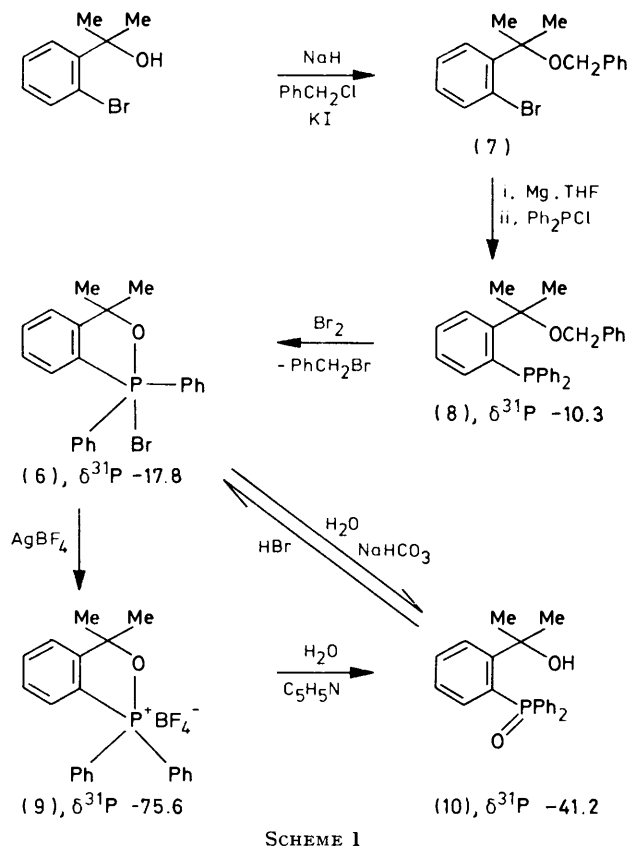


crude product showed an equimolar mixture of benzyl bromide and compound (6). A parallel reaction of triphenylphosphine and bromine in chloroform results in a heavy precipitate of compound (4). When an excess of bromine was added to compound (8), a by-product, a ring-brominated derivative of (6), was detected by field desorption mass spectrometry. Since the latter is practically insoluble in ether, it is best prepared in this solvent; on isolation from the ether solution it was distilled and characterized by ^1H n.m.r. spectroscopy.

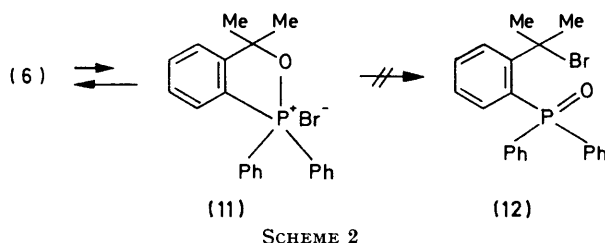


SCHEME 1

The high-field ^{31}P n.m.r. chemical shift of compound (6) (-17.8 p.p.m.) is indicative of a phosphorane,¹⁰ in this case one containing a covalent P-Br bond. This structure is supported by the observation of an intense molecular ion in the field desorption mass spectrum of (6). The field desorption mass spectrum of the products from the reaction of (8) with an excess of bromine in chloroform showed an additional molecular ion at m/e 476, accompanied by an $M - \text{Br}$ at m/e 397. This suggested the presence of a further bromoalkoxyphosphorane resulting from ring bromination of compound (6). Further confirmation of the covalent P-Br bond in (6) was obtained by the preparation of the ionic alkoxyphosphonium tetrafluoroborate, (9) (Scheme 1),^{7,11} from compound (6) and silver tetrafluoroborate. The ^{31}P n.m.r. chemical shift of (9) (75.6 p.p.m.), typical of alkoxyphosphonium salts,¹⁰ is observed 93.4 p.p.m. downfield from that of (6), thus substantiating the structural

assignment for the latter. A low-field multiplet assigned to the proton on the fused ring system *ortho* to phosphorus is seen at δ 8.43 in the ^1H n.m.r. of (6). This can also be considered evidence for an apical covalent P-Br bond. Several analogous chlorosulphuranes have shown this characteristic feature.^{7,12} The only reported bromoalkoxysulphurane⁸ shows the corresponding signal for the *ortho* proton at 8.62 p.p.m. This deshielding effect is believed to be due to the close proximity of the *ortho* proton to the magnetically anisotropic hypervalent bond to the halogen.

Surprisingly, bromoalkoxyphosphorane (6), in CDCl₃ solution, did not react appreciably with water at ambient temperature within 30 min. Both compounds (6) and (9) were rapidly hydrolysed, however, in the presence of aqueous pyridine or sodium hydrogencarbonate to give the phosphine oxide (10) (*vide infra*).



SCHEME 2

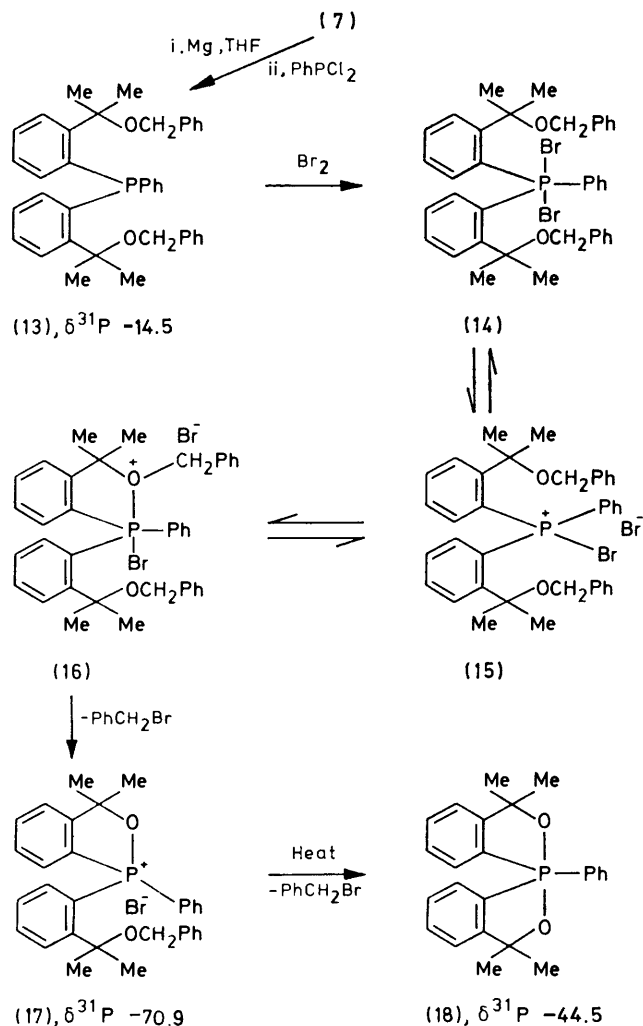
The thermal stability of compound (6) may be explained in terms of the small amount of (11) in equilibrium with (6) and the operation of the gem-dimethyl (Thorpe-Ingold) and five-membered ring effects,⁸ as well as from the steric hindrance to bromide attack at the tertiary α -carbon of (11), which would produce the Arbusov reaction product (12) (Scheme 2).

Dioxyphosphoranes, analogous to (18) (Scheme 3) have recently been prepared¹³ by brominolysis of phosphinobisethers, analogous to (13). We have reasoned that bromoalkoxyphosphoranes might have been intermediates in these reactions. In order to test this possibility, we have prepared the phosphine (13), as outlined in Scheme 3.

Like compound (8), (13) reacts spontaneously with bromine to give benzyl bromide but in this reaction an alkoxyphosphonium bromide (17) is produced, not a bromophosphorane. Indeed, (17) is thermally less stable than (6), and is converted into the more stable dioxyphosphorane (18) when heated (Scheme 3). The very facile debenylation of compounds (8) and (13) upon reaction with bromine can be described in terms of anchimeric electrophilic participation by phosphorus, as shown for (13) in Scheme 3. Intermediate, or transition state (16) is expected to be stabilized by the five-membered ring effect.⁸ Spectroscopic data discussed below provides some support for the postulated intermediacy of (16). The debenylation of (17) might proceed by a similar mechanism.

Compound (17) shows four non-equivalent methyl groups and two non-equivalent benzylic protons in its ^1H n.m.r. spectrum, in accord with the assigned structure.

At ambient temperature, moreover, the ^{31}P n.m.r. chemical shift (70.9 p.p.m.) suggests a four-co-ordinate phosphonium-type structure such as that postulated for (17). Accordingly, no aromatic protons were found for (17) in the low-field range of the ^1H n.m.r. spectrum where *ortho*-protons in (6) and in spirophosphoranes related to (6) are found.

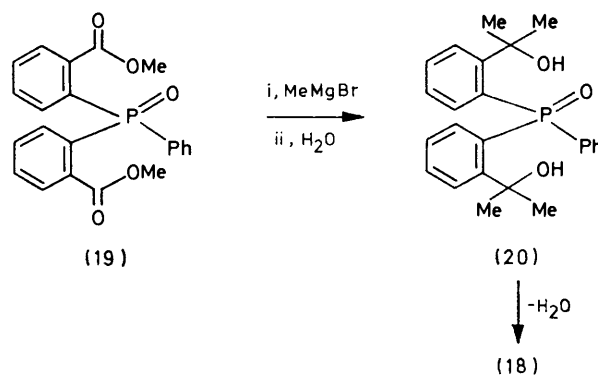


SCHEME 3

The four-co-ordinate phosphonium bromide structure found for (17) by both ^{31}P and ^1H n.m.r. (see Experimental section) is to be contrasted with the bromoalkoxyphosphorane structure of compound (6), discussed above. These two stable species differ only by a bulky *ortho*-substituent. This is a good demonstration of how structure and bonding in P^{V} and P^{IV} compounds are sensitive to the nature of substituents at phosphorus. Increase in the size of substituents should destabilize the *a priori* more crowded five-co-ordinate species, as compared with the four-co-ordinate P^{IV} structure.

The reaction of an excess of methylmagnesium bromide with the diester (19), followed by hydrolysis (Scheme 4), provides an alternative route to the phosphorane (18).

The spontaneous intramolecular dehydration of compound (20) (Scheme 4) is analogous to that of related diols¹³ and diacids which produce diacyloxyphosphoranes *via* cyclodehydration.¹⁴ The unusual stability of the phosphorane (18) is parallel to that of other five-membered ring spirobicyclic phosphoranes^{13,14} and sulphuranes.⁸



SCHEME 4

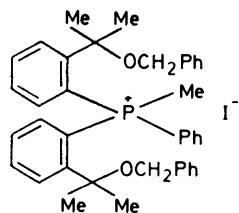
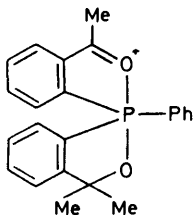
The phosphorane (18) exhibits a typical high-field ^{31}P n.m.r. peak ($\delta = -44.5$). In addition, the ^1H n.m.r. peaks for the diastereotopic¹⁵ methyl groups are well separated at δ 1.16 and 1.58, the methyl group giving rise to the high field (δ 1.16) peak appearing to occupy a position directly above the PhP group in the region shielded by its ring current. The low-field multiplet at δ 8.34–8.55, corresponding to two protons *ortho* to phosphorus, reflects the proximity of each such proton to an apical $\text{P}-\text{O}$ bond.^{7,12} (*Vide supra*).

The phosphine (13) possesses two equivalent sets of prochiral geminal groups¹⁵ (giving two methyl peaks in both ^1H and ^{13}C n.m.r.) and two sets of geminal methylene protons (giving an AB pattern).¹⁶ However, quaternisation of compound (13) with methyl iodide, produces the methiodide (21), which exhibits chemical-shift nonequivalence for every geminal methyl and every benzylic proton at room temperature. Variable-temperature experiments establish a coalescence temperature of 80°C for the merging of two methyl singlets separated by 30 Hz at 28°C . From the Gutowsky–Holm equation,¹² a free energy of activation (ΔG^\ddagger) of *ca.* 18 kcal/mol at 80°C is calculated for the observed equilibration process. Sterically hindered rotation around a $\text{C}-\text{P}$ bond could account for these data.

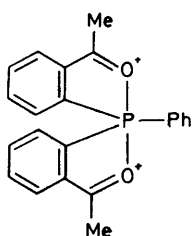
An example of anisogamous (non-equivalent in spin coupling) anisochronous nuclei¹⁶ is provided by the ^{13}C n.m.r. spectrum of compound (13). The coupling constants $^4J_{\text{CP}}$ for the geminal methyls in compound (13) are 0 and 3 Hz; on exceptionally large $^4J_{\text{CP}} = 10$ Hz is found for the geminal methyls of compound (8).

The 70 eV electron-impact mass spectrum of compound (18) shows only two prominent peaks, while the molecular ion abundance is 0.2% of the base peak. Loss of one methyl group from the molecular ion produces the stable $M - \text{CH}_3^+$ ion (base peak), which constitutes 68% of the

total ion current. The only other prominent ion is of *m/e* 173 (11% of the base peak) which is the doubly charged $M - 2\text{CH}_3^{2+}$ ion. Structures such as (22) and (23) would account for this observation.

(21), $\delta^{31}\text{P}$ 40.0

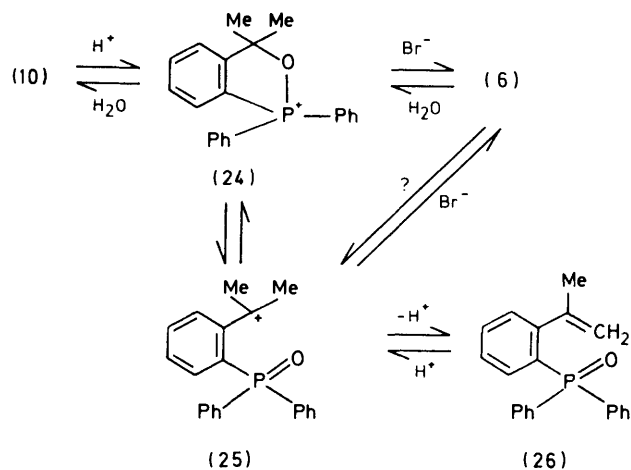
(22)



(23)

Usually, doubly charged ion peaks are very much less intense than the related singly charged ions. The ion (23) is 22 times as abundant as *m/e* 346, the singly charged $M - 2\text{CH}_3^+$ ion. This is a further indication of the exceptional stability of (22) and (23).

The low level of reactivity of compound (6) towards water and the need for hydrogencarbonate to complete



SCHEME 5

its hydrolysis suggested to us that the hydrolysis product, the phosphine oxide (10), might be converted back into (6). This has been achieved by treatment of compound (10) with aqueous hydrobromic acid (48%). A possible equilibrium for these reactions is indicated by the finding of variable amounts of the olefin (26) accompanying the phosphorane (6) in the reaction of the phosphine oxide (10) and HBr. The olefin-phosphorane ratio was found to depend on the acid and bromide ion

concentration. The higher the acid concentration and the lower the bromide concentration, the higher is the olefin content in the reaction mixture. Scheme 5 may account for these observations.

EXPERIMENTAL

N.m.r. chemical shifts are reported in p.p.m. downfield from Me_4Si for ^1H and ^{13}C , and in p.p.m. downfield from 85% H_3PO_4 for ^{31}P . Unless otherwise stated, n.m.r. spectra were obtained for CDCl_3 solutions. Electron-impact mass spectra were obtained at 70 eV and 150–200 °C source temperature. The usual work-up included chloroform extraction, drying over MgSO_4 , filtration, evaporation of the solvent and either distillation or recrystallization, as indicated.

Benzyl-1-(2-bromophenyl)-1-methylethyl Ether (7).—1-(2-Bromophenyl)-1-methylethanol¹⁷ (26 g, 121 mmol), benzyl chloride (40 g, 350 mmol), potassium iodide (2.5 g, 15 mmol), and sodium hydride (3 g, 125 mmol) * were mechanically stirred and heated carefully to allow for controlled hydrogen evolution through a wide-mouthed condenser and CaCl_2 drying tube. The mixture was then stirred and heated for 11 h at 95 ± 5 °C internal temperature. The reaction progress was followed by t.l.c. (silica–benzene). The reaction mixture was cooled, partitioned between water (100 ml) and CH_2Cl_2 (100 ml), worked up, and fractionally distilled to give recovered benzyl chloride at 38 °C/0.5 Torr, and the desired ether (7) (27 g, 73%) which was collected between 140–150 °C/0.6 Torr (b.p. 146 °C/0.6 Torr), ^1H n.m.r. δ 1.76 (6 H, s, Me), 4.22 (2 H, s, CH_2), and 6.95–7.65 (9 H, m, H-Ar).

Diphenyl-2-(1-methyl-1-benzyloxyethyl)phenylphosphine (8).—The bromoether (7) (24.4 g, 80 mmol), magnesium shavings (1.9 g, 78 mg-atom), 1,2-dibromoethane (0.2 g, 1.06 mmol), and dry tetrahydrofuran (THF) (75 ml) were stirred and refluxed until most of the magnesium was dissolved. The solution was then externally cooled by ice-water, and a solution of freshly distilled diphenylphosphinous chloride (17.6 g) in dry THF (15 ml) was added dropwise. This mixture was refluxed for 1 h, cooled, and hydrolysed with 10% sulphuric acid. The usual work-up gave the phosphine (8) (8.3 g, 25%), m.p. 71–72 °C (EtOH), ^1H n.m.r. δ 1.84 (6 H, s, Me), 4.29 (2 H, s, CH_2), and 6.95–7.60 (19 H, m, H-Ar); ^{31}P n.m.r. δ -10.3; ^{13}C n.m.r. δ 28.8 (J_{CP} 10 Hz, Me), 64.1 (CH_2), and 79.1 (CMe_2); mass spectroscopy *m/e* 410 (M^+ , 0.2%), 319 ($M - \text{C}_7\text{H}_7$, 48), 304 ($M - \text{C}_7\text{H}_7 - \text{Me}$, 100), 303 ($M - \text{C}_7\text{H}_7\text{O}$, 18), 289 ($M - \text{C}_7\text{H}_7 - 2\text{Me}$, 20), 276 (18), 183 ($\text{C}_{12}\text{H}_8\text{P}$, 12), and 91 (C_7H_7 , 23).

2-(1-Benzyloxy-1-methylethyl)phenyl(methyl)diphenylphosphonium Iodide.—The phosphine (8) (0.5 g, 1.2 mmol) and methyl iodide (0.5 g, 3.9 mmol) were dissolved in dry ether (20 ml) and left in the dark for 2 days. Filtration gave the crystalline methiodide (0.6, 89%), m.p. 120 °C, ^1H n.m.r. δ 1.70 (6 H, s, Me), 2.92 (3 H, d, $^2J_{\text{HP}}$ 13 Hz, MeP), 4.25 (2 H, s, CH_2), and 6.70–7.80 (19 H, m, H-Ar); ^{31}P n.m.r. δ +28.4; ^{13}C n.m.r. δ 15.9 (J_{CP} 65 Hz, MeP), 29.1 (Me), 65.0 (CH_2), and 81.2 (CMe_2).

Bis[2-(1-methyl-1-benzyloxyethyl)phenyl]phenylphosphine (13).—A Grignard reagent was made from compound (7) (24.4 g, 0.08 mol) as described above for compound (8).

* Sodium hydride was prepared by twice washing with pentane (30 ml) 6 g of the commercial 57% compound in mineral oil.

Phenylphosphonous dichloride (7 g, 39 mmol) in dry THF (10 ml) was added dropwise to the stirred and externally cooled Grignard solution. The resulting mixture was refluxed for 1 h, cooled, and decomposed with 10% sulphuric acid. The usual work-up and recrystallisation from ethanol gave the phosphine (13) (6.5 g, 30%), m.p. 93–94 °C, ^1H n.m.r. δ 1.62 (6 H, s, Me), 1.83 (6 H, s, Me), 3.93 (2 H, d, $^2J_{\text{HH}}$ 12.5 Hz, CHPh), 4.14 (2 H, d, $^2J_{\text{HH}}$ 12.5 Hz, CHPh, AB pattern), 6.90–7.60 (23 H, m, H-Ar); ^{31}P n.m.r. δ -14.5; ^{13}C n.m.r. δ 28.6 (Me), 29.0 ($^4J_{\text{CP}}$ 3 Hz), 64.1 (CH_2), and 79.4 (CMe_2); mass spectroscopy m/e 346 (6%), 225 (6), 119 (100), and 91 (20).

Methylphenylbis[2-(1-methyl-1-benzyloxyethyl)phenyl]-phosphonium Iodide (21).—The phosphine (13) (0.2 g, 0.36 mmol) and methyl iodide (0.2 g, 1.6 mmol) were dissolved in dry ether (10 ml) and left in the dark for 2 days. The precipitated crystalline compound (21) (0.18 g, 73%) was filtered off, m.p. 216 °C, ^1H n.m.r. δ 1.23 (3 H, s, Me), 1.38 (3 H, s, Me), 1.61 (3 H, s, Me), 1.76 (3 H, s, Me), 2.60 (3 H, d, $^2J_{\text{PH}}$ 14 Hz, MeP), 3.81 (1 H, d, $^2J_{\text{HH}}$ 12.5 Hz, CHPh), 4.38 (1 H, d, $^2J_{\text{HH}}$ 12.5 Hz, CHPh, AB pattern), 4.10 (1 H, d, $^2J_{\text{HH}}$ 13 Hz, CHPh), 4.48 (1 H, d, $^2J_{\text{HH}}$ 13 Hz, CHPh, AB pattern), and 6.24–7.86 (23 H, m, H-Ar); ^1H n.m.r. (*o*-dichlorobenzene) δ 1.04 (3 H, s, Me), 1.08 (3 H, s, Me), 1.34 (3 H, s, Me), 1.48 (3 H, s, Me), 2.31 (3 H, d, $^2J_{\text{HP}}$ 14 Hz, MeP), 3.48 (1 H, d, $^2J_{\text{HH}}$ 12 Hz, CHPh), 4.16 (1 H, d, $^2J_{\text{HP}}$ 12 Hz, CHPh, AB pattern), 3.79 (1 H, d, $^2J_{\text{HH}}$ 13 Hz, CHPh), and 4.30 (1 H, d, $^2J_{\text{HH}}$ 13 Hz, CHPh, AB pattern); ^{31}P n.m.r. δ +40.0; ^{13}C n.m.r. δ 22.4 ($^1J_{\text{CP}}$ 72 Hz, MeP), 28.5 (Me), 28.9 (Me), 29.5 (2 Me), 64.6 (CH_2), 65.0 (CH_2), 80.5 (CMe_2), and 81.3 (CMe_2).

1-Bromo-3,3-dimethyl-1,1-diphenyl-3H-2,1-benzoxaphosphole (6).—Phosphine (8) (0.5 g, 1.2 mmol) was stirred with cooling in dry ether (20 ml), while being titrated with 10% bromine solution in carbon tetrachloride. The ether was decanted from the white precipitate of the bromoalkoxyphosphorane (6), which was twice washed with dry ether. The ether solution yielded benzyl bromide upon fractional distillation. The product (6) was dried at 40 °C and 0.5 Torr (0.35 g, 73%), m.p. 110 °C, ^1H n.m.r. δ 1.96 (6 H, s, Me), 7.25–8.00 (13 H, m, H-Ar), 8.33–8.53 (1 H, m, H-ortho to P); ^{31}P n.m.r. δ -17.8; ^{13}C n.m.r. δ 30.4 (Me), 100.5 (CMe_2); field desorption mass spectroscopy m/e 398 (M^+ , 25%), 319 (M - Br, 100).

3,3-Dimethyl-1,1-diphenyl-3H-2,1-benzoxaphospholium Tetrafluoroborate (9).—Bromoalkoxyphosphorane (6) (0.1 g, 2.5 mmol) was dissolved in either 1,2-dichloroethane or CDCl_3 and silver tetrafluoroborate solution in 1,2-dichloroethane was added dropwise until precipitation of silver bromide ceased. Filtration and dilution of the filtrate with dry ether precipitated the crystalline salt (9) (80 mg, 78%), m.p. 158 °C, ^1H n.m.r. δ 1.91 (6 H, s, Me) and 7.50–8.23 (14 H, m, H-Ar); ^{31}P n.m.r. δ +75.6; ^{13}C n.m.r. δ 29.9 (Me) and 100.3 ($^2J_{\text{COP}}$ 2 Hz, CMe_2).

2-(1-Hydroxy-1-methylethyl)phenyl(diphenyl)phosphine Oxide (10).—The phosphine (8) (0.55 g, 1.34 mmol), was dissolved in dry chloroform (3.5 ml) and bromine (0.26 g, 1.63 mg-atom) was added dropwise. The ^{31}P n.m.r. was recorded (δ -17.8) and then water (0.2 g) was added to the n.m.r. tube with vigorous shaking. The ^{31}P n.m.r. showed

practically no change. Addition of concentrated sodium hydrogencarbonate (1 ml) released CO_2 when the tube was shaken, and ^{31}P n.m.r. spectroscopy showed a new signal at δ +41.2 while the δ -17.8 signal disappeared. Work-up gave the phosphine oxide (10) (0.35 g, 78%), m.p. 148 °C (cyclohexane), ^1H n.m.r. 1.63 (6 H, s, Me), 6.30br (1 H, s, HO), 7.00–7.63 (14 H, m, H-Ar); ^{31}P n.m.r. δ +41.2; mass spectroscopy m/e (no M^+), 321 (M - Me, 34%), 318 (M - H_2O , 100), 317 (M - H - H_2O , 50), 303 (M - Me - H_2O , 45), 241 (M - H_2O - Ph, 66), and 227 (77).

3,3,3',3'-Tetramethyl-1-phenyl-1,1'-spirobi[3H-2,1-benzoxaphosphole] (18).—Methylmagnesium bromide (2.9M; 20 ml, 58 mmol) was added dropwise to a stirred benzene (100 ml) solution of bis-(2-methoxycarbonylphenyl)phenylphosphine oxide (21) (4 g, 10.2 mmol),* and the mixture was refluxed for 1.5 h. Quenching with aqueous ammonium chloride followed by work-up and two recrystallisations from aqueous ethanol gave phosphorane (18) (3 g, 78%), m.p. 195 °C, ^1H n.m.r. δ 1.16 (6 H, s, Me), 1.58 (6 H, s, Me), 7.03–7.70 (11 H, m, H-Ar), and 8.34–8.55 (2 H, m, H-ortho to P); ^{31}P n.m.r. δ -44.5; ^{13}C n.m.r. δ 29.9 (Me), 31.4 (Me), 77.0 ($^2J_{\text{COP}}$ 2 Hz, CMe_2); mass spectroscopy m/e 376 (M^+ , 0.2%), 361 (M - Me, 100), 346 (M - 2 Me, 0.5), and 173 (M - 2 Me^{2+} , 11). Neat compound (17) when heated at 100 °C for 10 min yielded an equimolar mixture of benzyl bromide and (18); the latter was characterized by ^1H n.m.r. spectroscopy.

1-[2-(1-Benzyloxy-1-methylethyl)phenyl]-3,3-dimethyl-1-phenyl-3H-2,1-benzoxaphospholium Bromide (17).—The phosphine (13) (0.5 g, 0.9 mmol) was dissolved in dry chloroform (10 ml) and the solution cooled, and titrated with 10% Br_2 solution in CCl_4 with stirring. The resulting solution was added to dry ether (100 ml). The ether was decanted off and the white solid product was twice washed with dry ether and dried *in vacuo* to give compound (17) (0.35 g, 70%), m.p. 98 °C, ^1H n.m.r. δ 1.63 (3 H, s, Me), 1.69 (3 H, s, Me), 1.74 (3 H, s, Me), 1.93 (3 H, s, Me), 4.40 (1 H, d, $^2J_{\text{HH}}$ 12.5 Hz, CHPh), 4.60 (1 H, d, $^2J_{\text{HH}}$ 12.5 Hz, CHPh, AB pattern), and 6.75–8.10 (18 H, m, H-Ar); ^{31}P n.m.r. δ +70.9.

Reaction of Compound (10) with 48% Hydrobromic Acid.—The phosphine oxide (10) was dissolved in CDCl_3 and variable amounts of 48% HBr were added. In one case sodium bromide was also added. In each experiment, the ^1H n.m.r. spectrum was recorded, and the ratio (26)/(6) was calculated from the integration of the appropriate signals. The ratio olefin/bromoalkoxyphosphorane was 1/0.8 for a large excess of HBr; 1/1.4 for 50% molar excess of HBr; 1/3.4 for 50% molar excess HBr with one equivalent added sodium bromide; ^1H n.m.r. [for (26)] δ 1.82br (3 H, s, Me), 4.65 (1 H, m, CH), 4.87 (1 H, m, CH), and 7.10–7.60 (14 H, m, H-Ar); ^1H n.m.r. [for (6)] δ 1.96 (6 H, s, Me), 7.00–7.95 (13 H, m, H-Ar), and 8.30–8.50 (1 H, m, H-ortho to P).

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REFERENCES

- For a review, see R. G. Harvey and E. R. De Sombre, *Top. Phosphorus Chem.*, 1964, **1**, 57.
- (a) A. Skowronska, J. Miloljczak, and J. Michalski, *J. Chem.*

* Ref. 15 and unpublished results by Y. Segall and I. Granoth. The diester was made by refluxing 50% aqueous dioxan solution of the dipotassium salt of bis-2-carboxyphenylphenylphosphine oxide with a 50% excess of methyl iodide, m.p. 197 °C, ^1H n.m.r. δ 3.43 (6 H, s, Me) and 7.30–7.90 (13 H, m, H-Ar).

- Soc. Chem. Commun.*, 1975, 791; (b) D. B. Denney, D. Z. Denney, and G. Di Miele, *Phosphorus Sulfur*, 1978, **4**, 125; (c) J. Michalski, J. Mikoljczak, M. Pakulski, and A. Skowronska, *ibid.*, 1978, **4**, 233.
- ³ J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, 1965, **30**, 2635; 2639.
- ⁴ A. G. Anderson, jun., and F. J. Freenor, *J. Am. Chem. Soc.*, 1964, **86**, 5037.
- ⁵ L. A. Jones, C. E. Sumners, jun., B. Franzus, T. T.-S. Huang, and E. I. Snyder, *J. Org. Chem.*, 1978, **43**, 2821.
- ⁶ D. Dakternieks, G. V. Rosenthaler, and R. Schmutzler, *J. Fluorine Chem.*, 1978, **11**, 387.
- ⁷ T. M. Balthazor and J. C. Martin, *J. Am. Chem. Soc.*, 1975, **97**, 5634; J. C. Martin and T. M. Balthazor, *ibid.*, 1977, **99**, 152.
- ⁸ (a) J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, 1974, **96**, 3155; (b) J. C. Martin and E. F. Perozzi, *Science*, 1976, **191**, 154.
- ⁹ I. Granoth and J. C. Martin, *J. Am. Chem. Soc.*, 1978, **100**, 5229, 7434; *ibid.*, 1979, **101**, 4618, 4623.
- ¹⁰ M. M. Crutchfield, C. H. Dungun, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, 1967, **5**, 1.
- ¹¹ C. R. Johnson and J. J. Rigau, *J. Am. Chem. Soc.*, 1969, **91**, 5398.
- ¹² L. J. Adzima, C. C. Chiang, I. C. Paul, and J. C. Martin, *J. Am. Chem. Soc.*, 1978, **100**, 953; G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, 1977, **99**, 4390.
- ¹³ D. Hellwinkel and W. Krapp, *Chem. Ber.*, 1978, **111**, 13.
- ¹⁴ Y. Segall and I. Granoth, *J. Am. Chem. Soc.*, 1978, **100**, 5130.
- ¹⁵ W. B. Jennings, *Chem. Rev.*, 1975, **75**, 307.
- ¹⁶ W. McFarlane, *Chem. Commun.*, 1968, 229.
- ¹⁷ W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, 1971, **93**, 6205. The published procedure was used, replacing the acid quench of the Grignard reaction by aqueous ammonium chloride.