Carbonium Ion Rearrangements: Competitive Migration of the Electronically Contrasted Groups Methyl and Diphenylphosphinyl

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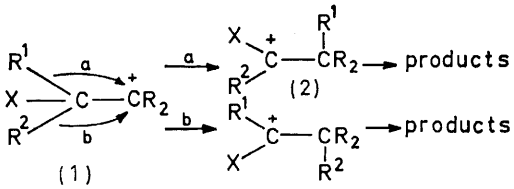
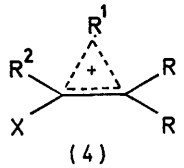
Carbonium ion rearrangements are described in which either a methyl group or the electronegative diphenylphosphinyl group can migrate. When a very careful balance between electronic effects is made, the two groups migrate competitively with the Ph_2PO migration slightly predominating. It is suggested that it is the ability of the group which stays behind to support the positive charge rather than ' migratory aptitude ' which is important in these reactions.

THE idea of ' migratory aptitude ' evolved from competition experiments in which one of two groups [R^1 or R^2 in (1)] on the same atom (the migration origin) could migrate to the migration terminus, leaving the other behind.[1] If R^1 migrated in preference to R^2, it was said to have a higher migratory aptitude and the ratio of products formed by R^1 and R^2 migration was used to set up a quantitative scale of migratory aptitudes.[2] Thus the concept grew up that a group able to bear positive charge was also a good migrating group.[3]



It was in a sense fortunate that this apparently sensible approach gave useful results as it has some serious flaws, one of which was at once apparent on careful inspection of the quantitative scale of migratory aptitudes: that is, that the scale was not entirely self consistent. A migratory aptitude for R^1 determined from competition between R^1 and R^2 was not the same as that from competition between R^1 and R^3. Nor is this surprising since R^1 migration in (1) leaves a cation (2) substituted by X and R^2, whereas R^2 migration leaves a cation (3) substituted by X and R^1. These cations do not have the same stability and some of this difference is reflected in the stability of the transition state or intermediate (4), drawn here for R^1 migration.

In other words, the transition state or intermediate (4) for a migration contains three places where positive



charge may be expected: the migration origin, the migration terminus, and the migrating group. If we want to establish a scale of migratory aptitudes with relevance outside the particular system under study we must vary only one of these at a time.

Another drawback of the early experiments was that the ' spectator group ' [X in (1)] in fact played an important role in driving the reaction forward: it was usually an oxygen atom and hence provided lone pair electrons to overlap with the developing cation at the migration origin. This is a drawback as it reduces the dependence of the stability of the transition state on the other substituents and it is not so much a ' spectator ' as a ' suppressor ' group.† It was the good fortune of the early investigators that these two disadvantages nearly cancel each other out.

In spite of these disadvantages, the study of rearrangement reactions has played a valuable part in the elucidation of carbonium ion chemistry, and could play a more valuable part as the disadvantages are overcome. To this end we have extended the scope of carbonium ion rearrangement reactions into migrations of more electronegative groups than the usual alkyl and aryl groups and we have attempted to do so in systems which do not suffer from these disadvantages. We have already

† There are other disadvantages too: stereochemistry, conformation, equilibration of cations, *etc.*[4]

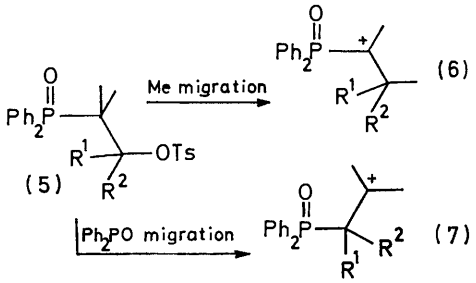
[1] L. M. Tiffeneau and A. Orekhoff, *Bull. Soc. chim. France*, 1924, **35**, 1639; *Ann. Reports*, 1930, **27**, 114.

[2] W. E. Beckmann and F. H. Moser, *J. Amer. Chem. Soc.*, 1932, **54**, 1124.

[3] C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' London, Bell, 1953, p. 476.

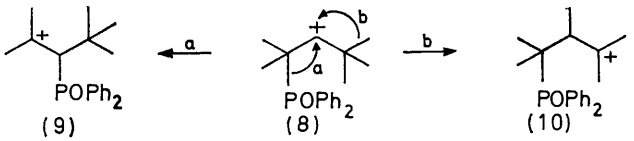
[4] D. Bethell and V. Gold, ' Carbonium Ions: an Introduction,' Academic Press, London and New York, 1967, p. 212.

shown [5] that migration of the diphenylphosphinyl (Ph_2PO) group is preferred to methyl migration in simple alkyl systems [*e.g.* (5)]. Whether R^1 and R^2 are H or Me, no product from methyl migration is formed, and very high yields of products from the cation (7) are found in every case. This is, of course, a particularly unfair competition as the cation left behind by methyl migration (6) is very unstable and it is this feature which decides the course of the reaction. Thus, while groups able to bear a positive charge (Ar, Me) stabilise the migrating group in the transition state or intermediate (4) more than the developing cation at the migration origin and thus show high ' migratory aptitude ', electronegative groups *de*-stabilise the developing cation at the migration origin more than that on the migrating group and so also show high ' migratory aptitude '.



A direct test for this hypothesis is clearly to construct a molecule where competitive rearrangement can occur to leave behind the same cation whether Ph_2PO or any other migration occurs. This, paradoxically, requires two migration origins, one on either side of a common migration terminus. The system we chose was the substituted pentyl cation (8) in which either Ph_2PO or methyl migration leaves behind a simple tertiary alkyl cation [(9) or (10) respectively].

The cation (8) was produced by the action of strong acid on the alcohol (11); this led to the recovery of some starting material and a 90% yield of an isomeric alcohol, still containing the $Ph_2PO{\cdot}CMe_2$ group [the mass spectrum showed this fragment, *m/e* 244 (40%), with a metastable peak at 181·0 for the decomposition of M^+ 300 (1%) to it]. However, in the n.m.r. spectrum the

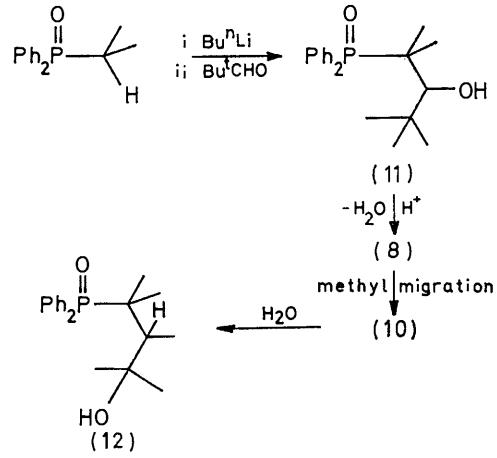


(a) Ph_2PO migration
(b) methyl migration

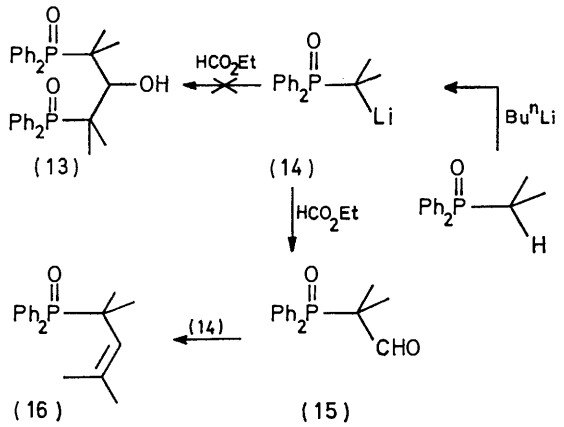
t-butyl group had been replaced by two diastereotopic methyl groups, and a distinct methyl group coupled to a methine proton. This product clearly arises from methyl migration and is assigned the structure (12). No product of Ph_2PO migration could be detected by t.l.c. or n.m.r.

[5] P. F. Cann, D. Howells, and S. Warren, *Chem. Comm.*, 1971, 1148; D. Howells and S. Warren, *J.C.S. Perkin II*, 1973, 1472.

It was disturbing that we found no Ph_2PO migration at all in this system as it did seem possible that steric



factors might prevent route (a) and thus invalidate the competition between the two migrating groups. The best control experiment seemed to be the solvolysis of a derivative of the symmetrical alcohol (13) and so we attempted to synthesise this by the action of ethyl formate on the lithium derivative (14). However this reaction gave instead the olefin (16). Presumably the



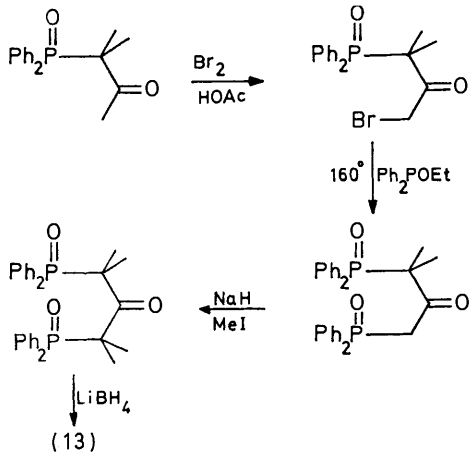
aldehyde (15) is indeed formed as an intermediate, but it reacts anomalously with the lithium derivative (14) by the Wittig reaction.

Lithium derivatives normally give 2-hydroxyalkylphosphine oxides on reaction with carbonyl compounds, only the sodium or potassium derivatives giving the Wittig reaction.[6] We were forced to synthesise the alcohol (13) by the more pedestrian route outlined in Scheme 1.

Solvolysis of the mesylate of the symmetrical alcohol (13) in buffered acetic acid gave an olefin (90%) and an alcohol (10%) derived from the same cation (16), that is the one formed by Ph_2PO migration. The alcohol (19) decomposes spontaneously at room temperature by a Wittig process to give the olefin (16). The olefin (18)

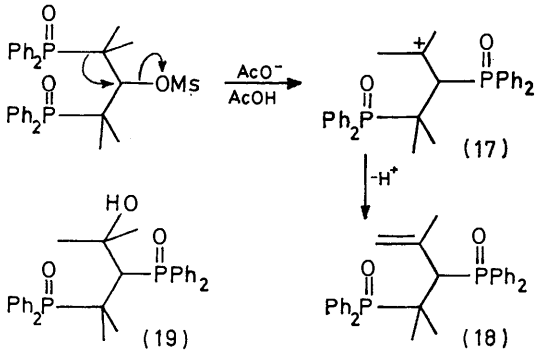
[6] L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *Chem. Ber.*, 1959, **92**, 2499.

shows restricted rotation about the central, very crowded, carbon–carbon single bond (n.m.r. spectrum) at room temperature,[7] but heating to 160° gives the spectrum expected for structure (18).

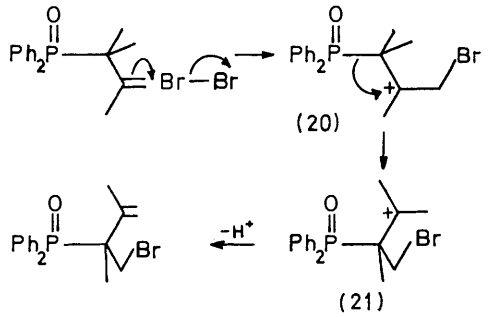


SCHEME 1

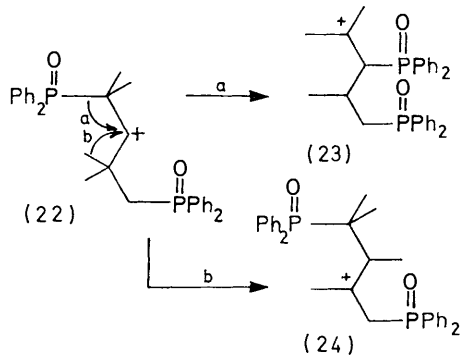
Diphenylphosphinyl migration should therefore be possible in cation (8) but we were not satisfied that the competition in this system was entirely ' fair ' as cations (9) and (10) differ in that the destabilising Ph_2PO substituent is nearer the positive charge in the former. This



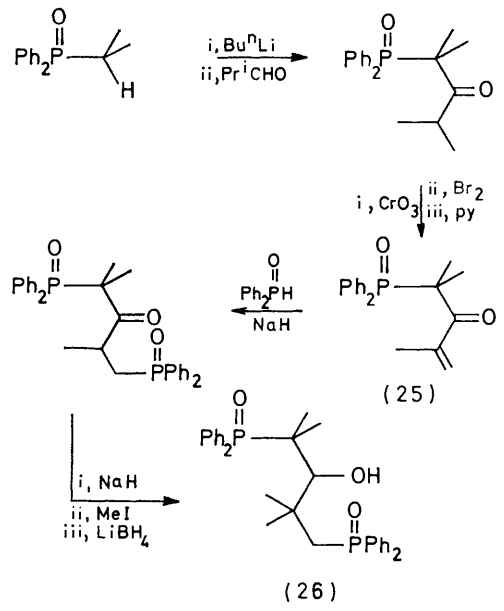
effect, small as it appears to be, may be decisive. It is certainly enough to drive another rearrangement,[5] that



of the cation (20) to (21). This time the *migrating* group is Ph_2PO, and the *destabilising* substituent, Br, a group of comparable electronegativity,* occupies an identical position relative to the positive charge in cations (20) and (21) as the Ph_2PO group does in cations (9) and (10). The best way to resolve this problem seemed to be to introduce another Ph_2PO group into the system (22) so that both rearranged cations (23) and (24) are destabilised to the same extent by the nearer and dominant Ph_2PO group.



The alcohol (26) from which cation (22) is derived was synthesised by making use of the Michael addition[9] of Ph_2PO^- to the very crowded ketone (25) as in Scheme 2.



SCHEME 2

Solvolysis of the mesylate of the alcohol (26) in buffered acetic acid gave two major products with very small amounts (*ca.* 1%) of three other as yet unidentified products. The major products were isomeric olefins, *M* 512 (mass spectra), and they are assigned structures (27) and (28) from their n.m.r. spectra.† Olefin (27) is clearly formed by Ph_2PO migration *via* cation (23) and

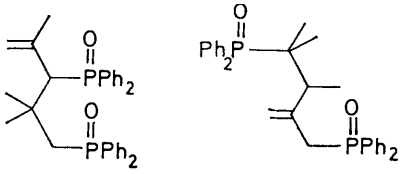
* *E.g.* pK_a $Ph_2PO{\cdot}CH_2CO_2H$ = 3·62, $BrCH_2CO_2H$ = 2·86.[8]

† The n.m.r. spectrum of (28) is straightforward but that of (27) shows that there is restricted rotation about the central crowded bond.[7]

[7] D. Howells and S. Warren, *Tetrahedron Letters*, 1973, 675.
[8] D. J. Martin and C. E. Griffin, *J. Org. Chem.*, 1965, **30**, 4034.
[9] P. F. Cann, M. R. Williams, and S. Warren, *J.C.S. Perkin I*, 1972, 2377.

olefin (28) by methyl migration *via* cation (24). They are formed in 70 and 25% yields respectively.

It is tempting to assign relative migratory aptitudes of 70 : 25 to the Ph_2PO and methyl groups on the grounds that we have now allowed for all the factors which invalidated earlier competition experiments. To do this



(27) (28)

would be to fall into the very trap we are trying to avoid. The rearrangements (8) ⟶ (10), (20) ⟶ (21), and (22) ⟶ (23) + (24) show that very subtle electronic factors are enough to tip the balance in favour of Ph_2PO or methyl migrations: and we would like to emphasise that it is only in the last of these that competition, in the sense of the two migrations occurring in the same molecule, is actually observed. In all other cases, only one group migrates, so that these subtle electronic factors are enough to tip the balance completely from one side to the other. Even our final system, cation (22), does not lead to two *identical* cations. Though cations (23) and (24) are balanced in terms of the nearer and dominant Ph_2PO group, the position of the more distant Ph_2PO group is different. Allowing for this factor would mean building a formidable molecule, and we feel that competition experiments are fundamentally inadequate if a quantitative scale of migratory aptitudes is wanted.

A surprising positive conclusion which emerges from this work is that in our most carefully balanced system (22) there is very little difference in migrating ability between Ph_2PO and methyl: it seems that the dominant factor in carbonium ion rearrangements which do not involve π- or *n*-participation is not the ability of the migrating group, but the ability of the group which stays behind, to support a positive charge.

EXPERIMENTAL

I.r. spectra were run on Pye–Unicam SP 100 and Perkin-Elmer 257 machines, n.m.r. spectra on Varian HA 100, XL, and Perkin-Elmer R12 machines, and mass spectra on A.E.I. MS9 and MS12 machines. T.l.c. was run on silica gel GF_{254}.

2-Diphenylphosphinyl-2,4,4-trimethylpentan-3-ol (11).— Isopropyldiphenylphosphine oxide [5] (2 g, 0·008 mol) in ether (50 ml) was treated with n-butyl-lithium (7·0 ml, 1·2M in hexane, 0·008 mol) at room temperature under nitrogen. The bright red solution was stirred for 0·5 h, and pivalaldehyde (0·6 g, 0·008 mol) in ether (20 ml) was added dropwise with stirring over 10 min, during which time the red colour disappeared. The solution was treated with water (50 ml), the layers separated, and the aqueous layer extracted with ether (2 × 50 ml). The combined ether layers were dried ($MgSO_4$) and evaporated. A small amount of starting material crystallised out at this point and was removed. Further evaporation and recrystallisation from ethyl acetate–light petroleum (b.p. 100—120°) gave the alcohol (11) (1·2 g, 48%), m.p. 98—99°, R_F (EtOAc) 0·8, $\nu_{max.}$ ($CHCl_3$) 3400 (OH) cm^{-1}, τ ($CDCl_3$) 1·9—2·7 (10H, m, Ph_2PO) 5·30 (1H, s, OH), 6·36 (1H, d, J_{PH} 12 Hz, $PCMe_2$·C*H*), 8·64 (6H, d, J_{PH} 16 Hz and further fine splitting, $PCMe_2$), and 9·04 (9H, s, CMe_3), *m/e* 330 (M^+, 1%), 244 (Ph_2PO·$HCMe_2$, 71), and 201 (Ph_2PO^+, 100) (Found: C, 72·8; H, 8·1; P, 9·6. $C_{20}H_{27}O_2P$ requires C, 72·7; H, 8·2; P, 9·4%).

Treatment of the Alcohol (11) *with Phosphoric Acid.*—The alcohol (13) (0·3 g) was dissolved in 85% phosphoric acid (5 ml) and allowed to stand for 24 h. Water (50 ml) was added, the solution was neutralised with sodium hydrogen carbonate solution, and extracted with chloroform (3 × 50 ml). The extracts were dried ($MgSO_4$), concentrated by evaporation, and subjected to preparative t.l.c. developed in chloroform. The two layers revealed by u.v. light were scraped off, extracted with chloroform, and evaporated to give starting material (10%; R_F 0·8), and *4-diphenylphosphinyl-2,3,4-trimethylpentan-2-ol* (12) (90%; R_F 0·4), m.p. 120—121° [from ethyl acetate–light petroleum (b.p. 100—120°)], $\nu_{max.}$ ($CHCl_3$) 3300 (OH) cm^{-1}, τ ($CDCl_3$) 1·9—2·7 (10H, m, Ph_2PO), 3·70 (1H, s, OH), 7·86 (1H, dq, J_{PH} 9·0, J_{HH} 7 Hz, $PCMe_2$·C*H*Me), 8·66 (6H, dd, J_{PH} 16 Hz, $PCMe_2$ *), 8·76 (3H, s, $HOCMe_2$ *) and 8·81 (3H, s, $HOCMe_2$ *), and 9·10 (3H, d, J_{HH} 7 Hz, HC*Me*), *m/e* 330 (M^+, 1%), 244 (Ph_2PO·$CHMe_2$, 40), and 201 (Ph_2PO^+, 100), *m** 181·0 (330 ⟶ 244) and 167·0 (244 ⟶ 201) (Found: C, 72·8; H, 8·2; P, 9·65. $C_{20}H_{27}O_2P$ requires C, 72·7; H, 8·2; P, 9·4%).

1-Bromo-3-diphenylphosphinyl-3-methylbutan-2-one.— 3-Diphenylphosphinyl-3-methylbutan-2-one [5] (6·5 g) in acetic acid (100 ml) was heated to 90° and bromine (1·14 ml) in acetic acid (20 ml) was added slowly over 1·5 h. The solution was poured into water (500 ml), neutralised with sodium hydrogen carbonate, and extracted with chloroform (3 × 250 ml). The combined chloroform extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give an oily mixture of ketone (10%), bromo-ketone (80%), and dibromo-ketone (10%). A small amount of the *bromo-ketone* was purified by preparative t.l.c. (EtOAc), m.p. (from di-isopropyl ether) 64—65°, R_F (EtOAc) 0·6, $\nu_{max.}$ 1725 (C=O), 1440 (PPh), and 1183 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—2·6 (10H, m, Ph_2PO), 5·68 (2H, s, CH_2Br), 8·48 (6H, d, J_{PH} 15 Hz, $PCMe_2$), *m/e* 366 (M^+, 1%, ^{81}Br), 364 (M^+, 1, ^{79}Br), 285 (M − Br, 92), 219 (70), and 201 (Ph_2PO^+, 100).

1,3-Bisdiphenylphosphinyl-3-methylbutan-2-one.— The crude reaction mixture from the bromo-ketone preparation (7·1 g) was heated to 160° in a stream of nitrogen and ethyl diphenylphosphinite [10] (4·6 g) was added. The mixture was cooled, triturated with ethyl acetate, and the solid product recrystallised from ethyl acetate to give the *ketone* (3·8 g, 42%), m.p. 150—151°, R_F (4% MeOH in $CHCl_3$) 0·2, $\nu_{max.}$ 1700 (C=O), 1440 (PPh), and 1173 (P=O) cm^{-1}, τ ($CDCl_3$) 2·1—2·8 (20H, m, 2 × Ph_2PO), 5·94 (2H, d, J_{PH} 13 Hz, PCH_2), 8·57 (6H, d, J_{PH} 15 Hz, $PCMe_2$), *m/e* 486 (M^+, 7%), 285 (M − Ph_2PO, 55), 244 (Ph_2PO·$CHMe_2$, 70), 231 (50), 219 (70), and 201 (Ph_2PO^+, 100) (Found: C, 71·7; H, 5·7; P, 12·6. $C_{29}H_{28}O_3P_2$ requires C, 71·6; N, 5·8; P, 12·7%).

2,4-Bisdiphenylphosphinyl-2,4-dimethylpentan-3-one.— The above ketone (3·7 g) in tetrahydrofuran (100 ml) was heated under reflux with sodium hydride [380 mg from

* Diastereotopic.

[10] B. A. Arbuzov and N. P. Crechkin, *Zhur. obshchei Khim.*, 1950, **44**, 5832.

760 mg of a 50% dispersion in oil washed with light petroleum (2 × 50 ml)] and excess methyl iodide (50 ml) for 12 h. The solution was treated with saturated ammonium chloride solution (50 ml) and extracted with chloroform (3 × 100 ml). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. Trituration of the oily product with ether and recrystallisation from ethyl acetate gave the *ketone* (3·5 g, 88%), m.p. 150—152°, R_F (4% MeOH in $CHCl_3$) 0·25, $\nu_{max.}$ 1670 (C=O), 1440 (PPh), and 1175 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—2·8 (20H, m, 2 × Ph_2PO) and 8·48 (12H, d, J_{PH} 16 Hz, $PCMe_2$), *m/e* 514 (M^+, 15%), 244 ($Ph_2PO{\cdot}CHMe_2$, 80), 231 (50), and 201 (Ph_2PO^+, 100) (Found: C, 72·3; H, 6·2; P, 12·1. $C_{31}H_{32}O_3P_2$ requires C, 72·3; H, 6·3; P, 12·0%).

2,4-*Bisdiphenylphosphinyl*-2,4-*dimethylpentan*-3-*ol* (13).—The fully methylated ketone (3·2 g) in dry tetrahydrofuran (200 ml) was treated with lithium borohydride (400 mg). Saturated ammonium chloride solution (150 ml) was added, and the aqueous layer extracted with chloroform (2 × 250 ml). The combined organic layers were dried ($MgSO_4$) and evaporated. Trituration of the oily product with ether and recrystallisation from ethanol gave the symmetrical *alcohol* (13) (3·2 g, 99%), m.p. 204—206°, R_F (4% MeOH in $CHCl_3$) 0·3, $\nu_{max.}$ ($CHCl_3$) 3260br (OH), 1440 (PPh), and 1160 (P=O) cm^{-1}, τ ($CDCl_3$) 1·8—2·7 (20H, m, 2 × Ph_2PO), 3·90 (1H, s, with fine splitting, HCO*H*), 6·16 [1H, t, J_{PH} 8·5 Hz with further fine splitting, $PCMe_2CH$-(OH)CMe_2P], 8·63 (6H, d, J_{PH} 17 Hz, $PCMe_2$ †), and 8·66 (6H, d, J_{PH} 17 Hz, $PCMe_2$ †), *m/e* 516 (M^+, 1%), 315 (M — Ph_2PO, 50), 298 (315 — OH, 58), 273 (298 — Me, 48), 244 ($Ph_2PO{\cdot}CHMe_2$, 70), 219 (65), and 201 (Ph_2PO^+, 100) (Found: C, 72·0; H, 6·2; P, 12·2. $C_{31}H_{34}O_3P_2$ requires C, 72·0; H, 6·6; P, 12·0%).

2,4-*Bisdiphenylphosphinyl*-2,4-*dimethyl*-3-*methylsulphonyloxypentane*.—The alcohol (13) (1·3 g) in suspension in dry tetrahydrofuran (50 ml) was stirred with n-butyl-lithium (1·3 ml, 1·9M in hexane) and after 10 min with methanesulphonyl chloride (0·3 g) in dry tetrahydrofuran (10 ml). Saturated ammonium chloride solution (50 ml) was added and the aqueous layer was washed with chloroform (3 × 50 ml). The combined organic layers were washed with sodium hydrogen carbonate solution (50 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated. Preparative t.l.c. eluted with 4% MeOH in $CHCl_3$ gave the *mesylate* (610 mg, 38%), m.p. 165—166° (from di-isopropyl ether), $\nu_{max.}$ 1440 (PPh), 1350, 1165 (S=O), and 1180 (P=O) cm^{-1}, τ ($CDCl_3$) 1·6—2·7 (20H, m, 2 × Ph_2PO), 4·82 (1H, t, J_{PH} 18 Hz, $PCMe_2{\cdot}CHOSO_2Me{\cdot}CMe_2P$), 6·58 (3H, s, $MeSO_2$), 8·31 (6H, d, J_{PH} 17 Hz, $PCMe_2$†), and 8·66 (6H, d, J_{HP} 14 Hz, $PCMe_2$†).

Solvolysis of the Mesylate of the Symmetrical Alcohol (13).—The mesylate (600 mg) in acetic acid (20 ml) containing sodium acetate (164 mg) was maintained at 75 ± 0·5° in a thermostatted water bath. After 24 h (*ca.* 12 half-lives) the solution was poured into water (50 ml) and extracted with chloroform (3 × 50 ml) and the combined chloroform layers were washed with sodium hydrogen carbonate solution (3 × 50 ml), dried ($MgSO_4$), and evaporated. Preparative t.l.c. with 4% MeOH in chloroform gave 3,4-*bisdiphenylphosphinyl*-2,4-*dimethylpent*-1-*ene* (18) (438 mg, 90%), m.p. >300°, R_F 0·5, $\nu_{max.}$ ($CHCl_3$) 1632 (C=C), 1440 (PPh), 1187, and 1175 (P=O) cm^{-1}, *m/e* 498 (M^+, 1%), 297 (M — Ph_2PO, 70), 255 (M — $Ph_2PO{\cdot}CMe_2$, 15), and 201 (Ph_2PO^+, 100) (Found: C, 74·8; H, 6·5; P, 12·2. $C_{31}H_{32}O_2P_2$ requires C, 74·7; H, 6·4; P, 12·4%). The 100 MHz n.m.r. spectrum of this compound is temperature dependent [7] and only at 160° gives the pattern expected for this structure (18): τ ($CDCl_3$) 2·0—2·8 (20H, m, 2 × Ph_2PO), 4·8 (1H, m, C=CH), 5·5 (1H, m, C=CH), 6·0 (1H, m, PC*H*·C=C), 8·11 (3H, d, J_{PH} 17 Hz, $PCMe_2$ *), 8·68br (3H, s, C=CMe), 8·85 (3H, d, J_{PH} 16 Hz, $PCMe_2$ *). The minor product (19) (49 mg, 10%, R_F 0·4) was unstable in solution in chloroform with a half-life at room temperature of *ca.* 2 h. From its spectra and decomposition product (16) it was identified as 3,4-bisdiphenylphosphinyl-2,4-dimethylpentan-2-ol (19), $\nu_{max.}$ ($CHCl_3$) 3400, 3170 (OH), 1440 (PPh), 1185, and 1160 (P=O) cm^{-1}, τ ($CDCl_3$) 1·8—2·7 (20H, m, 2 × Ph_2PO), 6·5 (1H, dd, J_{PH} 15, J_{PH} 10 Hz, PC*H*CP), 8·10 (3H, d, J_{PH} 17 Hz $PCMe_2$ *), 8·65 (3H, d, J_{PH} 19 Hz, $PCMe_2$ *), 8·44 (3H, s, Me_2COH *), and 8·85 (3H, s, Me_2COH *). The decomposition product was 2,4-*dimethyl*-4-*diphenylphosphinylpent*-2-*ene* (16), R_F (4% MeOH in $CHCl_3$) 0·5, $\nu_{max.}$ ($CHCl_3$) 1440 (PPh) and 1170 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—2·8 (10H, m, Ph_2PO), 4·86 (1H, m, MeC=C*H*CP), 8·33 (3H, d, J_{HH} 5 Hz, *Me*C=CH), 8·68 (6H, d, J_{PH} 15 Hz, $PCMe_2$), 8·82br (3H, s, *Me*C=C), *m/e* 298 (M^+, 25%), 245 (M — C_4H_5, 10), 202 (Ph_2POH, 60), and 186 (Ph_2PH, 100). The same product was obtained from the action of n-butyl-lithium and ethyl formate on isopropyldiphenylphosphine oxide and when the alcohol (13) (100 mg) in tetrahydrofuran (50 ml) containing sodium hydride (20 mg of 50% suspension in oil) was allowed to stand for 48 h.

2-*Diphenylphosphinyl*-2,4-*dimethylpentan*-3-*ol* (*see Scheme* 2).—Isopropyldiphenylphosphine oxide [5] (10 g) in dry ether (250 ml) was stirred with n-butyl-lithium (22 ml, 1·9M in hexane) for 0·5 h under nitrogen. The red colour was discharged by titrating with freshly distilled isobutyraldehyde (3·6 ml) in dry ether (50 ml). Saturated ammonium chloride solution (100 ml) was added and the aqueous layer extracted with ether (150 ml). The combined ether layers were dried ($MgSO_4$) and evaporated. The solid residue was recrystallised from di-isopropyl ether to give the *alcohol* (12·6 g, 98%), m.p. 117—118°, R_F (EtOAc) 0·7, $\nu_{max.}$ ($CHCl_3$) 3310 (OH), 1440 (PPh), and 1170 (P=O) cm^{-1}, τ ($CDCl_3$) 1·8—2·7 (10H, m, Ph_2PO), 5·35br (1H, s, OH), 6·22 (1H, dd, J_{PH} 12, J_{HH} 2 Hz, PCC*H*·$CHMe_2$), 8·23 (1H, m, CH·C*H*Me_2), 8·70 (3H, d, J_{PH} 17 Hz, $PCMe_2$ *), 8·80 (3H, d, J_{PH} 17 Hz, $PCMe_2$ *), 9·05 (6H, d, J_{HH} 7 Hz, CH*Me*$_2$), *m/e* 316 (M^+, 1%), 315 (2), 273 (M — C_3H_7, 90), 244 (273 — CHOH, 100), and 201 (Ph_2PO^+, 69) (Found: C, 72·4; H, 7·8; P, 9·9. $C_{19}H_{25}O_2P$ requires C, 72·2; H, 7·9; P, 9·8%).

2-*Diphenylphosphinyl*-2,4-*dimethylpentan*-3-*one*.—The solid residue of the above alcohol (12·0 g) in acetone (200 ml) was oxidised for 0·5 h with sodium dichromate (6 g) in dilute sulphuric acid (200 ml). Water (400 ml) was added and the solution extracted with ether (3 × 250 ml). The combined ether extracts were washed with brine (2 × 200 ml), dried ($MgSO_4$), and evaporated to give an oil (11·8 g, 98%), crystallised, and recrystallised from di-isopropyl ether as needles of the *ketone*, m.p. 138—139°, R_F (EtOAc) 0·5, $\nu_{max.}$ 1695 (C=O), 1440 (PPh), and 1177 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—2·7 (10H, m, Ph_2PO), 6·57 (1H, septuplet, J_{HH} 7 Hz, *H*CMe_2), 8·52 (6H, d, J_{PH} 15 Hz, $PCMe_2$), and 9·13 (6H, d, J_{HH} 7 Hz, CH*Me*$_2$), *m/e* 314 (M^+, 7%), 271 (M — C_3H_7, 7), 244 (271 — CO, 90), and 201 (Ph_2PO^+, 100) (Found: C, 72·6; H, 7·2; P, 9·6. $C_{19}H_{23}O_2P$ requires C, 72·6; H, 7·4; P, 9·8%).

4-*Bromo*-2-*diphenylphosphinyl*-2,4-*dimethylpentan*-3-*one*.—The oily ketone (11·0 g) was heated under reflux for 18 h

* Diastereotopic.

† Prochiral centres about another prochiral centre.

with bromine (50 ml) in acetic acid (250 ml) containing a few drops of 48% HBr. The solution was poured into water (1 l), sodium carbonate was added to remove the bromine colour, and the solution was extracted with chloroform (3 × 300 ml). The combined chloroform extracts were washed with aqueous sodium thiosulphate solution (200 ml) and brine (200 ml), dried ($MgSO_4$), and the chloroform evaporated. The oily residue slowly crystallised and was recrystallised from di-isopropyl ether to give the *bromo-ketone* (11·0 g, 80%), m.p. 138—139°, R_F (EtOAc) 0·5, $\nu_{max.}$ 1683 (C=O), 1440 (PPh), and 1177 (P=O) cm^{-1}, τ ($CDCl_3$) 1·8—2·7 (10H, m, $POPh_2$), 8·23 (6H, d, J_{PH} 15 Hz, $PCMe_2$), and 8·23 (6H, s, $CBrMe_2$), *m/e* 394 (M^+, 8, ^{81}Br), 392 (M^+, 8, ^{79}Br), 313 (M — Br, 65), 244 (313 — C_4H_6O, 60), and 201 (Ph_2PO^+, 100) (Found: C, 58·0; H, 5·6; P, 8·1. $C_{18}H_{22}BrO_2P$ requires C, 58·0; H, 5·6; P, 7·9).

2,4-*Dimethyl*-4-*diphenylphosphinylpent*-1-*en*-3-*one* (25).—The bromo-ketone (10·5 g) was heated in pyridine (250 ml; freshly distilled from calcium hydride) at 120° for 48 h. The solution was poured into hydrochloric acid (1 l, 6M) and extracted with chloroform (3 × 300 ml). The combined chloroform extracts were washed with brine (250 ml), dried ($MgSO_4$), and evaporated to give a dark brown oil. Column chromatography on Fison's silica gel eluted with 4 : 1 dichloromethane–chloroform gave the crystalline *enone* (25) (4·5 g, 54%), m.p. 119—120° (from di-isopropyl ether), $\nu_{max.}$ ($CHCl_3$) 1690 (C=O), 1656 (C=C), 1440 (PPh), and 1195 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—2·7 (10H, m, Ph_2PO), 3·83 (3H, s, allylic broadening, C=CMe), 8·49 (6H, d, J_{PH} 15 Hz, $PCMe_2$), *m/e* 312 (M^+, 75%), 243 ($Ph_2PO{\cdot}CHMe_2$, 15), 220 (60), 202 (Ph_2POH, 100), and 201 (Ph_2PO^+, 90%).

1,4-*Bisdiphenylphosphinyl*-2,2,4-*trimethylpentan*-3-*one*.[9]—The enone (25) (4·2 g) and diphenylphosphine oxide [5] (2·8 g) in tetrahydrofuran (250 ml) were stirred with sodium hydride [700 mg, 50% dispersion in oil, washed with light petroleum (2 × 50 ml)] for 2 h. Methyl iodide (25 ml) was added and the solution was heated under reflux for 12 h. Saturated ammonium chloride (200 ml) was added, the aqueous layer was extracted with chloroform (2 × 250 ml), and the combined chloroform layers were dried ($MgSO_4$) and evaporated to give an oil which crystallised on trituration with ether. Recrystallisation from chloroform–di-isopropyl ether gave the *ketone* (4·5 g, 60%), m.p. 136—137°, R_F (4% MeOH in chloroform) 0·15, $\nu_{max.}$ ($CHCl_3$) 1675 (C=O), 1440 (PPh), and 1175 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·7 (20H, m, 2 × Ph_2PO), 7·25 (2H, d, J_{PH} 10 Hz, PCH_2), 8·30 (6H, d, J_{PH} 15 Hz, $PCMe_2$), and 8·65 (6H, s, $COCMe_2$), *m/e* 528 (M^+, 3%), 499 (20), 443 (10), 401 (16), 273 (35), and 201 (Ph_2PO^+, 100) (Found: C, 72·8; H, 6·3; P, 11·4. $C_{32}H_{34}O_3P_2$ requires C, 72·7; H, 6·5; P, 11·7%).

1,4-*Bisdimethylphosphinyl*-2,2,4-*trimethylpentan*-3-*ol* (26).—Lithium borohydride (400 mg) was added to the above ketone (4·2 g) in dry tetrahydrofuran (200 ml). After 10 min saturated ammonium chloride (150 ml) was added, the aqueous layer was extracted with chloroform (2 × 250 ml), and the combined organic layers were dried ($MgSO_4$) and evaporated. Recrystallisation from ethanol gave the *alcohol* (26) (4·1 g, 98%), m.p. 229—231°, R_F (4% MeOH in $CHCl_3$) 0·2, $\nu_{max.}$ ($CHCl_3$) 3250br (OH), 1440 (PPh), and 1160 (P=O) cm^{-1}, τ ($CDCl_3$) 1·7—2·8 (20H, m, 2 × Ph_2PO), 4·10br (1H, s, OH), 6·15 (1H, d, J_{PH} 10 Hz, $PCMe_2CHOH$), 7·50 (2H, ABP system, J_{AB} 15, J_{AP} 14, J_{BP} 10 Hz, PCH_2), 8·61 (3H, d, J_{PH} 15 Hz, $PCMe_2$ *), 8·63 (3H, d, J_{PH} 15 Hz, $PCMe_2$ *), 8·85 (3H, s, CMe_2 *), and 9·00 (3H, s, CMe_2 *), *m/e* 530 (M^+, 1%), 497 (M — Me, 1), 329 (M — Ph_2PO, 15), 311 (329 — H_2O, 60), 297 (26), 273 (30), 255 (273 — H_2O, 45), 244 ($Ph_2POCHMe_2$, 15), and 201 (Ph_2PO^+, 100) (Found: C, 72·6; H, 6·7; P, 11·5. $C_{32}H_{36}O_3P_2$ requires C, 72·4; H, 6·8; P, 11·7%).

1,4-*Bisdiphenylphosphinyl*-2,2,4-*trimethyl*-3-*methylsulphonyloxypentane*.—A suspension of the alcohol (26) (1 g), and n-butyl-lithium (1 ml, 1·9M solution in hexane) was stirred for 10 min, and methanesulphonyl chloride (0·23 g) in dry tetrahydrofuran (10 ml) was added. Saturated ammonium chloride solution (20 ml) was added, and the aqueous layer was extracted with chloroform (3 × 50 ml). The combined organic layers were washed with sodium hydrogen carbonate solution (50 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated. Preparative t.l.c. with 4% methanol in chloroform as eluant gave the *mesylate* (400 mg, 33%), m.p. 174—175°, R_F (4% MeOH in $CHCl_3$) 0·25, $\nu_{max.}$ ($CHCl_3$) 1440 (PPh), 1345, 1167 (S=O), and 1175 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·8 (20H, m, 2 × Ph_2PO), 5·30 (1H, d, J_{PH} 18 Hz, $PCMe_2CHOSO_2Me$), 7·02 (3H, s, $MeSO_2$), 7·04 (2H, m, PCH_2), 8·52 (3H, d, J_{PH} 13 Hz, $PCMe_2$ *), 8·73 (3H, s, CMe_2 *), and 8·77 (3H, s, CMe_2 *).

Solvolysis of the Mesylate of Alcohol (26).—The mesylate (350 mg) in acetic acid (10 ml) containing sodium acetate (82 mg) was maintained at 75 ± 0·5° in a thermostatted water-bath for 24 h (*ca.* 12 half-lives). The solution was poured into water (50 ml) and extracted with chloroform (3 × 50 ml). The combined chloroform extracts were washed with sodium hydrogen carbonate solution (3 × 50 ml), dried ($MgSO_4$), and evaporated. Preparative t.l.c. eluted with 4% methanol in chloroform gave three minor products (*ca.* 1% each) and two major products, R_F 0·5 and 0·3, identified as the following. 3,5-*Bisdiphenylphosphinyl*-2,4,4-*trimethylpent*-1-*ene* (27) was formed in 70% yield (205 mg), m.p. (from aqueous ethanol) 101—102°, R_F 0·5, $\nu_{max.}$ ($CHCl_3$) 1630wk (C=C), 1440 (PPh), and 1175 (P=O) cm^{-1}, *m/e* 512 (M^+, 100%), 421 (20), 311 (M — Ph_2PO, 25), 298 (M — Ph_2POCH, 20), 255 ($Ph_2PO{\cdot}CHCMeCH_2$, 60), 241 (255 — CH_2?, 10), and 201 (Ph_2PO^+, 50) (Found: C, 74·9; H, 6·9; P, 12·1. $C_{32}H_{34}O_2P_2$ requires C, 75·0; H, 6·7; P, 21·1%). The 100 MHz n.m.r. spectrum of this compound [7] shows restricted rotation about a carbon–carbon single bond at 34°, but at 120° the expected pattern for structure (27) is observed: τ ($CDCl_3$) 1·9—2·8 (20H, m, 2 × Ph_2PO), 4·70br (1H, s, C=CH), 5·13br (1H, s, C=CH), 6·08 (1H, m, CHP), 7·3H (2H, m, CH_2P), 8·37br (3H, s, $MeC{=}CH_2$), 8·84 (3H, s, CMe_2 *), and 8·91 (3H, s, CMe_2 *). 4-*Diphenylphosphinyl*-2-*diphenylphosphinylmethyl*-3,4-*dimethylpent*-1-*ene* (28) was formed in 25% yield (73 mg), m.p. 161—162°, R_F 0·3, $\nu_{max.}$ ($CHCl_3$) 1440 (PPh), 1185, and 1175 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·7 (20H, m, 2 × Ph_2PO), 4·84 (1H, d, J_{HH} 4 Hz, C=CH), 5·14 (1H, d, J_{HH} 4 Hz, C=CH), 6·92 (2H, m, $PCH_2C{=}C$), 7·40 (1H, m, PCCHMe), 8·74 (3H, d, J_{HH} 2 Hz, CHMe), 8·82 (3H, d, J_{PH} 14 Hz, $PCMe_2$ *), and 8·83 (3H, d, J_{PH} 14 Hz, $PCMe_2$ *), *m/e* 512 (M^+, 1%), 312 (66), 311 (M — Ph_2PO, 70), 269 (M — Ph_2CMe_2, 80), 256 (50), 244 ($Ph_2POCHMe_2$, 30), and 201 (Ph_2PO^+, 100) [Found: M^+, 512·2069 (mass spectrum). $C_{32}H_{34}O_2P_2$ requires M^+, 512·2034].

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* Diastereotopic.