Dibenzophospholium Salts and Ylides. Preparation, Properties, and Wittig Olefin Synthesis

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The spectral properties, hydrolyses, and Wittig olefin syntheses of *P*-benzoyl- and -alkoxycarbonyl-methylene-*P*-phenyldibenzophospholes and their salts are compared with those of the corresponding triphenylphosphonium derivatives. The mechanistic implications of the differences in stereoselectivity and of the similarity of the kinetics of the Wittig reaction for the two series are discussed.

OUR previous studies of the dibenzophosphole ring systems have dealt with the expansion of the heterocyclic ring,[1] the preparation of pentaco-ordinate derivatives,[2] and the [1]H n.m.r.[3] and [31]P n.m.r.[4] spectra. We now report the preparation and properties of the salts and stabilised ylide derivatives of *P*-phenyldibenzophosphole.

The *P*-phenyldibenzophospholium salt precursors (1) were prepared from phenyldibenzophosphole and suitable α-halogenocarbonyl compounds in the usual manner. The benzoylmethylenephosphorane (2) was

prepared in methanolic solution by treatment of compound (1; R = Ph, X = Br) with sodium methoxide. The ylide precipitated from solution. The methoxycarbonylphosphorane (3) was converted into the oxide by this reagent and was therefore prepared by use of sodium hydride or lithium diethylamide as base. The diphosphorane (4) was prepared from *P*-phenyldibenzophosphole and dimethyl acetylenedicarboxylate.[5]

The i.r. spectra confirmed the ylide nature of the

[1] E. M. Richards and J. C. Tebby, *J. Chem. Soc.* (*C*), 1971, 1064; *Chem. Comm.*, 1967, 957.

[2] E. M. Richards and J. C. Tebby, *J. Chem. Soc.* (*C*), 1970, 1425.

[3] D. W. Allen, I. T. Millar, and J. C. Tebby, *Tetrahedron Letters*, 1968, 745.
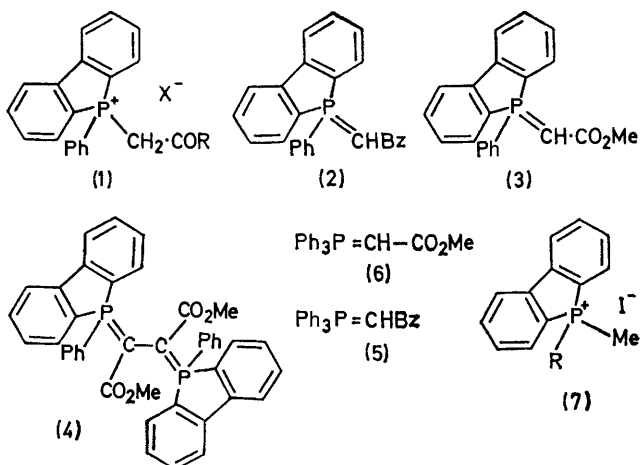
[4] D. W. Allen and J. C. Tebby, *J. Chem. Soc.* (*B*), 1970, 1527.

[5] M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc.* (*C*), 1967, 2442; M. A. Shaw and J. C. Tebby, *ibid.*, 1970, 5.

products. They contained the usual low frequency carbonyl bands, at 1500 for (2) and 1620 cm^{-1} for (3), but the wavenumbers were slightly lower than those of the analogous triphenylphosphoranes. This suggests

that there is less p_π–d_π back bonding to phosphorus in the heterocyclic ylides.

The ^{1}H n.m.r. spectra of the salts (1) and the ylides supported their assigned structures. The PCH coupling constants (see Table 1) of the heterocyclic ylides (2) and

TABLE 1

PCH coupling constants

Heterocycle	J_{PCH}	Triphenylphosphon-ium derivative	J_{PCH}
(7; R = Ph)	(−)14·5	Ph$_3$P̟Me I$^-$	(−)13·5
(1; R = OMe, X = Cl)	(−)14	Ph$_3$P̟·CH$_2$·CO$_2$Me Cl$^-$	(−)13·5
(1; R = Ph, X = Br)	(−)12	Ph$_3$P̟·CH$_2$Bz Br$^-$	(−)12·5
(3)	(+)26	Ph$_3$P=CH·CO$_2$Me (6)	(+)22
(2)	(+)28	Ph$_3$P=CH·Bz (5)	(+)25

(3) were considerably larger than those of the corresponding triphenylphosphoranes, (5) and (6) respectively, whereas there was relatively little difference between the two series of phosphonium salts. It is already well established [3,6] that the geminal PCH coupling constants of phosphonium salts are little affected by the inclusion of the phosphorus atom in a small ring. Thus a change in hybridisation of the phosphorus bonding orbitals would not be expected to be the cause of the increase in the coupling constant for the stabilised ylides (2) and (3). The increase is attributed to the increase in enolate character indicated by the i.r. spectra. This conclusion is based on the assumptions that the coupling constants are positive [7] and that the s-character of the bonding orbitals of the α-carbon atom is increased by increased enolate character. The latter assumption is supported by the larger coupling constant of the keto-phosphorane (5) than of the ester-phosphorane (6).

Surprisingly, the ylides (3) and (4) showed only singlet methoxy-group resonances in their n.m.r. spectra. The

[6] L. D. Quin and T. P. Burkett, *J. Amer. Chem. Soc.*, 1970, **92**, 4303.

resonance for (3) was unchanged in the temperature range −50 to +60°. These results contrast with those of triphenyl derivatives and suggest that the heterocyclic ylides are restricted to one conformation, probably that with the Z (cisoid) geometry.

The ^{31}P n.m.r. data are given in Table 2. Previous studies [4] of ^{31}P n.m.r. spectra of similar heterocyclic

TABLE 2

^{31}P N.m.r. chemical shifts of salts and ylides derived from triphenylphosphine or P-phenyldibenzophosphole

	δ_P (p.p.m.)	$\Delta\delta_P$
Methiodide (7; R = Me) [a]	−27	} 8
Ph$_2$P̟Me$_2$ I$^-$	−19	
Methiodide (7; R = Ph)	−21·5	} 3·5
Ph$_3$P̟Me I$^-$	−25	
Salt (1; R = Ph, X = Br)	−24	} 2
Ph$_3$P̟·CH$_2$Bz Br$^-$	−22	
Ylide (2)	−17	} 0
Ph$_3$P=CHBz	−17	

[a] Ref. 9.

phosphonium salts possessing at least two aliphatic substituents showed that the participation of the phosphorus atom in a five-membered ring produced an appreciable downfield shift ($\Delta\delta_P$ 8 p.p.m.) for the ^{31}P resonance. The monoalkyl salts [see (7; R = Ph)] show this effect to a much lesser extent. The ylide (2) had a chemical shift identical with that of the triphenyl-phosphorane, but this may well be due to cancelling of effects. A small deshielding effect produced by the ring could be cancelled by shielding produced by improved P̟···Ō stabilisation, as might be expected when a small ring is present and as suggested by the predominance of one conformation in the ester (3).

The u.v. spectra were dominated by bands arising from the dibenzophospholium chromophore. However the spectrum of the ylide (2) contained an additional inflection at 320 nm which is attributed to the de-localised carbanion.

The Wittig reactions (olefin synthesis) of the hetero-cyclic and 'acyclic' ylides have been compared. The stereochemical course of the reactions of the benzoyl ylides with benzaldehyde and acetaldehyde in benzene and ethanol solutions is summarised in Table 3. The heterocyclic ylide (2) gave more cis-olefin in all instances.

TABLE 3

cis-Olefin (%) obtained in Wittig reactions of benzoyl ylides

	Acetaldehyde at 25°		Benzaldehyde at 80°	
Ylide	Ethanol	Benzene	Ethanol	Benzene
(2)	21·4	27·6	12·9	22·1
(5)	14·0	11·8	10·1	11·6

The kinetics of the reactions with benzaldehyde in benzene have been studied. The rates for the benzoyl ylides at 80° were followed by i.r. spectroscopy and the

[7] I. F. Wilson and J. C. Tebby, *J.C.S. Perkin I*, 1972, 31; J. C. Tebby in 'Organophosphorus Chemistry,' Chem. Soc. Specialist Report, 1970, vol. 1, p. 296.

rates for the ethoxycarbonyl derivatives at 25° were followed by a more accurate titrimetric method. In both cases the rates of the heterocyclic and non-hetero-cyclic ylides were similar. The rate constants obtained by the titrimetric method were $2·8 \pm 0·2 \times 10^{-3}$ dm^{-3} mol s^{-1} for the heterocyclic ylide (8) and $1·73 \pm 0·05 \times 10^{-3}$ for ethoxycarbonylmethylenetriphenylphosphorane (9).[8] The rates were strongly dependent on the method of purification of benzene. This has been noted before.[8,9]

(8)   (12)
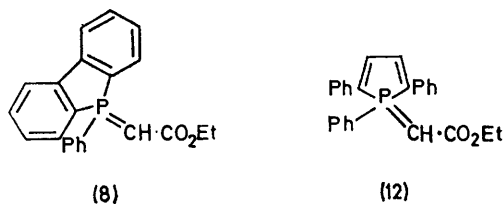
The similarity of the rates is in accord with the accepted mechanism of the Wittig reaction.[10] The formation of the betaines (10) (see Scheme 1) is the rate-determining step and is little affected by the participation of the phosphorus atom in a ring; the slight acceleration can be attributed to increased enolate character in the heterocycles. However the small ring does have an effect on the cis–trans ratio of the olefins formed in the Wittig reaction (see Table 3). The increased proportion of cis-olefin from the heterocyclic ylide is attributed to reduced equilibration of the threo- and erythro-isomers of (10) caused by an increase in their rates of decomposition via the (now stabilised) oxaphosphetan (11).
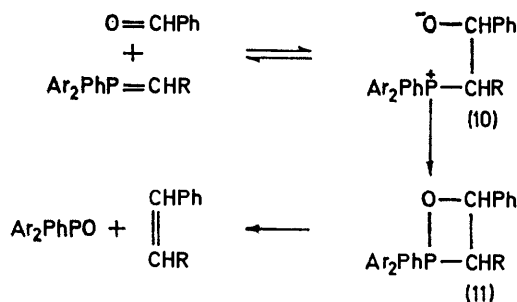
SCHEME 1

The Wittig reactions of another heterocyclic ylide (12) have been studied previously.[11] No kinetic data were

* Recent work [16] indicates that modest increases in the electro-negativity of the groups attached to phosphorus greatly increase the rate-determining role of steps (a) and (b).

† It is also possible that stable ylides are intermediates (i.e. precursors to the hydroxyphosphoranes) in the hydrolysis of the salts described in this paper. However this should not alter the rationalisation since we consider that the energy barrier to hy-droxyphosphorane formation should be similar for the salt and the ylide. This cannot apply to reactive ylides which are not readily formed from the corresponding salts in dilute aqueous alkali. Further, salts such as triphenylalkylphosphonium halides are relatively slowly hydrolysed in dilute alkali, whereas the corresponding reactive ylides are readily hydrolysed by water.[18] This may be attributed to the ready conversion of the 'high-energy' reactive ylides into the hydroxyphosphoranes, whereas the corresponding 'low-energy' salts face a large energy barrier.

presented but the compound appeared to be less reactive than the corresponding triphenylphosphorane. This was attributed to greater steric hindrance in (12).

The studies of heterocyclic ylides have a bearing on an alternative mechanism of the Wittig reaction in which a pentaco-ordinate intermediate is formed directly from the ylide and aldehyde. This mechanism has been put forward in order to explain the stereospecific formation of cis-olefin from reactive ylides in non-polar solvents.[12] However such a mechanism would be expected to be more applicable to stabilised ylides which have reduced nucleophilic character, as suggested by the original proposers of this mechanism.[13] The mechanism has been widely discussed in the literature [14] and also finds supporting evidence in the reactions of betaine ylides.[15] However the absence of fast reactions for the hetero-cyclic ylides, the increase in the proportion of cis-olefin, and the kinetic evidence of other workers [9] show conclusively that the mechanism does not apply to stabilised ylides.

The hydrolyses of the heterocyclic phosphonium salts (1) were more ready than the hydrolyses of the corre-sponding triphenylphosphonium salts. In fact hydro-lysis was the major problem in the preparation of the heterocyclic ylides. The rate of hydrolysis of compound (1; R = Ph, X = Br) was too great to be measured at 0° ($t_{\frac{1}{2}}$ <1 min), whereas the triphenylphosphonium salt had a half life of ca. 2 h; thus the rates of hydrolysis differ by a factor of at least 120.

The hydrolyses of phosphonium salts are normally second order in hydroxide ion in accordance with Scheme 2. Step (c), normally the slowest,* is much
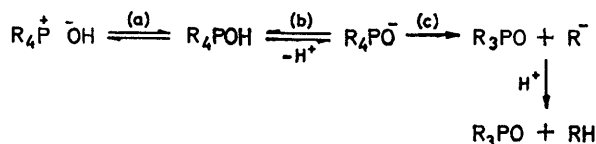
SCHEME 2

faster (and not 'rate-determining') when the leaving group (R$^-$) is a stabilised carbanion such as the p-nitrobenzyl anion.[17] We expect this step to be faster still when the leaving group (R$^-$) is an enolate anion, as in the hydrolyses described in this paper.† The second

[8] C. Ruchardt, P. Panse, and S. Eichler, Chem. Ber., 1967, 100, 1144.

[9] A. J. Speziale and D. E. Bissing, J. Amer. Chem. Soc., 1963, 85, 3878.

[10] A. W. Johnson, 'Ylid Chemistry,' Academic Press, 1966, 152.

[11] M. B. Hocking, Canad. J. Chem., 1966, 44, 1581.

[12] W. P. Schneider, Chem. Comm., 1969, 785.

[13] L. D. Bergelson and N. M. Shemyakin, Tetrahedron, 1963, 19, 149.

[14] R. F. Hudson, Chem. in Britain, 1971, 7, 287; I. Ugi, D. Marquarding, H. Kwsacek, G. Gokel, and P. Gillespie, Angew. Chem. Internat. Edn., 1970, 9, 728.

[15] J. Reucroft and P. G. Sammes, Quart. Rev., 1971, 25, 135.

[16] D. W. Allen, B. G. Hutley, and M. J. T. Mellor, J.C.S. Perkin II, 1972, 63.

[17] G. Aksnes and L. J. Brudvik, Acta Chem. Scand., 1967, 21, 745.

[18] R. F. Hudson, 'Structure and Mechanism in Organo-Phosphorus Chemistry,' Academic Press, New York, 1965, 222.

step (b) is not likely to be affected by the inclusion of the phosphorus atom in a small ring and therefore the rate enhancement observed for the heterocyclic salts may be attributed mainly to an increase in the equilibrium constant of the first step (a), due to stabilisation of the hydroxyphosphorane.[19]

EXPERIMENTAL

The n.m.r. spectra were obtained with a Perkin-Elmer R10 instrument, the i.r. spectra with a Unicam SP 200 instrument, and the u.v. spectra with a Beckman DB-G grating spectrophotometer. The ^{31}P chemical shifts are relative to 85% phosphoric acid. The salts and ylides were very susceptible to hydrolysis by moist air and wholly satisfactory analyses were not obtained for some compounds.

P-*Methoxycarbonylmethyl*-P-*phenyldibenzophospholium Chloride* (1; R = OMe, X = Cl).—*P*-Phenyldibenzophosphole [20] (2·60 g, 10 mmol) and methyl chloroacetate (1·3 g, 12 mmol) in dry benzene (20 ml) were heated under reflux for 4 h. The white crystalline *solid* was separated (2 g, 55%); m.p. 184° (from chloroform–ethyl acetate). The mother liquors, when poured into ether, gave an oil, which, when dissolved in chloroform and triturated with ethyl acetate, gave a further 200 mg of the salt; τ (CDCl$_3$) 1·1— 2·4 (12H, m), 4·25 (2H, d, J_{PH} 14 Hz), and 6·35 (3H, s) (Found: C, 68·9; H, 4·9. C$_{21}$H$_{18}$ClOP requires C, 68·4; H, 4·9%).

P-*Phenacyl*-P-*phenyldibenzophospholium Bromide* (1; R = Ph, X = Br).—*P*-Phenyldibenzophosphole (2·60 g, 10 mmol) and phenacyl bromide (2·2 g, 11 mmol) in dry benzene (20 ml) were heated under reflux for 4 h. The crystalline *solid* was separated (4·5 g, 98%); m.p. 247— 249° (from chloroform–ethyl acetate), τ (CDCl$_3$) 1·4—2·6 (18H, m) and 4·57 (2H, d, J_{PH} 12 Hz), $\lambda_{max.}$ 333 (ε 6000), 275 * (18,000), and 242 † nm (53,000) (Found: C, 68·3; H, 4·7. C$_{26}$H$_{20}$BrOP requires C, 68·0; H, 4·4%).

P-*Benzoylmethylene*-P-*phenyldibenzophosph*(v)*ole* (2).—The phosphonium salt (1; R = Ph, X = Br) (2·34 g, 5 mmol) was partly dissolved in dry methanol (25 ml). Sodium methoxide (5·5 mmol) was added under nitrogen. After 10 min the pale yellow *ylide* began to precipitate. After 4 h the solid was separated (1·2 g, 63%); m.p. 204—206° (from chloroform–ethyl acetate), τ (CDCl$_3$) 1·7—2·8 (18H, m) and 5·6 (1H, d, J_{PH} 28 Hz), $\lambda_{max.}$ 330 (ε 9000), 320infl (9000), 275 * (14,000), and 240 † nm (54,000) (Found: C, C, 83·4; H, 5·7. C$_{26}$H$_{19}$OP requires C, 82·5; H, 5·0%).

Reactions of Benzoylmethylenetriphenylphosphorane and the Ylide (2) *with Aldehydes.*—The solution of the ylide (0·19 g, 0·5 mmol) in the appropriate solvent (2·5 ml) was treated with the aldehyde (0·6 mmol). The acetaldehyde reaction mixtures were left at room temperature overnight and then heated under reflux for 5 min. The benzaldehyde reaction mixtures were heated under reflux for 2 h. The solutions were analysed by g.l.c. for *cis–trans* ratio and total yield of olefin (Pye 104 chromatograph; PEGA 20 m column at 175—225°). The *trans*-olefins were identified by comparison of their retention times with those of authentic samples. The yields of olefins were almost quantitative; the *cis–trans* ratios are presented in Table 3.

P-*Methoxycarbonylmethylene*-P-*phenyldibenzophosph*(v)*ole* (3).—(a) The phosphonium salt (1; R = OMe, X = Cl)

(368 mg, 1 mmol) was suspended in dry benzene (10 ml) under nitrogen and treated with lithium diethylamide (1·05 mmol) (from butyl-lithium and diethylamine). The mixture was stirred for 3 h, filtered, and evaporated, and the resultant orange oil was triturated with ether. The yellow solid (150 mg, 46%) had an i.r. spectrum very similar to that of the product prepared by method (b).

(b) The phosphonium salt (1; R = OMe, X = Cl) (368 mg, 1 mmol) was suspended in dry benzene (10 ml) and treated with sodium hydride (2·5 g, 10 mmol). Absolute ethanol (0·05 ml) was added and the mixture was stirred overnight. The solution was filtered and the benzene removed under vacuum to give a yellow solid (200 mg, 65%). The i.r. spectrum indicated that a small amount of *P*-phenyldibenzophosphole *P*-oxide was present. The ylide was so readily hydrolysed in the atmosphere that analyses corresponding to the molecular formula were not obtained; τ (CDCl$_3$) 2·15—2·9 (13H, m), 6·45 (3H, s), and 7·12 (1H, d, J_{PH} 26 Hz).

P-*Ethoxycarbonylmethyl*-P-*phenyldibenzophospholium Chloride* (1; R = OEt, X = Cl).—The *salt*, prepared in a similar manner to the methyl ester, had m.p. 186°, $\nu_{max.}$ 700, 725, 770, 780, 810, 895, 1025, 1070, 1085, 1115, 1130, 1165, 1200, 1320, 1385, 1405, 1450, 1475, 1595, and 1710 cm^{-1}, τ (CDCl$_3$) 1·0—2·6 (13H, m, ArH), 4·47 (2H, d, J_{PH} 14·5 Hz, P·CH$_2$), 5·94 (2H, q, J_{HH} 7·1 Hz, CH$_2$), and 8·97 (3H, t, CH$_3$) (Found: C, 69·4; H, 4·9. C$_{22}$H$_{20}$ClOP requires C, 69·0; H, 5·2%).

P-*Ethoxycarbonylmethylene*-P-*phenyldibenzophosphole* (8). —The phosphonium salt (1; R = OEt, X = Br) (1 mmol) was suspended in dry benzene (10 ml) and treated with sodium hydride (2·5 g, 10 mmol) and methanol (0·05 ml). The mixture was worked up as for the methyl ester to give a yellow oil, ν_{CO} 1630 cm^{-1}, τ (CDCl$_3$) 2·2—3·1 (13H, m, ArH), 6·20 (2H, d, J_{HH} 7 Hz, CH$_2$), 7·26br (1H, s, methine), and 8·82 (3H, t, Me).

Dimethyl 2,3-*Bis*-5-*phenyldibenzophosph*(v)*ol*-5-*ylidene-succinate.*—The diphosphorane (4), prepared [5] from 5-phenyldibenzophosphole and dimethyl acetylenedicarboxylate, had m.p. 100—105°, $\nu_{max.}$ (KBr) 700, 725, 730, 760, 775, 845, 1065, 1085, 1165, 1270, 1360, 1440, 1570, 1585, and 1605 cm^{-1}, τ (CDCl$_3$) 2·2—2·9 (26H, m) and 6·24 (6H, s) (Found: H, 5·1. C$_{42}$H$_{32}$O$_4$P$_2$ requires H, 4·8%).

Kinetics of Wittig Reactions.—(a) The reactions of the benzoyl ylides (2) and (5) with freshly distilled benzaldehyde in thiophen-free, sodium-dried benzene at 80° (reflux) under nitrogen were followed by i.r. spectroscopy. The rates of disappearance of the aldehyde carbonyl absorptions at 1700 cm^{-1} and the rates of appearance of olefin carbonyl absorption at 1660 cm^{-1} were plotted against time. The slopes showed that the reaction of the heterocyclic ylide (2) was 2—3 times faster than that of (5).

(b) The reactions of the ethoxycarbonyl ylides (8) and (9) with benzaldehyde in benzene at 25·0 °C under nitrogen were followed by a titrimetric method. Solutions of benzaldehyde (0·08M) and the ylides (0·08M) were separately allowed to equilibrate at 25·0° for 2 h. The solutions were mixed under nitrogen. Samples (0·4—0·8 cm^3) were taken at intervals, added to excess of hydrochloric acid (25 cm^3; 0·00016M), and titrated against sodium hydroxide (0·0008M).[9] The end points were determined conductimetrically to an accuracy of $\pm$0·1 cm^3.

* Structured band (5 peaks) centred at this wavelength.
† Structured band (3 peaks) centred at this wavelength.

[19] F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.
[20] H. Hoffman, *Chem. Ber.*, 1962, **95**, 2563; L. Horner, G. Mummenthey, H. Moser, and P. Beck, *ibid.*, 1966, **99**, 2782.

Kinetics of Hydrolysis of Methoxycarbonylmethyltriphenyl-phosphonium Chloride and the Heterocyclic Salt (1; R = OMe, X = Cl).—Solutions of the salts (0·02M) in 50% aqueous ethanol (5 cm³) at 0° were mixed with sodium hydroxide in 50% aqueous ethanol (5 cm³; 0·02M) at 0°.

Samples (1 cm³) of the reaction mixture were added to excess of hydrochloric acid (25 cm³; 0·000625M) and conductimetrically titrated with sodium hydroxide (0·0032M). The solutions were standardised against borax.