Tetrahedron. Vol. 28, pp. 343 to 352. Pergamon Press 1972. Printed in Great Britain

TETRAPHENYLCYCLOPENTADIENYLIDES

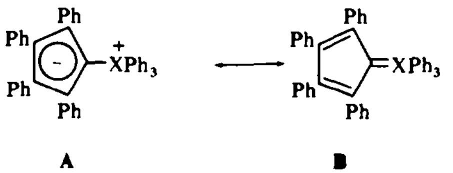
B. H. FREEMAN, D. LLOYD* and M. I. C. SINGER
Department of Chemistry, United College of St. Salvator and St. Leonard, University of St. Andrews, St. Andrews, Fife, Scotland

(*Received in the UK* 12 *August* 1971; *Accepted for publication* 16 *September* 1971)

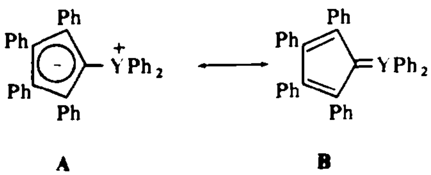
Abstract—The properties of a number of heteronium tetraphenylcyclopentadienylides with a variety of hetero-atoms are reported, including their UV spectra, basicities, and reactivities towards aldehydes and nitrosobenzene. These properties are very dependent on the identity of the hetero-atoms; with elements of either Group V or Group VI of the periodic table the dipolar and nucleophilic character of the ylides increases and their stability decreases as one descends the periodic table.

THERE has been much recent interest in the comparisons of ylides having different hetero-atoms, and in particular in the comparison of sulphonium and arsonium ylides with the extensively examined phosphonium ylides.

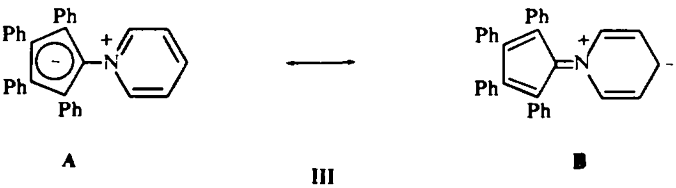
The preparation of various tetraphenylcyclopentadienylides (I, II and III) by thermal decomposition of diazotetraphenylcyclopentadiene in the presence of appropriate carbene-acceptors has provided a unique series of stabilised heteronium ylides, differing solely in the identity of the hetero-atoms. This series includes the first isolated examples of stibonium,[1] bismuthonium,[2] selenonium,[3] and telluronium[4] ylides as well as pyridinium,[5] phosphonium,[6,7] arsonium[8] and sulphonium[9] ylides. Comparative studies on these ylides are now reported.



I; X = P, As, Sb or Bi



II; Y = S, Se or Te



III

The phosphonium ylide (I; X = P) was also prepared from 5-bromo-1,2,3,4-tetraphenylcyclopentadiene by a modification of the salt method for the preparation of ylides. Earlier work[6] had suggested that this was not possible but the use of a modified method[10] has enabled its preparation in high yield.

---

* Author to whom correspondence should be addressed.

All of these ylides have been isolated as solids, many of them crystalline. They were insoluble or almost so in water, ethanol, ether or light petroleum but dissolved in chloroform or benzene. In both the Group V and Group VI series the m.ps tend to be lower with increasing atomic weight of the hetero-atoms (X = P, As, Sb, Bi; m.p. = 297–299°, 228–230°, 196–198°, *ca* 165°; Y = S, Se, Te; m.p. = 216–218°, 189–190°, 193·5°).

They are far more stable than most ylides because the carbanionic portions of the molecules in their dipolar canonical forms (IA, IIA) consist of cyclopentadienide anions which are stabilised by having delocalised sextets of π-electrons. The triphenylphosphonium, triphenylarsonium, diphenylsulphonium and diphenylselenonium ylides are completely stable in air, although exposure to sunlight caused darkening of the exposed surfaces in the case of these Group VI ylides. The pyridinium and triphenylstibonium ylides are stable as solids but decompose slowly in solution, while the triphenylbismuthonium and diphenyltelluronium ylides decompose slowly in the solid state and more rapidly in solution.

The relative stabilities can be correlated with the nature of the bond linking the hetero-atom to the 5-membered ring and the relative contributions of what will be called the 'dipolar' (A) and 'covalent' (**B**) canonical forms.

TABLE 1. LONGEST WAVELENGTH ABSORPTION MAXIMA OF HETERONIUM TETRAPHENYLCYCLOPENTADIENYLIDES

Ylide:	III		I, X = P	I, X = As	I, X = Sb	I, X = Bi	
λ_{max}(nm):	538	595	288	291	349	525	596
Solvent	EtOH	PhH	EtOH*	EtOH*	$CHCl_3$*	EtOH	PhH

Ylide:	II, Y = S	II, Y = Se	II, Y = Te	
λ_{max}(nm):	292(sh328)	294(sh347)	335(sh280)	347(sh280)
Solvent:	PhH*	EtOH*	MeOH	PhH

* The wavelength of the absorption maximum does not vary with the solvent in these cases. The solvent used for quantitative measurement depended on the solubility of the particular ylide.

In the case of the pyridinium ylide (III) there can be little stabilisation due to the contribution of form **B** but in the other cases both forms would be expected to contribute significantly. However it would be expected that as one goes down the periodic table the increasing size of the hetero-atoms and the more diffuse *d*-orbitals would lower the effectiveness of the overlap between the 2*p*-orbitals of the carbanionic moieties and the vacant n*d*-orbitals of the hetero-atoms, leading to decreased contributions from the covalent forms to the structures of the molecules and, in turn, to decreased stabilities. In addition, the trend towards lower stability on descending the table should be increased by the decreased electrostatic interaction between the carbanionic moieties and the heteronium atoms due to the greater lengths of the carbon-hetero-atom bonds and the lower electronegativity of the hetero-atoms.

The differing contributions of the covalent forms to the overall structure are apparent from the electronic spectra of the ylides. (Table 1)

With decreasing contributions from the covalent form the absorption maxima shift to longer wavelengths. In particular there is a striking difference between the pyridinium and triphenylbismuthonium ylides and the other ylides. The latter are yellow and, with the exception of the diphenyltelluronium ylide which shows a small solvent shift, the wavelength at which they absorb is independent of the solvent. In contrast the pyridinium and bismuthonium ylides are dark blue-purple and show solvatochromism. Similar solvatochromism has been observed[11, 12] and commented upon[12] in the case of unsubstituted pyridinium cyclopentadienylide. It must be inferred that there is considerable similarity between the electronic structures of the triphenylbismuthonium and pyridinium ylides, whence it would appear that for the former, as for the latter ylide, the contribution of the covalent form is minimal. This is presumably because the overlap of the very large and diffuse 6*d*-orbitals of bismuth with the pπ-orbitals of the cyclopentadienide ring is also minimal. Pentaphenylbismuth is also deep violet whereas pentaphenyl-phosphorus, -arsenic and -antimony are colourless or yellow.[13] This sharp difference between the pyridinium and bismuthonium ylides and all the other ylides is surprising, but in the case of the other heteronium ylides no absorption at comparable long wavelength was observed even in highly concentrated solutions. It is still possible of course that there is such absorption but that it is of very low intensity.

Increased contribution of the covalent forms **B** to the structure of the ylides results in their having an overall lower polarity and, in general, the ease with which they are attacked by either nucleophilic or electrophilic reagents can be correlated with a decreased contribution of the covalent form.

Thus the triphenyl-phosphonium and -arsonium and diphenyl-sulphonium and -selenonium ylides were recovered unchanged after they had been heated in refluxing ethanolic potassium hydroxide for 18 hr., whereas the triphenyl-stibonium and -bismuthonium and diphenyltelluronium ylides were rapidly attacked and decomposed by alkali. Attempts to recrystallise the stibonium ylide from ethanol led to its almost complete conversion into tetraphenylcyclopentadiene and triphenylstibine oxide.

The ylides having Group V hetero-atoms, but not those having Group VI hetero-atoms, were basic and formed salts. Thus the triphenyl-phosphonium, -arsonium and -stibonium ylides were soluble in dilute mineral acids and gave crystalline perchlorates, but the stibonium perchlorate had to be filtered off rapidly to prevent its hydrolysis. The triphenylbismuthonium ylide however decomposed at once on admixture with dilute or concentrated mineral acids. The diphenyl-sulphonium and -selenonium ylides were insoluble in acids; addition of perchloric acid to an ethanolic solution of the diphenyltelluronium ylide produced no change in its UV spectrum, indicating that it is not protonated to any extent under these conditions.

Johnson[14] has shown that the pK_a values for the dissociation of a series of phenacylheteronium salts into the related stabilised α-keto-ylides are in the order S>P>As. The pK_a values for the perchlorates of the ylides (I; X = P, As or Sb) were determined spectroscopically in 95% ethanol using Johnson's method[15] so that the results he obtained and those presently described should be comparable; these values cannot of course be compared with pK_a values determined in aqueous solution but should be mutually consistent. For the perchlorates of (I; X = P) and (I; X = As) pK_a = 5·3, 7·6, respectively. An accurate value could not be obtained for the perchlorate of (I; X = Sb) owing to the rapid hydrolysis of both salt and ylide which took place in 95% ethanol but rough measurements suggested its $pK_a > 7{\cdot}6$. These results indicate that the basicity of the ylides lies in the order

$$\mathrm{Sb} > \mathrm{As} > \mathrm{P} \gg \mathrm{Se} \sim \mathrm{S},$$

which suggests in turn that their polarity lies in the same order, as also inferred from their spectra and stability.

The reactivities of these ylides with carbonyl compounds in Wittig reactions would also be expected to correlate with their polarity and this is borne out by the results given in Table 2.

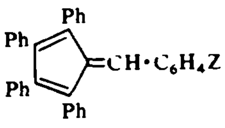
TABLE 2. REACTIVITIES OF TETRAPHENYLCYCLOPENTADIENYLIDES WITH ALDEHYDES

Ylide:	(II, Y = S)	(II, Y = Se)	(II, Y = Te)	(I, X = P)	(I, X = As)	(I, X = Sb)
Yield of Fulvene from benzaldehyde:*	0	0	-	0	16%	40%
Yield of Fulvene from *p*-Nitrobenzaldehyde:*	0	0	†	0	95%	99%

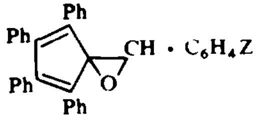
* Yield after ylide and aldehyde had been heated in refluxing carbon tetrachloride for 18 hr.

† Decomposition of the ylide supervened.

It is noteworthy that both the arsonium and stibonium ylides gave rise to fulvenes (IV) and not epoxides (V), especially since the only other reported reaction of a stibonium ylide with a carbonyl compound, namely that between triphenylstibonium methylide and benzophenone produced triphenylstibine and diphenylacetaldehyde, which the authors suggested was formed by rearrangement of an intermediate epoxide.[16, 17]

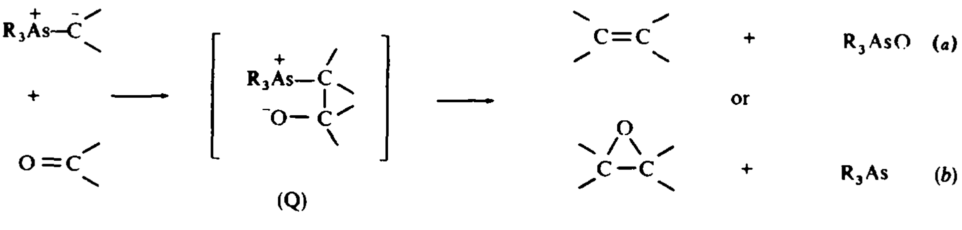


IV



V $Z = H$ or $p\text{-NO}_2$

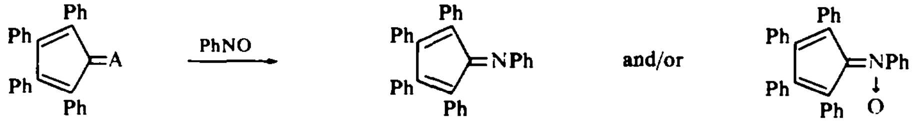
It has been suggested that the more stabilised arsonium ylides give rise to olefins and triphenylarsine oxide whereas less stabilised arsonium ylides produce epoxides and triphenylarsine.[18, 19] In each case reaction presumably proceeds *via* the betaine adduct (Q)



Thereafter either a cyclic rearrangement of the electrons ensues giving rise to the olefin or else nucleophilic displacement of the arsonium group by the oxygen provides the epoxide. Two factors may promote the former course, namely the production of the oxide bond and of the olefinic bond. In the case of phosphonium ylides the great bond strength of the phosphine oxide bond drives the reaction exclusively to the formation of olefin. The strength of the arsine oxide bond is much less so that this is of less significance and the course of the reaction will be determined much more by the nature of the olefinic bond which is formed. In the case of unstabilised arsonium ylides, such as arsonium methylides, an isolated double bond is formed but in the case of stabilised ylides, such as α-keto-ylides or cyclopentadienylides, the newly formed olefinic bond forms part of a conjugated system and there is more energetic gain in its formation. If it is assumed that the relative energies of the transition states leading from the betaines to the final products reflect the stabilities of these products, the above considerations explain why both the arsonium and stibonium cyclopentadienylides form fulvenes rather than fulvene epoxides. A similar suggestion has been made in connexion with results obtained with phenacylides.[19]

Samples of the fulvenes were also prepared from tetraphenylcyclopentadiene and the aldehydes by established methods[20] and had identical m.p. and spectra.

A similar pattern of reactivity obtained in the reactions of these ylides with nitrosobenzene to produce either the anil (VI) or anil oxide (VII), as shown in Table 3.

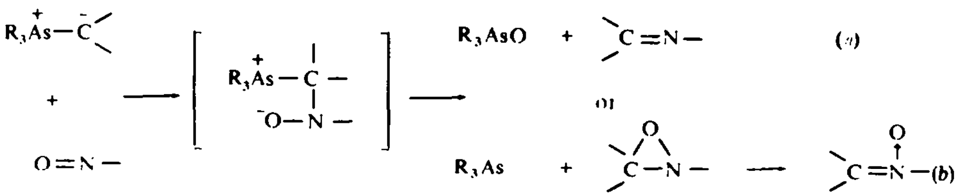


VI VII

TABLE 3. REACTIVITIES OF TETRAPHENYLCYCLOPENTADIENYLIDES WITH NITROSOBENZENE

Ylide:	(II, Y = S)	(II, Y = Se)	(I, X = P)	(I, X = As)	(I, X = Sb)
Reaction time	18 hr.	18 hr.	18 hr.	4 hr.	10 min.
Yield of anil (VI)	0	0	0	35%	0
Yield of anil oxide (VII)	5%	80%	0	48%	80%

It is of interest that in this case only the arsonium ylide gave some anil as well as anil oxide. Reaction is presumed to follow similar paths to those involving carbonyl compounds, *viz.*



Similar considerations will determine the nature of the final products but there will be less energetic gain in path (*a*) in this case, for the anils formed from cyclopentadienylides may be to some extent destabilised by conjugation with the five-membered ring since such conjugation leads to the formation of an anti-aromatic electronic system in the cyclopentadiene ring. In consequence, whereas all the present ylides follow reaction path (*a*) in the case of reaction with aldehydes, only the arsonium ylide follows this path in reactions with nitrosobenzene, and even in this case not as the major reaction path. That any anil is formed in this case reflects the greater strength of the arsine oxide bond compared with the sulphur-, selenium- and stibine-oxide bonds. The phosphonium ylide which might be expected to follow path (*a*) predominantly because of the great strength of the phosphine oxide bond was however unsufficiently reactive to give any product with nitrosobenzene.

Neither the anil (VI) nor the anil oxide (VII) had been reported previously. Authentic samples, which were identical with those obtained from the ylides, were made by reaction of nitrosobenzene with, respectively, tetraphenylcyclopentadiene and diazotetraphenylcyclopentadiene; the same method had been used to prepare an anil oxide from diazofluorene.[21] The product (VII) showed strong absorption bands characteristic of aryl amine oxides at 898 and 1290 cm^{-1}.[22] It could be reduced to the anil (VI) by reaction with triphenylphosphine in benzene, thus confirming its structure.

No fulvenes, anil or anil oxide could be found from similar reactions of aldehydes or nitrosobenzene with the diphenyltelluronium ylide (II, Y = Te) or the triphenylbismuthonium ylide (I, X = Bi): in every case decomposition of the ylides apparently supervened.

It may be noted that the apparent nucleophilicity of these ylides

$$(\mathrm{Sb} > \mathrm{As} > \mathrm{Se} > \mathrm{S} > \mathrm{P})$$

does not run entirely parallel with their basicities

$$(\mathrm{Sb} > \mathrm{As} > \mathrm{P} > \mathrm{S} \sim \mathrm{Se}).$$

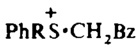
This series of compounds thus provides an excellent example of the pitfalls of assuming precise correlation between these two types of properties, the latter of which involves a relatively simple equilibrium while the former involves a more complex sequence of events. The difference in this case may be connected with the lesser steric hindrance to attack by nucleophiles on the sulphonium and selenonium ylides compared with the phosphonium ylide.

The results described entirely confirm Johnson's suggestion[14, 23] that, on descending Group V of the Periodic Table, the tetravalent heteronium atoms are less able or willing to undergo valence shell expansion.

Triphenylphosphonium fluorenylide has been shown to react with dichlorocarbene to form a dichlorofulvene but no such reaction occurred with triphenylphosphonium cyclopentadienylide,[24] a difference ascribed by the authors to the greater delocalisation of the negative charge in the latter ylide. No formation of a dichlorofulvene could be detected under similar conditions from the ylides (I; X = P, As or Sb) and the phosphonium and arsonium ylides were recovered unchanged from the reaction mixtures. Diazo-2,3,4,5-tetraphenylcyclopentadiene also did not react with this carbene.

Johnson has commented[25] on the fact that alkyl heteronium ylides are more reactive towards electrophiles than are aryl heteronium ylides. Methylphenylsulphonium tetraphenylcyclopentadienylide (VIII) was prepared by the general method from diazotetraphenylcyclopentadiene and thioanisole. This ylide was stable when stored

VIII



$PhR\overset{+}{S}\cdot CH_2Bz$

IX

in the dark but darkened rapidly on exposure to light. Unlike its diphenylsulphonium analogue it was hydrolysed by aqueous-ethanolic sodium hydroxide. In water it was completely hydrolysed in *ca* 15 min. With perchloric acid it gave a crystalline perchlorate but this salt was not stable and slowly evolved thioanisole. Its pK_a was not determined because of its ready hydrolysis in 95% ethanol: however the fact that a salt could be obtained indicates that the ylide is more basic than the ylides (II), It has been shown[14] that the pK_a of the methylphenylsulphonium ylide salt (IX, R = Me) is greater than that of the diphenylsulphonium ylide salt (IX, R = Ph), and these authors attributed the difference to the greater inductive withdrawal of electrons by the phenyl group compared to the Me group, leading in turn to better pπ-dπ overlap between the sulphur atom and the carbanionic portion of the molecule.

The ylide (VIII) was also more reactive towards nitrosobenzene than its diphenyl analogue (II, Y = S) and gave, after 18 hr., an 81% yield of the anil oxide (VII). It did not however react with benzaldehyde, *p*-nitrobenzaldehyde or 2,6-dinitrobenzaldehyde.

EXPERIMENTAL

Light petroleum had b.p. 40–60°.

Triphenylphosphonium tetraphenylcyclopentadienylide from 5-bromo-1,2,3,4-tetraphenylcyclopentadiene. The bromocyclopentadiene (0·45 g) and triphenylphosphine (0·786 g) were heated on an oil-bath at 150° for 10 min. The mixture was cooled and addition of ether (15 ml) produced a yellow ppt of triphenyl(2,3,4,5-tetraphenylcyclopentadienyl)phosphonium bromide (0·68 g, 96%). To a soln of this salt in EtOH (8 ml) perchloric acid (70%, 0·2 ml) was added, followed by ether (15 ml). The resultant perchlorate (0·66 g, 90%) was filtered off, washed with ether, recrystallized from MeOH and was identical (m.p., IR) with authentic samples.[6,7] 2N NaOH (2 ml) was added to a soln of this perchlorate (0·365 g) in EtOH (15 ml) and the mixture was shaken vigorously for 10 min and then kept for 3 hr. The pale yellow ppt (0·29 g, 93%) was filtered off and recrystallized from benzene-nitromethane to give the ylide, identical (m.p., IR) with authentic samples.[6,7]

Ethanolysis of triphenylstibonium tetraphenylcyclopentadienylide. A soln of the ylide (0·36 g) in EtOH (15 ml) was heated under reflux for 5 min and cooled. Crystals of 1,2,3,4-tetraphenylcyclopentadiene separated (0·156 g, 85%). The filtrate was evaporated, water was added to the residue and the mixture was boiled for 3 min, decanted while hot and cooled. Triphenylstibine oxide (0·074 g, 40%) precipitated.

Attempted alkaline cleavage of tetraphenylcyclopentadienylides. The triphenylarsonium ylide (I, X = As: 0·34 g) was added to a soln of NaOH (1 g) in EtOH (25 ml) and the mixture was heated under reflux for 18 hr. It was then poured into water (50 ml) and extracted with chloroform. The extract was washed with water and dried (Na_2SO_4). Solvent was removed and ether was added to the residue: the solid ylide was thus recovered quantitatively. Similar results were obtained when I (X = P) and II (Y = S or Se) were used.

pK_a Determinations. pK_a determinations were carried out spectrophotometrically, using aqueous EtOH (95%) as solvent throughout. (*cf* ref 15). Solns of each ylide perchlorate (*ca* 4 mg) in EtOH (95%, 10 ml) were made and aliquots (1 ml) of each soln were diluted to 10 ml with, severally, 0·1M HCl, 0·1M KOH, and an appropriate buffer soln made either from tris(hydroxymethyl)aminomethane hydrochloride or formic acid-potassium hydroxide and whose apparent pH was determined potentiometrically. The absorbance of each set of 3 solns was recorded at 5 wavelengths in the region where the ylides absorb strongly (260-350 nm) and the conjugate salts are nearly transparent. The pK_a values were then calculated from these absorbances,[26] and are the averages of determinations using at least 2 different buffers, the value for each buffer being the average of the values obtained at each of the 5 different wavelengths.

Reaction of ylides (I) *and* (II) *with benzaldehyde.* Solns of equiv amounts (1 mmole) of the ylides and freshly distilled benzaldehyde in CCl_4 (25 ml) were heated under reflux for 18 hr. Solvent was then removed. In the case of the triphenylphosphonium, diphenylsulphonium and diphenylselenonium ylides, following addition of ether to the residue, the original ylides were filtered off and recovered quantitatively.

In the case of the triphenylarsonium ylide, ether was added, unreacted ylide (0·3 g) was filtered off, the ether was evaporated and the residue, in a small amount of benzene, was applied to an alumina column. Elution with light petroleum-benzene (4:1) gave 2,3,4,5,6-pentaphenylfulvene (0·073 g, 16%) as red-brown prisms, m.p. and mixed m.p. 197–199°. A second fraction, eluted by benzene, gave after removal of solvent and trituration with EtOH, tetraphenylcyclopentadienone (0·004 g, 1·3%), black crystals, m.p. 214–216°. Finally elution with MeOH gave a yellow soln from which solvent was evaporated. Water was added to the residue and the mixture was boiled for 5 min. When it was cooled triphenylarsine oxide (0·026 g, 8%), m.p. 192°, crystallized out. When chloroform replaced CCl_4 as solvent similar results were obtained, including a 17% yield of fulvene.

In the case of the triphenylstibonium ylide, the solvent was removed and a soln of the residue in a small amount of benzene was applied to an alumina column. Light petroleum-benzene (4:1) eluted a red band and a yellow band. Solvent was removed from the former and the residue was recrystallized from AcOH to give 2,3,4,5,6-pentaphenylfulvene (0·184 g, 40%). Removal of solvent from the second fraction, followed by trituration with EtOH, gave 1,2,3,4-tetraphenylcyclopentadiene (0·055 g, 15%). Elution with methanol provided triphenylstibine oxide (0·092 g, 25%).

Reaction of ylides (I) *and* (II) *with* p-*nitrobenzaldehyde.* A mixture of the ylide (1 mmole) and *p*-nitrobenzaldehyde (0·151 g, 1 mmole) in CCl_4 (25 ml) was heated under reflux for 4 hr. Removal of the solvent and addition of ether provided a quantitative recovery of the triphenylphosphonium, diphenylsulphonium and diphenylselenonium ylides. The products from the triphenylarsonium and triphenylstibonium ylides were each dissolved in the minimum amount of benzene and applied to an alumina column. Elution with benzene gave a brown band and soln, wherefrom removal of solvent and trituration with nitromethane produced red crystals of 6-*p*-nitrophenyl-2,3,4,5-tetraphenylfulvene, m.p. and mixed m.p. 232–234° (0·48 g, 95%, from arsonium ylide: 0·49 g, 99%, from stibonium ylide). Further elution of the column with MeOH gave respectively, triphenylarsine oxide (0·12 g, 41%) and triphenylstibine oxide (0·184 g, 50%).

6-p-*Nitrophenyl*-2,3,4,5-*tetraphenylfulvene.* A mixture of tetraphenylcyclopentadiene (0·749, 2 mmole), *p*-nitrobenzaldehyde (0·377 g, 2·5 mmole), NaOH (2 g) and MeOH (50 ml) was heated under reflux for 6 hr. The brown ppt was filtered off and recrystallized from nitromethane to give the fulvene (0·6 g, 60%) as red-brown needles, m.p. 232–234° (lit.[27] 227–228°), $\lambda_{max}(CHCl_3)$ 273, 353 nm (log ε = 3·59, 3·45). (Found: C, 84·0; H, 4·8; N, 3·5. Calc. for $C_{36}H_{25}NO_2$: C, 84·0; H, 5·6; N, 3·2%).

Reaction of ylides (I) *and* (II) *with nitrosobenzene*

(a) A soln of I (X = As: 0·67 g, 1 mmole) and nitrosobenzene (0·107 g, 1 mmole) in benzene (25 ml) was heated under reflux for 6 hr, a further portion of nitrosobenzene (0·054 g) being added after 3 hr. The soln was then concentrated to 5 ml and chromatographed on alumina. Elution with light petroleum-benzene (2:1) removed a red band which TLC showed to be a mixture of a red and a colourless product. Light petroleum-benzene (1:5) then removed a trace amount of tetraphenylcyclopentadienone. Benzene eluted a green band as a red-green soln, which on removal of solvent and trituration with EtOH (5 ml) gave VII (0·23 g, 48%), identical (m.p., IR) with an authentic sample. Finally elution with chloroform removed a yellow band which, on removal of solvent and recrystallization from water afforded triphenylarsine oxide (0·032 g, 10%). The initially eluted red band was treated thus. Alumina (5 g) was added to the eluted soln and solvent was evaporated off. The residue was applied to an alumina column with light petroleum. Light petroleum-benzene (10:1) eluted a colourless product which, after removal of solvent and recrystallization from EtOH, proved to be triphenylarsine (0·10 g, 33%). Light petroleum-benzene (1:2) then removed a red product which was recrystallized from nitromethane and was identical (m.p., IR) with an authentic sample of VI (0·16 g, 35%), crimson plates.

(b) A soln of I (X = Sb: 0·36 g, 0·5 mmole) and nitrosobenzene (0·053 g, 0·5 mmole) in benzene (15 ml) was heated under reflux for 10 min. Solvent was removed and the residue was chromatographed on alumina. Light petroleum-benzene (1:1) removed triphenylstibine (0·12 g, 70%), benzene removed a trace of tetraphenylcyclopentadienone and chloroform eluted VII (0·19 g, 81%).

(c) When a soln of II (Y = S; 0·55 g, 1 mmole) and nitrosobenzene (0·106 g, 1 mmole) in benzene (20 ml) had been heated under reflux for 18 hr little change of colour occurred. After 3 hr furhter nitrosobenzene (0·05 g) was added. Solvent was removed and ether (10 ml) added and unchanged ylide (0·37 g, 67%) was filtered off. Chromatography of the residue on alumina with chloroform gave VII (0·024 g, 5%).

(d) By the method described in (c), II (Y = Se; 0·601 g, 1 mmole) gave VII (0·38 g, 80%).

(e) The ylide I (X = P) was recovered quantitatively [*cf* para (c)] from attempted reactions with nitrosobenzene.

2,3,4,5-*Tetraphenylcyclopentadienone anil* (VI). NaOEt [1 ml; from Na (0·5 g) in EtOH (10 ml)] was added to a soln of 1,2,3,4-tetraphenylcyclopentadiene (0·74 g; 2 mmole) and nitrosobenzene (0·214 g, 2 mmole) in benzene (20 ml) and the mixture was heated under reflux for 10 min, cooled, diluted with light petroleum, and kept at room temp. Red crystals separated which were filtered off and recrystallized from nitromethane to give the *anil* (0·35 g, 38%), crimson plates, m.p. 235°, λ_{max}(CHCl$_3$) 256, 325 sh, 450 nm (log ε = 3·76, 3·23, 2·65). (Found: C, 90·8; H, 5·9; N, 3·2. $C_{35}H_{25}N$ requires: C, 91·6; H, 5·6; N, 3·1%).

N-*Phenyl*-2,3,4,5-*tetraphenylcyclopentadienone ketoxime*. (VII). A soln of diazo-2,3,4,5-tetraphenylcyclopentadiene (0·79 g, 2 mmole) and nitrosobenzene (0·214 g, 2 mmole) in chloroform (20 ml) was heated under reflux for 18 hr, a further quantity of nitrosobenzene (0·107 g) being added after 6 hr. After removal of solvent the residue was applied in benzene to an alumina column. Elution with light petroleum-benzene (1:1) removed unchanged diazo-compound (0·31 g); benzene removed a trace of tetraphenylcyclopentadienone and a small amount of nitrosobenzene. Chloroform then eluted a green band. Removal of solvent and addition of ethanol (10 ml) produced the khaki-green *ketoxime* (0·19 g, 22%), which was filtered off and had m.p. 224–226° (from n-propanol), λ_{max}(CHCl$_3$) 250, 363 nm (log ε = 3·53, 3·45). (Found: C, 88·2; H, 5·1; N, 2·9. $C_{35}H_{25}NO$ requires: C, 88·4; H, 5·25; N, 2·9%).

Conversion of ketoxime (VII) *into anil* (VI). The ketoxime (0·237 g, 0·5 mmole) and triphenylphosphine (0·262 g, 1 mmole) in benzene (20 ml) were heated under reflux for 4 hr. Solvent was evaporated and the residue was chromatographed on alumina. Light petroleum-benzene (1:1) removed triphenylphosphine and benzene eluted the anil (0·184 g, 80%), identical with an authentic sample.

Attempted reaction of ylides (I) *with dichlorocarbene*. t-BuOK (0·3 g) was added to a soln of I (X = As; 0·335 g, 0·5 mmole) in benzene (20 ml), which was then stirred at room temp while chloroform (0·3 ml) was added and for a further 48 hr. The soln was then filtered, washed well with water and dried (Na_2SO_4). Solvent was evaporated. Addition of ether produced a ppt of unchanged ylide (0·25 g, 75%). Chromatography of the evaporated filtrate (alumina; light petroleum, benzene) gave triphenylarsine (0·01 g) and tetraphenylcyclopentadienone (0·018 g) but no 6,6-dichloro-2,3,4,5-tetraphenylfulvene. Similar results were obtained from I (X = P or Sb) save that in the latter case, 1,2,3,4-tetraphenylcyclopentadiene was recovered instead of the ylide.

Methylphenylsulphonium tetraphenylcyclopentadienylide (VIII) *and its perchlorate*. Diazotetraphenylcyclopentadiene (3·96 g) was heated in thioanisole (3·72 g) at 150° for 10 min under oxygen-free nitrogen. Ether (15 ml) was added to the cooled mixture and the very pale yellow *ylide* (3·2 gm 65%) separated and was filtered off. It had m.p. 204–206° (dec) (from light petroleum-benzene), λ_{max} (EtOH) 294, 347sh nm (log ε = 4·30, 3·61), τ (CDCl$_3$) 2·85m (25H), 7·24s (3H). (Found: C, 87·9; H, 5·1. $C_{36}H_{28}S$ requires: C, 87·8; H, 5·7%). Addition of perchloric acid (70%, 1 ml) to a soln of this ylide (0·49 g) in EtOH (10 ml) produced an immediate yellow ppt. Ether (10 ml) was added and the *perchlorate* was filtered off, washed with EtOH and had m.p. 155° (dec), yellow needles (from AcOH with addition of ether to initiate crystallization), λ_{max}(EtOH) 252, 335 nm (log ε = 4·20, 3·61). (Found: C, 72·8; H, 4·95. $C_{36}H_{29}ClO_4S$ requires: C, 73·0; H, 4·9%).

Reaction of methylphenylsulphonium ylide (VIII) *with nitrosobenzene*. A soln of the ylide (0·49 g, 1 mmole) and nitrosobenzene (0·106 g, 1 mmole) in benzene (20 ml) was heated under reflux for 15 hr, further nitrosobenzene (0·05 g) being added after 3 hr. Solvent was removed, ethanol (15 ml) was added to the residue, and the mixture was boiled for 2 min. Filtration of the hot mixture removed unreacted ylide (0·05 g). From the cooled filtrate crystals of N-phenyl-2,3,4,5-tetraphenylcyclopentadienone ketoxime (0·385 g, 81%) separated out.

ACKNOWLEDGEMENTS

We are grateful to the University of St. Andrews and the S.R.C. for research scholarships given, respectively, to M.I.C.S. and B.H.F.

REFERENCES

[1] D. Lloyd and M. I. C. Singer, *Chem. & Ind.* 787 (1967)

[2] D. Lloyd and M. I. C. Singer, *Chem. Comm.* 1042 (1967)

[3] D. Lloyd and M. I. C. Singer, *Ibid.* 390 (1967)

[4] B. H. Freeman and D. Lloyd, *Ibid.* 924 (1970)

[5] I. B. M. Band, D. Lloyd, M. I. C. Singer and F. I. Wasson, *Ibid.* 544 (1966); D. Lloyd and M. I. C. Singer, *J. Chem. Soc.* (C) 2939 (1971)

[6] D. Lloyd, M. I. C. Singer, M. Regitz and A. Liedhegener, *Chem. & Ind.* 324 (1967)

[7] M. Regitz and A. Liedhegener, *Tetrahedron* **28**, 2701 (1967)

[8] D. Lloyd and M. I. C. Singer, *Chem. & Ind.* 510 (1967)

[9] D. Lloyd and M. I. C. Singer, *Ibid.* 118 (1967)

[10] D. Lloyd and M. I. C. Singer, *J. Chem. Soc.* (C) 2941 (1971)

[11] D. Lloyd and J. S. Sneezum, *Chem. & Ind.* 1221 (1955); *Tetrahedron* **3**, 334 (1958)

[12] E. M. Kosower and B. G. Ramsey, *J. Am. Chem. Soc.* **81**, 856 (1959)

[13] G. Wittig and M. Rieber, *Liebigs Ann.* **562**, 187 (1949); G. Wittig and K. Clauss, *Ibid.* **577**, 26 (1952); G. Wittig and D. Hellwinkel, *Chem. Ber.* **97**, 741, 769, 789 (1964)

[14] A. Wm. Johnson and R. T. Amel, *Canad. J. Chem.* **46**, 461 (1968)

[15] A. Wm. Johnson, S. Y. Lee, R. A. Swor and L. D. Royer, *J. Am. Chem. Soc.* **88**, 1953 (1966)

[16] M. Henry and G. Wittig, *Ibid.* **82**, 563 (1960)

[17] See also A. Wm. Johnson, *Ylid Chemistry* pp. 296–7, 301–2, Academic Press, New York and London (1966)

[18] N. A. Nesmeyanov, V. V. Pravdina and O. A. Reutov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk* 1474 (1965); A. Wm. Johnson, ref. 17, p. 298; S. Trippett and M. A. Walker, *J. Chem. Soc.* (C) 1114 (1971)

[19] A. Wm. Johnson and H. Schubert, *J. Org. Chem.* **35**, 2678 (1970)

[20] A. Lowenbein and G. Ulich, *Ber. Dtsch. Chem. Ges.* **58**, 2662 (1925)

[21] H. Staudinger and K. Miescher, *Helv. Chim. Acta* **2**, 554 (1919)

[22] See E. Ochiai, *Aromatic Amine Oxides* pp. 114ff. Elsevier, Amsterdam (1967)

[23] A. Wm. Johnson, ref. 17, pp. 284 ff., 296

[24] R. Oda, Y. Ito and M. Okano, *Tetrahedron Letters* 7 (1964)

[25] A. Wm. Johnson and R. B. LaCount, *Tetrahedron* **9**, 130 (1960)

[26] L. A. Flexser, L. P. Hammett and A. Dingwall, *J. Am. Chem. Soc.* **57**, 2103 (1935)

[27] D. Taber, N. Picus, E. I. Becker and P. E. Spoerri, *Ibid.* **77**, 1010 (1955)