Rearrangements of Secondary and Tertiary Carbonium Ions by Diphenylphosphinyl Migration

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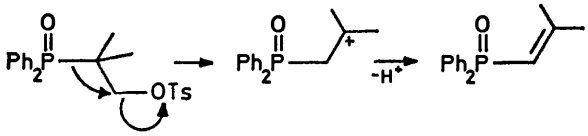
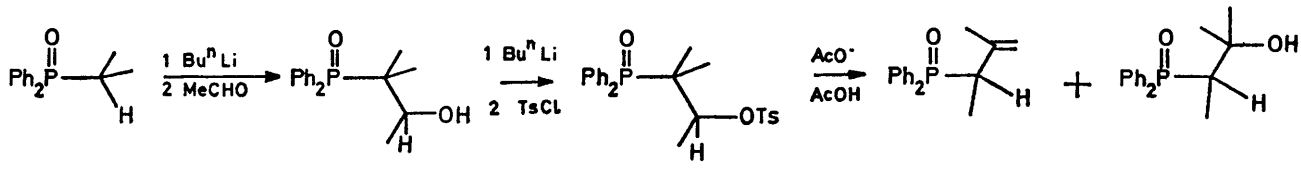
Secondary and tertiary carbonium ions with a β-diphenylphosphinyl substituent, generated by solvolysis of sulphonates, or electrophilic attack on suitable olefins, rearrange exclusively by diphenylphosphinyl migration. The preference for this supposedly unfavourable reaction pathway is investigated.

WHEN we first observed[1] migration of the electronegative diphenylphosphinyl (Ph_2PO) group in the solvolysis of the tosylate (1), we supposed that this apparently unfavourable reaction might occur because (i) this is the only pathway to the stable tertiary alkyl cation (2), and (ii) the alternatives are unattractive: methyl migration would give an unstable α-phosphinyl



(1) (2) (3)

cation, and direct displacement would be unfavourable at a neopentyl position.



(4) (5) (6) (7)

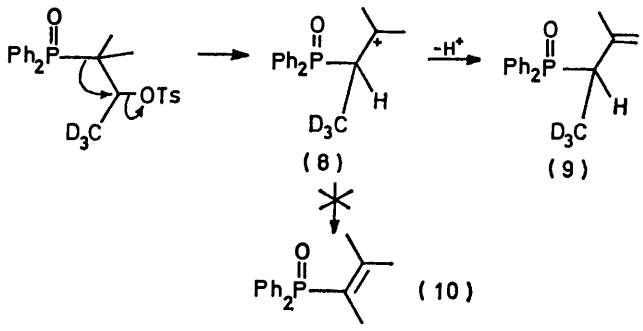
We also observed that the reaction occurred some 200 times slower than the corresponding methyl migration in neopentyl tosylate and this seemed to confirm that Ph_2PO migration was not instrinsically preferred to methyl migration. We have now investigated[2] two further types of rearrangement which show that Ph_2PO migration occurs even when the driving force to produce a tertiary cation is absent, and when a reasonable alternative pathway, elimination to give an olefin, is available.

Solvolysis of the tosylate of the secondary alcohol (5), prepared by Horner's method[3] from the phosphine oxide (4) did indeed give an olefin, but it was not the olefin from elimination, but rather an isomeric olefin (6) with a rearranged structure. A small amount (4%) of a rearranged alcohol (7) was also formed, but under strictly anhydrous conditions, the olefin (6) was the only product.

Ambiguities in the reaction pathway[2] were resolved by using the [1,1,1-$^2H_3$]alcohol. The tosylate from this alcohol was deuteriated only in the methyl group shown but the product was deuteriated in the methyl group next to phosphorus (9). The reaction must therefore occur by Ph_2PO migration giving the tertiary cation (8) as an intermediate.

The conjugated olefin (10) is not formed in this reaction, nor can the unconjugated olefin (6) be isomerised to (10) in strong acid, in contrast to the system with one less methyl group (3).[1] Presumably the rather inefficient p_π(C=C)–d_π(P=O) overlap does not outweigh steric crowding in the tetrasubstituted olefin (10).

With the fully methylated tertiary alcohol (11), elimination to give the olefin (12) is very easily induced. Attempts to make derivatives with TsCl in pyridine, methanesulphonyl chloride (MsCl) and Et_3N, or HBr give (12) in high yield. If the tertiary cation (13) is an intermediate in some of these reactions, it seemed possible that Ph_2PO migration might occur, making the cation degenerate. We therefore prepared the alcohol (11)



(8) (9) (10)

from [$^2H_6$]acetone and found that treatment with MsCl and Et_3N gave the olefin (12) without any scrambling of deuterium, but that acid gave the olefin (12) with equal amounts of deuterium in all eleven positions.

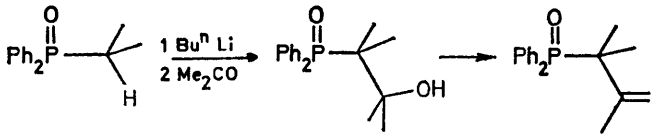
The degenerate rearrangement (13) is clearly responsible for this, and can be initiated in another way.

[1] P. F. Cann, D. Howells, and S. Warren, *J.C.S. Perkin II*, 1972, 304.

[2] Preliminary communication, P. F. Cann, D. Howells, and S. Warren, *Chem. Comm.*, 1971, 1148.

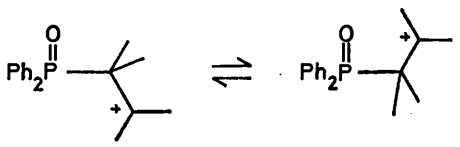
[3] L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *Chem. Ber.*, 1969, **92**, 2499.

When the olefin (12) was dissolved in [^{2}H]trifluoroacetic acid in an n.m.r. tube at 34°, the signals for the olefinic



(11) (12)

and allylic methyl protons disappeared together with a half-life of *ca.* 5 h, while the signals for the remaining methyl groups disappeared with a half-life of *ca.* 70 h.

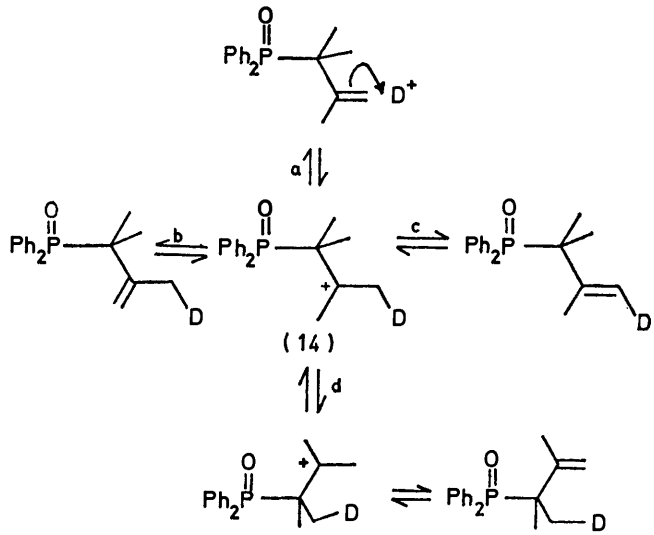


(13)

These rates could not unfortunately be compared with those for 2,3,3-trimethylbut-1-ene as this olefin rapidly formed a trifluoroacetate ester under these conditions.

The deuteriated cation (14) therefore partitions between direct loss of a proton (path a, b, c) and Ph_2PO migration (path d) with the former predominating by an order of magnitude. Olah [4] has already shown that the methyl analogue (15) is a degenerate cation and not a non-classical ion.

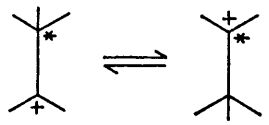
If we add electrophilic bromine, instead of a proton, to the olefin (12) a single rearranged brominated olefin is formed in nearly quantitative yield (96% with bromine in chloroform at −78°). The n.m.r. spectrum of this



(14)

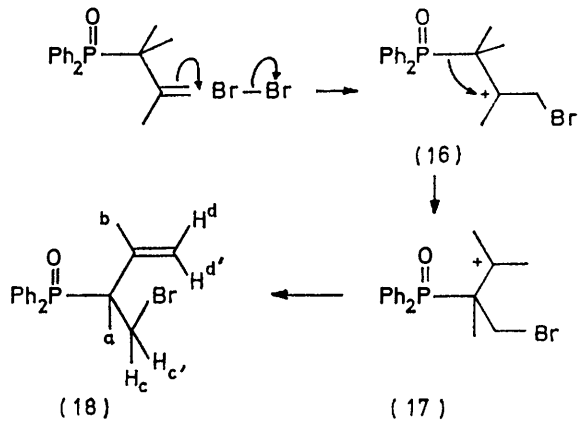
compound showed an undisturbed isopropenyl group but that one of the methyl groups next to phosphorus had been replaced by the characteristic ABP pattern of a diastereotopic CH_2Br group. The product (18) (n.m.r. data in Experimental section) is clearly that derived from a Ph_2PO migration from one tertiary cation (16) to another (17). No product from the deprotonation of the first cation (16) is formed, and the rearrangement (16) ⟶ (17), unlike that of (14), is essentially irreversible.

Diphenylphosphinyl migration is always preferred to methyl migration because the cations produced [*e.g.* (2), (8), or (17)] are more stable than the alternatives; it can



(15)

occur fast enough [as in (13)] to give a degenerate cation, and can be directed by very small electronic effects [the rearrangement (16) ⟶ (17) is irreversible because the electronegative bromine atom in (17) is one more carbon atom away from the positive charge than in (16)].



(18) (17)

The high yield produced in this reaction under very mild conditions serves to emphasise that migration of the Ph_2PO group, and presumably of other groups of comparable electronegativity, occurs even when good alternative pathways are available and when the cation at the end is not emphatically more stable than that at the start.

EXPERIMENTAL

I.r. spectra were taken on Pye–Unicam SP 100 and Perkin-Elmer 257 machines; n.m.r. spectra on Varian HA 100, 100 XL, and Perkin-Elmer R-12 machines, and mass spectra on A.E.I. MS9, MS902, and MS12 spectrometers. T.l.c. was run on silica gel GF 254 and column chromatography on Fison's silica 100—120 mesh.

Isopropyl(diphenyl)phosphine Oxide.—A solution of diphenylphosphine oxide (12·0 g), prepared by the method of Hunt and Saunders,[5] in dry tetrahydrofuran (150 ml) was stirred with sodium hydride [1·7 g from 3·4 g 50% suspension in oil; washed with light petroleum (2 × 20 ml)] for 10 min. Excess of isopropyl bromide (20 ml) was added and the mixture was heated under reflux for 2 h. The

[4] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, 1969, **91**, 5801.

[5] B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 1957, 2413.

mixture was filtered to remove sodium bromide and most of the solvent was removed under reduced pressure. The residue was dissolved in chloroform (100 ml), washed with water (2 × 50 ml), and dried ($MgSO_4$). Evaporation gave isopropyl(diphenyl)phosphine oxide (13·5 g, 93%), recrystallised from ethyl acetate, m.p. 144—145° (lit.,[6] 145—146°), R_F (EtOAc) 0·2, $\nu_{max.}$ 1436 (P–Ph) and 1180 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—2·7 (10H, m, Ph_2PO), 7·5 (1H, octet, $J_{PH} = J_{HH} = 7$ Hz, PC*H*Me_2), and 8·85 (6H dd, J_{PH} 16, J_{HH} 7 Hz, PCH*Me*$_2$), *m/e* 244 (M^+, 7%) and 201 (Ph_2PO^+, 100).

3-*Diphenylphosphinyl*-3-*methylbutan*-2-*ol* (5).—Isopropyl(diphenyl)phosphine oxide (3 g) in dry ether (100 ml) under nitrogen was stirred with n-butyl-lithium (10·5 ml; 1·2M in hexane) for 30 min. The deep red solution was cooled in dry ice–acetone and acetaldehyde (0·6 g) in dry ether (50 ml) was added over 10 min. The treatment with n-butyl-lithium and acetaldehyde was repeated, then water (100 ml) was added. The aqueous layer was separated and extracted with chloroform (3 × 50 ml). The combined organic layers were dried ($MgSO_4$), and evaporated, and the product was recrystallised [ethyl acetate–light petroleum (b.p. 100—120)] to give the *alcohol* (5), m.p. 196—197°, R_F (EtOAc) 0·4, $\nu_{max.}$ 3350 (OH) and 1444 (P–Ph) cm^{-1}, (*m/e* 288 M^+, 1%), 242 ($Ph_2PO{\cdot}CMe_2^+$, 13), and 201 (Ph_2PO^+, 100), τ ($CDCl_3$) 1·9—2·7 (10H, m, Ph_2PO), 5·1 (1H, s, OH), 5·9 (1H, dq, J_{PH} 10, J_{HH} 5 Hz, $PCMe_2{\cdot}CH$Me), 8·8 (3H, d, J_{PH} 16 Hz, $PCMe_2$*), 8·9 (3H, d, J_{PH} 16 Hz, $PCMe_2$*), and 8·96 (3H, d, J_{HH} 5 Hz, CH*Me*) (Found: C, 70·5; H, 7·2. $C_{17}H_{31}O_2P$ requires C, 70·8; H, 7·3%).

2-*Diphenylphosphinyl*-1,2-*dimethylpropyl Toluene*-p-*sulphonate*.[7]—The alcohol (5) (1·0 g) in dry ether (100 ml) was stirred under nitrogen with n-butyl-lithium (3·0 ml; 1·5M solution in hexane) and toluene-*p*-sulphonyl chloride (0·9 g) for 0·5 h. Water (100 ml) was added, the ethereal layer was separated, washed with sodium hydrogen carbonate solution (50 ml), dilute HCl (50 ml), and brine (50 ml), dried ($MgSO_4$), and the ether was removed under reduced pressure. Column chromatography of the oily product (4 : 1 dichloromethane–chloroform) gave the crystalline *tosylate* (1·0 g, 66%) m.p. 142–143° (from ethyl acetate), R_F (EtOAc) 0·5, $\nu_{max.}$ 1440 (P–Ph), 1350, 1170 (S=O), and 1185 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·9 (14H, m, Ar), 5·20 (1H, quintet, $J_{PH} = J_{HH} = 6$ Hz), 7·70 (3H, s, *Me*Ar), 8·67 (3H, d, J_{PH} 14 Hz*), 8·84 (3H, d, J_{PH} 16 Hz*), and 8·67 (3H, d, J_{HH} 6 Hz).

Solvolysis of the Tosylate of the Alcohol (5).—The tosylate (400 mg) was kept at 70° for 24 h (*ca.* 12 half-lives) in acetic acid (20 ml) containing sodium acetate (164 mg). The solution was poured into water (100 ml) and extracted with chloroform (3 × 50 ml). The combined chloroform layers were washed with sodium hydrogen carbonate solution (2 × 50 ml) and with brine (50 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The resulting oil was triturated with di-isopropyl ether to give crystals of the major product, 3-*diphenylphosphinyl*-2-*methylbut*-1-*ene* (6) (290 mg, 96%), m.p. 113—114° (from chloroform–isopropyl ether), *m/e* 270 (M^+, 50%) and 201 (Ph_2PO^+, 100), $\nu_{max.}$ 1640 (C=C), 1440 (P–Ph), and 1175 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·7 (10H, m, Ph_2PO), 5·20 (2H, m, $C{=}CH_2$), 6·90 (1H, quintet, $J_{PH} = J_{HH} = 7$ Hz), 8·30 (3H, s, allylic broadening, C=CMe), and 8·66 (3H, dd, J_{PH} 16, J_{HH} 7 Hz, PCH*Me*) (Found: C, 75·4; H, 7·1; P, 11·2. $C_{17}H_{19}OP$ requires C, 75·6; H, 7·1; P, 11·5%).

Preparative t.l.c. (EtOAc) gave the minor product, 3-*diphenylphosphinyl*-2-*methylbutan*-2-*ol* (7) (10·4 mg, 4%), m.p. 149—157° (from chloroform–isopropyl ether), R_F (EtOAc) 0·3, *m/e* 288 (M^+, 7%), 273 ($M - CH_3$, 28), 230 ($M - Me_2CHOH$, 93), and 201 (Ph_2PO^+, 100), $\nu_{max.}$ ($CHCl_3$ solution), 3350 (OH), 1440 (P–Ph), and 1180 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—2·6 (10H, m, Ph_2PO), 5·26 (1H, s, OH), 7·25 (1H, dq, J_{PH} 11, J_{HH} 7 Hz, PC*H*Me), 8·72 (6H, s, CMe_2), and 8·84 (3H, dd, J_{PH} 17, J_{HH} 7 Hz, PCH*Me*) (Found: C, 70·9; H, 7·3; P, 10·5. $C_{17}H_{21}O_2P$ requires C, 70·8; H, 7·3; P, 10·7%).

Solvolysis of the Tosylate under Strictly Anhydrous Conditions.—The solvolysis was repeated in acetic acid dried by distillation from a solution of acetic acid, acetic anhydride, and chromium trioxide[8] and sodium acetate dried in a vacuum oven at 100° and 5 mmHg. Only a trace of the alcohol (7) could be detected.

Attempted Isomerisation of the Olefin (6) *to its Conjugated Isomer* (10).—The olefin (6) (100 mg) was kept at room temperature for 24 h in syrupy phosphoric acid (85%, 7 ml), poured into water (50 ml), and extracted with chloroform (3 × 50 ml). The combined chloroform layers were washed with sodium hydrogen carbonate solution (2 × 50 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Preparative t.l.c. gave the olefin (6) (40%) and the alcohol (7) (60%).

3-*Diphenylphosphinyl*-3-*methylbutan*-2-*one*.—The alcohol (5) (2·4 g) in acetone (100 ml) was treated with sodium dichromate (3 g) in dilute sulphuric acid (50 ml) for 1 h. Water (200 ml) was added and the solution was extracted with chloroform (3 × 150 ml). The combined chloroform layers were washed with brine (2 × 100 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography (with 4 : 1 dichloromethane–chloroform) gave the oily ketone, R_F (EtOAc) 0·5, *m/e* 286 (M^+, 55%), 244 ($M - CH_2CO$, 35), and 201 (Ph_2PO^+, 100), $\nu_{max.}$ 1700 (C=O), 1440 (P–Ph), and 1183 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—2·7 (10H, m, $POPh_2$), 7·86 (3H, s, $COCH_3$), and 8·52 (6H, d, J_{PH} 15 Hz).

[1,1,1-$^2H_3$]-3-*Diphenylphosphinyl*-3-*methylbutan*-2-*one*.—The ketone (250 mg) was refluxed with anhydrous potassium carbonate (3 g) in deuterium oxide (7 ml) for 24 h, and poured into chloroform (50 ml). The chloroform layer was washed with water (2 × 50 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the oily deuteriated ketone, *m/e* 289 (M^+, 55%), 288 (1), 245 (32), 244 (2), and 201 (100%) showing more than 98% deuterium incorporation, $\nu_{max.}$ 1693 (C=O), 1440 (P–Ph), and 1185 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—2·7 (10H, m) and 8·52 (6H, d, J_{PH} 15 Hz).

[1,1,1-$^2H_3$]-3-*Diphenylphosphinyl*-3-*methylbutan*-2-*ol*.—The deuteriated ketone (240 mg) in tetrahydrofuran (7 ml) was treated with excess of lithium borohydride. After 10 min saturated aqueous ammonium chloride solution was slowly added and the solution was extracted with chloroform (3 × 30 ml). The combined chloroform layers were dried ($MgSO_4$) and evaporated to give the deuteriated alcohol (230 mg, 95%), recrystallised from ethyl acetate–light petroleum, m.p. 191—194°, $\nu_{max.}$ 3190 (OH), 2225 (CD), 1440 (P–Ph), and 1135 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·8 (10H, m,

* Diastereotopic.

[6] B. A. Arbuzov, *J. Russ. Phys. Chem. Soc.*, 1916, **42**, 395.

[7] This method is described by H. C. Brown, R. Berneimer, C. J. Kim, and S. E. Sheppelc, *J. Amer. Chem. Soc.*, 1967, **89**, 370.

[8] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, ' Purification of Laboratory Chemicals,' Pergamon, London, 1966.

$POPh_2$), 4·7 (1H, s, OH), 6·05 (3H, d, J_{PH} 11 Hz, further fine splitting, $CHCD_3$), 8·85 (3H, d, J_{PH} 16 Hz, $PCMe_2$*), and 8·96 (3H, d, J_{PH} 16 Hz, $PCMe_2$*), *m/e* 291 (M^+, 5%), 244 (25), 243 (100), 242 (25), and 201 (Ph_2PO^+, 75%).

[α-*Me*-$^2H_3$]-2-*Diphenylphosphinyl*-1,2-*dimethylpropyl Toluene*-p-*sulphonate*.—The deuteriated alcohol was converted into its tosylate by the method used for the undeuteriated compound, $\nu_{max.}$ 2250 (CD), 1440 (PPh), 1370, 1175 (S=O), and 1190 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·8 (14H, m, ArH), 5·20 (1H, d, J_{PH} 6 Hz, some further fine splitting, $PCMe_2$·*C*HOTs·CD_3), 7·59 (3H, s, Ar*Me*), 8·67 (3H, d, J_{PH} 15 Hz, $PCMe_2$*), 8·85 (3H, d, J_{PH} 14 Hz, $PCMe_2$*).

Solvolysis of the Deuteriated Toluene-p-*sulphonate*.—The procedure used for the undeuteriated tosylate gave [4,4,4-$^2H_3$]-3-diphenylphosphinyl-2-methylbut-1-ene, $\nu_{max.}$ 2220 (CD), 1635 (C=C), 1440 (P–Ph), and 1180 (P=O) cm^{-1}, τ 2·0—2·7 (10H, m, $POPh_2$), 5·20 (2H, m), $C=CH_2$), 6·90 (1H m, $PCHCD_2$), and 8·27br (3H, s, C=CMe), there was no signal at τ 8·6, *m/e* 273 (M^+, 35%), 255 (M – CD_3, 5), 232 (M – $MeC=CH_2$, 3), and 201 (Ph_2PO^+, 100).

3-*Diphenylphosphinyl*-2,3-*dimethylbutan*-2-*ol* (11).—Isopropyl(diphenyl)phosphine oxide (4·0 g) in dry ether (100 ml) under nitrogen was stirred with n-butyl-lithium (14·0 ml; 1·2M in hexane) at room temperature for 0·5 h. The solution was cooled in a dry ice–acetone bath and acetone (1·0 g) in dry ether (50 ml) added dropwise over 10 min. The solution was allowed to warm to room temperature, and n-butyl-lithium was added until no further red colour appeared. The colour was removed by addition of acetone in ether in a dry ice–acetone bath, and this recycling procedure was repeated twice more. Water (100 ml) was added, the layers separated, and the aqueous layer extracted with chloroform (3 × 50 ml). The combined organic layers were dried ($MgSO_4$) and evaporated to give the *tertiary alcohol* (11), and recrystallised from chloroform–isopropyl ether or ethyl acetate–light petroleum, m.p. 132—133° (4·0 g, 81%). R_F (EtOAc) 0·6, *m/e* 302 (M^+, 1%), 244 (Ph_2PO·CMe_2H^+, 90), and 202 (Ph_2POH, 100), $\nu_{max.}$ 3360 (OH), 1440 (P–PH), and 1190 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·7 (10H, m, Ph_2PO), 4·44 (1H, s, OH), 8·72 (6H, d, J_{PH} 17 Hz, $PCMe_2$), and 8·82 (6H, s, Me_2C) (Found: C, 71·4; H, 7·3; P, 10·3. $C_{18}H_{23}O_2P$ requires C, 71·5; H, 7·7; P, 10·2%).

3-*Diphenylphosphinyl*-2,3-*dimethylbut*-1-*ene* (12).—The tertiary alcohol (11) (1·5 g) was dissolved in syrupy phosphoric acid (85%; 10 ml) and after 15 min water (50 ml) was added and the solution extracted with chloroform (3 × 50 ml). The combined chloroform extracts were dried ($MgSO_4$) and evaporated, and the residue was recrystallised from di-isopropyl ether or ethyl acetate–light petroleum (b.p. 100—120°) to give the *olefin* (12) (1·2 g, 84%), m.p. 140—141°, R_F (EtOAc) 0·7, $\nu_{max.}$ 1645 (C=C), 1450 (PPh), and 1190 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·7 (10H, m, $POPh_2$), 5·1 (1H, d, J_{HH} 4 Hz, broadened by allylic coupling, *trans-HC*=CMe), 5·24 (1H, d, J_{HH} 4 Hz, *cis-HC*=CMe), 8·24 (3H, d, J_{HH} 1 Hz, CH_2=C*Me*), and 8·62 (6H, d, J_{PH} 15 Hz, $PCMe_2$), *m/e* 284 (60%), 244 (M – C_3H_4, 40), and 201 (Ph_2PO^+, 100) (Found: C, 75·9; H, 7·4; P, 10·9. $C_{18}H_{21}OP$ requires C, 76·0; H, 7·4; P, 10·9%).

[$^2H_6$]-2,3-*Dimethyl*-3-*diphenylphosphinylbutan*-2-*ol*.—Isopropyl(diphenyl)phosphine oxide (1 g) was combined with [$^2H_6$]acetone by the method used for the undeuteriated compound to give the [$^2H_6$]alcohol deuteriated only on the methyl groups next to the hydroxy-group (0·9 g, 68%), *m/e* 308 (M^+, 1%), 290 (M – H_2O, 10), and 244 (Ph_2PO·$CHMe_2^+$, 100), $\nu_{max.}$ 3470 (OH), 2215 (CD), 1440 (PPh), and 1155 (P=O) cm^{-1}, τ ($CDCl_3$), 1·8—2·6 (10H, m, Ph_2PO), 8·55 (6H, d, J_{PH} 17 Hz, $PCMe_2$), and 8·80 [0·5H, s, C(OH)-Me_2]. The compound is 91% deuteriated in the C(OH)Me_2 positions.

Conversion of the [$^2H_6$]*Alcohol into the Deuteriated Olefin*.—(a) *With methanesulphonyl chloride and triethylamine*. The deuteriated alcohol [$^2H_6$]- (11) (100 mg) in dichloromethane (5 ml) was cooled to 0° and treated with triethylamine (0·01 ml) and methanesulphonyl chloride (0·03 ml). After 12 h the solution was washed with ice–water, cold dilute HCl, sodium carbonate solution, and brine. Evaporation of the solvent and preparative t.l.c. (EtOAc) gave the deuteriated olefin, $\nu_{max.}$ 2250 (CD), 1640 (C=C), 1440 (PPh), and 1885 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·6 (10H, m, $POPh_2$), 5·0br (0·2H, d, J_{HH} 4 Hz, HC=C), 5·3 (0·2H, d, J_{HH} 4 Hz, HC=C), 8·3 (1H, d, J_{PH} 1 Hz, C=CMe), and 8·56 (6H, d, J_{PH} 15 Hz, $PCMe_2$). The compound is deuteriated only at the H_2C=C–CH_3 positions.

(b) *With phosphoric acid*. The deuteriated alcohol [$^2H_6$]-(11) (100 mg) was dissolved in syrupy phosphoric acid (85%; 10 ml) at room temperature. After 5 min, neutralisation and extraction as before gave the deuteriated olefin (90 mg, 90%), m.p. 106—107°, $\nu_{max.}$ 2240, 2270 (CD), 1640 (C=C), 1440 (PPh), and 1180 (P=O) cm^{-1}, τ ($CDCl_3$), 1·9—2·6 (10H, m), 5·0 (0·4H, d, J_{HH} 4 Hz, HC=C), 5·2 (0·4H, d, J_{HH} 4 Hz, HC=C), 8·2 (2H, d, J_{HH} 1 Hz, HC=CMe), and 8·55 (4H, d, J_{PH} 15 Hz, $PCMe_2$). The compound is nearly equally deuteriated at all except the aromatic positions.

Reaction of the Olefin (12) *with* [^2H]*Trifluoroacetic Acid*.—The olefin (12) (62 mg) was dissolved in [^2H]trifluoroacetic acid (700 mg) in an n.m.r. tube in a heated block (34°). The 100 MHz spectrum was recorded at hourly intervals and the degree of deuteriation assessed by comparing the integreated area of each peak with that of the peaks of the aromatic hydrogen atom which did not diminish with time.

Bromination of the Olefin (12).—The olefin (12) (100 mg) in chloroform (5 ml) was cooled to −78° in a dry ice–acetone bath, and a solution of bromine (53 mg) in chloroform (5 ml) was added. After 0·5 h the solution was allowed to warm, washed with aqueous sodium thiosulphate (2 × 20 ml) and water (20 ml), dried ($MgSO_4$), evaporated, and subjected to preparative t.l.c. (EtOAc). Recrystallisation from di-isopropyl ether gave 4-*bromo*-3-*diphenylphosphinyl*-2,3-*dimethylbut*-1-*ene* (18) (121 mg, 96%), m.p. 94—95°, R_F (EtOAc) 0·55, $\nu_{max.}$ 1630 (C=C), 1440 (PPh), and 1175 (P=O) cm^{-1}, τ 8·56 (3H, d, $J_{a,P}$ 15 Hz, a-H_3), 8·20 (3H, s, b-H_3), 5·8 and 6·3 (1H each, ABP systems, J_{AB} 10, J_{AP} 4, J_{BP} 5 Hz, c- and c′-H), and 4·85 and 5·24 (1H each, AB system, J_{AB} 5 Hz, some allylic broadening, d- and d′-H) [Found: 364·0457; 362·0480 (high resolution mass spectrum). $C_{18}H_{20}OP^{81}Br$ requires 364·0415. $C_{18}H_{20}OP^{79}Br$ requires 362·0432 (each 3%)], *m/e* 283 (M – Br, 60%) and 201 (Ph_2PO^+, 100).

Bromination under the same conditions with either pyridinium bromide perbromide (114 mg) or phenyltrimethylammonium perbromide (130 mg) gave the same product in nearly quantitative yield. In all these experiments, traces of two other products were detected by t.l.c.

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* Diastereotopic.