Carbonium Ion Rearrangements: Electronic and Conformational Control in the Migration of the Electronegative Group Diphenylphosphinyl

By **David Howells** and **Stuart Warren,*** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

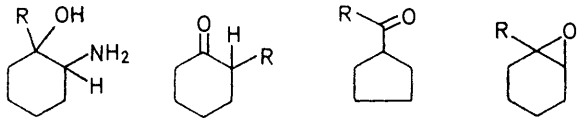
In contrast to the pinacolyl derivatives (6) and (21), *cis*- and *trans*-2-diphenylphosphinyl-2-methylcyclohexyl tosylates (14a and b) give neither methyl nor diphenylphosphinyl migrations on solvolysis. Instead, two different olefins, 3-diphenylphosphinyl-3-methylcyclohexene from (14a) and the 4-diphenylphosphinyl-4-methyl isomer from (14b), are formed in high yield. The conformations of the tosylates and the structures of the olefins were elucidated by deuterium labelling and the use of the n.m.r. shift reagent $Eu(dpm)_3$. The rates of solvolysis are slow compared with methyl or diphenylphosphinyl migration and it is suggested that electronic and not conformational factors control the corresponding acyclic rearrangements.

SOME carbonium ion rearrangements are controlled largely by the conformation of the reagents. The deamination of aminocyclohexanols (1) and decanols can initiate three possible pathways: migration of the exocyclic substituent R to give a cyclohexanone (2), migration of a ring bond to give a ring-contracted ketone (3), or epoxide (4) formation. Each diastereoisomer of the starting material gives only those products resulting from migration or participation of the group which is antiperiplanar to the leaving group.[1] Even acyclic compounds, lacking the fixed conformations of the cyclic compounds, may show substantial conformational control.[2] Three conformations of compounds such as (5) are normally populated. Each has one

[1] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Interscience, New York, 1965, p. 105.

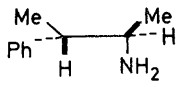
[2] E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 144.

group (Ph, Me, or H) antiperiplanar to the leaving group, and the proportion of migration of each of these groups on deamination can simply reflect the proportion

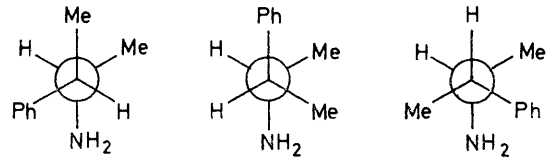


(1) (2) (3) (4)

of the molecules in each conformation. In this particular case,[3] 32% of the products arise by methyl migration from the most stable conformation (5a), and 24% each



(5)



(5a) (5b) (5c)

by phenyl or hydride shifts from the less stable conformations (5b and c).

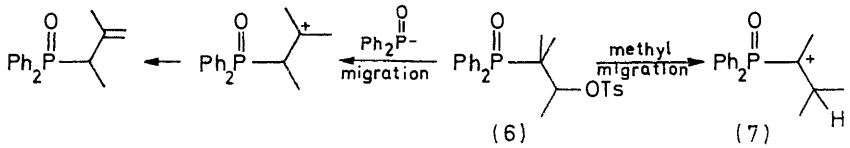
In a series of papers[4] concerned with rearrangements where either the methyl or diphenylphosphinyl groups can migrate, we have claimed that these reactions are controlled by electronic factors, chief of which is the relative stability of the cations produced at the migration origin by the rearrangement. In compounds such as (6), no methyl migration occurs, and we have explained this by the instability of the β-phosphinyl cation (7) which would result. Though we have been able to explain all our results this way, an almost equally valid explanation might have been that the two largest groups in the molecule are Ph_2PO and the leaving group OTs, that these will therefore be antiperiplanar in the most populated conformation, and the almost universal preference for diphenylphosphinyl migration simply reflects this.

One piece of evidence which seemed to support this conformational explanation, was that the only compound which did show exclusive methyl migration[4] was the alcohol (8) where the Ph_2PO and OH groups would not be antiperiplanar, but, inevitably, the OH and *one* of the methyl groups on the t-butyl group would be.

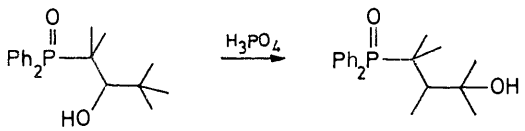
Nevertheless, we have not found methyl migration from a carbon with a Ph_2PO substituent, and it seemed that the best check for conformational control would be to construct a molecule in which such a methyl group would be constrained antiperiplanar to the leaving group. Conformational control predicts methyl migration in this situation while electronic control predicts that migration of neither group will occur: some other reaction pathway must be found.

We chose to make the two diastereoisomeric alcohols (13a and b) for this purpose. Addition of diphenylphosphinyl anion[5] to cyclohexene oxide gave the alcohol (9) and this gave the ketone (10) with Jones reagent. Methylation of this ketone was troublesome, sodium hydride, butyl-lithium, or trityl-lithium with methyl iodide in tetrahydrofuran all giving the trimethyl-ketone (11). Methylation with sodium ethoxide and methyl iodide in ethanol however did give the monomethyl-ketone (12). Presumably, in the absence of a proton donor, which would allow equilibration to the more stable enolate ion, kinetic enolisation occurs twice at the 6-position followed by the slower but thermodynamically more favourable enolisation at the 2-position.

Reduction of the ketone (12) with lithium borohydride in tetrahydrofuran gave a mixture of the two alcohols (13a and b) which could not be separated by t.l.c. Fortunately, reduction with sodium borohydride in methanol gave almost entirely one of the alcohols (13a) which crystallised from the reaction mixture. This later proved to be the compound with the OH and Ph_2PO groups *trans*. The other alcohol was obtained by fractional crystallisation of the original mixture.



(6) (7)



(8)

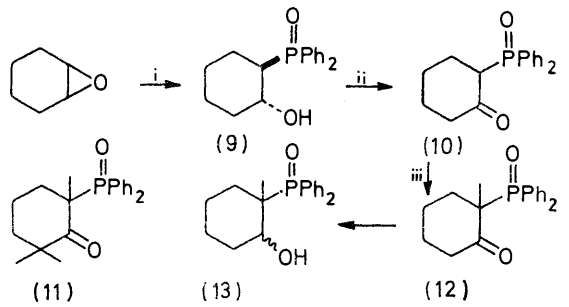
The n.m.r. spectra of the alcohols were unhelpful, but the two tosylates (14a and b) gave n.m.r. spectra containing clear AXYP patterns for the methine C*H*OTs proton (H*). The coupling constants were assigned after the deuteriated compounds (14a; $H^a = H^e = D$) and (14b; $H^a = H^e = D$) had been made since the only surviving coupling in these compounds was to phosphorus. The other two couplings must be to adjacent

[3] B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Amer. Chem. Soc.*, 1957, **79**, 6160.

[4] D. Howells and S. Warren, *J.C.S. Perkin II*, 1973, 1472, 1645; P. F. Cann, D. Howells, and S. Warren, *ibid.*, 1972, 304.

[5] P. F. Cann, S. Warren, and M. R. Williams, *J.C.S. Perkin I*, 1972, 2377.

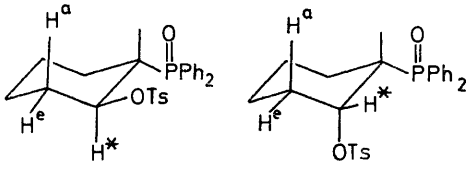
axial and equatorial protons and the coupling constants [6] as well as the relative chemical shifts [7] were characteristic of an axial methine proton in (14a) and of an equatorial



Reagents: i, $Ph_2P(O)H$–NaH; ii, Jones reagent; iii, NaOEt–MeI–EtOH

methine proton in (14b). Evidently the very large Ph_2PO group fixes the conformation so that the tosyl group is equatorial in (14a) and axial in (14b).

Solvolyses of the tosylates (14a) and (14b) in acetic acid were remarkably slow, having half-lives of *ca.* 170 and 100 h respectively. Each tosylate gave a different, isomeric olefin, M^+ 296 (mass spectra), both showing intact PCMe groups in their n.m.r. spectra, so that neither Ph_2PO nor methyl migration had occurred in either case. The olefin from the equatorial tosylate (14a) showed two olefinic protons in the n.m.r. spectrum at τ 4·00 and 4·32 only one of which was shifted substantially downfield when the spectrum was run in the



(14a) (14b)

(14a)	(14b)
H* τ 5·18	H* τ 4·80
J_{H^*P} 18 Hz	J_{H^*P} 9 Hz
$J_{H^*H^a}$ 9 Hz	$J_{H^*H^a}$ 1·5 Hz
$J_{H^*H^e}$ 3 Hz	$J_{H^*H^e}$ 4 Hz

presence of the europium shift reagent $Eu(dpm)_3$.[8] Among the other protons, in the molecule, only the PC*Me*, and the *ortho*-aromatic protons were shifted by

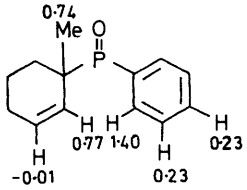
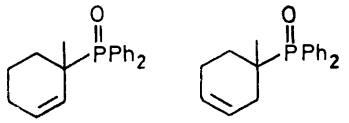


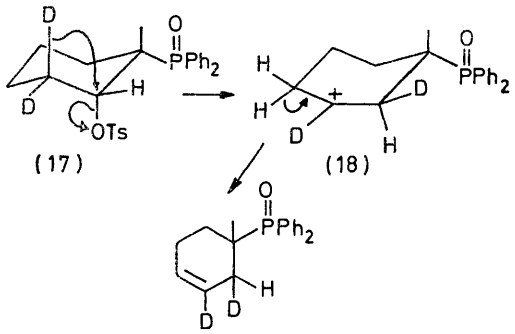
FIGURE Δδ With 0·12 mol $Eu(dpm)_3$ in $CDCl_3$

comparable amounts (Figure). This olefin could also be obtained by an elimination reaction on the tosylate (14a) with tetra-n-butylammonium acetate in benzene and is assigned structure (15).

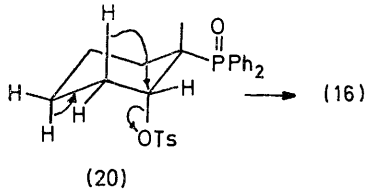


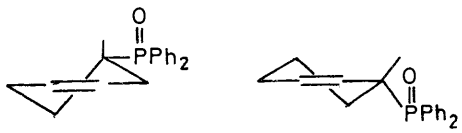
(15) (16)

The olefin from the axial tosylate (14b) had a slightly different n.m.r. spectrum, particularly in the olefinic region. The only other olefin with an unrearranged skeleton is (16) and this would have to arise by a hydride shift and an elimination. To confirm this, the di-deuterio-tosylate (17b) was prepared by exchanging deuterium into the ketone (12) and then making the tosylate as before. Solvolysis of this tosylate gave the olefin (19) with two deuterium atoms, one olefinic, and one in the methylene envelope.



It is at first puzzling that the cation (18) should give only the olefin (19) and none of its isomer. Two explanations are possible. The elimination may be concerted with the hydride shift (20) after the style





(16) (15)

equatorial diphenylphosphinyl group

pseudo-equatorial diphenylphosphinyl group

of the steroid backbone rearrangements, or the very large Ph_2PO group may exert steric control by oc-

[6] D. H. Williams and I. Fleming, 'Spectroscopic Methods in Organic Chemistry,' McGraw-Hill, London, 1966, p. 109; H. Booth, *Tetrahedron Letters*, 1965, 411.

[7] D. H. Williams and N. S. Bhacca, *J. Amer. Chem. Soc.*, 1964, **86**, 2742.

[8] J. K. M. Sanders and D. H. Williams, *Nature*, 1972, **240**, 385; J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Amer. Chem. Soc.*, 1972, **94**, 5325.

cupying a genuine equatorial position in (16) rather than a pseudoequatorial position in (15). The latter explanation is credible only because the steric demands of the Ph_2PO group are very large. The *trans*-tosylate (14a) must almost never, for example, occupy the diaxial conformation or diphenylphosphinyl migration would surely occur as it does in the analogous, free-rotating, secondary tosylate (6).

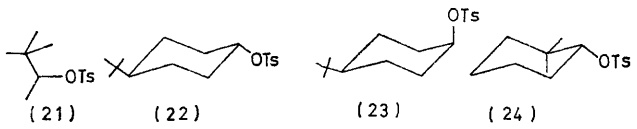
Another factor influenced our final conclusions. Elimination occurs in these molecules not because it is a particularly favourable pathway but because no other pathway is open. There are two pieces of evidence for this: molecules such as the secondary tosylate (6) which could also eliminate to give an olefin prefer to rearrange.[4] More directly, the eliminations in the cyclohexyl compounds (14a and b) are slower than any of the rearrangements we have observed on other secondary tosylates by about two orders of magnitude, and are slower than the solvolyses of analogous cyclohexyl compounds lacking the phosphorus atom (Table).

Rates of solvolysis of secondary tosylates in acetic acid at 75° (s^{-1})

Compound	Reaction and rate (reference)	Diphenylphosphinyl analogue	Reaction and rate
(21)	Methyl migration, $2{\cdot}4 \times 10^{-4}$ (ref. 10)	(6)	Ph_2PO Migration $1{\cdot}9 \times 10^{-4}$ [a]
(22)	72% Elimination 24% substitution, $3{\cdot}8 \times 10^{-5}$ [b]	(14a)	Elimination, $1{\cdot}2 \times 10^{-6}$ [c]
(23)	88% Elimination 12% substitution, $1{\cdot}0 \times 10^{-4}$ [d]	(14b)	Hydride shift and elimination, $2{\cdot}0 \times 10^{-6}$ [c]
(24)	68% Ring contraction 27% methyl migration 4% elimination $2{\cdot}7 \times 10^{-4}$ [b]		

[a] Rate determined titrimetrically: see Experimental section. [b] S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, 1955, **77**, 5562. [c] Very slow reactions: half-lives determined by t.l.c., [d] Rate extrapolated from published data (A. P. Krapcho, J. E. McCullogh, and K. V. Nahabedian, *J. Org. Chem.*, 1965, **30**, 139).

We conclude that conformational control can prevent migration of either group but cannot be responsible for one group migrating rather than another. The control observed in the rearrangements of simple diphenylphosphinyl compounds such as (6) is therefore electronic



control and not a conformation effect. Further, the accumulated evidence about the reactions of all these secondary tosylates, namely: (1) the reaction is stereospecific at both the migrating phosphorus atom and the migration terminus;[9] (2) the rate of solvolysis of the tosylate (6) is nearly the same as that of pinacolyl tosylate (21) and some three times greater than that of isopropyl tosylate;[10] (3) rearrangement of the diphenylphosphinyl group can be completely prevented by conformational control, the axial and equatorial tosylates (14a and b) giving different products; and (4) the reactions are subject to the most rigorous electronic control giving rise to single products in high yields, indicates that they must be concerted reactions [with the exception of that of (14a)] in which loss of tosylate and diphenylphosphinyl, methyl, or hydride migration occur together in the rate-limiting step.

[9] F. H. Allen, O. Kennard, L. Nassimbeni, R. G. Shepherd, and S. Warren, *Nature*, 1974, **248**, 670.

[10] S. Winstein, B. K. Morse, E. Grunwald, K C. Schneider, and J. Corse, *J. Amer. Chem. Soc.*, 1952, **74**, 1113.

EXPERIMENTAL

Spectroscopic and chromatographic techniques have been described previously.[4]

trans-2-*Diphenylphosphinylcyclohexanol* (9).—Diphenylphosphine oxide[11] (10·0 g) in dry ether (150 ml) was treated with sodium hydride (1·5 g; from 3·0 g 50% suspension in oil washed with light petroleum) and after 10 min cyclohexene oxide[12] (4·8 g) in dry ether (50 ml) was added. The solution was heated under reflux for 24 h, water (100 ml) added, and the aqueous layer separated and extracted with ether (2 × 100 ml). The combined ethereal layers were dried ($MgSO_4$) and the ether evaporated. The resulting oil was triturated and recrystallised from aqueous ethanol to give the alcohol (9) (11·5 g, 78%), R_F (EtOAc) 0·3, m.p. 151—152° (lit.,[13] 153—155°), $\nu_{max.}$ 3300 (OH), 1440 (P–Ph), and 1180 (P=O) cm^{-1}, τ ($CDCl_3$) 2·08—2·72 (10H, m, Ph_2PO), 4·80br (1H, s, OH), 6·20 (1H, m, C*H*OH), 7·48 (1H, m, PC*H*), and 7·9—9·0 (8H, m, methylene envelope), *m/e* 300 (15%, M^+) and 201 (100, Ph_2PO^+).

2-*Diphenylphosphinylcyclohexanone* (10).—The alcohol (9) (10·1 g) in acetone (250 ml) was treated with Jones reagent[14] (9·5 ml) for 30 min. The solution was decanted and evaporated, the residue taken up in chloroform (150 ml), washed with brine (3 × 100 ml), dried ($MgSO_4$), and chloroform evaporated. Column chromatography on alumina, eluting with chloroform, gave the crystalline *ketone* (10) (4·2 g, 42%), m.p. 144—145° (from chloroform–di-isopropyl ether), R_F (EtOAc) 0·5, $\nu_{max.}$ 1705 (C=O), 1442 (P–Ph), and 1183 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—2·7 (10H, m, Ph_2PO), 6·5 (1H, m, PC*H*), 7·3 (2H, m, CH_2CO), and 7·4—8·7 (6H, m, methylene envelope), *m/e* 298 (40%, M^+) and 201 (100, Ph_2PO^+) (Found: C, 72·6; H, 6·5; P, 10·5. $C_{18}H_{19}O_2P$ requires C, 72·5; H, 6·4; P, 10·4%).

2-*Diphenylphosphinyl*-2-*methylcyclohexanone* (12).—A solution of the ketone (12) (4·0 g) in ethanol (150 ml) was treated with sodium hydride (700 mg of 50% suspension in oil) and methyl iodide (15 ml) and heated under reflux for 12 h. More sodium hydride (350 mg) was added and the solution heated under reflux for 12 h. The ethanol was evaporated under reduced pressure, the residue dissolved in chloroform (150 ml), washed with water (100 ml) and brine (100 ml), dried, and the solvent evaporated to give the crystalline *ketone* (12) (3·8 g, 92%), m.p. 116—117° [from light petroleum (b.p. 60—80°)], R_F (2% methanol in ether on alumina plates) 0·5, $\nu_{max.}$ 1695 (C=O), 1440 (P–Ph), and 1170 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·8 (10H, m, Ph_2PO), 7·0—8·6 (8H, m, methylene envelope), and 8·71 (3H, d,

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

[12] V. Dev, *J. Chem. Educ.*, 1970, **47**, 476.

[13] K. Isslieb and H. R. Roloff, *Chem. Ber.*, 1965, **98**, 2091.

[14] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39.

J_{PH} 15 Hz, PC*Me*), *m/e* 312 (50%, M^+), 311 (18, M − H), 284 (23, M − CO), 243 (47, $Ph_2PO{\cdot}CMe_2^+$), 219 [75, $Ph_2P(OH)_2^+$], 202 (100, Ph_2POH), and 201 (80, Ph_2PO^+) (Found: C, 72·6; H, 6·8; P, 10·0. $C_{19}H_{21}O_2P$ requires *C*, 73·1; H, 6·8; P, 9·9%).

Methylation of the ketone (12) with an excess of methyl iodide and sodium hydride, trityl-lithium, or butyl-lithium in tetrahydrofuran gave only 2-diphenylphosphinyl-2,6,6-trimethylcyclohexanone (11), τ 1·7—2·6 (10H, s, Ph_2PO), 7·5—9·1 (6H, methylene envelope), 8·46 (3H, d, J_{PH} 16 Hz, PC*Me*), 8·86 * (3H, s, CMe), and 8·99 * (3H, s, CMe).

t-2-*Diphenylphosphinyl*-c-2-*methyl*-r-*cyclohexanol* (13a).—The ketone (12) (1·0 g) in methanol (50 ml) was treated with sodium borohydride (200 mg) for 30 min. The solvent was evaporated under reduced pressure and the residue dissolved in chloroform, washed with saturated ammonium chloride solution (2 × 50 ml), dried ($MgSO_4$), and chloroform evaporated to give the crystalline *alcohol* (13a) (980 mg, 98%), m.p. 213—214° (from chloroform–di-isopropyl ether), R_F (30% methanol in chloroform) 0·4, $\nu_{max.}$ 3300 (OH), 1440 (P–Ph), and 1160 (P=O) cm^{-1}, τ ($CDCl_3$) 1·8—2·7 (10H, m, methylene envelope), and 8·80 (3H, d, J_{PH} 18 Hz, PC*Me*), *m/e* 314 (4%, M^+), 286 (17, M − CO), 243 (100, $Ph_2PO{\cdot}CMe_2^+$), 219 [8, $Ph_2P(OH)_2^+$], 202 (44, Ph_2POH), and 201 (30, Ph_2PO^+) (Found: C, 72·6; H, 7·5; P, 9·7. $C_{19}H_{28}O_2P$ requires C, 72·6; H, 7·4; P, 9·9%).

t-2-*Diphenylphosphinyl*-c-2-*methylcyclohexyl* r-*Toluene*-p-*sulphonate* (14a).—The alcohol (13a) (520 mg) in dry ether (25 ml) was treated with n-butyl-lithium (1 ml of 1·9M solution in hexane) for 10 min and then toluene-*p*-sulphonyl chloride (325 mg) was added. After 30 min the solution was washed with water (2 × 25 ml), dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The resulting oil was purified by preparative t.l.c. (EtOAc) to give the crystalline tosylate (14a) (590 mg, 82%), m.p. 167—168°, R_F (EtOAc) 0·6, $\nu_{max.}$ 1440 (P–Ph), 1365 and 1178 (S=O), and 1190 (P=O) cm^{-1}, τ ($CDCl_3$) 2·0—3·0 (14H, m, Ar), 5·28 (1H, ddd, J_{HP} 18, J_{HH} 9, J_{HH} 3 Hz, $CH_2CHOTs{\cdot}CP$), 7·60 (3H, s, *Me*Ar), 8·0—9·0 (8H, methylene envelope), and 8·83 (3H, d, J_{PH} 15 Hz, PC*Me*).

Solvolysis of Tosylate (14a).—The tosylate (14a) (240 mg) was allowed to solvolyse in acetic acid (10 ml) containing sodium acetate (82 mg) at 75° for 4 weeks. The solution was poured into water (100 ml) and extracted with chloroform (3 × 50 ml). The chloroform extracts were dried ($MgSO_4$) and the solvent evaporated under reduced pressure. Preparative t.l.c. (3% methanol in chloroform) gave the tosylate (14a) (13 mg, 8·3%), a trace (*ca.* 1%) of an unidentified product, and 3-*diphenylphosphinyl*-3-*methylcyclohexene* (15) (143 mg, 91%), m.p. 85—89°, R_F (3% methanol in chloroform) 0·55, $\nu_{max.}$ 1635 (C=C), 1440 (P–Ph), and 1177 (P=O) cm^{-1}, τ ($CDCl_3$) 1·8—2·7 (10H, m, Ph_2PO) and 5·16 (2H, m, HC=CH), *m/e* 296 (32%, M^+), 202 (100, Ph_2PO), and 201 (35, Ph_2PO^+). The n.m.r. spectrum of this compound was modified by the addition of up to 0·12 mol. equiv. of $Eu(dpm)_3$ [8] (see text).

c-2-*Diphenylphosphinyl*-t-2-*methyl*-r-*cyclohexanol* (13b).—The ketone (12) (500 mg) in dry tetrahydrofuran (25 ml) was treated with lithium borohydride. After 10 min saturated ammonium chloride solution (25 ml) was added, the aqueous layer separated and was extracted with chloroform, the combined organic layers were dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The crystalline residue was fractionally recrystallised from chloroform–di-isopropyl ether. The first crop (260 mg) was mainly the *trans*-alcohol (13a) but the second crop (150 mg) was mainly the *cis*-alcohol (13b). This was recrystallised again from the same solvent to give pure cis-*alcohol* (13b), m.p. 214—215°, R_F (3% methanol in chloroform) 0·4, $\nu_{max.}$ 3220 (OH), 1440 (P–Ph), and 1150 (P=O) cm^{-1}, τ ($CDCl_3$) 1·8—2·7 (10H, m, Ph_2PO), 4·60 (1H, s, OH), 6·04 (1H, m, C*H*OH), 8·0—8·9 (8H, methylene envelope), and 8·73 (3H, d, J_{PH} 18 Hz, PC*Me*), *m/e* 314 (6%, M^+), 286 (18, M − CO), 243 (100, $Ph_2PO{\cdot}CMe_2^+$), 202 (36, Ph_2POH), and 201 (30, Ph_2PO^+).

c-2-*Diphenylphosphinyl*-t-2-*methylcyclohexyl* r-*Toluene*-p-*sulphonate* (14b).—This tosylate was prepared in the same way as the *trans*-compound from the alcohol (13b) (150 mg). Preparative t.l.c. (multiple elution with chloroform) gave the crystalline cis-*tosylate* (14b) (110 mg, 49%), m.p. 153—154°, R_F (EtOAc) 0·6, $\nu_{max.}$ 1438 (P–Ph), 1350 and 1170 (S=O), and 1190 (P=O) cm^{-1}, τ ($CDCl_3$) 1·6—3·0 (14H, m, Ar), 4·90 (1H, ddd, J_{PH} 9, J_{HH} 4, J_{HH} 1·5 Hz, $CH_2CHOTs{\cdot}CP$), 8·0—9·0 (8H, methylene envelope), and 8·76 (3H, d, J_{PH} 16 Hz, PC*Me*).

Solvolysis of the cis-*Tosylate* (14b).—This compound (110 mg) was solvolysed in the same way as the *trans*-tosylate. Preparative t.l.c. (3% methanol in chloroform) gave 4-*diphenylphosphinyl*-4-*methylcyclohexene* (16) (69 mg, 98%), R_F (3% methanol in chloroform) 0·55, $\nu_{max.}$ 1440 (P–Ph) and 1175 (P=O) cm^{-1}, τ ($CDCl_3$) 1·6—2·7 (10H, m, Ph_2PO), 4·06 (2H, m, HC=CH), 7·7—8·5 (6H, methylene envelope), and 8·66 (3H, d, J_{PH} 15 Hz, PC*Me*), *m/e* 296 (4%, M^+), 295 (6, M − H), 236 (100), and 199 (14).

[6,6-$^2H_2$]-2-*Diphenylphosphinyl*-2-*methylcyclohexanone*.—The ketone (12) (200 mg) was heated under reflux with anhydrous potassium carbonate (3 g) in deuterium oxide (7 ml) for 24 h. The solution was extracted with chloroform (50 ml), the chloroform layer washed with water (2 × 50 ml), dried ($MgSO_4$), and the solvent evaporated under reduced pressure to give the deuteriated ketone (195 mg), $\nu_{max.}$ 2220 (C–D), 1695 (C=O), 1440 (P–Ph), and 1180 (P=O) cm^{-1}, τ ($CDCl_3$) 1·8—2·9 (10H, m, Ph_2PO), 7·5—8·5 (6H, methylene envelope), and 8·65 (3H, d, J_{PH} 15 Hz, PCMe), *m/e* 314 (43%, M^+), 313 (15), 219 [75, $Ph_2P(OH)_2^+$], and 202 (100, Ph_2POH). The mass spectrum shows >98% deuteriation in the CH_2CO position.

[6,6-$^2H_3$]-t-2-*Diphenylphosphinyl*-c-2-*methylcyclohexyl* r-*Toluene*-p-*sulphonate*.—The dideuteriated *trans*-tosylate was prepared in the same way as the undeuteriated *trans*-tosylate (14a). The n.m.r. spectrum showed two deuterium atoms were still present in the same positions, τ ($CDCl_3$) 1·5—3·0 (14H, m, Ar), 5·28 (1H, d, J_{PH} 18 Hz, $CD_2CHOTs{\cdot}CP$), 7·58 (3H, s, *Me*Ar), 7·5—8·7 (6H, methylene envelope), and 8·73 (3H, d, J_{PH} 15 Hz, PC*Me*).

[6,6-$^2H_2$]-c-2-*Diphenylphosphinyl*-t-2-*methylcyclohexyl* r-*Toluene*-p-*sulphonate* (17).—The dideuteriated *cis*-tosylate was prepared in the same way as the undeuteriated *cis*-tosylate (14b). The n.m.r. spectrum showed the presence of 2 deuterium atoms in the CH_2CO position, τ ($CDCl_3$) 1·5—3·0 (14H, m, Ar), 4·83 (1H, d, J_{PH} 9 Hz, $CD_2CHOTs{\cdot}CP$), 7·69 (3H, s, *Me*Ar), 8·0—8·7 (6H, methylene envelope), and 8·76 (3H, d, J_{PH} 17 Hz, PC*Me*).

Solvolysis of the Deuteriated cis-*Tosylate* (17).—This compound was solvolysed in the same way as the undeuteriated compound to give [1,2-$^2H_2$]-4-diphenylphosphinyl-4-methylcyclohexene (19), τ ($CDCl_3$) 1·5—2·7 (10H, m, Ph_2PO) and 4·05 (1H, m, HC=CD).

* Diastereotopic methyl groups.

Rates of Solvolyses of Tosylates (14a) *and* (14b).—These (Table) were determined approximately from half-life estimates from t.l.c. separations. This method is very inaccurate (±20%) but is suitable for these very slow reactions.

[15] S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1948, **70**, 821.

Rate of Solvolysis of Tosylate (6).—The rate was determined titrimetrically [15] at 74·5° in acetic acid giving $k = 1{\cdot}92 \times 10^{-4}$ s^{-1}.

We thank the S.R.C. for a grant (to D. H.).

[4/144 *Received*, 24*th January*, 1974]