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TRITOLYLARSONIUM AND TRIS(METHOXYPHENYL)ARSONIUM YLIDES

THE EFFECTS OF *ortho*-SUBSTITUENTS IN TRIARYLARSONIUM GROUPS ON THE PROPERTIES OF YLIDES

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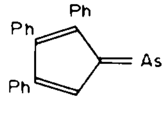
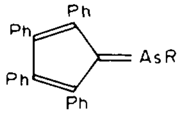
Abstract—A number of tritolylarsonium and tris(methoxyphenyl)arsonium cyclopentadienylides and other ylides have been prepared and their properties (basicity, NMR spectra, reactions with aldehydes and nitrosobenzene, acetylation, and methanolysis) have been investigated. Substituents in the *m*- or *p*-positions of triarylarsonium groups have little effect on properties, but *o*-substituents result in markedly lower reactivity and lower basicity, and these ylides were also more difficult to prepare. NMR spectra gave indication of crowding in some of these *o*-substituted ylides. The effects of the *o*-substituents are discussed. *p*-Methyl- and *p*-methoxy-substituents increased the proportion of anil to ketoxime formed in reactions with nitrosobenzene, but the *o*-methoxy analogue gave only ketoxime.

In studies of ylides relatively little attention has been paid to the effect on their properties of different substituents on the heteronium atom. Johnson and LaCount showed that in the case of phosphonium fluorenylides replacement of a triphenylphosphonium group by a trialkylphosphonium group resulted in decreased stability and increased basicity of the ylide, and an increase in its ylidic reactivity.[1] In the case of triarylarsonium ylides the effects of *p*-substituents in the *As*-phenyl groups on the course of Wittig reactions which may lead to the formation either of alkenes or of epoxides indicated that they had little effect,[2,3] save in the case of a tris(*p*-dimethylamino)arsonium ylide.[2] An investigation of the reactions of a series of *p*-substituted triarylarsonium benzylides with benzaldehyde showed that as the substituents became more electron-donating so the proportion of alkene to epoxide increased; this was even more marked when alkyl groups replaced aryl groups.[4]

Triarylarsinedihalides have been shown to have anomalous conductivity when the aryl substituents are *o*-substituted.[5] It therefore seemed of interest to investigate the properties of O-substituted triarylarsonium ylides. In the present account the results obtained with tris-(*o*-methoxyphenyl)- and tri-*o*-tolyl-arsonium ylides are described. *p*- and *m*-Substituted analogues were also studied for comparative purposes.

Basicity. Measurements of the basicity of some triarylarsonium acylylides showed that as the electron-donating character of the *p*-substituent in the aryl groups increased, e.g. from H to Me to OMe, so the basicity increased.[6] Replacement of a triarylarsonium group by a trimethylarsonium group also led to a more basic ylide.[7] In the present work the pK_a values of the perchlorate salts of ylides (I and II), made by addition of perchloric acid to suspensions of the corresponding ylides in ethanol, were determined in 95%-ethanol by the method previously used by Johnson.[8] Solubility characteristics required the use of this solvent. Results are not comparable with those obtained in aqueous solution but are comparable with earlier results using the same solvent.[8,9] Results are shown in Table 1.


(I)


(II)

(a) R = Ph; (b) R = *p*-tolyl; (c) R = *m*-tolyl; (d) R = *o*-tolyl; (e) R = *p*-methoxyphenyl; (f) R = *o*-methoxyphenyl

Table 1. pK_a Values for perchlorates of ylides

Ylide	(Ia)	(Ib)	(Ic)	(Id)	(IIa)	(IId)
pK_a	6.6	7.0	6.9	5.8	7.5	7.0

These results are in accord with earlier work in that the *p*-tolyl ylide is more basic than its phenyl analogue[6] and the triphenylcyclopentadienylides are less basic than their tetraphenylcyclopentadienylide analogues.[9] The latter differences may be associated with steric factors.[9] The *m*-tolyl ylide also appears to be more basic than its phenyl counterpart but both *o*-tolyl ylides (Id, IId) are apparently less basic.

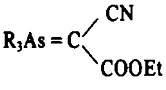
The increased basicity caused by electron-donating *p*-substituents in the aryl rings has been associated with more dipolar character and less double-bond character in the ylide bond in these cases. Possible causes of the effects of *o*-substituents will be considered later in this report.

^{1}H-NMR spectra. In the spectra of tri-*o*-tolylarsonium tetraphenylcyclopentadienylide (IId) the Me groups ap-

pear as a broad singlet at δ 1.85 at 70°, but as three peaks at δ 1.1, 1.5 and 2.75 at −45°. Coalescence temperature for these peaks is at ~10°. With four substituent phenyl and three *o*-tolyl groups this molecule is likely to be crowded and this is thus reflected in the spectra. The triphenylcyclopentadiene analogue (Id) gives only one peak for its Me groups, which is shifted 0.3 ppm upfield compared to the tri-*p*-tolyl derivative (Ib) due to shielding from the faces of adjacent aryl rings. Tris-(*o*-methoxyphenyl)arsonium tetraphenylcyclopentadienylide (IIf) shows only one sharp singlet at δ 3.2, however, even down to −50°, reflecting the lesser steric requirements of OMe groups compared to Me groups.[10]

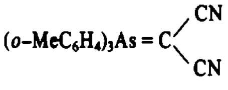
The Et groups of the cyano(ethoxycarbonyl)ylides (III) provide very broad signals because of restricted rotation about the EtOOC–C bond due to its partial double-bond character (see Ref. 11).

Wittig reactions with benzaldehydes. The triphenyl- and *m*- and *p*-substituted triphenyl-arsonium ylides (Ia–c, e) all reacted with benzaldehyde or *p*-nitrobenzaldehyde in benzene to give 55–60% and 85–95% yields, respectively, of fulvenes. The *o*-substituted ylides (Id, f) did not react with either of these aldehydes, but ylide (If) gave a low yield (33%) of fulvene with 2, 4-dinitrobenzaldehyde. Similarly, although ylides (IIa, b, e) gave fulvenes with benzaldehyde, albeit in low yield, ylides (IId, f) did not react with either *p*-nitrobenzaldehyde or 2, 4-dinitrobenzaldehyde.



$$R_3As=C\begin{matrix}\diagup CN\\ \diagdown COOEt\end{matrix}$$

(III)



$$(o\text{-}MeC_6H_4)_3As=C\begin{matrix}\diagup CN\\ \diagdown CN\end{matrix}$$

(IV)

(a) R = Ph
(b) R = *p*-tolyl
(c) R = *o*-tolyl
(d) R = *o*-methoxyphenyl

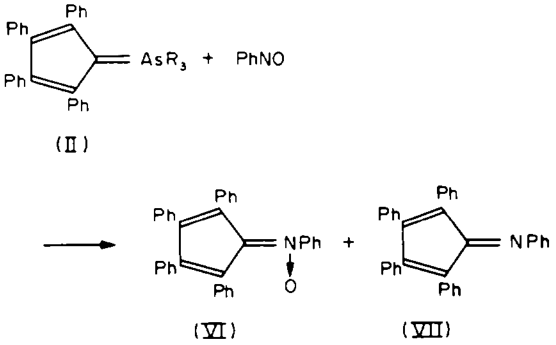
$(o\text{-}MeC_6H_4)_3As=CHPh$

(V)

Ylides (IIIa, b) gave very high yields of alkene on reaction with *p*-nitrobenzaldehyde but, as in the case of the cyclopentadienylides, the *o*-substituted ylides (IIIc, d) failed to react. With the more reactive 2, 4-dinitrobenzaldehyde the *o*-methoxyphenyl derivative (IIId) gave a poor yield of alkene but the *o*-tolyl derivative (IIIc) again did not react. The tri-*o*-tolylarsonium ylide (IV) also did not react with either *p*-nitro- or 2,4-dinitro-benzaldehyde, although its triphenylarsonium analogue provided a 61% yield of alkene on reaction with *p*-nitrobenzaldehyde.[1]

All the foregoing ylides are examples of "stable" arsonium ylides but the benzylylide (V) is a "semi-stabilised" ylide.[12] As stable ylides the former provide alkenes on reaction with aldehydes but the latter might give either an alkene or an epoxide, or a mixture of both,[4,12] When this ylide (V) was generated by the action of phenyl lithium on its tetrafluoroborate salt in the presence of benzaldehyde a mixture of *trans*-stilbene (7%) and *trans*-stilbene oxide (66%) was formed. This ratio is very similar to that previously reported (1 : 11) for triphenylarsonium benzylylide.[4] Tris-*p*-methoxyphenylarsonium benzylylide provided stilbene and stilbene oxide in the ratio (1 : 6.5)[4] and it thus appears that the electron-donating effect of the *o*-Me, like the *p*-OMe group, on the course of these reactions is not great, but is slightly more so in the latter case.

Reactions with nitrosobenzene. Reactions of arsonium ylides with notrosobenzene are more finely balanced than those with aldehydes and may provide ketoximes and/or anils,[9] e.g.



The triphenylcyclopentadienylides (Ia–c, e) all gave good yields (>70%) of ketoxime only, whereas the *o*-substituted analogues (Id, f) did not react. The yield of ketoxime obtained from Ia was greatly improved from that previously reported[9] by using a dry-filled column rather than a liquid filled column in the work-up procedure.

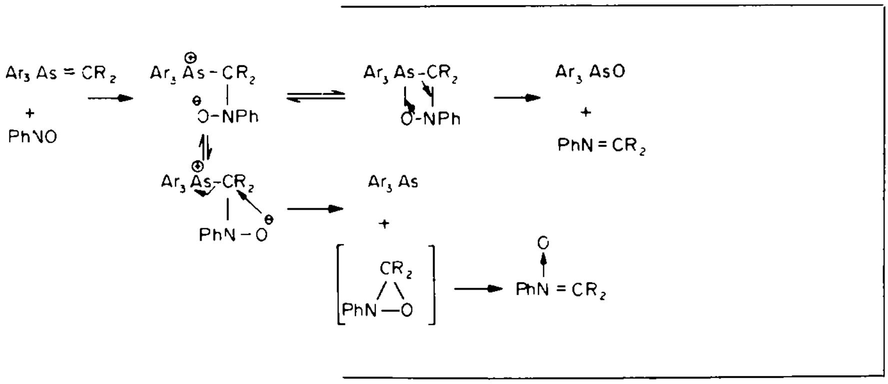
A similar improvement was noted in the reaction involving tetraphenylcyclopentadienylide (IIa). Furthermore this change of method eliminated contamination of the products by tetraphenylcyclopentadienone. Results obtained with tetraphenylcyclopentadienylides are shown in Table 2.

The presence of an electron-donating substituent (Me or OMe) in the *p*-positions of the triarylarsonium moiety thus results in a change of the ketoxime: anil ratio from 1 : 1 to 1 : 2. This resembles the change of epoxide: alkene

Table 2. Percentage yields of products from reactions of ylides (II) with nitrosobenzene

Ylide	Solvent	Ketoxime (VI)	Triarylarsine	Anil (VII)	Triarylarsine Oxide	Recovered Ylide
IIa	benzene	44	46	49	22	—
IIb	benzene	28	28	57	30	—
IIe	benzene	26	24	48	48	—
IId	benzene	0	0	0	0	89
IId	chloroform	15	14	0	0	68
IIf	benzene	0	0	0	0	89
IIf	chloroform	trace	0	0	0	80

ratio previously described in reactions of arsonium ylides with aldehydes when electron-donating substituents are introduced at the As atom.[4] Reactions of ylides with nitrosobenzene are assumed to follow a similar path to those with carbonyl compounds, *viz.*



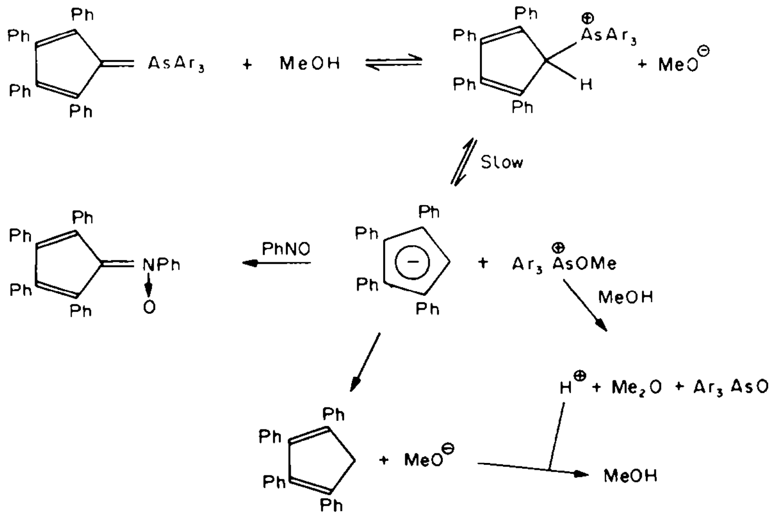
Comment has been made[4,12] that, in the case of reactions with carbonyl compounds, cleavage of the As–C bond which is formed in the intermediate betaine takes place in an opposite sense depending on whether an alkene or an epoxide is formed. Hence electron-donating substituents on arsenic should favour alkene formation. Similar considerations should then affect the formation of anils and ketoximes, with electron-donating substituents on arsenic favouring the former, as is found.

o-Substituents in the arylarsonium moiety lower reactivity towards nitrosobenzene but there is a solvent effect in the case of the tri-*o*-tolylarsonium ylide (IId), which gave some product in chloroform but not in benzene. It was recognised some time ago that Wittig reactions of phosphonium ylides were accelerated when chloroform replaced benzene as solvent.[13] Rather surprisingly ylide IId gave only ketoxime, contrasting with the results obtained from its *p*-substituted isomer.

In order to investigate the generality of solvent effects triphenylarsonium tetraphenylcyclopentadienylide was treated with nitrosobenzene in different solvents. In carbon tetrachloride or chloroform the ratios of products remained essentially the same (in CCl_4 ketoxime 45%, anil 52%; in $CHCl_3$ ketoxime 39%, anil 32%), although chloroform may have induced a slight shift towards ketoxime formation. In dry methanol, however, only the ketoxime was formed, in 19% yield. Ketoxime should be accompanied by triphenylarsine but instead triphenylarsine oxide and tetraphenylcyclopentadiene were the other products. This result, plus the fact that use of a much smaller amount of methanol as solvent resulted in a 74% conversion of the dissolved ylide into ketoxime (not all dissolved in the limited amount of solvent available), suggested that an alternative mechanism was operating. Similar results were obtained with the tri-*p*-tolyl- and tris-(*p*-methoxyphenyl)-arsonium ylides (IIb, e) the products being ketoxime (VI) (47%), triarylarsine oxide and tetraphenylcyclopentadiene.

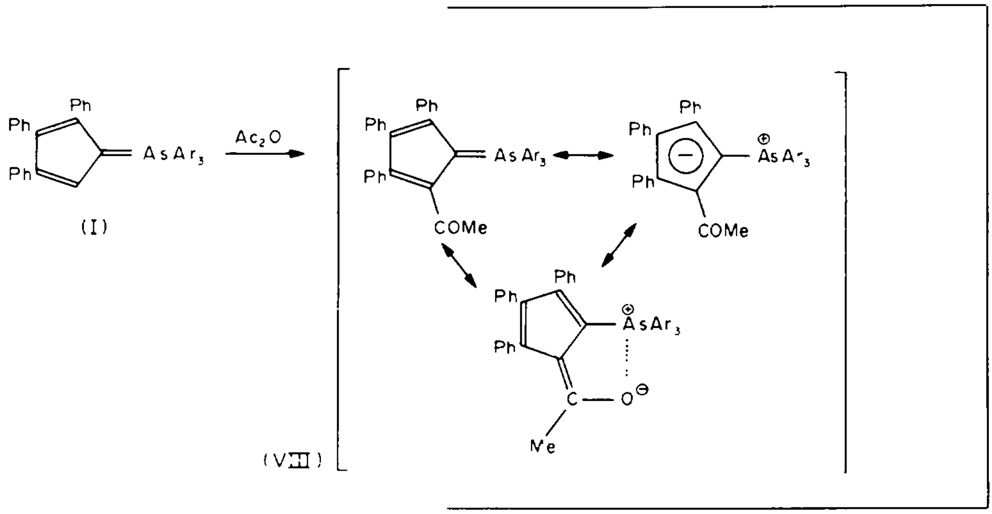
It had been noted by other workers that triphenylphosphonium *p*-nitrobenzylide decomposed in ethanol to give triphenylphosphine oxide and *p*-nitrotoluene.[14] Evidence was provided that the ylide and alcohol were in equilibrium with protonated ylide and alkoxide ion and that reaction proceeded from interaction of these species.[14]

A similar mechanism could be applied to explain the reactions of ylides (IIa, b, e) with nitrosobenzene in methanol, as follows:



It had been found earlier that ylide IIa is not attacked by ethanolic sodium hydroxide.[9] In accord with the above reaction scheme it is now found that ylides IIb, e are cleaved by boiling methanol to give tetraphenylcyclopentadiene and triarylarsine oxide. The lack of reactivity towards ethanolic hydroxide reported previously seems likely to be due to the insolubility of the ylide in the reaction medium.

Acetylation of triphenylcyclopentadienylides (I). Triphenylarsonium,[9] tri-*p*-tolyl-, tris-(*p*-methoxyphenyl)- and tris-(*o*-methoxyphenyl)-arsonium triphenylcyclopentadienylides all reacted readily with acetic anhydride, with acetylation of the unsubstituted site in the cyclopentadiene ring.



(I)

(VIII)

No IR absorption attributable to the CO group appears above 1600 cm^{-1} in the spectra of any of these acetylated ylides. This is because of intramolecular interaction between the CO group, which carries a significant negative charge, and the adjacent positively charged As atom (see VIII).[15] In the NMR spectra of VIII (Ar = o-MeC$_6$H$_4$), the OMe groups appear as three singlets (δ 2.8, 3.0, 3.8) at −10°, coalescing at ~20°; the intramolecular O... As interaction presumably increases steric crowding in this molecule, similar to that in compound IIf.

In contrast no reaction took place when tri-*o*-tolylarsonium triphenylcyclopentadienylide was heated in acetic anhydride and unchanged ylide was recovered. It seems unlikely that the cyclopentadiene ring has insufficient electron density to react, despite the lower basicity of this tri-*o*-tolyl derivative compared to the other ylides (I), since the even less basic triphenylphosphonium triphenylcyclopentadienylide is readily acetylated under similar conditions.[9] Steric factors provide a more likely explanation, the difference between the tri-*o*-tolyl and tris-(*o*-methoxyphenyl) derivatives correlating with the difference in steric crowding between these two compounds indicated by their NMR spectra (See above.)

DISCUSSION

The *p*-substituted triarylarsonium ylides appear to resemble fairly closely their triphenylarsonium analogues, the only evident differences being small increases in their basicity and in the ratio of anil to ketoxime formed in reactions with nitrosobenzene, as described and discussed above.

The *o*-substituted triarylarsonium ylides differ substantially, however, in their behaviour. Factors influencing their behaviour may be considered in terms of electronic, stereoelectronic and steric effects, although all these factors must be interwoven with each other.

It has been suggested that in triphenylphosphonium ylides the main interaction of the phenyl groups with the phosphorus atom is inductive (withdrawal of electrons).[16] Other evidence is also available of the electron-withdrawing effects of phenyl groups on hetero-atoms, especially when geometry of the molecules hinders or precludes conjugative interaction.[17] Electron-withdrawal by substituents on the As atom should make an ylide more stable, less basic and less reactive towards nucleophiles generally. This at first sight perverse behaviour may be interpreted in terms of resultant better overlap between the carbanion electrons and vacant 3*d* orbitals of the As atom in the more stable ylides, leading to more double-bond character in the ylide-C–As bond. This in turn may be connected with contraction of the 3*d* orbitals on arsenic caused by electron-withdrawing substituents thereby improving the overlap, or, considered in another way, by the premise that the more that substituent groups on arsenic draw electrons away from that atom the more scope there is for the ylide C atom to donate electrons to the arsenic. (The opposite will obtain for electron-donating substituents.) Furthermore, and inseparable from the overlap effects, electron-withdrawing substituents on arsenic will increase the electrostatic interaction between that atom and the carbanionic centre.

If, however, aryl groups may have some smaller electron-donating conjugative effect as well, then any steric factors due to crowding would affect the latter more than the inductive effects so that the overall effect of such steric factors could be to increase the electron-withdrawing character of these aryl groups, hence lowering the basicity and nucleophilic reactivity of the ylide. This is a possible contributing factor to the properties of the *o*-substituted arylarsonium ylides. Steric as well as stereoelectronic factors must also be reckoned with, however, for it is likely that the rate-determining step in the Wittig-type reactions of the present ylides, since they are "stable" ylides, is initial betaine formation, and steric hindrance due to the *o*-substituents could well play an important role.

o-Methoxyphenyl groups on arsenic lower the basicity and reactivity less than *o*-tolyl groups do, which suggests that steric rather than stereoelectronic effects predominate. OMe groups are conjugatively electron-donating but inductively electron-withdrawing, wherefore, if stereoelectronic effects were the more important, the resultant overall effect of *o*-OMe groups should be to favour their inductive effect. Thus they should decrease the basicity and reactivity of an ylide more strongly than an *o*-Me substituent, which is not in fact the case. Thus it seems likely that as far as basicity and reactivity towards aldehydes are concerned, simple steric crowding effects may be the prime cause of the differences shown by the *o*-substituted ylides.

However in the case of the reactions with nitrosobenzene the increased ketoxime: anil ratio shown by the *o*-methoxyphenyl derivative compared to its triphenyl analogue, whereas the *p*-methoxyphenyl derivative shows a decreased ketoxime: anil ratio, may indicate that in this instance, presumably for steric reasons, the inductive effect of the *o*-OMe group is indeed over-riding its small conjugative effect.

Preparation of ylides. The triphenyl- and tetraphenylcyclopentadienylides (I, II) were prepared from the corresponding diazocyclopentadienes by an improved method[18] in which the reactants are heated together with bis(acetylacetonato)copper(II) in boiling benzene. Yields were higher than those reported in previous work.[19]

Ylides III and IV were prepared by reactions of the appropriate triarylarsine oxides with ethyl cyanoacetate or dicyanomethane in acetic anhydride. This method failed, however, to provide tri-*o*-tolylarsonium ylides when tri-*o*-tolylarsine oxide was heated in acetic anhydride with either dimethyl malonate, ethyl acetoacetate or acetylacetone. Unchanged arsine oxide was recovered. No reaction took place between tri-*o*-tolylarsine oxide and acetylacetone in triethylamine containing phosphorus pentoxide. When tri-*o*-tolylarsine oxide and nitromethane were heated together in acetic anhydride no ylide was formed but tri-*o*-tolylarsine was produced. Tri-*o*-tolylarsine oxide is not changed when heated in nitromethane or acetic anhydride alone and the mechanism for its deoxygenation in the mixture is not known. Methods for the conversion of triphenylarsine oxide into triphenylarsine are reported to be rare,[20] and this present example represents a simple method for carrying out such a conversion. It is not, however, applicable to triphenylarsine oxide since the latter compound reacts with a mixture of nitromethane and acetic anhydride to give triphenylarsonium acetylnitromethylide.[11] These failures of tri-*o*-tolylarsine oxide to undergo reaction may again be associated with steric hinderance; there is no obvious correlation between the pK_a values of the active methylene compounds mentioned and their reactivities towards tri-*o*-tolylarsine oxide.

Tri-*o*-tolylarsine was similarly much less reactive towards benzyl bromide than are many triarylarsines and triethylarsine,[21] and no product was obtained in a variety of solvents, with or without a small amount of sodium iodide present. Benzyl tri-*o*-tolylarsonium tetrafluoroborate was obtained in low yield by adding silver tetrafluoroborate to a mixture of the reactants in 1,2-dichloroethane.

EXPERIMENTAL

NMR spectra were recorded in $CDCl_3$.

IR spectra were recorded using Nujol mulls. Light petroleum had b.p. 60–80°.

Triphenylarsonium 2, 3, 4-*triphenylcyclopentadienylide* (Ia). A mixture of diazo-2, 3, 4-triphenylcyclopentadiene (3.2 g, 10 mmol), triphenylarsine (4.6 g, 15 mmol) and bis(acetylacetonato)copper(II) (0.2 g, 0.8 mmol) in benzene (100 ml) was heated under reflux for 2 h. Solvent was then evaporated and the residual oil was triturated with ether–light petroleum to provide the ylide. Excess catalyst was removed by heating a suspension of the product in EtOH for several min. The yellow-orange ylide (5.1 g, 85%) had m.p. 199–201° (from benzene–light petroleum) (lit. m.p. 198–200°[19]).

Other triarylarsonium 2, 3, 4-*triphenylcyclopentadienylides.* These were prepared similarly except that 11 mmol of triarylarsines were used. 2, 3, 4-Triphenylcyclopentadienylides, yellow crystals from benzene-light petroleum (1 : 1) were as follows:

Tri-p-*tolylarsonium* (Ib), (5.3 g, 83%), m.p. 219–221°, δ 2.4 s (9H), 6.2–7.4 m (28H) (Found: C, 82.15; H, 6.0. $C_{44}H_{37}As$ requires; C, 82.5; H, 5.8%).

Tri-m-*tolylarsonium* (Ic) (3.2 g, 50%), m.p. 182–184°, δ 2.3 s (9H), 6.2–7.5 m (28H) (Found: C, 82.5; H, 5.8. $C_{44}H_{37}As$ requires; C, 82.5; H, 5.8%).

Tri-o-*tolylarsonium* (Id), (5.13 g, 80%), m.p. 237–240°, δ 2.15 s (9H), 6.7–7.7 m (28H) (Found: C, 82.85; H, 5.75. $C_{44}H_{37}As$ requires; C, 82.5; H, 5.8%).

Tris(p-*methoxyphenyl*)*arsonium* (Ie), (6.0 g, 87%), m.p. 246–248°, δ 3.8 s (9H), 6.2–7.5 m (28H) (Found: C, 76.1; H, 5.7. $C_{44}H_{37}AsO_3$ requires; C, 76.7; H, 5.4%).

Tris-(o-*methoxyphenyl*)*arsonium* (If), (5.8 g, 84%), m.p. 235–237°, δ 3.35 s (9H), 6.4–7.6 m (28H) (Found: C, 76.2; H, 5.4. $C_{44}H_{37}AsO_3$ requires; C, 76.7; H, 5.4%).

Perchlorates of triarylarsonium 2, 3, 4-*triphenylcyclopentadienylides.* Perchloric acid (70%, 0.1 ml) was added to a suspension of the ylide (5 mmol) in ethanol (5 ml). The soln was filtered and addition of ether precipitated the perchlorate which was recrystallised from EtOH. Salts of the following 2, 3, 4-triphenylcyclopentadienylides were obtained: *Tri*-p-*tolylarsonium* (89%), m.p. 158–160° (Found: C, 71.0; H, 4.8. $C_{44}H_{38}AsCIO_4$ requires; C, 71.3; H, 5.2%); *tri*-m-*tolylarsonium* (83%), m.p. 218–219° (Found: C, 71.0; H, 5.15. $C_{44}H_{38}AsCIO_4$ requires C, 71.3, H, 5.2%) *tri*-o-*tolylarsonium* (91%), m.p. 201–203° (Found: C, 71.9; H, 5.1. $C_{44}H_{38}AsCIO_4$ requires; C, 71.3; H, 5.2%).

Triphenylarsonium 2, 3, 4, 5-*tetraphenylcyclopentadienylide* (IIa). A mixture of diazo-2, 3, 4, 5-tetraphenylcyclopentadiene (3.96 g, 10 mmol), triphenylarsine (4.6 g, 15 mmol), bis(acetylacetonato)copper(II) (0.4 g, 1.5 mmol) and benzene (100 ml) was heated under reflux for 2 h. Solvent was evaporated and trituration of the residual oil with ether-light petroleum provided the cyclopentadienylide, which was freed from excess catalyst by warming with EtOH. The ylide (5.54 g, 82%) had m.p. 228–230° (lit. m.p. 228–230°[19]).

Other triarylarsonium 2, 3, 4, 5-*tetraphenylcyclopentadienylides.* These ylides were prepared similarly to their triphenylarsonium analogue save that 11 mmol of tritolylarsines and 10 mmol of tris(methoxyphenyl)arsines were used. 2, 3, 4, 5-Tetraphenylcyclopentadienylides, yellow crystals from benzene-light petroleum (1 : 1), were as listed:

Tri-p-*tolylarsonium* (IIb), (3.2 g, 49%), m.p. 226–228°, δ 2.3 s (9H) 6.5–7.4 m (32H) (Found: C, 84.2; H, 5.8. $C_{50}H_{41}As$ requires; C, 83.8; H, 5.8%).

Tri-o-tolylarsonium (IId), (5.4 g, 75%), m.p. 226–228°, δ(70°) 1.85 s (broad), 6.7–7.6 m; (−45°) 1.1 s (broad), 1.5 s (broad), 2.8 s (broad), 6.3 − 7.6 m (Fouhd: C, 83.4; H, 5.6. $C_{50}H_{41}As$ requires; C, 83. 8; H, 5.8%).

Tris-(p-*methoxyphenyl*) (IIe), (3.74 g, 70%), m.p. 127–130°, δ 3.8 s (9H), 6.5–7.4 m (32H) (Found: C, 78.5; H, 5.0. $C_{50}H_{41}AsO_3$ requires: C, 78.5; H, 5.4%).

Tris-(o-*methoxyphenyl*) (IIf), (5.9 g, 78%), m.p. 213–215°, δ 3.2 s (9H), 6.4–7.5 m (32H) (Found: C, 78.2; H, 5.1. $C_{50}H_{41}AsO_3$ requires C, 78.5; H, 5.4%).

Tri-o-tolyl(2, 3, 4, 5-tetraphenylcyclopentadienyl)arsonium perchlorate. Prepared as the perchlorates of the 2, 3, 4-triphenylcyclopentadienylides this *perchlorate* (88%) had m.p. 156–157° (found: C 73.2; H, 4.9, $C_{50}H_{42}AsClO_4$ requires; C, 73.5; H, 5.2%).

Triarylarsonium cyano(ethoxycarbonyl)methylides. The triphenylarsonium ylide was prepared as described.[11] For other analogues a mixture of ethyl cyanoacetate (0.68 g, 6 mmol) and triarylarsine oxide (5 mmol) in freshly distilled Ac_2O (10 ml) was heated under reflux for 10 min. Water (100 ml) was added to the cooled soln and the resultant suspension was scratched to induce it to crystallise. After 4 hr the crystalline solid was filtered off, washed with ether and recrystallised from benzene-light petroleum (1:1), providing thereby the following cyano(ethoxycarbonyl)methylides:

Tri-p-tolylarsonium (IIb), (1.70 g, 75%), m.p. 231–3°, δ 1.25 t (3H), 2.4 s (9H), 4.1 q (2H), 7.2–7.7 m (12H), ν_{max}. 1590, 1650, 2180 cm^{-1} (Found: C, 67.7; H, 5.7; N, 3.0. $C_{26}H_{26}AsNO_2$ requires; C, 68.0; H, 5.7; N, 3.0%).

Tri-o-tolylarsonium (IIIc), (1.72 g, 75%), m.p. 229–231°, δ 1.2 t (3H) 2.25 s (9H), 4.05 q (2H), 7.2–7.7 m (12H), ν_{max}.1635, 2180 cm^{-1} (Found: C, 67.7; H, 5.8; N, 3.0. $C_{26}H_{26}AsNO_2$ requires; C, 68.0; H, 5.7; N, 3.0%).

Tris-(o-methoxyphenyl)arsonium (IIId), (2.25 g 89%), m.p. 233–235°, δ 1.2 t (3H), 3.6 s (9H), 4.0 q (2H), 6.8–7.7 m (12H), ν_{max}. 1580, 1610, 2185 cm^{-1} (Found: C, 61.8; H, 5.5; N, 2.6. $C_{26}H_{26}AsNO_5$ requires; C, 61.5; H, 5.2; N, 2.6%).

Tri-o-tolylarsonium dicyanomethylide (IV). A mixture of dicyanomethane (0.33 g, 5 mmol) and tri-*o*-tolylarsine oxide (1.82 g, 5 mmol) in Ac_2O (10 ml) was heated under reflux for 2 min. Water (100 ml) was added to the cooled soln whereupon the *ylide* (1.66 g, 81%) crystallised out, m.p. 250–251° (from EtOH), δ 2.35 s (9H), 7.2–7.7 m (12H), ν_{max}. 2140, 2170 cm^{-1} (Found: C, 70.0; H, 4.8; N, 6.8. $C_{24}H_{21}AsN_2$ requires; C, 69.9; H, 5.1; N, 6.8%).

Reaction of tri-o-tolylarsine oxide with nitromethane and acetic anhydride. When these three reagents (0.36 g, 5 ml, 5 ml respectively) were heated under reflux for 5 min and water was then added, tri-*o*-tolylarsine (0.18 g, 50%) precipitated out.

Benzyltri-o-tolylarsonium tetrafluoroborate. Benzyl bromide (13.6 g, 50 mmol) was added to a soln of tri-*o*-tolylarsine (6.92 g, 20 mmol) in 1, 2-dichloroethane (30 ml) and the mixture was stirred at room temp. under N_2 for 3 hr. Silver tetrafluoroborate (3.9 g, 20 mmol) was then added dropwise and the mixture was stirred for 1 week. A ppt was filtered off and solvent was evaporated from the filtrate leaving an orange oil which was purified by washing with boiling benzene and recrystallisation of the resultant solid twice from EtOH-ether, providing the *tetrafluoroborate* (1.5 g, 14%), m.p. 197–199°, δ 2.1 s (9H), 4.8 s (2H), 7.0–7.8 m (17H) (Found: C, 63.8; H, 5.35. $C_{28}H_{28}AsBF_4$ requires; C, 63.9; H, 5.35%).

pK_a Determinations. pKa determinations were carried out as described in an earlier paper,[9] utilising a method previously used for other ylides.[8]

Reactions of 2, 3, *4-triphenylcyclopentadienylides with benzaldehyde.* A mixture of the ylide (0.5 mmol) and freshly distilled benzaldehyde (0.5 mmol) in benzene (30 ml) was heated under reflux for 18 hr, a further quantity of benzaldehyde (0.25 mmol) being added after 1 hr. Solvent was removed and the residue was dissolved in a small amount of benzene. Addition of ether precipitated unchanged ylide. Solvent was removed and the residue was chromatographed on a silica column prepared with light petroleum. Elution with light petroleum-benzene (2:1) provided 1, 2, 3, 6-tetraphenylfulvene, m.p. 173–175°, identical with an authentic sample. MeOH eluted triarylarsine oxide. Yields obtained were as follows. From ylide Ia, 58%, Ib, 57%; Ic, 55%; Ie, 58%. Ylide Ia gave a 55% yield when chloroform replaced benzene as solvent.

Reactions of 2, 3, *4-triphenylcyclopentadienylides with* p-*nitrobenzaldehyde.* A mixture of ylide (0.5 mmol), *p*-nitrobenzaldehyde (0.075 g, 0.5 mmol) and benzene (30 ml) was heated under reflux for 4 hr. Solvent was removed and the residue, dissolved in the minimum amount of benzene, was applied to a silica column prepared with benzene–light petroleum (1:1). Benzene eluted 6-*p*-nitrophenyl-1, 2, 3-triphenylfulvene, which, after trituration with, and recrystallisation from EtOH, had m.p. 162–164°, identical with an authentic sample. Triphenylarsine oxide was eluted with MeOH. Yields obtained were as follows. From ylide (Ia), 92%; (Ib), 86%; (Ic), 58%; (Ie), 91%. No fulvene was obtained from ylides (Id, f) and arsonium ylide was recovered unchanged (84, 87%) when solvent was removed from the reaction mixture and the residue was triturated with ether.

Reactions of 2, 3, *4-triphenylcyclopentadienylides with* 2, *4-dinitrobenzaldehyde.* A mixture of Ia (0.598 g 1 mmol), 2, 4-dinitrobenzaldehyde (0.198 g, 1 mmol) and benzene (50 ml) was heated under reflux for 3 hr. After removal of solvent the residue, dissolved in a minimum amount of benzene, was applied to a column prepared with benzene-light petroleum (1:1). Benzene eluted 6-(2, *4-dinitrophenyl*)-1, 2, *3-triphenylfulvene* (0.414 g, 88%), brown needles m.p. 197–199° (from nitromethane) (Found: M^+ 472 · 1426. $C_{30}H_{20}N_2O_4$ requires; *M* 472 · 1423). MeOH eluted triphenylarsine oxide (0.30 g, 92%).

When solvent was removed from a mixture of Id (0.321 g, 0.5 mmol), 2, 4-dinitrobenzaldehyde (0.1 g, 0.5 mmol) and benzene (25 ml) which had been heated under reflux for 24 hr, addition of ether–light petroleum (1:1) provided unchanged ylide (0.31 g, 96%).

Removal of solvent from a mixture of If (0.69 g, 1 mmol), 2,4-dinitrobenzaldehyde (0.196 g, 1 mmol) and benzene (30 ml), which had been heated for 3 hr, followed by dissolution of the residue in a minimum quantity of benzene and addition of ether, precipitated unchanged ylide (0.47 g, 68%). Evaporation of solvent from the filtrate, followed by chromatography as described above provided 6-(2, 4-dinitrophenyl)-1, 2, 3-triphenylfulvene (0.156 g, 33%), identical with the previously prepared sample.

Reactions of 2, 3, 4, *5-tetraphenylcyclopentadienylides with benzaldehyde.* A mixture of the ylide (0.5 mmol) and freshly distilled benzaldehyde (0.053 g, 0.5 mmol) in benzene (25 ml) was heated under reflux for 20 hr, a further sample of benzaldehyde (0.026 g, 0.25 mmol) being added after 5 hr. Removal of solvent and trituration of the residue with ether precipitated unchanged ylide, which was filtered off and washed with ether. Solvent was removed from the filtrate and the residue was dissolved in a small amount of benzene and applied to a silica column prepared with benzene–light pertoleum (1:1). Benzene eluted 1, 2, 3, 4, 6-pentaphenylfulvene which was freed from solvent, triturated with EtOH, recrystallised from AcOH and was identical with an authentic sample. MeOH eluted triarylarsine oxide. Yields of fulvene were from ylide IIa, 19%; IIb, 20%; IIe, 17%, and recovered ylide was IIa, 81%; IIb, 77%; IIe, 84%.

Reactions of cyano(ethoxycarbonyl)methylides (III) *with* p-*nitrobenzaldehyde.* A mixture of ylide (0.5 mmol), *p*-nitrobenzaldehyde (0.5 mmol) and benzene (25 ml) was heated under reflux for 18 hr. Solvent was evaporated and the residue was triturated with EtOH. Ethyl *p*-nitrobenzylidenecyanoacetate, which crystallised and was recrystallised from EtOH, was identical with an authentic sample.[11] Yields were from IIIa 90%, IIIb 89%.

Reaction of tris-(o-*methoxyphenyl*)- *and triphenyl-arsonium cyano(ethoxycarbonyl)methylides with* 2, *4-dinitrobenzaldehyde.* A mixture of IIId (0.507 g, 1 mmol), 2, 4-dinitrobenzaldehyde (0.2 g, 1 mmol) and benzene (25 ml) was heated under reflux for 18 hr. Solvent was removed and trituration of the residue in ether–light petroleum (1:1) provided unchanged ylide (0.23 g, 45%), which was filtered off. The filtrate was freed from solvent and applied to a silica column prepared from benzene. $CHCl_3$ eluted *ethyl* 2, *4-dinitrobenzylidenecyanoacetate* (0.053 g, 18%), m.p. 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%). Compound IIIa similarly provided the identical alkene (95%) and no ylide was recovered.

Reactions of 2, 3, *4-triphenylcyclopentadienylides* (I) *with nitrosobenzene.* A soln of ylide (0.5 mmol) and nitrosobenzene (0.053 g, 0.5 mmol) in benzene (25 ml) was heated under reflux for 6 hr. After 3 hr heating further nitrosobenzene (0.027 g, 0.25 mmol) was added. Solvent was evaporated and the residue was dissolved in CH_2Cl_2. Approximately 5 times the weight of silica was added to the soln and solvent was then removed. This was repeated twice and the product-absorbent mixture was applied to the top of a dry silica column. Addition of benzene separated a green-red band from the top of the column. This segment was cut from the column and treated with $CHCl_3$ which extracted N-phenyl-2, 3, 4-triphenylcyclopentadienone ketoxime, which, after removal of the $CHCl_3$ and trituration with EtOH gave green crystals, m.p. 160–162° (from EtOH) identical with an authentic sample.[9] Extraction of the bottom part of the column with $CHCl_3$ provided triphenylarsine. Yields (%) were as follows: Ketoxime: from Ia, 72; Ib, 73; Ic, 77; Ie, 77. Arsine: from Ia, 72; Ib, 64; Ic, 69; Ie, 61. Ylides Id and If gave no ketoxime from attempted reactions in benzene or $CHCl_3$ and were recovered in 96% yield from benzene and 92–93% yield from $CHCl_3$.

Reactions of 2, 3, 4, 5-*tetraphenylcyclopentadienylides* (II) *with nitrosobenzene.* Ylide (1 mmol), nitrosobenzene (0.107 g, 1 mmol) and benzene (25 ml) were heated under reflux for 6 hr, a further sample of nitrosobenzene (0.054 g, 0.5 mmol) being added after 3 hr. Solvent was removed and the mixture of products was applied to a dry silica column as described in the previous paragraph. On development with benzene, 3 bands appeared. The green second band was cut from the column and extracted with $CHCl_3$ to give, after removal of solvent and trituration with ethanol, N-phenyl-1, 2, 3, 4-tetraphenylcyclopentadienone ketoxime, khaki-green needles, m.p. 223–225° (from EtOH).[9] The third band was extracted with $CHCl_3$ to provide triarylarsine oxide. The first red band was extracted with $CHCl_3$ and the residue was applied to another dry silica column. Development of this column with benzene–light petroleum (1:4) gave a colourless band and left a red band at the top of the column. Extraction of the former with $CHCl_3$ and removal of the solvent give triphenylarsine. The red band was extracted with $CHCl_3$ and removal of the solvent and trituration with EtOH gave N-phenyl-2, 3, 4, 5-tetraphenylcyclopentadienone anil, crimson prisms m.p. 233–235° (from nitromethane).[9] Similar reactions were also carried out in other solvents but the same work-up technique was used. Yields are given in Table 2 and in the text following that Table.

Methanolysis of triarylarsonium 2, 3, 4, 5-*tetraphenylcyclopentadienylides.* The tri-*p*-tolyl ylide (0.36 g, 0.5 mmol) was heated in boiling MeOH for 18 hr. On removal of solvent no unchanged ylide was obtained when the residue was triturated with ether–light petroleum. This residue was applied to a silica column prepared with light petroleum. Benzene eluted 1, 2, 3, 4-tetraphenylcyclopentadiene (0.12 g, 65%) followed by a red intractable tar (0.05 g). MeOH eluted tri-*p*-tolylarsine oxide (96%). Similarly the tris-(*p*-methoxyphenyl) ylide gave tetraphenylcyclopentadiene (16%) and an oil (0.17 g) containing tris-(*p*-methoxyphenyl)arsine oxide.

Acetylation of 2, 3, 4-*triphenylcyclopentadienylides.* A soln of ylide separated out. The following triarylarsonium 2-acetyl-3, 4, 5-triphenylcyclopentadienylides were prepared. *Tri*-p-*tolyl* ylide separated out. The following triarylarsonium 2-acetyl-3, 4, 5-triphenylcyclopentadienylides were prepared. *Tri*-p-*tolyl* (0.23 g, 68%), m.p. 257–259° [from benzene-light petroleum (1:1)] δ 1.7 s (3H, 2.3 s (9H), 6.5–7.5 m (27H) (Found: C, 81.0; H, 5.5. $C_{46}H_{39}AsO$ requires; C, 80.9; H, 5.8%); *tris*-p(*methoxyphenyl*) (some Ac_2O was removed before scratching, 0.238 g, 65%), m.p. 249–252° [from benzene–light petroleum (1:1)] δ 1.7 s (3H), 3.8 s (9H), 6.6–7.5 m (27H) (Found: C, 75.8; H, 5.0. $C_{46}H_{39}AsO_4$ requires C, 76.5; H, 5.4% *tris*-o-(*methoxyphenyl*) (0.245 g, 67%), m.p. 278–280° [from benzene–light petroleum (1:1)], δ 1.6 s (3H), 3.1 s, broad (9H), 6.5–7.8 m (27H), δ, at −10° 1.6 s (3H), 2.8 s (3H), 3.0 s (3H), 3.8 s (3H), 6.5–7.8 m (27H) (Found: C, 75.8; H, 5.5. $C_{46}H_{39}AsO_4$ requires; C, 75.6; H, 5.4%). An attempted reaction using the tri-*o*-tolylarsonium ylide provided only unchanged ylide (91%).

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