

The Effects of Substituents at Phosphorus on the Mode of Decomposition of Phosphonium Betaines in Protic Solvents

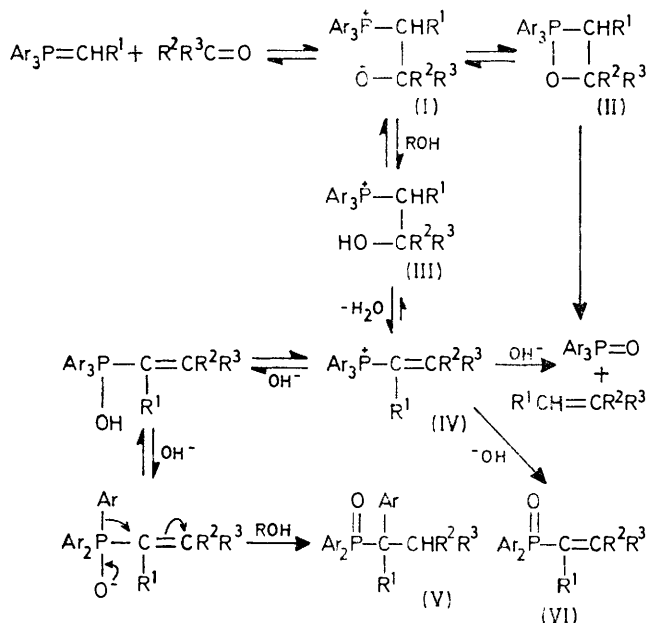
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A delicate balance of steric and electronic effects controls the course of decomposition of phosphonium betaines generated in protic solvents. Electron-withdrawing heteroaryl substituents (*e.g.* 2-furyl and 2-thienyl) promote intramolecular betaine collapse to form the normal Wittig products, as also does enclosure of the phosphorus in the dibenzophosphole ring system. Except in such cyclic systems, both electron-donating and bulky groups (*e.g.* *o*-tolyl and *t*-butyl) reduce the rate of intramolecular collapse and allow a dehydration step to occur, with the formation of a vinylphosphonium intermediate (IV). The decomposition of (IV) leading to abnormal products depends on the carbanionic stability of the group cleaved from phosphorus. Carbanions of moderate stability such as phenyl, *p*-methoxyphenyl, or *m*-chlorophenyl require the additional stabilisation of negative charge afforded in the transition state of the reaction leading to the rearrangement product (V). For carbanions of greater stability, such as 2-heteroaryl and *m*-trifluorophenyl carbanions, simple cleavage of the leaving group can occur, with formation of the vinylphosphine oxide (VI). The presence of an aryl substituent on the carbon α to phosphorus promotes betaine collapse to the normal Wittig products even when the phosphorus bears a *t*-butyl group [as in the reaction of the salt (XIII) with benzaldehyde in the presence of ethoxide ion].

THE Wittig reaction between a phosphonium salt and a carbonyl compound in the presence of alkoxide ion in protic solvents may occur by 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* an oxyphosphorane (II).¹ Alternatively, protonation of the betaine may occur to give the β -hydroxyalkylphosphonium salt (III), which subsequently may eliminate water to form the vinylphosphonium salt (IV). Hydrolysis of the latter may then occur 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 and (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 the nature of the substituents R¹, R², and R³,^{2,3,6,7} on the electron-withdrawing character of the substituents at phosphorus,⁸ and on the steric constraints placed on the phosphorus atom by its incorporation into a small ring system.⁹ When R¹ = H, and either R² or R³ is an electron-withdrawing group such as phenyl or methoxycarbonyl, then the rearrangement products (V) are formed preferentially when the substituents at phosphorus are phenyl, *m*-chlorophenyl, or *p*-methoxyphenyl, that group migrating which is the more stable as a carbanion.^{3,7} However, when R¹ = Ph or Me, the normal Wittig products (olefin and phosphine oxide) are formed from collapse of the phosphonium betaine *via* the oxyphosphorane (II).^{6,7} If the electrophilicity of the phos-

phonium centre in the betaine is increased by attachment of the electron-withdrawing 2-furyl substituent, then even when R¹ = H, the normal Wittig products are formed preferentially.⁸ In addition, betaine collapse *via* the oxyphosphorane is also facilitated even when R¹ = H by enclosure of the phosphorus in the small, strained dibenzophosphole ring system, owing to the formation of



SCHEME

a strain-free spirophosphorane in which both four- and five-membered rings span apical-equatorial positions.⁹ We have continued to investigate steric and electronic

¹ G. Wittig and U. Schollkopf, *Chem. Ber.*, 1954, **87**, 1318.

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 Preliminary communication, D. W. Allen, 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.

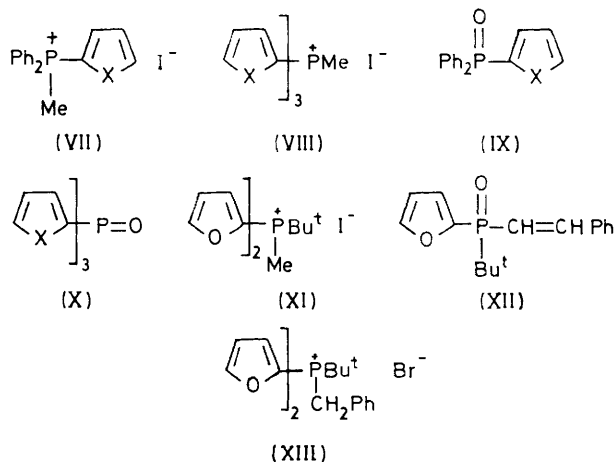
⁷ S. Trippett and B. J. Walker, *J. Chem. Soc.*, 1966, 887.

⁸ D. W. Allen, B. G. Hutley, and T. C. Rich, *J.C.S. Perkin II*, 1973, 820.

⁹ D. W. Allen, B. G. Hutley, and K. Polasik, *J.C.S. Perkin I*, 1975, 619.

effects of substituents at phosphorus on the mode of decomposition of phosphonium betaines in protic solvents, and now report as follows.

The reaction of methyltriphenylphosphonium iodide and benzaldehyde in ethanolic sodium ethoxide [or alternatively the reaction of triphenylphosphine and styrene oxide, which leads directly to the betaine (I; Ar = Ph, R¹ = R² = H, R³ = Ph)] yields predominantly the rearrangement product (V; Ar = R³ = Ph;

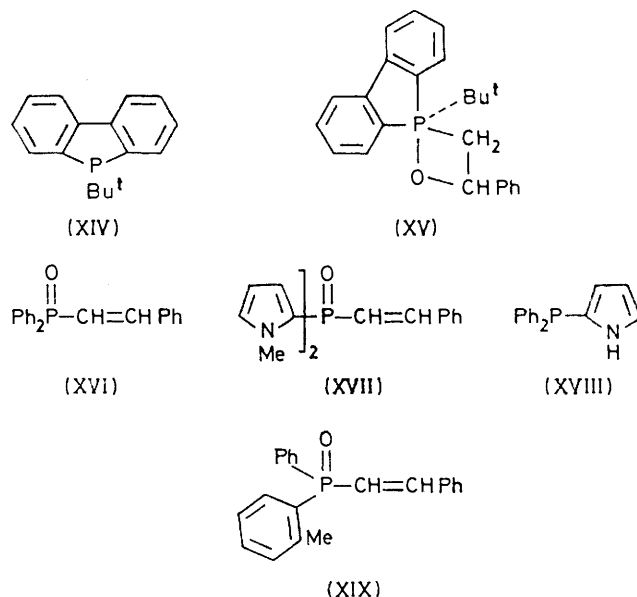


R¹ = R² = H) *via* a vinylphosphonium intermediate.^{3,7} In contrast, the analogous reactions of the phosphonium salts (VII and VIII; X = O) yield the normal Wittig products of styrene and the phosphine oxides (IX and X; X = O, respectively).⁸ On the basis of earlier work on the chemistry of heteroarylphosphonium salts,¹⁰ it was suggested that the 2-furyl substituents act as electron-withdrawing groups which favour intramolecular collapse of the betaine (I). We now find that the presence of the 2-thienyl substituent at phosphorus has the same result. Thus the betaines (I) derived from the reactions of tri-2-thienylphosphine or diphenyl-(2-thienyl)phosphine with styrene oxide in ethanol collapse to give styrene and the phosphine oxides (IX and X; X = S, respectively). Although on the basis of our earlier work¹⁰ the 2-thienyl group is less strongly electron-withdrawing than 2-furyl when attached to a second-row element, it is nevertheless still appreciably more electron-withdrawing than phenyl, and this is reflected in the increased rate of betaine collapse *via* the oxyphosphorane (II).

The presence of bulky groups at phosphorus has been shown to have a marked influence on the course of alkaline hydrolysis of phosphonium salts; in such crowded systems, loss of the substituent which forms the most stable carbanion may not necessarily occur.¹¹ Since both competing routes for the Wittig reaction in a protic solvent involve nucleophilic attack at a phosphonium centre, we have studied the effect of introducing bulky groups at phosphorus both on the preferred mechanistic course and on the products of such reactions.

¹⁰ D. W. Allen, B. G. Hutley, and M. T. J. Mellor, *J.C.S. Perkin II*, 1972, 63.

Introduction of a *t*-butyl group at phosphorus has a marked effect on the course of the Wittig reactions of methylphosphonium salts. Thus the major product of the reaction of the salt (XI) with benzaldehyde in ethanolic sodium ethoxide is the vinylphosphine oxide (XII), arising by loss of furan from a vinylphosphonium intermediate. However, the Wittig reaction of the benzyl-(2-furyl)-*t*-butylphosphonium salt (XIII) with benzaldehyde proceeds normally to give stilbene and di-(2-furyl)-*t*-butylphosphine oxide, again reflecting the dominant role of the substituent R¹ in the decomposition of the betaine, as established for phenylphosphorus systems.^{6,7} In contrast, the reaction of *t*-butyldiphenylphosphine with styrene oxide gives a complex mixture of products which are difficult to separate and identify with certainty. The only phosphorus-containing product fully characterised was the normal Wittig product, diphenyl-*t*-butylphosphine oxide, which however was isolated in only very small yield. The complexity of the products indicates that betaine collapse is slow, owing to both the steric effect of the *t*-butyl group and the reduced electron-withdrawing effects of the substituents at phosphorus, leading to the vinylphosphonium intermediate. However, the betaine derived from the reaction of 5-*t*-butyldibenzophosphole (XIV) with styrene oxide undergoes decomposition to form only the normal Wittig products, styrene and the dibenzophosphole oxide, in a clean reaction. In this case (as for the related reaction of 5-phenyldibenzophosphole⁹) the



dominant factor seems to be relief of steric strain in forming the spirophosphorane (XV), in which both four- and five-membered rings span apical-equatorial positions, the *t*-butyl substituent occupying an equatorial position.

Replacement of the 2-furyl substituents in the salts (VII and VIII; X = O) by the 1-methylpyrrol-2-yl substituent also reduces the rate of betaine collapse and

¹¹ J. R. Corfield, N. J. De'ath, and S. Trippett, *J. Chem. Soc. (C)*, 1971, 1930.

leads to abnormal products. Thus the Wittig reactions of the salts (VII and VIII; X = NMe) with benzaldehyde give the vinylphosphine oxides (XVI) and (XVII), respectively, together with 1-methylpyrrole. The 1-methylpyrrol-2-yl substituent may reduce intramolecular betaine collapse in two ways: (i) by its reduced electron-withdrawing effect as compared with the 2-furyl and 2-thienyl groups¹² and (ii) by a possible steric effect of the 1-methyl group.¹³ In order to investigate these effects more fully, we have studied the reaction between diphenyl(pyrrol-2-yl)phosphine (XVIII) and styrene oxide in ethanol. This reaction also leads to the vinylphosphine oxide (XVI) (together with pyrrole) as the major product (although substantial quantities of the normal Wittig products are also formed). It seems, therefore, that it is the overall electronic effect of the pyrrole ring system on the electrophilicity of the phosphonium centre which is largely responsible for the course of the reaction, the steric effect of the *N*-methyl substituent playing a minor role. Additionally, the relative ease of carbanionic cleavage of the pyrrol-2-yl group from the vinylphosphonium intermediate is doubtless of importance. We have shown previously that the 1-methylpyrrol-2-yl substituent is cleaved in preference to phenyl on alkaline hydrolysis of mixed (1-methylpyrrol-2-yl)phenylphosphonium salts.¹²

We have also studied the effects of various substituted phenyl groups (*o*-tolyl, *o*-chlorophenyl, *o*-methoxyphenyl, and *m*-trifluoromethylphenyl) on the mode of betaine decompositions by investigating the reactions of either the phosphines $\text{Ph}_2\text{P}\cdot\text{C}_6\text{H}_4\text{X}$ with styrene oxide in refluxing ethanol, or the methiodides $\text{MePh}_2\text{P}^+\cdot\text{C}_6\text{H}_4\text{X}^-$ with benzaldehyde in ethanolic sodium ethoxide. Previous work has shown that reactions of this type which involve *m*-chlorophenyl or *p*-methoxyphenyl substituents at phosphorus result in the rearranged oxides (V), with the group most stable as a carbanion migrating preferentially.^{7,9} The reaction of diphenyl(*o*-tolyl)phosphine with styrene oxide (and that of the corresponding methiodide with benzaldehyde) gives a mixture containing two isomeric rearrangement products (V) in which either phenyl or *o*-tolyl groups have migrated from phosphorus to adjacent carbon, and also two vinylphosphine oxides, (XVI) and (XIX), corresponding to cleavage of phenyl or *o*-tolyl groups from a vinylphosphonium intermediate. The reaction of (*o*-chlorophenyl)diphenylphosphine with styrene oxide gives predominantly the vinylphosphine oxide (XVI), together with chlorobenzene. The major products from the reaction of (*o*-methoxyphenyl)diphenylphosphine with styrene oxide are the vinylphosphine oxide (XVI) and a mixture of rearrangement products (V). In addition, both (*o*-methoxyphenyl)diphenylphosphine oxide and methyl-diphenylphosphine oxide are formed, the latter arising from dissociation

of the betaine to the ylide and benzaldehyde, protonation of the ylide being followed by hydrolysis with loss of the *o*-methoxyphenyl group. Both styrene and anisole are present in the reaction mixture.

The most significant result of this group of substituted phenyl compounds, however, is that from the Wittig reaction of the methiodide of diphenyl(*m*-trifluoromethylphenyl)phosphine with benzaldehyde, which gives predominantly the vinylphosphine oxide (XVI) together with trifluoromethylbenzene. No rearrangement products appear to be formed. This reaction thus resembles that of the pyrrol-2-ylphosphine with styrene oxide, and this suggests that the key factor is the stability of the forming carbanionic leaving group. In the case of the above *ortho*-substituted phenyl groups, it could be argued that in addition to the relative stability of the *o*-chlorophenyl and *o*-methoxyphenyl carbanions as compared with phenyl, the steric effect of the *ortho*-substituent is also likely to be of importance; in the case of the *meta*-trifluoromethyl substituent, the steric effect should be much reduced.

Clearly a delicate balance of steric and electronic effects controls the course of Wittig reactions conducted in protic solvents. The ultimate fate of the phosphonium betaine (I) is determined by the relative rates of the intramolecular collapse and dehydration steps. Electron-withdrawing substituents at phosphorus (*e.g.* 2-furyl and 2-thienyl, but not *m*-trifluoromethylphenyl) promote intramolecular betaine collapse, as also does enclosure of phosphorus in a small ring system. In contrast (except in such cyclic systems), both electron-donating and bulky groups (*e.g.* *o*-tolyl and *t*-butyl) reduce the rate of intramolecular collapse and allow the dehydration step to occur, with the formation of a vinylphosphonium intermediate (IV). The decomposition of (IV) leading to abnormal products depends on the carbanionic stability of the group cleaved from phosphorus. Carbanions of moderate stability such as phenyl, *p*-methoxyphenyl, and *m*-chlorophenyl require the additional stabilisation of negative charge afforded in the transition state of the rearrangement reaction. For carbanions of greater stability, such as the 2-heteroaryl and *meta*-trifluoromethylphenyl carbanions, simple cleavage of the leaving group can occur, with formation of the vinylphosphine oxide.

EXPERIMENTAL

¹H N.m.r. spectra were recorded at 60 MHz with a JEOL spectrometer (Me₄Si as internal standard). Mass spectra were recorded at 70 eV with an A.E.I. MS30 spectrometer.

Operations involving organolithium intermediates or tertiary phosphines were conducted under nitrogen.

Synthesis of Phosphines and Derivatives.—Tri-(2-thienyl)phosphine,¹⁴ diphenyl-(2-thienyl)phosphine,¹³ 5-*t*-butyldibenzophosphole,¹⁵ diphenyl-*t*-butylphosphine,¹⁶ 1-methylpyrrol-2-yl-diphenylphosphine,¹² tris-(1-methylpyrrol-2-yl)phosphine,¹² diphenyl(pyrrol-2-yl)phosphine,¹³ (*o*-methoxy-

¹² D. W. Allen, B. G. Hutley, and M. T. J. Mellor, *J.C.S. Perkin II*, 1974, 1690.

¹³ D. W. Allen, J. R. Charlton, and B. G. Hutley, *Phosphorus*, 1976, **6**, 191.

¹⁴ K. Issleib and A. Brack, *Z. anorg. Chem.*, 1957, **292**, 245.

¹⁵ D. W. Allen, F. G. Mann, and I. T. Millar, *J. Chem. Soc. (C)*, 1971, 3937.

¹⁶ S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, 1967, **32**, 781.

phenyl)diphenylphosphine,¹⁷ (*o*-chlorophenyl)diphenylphosphine,¹⁸ and diphenyl(*o*-tolyl)phosphine¹⁹ were prepared and, where appropriate, converted into phosphonium salts and phosphine oxides, as described in the literature.

Bis-(2-furyl)-*t*-butylphosphine.—To an ice-cold solution of 2-furyl-lithium (0.2 mol) [prepared from *n*-butyl-lithium (0.2 mol) and furan (>0.2 mol) in ether (100 cm³)] was added, dropwise with stirring, a solution of *t*-butylphosphonous dichloride (12 g, 0.075 mol) in benzene (40 cm³). The resulting solution was heated under reflux for 1 h before cooling and hydrolysing with aqueous ammonium chloride (10% w/v; 100 cm³). The organic layer was separated, dried (Na₂SO₄), and evaporated. The residue was distilled under reduced pressure to give the phosphine (4.8 g, 28%), b.p. 78–82° at 0.6 mmHg, τ (CDCl₃) 2.3 (2 H, m), 3.2 (2 H, m), 3.7 (2 H, m), and 8.95 (9 H, d, ³J_{PCH} 13 Hz); the *methiodide* (XI) had m.p. 185° (from EtOH–EtOAc–Et₂O) (Found: C, 43.2; H, 5.15. C₁₃H₁₈IO₂P requires C, 42.85; H, 4.95%); τ (CDCl₃) 2.05 (4 H, m), 3.20 (2 H, m), 7.15 (3 H, d, ²J_{PCH} 13 Hz), and 8.59 (9 H, d, ³J_{PCH} 18 Hz). Oxidation of the phosphine with hydrogen peroxide in acetone gave the phosphine oxide, m.p. 67°, as a hygroscopic solid, *M*⁺ 238, τ (CDCl₃) 2.15 (2 H, m), 2.70 (2 H, m), 3.37 (2 H, m), and 8.72 (9 H, d, ³J_{PCH} 16 Hz). Treatment of the phosphine with benzyl bromide gave *benzyl-di*-(2-furyl)-(*t*-butyl)phosphonium bromide (XII), m.p. 211–212° (from EtOH–EtOAc–Et₂O) (Found: C, 58.2; H, 5.8. C₁₉H₂₂BrO₂P requires C, 58.0; H, 5.65%); τ (CDCl₃) 1.74 (2 H, m), 1.90 (2 H, m), 2.73 (5 H, s), 3.10 (2 H, m), 4.98 (2 H, d, ²J_{PCH} 12 Hz), and 8.45 (9 H, d, ³J_{PCH} 19 Hz).

Diphenyl-(*m*-trifluoromethylphenyl)phosphine.—To the Grignard reagent prepared from *m*-bromotrifluoromethylbenzene (9.0 g) and magnesium (1.5 g) in ether (90 cm³) was added a solution of diphenylphosphinous chloride (4.5 g) in ether (40 cm³), and the resulting solution was heated under reflux for 1 h before being cooled in ice and hydrolysed with ammonium chloride solution (10% w/v; 50 cm³) and dilute hydrochloric acid (2M; 100 cm³). The organic layer was separated, dried, and evaporated to give the crude phosphine, which resisted crystallisation from a range of solvents. The *methiodide* had m.p. 180–181° (from EtOH–EtOAc) (Found: C, 51.0; H, 3.5. C₂₀H₁₇F₃IP requires C, 50.85; H, 3.65%); the *oxide* had m.p. 115–116° (from EtOH–hexane) (Found: C, 65.95; H, 4.05. C₁₈H₁₄F₃OP requires C, 65.9; H, 4.05%).

Reactions of Phosphines with Styrene Oxide.—General procedure. The phosphine (10⁻³ mol) and styrene oxide (2 × 10⁻³ mol) were heated together in ethanol (2 cm³) for 24 h. The solution was then analysed by g.l.c. for the presence of styrene and appropriate hydrocarbons arising from cleavage of aryl or heteroaryl groups from phosphorus. It was then evaporated and the residue subjected to preparative t.l.c. on 20 × 20 cm preparative plates coated (1 mm) with Kieselgel HF 256 (solvent 1 : 1 hexane–ethyl acetate). Individual bands were extracted with methanol to yield the phosphine oxide products.

(A) Diphenyl-(2-thienyl)phosphine and styrene oxide gave styrene (41%) and diphenyl-(2-thienyl)phosphine oxide, m.p. 117°, identical with an authentic specimen.

(B) Tri-(2-thienyl)phosphine and styrene oxide gave styrene (40%) and tri-(2-thienyl)phosphine oxide, identical with an authentic specimen.

¹⁷ W. E. McEwen, W. I. Shiau, Younn-Ing Yeh, D. N. Schulz, R. U. Pagilagan, J. B. Levy, C. Symmes, jun., G. O. Nelson, and I. Granth, *J. Amer. Chem. Soc.*, 1975, **97**, 1787.

¹⁸ F. A. Hart, *J. Chem. Soc.*, 1960, 3324.

(C) G.l.c. analysis of the product from diphenyl(pyrrol-2-yl)phosphine and styrene oxide showed the presence of styrene (26%), pyrrole, benzaldehyde, and unchanged styrene oxide. T.l.c. gave diphenyl-(β -styryl)phosphine oxide (32%), m.p. 168° (lit.,²⁰ 168–169°) (Found: C, 79.1; H, 5.85. Calc. for C₂₀H₁₇OP: C, 78.95; H, 5.6%), identical with an authentic specimen, and *diphenyl*-(pyrrol-2-yl)-phosphine oxide (24%), m.p. 184–185° (from EtOH–hexane) (Found: C, 72.55; H, 5.45. C₁₆H₁₄NOP requires C, 71.9; H, 5.3%), identical with a sample prepared by oxidation of the phosphine.

(D) G.l.c. analysis of the product from (*o*-methoxyphenyl)-diphenylphosphine and styrene oxide showed the presence of styrene (15%) and anisole (15%). T.l.c. gave diphenyl-(β -styryl)phosphine oxide (15%), a mixture of rearranged phosphine oxides, (1,2-diphenylethyl)-(*o*-methoxyphenyl)-phenylphosphine oxide and [1-(*o*-methoxyphenyl)-2-phenylethyl]diphenylphosphine oxide (30% total); *m/e* 412 (*M*⁺) 232 [(*o*-MeO·C₆H₄)PhPOH], 210 [PhCH=CH-(*o*-MeO·C₆H₄)], 202 (Ph₂POH), and 180 (PhCH=CHPh), in accord with the very specific fragmentation pattern established for such compounds.²¹ In addition, (*o*-methoxyphenyl)diphenylphosphine oxide (15%), m.p. 165–166° (from hexane–EtOH) (Found: C, 74.1; H, 5.55. C₁₉H₁₇O₂P requires C, 74.0; H, 5.55%), *M*⁺ 308, identical with a sample prepared by oxidation of the phosphine, and methyl-diphenylphosphine oxide were isolated and identified.

(E) G.l.c. analysis of the product from (*o*-chlorophenyl)-diphenylphosphine and styrene oxide showed the presence of styrene (12%), chlorobenzene (55%), and benzaldehyde. T.l.c. gave diphenyl(methyl)phosphine oxide (20%), together with diphenyl-(β -styryl)phosphine oxide and (*o*-chlorophenyl)diphenylphosphine oxide, which were incompletely separated.

(F) G.l.c. analysis of the product from diphenyl(*o*-tolyl)-phosphine and styrene oxide indicated the presence of styrene (8%), together with both benzene and toluene. T.l.c. gave a mixture of the isomeric rearranged phosphine oxides, diphenyl-[2-phenyl-1-(*o*-tolyl)ethyl]phosphine oxide and (1,2-diphenylethyl)phenyl-(*o*-tolyl)phosphine oxide (20% total) (Found: C, 81.7; H, 6.5. Calc. for C₂₇H₂₅OP: C, 81.8; H, 6.35%); *m/e* 396 (*M*⁺), 216 [Ph(*o*-MeC₆H₄)POH], 202 (Ph₂POH), 194 [PhCH=CH(*o*-MeC₆H₄)], and 180 (PhCH=CHPh), in accord with the specific fragmentation pattern found for such compounds.²¹ Also isolated was a mixture of substituted vinylphosphine oxides, phenyl-(*o*-tolyl)-(β -styryl)phosphine oxide (*M*⁺ 318) and diphenyl-(β -styryl)phosphine oxide (*M*⁺ 304), which could not be separated (20% total).

(G) G.l.c. analysis of the product from diphenyl-(*t*-butyl)-phosphine and styrene oxide indicated the presence of styrene (14%) and benzene (<5%). T.l.c. revealed the presence of a number of phosphine oxides, which were incompletely separated from each other. The only product identified with certainty was diphenyl-*t*-butylphosphine oxide, m.p. 131° (lit.,²² 131°), *M*⁺ 258.

(H) G.l.c. analysis of the product from 5-*t*-butyldibenzo-phosphole and styrene oxide showed the presence of styrene,

¹⁹ M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, 1969, **91**, 6266.

²⁰ A. M. Aguiar and D. J. Daigle, *J. Org. Chem.*, 1965, **30**, 2826.

²¹ D. W. Allen, J. C. Tebby, and D. H. Williams, *Tetrahedron Letters*, 1965, 2361.

²² D. Seyferth, M. A. Eisert, and J. K. Heeren, *J. Organometallic Chem.*, 1964, **2**, 101.

and t.l.c. separation gave 5-*t*-butyldibenzophosphole 5-oxide, m.p. 159–160° (from MeOAc–hexane), identical with a specimen prepared by oxidation of the phosphine (Found: C, 75.1; H, 6.75. $C_{16}H_{17}OP$ requires C, 74.95; H, 6.7%), M^+ 256.

Wittig Reactions of Methylphosphonium Salts with Benzaldehyde.—General procedure. To a solution of the phosphonium salt (10^{-3} mol) in ethanol (2 cm³) containing sodium ethoxide (10^{-3} mol) was added freshly distilled benzaldehyde (10^{-3} mol), and the resulting solution was kept at room temperature under nitrogen for 7 days. The solution was then analysed by g.l.c. for the presence of styrene and other hydrocarbons, and the phosphine oxide products were separated by t.l.c. as in the case of the reactions of phosphines with styrene oxide.

(A) *Di*-(2-furyl)methyl-(*t*-butyl)phosphonium iodide. G.l.c. analysis showed the absence of styrene, but the presence of furan (g.l.c.–mass spectrometry, M^+ 68). T.l.c. followed by fractional sublimation gave as the major product (2-furyl)-(β-styryl)-(t-butyl)phosphine oxide, m.p. 102–104° (after sublimation) (Found: C, 69.5; H, 7.05. $C_{16}H_{19}PO_2$ requires C, 70.05; H, 7.0%), M^+ 274, τ (CDCl₃) 2.1–3.9 (10 H, m, aromatic, olefinic, and furan ring protons), 8.8 (9 H, d, $^3J_{PCH}$ 16 Hz, Bu^tP); also isolated as a hygroscopic oil (the minor product from fractional sublimation) was (2-furyl)-methyl-(t-butyl)phosphine oxide, *m/e* 186 (M^+), 129 ($M - Bu^t$), and 114 ($M - Bu^t - Me$), τ (CDCl₃) 2.35 (1 H, m), 2.95 (1 H, m), 3.55 (1 H, m), 8.3 (3 H, d, $^2J_{PCH}$ 12 Hz, PMe), and 8.8 (9 H, d, $^3J_{PCH}$ 15 Hz, PBu^t).

(B) *Methyl*(diphenyl)-(m-trifluorophenyl)phosphonium iodide. G.l.c. analysis showed the presence of styrene (16%), together with trifluoromethylbenzene (g.l.c.–mass spectrometry M^+ 146). T.l.c. gave diphenyl-(β-styryl)phosphine oxide, together with diphenyl-(m-trifluorophenyl)phosphine oxide, identified by comparison with authentic materials.

(C) *Methyl*-(1-methylpyrrol-2-yl)diphenylphosphonium iodide. G.l.c. analysis showed the presence of styrene (<5%) and 1-methylpyrrole. T.l.c. gave diphenyl-(β-styryl)phosphine oxide (53%).

(D) *Methyltris*-(1-methylpyrrol-2-yl)phosphonium iodide. G.l.c. analysis showed the presence of styrene (5%) and 1-methylpyrrole. T.l.c. gave bis-(1-methylpyrrol-2-yl)-β-styrylphosphine oxide as an oil which resisted crystallisation, M^+ 310, τ (CDCl₃) 2.20–3.25 (9 H, m), 3.47–3.95 (4 H, m), and 6.14 (6 H, s).

Wittig Reaction of Benzyl-di-(2-furyl)-(t-butyl)phosphonium Bromide (XIII) with Benzaldehyde.—The salt (XIII) (0.5×10^{-3} mol), benzaldehyde (10^{-3} mol), and sodium ethoxide (0.5×10^{-3} mol) in ethanol (2 cm³) were kept at room temperature for 7 days. The mixture was poured into dilute hydrochloric acid (10 cm³) and the resulting mixture extracted with hexane (3×5 cm³), and then with chloroform (3×5 cm³). On evaporation, the dried hexane extract gave *trans*-stilbene (95%), and the chloroform extract gave di-(2-furyl)-(t-butyl)phosphine oxide, identical with an authentic specimen.

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