AN INVESTIGATION OF SOME IODONIUM AND ARSONIUM YLIDES

being a Thesis

presented by

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to the

UNIVERSITY OF ST. ANDREWS

in application for

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St. Andrews. October, 1980.

TO MUM , DAD AND SANDRA

DECLARATION.

I declare that this Thesis is based on the results of experiments carried out by me, that it is my own composition and has not previously been presented for a Higher Degree.

The work was carried out in the Department of Chemistry of the University of St. Andrews, under the direction of Dr. D.M.G. Lloyd.

CERTIFICATE.

I hereby certify that Mr. William A. Macdonald, B.Sc., has spent eleven terms at research work under my supervision, has fulfilled the conditions of the Resolution of the University Court 1967, No. 1, and is qualified to submit the accompanying thesis in application for the degree of Ph.D.

Director of Research.

UNIVERSITY CAREER.

I entered the University of St. Andrews as an undergraduate in October 1973 and graduated B.Sc. with First Class Honours in Chemistry in July 1977.

The research described in this thesis was carried out between October 1977 and July 1980, during which time I held a Research Studentship awarded by the University of St. Andrews.

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SUMMARY.

Section 1. AN INVESTIGATION OF SOME IODONIUM YLIDES.

Attempts to prepare iodonium ylides from dibenzoylcyclopentadiene, 1,4-diphenylcyclopentadiene or fluorene, and an iodinimine from *p*-toluamide were unsuccessful.

The reactions of phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide and phenyliodonium bis(methoxycarbonyl)methylide with *p*-nitrobenzaldehyde were studied and it was concluded that the iodonium ylides decomposed rather than react with *p*-nitrobenzaldehyde in the Wittig reaction.

The copper catalysed decomposition of these iodonium ylides and of phenyliodonium-benzoylacetmethylide and-dibenzoylmethylide in the presence of triphenylarsine and other carbene acceptors was investigated. These four iodonium ylides were heated with triphenylarsine in the presence of a variety of copper and other transition metal compounds, and only copper compounds were found to be effective as catalysts. The results suggest that the catalyst has an organisational role and furthermore, complexing with the ylide may well weaken the $\overset{-}{C} - \overset{+}{I}$ bond and then stabilise the intermediate carbene.

Section 2. AN INVESTIGATION OF SOME TRIARYLARSONIUM YLIDES.

The preparation of triphenylarsonium ylides by the thermal decomposition of diazo-2,3,4-triphenylcyclopentadiene or diazo-2,3,4,5-tetraphenylcyclopentadiene in the presence of triphenylarsine has been improved by using copper acetylacetonate to catalyse the reaction and the reaction has been extended to the preparation of tri-*p*-tolyl, tri-*m*-tolyl, tri-*p*-methoxyphenyl, tri-*o*-tolyl, and tri-*o*-methoxyphenylarsonium ylides.

An attempt to prepare tri-*o*-tolylarsonium 2,4-diphenylcyclopentadiene by condensing 1,4-diphenylcyclopentadiene with tri-*o*-tolylarsine oxide was unsuccessful as were attempts to prepare various tri-*o*-tolylarsonium ylides of β-dicarbonyl compounds in a similar manner. Tri-*o*-tolylarsine oxide was successfully condensed with ethyl cyanoacetate and dicyanomethane to give the corresponding arsonium ylides. Tri-*p*-tolyl, and tri-*p*-methoxyphenylarsonium cyanoethoxycarbonylmethylides were prepared in an analogous manner.

pK_a measurements of some triarylarsonium 2,3,4-triphenylcyclopentadienylides and 2,3,4,5-tetraphenylcyclopentadienylides suggested that the tri-*o*-tolylarsonium ylides were less basic than the triphenylarsonium ylides, and that tri-*p*-tolylarsonium 2,3,4-triphenylcyclopentadienylide was more basic than the corresponding triphenylarsonium ylide. The reactions of these and of other triarylarsonium ylides with carbonyl compounds and with nitrosobenzene were investigated to see if their reactivity paralleled their basicity. The para-substituted ylides were not found to be more reactive than triphenylarsonium ylides, but the ortho-substituted ylides were far less reactive. Tri-*o*-methoxyphenylarsonium 2,3,4-triphenylcyclopentadienylide was found to be more reactive than the corresponding tri-*o*-tolylarsonium ylide. Furthermore, in the reaction of the triarylarsonium 2,3,4,5-tetraphenylcyclopentadienylides with nitrosobenzene, donating substituents on the phenyl group of the arsenic influenced the reaction course.

The acetylation of the triarylarsonium 2,3,4-triphenylcyclopentadienylides was studied.

Tri-*p*-tolylarsonium- and tri-*p*-methoxyphenylarsonium-2,3,4,5-tetraphenylcylcopentadienylides were found to undergo methanolysis to give 1,2,3,4-tetraphenylcyclopentadiene and the corresponding triarylarsine oxide.

The reactions of the triarylarsonium cyanoethoxycarbonylmethylides with carbonyl compounds followed the same trend shown by the triarylarsonium 2,3,4-triphenylcyclopentadienylides. Tri-*o*-tolylarsonium dicyanomethylide was found to be unreactive.

Tri-*o*-tolylarsonium benzylide reacted with benzaldehyde to give the same ratio of products as did triphenylarsonium benzylide.

The factors that could influence the reactivity of these triarylarsonium ylides are discussed and it is proposed that the unreactivity of the ortho-substituted ylides is mainly due to steric factors.

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PART II.

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EXPERIMENTAL

EXPERIMENTAL (continued)

PART I. INTRODUCTION.

1. YLIDES.

Ylides have been defined[1] as compounds in which a carbanionic centre is attached to a heteroatom that carries a high degree of positive charge, and can be represented by the general formula (1a) although there may also be a contribution from a covalent structure (1b).

(a) 1 (b)

The precise nature of the C-X bonding is very much in debate. In the apolar form (1b) the most usual description is in terms of overlap between a filled 2pπ orbital of the methylene carbon, which is believed to be sp^2 hybridized[2,3] and a vacant d-orbital of the heteroatom. Frequently in this account ylides will be represented in formulae by only one canonical form, but it is generally assumed that the other form(s) also contribute to the overall structure.

The special feature of ylides that makes them worthy of study is the stabilisation of the potential carbanionic centre afforded by the adjacent heteronium group. Thus many ylides are isolable as crystalline solids whereas normal carbanions are very reactive towards atmospheric components. Ylides also have special chemical properties which are different from those of simple carbanions and these will be discussed in section 4(c).

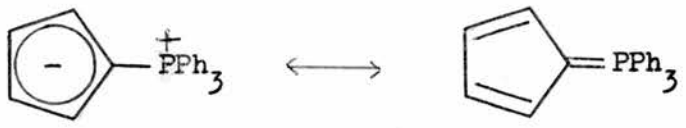
The fact that some ylides are sufficiently stable to be isolated has been attributed to the structural and electronic features which may contribute to stabilisation of the ylidic carbanion. This stabilisation is thought to result from delocalisation of the non-bonded electrons of the carbanion, and is afforded by both the heteronium group (X) and the two carbanion substituents (R, R^1). The nature and effects of these substituents will be discussed in turn.

The heteronium group (X) usually contains an atom belonging to group V or VI of the Periodic Table, commonly nitrogen, phosphorus, arsenic or sulphur[1], although stable ylides have been prepared where the heteroatom is antimony[4], bismuth[5], selenium[6,7], tellurium[8], iodine[9,10], bromine and chlorine[11]. There is evidence for the transient existence of oxygen ylides[12] and the existence of xenonium ylides has also been proposed[13].

In the case of elements of the 2nd row (and below), stabilisation is generally considered to result from delocalisation of the non-bonded electrons on the carbanion into vacant low-lying orbitals of the heteroatom, in the case of phosphorus and sulphur the 3d-orbitals. In this way the heteroatom can expand its valence shell to accommodate ten electrons, a phenomenon well known in phosphorus and sulphur chemistry. The properties of arsenic and antimony are similar to those of phosphorus and sulphur and similar stabilisation of the adjacent carbanion by overlap of the d-orbitals can be expected. The conversion of the arsine or stibine into a quaternary salt will contract the normally diffuse 4d- and 5d-orbitals and make effective overlap possible.

Presumably in the case of ylides containing heteroatoms other than the 1st row elements, similar factors apply.

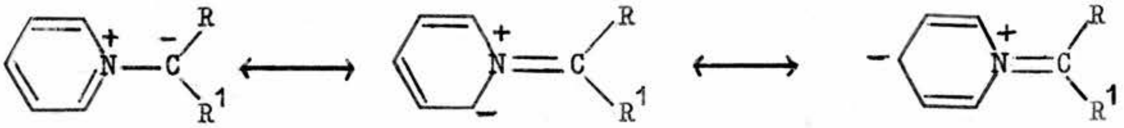
Thus, this involvement of the d-orbitals in π bonding results in a contribution from the covalently bound canonical form (1b) and the extent to which each of the canonical forms (1a) and (1b) contribute to the resonance hybrid can be used to rationalise the observed physical and chemical properties. For instance, the dipole moment of 7.0D for triphenylphosphonium cyclopentadienylide (2a) has been taken to show that the covalently bound canonical form (2b) contributes approximately 50% to the resonance hybrid[14].



(2a) (2b)

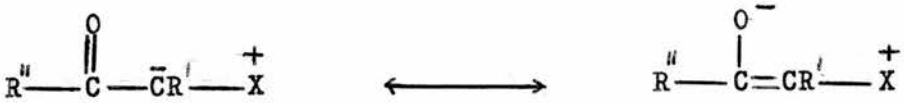
It is worth noting that there are alternative descriptions to the one given above which do not invoke the use of d-orbitals, for instance the qualitative 3-centre-4- electron bonding theory as described by Musher[13], but discussion of these is beyond the scope of this thesis and for our purposes the use of d-orbitals, although not completely justified, provides a satisfactory basis for the experimental evidence.

In the case of the 1st row elements, valence shell expansion cannot occur because the 3s-orbitals of nitrogen (and oxygen), the next available vacant orbitals, are of too high an energy to interact with those of the carbanion. Stabilisation of the ammonium ylide is generally assumed to take place by electrostatic interaction of the opposite charges and thus an ammonium group is much less effective for carbanion stabilisation than heteronium groups that can invoke the use of d-orbitals for $p\pi - d\pi$ bonding. Accordingly this gives rise to ylides of lower stability compared to the phosphorus, sulphur and arsenic analogues. Stability is greater in the case of pyridinium ylides and this is probably due to stabilisation of the carbanion by resonance interaction with the pyridinium ring as well as electrostatic interaction with it (3).



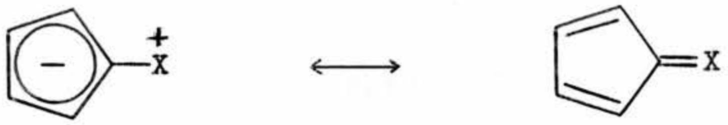
(3)

The carbanion substituents R and R^1 also afford stabilisation by delocalisation of the electron pair on the carbanion and this can be achieved in two ways. First, attachment of electron withdrawing groups can afford stabilisation by inductive and/or conjugative effects. For instance, the carbonyl group in ((1) R = R''CO) affords stabilisation by a contribution from the enolate structure (4b).



(4a) (4b)

Similar stabilisation results from use of cyano, sulphonyl or nitro groups, while groups with a purely inductive effect such as pentafluorophenyl are also of value. The second method entails the incorporation of the carbanion into an aromatic system such as the cyclopentadienide (5), indenide or fluorenide ring systems, which have stable sextets of π electrons[15].



(5a) (5b)

2. PREPARATION OF YLIDES.

The commonest method used for the preparation of ylides is the so-called "salt method". In this method a suitable heteronium salt is prepared which has an acidic hydrogen atom on one of the substituent groups. Treatment with base removes this hydrogen atom and provides the ylide as illustrated by the preparation of the phenacylides (6)[16,17,18].

$$\overset{+}{X}\text{-}CH_2COPh \quad Br^- \xrightarrow{\text{base}} X{=}CHCOPh$$

$$X = PR_3, AsR_3, SR_2 \qquad\qquad (6)$$

Another method starts from the dihalogeno-compounds (7) which reacts with a compound having a reactive methylene group, in the presence of base, to give an ylide[19].

$$\mathrm{Ph_3XCl_2 + CH_2(CN)_2 \xrightarrow{Et_3N} Ph_3X{=}C(CN)_2}$$

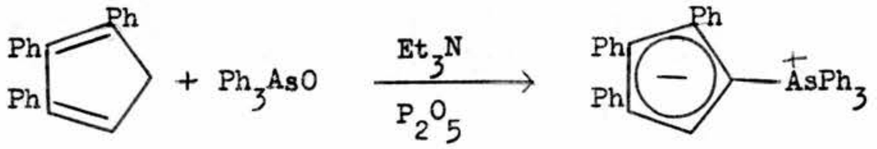
(7)

X = As,P.

A third method, by means of which sulphonium and arsonium ylides have been prepared, involves the reaction of reactive methylene compounds e.g.(8)[20] and (9)[21] with sulphoxides or arsine oxides in the presence of a suitable catalyst such as phosphorus pentoxide or acetic anhydride.

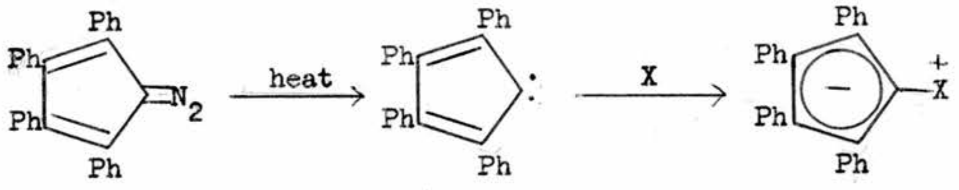
$$\mathrm{CH_2(CN)_2 + MeSO_2 \xrightarrow[\text{or } Et_3N,P_2O_5]{Ac_2O} Me_2S{=}C(CN)_2}$$

(8)



(9)

Ylides with a wide range of different heteroatoms have been prepared by utilising a futher method involving the thermal or photolytic decomposition of diazo-compounds in the presence of a carbene acceptor. An example of this method is (10)[4,5,6,8,22].



(10)

X = pyridine, PPh_3, $AsPh_3$, $SbPh_3$, $BiPh_3$, SPh_2, $SePh_2$, $TePh_2$.

This method has been extended and improved by the addition of a copper catalyst to the reaction mixture and this will be discussed in more detail in section 6.

3. PHYSICAL PROPERTIES OF YLIDES.

The structure of most of the ylides so far prepared have been determined on the basis of their chemical properties and also by physical means. Most of the properties of ylides which are of interest concern either directly or indirectly their relative stabilities and this is intimately connected with the polarity of the ylide bond. Much important information about the nature of bonding in ylides, particularly the carbon to heteroatom bond, has been derived from X-ray and dipole moment studies, and basicity (pK_a) measurements. Other techniques that have been used to study the physical parameters of the ylides include ultra-violet and infra-red spectroscopy, nuclear magnetic resonance spectroscopy (both of ^1H and ^{13}C nuclei) and mass spectrometry. These will be discussed in turn.

X-ray studies of some phosphorus[23], sulphur[24,25] and arsenic[26] ylides have shown that the ylide carbon to heteroatom distance is intermediate between a $C - X$ single bond and a $C = X$ double bond and this provides evidence for π bonding in ylides. For instance, in the phosphonium ylides studied, the ylide carbon to phosphorus distance was found to lie in the range 1.66 - 1.74 Å, a distance intermediate between the values known for $C - P$ single bonds[27] (1.85Å) and those for $C = P$ double bonds[28] (1.66Å). The overlap of a filled 2p - orbital of the methylene carbon, which is believed to be sp^2 hybridised[2,3], with a vacant 3d-orbital of phosphorus is envisaged, and the value of the overlap integral has been shown[29] to be sufficient for formation of a $p\pi - d\pi$ bond. Triphenylphosphonium methylide (11) was found to have a carbon to phosphorus bond

$$Ph_3\overset{+}{P} \text{ —— } \overset{-}{C}RR^1 \qquad\qquad Ph_3P = CRR^1$$

(11a) (11b)

length of 1.66Å which indicates an almost fully covalent C = P double bond consistent with the lack of stabilisation of the dipolar form (11a). In compounds where stabilisation of the dipolar structure is enhanced by the attachment of electron withdrawing groups (e.g. $R = SO_2C_6H_4Me_{(\underline{p})}$, $R^1 = H$), the ylide carbon to phosphorus bond length is longer (1.71Å), showing an increased contribution of the dipolar structure (11a). This is consistent with other physical data.

In the case of the one nitrogen ylide on which X-ray measurements have been reported[30], namely pyridinium dicyanomethylide (12), the ylide carbon to nitrogen bond distance is 1.41Å which is only slightly shorter than the distance calculated for a C - N single bond[28] (1.47Å). This illustrates the inability of nitrogen to undergo valence shell expansion.

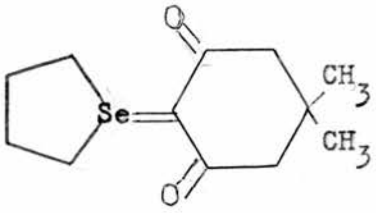
$$C_6H_5\overset{+}{N} - \overset{-}{C}(CN)_2$$

(12)

The structures of the stabilised selenonium ylides (13)[31] and (14)[32] have been studied by X-ray crystallography. In both molecules the

$Ph_2Se{=}C(COMe)_2$

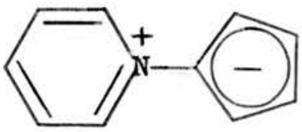
(13)



(14)

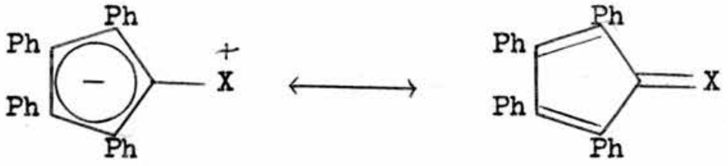
length of the ylide C - Se bond indicates a large contribution from the dipolar form.

Since all ylides have some measure of dipolar character, they all have dipole moments, which for many ylides commonly lie in the range 5.0 to 7.0D. These dipole moment measurements give a good indication of the extent of the delocalisation of charge in the molecule and may be used to assess the contribution made by the dipolar forms. Thus the dipole moment of the completely dipolar pyridinium cyclopentadienylide (15) is 13.5D[33], whereas the dipole moment of the only partially dipolar triphenylphosphonium cyclopentadienylide (2) is 7.0D[14] (see section 1).



(15)

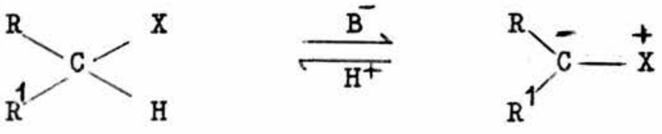
A study of the dipole moments of a series of tetraphenylcyclopentadienylides (16) showed that the order of increasing contribution of the



(16a) (16b)

dipolar canonical form was S < P < As. The triphenylstibonium tetraphenylcyclopentadienylide had an anomalously low dipole moment[34].

Many ylides are soluble in dilute aqueous acid while they are insoluble in water. In other words they are basic and can undergo the reverse reaction used in their formation from salts by basification, with the resulting formation of a conjugate acid (17), and a study of the relative basicity of a series of ylides can shed light on the electronic characteristics of ylides in general.



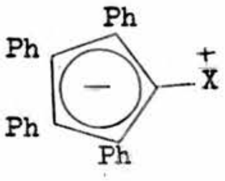
(17) (1a)

The degree of acidity of the conjugate acid (17) is believed to be primarily dependent on the degree of delocalisation of the carbanion electron pair in the resulting ylide (1). As mentioned previously, stabilisation of the carbanionic carbon in a given ylide is achieved either by orbital overlap with the heteroatom (X), or by the attachment of groups (R, R^1) which can delocalise the negative charge. Thus, highly stabilised ylides have a low pK_a and a low basicity, while unstabilised ylides have a high pK_a and high basicity.

The acid dissociation constants (pK_a values) of the conjugate acids of ylides can be measured using spectroscopic methods and comparisons of the acidifying effects of various heteroatoms have been carried out in two series of ylides where the structures are identical except for the alteration of the heteroatom, namely (18)[35] and (16)[36].

Ph-CO-CH=X $\qquad$ X = Ph_3P, Ph_3As, Ph_2S

(18)



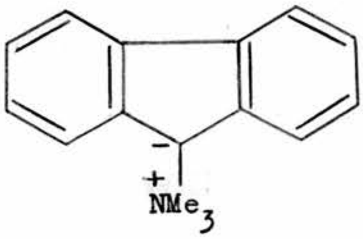
X = Ph_3P, Ph,As, Ph_3Sb, (Ph_3Bi)
Ph_2S, Ph_2Se

(16)

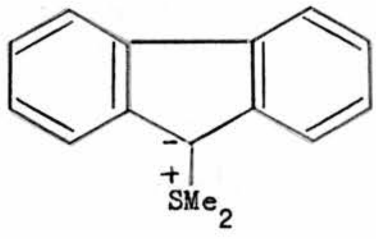
In each case the order of basicity of the ylides as established by pK_a measurements was found to be Sb > As > P > Se > S. This is in agreement with the order established by dipole measurement studies (with the exception of antimony, where the ylide had an anomalously low dipole moment)[34]. The increased basicity as one progresses along the above series is attributed to the decreasing effectiveness of the $p_\pi - d_\pi$ overlap between the carbanionic moiety and the heteroatom and this is believed to be due to the increase in size of the heteroatom, and the d-orbitals becoming more diffuse in character. In addition, the decreasing electrostatic interaction between the carbanionic moieties and the heteronium atom due to the greater length of the C - X bonds and the lower electronegativity of the heteroatom as one goes down the periodic table, would also be expected to result in an increase in basicity.

These arguments can also be used to explain the increased contribution of the dipolar canonical form as one progresses along the above series from sulphur to arsenic.

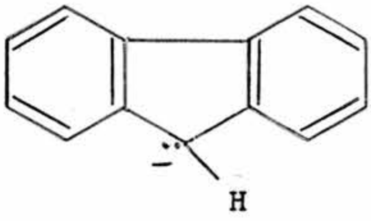
The inability of nitrogen to undergo valence shell expansion is demonstrated strikingly by a comparison of the pK_a's of the conjugate acids of two ylides in the fluorene series, (19) and (20).



(19)



(20)



(21)

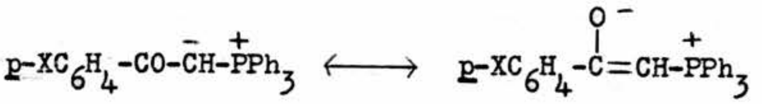
The fluorenyl anion (21) can be formed from fluorene by treatment with a variety of bases such as butyllithium, and the pK_a of the conjugate acid, fluorene, is about 25[37]. By comparison the conjugate acid of the nitrogen ylide (19)[38] has a pK_a only a little less than that of fluorene and the pKa of the conjugate acid of the sulphonium ylide (20) is 7.3[39]. This very low basicity of the ylide (20) reflects the ability of the dimethylsulphonium group to stabilise an adjacent carbanion by use of its vacant low-lying 3d-orbitals, whereas the high basicity of the trimethylammonium ylide can be taken as strong evidence that this stabilisation is absent, which, as stated earlier (see section 1) is because the next available empty orbitals of the nitrogen are unable to interact with those of the carbanion.

The nature of the substituent groups on the heteroatom also has an important effect on the pK_a of the ylide. In the series (18) quoted above, the groups were phenyl, but similar measurements were also made for X = Me_2S, Me_3P, Me_3As, MeSPh, Me_2PPh, Me_2AsPh or Bu_3P, Bu_3As. In both cases a similar order is found with respect to change of heteroatom. On changing the substituent groups progressively from phenyl to methyl, a marked increase is found in the basicity of the ylide in each series. The dipole moment has also been found to increase on changing from triphenyl to tri-n-butylphosphine in the phosphonium fluorenylides[40,41]. There must therefore be more double bond character in the carbon-phosphorous bond of the triphenylphosphonium ylide than of the trialkylphosphonium ylide and the 3d-orbitals of the triphenylphosphonium group must provide better overlap with the filled 2p-orbitals of the carbanion than do those of the trialkylphosphonium group. From the proposal of Jaffe[42] and Craig[29,43] that π bonding with an atom carrying vacant d-orbitals is more efficient when the atom carries a positive charge, it follows that a lower electron density is induced on the phosphorus atom by the phenyl substituents than by the methyl or n - butyl substituents. The phenyl groups are therefore electron withdrawing with respect to the alkyl groups. There are other instances when the phenyl group has been observed to be electron withdrawing. For example, a study of the pK_a values of bicyclic quinuclidine systems incorporating a phenyl ring showed that the phenyl group has an electron withdrawing effect[44].

In a series of tri (p - X - phenyl) phosphonium fluorenylides, it was found[41] that when X was an electron withdrawing group the ylide was less basic than when X was hydrogen, and the converse applied when

X was an electron donating group. These reports substantiate the foregoing account of the increased stability of arylphosphonium ylides over their alkyl counterparts and presumably the same considerations apply to the other heteronium ylides.

The effect of the carbanion substituents ((1), R, R^1) is somewhat simpler to evaluate. The order of decreasing basicity for ylides of a given heteroatom parallels the abilities of the substituents (R, R^1) to delocalise the electrons on the carbanion. A study of the pK_a values of the conjugate acids of a series of acylated triphenylphosphonium methylides[45] (22), showed that the pK_a's of the salts lay in the order $X = NO_2 < H < OMe$.

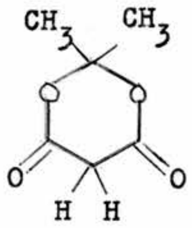


$$\underline{p}\text{-}XC_6H_4\text{-}CO\text{-}\overset{-}{C}H\text{-}\overset{+}{P}Ph_3 \longleftrightarrow \underline{p}\text{-}XC_6H_4\text{-}\overset{O^-}{\overset{|}{C}}{=}CH\text{-}\overset{+}{P}Ph_3$$

(22a) (22b)

Thus, when R = _p_ - nitrophenyl the carbonyl group is more electron deficient and therefore better able to accept electron density from the carbanion by resonance. The converse is true for the _p_ - anisyl case.

Evidence for resonance interaction of the ylide carbanion with an electron withdrawing group such as CO, CN, NO_2, SO_2 can be obtained by the use of infra-red spectroscopy. A study of the infra-red spectra of a series of arsonium ylides stabilised by such groups showed[46] that the delocalisation of the negative charge into these groups resulted in the stretching frequency being uniformly low. For instance, the carbonyl absorption frequencies of 2,2 - dimethyl - 1,3 - dioxan - 4,6 - dione (Meldrums acid) (23) occur at 1740 and 1785 cm^{-1} whereas triphenylarsonium - 2,2 - dimethyl - (4,6 - dioxo - 1,3 - dioxan) - ylide (24) shows two absorptions at 1685 and 1635 cm^{-1}.



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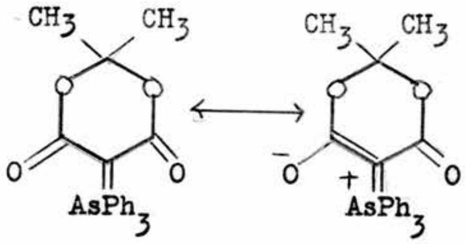
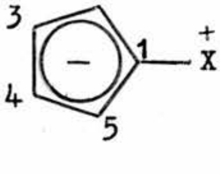


(24)

The stretching frequencies of the above series of arsonium ylides are lower than the frequencies associated with the corresponding phosphonium ylides. This is in keeping with the assumption that the dipolar canonical form makes a greater contribution to the overall structure of arsonium ylides than it does in phosphonium ylides.

^{1}H and ^{13}C nuclear magnetic resonance spectroscopy can be very useful in showing the extent and location of charge in ylides. In those ylides where the carbanion is incorporated into an aromatic system, for instance the cyclopentadienylides (25), an examination of the vicinal proton coupling constants of the three ylides has shown that there is

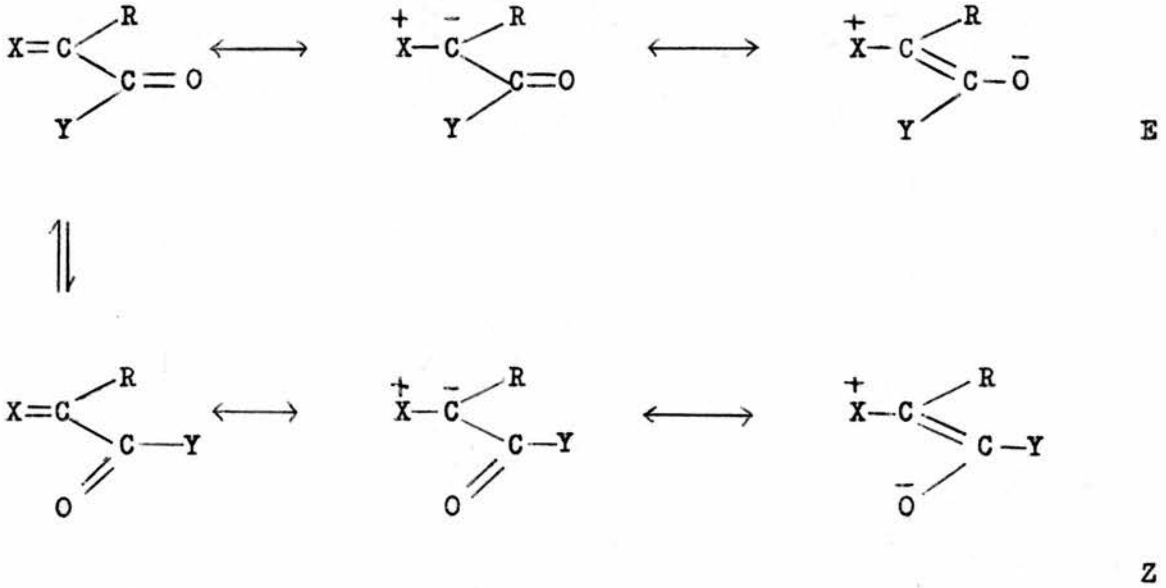


X = SMe$_2$, PPh$_3$, AsPh$_3$.

(25)

extensive delocalisation of the negative charge throughout the ring[47]. A more detailed comparison of the differences in the bond orders of the $C_2 - C_3$ and $C_3 - C_4$ bonds has shown that the greatest charge delocalisation occurs when X = $AsPh_3$, which is in accord with dipole moment studies.

There has been considerable interest[48, 49, 50] in the configurational stability of carbonyl substituted ylides and the possible geometric isomerism about the α,β - C - C bond, which will have partial double bond character due to contributions from enolate forms (26).



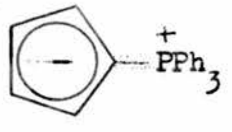
X PPh_3,$AsPh_3$,SMe_2

(26)

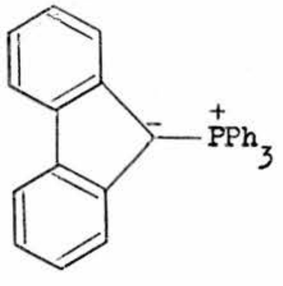
Variable temperature studies on phosphonium[48,49], arsonium[49,50,46] and sulphonium[50,51] ylides have provided data confirming such isomerism and also the energy barrier to interconversion of the isomers. The cisoid - structures (26 Z) were found generally to be the major contributing forms.

^1H nuclear magnetic resonance spectra may also give some information on the hybridisation about the carbon atom in ylides. In triphenylphosphonium methylide the ylide carbon appeared to be sp^2 hybridised, but in triphenylarsonium methylide the ylide carbon appeared to be sp^3 hybridised[52].

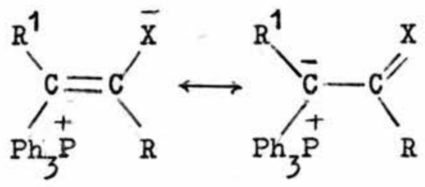
Little has been reported on the ^{13}C nuclear magnetic resonance spectra of ylides. A report of the ^{13}C spectra of some phosphonium ylides (2) (27) and (28) suggested[53] that the negative charge was



(2)



(27)



(28) (28b)

more delocalised in the cyclopentadienylide (2) than in the fluorenylide (27) and that with ylides of the type (28) the charge appeared to be localised on the ylide carbon as exemplified by (28b). The methylene carbon was considered to be sp^2 hybridised.

No information on arsonium ylides has been obtained from ^{13}C spectroscopy and generally in the ^{13}C spectra of arsonium ylides the signal of the carbanion carbon adjacent to the arsenic is not apparent[54].

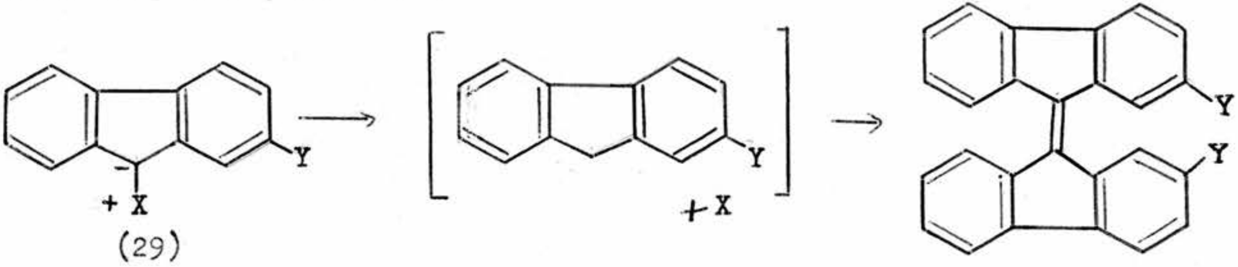
Further information about the extent to which each of the canonical forms contributes to the resonance hybrid can be obtained from ultraviolet spectroscopy. In the series of tetraphenylcyclopentadienylides (16), the absorption maxima shift to longer wavelengths as the group is descended (ie, from P to Bi), indicating increased contribution from the dipolar form. This is in agreement with the data obtained from other physical methods. From the observations that only the bismuthonium and pyridinium ylides are deeply coloured and show solvatochromism it can be inferred that there is considerable similarity between the electronic structure of the two ylides. The apolar canonical form is not possible for the pyridinium ylide and it would therefore appear likely that this apolar form is not possible for the bismuthonium ylide, presumably because overlap of the very large and diffuse 6d-orbitals of bismuth with the orbitals of the cyclopentadiene ring is minimal.

Finally, mass spectrometry can give information on the stability of the ylide carbon-heteroatom bond. The characteristic fragmentation pattern of the triphenylarsonium ylides is the loss of the carbanionic moiety followed by breakdown of the triphenylarsine portion[46]. However, little information is available about electron-impact induced fragmentation of ylides.

4. CHEMICAL PROPERTIES OF YLIDES.

a) Chemical Stability.

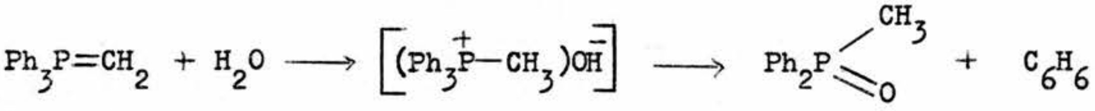
The chemical reactivity of ylides is related to the polarity of the ylide bond and the extent to which the carbanionic centre is stabilised. Ylides may decompose to give a carbene and a neutral molecule, the ease with which this takes place being related to the strength of the ylide bond (this is similar to the reaction that occurs in the mass spectrometer). Phosphonium and arsonium ylides, in general, do not appear to be thermodynamically unstable, whereas, in comparison, sulphonium and ammonium ylides show a greater tendency to decompose spontaneously via the formation of a carbene intermediate. An example of this is provided by the fluorenylides[55,56] (29) which are believed to react with another molecule of ylide to give the isolated product, an olefin.



(29)

X= SMe_2, Y = NO_2 X = NMe_3, Y = H

Many ylides are unaffected by atmospheric components, particularly oxygen and moisture. Stabilised phosphonium, arsonium and sulphonium ylides are usually inert to oxygen, whereas their nitrogen counterparts often decompose rapidly when kept in air and more slowly under nitrogen. The order of stability to hydrolysis of ylides of a given heteroatom appears to parallel the basicity of the ylides. For instance, whereas triphenylphosphonium alkylides hydrolyse spontaneously in the presence of moisture more stable ylides such as the fluorenylide must be heated under reflux with alcoholic sodium hydroxide to effect complete hydrolysis[57], and triphenylphosphonium cyclopentadienylide is inert to such conditions[58]. The initial attack is believed to proceed by formation of an unstable phosphonium (or arsonium) hydroxide (30) which decomposes rapidly to give the phosphine (or arsine) oxide[59].



$$Ph_3P{=}CH_2 + H_2O \longrightarrow \left[(Ph_3\overset{+}{P}{-}CH_3)\overset{-}{OH}\right] \longrightarrow Ph_2P(CH_3){=}O + C_6H_6$$

(30)

In the case of sulphonium ylides the sulphonium hydroxide (31) decomposes to give a sulphide and an alcohol[60].

$$R_2C{=}S(CH_3)_2 + H_2O \rightarrow \left[R_2CH{-}\overset{+}{S}(CH_3)_2\ \overset{-}{OH}\right] \rightarrow R_2CHOH + (Me_2)S$$

(31)

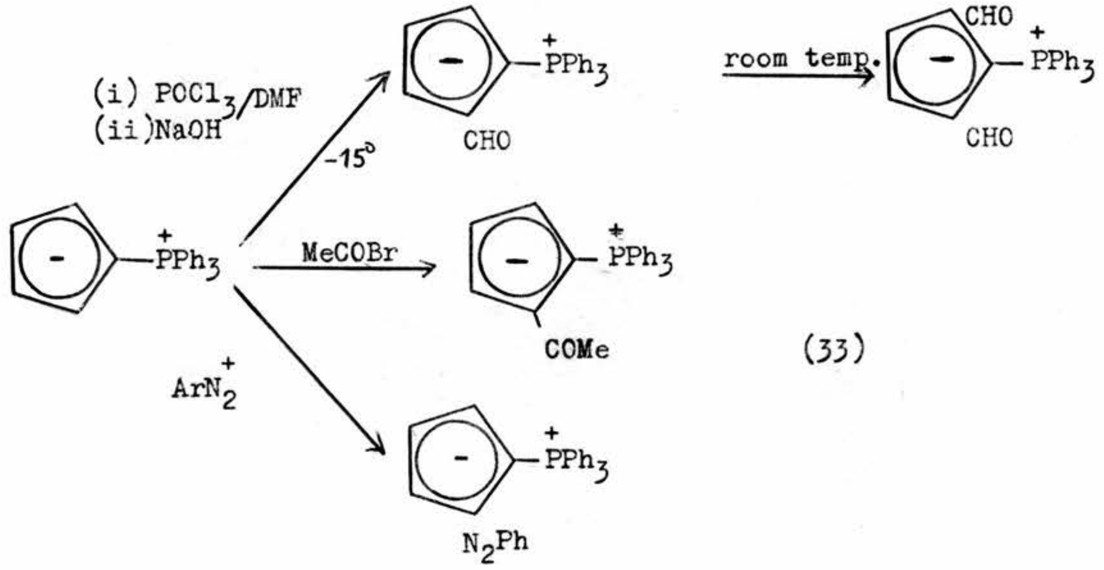
b) Carbanionic reactions.

If an ylide is sufficiently dipolar, electrophiles may attack it at the carbanionic centre. The heteronium group plays no role other than stabilisation of the carbanion, and is retained in the product. Reactions of this type include reactions with a wide variety of electrophiles and an example is shown in (32)[46].

$$Ph_3\overset{+}{As}{-}\overset{-}{C}HCOPh \xrightarrow{(PhCO)_2O} \underset{(PhCO_2^-)}{\left[Ph_3\overset{+}{As}{-}CH(COPh)_2\right]} \longrightarrow Ph_3\overset{+}{As}{-}\overset{-}{C}(COPh)_2$$

(32)

If the negative charge is delocalised onto other parts of the molecule reaction may ensue at an atom not directly attached to the heteroatom as shown in (33)[61, 62].

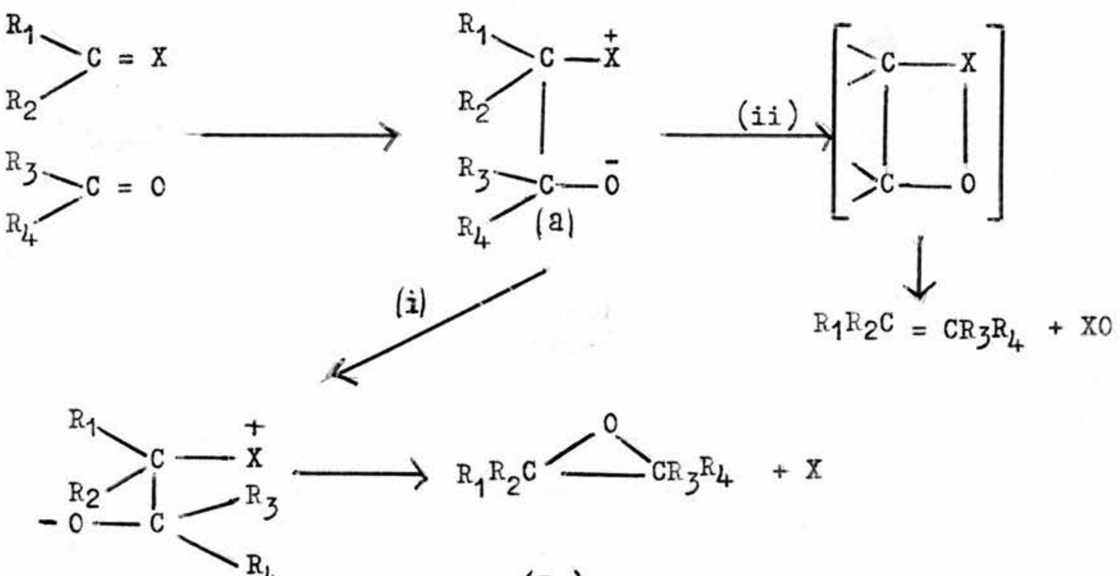


(33)

c) <u>The Wittig Reaction</u>.

The Wittig reaction, involving a condensation-elimination reaction between an ylide and an aldehyde or ketone, is of great synthetic importance and variations in the mode of reactions of ylides with carbonyl compounds are of great interest.

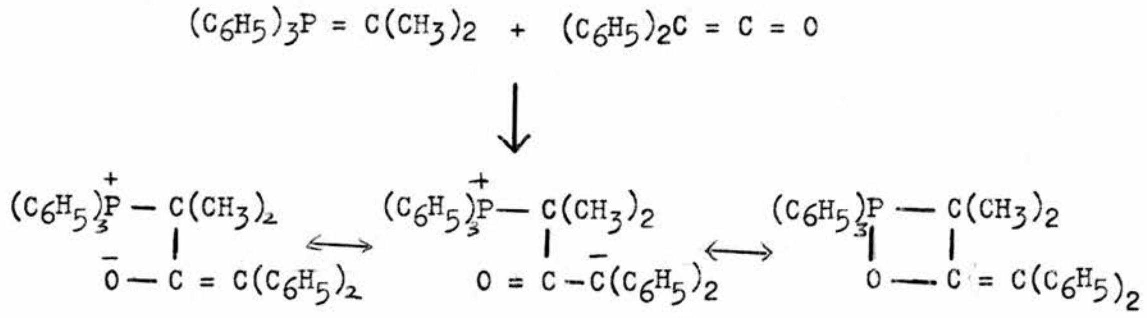
Phosphonium ylides react with carbonyl compounds to give olefins while sulphonium ylides give exclusively epoxides, but arsonium ylides can give either product. The reation is believed to proceed via a betaine intermediate. (34a)



(34)

There is considerable evidence to support the proposal that betaines are intermediates in the Wittig reaction and it has been possible to isolate the betaines as their conjugate acids from the reaction of some phosphonium ylides with carbonyl compounds[63].

The isolation and characterisation of a betaine obtained from the reaction of triphenylphosphonium isopropylidene with diphenylketene provided an opportunity to obtain evidence pertaining to the structure of the betaine - mainly to the question of open chain structure (35a) versus the cyclic structure (35b)[64].



(35a) (35b)

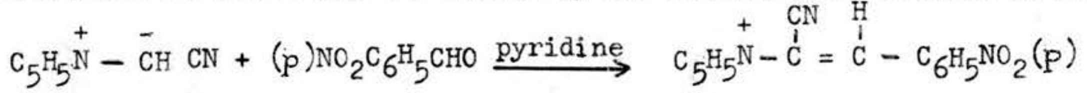
Dipole moment and P^{31} nuclear magnetic resonance studies suggest that the betaine structure involves considerable association between the oxyanion and the phosphonium group and therefore structure (35b) contributes appreciably in this case.

The reaction initially involves the nucleophilic attack by an ylide carbanion on the carbonyl carbon to form a betaine intermediate and the inability of some very stable ylides to react is attributed to their lack of nucleophilicity as a result of increased delocalisation of the carbanion's negative charge.

Whether the reaction follows path (34i) or (34ii) is influenced by the strength of the X=O bond and the leaving abilities of the group X. The apparent driving force for path (34i) in the case of phosphonium ylides, is the formation of the P=O bond, a high energy bond. The S=O bond is a weaker bond; the driving force to path (34i) is thus diminished and nucleophilic substitution of the heteroatom by the oxygen to give the epoxide takes place instead. In addition, the sulphide group is a good leaving group and these two factors together may explain why epoxide formation is favoured over olefin formation from the betaine.

Arsonium ylides exhibit intermediate behaviour. The As=O bond is intermediate in strength between the P=O and the S=O bond and the triarylarsonium group is a good leaving group. Thus the Wittig reaction may proceed by either path (34i) or (34ii) and the factors affecting the mechanism of this reaction will be discussed in more detail later.

In a similar manner to arsonium ylides, stibonium ylides can react with carbonyl compounds to give a mixture of the alkene and the alkene oxide, but with selenonium ylides only the epoxide is obtained. Pyridinium ylides also react with aldehydes, but in a manner different from other ylides. The reaction is analogous to that of any active methylene compound with an aldehyde, the Knoevenagel reaction (36).



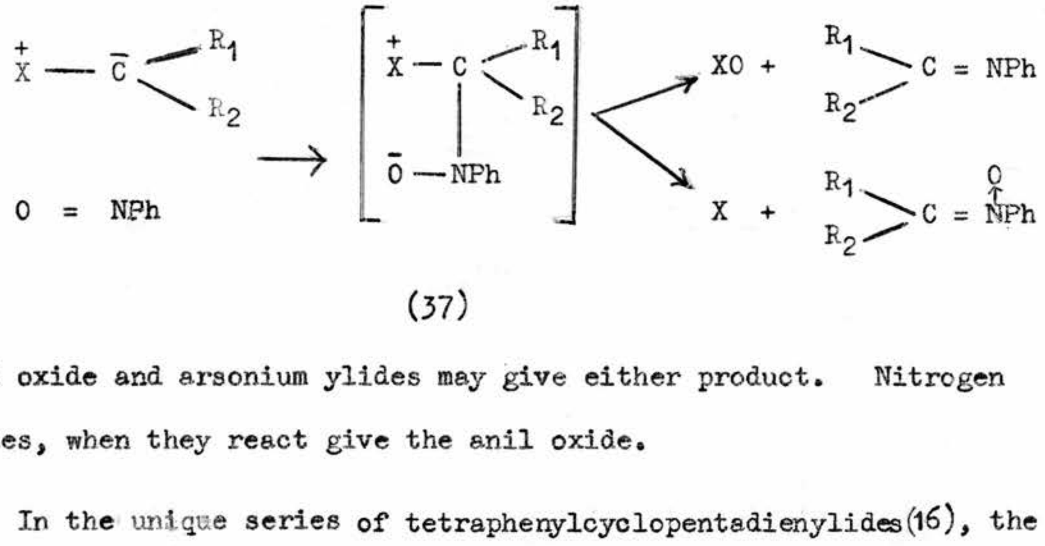
$$C_5H_5\overset{+}{N} - \overset{-}{C}H\ CN + (p)NO_2C_6H_5CHO \xrightarrow{\text{pyridine}} C_5H_5\overset{+}{N} - \overset{CN}{C} = \overset{H}{C} - C_6H_5NO_2(p)$$

(36)

An olefin is formed but the pyridinium group is retained[65].

There are no reported cases of ammonium ylides reacting with carbonyl compounds to give Wittig products, but there are instances of the intermediate betaine being obtained[66].

An analogous reaction is that of ylides with nitrosobenzene and the reaction follows a similar pathway as shown in (37). Again phosphonium ylides normally give the anil, sulphonium ylides the anil oxide and arsonium ylides may give either product. Nitrogen ylides, when they react give the anil oxide.

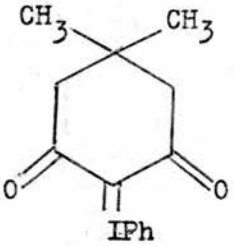


(37)

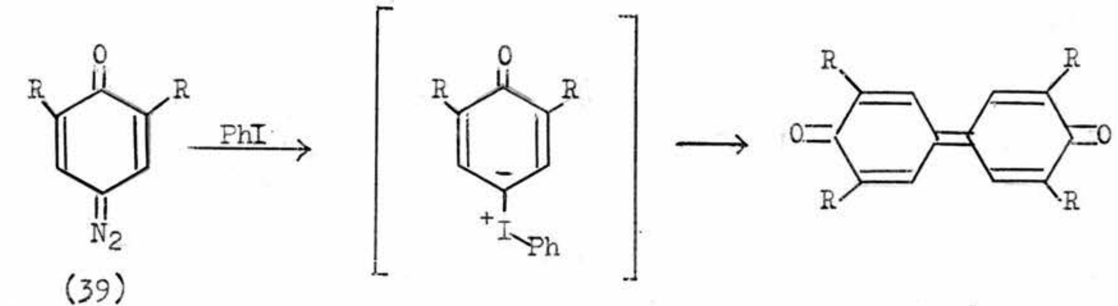
In the unique series of tetraphenylcyclopentadienylides (16), the nucleophilicity of the ylides as indicated in the reaction with aldehydes and nitrosobenzene has been shown to lie in the order Sb > As > Se > S > P, which does not exactly parallel the order of their basicities [26] (see section 3). This illustrates the general principle that a precise correlation of these properties cannot be assumed for the good reason that basicities are concerned only with the measurements of a simple equilibrium involving a small electrophile (proton), whereas nucleophilic attack on reagents such as aldehydes involves a more complex series of events and is subject to greater steric effects.

5. IODONIUM YLIDES.

Iodonium ylides have been known to exist since the late 1950's when the preparation of phenyliodonium 4, 4 -dimethyl -2, 6 - dioxo-cyclohexylide (38) was reported[67]. Since then iodonium ylides of a large number of β-dicarbonyl compounds[9] have been prepared, and, in addition, iodonium ylides wherein the anionic moiety is part of a cyclopentadiene system[10] or of a heterocyclic system such as imidazole[11], pyrazole,[68] indole[69] and pyrole[69] have been obtained. In all the ylides that have been isolated to date, the carbanion is stabilised by electron withdrawing groups. No non-stabilised iodonium ylides have been isolated although they have been proposed as reaction intermediates when carbenes are generated in the presence of alkyl or aryl iodides. An illustration of this is the photolysis of compound (39) in the presence of iodobenzene to give the diphenoquinone.[70] (40).



(38)



(39)

$R = C(CH_3)_3$

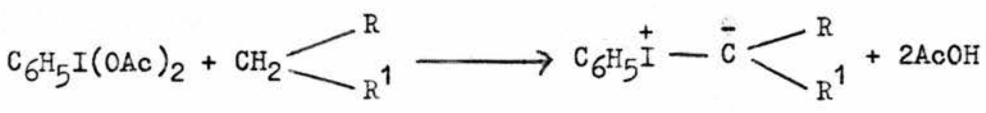
(40)

For the iodine to stabilise an adjacent carbanion it must utilise the large and diffuse 5d-orbitals and it would be expected that overlap between these orbitals and the filled 2p-orbital of the carbon would be poor. Thus, the ylides would be expected to exist mainly in the dipolar form and physical evidence tends to support this.

The preparation and properties of iodonium ylides will be discussed in this section.

a) Preparation.

Extensive work has been carried out on the preparation of phenyliodonium ylides of β-dicarbonyl compounds. It was found that (diacetoxyiodo)benzene reacts with compounds bearing reactive methylene groups, in the presence of base, to give the phenyliodonium ylides (41) and that by using the appropriate (diacetoxyiodo)arene compound, iodonium ylides with substituents on the phenyl group can be prepared[71].



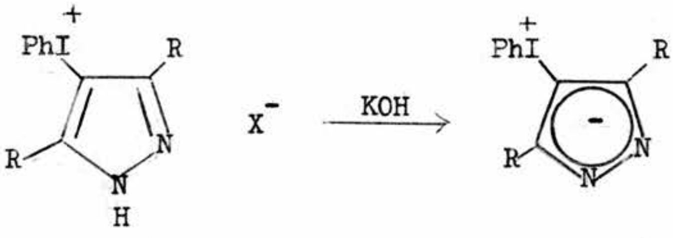
$$C_6H_5I(OAc)_2 + CH_2 < \genfrac{}{}{0pt}{}{R}{R^1} \longrightarrow C_6H_5\overset{+}{I} - \overset{-}{C} < \genfrac{}{}{0pt}{}{R}{R^1} + 2AcOH$$

(41)

This reaction is analogous to the base catalysed condensation of triphenylarsine oxide with reactive methylene compounds (see section 2).

This method has been extended to the preparation of phenyliodonium ylide derivatives of pyrrole and indole[69].

Treatment of some pyrazoles with (diacetoxyiodo)benzene and p-toluenesulphonic acid yields the iodonium tosylate which can be converted into the corresponding salt (42) by an acid HX. Treatment of the salt (42) with potassium hydroxide gives the iodonium ylide (43) in good yields[68].



(42) (43)

Similarly, the reaction of (diacetoxyiodo)arenes with p-toluenesulphonamide in the presence of base results in the formation of a new type of iodonium ylide, aryliodonium-N-tosylimine (44)[72]. These compounds are

$$ArI(OAc)_2 + (\underline{p})\text{-}\ CH_3C_6H_4SO_2NH_2 \xrightarrow[MeOH]{KOH} ArI = NSO_2C_6H_4CH_3(\underline{p}) \quad + 2AcOH$$

$$Ar = C_6H_5,\ \ p\text{-}CH_3C_6H_4,\ \ p - ClC_6H_4 \qquad\qquad (44.)$$

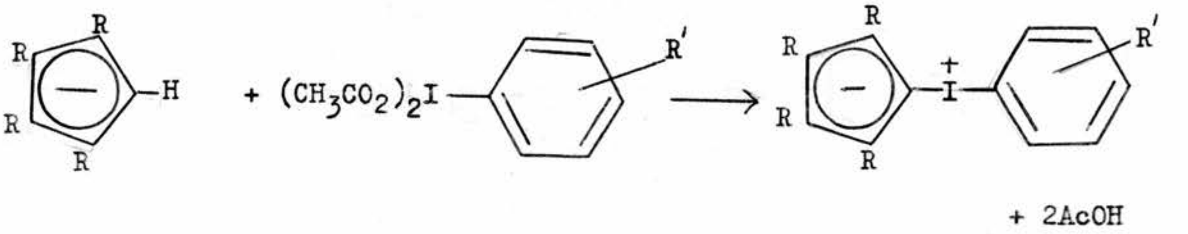
analogous to the phosphinimines (45). Phosphinimines are isoelectronic with phosphonium ylides and their chemistry is very similar.

$$R_3\overset{+}{P} — \overset{-}{N} — R^1 \longleftrightarrow R_3P = N — R^1$$

(45)

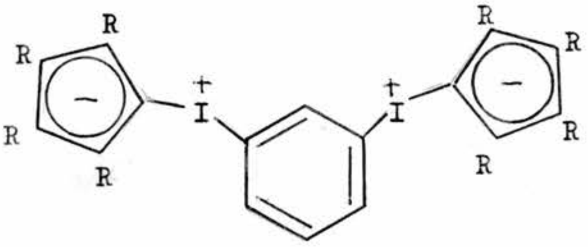
When the imine (44) is stirred with β-dicarbonyl compounds at temperatures from -7 to -20°C the phenyliodonium group is transferred to the latter moiety and this gives another route by which phenyliodonium ylides may be obtained.

Cyclopentadienyl anions with three or four electron withdrawing groups such as CN, CO_2Et or CHO undergo reaction with (diacetoxyiodo) benzenes to give iodonium ylides (46)[10]. The alkali metal salts react with the substrates in glacid acetic acid or in acetonitrile at temperatures between 0-20°C.



(46)

In a similar manner systems with multiple iodonium ylidic centres (47) have been prepared[73].



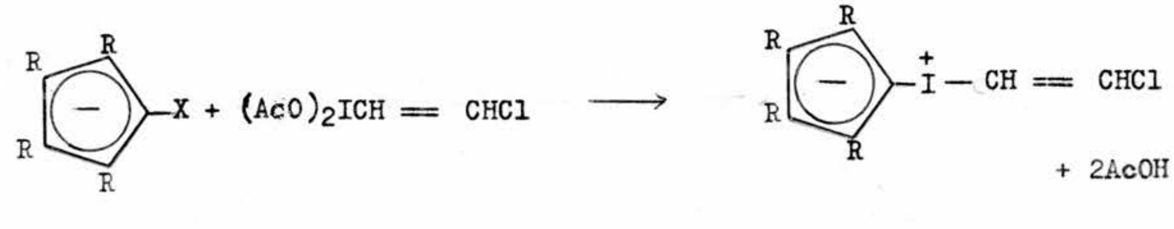
(47)

Increasing cyano-substitution lowers the nucleophilicity of the cyclopentadienyl anion with the result that phenyliodonium 1,2,3,4, - tetracyanocyclopentadienylide cannot be prepared under the above conditions[10]. However, this cyclopentadienyl anion will react with (diacetoxyiodo)benzene in the presence of sulphuric acid. It is assumed that the reaction proceeds via the protonation of (diacetoxyiodo)benzene; a similar reaction occurs in the presence of perchloric acid. This is analogous to the preparation of diphenyliodonium salts from (diacetoxyiodo)benzene and aryl derivatives in the presence of sulphuric acid as shown in (48)[74].

$$ArI(OAc)_2 + Ar^1H + H_2SO_4 \longrightarrow Ar\overset{+}{I}Ar^1 \; HOSO_3^- + 2AcOH$$

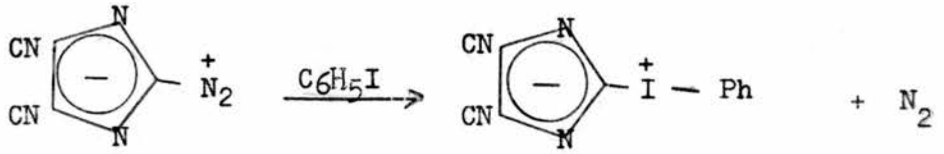
(48)

Substituted cyclopentadienyl anions also react with 2 - (diacetoxyiodo) vinyl chloride in acetonitrile at 20°C to give the previously unknown aliphatic iodonium ylides (49)[10].



(49)

One other preparation of interest is that of phenyliodonium dicyanoimidazylide (50) from diazodicyanoimidazole. When diazodicyanoimidazole is heated in iodobenzene the ylide (50)[11] is formed. This reaction is similar to the preparation of other heteronium ylides from the decomposition of diazo-compounds in the presence of carbene acceptors (see section 2).

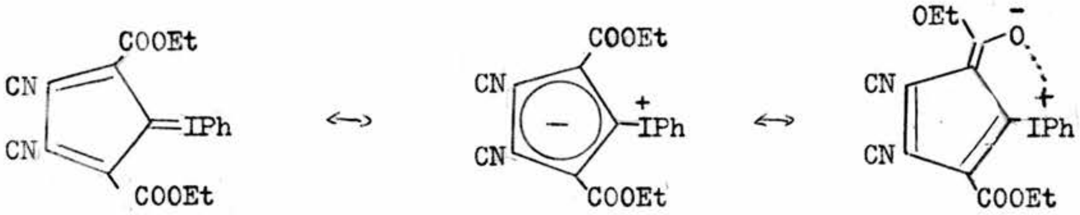


(50)

b) Physical Properties.

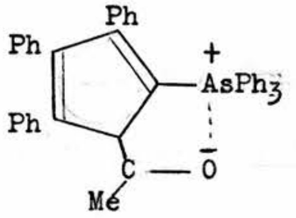
Little has been reported on the physical properties of iodonium ylides and only X-ray studies and infra-red spectroscopy have been utilised to study the nature of the bonding in iodonium ylides.

Phenyliodonium 2,5 - diethoxy carbonyl -3,4 - dicyanocyclopentadienylide (51) is the only iodonium ylide to date to have been studied by X-ray analysis[75].



(51a) (51b) (51c)

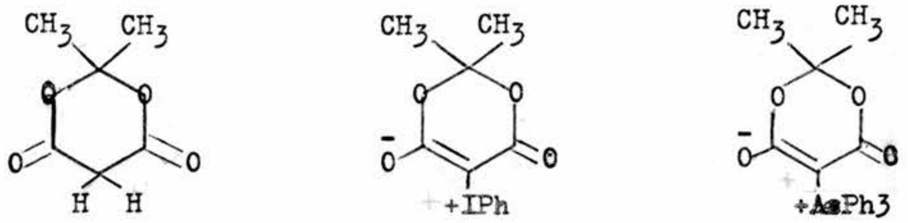
The two C-I bonds were found to be nearly the same length (2.08 Å) and it therefore appears that there is little contribution from the apolar canonical form (51a). In addition, it was observed that the I-O distance (2.96 Å) was considerably less than the van der Waals distance (3.5 Å). This suggests that the negative charge is being delocalised by the ester groups and that there is an intramolecular association between the oxygen and the iodine as implied by the canonical form (51c). This intramolecular association between an oxygen and a heteroatom has been observed before in the case of triphenylarsonium 2 - acetyl -3,4,5 - triphenylcyclopentadienylide (52) where the oxygen atom of the ester group was found to interact considerably with the arsenic[26].



(52)

Thus, the similarity of C-I bond lengths and the contribution from the canonical form (51c) provides strong evidence that the iodonium ylide (51) exists mainly as the dipolar canonical form (s). This lack of contribution from the apolar form (51a) is presumably because of the poor overlap between the 2p-orbital of the carbon and the 5d-orbitals of the iodine. In addition the low electronegativity and the large size of the iodine atom would contribute to a decreased p_{π}- d_{π}overlap.

A study of the carbonyl absorption frequency in the infra-red spectra of iodonium ylides of β - dicarbonyl compounds shows the increased single bond character of the ylide carbonyl group due to a contribution from the enolate form, as illustrated by the series (53) and (54). In comparison with arsonium ylides, the stretching frequency of the carbonyl groups of iodonium ylides would appear to be less, suggesting an increased contribution from the dipolar form. This is in agreement with the X-ray studies and again presumably results from the poor pπ- 5dπ overlap.



ν C = 0 1740, 1785 1630 1685, 1635 cm^{-1}

(53)

$(CH_3OCO)_2CH_2$ $(CH_3OCO)_2C = IPh$ $(CH_3OCO)_2C = AsPh_3$

ν C = 0 1750 1675 1700 cm^{-1}

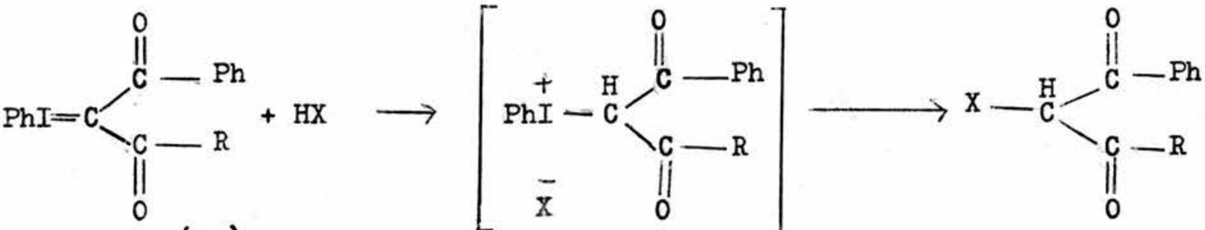
(54)

c) Chemical Properties.

Iodonium ylides decompose slowly at room temperature and the rate at which decomposition takes place depends on how well stabilised the negative charge on the carbanion is. Thus, the cyclopentadienylides stabilised by electron withdrawing groups can be recrystallised from hot solvent and have high melting points[10]. Similarly phenyliodonium 2,2 - dimethyl - (4,6-dioxo -1,3 - dioxan) - ylide can be recrystallised from ethanol[9]. However, the iodonium ylides of other β -dicarbonyl compounds generally decompose when heated in solution. The iodonium ylide (38) is more stable, but when it is heated in solution the phenyl ether is obtained.[76] The iodonium ylides are all light sensitive, but they can be stored in the dark at -20°C for long periods.

The iodonium ylides are not hydrolysed readily in water, and in the preparation of many iodonium ylides water is used to precipitate out the ylide from the reaction solution. Furthermore, several of the phenyliodonium cyclopentadienylides can be recrystallised from a DMSO/water mixture.

In the presence of mineral acids, iodonium ylides of β - dicarbonyl compounds such as (55) are protonated and then undergo nucleophilic substitution [77]. On the other hand, stabilised phosphonium, arsonium and sulphonium ylides can be protonated to give the conjugate acid, but the reaction goes no further and this gives an indication of the relative weakness of the C-I bond.



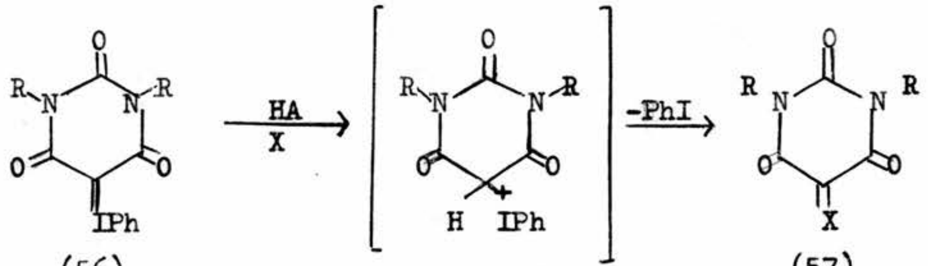
(55)

+ PhI

$X = Cl, Br; R = CH_3$, Ph.

Acids that have a sufficiently high acidity for the protonation of the ylide (55) and have an anion that is sufficiently nucleophilic will undergo this reaction. For example, phenyliodonium dibenzoylmethylide reacts with trichloroacetic acid, p-nitrobenzoic acid[77] and the tosylates of aliphatic amino acids[78] to give the corresponding acyloxy derivatives. However, reaction with picric acid does not give the desired product, presumably because the picrate anion has only weak nucleophilic properties[77].

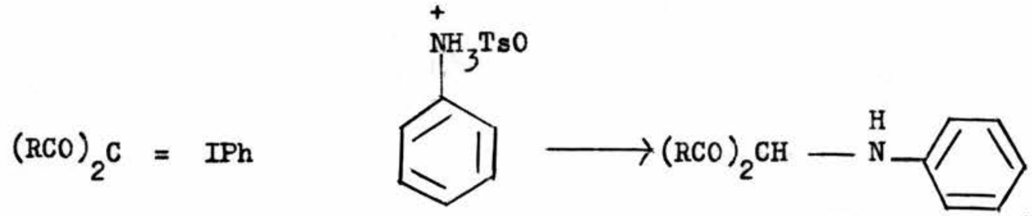
This cleavage reaction has been used to prepare ylides of other heteroatoms. For instance, the protonation of the phenyliodonium ylide (56) with p - toluenesulphonic acid in the presence of nucleophilic reagents such as dimethylsulphide or pyridine results in the formation of the dimethylsulphonium and pyridinium ylides (57)[79].



(56) (57)

$A = TxO^-$ X = pyridine, dimethylsulphide.

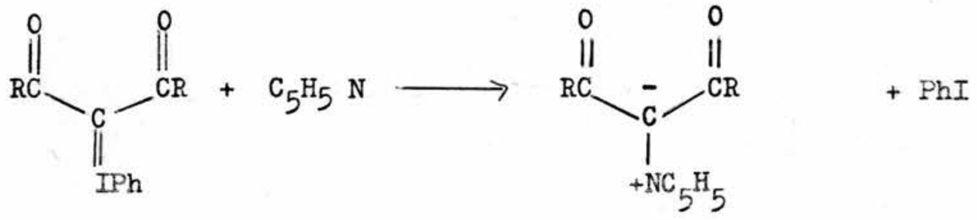
Although with the tosylates of aliphatic amino acids acyloxy derivatives are formed, the reaction of the tosylates of aromatic amino acids with iodonium ylides takes a different course and the N- substituted amino acids (58) are formed. p-Nitroaniline tosylate reacts similarly[80].



+PhI + TsOH (58)

This unexpected course of reaction may be explained by the strongly acidic properties of the $\overset{+}{N}H_3$ group of aromatic tosylates which results in protonation of the ylide, followed by nucleophilic attack by the nitrogen atom on the protonated carbon atom of the ylide.

Iodonium ylides of β-dicarbonyl compounds were found to undergo thermal cleavage in the presence of pyridine to give the corresponding pyridinium ylide (59)[81].

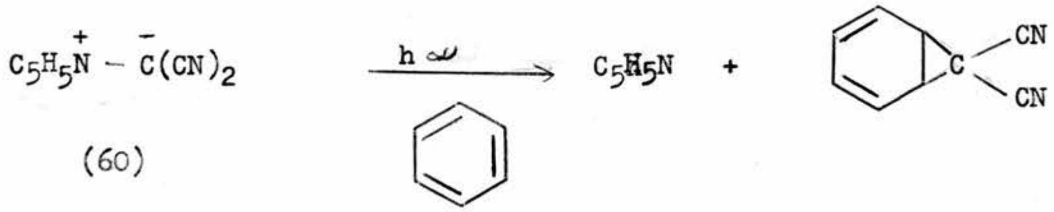


(59)

It was found that the addition of copper salts to the reaction mixture considerably raised the yield of pyridinium ylide product[82]. Of copper iodide, copper cyanide, copper sulphate, copper powder and copper acetylacetonate, the latter was found to be the best catalyst and its good solubility in organic solvents made it possible to carry out the cleavage reaction in a homogeneous medium. In addition, the presence of a copper catalyst was found to change the course of the reaction in some instances. Whereas the thermal decomposition of the iodonium ylide (38) in the presence of pyridine only yielded phenyl 2-iododimedonyl ether, with the addition of copper acetylacetonate a considerable amount of the pyridinium ylide was formed as well.

This catalytic cleavage has been carried out in the presence of compounds other than pyridine. Iodonium ylides have been treated with quinoline, isoquinoline, dimethyl sulphide and triphenyl phosphine to give the corresponding ylides[83].

The thermal and copper catalysed decompositions of these iodonium ylides are thought to occur via a diacylcarbene intermediate which reacts with a carbene acceptor such as pyridine[81]. The analogous decomposition of sulphonium and ammonium ylides has been mentioned previously (section 4(a)). More conclusive evidence of a carbene intermediate has been obtained from the photochemical cleavage of pyridinium dicyanomethylide (60) in the presence of benzene with the formation of 7,7 - dicyanonorcaradiene[84]. Similarly in the photolytic decomposition of dimethylsulphonium phenacylide in cyclohexene, 7 - benzoylnorcarane is formed[85].



(60)

In the case of iodonium ylides evidence for a carbene intermediate comes from an investigation of the decomposition of the iodonium ylides(38) and (61) in ethanol which was studied alongside the decomposition of diazodimedone[86]. The formation of the obtained products could best be rationalised by assuming cleavage of the I-C bond in the ylides to yield a diketocarbene. Furthermore, the copper catalysed decomposition of the iodonium ylides (38) and (61) gave different products from the thermal decomposition. From this and by comparison with the products obtained from the thermal and photochemical decomposition of diazodimedone, it was deduced that the carbene obtained from the thermal decomposition of the ylides (38) and (61) was in the triplet state, whereas the carbene obtained from the copper catalysed decomposition was in the singlet state. The

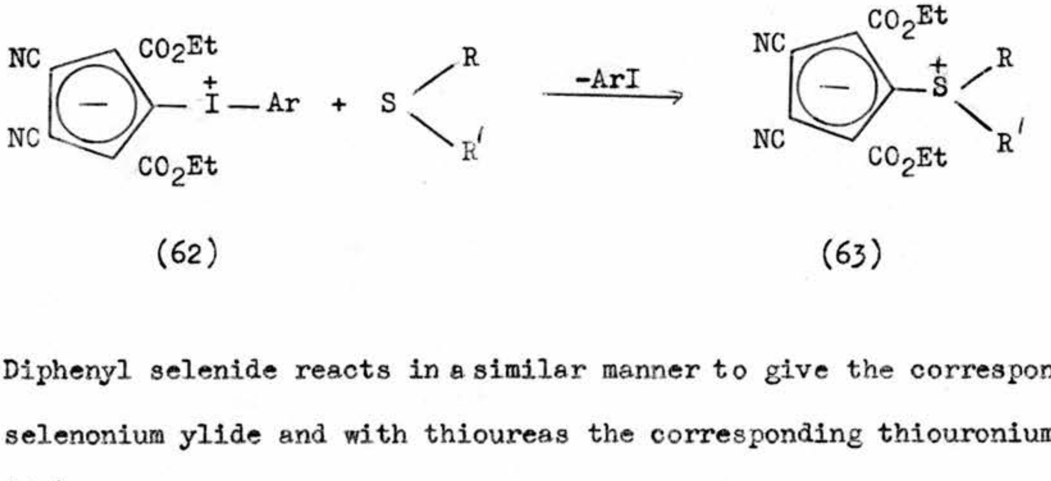
$$(PhCO)_2C = IPh$$

(61)

thermolysis of diazo-compounds in copper-catalysed reactions is known to provide singlet carbenes or carbenoid species[87].

The role of the catalyst has not been established accurately. It is assumed that the influence of the catalyst can be explained by the capacity of the copper atom to form co-ordinate bonds with the oxygen atom of the carbonyl groups. This may favour cleavage of the C-I bond and stabilise the intermediate carbene[82].

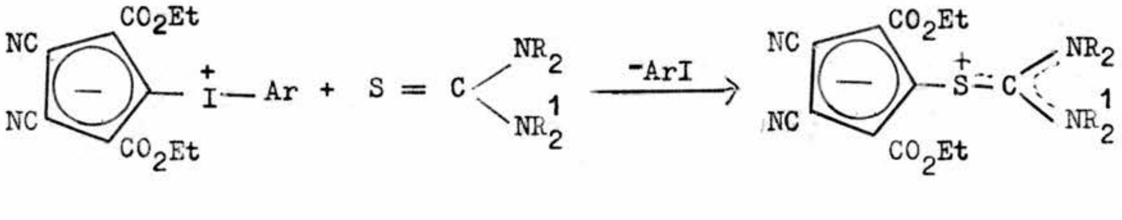
In an analogous reaction, aryliodonium cyclopentadienylides stabilised by electron withdrawing groups such as (62) undergo thermal cleavage in the presence of thioethers to form sulphonium cyclopentadienylides (63)[88]. The reactions were generally carried out either in excess thioethers at temperatures of about 130°C or in refluxing acetonitrile.



(62)

(63)

Diphenyl selenide reacts in a similar manner to give the corresponding selenonium ylide and with thioureas the corresponding thiouronium ylides (64) are obtained.



(64)

Similarly, the aryliodonium cyclopentadienylides react with triphenylphosphine and triphenylarsine in melt conditions, in the presence of catalytic amounts of Cu(I) salts or copper acetylacetonate, at temperatures of 140°C-150°C to give the corresponding phosphonium and arsonium ylides. In the absence of copper compounds, the reaction temperature had to be increased to 180°C and only the arsonium ylide was obtained in useful yields.

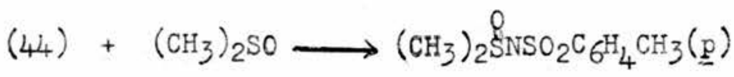
Phenyliodonium N-tosylimine (44) undergoes thermal cleavage at 100°C in the presence of thioanisole or triphenylphosphine as shown in (65) and it is proposed that the reaction proceeds via a sulphonyl nitrene intermediate[72].

$$\underset{(44)}{C_6H_5I = NSO_2C_6H_4CH_3(p)} + X \longrightarrow X = NSO_2C_6H_4CH_3(p) + PhI$$

$X =$ MeSPh, PPh_3.

(65)

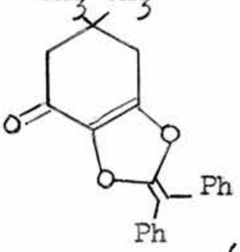
The imine (44) also reacts with DMSO at room temperature with the formation of dimethyloxysulphonium-N-tosylimine (66). Since the imine (44) does not decompose at room temperature it is proposed that the reaction does not proceed via nitrene formation but via a substitution reaction on the nitrogen of the imine (44).



$$(44) + (CH_3)_2SO \longrightarrow (CH_3)_2\overset{O}{S}NSO_2C_6H_4CH_3(\underline{p})$$

(66).

Related substitution reactions have been reported in the literature. Whereas the phenyliodonium dimedonylide (38) reacts with diphenylketone to afford an acetal (67) and a lactone (68) presumably through the betaine (69), and reacts with phenyl isocyanate to give the azalactone[89], reaction with phenyl isothiocyanate takes a different course and no adduct (70) is obtained[90]. Instead the main products were compounds (71) and (72) and it is proposed that the reaction is initiated by displacement of PhI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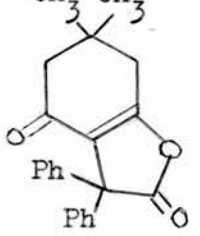
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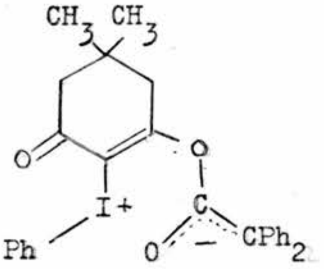
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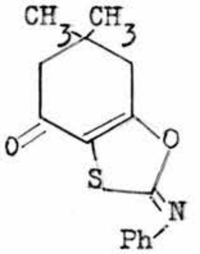
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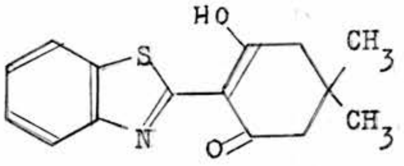
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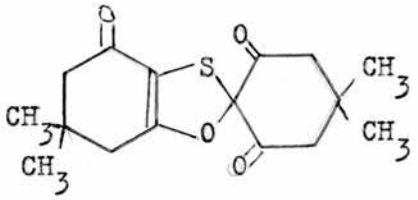
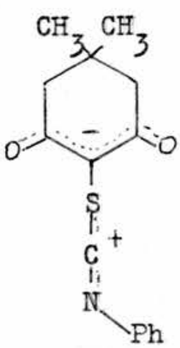

(72)

from the ylide (38) by phenyl isothiocyanate with the formation of a sulphur ylide (73). This ylide can then undergo an intramolecular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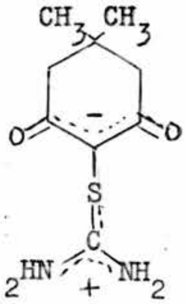
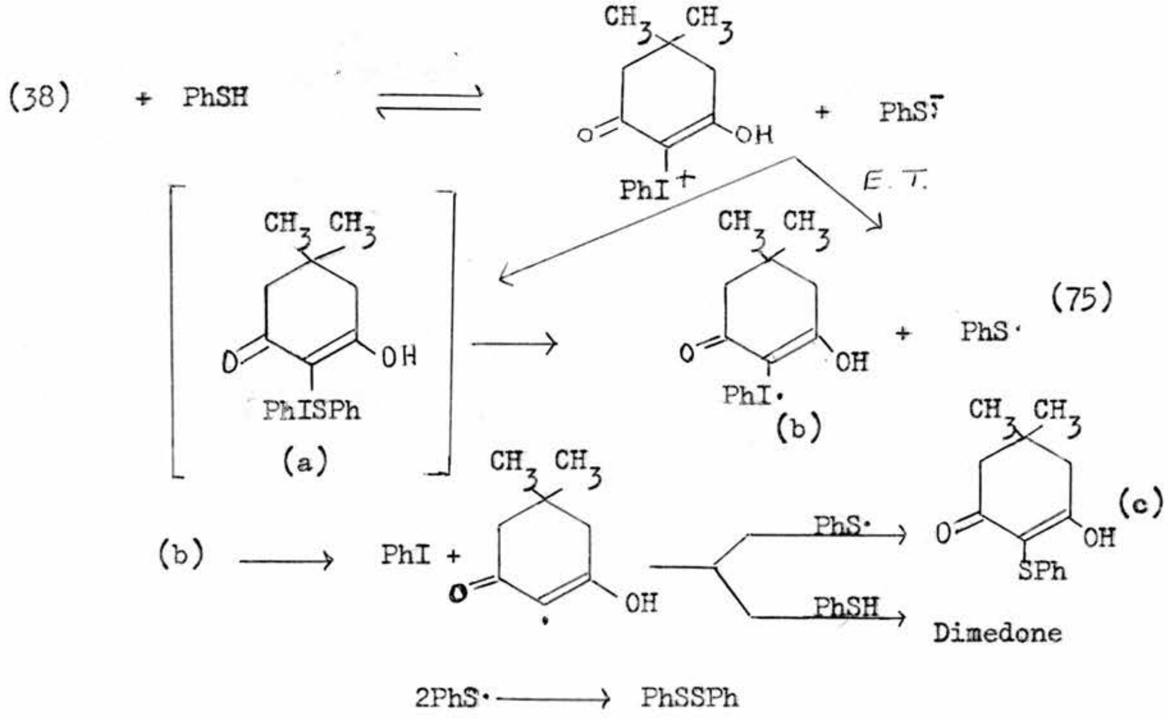

(74)

rearrangement which eventuates in compound (71), or fragment to give phenyl isocyanate and ultimately compound (72). Corrobative evidence that compounds containing the C=S moiety can displace iodobenzene for the ylide (38) was sought and it was found that the ylide (38) reacts with thiourea at room temperature to give the thiouronium ylide (74).

In contrast, a study of the reaction of the ylide (38) with thiophenol showed that an oxidation-reduction reaction to give diphenylsulphide, dimedone and iodobenzene was the main reaction and that the substitution adduct (75c) was a minor product[91]. The oxidation of thiophenol by the ylide (38) apparently proceeds by initial protonation of the ylide by the thiophenol and subsequent electron transfer from the resulting thiophenoxide ion to the conjugate acid of the ylide as shown in (75). The electron transfer process may proceed through the intermediate (75a) which suffers subsequent iodine sulphur bond homolysis.



(75)

The general reaction pattern does not change with para-substituted thiophenols, but the ratio of substitution/oxidation is dependent on the electron donating capacity of the substituent and the yield of oxidation product increases as the electrophilicity of the substituents increases.

This oxidation-reduction reaction is not restricted to aromatic thiols and a similar reaction occurs with methanethiol and hydrogen sulphide, but the ratio of oxidation product to substitution product is lower.

6. THE COPPER CATALYSED PREPARATION OF YLIDES.

Carbenes are recognised as the most common intermediates in the photolysis and thermolysis of diazo-alkanes[87]. Diazo-2,3,4,5-tetraphenylcyclopentadiene decomposes when heated at its melting point evolving nitrogen, and if this decomposition is carried out in a solvent having a heteroatom such as N, S, P, As, Se, Te or Bi, the resulting carbene reacts with the lone pair of electrons on the heteroatom forming 2,3,4,5-tetraphenylcyclopentadienylide (16).

(16)

X = $AsPh_3$, PPh_3, $SbPh_3$, $BiPh_3$, SPh_2, $SePh_2$, $TePh_2$, pyridine

When either 2-methyl-3,4,5-triphenyl-, 2,3,4-triphenyl-, 2,3,5-triphenyl- or 2,5-diphenyl-diazocyclopentadiene was heated with triphenylarsine in the melt conditions, however, little or no arsonium ylide was obtained[92]. If, on the other hand copper-bronze powder was also mixed and heated with the reactants all these diazocyclopentadienes gave arsonium cyclopentadienylides. In addition to providing cyclopentadienylides where they could not otherwise be obtained, admixture of copper-bronze with the reactants appears in general to result in a marked increase in the yield of ylides.

This preparation of arsonium ylides by a thermal decomposition is not limited to cyclopentadienes and the method has been extended to other series of diazo-compounds as illustrated by (76). This reaction only takes place in the presence of a copper catalyst[46].

$$(EtOOC)_2C = N_2 + AsPh_3 \xrightarrow[150^\circ]{CuBr} (EtOOC)_2C = AsPh_3 + N_2$$

(76)

Furthermore, in the presence of a copper-bronze catalyst the ylide forming reaction may be carried out a markedly lower temperatures and in solution. Thus, the decomposition of diazocyclopentadienes have been carried out in refluxing benzene, cyclohexane or ethanol and good yields of the arsonium ylides have been obtained[92].

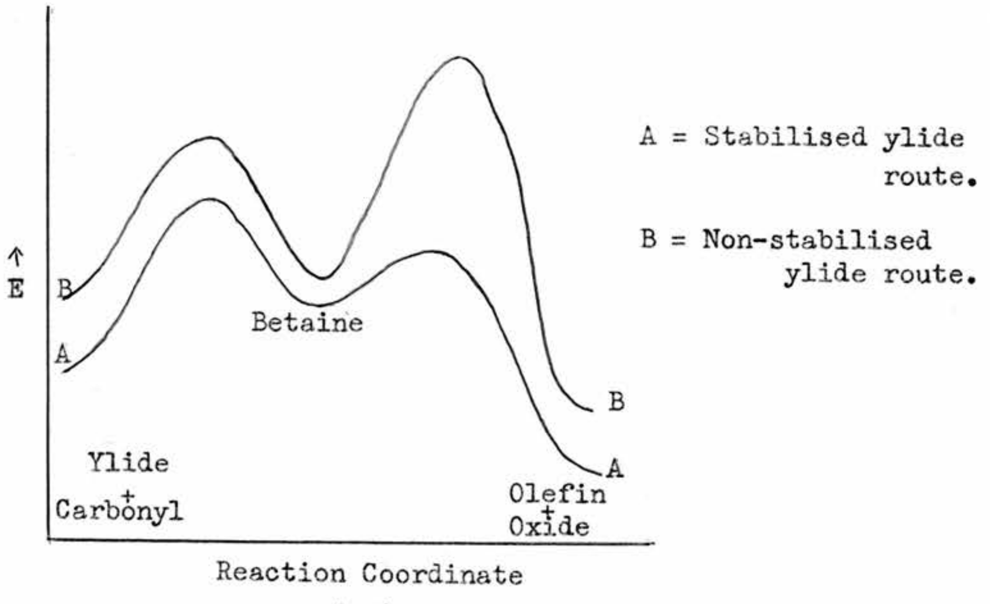
The copper catalysed decomposition of diazo-alkanes is normally free of products resulting from the insertion of carbenes into C-H bonds, and the decomposition of diazo-alkanes catalysed by a chiral complex yields optically active products[93]. These results suggest that free carbenes do not play a role in the copper-catalysed decomposition of diazoalkanes and that a carbene-copper complex is involved. A study of the homogeneous catalysed addition of ethyl diazoacetate to olefins utilising (trialkyl phosphite) - copper (1) chloride complexes revealed systematic changes in the isomeric cyclopropane product distribution as a function of the steric bulk and electronic effects of the ligand, proving the intermediacy of a carbene-metal-olefin complex[94].

The use of copper catalysts to catalyse the decomposition of iodonium ylides in the presence of a carbene acceptor to give another heteronium ylide has already been discussed (section 4(c)). Presumably the intermediate in these reactions also involves a carbene-metal complex.

7. THE WITTIG REACTION.

a) Phosphonium ylides.

Various studies of the reactions of phosphonium ylides with carbonyl compounds have suggested that the mechanism of the Wittig reaction is perhaps best summarised by the energy profiles shown in (77)[95,96,97,98].



(77).

It appears that stabilised ylides, that is ylides that can be isolated, react with carbonyl compounds in a slow, reversible first step (betaine formation) which is followed by fast decomposition. In the case of non-stabilised ylides the reverse would seem to be the case and the decompositions of the betaine products is the slow step. It would therefore be expected that changes in the structure of stabilised ylides would be reflected in the betaine formation step which depends on the nucleophilicity of the ylide and the electrophilicity of the reacting carbonyl group. In contrast, changes in the structure of non-stabilised ylides would be reflected in the betaine decomposition which depends on the ease of oxyanion transfer to phosphorus and on the stability of the olefinic product.

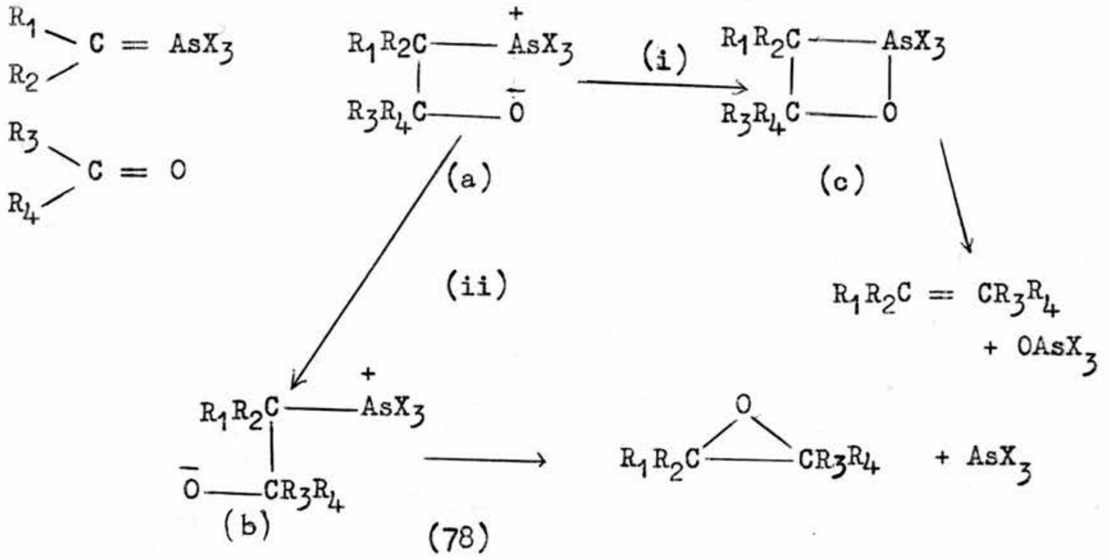
The nucleophilicity of phosphonium ylides is directly related to the ability of the carbanion substituents to delocalise the negative charge and therefore the reactivity of a given ylide in the Wittig reaction should be related to the basicity of that ylide. In a study of the reaction of a series of stabilised ylides, triphenylphosphonium acylmethylides, with benzaldehyde it was found that the overall reaction depended on the rate of betaine formation and that the most basic ylides were also the most reactive[96]. Similarly, the effect of electron donating substituents on phosphorus in the Wittig reaction is to increase the overall reaction rate as the substituents become more electron donating and the nucleophilicity of the ylide is increased[97].

However, in the case of non-stabilised ylides, the effect of electron donating groups on phosphorus such as tri(p-methoxyphenyl), tripiperidyl and trimorpholino is to decrease the overall rate of reaction[98]. All would undergo the initial step of the Wittig reaction to form a betaine, but there was considerable difficulty in effecting its decomposition to olefin and phosphine oxide. Substitution on phosphorus by electron donating groups would be expected to increase the electron density on phosphorus making subsequent nucleophilic attack by the oxyanion of the betaine more difficult and permitting build up and isolation of betaine from the reaction. Subsequently, triphenylphosphonium methylide reacts with benzophenone to give the olefin, but with trimethylphosphonium methylide only the betaine is obtained[98]. The alkyl groups are electron donating and will hinder the decomposition whereas the phenyl groups appear to be electron withdrawing (see section 3(a)) and make the phosphorus atom more susceptible to nucleophilic attack. These observations are consistant with the energy profile shown in (77).

b) Arsonium ylides.

Interest in arsonium ylides has arisen because arsenic appears to lie between sulphur and phosphorus in its effect on the properties of ylides. A study of arsonium ylide chemistry may discover unique chemical or physical properties and/or shed light on the mechanism of reactions of phosphonium and sulphonium ylides, both of which results would have recognised importance in preparative chemistry.

As mentioned in section 3(c), the As = O bond is intermediate in strength between the P = O and S = O bond and the triarylarsine group is a good leaving group, and arsonium ylides can react with carbonyl compounds to give an alkene and/or an epoxide as illustrated in the scheme below in (78). For the formation of the alkene (path 78(i)), the betaine is thought to take up a cis arrangement (78(a)) and the reaction is believed to proceed through the neutral pentacovalent



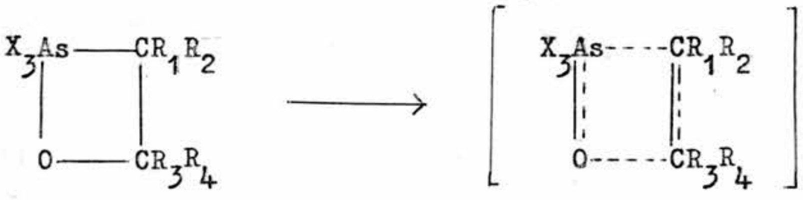
(78)

four-membered transition state (78(c)). However, for the formation of the epoxide (path 78 (ii)), the betaine must take up the trans arrangement (78 (b)) and this is then followed by intramolecular nucleophilic substitution of the triarylarsine group by the oxygen atom to give the epoxide.

Studies of the reaction of arsonium ylides with carbonyl compounds indicated[99,100] that stabilised arsonium ylides, that is ylides where the carbanion is stabilised by electron withdrawing groups such as phenacylide[100], carbomethoxymethylide[101], fluorenylide[102] and cyclopentadienylide[103], afforded only olefinic products. On the other hand non-stabilised arsonium ylides such as methylide[104] and ethylide[105] afford almost exclusively epoxides or products resulting from their rearrangement while semi-stabilised arsonium ylides such as benzylides[106,107] and 2-napthylmethylides[108] may react with carbonyl compounds to give the olefin and/or the epoxide.

In a more detailed study of the factors controlling the direction of elimination from the betaine the reaction of triarylarsonium p-substituted benzylides with various benzaldehydes was studied[109] and it was found that when the substituent on the benzylide was strongly electron withdrawing (e.g. p - $NO_2C_6H_4$, p - CNC_6H_4) the trans-olefin was obtained, whereas with unsubstituted benzylides the trans-epoxide was formed.

Obviously, the substituents R_1 and R_2 on the carbanion in the scheme shown in (78) are having a strong influence on whether path (78(i)) or (78(ii)), the product determining step, is followed. It has been suggested that in the transition state (79) for olefin formation from the five-co-ordinate intermediate (78(c)), breaking of the As - C bond is in advance of other electronic shifts and that the α- carbon bears a fractional negative charge. Stabilisation of this charge would lead to faster olefin formation and thus when the substituents on the α - carbon are electron withdrawing olefin formation is preferred.



(78(c)) (79)

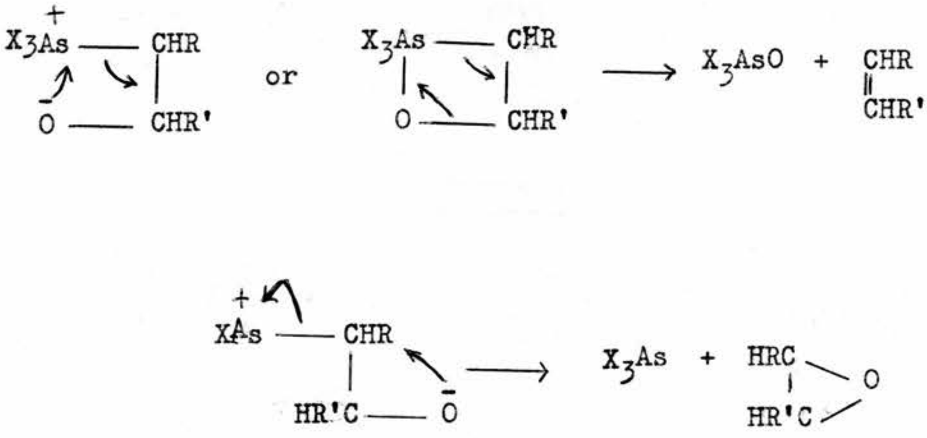
In addition to substituents attached to the carbanion affecting the reaction course, the electronic character of the substituents at the arsenic atom can also have a pronounced influence on the direction of elimination from the betaines. In an investigation of the reaction of p-substituted arylarsonium methylides ($(pXC_6H_4)_3As = CH_2$) with benzaldehyde[110] it was found that variations in the nature of the substituent X had little effect on the product distribution of alkene/epoxide which was generally in the range of 1-5% alkene, 95-99% oxide. However, if the substituent X = NMe_2, 92% of the trans-alkene was obtained.

In a subsequent more systematic study, the effect of the substituents at arsenic on the product ratio of alkene to epoxide in the reaction of various arsonium benzylides with benzaldehyde was investigated[111] and the results are shown in table (1).

	$X_2YAs^+-CH_2PhBr^-$		Yields	
			cis + trans stilbene oxide	cis + trans stilbene
	X	Y	%	%
(a)	C_6H_5	C_6H_5	79	7
(b)	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	66	10
(c)	C_6H_5	p-$(CH_3)_2NC_6H_4$	65	11
(d)	p-$(CH_3)_2NC_6H_4$	C_6H_5	57	15
(e)	p-$(CH_3)_2NC_6H_4$	p-$CH_3OC_6H_4$	33	12
(f)	p-$(CH_3)_2NC_6H_4$	p-$(CH_3)_2NC_6H_4$	24	25
(g)	C_6H_5	C_2H_5	47	27
(h)	C_2H_5	C_6H_5	13	62
(i)	n-C_3H_7	C_6H_5	18	70
(j)	C_2H_5	C_2H_5	1	87

The results clearly show that electron donating substituents such as alkyl groups at the arsenic atom promote the formation of the alkene. It is also worth noting the relatively small effect due to mesomeric effects as compared to the inductive effect. It is assumed that in the two distinct paths (78(i)) and (78(ii)) the heterolytic cleavage of the

As-C bond occurs in the opposite sense depending upon whether an alkene or an epoxide is formed as shown in (80). In the former case electrons are displaced towards the carbon and in the latter case towards the arsenic atom. Thus, electron donating substiuents should increase the



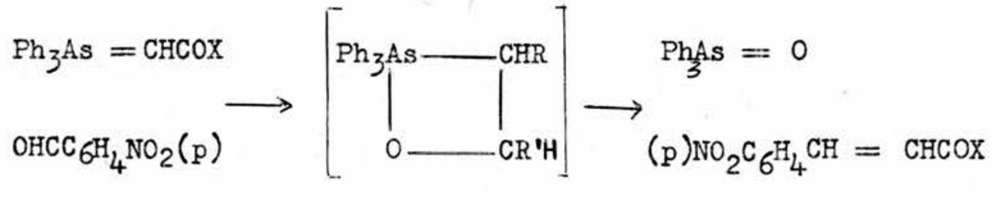
(80)

product ratio of alkene to epoxide and the results in table (1) support this view. However, although these results illustrate that the nature of the arsonium group influences the course of the reaction it can be seen that it does not do so in a manner that can be correlated with the relative stabilities of the arsonium ylides.

A kinetic study of the reaction between stabilised arsonium ylides and p-nitrobenzaldehyde showed that in this case the order of reactivity of the ylides paralleled the order of basicity and that for the reaction of triarylarsonium phenacylide ($R_3As = CHCOPh$) with p-nitrobenzaldehyde to give an olefin, the order of decreasing reactivity is
R = p-anisyl > p-tolyl > phenyl[112].

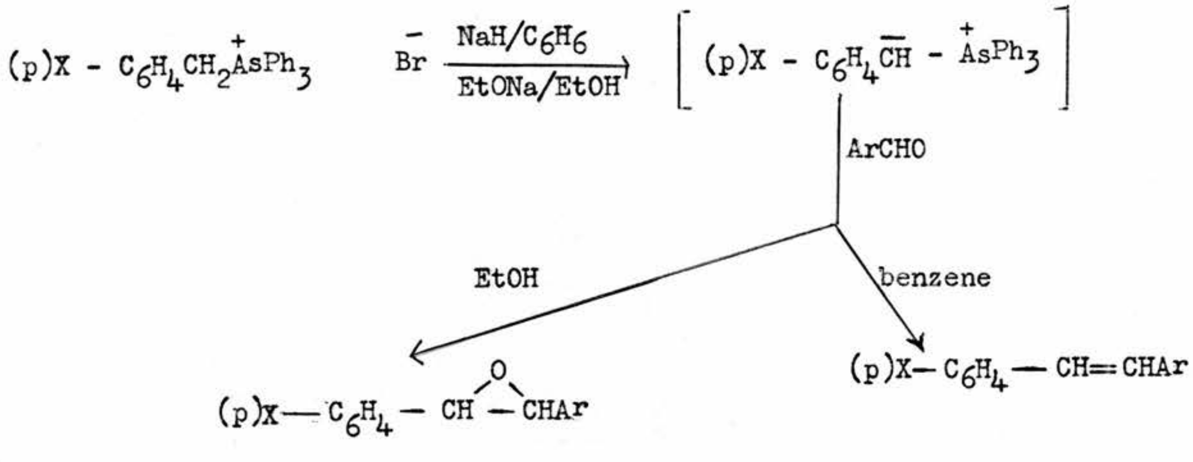
Thus, both the nature of the carbanionic moiety and the electronic nature of the substituents at arsenic influence the course of the Wittig reaction for arsonium ylides. Alkene formation is favoured as the substituents $R_{1,2}$ in (78) becomes more electron withdrawing and the substituent R_3 becomes more electron donating. However, at present the relative importance of the two effects is not assessable.

If the Wittig reaction proceeds via a betaine intermediate then solvents might also be expected to play a part in determining the course of the reaction. Frøyen (1971)[112] observed that the rate of reaction between stabilised arsonium ylides and p-nitrobenzaldehyde was faster when the reaction was carried out in benzene than in the more polar solvents DMF and DMSO. He argued that this indicates that a concerted mechanism is operative where the neutral pentacovalent cyclic transition state is formed in one step without any intermediacy of a betaine as shown in (81).



(81)

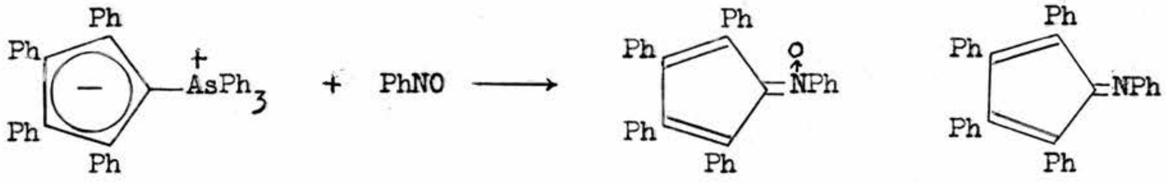
Other workers[113,114] working independently, have also found that for less stabilised arsonium ylides, solvent has an effect on the course of the reaction. Triphenylarsonium p-chlorobenzylide and triphenylarsonium benzylide react with carbonyl compounds in ethanol to give epoxides, but if the reaction is carried out in benzene, olefins are obtained as shown in (82).



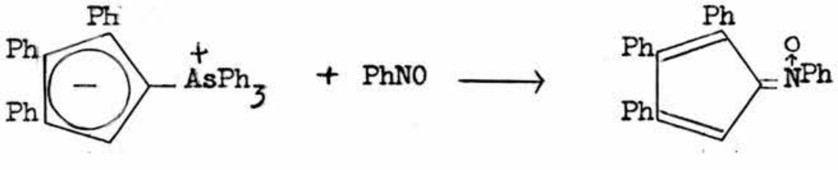
(82)

If the reaction proceeds as shown in the scheme in (78), then polar solvents should stabilise by solvation and thus favour the betaine (78(b)), whose presence is essential for epoxide formation, while non-polar solvents should favour the neutral four-centred intermediate (78(c)) with the resulting formation of the alkene. These observations accord with the results above.

Arsonium ylides react with nitrosobenzene to give an anil oxide



(83)



(84)

and/or an anil as shown in the examples (83)[36] and (84)[115]. The anil oxide is thought to arise via an oxazirane as intermediate which rapidly isomerises to an anil oxide. This reaction is thus analogous to the reaction of ylides with carbonyl compounds and presumably the factors mentioned in this section will influence this reaction in a similar manner.

In conclusion, the mechanism of the Wittig reaction is far from simple and it is influenced by the nature of the heteroatom, the substituents at the heteroatom and the solvent in which the reaction is carried out.

PART II. DISCUSSION.

The iodonium ylides described in the literature have as an anionic part either a β-dicarbonyl system[9], a heterocyclic system[11,68,69], or a cyclopentadiene system.[10] The phenyliodonium cyclopentadienylides that have been prepared to date are strongly stabilised by electron withdrawing groups attached to the cyclopentadiene ring.

An attempt was made to prepare some less stabilised phenyliodonium cyclopentadienylides. In addition, the reaction of p-toluamide with (diacetoxyiodo)benzene, which might provide a phenyliodimine, was investigated. Some further reactions of previously known iodonium ylides were studied and the copper catalysed thermal decomposition of phenyliodonium ylides was investigated in more depth. These reactions are discussed in section 1.

In a study of the effect of varying the position of a methyl group on the ability of tritolylarsine dihalides to ionise in non-aqueous solvents by Dr. G.S. Harris of the University of St. Andrews, it was found that one of the halogens of tri-o-tolylarsine dihalide ionised readily, whereas the tri-p-tolyl and tri-m-tolyl-arsine dihalides ionised only slightly.

The preparation and reactions of a variety of para, ortho and meta substituted triarylarsonium ylides were studied to see if the position of the substituent affected the properties of the arsonium ylides. This work is discussed in section 2.

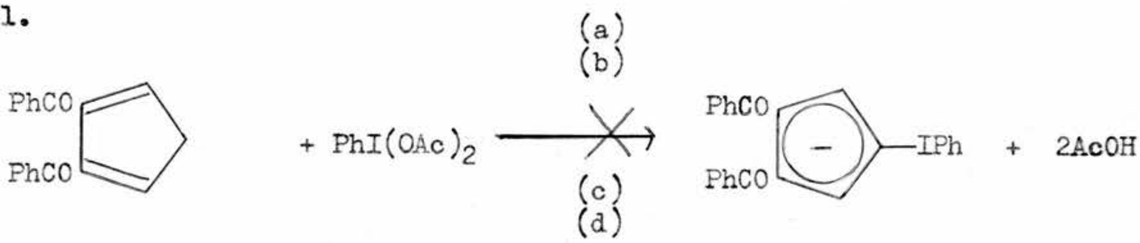
For the sake of brevity some of the compounds discussed in this thesis are illustrated by formulae which in fact represent only one of the possible contributing canonical forms of the compounds in question.

1. AN INVESTIGATION OF SOME IODONIUM YLIDES.

(i) THE ATTEMPTED PREPARATION OF AN IODONIUM YLIDE.

(a) From Dibenzoylcyclopentadiene.

Dibenzoylcyclopentadiene (2-benzoyl-6-phenyl-6-hydroxyfulvene) reacts with triphenylarsine in acetic anhydride to give triphenylarsonium 3,4-dibenzoylcyclopentadienylide [116]. An attempt was made first to prepare phenyliodonium 3,4-dibenzoylcyclopentadienylide by condensing (diacetoxyiodo)benzene with dibenzoylcyclopentadiene in an analogous reaction as shown in (85a), but the reaction gave an intractable black oil.



(a) $(CH_3CO)_2O$ (b) Et_3N, P_2O_5 (c) KOH (d) PhLi.

(85)

Arsine oxides (and sulphoxides) have also been condensed with reactive methylene compounds in the presence of triethylamine and phosphorus pentoxide [46,20], but an attempt to prepare the iodonium ylide in a similar manner to that shown in (85b) also failed.

The iodonium ylides of β-dicarbonyl compounds are prepared in milder conditions by reacting the reactive methylene compound with (diacetoxyiodo)benzene in the presence of potassium hydroxide, but an attempt to apply this method to the preparation of the iodonium ylide of dibenzoylcyclopentadiene, as shown in (85c), was unsuccessful.

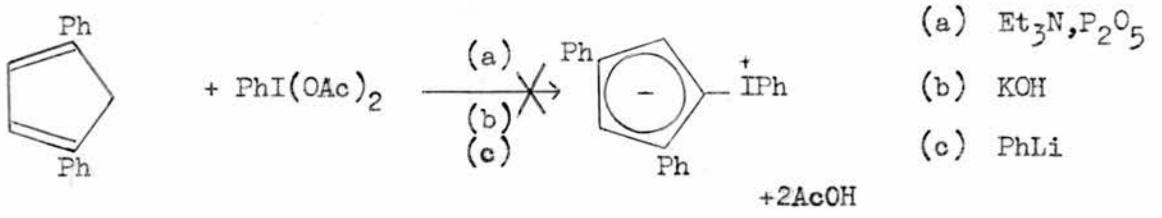
This reaction was repeated, but phenyllithium was used as the base as shown in (85d). This reaction gave an intractable black oil.

Another method by which triphenylarsonium ylides have been prepared is by the reaction of reactive methylene compounds with triphenylarsonium dichloride instead of triphenylarsine oxide[117]. When dibenzoylcyclopentadiene was stirred with iodobenzene dichloride in the presence of potassium hydroxide however, a black oil was again formed.

It was found that on the addition of dibenzoylcyclopentadiene to (diacetoxyiodo)benzene in methanol, not necessarily in the presence of base, the solution turned black. Dibenzoylcyclopentadiene is a fairly strong acid and it is possible that it may react with (diacetoxyiodo)benzene in an alternative way to give unknown products.

(b) From 1,4 - Diphenylcyclopentadiene.

Triphenylarsine oxide can be condensed with 1,4 -diphenylcyclopentadiene in triethylamine in the presence of phosphorus pentoxide to give triphenylarsonium 2,4 - diphenylcyclopentadienylide[92], but an attempt to prepare phenyliodonium 2,4 - diphenylcyclopentadienylide using this method as shown in (86a) gave a black oil which was not treated further.



(86)

Similarly, the reaction of 1,4 - diphenylcyclopentadiene and (diacetoxyiodo)benzene in the presence of potassium hydroxide, as shown in (86b), failed to result in the formation of an iodonium ylide and unchanged 1,4 - diphenylcyclopentadiene was recovered. It appeared that potassium hydroxide was not a strong enough base to give the 1,4 - diphenylcyclopentadienyl anion and therefore the reaction was repeated using phenyllithium as base as shown in (86c). This time an intractable oil was obtained. The 1,4 - diphenylcyclopentadienyl anion appeared to be formed in this case and it is possible that the iodonium ylide was formed, but decomposed under the reaction conditions.

(c) From Fluorene.

Fluorenylides containing a wide variety of heteroatoms are known[1]. An attempt to prepare phenyliodonium fluorenylide by the reaction of fluorene and (diacetoxyiodo)benzene in the presence of phenyllithium resulted in an intractable oil being obtained. The fluorenyl anion was formed and therefore it is again possible that the iodonium ylide was formed but decomposed under the reaction conditions.

(d) From p-Toluamide.

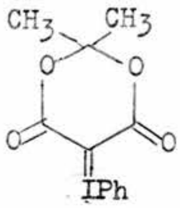
(Diacetoxyiodo)benzene reacts with p-toluenesulphonamide in the presence of potassium hydroxide at room temperature to give phenyliodonium-N-tosylimine [72]. When p-toluamide was stirred with (diacetoxyiodo)benzene in the presence of potassium hydroxide however, it gave an oil that could not be induced to crystallise. The reaction was repeated using phenyllithium and sodium hydride as base. In both cases an intractable oil resulted. Again, it is possible that phenyliodonium-N-tolylimine was formed, but the absence of an electron withdrawing group such as the sulphonyl group may mean that the imine is not sufficiently stabilised and that it decomposes under the reaction conditions.

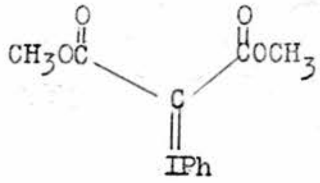
(e) Summary.

The various attempts to prepare the iodonium ylides mentioned in this section all failed. All the iodonium ylides prepared to date have been prepared at room temperature. It is highly likely that in the vigorous reaction conditions of the condensation reactions involving acetic anhydride or triethylamine and phosphorus pentoxide any iodonium ylide formed would rapidly decompose. The reactions of dibenzoylcyclopentadiene with (diacetoxyiodo)benzene are difficult to comment upon because the reactants appear to react together in non-basic conditions. With 1,4 - diphenylcyclopentadiene and fluorene it is likely that (diacetoxyiodo)benzene reacted with the corresponding anion and it would therefore appear that, if the iodonium ylide is formed, it is decomposing under the reaction conditions. The phenyliodonium cyclopentadienylides that have been prepared previously (see Introduction) have been heavily stabilised by four electron withdrawing groups attached to the cyclopentadiene ring. The phenyl groups of 1,4 - diphenylcyclopentadiene and fluorenylide presumably do not stabilise the anion sufficiently to prevent decompostion of the ylide. A similar argument can be applied to p-toluamide.

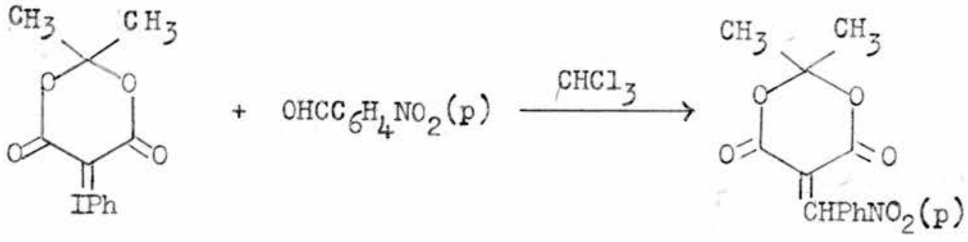
(ii) WITTIG REACTION.

Although a large number of phenyliodonium ylides of β-dicarbonyl compounds have been prepared, there has been no report of how these ylides or other iodonium ylides react in the Wittig reaction. The reaction of the two phenyliodonium ylides (87) and (88) with p-nitrobenzaldehyde was studied.


(87)


(88)

A mixture of phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (87) and p-nitrobenzaldehyde, in chloroform, was heated under reflux for four hours. Work up gave an 8% yield of p-nitrobenzylidene-2,2-dimethyl-4,6-dioxo-1,3-dioxan (89). When the reaction was repeated in benzene or methanol,


(87) (89)

however, no p-nitrobenzylidene-2,2-dimethyl-4,6-dioxo-1,3-dioxan was obtained. Unchanged iodonium ylide (87) was not recovered, but the presence of iodobenzene in the reaction residue indicated that the ylide had decomposed during the reaction. A previous study of the reaction between stable phosphonium ylides and carbonyl compounds indicated that solvent affected the rate of the reaction and that the reaction was six times faster in chloroform than in benzene and about one thousand times faster in methanol than in benzene[97]. It is therefore surprising that in the case of the iodonium ylide (87) reaction occured in chloroform and not in methanol. Benzoic acid has been reported to catalyse the Wittig reaction[118] and a possible explanation for the reaction of iodonium ylide (87) in chloroform is that trace amounts of hydrochloric acid in the chloroform catalysed the reaction. The hydrochloric acid probably protonated the carbonyl group making it more susceptible to the attack of the nucleophilic ylide.

Triphenylarsonium bis(methoxycarbonyl)methylide (90), which was prepared in this present work by treating phenyliodonium bis(methoxycarbonyl)methylide (88) with triphenylarsine in the presence of a copper catalyst (see later), reacted with p-nitrobenzaldehyde to give dimethyl p-nitrobenzylidenemalonate (91) in an 83% yield (c.f. triphenylarsonium bis(ethoxycarbonyl)methylide and tri-(n-butyl)arsonium bis(methoxycarbonyl) methylide which have been reported to react with p-nitrobenzaldehyde, give diethyl or dimethyl p-nitrobenzalidenemalonate in an 82% and a 93% yield respectively)[46]. On the other hand, triphenylarsonium

$$(CH_3OCO)_2C = AsPh_3 + OHCC_6H_4NO_2(p) \longrightarrow (CH_3OCO)_2C = CHC_6H_4NO_2(p)$$

(90) (91)

2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide does not undergo reaction with p-nitrobenzaldehyde.

Phenyliodonium bis(methoxycarbonyl)methylide (88) would therefore be expected to be a more reactive ylide than the iodonium ylide (87), but in fact it did not react with p-nitrobenzaldehyde in benzene, chloroform or methanol. Again the iodonium ylide (88) was not recovered and the presence of iodobenzene and 1,1,2,2-tetrakis(methoxycarbonyl)ethene indicated that the ylide had decomposed during the reaction.

The fact that neither of the iodonium ylides (87) and (88) reacted with p-nitrobenzaldehyde in methanol or benzene, but that both ylides decomposed instead, suggests that iodonium ylides, like ammonium ylides, are less stable in a reactive sense under the conditions of the Wittig reaction than are, for example, arsonium ylides.

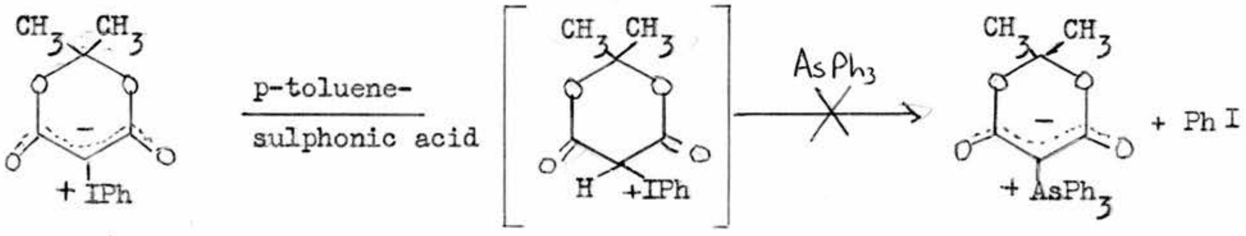
(iii) CLEAVAGE REACTIONS.

Iodonium ylides undergo thermal cleavage and in the presence of a carbene acceptor such as pyridine can give the corresponding heteronium ylide [81]. Furthermore, it is known that the presence of a copper catalyst aids this reaction (see Introduction).

Little information has been reported on the decomposition of iodonium ylides in the presence of triphenylarsine and these reactions were investigated. The decomposition of the iodonium ylides in the presence of other carbene acceptors was also studied.

(a) Phenyliodonium 2,2-dimethyl-(4,6-dioxo-1,3-dioxan)-ylide.

Phenyliodonium 2,2-dimethyl-(4,6-dioxo-1,3-dioxan)-ylide (87) has been reported to react with dimethylsulphide in the presence of p-toluenesulphonic acid to give the corresponding sulphonium ylide [7]. Before studying the thermal cleavage reactions of the iodonium ylide (87), an attempt was made to prepare triphenylarsonium 2,2-dimethyl-(4,6-dioxo-1,3-dioxan)-ylide(92),by cleaving the iodonium ylide with p-toluenesulphonic acid at room temperature in the presence of triphenylarsine, but this reaction was unsuccessful. Likewise, it was found that thioanisole would not react with the iodonium ylide (87) under similar conditions. Thioanisole is less nucleophilic than dimethylsulphide and this likely explains why no substitution reaction

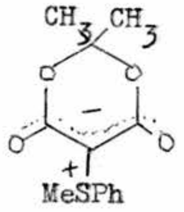


(87) (92)

occurred. Presumably triphenylarsine is also less nucleophilic than dimethylsulphide, but the possibility that there may be steric hindrance to the substitution of the iodobenzene group by the bulky triphenylarsine group must also be **taken into account.**

Attempts to prepare the triphenylarsonium ylide (92) by heating a mixture of the iodonium ylide (87) and triphenylarsine in the melt or in ethanol were unsuccessful. The triphenylarsonium ylide (92) was obtained in good yields however, when the mixture of the iodonium ylide (87) and triphenylarsine in ethanol was heated in the presence of copper acetylacetonate. This reaction was repeated using various concentrations of copper catalyst and it was found that if less than 0.15 mole of copper acetylacetonate was used per 1 mole of iodonium ylide no reaction took place. In addition, if the reaction was carried out in methylene chloride instead of ethanol, the reaction was not particularly successful and in one case unchanged iodonium ylide was recovered and in the other case an impure sample of the arsonium ylide was obtained.

The catalytic cleavage of the iodonium ylide (87) in the presence of thioanisole in ethanol resulted in the formation of the methylphenylsulphonium ylide (93), but with triphenylphosphine and

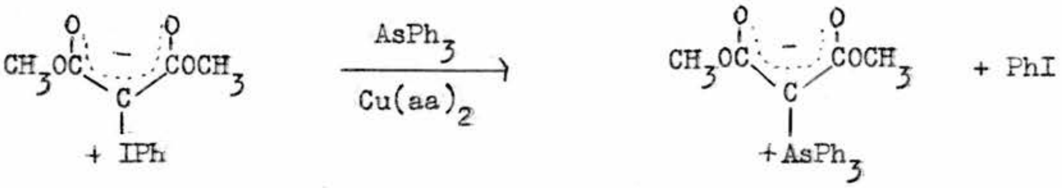


(93)

dimethylsulphoxide, the phosphonium and sulphoxonium ylides were not obtained. In some instances the unchanged iodonium ylide was recovered, but in other cases an oil was obtained. The recovery of iodonium ylide seemed to depend on how fresh the ylide sample was.

(b) Phenyliodonium bis(methoxycarbonyl)methylide.

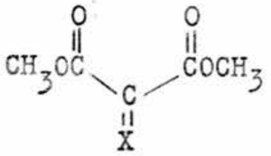
This ylide was found to be more reactive than the iodonium ylide (87). The arsonium ylide (90) could be obtained in reasonable yields by heating a mixture of triphenylarsine and the iodonium ylide (88) in ethanol in the presence of copper acetylacetonate, but again if the reaction was carried out in the absence of catalyst no arsonium ylide was obtained.



(87) (90)

Only a trace amount of catalyst , 5m.mole of copper acetylacetonate per 1 mole of iodonium ylide (88), was required to effect the catalytic decomposition of this ylide and the iodonium ylide also reacted readily with triphenylarsine in methylene chloride.

The catalytic decomposition of the iodonium ylide (88) was also carried out in the presence of thioanisole, diphenylsulphide, dimethylsulphoxide and triphenylphosphine and the corresponding ylides (94), (95), (96) and (97) were obtained.



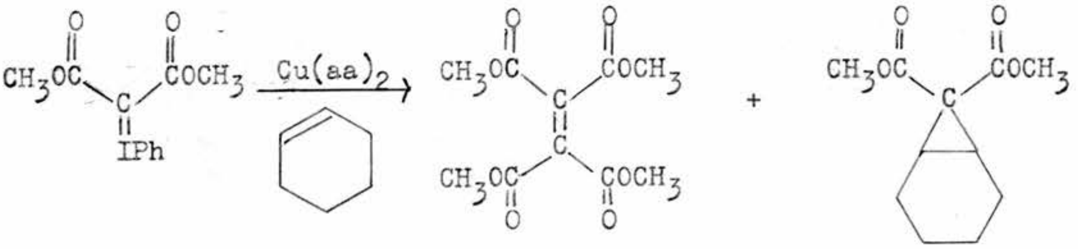
(94) $X = MeSPh$

(95) $X = Ph_2S$

(96) $X = Me_2SO$

(97) $X = Ph_3P$

An attempt to use this method to prepare triphenylstibonium bis(methoxycarbonyl)methlide by reacting triphenylantimony with the iodonium ylide (88) failed, as did an attempt to react the iodonium ylide with thiourea. Presumably, either these compounds are not sufficiently good carbene acceptors to undergo this reaction, or the ylide is formed but decomposes under the reaction conditions. The decomposition of the ylide (87) in cyclohexene in the presence of copper acetylacetonate resulted in the formation of 1,1,2,2, - tetrakis(methoxycarbonyl)ethene (98) and 7,7 - bis(methoxycarbonyl) bicyclo[4,1,0]heptane (99). This is strong evidence that an intermediate carbene is being generated when the iodonium ylide is decomposed in the presence of a copper catalyst. The products (98) and (99) were formed in approximately equal amounts.

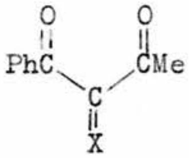


(98) (99)

(c) <u>Phenyliodonium benzoylacetmethylide</u>.

This iodonium ylide (100) reacted with triphenylarsine in ethanol in the presence of copper acetylacetonate to give the triphenylarsonium ylide (101). A minimum ratio of 0.03 mole of copper acetylacetonate per 1 mole of iodonium ylide was required to obtain optimum yields of the arsonium ylide. If 8m.mole of catalyst per 1 mole of iodonium ylide was used, the arsonium ylide was obtained in small yields and below this ratio no arsonium ylide was obtained.

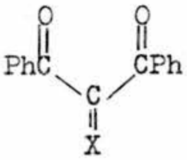
The copper catalysed decomposition of the iodonium ylide (100) in thioanisole gave the corresponding methylphenylsulphonium ylide (102).



(100) X = IPh. (101) X = $AsPh_3$. (102) X = MeSPh.

(d) Phenyliodonium dibenzoylmethylide.

This iodonium ylide (103) reacted with triphenylarsine and thioanisole in the presence of copper acetylacetonate (8m.mole per 1 mole of iodonium ylide) to give the corresponding triphenylarsonium and methylphenylsulphonium ylides (104) and (105) respectively.



(103) X = IPh. (104) X = $AsPh_3$. (105) X = MeSPh.

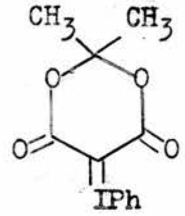
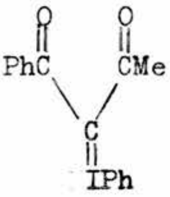
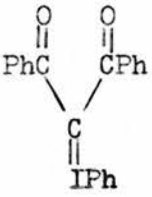
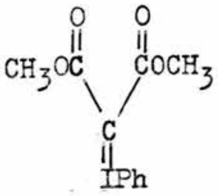
(e) Conclusion.

The phenyliodonium ylides studied reacted readily with triphenylarsine and some other carbene acceptors, but only when the ylide was decomposed in the presence of a copper catalyst and it is interesting to compare this lack of reactivity in the absence of catalyst with the lack of reactivity of some substituted diazocyclopentadienes with triphenylarsine in similar conditions (see Introduction, section 6).

The formation of the addition product (99) and the dimer (98) from the copper catalysed decomposition of the iodonium ylide (88) in cyclohexene substantiates the evidence in the Introduction, section 5(c), that iodonium ylides decompose via a carbene intermediate. The fact that reaction only occurs in the presence of a copper catalyst suggests the intermediacy of a ketocarbene-metal chelate complex which stabilises the carbene sufficiently to enable it to react preferentially with the required substrate. In addition, complexing of the copper with the iodonium ylides may well favour the cleavage of the X_2C - I bond. The possibility of the participation of copper compounds in the cleavage of diaryliodonium compounds has been mentioned in the literature [119]. It is interesting to note that the intermediate reacts preferentially with triphenylarsine (or thioanisole etc.) rather than with ethanol and it is likely that the catalyst has an organisational role and brings the reactants together.

There would appear to be a minimum temperature below which the iodonium ylides will not decompose, but this varies from ylide to ylide. Whereas the iodonium ylide (88) reacted with triphenylarsine in methylene chloride, the copper catalysed decomposition of iodonium ylide (87) in methylene chloride was not particularly successful.

Table 2.

	 (87)	 (100)	 (103)	 (88)
Reaction Time (hrs.)	2	2	1½	1½
Catalyst concentration per mole of ylide.	0.15 mole	30m.mole	8m.mole	5m.mole
Copper compounds ligands	% Yield of arsonium ylide.			
(a) acetylacetone	81	81	81	69
(b) benzoylacetone	82	85	81	74
(c) dibenzoylmethane	0	81	81	63
(d) acetylacetone monoanil	82	81	81	71
(e) acetylacetone bisanil	80	82	83	74
(f) dipivaloylmethane	75	82	83	74
(g) $(CH_2NHCMe{=}CHCOMe)$	0	64	69	57
(h) acetate	31	82	73	63
(i) pyridine$_2$ chloride$_2$	0	81	73	50
(j) chloride	0	72	82	45
(k) dicyclohexyl-18-crown-6	0	0	0	52
(l) copper bronze	50	0	0	52
(m) tartrate	0	0	0	46.5
(n) 5,12-dimethyl-7,14-diphenyl -1,4,8,11-tetra-aza cyclotetradeca-4,11-diene	0	0	0	54
rhodium acetylacetonate	0	0	0	43

No reaction with nickel, platinum, paladium, zinc, uranyl or vanadyl acetylacetonate.

(iv) THE CATALYTIC DECOMPOSITION OF SOME IODONIUM YLIDES.

Although it is known that salts and complexes catalyse the decomposition of iodonium ylides, little has been reported on how these compounds function as catalysts. To try to gain some information on the factors influencing the effectiveness of copper compounds as catalysts, the iodonium ylides (87), (88), (100) and (103) were decomposed in the presence of triphenylarsine using copper complexes with ligands of various sizes, and copper salts as catalysts. The reactions were carried out in ethanol and the same batch of ylide was used for each series of reactions. The amount of catalyst used per mole of ylide and the yield of the corresponding arsonium ylide obtained are given in Table(2).

From Table (2) the general observation can be made that the copper compounds are good catalysts for the decomposition of all four ylides, but that their effectiveness varies from ylide to ylide. Iodonium ylide (88) reacted with triphenylarsine in the presence of almost any copper containing compounds, whereas the iodonium ylide (87) only reacted with triphenylarsine in the presence of a smaller range of compounds. Furthermore, the minimum concentration of copper catalyst per ylide for the reaction to occur varied from ylide to ylide, with ylide (88) requiring the lowest concentration and ylide (87) the highest. In all four cases however, the homogeneous catalysed reactions were more successful than the reactions catalysed by copper bronze.

In the solid state, copper acetylacetonate is square planar. If the copper compounds catalyse the decomposition of the iodonium ylides by a template effect in solvent, in complexation with the reactants this square planar state may be distorted and the reactants may occupy positions 'cis' to one another. If this is the case, then it might be expected that steric factors and also conformational factors ie. whether the reactants are adjacent to one another, would be important. In the case of complexes with bulky ligands such as compounds (c) and (f) (see Table 2), there could be steric hindrance to the complexing of the iodonium ylides with copper, and furthermore these ligands would hinder the approach of triphenylarsine. This should result in there being a lower yield of arsonium ylide and for the catalytic decomposition of iodonium ylide (87) by compound (c) this would indeed appear to be the case. This catalyst is however, not readily soluble in ethanol. Iodonium ylide (87) requires the highest catalyst to ylide ratio for reaction to take place and the lack of reaction in this case is probably because the catalyst was not sufficiently soluble in ethanol to reach this minimum concentration. This explanation is substantiated by the fact that the other three ylides all reacted with triphenylarsine in the presence of this catalyst. The inability of some copper salts to catalyse the decomposition of iodonium ylide (87) may again be due to their insolubility in ethanol and it is interesting to note that copper acetate which is reasonably soluble in ethanol will catalyse this reaction.

Compounds such as (k) and (n) with which the reactants would have to complex 'trans' to one another were not good catalysts, suggesting that conformational factors are important.

None of nickel, platinum, paladium, zinc, uranyl or vanadyl acetylacetonate was effective as a catalyst for this reaction. Rhodium acetylacetonate catalysed the decomposition of iodonium ylide (88) to give the arsonium ylide but the ylide obtained was not as pure as that obtained from the copper catalysed reactions and furthermore, this compound did not catalyse the decomposition of the other three iodonium ylides to give the corresponding arsonium ylides. It is difficult to say why only copper compounds are effective as catalysts, but the favourable reduction potential of the Cu^{2+} ion may be important.

Summarising the observations made this far, it would appear that the iodonium ylides require a certain minimum ratio of catalyst to ylide before reaction takes place and this ratio varies from ylide to ylide, with the result that in the case of iodonium ylide (87) the insolubility of some of the complexes and salts in ethanol impairs their ability to function as catalysts. Furthermore, copper complexes in which the reactants could not be adjacent to one another were not effective as catalysts. From this second observation, that if the reactants are 'trans' to one another reaction is hindered, it appears that the reactants must complex 'cis' to one another for reaction to take place. In the case of the complexes (a)-(f) it is possible that they distort in solution allowing the reactant to complex adjacent to one another and that this would favour reaction.

Another factor that might be involved is how well the ylides complex with copper. High electron density favours complexing and therefore dimethylmalonate with its two methoxy groups might be expected to be a better ligand than benzoylacetone, dibenzoylmethane or Meldrum's Acid.

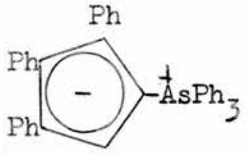
In conclusion, it is not possible to say exactly how the catalyst functions, but the evidence of this work suggests that conformational factors are important and that the catalyst has an organisational role and brings the reactants together. In addition, the catalyst may well weaken the $\overset{-}{C} - \overset{+}{I}$ band and then stabilise the intermediate carbene sufficiently that it can react preferentially with the triphenylarsine.

2. AN INVESTIGATION OF SOME TRIARYLARSONIUM YLIDES.

(i) PREPARATION OF ARSONIUM YLIDES.

(a) Triarylarsonium 2,3,4-triphenylcyclopentadienylides.

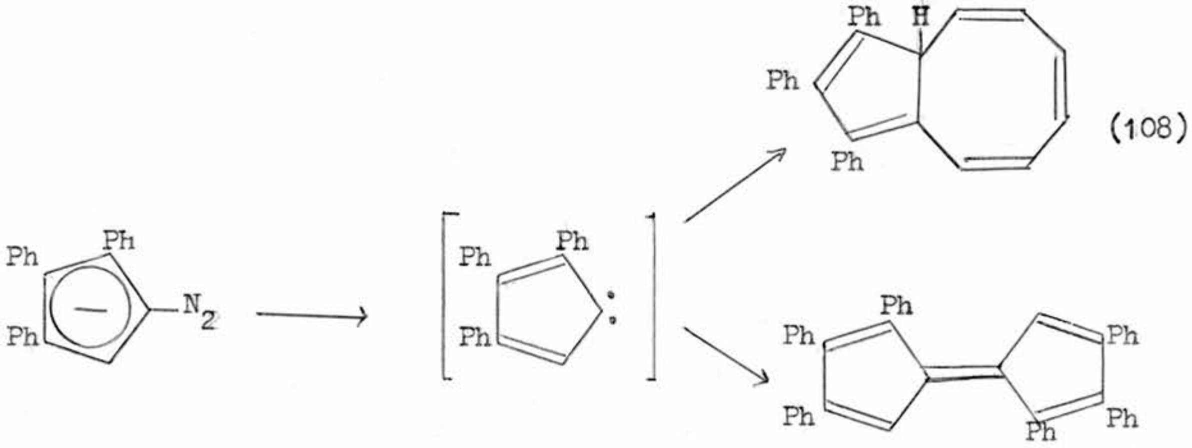
Diazo-2,3,4-triphenylcyclopentadiene is known to react with triphenylarsine in melt conditions, or in benzene solution in the presence of copper-bronze, to give triphenylarsonium 2,3,4-triphenylcyclopentadienylide (106) in yields of 52 and 35% respectively [92].



(106)

It has now been found that this preparation can be improved by using copper acetylacetonate instead of copper-bronze as the catalyst. The decomposition was carried out in benzene, and removal of the solvent and trituration of the residue with ether gave the arsonium ylide (106) in an 85% yield.

As with copper-bronze, the presence of this catalyst allowed the reaction to be carried out at temperatures below the melting point of diazo-2,3,4-triphenylcyclopentadiene, but in this case the reaction was carried out in a homogeneous medium. Diazo-2,3,4-triphenylcyclopentadiene decomposes to give a carbene which then reacts with a carbene acceptor such as triphenylarsine (see Introduction, section 6) and in this case the reaction is likely to proceed via a carbene - copper chelate complex. The good yield of the triphenylarsonium ylide (106) demonstrates that this reactive intermediate is selective and that it reacts preferentially with triphenylarsine rather than with itself or with benzene.

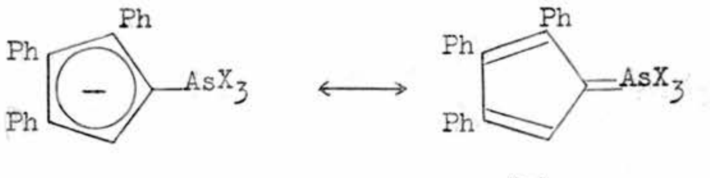


(108)

(107)

Diazo-2,3,4-triphenylcyclopentadiene has been decomposed in ethanol heated under reflux to give the fulvene (107) [120] and photolytic decomposition of the same diazo-compound in benzene gave the product (108) [121]. It is interesting to compare the copper catalysed decomposition of diazo-2,3,4-triphenylcyclopentadiene with the copper catalysed decomposition of iodonium ylides discussed earlier. In both cases the reactions were more successful when they were carried out in a homogeneous medium and in addition, both reactions are thought to occur via a carbene-copper intermediate. Presumably the factors that influence the efficiency of copper compounds as catalysts mentioned earlier would apply to the copper catalysed decomposition of diazocyclopentadienes, but the insolubulity of some of the copper compounds, especially the salts, in benzene precluded their use in this case. Copper acetylacetonate is soluble in benzene in the catalytic amounts used.

This method was extended to the preparation of other triarylarsonium ylides and the decomposition of diazo-2,3,4-triphenylcyclopentadiene in the presence of tri-p-tolyl-, tri-p-methoxyphenyl-, tri-m-tolyl-, tri-o-tolyl- and tri-o-methoxyphenyl-arsine in a similar manner to that described above for triphenylarsine gave the corresponding arsonium ylides (109), (110), (111), (112) and (113) in good yields.



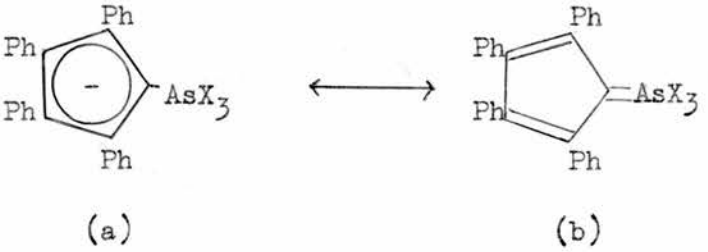
(a) (b)

(109) X = p-tolyl.
(110) X = p-methoxyphenyl.
(111) X = m-tolyl.
(112) X = o-tolyl.
(113) X = o-methoxyphenyl.

(b) Triarylarsonium 2,3,4,5 - tetraphenylcyclopentadienylides.

Triphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (114) has previously been prepared by decomposing diazo - 2,3,4,5 - tetraphenylcyclopentadiene in the presence of triphenylarsine in the melt[103]. Again it was found that if copper acetylacetonate was used in the ylide forming reaction, the reaction could be carried out in solution at markedly lower temperatures and that the triphenylarsonium ylide was obtained in better yields than before. The mechanism of the reaction is assumed to be the same as that discussed for diazo-2,3,4 - triphenylcyclopentadiene.

Tri-o-tolylarsonium and tri-o-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylides (115) and (116) were prepared in an analogous manner by reacting diazo-2,3,4,5 - tetraphenylcyclopentadiene with tri-*o*-tolylarsine and tri-*o*-methoxyphenylarsine respectively. Both ylides were obtained in good yields.



(a) (b)

(114) X = Ph_3
(115) X = *o*-tolyl.
(116) X = *o*-methoxyphenyl.
(117) X = *p*-tolyl.
(118) x = *p*-methoxyphenol.

Tri-*p*-tolylarsonium and tri-*p*-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylides (117) and (118) proved slightly more awkward to obtain. The ylide forming reaction was carried out with tri-*p*-tolylarsine and tri-*p*-methoxyphenylarsine as described above for triphenylarsine, but suprisingly trituration of the residue remaining after the removal of the solvent with ether did not precipitate out the desired ylides and in fact the residue dissolved in ether. The addition of light petroleum to the ether solution however, precipitated out the arsonium ylides (117) and (118) respectively, but the yields obtained were not as high as that of the other triarylarsonium ylides prepared. Diazo-2,3,4,5 - tetraphenylcyclopentadiene must react with an equimolar amount of tri-*p*-methoxyphenylarsine, otherwise the excess arsine contaminates the ylide product.

(c) Attempted Preparation of Tri-o-tolylarsonium 2,4-diphenylcyclopentadienylide.

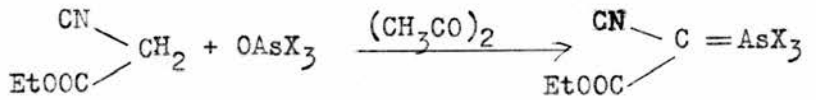
Triphenylarsonium 2,4-diphenylcyclopentadienylide has been prepared by the condensation of triphenylarsine oxide with 1,4-diphenylcyclopentadiene in triethylamine in the presence of phosphorus pentoxide [92]. However, an attempt to prepare tri-*o*-tolylarsonium

2,4 - diphenylcyclopentadienylide using this method failed and tri-*o*-tolylarsine oxide was recovered.

(d) Miscellaneous Triarylarsonium Ylides.

In addition to the preparation of arsonium ylides by the decomposition of diazo-compounds in the presence of triphenylarsine, another method by which triphenylarsonium ylides are commonly formed is by condensing triphenylarsine oxide with reactive methylene compounds[46]. This method was used to prepare some other triarylarsonium ylides.

Tri-*p*-tolyl, tri-*o*-tolyl and tri-*o*-methoxyphenyl-arsonium cyanoethoxycarbonylmethylides (119), (120), and (121) were formed in good yields from the condensation of the corresponding arsine oxide with ethyl cyanoacetate in acetic anhydride.



$$\begin{matrix}CN \\ EtOOC\end{matrix} CH_2 + OAsX_3 \xrightarrow{(CH_3CO)_2} \begin{matrix}CN \\ EtOOC\end{matrix} C = AsX_3$$

(119) X = *p*-tolyl; (120) X = *o*-tolyl; (121) X = *o*-methoxyphenyl.

Tri-*o*-tolylarsonium dicyanomethylide (122) was prepared in a similar manner, but when this method was applied to the preparation

$$(CN)_2CH_2 + OAs(\underline{o}\text{-tolyl})_3 \longrightarrow \underset{(122)}{(CN)_2C = As(\underline{o}\text{-tolyl})_3}$$

of tri-*p*-tolylarsonium dicyanomethylide a brown oil resulted which could not be induced to crystallise. An infra-red spectrum of the oil had no peak at approximately 880 cm^{-1} corresponding to the As=O bond. It therefore appears likely that the ylide was formed, but that it does not crystallise readily.

No tri-o-tolylarsonium ylides were formed when tri-o-tolylarsine oxide was heated with dimethyl malonate, ethyl acetoacetate or acetylacetone, in acetic anhydride. In each case an infra-red spectrum of the reaction product showed a peak at approximately 880 cm^{-1} corresponding to the As=O bond, indicating the presence of unchanged tri-o-tolylarsine oxide. Similarly, an attempt to condense acetylacetone with tri-o-tolylarsine oxide in the presence of triethylamine and phosphorus pentoxide failed and an infra-red spectrum of the residue again showed that tri-o-tolylarsine oxide was present.

The condensation of nitromethane with tri-o-tolylarsine oxide in the presence of triethylamine and phosphorus pentoxide also failed. When this reaction was repeated in acetic anhydride, tri-o-tolylarsine was obtained from the work up. Tri-o-tolylarsine oxide is stable in nitromethane or acetic anhydride and it is surprising that a combination of the two results in the reduction of the arsine oxide to the arsine. If the ylide was formed it is unlikely that it would decompose to give tri-o-tolylarsine. There is no obvious mechanism for this reaction.

As the above condensation reactions were not successful, the preparation of tri-o-tolylarsonium ylides by another route was investigated. Ethyl acetoacetate was added to a solution of triphenyl - and tri-o-tolyl **arsine dibromide respectively** in the presence of triethylamine. In both cases, the corresponding triarylarsine oxides were isolated from the reaction mixture. Presumably, either the ethyl acetoacetate anion is not sufficiently nucleophilic to attack the dibromide or the dibromide hydrolyses before reaction can take place.

There is no obvious reason why tri-*o*-tolylarsine oxides should not condense with the above β-dicarbonyl compounds and yet react with the cyano-substituted compounds, since from Table (3) it can be seen that the cyano-substituted compounds are not more acidic than the β-dicarbonyl compounds.

Table (3)

	pK_a
Acetylacetone	9
Ethyl cyanoacetate	9
Ethyl acetoacetate	11
Dicyanomethane	11
Diethyl malonate	13
Nitromethane	16

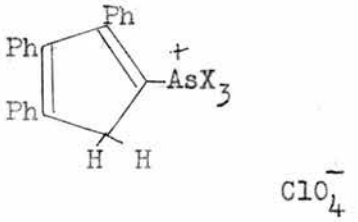
Similarly, tri-*o*-tolylarsine oxide would not condense with 1,4-diphenylcyclopentadiene, whereas triphenylarsine oxide would [92].

Tri-*o*-tolylarsine was also found to be unusually unreactive and whereas triphenylarsine and a variety of triethyl - and *p*-substituted triaryl - arsines are known to react with benzyl bromide [122], attempts to prepare benzyltri-*o*-tolylarsonium bromide by reacting tri-*o*-tolylarsine and benzyl bromide neat, in benzene, ethanol, butanol, nitromethane or in nitromethane in the presence of sodium iodide, all failed. In a similar manner tris(*p*-chlorophenyl)arsine would not react with benzyl bromide, and silver tetrafluoroborate had to be added to eliminate the bromide ion from the system [122]. Whereas the chloro group has an electron withdrawing effect, the methyl group is an electron repeller and the ortho-methyl groups would be expected to make the arsenic more nucleophilic. In addition, the Ph-As bond should be sufficiently long that there would be little steric hindrance from the methyl groups. There is therefore no obvious reason why reaction does not take place, but steric factors are possibly the most likely.

(ii) PHYSICAL PROPERTIES.

(a) Triarylarsonium 2,3,4-triphenylcyclopentadienylides.

The triarylarsonium 2,3,4-triphenylcyclopentadienylides (109), (110), (111), (112) and (113) were faintly yellow crystalline compounds with melting points in the range 220-240°, except for the tri-m-tolylarsonium ylide (110) which had a melting point of 181-184° . They were all stable at room temperature and the ylides were insoluble in water, ethanol, ether and light petroleum, but dissolved in benzene and chloroform. The ortho-substituted ylides (112) and (113) were found to be more insoluble in general that the other ylides. The ylides dissolved in dilute mineral acids and the ylides (109), (111) and (112) were dissolved in perchloric acid to give the yellow crystalline perchlorates (123), (124) and (125), presumably with protonation taking place at the 5-position thereby giving compounds with most conjugation [115].



(123) X = p-tolyl.

(124) X = m-tolyl.

(125) X = o-tolyl.

The pK_a's of the perchlorates (123), (124) and (125) were determined spectroscopically in 95% ethanol solution using the same method as Johnson [41]. Solubility characteristics required the use of this solvent and as a result the pH values of the buffers measured with the pH meter differed from those expected for aqueous solution. Therefore the pK_a values determined for the salts are only relative and cannot be compared to values determined in aqueous media. The pK_a of tri-p-tolyl(2,3,4-triphenylcyclopentadienyl)arsonium perchlorate (123) was 7.0 and the corresponding tri-m-tolyl and tri-o-tolyl perchlorates (124) and (125) had pK_a's of 6.9 and 5.8 respectively. The pK_a of triphenyl-(2,3,4-triphenylcyclopentadienyl)arsonium perchlorate, carried out under identical conditions, was 6.6. These results indicate that the tri-p-tolyl and tri-m-tolylarsonium ylides (109) and (111) are more basic than the triphenylarsonium ylide (106). The inductive effect of the methyl group of the tolyl substituents would be expected to increase the electron density at the arsenic atom with respect to the unsubstituted phenyl groups, with the result that these ylides would be more basic and have more single bond character. The positive arsenic would induce a fractional positive change on the benzene ring at positions ortho and para to itself, with the result that the p-tolyl substituent would be expected to have a greater effect than the m-tolyl substituent.

Surprisingly, the pK_a measurement of the tri-o-tolyl arsonium perchlorate (125) indicates that the tri-o-tolyl arsonium ylide (112) is less basic than the triphenylarsonium ylide (106) , which in turn suggests that the apolar form (112b) contributes more to the overall structure than does the apolar structure to the triphenylarsonium ylide (106). This is the opposite to what might be expected. The factors that could be causing this will be discussed once the reactions of the triarylarsonium ylides have been mentioned.

The dipole moments of these ylides, shown in Table 4 did not follow the same pattern as the pK_a measurements, but instead all the substituted ylides had a dipole moment greater than the triphenylarsonium ylide (106), suggesting that the ylides all have a larger contribution from the dipolar form. The order of the dipole moments did not follow a meaningful pattern.

Table 4

Heteroatom group	M
(106) Ph	8.08 ± 0.1D
(109) p-tolyl	9.35 ± 0.2D
(111) m-tolyl	8.70 ± "
(110) p-methoxyphenyl	8.77 ± "
(112) o-tolyl	8.8 ± "
(113) o-methoxyphenyl	9.49 ± 0.04

The N.M.R. spectra of these ylides showed a complex centred at 7.0δ corresponding to twenty-seven phenyl protons and a singlet corresponding to nine methyl or methoxy protons. Interestingly, in the case of the tri-o-tolylarsonium ylide (112) the methyl groups appeared 0.3 δ upfield from the methyl peak of tri-o-tolylarsine whereas the methyl groups of the tri-p-tolylarsonium ylide (109) had the same shift as the methyl groups of tri-p-tolylarsine. Similarly, the methoxy peak of tri-o-methoxyphenylarsonium ylide (113) was displaced 0.25 δ upfield from the methoxy peak of tri-o-methoxyphenylarsine, whereas again the methoxy peak of tri-p-methoxyphenylarsonium ylide (111) and tri-p-methoxyphenylarsine occurred at the same shift. Presumably, the ortho substituents are lying over the face of the phenyl rings of the triphenylcyclopentadiene, with the result that the magnetic anisotropic effect of the benzene nuclei shield the methyl or methoxy nuclei.

(b) Triarylarsonium 2,3,4,5 - tetraphenylcyclopentadienylides.

The triarylarsonium 2,3,4,5 - tetraphenylcyclopentadienylides (115), (116), (117) and (118) were crystalline compounds, varying in colour from pale yellow to orange and they had melting points of over 210° except for the tri-p-methoxyphenylarsonium ylide (118) which had an unusually low melting point of 127-130°. All the ylides were stable at room temperature and the ortho-substituted ylides (115) and (116) were insoluble in ether, methanol and light petroleum, but they dissolved in benzene and chloroform. The para-substituted ylides (117) and (118) on the other hand, dissolved in methanol, benzene and chloroform and were partially soluble in ether, but were insoluble in light petroleum.

The tri-o- tolylarsonium ylide dissolved in perchloric acid to give tri-o-tolyl(2,3,4,5-tetraphenylcyclopentadienyl)arsonium perchlorate. The pK_a of this perchlorate determined in 95% ethanol was 7.0 whereas the pK_a of triphenylarsonium(2,3,4,5-tetraphenylcyclopentadienyl) arsonium perchlorate was 7.5. This indicates that the tri-o-tolylarsonium ylide (115) is less basic than the triphenylarsonium ylide (114) and the position is exactly analogous to the triarylarsonium 2,3,4-triphenylcyclopentadienylide system. In other words, (115b) appears to contribute more to the overall structure of the tri-o-tolylarsonium ylide (115) than does (114b) to the overall structure of the triphenylarsonium ylide (114).

The N.M.R. spectra of the tri-o-tolylarsonium ylide (115) at 70° showed a multiplet centres on approximately 7.0δ and a broad singlet at 1.85δ. At -45° three peaks at 1.1δ 1.5δ and 2.75δ were observed and the methyl peaks coalesced at approximately 10°. The ortho-methyl groups appear to be hindering rotation about the $\overset{+}{As} - \overset{-}{C}$ bond. Tri-o-methoxyphenylarsonium ylide (116) showed a complex centred at approximately 7.0δ and a sharp singlet at 3.2δ. The solution was cooled to -50°, but the methoxy peak showed no sign of separating into more than one peak. The insolubility of these ylides in acetone and D.M.S.O. meant that the N.M.R.'s were carried out in chloroform and this limited the temperature range that could be studied. The spectra clearly showed however, that the ortho-methyl groups sterically hinder rotation about the $\overset{+}{A}s$ - phenyl bond more than the ortho-methoxy groups. Again, as with the triarylarsonium 2,3,4-triphenylcyclopentadienylide analogues, the ortho-methyl and ortho-methoxy peaks were shifted upfield from the corresponding peaks of tri-o-tolyl and tri-o-methoxyphenylarsine, presumably for the same reason. Tri-p-tolylarsonium ylide (117) and tri-p-methoxyphenylarsonium ylide (118) showed multiplets centred at approximately 7.0δ and singlets at 2.35δ and 3.8δ respectively.

(c) Triarylarsonium cyanoethoxycarbonylmethylides.

The triarylarsonium cyanoethoxycarbonylmethylides (119), (120) and (121) were colourless crystalline compounds with melting points of about 230°. They were all stable at room temperature and were soluble in benzene, chloroform, carbon tetrachloride and methanol, but were insoluble in ether, light petroleum and water.

In the infra-red spectrum of the ylides, the stretching frequencies associated with the electron withdrawing substituents on the ylides were uniformly low because of the delocalisation of the negative charge into these groups. Thus, the carbonyl group showed an absorption in the range 1605-1650 cm^{-1}, and the cyanide group showed a peak at 2175 cm^{-1}.

The N.M.R. spectra are recorded in the spectra section, but it is worth noting that, unlike the triarylarsonium ylides (112), (113), (115) and (116), the ortho-methyl and-methoxy peaks were not shifted significantly upfield from the methyl and methoxy peaks of tri-o-tolyl- and tri-o-methoxyphenyl-arsine.

(d) Tri-o-tolylarsonium dicyanomethylide.

The properties of tri-o-tolylarsonium dicyanomethylide were similar to those of the triarylarsonium cyanoethoxycarbonylmethylides. The colourless compound had a melting point of 250° and showed peaks at 2140 and 2170 cm^{-1} in the infra-red spectrum corresponding to the cyanide groups. The N.M.R. spectrum showed a complex centred on approximately 7.4δ and a singlet at 2.35δ. Again this peak was not shifted upfield significantly from the methyl peak of tri-o-tolylarsine.

(iii) REACTIONS OF THE ARSONIUM YLIDES.

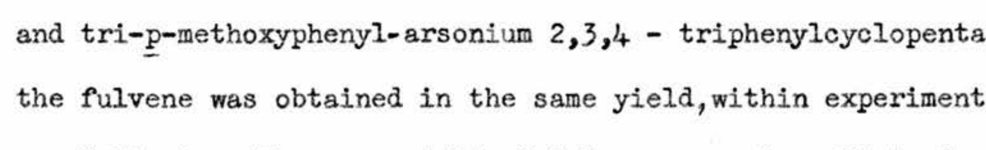
(a) Triarylarsonium 2,3,4 - triphenylcyclopentadienylides.

1. Carbonyl compounds.

The pK_a values of the triarylarsonium ylides suggested that tri-o-tolylarsonium ylide (112) had more double bond character than triphenylarsonium ylide (106), while p-tolylarsonium ylide (109) appeared to have more single bond character. Changes in pK_a values are often reflected by changes in reactivity. The reactions of triarylarsonium ylides with carbonyl compounds were investigated to see if this was indeed the case.

Triphenylarsonium 2,3,4 - triphenylcyclopentadienylide (106) had previously reacted with benzaldehyde in carbon tetrachloride [115], but because of the insolubility of the ortho-substituted ylides in this solvent the reactions were now all carried out in benzene.

Triphenylarsonium 2,3,4 - triphenylcyclopentadienylide reacted with benzaldehyde in benzene over 18 hours to give a 58% yield of 1,2,3,6 - tetraphenylfuvene as shown in (126) and with tri-p-tolyl -, tri-m-tolyl - and tri-p-methoxyphenyl-arsonium 2,3,4 - triphenylcyclopentadienylides the fulvene was obtained in the same yield, within experimental error - see Table 4. The same yield of fulvene was also obtained when triphenylarsonium ylide (106) reacted with benzaldehyde in chloroform.

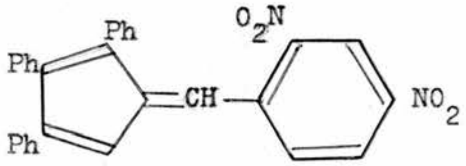


X = Ph, p-tolyl, p-methoxyphenyl, m-tolyl.

(126)

In a similar manner all four ylides reacted with p-nitrobenzaldehyde in benzene over four hours to give 6-p-nitrophenyl-1,2,3, - triphenylfulvene in yields of approximately 90%. Tri-o-tolyl - and tri-o-methoxyphenyl-arsonium 2,3,4- triphenylcyclopentadienylides (112) and (113) however, did not react with p-nitrobenzaldehyde under similar conditions, nor when the reactants were heated together for eighteen hours. In both cases unchanged arsonium ylide was recovered.

The ortho-substituted ylides (112) and (113) were next treated with 2,4- dinitrobenzaldehyde to try to estimate how unreactive these ylides are. Triphenylarsonium ylide (106) reacted with 2,4-dinitrobenzaldehyde to give an 88% yield of the fulvene (127). Tri-o-tolylarsonium ylide (112) did not react with 2,4-dinitrobenzaldehyde, but tri-o-methoxyphenylarsonium ylide (113) reacted partially to give a 33% yield of the fulvene (127).



(127)

The ortho-substituted ylides (112) and (113) were thus less reactive than the para-substituted or the unsubstituted ylides as was expected from the pK_a measurements. The reaction of the para-substituted ylides (109) and (100) with benzaldehyde showed that these ylides were not more reactive than the triphenylarsonium ylide (106), and this was contrary to expectation.

2. Nitrosobenzene.

Nitrosobenzene behaves in a similar way to carbonyl compounds in its reaction with ylides. The arsonium ylides (106), (109), (110) and (111) reacted with nitrosobenzene to give N-phenyl-2,3,4-triphenylcyclopentadienone ketoxime (128) in similar yields. Instead of chromatographing the reaction mixture on a liquid filled column, the reaction mixture was chromatographed on a 'dry filled' column and by using this method a yield of over 70% of the ketoxime (128) was obtained instead of a yield of 17% as obtained previously [115].

(128)

X = Ph , p-tolyl , p-methoxyphenyl , m-tolyl .

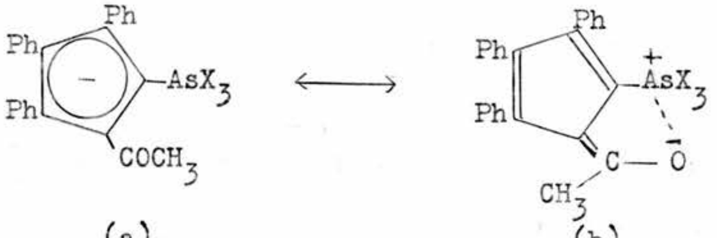
Neither of the ortho-substituted ylides (112) and (113) reacted with nitrosobenzene in benzene nor in chloroform. In both cases the unchanged ylide was recovered.

3. N,N-dimethylamino-4-nitrosobenzene.

An attempted reaction of triphenylarsonium 2,3,4-triphenylcyclopentadiene with N,N-dimethylamino-4-nitrosobenzene was unsuccessful and unchanged arsonium ylide was recovered. The Me_2N group deactivates the nitroso group sufficiently that nucleophilic attack by the ylide would not take place.

4. Acetylation.

Cyclopentadienes, by virtue of the high charge density on the five membered ring, are prone to electrophilic attack (see Introduction, section 3). The acetylation of tri-p-tolyl-,tri-p-methoxyphenyl - and tri-o-methoxyphenyl-arsonium 2,3,4-triphenylcyclopentadienylides took place readily when each ylide was heated to reflux in acetic anhydride to give the ylides (129), (130) and (131) respectively.



(a) (b)

(129) X = p-tolyl; (130) X = p-methoxyphenyl;

(131) X = o-methoxyphenyl.

The infra-red spectrum of each of these ylides did not show a carbonyl absorption above 1600 cm^{-1} and below this value the presence of absorption due to the phenyl groups made it difficult to interpret the spectra. It is interesting to compare these carbonyl absorption peaks with those of arsonium ylides that have been acetylated in the 3 or 4 position which occur about 1640 cm^{-1}[92]. The polarisation of the carbon-oxygen bond in the ylides (129), (130) and (131) is being exaggerated even further when the carbonyl group is in close proximity to the arsenic atom, presumably by interaction between the positive arsenic and the negative oxygen as shown in canonical structure (129-131b).

The N.M.R. spectra of the tri-p-tolylarsonium and tri-p-methoxyphenylarsonium 5-acetyl-2,3,4-triphenylcyclopentadienylides (129) and (130) showed complexes centred on approximately 7.0δ and singlets at 1.7δ corresponding to the acetyl group. The methyl and methoxy peaks showed at 2.3δ and 3.8δ respectively. The methyl peak of the acetyl group occurred further upfield than usual, presumably as a result of the contribution from the structure (129-130b) which would have the effect of reducing the deshielding normally associated with the carbonyl group.

The methoxy groups of tri-o-methoxyphenylarsonium 5-acetyl-2,3,4-triphenylcyclopentadienylide (131) exhibited coalescence at approximately 20°, and at -10° , three singlets at 3.8δ, 3.0δ and 2.8δ were observed (c.f. the spectra of tri-o-tolylarsonium ylide (115)). This steric hindrance to rotation about the $\overset{+}{As} - \overset{-}{C}$ bond presumably arises from the contribution from the structure (131b).

Tri-o-tolylarsonium 2,3,4-triphenylcyclopentadienylide was not acetylated under similar conditions and the unchanged arsonium ylide was recovered. The pK_a of the tri-o-tolylarsonium ylide (112) indicated that this ylide has more double bond character than the triphenylarsonium ylide (106), but it is unlikely that the cyclopentadiene ring of the tri-o-tolylarsonium ylide (112) does not have a sufficiently high electron density to undergo electrophilic attack, as the corresponding phosphonium ylide which is even less basic ($pK_a = 4.2$ as opposed to the arsonium ylide $pK_a = 5.8$) undergoes acetylation[115]. It is more likely that the ortho-methyl groups sterically hinder the electrophilic attack by the bulky acetic anhydride group. This substantiates the conclusion derived from the N.M.R. spectra's of the triarylarsonium 2,3,4,5-tetraphenylcyclopentadienylides that the ortho-methyl groups afford more steric hindrance that the ortho-methoxy groups.

5. Summary of Reactions of Triarylarsonium 2,3,4-triphenylcyclopentadienylides

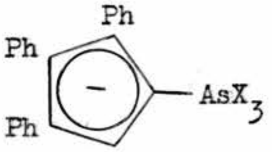


Table 4. Reactivity of ylides with aldehydes.

X	% Yield of fulvene from reaction in benzene at reflux temp. from - benzaldehyde	p-nitrobenzaldehyde	2,4-dinitrobenzaldehyde.
(106) Ph	58	92	88
(107) p-tolyl	56.5	86	-
(110) p-methoxyphenyl	55	87.5	-
(111) m-tolyl	58	90.5	-
(112) o-tolyl	-	0	0
(113) o-methoxyphenyl	-	0	33

Table 5. Reactivity of ylides with nitrosobenzene.

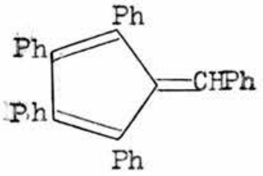
X	Yield of products after reaction in benzene at reflux temp. ketoxime(128)
(106) Ph	72
(109) p-tolyl	73
(110) p-methoxyphenyl	77
(111) m-tolyl	77
(112) o-tolyl	0
(113) o-methoxyphenyl	0

The yields of unchanged ylide recovered are recorded in the Experimental, Part III

(b) Triarylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

1. Carbonyl compounds.

The para-substituted arsonium ylides (117) and (118) both reacted with benzaldehyde in benzene to give a 20% yield of 1,2,3,4,6 - pentaphenylfulvene (132), as did the triphenylarsonium ylide (114) (see Table 6).

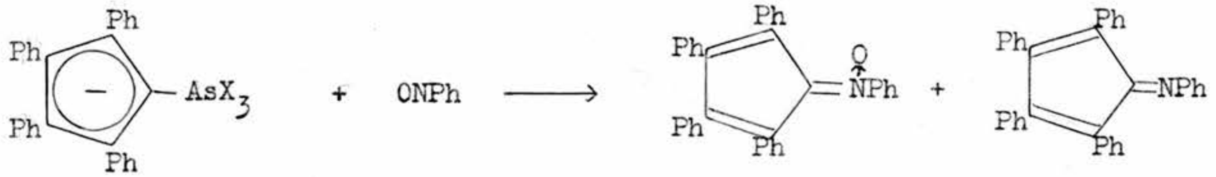


(132)

On the other hand, like the triphenylcyclopentadienylide analogues, neither of the ortho-substituted arsonium ylides (115) and (116) reacted with p-nitrobenzaldehyde in benzene nor in chloroform. In addition neither ylide reacted with 2,4-dinitrobenzaldehyde. In all the above reactions unchanged arsonium ylide was also recovered.

2. Nitrosobenzene.

The triphenylarsonium ylide (114) had previously reacted with nitrosobenzene in benzene to give a 48% yield of N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (133) and a 35% yield of N-phenyl 2,3,4,5 - tetraphenylcyclopentadienone anil (134)[36]. It was now found that the work up for this reaction could be improved by using a 'dry filled' column instead of a 'liquid filled' column. The product (134) was obtained in a better yield of 48% and the reaction products were not contaminated with 2,3,4,5 - tetraphenycyclopentadienone.

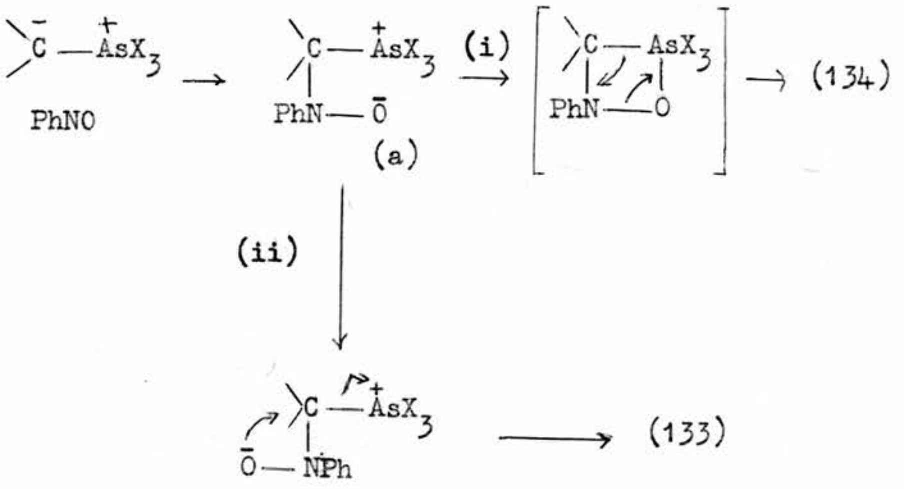


(133) (134)

X = Ph, p-tolyl, p-methoxyphenyl.

The para-substituted ylides (117) and (118) also reacted with nitrosobenzene to give the ketoxime (133) and the anil (134), but the ratio of anil:ketoxime changed from 1:1 to approximately 2:1. For the tri-p-tolylarsonium ylide (117) the yield of products (133) and (134) was 29% and 60%, and for the tri-p-methoxyphenylarsonium ylide (118) the yield was 25% and 48% respectively.

The mechanism of the reaction is believed to involve the betaine intermediate (135a). Obviously the para-substituents are having a



(135)

strong influence on whether path (135i) or (135ii) is followed (see Introduction : section 7). Assuming that the heterolytic cleavage of the $\overset{+}{As}-\overset{-}{C}$ bond occurs in the opposite sense depending upon whether an alkene or an epoxide is formed as shown by the arrows in (135), electron denoting substituents would be expected to increase the ratio of anil to ketoxime and the above results support this view.

The ortho-substituted ylides (115) and (116) did not react with nitrosobenzene in benzene and the unchanged ylides were recovered. When the reactions were repeated in chloroform, surprisingly the tri-*o*-tolylarsonium ylide (115) underwent partial reaction to give a 15% yield of the ketoxime (133). Unchanged arsonium ylide (65%) was also recovered. With tri-*o*-methoxyphenylarsonium ylide (116) a trace amount of what was thought to be the ketoxime (133) was obtained.

3. Effect of Solvent.

Solvent can play a part in determining the course of the Wittig reaction (see Introduction : section 7). The triphenylarsonium ylide (114) was therefore treated with nitrosobenzene in various solvents to see if the product ratio would alter, but when the reaction was carried out in carbon tetrachloride or chloroform there was no significant change in the product distribution from that obtained in benzene. When the reaction was carried out in 400 ml. of absolute methanol however, only the ketoxime (133) was obtained in a yield of 19%. This reaction was repeated in a smaller quantity of methanol (50ml.). Not all the ylide dissolved in methanol, but, of that which did, a 74% yield of the ketoxime (133) was obtained. Similarly both tri-*p*-tolyl- and tri-*p*-methoxyphenyl-arsonium 2,3,4,5-tetraphenylcyclopentadienylides gave only the ketoxime in a 47% yield from their reaction with nitrosobenzene in absolute methanol. Further investigation of these reactions revealed however, that no triarylarsine was present as would be expected if the ketoxime was formed, and that the reaction residues contained 1,2,3,4-tetraphenylcyclopentadiene. Obviously the reaction was not a Wittig reaction and the presence of 1,2,3,4-tetraphenylcyclopentadiene suggested that the ylides were decomposing.

Earlier reports have stated that triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide is stable to hydrolysis by an alcoholic potassium hydroxide solution [36]. Contrary to this, both the para-substituted ylides (117) and (118) decomposed to give 1,2,3,4-tetraphenylcyclopentadiene and the corresponding arsine oxide when heated in absolute methanol overnight. It therefore appears that the triarylarsonium ylides are subject to hydrolysis and the reason that unchanged triphenylarsonium ylide (114) was recovered from the alcoholic potassium hydroxide solution was because of the insolubility of this ylide in alcohol.

It has been reported that the ethoxide catalysed decomposition of triphenyl-p-nitrobenzylphosphonium bromide afforded the same products as were obtained by the reaction of triphenylphosphonium p-nitrobenzylide with ethanol, leading to the conclusion that a pre-equilibrium condition existed for the decomposition reaction [123]. The mechanism for the reaction was portrayed as shown in (136). Reaction of the ylide with O-deuteroethanol afforded di- and trideuteronitrotoluene, indicating clearly that pre-equilibrium occurred with the alcoholic deuterium being removed by the ylidic carbanion.

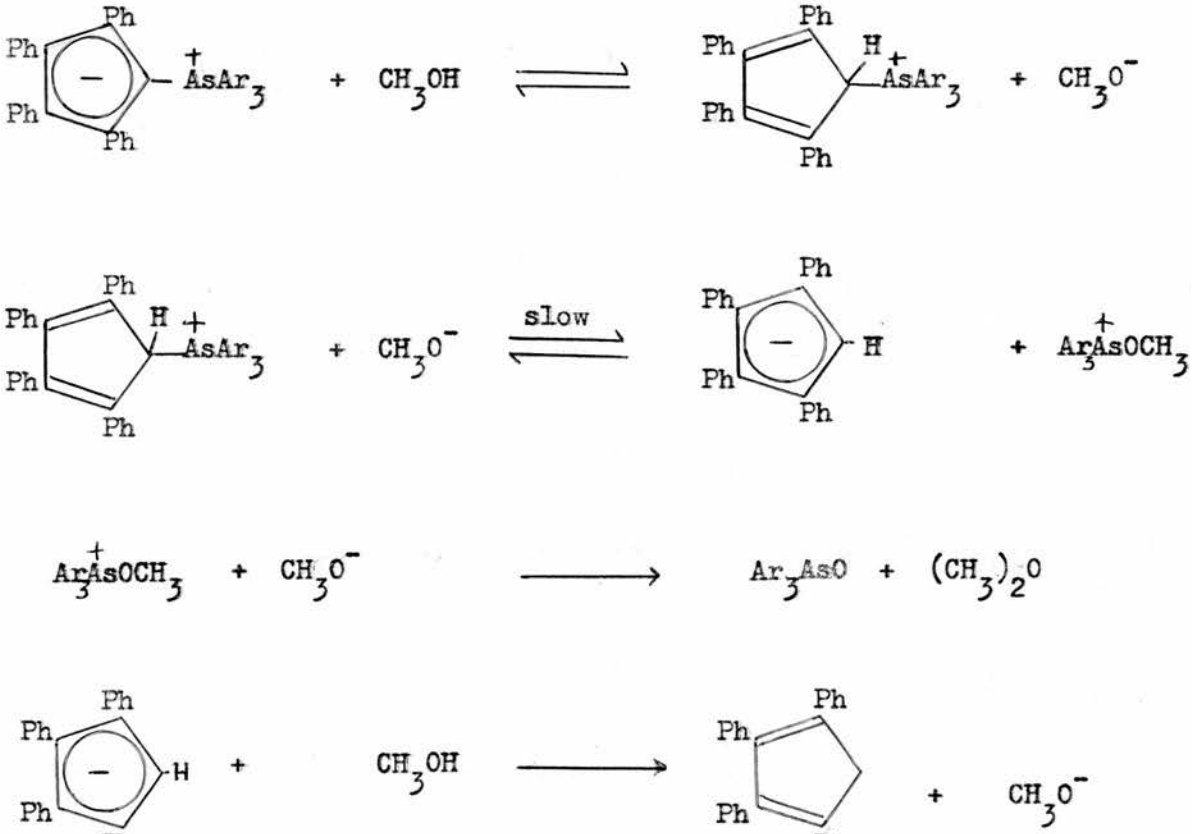
$$Ph_3P{=}CHC_6H_4NO_2(p) + C_2H_5OH \rightleftharpoons Ph_3\overset{+}{P}{-}CH_2C_6H_4NO_2(p) + C_2H_5O^-$$

$$Ph_3\overset{+}{P}{-}CH_2C_6H_4NO_2(p) + C_2H_5O^- \overset{\text{slow}}{\rightleftharpoons} Ph_3\overset{+}{P}OC_2H_5 + \overset{-}{C}H_2C_6H_4NO_2$$

$$Ph_3\overset{+}{P}OC_2H_5 + C_2H_5O^- \longrightarrow (C_2H_5)_2O + Ph_3PO$$

$$^-CH_2C_6H_4NO_2 + C_2H_5OH \longrightarrow CH_3C_6H_4NO_2 + C_2H_5O^-$$

Presumably the methanolysis of the triarylarsonium 2,3,4,5-tetraphenylcyclopentadienylides (117) and (118) occurred by a similar mechanism as shown in (137)



(137)

When this reaction occurred in the presence of nitrosobenzene, the nitrosobenzene probably underwent nucleophilic attack by the 2,3,4,5- tetraphenylcyclopentadienyl anion to give the ketoxime (133), but this reaction competed with the reaction of the anion with methanol. As mentioned earlier, when the triphenylarsonium ylide (114) reacted with nitrosobenzene in methanol, the yield of ketoxime (133) decreased as the solution became more dilute.

4. Summary of Reactions of Triarylarsonium 2,3,4,5 - tetraphenylcyclopentadienylides.

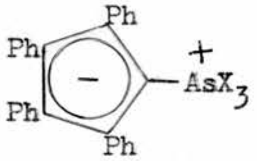


Table 6.

Reactivity of Ylides with aldehydes.

% Yield of fulvene from reaction in benzene at reflux temp. from -

	X	benzaldehyde	p-nitrobenzaldehyde	2,4-dinitrobenzaldehyde.
(114)	Ph	19	-	-
(117)	p-tolyl	20	-	-
(118)	p-methoxyphenyl	17	-	-
(115)	o-tolyl	-	0	0
(116)	o-methoxyphenyl	-	0	0

Table 7.

Reactivity of Ylides with nitrosobenzene.

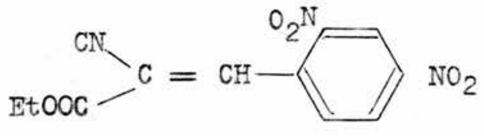
% Yield from reaction in benzene

	X	ketoxime (133)	anil (134)
(114)	Ph	44	48.5
(117)	p-tolyl	28	57
(118)	p-methoxyphenyl	26	48
(115)	o-tolyl	0	0
		15 (chloroform)	0
(116)	o-methoxyphenyl	0	0
		trace(chloroform)	0

The % yield of unchanged arsonium ylide is recorded in the Experimental, Part III.

(c) Triarylarsonium cyanoethoxycarbonylmethylides.

The reactivity of these ylides with carbonyl compounds followed the same trend as that shown by the triarylarsonium 2,3,4-triphenylcyclopentadienylides. Triphenylarsonium- and tri-p-tolylarsonium-cyanoethoxycarbonylmethylides reacted with p-nitrobenzaldehyde in benzene to give a 90% yield of the ethyl-p-nitrobenzylidenecyanoacetate. Tri-p-tolylarsonium cyanoethoxycarbonylmethylide and p-nitrobenzaldehyde in methanol also gave similar yields of ethyl-p-nitrobenzylidenecyanoacetate. Again neither tri-o-tolylarsonium - nor tri-o-methoxyphenylarsonium-cyanoethoxycarbonylmethylides (120) and (121) reacted with p-nitrobenzaldehyde. The reaction of ylide (120) and p-nitrobenzaldehyde was also carried out in toluene and the unchanged arsonium ylide was again recovered. Furthermore, whereas triphenylarsonium cyanoethoxycarbonylmethylide reacted with 2,4-dinitrobenzaldehyde quantitatively to give ethyl 2,4-dinitrobenzylidenecyanoacetate (138), the tri-o-methoxyphenylarsonium ylide (121) reacted only partially to give an 18% yield of the product (138), and the tri-o-tolylarsonium ylide (120) did not react at all.



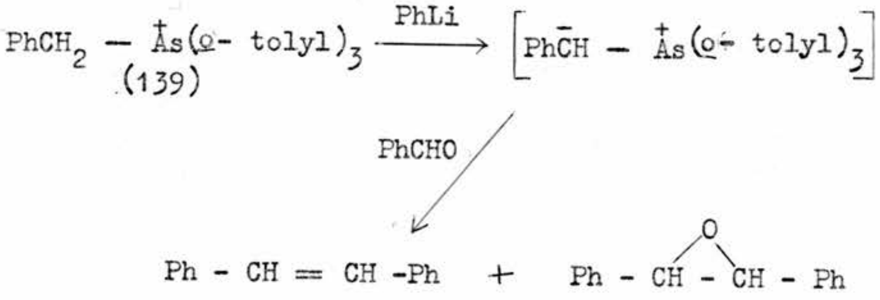
(138)

(d) Tri-o-tolylarsonium dicyanomethylide.

This arsonium ylide (122) did not react with p-nitrobenzaldehyde or 2,4-dinitrobenzaldehyde and the unchanged ylide was recovered in both cases.

(e) Tri-o-tolylarsonium benzylide.

As mentioned earlier it was found that tri-o-tolylarsine would not react with benzyl bromide to give the bromide salt. The addition of silver tetrafluoroborate however, eliminated the bromide ion from the system and benzyltri-o-tolylarsonium tetrafluoroborate (139) was obtained. This salt was treated with phenyllithium to generate tri-o-tolylarsonium benzylide which then reacted *in situ* with benzaldehyde.



Work up gave a 7% yield of the trans-stilbene and a 66% yield of trans-stilbene oxide. Comparing this result with the result in Table (1), it can be seen that the ratio of stilbene to stilbene oxide is approximately the same as that obtained with triphenylarsonium - and tri-p-methoxyphenylarsonium benzylide. Electron donating substituents at the arsenic atom promote alkene formation as discussed in the Introduction, section 7, but it would appear that the ortho-tolyl group like the para-methoxyphenyl group, is not having a marked effect on the reaction course. Presumably the inductive effect of the methyl groups or the donating effect of the methoxy groups is negligible compared to the electron withdrawing effect of the phenyl ring.

(iv) Conclusion.

Summarising the reactions of the triarylarsonium ylides it can be seen that the ortho-substituted ylides which were studied were far less reactive than the corresponding triphenylarsonium ylides and, whereas the triphenylarsonium ylides in some cases reacted with benzaldehyde, the tri-o-tolylarsonium ylides would not react with 2,4-dinitrobenzaldehyde, and the tri-o- methoxyphenylarsonium ylides only reacted partially. The para-substituted ylides were not found to be more reactive than the corresponding triphenylarsonium ylides. There are several factors that could influence the reactivity of these triarylarsonium ylides and these will be discussed in turn.

(a) Electronic Effects.

As discussed in the Introduction, for stabilised phosphonium ylides the most basic ylides are also the most reactive, and electron withdrawing substituents on the phosphorus atom make the ylide more stable and less basic. The phenyl groups in triphenylphosphonium ylides were found to be electron withdrawing. Electron donating substituents on the benzene ring increased the basicity of the ylides. In this work however, it was found that this increase in basicity arising from electron donating substituents in a para position was not paralleled in the reactivity of these substituted ylides, and the tri-p-tolylarsonium ylides (109) and (117) and the tri-p-methoxyphenylarsonium ylides (110) and (118) reacted with benzaldehyde to give the same yield of fulvene as the corresponding triphenylarsonium ylides (106) and (114). In addition, from the reaction of tri-o-tolylarsonium benzylide with benzaldehyde, and from the work carried out by Gosney et al. (see Introduction, Table (1)), it can be seen that electron donating or repelling substituents on the benzene ring are having a negligible effect on the pathway that the reaction takes compared to that taken by the triphenylarsonium benzylide example. It would therefore appear that the donating effect of these groups is insignificant beside the inductive effect of the phenyl groups.

As well as having an electron withdrawing effect, the benzene ring may also have a small mesomeric effect which acts in the opposite sense and increases the electron density at the arsenic. If this is the case then a substituent on the ortho position may sterically distort the triarylarsine group,thereby diminishing this mesomeric interaction. The arsenic would then have a lower charge density and would interact more with $\bar{C}$,with the result that the ylide would be less basic and less reactive. This is in keeping with the unexpectedly low pK_a of the tri-o-tolylarsonium ylides (112) and (115).

(b) Kinetic Effects.

The betaine decomposition step is the rate determining for unstable phosphonium ylides and electron donating groups hinder this step by increasing the electron density on the phosphorus, making subsequent nucleophilic attack by the oxyanion of the betaine more difficult (see Introduction). The situation with the triarylarsonium ylides studied is not analogous however, as these ylides are stable and the betaine formation step is most likely to be the rate determining step. Electron donating substituents would help, not hinder this step.

(c) Steric Effects.

Substituents on the ortho position could lower the reactivity of the ylides by -

a) hindering the reactants coming together,

b) introducing crowding in the formation of the betaine,

c) hindering the attack of the oxyanion of the betaine on the triarylarsine moiety.

It is likely that both electronic and steric factors are involved in the lowered reactivity of the ortho-substituted ylides, but it is difficult to say which factor dominates. The observation that the tri-o-methoxyphenylarsonium ylides appear to be more reactive than the tri-o-tolylarsonium ylides casts some light on the situation however. Whereas the methyl group has an inductive electron repelling effect, the methoxy group has an inductive electron withdrawing effect as well as a mesomeric electron donating effect, and if a substituent on the ortho-position sterically distorts the triarylarsine group, thereby diminishing the mesomeric interaction, the inductive effect of the methoxy group may become more important. The arsenic would have a lower charge density with the result that the ylide would have more double bond character and be more stable. This is the opposite to what was found. In addition, other evidence in this work has already suggested that the donating or repelling effects of the methoxy or methyl groups are negligible compared to the electron withdrawing effect of the phenyl groups.

If electronic effects are not of major importance, it is likely that the over-riding influence may be steric. Some support for this can be gained from the fact that tri-o-methoxyphenylarsonium ylide (113) could be acetylated, whereas tri-o-tolylarsonium ylide (112) was not. It was argued that the methyl group sterically hindered the reaction from taking place, and from this, and from the observation derived from N.M.R. studies that the tri-o-tolyl groups hinder rotation about the $\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{As}}$ bond more than the tri-o-methoxyphenyl groups, it would appear likely that the ortho-methyl groups cause more steric hindrance than the ortho-methoxy groups.

Tri-o-tolyarsonium ylide (115) reacted with nitrosobenzene in chloroform to give the ketoxime (133), but the reaction did not take place in benzene. Tri-o-methoxyphenylarsonium ylide (116) did not react significantly with nitrosobenzene in chloroform or benzene. The reason why tri-o-tolylarsonium ylide (115) reacted with nitrosobenzene and tri-o-methoxyphenylarsonium ylide (116) did not react, and why the reaction occurred in chloroform and not in benzene, is not clear. Chloroform was used as the solvent in some of the other reactions of ortho-substituted ylides and triarylarsonium ylides, but this was the only reaction where it had this effect.

The reaction of triarylarsonium ylides with nitrosobenzene is a more sensitive reaction than the reaction of the ylides with carbonyl compounds, and whereas electron donating substituents on the benzene rings had little effect on the reactions of triarylarsonium benzylides with benzaldehyde, in the reaction of triarylarsonium 2,3,4,5-tetraphenylcyclopentadienylides with nitrosobenzene, electron donating substituents did influence the reaction path.

Thus, taking all the evidence together, the ortho substituents may well distort the triarylarsonium group, thereby diminishing the mesomeric interaction between the phenyl group and the arsenic, but it is unlikely that this electronic effect would lower the reactivity sufficiently to account for the large difference in reactivity of these ylides when compared to the triphenylarsonium ylides. It seems more likely that it is the steric factors that dominate and that ortho-substituents sterically hinder reaction in one of the ways mentioned earlier.

3. MISCELLANEOUS REACTIONS.

The Attempted Reaction of A Thiouronium Alkylide with Benzaldehyde.

Thiouronium ylides studied to date react with aldehydes to give alkenes[130],but they have all been stable ylides and there have been no reports of the reaction of an unstable thiouronium ylide in the Wittig reaction.

It was proposed to prepare a thiouronium alkylide and react this *in situ* with *p*-nitrobenzaldehyde,but an attempt to prepare S-isopropyl *N*,*N*,*N*'*N*'-tetramethylthiouronium bromide was unsuccessful. Iodobutane however reacted with *N*,*N*,*N*'*N*'- tetramethylthiourea in butanol to give S-butyl *N*,*N*,*N*'*N*'- tetramethylthiouronium iodide. This salt was treated with phenyllithium and then reacted with *p*-nitrobenzaldehyde *in situ*. Work up gave an oil and mass spectroscopy and N.M.R. studies of the fractions obtained from chromatography showed that *N*,*N*,*N*'*N*'-tetramethylurea and butyldisulphide were present. It therefore appears likely that the iodide salt was cleaved by the base to give *N*,*N*,*N*'*N*'-tetramethylurea and *n*-butylmercaptan which was oxidised to give butyldisulphide.

PART 3

EXPERIMENTAL.

MATERIALS AND APPARATUS.

N.M.R. Spectra were carried out on a Varian HA100 spectrometer operating at 100 MHz and a Brucker WP 80 operating at 80 MHz with tetramethylsilane as internal standard.

Infra-red spectra were obtained with a Perkin-Elmer 257 instrument

Ultra-Violet spectra were measured with a Unicam SP 800 instrument.

Microanalyses were carried out by Mrs. S Smith, St. Andrews University.

G.C. was carried out on a 2% 20M carbowax column using α -methylstilbene as reference standard.

Column chromatography was carried out on silica gel, Grade M.60.

'Dry filled' column chromatography was carried out on silica Woelm T.S.C.

Light petroleum refers to light petroleum 60 - 80°.

Phenyliodonium 2,2-dimethyl-(4,6-dioxo-1,3-dioxan)-ylide, -bis(methoxycarbonyl)methylide,- benzoylacetmethylide and-dibenzoylmethylide were prepared as described by Neiland et al [9,77,124].

Triarylarsines and triarylarsine oxides were prepared as decribed by Goddard [125].

1. THE ATTEMPTED PREPARATION OF SOME PHENYLIODONIUM YLIDES.

(i) Phenyliodonium 3,4-dibenzoylcyclopentadienylide.

(a) A mixture of (diacetoxyiodo)benzene (0.32g., 1m.mole) and 2-benzoyl-6-phenyl-6-hydroxyfulvene (dibenzoylcyclopentadiene) (0.274g., 1m.mole) in acetic anhydride (10ml.) was warmed on a steam bath. The solution immediately turned black and after 0.5 hours the mixture was cooled. The addition of ether to the reaction mixture gave an intractable black oil.

(b) (Diacetoxyiodo)benzene (0.32g., 1m.mole) was added to a suspension of dibenzoylcyclopentadiene (0.274g., 1m.mole) in triethylamine (10ml.). The mixture was stirred for 18 hours and the solvent was removed to give a black/brown oil which could not be induced to crystallise.

(c) (Diacetoxyiodo)benzene (0.32g., 1m.mole) was dissolved in methanol (10ml.) and potassium hydroxide (0.112g., 2m.mole) followed by dibenzoylcyclopentadiene (0.274g., 1m.mole) was added. The resulting black solution was stirred for 20 minutes and then heated and filtered hot. Water (20ml.) was added to the filtrate and a black oil formed which could not be induced to crystallise.

The experiment was repeated, but the mixture was not heated and the methanol was removed at reduced pressure. A crude black solid that was not treated further was obtained.

(d) Iodobenzene dichloride (0.275g., 1m.mole) in methanol (5ml.) was added to a mixture of dibenzoylcyclopentadiene (0.274g., 1m.mole) and potassium hydroxide (0.112g., 2m.mole) in methanol (10ml.). After

20 minutes the black solution was filtered to give an intractable black oil.

(e) Phenyl lithium (1.25 ml., 1.6M) was added to a solution of dibenzoylcyclopentadiene (0.274g., 1m.mole) in dry benzene (30ml.) under a nitrogen atmosphere. (Diacetoxyiodo)benzene (0.32g., 1m.mole) in benzene (30ml.) was added dropwise and the solution turned black. The solution was stirred for 15 minutes and the benzene solution was then washed with water. The solvent was removed to give an intractable black oil.

(f) A sample of dibenzoylcyclopentadiene was added to (diacetoxyiodo)benzene in methanol. The solution turned black and was not treated further.

(ii) Phenyliodonium 2,4-diphenylcyclopentadienylide.

(a) A mixture of 1,4-diphenylcyclopentadiene (0.218g., 1m.mole), (diacetoxyiodo)benzene (0.322g., 1m.mole) and potassium hydroxide (0.112g., 2m.mole) in methanol (100ml.) was stirred for 2 hours. The solution was heated and then filtered hot. The addition of water gave a yellow solid which was found to be unchanged 1,4-diphenylcyclopentadiene.

The reaction was repeated, but the solution was not heated. The addition of water gave unchanged 1,4-diphenylcyclopentadiene.

(b) Phosphorus pentoxide (0.25g.) was added to a mixture of 1,4-diphenylcyclopentadiene (0.218g., 1m.mole) and (diacetoxyiodo)benzene (0.322g., 1m.mole) in triethyamine (15ml.) and the mixture was heated under reflux for 18 hours. After the initial 8 hours a further quantity of phosphorus pentoxide (0.25g.) was added. The solvent was decanted while hot and then was removed to give an intractable black oil.

(c) Phenyllithium (1.25ml., 1.6M) was added to a solution of 1,4-diphenylcyclopentadiene (0.218g., 1m.mole) in dry benzene (50 ml.) under a nitrogen atmosphere and a white precipitate formed. (Diacetoxyiodo)benzene (0.322g. 1m.mole) in benzene (20 ml.) was added dropwise and the orange solution was stirred for 15 min. The benzene solution was washed with water and then dried over sodium sulphate. The solvent was removed to give an intractable oil.

(iii) Phenyliodonium fluorenylide.

Phenyllithium (2.5ml., 1.6M) was added to a solution of fluorene (0.332g., 2m.mole) in dry benzene (30 ml.). (Diacetoxyiodo)benzene (0.64g., 2m.mole) in benzene (20 ml.) was added dropwise and the suspension was stirred for 2 hours. The benzene solution was washed with water and then dried over sodium sulphate. The solvent was removed to give an intractable oil.

(iv) Phenyliodonium-N-toluimine.

(a) p-Toluamide (0.675g., 5m.mole) was added to a solution of potassium hydroxide (0.7g., 12.5m.mole) in methanol (20 ml.) The solution was cooled to below 10° and (diacetoxyiodo)benzene (1.6g., 5m.mole) was added. The solution was stirred for a further 3 hours and then water was added to the solution to give an orange coloured oil. This oil could not be induced to crystallise.

(b) Phenyllithium (6.25ml., 1.6M) was added to a solution of p-toluamide (0.675g., 5m.mole) in dry T.H.F. (30 ml.) and a solid formed.

A solution of (diacetoxyiodo)benzene (1.6g., 5m.mole) in T.H.F. (20 ml.) was added and a red coloured solution resulted. The solution was stirred for 1 hour and then the solvent was removed. The residue was dissolved in chloroform (50 ml.) and the solution was washed with water (2 times) and dried over sodium sulphate. The solvent was removed to give an intractable red oil.

(c) Experiment (1(iv)b) was repeated on the same scale using sodium hydride (10m.mole) as the base. Work up gave an intractable oil.

2. REACTIONS OF PHENYLIODONIUM 2,2-DIMETHYL (4,6-DIOXO-1,3-DIOXAN)-YLIDE.

(i) p-Nitrobenzaldehyde.

A mixture of phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (1.73g., 5m.mole) and p-nitrobenzaldehyde (0.8g., 5m.mole) in chloroform (30 ml.) was heated under reflux for 4 hours. The solution was extracted with a saturated solution of sodium metabisulphite to remove p-nitrobenzaldehyde. The chloroform layer was dried over sodium sulphate and the solvent was removed to give an orange oil which gave, on trituration with ether, p-nitrobenzylidene-2,2-dimethyl-4,6-dioxo-1,3-dioxan (0.11g., 8%), identical with a sample propared from Meldrums acid and p-nitrobenzaldehyde.

The reaction was repeated on the above scale, but the reaction mixture was chromatographed on a silica column prepared with light petroleum, instead of being extracted with sodium metabisulphite. Iodobenzene (0.45g., 44%) was eluted with light petroleum followed by p-nitrobenzaldehyde (0.55g., 69%) and p-nitrobenzylidene-2,2-dimethyl-4,6-dioxo-1,3-dioxan (0.05g., 4%). The alkene spread on the column and was not eluted in a sharp band. A yellow oil containing a mixture of unknown compounds, including possibly the alkene, was eluted with chloroform.

The reaction was repeated on the same scale as above, but using benzene (75 ml.) as the solvent. The solution was extracted with sodium metabisulphite, but on work up no p-nitrobenzylidene-2,2-dimethyl-4,6-dioxo-1,3-dioxan was obtained from the residual oil.

The reaction was repeated on the same scale as above, but using methanol as the solvent. Again no p-nitrobenzylidene-2,2-dimethyl-4,6-dioxo-1,3-dioxan was obtained after the work up.

(ii) Triphenylarsine.

(a) Phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (0.34g., 1m.mole) and triphenylarsine (0.92g., 3m.mole) were dissolved in methanol (50 ml) and several crystals of p-toluenesulphonic acid were added to the solution. The solution was stirred for 2 days and the solvent was removed to give an unknown oily compound.

(b) A mixture of phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (0.346g., 1m.mole) and triphenylarsine (0.92g., 3m.mole) was heated on a steam bath for 0.5 hours. Ether was added to the melt and an intractable brown oil was formed.

(c) A mixture of phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (0.346g., 1m.mole) and triphenylarsine (0.92g., 3m.mole) in ethanol (25 ml.) was heated under reflux for 2 hours. The solvent was removed, but trituration of the residual oil with ether would not induce it to crystallise.

(d) A mixture of phenyliodonium 2,2,-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (0.346g., 1m.mole), triphenylarsine (0.92g., 3m.mole) and copper acetylacetonate (0.04g., 0.15m.mole) in ethanol (25 ml.) was heated under reflux for 2 hours. The cooled solution was filtered and the solvent was removed. Trituration of the residue with ether gave triphenylarsonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (0.36g., 80%). A sample was recrystallised from a benzene/light petroleum mixture (1:1) to give colourless crystals, mpt 186-187° (lit.mpt 187°)[46].

The reaction was repeated using different amounts of copper acetylacetonate. It was found that if less than 0.1m.mole of copper acetylacetonate was used no reaction took place.

The reaction was repeated twice using methylene chloride instead of ethanol as the solvent. In one case unchanged iodonium ylide was recovered and in the other case impure arsonium ylide was obtained.

(iii) <u>Thioanisole</u>.

A mixture of phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (0.34g., 1m.mole), thioanisole (0.37g., 3m.mole) and copper acetylacetonate (0.04g., 0.15m.mole) in ethanol (25 ml.) was heated under reflux for 2 hours. The solvent was removed and trituration of the residual oil with ether gave methylphenylsulphonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (0.2g., 75%). A sample was recrystallised from a benzene/light petroleum mixture as white crystals, mpt 133-135°. (Found C, 58.9: H, 5.2. $C_{13}H_{14}O_4S$ requires C, 58.6; 5.3%).

(iv) <u>Triphenylphosphine</u>.

A mixture of phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (0.346g., 1m.mole), triphenylphosphine (0.524g., 2m.mole) and copper acetylacetonate (0.04g., 0.15m.mole) in ethanol (25 ml.) was heated under reflux for 2 hours. The solvent was removed and trituration of the residual oil with ether gave unchanged iodonium ylide (0.2g., 58%).

(v) Dimethylsulphoxide

A mixture of phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide (0.346g., 1m.mole), dimethylsulphoxide (0.23g., 3m.mole) and copper acetylacetonate (0.04g., 0.15m.mole) in ethanol (25ml) was heated under reflux for 2 hours. The solvent was removed to give a black oil which was not treated further.

3. REACTIONS OF PHENYLIODONIUM BIS(METHOXYCARBONYL)METHYLIDE.

(i) p-Nitrobenzaldehyde.

A mixture of phenyliodonium bis(methoxycarbonyl)methylide (1.67g., 5m.mole) and *p*-nitrobenzaldehyde (0.75g., 5m.mole) in benzene (25 ml) was heated under reflux for 14 hours. The solvent was removed, but trituration of the residue with ether did not induce the oil to crystallise. The ether was removed and the residue was applied to a silica column prepared from light petroleum. Iodobenzene (0.45g., 44%) was eluted with light petroleum, and *p*-nitrobenzaldehyde (0.5g., 66%) was eluted with a benzene/light petroleum mixture. A further fraction was eluted with chloroform which gave 1,1,2,2-tetrakis(methoxycarbonyl)ethene (0.1g., 15%), identical with the sample prepared in Experiment (3ii). An intractable yellow oil was eluted with methanol.

The reaction was repeated on 1/5 scale using chloroform as the solvent. The solvent was removed and again no precipitate was found when the oil was triturated with ether. The oil was dissolved in chloroform (50 ml.) and the solution was extracted twice with a saturated sodium metabisulphite solution and then washed with water. The chloroform solution was dried over sodium sulphate and the solution was removed. Trituration of the residual yellow oil gave a trace amount of 1,1,2,2-tetrakis(methoxycarbonyl)ethene (0.01g., 2%).

Triphenylarsonium bis(methoxycarbonyl)methylide + p-nitrobenzaldehyde.

A mixture of triphenylarsonium bis(methoxylcarbonyl)methylide (0.44g., 1m.mole) and p-nitrobenzaldehyde (0.155g., 1m.mole) in benzene (25 ml) was heated under reflux for 8 hours. The solvent was removed and trituration of the residue with ether gave a mixture of dimethyl p-nitrobenzylidenemalonate and triphenylarsine oxide. This was dissolved in the minimum volume of ethanol and the mixture was cooled to -70° to give pure dimethyl p-nitrobenzylidenemalonate (0.22g., 83%) which was filtered off. A sample was recrystallised from ethanol as pale yellow needles, mpt 136-138°, identical with an authentic sample[126].

(ii) Cyclohexene.

A mixture of phenyliodonium bis(methoxycarbonyl)methylide (6.6g., 20m.mole) and copper acetylacetonate (0.03g., 0.11m.mole) in cyclohexene (20 ml.) was heated under reflux for 3 hours. The solution was cooled and a white precipitate formed. This was filtered off to give 1,1,2,2-tetrakis(methoxycarbonyl)ethene (1.07g., 41%) and a sample recrystallised from benzene gave colourless needles mpt 123-5°. (Found C,46.4; H,4.9. $C_{10}H_{12}O_8$ requires C,46.2; H,4.7%). The solvent was removed from the filtrate and the residue was applied to a silica column prepared from light petroleum. Iodobenzene (0.38g., 93%) was eluted with this solvent. Another fraction was eluted with benzene which gave, after removal of solvent, 7,7-bis(methoxycarbonyl)bicyclo [4,1,0]heptane (1.65g., 38%). A sample recrystallised from light petroleum gave white needles mpt 91-2°. (Found C,62.3; H,7.6. $C_{11}H_{16}O_4$ requires C,62.3; H,7.6%).

(iii) Triphenylarsine.

(a) A mixture of phenyliodonium bis(methoxycarbonyl)methylide (0.167g., 0.5m.mole) and triphenylarsine (0.45g., 1.5m.mole) in ethanol (20 ml.) was heated under reflux for 2 hours. The solvent was removed and a yellow oil remained that could not be induced to crystallise.

(b) A mixture of phenyliodonium bis(methoxycarbonyl)methylide (0.334g., 1m.mole), triphenylarsine (0.92g., 3m.mole) and copper acetylacetonate (1.3mg., 5μ.mole) in ethanol (25 ml.) was heated under reflux for 1.5 hours. The cooled solution was filtered and the solvent was removed. Trituration of the residue with ether gave triphenylarsonium bis(methoxycarbonyl)methylide (0.3g., 69%). A sample was recrystallised from a benzene/light petroleum mixture to give colourless crystals, mpt 186-8°. (Found C,63.1; H,4.9, $C_{23}H_{21}O_4As$ requires C,63.3; H,4.8%).

The reaction was repeated using methylene chloride instead of ethanol. The arsonium ylide (0.28g., 64%) was obtained.

(iv) Thioanisole.

A mixture of phenyliodonium bis(methoxycarbonyl)methylide (0.668g., 2m.mole), thioanisole (0.74g., 6m.mole) and copper acetylacetonate (3mg., 0.011 m.mole) in methylene chloride (30 ml.) was heated under reflux for 2 hours. The cooled solution was filtered and the solvent was removed. Ether was added to the residual oil and after leaving the mixture at 0° overnight a precipitate formed. This was filtered off and washed with ether to give methylphenylsulphonium bis(methoxycarbonyl)methylide (0.27g., 53%). A sample recrystallised from benzene gave crystals, mpt 128-130° (lit. 126-127°)[127].

(v) Diphenylsulphide.

A mixture of phenyliodonium bis(methoxycarbonyl)methylide (0.668g., 2m.mole), diphenylsulphide (0.74g., 4m.mole) and copper acetylacetonate (3mg., 0.01m.mole) in ethanol (30 ml.) was heated under reflux for 4 hours. The cooled solution was filtered and the solvent was removed. Trituration of the residue gave diphenylsulphonium bis(methoxycarbonyl)methylide (0.33g., 52%). A sample recrystallised from benzene gave crystals, mpt 128-130° (lit. 127-128°)[127].

(vi) Dimethylsulphoxide.

A mixture of phenyliodonium bis(methoxycarbonyl)methylide (0.668g., 2m.mole), dimethylsulphoxide (0.47g., 6m.mole) and copper acetylacetonate (3mg., 0.01m.mole) in ethanol (30 ml) was treated in an identical manner to that described in Experiment (3(iii)b). Work up gave dimethylsulphonium bis(methoxycarbonyl) methylide (0.145g., 34%). A sample recrystallised from benzene gave crystals, mpt 159-160° (lit. 157°)[127].

(vii) Triphenylphosphine.

A mixture of phenyliodonium bis(methoxycarbonyl)methylide (0.334g., 1m.mole), triphenylphosphine (0.524g., 2m.mole) and copper acetylacetonate (1.3mg., 0.005m.mole) in ethanol (20 ml.) was treated in an identical manner to that described in Experiment (3(iv)b). Work up gave triphenylphosphonium bis(methoxycarbonyl)methylide (0.24g., 66%). A sample recrystallised from benzene/light petroleum gave white crystals, mpt 185-188°. (Found C, 70.4; H, 5.2. $C_{23}H_{21}O_4P$ requires C, 70.4; H, 5.4%).

(viii) Triphenylantimony.

A mixture of phenyliodonium bis(methoxycarbonyl) methylide (0.334g., 1m.mole), triphenylantimony (0.353g., 1m.mole) and copper acetylacetonate(1.3mg., 0.005m.mole) in ethanol (20ml.) was heated under reflux for 2 hours. The solvent was removed and trituration of the residue with ether gave unchanged triphenylantimony.

(ix) Thiourea.

A mixture of phenyliodonium bis(methoxycarbonyl) methylide (o.334g., 1m.mole), thiourea (0.152g., 2m.mole) and copper acetylacetonate(1.3mg., 0.005m.mole) in ethanol (20ml.) was heated under reflux for 2 hours. The solvent was removed to give an oil which could not be induced to crystallise.

4. REACTIONS OF PHENYLIODONIUM BENZOYLACETMETHYLIDE.

(i) Triphenylarsine.

A mixture of phenyliodonium benzoylacetmethylide (0.366g., 1m.mole), triphenylarsine (0.92g., 3m.mole) and copper acetylacetonate (8mg., 0.03m.mole) in ethanol (25 ml.) was heated under reflux for 2 hours. The cooled solution was filtered and the solvent was removed. Trituration with ether gave triphenylarsonium benzoylacetmethylide (0.38g., 81%). A sample was recrystallised from a benzene/light petroleum mixture as colourless crystals, mpt. 174-5° (lit. 174°).[46]

The reaction was repeated, but a smaller amount of copper acetylacetonate (2mg., 0.008 m.mole) was used. Work up gave triphenylarsonium benzoylmethylide (0.07g., 15%). The reaction was repeated without copper acetylacetonate. Work up gave an intractable oil which was not treated further.

(ii) Thioanisole.

A mixture of phenyliodonium benzoylacetmethylide (0.366g., 1m.mole), thioanisole (0.37g., 3m.mole) and copper acetylacetonate (8mg., 0.03m.mole) in ethanol (25 ml.) was heated under reflux for 5 hours. The cooled solution was filtered and the solvent was removed. Trituration with ether gave methylphenylsulphonium benzoylacetmethylide (0.11g., 39%). A sample recrystallised from benzene/light petroleum gave colourless crystals, mpt 136-138° (lit.138°)[128]

5. REACTIONS OF PHENYLIODONIUM DIBENZOYLMETHYLIDE.

(i) Triphenylarsine.

A mixture of phenyliodonium dibenzoylmethylide (0.428g., 1m.mole), triphenylarsine (0.92g., 3m.mole) and copper acetylacetonate (2mg., 8µ.mole) in ethanol (25 ml.) was heated under reflux for 2 hours. The cooled solution was filtered and the solvent was removed. Trituration of the residue with ether gave triphenylarsonium dibenzoylmethylide (0.35g., 81%). A sample was recrystallised from a benzene/light petroleum mixture (1:1) to give crystals, mpt 219-220° (lit.208-210°).[46] (Found C 74.7; H, 4.8. $C_{33}H_{25}O_2As$ requires C, 75.0; H, 4.8%)

(ii) Thioanisole.

A mixture of phenyliodonium dibenzoylmethylide (0.428g., 1m.mole), thioanisole (0.37g., 3m.mole) and copper acetylacetonate (2mg., 8µ.mole) in ethanol (25 ml.) was treated under reflux for 2 hours. The cooled solution was filtered and the solvent was removed to give, on trituration with ether, methylphenylsulphonium dibenzoylmethylide (0.22g., 64%). A sample was recrystallised from a benzene/light petroleum mixture to give colourless crystals, mpt. 170-171° (lit.178-9°)[129].

6. THE COPPER CATALYSED DECOMPOSITION OF SOME IODINE YLIDES.

(i) Phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide.

A mixture of phenyliodonium 2,2-dimethyl(4,6-dioxo-1,3-dioxan)ylide (0.346g., 1m.mole) and triphenylarsine (0.61g., 2m.mole) in ethanol (25 ml.) was heated under reflux for 2 hours in the presence of the catalysts listed in Table (2). The reactions were worked up in an identical manner to that described in Experiment (2(ii)d) and the results are in Table (2).

(ii) Phenyliodonium bis(methoxycarbonyl)methylide.

A mixture of phenyliodonium bis(methoxycarbonyl)methylide (0.33g., 1m.mole) and triphenylarsine (0.61g., 2m.mole) in ethanol (25 ml.) was heated under reflux for 1.5 hours in the presence of the catalysts listed in Table (2). The reactions were worked up in an identical manner to that described in Experiment (3(iii)b) and the results are in Table (2).

(iii) Phenyliodonium benzoylacetmethylide.

A mixture of phenyliodonium benzoylacetmethylide (0.366g., 1m.mole) and triphenylarsine (0.61g., 2m.mole) in ethanol (25 ml.) was heated under reflux for 2 hours in the presence of the catalysts listed in Table(2). The reactions were worked up in an identical manner to that described in Experiment (4(i)) and the results are in Table (2)

(iv) Phenyliodonium dibenzoylmethylide.

A mixture of phenyiodonium dibenzoylmethylide (0.428g., 1m.mole) and triphenylarsine (0.61g., 2m.mole) in ethanol (25 ml.) was heated under reflux for 1.5 hours in the presence of the catalysts listed in Table (2). The reactions were worked up in an identical manner to that described in Experiment (5(i)) and the results are in Table (2).

7. PREPARATION OF TRIARYLARSONIUM 2,3,4-TRIPHENYLCYCLOPENTADIENYLIDES.

(i) Triphenylarsonium 2,3,4-triphenylcyclopentadienylide.

A mixture of diazo-2,3,4-triphenylcyclopentadiene (3.2g., 10m.mole), triphenylarsine (4.6g., 15m.mole) and copper acetylacetonate (0.2g., 0.8m.mole) in benzene (100 ml.) was heated under reflux for 2 hours. The solvent was removed and on triturating the residual oil with ether/light petroleum, triphenylarsonium 2,3,4-triphenylcyclopentadienylide (5.1g., 85%) was obtained. The excess catalyst was removed by heating a suspension of the reaction product in ethanol for several minutes. The ylide was recrystallised from a benzene/light petroleum mixture as yellow/orange crystals, mpt 199-201° (lit. 198-200°)[92].

(ii) Tri-p-tolylarsonium 2,3,4-triphenylcyclopentadienylide.

Diazo-2,3,4-triphenylcyclopentadiene (3.2g., 10m.mole) and tri-p-tolyarsine (3.8g., 11m.mole) were treated in an identical manner to that described in Experiment (7(i)a) to give tri-p-tolylarsonium 2,3,4-triphenylcyclopentadienylide (5.3g., 83%). Yellow crystals, mpt 219-221° from a benzene/light petroleum mixture (1:1). (Found C, 82.15; H, 6.0. $C_{44}H_{37}As$, requires C, 82.5; H, 5.8%).

Perchloric acid (0.1 ml.) was added to a suspension of tri-p-tolylarsonium 2,3,4-triphenylcyclopentadienylide (0.32g., 5m.mole) in ethanol (5 ml.). The solution was filtered and on the addition of ether a colourless precipitate formed. The solid was filtered and recrystallised from ethanol to give tri-p-tolyl(2,3,4-triphenylcyclopentadienyl)arsonium perchlorate (0.33g., 89%), mpt 158-160°. (Found C, 71.0; H, 4.8. $C_{44}H_{38}ClO_4As$ requires C, 71.3; H, 5.2%).

(iii) Tri-p-methoxyphenylarsonium 2,3,4-triphenylcyclopentadienylide.

Diazo-2,3,4-triphenylcyclopentadiene (3.2mg., 10m.mole) and tri-p-methoxyphenylarsine (4.3g., 11m.mole) were treated in an identical manner to that described in Experiment (7(i)a) to give tri-p-methoxyphenylarsonium 2,3,4-triphenylcyclopentadienylide (6.0g., 87%). Yellow crystals, mpt 246-8° from benzene/light petroleum (1:1). (Found C, 76.1; H, 5.7. $C_{44}H_{37}O_3As$, requires C, 76.7; H, 5.4%).

(iv) Tri-m-tolylarsonium 2,3,4-triphenylcyclopentadienylide.

Diazo-2,3,4-triphenylcyclopentadiene (3.2g., 10m.mole) and tri-m-tolylarsine (3.8g., 11m.mole) reacted in an identical manner to that described in (7(i)) to give tri-m-tolylarsonium 2,3,4-triphenylcyclopentadienylide (3.2g., 50%). Yellow crystals, mpt. 182-4° from benzene/light petroleum (1:1). (Found C, 82,5; H, 5.8. $C_{44}H_{37}As$ requires C, 82.5; H, 5.8%).

Tri-m-tolyl(2,3,4-triphenylcyclopentadienyl) arsonium perchlorate (0.30g., 83%), mpt 218-219° was prepared in an identical manner to that described in Experiment (7(ii)). (Found C, 71.0; H, 5.15. $C_{44}H_{38}ClO_4As$ requires C, 71.3; H, 5.2%).

(v) Tri-o-tolylarsonium 2,3,4-triphenylcyclopentadienylide.

Diazo-2,3,4-triphenylcyclopentadiene (3.2g., 10m.mole) and tri-o-tolylarsine (3.8g., 11m.mole) were treated in an identical manner to that described in Experiment (7(i)a) to give tri-o-tolylarsonium 2,3,4-triphenylcyclopentadienylide (5.13g., 80%). Yellow crystals, mpt. 237-240° from benzene/light petroleum (1:1). (Found C, 82.86; H, 7. ; $C_{44}H_{37}As$ requires C, 82.5; H, 5.8%).

Tri-o-tolyl(2,3,4-triphenylcyclopentadienyl)arsonium perchlorate (0.33g., 91%) mpt 210-203° was prepared in an identical manner to that described in (7(ii)). (Found C, 71.9; H, 5.1. $C_{44}H_{38}ClO_4As$ requires C, 71.3; H, 5.2%).

(vi) Tri-o-methoxyphenyl arsonium 2,3,4-triphenylcyclopentadienylide.

Diazo-2,3,4-triphenylcyclopentadiene (3.2g., 10m.mole) and tri-o-methoxyphenylarsine (4.3g., 11m.mole) were treated in an identical manner to that described in (7(i)a) to give tri-o-methoxyphenylarsonium 2,3,4-triphenylcyclopentadienylide (5.8g., 84%). Yellow crystals, mpt. 235-7° from benzene/light petroleum (1:1). (Found C, 76.2; H, 5.4. $C_{44}H_{37}O_3As$ requires C, 76.7; H, 5.4%).

8. PREPARATION OF TRIARYLARSONIUM 2,3,4,5-TETRAPHENYLCYCLOPENTADIENYLIDES.

(i) Triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide.

Diazo-2,3,4,5-tetraphenylcyclopentadiene (3.96g., 10m.mole) and triphenylarsine (4.6g., 15m.mole) in benzene (100 ml.) was heated under reflux in the presence of copper acetylacetonate (0.4g., 1.5m.mole) for 2 hours. The solvent was removed and on triturating the residual oil with an ether/light petroleum mixture it gave triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (5.54g., 82%). The excess catalyst was removed by warming the crude reaction product in ethanol. The ylide was recrystallised from a benzene/light petroleum mixture (1:1) to give yellow crystals, mpt. 228-230° (lit. mpt 228-230°)[103].

(ii) Tri-p-tolylarsonium 2,3,4,5-tetraphenylcyclopentadienylide.

Diazo-2,3,4,5-tetraphenylcyclopentadiene (3.96g., 10m.mole) and tri-p-tolylarsine (4.0g., 11m.mole) in benzene (100ml.) were heated under reflux in the presence of copper acetylacetonate (0.4g., 1.5m.mole) for 2 hours. The solution was cooled and filtered to remove the excess catalyst. The solvent was removed and trituration of the residual oil with light petroleum gave tri-p-tolylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (3.2g., 49%). Yellow crystals, mpt. 226-8° from a benzene/light petroleum mixture (1:1). (Found C, 84.2; H, 5.8. $C_{50}H_{41}As$ requires C, 83.8; H, 5.8%).

(iii) Tri-p-methoxyphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide.

Diazo-2,3,4,5-tetraphenylcyclopentadiene (3.96g., 10m.mole) and tri-*p*-methoxyphenylarsine (3.96g., 10m.mole) were treated in an identical manner to that described in (8(ii)) to give tri-*p*-methoxyphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (3.74g., 70%). Orange/yellow crystals, mpt, 127-130° from a benzene/light petroleum mixture. (Found C, 78.5; H, 5.0. $C_{50}H_{41}O_3As$ requires C, 78.5; H, 5.4%).

(iv) Tri-o-tolylarsonium 2,3,4,5-tetraphenylcyclopentadienylide.

Diazo 2,3,4,5-tetraphenylcyclopentadiene (3.96g., 10m.mole) and tri-*o*-tolylarsine (93.8g., 11m.mole) were treated in an identical manner to that described in Experiment (8(i)) to give tri-*o*-tolylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (5.4g., 75%). Yellow crystals, mpt 226-228° from a benzene/light petroleum mixture (1:1). (Found C, 83.4; H, 5.6. $C_{50}H_{41}As$ requires C, 83.8; H, 5.8%).

Perchloric acid (0.1 ml.) was added to a suspension of tri-*o*-tolylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (0.358g., 0.5m.mole) in ethanol (5 ml.). The solution was filtered and on addition of ether a yellow precipitate formed. The solid was filtered off and recrystallised from ethanol to give tri-*p*-tolyl(2,3,4,5-tetraphenylcyclopentadienyl)arsonium perchlorate (0.36g., 88%)mpt.156-7°. (Found C, 73.2; H, 4.9. $C_{50}H_{42}O_4Cl$ As requires C, 73.5; H, 5.2%).

(v) Tri-o-methoxyphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide.

Diazo 2,3,4,5-tetraphenylcyclopentadiene (3.96g., 10m.mole) and tri-o-methoxyphenylarsine (3.96g., 10m.mole) were treated in an identical manner to that described in Experiment (8(i)) to give tri-o-methoxyphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (5.9g., 78%). Yellow/orange crystals, mpt 213-5° from a benzene/light petroleum mixture (1:1). (Found C, 78.2; H, 5.1. $C_{50}H_{41}O_3As$ requires C, 78.5; H, 5.4%)

9. ATTEMPTED PREPARATION OF TRI-O-TOLYLARSONIUM 2,4-DIPHENYLCYCLOPENTADIENYLIDE.

Phosphorus pentoxide (1.0g.) was added to a mixture of tri-o-tolylarsine oxide (0.346g., 0.5m.mole), 1,4-diphenylcyclopentadiene (0.108g., 0.5m.mole) and triethylamine (40 ml.) and the mixture was heated under reflux for 24 hours. After the initial 4 hours, further phosphorus pentoxide (0.5g) was added. Water (100ml.) was added to the reaction mixture and the resultant suspension was extracted with methylene chloride. The extract was washed well with water, dried over sodium sulphate and the solvent was evaporated. Trituration of the residue with ether yielded unchanged tri-o-tolylarsine oxide (0.195., 56%) but no arsonium ylide.

10. PREPARATION OF MISCELLANEOUS TRIARYLARSONIUM YLIDES.

(i) Tri-p-tolylarsonium cyanoethoxycarbonylmethylide.

A mixture of ethyl cyanoacetate (0.68g., 6m.mole) and tri-p-tolylarsine oxide (1.82g., 5m.mole) in freshly distilled acetic anhydride (10ml.) was heated under reflux for 10 minutes. Water (100ml.) was added to the cooled solution and the resultant suspension was scratched to make it crystallise. After 4 hours the crystalline solid was filtered off and washed with ether to give tri-p-tolylarsonium cyanoethoxycarbonylmethylide (1.70g., 75%). The ylide was crystallised from a benzene / light petroleum mixture (1:1) to give colourless crystals, mpt. 231-3°. (Found C, 67.7; H, 5.7; N, 3.0. $C_{26}H_{26}NO_2As$ requires C, 68.0; H, 5.7; N, 3.0%).

(ii) Tri-o-tolylarsonium cyanoethoxycarbonylmethylide.

A mixture of ethyl cyanoacetate (0.68g., 6m.mole) and tri-o-tolylarsine oxide (1.82g., 5m.mole) was treated in a similar manner to that described in Experiment (10(i)) to give tri-o-tolylarsonium cyanoethoxycarbonylmethylide (1.72g., 75%) Colourless crystals from ethanol, mpt. 229-231°. (Found C, 67.7; H, 5.8; N, 3.0. $C_{26}H_{26}NO_2As$ requires C, 68.0; H, 5.7; N, 3.0%.).

(iii) Tri-o-methoxyphenylarsonium cyanoethoxycarbonylmethylide.

A mixture of ethyl cyanoacetate (0.68g., 6m.mole) and tri-o-methoxyphenylarsine oxide (2.06g., 5m.mole) was treated in a similar manner to that described in Experiment (10(i)) to give tri-o-methoxyphenylarsonium cyanoethoxycarbonylmethylide (2.25g., 89%). Colourless crystals from ethanol, mpt. 233-5°. (Found C, 61.8; H, 5.5; N, 2.6. $C_{26}H_{26}O_5NAs$ requires C, 61.5; H, 5.2; N, 2.6%)

(iv) Tri-p-tolylarsonium dicyanomethylide.

A mixture of dicyanomethane (0.33g., 5m.mole) and tri-p-tolylarsine oxide (1.82g., 5m.mole) in acetic anhydride (10ml.) was heated under reflux for 15 minutes. Water (100ml.) was added to the cooled reaction mixture, but the brown oily suspension would not crystallise. An infra-red spectrum of the oil suggested that there was no tri-p-tolylarsine oxide present.

(v) Tri-o-tolylarsonium dicyanomethylide.

A mixture of dicyanomethane (0.33g., 5m.mole) and tri-o-tolylarsine oxide (1.82g., 5mmole) in acetic anhydride (10ml.) was heated under reflux for 2 minutes. Water (100ml.) was added to the cooled solution whereupon tri-o-tolylarsonium dicyanomethylide (1.66g., 81%) crystallised from the oil. The ylide was recrystallised from ethanol as colourless crystals, mpt. 250-251°. (Found C, 70.0; H, 4.8; N, 6.8. $C_{24}H_{21}N_2As$ requires C, 69.9; H, 5.1; N, 6.8%).

(vi) Attempted Preparation of Tri-o-tolylarsonium nitromethylide.

(a) A suspension of tri-o-tolylarsine oxide (0.36g., 1m.mole), phosphorus pentoxide (0.3g.,) and triethylamine (5ml.) in nitromethane (10ml.) was heated under reflux for 4 hours during which time further phosphorous pentoxide was added (0.3g.). The solvent was removed and the residue was extracted with chloroform; the extracts were washed well with water and dried. Removal of the solvent gave only unchanged tri-o-tolylarsine oxide (0.2g., 56%).

(b) A mixture of tri-o-tolylarsine oxide (0.36g., 1m.mole) and nitromethane (5ml.) in acetic anhydride (5ml.) was heated under reflux for 5 minutes. Water (50ml.) was added to the cooled solution and a white solid formed. This was filtered off and found to be tri-o-tolylarsine (0.18g., 50%).

The reaction was repeated but the reaction mixture was left at room temperature for one week instead of being heated in solution. On work up tri-o-tolylarsine was obtained (0.19g., 53%).

(vii) Attempted preparation of Triphenylarsonium ethoxycarbonylacetmethylide.

To a solution of triphenylarsine (0.306g., 1m.mole) in chloroform (20ml.), bromine (0.16g., 2m.mole) was added dropwise until a red colour remained in the solution. Ethyl acetoacetate

(0.13g., 1m.mole) followed by triethylamine (5ml.) were added and a white precipitate of triethylamine bromide formed. This was filtered off and the solvent was removed from the filtrate. The residual oil was triturated with ether and this gave triphenylarsine oxide (0.22g., 68%).

(viii) Attempted Preparation of Tri-o-tolylarsonium ethoxycarbonylacetmethylide.

(a) Tri-*o*-tolylarsine (0.346g., 1m.mole) was treated in an identical manner to that described in Experiment (10(vii)). The work up gave a mixture of tri-*o*-tolylarsine oxide and ethyl acetoacetate.

(b) A mixture of tri-o-tolylarsine oxide (0.346., 1m.mole) and ethyl acetoacetate (0.13g., 1m.mole) in acetic anhydride (2ml.) was heated under reflux for 10 minutes. Water (50ml.) was added to the cooled solution and an oil was obtained that could not be induced to crystallise. An infra-red spectrum of the oil showed that tri-*o*-tolylarsine oxide was present in the oil.

(ix) Attempted Preparation of Tri-o-tolylarsonium bis(methoxycarbonyl) methylide.

A mixture of tri-*o*-tolylarsine (0.346g., 1m.mole) and dimethyl malonate (0.16g., 1m.mole) was treated in an identical manner to that described in Experiment (10(i)). The work up gave a brown oil that would not crystallise. An infra-red spectrum of the oil showed that tri-*o*-tolylarsine oxide was present.

(x) Attempted Preparation of Tri-o-tolylarsonium diacetylmethylide.

(a) A mixture of tri-o-tolylarsine (0.346g., 1m.mole) and acetylacetone (0.10g., 1m.mole) was treated in an identical manner to that described in Experiment (10(i)). The work up gave a brown oil that would not crystallise. An infra-red spectrum of the oil showed that tri-o-tolylarsine oxide was present.

(b) A mixture of tri-o-tolylarsine (0.346g., 1m.mole), acetylacetone (0.1g., 1m.mole) and phosphorus pentoxide (0.25g.) in triethylamine (45ml.) was heated under reflux for 8 hours. After the first 4 hours further phosphorus pentoxide (0.1g.) was added. The solvent was evaporated and water (25ml.) was added to the oily residue. The resultant suspension was extracted with methylene chloride and the combined extracts were washed with water and dried over sodium sulphate. The solvent was removed to give a brown oil and an infra-red spectrum of the oil revealed that tri-o-tolylarsine oxide was present.

11. TRI-O-TOLYLARSONIUM BENZYLIDE.

(i) Benzyltri-o-tolylarsonium bromide.

A mixture of tri-o-tolylarsine (0.346g., 1m.mole) and benzyl bromide (0.256g., 1.5m.mole) in benzene (20ml.) was heated under reflux for 8 hours. The solvent was removed from the solution, but on triturating the residue with ether or light petroleum no benzyltri-o-tolylarsonium bromide was obtained.

The reaction was repeated as above but using ethanol,butanol, nitromethane and nitromethane with a small amount of sodium iodide as the reaction solvents. No benzyltri-o-tolylarsonium bromide was obtained in any of these solvents.

(ii) Benzyltri-o-tolylarsonium tetrafluoroborate.

Benzyl bromide (13.6g., 50m.mole) was added to a solution of tri-o-tolylarsine (6.92g., 20m.mole) in 1,2-dichloroethane (30ml.) and the mixture was stirred at room temperature under a nitrogen atmosphere for 3 hours. Silver tetrafluoroborate (3.9g., 20m.mole) was then added dropwise and a white precipitate formed. The mixture was stirred for one week and the precipitate was filtered off. The solvent was removed to give an orange oil which was purified by washing with boiling benzene and recrystallising the remaining solid from an ethanol / ether mixture (2 times) to give benzyltri-o-tolylarsonium tetrafluoroborate (1.5g., 14%), mpt. 197 - 199°. (Found C, 63.8; H, 5.35; $C_{28}H_{28}AsBF_4$ requires C, 63.9; H, 5.35%)

(iii) Reaction of Tri-o-tolylarsonium benzylide and Benzaldehyde.

n - Butyl lithium (0.7ml., 1.6M) was added to a suspension of benzyl tri-o-tolylarsonium tetrafluoroborate (0.525g., 1m.mole) in dry T.H.F. (20ml.) under a nitrogen atmosphere. An orange coloured solution resulted. Freshly distilled benzaldehyde was added after 15 minutes and the orange colour disappeared. The solution was allowed to stir overnight. After 24 hours the solution was made up to 50ml. with chloroform and the solution was analysed by G.C. (2% 20M carbowax column; 180°C) using α-methylstilbene as the reference standard. The product yields were trans-stilbene (12mg., 7%) and trans-stilbene oxide (128mg., 66%).

12. REACTIONS OF TRIARYLARSONIUM 2,3,4 - TRIPHENYLCYCLOPENTADIENYLIDES.

(i) Benzaldehyde.

(a) Triphenylarsonium 2,3,4 - triphenylcyclopentadienylide.

A mixture of triphenylarsonium 2,3,4 - triphenylcyclopentadienylide

(0.3g., 0.5m.mole) and freshly distilled benzaldehyde (0.053g., 0.5m.mole) in benzene (30ml.) was heated under reflux for 18 hours, with the addition of a further quantity of benzaldehyde (0.025g., 0.25m.mole) after one hour. The solvent was removed and the residue was dissolved in a small quantity of benzene. The addition of ether precipitated unchanged arsonium ylide from solution (0.1g., 33%). After removing the solvent, the residue was chromatographed on a silica column prepared with light petroleum. Elution with a (2:1) mixture of light petroleum and benzene brought off a brown band which gave a red-brown solution. Removal of the solvent gave 1,2,3,6 - tetraphenylfulvene (0.11g., 58%). A sample was recrystallised from nitromethane as pale red-brown needles, mpt. 173 - 175° (lit. 175°)[115]. Triphenylarsine oxide (0.065g., 40%) was eluted with methanol.

The reaction was repeated on the same scale, but chloroform was used instead of benzene. Work up gave 1,2,3,6 - tetraphenylfulvene (0.105g., 55%).

(b) Tri-p-tolylarsonium 2,3,4 - triphenylcyclopentadienylide.

Tri-*p*-tolylarsonium 2,3,4 - triphenylcyclopenyadienylide (0.32g., 0.5m.mole) was subjected to the same procedure as described in Experiment (12(i)a. Unchanged ylide (0.05g., 15%) was recovered from the reaction mixture and chromatography of the remaining residue gave 1,2,3,6 - tetraphenylfulvene (0.108g., 56.5%), identical to the compound prepared in Experiment (12(i)a).

(c) Tri-p-methoxyphenyl 2,3,4 - triphenylcyclopentadienylide.

Tri-*p*-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide (0.345g., 0.5m.mole) was subjected to the same procedure as described in

Experiment (12(i)a). Unchanged ylide (0.109g., 55%) was recovered and chromatography of the remaining reaction mixture gave 1,2,3,6 - tetraphenylfulvene (0.11g., 58%), identical to the compound prepared in Experiment (12(i)a).

(d) Tri-m-tolylarsonium 2,3,4 - triphenylcyclopentadienylide.

Tri-*m*-tolylarsonium 2,3,4- triphenylcyclopentadienylide (0.32g., 0.5m.mole) was subjected to the same procedure as described in Experiment (12(i)a). No unchanged ylide was recovered from the residue and chromatography of the reaction mixture gave 1,2,3,6-tetraphenylfulvene (0.105g., 55%) identical to the compound prepared in Experiment (12(i)a).

(ii) p-Nitrobenzaldehyde.

(a) Triphenylarsonium 2,3,4- triphenylcyclopentadienylide.

A mixture of triphenylarsonium 2,3,4-triphenylcyclopentadienylide (0.3g., 0.5m.mole) and *p*-nitrobenzaldehyde (0.075g., 0.5m.mole) in benzene (30ml.) was heated under reflux for 4 hours. The solvent was removed and the residue was taken up in a minimum amount of benzene and applied to a silica column prepared with a mixture of benzene / light petroleum (1:1). A single brown band was eluted with benzene to give, after removal of solvent and trituration with ethanol, 6-*p*-nitrophenyl - 1,2,3-triphenylfulvene (0.197g., 92%). A sample was recrystallised from ethanol as red-brown needles, mpt. 162-164° (lit. 163-165°) [115]. Triphenylarsine oxide (0.15g., 94%) was eluted with methanol.

(b) Tri-p-tolylarsonium 2,3,4- triphenylcyclopentadienylide.

Tri-*p*-tolylarsonium 2,3,4 - triphenylcyclopentadienylide (0.32g., 0.5m.mole) was treated in an identical manner to that described in Experiment (12(ii)a). The work up gave 6-*p*-nitrophenyl - 1,2,3-

triphenylfulvene (0.184g., 86%) identical to the compound prepared in Experiment (12(ii)a) and tri-p-tolylarsine oxide (0.165g., 90%).

(c) Tri-p-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide.

Tri-p-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide (0.345g., 0.5m.mole) was treated in an identical manner to that described in Experiment (12(ii)a). The work up gave 6-p-nitrophenyl - 1,2,3 - triphenylfulvene (0.194g., 90.5%) identical to the compound prepared in Experiment (12(ii)a) and tri-p-methoxyphenylarsine oxide (0.2g., 96%).

(d) Tri-m-tolylarsonium 2,3,4 - triphenylcyclopentadienylide.

Tri-m-tolylarsonium 2,3,4 - triphenylcyclopentadienylide (0.32g., 0.5m.mole) was treated in an identical manner to that described in Experiment (12(ii)a). The work up gave 6-p-nitrophenyl - 1,2,3 - triphenylfulvene (0.187g., 57.5%) identical to the compound prepared in Experiment (12(ii)a) and tri-m-tolylarsine oxide (0.176g., 96%).

(e) Tri-o-tolylarsonium 2,3,4 - triphenylcyclopentadienylide.

A mixture of tri-o-tolylarsonium 2,3,4 - triphenylcyclopentadienylide (0.32g., 0.5m.mole) and p-nitrobenzaldehyde (0.075g., 0.5m.mole) in benzene (30ml.) was heated under reflux for 18 hours. On removing the solvent and triturating the residual oil with ether, unchanged arsonium ylide (0.27g., 84%) was recovered.

(f) Tri-o-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide.

A mixture of tri-o-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide (0.345g., 0.5m.mole) and p-nitrobenzaldehyde (0.075g., 0.5m.mole) was treated in an identical manner to that described in Experiment (12(ii)e) The work up gave unchanged arsonium ylide (0.30g., 87%).

(iii) 2,4 - Dinitrobenzaldehyde.

(a) Triphenylarsonium 2,3,4 - triphenylcyclopentadienylide.

A mixture of triphenylarsonium 2,3,4 - triphenylcyclopentadienylide (0.598g., 1m.mole) and 2,4 - dinitrobenzaldehyde (0.198g., 1m.mole) in benzene (50ml.) was heated under reflux for 3 hours. The solvent was removed and the residue was taken up in a small amount of benzene and applied to a silica column prepared with a (1:1) mixture of benzene/ light petroleum. A brown band was eluted with benzene and removal of the solvent gave 6-(2,4-dinitrophenyl) - 1,2,3 - triphenylfulvene (0.414g., 88%). A sample was recrystallised from nitromethane as brown needles, mpt. 197 - 199°. (Molecular weight 472 . 1426. $C_{30} H_{20} N_2 O_4$ required 472 . 1423). Triphenylarsine oxide was eluted with methanol (0.30g., 92%).

(b) Tri-o-tolylarsonium 2,3,4 - triphenylcyclopentadienylide.

A mixture of tri-o-tolylarsonium 2,3,4 - triphenylcyclopentadienylide (0.321g., 0.5m.mole) and 2,4 - dinitrobenzaldehyde (0.1g., 0.5m.mole) in benzene (25ml.) was heated under reflux for 24 hours. On removal of the solvent and the addition of an ether / light petroleum mixture (1:1) unchanged arsonium **ylide** (0.31g.,96%) was recovered.

(c) Tri-o-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide.

A mixture of tri-o-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide (0.69g., 1m.mole) and 2,4 - dinitrobenzaldehyde (0.196g., 1m.mole) in benzene (30ml.) was heated under reflux for 3 hours. The solvent was removed and the residue was dissolved in a small amount of benzene. Ether was added to the solution whereupon unchanged arsonium ylide precipitated out of solution

(0.47g., 68%). The solvent was removed and the residue was chromatographed in an identical manner to that described in Experiment (12(iii)a) to give 6-(2,4-dinitrophenyl)-1,2,3-triphenylfulvene (0.156g., 33%) identical to the compound prepared in Experiment (12(iii)a).

(iv) Nitrosobenzene.

(a) Triphenylarsonium 2,3,4-triphenylcyclopentadienylide.

Triphenylarsonium 2,3,4-triphenylcyclopentadienylide (0.3g., 0.5m.mole) and nitrosobenzene (0.530g., 0.5m.mole) in benzene (25ml.) was heated under reflux for 6 hours. (After the initial 3 hours a further quantity of nitrosobenzene (0.027g., 0.5m.mole) was added). The solvent was removed and the residual oil was dissolved in methylene chloride. Approximately 5 times the weight of silica was added to the solution and the solvent was then **removed**. This was repeated twice and the compound - absorbent mixture was then applied to the top of a dry silica column. Benzene was added to the column and a green/red band separated from the top of the column. This segment was cut from the column and extracted with chloroform to give, after removal of solvent and trituration with ethanol, N-phenyl-2,3,4-triphenylcyclopentadienone ketoxime (0.143g., 72%). A sample was recrystallised from ethanol to give green needles mpt 160-2° (lit. mpt. 156-158°)[115]. Extraction of the bottom part of the column with chloroform gave triphenylarsine (0.11g., 72%).

(b) Tri-p-tolylarsonium 2,3,4-triphenylcyclopentadienylide.

Tri-p-tolylarsonium 2,3,4-triphenylcyclopentadienylide (0.321g., 0.5m.mole) was treated in a similar manner to that described in Experiment (12(iv)a). The work up gave N-phenyl-2,3,4 triphenylcyclopentadienone ketoxime (0.146g., 73%), identical to the compound prepared in Experiment (12(iv)a), and tri-p-tolylarsine (0.117g., 64%).

(c) Tri-p-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide.

Tri-p-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide (0.345g., 0.5m.mole) was treated in a similar manner to that described in Experiment (12(iv)a). The work up gave N-phenyl-2,3,4-triphenylcyclopentadienone ketoxime (0.153g., 77%), identical to the compound prepared in Experiment (12(iv)a), and tri-p-methoxyphenylarsine (0.127g., 61%).

(d) Tri-m-tolylarsonium 2,3,4 - triphenylcyclopentadienylide.

Tri-m-tolylarsonium 2,3,4 - triphenylcyclopentadienylide (0.321g., 0.5m.mole) was treated in a similar manner to that described in Experiment (12(iv)a). The work up gave N-phenyl-2,3,4 - triphenylcyclopentadienone ketoxime (0.154g., 77%), identical to the compound prepared in Experiment (12(iv)a), and tri-m-tolylarsine (0.125g.,69%).

(e) Tri-o-tolylarsonium 2,3,4 - triphenylcyclopentadienylide.

A mixture of tri-o-tolylarsonium 2,3,4 - triphenylcyclopentadienylide (0.321g., 0.5mmole) and nitrosobenzene (0.053g., 0.5m.mole) in benzene (30ml.) was heated under reflux for 6 hours. (After 3 hours a further quantity of nitrosobenzene (0.026g., 0.25m.mole) was added). The solvent was removed and on the addition of an ether / light petroleum mixture (1:1) unchanged arsonium ylide (0.31g., 96%) was recovered.

The reaction was repeated using chloroform as the solvent. Unchanged arsonium ylide (0.30g., 93%) was recovered.

(f) Tri-o-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide.

Tri-o-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide (0.345g., 0.5m.mole) was treated in a similar manner to that described in

Experiment (12(iv)a). Work up gave unchanged arsonium ylide (0.330g., 96%).

The reaction was repeated using chloroform as the solvent. Unchanged arsonium ylide (0.195g., 92%) was recovered.

(v) N,N-dimethylamino-4-nitrosobenzene.

Triphenylarsonium 2,3,4-triphenylcyclopentadienylide.

A mixture of triphenylarsonium 2,3,4-triphenylcyclopentadienylide (0.598g., 1m.mole) and N,N-dimethylamino-4-nitrosobenzene (0.15g., 1m.mole) in benzene (30ml.) was heated under reflux for 24 hours. The solvent was removed and on adding ether to the residual oil unchanged arsonium ylide (0.5g., 84%) was recovered.

(vi) Acetylation.

(a) Tri-p-tolylarsonium 2,3,4-triphenylcyclopentadienylide.

A solution of tri-p-tolylarsonium 2,3,4-triphenylcyclopentadienylide (0.32g., 0.5m.mole) in ecetic anhydride (5ml.) was heated to reflux for 3 minutes, and then cooled. On scratching the walls of the flask, tri-p-tolylarsonium-5-acetyl-2,3,4-triphenylcyclopentadienylide was obtained (0.23g., 68%). A sample was recrystallised from a benzene/light petroleum mixture to give crystals, mpt. 257-259°. (Found C, 81.0; H, 5.5; $C_{46}H_{39}O$ As requires C, 80.9; H, 5.8%).

(b) Tri-p-methoxyphenylarsonium 2,3,4-triphenylcyclopentadienylide.

A solution of tri-p-methoxyphenylarsonium 2,3,4-triphenylcyclopentadienylide (0.345g., 0.5m.mole) in acetic anhydride (5ml.) was heated to reflux for 3 minutes. On reducing the acetic anhydride in bulk and scratching the residue, tri-p-methoxyphenylarsonium 5-acetyl-2,3,4-triphenylcyclopentadienylide was obtained (0.328g., 65%). Crystals, mpt. 249-252° from a benzene/light petroleum mixture (1:1). (Found C, 75.8; H, 5.0; $C_{46}H_{39}O_4$ As requires C, 76.5; H, 5.4%).

(c) Tri-o-tolylarsonium 2,3,4 - triphenylcyclopentadienylide.

A solution of tri-o-tolylarsonium 2,3,4 - triphenylcyclopentadienylide (0.32g., 0.5m.mole) in acetic anhydride (5ml.) was heated under reflux for 3 minutes. On cooling and scratching, unchanged arsonium ylide was recovered (0.29g., 91%).

(d) Tri-o-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide.

Tri-o-methoxyphenylarsonium 2,3,4 - triphenylcyclopentadienylide (0.345g., 0.5m.mole) was treated in an identical manner to that described in Experiment (12(vi)a) to give tri-o-methoxyphenylarsonium 5 - acetyl - 2,3,4 - triphenylcyclopentadienylide (0.245g., 67%). Crystals mpt. 278-280° from a benzene /light petroleum mixture (1:1). (Found C, 75.8; H, 5.5; $C_{46}H_{39}O_4As$ requires C, 75.6; H, 5.4%).

13. REACTIONS OF TRIARYLARSONIUM 2,3,4,5 - TETRAPHENYLCYCLOPENTADIENYLIDES.

(i) Benzaldehyde.

(a) Triphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of triphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.337g., 0.5m.mole) and freshly distilled benzaldehyde (0.053g., 0.5m.mole) in benzene (25ml.) was heated under reflux for 20 hours. (After 5 hours a further quantity of benzaldehyde (0.026g.,0.25m.mole) was added) The solvent was removed and the residue was triturated with ether whereupon a pale yellow precipitate appeared. This was filtered off and washed with ether to give unchanged arsonium ylide (0.272g., 81%). The mother-liquor, on removal of the solvent, was dissolved in a small amount of benzene and applied to a silica column prepared with a benzene / light petroleum mixture (1:1). A brown band was eluted with benzene. Evaporation of the solvent and trituration of the residue with ethanol gave

1,2,3,4,6 - pentaphenylfulvene (0.043g., 19%). A sample recrystallised from glacial acetic acid gave red-brown prisms mpt 197 - 200° (lit 200-201°)[36]. A pale yellow band remained at the top of the column and this was eluted with methanol. The solvent was removed and triphenylarsine oxide (0.375g., 23%) was obtained.

(b) Tri-p-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of tri-p-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.358g., 0.5m.mole) and benzaldehyde (0.053g., 0.5m.mole) in benzene (25ml.) was heated under reflux for 20 hours. (After 5 hours a further quantity of benzaldehyde (0.026g., 0.25m.mole) was added). The solvent was removed, the residue was dissolved in a small amount of benzene, and on the addition of light petroleum a yellow precipitate formed. This was filtered off and washed with light petroleum to give unchanged arsonium ylide (0.276g., 77%). The mother liquor was chromatographed in an identical manner to that described in Experiment (13(i)a) to give 1,2,3,4,6 - pentaphenylfulvene (0.046g., 20%) identical to the compound prepared in Experiment (13(i)a).

(c) Tri-p-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of tri-p-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.382g., 0.5m.mole) and benzaldehyde (0.053g., 0.5m.mole) was treated in an identical manner to that described in Experiment (13(i)b). Unchanged arsonium ylide (0.321g., 84%) was recovered from the reaction mixture and chromatography of the remaining residue gave 1,2,3,4,6 - pentaphenylfulvene (0.039g., 17%) identical to the compound prepared in Experiment (13(i)a).

(ii) p-Nitrobenzaldehyde.

(a) Tri-o-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of tri-o-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.358g., 0.5m.mole) and p-nitrobenzaldehyde (0.075g., 0.5m.mole) in benzene (30ml.) was heated under reflux for 18 hours. The solvent was removed and trituration of the residual oil with ether gave unchanged arsonium ylide (0.315g., 88%).

The reaction was repeated using chloroform as the solvent. Unchanged arsonium ylide was recovered quantitatively.

(b) Tri-o-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of tri-o-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.382g., 0.5m.mole) and p-nitrobenzaldehyde (0.075g., 0.5m.mole) was treated in an identical manner to that described in Experiment (13(ii)a). Unchanged arsonium ylide (0.325g.,85%) was recovered.

(iii) 2,4-Dinitrobenzaldehyde.

(a) Tri-o-tolylarsonium 2,3,4,5-tetraphenylcyclopentadienylide.

A mixture of tri-o-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.358g.,0.5m.mole) and 2,4-dinitrobenzaldehyde (0.098g., 0.5m.mole) in benzene (30ml.) was heated under reflux for 18 hours. The solvent was removed and trituration of the residue with ether gave unchanged arsonium ylide (0.314g., 88%).

(b) Tri-o-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of tri-o-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.382g., 0.5m.mole) and 2,4 - dinitrobenzaldehyde (0.098g., 0.5m.mole) was treated in an identical manner to that described in Experiment (13(iii)a). Unchanged arsonium ylide (0.333g., 87%) was recovered.

(iv) Nitrosobenzene.

(a) Triphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of triphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.674g., 1m.mole) and nitrosobenzene (0.107g., 1m.mole) in benzene (25ml.) was heated under reflux for 6 hours. (After the initial 3 hours a further quantity of nitrosobenzene (0.054g., 0.5m.mole) was added). The solvent was removed, the residue was adsorbed on to silica (as described in Experiment (12(iv)a)) and then deposited on the top of a dry silica column. The column was developed with benzene and 3 bands were obtained. The green second band was cut from the column and extracted with chloroform to give, after removal of the solvent and trituration with ethanol, N-phenyl-1,2,3,4,5-tetraphenylcyclopentadienone ketoxime (0.21g., 44%). A sample was crystallised from ethanol as khaki-green needles, mpt. 223-5° (lit. mpt. 224-226°)[36]. The third band was extracted with chloroform to give, after removal of solvent, triphenylarsine oxide (0.01g., 22%).

The first red band was extracted with chloroform and the residue was reapplied to a second dry silica column. Development of the column with a benzene / light petroleum mixture (1:4) gave a colourless band, and a red band was left at the top of the column. The red band was extracted with chloroform to give, after removal of the solvent and trituration with ethanol, N-phenyl-2,3,4,5 - tetraphenylcyclopentadienone anil (0.223g., 48.5%). A sample was crystallised from nitromethane as crimson prisms, mpt. 233 - 235° (lit. mpt. 232-235°).[36] The colourless band of the dry column after extraction with chloroform and removal of the solvent, gave triphenylarsine (0.070g., 46%).

The reaction was repeated on half the above scale, but using chloroform as the solvent. Work up gave N-phenyl - 2,3,4,5 - tetraphenylcyclopentadienone ketoxime (0.093g., 39%) and N-phenyl 2,3,4,5 - tetraphenylcyclopentadienone anil (0.074g., 32%), identical with the above compounds.

The reaction was repeated again on half the above scale, but carbon tetrachloride was used as the solvent. Work up gave N-phenyl 2,3,4,5- tetraphenylcyclopentadienone Ketoxime (0.107g., 45%) and N-phenyl 2,3,4,5 - tetraphenylcyclopentadienone anil (0.12g., 52%).

A mixture of triphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.34g., 0.5m.mole) and nitrosobenzene (0.053g., 0.5m.mole) in absolute methanol (400ml.) was heated under reflux for 8 hours. A further quantity of nitrosobenzene (0.027g., 0.25m.mole) was added after 4 hours. The reaction was worked up in an identical manner to that described above to give N-phenyl - 2,3,4,5 - tetraphenylcyclopentadienone ketoxime (0.046g., 19%), but no N-phenyl 2,3,4,5 - tetraphenylcyclopentadienone anil or triphenylarsine was recovered. Instead a red oily compound (0.13g.) that contained 1,2,3,4 - tetraphenylcyclopentadiene was obtained.

The reaction was repeated on the same scale, but the reaction was carried out in absolute methanol (50ml.). After 10 hours arsonium ylide (0.12g., 36%) was filtered off from the solution . The solvent was then removed and the residue was chromatographed in an identical manner to that described above to give N-phenyl - 2,3,4,5 - tetraphenylcyclopentadienone ketoxime (0.11g., 74% of the dissolved ylide) and triphenylarsine oxide (0.071g., 65%). Again no N-phenyl 2,3,4,5 - tetraphenylcyclopentadienone anil or triphenylarsine was recovered but the same red oily compound (0.065g) as described above was obtained.

(b) Tri-p-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of tri-p-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.358g., 0.5m.mole) and nitrosobenzene (0.053g., 0.5m.mole) was treated in an identical manner to that described in Experiment (13(iv)a) to give N-phenyl-2,3,4,5- tetraphenylcyclopentadienone Ketoxime (0.067g., 28%) and N-phenyl-2,3,4,5- tetraphenylcyclopentadienone anil (0.131g., 57%) identical with the compounds prepared in Experiment (13(iv)a). Tri-p-tolylarsine (0.048g., 28%) and tri-p-tolylarsine oxide (0.11g., 30%) were also obtained.

A mixture of tri-p-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.358g., 0.5m.mole) and nitrosobenzene (0.053g., 0.5m.mole) in absolute methanol (50ml.) was treated in an identical manner to that described above. Work up gave N-phenyl-2,3,4,5- tetraphenylcyclopentadienone ketoxime (0.11g., 48%), tetracyclone (0.003g., 2%), and a red oil (0.22g) which contained 1,2,3,4 - tetraphenylcyclopentadiene.

(c) Tri-p-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of tri-p-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.382g., 0.5m.mole) and nitrosobenzene (0.053g., 0.5m.mole) was treated in a similar manner to that described in Experiment (13(iv)a). Extraction of the green band in the first column gave N-phenyl 2,3,4,5 - tetraphenylcyclopentadienone Ketoxime (0.062g., 26%) identical with the compound prepared in Experiment (13(iv)a). The band at the top of the column was extracted with chloroform, and after removal of the solvent was found to be a mixture of unchanged arsonium ylide and tri-p-methoxyphenylarsine oxide (0.096g.). N-phenyl-2,3,4,5-tetraphenylcyclopentadienone anil (0.11g., 48%), identical with the compound obtained in Experiment (13(iv)a), and tri-p-methoxyphenylarsine (0.048g.,24%) were separated on the second dry column by using a light petroleum / ether mixture (5:1).

A mixture of tri-p-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.38g., 0.5m.mole) and nitrosobenzene (0.053g., 0.5m.mole) in methanol (30ml.) was treated as above. Work up gave N-phenyl-2,3,4,5 - tetraphenylcyclopentadienone Ketoxime (0.11g., 47%) and a red oil/solid (0.04g.).

(d) Tri-o-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of tri-o-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.716g., 1m.mole) and nitrosobenzene (0.107g., 1m.mole) in chloroform (25ml.) was heated under reflux for 8 hours. (After the initial 4 hours a further quantity of nitrosobenzene (0.054g., 0.5m.mole) was added). The solvent was removed and the residue was triturated with ether, whereupon a pale yellow precipitate formed. This was filtered off to give unchanged arsonium ylide (0.47., 65%). The solvent was removed from the filtrate and the residue was applied to a dry silica column. Development of the column with benzene gave first a red band and then a green band. The green band was cut from the column and extracted with chloroform. Removal of the solvent and trituration with ethanol gave N-phenyl-2,3,4,5- tetraphenylcyclopentadienone ketoxime (0.073g., 15%). The red band was extracted with chloroform and the residues applied to a second dry column which was developed with a benzene/ light petroleum mixture to give a clear column with a red top. Extraction of the column gave tri-o-tolylarsine (0.049g., 14%) and a trace amount of the unknown red compound (0.02g.)

A mixture of tri-o-tolylarsonium 2,3,4,5 -tetraphenylcyclopentadienylide (0.716g., 1m.mole) and nitrosobenzene (0.107g., 1m.mole) in benzene (25ml.) was heated under reflux for 18 hours. (After the initial 4 hours a further quantity of nitrosobenzene (0.054g., 0.5m.mole) was added). The solvent was removed and on triturating the residue with ether, unchanged arsonium ylide (0.64g., 89%) was recovered.

(e) Tri-o-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

A mixture of tri-o-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.382g., 0.5m.mole) and nitrosobenzene (0.053g., 0.5m.mole) in benzene (25ml.) was heated under reflux for 8 hours. (After the initial 4 hours a further quantity of nitrosobenzene (0.025g., 0.5m.mole) was added). The solvent was removed and on triturating the residue with an ether / light petroleum mixture (1:1), unchanged arsonium ylide (0.34g., 89%) was recovered.

The reaction was repeated on the same scale, but with chloroform (25ml.) as the solvent. The work up gave unchanged arsonium ylide (0.305g., 80%). This was filtered off and the solvent was removed from the filtrate. The remaining residue was chromatographed on a dry silica column to give what appeared to be a trace amount of N-phenyl-2,3,4,5 - tetraphenylcyclopentadienone Ketoxime. There was no red band on the column corresponding to N-phenyl-2,3,4,5 - tetraphenylcyclopentadienone anil.

(v) Decomposition of Triarylarsonium 2,3,4,5 - tetraphenylcyclopentadienylides in Methanol.

(a) Tri-p-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

Tri-p-tolylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide (0.36g., 0.5m.mole) in absolute methanol (70ml.) was heated under reflux for 18 hours. The solvent was removed , but no unchanged arsonium ylide was recovered on triturating the residue with an ether / light petroleum mixture. The residue was chromatographed on a silica column prepared from light petroleum

1,2,3,4 - tetraphenylcyclopentadiene (0.12g., 65%) was eluted with benzene. The next layer eluted with benzene gave after removal of solvent, a red intractable tar (0.05g.). Tri-p-tolylarsine oxide (0.2g., 96%) was eluted with methanol.

(b) Tri-p-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadienylide.

Tri-p-methoxyphenylarsonium 2,3,4,5 - tetraphenylcyclopentadiene (0.38g., 0.5m.mole) in absolute methanol (30ml.) was heated under reflux for 18 hours. Work up as in Experiment (13(v)a), gave 1,2,3,4 - tetraphenylcyclopentadiene (0.14g., 16%) and an oil (0.17g.) which contained tri-p-methoxyphenylarsine oxide.

14. REACTION OF TRIARYLARSONIUM CYANOETHOXYCARBONYLMETHYLIDE.

(i) p-Nitrobenzaldehyde.

(a) Triphenylarsonium cyanoethoxycarbonylmethylide.

A mixture of triphenylarsonium cyanoethoxycarbonylmethylide (0.21g., 0.5m.mole) and p-nitrobenzaldehyde in benzene (25ml.) was heated under reflux for 18 hours. The solvent was removed and on triturating the residue with ethanol a white solid crystallised. This was filtered off and found to be ethyl p-nitrobenzylidenecyanoacetate (0.111g., 90%). A sample was recrystallised from ethanol as yellow/white coloured crystals, mpt. 166 - 167° (lit. 166 - 167°)[46].

(b) Tri-p-tolylarsonium cyanoethoxycarbonylmethylide.

A mixture of tri-p-tolylarsonium cyanoethoxycarbonylmethylide (0.344g., 0.75m.mole) and p-nitrobenzaldehyde (0.155g., 0.75m.mole) in benzene (25ml.) was treated in an identical manner to that described in Experiment (14(i)a). The work up gave ethyl p-nitrobenzylidenecyanoacetate (0.165g., 89%) identical to the compound prepared in Experiment (14(i)a).

The reaction was repeated in methanol as the solvent. Ethyl p-nitrobenzylidenecyanoacetate (0.151g., 82%) was obtained identical to the compound prepared in Experiment (14(i)a).

(c) Tri-o-tolylarsonium cyanoethoxycarbonylmethylide.

A mixture of tri-*o*-tolylarsonium cyanoethoxycarbonylmethylide (0.46g., 1m.mole) and *p*-nitrobenzaldehyde (0.153g., 1m.mole) in benzene was heated under reflux for 18 hours. The solvent was removed and on the addition of ether unchanged arsonium ylide (0.435g., 95%) was recovered.

The reaction was repeated in toluene and again the arsonium ylide was recovered quantitatively.

(d) Tri-o-methoxyphenylarsonium cyanoethoxycarbonylmethylide.

A mixture of tri-o-methoxyphenylarsonium cyanoethoxycarbonylmethylide (0.253g., 0.5m.mole) and *p*-nitrobenzaldehyde (0.075g., 1m.mole) in benzene was treated in an identical manner to that described in Experiment (14(i)c). Work up gave unchanged arsonium ylide (0.23g., 91%).

(ii) 2,4 - Dinitrobenzaldehyde.

(a) Triphenylarsonium cyanoethoxycarbonylmethylide.

A mixture of triphenylarsonium cyanoethoxycarbonylmethylide (0.42g., 1m.mole) and 2,4 - dinitrobenzaldehyde.(0.2g., 1m.mole) in benzene (25ml.) was heated under reflux for 18 hours. The solvent was removed, and the residue was dissolved in a small quantity of benzene and chromatographed on a silica column prepared with a (1:1) mixture of benzene / light petroleum. An orange/brown layer was eluted with chloroform and on removal of the solvent this was found to be ethyl 2,4 - dinitrobenzylidenecyanoacetate (0.275g., 95%). A sample was recrystallised from an ethyl acetate / light petroleum mixture to give crystals mpt. 121-122°. (Found C, 49.4; H, 2.8; N, 15.0; $C_{12}H_9O_6N_3$ requires C, 49.5; H, 3.1; N, 14.4%).

(b) Tri-o-tolylarsonium cyanoethoxycarbonylmethylide.

A mixture of tri-*o*-tolylarsonium cyanoethoxycarbonylmethylide (0.46g., 1m.mole) and 2,4-dinitrobenzaldehyde (0.2g., 1m.mole) in benzene (25ml.) was heated under reflux for 18 hours. The solvent was removed and on the addition of ether, unchanged arsonium ylide (0.43g., 93%) was recovered.

(c) Tri-o-methoxyphenylarsonium cyanoethoxycarbonylmethylide.

A mixture of tri-*o*-methoxyphenylarsonium cyanoethoxycarbonylmethylide (0.507g., 1m.mole) and 2,4-dinitrobenzaldehyde (0.2g., 1m.mole) was heated in benzene (25ml.) under reflux for 18 hours. The solvent was removed and on triturating the residue with an ether / light petroleum mixture (1:1), unchanged arsonium ylide (0.23g., 45%) was recovered. After filtering off the unchanged ylide the solvent was removed from the filtrate and the remaining residue was applied to a silica column prepared from benzene. A brown band was eluted with chloroform and this gave after removal of solvent, ethyl 2,4-dinitrobenzylidenecyanoacetate (0.053g., 18%) identical with the compound prepared in Experiment (14(ii)a).

15. REACTIONS OF TRI-O-TOLYLARSONIUM DICYANOMETHYLIDE.

(a) Tri-o-tolylarsonium dicyanomethylide.

A mixture of tri-*o*-tolylarsonium dicyanomethylide (0.41g., 1m.mole) and p-nitrobenzaldehyde (0.153g., 1m.mole) in benzene (25ml.) was heated under reflux for 18 hours. The solvent was removed and trituration of the residue with ether gave unchanged arsonium ylide (0.365g., 89%).

(b) Tri-o-tolylarsonium dicyanomethylide.

A mixture of tri-o-tolylarsonium dicyanomethylide (0.41g., 1m.mole) and 2,4-dinitrobenzaldehyde (0.2g., 1m.mole) in benzene (25ml.) was heated under reflux for 18 hours. The solvent was removed and trituration of the residue with ether gave unchanged arsonium ylide (0.375g., 91%).

pK_a DETERMINATIONS.

Optical density measurements for the pK_a determinations were carried out on a Unicam S.P. 800 spectrophotometer. pH determinations were carried out with a Beckman Research pH Meter equipped with glass and saturated calomel electrodes. All optical density measurements and pH determinations were recorded at 25°.

95% Ethanol was the solvent used for all the solutions of acids, bases, buffers and ylide perchlorates. The acid solution was 0.1M HCl prepared by adding water (50ml.) and ethanol (950ml.) to concentrated hydrochlic acid (9.3ml.). The base solution was 0.1M KOH prepared by dissolving potassium hydroxide (5.61g.) in water (50ml.) and ethanol (950ml.).

Ten buffered solutions were prepared in a 95% ethanol-water solution. The apparent pH of each buffer was 8.64 (8.9), 8.45 (8.6),7.85 (8.0), 7.68 (7.8), 7.01 (7.2), 6.57 (4.0), 6.02 (3.6), 5.82 (3.4), 5.65 (3.2),* 5.43 (3). The first five were Tris-HCl buffers (Tris-tris-(hydroxymethyl) aminomethane) and the other five were formicacid-potassium hydroxide buffers.

Stock solutions of each ylide perchlorate were prepared by dissolving the salt (ca. 4mg.) in 95% ethanol (10ml.). Aliquots (1ml.) of each stock solution were diluted to 10ml. separately with the acidic solution , the basic solution and the appropriate buffer solution.

* (The values in parentheses are the pH values of the same buffers when prepared in aqueous media).

The absorbancy of the three solutions was recorded at five wavelengths in the region (260-350nm.) where the ylides absorbed strongly and the conjugate salts were nearly transparent. The pK_a values were calculated as follows.

$$pK_a = pH + \log \frac{B - b}{b - A}$$

where B = absorbancy of the stock aliquot in basic solution,

b = absorbancy of the stock aliquot in buffered solution,

A = absorbancy of the stock aliquot in acid solution, and

pH = pH of the buffer solution used.

The values recorded were the average of the pK_a's determined using at least two different buffers. The pK_a determined using any given buffer solution was the average of the pK_a values determined at five different wavelengths.

Results.

Ylide	pK_a
(106)	6.6
(109)	7.0
(111)	6.9
(112)	5.8
(114)	7.5
(115)	7.0

17. MISCELLANEOUS REACTIONS.

(i) Attempted Preparation of S-isopropyl N,N,N^1,N^1 - tetramethylthiouronium bromide.

A mixture of 2 - bromopropane (0.246g., 2m.mole) and N,N,N^1,N^1 tetramethylthiourea (0.264g., 2m.mole) in butanol (25ml.) was heated under reflux for 5 hours. The solvent was removed to give an oil that was found to be a mixture of starting materials.

(ii) Preparation of S-butyl N,N,N^1N^1-tetramethylthiouronium iodide.

A mixture of 1-iodobutane (9.2g., 50m.mole) and N,N,N^1,N^1-tetramethylthiourea (6.6g., 50m.mole) in butanol (50ml.) was heated under reflux for 4 hours. Ether was added to the cooled solution and a white precipitate formed which was filtered off to give S-butyl N,N,N^1,N^1-tetramethylthiouronium iodide (13.4g., 85%). A sample was recrystallised from benzene as white crystals mpt. 103-4°. (Found C, 34.3; H, 6.8; N, 8.6. $C_9 H_2 N_2 S Br$ requires C, 34.2; H, 6.7; N, 8.8%).

(iii) The Attempted Reaction of S-butyl N,N,N^1,N^1-tetramethylthiouronium iodide with p-Nitrobenzaldehyde.

Phenyllithium (16ml. 1.6M) was added to a suspension of S-butyl N,N,N^1,N^1-tetramethylthiouronium iodide (6.72g., 25m.mole) in dry benzene (60ml.) under a nitrogen atmosphere. The resulting solution was stirred for 1 minute and then *p*-nitrobenzaldehyde (3.83g., 25m.mole) in benzene (20ml.) was added. The dark brown solution was stirred for a further hour, and was extracted thoroughly with water and then by a saturated solution of sodium metabisulphite. The benzene layer was dried over sodium sulphate and removal of the solvent left a residual dark red oil. This oil was chromatographed on a silica column prepared with benzene/light petroleum (1:1). Mass spectra and N.M.R. spectroscopy of the various fractions that were eluted from the column showed that N,N,N^1,N^1 - tetramethylurea, butyldisulphide and the products from the disproportionation of p-nitrobenzaldehyde were present.

18. SPECTRA.

(i) N.M.R. SPECTRA.

Chemical shifts (δ) are given in p.p.m. relative to tetramethylsilane as internal standard, with relative intensities in parentheses. Deuteriochloroform was the solvent unless otherwise stated.

(a) 2,2-dimethyl(4,6-dioxo-1,3-dioxan)-ylide.

(93) methylphenylsulphonium 7.95-7.2(5)m 3.4(3)s 1.7(6)s

(b) bis(methoxycarbonyl)methylides.

(90) $(CH_3OCO)_2$= As Ph_3 7.85-7.25(15)m 3.35(6)s

(97) $(CH_3OCO)_2$ = PPh_3 7.9 -7.2 (15)m 3.3 (6)s

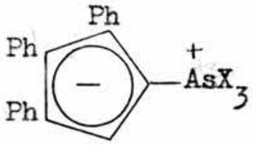
(c) 1,1,2,2-Tetrakis(methoxycarbonyl)ethene.

(98) 3.9s

(d) 7,7,bis(methoxycarbonyl)bicyclo(4,1,0)heptane.

(99) 3.8(3)s 3.7(3)s 2.1-2.5(6)m 1.5-0.9(4)m

(e) Triarylarsonium 2,3,4-triphenylcyclopentadienylides.

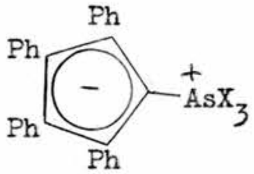


	X		
(109)	p-tolyl	7.4-6.2(28)m	2.4(9)s
(110)	p-methoxyphenyl	7.5-6.2(28)m	3.8(9)s
(111)	m-tolyl	7.5-6.2(28)m	2.3(9)s
(112)	o-tolyl	7.7-6.6(28)m	2.15(9)s
(113)	o-methoxyphenyl	7.6-6.4(28)m	3.35(9)s

(f) Triarylarsonium 5-acetyl-2,3,4-triphenylcyclopentadienylides.

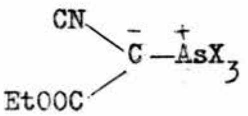
(129)	p-tolyl	7.5-6.5(27)m	2.3(9)s		1.7(3)s	
(130)	p-methoxyphenyl	7.5-6.6(27)m	3.8(9)s		1.7(3)s	
(131)	o-methoxyphenyl	7.8-6.5(27)m	3.1(9)s(broad)		1.6(3)s	
(131)	at -10°	7.8-6.5(27)m	3.8(3)s	3.0(3)s	2.8(3)s	1.6(3)s
(131)	coalesced at 20°					

(g) Triarylarsonium 2,3,4,5-tetraphenylcyclopentadienylides.



	X				
(117)	p-tolyl	7.4-6.5(32)m		2.3(9)s	
(118)	p-methoxyphenyl	7.4-6.5(32)m		3.8(9)s	
(115)	o-tolyl at 70°	7.6-6.7m		1.85s (broad)	
(115)	o-tolyl at-45°	7.6-6.3m	2.8s (broad)	1.5s (broad)	1.1s (broad)
(115)	o-tolyl coalesced at Approximately 10°				
(116)	o-methoxyphenyl	7.5-6.4(32)m		3.2(9)s	

(h) Triarylarsonium cyanoethoxycarbonylmethylides.



	X				
(119)	p-tolyl	7.7-7.2(12)m	4.1 q	2.4(9)s	1.25t
(120)	o-tolyl	7.7-7.2(12)m	4.05 q	2.25(9)s	1.2t
(121)	o-methoxyphenyl	7.7-6.8(12)m	4.0 q	3.6(9)s	1.2t

These compounds exhibit internal rotation about the enolate α,β c-c bond resulting in considerable broadening of the ethyl resonances.

(i) Tri-o-tolylarsonium dicyanomethylide.

(122)	7.7-7.2(12)m	2.35(9)s

(j) Ethyl 2,4-dinitrobenzylidenecyanoacetate.

(138)	9.2-8.0(3)m	4.45(2)q	1.45(3)t

(k) Benzyltri-o-tolylarsonium tetrafluoroborate.

(139)	7.8-7.0(17)m	4.8(2)s	2.1(3)q

(l) Triarylarsines.

Tri-p-tolylarsine	7.7-6.9(12)m	2.35(9)s
Tri-p-methoxyphenylarsine	7.4-6.75(12)m	3.8(9)s
Tri-m-tolylarsine	7.4-6.9(12)s(broad)	2.3(9)s
Tri-o-tolylarsine	7.4-6.6(12)m	2.45(9)s
Tri-o-methoxyphenylarsine	7.2-6.5(12)m	3.65(9)s

m = multiplet, q = quartet, t = triplet, d = doublet, s = singlet

(ii) I.R. SPECTRA.

α max is given in cm^{-1}. The infra-red spectra was carried out in a nujol mull.

(i) Triarylarsonium cyanoethoxycarbonylmethylides.

(119)	Tri-p-tolylarsonium cyanoethoxycarbonylmethylides		2180, 1650, 1590.
(120)	Tri-o-tolylarsonium	do.	2180, 1635.
(121)	Tri-o-methoxyphenylarsonium	do.	2185, 1610, 1580.

(ii)	Tri-o-tolylarsonium dicyanomethylide		
(122)			2170, 2140.

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