Rapid Intramolecular Collapse of Betaines derived from 5-Phenyldibenzophospholes as compared with those derived from Acyclic Triarylphosphines; Mechanism of the Wittig Reaction in Protic Solvents

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The reaction of 5-phenyldibenzophosphole or its 2,8-dimethoxy-derivative (VII; R = H or OMe) with styrene oxide in ethanol yields solely the normal Wittig products, styrene and the 5-phenyldibenzophosphole 5-oxide (VIII; R = H or OMe). In contrast, the corresponding reactions of the acyclic triarylphosphines, triphenylphosphine and bis-(p-methoxyphenyl)phenylphosphine, predominantly yield rearranged phosphine oxides, the normal Wittig products being formed only to a small extent. These results are accommodated in a scheme in which rapid collapse of the initially formed cyclic, ring-strained, phospholium betaine (XI; R = H or OMe) occurs to form the normal Wittig products via the unstrained spiro-oxaphosphetan (XII; R = H or OMe). In the case of acyclic phosphonium betaines, collapse via the oxaphosphetan does not occur so rapidly, and the alternative route involving protonation and dehydration of the betaine to form the vinylphosphonium salt (IV) is followed. Hydrolysis of the latter predominantly yields the rearranged phosphine oxides (V).

The reaction of 5-phenyldibenzophosphole with phenylacetylene in wet diethylene glycol proceeds via the vinylpholium salt (XIV; R = X = Ph) to form the ring-expanded phosphine oxide (XVI; R = X = Ph) and the ring-opened phosphine oxide (XVII).

THE Wittig reaction between a phosphonium salt and a carbonyl compound in the presence of alkoxide ion in protic solvents may occur by either of two competing mechanistic courses (see Scheme). On the one hand, the initially formed betaine (I) may undergo rate-determining collapse to the normal Wittig products (*i.e.* olefin and phosphine oxide) via the oxaphosphetan (II).[1] Alternatively, protonation of the betaine may occur to give the hydroxyethylphosphonium salt (III) which subsequently may eliminate water to form the vinylphosphonium salt (IV). Hydrolysis of the latter may then take place by one or more of the following routes: (i) with cleavage of the vinylic substituent to give the normal Wittig products;[2] (ii) with migration of an aryl group from phosphorus to adjacent carbon to form the rearrangement product (V);[3] (iii) with loss of a substituent other than the vinylic group to form a vinylphosphine oxide (VI).[4,5]

The preferred course has been shown to depend on (i) the nature of the substituents R[1], R[2], and R[3];[2,3,6] (ii) the steric and electronic character of the P-substituents.[5,7]

When the P-substituents are strongly electron-withdrawing, the phosphonium centre is highly electrophilic, and collapse of the betaine (I) via the oxaphosphetan (II) is favoured.[7] When the P-substituents are less strongly electron-withdrawing or bulky, *e.g.* t-butyl, the rate of intramolecular collapse is reduced, and the alternative route involving protonation and dehydration of the betaine to form the vinylphosphonium salt (IV) is favoured. We now show that enclosure of the phosphorus atom in a small ring also favours rapid intramolecular collapse of the betaine to form normal Wittig products.

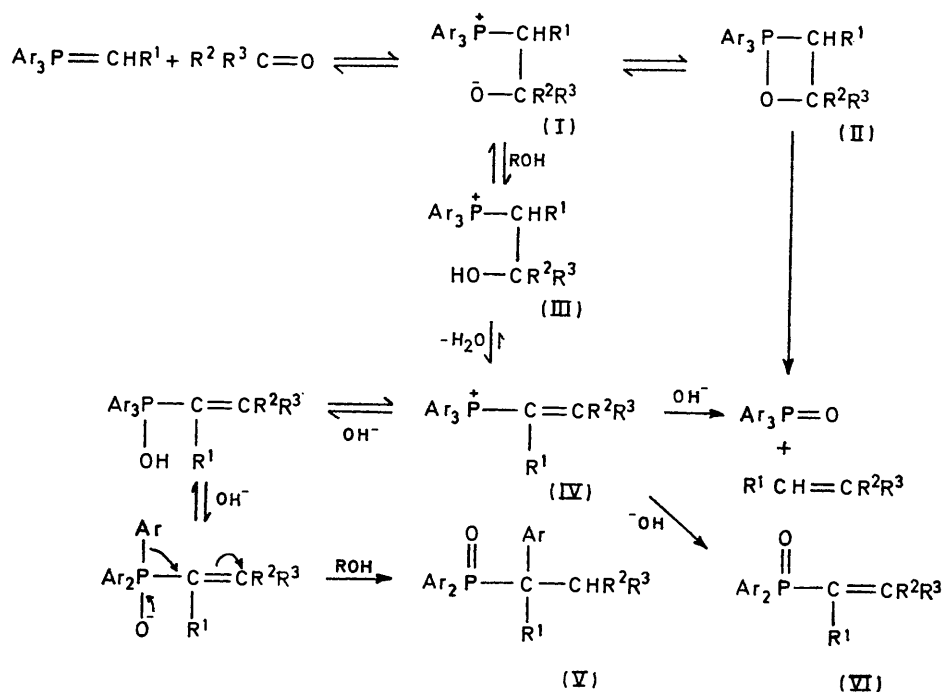The reaction of methyltriphenylphosphonium iodide

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[2] E. E. Schweizer, D. M. Crouse, T. Minami, and A. T. Wehman, *Chem. Comm.*, 1971, 1000.

[3] E. M. Richards and J. C. Tebby, *J. Chem. Soc. (C)*, 1971, 1059.

[4] J. W. Rakshys and S. V. McKinley, *Chem. Comm.*, 1971, 1336.

[5] D. W. Allen, P. Heatley, B. G. Hutley, and M. T. J. Mellor, *Tetrahedron Letters*, 1974, 1787.

[6] D. J. H. Smith and S. Trippett, *J.C.S. Chem. Comm.*, 1972, 191.

[7] D. W. Allen, B. G. Hutley, and T. C. Rich, *J.C.S. Perkin II*, 1973, 820.

with benzaldehyde in the presence of ethanolic sodium ethoxide yields predominantly the rearrangement product (V; Ar = R^2 = Ph, R^1 = R^3 = H). This product is
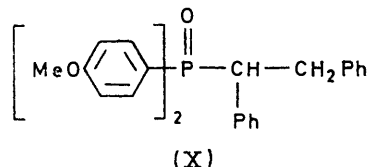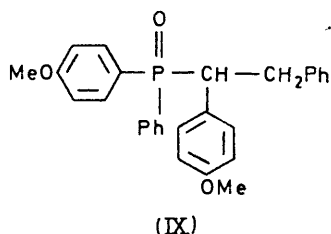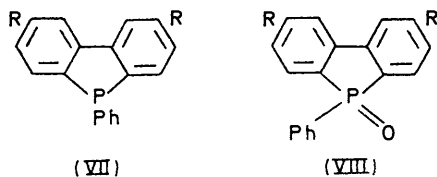
course of the reactions between the 5-phenyldibenzo-phospholes (VII; R = H or OMe) and styrene oxide, in ethanol.

SCHEME

also isolated from the reaction of triphenylphosphine with styrene oxide in ethanol.[8] Both reactions involve

initial formation of the betaine (I), which after proton-ation loses water to form the vinylphosphonium salt. Hydrolysis of the latter occurs with $P \longrightarrow C$ aryl migration to form (V).[3] We have now investigated the

In contrast to that of triphenylphosphine, the reaction of 5-phenyldibenzophosphole (VII; R = H) with styrene oxide yields solely the normal Wittig products, styrene and the phosphole oxide (VIII; R = H). Similarly, the reaction of the 2,8-dimethoxy-derivative (VII; R = OMe) with styrene oxide yields styrene and the oxide (VIII; R = OMe), whereas the corresponding reaction of the acyclic bis-(p-methoxyphenyl)phenylphosphine yields mainly a mixture of rearrangement products, (IX) and (X), together with a smaller amount of the normal Wittig products.

The formation of the normal Wittig products in the reactions of the dibenzophospholes (VII) can be accom-modated in terms of rapid intramolecular attack by the O^- of the betaine (XI) at the phosphonium centre to form the spiro-oxaphosphetan (XII) in which both the four- and the five-membered ring span apical–equatorial posi-tions in the trigonal bipyramidal phosphorane, followed by collapse of the latter to the phosphole oxide and styrene. We have shown previously [9] that dibenzophos-pholium salts undergo alkaline hydrolysis extremely rapidly in comparison with their acyclic analogues, nucleophilic attack at phosphorus being facilitated by the formation of the hydroxyphosphorane in which the five-membered ring spans the apical and equatorial positions.

Intramolecular collapse of betaines derived from acyclic phosphorus compounds occurs more slowly, and the alternative route involving protonation of the betaine

[8] S. Trippett and B. J. Walker, *J. Chem. Soc.*, 1966, 887.
[9] D. W. Allen and I. T. Millar, *J. Chem. Soc. (B)*, 1969, 263.

is able to occur, leading to the vinylphosphonium salt and subsequently the rearrangement products.

(XI)   (XII)

(XIII)
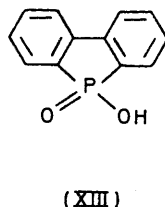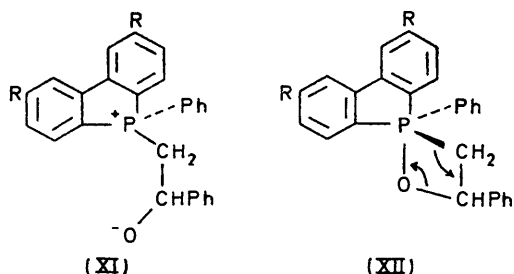
Richards and Tebby [10] have shown that when a 5-substituted dibenzophosphole reacts with methyl propiolate (an electrophilic acetylene) in the presence of

(XIV)   (XV)

(XVII)   (XVI)
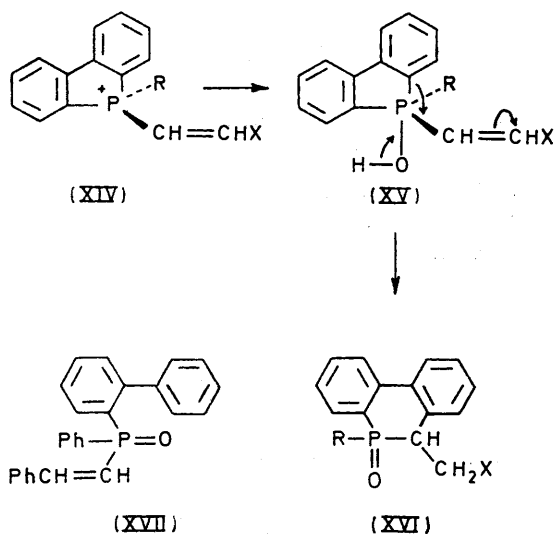
water, the initially formed vinylphosphonium salt (XIV; R = Me or Ph, X = CO₂Me) undergoes alkaline hydrolysis *via* the oxyphosphorane (XV) with migration of an apical *P*-aryl group to the equatorially disposed carbon atom of the vinyl group, resulting in ring expansion to form the dibenzophosphorin oxide (XVI; R = Me or

Ph, X = CO₂Me). In order to investigate the ultimate fate of the vinylphospholium salt (XIV; R = Ph, X = Ph), which could arise in the course of the reaction of 5-phenyldibenzophosphole (VII; R = H) with styrene oxide, we have studied the reaction of the phosphole with phenylacetylene in refluxing, wet diethylene glycol. The major product isolated was the ring-expansion product (XVI; R = X = Ph) (26% yield); a much smaller amount of the ring-opened vinylphosphine oxide (XVII) (6% yield) was also isolated. Thus, the vinylphospholium salt (XIV; R = X = Ph) is undergoing subsequent hydrolysis either with migration of the apical *P*-aryl group to carbon to form (XVI) or with apical cleavage to form (XVII). We have shown previously that ring opening occurs in the alkaline hydrolysis of other 5-phenyldibenzophospholium salts.[11]

Clearly, the reaction of 5-phenyldibenzophospholes with styrene oxide in ethanol cannot involve the vinylphospholium salts to any significant extent, and the formation of the normal Wittig products supports the above suggestion of rapid intramolecular collapse of the initially formed betaines. It is of interest to consider the factors promoting betaine collapse. It seems likely that the position of the equilibrium between the betaine (XI) and the spiro-oxaphosphetan (XII) lies well in favour of the latter. It has been demonstrated that spirophosphoranes show a greater tendency to exist in the penta-coordinate state than is the case for the corresponding monocyclic systems.[12] A major factor involved here is relief of strain in the cyclic dibenzophospholium betaine (XI) on assuming the oxaphosphetan struture (XII), in which the endocyclic CPC angle is 90°. In the phospholium betaine (XI), there is likely to be considerable ring strain. A recent *X*-ray study [13] of the related cyclic phosphinic acid (XIII) has shown that the corresponding bond angle is 93·4°. The increase in ring strain on passing from the parent dibenzophosphole (in which the bond angle is likely to be *ca.* 90° by analogy with that reported for 1-benzylphosphole [14]) to the quaternary derivative, may well be responsible for the reduced rate of quaternisation of 5-phenyldibenzophosphole relative to triphenylphosphine,[15] and also for the increased rate of retrocyanoethylation of cyanoethylphospholium salts as compared with their acyclic analogues,[16] rather than an effect based on phosphole aromaticity.

The increased proportion of *cis*-olefin formed in the reactions of aldehydes with stabilised dibenzophospholium ylides has been attributed [17] to the reduced equilibration of the *threo*- and *erythro*-isomers of the dibenzophospholium betaine caused by an increase in the rate of betaine decomposition (*via* the more stable spiro-oxaphosphetan). Our present results support this suggestion.

[10] E. M. Richards and J. C. Tebby, *J. Chem. Soc. (C)*, 1971, 1064; *Chem. Comm.*, 1967, 957.
[11] D. W. Allen and I. T. Millar, *J. Chem. Soc. (C)*, 1969, 252; D. W. Allen, I. T. Millar, and F. G. Mann, *J. Chem. Soc. (C)*, 1967, 1869.
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[15] D. W. Allen, J. R. Charlton, and B. G. Hutley, *Phosphorus*, 1975, **5**, 9.
[16] W. B. Farnham and K. Mislow, *J.C.S. Chem. Comm.*, 1972, 469.
[17] I. F. Wilson and J. C. Tebby, *J.C.S. Perkin I*, 1972, 2713.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded at 60 MHz on a JEOL spectrometer. G.l.c. analyses were carried out with a Pye-Unicam G.C.V. chromatograph equipped with a 5 ft column of 8% Apiezon L on Celite, and a flame ionisation detector. T.l.c. was carried out with preparative plates having a 1 mm thickness of silica gel CT. Each plate was developed several times in 1 : 1 petroleum (b.p. 60—80°)–ethyl acetate. Mass spectra were recorded on an A.E.I. MS30 instrument at 70 eV.

Reactions of Phosphines with Styrene Oxide in Ethanol.— (*A*) 5-Phenyldibenzophosphole (0·26 g) and styrene oxide (0·24 g, 2 mol. equiv.) were heated under reflux in ethanol (2 ml) for 24 h. G.l.c. analysis of the resulting solution confirmed the presence of styrene (47%). Evaporation of the solution and preparative t.l.c. of the residue gave 5-phenyl-dibenzophosphole 5-oxide (VIII; R = H) (40%), m.p. 166—167° (lit.,[18] 166—168°); *m/e* 276 (M^+); i.r. spectrum identical with that of an authentic specimen. Although the developed t.l.c. plate showed two other faint bands of similar polarity to (VIII; R = H), no other phosphine oxides could be isolated or identified.

(*B*) 2,8-Dimethoxy-5-phenyldibenzophosphole [19] (0·126 g) and styrene oxide (0·061 g, 1 mol. equiv.) were heated under reflux in ethanol (1 ml) for 24 h. G.l.c. analysis of the resulting solution confirmed the presence of styrene and evaporation gave 2,8-*dimethoxy-5-phenyldibenzophosphole 5-oxide* (VIII; R = OMe) (49%), m.p. 255—257° (Found: C, 69·1; H, 5·4; $C_{20}H_{17}O_3P, 0·5H_2O$ requires C, 69·55; H, 5·2%); τ (CDCl$_3$) 2·42 (11H, m) and 6·02 (6H, s); *m/e* 336 (M^+). No other phosphine oxides were isolated or detected.

(*C*) Bis-(*p*-methoxyphenyl)phenylphosphine (0·322 g) and styrene oxide (0·240 g, 2 mol. equiv.) were heated under reflux in ethanol (2 ml) for 24 h. G.l.c. analysis of the resulting solution indicated the formation of styrene (25%). Evaporation of the solution followed by preparative t.l.c. of the residue gave bis-(*p*-methoxyphenyl)phenylphosphine

oxide (23%), identical with an authentic specimen, and a mixture of the isomeric phosphine oxides (IX) and (X) (70% total yield), which could not be separated further (Found: C, 76·05; H, 6·05. Calc. for $C_{28}H_{27}O_3P$: C, 76·0; H, 6·15%); τ (CDCl$_3$) 1·8—3·5 (aromatic H), 6·2 (s, CH$_3$O), 6·4 (s, CH$_3$O), and 6·6 (m, benzylic H); *m/e* 442 (M^+), 262 [(*p*-MeOC$_6$H$_4$)$_2$POH)], 232 [*p*-MeOC$_6$H$_4$(Ph)POH], 210 (*p*-MeOC$_6$H$_4$·CH=CHPh), and 180 (PhCH=CHPh), in accord with the specific fragmentation pattern established for such compounds.[20]

Reaction of 5-Phenyldibenzophosphole with Phenylacetylene. —5-Phenyldibenzophosphole (0·260 g), phenylacetylene (0·20 g, 2 mol. equiv.), and water (0·05 ml) were heated together under reflux in wet diethylene glycol (2 ml) for 24 h. The solvent was then evaporated off under reduced pressure, and the tarry residue separated by preparative t.l.c. to give (a) 6-*benzyl-5,6-dihydro-5-phenyldibenzophosphorin 5-oxide* (XVI; R = X = Ph) (26%), m.p. 136—137° [from petroleum (b.p. 40—60°)–toluene] (Found: C, 82·3; H, 5·8. $C_{26}H_{21}OP$ requires C, 82·05; H, 5·55%); *m/e* 380 (M^+), 303 (M − Ph), 265, and 251; τ (CDCl$_3$) 1·5—3·7 (18H, m) and 6·0—7·6 (3H, m); λ$_{max.}$ (EtOH) 217 (ε 34,865), 235infl. (24,700), 268 (8550), 273 (9405), and 284 nm (6650) (u.v. spectrum very similar to those of other dibenzophosphorin 5-oxides,[10,11] and markedly different from those of dibenzo-phosphole oxides and ring-opened biphenyl-2-ylphosphine oxides [10,11]); and (b) biphenyl-2-yl(phenyl)(styryl)phosphine oxide (XVII) (6%), isolated as a gum which resisted crystallisation; *m/e* 380 (M^+), 303 (M − Ph), 277 (M − PhCH=CH), and 265; τ (CDCl$_3$) 2·0—3·0 (aromatic H only); λ$_{max.}$ (EtOH) 212 (ε 36,337) and 269 nm (19,000) (u.v. spectrum showed considerable differences from those of dibenzo-phosphole and dibenzophosphorin oxides [10,11]).

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[20] D. W. Allen, J. C. Tebby, and D. H. Williams, *Tetrahedron Letters*, 1965, 2361.