Reactions of Bromonitroalkenes with Tervalent Phosphorus. Part I. Reaction in Aprotic Solvents

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The reaction of a variety of 2-substituted 1-bromo-1-nitroethylenes with triphenylphosphine in benzene or ethyl acetate gave good yields of cyanomethyl(triphenyl)phosphonium salts, which on treatment with base afforded the corresponding ylides. An analogous cyanomethylphosphonate was obtained from a reaction with triethyl phosphite. Three alternative sites of initial attack by phosphine are considered in an attempt to explain the deoxygenation reaction; efforts to gain evidence for one of these (initial attack at halogen) were only partially successful.

UNLIKE their aromatic counterparts,[1] the reactions of aliphatic nitro-compounds with tervalent phosphorus have not been extensively investigated. In the few cases where these reactions have been studied, formal reduction of the nitro-group has taken place, generally through elimination of phosphine oxide.[2] The present study was initiated to gain further information about these reactions, with the ultimate objective of the synthesis of the so far unknown α-nitroalkylphosphonium salts.

2-Substituted 1-bromo-1-nitroethylenes (1) react with triphenylphosphine in dry aprotic solvents to give cyanomethyl(triphenyl)phosphonium bromides (2) and

$$RCH{=}CBr{\cdot}NO_2 + 3Ph_3P \longrightarrow Ph_3\overset{+}{P}{-}CHR{\cdot}CN\ Br^- + 2Ph_3PO$$
(1) (2)

$$Ph_3P{=}CR{\cdot}CN$$
(3)

$$PhCHBr{\cdot}CN + Ph_3P \longrightarrow Ph_3\overset{+}{P}{\cdot}CHPh{\cdot}CN\ Br^-$$
(4)

$$PhCH{=}CBr{\cdot}NO_2 + (EtO)_3P \longrightarrow (EtO)_2\overset{O}{\overset{\|}{P}}CHPh{\cdot}CN + (EtO)_3PO$$
(5)

triphenylphosphine oxide. The yield swere highest when 3 mol. equiv. of triphenylphosphine were used. The results from a variety of bromonitroethylenes are outlined in the Table. Reactions of 1-bromo-1-nitro-2-(4-nitrophenyl)ethylene and its 2-(2,4-dinitrophenyl) analogue with triphenylphosphine gave triphenylphosphine

Reaction of 1-bromo-1-nitroethylenes with triphenylphosphine

(1)	R	Salt (2) (%)	Ph_3PO (%)
a	Ph	80	89
b	4-MeC_6H_4	68	67
c	4-$MeO{\cdot}C_6H_4$	66	84
d	3-$O_2N{\cdot}C_6H_4$	65	64
e	3-ClC_6H_4	69	71
f	Me	66	70

oxide as the only isolable product; a similar reaction with 1-chloro-1-nitro-2-phenylethylene gave phosphine oxide and an unidentified red oil.

The salts obtained were readily converted into the corresponding ylides (3) by treatment with dilute aqueous sodium hydroxide. Attempts to carry out a Wittig reaction with these ylides were unsuccessful; even heating to 150 °C with benzaldehyde in dimethyl sulphoxide gave no apparent reaction.

The salts (2) were identified on the basis of spectral data. In all aryl-substituted cases the n.m.r. spectra showed one low-field doublet (J 18 Hz) between τ 0·14 and 0·93 (which disappeared on conversion into the corresponding ylide), as expected for a highly deshielded proton α to phosphorus. The salt (2f) obtained from 1-bromo-1-nitropropene (1f) showed an eight-line multiplet at τ 1·92 and a doublet of doublets at τ 8·32 (J_{HH} 6, J_{PH} 17 Hz), which became a doublet (J 13 Hz) on conversion into the ylide (3). The salts (2) showed no normal nitro or cyano i.r. stretching absorptions, but the corresponding ylides (3) showed absorptions between 2120 and 2150 cm^{-1} attributed to CN stretching. Molecular ions were observed in the mass spectra of the ylides (3), but the highest m/e values for the salts (2) corresponded to the fragment M — HBr.

Chemical confirmation of the salt structures was obtained by the preparation of an authentic sample of α-cyanobenzyl(triphenyl)phosphonium bromide from α-bromobenzyl cyanide (4) and triphenylphosphine. The halide (4) was conveniently prepared by the reaction of benzyl cyanide with *N*-bromosuccinimide. Finally hydrolysis of the ylide (3a) with refluxing aqueous 5N-sodium hydroxide, followed by acidification, gave phenylacetic acid and triphenylphosphine oxide in high yield.

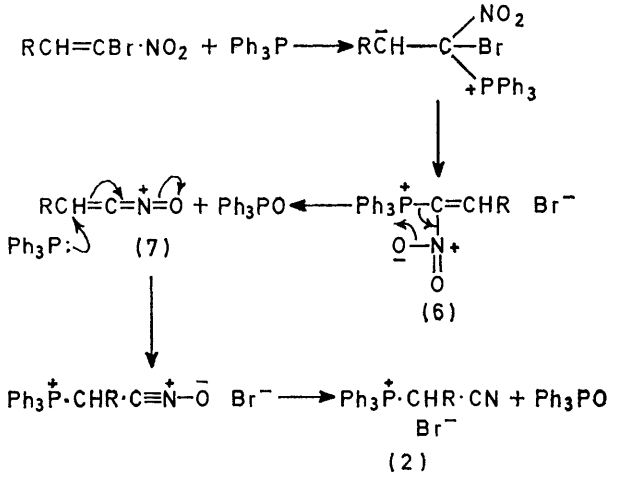
A similar deoxygenation reaction takes place with triethyl phosphite, which with 1-bromo-1-nitro-2-phenylethylene under anhydrous conditions gave diethyl α-cyanobenzylphosphonate (5) and triethyl phosphate in high yield. The identification of the phosphonate (5) is based on its mass and n.m.r. spectra; the latter shows a one-proton doublet at τ 2·35 (J_{PH} 15 Hz) and peaks characteristic of $(EtO)_2P(O)$ at τ 5·86 and 8·72. In early experiments considerable amounts of diethyl phosphite were also formed, but this was shown to be due to traces of water in the reaction mixture.

At least three alternative sites of initial attack by

[1] J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.
[2] S. Trippett, B. J. Walker, and H. Hoffmann, *J. Chem. Soc.*, 1965, 7140; M. Ohno and I. Sakai, *Tetrahedron Letters*, 1965, 4541; M. Ohno and N. Kawabe, *ibid.*, 1966, 3935.

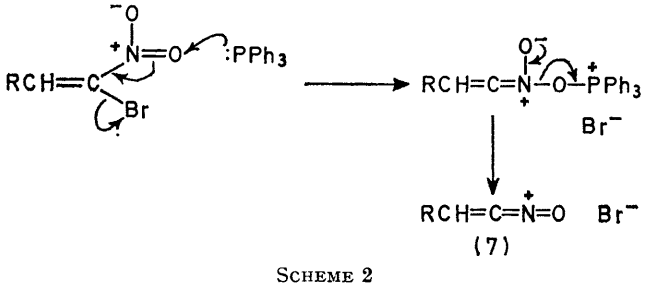
phosphine can be envisaged to explain the formation of the salts (2). Attack at halogen attached to carbon followed by elimination would give the α-nitro-salt (6). Such salts have never been isolated and that they should readily eliminate phosphine oxide is not unreasonable. Further addition of phosphine followed by deoxygenation as shown (Scheme 1) would lead to the isolated products. However, phosphine additions to the double bond would be expected to occur in the opposite sense,[3] owing to the polarity of this bond, although small contributions through a reversible step could be envisaged.

Attack of phosphine at the oxygen of the nitro-group followed by elimination of phosphine oxide (Scheme 2) would give an intermediate (7) common to Scheme 1. By analogy with the Perkow reaction [4] a similar scheme involving initial attack at nitrogen followed by rearrangement, can be envisaged.



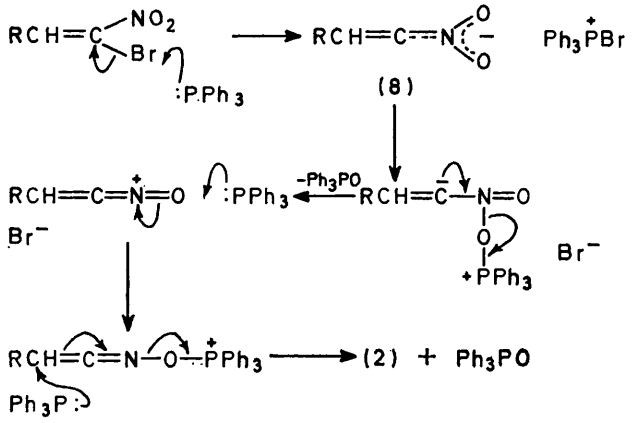
SCHEME 1

Finally, initial attack could occur at the halogen to give the ion pair (8), which through progressive deoxygenation and final addition of phosphine would give the



SCHEME 2

observed products (Scheme 3). In an attempt to gain support for this last mechanism the reactions were repeated with methanol as solvent, since reactions involving initial attack on halogen are known to be suppressed in this solvent through hydrolysis of the ion pair corresponding to (8). However, although in some cases small yields of methyltriphenylphosphonium bromide and nitroalkene [the expected products of hydrolysis of (8)]



SCHEME 3

were obtained, the main course of the reaction was completely changed.[5]

EXPERIMENTAL

M.p.s were taken on a Kofler micro hot-stage apparatus. I.r., mass, and n.m.r. spectra were obtained with a Perkin-Elmer model 457, an A.E.I. MS-902, and a Varian HA-100 spectrometer (tetramethylsilane as an internal reference), respectively.

Halogenonitroalkenes.— 1-(2,4-*Dinitrophenyl*)-2-*nitroethylene*. 1-(2,4-Dinitrophenyl)-2-nitroethyl nitrate [6] (12·7 g, 0·042 mol) was refluxed in methanol (250 ml) for 3 h. The volume was then reduced to 100 ml by distillation and the resulting light yellow solution was kept at 0—5° for 2 h. Filtration and recrystallisation from methanol gave 1-(2,4-dinitrophenyl)-2-nitroethylene (4·3 g, 43%), m.p. 105—107°.

1,2-*Dibromo*-1-(2,4-*dinitrophenyl*)-2-*nitroethane*. To 1-(2,4-dinitrophenyl)-2-nitroethylene [6] (4·3 g, 0·018 mol) in chloroform (30 ml) was added bromine (2·9 g, 0·93 ml, 0·018 mol) at room temperature. The solution was refluxed for 30 min and the solvent was removed under reduced pressure to give an oil which slowly solidified. Crystallisation from methanol gave white crystals of 1,2-*dibromo*-1-(2,4-*dinitrophenyl*)-2-*nitroethane* (5·6 g, 78%), m.p. 140—141°; $\nu_{max.}$ (KBr) 1575, 1540, and 1345 cm^{-1}; *m/e* 356(5%), 354(10), 164(100), 109(15), 91(13), 82(46), and 80(46) (Found: C, 23·7; H, 1·5; Br, 40·1. $C_8H_5Br_2N_3O_6$ requires C, 24·1; H, 1·3; Br, 40·1%).

1-*Bromo*-2-(2,4-*dinitrophenyl*)-1-*nitroethylene*. To 1,2-dibromo-1-(2,4-dinitrophenyl)-2-nitroethane (3·99 g, 0·01 mol) in ethanol (100 ml), at 0—5°, was added anhydrous potassium acetate (0·98 g, 0·01 mol) in ethanol (25 ml) in one portion. The solution was allowed to reach room temperature and then heated at 60° for 30 min. The volume was reduced to 60 ml under reduced pressure, cold water (25 ml) was added, and the solid was filtered off and washed with water. Recrystallisation from ethanol gave light yellow needles of the *olefin* (1·7 g, 53%), m.p. 115—116; $\nu_{max.}$ (KBr) 1535, 1345, and 1325 cm^{-1}; *m/e* 319(4%), 317(4), 169(24), 167(24), 165(27), 164(100), 134(25), 118(44),

[3] G. Pattenden and B. J. Walker, *J. Chem. Soc.* (*C*), 1969, 531.
[4] P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, 1965, **21**, 1961.
[5] C. J. Devlin and B. J. Walker, *Chem. Comm.*, 1970, 917; and unpublished results.
[6] L. F. Fieser and W. H. Daudt, *J. Amer. Chem. Soc.*, 1946, **68**, 2248.

and 109(21); τ ($CDCl_3$) 0·93 (1H, d), 1·17 (1H, s), 1·42 (1H, dd), and 2·15 (1H, d) (Found: C, 30·3; H, 1·2; Br, 25·2. $C_8H_4BrN_3O_6$ requires C, 30·2; H, 1·3; Br, 25·2%).

1,2-*Dibromo*-1-*nitro*-2-(3-*nitrophenyl*)*ethane*.[7] To 1-nitro-2-(3-nitrophenyl)ethylene [8] (1·94 g, 0·01 mol) in chloroform (25 ml) was added bromine (1·6 g, 0·52 ml, 0·01 mol), and the solution was refluxed for 12 h. The chloroform was removed under reduced pressure and the residue, crystallised from ethanol, gave white crystals of 1,2-dibromo-1-nitro-2-(3-nitrophenyl)ethane (2·6 g, 73%), m.p. 154—156° (lit.,[7] 158°); $\nu_{max.}$ (KBr) 1575, 1520, and 1350 cm^{-1}; *m/e* 356(1%), 354(2), 229(46), 227(46), 194(40), 147(46), 118(33), 102(100), and 101(100).

1-*Bromo*-1-*nitro*-2-(3-*nitrophenyl*)*ethylene* (1d).[7] To 1,2-dibromo-1-nitro-2-(3-nitrophenyl)ethane (2·1 g, 0·006 mol) in ethanol (100 ml) was added anhydrous sodium acetate (0·49 g, 0·006 mol) in ethanol (40 ml) in one portion. The resulting solution was heated at 60° for 30 min. The volume was reduced (50 ml) under reduced pressure and the solution was stored at 0° for 12 h. The yellow needles were filtered off, washed with water (2 × 50 ml), dried, and recrystallised from ether–ethyl acetate (2 : 1) to give the olefin (1d) (1·2 g, 73%), m.p. 113—114° (lit.,[7] 114—115°) $\nu_{max.}$ (KBr) 1525 and 1305 cm^{-1}; *m/e* 274(30%), 272(30), 198(30), 196(30), 147(45), 101(100), and 89(35); τ ($CDCl_3$) 1·20 (1H, t), 1·32 (1H, s), 1·61 (1H, dq), 1·85 (1H, dq), and 2·27 (1H, t) (Found: C, 35·1; H, 1·15; Br, 29·5. $C_8H_5BrN_2O_4$ requires C, 35·2; H, 1·8; Br, 29·3%).

1-Bromo-1-nitro-2-(4-nitrophenyl)ethylene,[9] m.p. 135—136°, *m/e* 274 and 272, τ [$(CD_3)_2SO$] 1·54—1·98(m), was prepared in a similar way.

1,2-*Dibromo*-1-(3-*chlorophenyl*)-2-*nitroethane*. To 1-(3-chlorophenyl)-2-nitroethylene [10] (4·22 g, 0·023 mol) in chloroform (40 ml), bromine (3·68 g, 1·18 ml, 0·023 mol) was added dropwise at room temperature. The resulting solution was refluxed for 12 h. Then the chloroform was removed under reduced pressure and the residue was recrystallised from ethanol to give white crystals of 1,2-*dibromo*-1-(3-*chlorophenyl*)-2-*nitroethane* (5·5 g, 70%), m.p. 64—65°; $\nu_{max.}$ (KBr) 1565 and 1345 cm^{-1}; *m/e* 347(3%), 345(12), 343(17), 220(20), 218(100), 216(73), 185(16), and 183(53) (Found: C, 28·0; H, 1·8. $C_8H_6Br_2ClNO_2$ requires C, 28·0; H, 1·7%).

1-*Bromo*-2-(3-*chlorophenyl*)-1-*nitroethylene* (1e). To 1,2-dibromo-1-(3-chlorophenyl)-2-nitroethane (3·78 g, 0·011 mol) in ethanol (100 ml), anhydrous potassium acetate (1·08 g, 0·011 mol) in ethanol (25 ml) was added. The solution was stirred for 2 h at room temperature, then refluxed for 30 minutes, cooled, and filtered. The filtrate was evaporated to dryness under reduced pressure. Water (100 ml) and ether (100 ml) were added to the residue. The ether layer was washed with water (2 × 100 ml) and dried ($MgSO_4$). Removal of the ether gave an oil which was dissolved in hot light petroleum (b.p. 40—60°) and kept overnight at 0°. Yellow needles of 1-*bromo*-2-(3-*chlorophenyl*)-1-*nitroethylene* (2·1 g, 73%), m.p. 37—38°, were obtained; $\nu_{max.}$ (KBr) 1540 and 1310 cm^{-1}; *m/e* 265(3%), 263(10), 136(100), and 108(8) (Found: C, 36·4; H, 2·0. $C_8H_5BrClNO_2$ requires C, 36·5; H, 1·9%).

1,2-*Dibromo*-3-*nitropropane*. To 1-nitropropene [11] (4·18 g, 0·048 mol) in chloroform (40 ml), bromine (7·68 g, 2·48 ml, 0·048 mol) was added dropwise at room temperature. The solution was refluxed for 6 h (until it became colourless). The chloroform was removed under reduced pressure and fractional distillation gave an oil, 1,2-dibromo-3-nitropropane [12] (10·5 g, 89%), b.p. 50—52° at 0·1 mmHg, n_D^{20} 1·5248; $\nu_{max.}$ (film) 1565 and 1350 cm^{-1}; *m/e* 203(50%), 201(100), 199(50), 121(70), and 119(70); τ ($CDCl_3$) 4·03 (1H, d), 5·38 (1H, octet), and 8·12 (3H, d).

1-*Bromo*-1-*nitropropene* (1f). To 1,2-dibromo-3-nitropropane (8·65 g, 0·035 mol) in ether (150 ml), protected from moisture by calcium chloride drying tubes, was added finely ground anhydrous potassium acetate (3·43 g, 0·035 mol). The mixture was stirred at room temperature for 12 h, then the solid was filtered off and the ether layer was washed with water (100 ml) and dried ($MgSO_4$). Careful removal of the ether under reduced pressure followed by fractional distillation gave a yellowish lachrymatory liquid, 1-bromo-1-nitropropene [13] (4·1 g, 71%), b.p. 58° at 10 mmHg, $n_D^{19.5}$ 1·5139; $\nu_{max.}$ (film) 1550 and 1315 cm^{-1}; *m/e* 167(8%), 121(14), 119(14), 76(76), and 59(100); τ ($CDCl_3$) 2·24 (1H, q) and 7·98 (3H, d).

Reactions of 1-*Bromo*-1-*nitroethylenes with Triphenylphosphine*.—(*a*) To 1-bromo-1-nitro-2-phenylethylene (1a) [14] (2·74 g, 0·012 mol) in benzene (100 ml), triphenylphosphine (9·43 g, 0·036 mol) in benzene (100 ml) was added gradually during 15 min at room temperature. The solution was stirred at room temperature for 24 h. The precipitate was filtered off, washed with ethyl acetate (3 × 50 ml) and ether (3 × 50 ml), and recrystallised from chloroform–ethyl acetate to give a white crystalline solid, α-*cyanobenzyl*(*triphenyl*)*phosphonium bromide* (2a) (4·4 g, 80%), m.p. 255—256°; $\nu_{max.}$ (KBr) 2660, 1580, 1485, 1435, and 1105 cm^{-1}; *m/e* 377; τ ($CDCl_3$) 0·75 (1H, d, J_{PH} 18 Hz) and 2·18 (20H, m) (Found: C, 67·8; H, 4·3; Br, 18·0. $C_{26}H_{21}BrNP$ requires C, 68·1; H, 4·6; Br, 17·5%).

The filtrate and washings were evaporated to dryness under reduced pressure and the residue (7·4 g) was dissolved in ethyl acetate (50 ml) and chromatographed on alumina (700 g). Elution with ether gave traces of triphenylphosphine and elution with ethyl acetate gave triphenylphosphine oxide (5·9 g), m.p. and mixed m.p. 153—154°.

(*b*) 1-Bromo-1-nitro-2-(*p*-tolyl)ethylene (1b) [15] (2·90 g, 0·012 mol) in ethyl acetate (200 ml) was added to a solution of triphenylphosphine (9·43 g, 0·036 mol) in ethyl acetate (100 ml) at room temperature during 15 min. The resulting solution was stirred for 24 h. The semi-solid was filtered off, washed with ethyl acetate (100 ml) and ether (200 ml), and recrystallised from chloroform–ethyl acetate to give a semicrystalline solid, α-cyano-4-methylbenzyl(triphenyl)-phosphonium bromide (2b) (3·8 g, 68%), m.p. 164—168°; $\nu_{max.}$ (KBr) 2780, 1585, 1485, 1440, and 1100 cm^{-1}; *m/e* 391; τ ($CDCl_3$) 0·88 (1H, d, J_{PH} 18 Hz), 2·26 (15H, m), 2·98 (4H, m), and 7·70 (3H, d, J_{PH} 3 Hz), for which a satisfactory analysis was not obtained. Chromatography of the residue on alumina gave triphenylphosphine oxide (4·4 g, 67%), m.p. and mixed m.p. 153—154°.

(*c*) By a similar procedure 1-bromo-2-(4-methoxyphenyl)-1-nitroethylene (1c) [16] gave semicrystalline α-cyano-4-

[7] J. W. Baker, *J. Chem. Soc.*, 1931, 2416.
[8] K. H. Slotta and G. Szyszka, *Ber.*, 1935, **68**, 184.
[9] J. Thiele and S. Haeckel, *Annalen*, 1902, **325**, 1.
[10] N. Campbell, W. Anderson, and J. Gilmore, *J. Chem. Soc.*, 1940, 446.
[11] G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1947, 1471.
[12] E. Schmidt and G. Rutz, *Ber.*, 1928, **61**, 2142.
[13] E. A. Braude, E. R. H. Jones, and G. G. Rose, *J. Chem. Soc.*, 1947, 1104.
[14] W. E. Parham and J. L. Bleasdale, *J. Amer. Chem. Soc.*, 1951, **73**, 4664.
[15] D. E. Worrall, *J. Amer. Chem. Soc.*, 1938, **60**, 2841.
[16] K. W. Rosenmund and K. Kuhnheun, *Ber.*, 1923, **56**, 1262.

methoxybenzyl(triphenyl)phosphonium bromide (2c) (66%), m.p. 135—140° (chloroform–ethyl acetate); $\nu_{max.}$ (KBr) 2790, 1600, 1505, 1435, and 1100 cm^{-1}; *m/e* 407; τ ($CDCl_3$) 0·93 (1H, d, J_{PH} 18 Hz), 2·22 (15H, m), 3·10 (4H, m) and 6·30 (3H, s).

(*d*) 1-Bromo-1-nitro-2-(3-nitrophenyl)ethylene (1d) gave α-cyano-3-nitrobenzyl(triphenyl)phosphonium bromide (2d) (75%), m.p. 140—144°, as a semicrystalline solid. A crystalline sample, m.p. 215—216° was however obtained by successive recrystallisations from chloroform–ethyl acetate; $\nu_{max.}$ (KBr) 2680, 1590, 1525, 1440, 1350, and 1100 cm^{-1}; *m/e* 422; τ ($CDCl_3$) 0·14 (1H, d, J_{PH} 18 Hz) and 2·20 (19H, m).

(*e*) 1-Bromo-2-(3-chlorophenyl)-1-nitroethylene (1e) gave semicrystalline α-cyano-3-chlorobenzyl(triphenyl)phosphonium bromide (2e) (79%), m.p. 148—151° (from chloroform–ethyl acetate); $\nu_{max.}$ (KBr) 2785, 1575, 1435, and 1100 cm^{-1}; *m/e* 413, 412, and 411; τ ($CDCl_3$) 0·46 (1H, d, J_{PH} 18 Hz), 2·22 (15H, m), and 2·85 (4H, m).

(*f*) 1-Bromo-1-nitropropene (1f) gave *α-cyanoethyl(triphenyl)phosphonium bromide* (2f) (66%) as white crystals (from chloroform–ethyl acetate), m.p. 188—189°; $\nu_{max.}$ (KBr) 2780, 1590, 1485, 1440 and 1100 cm^{-1}; *m/e* 315; τ ($CDCl_3$) 1·92 (1H, 8 lines), 2·22 (15H, m), and 8·32 (3H, q, J_{HH} 6, J_{PH} 17 Hz) (Found: C, 63·4; H, 4·5. $C_{21}H_{19}BrNP$ requires C, 63·6; H, 4·8%).

Preparation of Ylides from the Phosphonium Salts (2).—α-Cyanobenzyl(triphenyl)phosphonium bromide (2a) (4·12 g, 0·009 mole) in chloroform (300 ml) was shaken with cold aqueous 5N-sodium hydroxide (25 ml) for 5 min. The chloroform layer was washed with water (3 × 50 ml), dried ($MgSO_4$), and evaporated to give an oil which crystallised when triturated with ether (3 ml). Recrystallisation from ethyl acetate–ether (4 : 1) gave yellow crystals of *α-cyanobenzylidene(triphenyl)phosphorane* (3a) (2·1 g, 70%), m.p. 203—204°; $\nu_{max.}$ (KBr) 2145, 1595, 1495, 1435, and 1100 cm^{-1}; *m/e* 377(100%), 262(23), 183(75), 108(18), and 77(14) (Found: C, 82·5; H, 5·6; P, 8·3. $C_{26}H_{20}NP$ requires C, 82·7; H, 5·4; P, 8·2%).

α-Cyano-4-methylbenzyl(triphenyl)phosphonium bromide (2b) gave yellow crystals of *α-cyano-4-methylbenzylidene(triphenyl)phosphorane* (0·55 g, 47%), m.p. 214—215°; $\nu_{max.}$ (KBr) 2150, 1610, 1510, 1440, and 1100 cm^{-1}; *m/e* 391 and 351; τ ($CDCl_3$) 2·38 (15H, m), 3·19 (4H, m), and 7·85 (3H, s) (Found: C, 83·2; H, 5·4; P, 8·0. $C_{27}H_{22}NP$ requires C, 82·9; H, 5·6; P, 7·9%).

α-Cyano-4-methoxybenzyl(triphenyl)phosphonium bromide (2c) gave *α-cyano-4-methoxybenzylidene(triphenyl)phosphorane* (54%) as yellow crystals, m.p. 211—212° (ethyl acetate); $\nu_{max.}$ (KBr) 2815, 2140, 1585, 1495, 1435, 1240 and 1100 cm^{-1}; *m/e* 407 and 392; τ ($CDCl_3$) 2·4 (15H, m), 3·3 (4H, m), and 6·34 (3H, s) (Found: C, 79·4; H, 4·5; P, 7·9. $C_{27}H_{21}NOP$ requires C, 79·8; H, 4·5; P, 7·6%).

α-Cyano-3-nitrobenzyl(triphenyl)phosphonium bromide (2d) gave *α-cyano-3-nitrobenzylidene(triphenyl)phosphorane* (65%), as orange-red crystals (from ethyl acetate), m.p. 220—222°; $\nu_{max.}$ (KBr) 2145, 1610, 1525, 1480, 1440, 1345, and 1105 cm^{-1}; *m/e* 422, 396, and 392 (Found: C, 73·9; H, 5·2; P, 7·6. $C_{26}H_{19}N_2O_2P$ requires C, 73·9; H, 4·5; P, 7·3%).

α-Cyano-3-chlorobenzyl(triphenyl)phosphonium bromide (2e) gave *α-cyano-3-chlorobenzylidene(triphenyl)phosphorane* (65%) as yellow crystals (from ethyl acetate), m.p. 195—198°; $\nu_{max.}$ (KBr) 2145, 1588, 1475, 1440 and 1100 cm^{-1}; *m/e* 413, 412, 411, and 410 (Found: C, 76·2; H, 4·3; Cl, 8·8. $C_{26}H_{19}ClNP$ requires C, 75·8; H, 4·6; Cl, 8·6%).

α-Cyanoethyl(triphenyl)phosphonium bromide (2f) gave α-cyanoethylidene(triphenyl)phosphorane (67%) as white crystals [from ethyl acetate–light petroleum (b.p. 40—60°)], m.p. 172—174° (lit.,[17] 176°); $\nu_{max.}$ (KBr) 2120, 1480, 1438, and 1110 cm^{-1}; *m/e* 315; τ ($CDCl_3$) 1·44 (15H, m) and 8·30 (3H, d, J_{PH} 13 Hz) (Found: C, 79·9; H, 5·9. Calc. for $C_{21}H_{18}NP$: C, 80·0; H, 5·7%).

α-Cyanobenzyl(triphenyl)phosphonium bromide (2a).—(*a*) Benzyl cyanide (11·7 g, 0·100 mol), *N*-bromosuccinimide (17·8 g, 0·100 mol), and benzoyl peroxide (1·2 g, 0·005 mol) were refluxed in carbon tetrachloride (250 ml) for 4 h. The solution was then cooled and filtered, and the carbon tetrachloride was removed under reduced pressure. Fractional distillation of the residue gave α-bromobenzyl cyanide (10·8 g, 55%), b.p. 74—76° at 0·5 mmHg (lit.,[18] 137—139° at 15 mmHg).

(*b*) α-Bromobenzyl cyanide (8·82 g, 0·045 mol) and triphenylphosphine (11·79 g, 0·045 mol) in benzene (200 ml) were stirred for 24 h at room temperature. The solid was filtered off, washed with ethyl acetate (3 × 100 ml) and ether (100 ml), and recrystallised from chloroform–ethyl acetate to give white crystals of α-cyanobenzyl(triphenyl)-phosphonium bromide (8·0 g, 39%), m.p. 255—256°, identical with the salt isolated previously.

Hydrolysis of α-Cyanobenzylidene(triphenyl)phosphorane.—α-Cyanobenzylidene(triphenyl)phosphorane (0·75 g, 0·002 mol) in ethanol (70 ml) and aqueous 5N-sodium hydroxide (50 ml) was refluxed for 12 h. The solution was cooled, diluted with water (120 ml), and extracted with ethyl acetate (2 × 100 ml). The extract was washed with water (2 × 100 ml) and dried ($MgSO_4$). Evaporation gave triphenylphosphine oxide (0·43 g, 83%), m.p. and mixed m.p. 153—154°.

The aqueous portion was neutralised with concentrated hydrochloric acid at 0° and extracted with ether (3 × 200 ml). Evaporation of the dried extract gave white crystals of phenylacetic acid (0·18 g, 65%), m.p. and mixed m.p. 76—77°; *m/e* 137(5%), 136(58), 92(35), 91(100), 77(3), 65(23), 63(100), and 51(8).

Reaction of Triethyl Phosphite with 1-Bromo-1-nitro-2-phenylethylene.—To the olefin (1a) (3·42 g, 0·015 mol) in benzene (70 ml) at room temperature, triethyl phosphite (7·47 g, 0·045 mol) in benzene (40 ml) was added in one portion with stirring under dry nitrogen. An exothermic reaction occurred and a bronze colour developed which gradually changed to yellow within 1 h. The solution was stirred for 14 h. The solvent was removed under reduced pressure, care being taken to maintain the bath temperature at *ca.* 20°. The residue was chromatographed on silica gel (500 g). Elution with ether gave an oil (2·7 g) which on distillation gave diethyl α-cyanobenzylphosphonate (1·9 g, 51%) as a yellowish oil, b.p. 120—124° at 0·03 mmHg; $\nu_{max.}$ (film) 2980, 2900, 2240, 1535, 1260, 1030, and 960 cm^{-1}; *m/e* 252(6%), 240(5), 117(93), 116(50), 109(83), 105(100), 81(42), and 77(25); τ ($CDCl_3$) 2·35 (1H, d, J_{PH} 15 Hz), 2·58 (5H, m), 5·86 (4H, m), and 8·72 (6H, m). The n.m.r. spectrum also showed an unidentified impurity singlet at τ 7·84. Elution with ethyl acetate gave a sweet-smelling liquid from which triethyl phosphate (3·9 g, 72%) was distilled; b.p. 96—98° at 10 mmHg.

[17] S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1959, 3874.
[18] J. D. Loudon and I. Wellings, *J. Chem. Soc.*, 1959, 1780.

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