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PREPARATION AND PROPERTIES OF SOME STABLE ARSONIUM YLIDES

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Abstract—Stable crystalline arsonium ylides have been prepared by thermal decomposition of diazo compounds in the presence of triphenylarsine, and by condensation reactions of reactive methylene compounds with triphenylarsine oxide. The spectra of these ylides, and their reactions with benzaldehydes are discussed. Like other stabilised arsonium ylides they give alkenes rather than epoxides in Wittig reactions. They are generally more polar than their phosphonium analogues and also are more reactive in the Wittig reaction. With diphenylcyclopropenone some more reactive arsonium ylides form α-pyrones.

Sulphonium and especially phosphonium ylides have been intensively investigated but much less attention has been paid to the related arsonium ylides.[1]

Whereas phosphonium ylides form olefins and sulphonium ylides form epoxides as the products of Wittig reactions, arsonium ylides can give rise to either olefins, epoxides, or a mixture of both types of product. It seems that the more stabilised arsonium ylides afford olefins but the less stabilised arsonium ylides afford either epoxides or their rearrangement products.[2–10]

Stabilised phosphonium and sulphonium ylides are of less value as reagents in Wittig reactions since they either do not react or at best react sluggishly. Since we had shown[4,5,11] that arsonium cyclopentadienylides take part in Wittig reactions wherein their phosphonium or sulphonium analogues fail to react, it seemed worthwhile to examine more generally the reactivity of arsonium ylides.

It was first necessary to make a suitable range of stable arsonium ylides. The first arsonium ylides were prepared either by the action of base on suitable arsonium salts[1,12–14] or by the reaction between triphenylarsine dichloride and reactive methylene compounds.[15] Stabilised arsonium ylides have been prepared by acylation of other arsonium ylides.[2,16] The salt method sometimes fails to provide arsonium ylides since attempted conversion of a halogen compound into an arsonium salt leads instead to nucleophilic removal of the halogen atom and formation of a carbanion,[17] especially when this carbanion is stabilised by appropriate electron-withdrawing substituent groups. Similar results have been noted in the attempted formation of some phosphonium salts as precursors of stabilised ylides.[18]

Arsonium cyclopentadienylides have previously been prepared by us by carbenic decomposition of diazocyclopentadienes in the presence of triphenylarsine[19,20] and by condensation of triphenylarsine oxide with cyclopentadienes.[18,21,22] In the present work the general application of these methods is discussed together with the properties of the resultant arsonium ylides.

Preparation of arsonium ylides from arsine oxides

A wide range of arsonium ylides (**1–13**; **15–17**) was prepared by condensation of compounds having reactive methylene groups with triphenylarsine oxide either in refluxing acetic anhydride or in refluxing triethylamine in the presence of phosphorus pentoxide. In these reactions the major product was isolated in crystalline form and characterised as an arsonium ylide by analysis and spectroscopic studies. The yields obtained are listed in Table 1 and elemental analyses and m.ps in Table 2.

The structure of a number of these ylides was confirmed by alternative syntheses involving acylation of mono-β-ketoylides (**18**). Such ketoylides were prepared by the 'salt' method and then acylated by reaction with acetic or benzoic anhydrides. Details are given in Table 3.

Similarly, carbamoylation of triphenylarsonium acetonylide (**18**, R = Me) with phenyl isocyanate gave the ylide **12** (82%) and reaction of triphenylarsonium ethoxycarbonylmethylide (**18**, R = OEt) with ethyl chloroformate in the presence of triethylamine gave ylide **14** (21%).

No O-acylated products were encountered, although O-acylation of triphenylarsonium phenacylide with benzoyl bromide has been reported.[2] These authors suggested that O-acylation was the result of kinetic control of the reaction whereas thermodynamic control resulted in the formation of C-acylated products.

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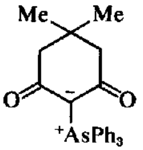

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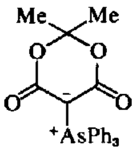

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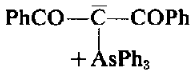
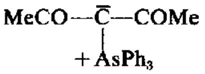


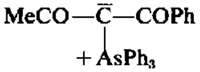
$\mathrm{PhCO{-}\underset{^{+}AsPh_3}{\bar{C}}{-}COPh}$

3



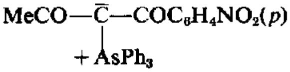
$\mathrm{MeCO{-}\underset{^{+}AsPh_3}{\bar{C}}{-}COMe}$

4



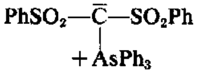
$\mathrm{MeCO{-}\underset{^{+}AsPh_3}{\bar{C}}{-}COPh}$

5



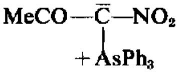
$\mathrm{MeCO{-}\underset{^{+}AsPh_3}{\bar{C}}{-}COC_6H_4NO_2(\mathit{p})}$

6



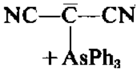
$\mathrm{PhSO_2{-}\underset{^{+}AsPh_3}{\bar{C}}{-}SO_2Ph}$

7



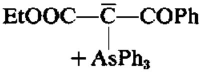
$\mathrm{MeCO{-}\underset{^{+}AsPh_3}{\bar{C}}{-}NO_2}$

8



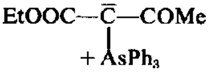
$\mathrm{NC{-}\underset{^{+}AsPh_3}{\bar{C}}{-}CN}$

9



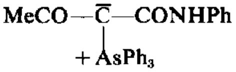
$\mathrm{EtOOC{-}\underset{^{+}AsPh_3}{\bar{C}}{-}COPh}$

10



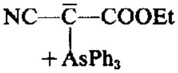
$\mathrm{EtOOC{-}\underset{^{+}AsPh_3}{\bar{C}}{-}COMe}$

11



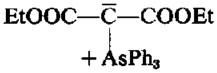
$\mathrm{MeCO{-}\underset{^{+}AsPh_3}{\bar{C}}{-}CONHPh}$

12



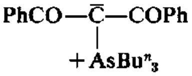
$\mathrm{NC{-}\underset{^{+}AsPh_3}{\bar{C}}{-}COOEt}$

13



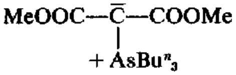
$\mathrm{EtOOC{-}\underset{^{+}AsPh_3}{\bar{C}}{-}COOEt}$

14



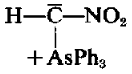
$\mathrm{PhCO{-}\underset{^{+}AsBu^{n}_3}{\bar{C}}{-}COPh}$

15



$\mathrm{MeOOC{-}\underset{^{+}AsBu^{n}_3}{\bar{C}}{-}COOMe}$

16



$\mathrm{H{-}\underset{^{+}AsPh_3}{\bar{C}}{-}NO_2}$

17

Compounds with strongly activated Me groups, such as nitromethane, reacted with triphenylarsine oxide in acetic anhydride to give not the monosubstituted ylide **17** but instead the acetylated ylide **8**. Presumably the ylide **17** is formed first and is immediately acetylated by the solvent. Arsonium cyclopentadienylides acetylated in the 5-membered ring have been obtained similarly from condensation reactions of cyclopentadienes and triphenylarsine oxide in acetic anhydride.[18,21]

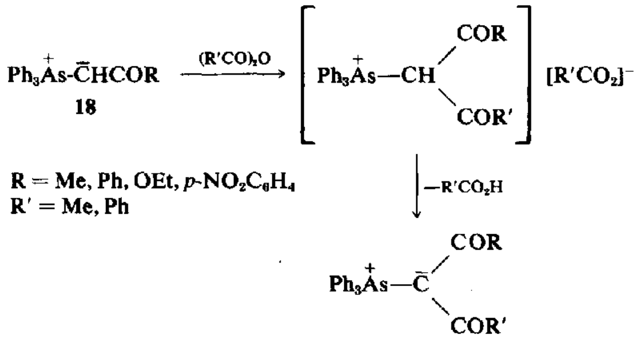
Table 1. Reaction conditions and yields of ylides

Ylide	Carbon Acid employed	Yield, % 'Arsine Oxide' method $+\mathrm{Ac_2O}$	$+\mathrm{P_2O_5/Et_3N}$	'Carbene' method (reaction temp, catalyst)
1	$\mathrm{Me_2\overset{\ulcorner CH_2CO \urcorner}{CH\cdot CH_2COCH_2}}$	85	39	64(150°, CuBr)
2	$\mathrm{Me_2\overset{\ulcorner O\cdot CO \urcorner}{CH\cdot O\cdot CO\cdot CH_2}}$	42	dec.	40(150°, CuBr)
3	$\mathrm{(PhCO)_2CH_2}$	73	44	79(150°, CuBr)
4	$\mathrm{Ac_2CH_2}$	33	48	34(150°, Cu)
5	$\mathrm{AcCH_2COPh}$	27	44	54(150°, CuBr)
6	$p\text{-}\mathrm{NO_2C_6H_4COCH_2Ac}$	35	no reaction	—
7	$\mathrm{(PhSO_2)_2CH_2}$	52	—	96(150°, Cu)
8	$\mathrm{MeNO_2}$	28	see **17**	—
9	$\mathrm{(NC)_2CH_2}$	41	16	—
10	$\mathrm{PhCOCH_2CO_2Et}$	61	13	73(150°, CuBr)
11	$\mathrm{AcCH_2CO_2Et}$	68	22	56(120°, CuBr)
12	$\mathrm{AcCH_2CONHPh}$	81	21	–
13	$\mathrm{EtO_2CCH_2CN}$	89	72	–
14	$\mathrm{(EtO_2C)_2CH_2}$	no reaction	no reaction	61(150°, Cu)
15	$\mathrm{(PhCO)_2CH_2}$	dec.	33	–
16	$\mathrm{(MeO_2C)_2CH_2}$	dec.	59	–
17	$\mathrm{MeNO_2}$	see **8**	64	–

Table 2. M.ps and analytical data of arsonium ylides

Ylide	m.p.°C	Recrystn. solvent	Formula	Elemental analysis, % Calcd. C	H	N	Found C	H	N
1	188–190	benzene-hexane	$C_{26}H_{25}AsO_2$	70·3	5·7		70·1	5·6	
2	187 dec.	benzene-light pet.	$C_{24}H_{21}AsO_4$	64·3	4·7		64·4	4·9	
3	209–212[a]	benzene-light pet.	$C_{33}H_{25}AsO_2$	75·0	4·8		74·6	5·0	
4	152–154	benzene-hexane	$C_{23}H_{21}AsO_2$	68·3	5·2		68·1	5·5	
5	165–167[b]	benzene-hexane	$C_{28}H_{23}AsO_2$	72·1	5·0		72·1	5·0	
6	192–194	benzene-light pet.	$C_{28}H_{22}AsNO_4$	65·8	4·3	2·7	65·6	4·1	2·7
7	244–246[c]	chlorobenzene	$C_{31}H_{25}AsO_4S_2$	62·0	4·2		62·3	4·4	
8	154–158	benzene-light pet.	$C_{21}H_{18}AsNO_3$	61·9	4·5	3·4	62·1	4·8	3·4
9	184–186[d]	ethanol	$C_{21}H_{15}AsN_2$	68·1	4·1	7·6	68·1	4·2	7·4
10	118–121[e]	ethyl acetate	$C_{29}H_{25}AsO_3$	70·2	5·1		70·4	5·4	
11	174–176	benzene-hexane	$C_{24}H_{23}AsO_3$	66·4	5·3		66·5	5·6	
12	198–201	nitromethane	$C_{28}H_{24}AsNO_2$	69·9	5·0	2·9	69·6	5·0	2·8
13	171–172	ethyl acetate-light pet.	$C_{23}H_{20}AsNO_2$	66·2	4·8	3·4	65·9	5·0	3·2
14	118–120	ether-hexane	$C_{25}H_{25}AsO_4$	64·7	5·3		64·4	5·4	
15	88–91	hexane	$C_{27}H_{37}AsO_2$	69·2	8·0		69·0	8·3	
16	oil								
17	170–172	nitromethane	$C_{19}H_{16}AsNO_2$	62·5	4·4	3·8	62·3	4·6	3·8

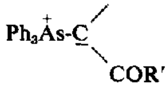
[a] lit.[2] m.p. 208–210°.
[b] lit.[2] m.p. 174°.
[c] lit.[15] m.p. 252–254°.
[d] lit.[15] m.p. 190–191°.
[e] lit.[51] m.p. 118–125°.



R = Me, Ph, OEt, p-$NO_2C_6H_4$
R' = Me, Ph

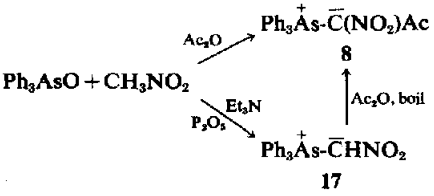
Details are given in Table 3.

Table 3. Acylation of monoketoylides $Ph_3\overset{+}{As}\text{-}\overset{-}{C}HCOR$ (**18**) with carboxylic anhydrides $(R'CO)_2O$

Product 	R	R'	Yield %
3	Ph	Ph	50[a]
4	Me	Me	71
5	Ph	Me	67
5	Me	Ph	48
6	p-$NO_2C_6H_4$	Me	65
10	OEt	Ph	72
11	OEt	Me	90

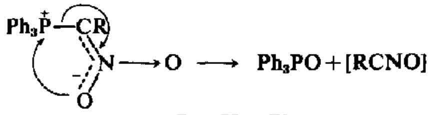
[a] Ref 2.

The unacylated ylide (**17**) could be obtained by using triethylamine and phosphorus pentoxide instead of acetic anhydride. The resultant ylide was converted into the acetylide by heating it briefly in acetic anhydride.



Since phosphonium ylides are in general more stable than arsonium ylides[2,23,24] it is at first sight surprising that triphenylarsonium nitromethylide

(17) is markedly more stable than its phosphonium analogue (19, R = H). The phosphonium ylide (19, R = H) decomposes by an intramolecular reaction to form triphenylphosphine oxide[25] but no such reaction ensues with the arsonium ylide (17).

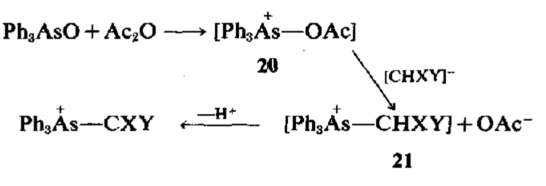


19: R = H or Ph

A similar mechanism was suggested[15] to account for the probable formation of benzonitrile oxide in an unsuccessful attempt to prepare the phosphonium ylide (19, R = Ph). Under the same conditions the corresponding arsonium ylide could be prepared and isolated. This difference in behaviour between the phosphonium and arsonium ylides may be correlated with the difference in strength of the P-O and As-O bonds;[26] the strength of the former provides a considerable driving force in this as in many other reactions, including those of the Wittig type.

The extension of the arsine oxide condensation reaction to trialkylarsine oxides has hitherto been restricted by their sensitivity to acetic anhydride, their hygroscopic nature, and a respect for the high toxicity of the precursor arsines from which they are prepared. Attempted condensations using tri-n-butylarsine oxide in acetic anhydride provided only intractable tars, but reaction of tri-n-butylarsine oxide with dibenzoylmethane in triethylamine and in the presence of phosphorus pentoxide gave the stable crystalline ylide (15). Under these conditions dimethyl malonate also reacted with tri-n-butylarsine oxide to give the ylide (16) but it did not react with the less nucleophilic triphenylarsine oxide either under these conditions or in acetic anhydride.

Sulphoxides condense similarly with reactive methylene compounds.[27–29] Reaction presumably proceeds in an analogous fashion, with initial formation of an acetoxy (20) or phosphorylated arsonium cation. This then reacts with a carbanion to form an arsonium salt (21) which is strongly acidic if X and Y are electron-withdrawing groups, and hence is readily converted into an ylide by loss of a proton, whose removal is assisted by the acetic anhydride or triethylamine.



$$Ph_3AsO + Ac_2O \longrightarrow [Ph_3\overset{+}{A}s\text{—}OAc]$$

20

$$\xrightarrow{[CHXY]^-}$$

$$Ph_3\overset{+}{A}s\text{—}\bar{C}XY \xleftarrow{-H^+} [Ph_3\overset{+}{A}s\text{—}CHXY] + OAc^-$$

21

It is necessary that the methylene reactant should be a fairly strong carbon acid; less acidic compounds such as diethyl malonate, phenylacetonitrile, acetophenone or fluorene do not react under these conditions.

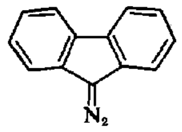
Sulphoxides also condense readily with reactive methylene compounds in the presence of dicyclohexylcarbodiimide,[30] but triphenylarsine oxide did not form ylides under identical conditions. Triphenylarsine sulphide did not react with methylene compounds under any of the above conditions.

Preparation of arsonium ylides from triphenylarsine and diazo-compounds

Triphenylarsonium cyclopentadienylides have been prepared by thermal decomposition of the appropriate diazocyclopentadiene in the presence of triphenylarsine.[19, 31] This method has now been extended to a number of other diazo compounds; the arsonium ylides prepared in this way are listed in Table 1. A mixture of the diazo compound and triphenylarsine under oxygen-free nitrogen was heated above the m.p. of the mixture. Nitrogen was evolved vigorously and the resultant products were identical with the ylides prepared from triphenylarsine oxide and a methylene compound. No ylides could be isolated, however, under identical conditions, from the decomposition of a number of monoacyldiazo compounds, namely ethyl diazoacetate, *p*-nitrobenzoyldiazomethane or benzoylphenyldiazomethane.

The preparation of arsonium cyclopentadienylides[31] and of other arsonium ylides from diazo compounds is greatly facilitated by the presence of copper, copper-bronze or copper salts. For example, attempts to prepare the bis(ethoxycarbonyl)ylide (14) by thermolysis of diethyl diazomalonate in the presence of triphenylarsine without the presence of a catalyst proved abortive whereas this ylide was obtained in 61% yield if the reactants were heated at 150° together with copper-bronze.

This conversion of diazo compounds into arsonium ylides represents a novel way of forming a C-As bond. It is assumed to involve initial formation of a carbene, by decomposition of the diazo compound with loss of nitrogen, followed by reaction of the electron-deficient carbene with a lone pair of electrons on the arsenic atom. Thermolysis of diazo compounds in copper-catalysed reactions is known to provide singlet carbenes or carbenoid species.[32] An alternative pathway might involve the intermediate formation of an arsazene. Such compounds are however unknown, and careful examination of reaction mixtures in the present work has failed to provide any indication of their formation. A thermogravimetric investigation of the reaction between triphenylarsine and tetraphenyldiazocyclopentadiene has supplied evidence of the intermediacy of a carbene[20] but this could be an atypical case because of the considerable



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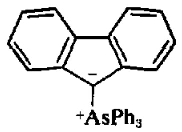

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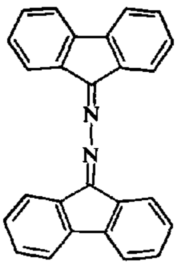

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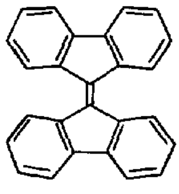

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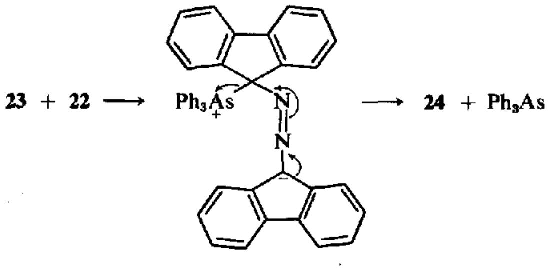
steric hindrance to arsazene formation which would obtain in this instance.

When 9-diazofluorene (**22**) was heated in molten triphenylarsine the product was not the arsonium ylide (**23**) but instead, and in almost quantitative yield, fluorenone ketazine (**24**). The same product resulted if 9-diazofluorene was heated with diphenyl sulphide; with triphenylphosphine a high yield of a phosphazene was obtained.[31] Thermal decomposition of 9-diazofluorene alone has been shown[33] to give bifluorenylidene (**25**) as the major product, probably formed by biphilic interaction between initially formed carbene and undecomposed diazofluorene with concomitant loss of nitrogen, together with only a small amount (*ca* 4%) of fluorenone ketazine, formed by an addition reaction of the carbene to diazofluorene.

It had been shown previously that diazo compounds can form ketazines by reaction with pyridinium[34] or phosphonium[34–36] ylides, so it seemed likely that in the present case partial conversion of diazofluorene into the arsonium ylide ensued and that the ylide then reacted with more diazofluorene to give the ketazine:



Evidence in support of this mechanism was obtained by mixing solutions of equimolar quantities of diazofluorene and the ylide (**23**) (prepared *via* the 'salt' method) at room temperature, when essentially quantitative yields of the ketazine (**24**) and of triphenylarsine were formed.

General properties of arsonium ylides

All of the triphenylarsonium ylides were isolated as non-hygroscopic crystalline solids. The tri-n-butylarsonium ylides (**15**) and (**16**) are less stable; ylide (**15**) is hygroscopic and also becomes brown when kept, while (**16**) decomposes readily in solution. The arsonium ylides are insoluble or almost so in water, ethanol, ether or light petroleum, and soluble in warm chloroform or benzene. The triphenylarsonium ylides are stable indefinitely in air as solids and in solution. They are recovered unchanged after being heated in refluxing ethanolic sodium hydroxide.

The great stability of these ylides is undoubtedly due to the delocalisation of negative charge which is possible in the 'dipolar' canonical form (**D**) when R and R′ are electron-withdrawing groups.

$$\begin{array}{ccc} Ph_3As{=}CRR' & \longleftrightarrow & Ph_3\overset{+}{As}{-}\overset{-}{C}RR' \\ \mathbf{C} & & \mathbf{D} \end{array}$$

This is illustrated by the typically low stretching frequencies for the CO and other substituent groups in their IR spectra (see below). The 'covalent' canonical form (C) makes a smaller contribution to the overall structure of arsonium ylides than to the overall structure of corresponding phosphonium ylides, since the overlap of *p*-orbitals of carbon with the *d*-orbitals of arsenic is less effective than with the *d*-orbitals of phosphorus. Arsonium ylides which do not have strongly electron-withdrawing groups **R** and **R′** are normally chemically unstable.

IR spectra (for details see Table 4)

The stretching frequencies associated with the electron-withdrawing substituents in the ylides are uniformly low because of the delocalisation of the negative charge into these groups. Thus the diesters (**2** and **14**) each show two intense CO absorptions (due to symmetric and asymmetric coupling between the two groups) at 1685, 1635 and 1670, 1595 cm^{-1} respectively In the keto-esters (**10** and **11**) both bands are shifted to lower frequency. In the case of the cyano-ester (**13**) the CO group causes a single peak at 1625 cm^{-1}. In the case of diacylylides (**3**–**6**) the coupled CO vibrations are less separated and appear at 1580–1555 cm^{-1} and 1515–1505 cm^{-1}. The absorptions at 2170–2105 cm^{-1} and 2145 cm^{-1} (CN) in ylides (**9** and **13**) respectively, at 1310, 1130 cm^{-1} (SO) in ylide (**7**), and at 1395, 1208 cm^{-1} (NO_2) in

Table 4. Spectral data of arsonium ylides

Ylide	Ultraviolet $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ)	Infrared[a,b] $\nu_{\max}^{\text{nujol}}$ cm^{-1}	PMR[c] τ (multiplicity, relative intensity)
1	213 (4·40), 265 (4·30)	1605, 1545	2·48 (s, 15); 7·65 (s, 4) 8·86 (s, 6)
2	224 (4·43), 240 (sh, 4·15), 265 (sh, 3·61)	1685, 1635	2·2–2·7 (m, 15), 8·20 (s, 6)
3	222 (4·56), 315 (3·95), 350 (sh, 3·59)	1581, 1568, 1505 (*1520*)[d]	2·2–3·15 (m)
4	216 (4·41), 2·75 (4·20)	1580, 1510 (*1580, 1545*)[d]	2·3–2·8 (m, 15), 7·63 (s, 6)
5	217 (4·43), 290 (3·96), 325 (sh, 3·55)	1578, 1555, 1515 (*1560, 1530*)[d]	2·2–2·8 (m, 20), 8·17 (s, 3)
6	215 (4·48), 267 (4·38), 325 (sh, 3·70)	1565, 1515 (*1570, 1530*)[d]	1·83 (d, 2, *J* 9 Hz), 2·18–2·76 (m, 17), 8·13 (s, 3)
7	217 (4·54), 265 (4·03), 285 (3·77)	1292, 1122 (*1310, 1130*)[e]	2·2–2·8 (m)
8	222 (4·40), 315 (4·06)	1595, 1395	2·46 (s, 15), 7·32 (s, 3)
9	223 (4·38), 265 (3·57)	2170, 2140, 2105 (*2200*)[e]	$2{\cdot}3_5$ (s, broad)
10	221 (4·50), 272 (4·11), 300 (3·86)	1640, 1523, 1500 (*1675, 1530*)[d]	2·2–2·75 (m, 20), 6·31 (q, 2), 9·42 (t, 3)
11	217 (4·37), 254 (4·10)	1645, 1535 (*1640, 1540*)[d]	2·2–2·8 (m, 15), 6·27 (q, 2), 7·50 (s, 3), 9·39 (t, 3)
12	223 (4·48), 244 (4·35), 281 (4·27)	1600, 1575, 1515	2·2–2·8 (m, 20), 8·51 (s, 3), −2·40 (s, broad, 1)
13	223 (4·45), 264 (3·80)	2145, 1625 (*2200, 1640*)[e]	see footnote *f*
14	223 (4·48), 238 (sh, 4·23), 270 (sh, 3·76)	1670, 1595 (*1700, 1630*)[e]	2·2–2·7 (m, 15), 6·13 (q, 4) 9·19 (t, 6)
15	210 (4·21), 230 (4·23), 255 (sh, 3·89), 318 (3·93)	1580, 1558, 1490	2·6–3·2 (m, 10), 7·3–9·3 (m, 27)
17	223 (4·39), 265 (3·76), 298 (3·81)	1395, 1208	2·38 (broad s)

[a] Only maxima in the carbonyl, sulphonyl, nitro and nitrile regions are reported.

[b] Values for the corresponding phosphorus compounds in italics.

[c] The PMR spectra were recorded in deuteriochloroform with tetramethylsilane as an internal standard. The multiplicity is indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

[d] Ref 52.

[e] Ref 53.

[f] Compound exhibits internal rotation about the enolate α,β carbon–carbon bond resulting in considerable broadening of the ethyl resonances (*cf* Ref 16): τ 2·4 (broad, s, 20H), 5·9 (broad, q, 2H), 8·7 (broad, t, 3H).

ylide **17** show that the negative charge is delocalised over these groups.

It may be noted that all these stretching frequencies are lower than those associated with the corresponding phosphonium ylides, which is in keeping with the assumption that the dipolar canonical forms make a greater contribution to the overall structure of arsonium ylides than they do in the case of phosphonium ylides.

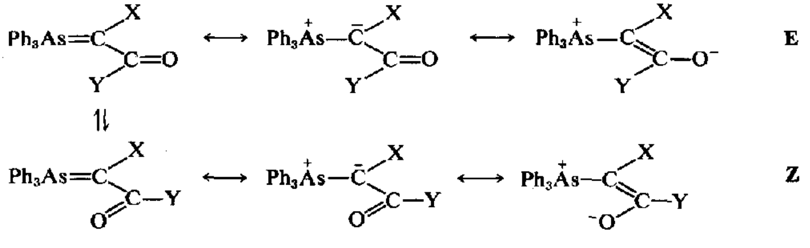
UV spectra (see Table 4)

The UV spectra of the ylides contain a broad band in the region 240–350 nm. As the conjugation is increased by means of electron-withdrawing substituents in the carbanionic moieties this absorbtion occurs at longer wavelength and is associated with a hyperchromic effect. The spectra of ylides (**9** and **14**) closely resemble those of their phosphonium analogues.[15]

NMR spectra (see Table 4)

There has been considerable interest[16,37] in the configurational stability of CO-substituted ylides and the possible geometric isomerism about the α,β-C—C bond, which will have partial double-bond character due to the contributions from enolate forms, *viz.* (see below).

Variable temperature studies on triphenyl-

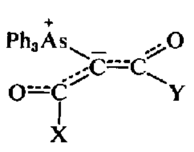


arsonium α(methoxycarbonyl)ylides have provided data confirming such isomerism and also the energy barriers to interconversion of the isomers.[16] The *cisoid* structures (Z) were shown to be the major contributing forms

Except in the case of ylide (13), the situation is of possible greater complexity in the case of the presently described ylides since both α-substituent groups can exist in *cisoid* or *transoid* forms leading to the possibility of four geometric isomeric arrangements (or three if the two substituents are identical).

The NMR spectra of these arsonium ylides were examined in detail for evidence of geometric isomers but no broadening or doubling of peaks due to the presence of long-lived conformers of any of the ylides could be detected, save in the case of ylide (13), where broadening of the signals was observed. Neither variable temperature spectroscopy, change of solvent, nor addition of anhydrous lithium bromide caused any change in the spectra of the other ylides.

Thus all of the present ylides, except (13), must either adopt exclusively one conformation or else the enolate forms play a relatively small part in the overall structure. The latter explanation appears to be unlikely since the IR spectra show that the substituent CO (and other) groups bear significant negative charges. It seems likely, therefore, that these ylides exist as (Z, Z) isomers e.g. **26**.



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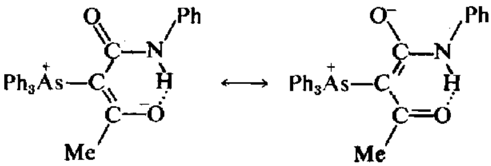
This is in accord with the earlier evidence[16] on mono-α-CO-substituted arsonium ylides, and is supported by the absence of any appreciable shielding effect on the acetyl Me groups of ylides (4–6) and (11). The observed chemical shifts for these groups are also similar to that of the Me group in triphenylarsonium acetonylide (18, R = Me; $\tau = 7{\cdot}90$) (*cf* ref 37*d*) and contrast with that of the Me group of ylide (12) which has a Z, E conformation. (See below).

This *cisoid*-structure is energetically favourable because of interaction between the As and O atoms. Evidence for such interaction has been provided by X-ray crystallographic examination of a triphenylarsonium 2-acetylcyclopentadienylide;[38] the *cisoid* conformation of the acyl group in the latter ylide is also confirmed by its dipole moment.[39] Similar considerations apply to those ylides wherein nitro- or sulphonyl groups take the place of CO groups. In the case of the diacylylides the Z, Z-conformation will be further favoured in that the two negatively charged O atoms are not only favourably disposed to interact with the arsonium atom but are also as far apart from each other as possible. Any destabilisation of this arrangement by steric interaction between X and Y can be relieved by a twisting of both groups with respect to each other around the α,β-C–C bonds. Such a skewed arrangement could account for the absence of any long-range P-H coupling to the Me groups in triphenylphosphonium diacetylmethylide which, like the monoacetyl analogue ($J_{PH} = 1{\cdot}8$ Hz[37a]), is expected to exist in a *cisoid* conformation. The chemical shift of the Me signal (τ 7·75) of the triphenylphosphonium diacetylmethylide is almost the same as that for the methyl group in its arsonium analogue (4), suggesting that the two compounds have the same configuration.

The one ylide (13) which shows some evidence of conformational mobility is the only one for which interaction between the As atom and O atoms of both α-substituent groups is not possible since one substituent in this case is a linear cyano-group. The $\alpha\alpha$-dicyanoylide (9) is of course not susceptible to NMR analysis of this sort.

The NMR spectrum of ylide (12) showed a broad singlet at τ-2·4, indicating intramolecular H-bonding of the amide proton with the CO group. Thus in this case there is a Z, E conformation, stabilised by the H-bonding. A similar Z, E conformation has been postulated for related sulphonium phenylcarbamoyl-acylylides.[69]



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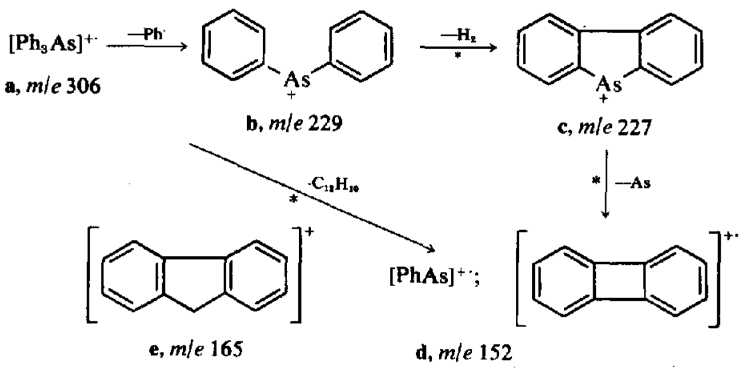
Support for this structure is provided by the strong shielding of the Me group (τ 8·52) by the triphenylarsonium group.

Mass spectra

Little information is available about electron-impact induced fragmentation of organo-arsenic compounds. Some generalisations and particular features concerning the behaviour of the arsonium ylides is now summarised and will be presented and discussed in more detail in a subsequent publication. The mass spectra were determined at 70 eV.

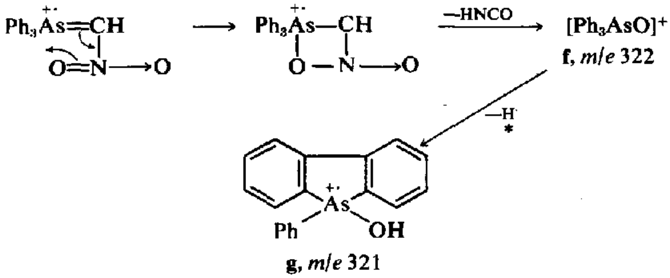
The characteristic fragmentation pattern of the triphenylarsonium ylides is the loss of the carbanionic moiety followed by breakdown of the triphenylarsine portion. In addition to prominent molecular ion and (M-1) peaks, the spectra have major peaks due to ions at *m/e* 306, 229, 227 and 152. These ions are consistent with the structural representations **a**, **b**, **c** and **d** respectively and are all reproduced in the separately determined spectrum of triphenylarsine itself. A doublet ion peak at *m/e* 152 occurs as the base peak in all spectra. An accurate mass determination in the case of ylide (**14**) showed these peaks to represent, respectively, fragments C_6H_5As (91%; Found: 151·9605; Calc. 151·9607) and $C_{12}H_8$ (9%; Found: 152·0622; Calc. 152·0626).



Medium or low abundance ions corresponding to the fluorenyl cation (**e**, *m/e* 165) were also present in the spectra of all the ylides which were examined, but not in the mass spectrum of triphenylarsine. No metastable ions can be detected which are related to the formation of e and its genesis remains uncertain.

Identification of the ylides is facilitated by the presence of diagnostic fragment ions formed by the loss of characteristic substituent groups from the carbanionic portion of the molecule. The spectrum of ylide (**14**) is presented as an example in Fig 1 and the (M-OEt) (*m/e* 429) and (M-CO_2Et) (*m/e* 391) ions are typical.

Of particular interest is the presence of significant rearrangement ions **f** and **g** in the spectrum of triphenylarsonium nitromethylide (**17**) arising from As-O bond formation. Although there is no confirmatory evidence from metastable peaks, such species are most plausibly formed by a four-centre oxygen transfer reaction:



Related rearrangement processes are found in both the electron-impact induced[40] and thermal[41] eliminations of triphenylphosphine oxide from stable alkylidene triphenylphosphoranes in which the stabilising groups contain carbonyl or sulphonyl functions. The select loss of triphenylarsine oxide from ylide (**17**) is presumably a reflection of the relative ease of oxygen transfer from nitro groups combined with the lower affinity for oxygen of arsenic *vis-a-vis* phosphorus. No thermochemical data is available for such As-O bonds, but As-O bonds are chemically much weaker than P-O bonds, and it is significant that the phosphorus analogue of **17** decomposes spontaneously at room temperature to triphenylphosphine oxide and fulminic acid, as discussed earlier in this paper. The dissociation energy of the As-O bond in As_4O_{10} has been deduced to be 93 kcal. compared with a value of 156 kcal. for the corresponding P-O bond in P_4O_{10}.[26]

Reaction of ylides with benzaldehydes. (For details see Table 5).

Of the disubstituted ylides (1–16) only the ylide (**14**) reacted with benzaldehyde to form an alkene (in 72% yield) and triphenylarsine oxide.

$$\underset{\mathbf{14}}{Ph_3\overset{+}{As}—\overset{-}{C}(CO_2Et)_2 + PhCHO} \xrightarrow[\text{reflux}]{CCl_4} PhCH{=}C(CO_2Et)_2 + Ph_3AsO$$

We believe however that this is the first reported example of a normal Wittig reaction involving an ylide stabilised by two CO groups attached to the carbanionic centre, although the corresponding

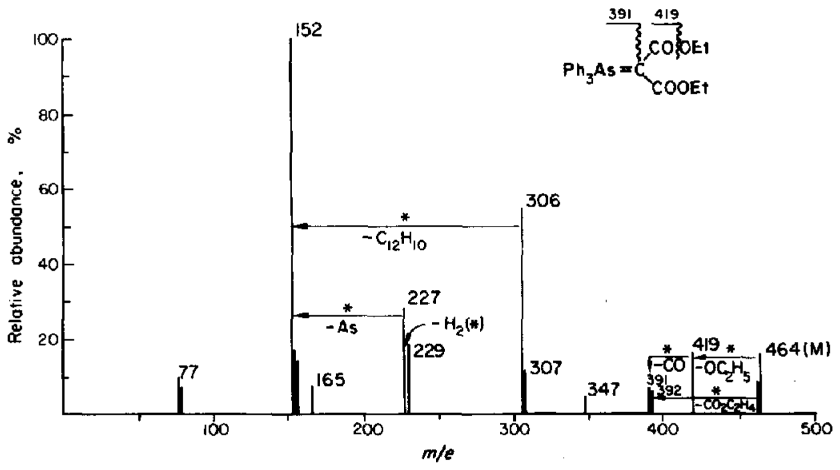


Fig 1. Mass spectrum of triphenylarsonium bis(ethoxycarbonyl)methylide (14).

Table 5. Reactivities of ylides with aldehydes in refluxing solvents

Ylide	Yield (per cent) of Olefin (solvent, reflux time) from benzaldehyde	from *p*-nitrobenzaldehyde
1→**8**	0	0
9	0	61 (dry benzene, 9 hr)
10	0	39 (CCl_4, 48 hr)
11	0	96 (CCl_4, 24 hr)
12	0	77 (benzene, 48 hr)
13	0	92 (CCl_4, 18 hr)
14	72 (CCl_4, 22 hr)	93 (CCl_4, 4 hr)
15	–	0
16	–	82 (CCl_4, 4 hr)
17	58 (benzene, 42 hr)	72 ($CHCl_3$, 24 hr)
18 (R = pNO$_2$C$_6$H$_4$)	84 (benzene, 48 hr)*	>95 (CCl_4, 10 min.)
(R = Ph)	~90 (THF)[b]	90 (benzene, 24 hr)*[a]
(R = Me)	90 (THF, 7 hr)*[b]	>95 (benzene, 10 min)
(R = OEt)	77 (ethanol, 24 hr)*[c]	
23	74 ($CHCl_3$, 3 hr)[d]	92 ($CHCl_3$, 3 hr)[d]

*Reaction carried out at room temperature.
[a]Ref 2, [b]Ref 6, [c]Ref 3, [d]Ref 13.

phosphonium ylide reacted in low yield with the very reactive carbonyl compound diphenylketene.[42] This indicates again therefore the greater reactivity of arsonium ylides *vis-a-vis* phosphonium ylides.

Many of the ylides (**9–14**; **16–18**; **23**) reacted with the more polar *p*-nitrobenzaldehyde to give alkenes and triphenylarsine oxide. The yields obtained show some rough inverse correlation with the likely delocalisation of the negative charge in the carbanionic portion of the ylides. The most strongly delocalised ylides (**1–8**) were completely unreactive even towards 2,4-dinitrobenzaldehyde. Kinetic studies of the reactions between stabilised arsonium and phosphonium ylides and *p*-nitrobenzaldehyde have shown similar trends.[43,44] However any assumption that there is complete correlation between basicity and nucleophilic reactivity of ylides is unwarranted. Significant divergencies may arise from other factors, *inter alia* from steric effects.[4,44]

Although alkylheteronium ylides are normally more reactive than their aryl counterparts,[45] the tri-n-butyl ylide **15**, like its triphenyl analogue, failed to react with benzaldehyde, *p*-nitrobenzaldehyde or 2,4-dinitrobenzaldehyde.

The results obtained accord with previous experiments with various heteronium fluorenylides[13] and cyclopentadienylides,[4,5,11,14] which indicated that arsonium ylides were more reactive than their phosphonium or sulphonium analogues. This difference was attributed to a greater contribution of the 'dipolar' canonical form to the structure of arsonium ylides than to the structure of phosphonium or sulphonium ylides, due to the greater ease with which the latter heteronium groups undergo valence shell expansion, and also to their increased electrostatic interaction. It has been shown[44] that the mechanisms of the reactions of stabilised arsonium ylides and of phosphonium ylides with carbonyl compounds in the Wittig reaction are similar. The equilibrium

(ylide + carbonyl compound) ⇆ (Wittig reaction intermediate)

will partially depend on the stability of the initial ylide and the progress of the reactions will thus vary inversely with relative stability of the ylides. Hence the equilibrium should be displaced towards the adduct for arsonium ylides *vis-a-vis* their phosphonium analogues.

It is also noteworthy that the reaction products obtained from these stabilised arsonium ylides were always alkenes and that there was no evidence of the formation of any epoxide in any instance. This accords with previous evidence that stabilised arsonium ylides always afford alkenes in Wittig reactions[2,4,6,7] whereas non-stabilised arsonium ylides give either epoxides,[3,8] or rearrangement products thereof.[9,10] The reasons for these differing reaction paths have been discussed elsewhere.[2–4]

In all cases authentic samples of the alkenes were prepared by established methods from the appropriate aldehydes and reactive methylene compounds, and were found to be identical with the products obtained from the Wittig reactions of the arsonium ylides, excepting only the products obtained from triphenylarsonium acetylethoxycarbonylmethylide (**11**). The NMR spectra of these products indicated that the ylide had reacted non-stereospecifically with *p*-nitrobenzaldehyde to produce a mixture of isomeric alkenes different from that produced in the condensation reaction. (For details see Experimental).

It had been reported that diphenylcyclopropenone reacted with pyridinium,[46–48] phosphonium[47] and sulphonium[47,49] acylylides to give α-pyrones. Triphenylarsonium phenacylide **18**, R = Ph), triphenylarsonium acetonylide **18**, R = Me) and triphenylarsonium ethoxycarbonylmethylide **18**, R = OEt) all reacted with diphenylcyclopropenone to give, respectively, 6-phenyl-, 6-methyl- and 6-ethoxy-3,4-diphenylpyran-2-ones in good yield. Reaction presumably involves initial attack on the ketone by the acyl oxygen rather than by a C atom as occurs in Wittig reactions. (see scheme below).

It is interesting to note that the phosphorus analogue of **18**, (R = OEt) reacted with diphenylcyclopropenone by a normal Wittig-type reaction to give a methylenecyclopropene derivative,[47,48a] although a pyrone has also been obtained from these reactants.[47] The ylides **4**, **11**, **16**, all of which have two electron-withdrawing substituent groups, did not react with diphenylcyclopropenone in refluxing benzene. Sulphonium diacylylides, with the exception of dimethylsulphonium diacetylmethylide, which is a more reactive ylide than arylheteronium ylides, similarly did not react with diphenylcyclopropenone, even under extreme conditions.[49] An alternative mechanism has been suggested[49,50] for the reaction of cyclopropenone with ylides, involving attack at C(2) of the cyclopropenone ring and formation of an intermediate ketene which cyclises to a pyrone.

EXPERIMENTAL

M.ps are uncorrected. Column chromatography was carried out over silica gel, Grade M.60. Light petroleum had b.p. 40–60°.

Preparation of materials. Triphenylarsine oxide, which was obtained commercially, contained water of hydration or crystallisation. In order to remove the water, a sample was heated at 140° *in vacuo* until the OH-absorption in the IR spectrum had disappeared. The cooled solid was stored in a desiccator until use.

Triphenylarsine was recrystallised from abs EtOH and dried *in vacuo* over P_2O_5 before use.

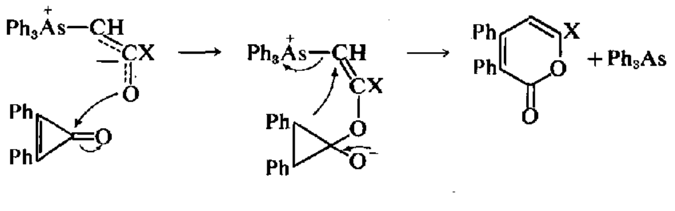
Tri-n-butylarsine oxide was prepared as described[54] and stored in a desiccator until use.

Bis(phenylsulphonyl)methane[55] and Meldrums acid[56] were prepared by literature methods. Other carbon acids were commercially available and were used without further purification.

9-Diazofluorene was prepared by the mercuric oxide dehydrogenation of fluorenone hydrazone.[57] Bis(phenylsulphonyl)diazomethane was obtained from the toluene-*p*-sulphonyl hydrazone.[58] All other diazo compounds were prepared by reaction of suitable substrates with toluene-*p*-sulphonyl azide.[59]

Synthesis of arsonium ylides

General procedures for the preparation of the ylides (**1**–**17**) from (a) arsine oxides and active methylene compounds, (b) triphenylarsine and diazo-compounds, and (c) by acylation of the β-keto-ylides (**18**) are illustrated by the following typical examples. The yields and physical



data of the ylides are listed in the appropriate Tables (1, 2 and 3) and are not reproduced here.

(a) *Preparation of ylides from active methylene compounds and arsine oxides with (i) acetic anhydride or (ii) triethylamine/phosphorus pentoxide as condensing agents.*

Triphenylarsonium 4,4-dimethyl-2,6-dioxocyclohexylide (1) *by method (i).* A mixture of triphenylarsine oxide (1·29 g, 0·004 mole), dimedone (0·56 g, 0·004 mole) and freshly distilled Ac_2O (10 ml) was heated under reflux for 10 min. Water (100 ml) was added to the cooled mixture and the resultant suspension was shaken periodically. After 2 hr the crystalline ppt was filtered off and recrystallised from benzene-hexane to give colourless prisms of the *ylide* (1·5 g).

Triphenylarsonium diphenylsulphonylmethylide (7) *by method (i).* Triphenylarsine oxide (0·97 g, 0·003 mole) was added to a soln of bis(phenylsulphonyl)methane (0·90 g, 0·003 mole) in Ac_2O (15 ml) and the mixture was heated under reflux for 2 min. On cooling and scratching, colourless crystals of the *ylide* separated and were filtered off, washed with ether and recrystallised from chlorobenzene (0·95 g).

Triphenylarsonium diacetylmethylide (4) *by method (ii).* A mixture of triphenylarsine oxide (1·29 g, 0·004 mole), acetylacetone (0·40 g, 0·004 mole) and P_2O_5 (1·0 g) in Et_3N (45 ml) was heated under reflux for 8 hr. After the first 4 hr further P_2O_5 (0·5 g) was added. Solvent was evaporated and water (100 ml) was added to the oily residue. The resultant suspension was extracted with CH_2Cl_2 and the combined extracts were washed with water, dried and concentrated to *ca* 5 ml. Chromatography on silica gel with benzene-EtOAc (1:5) as eluant afforded the *ylide* as a colourless oil (0·77 g) which crystallised on trituration with ether. An analytical sample was obtained by recrystallisation from benzene-hexane.

Triphenylarsonium dibenzoylmethylide (3) *by method (ii).* Dibenzoyl-methane (0·90 g, 0·004 mole) and P_2O_5 (1·0 g) were added to a suspension of triphenylarsine oxide (1·30 g, 0·004 mole) in Et_3N (60 ml) and the mixture was heated under reflux for 10 hr when a further portion (1·0 g) of P_2O_5 was added. After 20 hr the solvent was decanted while hot and cooled. Colourless crystals of the *ylide* deposited, which were filtered off, washed with ether and recrystallised from benzene-light petroleum (0·92 g).

Triphenylarsonium nitromethylide (17) *by method (ii).* A suspension of triphenylarsine oxide (1·50 g) and P_2O_5 (1·0 g) in nitromethane (45 ml) and Et_3N (20 ml) was heated under reflux for 4 hr during which time further P_2O_5 (1·0 g) was added. The soln was evaporated to dryness and the residue was extracted with chloroform; the extracts were washed well with water and dried. Removal of solvent and crystallisation of the crude product (1·1 g) from nitromethane gave the *ylide* as cream-coloured prisms.

(b) *Preparation of ylides from diazo-compounds*

Triphenylarsonium bis(ethoxycarbonyl)methylide (14). Diethyl diazomalonate (0·56 g, 0·003 mole) and triphenylarsine (2·76 g, 0·009 mole) were dissolved in anhyd ether (10 ml) and the soln was evaporated to dryness. Copper-bronze (0·5 g) was added and the process repeated. The reaction flask was flushed with oxygen-free N_2 for 10 min and plunged into an oil bath preheated to 150° (care!). After the evolution of N_2 had ceased (*ca* 15 min) the cooled mixture was leached with chloroform and the leachings were filtered. Solvent was evaporated and the oily residue was chromatographed on silica gel. Light petroleum removed triphenylarsine and benzene-EtOAc (1:1) eluted the *ylide* as a colourless oil (0·84 g) which crystallised from ether-hexane.

Triphenylarsonium benzoylacetmethylide (5). A finely ground mixture of acetylbenzoyldiazomethane (0·57 g, 0·003 mole), triphenylarsine (2·76 g, 0·009 mole) and cuprous bromide (0·6 g) was placed in a flask which was flushed continuously with oxygen-free N_2. The flask was immersed in an oil bath at 150° until N_2 ceased to be evolved (*ca* 5–10 min). Acetone (25 ml) was added to the cooled mixture and the insoluble material was filtered off. Removal of the solvent gave a viscous brown oil from which colourless crystals (0·75 g) of the *ylide* separated upon addition of ether.

Decomposition of 9-diazofluorene in molten triphenylarsine. 9-Diazofluorene (0·58 g, 0·003 mole), triphenylarsine (2·76 g, 0·009 mole) and copper-bronze (0·6 g) were mixed together and heated in a melt at 150° as described above. When it was cool, the mixture was shaken with chloroform, filtered, and the solvent was evaporated. Trituration of the residue with ether afforded glistening burgundy-coloured plates of fluorenone ketazine (0·51 g), m.p. 272–274°, undepressed by admixture with an authentic sample;[34] the product was also identified by its IR spectrum. Concentration of the mother liquor and chromatography of the residue on silica gel with benzene-light petroleum (1:1) as eluant gave triphenylarsine (2·68 g).

Reaction of triphenylarsonium fluorenylide (23) *with 9-Diazofluorene.* Triphenylarsonium fluorenylide (0·94 g, 0·002 mole) in anhyd CH_2Cl_2 (10 ml) was added during 10 min to a stirred soln of 9-diazofluorene (0·40 g, 0·002 mole) in CH_2Cl_2 (10 ml). The mixture was kept at room temp overnight and then concentrated to dryness. Addition of ether precipitated fluorenone ketazine (0·39 g) which was collected by filtration and identified by spectroscopic comparison with an authentic sample.[34] Examination of the filtrate by TLC indicated the absence of starting ylide, and the presence of triphenylarsine as well as unreacted 9-diazofluorene (minor).

(c) *Acylation of β-keto-ylides*

Triphenylarsonium p-*nitrobenzoylacetmethylide* (6). A soln of triphenylarsine (12·24 g, 0·04 mole) and *p*-nitrophenacyl bromide (9·80 g; 0·04 mole) in benzene was heated under reflux for 8 hr. Removal of solvent gave a viscous oil which crystallised from ether. Recrystallisation from EtOH-ether afforded *p*-nitrophenacyltriphenylarsonium bromide (13·8 g, 63%) as cream-coloured crystals, m.p. 144–147°; $\nu_{C=O}$ 1680 cm^{-1} (nujol).

To a slurry of this salt (5·0 g) in dry benzene (100 ml) NaH (3·0 g) as a dispersion in oil was added. The soln was stirred at room temp for 3 hr, filtered to remove any remaining solids, and concentrated *in vacuo*. When the residue was cooled triphenylarsonium *p*-nitrophenacylide (18, R = p-$NO_2C_6H_4$) was obtained as yellow crystals (3·61 g, 84%), m.p. 108–112°. Recrystallisation from benzene gave an analytical sample, m.p. 114–115° (lit.[60] 110–112°) (Found: C, 66·6; H, 4·4; N, 2·7; Calcd. for $C_{26}H_{20}AsNO_3$: C, 66·5; H, 4·3; N, 3·0%).

When a soln of the ylide (0·50 g) in dry benzene (15 ml) mixed with chromatography silica gel (5 g) was shaken overnight, this led to loss of the yellow colour. Filtration and evaporation of the solvent gave *p*-nitroacetophenone (0·14 g), identified by comparison (IR) with an authentic sample. Elution of the silica gel residue with EtOAc-EtOH (9:1) gave triphenylarsine oxide hydrate (0·36 g) as indicated by its IR spectrum.

A mixture of triphenylarsonium *p*-nitrophenacylide (0·32 g) and Ac_2O (10 ml) was heated briefly under reflux, cooled, and poured into water (100 ml), and the whole was extracted with CH_2Cl_2. The combined extracts were washed well with water, dried and evaporated. Chromatography of the residue on silica gel and elution with EtOAc-benzene (1:1) gave a yellow oil which crystallised from ether. Recrystallisation from benzene-light petroleum afforded the *ylide* (0·23 g) as yellow microcrystals, identical in m.p. and IR spectrum with a sample prepared from triphenylarsine oxide and *p*-nitroacetophenone (see above).

Triphenylarsonium acetyl(N-*phenylcarbamoyl*)*methylide* (**12**). Triphenylarsine (9·2 g) was added to a soln of bromoacetone (4·4 g) in nitromethane (60 ml) and the mixture was heated on a water bath for 2 hr. Solvent was evaporated and the residue was recrystallised from EtOH-ether to give acetonyltriphenylarsonium bromide (10·0 g, 75%) as colourless crystals, m.p. 164–166° (lit.[61] 165°).

Triphenylarsonium acetonylide (**18**, R = Me) was prepared from the *bromide* as described above. Recrystallisation from benzene-hexane gave an analytical sample as colourless prisms, m.p. 177–179° (lit.[12] (Nesmeyanov *et al.*) 165–166°; lit.,[61] 123°) (Found: C, 69·9; H, 5·5. Calcd. for $C_{21}H_{19}AsO$: C, 69·6; H, 5·3%).

A soln of the above ylide (1·1 g, 0·003 moles) in dry benzene (35 ml) was treated at room temp with phenyl isocyanate (0·36 g, 0·003 mole). After 24 hr the ppt was filtered off and recrystallised from nitromethane to give the ylide (**12**) (1·2 g) as colourless prisms. The product was identical (m.p., IR, UV) with that obtained from triphenylarsine oxide, acetoacetanilide and acetic anhydride.

Triphenylarsonium bis(*ethoxycarbonyl*)*methylide* (**14**). A soln of ethyl chloroformate (0·22 g) in anhyd acetonitrile (5 ml) was added to a stirred cooled soln of **18** (R = OEt, 0·78 g) in acetonitrile (20 ml) and Et_3N (2 ml). After 5 hr the mixture was evaporated to dryness and partitioned between chloroform and water. The organic layers were combined, washed with water and dried. The solvent was removed and the residue was chromatographed on silica gel. Elution with benzene-EtOAc (1:1) afforded the *ylide* as an oil which crystallised from ether-light petroleum as colourless prisms (0·18 g, 21%), identical with a sample prepared from triphenylarsine and ethyl diazomalonate (see above).

Triphenylarsonium benzoylacetmethylide (**5**). A mixture of triphenylarsonium acetonylide (0·72 g, 0·002 mole) and benzoic anhydride (0·45 g, 0·002 mole) was stirred in dry benzene (25 ml) for 24 hr. Solvent was evaporated and the oily residue crystallised from ether. Recrystallisation from benzene-hexane afforded the *ylide* as colourless microcrystals (0·45 g), identical (m.p., IR, UV) with the product prepared from acetylbenzoyldiazomethane and triphenylarsine (see above).

Reaction of arsonium ylides (**1–18**) *with aldehydes.* An equimolar amount of aldehyde was added to a soln of the ylide (0·001 mole) in solvent (30 ml). The mixture was heated under reflux for the prescribed period of time (see Table 5), and the solvent was then evaoorated *in vacuo*. In the case of the ylides (**1–8** and **15**) the addition of ether to the residue led to quantitative recovery of the original ylides. The other reactions were worked up as described (*vide infra*) to give the expected alkenes. The identity of the compounds was established by their m.p. IR and PMR spectra. The arsine oxide which formed concomitantly in each reaction was isolated in 75–95% yield. In the following recipes, the aldehyde used was always *p*-nitrobenzaldehyde unless stated otherwise.

(a) *From triphenylarsonium dicyanomethylide* (**9**). Trituration of the residue with ethanol gave *p*-nitrobenzalmalononitrile (0·12 g) as pale yellow crystals, identical in m.p. and IR spectrum with an authentic sample.[62]

(b) *From triphenylarsonium benzoylethoxycarbonylmethylide* (**10**). The residue was chromatographed on silica gel with benzene. Elution with benzene-chloroform (2:1) afforded ethyl *p*-nitrobenzylidenebenzoylacetate (0·12 g) as an oil which crystallised from EtOH as glistening plates, m.p. and mixed m.p. 114–116°, IR and PMR spectra identical with those of an authentic sample prepared from *p*-nitrobenzaldehyde and ethyl benzoylacetate: ν_{max} (nujol) 1716, 1667 and 1625 cm^{-1}, τ 8·81 (3H, t, *J* 7 Hz), 5·76 (2H, q, *J* 7 Hz), 1·8–2·7 (10 H, m). (Found: C, 66·1; H, 4·7; N, 4·3. Calc. for $C_{18}H_{15}NO_5$: C, 66·4; H, 4·7; N, 4·3%).

(c) *From triphenylarsonium ethoxycarbonylacetmethylide* (**11**). The residue was chromatographed on silica gel in benzene. Elution with benzene-chloroform (1:4) afforded ethyl *p*-nitrobenzylideneacetoacetate as an oil (0·26 g) which crystallised from benzene-hexane as pale yellow crystals, m.p. 53° (softening). The PMR spectrum indicated the compound to be a mixture of *cis-trans* isomers. It showed the presence of two Me groups at τ ($CDCl_3$) 7·64 and 7·55 and two benzylidene protons at τ 2·46 and 2·31, integrating in the ratio (1:2·6) respectively. Among other signals two overlapping triplets (Et groups) occurred at τ 7·83 and 8·64 (*J* = 7 Hz). A sample prepared from *p*-nitrobenzaldehyde and ethyl acetoacetate in boiling benzene, with piperidine as catalyst, showed similar isomerism in the corresponding ratio (0·9:1) (*cf* Ref 63).

(d) *From triphenylarsonium acetyl-*(N-*phenylcarbamoyl*)*methylide* (**12**). The residue was dissolved in benzene and applied to a silica gel column. Elution with benzene-EtOAc (3:1) afforded *p*-nitrobenzylideneacetoacetanilide (0·24 g) which crystallised from EtOH as colourless prisms, m.p. 145–147°; undepressed on admixture with a sample prepared from *p*-nitrobenzaldehyde and acetoacetanilide, ν_{max} (nujol) 3280, 1685, 1660, 1645, 1595, 1515 cm^{-1}, τ ($CDCl_3$) 0·82 (s, broad, 1H), 1·81 (d, 2H, *J* = 9 Hz), 2·1–2·9 (m, 8H), 7·53 (s, 3H). (Found: C, 65·7; H, 4·3; N, 8·8; Calcd. for $C_{17}H_{14}N_2O_4$: C, 65·8; H, 4·6; N, 9·0%).

(e) *From triphenylarsonium cyanoethoxycarbonylmethylide* (**13**). Addition of EtOH to the residue gave straw-coloured crystals of ethyl *p*-nitrobenzylidenecyanoacetate (0·23 g), m.p. 166–167°, undepressed on admixture with an authentic sample.[62]

(f) *From triphenylarsonium bis*(*ethoxycarbonyl*)*methylide* (**14**). The residue was dissolved in the minimum amount of benzene and chromatographed on silica gel. Elution with benzene-chloroform (1:1) afforded 0·27 g of diethyl *p*-nitrobenzylidenemalonate which crystallised from EtOH as pale yellow needles, identical (m.p., IR) with an authentic sample.[62]

A similar reaction with freshly distilled benzaldehyde followed by the usual workup gave diethyl benzylidenemalonate (0·18 g) as a colourless oil which was identified by comparison of its IR spectrum with an authentic sample.[62] The product was also identified by TLC.

(g) *From tri-(n-butyl)arsonium bis(methoxycarbonyl) methylide* (**16**). Trituration of the residue with ether produced colourless plates of dimethyl *p*-nitrobenzylidenemalonate (0·23 g), identical (m.p., IR) with an authentic sample.[64]

(h) *From triphenylarsonium nitromethylide* (**17**). Addition of EtOH to the residue afforded 0·13 g of *trans*-β,4-dinitrostyrene which was recrystallised from glacial AcOH as pale yellow microcrystals, identical (m.p., IR, UV) with an authentic sample.[65]

A similar process starting from benzaldehyde, followed by chromatography of the residue on silica gel with CH_2Cl_2 as eluant, gave ω-nitrostyrene (0·09 g), identified by spectroscopic comparison with an authentic sample.

(i) *From triphenylarsonium* p-*nitrophenacylide* (**18**, R = p-$NO_2C_6H_4$). The ppt which formed on cooling the mixture was collected by filtration and recrystallised from EtOAc to give pale-yellow microcrystals of 4,4′-dinitro-*trans*-chalcone (0·29 g), m.p. 202–205°, undepressed on admixture with an authentic sample.[66]

A similar reaction, but using freshly distilled benzaldehyde, resulted in substantial loss of the characteristic yellow colour of the ylide. Removal of solvent and crystallisation of the residue from EtOH gave 4′-nitrobenzylideneacetophenone as pale yellow microcrystals (0·21 g), identical with an authentic sample[67] (m.p., IR and UV spectra).

(j) *From triphenylarsonium acetonylide* (**18**, R = Me). Crystallisation of the residue from EtOH gave 4-nitrobenzylideneacetone as cream-coloured plates, m.p. 109–111° (lit.[68] 114–116°).

Reaction of triphenylarsonium phenacylide (**18**, R = Ph) *with diphenylcyclopropenone*. A soln of the ylide (2·12 g, 0·005 moles) and diphenylcyclopropenone (1·03 g, 0·005 moles) in abs benzene (20 ml) was stirred at room temp for 24 hr during which time a deep yellow colour developed. The soln was concentrated to *ca* 5 ml and chromatographed on silica gel. Light petroleum-benzene (2:1) eluted triphenylarsine (1·38 g, 90%) and benzene eluted 3,4,6-*triphenyl-2-pyrone* (1·39 g, 86%) as yellow crystals. Crystallisation of a sample from isopropyl alcohol gave golden coloured needles, identical (m.p., IR, UV and PMR) with an authentic sample.[47]

Reaction of triphenylarsonium acetonylide (**18**, R = Me) *with diphenylcyclopropenone*. A soln of the ylide (1·81 g, 0·005 moles) and diphenylcyclopropenone (1·03 g, 0·005 moles) in abs benzene (50 ml) was stirred at room temp for 36 hr. Solvent was evaporated and the residue was chromatographed on silica gel. Elution with light petroleum-benzene (2:1) gave triphenylarsine (1·23 g, 81%) and elution with benzene-EtOAc (9:1) gave 6-*methyl*-3,4-*diphenyl*-2-*pyrone* (1·04 g, 80%) as a colourless solid. Crystallisation from isopropyl alcohol gave colourless needles, m.p. 110–112° (*cf* lit.[47] m.p. 128–129°) identical by spectral comparison (IR, UV and PMR) with the product prepared by other workers.[47]

Reaction of triphenylarsonium ethoxycarbonylmethylide (**18**, R = OEt) *with diphenylcyclopropenone*. A soln of the ylide (1·96 g, 0·005 moles) and diphenylcyclopropenone (1·03 g, 0·005 moles) in abs benzene (20 ml) was stirred at room temp for 36 hr. After evaporation of the solvent, the residual oil was chromatographed on silica gel. Elution with light petroleum-benzene (2:1) gave triphenylarsine (1·32 g, 87%) as indicated by its IR spectrum. Further elution with benzene-chloroform (1:1) gave 6-*ethoxy*-3,4-*diphenyl*-2-*pyrone* (0·64 g, 44%), pale yellow needles m.p. 102–103° (from isopropyl alcohol). (Found: C, 77·8; H, 5·5. $C_{19}H_{16}O_3$ requires: C, 78·1; H, 5·5%); ν_{max} (nujol) 1718, 1620, 1530 cm^{-1}; $\lambda_{max}^{CH_2Cl_2}$ (log ϵ) 240 (4·16), 345 (3·95) nm; τ ($CDCl_3$) 2·6–3·1 (m, 10H), 4·49 (s, 1H), 5·68 (q, 2H, J = 7 Hz), 8·55 (t, 3H, J = 7 Hz).

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