</td>
<td>52.0</td>
</tr>
<tr>
<td>Radii (Å)</td>
<td>1.7 (N^3^-)</td>
<td>2.12 (P^3^-)</td>
<td>-</td>
<td>0.92 (Sb^3+)</td>
<td>1.0 (Bi^3+)</td>
</tr>
<tr>
<td>Ionic</td>
<td>0.70</td>
<td>1.10</td>
<td>1.21</td>
<td>1.41</td>
<td>1.52</td>
</tr>
<tr>
<td>Covalent</td>
<td>1.47</td>
<td>1.87</td>
<td>1.98</td>
<td>2.18</td>
<td>-</td>
</tr>
<tr>
<td>C-X (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electro-negativity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pauling (1960)</td>
<td>3.0</td>
<td>2.1</td>
<td>2.0</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Allred-Rochow</td>
<td>3.04</td>
<td>2.06</td>
<td>2.20</td>
<td>1.82</td>
<td>1.67</td>
</tr>
</tbody>
</table>

The electronic configurations of all the elements show the same outer shell arrangement, each having two paired electrons in an s-orbital and three unpaired electrons in p-orbitals.
Phosphorus like nitrogen, is essentially covalent in its chemistry whereas arsenic, antimony and bismuth become increasingly metallic (cationic). Because of the high ionisation potentials +5 ions do not exist, but for the 3-valent state, antimony and bismuth do show some cationic behaviour. The trends of the group are shown by the oxides which change from acidic for phosphorus to basic for bismuth. There is also an increase in the stability of the lower oxidation state with increasing atomic number. Thus bismuth pentoxide (Bi$_2$O$_5$) is the most difficult to prepare and the least stable. When nitrogen, being a first row element, has completed 2s and 2p orbitals it has only 3s orbital as the next available empty orbital. This accounts for the differences between it and other group V elements, since the remainder have available vacant orbitals of usable energy levels and hence are able to form a higher covalent state than nitrogen.

The essential differences between nitrogen and the other elements are shown in Table III, and, since these are the same factors which will account for the observed differences of phosphorus and arsenic they will each be discussed in turn.
Table III

Differences Between Nitrogen and Phosphorus and Arsenic

<table>
<thead>
<tr>
<th>Bonds</th>
<th>N</th>
<th>P As.</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(\Pi) - p(\Pi)</td>
<td>Very strong</td>
<td>None (a)</td>
</tr>
<tr>
<td>p(\Pi) - d(\Pi)</td>
<td>None</td>
<td>Weak to moderate, but important (b)</td>
</tr>
<tr>
<td>Valence Expansion</td>
<td>None</td>
<td>Valence Expansion. (c)</td>
</tr>
</tbody>
</table>

(a) p\(\Pi\) - p\(\Pi\) Bonds.

As would be expected from the electronic configurations, nitrogen, phosphorus and arsenic are able to form covalent \(\sigma\) bonds with three substituents, i.e. \(R_3M\). Other than nitrogen which is essentially \(sp^3\) hybridised, the hybridisation of the central atom appears to be between \(p^3\), requiring bond angles of 90°, and \(sp^3\) requiring bond angles of 109.5°. However the analogy with structures based on multiple bonds is limited to bare existence for phosphorus and arsenic. This disappearance of multiple bonded structures familiar for carbon, nitrogen and oxygen is general from first to other group elements. Evidently the conditions for good overlap to form \(p\sigma\) bonds, very favourable for 2p orbitals separated by 2p\(\sigma\) bonds, are much less so for the more diffuse (n)p orbitals separated by the longer (n)p\(\sigma\) bonds.

Thus compounds such as \(P(OR)_3\) exist but not \(N(OR)_3\) since the preferred arrangement is O=\(N(OR)\).
(b) $P\pi - d\pi$ Bonds.

Again the electron configuration suggests that tri-substituted compounds will be Lewis bases, and in fact they are able to act as donors because of their lone pairs. Nitrogen atom compounds can, however, have no function other than simple donation because of the lack of availability of orbitals of suitable energy levels. However when the atom, to which phosphorus or arsenic donates, has electrons in orbitals of the same symmetry as its empty d-orbitals, then back-donation may occur resulting in overall multiple bond character. Because of the relatively high energy of the d-orbitals and the unsymmetrical distribution of the bonding electrons (which leaves the bond polarised in the sense $N^6-X^6$), $(p\pi-d\pi)$ bonds are expected to be considerably weaker than $(p\pi)$ bonds.

The consequences of d-orbital are found by comparing the amine oxides $R_3N^6-O^6$ with phosphine oxides $R_3P^6-O^6$. All phosphorus-oxygen bond lengths, that have been measured, are shorter than the Schomaker-Stevenson calculated value of 1.71Å. (37), e.g. for trimethylphosphine oxide ($Me_3P-O$) the P-O bond is 1.46Å.

The dipole moment (38) is little more than half that expected for a single bond (39) and the bond strength is much higher than would be expected for the single bonded
Oxygen has two lone pairs available for overlap with the d-orbitals of phosphorus and so one might expect to form three bonds, which would give the symmetry, though not necessarily the strength, of a triple bond.

Further evidence for this type of bonding is supplied by phosphorus-fluorine bonds, the exceptional strength and shortening of which is well-known. Like oxygen, the halogens have two lone pairs available and thus a similar type 'triple' bond is possible, but these will be weaker because the halogen atom is neutral. These properties are reflected in the stability of the $\text{FPo}_3^{2-}$ anion ($\text{ClPO}_3^{2-}$ decomposes too fast for measurement) and the high nucleophilicity of fluoride ion in displacement reactions at phosphorus. It is apparently unimportant with chlorine partly, presumably because of its lower electronegativity and partly because $p\pi - d\pi$ bonding will be more efficient with 2p than with 3p orbitals.

(i) The Effectiveness of $p\pi - d\pi$ Bonding.

(1) By Dipole Moment Measurements.

An estimate of the effectiveness of $p\pi - d\pi$ bonding, (by overlap of 4d orbitals with the filled 2p orbitals of oxygen) in arsine oxides was made by Phillips and his workers. They calculated the apparent vector changes of moment which accompanied the formation of the oxides, sulphides or boro-
halides from amines, phosphines and arsines. For symmetrical bases the new bond is along the axis of symmetry so that the required vector was the algebraic difference of the moments of the donor molecules (X) and of the complex Y ($\Delta \mu_{x-y}$), provided the moment of the donor molecules remains unchanged.

The results they obtained are shown in Table IV.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$\Delta \mu_{x-y}$</th>
<th>Bond</th>
<th>$\Delta \mu_{x-y}$</th>
<th>Bond</th>
<th>$\Delta \mu_{x-y}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv N-O$</td>
<td>4.25</td>
<td>$\equiv N-BCl_3$</td>
<td>5.50</td>
<td>$\equiv P-PtCl_2$</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\equiv N-BF_3$</td>
<td>5.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv P-O$</td>
<td>2.89</td>
<td>$\equiv P-BCl_3$</td>
<td>5.8</td>
<td>$\equiv As.PtCl_2$</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>(2.66)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv As-O$</td>
<td>4.43</td>
<td></td>
<td></td>
<td>$\equiv As.PtCl_2$</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>(4.14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv Sb-S$</td>
<td>4.46</td>
<td></td>
<td></td>
<td>$\equiv Sb.PtCl_2$</td>
<td>6.12</td>
</tr>
</tbody>
</table>

From these results the authors point out that the vector changes ($\Delta \mu_{x-y}$) are not very different for all the nitrogen bonds in the formation of $\equiv N\rightarrow O$, $\equiv N\rightarrow BCl_3$ and $\equiv N\rightarrow BF_3$, ranging from 4.25 - 5.5. Also that the vector change $\Delta \mu_P \rightarrow BCl_3$ is about the same as $\Delta \mu_N \rightarrow BCl_3$.

Assuming then that the simple relation

$$\frac{\Delta \mu_N \rightarrow 0}{\Delta \mu_P \rightarrow 0} = \frac{\Delta \mu_N \rightarrow BCl_3}{\Delta \mu_P \rightarrow BCl_3}$$
holds, the expected value $\Delta \mu_P > 0$ would be 4.25, but since the observed value is only about 2.7 there is a large amount of double bond character. The values for $\Delta \mu_{As} \rightarrow 0$ and $\Delta \mu_{Sb} \rightarrow S$ are about the same as $\Delta \mu_N \rightarrow 0$, suggesting that overlap is not effective in these instances. However no definite conclusions were reached by the authors on this point since the values are considerably less than for

$$\Delta \mu_{As \rightarrow PtCl_2} \text{ and } \Delta \mu_{Sb \rightarrow PtCl_2}.$$ 

(2) By Use of pka Measurements

If arsenic, or antimony are to be involved in ylid formation they must be capable of stabilizing an adjacent carbanion. It is thought very debatable that effective overlap could occur between 4d or 5d orbitals on the arsenic and antimony with a 2 p-orbital on a carbon certainly if based on the neutral trivalent arsine or stibine. However conversion of the arsine or stibine into a quaternary salt, thereby forcing the central atom to carry a high degree of positive charge, probably would contract the normally diffuse d-orbitals such that effective overlap with a 2 p orbital could occur. Obviously as the element becomes larger and the principal quantum number of the d-orbital increases then the effectiveness of $2p-d^n$ bonding must decrease. Johnson and Amel(44) have attempted to measure the effectiveness of $p^n-d^n$ overlap for arsenic, phosphorus and sulphur by comparing the pka's of a series of phenacyl 'onium salts (56).
The authors consider that the $pK_a$ value indicates the relative effectiveness of the group $M$ in increasing the acidity of the 'onium salts (56) or in stabilizing the corresponding ylids (57). They view these two characteristics as being complementary if not synonymous.

Phenacylides are recognised to be stabilised by delocalisation of the negative charge by the carbonyl portion (57a) and by $p\pi-d\pi$ bonding (57b).

For example, Stephens [45] measured the bond length of $P-C$ in $\alpha$-halophenacylidenediophenylphosphoranes and showed that the measured ylid bond length (1.72 Å) is between the single bond length (1.87 Å) and the double bond length (1.33 Å), that the $C-CO$ bond (1.35 Å) is very close to the double bond length (1.33 Å) and that the $C-O$ bond (1.28 Å) is considerably longer than the double bond (1.23 Å).

Thus $pK_a$ value gives a measure of the driving force of the salt towards the formation of its ylid. The results obtained are shown in Table V.
Table V.

pka's of Phenacyl 'onium Salts.

<table>
<thead>
<tr>
<th>Compound M</th>
<th>pka</th>
</tr>
</thead>
<tbody>
<tr>
<td>((CH_3)_2S)</td>
<td>7.68</td>
</tr>
<tr>
<td>((CH_3)_3P)</td>
<td>8.60</td>
</tr>
<tr>
<td>((CH_3)_3As)</td>
<td>9.80</td>
</tr>
<tr>
<td>((CH_3)(C_6H_5)S)</td>
<td>6.66</td>
</tr>
<tr>
<td>((CH_3)_2(C_6H_5)P)</td>
<td>7.75</td>
</tr>
<tr>
<td>((CH_3)_2(C_6H_5)As)</td>
<td>9.45</td>
</tr>
<tr>
<td>((C_6H_5)_2S)</td>
<td>5.36</td>
</tr>
<tr>
<td>((C_6H_5)_3P)</td>
<td>5.60</td>
</tr>
<tr>
<td>((C_6H_5)_3As)</td>
<td>8.25</td>
</tr>
</tbody>
</table>

These clearly show that, in structurally parallel cases, the acidifying effects of the 'onium groups increase in the order As\(^+\) < P\(^+\) < S\(^+\) or in other words the effectiveness of p\(\pi\)-d\(\pi\) overlap for ylid stabilization is in the order S > P > As. This fact is perhaps substantiated by the altered values of pka when altering the nature of the substituent on the heteroatom. In all instances replacement of methyl by phenyl led to a decrease in the pka of the salt. This increase in acidity was attributed, by the authors, to the powerful inductive withdrawal effect of the phenyl group (relative to alkyl) which results in a decrease of electron density on
the heteroatom. Thus this gives better π\(\pi\)-d\(\pi\) overlap and affords more stabilization to the ylid.

(3) By Deuterium Exchange Measurements.

The problem of determining the importance of d-orbital resonance has also been attempted quantitatively by Doering and Hoffmann. They studied the rate of deuterium exchange of tetramethyl 'onium salts which would be determined by the difference in free energy between the starting product (in deuterium oxide solution) and the transition state for the exchange reaction. It was assumed that this transition state would be the one involved in the production of an intermediate ylid and that differences in heats of activation would be a reflection of the varying abilities of 'onium groups to stabilise the adjacent partial negative charge, (π\(\pi\)-d\(\pi\) bonding).

\[
\begin{array}{c}
\text{M} - \text{C} - \text{H} + \text{OD} \\
\text{H}
\end{array}
\rightarrow
\begin{bmatrix}
\text{M} - \text{C} - \text{H} & \text{OD} \\
\text{H} & \text{H}
\end{bmatrix}
\rightarrow
\begin{array}{c}
\text{H} - \text{OD} + \text{M} - \text{C} - \text{H} \\
\leftrightarrow \text{M} - \text{C} - \text{H}
\end{array}
\]

(58)
Even if the exchange was concerted the authors considered the carbon atom would still possess a negative charge in the transition state, differences in the attenuation of which would still be discernible through kinetic investigation.

They found that under identical conditions sulphonium phosphonium, arsonium and stibonium had incorporated respectively 98.0%, 74%, 7% and 1.0% of deuterium. Nitrogen, however, even at a higher temperature and much longer reaction time had only incorporated 1%.

Coulombic interaction should lead to the predication of more rapid exchange for the ammonium (C-N 1.47 Å) than phosphonium (C-P 1.87 Å). Since phosphonium exchanged faster by several orders of magnitudes than ammonium, Doering and Hoffmann conclude that a factor, namely d-orbital contribution, is noticeable. The difference of 6.6 k.cal. in the heat of activation gives quantitative confirmation to this hypothesis. (see Table VI).

<table>
<thead>
<tr>
<th>Salt</th>
<th>$\Delta H_{\text{exp}}$ (k.cal)</th>
<th>$\Delta S$ (cal. °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsuperscript{$\Theta$}</td>
<td>32.2 ± 0.6</td>
<td>-15 ± 2</td>
</tr>
<tr>
<td>P\textsuperscript{$\Theta$}</td>
<td>25.6 ± 0.2</td>
<td>+ 4 ± 1</td>
</tr>
<tr>
<td>S\textsuperscript{$\Theta$}</td>
<td>22.4 ± 0.5</td>
<td>- 1 ± 2</td>
</tr>
</tbody>
</table>
Further, the authors comment that in the absence of any resonance stabilization in the intermediate and assuming that only coulombic effects were operative, the heat of activation for the phosphonium salt would have been 41 k. cal. Thus the effective stabilization was in the vicinity of 15 k.cal/mole rather than the observed value.

The differences in the entropy values are also significant, since not only do they account for a good deal of the observed differences in the rates of deuterium exchange, but they are also in the direction expected if resonance stabilization is operative. Thus, if the resonance form (58c) is important in the transition state, a release of solvent would be expected to accompany conversion of the ionic salt into the less polar ylid. This would lead to a more favourable $\Delta S^\ddagger$, which was of course observed. It is also worth noticing here that Johnson's later work also places sulphur and phosphorus in this order. Unfortunately little information can be gained from Doering's experiments about arsonium or stibonium since only one experiment was carried out for each. Thus only one rate constant could be calculated and consequently no value for the heat or entropy of activation. Thus, although the rate of exchange was much lower for these latter salts, no sensible attempts can be made to evaluate them.

The authors, however, postulate that the decrease in
rate is probably due to the increase in bond length, which decreases the coulombic lowering of the activation energy. This assumes that the entropy of activations are constant for arsenic and antimony and that also the contribution of $p\pi-d\pi$ bonding remains roughly constant throughout. The authors suggest that this is reasonable because of the small decrease in strength shown by $\sigma$-bonds of increasing length. However they based this idea on the strength of phosphorus, arsenic and antimony $\sigma$-bonds with halogens which do only show a gradation of about 4 k.cal. at most. Unfortunately the more recent measurements of C-P, C-As, C-Sb show a difference of 11 k.cal. in the mean dissociation energy values and it should be realised that a difference in $k$ value of 100, results, when the entropy of activation term remains constant, for a difference in activation energy of only about 1 k.cal.

(c) Valence Expansion.

As mentioned previously unique reactions of ylids involves both heteroatom and carbonanion mechanistically during the course of a reaction. Thus in the Wittig reaction the initial nucleophilic attack of the ylid carbonanion on the carbonyl carbon leads to the formation of a betaine intermediate. This passes through a pentacovalent transition
state (60) to afford phosphine oxide and olefin.

\[
\begin{align*}
\text{R}_1 \text{R}_2 \text{C} & \quad \text{R}_3 \text{R}_4 \text{C} = 0 \\
\rightarrow & \\
\begin{aligned}
\text{R}_1 \text{R}_2 \text{C} & \quad \text{R}_3 \text{R}_4 \text{C} = 0 \\
\text{R}_1 \text{R}_2 \text{C} & \quad \text{R}_3 \text{R}_4 \text{C} = 0 \\
\end{aligned}
\end{align*}
\]

The final transition state (60) is probably superceeded by the formation of a pentacovalent intermediate (59a)

\[
\begin{align*}
\text{R}_1 \text{R}_2 \text{C} & \quad \text{R}_3 \text{R}_4 \\
\rightarrow & \\
\begin{aligned}
\text{R}_1 \text{R}_2 \text{C} & \quad \text{R}_3 \text{R}_4 \\
\text{R}_1 \text{R}_2 \text{C} & \quad \text{R}_3 \text{R}_4 \\
\end{aligned}
\end{align*}
\]

Therefore, the ability of the heteroatom to undergo valence expansion is very probably a necessary feature of a 'Wittig-type' reaction.

(1) For Nitrogen.

Evidence for valence expansion for nitrogen has been much sought after in the past. Schlenk and Holtz\(^{(48)}\) in 1916, made early attempts to demonstrate the existence of pentavalent nitrogen. They isolated tetramethylammonium triphenylmethide (61), but it was a highly coloured substance
undergoing typical carbanionic reactions.

\[
(C_6H_5)_3\text{C}Na + (CH_3)_4\text{NCl} \rightarrow (CH_3)_4\text{N}C(C_6H_5)_3
\]

However subsequent attempts by Hager and Marvel to prepare analogues, in which all five groups were more alike, failed. They concluded that the stability of Schlenk's product was due to the stability of the carbanion and not due to the formation of five valent nitrogen.

Later Wittig and Wetherling tried to prepare a pentacovalent nitrogen compound by allowing phenyl-lithium to react with tetramethylammonium bromide. It was not obtained, but an ylid complex \((62)\) was isolated.

\[
(CH_3)_3\text{N-CH}_3\text{Br} + C_6H_5\text{Li} \rightarrow (CH_3)_3\text{N-CH}_2\text{LiBr} + C_6H_6
\]

The thermodynamic instability and great reactivity, characteristic of carbanion chemistry only, led Doering and Hoffman to conclude that nitrogen ylids are stabilized only by electrostatic forces.

(2) For Phosphorus, Arsenic and Antimony.

The ability of phosphorus, arsenic and antimony to expand their octets has been indicated clearly by the isolation of
pentavalent derivatives. Examples include PF$_5$, PF$_5$Cl$_2$ \((51)\)
\((C_6H_5)_5P\)\(^{(52)}\) AsF$_5$, \((C_6H_5)_5As\)\(^{(53)}\)(54) SbP$_5$, SbCl$_5$, AsF$_6$\(^\Theta\)
and SbF$_6$.\(^{(55)}\)

The proposed hybridisation of orbitals for some compounds are shown in Table VII.

Table VII

<table>
<thead>
<tr>
<th>CO.NO.</th>
<th>Bonding</th>
<th>Geometry</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>(p^3) sp(^3)</td>
<td>Pyramidal</td>
<td>PH$_3$, AsCl$_3$, (C$_6$H$_5$)$_5$Sb.</td>
</tr>
<tr>
<td>4</td>
<td>sp(^3)</td>
<td>Tetrahedral</td>
<td>PH$_4$</td>
</tr>
<tr>
<td>5</td>
<td>sp(^3)d</td>
<td>Trigonal Bipyramidal</td>
<td>PF$_5$, AsF$_5$, (C$_6$H$_5$)$_5P$, (C$_6$H$_5$)$_5$As</td>
</tr>
<tr>
<td>6</td>
<td>sp(^3)d(^2)</td>
<td>Octahedral</td>
<td>PF$_6$(^\Theta), AsF$_6$(^\Theta), Sb(OH)$_6$ (3\Theta)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(SbF$_6$(^\Theta))(^n)</td>
</tr>
</tbody>
</table>

X-ray diffraction methods have shown the structure of penta-phenylphosphorane \(((C_6H_5)_5P)\) and presumably the isomorphous pentaphenylarsorane \(((C_6H_5)_5As)\) to be bipyramidal which is unlike the antimony analogue which has a square pyramidal geometry. Sodium hexafluoroantimonate contains the octahedral SbF$_6$.\(^\Theta\) ion consistent with the proposed hybridisation for antimony of sp\(^3\)d\(^2\).
Of the compounds studied in detail, i.e. PCl₅ and (C₆H₅)₅P, the two axial bonds are longer than the equatorial bonds (63).

The difficulty in assigning the orbitals involved is that the energy gained by forming five covalent bonds is smaller than any reasonable estimate of the energy required to promote an s-electron to a d-level. This led Pauling (56) originally to doubt that d-orbitals are involved at all, i.e. he proposed structures of the type PCl₄⁺Cl⁻ with five equivalent bonds, each having \( \frac{1}{3} \)th ionic character. The objection to this idea is that it does not require the bonding orbitals to be localised; however that pentacovalent compounds do have precise structures is well-known. Since the trigonal bipyramidal configuration is that expected (57) for compounds using sp³d hybridised orbitals and since the greater length of the axial bonds are predictable (58), it is usually accepted that a d-orbital must be involved. The extent to which hybridisation occurs, however, is still somewhat uncertain, so the higher states may well be stabilized partly by electrostatic forces. It is probably significant that the higher co-ordination numbers for \( P^V \) are most readily obtained when the more electronegative
groups such as halogen, alkoxy (59) or phenyl are present.

From all this data it is clear that arsenic, (and also antimony) can expand their outer valence shell to accommodate at least ten electrons.

**The Ease of Valence Expansion**

The most fruitful source for information of this type has been provided by the use of trivalent arsenic and phosphorus compounds as ligands in the formation of complexes with transitional metals.

According to Chatt (60) in 'complex chemistry' there are two kinds of acceptors,

(a) those which form their most stable complexes with the first ligand atom of each group; i.e. with N, O and F, and
(b) those which form their most stable complexes with the second or subsequent ligand atom.

This is in addition to the very great difference between the co-ordinating affinities of 1st and 2nd elements of each group.

With class (a) acceptors (or hard acids using Pearson's (61) general approach) Group V co-ordinating affinities lie in diminishing sequence $N > P > As > Sb > Bi$, and with class (b) acceptors (or soft acids) in the sequence $N << P < As > Sb > Bi$. 
The important feature of class (b) acceptors, in Chatts' opinion, is the presence of loosely held outer d-orbital electrons which can form π-bonds by donation to suitable ligands.

N.B. Both metals and non-metals can be either type (a) or (b) acids depending on their charge and size, i.e. the features which bring out class (a) behaviour are small size and high oxidation states, while class (b) behaviour is associated with low or zero oxidation states and/or large size. Since the features which promote class (a) behaviour are those which lead to low polarizability, it is convenient to call class (a) acids hard, whilst those leading to high polarizability (class (b)) are called soft acids - thus hard acids prefer hard bases and soft acids, soft bases.
Thus choosing suitable complex structures some measure of the relative nucleophilic strength of phosphorus and arsenic can be found.

Much study has been devoted to the displacement of carbon monoxide by other ligands and also to the interpretation of the change in frequencies of infrared absorption of the carbonyl group in the new acid-base complex.\(^{(63)(64)(65)(66)}\)

In a tetrahedrally co-ordinated metal complex such as Ni(CO)\(_4\) (64) the d-orbitals of the metal are so arranged that only two strong and two weak \(\pi\)-type bonds can be formed to the ligands.\(^{(67)}\) Thus the (Ni-C) bond will be an intermediate between the single and double bond form.

\[
\begin{align*}
\text{Ni} & \equiv \text{C} \equiv \text{O} \\
\text{C} & \equiv \text{C} \equiv \text{O} \\
\text{Ni} & \equiv \text{C} \equiv \text{O} \quad \text{Ni} \equiv \text{C} \equiv \text{O} \\
\end{align*}
\]

When the CO group is replaced by less strongly double-bonding ligands L, the canonical form with single metal to ligand bonds should make the greater contribution to the structure

\[
\begin{align*}
\text{L} & \equiv \text{Ni} \equiv \text{C} \equiv \text{O} \\
\text{L} & \equiv \text{C} \equiv \text{O} \\
\end{align*}
\]
So in going from (64) to (66) the bond order and the infrared frequency $\nu_{\text{CO}}$ would be expected to decrease. Since phosphines and arsines have almost identical electronegativities any marked differences between double bonding capacities (valence expansion) should appear as a difference in the carbonyl frequency ($\nu_{\text{CO}}$) in analogous carbonyl complexes. Abel and his co-workers studied the replacement of carbonyl in molybdenum hexacarbonyl (67) with phosphine, arsine and stibines as donors.

$$\text{Mo(CO)}_6 + 3L \rightarrow \text{Mo(CO)}_3L_3 + 3\text{CO} \quad (67)$$

$L = (C_6H_5)_3P, (C_6H_5)_3As$ or $(C_6H_5)_3Sb$

A pronounced increase in the carbonyl frequencies compared to those with nitrogen-donor derivatives was attributed to $\pi$-character in the metal-ligand bond. However the small differences in $\nu_{\text{CO}}$ in the complexes of phosphorus, arsenic or antimony was taken as indicative that the donor-acceptor properties of all three are essentially the same.

A very similar conclusion was reached by Chatt and Hart (68) when they studied a series of partially substituted nickel carbonyls. When nickel carbonyl reacts with ammonia, amines, ethers or sulphides, intractable substitution products, too unstable to be isolated, are obtained. It appears, therefore, that the ligand must be capable of a certain
minimum amount of \( \pi' \)-bonding to the metal to form isolable products. Studies of double bonding to platinum (II)\(^{(69)} \)
by the trialkyl derivatives of phosphorus, arsenic and antimony in such compounds as \( \text{cis-} \left[ (\text{PR}_3)_2 \text{PtCl}_2 \right] \) indicated that the double bond contributes significantly to the strength of the co-ordinate bond though its contribution to the electroneutrality of the donor and acceptor atoms concerned was rather small. (Dipole moment 10.7D\(^{(70)} \) for \( \left[ (\text{P(Et}_3)_2 \text{PtCl}_2 \right] \). In an attempt to estimate roughly the amount of \( \pi' \)-bonding of the \( \text{(Ni-P)} \) and \( \text{(Ni-As)} \) in nickel (0) complexes the dipole moments were measured, Table VIII.

<table>
<thead>
<tr>
<th>Table VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex</td>
</tr>
<tr>
<td>( \text{o-C}_6\text{H}_4\text{(Et}_2\text{P)}_2\text{Ni(CO)}_2 )</td>
</tr>
<tr>
<td>( \text{o-C}_6\text{H}_4\text{(Et}_2\text{As)}_2\text{Ni(CO)}_2 )</td>
</tr>
</tbody>
</table>

The moments are high and since the Ni-C-O group is almost non-dipolar, the large charge separation must reside in the (Ni-P) and Ni-As) bonds. They also suggest that there is no great difference between the double-bonding capacity of phosphorus and arsenic in the chelated nickel complexes.
In a later paper\(^{(86b)}\) Chatt and Hart studied the replacement of carbonyl in nickel carbonyl by aromatic tertiary phosphines and arsines since these should be more strongly \(\pi\)-bonding (according to their previous experience with platinous and palladous complexes). The dipole moments of such complexes were of the order 3.3D. Chatt and Hart calculated that, if there was an electron transfer of 0.5, and that since the bond lengths are about 2.23Å for (P-Ni) and 2.33Å for (As-Ni), the moments would be 5.4D and 5.6D respectively, if purely co-ordinate. This is 2.1 - 2.3D greater than the observed 3.3D and was attributed to partial neutralisation of the moment due to \(\pi\)-bonding. Again evidence points to a similar tendency for valence expansion for phosphorus and arsenic.

Horrocks and Taylor\(^{(71)}\) studied the infrared spectra of derivatives of tricarbonylnitrosylcobalt (Co(CO)\(_3\)NO) and, together with work carried out by Bigorgne, compiled a spectrochemical series for \(\pi\)-bonding, arrangement being in order of decreasing ability to withdraw charge from the central metal either by an inductive or \(\pi\)-electron accepting mechanism, (Table IX).
It is noticeable that arsenic compounds always appear above analogous phosphorus compounds, so infrared evidence suggests that arsenic is better able to expand its valence than phosphorus.

Evidence for the contrary of this was perhaps presented by Angelici and Basolo (72) when they studied the near-ultraviolet of various Mn(CO)$_4$L Br complexes. These complexes show one broad absorption band slightly shifted depending on the ligand (L) in the complex. The absorption maximum decreases in the order P(OC$_4$H$_9$)$_3$ > P(C$_4$H$_9$)$_3$ - CO - P(OC$_6$H$_5$)$_3$ > P C$_6$H$_5$Cl$_2$ > P(C$_6$H$_5$)$_3$ As > (C$_6$H$_5$)$_3$ Sb.

The Mn(CO)$_5$ Br absorption was assigned to a charge transfer transition from the (dxy) molecular orbital, primarily located on the metal, to the (Π*) molecular orbital, which is essentially located on the carbonyl, trans to bromide (73). If in cis (Mn(CO)$_4$L Br) the dxy-orbital is partially stabilised by

<table>
<thead>
<tr>
<th>Structure</th>
<th>As(OCH$_3$)$_3$</th>
<th>P(C$_6$H$_5$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbCl$_3$</td>
<td>P(OC$_2$H$_5$)$_3$</td>
<td>As(C$_2$H$_5$)$_3$</td>
</tr>
<tr>
<td>AsCl$_3$</td>
<td>P(OCH$_3$)$_3$</td>
<td>P(CH$_3$)$_3$</td>
</tr>
<tr>
<td>PCl$_3$</td>
<td>As(C$_6$H$_5$)$_3$</td>
<td>P(C$_2$H$_5$)$_3$</td>
</tr>
</tbody>
</table>
π-bonding to the ligand then the magnitude of this charge-transfer-transition may well be the π-bonding ability of the ligand.

Thus when \( L = M (C_6H_5)_3 \) and \( M = P, \text{ As or Sb} \), the π-bonding ability can be inferred as decreasing in the order \( (C_6H_5)_3P > (C_6H_5)_3\text{As} > (C_6H_5)_3\text{Sb} \). (Table X).

<table>
<thead>
<tr>
<th>L.</th>
<th>( \lambda_{\text{max}} )</th>
<th>( \varepsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (C_6H_5)_3P )</td>
<td>396</td>
<td>640</td>
</tr>
<tr>
<td>( (C_6H_5)_3\text{As} )</td>
<td>403</td>
<td>710</td>
</tr>
<tr>
<td>( (C_6H_5)_3\text{Sb} )</td>
<td>409</td>
<td>710</td>
</tr>
</tbody>
</table>

However, more recent work by Basolo and Thorsteinson\(^{(74)}\) perhaps helps to clarify this conflict. They studied the kinetics of substitution reactions of nitrosyltricarbonylcobalt (0) which is one of the few simple metal carbonyls that undergo substitution by a process which is dependent on the nature and concentration of the nucleophile. It, therefore, offers a unique opportunity to study the properties influencing nucleophilicity towards metals in low oxidation states, and since the reactions are second order, it is possible to determine the nucleophilic strength of ligands towards the substrate.
By analogy with previous work the carbonyl frequencies of this series of complexes suggest more back-donation for the (Co-As) bond than for the (Co-P) bond. (The authors, however, make no comment on this observation).

Further data, however, shows that the phosphorus ligand atom donors react faster than either nitrogen or arsenic. (Table XI).

Table XI.

Physical Properties of Nitrosyl dicarbonyl cobalt Complexes

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$k$ at 25° $M^{-1}$ sec$^{-1}$</th>
<th>Stretching frequencies $\nu_{CO}$ cm$^{-1}$</th>
<th>$\Delta$H NP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(n-C$_4$H$_9$)$_3$</td>
<td>$9 \times 10^{-2}$</td>
<td>2032</td>
<td>131</td>
</tr>
<tr>
<td>P(C$_6$H$_5$)$_3$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>2038</td>
<td>520</td>
</tr>
<tr>
<td>P(O$_4$C$_6$H$_5$)$_3$</td>
<td>$3.4 \times 10^{-5}$</td>
<td>2061</td>
<td>875</td>
</tr>
<tr>
<td>As(n-C$_4$H$_9$)$_3$</td>
<td>$9.0 \times 10^{-5}$</td>
<td>2039</td>
<td>-</td>
</tr>
<tr>
<td>As(C$_6$H$_5$)$_3$</td>
<td>$2.3 \times 10^{-6}$</td>
<td>2047</td>
<td>-</td>
</tr>
</tbody>
</table>

* $\Delta$HNP = difference in half-neutralisation potential between the ligand L and NN'diphenylquanidine in nitromethane.

The small $\Delta$HNP, the more basic L(75)

The data also indicated that for a given family of ligands the rate of reaction increased with increasing basicity of the reagent.(75) Unfortunately no quantitative values are available
for arsines, but they are well known to be weak bases.\(^{(76)}\)

These differences, say the authors, are in accord with the metal in the substrate being a class (b) or soft metal. Pearson would, therefore, predict that cobalt has a greater affinity for the soft phosphorus than the hard nitrogen atom i.e. the polarisability of the nucleophile is more important in determining its nucleophilic strength than its basicity. However since all the same arguments may be forwarded for arsenic, the authors suggest a third factor, namely $\Pi$-bonding, must also be of some significance. Thus, they say the presence of the best $\Pi$-bonding ligand atom, phosphorus, has the greater stabilizing influence on the 5-co-ordinated species in the displacement reaction, lowering the activation energy and increasing the rate of reaction. However since all but one experiment suggests that arsenic is an equal if not better $\Pi$-bonding ligand (the reference given by Basolo for the 'better $\Pi$-bonding' ability of phosphorus is actually the spectrochemical table\(^{(71)}\) already discussed here) this reasoning becomes invalid. Surely another explanation is simply that arsines compared to phosphines are always weaker bases and nucleophiles so that no matter what the reference acid is, arsines will form less stable complexes than their phosphine analogues. Also that the rate of exchange will be slower for arsenic than for phosphorus ligands since the greater size of arsenic will of necessity result in weaker
G-bonds, and consequently higher activation energies. Indeed Chatt and Hart\(^{(68)}\) had earlier concluded that, since evidence suggested equal double-bonding capacities for phosphorus and arsenic, the ready replacement of carbon monoxide by phosphorus compounds compared to arsenic compounds must be due to the much greater overall affinity of phosphorus for metals with filled d-orbitals i.e. to stronger G and T-bonding

On the whole, then, evidence presented by complex study suggests that arsenic is equally able to undergo valence expansion as is phosphorus.

The Effects of the Larger Atomic Size of Arsenic compared to Phosphorus.

(a) The Nucleophilicity of Phosphines and Arsines.

The large size of the arsenic atom leads to greater bond-lengths and weaker G-bonds (see later). It also results in the marked decrease of nucleophilicity of arsines compared to phosphines because the lone pair are not so readily donated. The rates of quaternisation observed for phosphines and arsines are evidence for this. Quaternisation is a simple nucleophilic displacement reaction,

\[ \text{R}_3\text{M} + \text{CH}_3\text{I} \rightarrow \text{R}_3\text{M} - \text{CH}_3 \text{I}^\Theta \]
It follows that the rate will depend directly on the nucleophilicity of the donating group, the strength of the new bond being formed and the strength of the bond being broken. Davies and Addis(76) observed qualitatively the ease of quaternisation of triphenyl bases with methyl iodide (Table XII).

Table XII.

Quaternisation of Triphenyl Bases.

<table>
<thead>
<tr>
<th>Base</th>
<th>Reaction with MeI</th>
<th>Dipole Moment $10^{18}$ e.s.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(C_6H_5)_3M$</td>
<td>None</td>
<td>0.26</td>
</tr>
<tr>
<td>Amine</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Phosphine</td>
<td>Violent</td>
<td>1.45</td>
</tr>
<tr>
<td>Arsine</td>
<td>With heating</td>
<td>1.07</td>
</tr>
<tr>
<td>Stibine</td>
<td>None</td>
<td>0.57</td>
</tr>
<tr>
<td>Bismuthine</td>
<td>None</td>
<td>0</td>
</tr>
</tbody>
</table>

They noticed the reactivity of the bases followed strictly the order of the dipole moments, i.e. the reactivity depended on the polarisability of the base.

The same authors made some quantitative measurements for certain quaternisations, the results of which are shown in Table XIII.
Table XIII

Velocity Coefficients for Quaternisations.

<table>
<thead>
<tr>
<th>Base</th>
<th>Alkyl Halide</th>
<th>Velocity Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_5(C_2H_5)_2M$</td>
<td>Ethyl iodide</td>
<td>0.73</td>
</tr>
<tr>
<td>Amine</td>
<td>&quot;</td>
<td>348</td>
</tr>
<tr>
<td>Phosphine</td>
<td>&quot;</td>
<td>50</td>
</tr>
</tbody>
</table>

These results show clearly arsines are much weaker nucleophiles than the corresponding phosphines.

(b) The Reactivity of Phosphonium and Arsonium Ylids.

It seems reasonable to predict that less stabilisation of an adjacent carbanion by an 'onium group will occur as Group V is descended from phosphorus to antimony. This will be expected because the coulombic forces decrease as the (C-M) bond increases (1.87Å, 1.95Å and 2.18Å) and also because of the decreasing electronegativities of the heteroatoms (2.1, 2.0 and 1.9). In addition, as previously mentioned, any $p\pi - d\pi$ bonding will become less effective as the size of the two atoms C and M become more dissimilar and the principal quantum number increases. Thus one would predict that arsonium ylids will be more reactive than the corresponding phosphonium ylids. This has been found during my research and indeed has already been demonstrated by
Johnson and LaCount (78) They determined a pKa of 7.8 for
9-fluorenyltriphenylarsonium bromide against 7.5 for the
analogous phosphonium bromide. This means the arsonium
ylid is the more basic and that there is less driving force
for its formation. The reason for this may be reduced
coulombic forces or equally it may be caused by less
effective $\pi^* - \pi$ bonding. Consequently the arsonium
fluorenylideneylid is the more reactive. This is shown
by its reactions with p-substituted benzaldehydes. In
contrast to the phosphonium ylid with which the reactivity
sequence is clearly $\text{pNO}_2 > \text{Cl} > \text{H} > \text{OCH}_3 > \text{N(CH}_3)_2 \quad (77)$ the
arsonium ylid reacts in good yield with all the benzaldehydes
e.g. the phosphorus analogue fails to react with p-dimethyla-
minobenzaldehyde, whereas the arsenic ylid reacts in 97% yield.

(c) The Strength of Certain Phosphorus and Arsenic Chemical
Bonds.

Arsonium ylids undergo a Wittig-type reaction, however
the products may be either olefin or epoxide. The
explanation for the obvious difference in behaviour of
phosphonium and arsonium ylids, when treated with carbonyl
compounds, is probably a two-fold one.

Firstly, the phosphine oxide bond is an exceptionally
strong one (D.E. 127 k.cal/mol) because of additional $\pi$-
bonding to the already strong $\sigma$-bond. Unfortunately no
quantitative value for the strength of the arsine oxide bond has been found, but suffice to say that the σ-bond will be weaker (because of greater bond length) and π-bonding is certainly less important.

The dipole moments of some phosphine and arsine oxides are known (Table XIII), but it is difficult to know just what the values mean without the necessary bond distance and bond angle. One would expect the moment to be larger in the arsenic compound than in the phosphorus one because of the greater bond length and also because of the reduced electronegativity of the hetero-atom.

<table>
<thead>
<tr>
<th>Compound</th>
<th>μ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((C_6H_5)_3P)</td>
<td>1.39</td>
</tr>
<tr>
<td>((C_6H_5)_3P) (\cdot) (\cdot) (\cdot) (\cdot)</td>
<td>4.28</td>
</tr>
<tr>
<td>((C_6H_5)_3As)</td>
<td>1.07</td>
</tr>
<tr>
<td>((C_6H_5)_3As) (\cdot) (\cdot) (\cdot) (\cdot)</td>
<td>5.50</td>
</tr>
</tbody>
</table>

Thus the driving force for the Wittig reaction in phosphorus chemistry, i.e. formation of the phosphine oxide bond, is not such a powerful one in the analogous arsenic chemistry, i.e. formation of the arsine oxide bond.

Secondly, the alternative route may be a direct result
of the weaker σ-bonds formed by arsenic with carbon, (Table XIV).

### Table XIV.

<table>
<thead>
<tr>
<th></th>
<th>Birr(^{(79)})( (C_6H_5)_3-M )</th>
<th>Mortimer(^{(80)})( (C_6H_5)_3-M )</th>
<th>Long and Sackman(^{(47)})*( (CH_3)_3-M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>72.4</td>
<td>71.3</td>
<td>65.3</td>
</tr>
<tr>
<td>As</td>
<td>57.0</td>
<td>60.3</td>
<td>51.5</td>
</tr>
<tr>
<td>Sb</td>
<td>61.3</td>
<td></td>
<td>49.7</td>
</tr>
<tr>
<td>Bi</td>
<td>46.8</td>
<td></td>
<td>33.8</td>
</tr>
</tbody>
</table>

* Chief uncertainty is the heats of atomisation of As, Sb and Bi

The strength of the \(M-C\) bonds, lies in the expected order suggested by the stretching force constants (2.99, 2.63, 2.18 and 1.82\(^{(47)}\) respectively) but the almost monotonic variation of the latter are not preserved in the values given for the mean bond dissociation energies. Long and Sackman suggest, therefore, the heat of atomisation is high for antimony and low for arsenic and bismuth.

In spite of doubts concerning the accuracy of these bond energies a quantitative value of the relative strengths may be found i.e. the \(As-C\) bonds are at least 11 k. cal. weaker than the \(P-C\) bonds. This will obviously be reflected in the ease with which an \(As-C\) bond can be cleaved during a
reaction i.e. that triphenylarsine will be a good leaving group. Thus when an alkyltriphenylarsorane reacts with a carbonyl compound to give an epoxide, the other product is triphenylarsine.

(d) The Object of Work presented in this Thesis.

The reactions that I have investigated were designed to make use of differences, arising essentially from the larger atomic size of arsenic, between phosphonium and arsonium ylids. Thus experiments were chosen to make use of the leaving ability of the triphenylarsine group as well as the knowledge that the formation of an arsine oxide \( \Theta \) \( (\text{H}_2\text{As}=\text{O}) \) or iminoarsorane \( (\text{R}_2\text{As}=\text{NH}) \) need not necessarily dictate the course of a reaction. It was also hoped to establish which factors effected the course of the Wittig reaction, when employing arsenic as the hetero-atom.
CHAPTER I.

Reaction of Alkylidenearsoranes with Carbonyl Compounds.

The object of this work was to establish the factors controlling the formation of either an olefin or an epoxide when an arsonium ylid reacts with a carbonyl compound. The course of the reaction is shown by the following general mechanism,

\[
\begin{align*}
\text{M} &\rightarrow \text{M}^+ + \text{C}< \\
\oplus &\rightarrow \bigl[ \begin{array}{c}
\oplus \\
0 \\
\text{C}< \\
\end{array} \bigr] \\
&\rightarrow \text{M} + \text{C}< \\
\text{M} &= R_3P, R_3As \text{ or } R_2S
\end{align*}
\]

\[(1)\]

It seems that arsonium ylids hold an intermediate position between phosphonium and sulphonium ylids in their behaviour towards carbonyl compounds. Initially all three types of ylids react identically by nucleophilic attack of the carbanion on the electrophilic carbonyl compound to form a zwitterionic intermediate, betaine \((1)\). This may then undergo elimination by path \((a)\) or \((b)\).

Phosphorus Betaines.

Phosphorus betaines follow exclusively path \((a)\), involving oxygen transfer to the heteroatom, forming phosphine oxide and olefin, i.e. a Wittig reaction\(^{81}\). The Wittig-olefin synthesis has received extensive study and has been applied successfully to the synthesis of many natural products\(^{82-85}\).
The reaction proceeds under mild conditions and there is no ambiguity in the position of the new double bond. The reaction is a two stage process, see above, and the rate determining step may be either the formation of the betaine (1), or its decomposition. Betaine formation will be rate determining when the nucleophilicity of the ylid and the electrophilicity of the carbonyl compound are reduced.

There is considerable evidence to support the proposal, originally advanced by Wittig, that betaines are intermediate in the Wittig reaction. For example when methylenetri(\(p\)-anisyl)phosphorane (2) reacts with benzaldehyde a 70% yield of betaine (3) results:

\[
\begin{align*}
(p-CH_2OC_6H_4)_3P-CH_2 + CH & \rightarrow (p-CH_2OC_6H_4)_3P-CH_2 \\
&s^+ \\
(2) & (3)
\end{align*}
\]

Under the same conditions methylenetri(p-tolyl)phosphorane (4) affords a 30% yield of betaine (5) together with a 55% yield of styrene (6).

\[
\begin{align*}
(p-CH_3OC_6H_4)_3P-CH_2 + CH & \rightarrow (p-CH_3OC_6H_4)_3P-CH_2 \\
&s^+ \\
(4) & (5)
\end{align*}
\]

\[
\begin{align*}
(p-CH_3OC_6H_4)_3P-CH_2 + CH & \rightarrow (p-CH_3OC_6H_4)_3P-CH_2 \\
&s^+ \\
(6)
\end{align*}
\]

i.e. when electron-donating groups are present in the phosphonium group the decomposition of betaine is slowed down, allowing its
isolation. Such effects occur only when the second stage is slow; thus fluorenylidetri(p-anisyl)phosphorane reacts normally to give benzalfluorene.

Wittig and Haag (88) have reported the isolation and characterisation of the betaine (9) obtained from the reaction of isopropylidenetriphenylphosphorane (7) with diphenylketene (8):

\[
\text{(7)} \quad \text{(8)} \quad \text{(9)}
\]

It is interesting that the physical properties of the betaine (9) suggest considerable association between the oxyanion and the phosphonium group.

Betaine decomposition is considered to proceed through either a four-membered cyclic intermediate (10a) or transition state (10b), by the initial attack of the oxyanion on the phosphonium group, finally giving the Wittig products.

\[
\text{(10a)} \quad \text{(10b)}
\]

The driving force for this path is presumably the formation of the strong phosphine oxide bond. This stage will be retarded by
groups which decrease the electropositive character and hence the oxygen affinity of the phosphorus and accelerated by substituents which can conjugate with the incipient double bond in the final transition state. The evidence for this second stage is provided by the nature of the products and also by observations that compounds of similar structure behave in ways predictable from a four centre intermediate or transition state. For example the betaine (12), which is produced by enolisation of the β-keto phosphonium salt (11), probably undergoes elimination to phosphine oxide and allene by the following mechanism. (89)

\[
\begin{align*}
(C_6H_5)_3P\text{-}C\text{-}O\text{-}C_2H_5 & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad (C_6H_5)_3P\text{-}C\text{-}O\text{-}C_2H_5 \\
\text{O=C} & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad \text{O=C} \\
\text{CH}_2 & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad \text{CH}_2 \\
\text{H} & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad \text{H}
\end{align*}
\]

(11) (12)

\[
\begin{align*}
(C_6H_5)_3P\text{-}O & \quad \rightarrow \quad (C_6H_5)_2P\text{-}O\text{-}C_2H_5 \\
\text{C}_2H_5O & \quad \rightarrow \quad \text{C}_2H_5O
\end{align*}
\]

Similarly Trippett (90) found that treatment of the hydroxy-phosphonium salt (13) with sodium ethoxide afforded a mixture of stereoisomeric stilbenes, presumably via a betaine intermediate.

\[
\begin{align*}
(C_6H_5)_2P\text{-}O\text{-}CH\text{-}C_6H_5 & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad (C_6H_5)_2P\text{-}O\text{-}CH\text{-}C_6H_5 \\
\text{H}_2O\text{-CH-}C_6H_5 & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad \text{H}_2O\text{-CH-}C_6H_5 \\
\text{CH}_3 & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad \text{CH}_3 \\
\text{H}_2O & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad \text{H}_2O \\
\text{CH}_3 & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \overset{\ominus}{\underset{\ominus}{\rightarrow}} \quad \text{CH}_3
\end{align*}
\]

(13)
The isolation, by Birum and Matthews,\(^{91}\) of a four membered cyclic intermediate \((16)\) has added considerable support for the proposed cyclic intermediate in a normal Wittig reaction. They reacted a bis-phosphorane \((14)\) with hexafluoroacetone \((15)\) and isolated the intermediate \((16)\). This intermediate decomposed, on heating, to give the expected Wittig products, \((17)\) and \((18)\).

\[
\begin{align*}
(\text{C}_6\text{H}_5)_3\text{P} &= \text{C} \rightleftharpoons (\text{C}_6\text{H}_5)_3\text{P} \text{C} \\
(\text{CF}_3)_2\text{C} &= 0 \\
(\text{CF}_3)_2\text{C} &= 0 \\
(\text{CF}_3)_2\text{C} &= 0
\end{align*}
\]

\((14)\) \hspace{1cm} \((15)\) \hspace{1cm} \((16)\) \hspace{1cm} \((17)\) \hspace{1cm} \((18)\)

**Sulphur Betaines.**

Sulphonium betaines decompose exclusively by path (b) involving the internal displacement of the sulphonium group by the oxyanion.

Thus Franzén and Driessen\(^{92}\) showed that methylenedimethylsulphorane \((19)\) reacts with carbonyl compounds to give the corresponding 1, or 1, 1-substituted ethylene oxides. \((20)\)

\[
\begin{align*}
(\text{CH}_3)_2\text{S} - \text{CH}_2^+ \quad \leftrightarrow \quad (\text{CH}_3)_2\text{S} + \text{CH}_2^- \\
(\text{19}) \quad \leftrightarrow \quad (\text{19}) \quad \rightarrow \quad (\text{19}) \quad \rightarrow \quad (\text{19})
\end{align*}
\]
1, 2-disubstituted epoxides were later prepared by Johnson\(^{(93)}\) by the reaction of substituted benzylidenediphenylsulphoranes \(^{(21)}\) with a series of carbonyl compounds.

\[
(C_6H_5)_2S - \text{CH Ar}
\]

With the information available it is possible only to speculate as to the reasons for the change in mechanisms. In spite of the greater ability of sulphur to stabilise an adjacent carbanion by valence shell expansion, sulphur appears more reluctant than phosphorus to form a pentacovalent intermediate. For example Ingold\(^{(94)}\) discovered that whereas the hydrolysis of phosphonium salts produced phosphine oxide and a hydrocarbon by direct attack of the hydroxide on tetravalent phosphorus,\(^{(95)}\) sulphonium salts afforded an olefin \(^{(22)}\) or alcohol \(^{(23)}\) together with a thioether by hydroxide attack on either an\(\alpha\)-carbon or \(\beta\)-hydrogen.

\[
R_4P + OH \rightarrow [R_4P - OH] \rightarrow OH \rightarrow RH + R_3P - O
\]

\[
R_2S + OH \rightarrow R^{1} - \text{CH} = \text{CH}_2 + R_2S \quad (22)
\]

\[
R - OH + R_2S \quad (23)
\]

This difference may well be the result of the difference in strength of the sulphur-oxygen bond \((\text{D.E. 89 k.cal/mole})\)^{(96)}
and the phosphorus-oxygen bond (D.E. 128 k.cal/mole). Also
the methylsulphide group is known to be an excellent leaving
group, because of the greater stability of sulphur in the
divalent state, and this factor may favour epoxide formation.
For example 9-fluorenyldimethylsulphonium bromide may be
hydrolysed in aqueous solution to 9-fluorenol, but attempts to
carry out analogous hydrolyses with phosphonium salts have
been fruitless\(^{(97)}\). Combination of the differences in
bond energies of the (P-O) bond and the (S-O) bond together
with the different 'leaving group abilities' of sulphide and
phosphine may well explain why sulphonium betaines eliminate
by path (b) to give epoxides\(^{(5)}\)

**Arsenic Betaines.**

Arsenic betaines, however, exhibit intermediate
behaviour since they are known to eliminate by path (a)
or by path (b). In the triphenylarsonium ylid series,
Johnson\(^{(77)}\) showed the fluorenylidene ylid led to exclusive
olefin formation (path (a)) while the benzyldiene ylid led to
equimolar formation of epoxide and olefin (path (a) and (b)),
and Wittig's experiments\(^{(13)}\) showed the methylene ylid led
to dominant formation of epoxide (path (b)). It seems that,
like sulphur, the potential formation of an arsenic-oxygen
bond is not a sufficient driving force to dictate the course
of reaction. Also the nature of the heteroatom component
cannot effect the ratio of path (a) product to path (b) product since the same arsine and arsine oxide were formed in the three examples above.

It seemed conceivable that the potential conjugation of substituents, on the carbanion of the ylid or on the carbonyl carbon, with the incipient double bond might be controlling the course of this reaction. In order to test this theory the reactions of a number of suitably substituted arsonium ylids with various carbonyl compounds were examined. The arsonium ylids were generated 'in situ' by treating the corresponding salts with sodium ethoxide in the presence of the carbonyl compounds. The equilibrium for the generation of reactive ylids from 'onium salts, using alkoxides, lies on the side of the salts.

\[
\begin{align*}
\text{(C}_6\text{H}_5\text{)}_3\text{As} & \text{CH}_2\text{R OH} \leftrightarrow \text{(C}_6\text{H}_5\text{)}_3\text{As} \text{CH R} + \text{R OH}
\end{align*}
\]

This method, therefore, can only be used for carbonyl compounds insensitive to alkoxide ions under the reaction conditions employed. Ethanol was employed as solvent throughout and all reactions were carried out at room temperature. Good yields of olefins or epoxides were found after twenty-four hours.

One anomalous reaction was observed during this series of experiments. When allyltriphenylarsonium bromide (24) was treated with sodium ethoxide in the presence of benzaldehyde the product was, unexpectedly, an arsonium salt. Evidence for
this was provided by its typical solubility properties together
with its infrared spectrum, which showed the characteristic
absorption bands of an arsonium salt at $1085\text{ cm}^{-1}$, (98) and
the presence of a strong band at $1147\text{ cm}^{-1}$, consistent with
an ether linkage. The p.m.r. of this compound was extremely
complex, consisting of a triplet ($3\text{H}$), doublet ($3\text{H}$) and
multiplets for ($1\text{H}$), ($3\text{H}$) and ($1\text{H}$). On the basis of these
physical properties, structure (25) was postulated for the
major product of this reaction.

\[
\begin{align*}
(C_6H_5)_3\text{As} - CH_2 - CH = CH_2 \text{Br} & \xrightarrow{OEt} (C_6H_5)_3\text{As} - CH_2 - CH - CH_3 \text{Br} \\
\text{(24)} & \quad \text{(25)}
\end{align*}
\]

It is thought reasonable that the p.m.r. should be difficult
to interpret, since in addition to the complex spectrum
predictable from first order principles, the presence of
the asymmetric carbon will make the $\delta$-protons to the arsonium
group magnetically non-equivalent. The expected chemical
shift for methylene protons $\delta$ to an arsonium group has been
found to be about $\tau 6.8$ so that presumably the lower complex
pattern ($1\text{H}$) $\tau 5.1 - 5.5$ forms half of the signal for the
non-equivalent methylene group the other half occurring,
together with the $-0-CH_2$ protons, at $\tau 5.8 - 6.8$ ($3\text{H}$).
However the very large $J$ value is disturbing. The complex
signal ($1\text{H}$) $\tau 7.2 - 7.8$ must then be due to the methyldiene
group.
Confirmation of this postulate was found in the treatment of the allyl salt with sodium ethoxide in ethanol in the absence of benzaldehyde, when the identical product was obtained. The reaction probably would take place by the following mechanism.

\[
\begin{align*}
(C\text{H}_3)_2\text{As-CH-CH-CH}_2 \quad &\xrightarrow{\text{OH}} \quad (C\text{H}_3)_2\text{As-CH-CH-CH}_2 \\
\text{Br} \quad &\xrightarrow{\text{H}} \quad \text{Br}
\end{align*}
\]

(24) (26)

\[
\begin{align*}
(C\text{H}_3)_2\text{As-CH=CH-CH}_3 \quad &\xrightarrow{\text{C}_2\text{H}_5\text{OH}} \quad (C\text{H}_3)_2\text{As-CH-CH-CH}_3 \\
\text{Br} \quad &\xrightarrow{\text{H}} \quad \text{Br}
\end{align*}
\]

(27) (25)

i.e. both resonance structures of allylidenetriphenylarsorane (26) are important, the electron density being distributed between the \(\alpha\)- and \(\gamma\)-carbon atoms. Also vinylarsonium salts (27), like vinylphosphonium salts, must undergo nucleophilic attack, at the double bond position.\(^{99}\)

A summary of results obtained for the series of experiments is given in Table (xy).
**Table (XV)**

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Arsonium Ylid.</th>
<th>Carbonyl Compound.</th>
<th>Olefin Epoxide yield % yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((\text{C}_6\text{H}_5)_2\text{As-CH-}\text{-NO}_2)</td>
<td>(\text{NO}_2\text{-CHO})</td>
<td>96 -</td>
</tr>
<tr>
<td>2</td>
<td>((\text{C}_6\text{H}_5)_2\text{As-CH-}\text{-NO}_2)</td>
<td>(\text{-CHO})</td>
<td>40 -</td>
</tr>
<tr>
<td>3</td>
<td>((\text{C}_6\text{H}_5)_2\text{As-CH-}\text{-CEO})</td>
<td>(\text{NO}_2\text{-CHO})</td>
<td>- 75</td>
</tr>
<tr>
<td>4</td>
<td>((\text{C}_6\text{H}_5)_2\text{As-CH-}\text{-CEO})</td>
<td>(\text{-CHO})</td>
<td>- 90</td>
</tr>
<tr>
<td>5</td>
<td>((\text{C}_6\text{H}_5)_2\text{As-CH-}\text{-CEO})</td>
<td>(\text{Cl-CHO})</td>
<td>- 76</td>
</tr>
<tr>
<td>6</td>
<td>((\text{C}_6\text{H}_5)_2\text{As-CH-}\text{-CEO})</td>
<td>(\text{-CHO})</td>
<td>- 51</td>
</tr>
<tr>
<td>7</td>
<td>((\text{C}_6\text{H}_5)_2\text{As-CH-}\text{-CEO})</td>
<td>(\text{NO}_2\text{-CHO})</td>
<td>- 86</td>
</tr>
<tr>
<td>8</td>
<td>((\text{C}_6\text{H}_5)_2\text{As-CH-}\text{-CEO})</td>
<td>(\text{CH}_3\text{-CHO})</td>
<td>- 56</td>
</tr>
<tr>
<td>9</td>
<td>((\text{C}_6\text{H}_5)_2\text{As-CH-}\text{-CEO})</td>
<td>(\text{-CHO})</td>
<td>67 -</td>
</tr>
<tr>
<td>10</td>
<td>((\text{C}_6\text{H}_5)_2\text{As-CH-}\text{-CEO})</td>
<td>(\text{CN-CHO})</td>
<td>- 87</td>
</tr>
</tbody>
</table>
Table (XV) (Continued).

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Arsonium Ylid</th>
<th>Carbonyl Compound</th>
<th>Olefin Epoxide % yield % yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>((C_6H_5)_2As-CH-H)</td>
<td>(\text{-CHO})</td>
<td>- 87</td>
</tr>
<tr>
<td>12</td>
<td>((C_6H_5)_3As-CH-\text{CO}_2\text{C}_2\text{H}_5)</td>
<td>(\text{-CHO})</td>
<td>77 -</td>
</tr>
<tr>
<td>13</td>
<td>((\text{CH}_3\text{O}-\text{Ph})_3As-CH-\text{NO}_2)</td>
<td>(\text{NO}_2-\text{-CHO})</td>
<td>95 -</td>
</tr>
<tr>
<td>14</td>
<td>((\text{CH}_3\text{O}-\text{Ph})_3As-CH-\text{NO}_2)</td>
<td>(\text{-CHO})</td>
<td>75 -</td>
</tr>
<tr>
<td>15</td>
<td>((\text{CH}_3\text{O}-\text{Ph})_3As-CH-\text{Ph})</td>
<td>(\text{NO}_2-\text{-CHO})</td>
<td>- 75</td>
</tr>
</tbody>
</table>

Discussion of Results.

The preferred course of arsenic betaine elimination appears to be by path (b) giving an epoxide and an arsine. Only when an electron-withdrawing group, capable of stabilising a carbanion, was present on the \(\text{<-}\)-carbon of the original ylid was the product of the reaction an olefin. In either case no stereoisomers were detected, i.e. only trans-olefin or trans-epoxide were identified, suggesting that the reaction between an arsonium ylid and an aldehyde is stereoselective.
Using the evidence established for phosphonium ylids, it seems reasonable that the first step of this reaction is reversible, forming both the erythro-(26) and the threo-(27) betaines.

\[
\begin{align*}
\text{erythro (26)} & \quad \text{threo (27)} \\
\begin{array}{c}
\text{(C}_6\text{H}_5)_3\text{As} - \text{C}_R^1 \quad \text{(C}_6\text{H}_5)_3\text{As} - \text{C}_R^1 \\
\Theta - \text{C}_R^2 \quad \Theta - \text{C}_R^2 \\
\end{array}
\end{align*}
\]

The erythro form would lead to either cis-olefin or trans-epoxide and the threo form would lead to either trans-olefin or cis-epoxide.

Epoxide Formation.

The mechanism for epoxide formation is most probably a trans-displacement reaction, occurring by rearside attack of the oxyanion on the carbon carrying the arsonium group. For this to happen the erythro and threo configurations would have to approach conformations (26a) and (27a) in the transition states.
In these conformations the \textit{threo}-form is clearly associated with the higher energy, since the three bulkiest groups are gauche to one another. So, provided that the first step is reversible, mainly the \textit{erythro}-form would be converted to epoxide, the \textit{threo}-form reverting to ylid and carbonyl compound. Experimentally the reactions have given exclusively \textit{trans}-epoxide.

The stereochemistry resulting from a \textit{trans}-displacement is analogous to that encountered and proposed by Read and Campbell\(^{100}\) for the conversion of the \textit{threo}- and \textit{erythro}-methohydroxides of 1,2-diphenyl-2-aminoethanol (28) into stilbene epoxides.
Also Speziale and Bissing\(^{(101)}\) have shown that the stereochemistry of the Wittig reaction between stabilised phosphonium ylids and carbonyl compounds is best accounted for by the reversible formation of the isomeric betaines.

**Olefin Formation.**

The mechanism for olefin formation probably involves the cis-elimination of triphenylarsine oxide by analogy with the Wittig reaction. This was demonstrated by Horner\(^{(102)}\) in 1964 when he proved that a phosphine oxide was produced with retention of its configuration at phosphorus i.e. cis-elimination had occurred. In the transition states the conformations of the isomeric betaines for olefin formation must approach (26b) and (27b).

\[
\begin{align*}
(C\text{$_6$H$_5$})_3\text{As-CH}_R^1 & \xrightarrow{\text{CH}_R^2} (C\text{$_6$H$_5$})_3\text{As}^+ \xrightarrow{\text{H}} \xrightarrow{\text{H}} H \xrightarrow{\text{H}} \xrightarrow{\text{H}} \xrightarrow{\text{cis-olefin}} (C\text{$_6$H$_5$})_3\text{As}^+ \xrightarrow{\text{H}} \xrightarrow{\text{H}} \xrightarrow{\text{H}} \xrightarrow{\text{cis-olefin}} (C\text{$_6$H$_5$})_3\text{As}^+ \xrightarrow{\text{H}} \xrightarrow{\text{H}} \xrightarrow{\text{H}} \xrightarrow{\text{cis-olefin}} (C\text{$_6$H$_5$})_3\text{As}^+ \xrightarrow{\text{H}} \xrightarrow{\text{H}} \xrightarrow{\text{H}} \xrightarrow{\text{cis-olefin}} \end{align*}
\]
In these conformers the erythro-form is associated with the higher energy because the bulky groups are eclipsed in the transition state. Therefore, the threo-form would be converted to olefin and arsine oxide and the erythro-form would revert to ylid and carbonyl. This agrees with the experimental results since only trans-olefins were isolated.

The deciding factor for the predominant course of elimination from an arsenic betaine will be governed by the relative rates of the formation of epoxides or olefins. Considering the original hypothesis that groups which can stabilize the incipient double bond will favour olefin formation in a concerted elimination postulated for the Wittig transition state (29), then either the ylid substituent, \( R^1 \), or carbonyl substituent, \( R^2 \), should be equally able to conjugate and hence stabilize the incipient double bond providing there is no sterid interference.

Experimental results show this idea is unsatisfactory, since although stabilisation is equally possible in the transition states for experiments 2, 3, 9 and 10, only experiments 2 and 2...
produce olefins. Only when an electron-withdrawing group was present on the \( \alpha \)-carbon of the ylid was the rate of formation of olefin faster than the rate of epoxide formation.

N.B. Kinetic data would be necessary to establish the actual effect the substituent had on the relative rates as it could either (a) hardly affect the rate of formation of epoxide or substantially decrease it, or (b) increase the rate of formation of olefin or hardly affect it; the outcome of both would result in the rate of olefin formation being greater than the rate of epoxide formation.
A more satisfactory explanation is offered by considering the formation of a pentacovalent arsenic intermediate (30) which undergoes a partial, non-concerted elimination. In the extreme case the following mechanism would be applicable.

\[
(C_6H_5)_3As \rightarrow [C_6H_5]_3As - \rightarrow (C_6H_5)_3As + (C_6H_5)_3As
\]

A partially non-concerted mechanism would mean that a considerable negative charge is developed on the carbon \( \alpha \) - to arsenic. It would seem likely, therefore, that such a mechanism would occur only when an electron-withdrawing group (\( R^1 \)) was present to stabilise this charge. This, of course, is borne out by experimental results. Also a partially non-concerted mechanism is probably the best explanation since the existence of the intermediate (31) might well result in a mixture of isomeric olefins.

The concept of a non-concerted elimination from the four-centred reaction is endorsed by some considerations made by
Corey\(^{(103)}\) when studying certain phosphonate esters.

Olefins may be prepared by treating phosphonate esters \((32)\) with a base and carbonyl compound.

\[
\begin{align*}
\text{(CH}_3\text{O)}_2\text{P} - \text{CH}_2 - X + \overset{\Theta}{\text{O}} & \underset{\text{B}}{\overset{\Theta}{\text{C}}} \text{R}_1 \text{R}_2 \rightarrow (\text{CH}_3\text{O})_2\text{P} - \text{CH} - X \\
(32) & \rightarrow (\text{CH}_3\text{O})_2\text{P} - \overset{\Theta}{\text{O}} + \overset{\Theta}{\text{C}} \text{R}_1 \text{R}_2
\end{align*}
\]

Unless \(X\) is a charge-stabilising, electron-withdrawing group then the intermediates \((33)\) formed are not directly applicable to olefin synthesis as they do not undergo efficient \textit{cis-}\n-cycloelimination. Corey considered that the slowness of elimination from the anion \((33)\) when \(X = \text{H or CH}_3\), relative to \(X = \text{CN or CO}_2\text{C}_2\text{H}_5\) etc. indicated that considerable negative charge accumulates at the carbon \(\alpha\)-to phosphorus in the transition state for olefin formation, i.e. cycloelimination is not completely concerted.

Experiments 13 and 14 using substituted benzyltri(p-methoxy-phenyl)arsenium salts were carried out in the hopes that the reduced electronegative character and hence oxygen affinity of the arsenic would slow down olefin formation in favour of epoxide formation. This was not so; the presence of the p-methoxy group was apparently not sufficiently effective to alter the relative
rates of olefin and epoxide formation.

Conclusion.

The preferred product of an arsenic Wittig reaction is an epoxide. The presence of a charge-stabilising group on the \( \alpha \)-carbon of an arsonium ylid results in olefin formation.
Experimental.

All experiments involving arsines or arsoranes were conducted under an oxygen-free nitrogen atmosphere. All liquid aldehydes were freshly distilled under an oxygen-free nitrogen atmosphere. The solvents were dried and distilled before use. Unless otherwise stated petrol refers to the fraction b.p 40-60°. Melting points were corrected.

Preparation of p-Nitrobenzyltriphenylarsonium Bromide.

p-Nitrobenzyl bromide (5g.) was refluxed in ethyl acetate with excess triphenylarsine (8 g.). After 4 hours the mixture was cooled and the arsonium salt filtered off (9 g.), m.p. (from chloroform-ethyl acetate) 156° (Lit\(^{150-152°}\)).

Reaction of p-Nitrobenzyltriphenylarsonium Bromide with p-Nitrobenzaldehyde in Ethanolic Sodium Ethoxide.

p-Nitrobenzaldehyde (1.2g.) was added, with mixing, to a solution of p-nitrobenzyltriphenylarsonium bromide (4 g.) in ethanol (50 ml), containing sodium (0.2 g.). A brilliant purple colour, which appeared on mixing, rapidly disappeared as a yellow solid precipitated. After 24 hours at room temperature, the solid was filtered off and shown to be trans - 4, 4' - dinitrostilbene (1.8 g.), m.p. (from acetic acid) 303-305° (Lit\(^{296 - 305°}\)), \(\nu_{max} 955, 975 \text{ cm}^{-1}\).
The mother liquor was concentrated, extracted with chloroform and the extract washed three times to remove sodium salts. After drying the chloroform extract it was chromatographed on basic alumina and gave triphenylarsine oxide (1.2 g.) on elution with a methanol-ether mixture (1:99), m.p and mixed m.p 189°, (Lit189°).

Reaction of p-Nitrobenzyltriphenyl arsonium Bromide with Benzaldehyde in Ethanolic Sodium Ethoxide.

The reaction conditions were the same as for the previous experiment. The quantities used were arsonium salt (4 g.), benzaldehyde (0.9 g.) and sodium (0.2 g.) in ethanol (50ml). The reaction mixture became a bright red colour and only changed to a pale red colour overnight. No precipitate separated out. After concentrating the mixture its chloroform extract was washed with water, dried and absorbed onto basic alumina. Elution with ether-petrol (20:80) gave trans-4-nitrostilbene (0.8 g.), m.p. 155° (Lit155°C), $\nu$ max 965, 975 cm$^{-1}$ (trans-olefin). Elution with ether-methanol (98:2) gave triphenylarsine oxide (2.15 g.), m.p. and mixed m.p. 189°.

Preparation of Benzyltriphenyl arsonium Bromide.

Excess triphenylarsine (10g.) was mixed with benzyl bromide (5 g.) and then heated together, without solvent, at 120°. The reaction mixture solidified. To obtain a good yield of this
arsonium salt it was found essential to have excess triphenylarsine. Recrystallisation from chloroform-ethyl acetate gave the arsonium salt (12 g.), m.p. 168° (Lit 168°).

Reaction of Benzyltriphenylarsonium Bromide with p-Nitrobenzaldehyde in Ethanolic Sodium Ethoxide.

A solution of the arsonium salt (4 g.) and p-nitrobenzaldehyde (1.3 g.) in ethanol (50 ml), containing sodium (0.2 g.), was set aside at room temperature. After 24 hours a solid separated from the reaction mixture. This was filtered off (1.5 g.) and shown to be trans-4-nitrostilbene epoxide, m.p. 127° (Lit 126°), ν max 840, 860 cm⁻¹ (epoxide), m/z 241, 224, 150. The chloroform extract of the concentrated mother liquor was washed, dried and chromatographed on basic alumina. Elution with petrol gave triphenylarsine (2.2 g.) m.p. and mixed m.p. 60°.

Reaction of Benzyltriphenylarsonium Bromide with Benzaldehyde in Ethanolic Sodium Ethoxide.

The reaction conditions were the same as for the previous experiment. The quantities used were arsonium salt (4 g.), benzaldehyde (0.9 g.), ethanol (50 ml) and sodium (0.2 g.). After 48 hours g.l.c. (2m Apiezon column at 200°C) showed the presence of trans-stilbene epoxide (90%) by comparison with a standard solution. No trace of stilbenes were detected.
Reaction of Benzyltriphenylarsonium Bromide and p-Chlorobenzaldehyde in Ethanolic Sodium Ethoxide.

A solution containing the arsonium salt (3 g.) and p-chlorobenzaldehyde (0.9 g.) in ethanol (50 ml) with sodium (0.15 g.), was left for 18 hours at room temperature. A white solid was filtered off (0.5 g.). The mother liquor was concentrated, extracted with chloroform and washed with water. The extract was then dried and chromatographed using a silica column. Elution with ether-petrol (10 : 90) gave triphenylarsine (1.0 g.), m.p. and mixed m.p. 60°C. Elution with ether gave a white solid (0.6 g.) identical with the first solid. This was shown to be trans-4-chlorostilbene epoxide (1.1 g.), m.p. 101-102°C (from ethyl acetate), $\nu_{max}$ 820, 845 (epoxide), cm$^{-1}$ m/e 230 for Cl = 35, 214, 124. (Found C, 72.35; H, 4.44; Cl, 15.40; calculated for C$_{14}$H$_{11}$ClO C, 72.9; H, 4.76; Cl, 15.39%). M.W. 230.

Preparation of p-Chlorobenzyltriphenylarsonium Bromide.

p-chlorobenzyl bromide (7 g.) and triphenylarsine (10.5 g.) were heated together, without solvent, for 2 hours at 100°C. No quaternisation occurred. On raising the temperature to 180°C for a further 2 hours, a small amount of arsonium salt (1.5 g.) was obtained. Reheating at 210°C for 2 hours gave a good yield of arsonium salt (13 g.), m.p. 162°C, $\nu_{max}$ 109 5 cm$^{-1}$ (arsonium salt) (Found C, 55.91; H, 3.82; Br, 15.5;...
calculated for C\textsubscript{25}H\textsubscript{21} As Br Cl C, 58.6 ; H, 4.1 ; Br, 15.6\%.

**Reaction of p-Chlorobenzyltriphenylarsonium Bromide with Benzaldehyde in Ethanolic Sodium Ethoxide.**

Benzaldehyde (0.35 g.) was added to a solution of p-chlorobenzyltriphenylarsonium bromide (1.5 g.) in ethanol - (50 ml) ethoxide (0.07 g. Na) and set aside overnight at room temperature. The reaction mixture was concentrated and extracted with chloroform. The chloroform extract was washed, dried and chromatographed on basic alumina. Elution with petrol gave triphenylarsine (0.4 g.) m.p and mixed m.p. 60°. Elution with ether-petrol (50 : 50) gave 4-chlorostilbene epoxide (0.35 g.). m.p. 101°C. The infrared spectra and melting point were identical with the compound previously identified as trans-4-chlorostilbene epoxide. Mixed m.p. (101°C) was not depressed.

Elution with ether-methanol (99 : 1) gave triphenylarsine oxide, m.p. and mixed m.p. 189°.

**Reaction of p-Chlorobenzyltriphenylarsonium Bromide with p-Nitrobenzaldehyde in Ethanolic Sodium Ethoxide.**

p-Nitrobenzaldehyde (0.3 g.) was dissolved in ethanol and added to a solution of the arsonium salt (1 g.) in ethanol (50 ml) containing sodium (0.04 g.). This was left overnight at room temperature, and then concentrated. The chloroform extract was
washed to remove sodium salts, dried and chromatographed on basic alumina. Elution with petrol gave triphenylarsine (0.58 g.), m.p. and mixed m.p. 60°. Elution with ether petrol (60 : 40) gave trans-4-chloro-4'-nitrostilbene epoxide m.p. 129°; \( \nu_{\text{max}} \) 850, 818 cm\(^{-1}\) (epoxide), m/e 275 (C1 35), 259, 135, 124, (Found: C, 61.10; H, 3.60; N, 5.1; calculated for \( \text{C}_{14}\text{H}_{10}\text{ClN}_{3} \) C, 61.00; H, 3.62; N, 5.08%). M.W. 275.

Reaction of Benzyltriphenylarsonium Bromide with p-Methoxy-benzaldehyde in Ethanolic Sodium Ethoxide.

The reaction conditions and method of work up were identical with those used for the previous experiment. The quantities used were benzyltriphenylarsonium bromide (3 g.), p-methoxy-benzaldehyde (0.9 g.), sodium (0.15 g.) and ethanol (50 ml). Elution of a silica column with petrol-ether (90 : 10) gave triphenylarsine (1.05 g.) m.p. and mixed m.p. 60°. Elution with petrol-ether (40 : 60) gave p-methoxystilbene epoxide (0.8 g.) m.p. 118° (Lit 118°); \( \nu_{\text{max}} \) 828 cm\(^{-1}\) (epoxide). Further elution gave triphenylarsine oxide (0.15 g.) m.p. and mixed m.p. 189°.

Preparation of p-Cyanobenzyltriphenylarsonium Bromide.

Excess triphenylarsine (10 g.) and p-cyanobenzyl bromide (6 g.) were heated together, without solvent, for 1 hour at 120° to give the arsonium salt. (14 g.) The salt was
exceptionally insoluble in chloroform or methylene chloride, m.p. 178°C (chloroform), $\nu_{\text{max}}$ 2260 cm$^{-1}$ (cyano group) 1095 cm$^{-1}$ (arsonium group). (Found C, 53.43; H, 3.90; Br, 15.9; Calculated for $C_{26}H_{21}$AsNBr C, 62.4; H, 4.2; Br, 15.9%)

**Reaction of p-Cyanobenzyltriphenylarsonium Bromide with Benzaldehyde in Ethanolic Sodium Ethoxide.**

A solution of the arsonium salt (2 g.) and benzaldehyde (0.45 g.) in ethanol (50 ml) containing sodium (0.1 g.) was set aside for 48 hours. This was evaporated nearly to dryness, extracted with chloroform and the chloroform extract washed with water and dried. Chromatography on basic alumina gave triphenylarsine (0.06 g.) m.p. and mixed m.p. 60° with petrol. Elution with petrol-ether (60:40) gave a white solid (0.55 g.) shown to be trans-4-cyanostilbene, m.p. 120° (Lit$^{110}$ 115°), $\nu_{\text{max}}$ 950, 965 cm$^{-1}$ (trans-olefin) $\lambda_{\text{max}}$ 320 (Lit$^{110}$ $\lambda_{\text{max}}$ trans 319). Elution with ether-methanol (98:2) gave triphenylarsine oxide (0.74 g.) m.p. and mixed m.p. 189°.

**Reaction of Benzyltriphenylarsonium Bromide with p-Cyanobenzaldehyde in Ethanolic Sodium Ethoxide.**

A solution of benzyltriphenylarsonium bromide (4 g.) and p-cyanobenzaldehyde (1.1 g.) in ethanol (50 ml) containing sodium (0.2 g.) was left at room temperature for 48 hours.
The reaction mixture was concentrated, extracted with chloroform and the chloroform extract was washed, dried and absorbed on basic alumina.

Elution with petrol gave triphenylarsine (1.75 g.), m.p. and mixed m.p. 60°. Elution with a petrol-benzene mixture (50 : 50) gave a white solid shown to be trans-4-cyano stilbene (1.3 g.), m.p. 69°, ν max 825, 845 cm⁻¹ (epoxide), % 221, 205, 115° (Found C, 81.5; H, 5.07; N, 6.49; calculated for C₁₅H₁₁NO C, 81.4; H, 5.01; N, 6.33%) M.W. 221.

Preparation of Methyltriphengylarsonium Iodide.

Triphenylarsine (10 g.) and methyl iodide (5 g.) were heated together, without solvent, for 30 minutes. The reaction mixture solidified and gave methyltriphenylarsonium iodide (14 g.) m.p. (from chloroform-ethyl acetate) 176° (Lit(13) 176°).

Reaction of Methyltriphengylarsonium Iodide with Benzaldehyde in Ethanolic Sodium Ethoxide.

The arsonium salt (4 g.) together with benzaldehyde (0.95 g.) in ethanol (50 ml) containing sodium (0.2 g.) was left overnight at room temperature. The g.l.c. of this solution, against a standard solution of styrene oxide using an Apiezon column at 145°, showed an 87% yield of styrene oxide. The g.l.c. also showed the absence of any styrene. The reaction mixture was treated in the same way as for previous experiments and gave
triphenylarsine (2.5 g.), m.p. and mixed m.p. 60°, on elution with petrol from an alumina column.

**Preparation of Ethoxycarbonylmethyltriphenylarsonium Bromide.**

The best method of preparation of this salt was found by refluxing a solution of triphenylarsine (10 g.) and ethyl bromoacetate (5 g.) in benzene for 12 hours. Providing excess triphenylarsine was used then the salt crystallised out on cooling, (10 g.) m.p. (from chloroform-ethyl acetate) 138° (lit (36) 138°).

**Reaction of Ethoxycarbonylmethyltriphenylarsonium Bromide with Benzaldehyde in Ethanolic Sodium Ethoxide.**

The arsonium salt (6.2 g.) was dissolved in ethanol (50 ml) containing sodium (0.29 g.) and benzaldehyde (1.4 g.) was added with mixing. The reaction mixture was left for 24 hours and then concentrated. Its chloroform extract was washed with water, dried and evaporated to dryness. This mixture was extracted with cold petrol (100-120°) leaving a white solid. This was shown to be triphenylarsine oxide (3.5 g.), m.p. and mixed m.p. 189°. The g.l.c. of the petrol extract (Apiezon column at 210°) showed trans-ethyl cinnamate (78% yield). This was confirmed by its isolation and distillation, b.p. 111°/2mm (lit (111) 144°/15 mm.).
Preparation of Allyltriphenylarsonium Bromide.

Triphenylarsine (4 g.) and allyl bromide (2 g.) were heated together, without solvent, at 70°. After 4 hours a small yield of arsonium salt (0.6 g.) was filtered off. The mother liquor, together with additional allyl bromide, was reheated to give more arsonium salt (2 g.) m.p. (from chloroform-ethyl acetate 181° (Lit.112) 180-181°).

Attempted Reaction of Allyltriphenylarsonium Bromide with Benzaldehyde in Ethanolic Sodium Ethoxide.

The allyltriphenylarsonium bromide (5 g.) was mixed with benzaldehyde (1.2 g.) in ethanol (50 ml) containing sodium (0.26 g.) and set aside for 48 hours at room temperature. The g.l.c. (Apiezon column at 220°) showed the presence of unreacted benzaldehyde and the complete absence of 1-phenylbutadiene. The reaction mixture was concentrated, extracted with chloroform and the chloroform extract washed with water, dried and concentrated. The addition of ethyl acetate caused the precipitation of a white solid, which was filtered off. This compound was shown to be 2-ethoxypropyltriphenylarsonium bromide (3 g.), m.p. (from chloroform-ethyl acetate) 203-204°, $\nu$ max 1147 cm$^{-1}$ (ether linkage) 1095 cm$^{-1}$ (arsonium salt); p.m.r. triplet (3 H) $\delta$ 9.2 (J=7 c.p.s), doublet (3 H) $\delta$ 8.5 (J=2.5 c.p.s), multiplet (1 H) $\delta$ 7.2 - 7.8, multiplet (3 H) $\delta$ 5.8 - 6.8 and multiplet (1 H) $\delta$ 5.1 - 5.5. (found C, 58.78; H, 5.45; Br, 17.30; calculated for $C_{25}H_{26}AsBrO$ C, 58.39; H, 5.49; Br, 16.89%.)
The mother liquor was chromatographed on basic alumina and gave triphenylarsine (1.25 g.) m.p. and mixed m.p. 60° on elution with petrol. Elution with ether gave a trace of a carbonyl compound (from infrared) and elution with ether-methanol (98 : 2) gave triphenylarsine oxide (0.3 g.), m.p. and mixed m.p. 189°.

Reaction of Allyltriphenylarsonium Bromide with Ethanolic Sodium Ethoxide.

The arsonium salt (1 g.) was dissolved in ethanol (50 ml.) containing sodium (0.05 g.) and left for 8 hours at room temperature. The reaction mixture was worked up as for the previous experiment. The identical product was obtained in high yield (1 g.) i.e. 2-ethoxypropyltriphenylarsonium bromide m.p. 203-204° (see above).

Preparation of p-Methoxytriphenylarsine.

p-Methoxybromobenzene (26 g.) was added to magnesium turnings (4 g.) dispersed in anhydrous diethylether (200 ml.) at such a rate as to maintain refluxing. After 2 hours, arsenic triiodide (22 g.) was added slowly, with caution, as a vigorous reaction ensued each addition. The addition of arsenic triiodide was stopped when the solution remained an orange colour. After 4 hours refluxing, the reaction mixture was poured onto hydrochloric acid and ice. Extracted with
chloroform, which, after suitable washings, was dried and evaporated to give p-methoxytriphenylarsine, m.p. (from ethanol) 158° (Lit.113) 158°, p.m.r. singlet (9) T 6.2 (OCH₃), multiplet (12) T 2.6 - 3.25 (p-substituted phenyl).

Preparation of p-Nitrobenzyltrip-methoxyphenyl)arsonium Bromide.

When p-nitrobenzyl bromide (1 g.) was heated with p-methoxytriphenylarsine (2 g.), without solvent, below 140°C, no quaternisation occurred. Raising the temperature to 160°C increased the amount of arsonium salt formed, but also resulted in much tarry matter. A compromise gave the impure arsonium salt in fair yield at 140°C for 8 hours. The buff-coloured oil was trituated with ether and solidified. Attempts to recrystallise gave an oil again. Eventually a whitish solid crystallised from a chloroform-ether solution after 6 months! m.p 108-110°, V max 1510, 1340 cm⁻¹ (nitro group), 1080, 1020 cm⁻¹ (arsonium group), p.m.r. singlet (9 H) T 6.3 (OCH₃), singlet (2 H) T 4.45 (methylene) multiplet (16 H) T 2.1 - 3.3 (aromatics).

Reaction of p-Nitrobenzyltrip-(p-methoxyphenyl)arsonium Bromide with p-Nitrobenzaldehyde in Ethanolic Sodium Ethoxide.

When sodium (0.04 g.) in ethanol (10 ml) was added to a solution of the arsonium salt (1 g.) in ethanol (40 ml) a brilliant purple colour developed. This rapidly disappeared on the addition of p-nitrobenzaldehyde (0.24 g.) and was replaced
by an immediate yellow precipitate. After 2 hours the solid was filtered off and shown to be 4, 4'-dinitrostilbene (0.42 g.) m.p and mixed m.p (from acetic acid) 303 - 304°. The mother liquor was treated as for previous experiments and absorbed onto alumina. Elution with methanol-ether (10 : 90) gave a very viscous yellow oil. Repeated attempts to crystallise this oil eventually gave a solid identified as p-methoxytriphenylarsine oxide (0.6 g.) m.p. (chloroform-petrol) 90 - 92° (Lit.113 92-94°), ν max 880 cm⁻¹ (arsine-oxide).

Reaction of p-Nitrobenzyltri(p-methoxyphenyl)arsonium Bromide with Benzaldehyde in Ethanolic Sodium Ethoxide.

When the arsonium salt (1 g.) in ethanol (50 ml.) containing sodium (0.04 g.) was treated with benzaldehyde (0.2 g.), the bright purple colour of the solution quickly disappeared. (this disappearance was much faster than for the analogous reaction without p-methoxy substituents on the arsonium group). The reaction mixture was worked up as for previous experiments and absorbed onto alumina. Elution with petrol-ether (50 : 50) gave trans-4-nitrostilbene (0.28 g.) m.p. (from ethanol) and mixed m.p. 155°. Eluting with methanol-ether (10 : 90) gave a yellow viscous oil, which eventually crystallised from chloroform-petrol, and was shown to be p-methoxytriphenylarsine oxide (0.6 g.), m.p and mixed m.p. 92 - 94°.
Preparation of Benzyltri(p-methoxyphenyl)arsonium Bromide.

p-Methoxytriphenylarsine (2 g.) and benzyl bromide were heated together, without solvent, at 140° and gave a colourless oil, insoluble in ether. Crystallisation was achieved from a very dilute solution of the salt in chloroform and ethyl acetate, m.p. 178°, $\nu$ max 1020, 1080 cm$^{-1}$ (arsonium salt). (Found C, 58.78; H, 5.10; calculated for C$_{28}$H$_{28}$AsBrO$_3$ C, 59.28; H, 4.97%)

Reaction of Benzyltri(p-methoxyphenyl)arsonium Bromide with p-Nitrobenzaldehyde in Ethanolic Sodium Ethoxide.

A solution of the arsonium salt (0.8 g.), p-nitrobenzaldehyde (0.21 g.) in ethanol (50 ml), containing sodium (0.3 g.), was set aside for 2 days. The solution had become a dark brown colour. Work up was as for previous experiments, followed by chromatography on a basic alumina column. Elution with a benzene-petrol mixture (10 : 90) gave p-methoxytriphenylarsine (0.5 g.) m.p. (from ethanol) and mixed m.p. 158°. Elution with ether-petrol (50 : 50) gave trans-4-nitrostilbene epoxide (0.25 g.) m.p. (from ethanol) and mixed m.p. 127°.
CHAPTER II.

Reaction of Alkylidene arsonaranes with Some Other Functional Groups.

Addition to Conjugated Double Bonds.

Alkylidene arsonaranes are powerful nucleophilic agents and should undergo the typical reactions of alkylation, acylation and Michael additions. The latter reaction was considered worthy of investigation as it seemed likely that the mode of reaction adopted by arsonium ylids could be either that taken by sulphonium or by phosphonium ylids when they undergo reaction with \( \alpha, \beta \)-unsaturated carbonyl compounds.

Corey and Chaykovsky\(^{114}\) reported that when sulphonium ylids are treated with \( \alpha, \beta \)-unsaturated aldehydes or ketones, epoxides are obtained in high yields. For example, methylenedimethylsulphorane (1) reacts with benzalacetophenone (2) to give the epoxide (3) in 87% yield, with no trace of the other possible product (4).

Additional studies by Corey et al\(^{114}\) and also Franzen and Driessen\(^{115}\) have shown that with less reactive carbonyl
compounds, e.g. esters, the alternative conjugate addition, to form cyclopropanes, may well occur or even predominate.

Thus the ylid (1) reacts with cinnamaldehyde to give the epoxide (5), but with ethyl cinnamate to give the cyclopropane derivative (6).

\[
\begin{array}{c}
\text{(CH}_3\text{)}_2\text{S-CH}_2 \\
\text{C}_6\text{H}_5\text{CH}=\text{CHCHO} \\
(\text{CH}_3\text{)}_2\text{S-CH}_2 \\
\text{C}_6\text{H}_5\text{CH}=\text{CH-CO}_2\text{C}_2\text{H}_5
\end{array} \rightarrow \begin{array}{c}
\text{C}_6\text{H}_5\text{CH}=\text{CH-CO}_2\text{C}_2\text{H}_5 \\
\text{C}_6\text{H}_5\text{CH}=\text{CH-CH-CH}_2 \\
\text{C}_6\text{H}_5\text{CH}=\text{CH-CO}_2\text{C}_2\text{H}_5
\end{array}
\]

(5)

(6)

It is interesting that these same \(\alpha, \beta\)-unsaturated carbonyl compounds do behave as Michael receptors with oxysulphonium ylids. For example the reaction of benzalacetophenone with methylenedimethyloxysulphorane (7) yields 95% of 1-benzoyl-2-phenylcyclopropane (4) and only a trace of the epoxide (3). Similarly ethyl cinnamate reacts to give 1-carboethoxy-2-phenylcyclopropane (6).

\[
\begin{array}{c}
\text{(CH}_3\text{)}_2\text{S-CH}_2 \\
\text{C}_6\text{H}_5\text{CH}=\text{CHCHO} \\
\text{(CH}_3\text{)}_2\text{S-CH}_2 \\
\text{C}_6\text{H}_5\text{CH}=\text{CH-CO}_2\text{C}_2\text{H}_5
\end{array} \rightarrow \begin{array}{c}
\text{C}_6\text{H}_5\text{CH}=\text{CH-CO}_2\text{C}_2\text{H}_5 \\
\text{C}_6\text{H}_5\text{CH}=\text{CH-CO}_2\text{C}_2\text{H}_5
\end{array}
\]

(7)

Oxysulphonium ylids are much more stable and less reactive than sulphonium ylids, as predicted from the data available on rates of base-catalysed hydrogen-deuterium exchange from the corresponding conjugate acids. For example the
methylenesulphonium ylid (1) reacts with 1,1-diphenylethylene (8) to give a 60% yield of 1,1-diphenylcyclopropane (9), but the methylenesulphonium ylid (7) does not react under identical reaction conditions.

\[
\begin{align*}
\text{(8)} & \quad \text{(9)} \\
(CH_3)_2S-CH_2 + \text{C}_6\text{H}_5-C=CH_2 & \rightarrow \text{C}_6\text{H}_5-C\text{CH}_2-CH_2
\end{align*}
\]

Phosphonium ylids may undergo reaction with activated carbon-carbon double bonds in three different ways. All three reaction paths can be accounted for by an initial Michael addition to give the betaine (12), followed by its decomposition by path (a), (b) or (c). \(^{(117)}\)

\[
\begin{align*}
\text{(10)} & \quad \text{(11)} \\
(C_6H_5)_3P-CHR^1 + R^2CH=CH-C-R^3 & \rightarrow (C_6H_5)_3P-C-CH-R^2 \quad H_0 \quad CH-C-R^3
\end{align*}
\]

\[
\begin{align*}
\text{(12)} & \\
\text{(a)} & \quad \text{(b)} & \quad \text{(c)} \\
(C_6H_5)_3P + CH=CH-R^2 & \quad (C_6H_5)_3P-C-CH-R^2 & \quad (C_6H_5)_3P-C-CH-R^3
\end{align*}
\]

The course of elimination of betaine (12) depends upon R^1 in the original alkylidene phosphorane (10). When R^1 is electron-
releasing the betaine decomposes by path (a); when $R^1$ is electron-attracting the betaine decomposes by path (b); and when $R^1$ is electron-attracting and $R^2$ is capable of ejection as an anion, then the third path (c) is followed.

The usual reaction of phosphonium ylids with $\alpha, \beta$-unsaturated aldehydes or ketones is the production of olefins a normal Wittig reaction. For instance Surmatis and Ofner\(^\text{118}\) prepared $\beta$-carotene by the reaction of a bis-phosphonium ylid with two molecules of $\beta$-ionyldeneacetaldehyde, i.e. no conjugate addition occurred. However, when the environment of the carbonyl group makes it unreactive then conjugative addition of the ylid occurs to give the betaine (12), which then decomposes by one of the paths described. One of the earliest examples was claimed by Inhoffen\(^\text{119}\) who said that 2-ketomethylenecyclohexane (13) underwent conjugate 1, 4-addition with cyclohexyldene-ethylidenetriphenylphosphorane (14) to give an intermediate (15). This, after a 1-3 hydride shift, broke down to give the triene (16) and triphenylphosphine oxide. However, the product (16) was characterised only by its ultraviolet spectrum.

\[ \text{C}_8\text{H}_{12}\text{O} + (\text{C}_6\text{H}_5)_3\text{P}-\text{CH-CH}= \rightarrow \left[ \begin{array}{c} \text{H} \\ \text{CH} \\ \text{CH} \end{array} \right] \]

\[ \left. \begin{array}{c} \text{F} \\ \text{C}_8\text{H}_{12} \end{array} \right] \]

\[ \left(13\right) \hspace{1cm} \left(14\right) \hspace{1cm} \left(15\right) \]

\[ \rightarrow \left(\text{C}_6\text{H}_5\right)_3\text{P}-\text{CH-CH}= \]

\[ \left(16\right) \]
Bohllmann reported that when cinnamylidenetriphenylphosphorane (17) was treated with cinnamylideneacetophenone (18) a diphenylhexatriene (20) was formed together with the expected olefin (21). He proposed that this product was a result of 1, 4 addition of the ylid to the carbonyl compound followed by thermal cleavage of a six-membered ring (19) to give the triene (20), triphenylphosphine oxide and phenylacetylene. However no phenylacetylene was isolated.

\[
\begin{align*}
\text{Mes-C-CH-CH-C}_6\text{H}_5 + (\text{C}_6\text{H}_5)_3\text{P-CH}_2 & \rightarrow \text{Mes-C-CH-CH-CH-C}_6\text{H}_5 + (\text{C}_6\text{H}_5)_3\text{P} \\
\text{Mes-C-CH-CH-C}_6\text{H}_5 + (\text{C}_6\text{H}_5)_3\text{P} & \rightarrow \text{Mes-C-CH-CH-C}_6\text{H}_5 + (\text{C}_6\text{H}_5)_3\text{P} \\
\end{align*}
\]
This reaction scheme is in accord with Bestman's observations, since $R^1$ of the phosphorane (10) is electron-releasing and decomposition of the intermediate occurs by path (a).

An example of the second type of stabilisation afforded the betaine (12), by path (b), was found by Bestman and Seng(122) when they treated carbomethoxytriphenylphosphorane (24) with methyl benzoylacrylate (25) and obtained the new ylid (26) by a 1,3-hydride shift.

$$\begin{align*}
\text{H} &\text{H} &\text{H} &\text{H} &\text{H} &\text{H} \quad \text{P} &\text{CH} &\text{CO}_2\text{Me} + \text{H} &\text{H} &\text{CO} &\text{CH} &\text{CH} &\text{CO}_2\text{Me} \rightarrow \text{H} &\text{H} &\text{H} &\text{H} &\text{H} &\text{H} \quad \text{P} &\text{CH} &\text{CH} &\text{CH} &\text{CO}_2\text{Me}
\end{align*}$$

The third type of reaction observed for phosphoranes was discovered by Trippett(123) when he added cyanomethylenetriphenylphosphorane (27) to either ethoxymethylene malonate (28) or to tetracyanoethylene (28b). In both experiments the product was a new ylid (29),(30) accompanied by simultaneous expulsion of ethoxide in the first reaction or cyanide in the second reaction, i.e. decomposition by path (c).
Reactions of Alkylidenearsonanes.

The chemistry of the conjugate addition of alkylidenearsonanes investigated suggests that arsonium ylids again exhibit intermediate behaviour between sulphonium and phosphonium ylids.

Methylenetriphenylarsorane reacts with both benzalacetomesitylene and benzalacetophenone to give respectively 1-mesitoyl-2-phenycyclopropane (32a) and 1-benzoyl-2-phenylcyclopropane (32b). These products were verified by the preparation of authentic samples using Corey's method. (124)

\[
(C_6H_5)_3As-CH_2 \xrightarrow{\text{Ar-C-CH=CH-C}_6H_5} \left[ (C_6H_5)_3As-CH_2 \xrightarrow{\text{C}_6H_5-CH-CH-C-Ar} \right] \rightarrow (C_6H_5)_3As+C_6H_5-CH-CH-C-Ar
\]

(32a) \( Ar = 2, 4, 6 \)-trimethylphenyl.

(32b) \( Ar = \text{phenyl.} \)
The formation of cyclopropanes is readily accounted for by the conjugate addition of the ylid to the \( \alpha, \beta \)-unsaturated ketone giving the intermediate betaine (31). This undergoes trans-elimination by rear-side attack of the carbanion on the carbon \( \alpha \) to the arsonium group, giving a cyclopropane with simultaneous expulsion of triphenylarsine. This mechanism is analogous to the one proposed for epoxide formation when arsonium ylids undergo reaction with carbonyl compounds and identical to that proposed for the decomposition of betaine (12) by path (a) when phosphonium ylids undergo reaction with \( \alpha, \beta \)-unsaturated carbonyl compounds.

It is interesting that even with a non-hindered ketone, arsonium ylids preferred to react at the double bond rather than the carbonyl bond (unlike phosphonium and sulphonium ylids).

However, when methylenetriphenylarsorane was treated with ethyl cinnamate, no trace of 1-carboethoxy-2-phenylcyclopropane (6) was found.

\[
(C_6H_5)_2As-CH_2 + C_6H_5-CH=CH-C=C_2H_5 \rightarrow C_6H_5-CH-CH=C-C_2H_5 + (C_6H_5)_2As \tag{6}
\]

There is clear indication that reaction of the ylid occurred at the carbonyl and not at the double bond, as the product is almost certainly the stable \( \beta \)-ketoalkyldenearsonane (34). Unfortunately the product was obtained as a red viscous oil, which failed to crystallise and could not be obtained analytically pure.
Its infrared spectrum showed a carbonyl absorption at 1510 cm\(^{-1}\) characteristic of the carbonyl stretching frequencies observed for acyldenearsoranes. Treatment of the product with hydrogen bromide gave a colourless oil, which again could not be obtained crystalline, but its infrared showed the presence of a new peak at 1720 cm\(^{-1}\), and the absence of the original 1510 cm\(^{-1}\). This kind of shift has been observed for a wide variety of acylphosphonium ylids and their salts\(^{(125)}\) the shift being attributed to increased single bond character due to delocalisation of the carbanion electrons through the carbonyl group.

\[
\begin{align*}
(C_6H_5)_3P-CH-C=CH\rightarrow (C_6H_5)_3P-CH=CH-C-R
\end{align*}
\]

The ultraviolet spectrum of the red oil showed \(\lambda_{\text{max}} 325 \ (\log E = 4.25)\) and \(\lambda_{\text{max}} 269 \ (\log E = 4.17)\) indicating a highly conjugated carbonyl compound. The mass spectrum gave the molecular weight as 450 (the expected value for cinnamoylmethylenetriphenylarsorane) and the following fragment patterns,

\[
\begin{align*}
(C_6H_5)_3As=CH - CH = CH - C_6H_5
\end{align*}
\]

It was hoped that alkaline hydrolysis of this product \((34)\) would confirm its structure, but unfortunately mostly black tarry decomposition products were obtained, from which only
triphenylarsine oxide was positively identified. Distillation caused the product to decompose and the only identified decomposition fragment was triphenylarsine.

A mechanism for the formation of (34) is proposed below,

\[
\begin{align*}
(C_6H_5)_3\text{As-CH}_2 & \\
C_6H_5-\text{CH=CH}-OC_2H_5 & \rightarrow (C_6H_5)_2\text{As-CH-C-CH=CH-C}_6H_5 + \text{OC}_2H_5 \\
\rightarrow (C_6H_5)_3\text{As-CH-C-CH=CH-C}_6H_5
\end{align*}
\]

i.e. the ethyl cinnamate acts as an acylating agent and gives rise to the new arsonium salt (35). Since the cinnamoyl group is acidifying and since the anion (\text{OC}_2H_5) is sufficiently basic, the acyl arsonium salt (35) is converted to its conjugate base, (cinnamoylmethylenetriphenylarsorane (34)).

Conclusion.

The reactions of alkylidenetriphenylarsoranes with \( \alpha, \beta \)-unsaturated carbonyl compounds may proceed by attack of the ylid on either the carbonyl carbon or the \( \beta \)-carbon atom.

Addition to the C,N Double Bond.

The reactions of alkylidenearsoranes with the C,O and C,C double bonds suggested that the ylids might also react with the C,N double bond.
Alkylidenesulphoranes undergo reaction with Schiff's bases to give aziridines. For example methylenedimethylsulphorane reacts smoothly with benzalaniline to give 1,2-diphenylaziridine (36) in 91% yield.

\[
\text{CH}_3\text{S-CH}_2 + \text{C}_6\text{H}_5\text{CH=NC}_6\text{H}_5 \rightarrow (\text{CH}_3)_2\text{S} + \text{C}_6\text{H}_5\text{CH-N-C}_6\text{H}_5
\]

(36)

The reaction of benzalaniline with methylenedimethyloxy sulphorane is more complex giving rise to 1,2-diphenylaziridine (36), 41%, but also to acetophenone anil (37) and the amino-sulphoxide (38).

\[
\text{C}_6\text{H}_5\text{CH-N-C}_6\text{H}_5 \quad \text{C}_6\text{H}_5\text{CH-NH-C}_6\text{H}_5 \quad \text{CH}_2\text{SOCH}_3
\]

(37) (38)

Speziale et al added benzalaniline to carboethoxymethylenedimethylsulphorane (39) and obtained the conjugated vinyl amine (41). They considered that this product arose from rearrangement of the primary product, 1,2-diphenyl-3-carboethoxyaziridine (40).

\[
\text{C}_6\text{H}_5\text{CH=NC}_6\text{H}_5 + (\text{CH}_3)_2\text{S-CH}_2\text{-CO}_2\text{C}_2\text{H}_5 \rightarrow \left[ \text{C}_6\text{H}_5\text{CH-N-C}_6\text{H}_5 \right]
\]

(39) (40)

\[
\text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 - \text{NH}
\]

(41)
This mechanism was suggested as the most likely by the authors because of the analogous reactions of other sulphonium ylids. Also the aziridine (40) was shown to open to give the product (41) under mild conditions.

Alkylidene phosphoranes are known to undergo two types of reactions with the C,N double bonds.

If the phosphonium ylids do not have a $\text{-CH}_2$ group to the phosphorus atom, then they undergo reaction with Schiff's bases, at $150 - 180^\circ$, to give olefins and iminophosphoranes. Thus benzylidene triphenylphosphorane gives with benzalaniline a 72% yield of trans-stilbene and phenyliminotriphenylphosphorane (43).

\[
\begin{align*}
(C_6H_5)_3P-CH-C_6H_5 & \quad \rightarrow \quad \left[ (C_6H_5)_3P-CH-C_6H_5 \right] \\
C_6H_5-N\text{-CH-C}_6H_5 & \quad \rightarrow \quad C_6H_5-N\text{-CH-C}_6H_5
\end{align*}
\]

\[
\rightarrow \quad \left( C_6H_5 \right)_3P=N C_6H_5 + C_6H_5-CH=CH-C_6H_5
\]

(42)

Phosphonium ylids with a $\text{-CH}_2$ group to the phosphorus atom react with a C,N double bond to form a betaine, sometimes isolable. This decomposes, on heating to give an allene, triphenylphosphine and an aniline. For example Bestman\(^{(117)}\) found that ethylidene triphenylphosphorane reacts with benzalaniline to give an isolable betaine (44). This decomposes
at 190° and 15 mm to phenyllallene (46), triphenylphosphine and aniline.

\[
\begin{align*}
\text{C}_6\text{H}_5-\text{N} & \quad \text{CH-CH}_2\text{P} \quad \text{C}_6\text{H}_5 \quad \text{at190°} \\
\text{C}_6\text{H}_5\text{N} & \quad \text{CH-C}_6\text{H}_5
\end{align*}
\]

Bestman suggests that after the initial nucleophilic attack of the ylid on the Schiff's bases, a 1,3 proton-shift occurs to give a new ylid (45). This then undergoes an intermolecular Hofmann degradation by an intramolecular elimination, (transfer of a proton from the \(\beta\)-position, with respect to phosphorus, to the lone pair on the nitrogen.)

It was found that alkylidenearsoranes undergo reaction with Schiff's bases to give aziridines in an analogous manner to alkylidenesulphoranes. This product was the predicted one by considerations of former results. It is envisaged that the arsonium ylids undergo nucleophilic attack at the electrophilic centre of the Schiff's base to give the betaine (47). This then expels triphenylarsine, probably by the rear-side attack of the nitrogen anion on the carbon \(\beta\) to the arsenic atom.
The aziridines were identified by spectral and elemental analysis. (Many side reactions occurred, particularly in experiment (2), above. The cleanest series involved generating and reacting the benzylidenetriphenylarsorane in ether, when yields of 50% aziridine were found. Use of benzene as solvent reduced the yield of aziridine to 20% or less.)

Using the previous knowledge that arsonium ylids, carrying a charge-stabilising group on the α-carbon, gave olefins when treated with carbonyl compounds, it was hoped that an analogous effect would be observed for this series of experiments, i.e. that betaine decomposition would occur by a cis-elimination to yield an iminoarsorane and an olefin, (analogous to phosphonium ylids). Thus it was hoped that the reaction of p-nitrobenzylidenetriphenylarsorane with p-methoxybenzalaniline would give 4-nitro-4'-methoxystilbene (49) and phenyliminoarsorane (50).
Initially this idea was tested by treating the arsonium salt and Schiff's base with ethanolic sodium ethoxide, the method employed so successfully for 'arsenic-Wittig' reactions. However, the products isolated were 4,4'-dinitrostilbene, and p-nitrotoluene, together with triphenylarsine and triphenylarsine oxide and not the expected 4-nitro-4'-methoxystilbene. It seemed that rather than the expected reaction taking place, alcoholysis of the p-nitrobenzyltriphenylarsonium salt was the faster reaction. Confirmation that these products were alcoholysis products was found by subjecting the arsonium salt to ethanolic sodium ethoxide. Five products were isolated, (a) triphenylarsine, (b) p-nitrotoluene, (c) 4,4'-dinitrobenezyl, (d) 4,4'-dinitrostilbene and (e) triphenylarsine oxide. Products (b), (c) and (e) can be directly accounted for by alcoholysis of the salt, probably by a mechanism as speculated below,
The p-nitrobenzyl anion could then protonate by reaction with the solvent, ethanol, to give p-nitrotoluene, or by attacking unchanged arsonium salt to give 4,4'-dinitrodibenzyl.

Products (a) and (d) probably arise by attack of the p-nitrobenzylidenetriphenylarsorane on unchanged salt to give a new arsonium salt (51), which then undergoes a Hofmann elimination to give the olefin, 4,4'-dinitrostilbene and triphenylarsine.
To prevent the alcoholysis of the arsonium salt occurring the salt was treated with Schiff's base and ethoxide in dimethylformamide. However, these reaction conditions proved equally unsuccessful giving unreacted starting materials or black tarry products. A final attempt was made by generating the ylid with butyl-lithium in ether followed by treatment with Schiff's base. There was clear indication that the p-nitrobenzylidene triphenylarsorane underwent reaction with the base because the purple colour (characteristic of this ylid\(^{21}\)) disappeared. However, after 24 hours refluxing, when the reaction mixture was plunged into water, the purple colour reappeared, suggesting that betaine formation probably had occurred, but that betaine elimination had not.
Experimental.

All experiments involving ylids were carried out under an oxygen-free nitrogen atmosphere. All solvents were dried and distilled before use. Unless otherwise stated petrol refers to the fraction, b.p. 40 - 60°. Melting points were corrected.

Preparation of Trimethyloxysulphonium Iodide.

Dimethylsulphoxide was dried by refluxing over calcium hydride followed by distillation under vacuum. The distilled dimethylsulphoxide (16 g.) and methyl iodide (30 ml) were refluxed for 9 days. The solid was filtered off (35 g.). Recrystallised from water, crushed and dried over P₂O₅ (127).

Preparation of Benzalacetomesitylene.

To a solution of acetomesitylene (15 g.) and benzaldehyde (10 g.) in ethanol (200 ml.) was added dropwise 2 N. sodium hydroxide (25 ml.), keeping the temperature at 0°C. After stirring the reaction mixture for a further hour, it was set aside for 16 hours. A small amount of solid separated and was filtered off. The mother liquor was concentrated until an oil separated out. Trituration with ethanol, produced a crystalline solid, m.p. (from ethanol) 61°, (Lit. (128) 63°), \( \nu_{\text{max}} 1640 \text{ cm}^{-1} \), (conjugated carbonyl) p.m.r. singlet (6H) \( \gamma 7.8 \), singlet (3H) \( \gamma 7.65 \), multiplet (7H) \( \gamma 2.3 - 3.2 \).
Preparation of 1-mesityl-2-phenylcyclopropane.

A solution of methylenedimethyloxysulphorane (0.03 mole) was prepared by treating trimethyloxysulphonium iodide (6.6 g.) with sodium hydride (1.5 g. of 50% NaH-mineral oil dispersion) in dimethylsulphoxide.\(^{126}\) The weighed amount of sodium hydride, as a mineral oil dispersion, had been previously washed three times with petrol, and decanted. When the preparation of the ylid was complete, the solution was cooled to 0\(^\circ\). Slow addition of a solution of benzalacetomesitylene (8.2 g.) in dimethylsulphoxide, however, caused the reaction mixture to go solid. The addition was continued at 15\(^\circ\). The solution gradually changed from colourless to a dark orange colour. When the addition of the ketone was complete, the reaction mixture was heated, overnight, at 50\(^\circ\). After cooling the mixture was poured into water, extracted with chloroform and the chloroform extract washed, dried and absorbed, with considerable difficulty, onto basic alumina. Elution with a petrol-benzene mixture (90 : 10) gave a colourless viscous oil. This was shown to be 1-mesityl-2-phenylcyclopropane, b.p. 188\(^\circ\) - 1 mm (Lit.\(^{121}\) 150\(^\circ\) - 0.1 mm), v\(_{\text{max}}\) 1670 (carbonyl), 1020-1040 cm\(^{-1}\), p.m.r. singlet (9H) \(\gamma\) 7.8 (all 3 methyl protons of the mesitylene group), complex multiplet (4H) \(\gamma\) 7.0 - 8.8 (cyclopropyl), multiplet (2H) \(\gamma\) 3.05 - 3.2 (aromatic), multiplet (5H) \(\gamma\) -0.65 - 3.0 (aromatic).
Reaction of Methylenetriphenylarsorane with Benzalacetomesitylene.

Methyltriphenylarsonium iodide (6 g.) was dispersed in ether (100 ml.) and butyl-lithium (29 ml. of 0.46 N) was slowly added. After 30 minutes the solution was a dark yellow colour. A solution of benzalacetomesitylene (3.4 g.) in ether (25 ml.) was added dropwise with very little apparent change in the colour of the reaction mixture. The ether was removed by distillation and replaced by tetrahydrofuran. The reaction mixture was refluxed for 8 hours and then concentrated. The concentrate was extracted with chloroform and the chloroform extract was washed, dried and absorbed on activated alumina. Volatile smelly arsines eluted first, together with triphenylarsine, which crystallised out (1.5 g.), m.p. and mixed m.p. 60°. Elution with petrol-benzene (99 : 1) gave a viscous oil, whose physical properties were identical with the previously identified 1-mesitoyl-2-phenylcyclopropane (1.6 g.) 48% yield (see previous preparation).

Preparation of Benzalacetophenone.

Benzaldehyde (21 g.) and acetophenone (24 g.) were dissolved in ethanol (200 ml.). The solution was cooled to 0° and sodium hydroxide (50 ml. of 2.5 N) was added slowly. After two hours a yellow solid had separated out from the reaction mixture. This was filtered off (36 g.), m.p. (from ethanol) 54.5 - 55.5° (Lit. 129) 57° uncorrected, \( \nu \) max 1640 cm\(^{-1}\) (conjugated carbonyl),
111.

p.m.r. multiplet (2H) $\gamma$ 7.95 - 8.15, multiplet (10H) $\gamma$ 7.2 - 7.8.

Preparation of 1-Benzoyl-2-phenycyclopropane.

Trimethyloxysulphonium iodide (6.6 g.) was dissolved in dry dimethylsulphoxide (60 ml.). To the cooled solution sodium hydride (1.5 g. of 50\% dispersion in mineral oil) was carefully added. When effervescence stopped, benzalacetophenone (5.5 g.) in dimethylsulphoxide (30 ml.) was added dropwise, followed by heating at 50° overnight. This mixture was poured into water, extracted with chloroform and the chloroform extract washed, dried and absorbed on basic alumina. Elution with petrol-benzene (90: 10) gave 1-Benzoyl-2-phenylcyclopropane, m.p. 50° (Lit.114 45.5 - 50°) $\nu$ max 1660(s), (carbonyl) 1030(s) cm.$^{-1}$, p.m.r. showed 3 multiplets, (1H) $\gamma$ 8.4 - 8.7, (1H) $\gamma$ 7.8 - 8.3 and (2H) $\gamma$ 6.9 - 7.5 (cyclopropyl protons), multiplet (8H) $\gamma$ 2.3 - 2.9, multiplet (2H) $\gamma$ 1.8 - 2.0 (aromatic protons).

Reaction of Methyleneetriphenylarsorane with Benzalacetophenone.

Methyltriphenylarsonium iodide (6 g.) was treated with butyl-lithium (12.3 mls. of 1.1M) in ether. After 1½ hours, benzalacetophenone (2.8 g.) was added dropwise in ether. The solution slowly changed from a dark brown colour to a pale yellow colour, when suddenly it turned to an emerald green colour, (this also occurred in a repeat experiment employing only 0.5 mole quantity of butyl-lithium to 1.0 mole of arsonium
salt). After refluxing for sixteen hours the solution was poured into water. The chloroform extract of this was washed, dried and absorbed on basic alumina. Elution with petrol gave triphenylarsine (1.9 g.), m.p. and mixed m.p. 60°. Elution with petrol-benzene (50 : 50) gave a yellow oil, which with trituration crystallised (1.5 g.). This was identified as 1-benzoyl-2-phenylcyclopropane by comparison with an authentic sample. Elution with petrol-ether (90 : 10) gave unreacted benzalacetophenone (0.6 g.). Elution with ether gave an unidentified white solid (0.45 g.), m.p. 241°, ν max 3,380 m (3° alcohol), 1680 s (carbonyl), 1590m, 1570w, 1210m, 1050m, 1010w, 895m, 790m, 765 760 750 m, 700 s cm⁻¹, m/e 519.

**Reaction of Methylene triphenylarsorane with Ethyl Cinnamate.**

To a dispersion of methyltriphenylarsonium iodide (8 g.) in ether was added butyl-lithium (16 mls. of 1.07 M). Freshly distilled ethyl cinnamate (3.2 g.) was added dropwise and then the reaction mixture was refluxed for 16 hours. A concentrated solution was then treated with chloroform and water and the chloroform extract was washed, dried and absorbed on basic alumina. Elution with petrol gave triphenylarsine (1.5 g.), m.p. and mixed m.p. 60°. Elution with petrol-benzene gave unreacted ethyl cinnamate (1.35 g.). Elution with either ether or ether-methanol (99 : 1) gave a red viscous oil (2.5 g.) which failed to crystallise, ν max 1630, 1600, 1570 (aromatic
conjugation), 1510s (ylid carbonyl), 1110, 1085, 1035m
(complex arsenic-carbon), 740, 690 cm\(^{-1}\) (substituted aromatics),
\(\lambda_{\text{max}}\) 325, \(\log \varepsilon = 4.25\), 269 m\(\mu\) \(\log \varepsilon = 4.17\), (a highly
conjugated carbonyl group). From a freshly prepared sample
a mass spectrum was obtained by using a lowered energy input,
giving the molecular weight as 450, with fragments of 347,
319 and 306. These physical properties indicated that the
red viscous oil was cinnamoylmethylenetriphenylarsorane.

Treatment of an ethanolic solution of the oil with aqueous
concentrated hydrobromic acid, caused the separation of a
colourless oil. This failed to crystallise, even in the
presence of tetrafluoroborate anions. However, the infrared
indicated that the product was in fact the corresponding
arsonium salt, 1720s (carbonyl) 1425m\(\mu\)cm\(^{-1}\) (arsonium-phenyl
stretching).

The attempted distillation of the red oil at 1 mm, resulted
in its decomposition at 200°. Triphenylarsine was the only
identified decomposition product.

Refluxing the red oil with aqueous sodium hydroxide (2N)
gave black tarry products, together with triphenylarsine oxide.

**Reaction of Benzylidenearsorane with Benzol (m-nitroaniline).**

Benzyltriphenylarsorium bromide (3.9 g.) was stirred with
butyl-lithium (7ml. of 1.2M) for 1 hour in ether. To the bright
orange solution was added benzol (m-nitroaniline) (1.85 g.).
The mixture was refluxed overnight and after concentrating extracted with benzene. The benzene extract was washed, dried and absorbed on basic alumina. Elution with petrol gave triphenylarsine (2.55 g.) m.p. and mixed m.p. 60°. Elution with benzene-petrol (20 : 80) gave a viscous oil, which later crystallised on triturating with petrol (0.6 g.) m.p. (from ethanol) 96°. The infrared spectrum was very complex, $\nu_{\text{max}}$ 1620 m, 1580 s, (aromatic double bonds) 1530 s, 1340 s, (nitro-group), 1260 m, 1210 m, 1080 m, 1030 m, 960 m, 880 m, 850 m, 800 m, 770 s, 740 s, 695 s cm$^{-1}$, $\lambda_{\text{max}}$ 243 (log $\varepsilon$ = 4.27) p.m.r. broad singlet (2H) $\gamma$ 6.4, multiplet (14H) $\gamma$ 2.15 - 3.65; $m/e$ 316, 300, 270, 240, 180, 90. Found C, 76.07; H, 5.18; N 8.98; calculated for $C_{20}H_{16}N_2O_2$ C, 75.96; H, 5.06; N, 8.85%.

M.W. 316. Identified as 1,3-nitrophenyl-2,3-diphenylaziridine.

Elution with ether-petrol (30 : 70), gave a bright yellow solid, identified as N-benzyl-m-nitroaniline (0.45 g.) m.p. and mixed m.p. 107°, $m/e$ 228, M.W. 228.

Elution with ether-petrol (50 : 50) gave a bright yellow solid shown to be m-nitroaniline (0.8 g.) m.p. and mixed m.p. 114°.

Reaction of Benzyltriphenylarsorane with p-Methoxybenzalaniline.

Benzyltriphenylarsonium bromide (3.9 g.) was stirred with butyl-lithium (7 mls. of 1.2M) in ether for 1 hour. To this was added a solution of p-methoxybenzalaniline (1.7 g.) in ether.

114.
After 24 hours refluxing the reaction mixture had changed from the original red colour to a yellow colour. This was concentrated, extracted with benzene, and the benzene extract washed, dried and absorbed onto alumina. Elution with petrol gave triphenylarsine (1.5 g.) m.p. and mixed m.p. 60°. Elution with petrol-benzene (95 : 5) gave a small amount (0.1 g.) of an unidentified yellow oil, \( \nu_{\text{max}} \) 1720 cm\(^{-1}\). Fractions from petrol-benzene mixtures from (70 : 30) to (40 : 60) gave a viscous yellow oil, later shown to be 2-(p-methoxyphenyl)-1,3-diphenylaziridine (0.7 g.). The oil failed to crystallise and a satisfactory analysis was not obtained. Its infrared was very complex and showed close similarities to the aziridine of the previous preparation; \( \nu_{\text{max}} \) 1600s, 1520s, 1245s, 1170m, 1160w, 1030s, 900m, 845m, 805s, 770, 760, 750 s., 695s cm\(^{-1}\), \( \lambda_{\text{max}} \) 236 (log \( E \) = 4.25), p.m.r. singlet (2H) \( \gamma \) 6.5, singlet (3H) \( \gamma \) 6.4, multiplet (14H) \( \gamma \) 2.85 - 3.5; \( m/e 301 \), 286, 210, 180, 90; M.W. of aziridine is 301. Elution with petrol-benzene (20 : 80) also gave a yellow oil (0.7 g.), which was contaminated with aziridine, and again was not obtained analytically pure. Its infrared spectrum suggested the compound contained a secondary amine (\( \nu_{\text{max}} \), 3,400 cm\(^{-1}\)). Its ultraviolet spectrum showed it to contain a conjugated olefin (\( \lambda_{\text{max}} \) 247, 296 m\( \mu \)). This compound was probably the ring-opened aziridine, i.e. \( \text{pCH}_3\text{O-C}_6\text{H}_4\text{CH=C-N-C}_6\text{H}_5 \), but
it could not be obtained free of aziridine. Elution with ether-petrol (50 : 50) gave N-benzylaniline (0.1 g.).

**Reaction of Benzylidenetriphenylarsorane with Benzalaniline**

Benzyltriphenylarsonium bromide (4 g.) was stirred with butyl-lithium (7 ml. of 1.2M) in ether for 1 hour. To the bright orange solution was added benzalaniline (1.4 g.). The reaction mixture was refluxed for 16 hours, cooled, concentrated and extracted with chloroform. The chloroform extract was washed with water, dried and absorbed onto basic alumina. Elution with petrol gave triphenylarsine (2 g.), m.p. and mixed m.p. 60°. Further elution with petrol gave 1,2,3-triphenylaziridine (0.8 g.), m.p. 88° (Lit. 88°); v max 1590s, 1490s, 1400w, 1340w, 1200m, 1070m, 1010m, 930m, 890m, 750 760s, 695s cm⁻¹; m/e 271, 180, 167. Molecular weight of 1,2,3-triphenylaziridine is 271.

**Attempted Reaction of p-Nitrobenzyltriphenylarsorane with Benzalaniline**

p-Nitrobenzyltriphenylarsorane bromide (5 g.) and p-methoxybenzalaniline (1.9 g.) were dissolved in ethanol (50 ml.) to which was added sodium (0.22 g.) in ethanol. The solution became a brilliant purple characteristic of the p-nitrobenzylidenetriphenylarsorane. This mixture was left for 4 days at room temperature during which time the purple colour disappeared.
A green-yellow solid was filtered off and shown to be 4,4'-dinitrostilbene m.p. and mixed m.p. 298 - 303°. The reaction mixture was concentrated and extracted with chloroform and water. The chloroform extract was dried, concentrated and upon addition of ethyl acetate a pale yellow solid precipitated. Identified as the original arsonium salt (1.5 g.), m.p. and mixed m.p. 156°. The mother liquor was absorbed onto basic alumina. Elution with petrol gave triphenylarsine (0.35 g.), m.p. and mixed m.p. 60°. A benzene-petrol mixture (10 : 90) gave a yellow solid, identified by comparison with authentic as p-nitrotoluene, m.p. and mixed m.p. 54°. Elution with ether-petrol (30 : 70) gave unreacted Schiff's base (0.7 g.). Elution with ether-methanol (99:1) gave triphenylarsine oxide (0.7 g.), m.p. and mixed m.p. 189°.

**Alcoholysis of p-Nitrobenzyltriphenylarsonium Bromide.**

p-Nitrobenzyltriphenylarsonium bromide (2.0 g.) was dissolved in absolute ethanol (distilled from calcium hydride) to which was added a solution of sodium ethoxide (0.09 g. sodium). The reaction mixture became a brilliant purple colour, which gradually faded to a yellow colour after 4 days at room temperature. A yellow solid precipitated and was filtered off. Identified as 4, 4'-dinitrostilbene (0.04 g.), m.p. and mixed m.p. 298 - 302°; $\nu$ max 960, 978 cm$^{-1}$ (trans-
olefin. The reaction mixture was concentrated and extracted with chloroform. The chloroform extract was washed, dried and absorbed on basic alumina. Elution with petrol gave triphenylarsine (0.15 g.) m.p. and mixed m.p. 60°. Elution with benzene-petrol (10:90) gave p-nitrotoluene (0.35 g.), m.p. and mixed m.p. 54°. Elution with ether-petrol (25:75) gave 4,4'-dinitrodibenzyl (0.02 g.), m.p. and mixed m.p. 180°. Elution with ether gave trace quantities of 4, 4'-dinitrostilbene. Elution with methanol-ether gave triphenylarsine oxide (0.5 g.) m.p. and mixed m.p. 189°.

**Attempted Reaction of p-Nitrobenzylidenetriphenylarsorane with p-Methoxybenzalaniline in Dimethylformamide.**

A solution of sodium ethoxide (0.09 g. sodium) in ethanol was heated under vacuum at 180° for 2 hours. After cooling, dimethylformamide (50 ml.) was introduced under nitrogen. To the dispersion was added a mixture of p-nitrobenzyltriphenylarsonium bromide (2 g.) and p-methoxybenzalaniline (0.8 g.). The reaction mixture remained a purple colour at room temperature, so it was heated at 70° for 12 hours. The mixture became a dark brown colour. The usual work up, however, failed to yield any 4-methoxy-4'-nitrostilbene or aziridine. Mostly unidentified tarry products were obtained together with triphenylarsine and unchanged Schiff's base.
Attempted Reaction of p-Nitrobenzylidenetriphenylarsorane with p-Methoxybenzalaniline in Ether.

p-Nitrobenzyltriphenylarsonium bromide (5 g.) was dispersed in ether and butyl-lithium (7.2 ml. of 1.3 M) was slowly added. The p-methoxybenzalaniline (1.9 g.) was introduced after 1 hour. No apparent change occurred at room temperature, so the reaction mixture was refluxed for 16 hours when the red colour disappeared. This mixture was poured into water, producing a brilliant purple colour, which only slowly disappeared. The chloroform extract was washed, dried and concentrated giving, on addition of ethyl acetate, unchanged arsonium salt (1.25 g.). Absorption chromatography yielded only triphenylarsine (1.5 g.) and unreacted Schiff's base (1.0 g.).
CHAPTER III.

The Preparation of Arsonium Ylids.

Preparation of 2-Ketoalkylidenearsoranes.

2-Ketoalkylidenearsoranes are termed 'stabilised ylids'. This implies only that they can be isolated, purified, stored in the atmosphere and used in subsequent experiments.

Horner and Oediger\(^{31}\) were the first to describe the preparation of stable arsonium ylids \(^1\). They condensed triphenylarsine dibromide with activated methylene compounds in the presence of amines.

\[ \text{R} = \text{R}^1 = \text{CN} \quad (a) \]
\[ \text{R} = \text{R}^1 = \text{SO}_2\text{C}_6\text{H}_5 \quad (b) \]
\[ \text{R} = \text{CN} \quad \text{R}^1 = \text{CO}_2\text{C}_2\text{H}_5 \quad (c) \]
\[ \text{R} = \text{NO}_2 \quad \text{R}^1 = \text{C}_6\text{H}_5 \quad (d) \]

Subsequently Nesmeyanov\(^{30}\) prepared the 2-ketoalkylidenearsoranes \(^2\), by the direct quaternisation of triphenylarsine with \(\alpha\)-brominated ketones or esters, followed by treatment of the arsonium salts with suitable bases. He concluded that the use of either sodamide in liquid ammonia or sodium methylate in methanol was necessary to remove the \(\alpha\)-proton.

\[ \text{R} = \text{R}^1 = \text{OCH}_3 \quad (a) \]
\[ \text{R} = \text{H} \quad \text{R}^1 = \text{CH}_3 \quad (b) \]
\[ \text{R} = \text{H} \quad \text{R}^1 = \text{C}_6\text{H}_5 \quad (c) \]
\[ \text{R} = \text{C}_6\text{H}_5 \quad \text{R}^1 = \text{OCH}_3 \quad (d) \]
The preparation of α-benzoylmethylenetriphenylarsorane (2c) was successfully repeated using Nesmeyanov's conditions, but only in low yield, because of the accompanying formation of triphenylarsine oxide. It was found, however, that the presence of a p-halogen substituent on the phenyl group facilitated the conversion of the arsonium salt to its ylid. Thus treatment of α-(p-bromobenzoyl)methyltriphenylarsonium bromide (3) with aqueous sodium hydroxide gave a good yield of ylid (4).

All attempts to prepare ethoxycarbonylmethylenetriphenylarsorane (5) from its salt, using sodium methylate in methanol, failed. Instead triphenylarsine oxide was isolated.

A successful method for preparing the ylid (5) was found by treating a chloroform solution of the salt with aqueous sodium hydroxide for exactly 4 minutes followed by rapid removal of excess base. Pure ylid was obtained directly, any recrystallisation caused the deterioration of the product, apparently because of the ease with which it undergoes hydrolysis.

Some of the subsequent reactions of β-ketoalkylidenearsoranes that I hoped to investigate necessitated the preparation of the unreported α-alkyl-β-ketoalkylidenearsoranes (6).
Alkyl
\((\text{C}_6\text{H}_5)_3\text{As} \overset{1}{\underset{\oplus}{\circ}} \underset{\oplus}{\circ} \circ \overset{1}{\underset{\oplus}{\circ}} \circ \text{Br}\)  
\((6)\)

(1) By Direct Quaternisation.

The first attempt to prepare these ylids was made using Nesmeyanov's method. This, however, required the quaternisation of a tertiary arsine with a secondary halide and, not surprisingly, all attempts failed, e.g. triphenylarsine failed to react with \(\alpha\)-bromopropiophenone in various solvents. In the absence of solvent, an abnormal reaction occurred giving triphenylarsine oxide hydrobromide as the major product. No trace of \(\alpha\)-benzylethyltriphenylarsonium bromide \((7)\) was detected.

\[
\begin{align*}
\text{(C}_6\text{H}_5)_3\text{As} + \text{Br-CH-CO-C}_6\text{H}_5 & \xrightarrow{\text{CH}_3^+} \ (\text{C}_6\text{H}_5)_3\text{As-CH-COC}_6\text{H}_5\text{Br} \\
\end{align*}
\]
\((7)\)

(2) By Alkylation of a \(\beta\)-Ketoalkyldenearsorane.

An alternative method was offered by the alkylation of the \(\beta\)-ketoalkyldenearsoranes \((2)\), a method successfully used for preparing \(\alpha\)-alkyl-\(\beta\)-ketoalkyldene phosphoranes \((10)\). For example Bestmann and Schulz\(^{132}\) discovered that the stable phosphorane \((8)\) could be alkylated to give a phosphonium salt \((9)\) if \(R\) had a +I effect or to give a higher alkylated ylid \((10)\) if \(R\) had a -I effect.
i.e. they proposed that the original alkylation product (9) was converted to its ylid (10), by the starting ylid (8) acting as a base. This process is called 'transylidation'.

In principle it would appear that any type of ylid of sufficient nucleophilicity should be capable of undergoing alkylation. Thus Wittig et al.\(^{4}(52)\) and Markl\(^{134}\) showed that alkyl- or arylmethylenetriphenylphosphoranes undergo alkylation in a straightforward manner. However, although Bestmann et al\(^{132}(135)\) noted that ester phosphoranes undergo C-alkylation with alkyl, allylic or benzylic halides, Ramirez and Dershowitz\(^{136}\) found that \( \alpha \)-ketomethylene ylids normally do not. For example they found that when phenacylidenedetriphenylphosphorane (11) undergoes reaction with ethyl iodide, the O-alkylated product (12) is obtained.

\[
\begin{align*}
\text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH}_2\text{CO}_2\text{Et} + \text{X} & \longrightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH} = \text{C}_6\text{H}_5 \text{X} \\
\text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH}_2\text{CO}_2\text{Et} + \text{C}_2\text{H}_5\text{I} & \longrightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH}_2\text{CO}_2\text{Et} \text{X} \\
\text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH}_2\text{CO}_2\text{Et} + \text{C}_2\text{H}_5\text{I} & \longrightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH} = \text{C}_6\text{H}_5 \text{X} \\
\text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH}_2\text{CO}_2\text{Et} + \text{C}_2\text{H}_5\text{I} & \longrightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH}_2\text{CO}_2\text{Et} \text{X} \\
\text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH}_2\text{CO}_2\text{Et} + \text{C}_2\text{H}_5\text{I} & \longrightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH}_2\text{CO}_2\text{Et} \text{X}
\end{align*}
\]
The explanation offered for the absence of O-alkylation with ester phosphoranes was that the ester group affords less stabilization. This is in agreement with the observations of Speziale et al\(^{(125)}\) that the ester phosphorane was more basic than the benzoyl ylid.

Although aware of the possibility of O-alkylation occurring with \(\beta\)-ketoarsoranes, the alkylation of \(p\)-bromo-phenacylidenetriphenylarsorane (4) and ethoxycarbonylmethylene-triphenylarsorane (5) with methyl iodide was attempted. Neither experiment yielded the hoped for arsonium salts (13a and b), but unexpectedly gave methyltriphenylarsonium iodide. This product is considered to have arisen from the initially formed arsonium salt (13) (the desired product) undergoing nucleophilic displacement by the iodide anion giving triphenylarsine and the \(\alpha\)-iodo compound (14). Under the reaction conditions used the triphenylarsine would quaternise with the excess methyl iodide.

\[
\begin{align*}
\text{(C}_6\text{H}_5)_2\text{As-CH-C-R} + \text{MeI} & \rightarrow (\text{C}_6\text{H}_5)_2\text{As-CH-C-R} & (13) \\
\text{(C}_6\text{H}_5)_2\text{As-Me} + \text{MeI} & \rightarrow \text{(C}_6\text{H}_5)_2\text{As-CH-C-R} & (14)
\end{align*}
\]

(a) \(R = p - \text{BrC}_6\text{H}_4\)

(b) \(R = \text{OC}_2\text{H}_5\)
Support for this idea was provided when \( p \)-bromophenacyl-triphenylarsonium iodide (3) was shown to undergo reaction with methyl iodide giving an 80% yield of methyltriphenylarsonium iodide together with triphenylarsine and decomposition products of \( p \)-bromophenacyl iodide, e.g. \( p \)-bromoacetophenone and free iodine.

\[
(C_6H_5)_3As-CH_2-C_6H_4Br(p) \rightarrow (C_6H_5)_3As + I-CH_2-C_6H_4Br(p)
\]

(3)

The concept of the decomposition of arsonium salts is not a new one and was offered, though wrongly, in 1921 as the explanation for the early failure to resolve arsonium compounds. It had also been found that heating arsonium salts could reverse the usual method of synthesis and, in fact, application of this type of reaction has been successfully applied in the synthesis of heterocyclic arsines (15).
To overcome this complication an alkylating agent was sought from which the resulting anion was not nucleophilic. Markl\(^{(134)}\) had reported alkylating benzylidene triphenylphosphorane \((16)\) with triethyloxonium tetrafluoroborate \((17)\), giving \(\alpha\)-phenylpropyltriphenylphosphonium tetrafluoroborate \((18)\) in 98\% yield.

\[
\begin{align*}
\text{reaction} & : \quad (\text{C}_6\text{H}_5)_3\text{P} = \text{CHC}_6\text{H}_5 + (\text{C}_2\text{H}_5)_3\text{OBF}_4^- \rightarrow (\text{C}_6\text{H}_5)_3\text{P} - \text{CHC}_2\text{H}_5 \text{BF}_4^- + (\text{C}_2\text{H}_5)_2\text{O} \\
\text{products} & : \quad (16) \quad (17) \quad (18)
\end{align*}
\]

Surprisingly all attempts to alkylate the ester arsonium ylid \((5)\) with triethyloxonium tetrafluoroborate failed to give the expected product \((19)\)

\[
\begin{align*}
\text{reaction} & : \quad (\text{C}_6\text{H}_5)\text{As} - \text{CH-CO}_2\text{Et} + (\text{C}_2\text{H}_5)_3\text{OBF}_4^- \rightarrow (\text{C}_6\text{H}_5)_3\text{As} - \text{CH-C}_2\text{H}_5 \text{BF}_4^- \\
\text{products} & : \quad (19)
\end{align*}
\]

The reaction at room temperature was very slow giving a high recovery of starting material. At 40\°C a reaction did occur producing a very viscous oil, the infrared of which showed the absence of a carbonyl peak. The oil solidified to a wax and the method was abandoned.

\(3\) By Acylation of Alkylarsonium Ylids.

A further method for preparing \(\alpha\)-alkyl- \(\beta\)-ketoalkylidenearsoranes \((6)\) was thought to be offered by the acylation of alkylidenearsonanes, again by analogy with phosphorus chemistry. This reaction was first discovered by Trippett\(^{(139)}\) and was
further investigated by Bestmann$^{(140)}$. He found that one equivalent of benzoyl chloride underwent reaction with two equivalents of methylenetriphenylphosphorane (20) to give one equivalent of benzoylmethylenetriphenylphosphorane (21) and one equivalent of methyltriphenylphosphonium chloride (22).

\[
\text{C}_6\text{H}_5\text{COCl} + (\text{C}_6\text{H}_5)_3\text{P}^=\text{CH}_2 \rightarrow (\text{C}_6\text{H}_5)_3\text{P}^=\text{CH}_2\text{CO} + \text{C}_6\text{H}_5\text{Cl}^-
\]

(20)

\[
(\text{C}_6\text{H}_5)_3\text{P}^=\text{CH}_2\text{CO} + (\text{C}_6\text{H}_5)_3\text{P}^=\text{CH}_2\text{Cl}^-
\]

(21) (22)

Bestmann and Arnason$^{(141)}$ and Trippett et al$^{(142)(143)}$ later provided many additional examples of the acylation of phosphoranes with acid halides.

By analogy with the previous reaction, it was hoped that $\alpha$-benzoylethylidenetriphenylarsorane (24a) would be obtained when ethylidenetriphenylarsorane (23) underwent reaction with benzoyl chloride.

\[
(\text{C}_6\text{H}_5)_3\text{As}^=\text{CH}-\text{CH}_3 + \text{R COCl} \rightarrow (\text{C}_6\text{H}_5)_3\text{As}^=\text{CH-COR} + \text{Cl}^-
\]

(23)

\[
(\text{C}_6\text{H}_5)_3\text{As}^=\text{CH-COR} + (\text{C}_6\text{H}_5)_3\text{As}^=\text{CH}_2\text{Cl}^-
\]

(24) (25)

(a) $\text{R} = \text{C}_6\text{H}_5$

(b) $\text{R} = \text{p-C1C}_6\text{H}_4$
However, all attempts to carry out this reaction failed to give the $\alpha$-methyl $\beta$-ketoalkylidenearsonane (24). Treatment of the ethyl arsonium salt (25) with butyl-lithium in ether, tetrahydrofuran or benzene followed by benzoyl chloride gave various arsines and numerous carbonyl-containing oils, some of which appeared to be arsonium salts.

The difficulty I had experienced previously when generating the $\alpha$-benzoylmethylene ylid (2c) from its salt unless there was a $\beta$-halosubstituent on the phenyl group, prompted the replacement of benzoyl chloride with $\beta$-chlorobenzoyl chloride. Again no evidence for $\alpha$-(p-chlorobenzoyl)ethylidenetriphenylarsorane (24b) was obtained.

During the course of work-up for these experiments it was noticed that 'butyl-containing' arsines and arsonium salts were complicating the already numerous reaction products. It was considered a possible explanation for the incorporation of butyl groups was, that ligand-exchange of the ethyl salt with butyl-lithium was occurring, i.e. nucleophilic attack on arsenic, to give (26).

\[
\begin{align*}
&\text{Bu}^\ominus \text{Li}^\oplus \\
&\left(\text{C}_6\text{H}_5\right)_2\text{As} - \text{C}_2\text{H}_5^- \rightarrow \left(\text{C}_6\text{H}_5\right)_2\text{As-C}_2\text{H}_5^- \\
&\left(\text{C}_6\text{H}_5\right)_2\text{Li}^- + \text{C}_6\text{H}_5^- \\
&\text{(26)}
\end{align*}
\]

To investigate this idea ethyltriphenylarsonium iodide was treated with butyl-lithium in tetrahydrofuran for four hours.
to obtain the ylid. The salt was then regenerated by the addition of acid. Should ligand-exchange have occurred the isolation of butylarsonium salts would be expected. In practice a 25% yield of starting material was recovered together with a further quantity of an impure arsionium salt. The p.m.r. of this oil indicated that its structure was closest to ethylidibutylphenylarsorium iodide (26% yield). In addition a 25% yield of triphenylarsine was recovered, together with some impure butylarsines.

To overcome this side reaction phenyl-lithium was employed since it was presumed that a less nucleophilic base would be more reluctant to undergo nucleophilic attack on the arsenic. However, treatment of the ethyl salt (25) with phenyl-lithium followed by p-chlorobenzoyl chloride failed, once more, to yield any trace of the α-methyl-β-ketoalkyldenearsorane (24b). But, in spite of the recovery of p-chlorobenzoic anhydride and acid which accounted for almost all of the p-chlorobenzoyl chloride used, a 69% yield of triphenylarsine was obtained.

Until this time it had been presumed that the formation of ethylidetriphenylarsorane (23) from its salt had occurred satisfactorily, especially as in the course of its generation the insoluble arsionium salt had dissolved giving a yellow-red colour, characteristic of the arsionium ylids previously prepared and successfully reacted.
However, the observation that a 25% recovery of triphenylarsine had been obtained in the regeneration experiment (p.129) coupled with the results of this last experiment led one to grave doubts about this assumption. It was concluded that these results could be accounted for in two ways,

(1) that the ethylidetriphenylarsorane was undergoing decomposition, or

(2) that the ethylidetriphenylarsorane had not been generated and that some alternative reaction was giving triphenylarsine.

In an effort to clarify the true situation two further experiments were carried out. The first involved treating the ethyl salt with phenyl-lithium at -30°C, followed by the addition of acid. (A homogeneous solution was obtained after two hours generation inferring that the arsonium salt had reacted). This experiment gave a 70% recovery of arsonium salt, against only 25% at room temperature, and a 13% yield of triphenylarsine (25% at room temperature). From this experiment it was concluded that if (1) was operative then decomposition of the ylid at -30°C was not a serious problem, but if (2) was operative then all this result meant was that the alternative reaction had been slowed down. The second experiment sorted this problem out. Treatment of the ethyl salt with phenyl-lithium at -30°C followed by the addition of
benzoyl chloride gave the merest indication of the expected product (ylid carbonyl 1520 cm\(^{-1}\)) together with major amounts of 'carbonyl-containing' arsionium compounds.

That benzoylation of an alkylidenearsorane was possible was established by treating benzylidene triphenylarsorane (27) with \(p\)-chlorobenzoyl chloride when the expected \(\stackrel{\text{\(\text{\(p\)-chlorobenzoyl}\)}}{\text{\(\text{\(-\_\)-}\)}}\text{-benzylidene triphenylarsorane (28) was obtained.}

\[
\begin{align*}
\text{\((C_6H_5)_3\text{As-CH-}	ext{C}_6\text{H}_5\)} & \rightarrow \text{\((C_6H_5)_3\text{As-CH-}	ext{COC}_6\text{H}_4\text{Cl(p)}\text{Cl}^\ominus\)} \\
\text{(27)} & \quad \downarrow \\
\text{\((C_6H_5)_3\text{As-CH-COC}_6\text{H}_4\text{Cl(p)}\text{Cl}^\ominus\)} & \rightarrow \text{\((C_6H_5)_3\text{As-CH-C}_6\text{H}_5\)} + \text{\((C_6H_5)_3\text{AsCH}_2\text{C}_6\text{H}_5\)}
\end{align*}
\]

These results showed that the complete lack of success to acylate ethylidene triphenylarsorane was due to unsatisfactory generation of the arsorane from its salt.

The Preparation of Alkylidenearsoranes from their Salts.

It was now apparent that a fundamental study of the experimental conditions for the preparation of an arsionium ylid from an arsionium salt was essential. A successful preparation had been accepted without question previously because the methylene and benzylidene arsionium ylids had been prepared and undergone reactions giving expected products. As events were
to show these ylids were the only ones successfully generated from their salts using organo-lithium bases.

The problem arose of how best to determine the quantity of ylid prepared, because of its rapid reaction with oxygen or water. Quenching reaction mixtures with acid at suitable intervals and measuring the quantity of arsonium salt presumed that the ylid solution did not contain dissolved unreacted arsonium salt. If it did then the amount of salt isolated would be in error and hence the yield of ylid. A better technique was offered by the reaction of the ylid with benzaldehyde followed by g.l.c. to find the yield of epoxide. It had been established previously that methyltriphenylarsonium iodide, in the presence of sodium ethoxide, underwent reaction with benzaldehyde giving a 90% yield of styrene oxide (29).

\[
\begin{align*}
\text{MeAr}^+ + \text{Ar}^- + \text{C}_6\text{H}_5\text{CHO} &\rightarrow \text{MeArCH}=\text{CH}_2 + \text{C}_6\text{H}_5\text{As}=\text{CH}_2 \\
\text{(29)}
\end{align*}
\]

It seemed reasonable, therefore, to assume that if an arsonium ylid was generated from its salt by an organo-lithium base that it would be successfully trapped by benzaldehyde.

Also it was decided to find the best reaction conditions for preparing the methylene ylid from its salt because it was known to give a good yield of styrene oxide when allowed to react with benzaldehyde. It was trusted that the same conditions could be used to prepare the ethylene ylid from its salt and hence prepare the elusive \(\gamma\)-methyl \(\beta\)-ketoarsonium ylid.
Treatment of Methyltriphenylarsonium Iodide with Butyl-Lithium.

**RUN I - in tetrahydrofuran at room temperature.**

The first trial experiments were carried out using butyl-lithium as base and tetrahydrofuran as solvent, at room temperature. Samples of the solution were taken and added to benzaldehyde, (dissolved in tetrahydrofuran). These samples were analysed for styrene oxide using gas-liquid chromatography. A summary of the results are found in Table (XVI).

<table>
<thead>
<tr>
<th>Generation Time (hrs.)</th>
<th>Yield of Styrene Oxide (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>5.2</td>
</tr>
<tr>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>1.5</td>
<td>0.12</td>
</tr>
<tr>
<td>3.0</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Since even the small yield of methylenetriphenylarsorane appeared to decompose at room temperature, the treatment was repeated at -37°C, **RUN II and RUN III, Table (XVII).**
Table (XVII).

<table>
<thead>
<tr>
<th>Generation Time (hrs.)</th>
<th>Yield of Styrene Oxide %</th>
<th>Generation Time (hrs.)</th>
<th>Yield of Styrene Oxide %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>4.3</td>
<td>4.0</td>
<td>24.2</td>
</tr>
<tr>
<td>1.58</td>
<td>8.2</td>
<td>6.0</td>
<td>13.6</td>
</tr>
<tr>
<td>3.0</td>
<td>14.7</td>
<td>8.0</td>
<td>6.8</td>
</tr>
<tr>
<td>4.0</td>
<td>22.6</td>
<td>10.0</td>
<td>trace.</td>
</tr>
</tbody>
</table>

The maximum yield of methylenetriphenylarsorane obtained using butyl-lithium in tetrahydrofuran was 24%.

Treatment of Methyltriphenylarsonium Iodide with Phenyl-Lithium.

RUN IV - in tetrahydrofuran at room temperature.

Exactly the same experimental techniques were used as for the previous runs. In this series it was particularly noticeable that the arsonium salt went into solution almost at the same rate as the addition of the base, to give a yellow-brown solution. Samples were taken over five hours and g.l.c. showed that no styrene oxide was formed. However, the quantitative recovery of benzaldehyde in all samples after the first five minutes meant that all the base had been rapidly used up, but not, apparently, to generate ylid. Many attempts were made to identify the products of this reaction but only triphenylarsine and biphenyl were isolated.
RUN V - in diethylether.

The failure to prepare the methylene ylid from its salt using phenyl-lithium in tetrahydrofuran led me to repeat Wittig's reaction conditions,\(^{13}\) i.e. using ether as solvent. When samples were taken from the reaction mixture and added to benzaldehyde in ether an immediate precipitation of a buff-coloured solid resulted. Gas chromatography of the filtrates, revealed the usage of benzaldehyde (Table (XVII)), but no trace of styrene oxide.

Table (XVIII).

<table>
<thead>
<tr>
<th>Generation Time (hrs.)</th>
<th>Consumption of Benzaldehyde (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>100</td>
</tr>
<tr>
<td>1.0</td>
<td>75</td>
</tr>
<tr>
<td>3.0</td>
<td>59.5</td>
</tr>
<tr>
<td>5.0</td>
<td>50</td>
</tr>
</tbody>
</table>

This suggested that the solid was probably a 'lithio-betaine' complex (29).

\[
\left[ \left( C_6H_5 \right)_3 As - CH_2 - CH - O \right]^\ominus \cdot LiI
\]

(29)

Confirmation of this was inferred when refluxing the solid in tetrahydrofuran produced styrene oxide and benzaldehyde in solution.
The methylene ylid was prepared again (Run Vb), using identical reaction conditions but allowing one hour reaction time. The ylid solution was divided into two parts, the first part was trapped by benzaldehyde in ether, the second by benzaldehyde in tetrahydrofuran, and they were both subsequently analysed for styrene oxide. It was considered that betaine formation in tetrahydrofuran might be inferior to betaine formation in ether since it was already established that ylid formation was effected by tetrahydrofuran (Run IV and V). This was found to be so. Betaine formation in tetrahydrofuran gave styrene oxide corresponding to an ylid yield of \(25\%\), whilst betaine formation in ether gave styrene oxide and benzaldehyde (by the reverse reaction) corresponding to an ylid yield of \(60\%\). Since the source of the ylid was identical tetrahydrofuran must affect either the ylid itself or the formation of betaine.

It was concluded that the use of tetrahydrofuran as solvent in the preparation and reaction of alkylidenearsonanes should be avoided.

_Treatment of Methyltriphenylarsyonium Iodide with Phenyl-Sodium - RUN VI._

The isolation of a 'lithio-betaine' complex, which could not be decomposed in refluxing ether led to the conclusion that a lithio-oxygen bond of considerable covalent character must
have been formed. This bond would presumably break down in tetrahydrofuran (because it is a better solvating agent than ether) leaving the betaine free to eliminate.

\[
\begin{align*}
\text{ether} & \quad \text{tetrahydrofuran} \\
(C_6H_5)_2\text{As-CH}_2 X \overset{\delta+\delta-}{\leftrightarrow} (C_6H_5)_2\text{As-CH}_2 X \overset{\delta+\delta-}{\leftrightarrow} \text{Li-O-CH-C}_6H_5 & \quad \text{Li-O-CH-C}_6H_5
\end{align*}
\]

A similar situation is perhaps demonstrated by the equilibrium which is set up by the cyclopropylanion (30) and its isomeric allylanion (31) (144).

\[
\begin{align*}
(C_6H_5)_2\text{CH-CH}_2 & \overset{\delta+\delta-}{\leftrightarrow} (C_6H_5)_2\text{CH-CH}_2\text{CH}_2\text{Li}
\end{align*}
\]

(30) tetrahydrofuran (31) ether.

In ether the equilibrium lies entirely to the right (31), in tetrahydrofuran entirely to the left. For the structure (30) to be stable the (C-Li) bond must be mainly ionic because stabilisation of the carbanion is presumably afforded by delocalisation through the phenyl groups, which offsets the strain of the cyclopropyl ring. In ether the lithium would form a bond with considerable covalent character, whereas in tetrahydrofuran the lithium would be expected to form an ionic bond, because this solvent is better at solvating Li\(^+\) than diethyl ether. Hence the equilibrium is where one would predict.

To overcome the practical difficulties of isolating and
transferring a 'lithio-betaine', it was decided to use phenyl-sodium as the base. The larger sodium atom would be expected to form an ionic bond even in diethyl ether, so that elimination of the betaine should occur directly in this solvent. This proved to be so. Generation of the methylene ylid with phenyl-sodium as base followed by addition to benzaldehyde gave styrene oxide in solution. However lower yields of ylid were usually obtained than when using phenyl-lithium as base. To ensure that this reduction in yield was not simply the inefficiency of the sodium-phenyl preparation, (it was necessary to prepare this base 'in situ'), several experiments were carried out using different molar ratios of base to one mole of arsonium salt. The highest yield of ylid (47%) was obtained using 1.5 mole of base/1.0 mole of arsonium salt. However when two moles of sodium-phenyl/one mole of salt was used, no styrene oxide could be detected. It was concluded that this method for the preparation of arsonium ylids was inferior to the previous method. (Run V).

Treatment of Methyltriphenylarsionium Iodide with t-Butyl-Lithium - Run VII.

The last base that was used was t-butyl-lithium, a very powerful base. The generation of the ylid was carried out using benzene as solvent because t-butyl-lithium attacks diethyl ether at room temperature giving ethylene and ethoxide.
Unfortunately the arsonium salt has a low solubility in benzene and the reaction was an extremely slow one. After six hours only 25% had undergone reaction to give an orange solution. Treatment of the solution with benzaldehyde gave only a 3% yield of styrene oxide, after one hour generation time reducing to 0.5% after three hours generation time. This method was abandoned.

Treatment of Ethyltriphenylarsonium Iodide with Phenyl-Lithium – Run VIII.

The best method found for generating methylenetriphenylarsorane from its salt was by using phenyl-lithium as the base, ether as the solvent and allowing 0.5 - 1 hour reaction time at room temperature.

Employing exactly these experimental conditions, the preparation of ethylidenetriphenylarsorane, from its salt, was attempted. The ylid solutions were again treated with benzaldehyde and analysed, this time, for α-phenyl-propylene oxide (32).

\[
\begin{align*}
\text{(C}_6\text{H}_5)_3\text{As-CH-CH}_3 & \rightarrow [\text{(C}_6\text{H}_5)_3\text{As-CH-CH}_3]_\Theta \rightarrow \text{(C}_6\text{H}_5)_3\text{As-C}_6\text{H}_5-\text{CH-CH-CH}_3 \\
\end{align*}
\]

A summary of the results is shown in Table (XIX).
Table (XIX).

RUN VIII

<table>
<thead>
<tr>
<th>Generation Time (hrs.)</th>
<th>Consumption of Benzaldehyde. %</th>
<th>Yield of α -phenyl-propylene Oxide. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>1.0</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>3.0</td>
<td>35</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

These results showed that all the phenyl-lithium had been consumed after five hours generation time (because no reaction occurred with the benzaldehyde) and that only minimal quantities of α -phenyl-propylene oxide had been formed. Once more the preparation of ethylidenetriphenylarsorane had failed. The experiment was repeated and analysis for benzene gave a theoretical quantity, and proved that phenyl-lithium had all been consumed. This meant that phenyl-lithium must be undergoing reaction with the ethylarsonium salt and all the possibilities considered are shown in the following diagram.
Gas liquid chromatography of the reaction mixture showed the absence of ethylbenzene (34) and thereby eliminated nucleophilic displacement reactions at the α-carbon atom. In order to search for butene (38), from rapid ylid decomposition, or ethylene (33), from a Hofmann-type elimination, the ethyl salt was treated with phenyl-lithium in a sealed vessel and analysed by gas liquid chromatography at room temperature. A peak with a retention time identical to that of butene was observed, but no ethylene was detected. Because of the uncertainty associated with this particular analysis, an attempt was made to trap the volatile products with bromine in carbon tetrachloride (connected to the exit nitrogen line). However, gas liquid chromatography of the carbon tetrachloride showed many products and one of the peaks could have been 2, 3-dibromobutane. The practical difficulty appeared to be that the diethyl ether (carried over
with the nitrogen) was being attacked by the bromine giving high yields of lachrymatory liquids which were swamping the wanted products. No conclusions were drawn, therefore, from this experiment.

The Preparation of n-Hexyl and n-Heptylarsonium Salts.

In order to obtain further knowledge about the probable reactions which occur when arsonium salts are treated with organo-lithium bases it seemed pertinent to prepare an arsonium salt containing a long alkyl chain. In this way the fragments of ylid decomposition or \( \beta \) -'Hofmann-type' elimination would be more readily identified. To this aim the preparation of the unknown n-hexyltriphenylarsonium salt was attempted.

Initially the direct quaternisation of triphenylarsine with n-hexyl bromide and iodide was attempted both with and without solvent and under pressure. All attempts failed to yield any arsonium salt.

The second method tried was the treatment of triphenylarsine with n-hexyl iodide in the presence of silver tetrafluoroborate. Franzen et al\(^{(145)}\) and Johnson et al\(^{(146)}\) discovered that phenylsulphide \(^{(39)}\) (for which normal alkylation procedures are useless) could be alkylated in good yield by treating it with a mixture of alkyl bromide and silver tetrafluoroborate. It is thought that this reagent facilitates the ionisation of the carbon-halogen bond.
Using Franzen's reaction conditions triphenylarsine was dissolved in n-hexyl iodide and silver tetrafluoroborate was cautiously introduced. The buff-coloured product was shown to be an arsonium tetrafluoroborate by its infrared spectrum. However its proton magnetic resonance spectrum showed the complete absence of a n-hexyl group. The elemental analysis gave C 60.73; H 4.34; As 23.29; F 10.43%. These figures indicated that the solid contained two arsenic atoms to one tetrafluoroborate anion (Atomic Weight As = 74.91, Atomic Weight F 19.00) and fitted closest to the empirical formula $2(C_6H_5)_2As\cdot HBF_4$. Refluxing the solid in sodium hydroxide did indeed give triphenylarsine, together with unreacted starting material and a brown tar. Further identification was not attempted.

The third approach for the preparation of a long-chain alkyl arsonium salt was offered by alkylation of a simple ylid by a straightforward nucleophilic displacement reaction. For example, the reaction of n-hexyl bromide with methylenetriphenylarsorane should give n-heptyltriphenylarsonium bromide (40).
The methylene ylid was prepared using the reaction conditions previously described and then treated with n-hexyl bromide. The product from this reaction was indeed the n-heptylarsonium salt, but unfortunately it was contaminated with methylarsonium salt. No technique was found which avoided this impurity, even though extreme care was exercised to exclude moisture and the ylid solution was filtered from starting materials. After much experimenting it was found that 90\% pure n-heptyl salt could be obtained from its solution in a chloroform and ethyl acetate mixture, from which methyltriphenylarsonium iodide was observed to crystallise out. The infrared spectrum of this salt showed the characteristic arsonium peaks at 1030 and 1005 cm\(^{-1}\). Its proton magnetic resonance spectrum showed a complex multiplet \(\gamma 7.8 - 9.5\), containing three major peaks at \(\gamma 8.4, 8.8\) and \(9.2\), which was the n-hexyl group, a multiplet \(\gamma 6.0 - 6.5\) which was attributed to the methylene group next to the positively charged arsenic atom, and a multiplet \(\gamma 2.0 - 2.65\) accounting for the aromatic protons.

The overall yield of this salt was 50\%. To try to improve this the use of the more reactive n-hexyl iodide was investigated. However this reaction did not give an n-heptylarsonium salt at all. The product obtained was an arsonium salt but its proton magnetic resonance spectrum showed that it did not contain the heptyl group. It was not identified.
Reaction of n-Heptyltriphenylarsonium Iodide with Phenyl-Lithium

The probable sites of attack of the phenyl-lithium on the n-heptylarsonium salt and the resulting products are shown in the diagram (41).

**DIAGRAM (41).**

\[
\begin{align*}
(C_6H_5)_3As + CH_2=CH-(CH_2)_4-CH_3 &+ C_6H_6 \\
\text{(a) attack at } &
\end{align*}
\]

\[
\begin{align*}
(C_6H_5)_3As \oplus & CH \quad CH \quad \text{(CH}_2\text{)}_4 \quad \text{CH}_3 \\
\text{(b) attack at } &
\end{align*}
\]

\[
\begin{align*}
\left[(C_6H_5)_4As(CH_2)_6CH_3\right] &\text{ decomp.} \\
\text{(c) attack at } &
\end{align*}
\]

\[
\begin{align*}
[C_6H_5)_3As \oplus \ominus - CH-(CH_2)_5-CH_2] &\text{ decomp.} \\
\text{(d) attack at } &
\end{align*}
\]

\[
\begin{align*}
C_6H_5-C_6H_5 &+ \left[(C_6H_5)_2As(CH_2)_6CH_3\right] \\
\text{(e) decomp.} &
\end{align*}
\]

\[
\begin{align*}
(C_6H_5)_3As + CH_3(CH_2)_5-CH=CH-(CH_2)_5CH_3 &\text{ decomp.} \\
\text{(f) decomp.} &
\end{align*}
\]

After treating the n-heptylarsonium salt with phenyl-lithium for seven days, the reaction mixture was subjected to gas chromatography. 1-Heptene (42) was positively identified in 35% yield. In other words at least 35% of the phenyl-lithium had attacked the \(\beta\)-hydrogen (path (a)) and a Hofmann elimination occurred.
Such eliminations have been known for a long time for sulphonium salts and recent work has shown that they proceed normally via an E-2 trans-elimination\(^5\). If the geometry of the salt is such as to prevent a trans-elimination and if the molecular structure is such as to provide no special stabilisation for a \(\sigma\)-carbanion (E-1\(_B\) route) and the base is strong enough, sulphonium ylids will undergo cis-elimination via an ylid intermediate.\(^{147}\) \(^{148}\)

Analysis of the n-heptyl reaction mixture at a higher temperature (210\(^\circ\)) revealed two further products. Both tetradec-7-ene (47) and heptylbenzene (48) were expected to chromatograph at this temperature, but since I had no authentic samples with which to compare the retention time, it was hoped to isolate these substances by column chromatography. These hopes were not justified.

Column chromatography gave a 26% yield of biphenyl (after correction for the biphenyl impurity present in the phenyl-lithium). This is considered to have arisen by the nucleophilic attack of the phenyl-lithium on the arsenic atom (path b) giving the pentacovalent intermediate, heptyltetraphenylarsorane (43).
This could then decompose by path (e) to give biphenyl (44) and heptyldiphenylarsine (45).

\begin{align*}
\text{C}_6\text{H}_5 & \rightarrow \text{CH}_3(\text{CH}_2)_6\text{As} & \rightarrow \text{CH}_3(\text{CH}_2)_6\text{As} + \text{C}_6\text{H}_5 - \text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5 & \rightarrow \text{C}_6\text{H}_5 & \rightarrow \text{C}_6\text{H}_5
\end{align*}

This mode of attack is quite reasonable since Wittig prepared pentaphenylarsorane (49) by the analogous reaction of treating tetraphenylarsonium chloride with phenyl-lithium for 3 days. This arsorane was a stable compound at room temperature but on heating it decomposed to biphenyl and triphenylarsine.

\[ (\text{C}_6\text{H}_4)_4\text{As} + \text{C}_6\text{H}_5\text{Li} \rightarrow (\text{C}_6\text{H}_5)_5\text{As} + \text{LiCl} \]

The only other products isolated from this experiment were triphenylarsine (45\% yield) and probably impure heptyldiphenylarsine (10\% yield). Unfortunately the higher boiling product was not eluted from the column.

In conclusion it was demonstrated that the reaction of an organo-lithium base with an arsonium salt is very complicated. At least two modes of attack were observed other than ylid formation, i.e. nucleophilic attack on the arsenic and attack at a \( \beta \) hydrogen giving a Hofmann-type elimination.
The Investigation of Other Methods of Preparation of Methylenetriphenylarsorane.

(1) Via a Pentacovalent Intermediate.

The mode of formation of methylenetriphenylarsorane from methyltriphenylarsonium iodide has been explained so far as the removal of the \( \alpha \)-proton by the phenyl anion.

\[
\begin{align*}
(C_6H_5)_3As-CH_2 + C_6H_5^- & \rightarrow (C_6H_5)_2As-CH + C_6H_5H \\
C_6H_5^- & \rightarrow C_6H_5H
\end{align*}
\]

However, an alternative route could equally be suggested proceeding through the five-covalent intermediate (50), which decomposes to the methylene ylid with corresponding loss of benzene.

\[
\begin{align*}
C_6H_5^-As-C_6H_5 + C_6H_5Li & \rightarrow C_6H_5^-As-C_6H_5H \\
C_6H_5^-As-C_6H_5H & \rightarrow (C_6H_5)_2As-CH_2 + C_6H_5H
\end{align*}
\]

(50)

Such a mode of formation has been shown by Seyferth\(^{149}\) to be involved in the preparation of methylenetriphenylphosphorane. He found that treatment of methyltriphenylphosphonium bromide with methyl-lithium gave in addition to the expected methane a 26% yield of benzene. A more striking example demonstrated by Seyferth was when he treated tetraphenylphosphonium bromide (51) with methyl-lithium, which, on the addition of cyclohexanone,
gave methylenecyclohexane (52) in 58% yield. In this case ligand-exchange followed by ylid formation must have taken place since the original phosphonium salt had no η-hydrogen and was incapable of forming an ylid directly.

\[
(C_6H_5)_4P\overset{\Theta}{\rightarrow} Br \overset{CH_3Li}{\rightarrow} [(C_6H_5)_4PCH_3] \overset{C_6H_5H}{\rightarrow} (C_6H_5)_3P=CH_2
\]

(51)

\[
(C_6H_5)_3P = 0 + \bigcirc \quad \text{CH}_2
\]

(52)

If this last type of reaction occurred readily for the corresponding tetraarylarsonium salt then such a mode of formation for arsonium ylids would overcome the disadvantages found when treating an alkylarylarsonium salt with a base.

\[
(C_6H_5)_4As\overset{\Theta}{\rightarrow} Cl \overset{CH_3Li}{\rightarrow} [(C_6H_5)_4AsCH_2] \overset{C_6H_6}{\rightarrow} (C_6H_5)_3As = CH_2
\]

(53)

However no reaction took place at all when tetraphenylarsonium chloride was stirred with methyl-lithium in refluxing ether. Seyferth\(^{149}\) had used a tetrahydrofuran-ether mixture (5:1) as solvent for his experiments, which I had initially avoided because of the previous difficulties encountered with tetrahydrofuran. However when this solvent was used for the arsenic reaction a theoretical yield of benzene was detectable after 5 hours, but no ylid was trapped by benzaldehyde. It was
presumed that an insufficient concentration of ylid had been built up to allow its detection. [This would necessitate that the rate of formation of the ylid from the pentacovalent intermediate was slower than the rate at which it decomposed.] Even more disturbing was that the reaction mixture was still heterogeneous. Later the solid was identified as tetraphenyl arsonium iodide, anion exchange having taken place to give the more insoluble salt. The recovery of a 56% yield of arsonium salt meant that more benzene had been formed than could be accounted for simply by the decomposition of the pentacovalent intermediate (53) to give the methylene ylid (2.4 mol. benzene/1 mol. arsonium salt).

The only explanation for the excess benzene that seemed reasonable was that triphenylarsine, a decomposition product, was undergoing reaction with the methyl-lithium, giving methylarsines (54).

\[
\begin{align*}
(C_6H_5)_3As + CH_3Li & \rightarrow (C_6H_5)_2AsCH_3 + C_6H_5Li \\
(C_6H_5)_2AsCH_3 + CH_3Li & \rightarrow C_6H_5As(CH_3)_2 + C_6H_5Li \\
(CH_3)_2C & \rightarrow CH_3 \\
C_6H_5As + C_6H_5Li & \rightarrow C_6H_5As-CH_2Li + C_6H_5H
\end{align*}
\]

This idea was investigated and reaction did take place between methyl-lithium and triphenylarsine to give benzene. When one equivalent of triphenylarsine was treated with three equivalents of methyl-lithium, followed by the addition of methyl iodide a 60% yield of trimethylphenylarsonium iodide was isolated (with
1.55 mol. benzene/1 mol. of arsine formed).

Exploitation of this reaction, by treating triphenylarsine and methyl-lithium in equivalent amounts followed by methyl iodide failed to give a good yield of dimethylphenylarsonium iodide but instead gave a mixture of the monomethyl, dimethyl and trimethyl-arsonium salts.

The attempted reaction of triphenylphosphine with methyl-lithium failed to give any benzene!

(2) Attempted Preparation of Methylenetriphenylarsorane using a Phosphorane.

This idea was based on the process of 'transylidation'. It was wondered what reaction would occur, if any, when an arsonium salt was introduced into a solution of a phosphorane. Presumably the following equilibrium would be set up when methyltriphenylarsonium iodide was added to a solution of methylenetriphenylphosphorane.

\[
(C_6H_5)_3P-CH_2 + (C_6H_5)_3As-CH_3 \rightleftharpoons (C_6H_5)_3As-CH_2 + (C_6H_5)_3P-CH_2 I
\]

The equilibrium products could be readily identified by subsequent reaction with benzaldehyde, when the phosphorane would give styrene and the arsorane would give styrene oxide.

When methyltriphenylarsonium iodide was added to methylenetriphenylphosphorane followed by subsequent reaction with benzaldehyde a 75% yield of styrene was obtained and no trace of styrene oxide was observed.
To encourage the equilibrium over to the right the more reactive dimethylphenylmethylenephosphorane was used. It was hoped that the +I effect of the methyl groups would increase the polarity of the phosphorus-carbon ylid bond and hence increase its basicity, since it was the relative basicity of the phosphorane and arsorane which would decide the final equilibrium. However, again no styrene oxide was detected in the final reaction mixture.

One of the practical difficulties associated with this idea was the insolubility of the arsonium salt in the phosphorane solution. It was expected, though, that the arsonium salt would be sufficiently soluble to set up an equilibrium. Reverse addition, however, showed that the observed experimental results were not the true equilibrium values because by adding trimethylphenylphosphonium iodide to methylenetriphenylarsorane in solution, a 50% yield of styrene oxide was obtained together with only a 5% yield of styrene.

It was concluded that different experimental conditions were needed to test the effectiveness of this idea to ensure that the rate at which equilibrium is established is faster than the rate at which arsonium ylids decompose.
Experimental.

All experiments were carried out under oxygen-free nitrogen. All solvents were carefully dried and distilled before use. Petrol refers to the fraction b.p 40-60° unless otherwise stated. Melting points were corrected. Proton magnetic resonance spectra were run in CDCl₃ unless otherwise stated.

Preparation of Phenacyltriphenylarsonium Bromide.

Triphenylarsine (6 g.) and phenacyl bromide (4 g.) were dissolved in benzene and refluxed for 8 hours. On cooling the arsonium salt separated out (8 g.), m.p. (chloroform-ethyl acetate) 176°, Lit.²¹ 178°; p.m.r. singlet (2 H) 5.5 (-CH₂ next to As⁺), multiplets (20 H) 1.4 - 1.85 and 2.0 - 2.65 (aromatic protons).

N.B. If the reaction is attempted without solvent, an abnormal reaction occurs yielding the hydrobromide of triphenylarsine oxide.

Preparation of Phenacylidenetriphenylarsorane.

Phenacyltriph enylarsonium bromide (6 g.) was dissolved in methanol and excess aqueous sodium hydroxide (20 mls. of 2 N) was added with cooling. The mixture was extracted with chloroform and the extract, after washing free of base, was dried and evaporated to give the arsorane (1.5 g.), 29.6% yield, m.p. (ethyl acetate-petrol) 158°, Lit.²⁰ 156°.
Only poor yields were obtained, but use of the stronger base, sodium ethoxide in ethanol resulted in even lower yields, because triphenylarsine oxide was also formed.

**Preparation of p-Bromophenacyltriphosphorylarsenium Bromide.**

Triphenylarsine (6 g.) and p-bromophenacyl bromide (6 g.) were dissolved in benzene and refluxed for 16 hours. The arsonium salt crystallised out (8.5 g.) m.p. (chloroform-ethyl acetate) 174° (Lit. 170 - 171°), p.m.r. singlet (2 H) 3.6, multiplets (19 H) 1.6 - 1.9 and 2.0 - 2.6.

**Preparation of p-Bromophenacylidene-triphosphorylarsorane.**

p-Bromophenacyltriphosphorylarsenium bromide (4 g.) was dissolved in chloroform. This was shaken for exactly 4 minutes with excess sodium hydroxide (20 mls. of 2 N). The chloroform extract was separated and rapidly washed free of base. After drying and concentrating, solid arsorane was obtained (2.8 g. = 81% yield), m.p. (ethyl acetate-petrol) 141 - 142°. Found C 61.92%; H 3.95%, calculated for C_{26}H_{20}AsBrO 062.06; H 3.95%; \nu max 1570 m (aromatic double bond), 1510 s (ylid carbonyl), 1085 w, 1080 m, 1070 m, 1200 w, 1005 m, (complex pattern observed for arsonium ylids), 840 m, 825 w, 770 w, 740 s, 685 s cm^{-1} (aromatic substitution patterns), p.m.r. a broad hump (1 H) 5.85 - 6.15 (maybe the ylid proton), multiplet (19 H) 2.1 - 2.9.
Attempted Quaternisation of Triphenylarsine with α-Bromopropiophenone.

Triphenylarsine (6 g.) and α-bromopropiophenone (4.2 g.) were dissolved in benzene and refluxed for 7 days. No arsonium salt was detected and triphenylarsine was recovered.

Refluxing triphenylarsine with α-bromopropiophenone gave triphenylarsine oxide, hydrobromide (1.5 g.) m.p. 165°. This was confirmed by preparing the hydrobromide by treating triphenylarsine oxide with concentrated hydrobromic acid. A highly crystalline solid was obtained, identical with the other product.

Reaction of p-Bromophenacylidenetriphenylarsorane with Methyl Iodide.

The arsorane (1.0 g.) was partially dissolved in ethyl acetate and to this was added a slight excess of methyl iodide (0.3 g.). The solution was refluxed for 1 hour, during which the colour of the solution changed from yellow to dark red. On cooling a solid separated, which was filtered off. Recrystallised from chloroform-ethyl acetate, m.p. 172°. From its analysis the compound was thought to be methyltriphenylarsonium iodide (0.3 g.). Found C 51.2; H 4.02%, calculated for C_{19}H_{18}As I; C 50.8; H 4.02%. This was found to be so, after further recrystallisations the melting point was raised to 176°, p.m.r. singlet (3 H) δ 6.85 (methyl), multiplet (15 H)
γ 2.0 - 2.5 (aromatic protons). No trace of ♣(p-bromobenzoyl) ethylenetriphenylarsorane was detected.

Preparation of Ethoxycarbonylmethyltriphenylarsonium Bromide.

Ethoxycarbonylmethyltriphenylarsonium bromide (5.0 g.) was dissolved in chloroform and shaken with excess sodium hydroxide (20 ml. of 2 N) for 4 minutes, with cooling. The chloroform extract was immediately washed free of base and dried. Evaporation to dryness gave a sweet-smelling oil, which initially dissolved in ether, but rapidly crystallised out (2.8 g.), m.p. 110° (attempted recrystallisation of this product gave less pure product because triphenylarsine oxide formed and could not be separated), Vmax. 1620 s (ylid ester-carbonyl), 1440 s (phenyl-arsenic bond), 1400 w, 1380 m, 1330 s, 1270 w, 1190 w, 1110 s, 1090 s, 1060 s, 1030 w, 1000 m (the last five form the familiar complex pattern associated with an arsonium ylid), 890 - 870 w (broad peak), 740 s, 690 s cm⁻¹ (mono-substituted aromatics), p.m.r. (CDCl₃) complex multiplet (3 H)γ 8.6 - 9.15 (methyl group), complex multiplet (2 H)γ 5.65 - 6.2 (methylene group), complex multiplet (15 H)γ 2.15 - 2.75, the 'ylid-proton' was not detected. Found C 66.80; H 5.40%, calculated for C₂₂H₂₁AsO₂ C 67.36; H 5.35%.

Reaction of Ethoxycarbonylmethyltriphenylarsorane with Methyl Iodide.

The arsorane (2.0 g.) was added to excess methyl iodide in
ethyl acetate. An immediate reaction occurred, resulting in the precipitation of a solid. This was filtered off and found to be identical with the product from the reaction of p-bromophenacyltriphenylarsorane and methyl iodide. It was identified as methyltriphenylarsonium iodide (1.3 g.), mixed m.p. 176°. The mother liquor was evaporated and its infrared spectrum showed a carbonyl at 1740 cm⁻¹, together with the characteristic peaks for an arsine.

**Reaction of p-Bromophenacyltriphenylarsonium Bromide with Methyl Iodide.**

The arsonium salt (3.0 g.) and methyl iodide (5 ml.) were dissolved in tetrahydrofuran and refluxed overnight. The solid was filtered off (1.5 g.) and was shown to be methyltriphenylarsonium iodide mixed m.p. 176°. Addition of ether led to the precipitation of a brown, crystalline solid (0.2 g.), m.p. 188°, \( V_{\text{max}} \) 1660 s, 1590 s, 1200 m, 1070 m, 1030 w, 1010 m, 970 w, 850 s, 750 s, 685 m cm⁻¹, p.m.r. showed only aromatic protons. This solid was unidentified. The infrared spectrum of the reaction mixture, after removal of solvent, showed a carbonyl at 1680 cm⁻¹ which may have been due to p-bromophenacyl iodide. The chloroform extract of this liquor was washed, dried and absorbed on neutral alumina. Elution with petrol gave a solid (0.4 g.) m.p. 47 - 48°. This was identified as p-bromoacetophenone, Lit. (150) m.p. 50°, p.m.r.
singlet (3 H) γ 7.45 (methyl protons), multiplet (4 H) γ 2.1 – 2.6 (aromatic protons).

Elution with chloroform-ether (50 : 50) gave methyltriphenylarsonium iodide (0.4 g.), total yield 81.4%.

Preparation of Triethylxonium Tetrafluoroborate.

Epichlorohydrin (14 g.) was added to boron trifluoride-etherate (19 g.) in ether (50 c.c.) at such a rate as maintained refluxing. An oil separated out initially, which after stirring for a further 2 hours, crystallised. These crystals were washed with ether and used immediately.

Reaction of Ethoxycarbonyltriphenylarsorane with Triethylxonium Tetrafluoroborate.

The arsorane (2.0 g.) was dissolved in tetrahydrofuran to which was added the triethylxonium tetrafluoroborate (1.0 g.) After stirring for 2 hours a white solid separated. This was filtered off (0.2 g.), m.p. 142°, $V_{\text{max}}$ 1740 s (ester carbonyl) broad band 1100 s – 1010 s (tetrafluoroborate), 1005 s (arsonium salt), 750, 740, 685 cm$^{-1}$ (aromatics). However treatment of ethoxycarbonylmethyltriphenylarsonium bromide with sodium tetrafluoroborate gave the same compound. Thus the product was ethoxycarbonylmethyltriphenylarsonium tetrafluoroborate. The infrared spectrum of the mother liquor, after removal of the solvent, showed the presence of unreacted arsorane (1640 cm$^{-1}$ carbonyl).
The experiment was repeated, but this time the reaction mixture was refluxed for 8 hours. Again a small yield of the same arsonium salt separated out. This was filtered off. The reaction mixture was concentrated and extracted with chloroform and water. The chloroform extract was dried, evaporated to remove the solvent, and the infrared spectrum was taken, $\nu_{\text{max}}$ 1720 w, 1440 m, 1300 w, 1240 w, 1210 w, broad 1110 - 1030 s, 1005 m, 850 w, 750 s, 685 m cm$^{-1}$. This showed that the expected product had not been formed and when the oil solidified to a wax, the experiment was abandoned.

**Reaction of Ethyltriphenylarsonium Iodide with Butyl-Lithium and Benzoyl Chloride.**

Ethyltriphenylarsonium iodide (10 g.) was dispersed in tetrahydrofuran (70 ml.) and stirred with butyl-lithium (21 mls. of 1.0 M) for 3 hours. Benzoyl chloride (1.5 g.) was added until the red colour was just discharged. The mixture was stirred overnight at room temperature and then concentrated. The remaining liquor was extracted with chloroform and water, the chloroform extract was dried and concentrated. On the addition of ethyl acetate a solid separated, but attempts to filter it off caused the solid to become an oil (3.0 g.), $\nu_{\text{max}}$ 1740 s, (ester carbonyl) 1600m, 1590 m, 1440 s (phenyl-arsonic) 1240 s, 1080 s, 1040 s, 1020 s (complex arsenic stretchings), 850 w, 740 s, 690 s cm$^{-1}$ (mono-substituted
aromatics). The oil remained unidentified, giving a very complex p.m.r., multiplet (15) \( \gamma 8.0 - 9.2 \), multiplet (4) \( \gamma 6.5 - 7.6 \) and multiplet (11) \( \gamma 2.0 - 3.0 \). The only conclusion drawn from this information was that a butyl group appeared to have become incorporated in the product.

The mother liquor was absorbed on neutral alumina and elution with petrol gave triphenylarsine (2.0 g.), mixed m.p. 60°. Elution with petrol-ether gave numerous oils, all of which were sweet-smelling and had carbonyl peaks varying from 1650 - 1750 cm\(^{-1}\).

The experiment was repeated using benzene and ether as solvents. Similar products resulted, but no trace of a compound with a carbonyl peak at 1510 cm\(^{-1}\) was observed.

**Reaction of Ethyltriphenylarsonium Iodide with Butyl-Lithium and p-Chlorobenzoyl Chloride.**

Ethyltriphenylarsonium iodide (10 g.) was stirred with butyl-lithium (21 ml. of 1 M.) in tetrahydrofuran (50 ml.) for 6 hours. p-Chlorobenzoyl chloride (1.9 g.) was added until the red colour was just dispelled. The solution was stirred at room temperature overnight and then concentrated. The concentrate was extracted with chloroform and the chloroform extract was washed, dried and evaporated under vacuum. The infrared spectrum of the total reaction mixture showed carbonyl peaks at 1680 m, 1730 s, 1760 s cm\(^{-1}\), but there was no peak at 1500 - 1520 cm\(^{-1}\), the expected position of an ylid carbonyl.
Chromatography from neutral alumina gave triphenylarsine (2.8 g.), mixed m.p. 60°. Elution with petrol-ether (90 : 10) gave a yellow oil (1.5 g.), \( \nu_{\text{max}} \) 1730 (carbonyl), 1600 m, 1440 s (phenyl-arsenic) 1280 s, 1170 w, \( \alpha \)-complex band-1120 s 1110 s and 1090 s, 1030 w, 1020 m, 1000 m, 850 m, 760 s, 735 s, 695 s cm\(^{-1}\) (aromatic substitution patterns); p.m.r. complex multiplet (9 H) \( \gamma \) 8.0 - 9.35, multiplet (1 H) \( \gamma \) 5.5 - 5.9, multiplet \( \gamma \) 1.95 - 2.2 and \( \gamma \) 2.5 - 3.0. This oil was not identified. It may have been a 'benzoyl-arsine' containing a butyl group, since addition of methyl iodide resulted in a reaction taking place and a new methyl peak appeared in the p.m.r. at \( \gamma \) 6.15.

Elution with ether-ethyl acetate (50 : 50) gave an unknown arsonium salt (3.0 g.), which failed to crystallise, \( \nu_{\text{max}} \) 1760 s, 1600 s, 1440 s, 1240 s, 1090 s, 1010 m, 995 m, 750 s, 685 m. Its p.m.r. was again very complex containing butyl-groups, multiplet (7) \( \gamma \) 7.85 - 9.35, multiplet (2) \( \gamma \) 5.95 - 6.95 and multiplet (13) \( \gamma \) 2.1 - 2.8.

This experiment was repeated in ether, but was equally unsuccessful. Again triphenylarsine, butyl-containing arsines and arsonium salts were isolated.

**Regeneration of Ethyltriphenylarsonium Iodide from Ethylidene-triphenylarsorane.**

Ethyltriphenylarsonium iodide (5 g.) was treated with butyl-lithium (11 ml. of 1.0 M.) in tetrahydrofuran for 4
hours at room temperature. Concentrated hydrochloric acid (1.1 ml.) was introduced and the reaction mixture was concentrated. A chloroform extract of this was washed, dried and concentrated. The addition of ethyl acetate caused the precipitation of ethyltriphenylarsonium iodide (1.25 g.), 25% recovery. The mother liquor was chromatographed on neutral alumina. Elution with petrol gave initially a viscous oil, with an 'alkyl-arssine odour', (0.4 g.) Its infrared showed the characteristic peaks associated with an arsine, 1070 (s), 1025 s, 1000 cm⁻¹. From the p.m.r. it was concluded that this oil was essentially butyldiphenylarsine, multiplet (9) Υ7.7 - 9.5 and multiplet (12) Υ2.15 - 3.3. Further elution with petrol gave pure triphenylarsine (0.8 g.) mixed m.p. 60°. Elution with chloroform gave an arsonium salt, which failed to crystallise (1.2 g) Υ max 1590 w, 1440 s (arsenic-phenyl band) 1340 w, 1310 w, 1260 m, 1190 w, 1160 w, 1090 s, 1040 w, 1000 s (arsenium salt), 900 m, 740 s, 690 s, (mono-substituted aromatics); p.m.r. complex multiplet (14) Υ 7.8 - 9.35, complex multiplet (5) Υ5.9 - 7.5 and aromatic complex (7) Υ1.85 - 2.5. This ratio was closest to ethyldibutyldiphenylarsonium cation, but this speculation was not verified because all attempts to solidify the oil failed.

Reaction of Benzyldenetriphenylarsorane with p-Chlorobenzoyl Chloride.

Benzyltriphenylarsonium bromide (5.0 g.) was stirred with
lithium-butyl (10.5 ml. of 1 M.) in a tetrahydrofuran-ether mixture (50:50) for 6 hours. p-Chlorobenzoyl chloride (1 g.) was added dropwise when a solid separated out. After stirring for a further 8 hours the solid was filtered off (1.1 g.) and shown to be benzyltriphenylarsonium bromide. The mother liquor was concentrated, extracted with chloroform and water and the chloroform extract washed, dried and concentrated. Addition of ether gave a solid (1.0 g.) which appeared to be a mixture of the desired α-(p-chlorobenzoylbenzylidenetriphenylarsorane and benzyltriphenylarsonium bromide, melting range 140 - 170°C. Column chromatography on neutral alumina was unsuccessful in separating them. Successive recrystallisations from ethyl acetate gave pure α-(p-chlorobenzoyl)benzylidenetriphenylarsorane (0.2 g.), m.p. 225 - 226°C, \( \nu_{\text{max}} \) 1575 m, 1510 s (ylid carbonyl), 1340 w, 1120 m, 1080 m, 1070 w, 1030 w, 1010 m, 1000 m, (complicated arsorane pattern) 940 m, 840 m (p-substituted aromatic), 750 s, 740 s, 695 m, 690 m cm\(^{-1}\) (mono-substituted aromatic). From the p.m.r. I was unable to find the position of the 'ylid-proton'. Found C 71.82; H 4.53%, calculated for \( \text{C}_{32}\text{H}_{25}\text{AsClO} \) C 71.75; H 4.48%.

Treatment of the arsorane (0.2 g.) in ethanol with excess perchloric acid gave a white solid, m.p. 220°C (from ethanol-water). Found C 60.32; H 4.31%, calculated for \( \text{C}_{32}\text{H}_{26}\text{AsCl}_2\text{O}_5 \) C 60.41; H 4.09%. 

163.
Reaction of Ethyltriphenylarsonium Iodide with Phenyl-Lithium and p-Chlorobenzoyl Chloride.

Ethyltriphenylarsonium iodide (10 g.) was stirred with phenyl-lithium (22.2 ml of 0.97 M) in a tetrahydrofuran-ether mixture (50:50) for 3 hours. p-Chlorobenzoyl chloride (1.9 g.) was introduced in ether, when the supposed red colour of the ylid disappeared after the first drops had been added. The reaction mixture was left at room temperature for 16 hours and then concentrated. A chloroform extract of the liquor was washed, dried and concentrated. A solid separated and was filtered off (1.2 g.). This was found to be p-chlorobenzoic anhydride m.p. 194°, Lit value 194°, $\nu_{\text{max}}$ 1790, 1725 cm$^{-1}$ (anhydride). Addition of ether to the mother liquor gave a further solid (0.2 g.), m.p. 242°, identified as p-chlorobenzoic acid, mixed m.p. 242°. The mother liquor was absorbed on neutral alumina and elution with petrol gave triphenylarsine (4.6 g.), yield 69.2%. Only trace yields of unidentified yellow oils were eluted with ether.

Reaction of Ethyltriphenylarsonium Iodide with Phenyl-Lithium at $-30^\circ$C.

Ethyltriphenylarsonium iodide (4.0 g.) was stirred with phenyl-lithium (9.6 ml. of 0.9 M.) in tetrahydrofuran (50 ml) at $-30^\circ$. After 2 hours the solution had become almost homogeneous and concentrated hydrochloric acid (1.0 ml.)
was added to regenerate the salt. The reaction mixture was worked up as for the previous experiment and the chloroform extract was treated with ethyl acetate causing the precipitation of ethyltriphenylarsonium iodide (2.8 g.), m.p. and mixed m.p. 160°. Column chromatography on neutral alumina gave triphenylarsine (0.35 g.), mixed m.p. 60°.

**Reaction of Ethyltriphenylarsonium Iodide with Phenyl-Lithium and Benzoyl Chloride at -30°.**

Ethyltriphenylarsonium iodide (15 g.) was stirred with phenyl-lithium (34 ml. of 0.95 M.) in tetrahydrofuran at -30°C, until the solution was almost homogeneous (2½ hours). Benzoyl chloride (2.3 g.) was introduced to the dark yellow solution, which changed to a light brown colour. After several hours a solid precipitated out, this was filtered off and shown to be recovered arsonium salt (6.65 g.). The mother liquor was concentrated, extracted with chloroform and the chloroform extract washed, dried and evaporated. The infrared spectrum of the brown reaction mixture showed carbonyl-peaks at 1840, 1825, 1680 and 1520 cm⁻¹. This appeared to have given a small yield of the desired arsorane. Treatment of a small portion of the mother liquor with perchloric acid caused the disappearance of the 1520 cm⁻¹ peak and the enhancement of the 1680 cm⁻¹ peak. The oil also showed a strong perchlorate anion (1080 - 1120 cm⁻¹) together with the characteristic arsonium peaks (1000 and 1030 cm⁻¹).
All attempts to isolate this ylid material failed, since it was not eluted from a neutral alumina column.

Quantitative Experiments to Find the Ideal Conditions for Obtaining Methyleneetriphenylarsorane from its Salt using Organo-Lithium Bases.

All solvents used in these experiments were carefully dried and distilled before use. Tetrahydrofuran was refluxed over calcium hydride and distilled onto sodium. Diethyl ether was refluxed over lithium aluminium hydride and distilled. Benzene was distilled over calcium hydride.

The estimation of products was carried out using a Gas Chromatography Ltd. S6 and the flame-ionisation detector. External standard solutions were used in the same solvent as the unknown.

The estimations of styrene oxide and benzaldehyde were made using an "Apiezon L" column, 6m x $\frac{3}{8}$" at 170°, with the flash heaters at 200°.

The estimations of benzene were made using the same column at 70°.

The complete results of all the quantitative experiments are found in the discussion part of this section.

Run I.

Methyltriphenylarsorium iodide (4 g.) was dispersed in
tetrahydrofuran (50 ml.) to which was added butyl-lithium (4.5 ml. of 2.0 M.) at room temperature. 10 ml. aliquots were taken from the reaction mixture and added to distilled benzaldehyde (0.2 ml) in 10 ml. of tetrahydrofuran, under nitrogen, at suitable intervals. These samples were subjected to g.l.c., and gave a maximum yield of ylid of 5.2%.

Run II and III.

These were exact repeats of Run I, except that the reaction was carried out at -38°C. This was maintained by the use of a chlorobenzene slurry bath with liquid nitrogen. All the samples were added to solutions of benzaldehyde in tetrahydrofuran, also cooled to -38°C. They were allowed to warm up to room temperature after 30 minutes. G.l.c. gave a maximum yield of 24.2%.

Run IV.

Methyltriphenylarsonium iodide (4 g.) was stirred with phenyl-lithium (6 ml. of 1.5 M.) in tetrahydrofuran (50 ml.) at room temperature. The solution became homogeneous almost immediately. The samples taken and subjected to g.l.c. showed that all the benzaldehyde was unreacted, but no styrene oxide was observed.
Run V (a).

Methyltriphenylarsonium iodide (4 g.) was treated with phenyl-lithium (6 ml. of 1.5 M) in ether (50 ml.) at room temperature. The solution became almost homogeneous after 45 minutes and was a dark red-brown colour. Samples were taken as before, but this time an immediate buff precipitate separated out. Each sample was filtered and the filtrates subjected to g.l.c. No styrene oxide was detected, but usage of benzaldehyde was observed.

The unknown solid was divided into two parts

(1) The first part was stirred with water which caused it to become very sticky. Extraction with chloroform gave, after drying and evaporating, an oil which now showed carbonyl absorption at 1695 cm\(^{-1}\).

(2) The solid was partially dissolved in tetrahydrofuran at room temperature and completely so after refluxing for 30 minutes. G.l.c. confirmed the presence of styrene oxide.

Run Vb.

The exact experimental reaction conditions were employed as for Run Va. After 1 hour, two samples (10 ml.) were taken.

(1) The first sample was added to benzaldehyde (0.2 ml.) in ether (10 ml.). The lithio-betaine was filtered off under nitrogen, and the solid was transferred to tetrahydrofuran. After refluxing for 30 minutes, g.l.c. analysis found a 49%
yield of styrene oxide, together with a 10.5% yield of benzaldehyde. The total yield of ylid was, therefore, 59.5%.

(2) The second sample was added to benzaldehyde (0.2 ml) in tetrahydrofuran (10 ml.). After stirring at room temperature for 30 mins. the sample was refluxed for a further 30 minutes. G.l.c. gave a 25% yield of styrene oxide. The reverse reaction was not detectable by this experiment.

Run VI.

Sodium-phenyl had to be prepared and used immediately. Sodium (0.7 g.) was melted under refluxing toluene. The solution was removed from the source of heat, stoppered and shaken very vigorously until the sodium solidified. This was repeated several times until a fine sodium sand was produced. This was transferred under benzene and chlorobenzene (1.7 g.) was added dropwise to maintain the temperature 25 - 30°. The grey sand was replaced by a black dispersion of phenyl-sodium. A 60% yield was presumed. Methyltriphenylarsonium iodide (4 g.) was added and after 30 minutes the benzene solution was only a pale yellow colour, a sample of which showed no styrene oxide after addition to benzaldehyde. A maximum yield was found after 2½ hours generating time when a 37% yield of ylid was determined.

The procedure was repeated using 1.5 mols. of phenyl-sodium/1 mol. of arsonium salt. After 2½ hours generation
time, a 47% yield of ylid was obtained.

Finally using 2 mols. of phenyl-sodium/1 mol. of arsonium salt no styrene oxide was detected at all. Samples of the red coloured solution did not discolourise on addition to benzaldehyde, but all the benzaldehyde was consumed.

Run VII.

Methyltriphenylarsonium iodide (6.0 g.) was stirred with t-butyl-lithium (8.5 ml. of 1.6 M) in benzene (50 ml.). The salt did not appear to react and after 6 hours reaction time only ¾ of the arsonium salt had dissolved to give an orange solution. The maximum yield of ylid was found to be 3.1% after 1 hour generation time.

Attempted Generation of Ethylidenetriphenylarsorane - Run VIIIa.

Ethyltriphenylarsonium iodide (4.0 g.) was treated with phenyl-lithium (5.4 ml. of 1.6 M) in diethyl-ether (50 ml.). Samples (5 ml.) were taken at suitable intervals and added to benzaldehyde (0.15 ml.) in 5 mls. of ether. Small precipitates formed in all of the test samples. Tetrahydrofuran was added and the samples refluxed for 30 minutes. G.l.c. analysis (Apiezon column at 200°) against a standard solution of L-phenyl-propylene oxide, gave a maximum yield of 10% ethylidenetriphenylarsorane, although all the phenyl-lithium had been consumed after 5 hours.
Run VIIIb.

The same quantities of reactants were used as in Run VIIIa, but no samples were taken. After 24 hours the total reaction mixture was analysed for benzene and ethylbenzene by g.l.c.

A theoretical yield of benzene confirmed the previous observation that all the phenyl-lithium had been consumed.

No ethylbenzene (Apiezon column at 140°C) was detected.

Run VIIIc.

Ethyltriphenylarsonium iodide (4 g.), phenyl-lithium (9.6 ml. of 0.9 M) and ether (50 ml.) were allowed to react in a sealed Schlenk tube for 24 hours at room temperature. The reaction mixture was analysed on g.l.c. for low-boiling gases. Standard solutions of both but-2-ene and ethylene in ether were successfully chromatographed at room temperature using a carbowax column. A peak, with an identical retention time to the standard solution of butene, was observed from the reaction mixture. No peak corresponding to the retention time for ethylene was observed.

Run VIIIId.

A repeat experiment of Run VIIIc was run, but this time the outlet of the Schlenk tube was connected to a Dreshnel bottle containing bromine (5 ml.) in dried carbon tetrachloride (25 ml.). The reaction was refluxed for 24 hours under a continuous flow
of nitrogen. The carbon tetrachloride solution was shaken with sodium metabisulphide, water and then dried and concentrated. The concentrate was subjected to g.l.c. using a carbowax column at 130°. Four major products were obtained, one of which corresponded to 2,3 dibromobutane.

However attempts to isolate this product failed.

**Attempted Quaternisation of Triphenylarsine and n-Hexyl Bromide.**

Triphenylarsine (10 g.) and n-hexyl bromide (5.4 g.) were refluxed, without solvent, for 16 hours. No solid separated out on cooling and triphenylarsine was recovered unchanged.

**Preparation of n-Hexyl Iodide.**

n-Hexyl bromide (20 g.) was treated with a ten-fold excess of sodium iodide as a saturated solution in anhydrous acetone (Finkelstein reaction). After refluxing for 4 hours, sodium bromide was filtered off. After concentrating the acetone solution it was treated with ether and water. The ether extract was washed, dried and distilled. n-Hexyl iodide distilled at b.p. 62°, Lit. 152 b.p. 767 180°.

**Attempted Quaternisation of Triphenylarsine and n-Hexyl Iodide.**

Triphenylarsine (5.0 g.) was dissolved in benzene and refluxed with n-hexyl iodide (3.5 g.) for 48 hours. No arsonium salt separated out, and triphenylarsine was recovered unreacted.
The reaction was repeated in both refluxing dimethylformamide and n-butanol with equal failure. Finally the quaternisation was attempted in n-butanol at 150°, but again a 90% recovery of triphenylarsine was obtained.

**Attempted Quaternisation of Triphenylarsine with n-Heptyl Iodide using Silver Tetrafluoroborate.**

This experiment was carried out in a dry box. The arsine (3.0 g.) was dissolved in excess n-hexyl iodide (10 g.) and silver tetrafluoroborate (2.2 g.) was slowly added over 15 minutes. Heat was evolved and silver iodide precipitated. This mixture was stirred overnight. Methylene chloride (50 ml.) was introduced and the solution was filtered free of silver iodide. Evaporation of the mother liquor gave a buff-coloured solid (2.2 g.). This solid proved difficult to crystallise, the best solvents for which were chloroform and ether. The melting point was not obtained; it discoloured at 280° and decomposed at 300°; \( \nu_{\text{max}} \) 1440 s (phenyl-arsenic), 1095 m, 1010 m (arsonium salt), 1055 s (tetrafluoroborate), 780 s, 695 s cm\(^{-1}\) (mono-substituted aromatic); p.m.r. multiplet (3H) \( \gamma \) 7.4 - 7.6, singlet (1 H) \( \gamma \) 6.8 and multiplet (15 H) \( \gamma \) 2.5 - 2.85. Found C 60.73; H 4.34; As 23.29; F 10.43%. It was concluded that this product was represented by the formula \( 2(C_6H_5)_2 \) As. HBF\(_4\).

When the solid (0.5 g.) was refluxed in sodium hydroxide (since no reaction occurred at room temperature), the product
turned grey and some decomposition occurred. Crystalline
triphenylarsine (0.18 g.) separated out on cooling. Unchanged
starting material (0.2 g.) was also recovered together with a
brown tar.

Reaction of Methylene triphenylarsorane with n-Hexyl Bromide.

Methyltriphenylarsonium bromide (8.0 g.) was stirred with
phenyl-lithium (10.5 ml. of 1.7 M) in ether for 1 hour at room
temperature. A solution of distilled n-hexyl bromide (2.55 ml.)
in ether was introduced. The red colour of the ylid disappeared
slowly and deposited a brown oil. After stirring for 16 hours
the reaction mixture was concentrated, extracted with chloroform
and water and the chloroform extract washed, dried and evaporated.
The viscous oily product was identified as a mixture of the
required n-heptyltriphenylarsonium iodide and methyltriphenyl-
arsonium iodide from the p.m.r. spectrum. This was an additive
spectra of these two components. From the integration value
of the methyl peak in methyltriphenylarsonium iodide, it was
possible to calculate the purity of the n-heptyl salt. For
example a typical p.m.r. showed a complex multiplet (9.6) $\gamma$ 8.0 - 9.5
(n-hexyl group), singlet (0.5) $\gamma$ 6.85 (methyl of methylarsonium
salt), multiplet (0.9) $\gamma$ 6.0 - 6.5 (-methylene group next to As$^2$),
and multiplet (13.4) $\gamma$ 2.15 - 2.7 (all aromatic protons). Hence
this sample contained 37% methyl arsonium salt in the n-heptyl
salt.
All attempts to avoid the impurity failed, even though great care was taken to avoid moisture and the ylid solution was filtered free of solid. The best purification was achieved by the addition of ethyl acetate to a refluxing solution of the salts in chloroform and setting aside for 14 days. During this time methyltriphenylarsonium iodide crystallised out. In this way 90% pure n-heptyltriphenylarsonium salt (4.9 g. = 4.4 g. of 100%) was obtained.

Reaction of Methylenetriphenylarsorane with n-Hexyl Iodide.

Methyltriphenylarsonium iodide (10 g.) was stirred with phenyl-lithium (13.2 ml. of 1.8 M.) in diethyl ether for 1 hour at room temperature. The ylid was filtered into n-hexyl iodide (4.7 g.) in ether and stirred overnight. The reaction was worked up as for the previous experiment. However treatment of the oily product with chloroform-ethyl acetate gave a white solid (5.0 g.) m.p. 151 - 153°. Recrystallisation from chloroform and ethyl acetate gave a constant melting point of 155°; $\nu_{\text{max}}$ 3350 m, 1445 s (phenylarsenic) 1345 w, 1320 w, 1260 w, 1230 s, 1190 w, 1160 w, 1120 m, 1080 s, 1030 w, 1005 s (arsonium salt), 975 m, 920 m, 745 s, 695 s cm$^{-1}$ (mono-substituted aromatic). However the p.m.r. spectrum was disappointing because it showed no heptyl group, singlet (3 H) $\gamma$ 8.5, singlet (1 H) $\gamma$ 6.85, singlet (1 H) $\gamma$ 5.9, multiplet (15 H) $\gamma$ 2.0 - 2.65.

The only interpretation of this spectrum was that the solid
was a mixture, but further recrystallisations failed to alter the ratio of the peaks or the melting point of the solid. Analysis found C 52.09; H 4.34%. The solid was not identified.

Reaction of n-Heptyltriphenylarsonium Iodide with Phenyl-Lithium.

The arsonium salt (90% pure) was freeze-dried for 16 hours to ensure the oil was dry. To this salt (6.1 g.) was added benzene (68 ml.) and phenyl-lithium (8.5 ml. of 1.5 M). The solution became orange and homogeneous, but later deposited a crude oil. After 7 days at room temperature the reaction mixture was subjected to g.l.c. ('Apiezon L column). With the column at 90° the presence of 1-heptene was confirmed (with an authentic sample), in a 55/° yield. With the column at 210° the presence of two further compounds were observed, but they were not identified because no authentic samples of heptylbenzene or tetradec-7,8-ene were available. The reaction mixture was concentrated, extracted with chloroform and water, and the chloroform extract was dried and concentrated. The addition of ethyl acetate caused an oil to separate, which was identified, by p.m.r., as unreacted heptyl salt (0.8 g.). The mother liquor was absorbed on silica. Elution with petrol gave biphenyl, (0.5 g.), mixed m.p. 71°. (The same phenyl-lithium (8.5 ml. of 1.5 M) when added to water and extracted with ether gave 0.1 g. of biphenyl). Therefore the true weight of biphenyl formed in this reaction was 0.4 g. (25.8% yield). Further
elution with petrol gave triphenylarsine (1.4 g.), mixed m.p. 60°. Elution with petrol-ether (90 : 10) gave 'foul-smelling arsine-type' oils (0.4 g.), $\nu_{\text{max}}$ 1440 m (phenyl-arsenic) 1070 m, 1020 m, 995 m (pattern characteristic of an arsine), 740 s, 695 s cm$^{-1}$ (mono-substituted aromatics). The p.m.r. suggested that the oils were probably impure heptyldiphenylarsines, complex multiplets at $\gamma 7.8 - 9.5$ and $\gamma 2.1 - 3.65$ (ratio: 11 : 17). The total oils were allowed to react with methyl iodide, which gave an arsonium salt, insoluble in ether, but again it failed to solidify. The p.m.r. of the crude oil showed a new peak $\gamma 6.15$, but these products were not identified further.

**Attempted Preparation of Methyleneetriphenylarsorane via a Pentacovalent Intermediate.**

(a) **In ether.**

Tetraphenylarsonium chloride (3.0 g.) was dispersed in ether and freshly prepared methyl-lithium (6.5 ml. of 1.25 M) was added at room temperature. After 7½ hours the mixture was analysed for benzene ('Apiezon column at 70°). No benzene was observed and it was concluded that no reaction had occurred.

(b) **In ether-tetrahydrofuran.**

Tetraphenylarsonium chloride (2.2 g.) was dispersed in a mixture of ether and tetrahydrofuran (1 : 5) and methyl-lithium (4.5 ml. of 1.25 M) was introduced. After 3 hours, at reflux, no apparent reaction had occurred to give the ylid since samples added to benzaldehyde did not precipitate a lithio-betaine
and no styrene oxide was detected. After 5 hours the reaction mixture was allowed to settle and the supernatant liquid was analysed for benzene. The solid was filtered off (1.5 g.) and the melting point was taken, 311°. This was later identified as tetraphenylarsonium iodide, m.p. 333°. Of the original starting material only 0.97 g. had reacted with the methyl-lithium. The quantity of benzene estimated by g.l.c. corresponded to 2.4 mol/l mol. of arsonium salt.

Reaction of Triphenylarsine with Methyl-Lithium

Triphenylarsine (0.006 mol = 2.0 g.) was dissolved in tetrahydrofuran (45 ml.) and methyl-lithium (0.018 mol = 15 ml. of 1.25 M) was introduced. After refluxing for 16 hours, g.l.c. of the mixture showed the formation of benzene (1.55 mol/l mol. of arsine). Excess methyl iodide was introduced to trap the methyl arsines as their methyl arsonium salts. After refluxing for 2 hours the solvent was removed and a chloroform extract of the oil was washed, dried and concentrated. A solid precipitated, which was difficultly soluble in chloroform (1.2 g.) m.p. (chloroform) 240 - 242°. This value suggested that the product isolated was trimethylphenylarsonium iodide, m.p. Lit. (4) 242°. This was confirmed by p.m.r. (D.D.M.S.O) singlet (9 H) δ 7.7, multiplet (5 H) δ 1.85 - 2.5; v_{max} 1425 s, 1095 s, 1000 s, 940 s, 875 m, 730 s, 685 m cm^{-1} Yield 57%.
Reaction of Triphenylarsine with Methyl-lithium II

Triphenylarsine (0.006 M = 2.0 g.) was dissolved in tetrahydrofuran (50 ml.) and methyl-lithium (0.006 M = 6 ml. of 1.1 M) was introduced. After refluxing for 12 hours the reaction mixture was subjected to g.l.c. (Apiezon column at 70°). The benzene detected corresponded to 0.78 mol./1.0 mol. of triphenylarsine. Methyl iodide was introduced and the work up was as for the previous experiment. An oily solid (1.55 g.) was shown, by p.m.r., to be a mixture of methyltriphenylarsonium Y6.9, dimethyldiphenylarsonium Y7.2 and trimethylphenylarsonium Y7.7, iodides.

An analogous reaction was attempted with triphenylphosphine and methyl-lithium. However no benzene was found in the reaction mixture.

Attempted Preparation of Methylenetriphenylarsorane using a Phosphorane.

Methyltriphenylphosphonium iodide (3.0 g.) was stirred with phenyl-lithium (5.7 ml. of 1.3 M) in ether for 1 hour. Solid methyltriphenylarsonium iodide (3.3 g.) was introduced and the mixture was stirred for 30 minutes. Benzaldehyde (0.8 g.) was slowly introduced causing the immediate separation of a white solid. The ether was removed by distillation and replaced with tetrahydrofuran. The reaction mixture was refluxed for 16 hours and then subjected to g.l.c. (Apiezon column at 150°). A 75% yield of styrene was found, but no trace of styrene oxide.
Reaction of Dimethylphenylmethylene phosphorane with
Methyltriphenylarsonium Iodide.

Trimethylphenylphosphonium iodide (2.0 g.) was stirred
with phenyl-lithium (6 ml. of 1.2 M) in ether for 30 minutes
giving a dark brown solution. Solid methyltriphenylarsonium
iodide (3.2 g.) was introduced and the reaction mixture was
vigorously stirred for 30 minutes. Benzaldehyde (0.8 g.) was
introduced causing the precipitation of a solid. The ether
was replaced with tetrahydrofuran and the reaction mixture
was refluxed overnight. G.l.c. showed a 52% yield of styrene,
but no trace of styrene oxide.

Reaction of Methylenetriphenylarsorane with
Trimethylphenylphosphonium Iodide.

Methyltriphenylarsonium iodide (3.2 g.) was stirred with
phenyl-lithium (5.5 ml. of 1.3 M) for 1 hour in ether. Solid
phosphonium salt (2.0 g.) was introduced and the reaction
mixture was vigorously stirred for 30 minutes. Benzaldehyde
(0.8 g.) was added and a solid precipitated. The ether was
distilled and replaced with tetrahydrofuran. After refluxing
for 16 hours, the mixture was subjected to g.l.c. A 46% yield
of styrene oxide was recorded together with a 5% yield of
styrene.
CHAPTER IV.

Some Reactions of $\beta$-Ketoalkylidenearsoranes.

(1) Reaction of $\beta$-Ketoalkylidenearsoranes with Carbonyl Compounds.

$\beta$-Ketoalkylidenearsoranes are more reactive than their phosphorus analogues. This was indicated, initially, by the difficulties encountered during the preparation of either benzoylmethylenetriphenylarsorane or ethoxycarbonylmethylene-triphenylarsorane from their corresponding arsonium salts. Further proof of their enhanced reactivity was gained when the ester arsoranes (1) readily underwent reaction with a variety of aldehydes and ketones. The reaction took place at room temperature and gave high yields of $\alpha,\beta$-unsaturated esters (3).

\[ \begin{align*}
(1) \quad \text{(C}_6\text{H}_5)_3\text{As-CH-COOR} + R^1\text{C} = 0 & \rightarrow \left[(\text{C}_6\text{H}_5)_3\text{As-CH-COOR}\right] \rightarrow (\text{C}_6\text{H}_5)_3\text{As} + \text{CHCOOR} \\
(2) \\
(3)
\end{align*} \]

\[ R = \text{C}_2\text{H}_5 \text{ or CH}_3 \]

(1) $R^1 = H \quad R^2 = \text{C}_6\text{H}_5$

(2) $R^1 = H \quad R^2 = \text{CH}_3\text{CH}_2\text{CH}_2$

(3) $R^1 = R^2 = \text{C}_2\text{H}_5$

(4) $R^1 \quad R^2 = \bigcirc$

N.B. An $\alpha,\beta$-unsaturated ester is the expected product from this reaction because the carbon $\alpha$ to arsenic in the ylid (1) has an electron-withdrawing group capable of stabilising
negative charge. From the earlier work in this thesis, when alkylideneasoranes underwent reaction with carbonyl compounds, this would make olefin-formation the fastest reaction, i.e. the three-betaines of (2) would undergo cis-elimination, via a pentacovalent intermediate, to give a trans-\(\alpha,\beta\)-unsaturated ester.

(2) Reaction of \(\beta\)-Ketoalkylideneasoranes with Conjugated Alkynes.

It was hoped that a \(\beta\)-ketoalkylideneasorane, less nucleophilic than an alkylideneasorane, would selectively attack at the triple bond of dimethyl acetylenedicarboxylate (4) to give the betaine intermediate (5). This could then eliminate triphenylarsine to give the cyclopropene derivative (6)

\[
\begin{align*}
\text{(4)} & \quad \begin{array}{c}
\text{MeO}_2\text{C} - \text{C} = \text{C} - \text{CO}_2\text{Me}
\end{array} \\
\text{H} & \quad \begin{array}{c}
(C_6\text{H}_5)_3\text{As-C-COR}
\end{array} \\
\text{MeO}_2\text{C} - \text{C} = \text{C} - \text{CO}_2\text{Me} & \quad \begin{array}{c}
(C_6\text{H}_5)_3\text{As-CH-COR}
\end{array} \\
\text{(5)} & \quad \begin{array}{c}
\text{MeO}_2\text{C} - \text{C} = \text{C} - \text{CO}_2\text{Me}
\end{array} \\
\text{CHCOR} & \quad \begin{array}{c}
(C_6\text{H}_5)_3\text{As-MeO}_2\text{C} - \text{C} = \text{C} - \text{CO}_2\text{Me}
\end{array}
\end{align*}
\]

When \(\beta\)-ketoalkylideneasoranes were treated with dimethyl acetylenedicarboxylate a reaction took place but no triphenylarsine was eliminated. Infrared and p.m.r. spectrums showed that the products were new arsonium ylids and that they were 1 : 1 adducts of the reactants. The presence of two methyl esters showed that the reaction had indeed taken place.
at the triple bond and that the adducts must have arisen by rearrangement of the intermediate betaines (5).

Hendrickson(153) had reported that benzoylmethylene-triphenylphosphorane (7) underwent reaction with dimethyl acetylenedicarboxylate giving the adduct (9) when methanol was used as solvent, but adduct (10) when ether was the solvent.

\[
(C_6H_5)_3P=CH-COC_6H_5 + MeO_2C-C≡C-CO_2Me \rightarrow \begin{array}{c}
\text{(C}_6\text{H}_5)_3P=CH-COC_6\text{H}_5 \\
\text{MeO}_2\text{C}-C≡C-CO_2\text{Me}
\end{array}
\]

Hendrickson(153) concluded that in the presence of 'mobile' protons, either in the donor or protic solvent, then collapse of betaine (8) occurred to the simple adduct (9), by a 1, 3 proton shift. When no 'mobile' protons were available the betaine (8) decomposed either by internal cyclisation to give adduct (10) or by further condensation with another molecule of acetylene.

By analogy the arsenic betaine could have formed product (11), involving a 1, 3 proton shift, or product (13), by a
1, 3 arsenic shift, via a four-membered cyclic intermediate.

![Diagram of molecular structures](image)

(a) $R = \text{BrC}_6\text{H}_4$

(b) $R = \text{OC}_2\text{H}_5$

The infrared spectrum of the 1:1 adduct from dimethyl acetylenedicarboxylate and $p$-bromobenzoylmethylenetriphenylarsorane included the peaks 1725 s, 1675 s, 1610 m, 1580 m, 1560 w cm$^{-1}$; there was no evidence of a peak at 1510 - 1520 cm$^{-1}$, characteristic of a carbonyl to the ylid bond. The p.m.r. spectrum showed the two ester methyls at $\gamma 6.4$ and $\gamma 6.25$, a singlet at $\gamma 4.15$ (olefinic proton) and aromatics at $\gamma 2.0 - 3.0$.

This information suggested that the adduct had the structure (13a). Substantiation for this was found when the adduct underwent reaction with perchloric acid and gave the arsonium perchlorate.

If the adduct had the structure (11a) then its salt (12a) would possess two unsaturated ester groups and a saturated ketone. If the adduct had the structure (13a) then the salt (14a) would
possess an unsaturated ketone, an unsaturated ester together with a saturated ester. The infrared spectrum of the arsonium salt had peaks at 1770 s, 1725 s, 1675 s, 1610 w, 1590 m cm\(^{-1}\). This could only fit \((14)\) since the 1770 cm\(^{-1}\) peak must be due to the saturated ester group. Therefore the adduct was assigned structure \((13)\).

The structure of the adduct from ethoxycarbonylmethylene-triphenylarsorane and dimethyl acetylenedicarboxylate was not assigned. This adduct underwent reaction with perchloric acid, but accompanying decomposition took place and no adduct salt was isolated.

Attempts were made to react \(\alpha\)-(p-chlorobenzoyl)benzylidene-triphenylarsorane with this acetylenic ester, because this arsorane does not possess an \(\alpha\)-hydrogen. However, no reaction took place; even at an elevated temperature the arsorane was recovered unchanged.

\((3)\) Reaction of \(\beta\)-KetoalkylideneArsoranes with Sulphenes.

The transitory existence of a sulphene \((16)\) was first proposed by Zincke and Brune\(^{(154)}\) in 1908 and later the intermediary of a sulphene was proposed to rationalise the course of three general reactions, (1) the reaction of sulphonyl halides \((15)\) with tertiary amines\(^{(155)}\) (2) the reaction of diazoalkanes with sulphur dioxide\(^{(156)}\) and (3) the photolysis of unsaturated sultones\(^{(157)}\).
Two groups, King et al (158) and Truce et al (159) simultaneously provided positive evidence (in 1964) for the existence of sulphenes. They observed that when sulphonyl halides were treated with triethylamine in an O-deutero-alcohol, only monodeuterated esters (17) were isolated and very little or no dideuterated material was detected. The formation of these products requires that deuterium be incorporated in an irreversible step and clearly indicates that the exchange could not have involved a carbanion of the sulphonyl halide or the sulphonate (18). It is explained by an elimination addition sequence involving a sulphone intermediate (16).

\[
\begin{align*}
RCH_2SO_2C1 & \xrightarrow{\left(C_2H_5\right)_2N} \left[RCH = SO_2\right] \xrightarrow{R'OD} \text{RCHD - SO}_3\text{R'} \\
(15) & \quad (16) & \quad (17)
\end{align*}
\]

\[
\begin{align*}
RCH_2SO_2X & \xleftarrow{E} \text{RCHSO}_2X + \text{BH} \xleftarrow{\text{etc}} X = \text{Cl} \text{ or OR'} \\
(18)
\end{align*}
\]

Ito, Okano and Oda (160) and Hamid and Trippett (161) have shown that stable phosphoranes, bearing an α-proton (19), undergo reaction with sulphone or phenylsulphone to give initially a betaine (20), which, after a 1,3 proton shift, gives a new phosphonium ylid (21).
The reaction of ethoxycarbonylmethylenetriphenylarsorane with phenylsulphene gave two products; a 1:1 adduct of the two reactants in 30% yield and trans-ethyl cinnamate in 24% yield.

The infrared spectrum of the adduct showed an 'ylid ester carbonyl' at 1650 cm\(^{-1}\), a sulphone (1260 and 1115 cm\(^{-1}\)) and the complex pattern associated with arsonium ylids (1090, 1070, 1035, 1000 cm\(^{-1}\)). Its p.m.r. spectrum showed an ethyl ester (triplet (3 H) \(\delta 9.25\) and quartet (2 H) \(\delta 6.1, J_{HH} = 7\) c/sec), a singlet (2 H) at \(\delta 5.45\) and aromatic protons (20 H) \(\delta 2.1\) - 3.0. This product was considered to be the arsenic analogue of (21a), i.e., \(\alpha\)-benzylsulphonyl-\(\alpha\)-ethoxycarbonylmethylenetriphenylarsorane (23). Its formation presumably occurred by nucleophilic attack of the arsorane on the electrophilic sulphene to give the betaine (22), which then underwent a 1,3 proton shift (visualised here as an intramolecular \(S_N^2\) process).
The yield of the second product, trans-ethyl cinnamate, increased to 44% when the reaction temperature was raised, together with an accompanying increase in the yield of triphenylarsine. It is considered that this product arose from the decomposition of a primary product, the episulphone (24) (the thermal instability of episulphones has been known as their general behaviour). The episulphone (24) could be formed from the betaine (22) simply by an internal nucleophilic displacement reaction, i.e. attack of the carbanion on the carbon α to arsenic and expulsion of triphenylarsine.

Since only trans-ethyl cinnamate was isolated this result shows a selective formation of the trans-episulphone because Neureiter\(^{(162)}\) has recently demonstrated that episulphones undergo a thermal cis-elimination, i.e. trans-episulphone gives trans-olefin.

This stereochemical feature may be explained, by analogy with early work in this thesis, by a preferred conformation of the betaine (22) selectively undergoing elimination to give the
three membered ring, i.e. the betaine formation is an equilibrium process.

Since this work was carried out, Ide and Yura\(^{163}\) have shown that stable sulfoxonium ylids, bearing an \(\alpha\)-proton, also undergo reaction with sulphenes. They found the analogous products, olefins in 63% yield and C-sulphonated products in 1.3% yield.

**Reaction of 8-ketoalkylidenearsoranes with Sulphines.**

Sulphines (25) have been prepared by the elimination of hydrogen chloride from sulphinyl chlorides using triethylamine in anhydrous solvents.\(^{164}(165)\) Hamid and Trippett\(^{161}\) have very recently reported that phenylsulphine does not behave as a nucleophile and does not, therefore, undergo typical ylid reactions. However, its behaviour as an electrophile was demonstrated.

When \(\alpha-\)\((\text{p-bromobenzoyl})\)methylenetriphenylarsorane was treated with a solution of phenylsulphine a 1 : 1 adduct was observed in 80% yield. This, by analogy with the previous reaction, would be formed by nucleophilic attack of the arsorane on the phenylsulphene to give the betaine (26a). A\textit{ priori} this could have formed a new ylid with structure (27a) by a 1,3 proton shift, or a new ylid (28a) by a 1,3 arsenic shift.
(a) \( R = \text{BrC}_{6}H_{4} \)
(b) \( R = \text{OEt} \).

The adduct isolated had a strong ylid carbonyl peak at 1520 cm\(^{-1}\) together with a sulphoxide peak at 1015 cm\(^{-1}\). The p.m.r. spectrum gave a broad singlet (2 H) \( \gamma 6.2 \) and a multiplet (24 H) \( \gamma 2.15 - 3.15 \). The product was considered to be \( \alpha \)-benzylsulphinyl-\( \alpha \)-(\( \mu \)-bromobenzoyl)methylene triphenylarsorane, structure (27a), since structure (28a) could not accommodate this physical data.

The reaction of ethoxycarbonylmethylene triphenylarsorane with phenylsulphine was more complex. The formation of two products was observed from the reaction mixture infrared spectrum, one with a carbonyl at 1650 cm\(^{-1}\) (an ylid ester) and another, unidentified product with a carbonyl at 1740 cm\(^{-1}\). The lower carbonyl-containing compound was isolated in 51% yield and was assigned the structure (27b).
Its infrared spectrum showed, in addition to the conjugated ester, a sulphoxide (1020 cm\(^{-1}\)) and a typical complex arsorane pattern (1000-1,100 cm\(^{-1}\)). However, the p.m.r. spectrum of this compound was not readily explained. It consisted of a multiplet (3 H) \(\gamma 8.65 - 9.35\), which was assigned to the methyl of the ester (also a multiplet in the simple ethoxycarbonyl-methylenetriphenylarsorane) two multiplets \(\gamma 4.4 - 4.8\) and \(\gamma 5.65 - 6.2\), which together integrated for four protons and were, therefore, assigned to the methylene of the ester group together with the benzyl protons, and a multiplet (20 H) \(\gamma 2.15 - 3.0\) for the aromatics. It was expected that the benzyl protons of structure (27b) would constitute an AB system by an inherent magnetic non-equivalence of the protons. However in this example the chemical shifts of the two benzylic protons differed by \(\gamma 1.2\). An exactly analogous compound (30a) had been prepared by Hamid and Trippett when the analogue phosphorane underwent reaction with phenylsulphine. Its infrared spectrum was almost identical and its p.m.r. spectrum showed exactly the same pattern, with a separation of chemical shifts of the two benzylic protons of \(\gamma 1.3\). It also was assigned structure (30a) rather than the alternative (31a).
In an attempt to confirm that the ylids had the assigned structures (27) for the arsenic ylid, (30) for the phosphorus ylid) several other sulphinylphosphoranes were prepared (30b-d). The p.m.r. spectrum of all these additional ylids confirmed an AB system for the benzyl protons, but, a maximum chemical shift difference of Υ 0.35 was observed. The large difference in chemical shift of the benzyl protons in the ester arsorane and phosphorane compared to the other arsorane and phosphoranes was not explained.

Finally some chemical reactions on the sulphinylmethylene ylids were carried out to gather further information about their structures.

(a) Wittig Reaction.

When the adduct obtained from phenylsulphine and p-bromobenzoylmethylenetriphenylphosphorane was treated with p-nitrobenzaldehyde, the olefin obtained was 1-(p-bromobenzoyl)-2-(p-nitrophenyl)ethylene (32). Formation of this product is...
envisioned as the initial loss of the sulphinyl group followed by subsequent reaction of the phosphorane with $\rho$-nitrobenzaldehyde. Providing, then, that the ylids do not interconvert under the reaction conditions used, this confirms that the structure of this adduct is (30c), since the alternative (31c) would give 1-phenyl-2-(\(\rho\)-nitrophenyl)ethylene. (33).

\[
(C_6H_5)_3P-C-COC_6H_4Br(\rho) \rightarrow [(C_6H_5)_3P=CH-COC_6H_4Br(\rho)] \\
\downarrow \rho-NO_2C_6H_4CHO \\
\rho-NO_2C_6H_4-CH=CH-COC_6H_4Br(\rho)
\]

(32)

\[
(C_6H_5)_3P+C-C_6H_5 \\
SO-CH_2COC_6H_4Br(\rho) \\
\downarrow \rho-NO_2C_6H_4CHO \\
\rho-NO_2C_6H_4-CH=CH-C_6H_5
\]

(33)

When the ester phosphorane (30a) was treated with $p$-nitrobenzaldehyde no reaction took place in refluxing tetrahydrofuran after 48 hours. The phosphorane (30a) was recovered unchanged.

(b) Salt Formation.

When the adduct, obtained from phenylsulphine and $\alpha$-acetyl methylenetriphenylphosphorane, was treated with
aqueous hydrobromic acid and subsequently with sodium tetrafluoroborate, the product obtained was \( \alpha \)-acetylmethyltriphenylphosphonium tetrafluoroborate (34). Again, by the same token, only structure (30c) could give rise to this product. Structure (31c) would have given benzyltriphenylphosphonium tetrafluoroborate (35). 

\[
\begin{align*}
(C_6H_5)_3P=\text{COCH}_3 & \xrightarrow{\text{HBr}} (C_6H_5)_2P=\text{CH_2COCH}_3 \quad \text{BF}_4^- \\
\text{SO-CH}_2C_6H_5 & \quad \text{BP}_4^- \\
(34) \\
\end{align*}
\]

\[
\begin{align*}
(C_6H_5)_3P=\text{C-C}_6H_5 & \xrightarrow{\text{HBr/\text{BF}_4^-}} (C_6H_5)_2P=\text{C}_2\text{C}_6H_5 \quad \text{BF}_4^- \\
\text{SO-CH}_2\text{COCH}_3 & \quad (35) \\
\end{align*}
\]

In conclusion the adducts obtained from the reaction of phenylsulphine and \( \beta \)-ketoalkylidenearsoranes or phosphoranes were assigned the structures (27) and (30) respectively.
Experimental.

All solvents were dried and distilled before use. Petrol refers to the fraction 40-60 unless otherwise stated. The g.l.c. measurements were made on a Gas Chromatography Ltd. S6. P.m.r. spectrum were run in CDCl₃, unless otherwise stated. Melting points were corrected.

Preparation of Diethylethoxycarbonylmethylphosphonate.

Triethyl phosphite (20 g.) and ethyl bromoacetate (25 g.) were gently warmed until a reaction commenced causing the mixture to reflux unaided for 5 minutes. After refluxing for 4 hours the mixture was distilled. The phosphonate (20 g.) was collected b.p. 116°, Lit. b.p. 143°.

Reaction of Diethylethoxycarbonylmethylphosphonate with Cyclohexanone.

The phosphonate (9.5 g.) and cyclohexanone (4.2 g.) were dissolved in dimethylformamide (30 ml.) and added to solid sodium ethoxide (from 1.05 g. sodium in ethanol). The reaction mixture was heated on a steam bath for 16 hours when it was diluted with water and extracted with benzene. The benzene extract was washed, dried and distilled. Ethyl cyclohexylideneacetate (5.0 g.) was collected b.p. 79°, Lit. 108°.
Reaction of Ethoxycarbonylmethyltriphenylarsonium Bromide with Cyclohexanone in Ethanolic Sodium Ethoxide.

The arsonium salt (5.0 g.) and cyclohexanone (1.04 g.) were added to ethanol (50 ml.) containing sodium (0.24 g.), and the reaction mixture was set aside, at room temperature, overnight. The solvent was removed and a chloroform extract of the concentrate was washed free of sodium salts, dried and evaporated. An ethanolic solution of the reaction mixture was subjected to g.l.c. (apiezon column at 200°). The authentic sample of ethyl cyclohexylideneacetate, confirmed the preparation of a 72% yield of this \( \alpha, \beta \)-unsaturated ester.

Reaction of Diethylethoxycarbonylmethylphosphonate with Diethyl Ketone.

The phosphonate (10 g.) and diethyl ketone (4.1 g.) in dried dimethylformamide (30 ml.) was added to solid sodium ethoxide (1.105 g. sodium) with cooling. The solution was set aside at room temperature and after 16 hours was diluted with water. An ether extract of this was washed, dried and distilled, ethyl 3-ethylpent-2-enoate was collected, b.p. 0.9 m.m. 40°, Lit. [167] b.p. 755 m.m. 188°.

Reaction of Ethoxycarbonylmethyltriphenylarsonium Bromide with Diethyl Ketone in Ethanolic Sodium Ethoxide.

The arsonium salt (4.0 g.) and diethyl ketone (0.73 g.)
were dissolved in ethanol (50 ml.) containing sodium (0.194 g.) and the reaction mixture was set aside for 24 hours. The work up was the same as for previous reactions. G.l.c. analysis gave a 51% of ethyl 3-ethylpent-2-enoate.

**Preparation of Ethyl Hex-2-enoate**

Ethoxycarbonylmethyltriphenylphosphonium bromide (30 g.) was dissolved in water (600 ml.) and sodium hydroxide (35 ml. of 2N) was carefully introduced, with stirring, until the solution was just alkaline. A yellow oil separated. This was extracted with chloroform, and, after washing, drying, and removal of the solvent, solid ethoxycarbonylmethylene-triphenylphosphorane was collected, m.p. (petrol-ethyl acetate) 120\(^\circ\). This was dissolved in benzene and, after the addition of butyraldehyde (5.2 g.), was refluxed for 24 hours. The solvent was removed and addition of petrol (60 - 80\(^\circ\)) gave triphenylphosphine oxide. The filtrate was distilled and ethyl hex-2-enoate was collected, b.p. 171 - 174\(^\circ\), Lit.\(^{(168)}\) 174 - 175\(^\circ\).

**Reaction of Ethoxycarbonylmethylene-triphenylarsorane with n-Butyraldehyde.**

The arsorane was prepared by shaking a chloroform solution of ethoxycarbonylmethyltriphenylarsoraniun bromide (10 g.) with excess 2N sodium hydroxide (20 ml.) for 4 minutes. After
washing and drying the chloroform, the arsorane was obtained (4.2 g.), in 50% yield. This was dissolved in benzene (60 ml.) and n-butyraldehyde (0.8 g.) was introduced. After refluxing for 24 hours, the solvent was removed. Addition of petrol gave triphenylarsine oxide, mixed m.p. 189°. G.l.c. of the filtrate gave an 80% yield (based on arsorane) of ethyl hex-2-enoate.

Reaction of \( \alpha \)-(2-bromobenzoyl)methylene triphenylarsorane with Dimethyl acetylenedicarboxylate.

Dimethyl acetylenedicarboxylate (0.28 g.) in tetrahydrofuran (10 ml.) was introduced into a solution of arsorane (1.0 g.) in tetrahydrofuran (40 ml.) The mixture became bright red immediately. After refluxing for 16 hours the solvent was evaporated leaving a red viscous liquid, which, after cooling and trituration with ether, solidified, m.p. 150 - 157°. This adduct was difficult to obtain crystalline. Chromatography from neutral alumina gave the adduct (13a) on elution with ether, m.p. 150 - 159°, i.e. no purer. Finally recrystallised from ethanol-water (0.7 g.) m.p. 164 -167°, \( \nu \)max 1725 s, 1675 s, 1610 m, 1580 m, 1560 w, 1420 s, 1340 w, 1260 w, 1230 s, 1210 w, 1170 s, 1080 s, 1010 m, 995 m, 950 w, 900 s, 855 w, 840 w, 810 s, 790 s, 695 w cm\(^{-1}\); p.m.r. singlet (3 H)\( \tau \) 6.74, singlet (3 H) \( \tau \) 6.25, singlet (1 H)\( \tau \) 4.15, multiplet (19 H)\( \tau \) 2.0 - 3.0.
Treatment of this ylid with perchloric acid gave a solid m.p. (chloroform-ethyl acetate) 144 - 148°.

$\nu_{\text{max}}$ 1770 s, 1725 s, 1675 s, 1610 w, 1590 m, 1310 m, 1280 m, 1250 m, 1220 m, broad 1100 - 1060 s, 1005 s, 960 m, 920 m, 910 m, 875 m, 845 w, 830 m, 790 s, 760 s, 745 s, 690 s cm$^{-1}$

p.m.r. singlet (3 H) $\gamma$6.4, singlet (3 H) $\gamma$6.2 (ester methyls), singlet (1 H) $\gamma$ 3.15 (conjugated olefin proton), multiplet (19 H) $\gamma$2.1 - 2.7 (aromatics), singlet (1 H) $\gamma$ 1.98 (proton $\alpha$ to arsorium group). This salt was 1,2-di(methoxycarbonyl)-3-$\eta$-bromobenzoyl-allyltriphénylarsonium bromide. Found C 51.24; H 3.84%; calculated for C$_{52}$H$_{27}$As Br Cl 0.9 C 51.52; H 3.62%.

Reaction of Ethoxycarbonylmethylene triphenylarsorane with Dimethyl Acetylendicarboxylate.

The acetylene (0.1 g.) in tetrahydrofuran (5 ml.) was introduced to a solution of the arsorane (0.25 g.) in tetrahydrofuran (10 ml.). After 2 days at room temperature the solvent was removed and addition of ether to the liquor caused the slow crystallisation of a yellow solid (0.2 g.) m.p. 146 - 150°, vigorous at 190°. Recrystallisation caused deterioration of the adduct (13b), $\nu_{\text{max}}$ 1720 m, 1690 m, 1650 s, 1575 w, 1520 m, 1420 m, 1320 m, 1240 s, 1170 w, 1125 s, 1080 w, 1055 w, 1040 m, 1015 w, 1000 m, 860 m, 840 m, 780 m, 740 s, 690 m cm$^{-1}$ p.m.r. triplet (3 H) $\gamma$ 9.0 J$_{HH}$ = 7 c/s (methyl of the ethyl ester), singlet (3 H) $\gamma$ 6.7 (methyl ester) multiplet
consisting of a quartet (–CH$_2$ of ethyl ester) and singlet of methyl ester (5 H $\gamma$ 5.95 – 6.5, singlet (1 H) $\gamma$ 5.3, (conjugated olefinic proton) and a multiplet (15 H) $\gamma$ 2.1 – 2.7 (aromatic protons). The adduct analysis found C 62.99; H 5.16; As 14.08%, calculated for C$_{28}$H$_{27}$AsO $\gamma$ C 62.95; H 5.05; As 14.02%.

**Reaction of Ethoxycarbonylmethylenetriphenylarsorane with Phenylsulphene.**

The arsorane (1.0 g.) and excess triethylamine (0.4 ml) were dissolved in tetrahydrofuran, which was ice-cooled. A solution of benzylsulphonyl chloride (0.48 g.) in tetrahydrofuran was added dropwise. The yellow solution was set aside for 24 hours, when it was subjected to g.l.c. (silicon column at 210°). **Trans-ethyl cinnamate** was identified in 24% yield. (When the reaction was refluxed for 24 hours a 44% yield of ethyl cinnamate was detected). The reaction mixture was concentrated and treated with chloroform and water. The chloroform extract was dried, concentrated and the addition of ether gave a white solid (0.3 g.), which was difficult to recrystallise m.p. (from chloroform and ether) 198°. (a further 0.13 g. of this adduct was obtained from the mother liquor by column chromatography on neutral alumina).

$\nu_{\max}$ 1650 s (ylid-ester carbonyl), 1440 s, 1280 m, 1260 s together with 1115 m (sulphone group), 1090 w, 1070 s, 1035 s,
1000 w (complex arsorane pattern), 920 m, 975 m, 780 m, 750 s, 749 s cm\(^{-1}\); p.m.r. triplet (3 H) \(\gamma \) 9.25, \(J_{HH} \approx 7.5\) c/sec., quartet (2 H) \(\gamma\) 6.1, \(J_{HH} \approx 7.5\) c/sec., singlet (2 H) \(\gamma\) 5.45, multiplet (20 H) \(\gamma\) 2.1 -3.0. Solid identified as \(\alpha\)-benzyl-sulphonyl-\(\alpha\)-ethoxycarbonylmethylenetriphenylarsorane (30% yield). Found C 62.7; H 5.03; S 5.36%, calculated for \(C_{29}H_{27}AsO_4S\) C 63.7, H 4.95; S 5.68%. Chromatography of the mother liquor on neutral alumina gave triphenylarsine (0.2 g.) with petrol, ethyl cinnamate (0.06 g.) with petrol-ether (95 : 5) (0.11 g. from g.l.c.) and adduct (0.13 g.) with ether.

**Reaction of \(\alpha\)-(\(\rho\)-bromobenzoyl)methylenetriphenylarsorane with Phenylsulphine.**

The arsorane (2.5 g.) and triethylamine (0.5 g.) in benzene were cooled in ice and benzylsulphinyl chloride (0.87 g.) was added dropwise. The bright yellow colour of the solution had become colourless after 16 hours. Triethylammonium chloride was filtered off. The mother liquor was washed, dried and evaporated. A crystalline solid (2.5 g.) was obtained. Recrystallisation from a chloroform-ether mixture gave a solid which incorporated diethyl ether. A nujol mull gave \(\nu_{max}\) 1580, 1565 m, 1520 s (ylid carbonyl), 1440 s, 1380 m, 1320 w, 1130 m, 1110 w, 1075 m, 1060 m, 1015 s (sulphoxide), 995 m, 990 m (complex
arsorane pattern), 840 m, 770 m, 740 s, 695 (s) cm\(^{-1}\); p.m.r. broad singlet (2 H) Y 6.2, multiplet (24 H) Y 2.15 - 3.15, and in addition inclusion of 0.5 mol. of diethyl ether. To avoid this the solid was recrystallised from ethanol and water. A nujol mull showed a carbonyl shift from 1520 s to 1495 cm\(^{-1}\). However, the p.m.r. now gave only a singlet (2 H) Y 6.2 and a multiplet (24 H) Y 2.15 - 3.15. This phenomena was reversible, and it was attributed to hydrogen bonding in the solid state. A solution spectra in chloroform of the solid, with carbonyl 1495 cm\(^{-1}\), gave the carbonyl peak 1520 - 1510 cm\(^{-1}\). This product was identified as \(\alpha\)-benzylsulphinyl-\(\alpha\)-(\(\beta\)-bromobenzoyl)methylene-triphenylarsorane. Found C 62.04; H 4.33; S 5.20%; calculated for C\(_{33}\)H\(_{26}\)AsBrO\(_2\)S, C 61.81; H 4.05; S 4.99%.

**Reaction of Ethoxycarbonylmethylene-triphenylarsorane with Phenylsulphine.**

The arsorane (4.35 g.) and triethylamine (1.52 ml.) were dissolved in tetrahydrofuran (50 ml.) and the solution was cooled in ice. Addition of benzyl sulphinyl chloride (1.9 g.) gave a bright yellow coloured solution and a solid separated. After 24 hours at room temperature the reaction mixture was subjected to g.l.c. (silicon column at 210°). No ethyl cinnamate was detected. (When the reaction was repeated in refluxing tetrahydrofuran a 7.2% yield of trans-ethyl cinnamate was found). After evaporation of the solvent a chloroform
extract was washed, dried and divided into two parts.

(1) The first part was evaporated and its infrared spectrum taken. This showed the presence of two carbonyl containing compounds, 1650 cm\(^{-1}\) (conjugated ester) and a 1740 cm\(^{-1}\) (a saturated ester). This mixture was dissolved in hot ethyl acetate and crystals slowly separated m.p. 139 - 140\(^{\circ}\). Recrystallisation from ethyl acetate gave a solid m.p. 140 - 142\(^{\circ}\). Repeated recrystallisations gave a solid (1.4 g.) m.p. 146.5 - 147.5 which remained constant, \(\nu_{\text{max}}\) 1650 s (ylid ester carbonyl) 1440 s, 1280 w, 1240 s, 1080 s (sulphoxide), 1065 m, 1020 s, 1010 m, 1000 (arsorane pattern), 965 m, 880 m, 745 s, 690 s cm\(^{-1}\); p.m.r. complex multiplet (3 H) \(\gamma 8.65\) - 9.35, two multiplets (4 H) \(\gamma 4.4\) - 4.8 and \(\gamma 5.65\) - 6.2, multiplet (20 H) \(\gamma 2.15\) - 3.0. This adduct was thought to be \(\alpha\)-benzylsulphinyl-\(\alpha\)-ethoxycarbonylmethylenetriphenylarsorane (51\% yield), however the analysis was consistently low. Found C 64.50; 64.64; H 5.32; 5.36\%, calculated for \(C_{29}H_{27}AsS_{0.5}\), C 65.9; H 5.11\%.

The mother liquor was enriched with carbonyl compound 1740 but all attempts to obtain this oil pure failed.

(2) The second part of the reaction mixture was chromatographed on neutral alumina. However decomposition of the products occurred as very little eluted. Elution with petrol gave triphenylarsine (0.1 g.), mixed m.p. 60\(^{\circ}\). Elution with ether-petrol (95:5) gave a trace amount of ethyl cinnamate.
(from its infrared spectrum only). Continued elution gave a small quantity of oil which decomposed to ethyl cinnamate on heating. There was insufficient to identify this oil. 
\[ \nu_{\text{max}} 1720 \text{ s.} \]

**Reaction of \( \alpha \)-acetilmethylenetriphenylphosphorane with Phenylsulphine.**

The phosphorane (4.0 g.) and triethylamine (1.27 g.) were dissolved in benzene (50 ml.) and benzylsulphinyl chloride (2.2 g.) was added dropwise with cooling. On warming an immediate precipitate formed. This was filtered after five hours, washed with water and was identified as \( \alpha \)-benzylsulphinyl-\( \alpha \)-acetilmethylenetriphenylphosphorane (4.0 g.) m.p. 201 d.

\[ \nu_{\text{max}} 1560 \text{ s (ylid carbonyl), (the starting phosphorane had an ylid carbonyl peak at 1540 s), 1440 s, 1380 s, 1295 s, 1195 m, 1110 s, 1055 s (sulphoxide), 1010 s, 940 w, 920 w, 870 w, 770 w, 775 m, 695 s cm}^{-1} \text{ p.m.r. singlet (3 H) } \gamma 7.45 \text{ (methyl), an AB system (2 H) } \gamma 5.45 \text{ and } \gamma 5.65, \gamma 5.70 \text{ and } 5.90 \text{ (benzyl protons), multiplet (20) } \gamma 2.15 - 3.0 \text{ (aromatics).} \]

Pound C 73.68; H 5.36; S 7.18%, calculated for C\(_{28}\)H\(_{25}\)O\(_2\)PS, C 73.64; H 5.48; S 7.02%. 
Attempted Preparation of \( \alpha \)-Benzylsulphinyl-\( \alpha \)-acetylmethyltriphenylphosphonium Tetrafluoroborate.

The adduct was dissolved in ethanol and addition of aqueous concentrated hydrobromic acid followed by sodium tetrafluoroborate gave an immediate precipitate. This solid was recrystallised from ethanol-water mixture, m.p. 151°C. Its infrared spectrum showed a saturated carbonyl (1710 cm\(^{-1}\)) and a broad tetrafluoroborate peak (1110 - 1020 s). However the p.m.r. had only a doublet (3 H) \( \gamma 7.65, J = 3\) c/sec, doublet (2H) \( \gamma 5.0, J_{\text{PH}} = 11\) c/sec. and a multiplet (15 H) \( \gamma 2.0 - 2.8\).

The compound appeared to be \( \alpha \)-acetylmethyltriphenylphosphonium tetrafluoroborate. This was prepared by a similar treatment of the acetylmethylene phosphorane, with acid and tetrafluoroborate. It was identical with the product from this reaction.

Found C 62.82; H 5.13%, calculated for \( \text{C}_{21}\text{H}_{20}\text{BF}_{4}\text{OP}, \) C 62.42; H 4.92%.

Reaction of \( \alpha \)-(\( p \)-bromobenzoyl)methylenetriphenylphosphorane with Phenylsulphine.

The phosphorane (4.0 g.) and triethylamine (0.94 g.) were dissolved in benzene and ice-cooled. Benzylsulphinyl chloride (1.67 g.) was added and almost immediately the yellow solution became colourless and deposited a solid. This solid was
filtered off and shown to be a mixture of triethylammonium chloride and product. The reaction mixture was washed with water, dried and evaporated. The product was dissolved in methylene chloride and addition of ether gave a cream solid. Total solids were recrystallised (4.0 g.) m.p. (from ethanol and water) 182.5 °.

$\nu_{\text{max}}$ 1590 m, 1575, 1520 s (ylid carbonyl), 1320 s, 1280 m, 1195 m, 1135 s, 1110 s, 1075 m, 1030 s (sulphoxide), 10005 s, 995 s, 920 m, 890 m, 840 m, 750 s, 720 s, 695 s cm$^{-1}$; p.m.r. the benzyl protons were an AB system (2 H) $\gamma$ 6.0 and 6.2, the aromatics formed three humps $\gamma$ 1.8 - 2.15 (2 H) and $\gamma$ 2.15 - 2.95 - 3.15 (22 H). Compound was $\alpha$-benzylsulphinyl-$\alpha$-($\beta$-bromobenzoyl)-methyleneetriphenylphosphorane. Found C 66.20; H 4.32; S 5.79%, calculated for C$_{35}$H$_{26}$BrO$_2$PS, C 66.23; H 4.35; S 5.35%.

During the work up a new carbonyl compound (1680) formed m.p. 172 °. $\nu_{\text{max}}$ 1680 s, 1600 s, 1380 m, 1260 s, 1220 m, 1160 m, 1055 m, 995 s, 750 s, 720 s, 695 s; p.m.r. singlet (2 H) $\gamma$ 5.95, multiplet (28?H) $\gamma$ 1.8 - 3.0. Found C 59.07; 58.94; H 4.37; 4.42%. This solid was not identified.

Reaction of the Adduct with $\beta$-Nitrobenzaldehyde.

The sulphinylphosphorane (see above), 1.0 g., was treated with $\beta$-nitrobenzaldehyde (0.25 g.) in ethanol. After 7 days at room temperature, no reaction had taken place. The reaction mixture was refluxed, and on cooling, needles crystallised out,
m.p. 162°, recrystallised from ethanol (0.35 g.) m.p. 165° constant.

\[ \nu_{\max} 1670 \text{ s (saturated carbonyl), 1590 m, 1520 s, 1350 s} \]
(nitro-group) 1440 m, 1110 s, 1070 m, 1020 s, 850 m, 835 w, 825 w, 790 w, 750 m, 695 s.

However the p.m.r. spectrum showed only \( \rho \)-substitution in the aromatics, and no aliphatic protons were visible; \( \text{m/e} \ 331 \) or 333, solid was identified as 1-(\( \rho \)-bromobenzoyl)-2-(\( \rho \)-nitrophenyl)ethylene.

Column chromatography gave triphenylphosphine oxide (0.3 g.) and more olefin (0.15 g.), m.p. 165°, Lit. value 166°, Mol. Wt 331/333.

**Reaction of \( \alpha \)-cyanomethylenetriphenylphosphorane with Phenylsulphine.**

\( \alpha \)-Cyanomethyltriphenylenphosphonium chloride (7.0 g.) was dissolved in chloroform and shaken with excess 2N sodium hydroxide for 2 minutes. The chloroform extract was washed, dried and evaporation at 30° gave the cyanophosphorane (5.6 g.), m.p. 193°, \( \nu_{\max} 2150 \text{ cm}^{-1} \).

The phosphorane (4.0 g.) and triethylamine (1.84 ml.) were dissolved in benzene and ice-cooled. Benzylsulphinyl chloride (2.3 g.) was introduced dropwise. After 5 hours at room temperature the benzene solution was washed, dried and evaporated. A white solid from ethyl acetate (30 d), (5.0 g.) m.p. 195°.
$\nu_{\text{max}}$ 2170 s (cyano), 1590 w, 1440 s, 1320 w, 1180 s, 1180 s, 1110 s, 1040 1030 s (sulphoxide), 980 s, 910 m, 870 m, 760 s, 725 s, 695 s cm$^{-1}$; p.m.r. benzyl protons (2 H), AB system $\gamma$ 5.4 and 5.75, multiplet (20 H)$\gamma$ 2.15 – 2.9. Found C 73.94; H 5.19; N 3.32%; calculated for C$_{27}$H$_{22}$NOPS, C 73.78; H 5.01; N 3.19%.
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