Solvolysis of Secondary Alkyl Tosylates with β-Dimethyl and β-Nitro, Sulphinyl, Sulphonyl, or Phosphonoyl Substituents: Fragmentation *vs.* Rearrangement [1]

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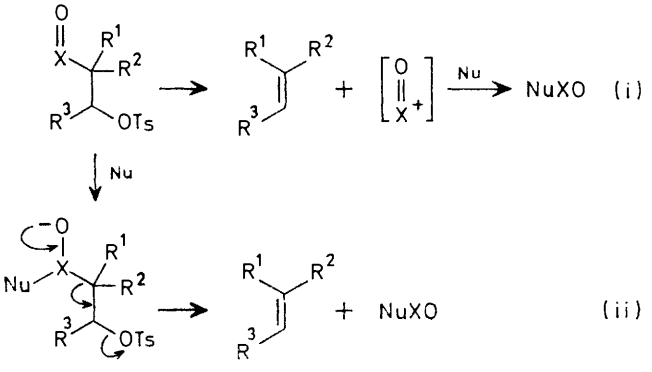
The title compounds either fragment or rearrange on solvolysis in carboxylic acids. The named functional group is either lost as an electrophilic fragment (nitro, phosphonoyl) or migrates to the secondary carbon atom (phenylsulphinyl, phenylsulphonyl, and in one case carbonyl). These results are compared with those for other electronegative groups where 1,4-participation becomes a third possibility.

ELECTRONEGATIVE substituents based on C=O, P=O, S=O, N=O, *etc.*, on neighbouring carbon atoms in an alkyl tosylate can take part in the solvolysis of the tosylate in three main ways.

(A) *Fragmentation.* The substituent may be lost in a fragmentation reaction, either as a cation (usually under acidic conditions) or after nucleophilic attack by the solvent or other nucleophile (usually under basic conditions). The former case (i), where the substituent contains a relatively electron-rich atom (usually O or N) has been extensively studied by Grob,[2] the latter (ii) particularly where X is C, by Nerdel and Weyerstahl and their co-workers.[3]

(B) *Participation.* An electron-rich atom (usually oxygen) in the substituent may carry out an intramolecular nucleophilic displacement of the tosylate (iii) to give a cyclic intermediate (1) which subsequently adds solvent or fragments to give the products. We have found that this is the normal mode of reaction for carbonyl



compounds of the general structure (2) which give unrearranged solvolysis products by this route.[4]

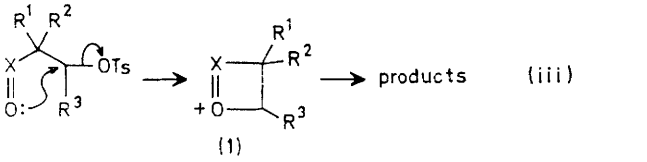
[1] Preliminary communication, P. K. G. Hodgson, R. G. Shepherd, and S. Warren, *J.C.S. Chem. Comm.*, 1974, 633.

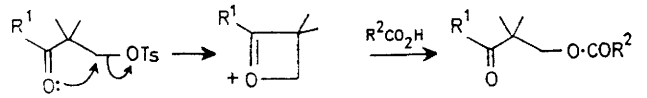
[2] C. A. Grob and P. W. Schiess, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1; C. A. Grob, *ibid.*, 1969, **8**, 535; C. A. Grob, W. Kunz, and P. R. Marbet, *Tetrahedron Letters*, 1975, 2613.

[3] K.-D. Klinkmüller, H. Marschall, and P. Weyerstahl, *Chem. Ber.*, 1975, **108**, 203, which gives references to earlier papers; see also A. Eschenmoser and A. Frey, *Helv. Chim. Acta*, 1952, 1660.

[4] P. K. G. Hodgson and S. Warren, *J.C.S. Chem. Comm.*, 1973, 756; *J.C.S. Perkin II*, 1975, 372.

(C) *Rearrangement.* Recent work on the migration of many electronegative groups including alkoxycarbonyl,[5] carbonyl,[6] nitro,[7] arylsulphonyl,[8] arylsulphinyl,[8] and

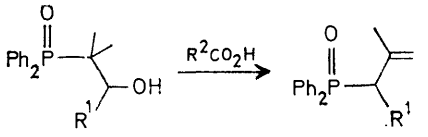




phosphonic acids [9] and esters [10] has exposed the fallacy that electronegative groups are ' poor migrating groups '. Our own work [11] on diphenylphosphinoyl-substituted alkyl tosylates [*e.g.* (3)] shows that Ph_2PO migration is normally the only reaction that occurs when these compounds are solvolysed.

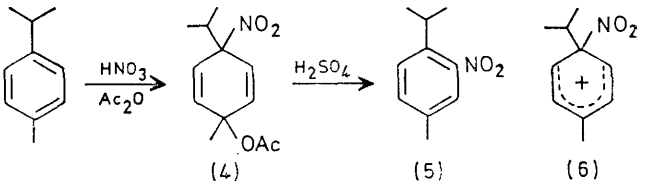
We have now extended our work on carbonyl [4] and phosphinoyl [11] compounds to those containing nitro, phosphonic acid and ester, phenylsulphonyl and phenylsulphinyl groups, and report [1] that whereas the last two groups migrate, fragmentation is the result of solvolysis of alkyl tosylates having the other groups in the β-position.

The nitro-group. The nitro-group is one of the most electronegative available to the organic chemist (σ_I 0.63, σ_R 0.70, σ^-_P 1.24) [12] yet there are now well established

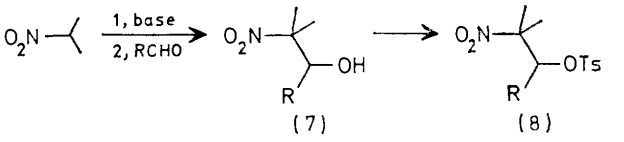


examples [7] of nitro-migration occurring after *ipso*-nitration of aromatic compounds [13] [*e.g.* (4) ⟶ (5)] *via* the cation (6).

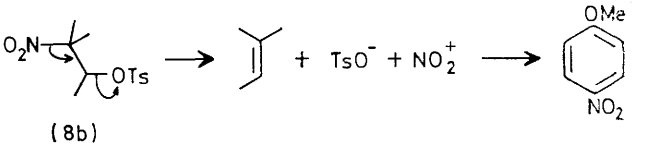
The nitroalkanols (7) needed for our work were prepared by Henry addition [14] and converted into tosylates (8) by the Nerdel [15] modification of the standard procedure. Both reactions gave low yields except in the case R = H. Solvolysis of the primary alkyl tosylate (8a) gave no reaction even after 18 days in trifluoroacetic



acid at 75 °C. The more reactive secondary tosylate (8b) was 90% converted after 12 days under these conditions, but no products (except sodium tosylate) remained in the reaction flask. This is expected if fragmentation to a pentene (9) and nitryl cation (NO_2^+) occurs. When the solvolysis was carried out in the presence of anisole, *p*-nitroanisole was formed, showing that some electrophilic nitrating species, presumably NO_2^+, was indeed produced.



a; R = H b; R = Me c; R = Ph



We were unable to make the tosylate of the secondary benzyl alcohol (8c) as treatment with tosyl chloride under a variety of conditions gave benzaldehyde as the only product. Benzaldehyde was also formed when the alcohol (8c) was treated directly with acid (trifluoroacetic, sulphuric, or phosphoric), conditions which bring about rearrangement in the corresponding diphenylphosphinoyl compound [parent alcohol of (3; R^1 = Ph)].[16] Benzaldehyde could arise from a reverse Henry addition, particularly in base, or from participation by the nitro-

[5] R. M. Acheson, *Accounts Chem. Res.*, 1971, **4**, 177; R. M. Acheson and R. F. Flowerday, *J.C.S. Perkin I*, 1974, 2335; J. Kagan, D. A. Agdeppa, and S. P. Singh, *Helv. Chim. Acta*, 1972, **55**, 2252; J. Kagan and D. A. Agdeppa, *ibid.*, p. 2255; J. N. Marx, J. C. Argyle, and L. R. Norman, *J. Amer. Chem. Soc.*, 1974, **96**, 2121.

[6] H. O. House and G. D. Ryerson, *J. Amer. Chem. Soc.*, 1961, **83**, 979; R. D. H. Murray, W. Parker, R. A. Raphael, and D. B. Jhaveri, *Tetrahedron*, 1962, **18**, 55; V. Tortorella, L. Toscano, C. Vetuschi, and A. Romeo, *J. Chem. Soc.* (*C*), 1971, 2422; H. Hart, I. Huang, and P. Lavrik, *J. Org. Chem.*, 1974, **39**, 999; P. Bakusis, G. C. Magalhães, H. Martins, and M. L. F. Bakuzis, *ibid.*, p. 2427; E. Lee-Ruff and P. Khazanie, *Canad. J. Chem.*, 1975, **53**, 1708.

[7] S. R. Hartshorn, *Chem. Soc. Rev.*, 1974, **3**, 167; A. Fischer and C. C. Greg, *J.C.S. Chem. Comm.*, 1974, 50.

[8] T. Durst and K.-C. Tin, *Tetrahedron Letters*, 1970, 2369; D. F. Tavares, R. E. Estep, and M. Blezard, *ibid.*, p. 2373.

[9] N. N. Girotra and N. L. Wendler, *Tetrahedron Letters*, 1969, 4647.

[10] B. A. Arbuzov in ' Chimie Organique du Phosphore,' Colloque Internationaux du Centre de la Recherche Scientifique, no. 182, Paris, 1970, p. 3; C. E. Griffin, *ibid.*, p. 95; R. H. Churi and C. E. Griffin, *J. Amer. Chem. Soc.*, 1966, **88**, 1824; C. E. Griffin and S. K. Kundu, *J. Org. Chem.*, 1969, **34**, 1532; M. Sprecher and E. Nativ, *Tetrahedron Letters*, 1968, 4405; M. Sprecher and D. Kost, *ibid.*, 1969, 703; 1970, 2535; 1975, 4483.

[11] P. F. Cann and S. Warren, *Chem. Comm.*, 1970, 1026; P. F. Cann, D. Howells, and S. Warren, *ibid.*, 1971, 1148; *J.C.S. Perkin II*, 1972, 304; D. Howells and S. Warren, *ibid.*, 1973, 1472, 1645; 1974, 992.

[12] O. Exner in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum, London, 1972, p. 37.

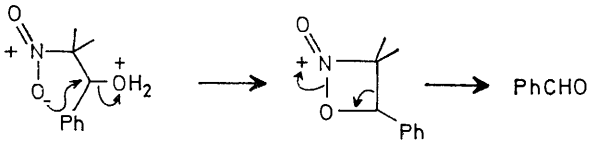
[13] R. C. Hahn and D. L. Strack, *J. Amer. Chem. Soc.*, 1974, **96**, 4335; M. W. Galley and R. C. Hahn, *ibid.*, p. 4337.

[14] L. Henry, *Compt. rend.*, 1895, **120**, 1265; *Bull. Soc. chim. France*, 1895, **13**, 999; H. H. Baer and L. Urbas in ' The Chemistry of the Nitro and Nitroso Groups,' ed. H. Feuer, Interscience, New York, 1970, part 2, p. 76.

[15] F. Nerdel, D. Frank, and H. Marschall, *Chem. Ber.*, 1967, **100**, 720.

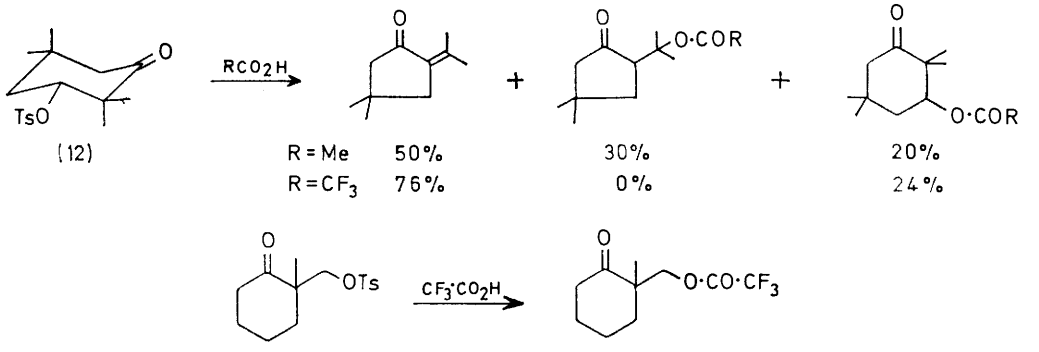
[16] A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1975, 148; *J.C.S. Perkin I*, 1976, 639; A. H. Davidson, C. Earnshaw, J. I. Grayson, and S. Warren, *J.C.S. Perkin I*, in the press.

group (10) followed by fragmentation (11). A similar sequence occurs in secondary tosylates with a β-benzoyl substituent.[4] We conclude that migration of the nitro-group in simple alkyl systems is unlikely to be a useful reaction.



(10) (11)

Carbonyl groups. Though 1,4-carbonyl participation is the reaction which occurs when most 2-oxoalkyl



(12) R = Me 50% 30% 20%
R = CF_3 76% 0% 24%

(13)

tosylates are solvolysed,[4] we have found one such compound in which the carbonyl group migrates. This is the substituted cyclohexanone (12),[17] whose carbonyl group is so placed that participation by the lone pairs of electrons on the oxygen atom is impossible. Mixtures of products are formed on solvolysis, not all resulting from rearrangement, so that even in this electronically and conformationally ideal system carbonyl migration is an inefficient process.

The more flexible cyclohexanone (13), whose base-catalysed rearrangements have become something of a *cause celèbre*,[18] reacts rather more slowly than the open chain analogue [4] (2; R^1 = Me) in trifluoroacetic acid to give the unrearranged ester. 1,4-Carbonyl participation is hindered here, but not excluded.

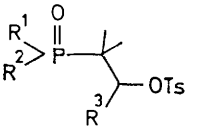
It may be that the strength of the acyl–carbon (C–CO) bond is so great that carbonyl migration is a poor reaction. In any event, it does not occur except in special cases such as the rearrangement of dienones or epoxides [5,6] where there is a strong driving force.

[17] A. Eschenmoser, H. Schinz, R. Fischer, and J. Colonge, *Helv. Chim. Acta*, 1951, **34**, 2329.

[18] E. Wenkert and D. P. Strike, *J. Org. Chem.*, 1962, **27**, 1883; E. Wenkert, P. Bakuzis, R. J. Baumgarten, C. L. Leicht, and H. P. Schenk, *J. Amer. Chem. Soc.*, 1971, **93**, 3208; F. Nerdel, D. Frank, and H. Marschall, *Angew. Chem. Internat. Edn.*, 1962, **1**, 457; *Chem. Ber.*, 1967, **100**, 720; K. B. Wiberg and G. W. Kline, *Tetrahedron Letters*, 1963, 1043; Y. Tsuda, T. Tanno, A. Ukai, and K. Isobe, *ibid.*, 1971, 2009; A. Barco, G. P. Polloni, M. Anastasia, G. Traverso, F. Taddei, and G. DeGiule, *Gazzetta*, 1969, **99**, 735; S. W. Baldwin and E. H. Page, *J.C.S. Chem. Comm.*, 1972, 1337; R. H. Bisceglia and C. J. Cheer, *ibid.*, 1973, 165; S. Wolff and W. C. Agosta, *ibid.*, p. 771; W. Kirmse and J. Alberti, *Chem. Ber.*, 1973, **106**, 236.

Phosphonic acid and ester groups. Our previous work [11] showed that, during the solvolysis of tosylates (14), phosphoryl substituents ($R^1 = R^2$ = EtO, R^3 = H) lead to fragmentation, but diphenylphosphinoyl substituents ($R^1 = R^2$ = Ph, R^3 = H, Alk, Ar) react exclusively by diphenylphosphinoyl migration. We have now investigated the phosphonoyl substituents (R^1 = Ph, R^2 = HO or MeO) to determine where the boundary lies between fragmentation and migration with the hope that we might be able to determine the stereochemistry of the migration, should it occur. The chiral $R^1(R^2O)PO$ function has been used by Musierowicz [19] and other workers [20] to determine or control the stereochemistry of reactions.

Since we wanted both the esters (R^1 = MeO) and the acids (R^1 = HO), we synthesised the benzyl esters (16) and (21) by methylation and reduction of the carboxylic ester (15) and the ketone (20), respectively, as in Schemes



(14)

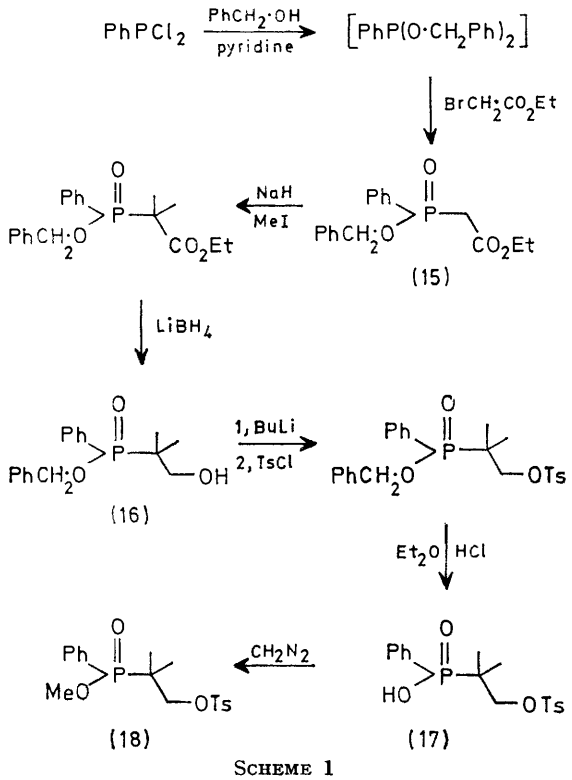
1 and 2. Iodoacetone was used in the synthesis of the ketone (20) as chloroacetone gave largely the enol-phosphonate (19). We found that the sequence tosylation, debenzylation, and methyl ester formation was best carried out in that order. Debenzylation by hydrogen chloride in ether gave good yields of the acids (17) and (22), whereas debenzylation with sodium iodide in acetone led to extensive decomposition and formation of sodium tosylate.

The solvolysis of either primary tosylate (17) or (18) in formic or trifluoroacetic acid was very slow, but after some days at 75 °C the starting materials were consumed and no identifiable products could be detected. In

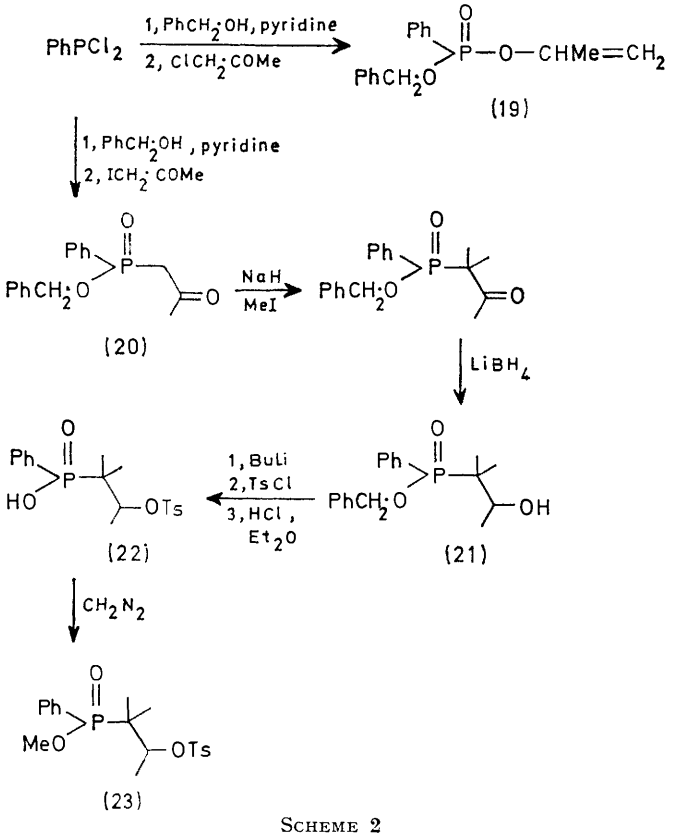
[19] S. Musierowicz, A. Wróblewski, and H. Krawczyk, *Tetrahedron Letters*, 1975, 437.

[20] J. Michalski and A. Ratajczak, *Chem. and Ind.*, 1960, 1241; M. Mikołajczyk and M. Para, *Chem. Comm.*, 1969, 1192; L. P. Reiff and H. S. Aaron, *J. Amer. Chem. Soc.*, 1970, **92**, 5275; G. R. van den Berg, D. H. J. M. Platenburg, and H. P. Benschop, *Chem. Comm.*, 1971, 606; W. B. Farnham, R. K. Murray, and K. Mislow, *ibid.*, p. 605.

particular, the characteristic lines of the $PCMe_2$ group were absent from the n.m.r. spectrum of the reaction

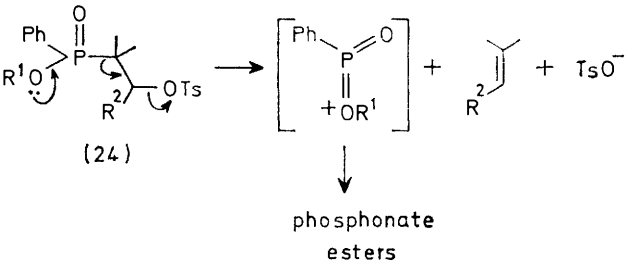


SCHEME 1



SCHEME 2

mixture, showing that P–C bond cleavage had occurred. The secondary tosylates (22) and (23) were more reactive (half-life *ca.* 30 min in formic acid at 75 °C), but again gave no clearly defined products. The acid (22) definitely fragmented (no $PCMe_2$ by n.m.r.) but the ester (23) gave small amounts of products which might, from their n.m.r. spectra, have been rearrangement products. It seems that fragmentation (24) is the normal mode of reaction of these compounds.



We decided not to investigate this system any further as, even if the methyl ester (23) had given clearly defined rearrangement products, we would not have been able to study the stereochemistry of the reaction as we could not completely separate the diastereoisomers of the ester (23) even by analytical high-pressure liquid chromatography. We have therefore synthesised the phosphine oxide (14; R^1 = Ph, R^2 = R^3 = Me) and have already reported [21] our demonstration of the stereospecificity of its rearrangement.

Phenylsulphonyl and phenylsulphinyl groups. By direct analogy with the phosphorus compounds, the two sulphur-based functional groups $PhSO_2$ and PhSO would seem the best candidates for rearrangement. The required sulphone (26) was made in only 25% yield by the addition of the carbanion from isopropyl phenyl sulphone (25) to acetaldehyde. The tosylate of this sulphone (27) was very unreactive indeed but did slowly rearrange in trifluoroacetic acid at 75 °C (half-life *ca.* 6 days) to give the allyl sulphone (28).

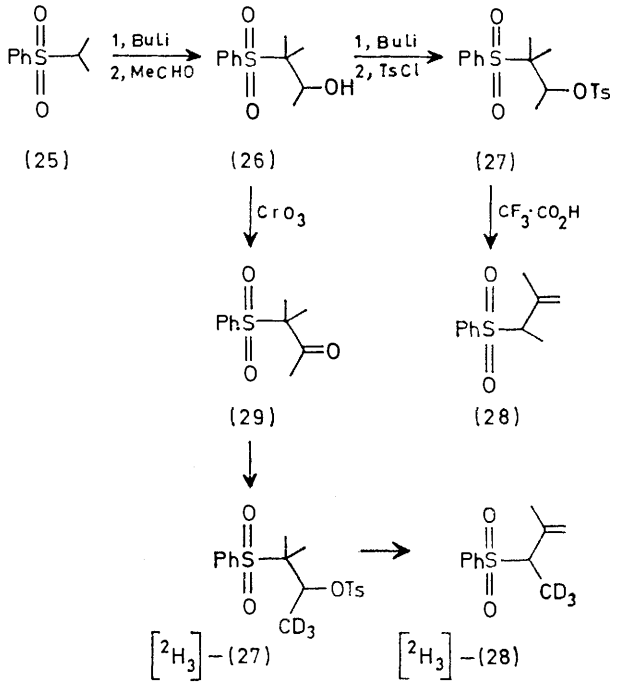
That the reaction involves migration of the phenylsulphonyl group was shown by preparing the deuteriated compound, [$^2H_3$]-(27), from the ketone (29). Rearrangement of [$^2H_3$]-(27) gave the allyl sulphone, [$^2H_3$]-(28), with only the α-methyl group deuteriated.

The required sulphoxide (31) was made similarly from the carbanion of isopropyl phenyl sulphoxide (30). This reaction gives a single crystalline isomer of the sulphoxide (31) albeit in only 30% yield, and the configuration of this isomer has been determined by *X*-ray crystallography [22] as (*SRS*,2*RS*). It gives a single tosylate, presumably of the same configuration. The solvolysis of this tosylate (32) in trifluoroacetic acid leads to decomposition, probably by protonation at the sulphoxide oxygen atom, but in acetic acid at 75 °C the allyl sulphoxide (33) is formed. This phenylsulphinyl migration

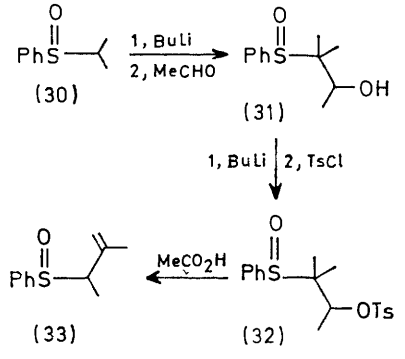
[21] F. H. Allen, O. Kennard, L. R. Nassimbeni, R. G. Shepherd, and S. Warren, *Nature*, 1974, **248**, 670; *J.C.S. Perkin II*, 1974, 1530.

[22] F. H. Allen, O. Kennard, G. M. Sheldrick, and O. Oeser, *Acta Cryst.*, 1976, **B32**, 274.

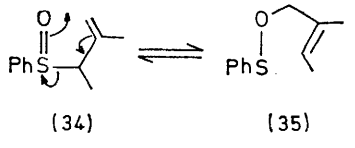
occurs at roughly four times the rate of the diphenylphosphinoyl migration of (3; R^1 = Me) under the same conditions (see Table 2).



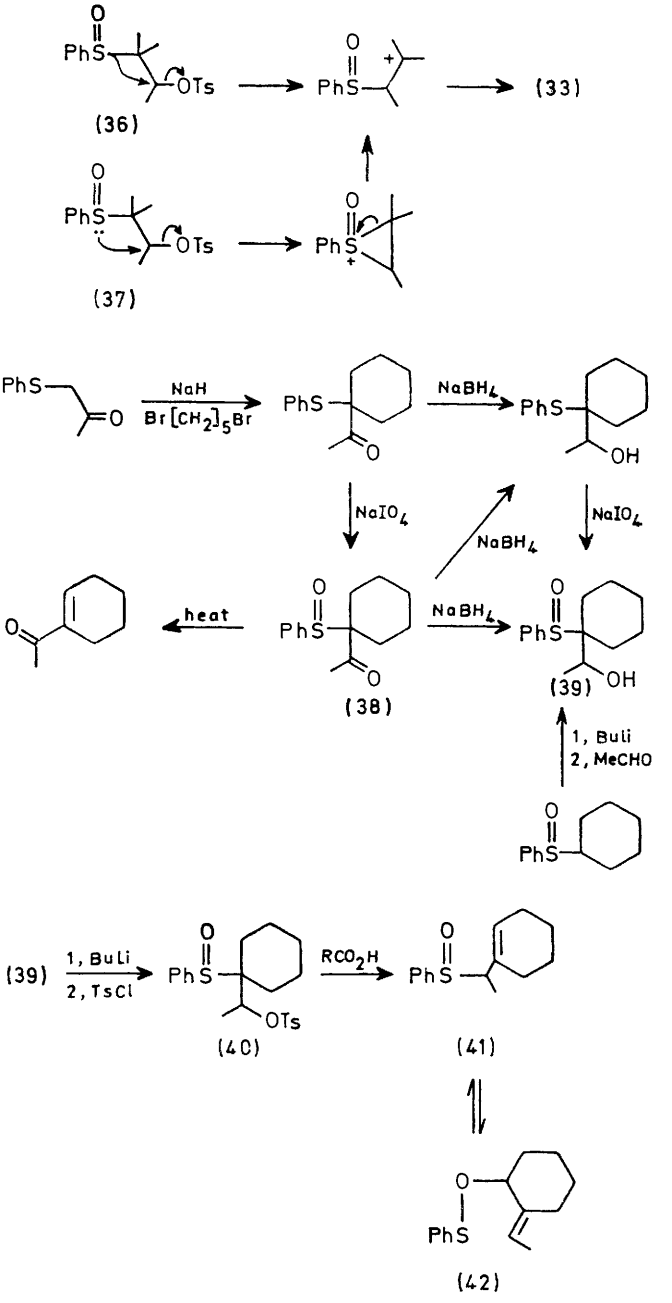
Under some conditions the allyl sulphoxide (33) is produced as a mixture of diastereoisomers, but in formic acid at 50—60 °C, the n.m.r. spectrum of the reaction



mixture shows that the reaction is stereospecific, though epimerisation of the product occurs after isolation even at −15 °C. The epimerisation presumably takes place by the [2,3] sigmatropic process (34) *via* the allyl sulphenate (35), a process known to racemise allyl sulphoxides.[23]



We were eager to determine the stereochemistry of the sulphoxide rearrangement as the straightforward process of σ-bond migration (36) should lead to inversion at C-2 but retention at sulphur, while *n*-participation by the lone pair of electrons on sulphur (37) should lead to inversion at both C-2 and sulphur. We therefore turned to the cyclohexyl compound (40), reasoning that the [2,3] sigmatropic shift on the product (41) would be relatively slow as the sulphenate ester (42) has an exocyclic double



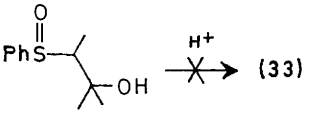
Scheme 3

bond. The alcohol (39) could be synthesised by any of the routes summarised in Scheme 3. None gave a very good yield, particularly that *via* the phenylsulphinyl ketone (38), as this decomposes very readily to acetyl-

[23] P. Bickart, F. W. Carson, J. Jacobus, E. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4869.

cyclohexene while its reduction gave a mixture of the alcohol (39) and the corresponding sulphide. The alcohol (39) could be separated into diastereoisomers, one of which * was converted into the tosylate (40). Solvolysis again gave a single isomer of the allyl sulphoxide (41) but this compound underwent epimerisation during work-up and we were again unable to isolate a stable crystal for *X*-ray spectroscopy.

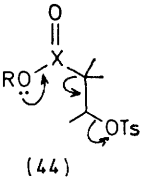
This was not the only unsatisfactory feature of the sulphoxide rearrangements, as many of the compounds such as the ketone (38) are thermally unstable. Almost all tended to give diphenyl disulphide on treatment with acids, black tars also being formed in the stronger acids (trifluoroacetic, sulphuric, and toluene-*p*-sulphonic in acetonitrile). The addition of the sulphoxide stabilised carbanions to acetaldehyde proceeds in only 20—30% yield [*e.g.* (30) ⟶ (31)], and the 2-hydroxyalkyl sulphoxide with the alternative substitution pattern (43) does not undergo dehydration to the allyl sulphoxide (33), unlike the corresponding phosphine oxide.[16] We have therefore abandoned our hopes [24] of developing these sulphoxide rearrangements into useful synthetic procedures and turned instead to the more tractable 2-hydroxyalkyl sulphides.[25]



(43)

Conclusions. Table 1 summarises our results and records the reaction pathway most commonly adopted by compounds of the general structure $XCMe_2$·CHR·OTs on solvolysis, and Table 2 gives some rates where they have been measured under comparable conditions. ' Good migrating groups ' with lone pairs of electrons (MeO) or π-electrons (aryl, alkenyl) migrate in preference to methyl because an intermediate replaces a transition state in the rearrangement. ' Poor migrating groups ' (H, PhSO, $PhSO_2$, Ph_2PO) migrate in preference to methyl to give the more stable cation, and not because their migration is intrinsically more favourable than methyl migration. Indeed, there clearly comes a point at which it is so unfavourable that other processes (participation for carbonyl and fragmentation for nitro) take over.

Exactly where this boundary lies is difficult to define, but some of the factors which place a given substituent on one side or the other are clear. (*a*) Among electronegative groups, the more electronegative the group, the slower the migration (*e.g.* $PhSO_2$ *vs.* Ph_2PO). Presumably nitro does not migrate for this reason. (*b*) The stronger the C–X bond, the less favourable either rearrangement or fragmentation become, and the more favourable participation becomes (*e.g.* PhCO *vs.* Ph_2PO). (*c*) Perhaps solely because of factor (*b*), but perhaps also because the X–C bond is longer and small C–X–C bond angles are more favourable, functional groups based on second row elements (P, S) migrate easily. (*d*) As recognised by Grob,[2] oxygen atoms in the substituent X encourage fragmentation [see (44)]. This factor helps the nitro-compound to fragment and is presumably decisive in the difference between the phosphinoyl and phosphonoyl substituents.



(44)

TABLE 1

Reaction pathways in $XCMe_2$·CHR·OTs solvolysis

X	Pathway for R = H	Pathway for R = Me
H	H migration [a]	H migration [a]
Me	Me migration [a]	Me migration [a]
Alkyl	Me and alkyl migration [b]	
Alkenyl	Alkenyl migration [c]	
Alkynyl	Alkynyl migration [d]	
Aryl	Aryl migration [a]	Aryl migration [a]
HO †		Alkyl migration [e]
MeO	MeO migration [f]	MeO ‡ migration [f]
PhS §		PhS migration [g]
PhSO		PhSO migration
$PhSO_2$		$PhSO_2$ migration
Ph_2PO	Ph_2PO migration [h]	Ph_2PO migration [h]
Ph(Me)PO		Ph(Me)PO migration
Ph(MeO)PO	Fragmentation	¶
Ph(HO)PO	Fragmentation	Fragmentation
$(EtO)_2PO$	Fragmentation [h]	
NO_2	Fragmentation	Fragmentation
PhCO	1,4-Carbonyl participation	1,4-Carbonyl participation [j]
MeCO	1,4-Carbonyl participation [j]	1,4-Carbonyl participation [j]

† $XC(Alk)_2CHR$·OTs in a steroid molecule. ‡ By silver-catalysed solvolysis of the bromide. § Rearrangement occurs when the alcohol is treated with TsOH. ¶ Mixed pathways; see text.

[a] Ref. 26. [b] J. R. Owen and W. H. Saunders, *J. Amer. Chem. Soc.*, 1966, **88**, 5809; R. L. Heidke and W. H. Saunders, *ibid.*, 5816. [c] R. S. Bly and R. T. Swindell, *J. Org. Chem.*, 1965, **30**, 10. [d] J. W. Wilson, *Tetrahedron Letters*, 1968, 2561. [e] S. S. Deshmane and H. Hirschmann, *J. Org. Chem.*, 1975, **40**, 3469. [f] S. Winstein and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1952, **74**, 1160. [g] Ref. 25. [h] Ref. 11. [i] Ref. 21. [j] Ref. 4.

TABLE 2

Approximate solvolysis rates for the secondary tosylates $XCMe_2$·CHMe·OTs (k_{obs}/s^{-1}; 75 °C)

X	CF_3·CO_2H	$MeCO_2H$
H [a]		2.0×10^{-4}
Me [a]		1.2×10^{-4}
Ph [a]		2.1×10^{-3}
Ph_2PO	$>10^{-3}$	1.9×10^{-4}
PhSO	*b*	7.7×10^{-4}
$PhSO_2$	1.4×10^{-6}	*c*

[a] Estimated from data at other temperatures for the brosylates from ref. 26. [b] Decomposes. [c] Too slow to be measured.

* This alcohol has the (1*RS*,S*SR*)-configuration as determined by F. H. Allen in our laboratories by *X*-ray crystallography.

[24] A. H. Davidson, P. K. G. Hodgson, D. Howells, and S. Warren, *Chem. and Ind.*, 1975, 455.

[25] P. Brownbridge and S. Warren, *J.C.S. Chem. Comm.*, 1975, 820.

[26] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, 1952, **74**, 113; S. Winstein and H. Marshall, *ibid.*, 1120.

The rates of solvolysis of all the secondary tosylates (Table 2) are within an order of magnitude except for $PhSO_2$ (very slow) and phenyl (fast) migration, and all except the sulphone (27) react faster than isopropyl tosylate by an order of magnitude. The primary tosylates (X = H,[26] Me,[26] Ph,[26] and Ph_2PO[11]) show much larger differences in rate. Presumably the transition state for the solvolysis of the secondary tosylates involves considerable C–O bond breaking and little (if any) participation by the migrating group.

EXPERIMENTAL

I.r. spectra were taken on a Perkin-Elmer 257, n.m.r. spectra on a Perkin-Elmer R12B, Hitachi Perkin-Elmer R24A, or Varian HA100D, mass spectra on an A.E.I. MS9 or MS30 and high resolution mass spectra on an A.E.I. MS902 machine. T.l.c. was run on silica gel GF 254 eluted with acetone (30%)–light petroleum (b.p. 60—80°) except where stated otherwise. Petrol refers to light petroleum (b.p. 60—80°). N.m.r. peaks marked with an asterisk are for diastereotopic protons. We have previously described [4] typical procedures for preparing and solvolysing tosylates.

*2-Methyl-2-nitropropyl Toluene-*p*-sulphonate* (8a). Anhydrous pyridine (2.5 ml) was added slowly to a mixture of 2-nitro-2-methylpropan-1-ol [14] (7a) (3 g) and toluene-*p*-sulphonyl chloride (4.75 g). The mixture was heated at 100 °C for 1 h, then cooled to room temperature, and water (10 ml) was added. Recrystallisation of the precipitate (from MeOH) gave the tosylate (8a) (4 g, 59%) as a white solid, m.p. 69—70° (lit.,[27] 73—74°), R_F 0.36, $\nu_{max.}$ ($CHCl_3$) 1 545 and 1 372 (NO_2), and 1 173 cm^{-1} (SO_2), τ ($CDCl_3$) 2.25 and 2.67 (4 H, ABq, *J* 8.4 Hz, Ar), 5.72 (2 H, s, CH_2·OTs), 7.54 (3 H, s, *Me*Ar), and 8.41 (6 H, s, $Me_2C{\cdot}NO_2$).

Trifluoroacetolysis of the Tosylate (8a).—The usual procedure [4] with the tosylate (546 mg), sodium trifluoroacetate (272 mg), and trifluoroacetic acid (15 ml) after 18 days at 75 °C gave unchanged tosylate (8a) (487 mg, 89%).

3-Methyl-3-nitrobutan-2-ol (7b).—The potassium fluoride-catalysed addition of acetaldehyde to 2-nitropropane [28] gave the alcohol (7b) (5%), b.p. 106—108° at 18 mmHg (lit.,[28] 82—84° at 5 mmHg), R_F 0.33, $\nu_{max.}$ 3 565 (OH), 1 398, and 1 374 cm^{-1}, τ 5.83 (1 H, q, *J* 7.2 Hz, C*H*Me), 7.24 (1 H, s, OH), 8.47 * and 8.49 * (each 3 H, s, $Me_2C{\cdot}NO_2$), and 8.84 (3 H, d, *J* 7.2 Hz, CH*Me*). The *toluene-*p*-sulphonate* (8b) prepared by the Nerdel method [15] had m.p. 66—67°, R_F 0.32, $\nu_{max.}$ 1 378, 1 352, 1 194, and 917 cm^{-1}, τ ($CDCl_3$) 2.25 and 2.67 (4 H, ABq, *J* 7.8 Hz, Ar), 4.93 (1 H, q, *J* 7.2 Hz, C*H*Me), 7.51 (3 H, s, *Me*Ar), 8.45 * and 8.50 * (each 3 H, s, Me_2CNO_2), and 8.67 (3 H, d, *J* 7.2 Hz, CH*Me*), *m/e* 287 (M^+, 9%), 244 (37), 165 (13), 155 (85), 91 (100), and 69 (54) (Found: M^+, 287.083 5. $C_{12}H_{17}NO_5S$ requires *M*, 287.0826).

Trifluoroacetolysis of the Tosylate (8b).—After 12 days the tosylate (8b) (9%) was the only organic material present. The normal procedure with the tosylate (8b) (141 mg), sodium trifluoroacetate (68 mg), anisole (500 mg), and trifluoroacetic acid (8 ml) gave *p*-nitroanisole (32 mg, 40%), identified by its i.r., n.m.r., and mass spectra.

2-Methyl-2-nitro-1-phenylpropan-1-ol (7c).—2-Nitropropane (71 g) and benzaldehyde (80.5 g) were slowly added to a cooled solution of sodium (3.5 g) in anhydrous methanol (270 ml) under nitrogen. The mixture was stirred for 24 h and acidified with acetic acid (75 ml). The methanol was evaporated off and the resulting oil partitioned between water and ether (150 ml). The ether layer was washed with water (100 ml), sodium hydrogen sulphite solution (4 × 100 ml), and water (100 ml), and dried ($MgSO_4$). Evaporation under reduced pressure, finally at 150 °C, gave an oil which crystallised on trituration with petrol (200 ml) for 2 h. The solid was collected, washed with petrol, dried (P_2O_5), and recrystallised from heptane to give the alcohol (7c) as a cream solid (46.9 g, 32%), m.p. 62—65° (lit.,[29] 68—70°), R_F 0.30, $\nu_{max.}$ 3 626 (OH), 1 400, 1 376, and 1 058 cm^{-1}, τ ($CDCl_3$) 2.68 (5 H, s, Ar), 4.76 (1 H, s, C*H*OH), 7.31 (1 H, s, OH), and 8.46 * and 8.59 * (each 3 H, s, $Me_2C{\cdot}NO_2$). Attempted preparation of the tosylate by the butyl-lithium method [11] or the Nerdel [15] method gave in each case benzaldehyde as the only product.

Acidic Solvolysis of the Alcohol (7c).—The alcohol (7c) (200 mg) in trifluoroacetic acid (7 ml) after 2.5 h at 75 °C gave benzaldehyde (100 mg, 93%) and a small amount of a nitroalkyl trifluoroacetate of unknown structure. Benzaldehyde (48 and 98%, respectively) was the only product when the alcohol was dissolved in phosphoric or sulphuric acid.

2,2,5,5-Tetramethylcyclohexane-1,3-dione.—The dione, prepared by the method of Halsall and Thomas,[30] had m.p. 95—96° (lit.,[31] 95°), R_F 0.41, $\nu_{max.}$ 1 735 and 1 702 cm^{-1} (CO), τ ($CDCl_3$) 7.51 (4 H s, CH_2), 8.78 (6 H, s, CO·CMe_2·CO), and 9.02 (6 H, s, CMe_2).

3-Hydroxy-2,2,5,5-tetramethylcyclohexanone.—A solution of sodium borohydride (228 mg) in absolute ethanol (60 mol) was added dropwise to a stirred solution of the above dione (3.36 g) in ethanol (100 ml) at 20 °C. After 22 h at 25 °C, the mixture was poured into saturated brine (200 ml) and extracted with ether (4 × 50 ml). The extracts were washed with saturated sodium carbonate solution (250 ml) and water (250 ml), and dried (Na_2SO_4). Evaporation, and recrystallisation of the residue from petrol gave the hydroxy-ketone as white crystals (1.5 g, 44%), m.p. 57—58° (lit.,[17] 54—55°), R_F 0.45, $\nu_{max.}$ (CCl_4) 3 630 (OH) and 1 713 (CO) cm^{-1}, τ (CCl_4) 6.39 (1 H, dd, J_{aa} 8, J_{ae} 7 Hz, CH_aOH), 7.62 * and 8.09 * (each 1 H, ABq, *J* 14 Hz, CH_2·CO), 8.32 (3 H, m, CH_2·CH and OH), 8.97 (6 H, s, 2 Me_a), 8.99 (3 H, s, Me_e), and 9.17 (3 H, s, Me_e). The toluene-*p*-sulphonate (12) prepared by the Nerdel [15] method as a cream solid had m.p. 81—83° (lit.,[17] 83°), R_F 0.38, $\nu_{max.}$ (CCl_4) 1 717 (CO) and 1 192 and 1 182 cm^{-1} (SO_2), τ (CCl_4) 2.33 and 2.78 (each 2 H, ABq, *J* 8.4 Hz, Ar), 5.56 (1 H, t, *J* 8 Hz, CH_2·C*H*OTs), 7.63 * and 8.02 * (each 1 H, ABq, *J* 14 Hz, CH_2·CO), 7.59 (3 H, s, *Me*Ar), 8.02 (2 H, d, *J* 8 Hz, CH_2·CHOTs), 8.95 (3 H, s, Me), 8.98 (3 H, s, Me), 9.12 (3 H, s, Me), and 9.14 (3 H, s, Me).

Trifluoroacetolysis of the Tosylate (12).—The usual procedure [4] with the tosylate (12) (243 mg), sodium trifluoroacetate (102 mg), and trifluoroacetic acid (10 ml) gave a yellow oil which contained 2-isopropylidene-4,4-dimethylcyclopentanone (76%) and 2,2,5,5-tetramethyl-3-trifluoroacetoxycyclohexanone (24%), identified by their n.m.r. spectra and separable by g.l.c. but not by t.l.c. A portion of the mixture (60 mg) was hydrolysed [32] with potassium hydrogen carbonate (200 mg) in methanol (8 ml) and water (4 ml) for 52 h at room temperature. The solution was

[27] J. L. Riebsomer, *J. Org. Chem.*, 1946, **11**, 182.
[28] S. Kambe and H. Yasuda, *Bull. Chem. Soc. Japan*, 1968, **41**, 1444.
[29] Wallace and Tiernan Inc., B.P. 916,789/1963 (*Chem. Abs.*, 1963, **59**, 2712h).
[30] T. G. Halsall and D. B. Thomas, *J. Chem. Soc.*, 1956, 2431.
[31] R. D. Desai, *J. Chem. Soc.*, 1932, 1079.
[32] A. Lardon and T. Reichstein, *Helv. Chim. Acta*, 1954, **37**, 388.

poured into water (25 ml) and extracted with ether (3 × 20 ml), and the extracts were washed with water (50 ml) and dried ($MgSO_4$). Evaporation gave a yellow liquid separated by preparative t.l.c. into 3-hydroxy-2,2,5,5-tetramethylcyclohexanone, identified by its i.r. and n.m.r. spectra, and 2-isopropylidene-4,4-dimethylcyclopentanone [17] as a colourless liquid (25 mg), R_F 0.58, $\nu_{max.}$ (CCl_4) 1 713 (CO) and 1 637 cm^{-1} (C=C), τ (CCl_4) 7.67 (2 H, m, CH_2·C=C), 7.86 (3 H, t, J 1 Hz, *Me*C=C·CH_2), 7.96 (2 H, s, CH_2·CO), 8.24 (3 H, s, *Me*C=C·CH_2, Me and CH_2 *cis*), and 8.96 (6 H, s, CMe_2), $\lambda_{max.}$ 252 nm (ε 7 700), *m/e* 152 (M^+, 71%), 137 (15), 96 (75), 68 (100), and 67 (20). (Found: M^+, 152.1203. $C_{10}H_{16}O$ requires M, 152.1200). I.r. and u.v. spectra of this compound are given in ref. 17.

2-*Methyl*-2-(p-*tolylsulphonyloxymethyl*)*cyclohexanone* (13).—This tosylate was prepared from the alcohol [33] by the usual method [4] as a yellow oil, R_F 0.33, $\nu_{max.}$ (CCl_4) 1 714 (CO) and 1 192 cm^{-1} (SO_2), τ(CCl_4) 2.30 and 2.73 (each 2 H, ABq, J 8.4 Hz, Ar), 6.12 (2 H, s, CH_2·OTs), 7.58 (3 H, s, *Me*Ar), 7.72 (2 H, m, CH_2CO), 8.24 (6 H, m, methylene envelope), and 8.92 (3 H, s, Me).

Trifluoroacetolysis of the Tosylate (13).—The usual procedure [4] with the tosylate (13) (296) mg), sodium trifluoroacetate (136 mg), and trifluoroacetic acid (10 ml) gave after 21 days a brown oil separated by preparative t.l.c. into the original tosylate (13) (80%) and 2-methyl-2-trifluoroacetoxymethylcyclohexanone [33] (20%) as colourless liquids identified by their i.r. and n.m.r. spectra.

Ethyl 2-[*Benzyloxy*(*phenyl*)*phosphinoyl*]*propionate*.—Dibenzyl phenylphosphonite was prepared by the method of Anand and Todd [34] but not distilled, as we find this leads to substantial amounts of benzyl benzyl(phenyl)phosphinate. Freshly distilled ethyl bromoacetate (42 g) was slowly added at 0 °C under nitrogen to crude dibenzyl phenylphosphinite (80 g); the mixture was kept overnight at 0 °C and allowed to reach room temperature. Ether (200 ml) was added, followed by triphenylphosphine (65.6 g) in ether (300 ml) and the mixture stirred until precipitation of benzyltriphenylphosphonium bromide was complete. The mixture was filtered, and the filtrate passed down a column of silica with chloroform as eluant to give a colourless oil, crystallised and recrystallised from hexane at about −15 °C. The *ester* (70 g, 89%) had R_F (EtOAc) 0.5, $\nu_{max.}$ ($CHCl_3$) 1 735 (CO), 1 445 (P–Ph), and 1 250 cm^{-1} (P=O), τ ($CDCl_3$) 2.5 (10 H, m, Ph), 5.06 (2 H, ABP system, $J_{AP} = J_{BP} = 8$, J_{AB} 11.5 Hz, PhCH_2*O), 6.07 (2 H, q, J 7 Hz, MeCH_2O), 6.97 (2 H, d, J_{HP} 18 Hz, PhCH_2P), and 8.97 (3 H, t, J 7 Hz, *Me*CH_2), *m/e* 318 (M,$^+$ 16%), 212 (18), and 91 (100).

Ethyl 2-[*Benzyloxy*(*phenyl*)*phosphinoyl*]-2-*methylpropionate*.—Sodium hydride (16 g; 60% suspension in oil washed with ether) was added in portions to the above ester (63.6 g) and methyl iodide (100 g) in tetrahydrofuran (200 ml) at 0 °C under nitrogen. After 1 H at 0 °C, the mixture was allowed to come to room temperature, ether (200 ml) was added, and the ethereal solution was extracted with saturated ammonium chloride solution. The organic phase was dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography as before gave a pale yellow oil (35 g, 50%), identified as the methylated *ester* by its spectra. It had R_F (EtOAc) 0.55, $\nu_{max.}$ ($CHCl_3$) 1 725 (C=O), 1 443 (P–Ph), and 1 255 cm^{-1} (P=O), τ ($CDCl_3$) 2.2—3.0 (10 H, m, Ph), 5.11 (2 H, ABP system, $J_{AP} = J_{BP} = 8$, J_{AB} 12 Hz, PhCH_2*O), 6.04 (2 H, q, J 7 Hz, MeCH_2O), 8.61 (3 H, d, J_{PH} 14 Hz, PCMe_2*), and 8.72 (3 H, d, J_{PH} 16 Hz, PCMe_2*), *m/e* 346 (M^+, 14%), 276 (28), 170 (15), 142 (18), and 91 (100).

2-[*Benzyloxy*(*phenyl*)*phosphinoyl*]-2-*methylpropan*-1-*ol* (16).—An excess of lithium borohydride (1.5 g) was added in portions to the methylated ester (15 g) in tetrahydrofuran (300 ml) under nitrogen. After 1 h, saturated ammonium chloride solution was added, the layers were separated, the aqueous layer was back extracted with ether (100 ml), and the combined organic layers were dried ($MgSO_4$). Removal of the solvents under reduced pressure gave the *alcohol* (16) (11 g), crystallised and recrystallised from hexane at low temperature. It had R_F 0.25 (EtOAc), $\nu_{max.}$ ($CHCl_3$) 3 400br (OH), 1 440 (P–Ph), and 1 185 cm^{-1} (P=O), τ (C_6D_6) 2.1—3.0 (10 H, m, Ph), 5.16 (2 H, ABP system, $J_{AP} = J_{BP} = 7$, J_{AB} 12 Hz, PhCH_2*O), 5.4br (1 H, s, OH), 6.24 (2 H, ABP system, $J_{AP} = J_{BP} = 16$, J_{AB} 11 Hz, CH_2*OH), 8.80 (3 H, d, J_{HP} 15 Hz, PCMe_2*), and 8.93 (3 H, d, J_{PH} 16 Hz, PCMe_2*), *m/e* 304 (M^+, 5%), 274 (10), 214 (15), 167 (15), 158 (20), 141 (92), 91 (100), and 77 (53).

The alcohol (16) (2.5 g) in tetrahydrofuran (80 ml) was treated with butyl-lithium (3.65 ml of 15% solution in hexane) in tetrahydrofuran (20 ml) and tosyl chloride (1.6 g) in tetrahydrofuran (20 ml). The solution was stirred for 0.5 h and washed with saturated ammonium chloride solution; the organic phase was dried ($MgSO_4$) and evaporated under reduced pressure to give the tosylate (3 g, 80%), crystallised and recrystallised from hexane at low temperature. It had R_F 0.6 (EtOAc), $\nu_{max.}$ ($CHCl_3$) 1 440 (P–Ph) and 1 175 and 1 185 cm^{-1} (P=O and SO_2), τ ($CDCl_3$) 2.2—3.0 (14 H, m, Ar), 5.16 (2 H, ABP system, $J_{AP} = J_{BP} = 8$, J_{AB} 12 Hz, PhCH_2*O), 6.03 (2 H, d, J_{HP} 10 Hz, CH_2·OTs), 7.61 (3 H, s, *Me*Ar), 8.94 (6 H, d, J_{HP} 15 Hz, PCMe_2), *m/e* 458 (M^+, 0.5%), 274 (3), 141 (4), and 91 (100).

2-[*Hydroxy*(*phenyl*)*phosphinoyl*]-2-*methylpropyl Toluene*-p-*sulphonate* (17).—The above tosylate (1.7 g) was treated with ether (35 ml) saturated with hydrogen chloride and stirred at room temperature for 24 h. The solvents were removed under reduced pressure, and the crystalline product washed with ether several times, the ether being removed by evaporation under reduced pressure. The product (1 g, 78%) was recrystallised from chloroform–di-isopropyl ether to give the *tosylate* (17), m.p. 161—162°, R_F 0.4 (2 : 3 MeOH–EtOAc), $\nu_{max.}$ 1 440 (P–Ph), 1 230 (P=O), and 1 190 and 1 170 cm^{-1} (SO_2), τ (CD_3OD) 2.1—2.8 (9 H, m, Ar), 6.02 (2 H, d, J_{HP} 9 Hz, CH_2OTs), 7.54 (3 H, s, *Me*Ar), 8.92 (6 H, d, J_{HP} 15 Hz, PCMe_2); the compound was too involatile for a mass spectrum to be obtained (Found: C, 55.4; H, 5.8; P, 8.1. $C_{17}H_{21}O_5PS$ requires: C, 55.4; H, 5.8; P, 8.4%).

Treatment of this hydroxyphosphinoyl compound (17) (100 mg) with diazomethane in ether gave the *methyl ester* (18) (104 mg, 100%), R_F 0.2, τ ($CDCl_3$) 2.1—2.8 (9 H, m, Ar), 5.91 (2 H, d, J_{HP} 8 Hz, CH_2OTs), 6.35 (3 H, d, J_{HP} 10.5 Hz, PO*Me*), 7.56 (3 H, s, *Me*Ar), and 8.87 (6 H, d, J_{HP} 15 Hz, PCMe_2).

Reaction of Dibenzyl Phenylphosphonite with Chloroacetone.—Crude dibenzyl phenylphosphonite [34] (100 mg) in acetonitrile (2 ml) was treated with chloroacetone (25 μl) overnight. Removal of the solvent under reduced pressure and preparative t.l.c. gave benzyl isopropenyl phenylphosphonate (19) (70 mg, 78%) as a colourless oil, R_F 0.7, $\nu_{max.}$ ($CHCl_3$) 1 660 (C=C–O), 1 442 (P–Ph), and 1 250 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.9 (10 H, m, Ar), 4.92 (2 H, m, PhCH_2O), 5.31 (1 H, m, vinyl H), 5.58 (1 H, m, vinyl H), and 8.13 (3 H, s, Me), *m/e* 288 (M^+, 4%) and 91 (100).

[*Benzyloxy*(*phenyl*)*phosphinoyl*]*propan*-2-*one* (20).—Crude

[33] W. C. Lumma and O. H. Ma, *J. Org. Chem.*, 1970, **35**, 2391.
[34] N. Anand and A. R. Todd, *J. Chem. Soc.*, 1951, 1867.

dibenzyl phenylphosphonite [34] (12 g) in acetonitrile (50 ml) was added to iodoacetone (3.3 ml) in acetonitrile (200 ml) under reflux in a nitrogen atomosphere. The mixture was heated under reflux for 5 min, cooled, and evaporated under reduced pressure. Column chromatography on silica [dichloromethane–chloroform (2 : 1) as eluant] gave the *ketone* (20) (5.4 g, 55%) as a colourless oil, R_F 0.55, $\nu_{max.}$ ($CHCl_3$) 1 715 (CO), 1 440 (P–Ph), and 1 235 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.8 (10 H, m, Ph), 5.01 (2 H, ABP system, $J_{AP} = J_{BP} = 8$, J_{AB} 12 Hz, PhCH_2*O), 6.62 (2 H, d, J_{HP} 19 Hz, PCH_2), and 7.73 (3 H, s, MeCO), *m/e* 288 (M^+, 73%), 182 (27), 125 (27), and 91 (100).

3-[*Benzyloxy(phenyl)phosphinoyl*]-3-*methylbutan*-2-*one*.—The ketone (20) (5.4 g) and methyl iodide (30 g) in tetrahydrofuran (350 ml) were treated with sodium hydride (1.6 g of 60% suspension in oil, washed with ether) and the mixture was stirred for 1 h. Aqueous ammonium chloride (200 ml) was added, the layers were separated, and the organic layer was dried ($MgSO_4$). Evaporation under reduced pressure gave a yellow oil which was used directly to prepare the alcohol (22). A small amount was purified by preparative t.l.c. to give the methylated *ketone*, R_F 0.6, $\nu_{max.}$ 1 705 (CO), 1 440 (*P*–Ph), and 1 235 cm^{-1} (P=O), τ ($CDCl_3$) 2.1—3.0 (10 H, m, Ar), 5.01 (2 H, ABP system, $J_{AP} = J_{BP} = 7$ Hz, J_{AB} 11.5 Hz, PhCH_2*O), 7.65 (3 H, s, MeCO), 8.58 * (3 H, d, J_{HP} 16 Hz, $PCMe_2$), and 8.65 * (3 H, d, J_{HP} 15 Hz, $PCMe_2$), *m/e* 316 (M^+, 7%), 274 (5), 210 (2), and 91 (100).

3-[*Benzyloxy(phenyl)phosphinoyl*]-3-*methylbutan*-2-*ol* (21).—The crude methylated ketone [from 5.4 g of ketone (20)] in tetrahydrofuran (300 ml) was treated with an excess of lithium borohydride (0.5 g). After 0.5 h, aqueous ammonium chloride (100 ml) was added, the layers were separated, the aqueous layer was back-extracted with ether (50 ml), and the combined organic layers were dried ($MgSO_4$). Removal of the solvents under reduced pressure and column chromatography with chloroform as eluant gave a mixture of the diastereoisomers of the alcohol (21) [3.8 g, 50% based on (20)]. The mixture did not separate even on alumina-coated plates (R_F 0.45 with ethyl acetate) and the n.m.r. spectrum showed it was a 60 : 40 mixture: τ ($CDCl_3$) 2.1—2.9 (10 H, m, Ar), 4.7—5.3 (2 H, two ABP systems in the ratio 60 : 40, each with $J_{AP} = J_{BP} = 7$, J_{AB} 14 Hz, PhCH_2*O), 5.65br (1 H, s, OH), 5.5—5.8 and 6.0—6.3 (1 H, two sextets, each J_{HH} 6.5, J_{HP} 13 Hz, MeC*H*OH), and 8.6—9.2 (9 H, 'm', Me), *m/e* 318 (M^+, 2%), 274 (16), and 91 (100).

These alcohols were converted into their toluene-*p*-sulphonates (70%) as above [(16) ⟶ (17)] and purified by column chromatography with 1 : 1 dichloromethane–chloroform as eluant. The mixture of diastereoisomers had R_F 0.75, $\nu_{max.}$ 1 440 (P–Ph) and 1 192 and 1 180 cm^{-1} (SO_2), τ ($CDCl_3$) 2.1—2.9 (14 H, m, Ar), 4.8—5.4 (3 H, m, ArCH_2O and MeC*H*OTs), 7.59 (3 H, s, *Me*Ar), 8.51 (3 H, d, *J* 6.5 Hz, *Me*CHOTs), and 8.7—9.2 (6 H, 8 lines, $PCMe_2$*), *m/e* 472 (M^+, 0.5%), 274 (3), 141 (4), 107 (42), and 91 (100).

2-[*Hydroxy(phenyl)phosphinoyl*]-1,2-*dimethylpropyl Toluene*-p-*sulphonate* (22).—The above tosylate mixture was debenzylated as before [(16) ⟶ (17)] to give the *tosylate* (22) (60%) as white crystals (from chloroform–di-isopropyl ether), m.p. 118—119° (decomp.), τ ($CDCl_3$) 2.1—2.8 (9 H, m, Ar), 5.23 (1 H, sextet, J_{HH} 6.5, J_{HP} 13 Hz, MeC*H*OTs), 7.54 (3 H, s, *Me*Ar), 8.50 (3 H, d, J_{HH} 6.5 Hz, *Me*CHOTs), 8.86 * (3 H, d, J_{HP} 16 Hz, PC*Me*), and 9.01 * (3 H, d, J_{HP} 17 Hz, PC*Me*). We were unable to obtain a satisfactory analysis for this compound and it was too involatile for a mass spectrum. Methylation with diazomethane as before [(17) ⟶ (18)] gave the *methyl ester* (23) (100%), R_F 0.4, τ ($CDCl_3$) 2.2—2.9 (9 H, m, Ar), 5.0—5.4 (1 H, m, MeC*H*OTs), 6.43 (3 H, d, J_{HP} 11 Hz, *Me*OP), 7.60 (3 H, s, *Me*Ar), 8.54 † (3 H, d, J_{HH} 6.5 Hz, *Me*CHOTs), 8.56 † (3 H, d, J_{HH} 6.5 Hz, *Me*CHOTs), and 8.8—9.2 (6 H, 8 lines, $PCMe_2$) (the peaks marked with an obelus, †, belong to the two diastereoisomers in the ratio 1 : 1); *m/e* 396 (M^+, 0.1%), 224 (5), 198 (5), 155 (100), and 141 (2). We were again unable to separate the diastereoisomers by chromatography.

Solvolysis of the Tosylates (17), (18), (22), *and* (23).—Each tosylate was solvolysed by the usual method [4] in trifluoroacetic acid (17) or formic (all) acids. The reaction mixture was worked up in the usual way and n.m.r. spectra were taken to determine the extent of fragmentation. The results are described in the main text.

3-*Methyl*-3-*phenylsulphonylbutan*-2-*ol* (26).—Isopropyl phenyl sulphone (25) (prepared by oxidation with peracetic acid [35] of the sulphide [36]) (18.4 g) in dry tetrahydrofuran was treated with butyl-lithium (66.7 ml of 1.5M-solution in hexane) at 0 °C in a nitrogen atmosphere. After 0.5 h the mixture was cooled to −78 °C and acetaldehyde (5 g) in dry tetrahydrofuran (25 ml) saturated with lithium bromide was added dropwise. The mixture was allowed to warm to room temperature and water (300 ml) was added. The layers were separated, the aqueous layer was extracted with ether (3 × 100 ml), and the combined organic layers were dried (Na_2SO_4). Evaporation gave a yellow oil which was purified on a silica gel column with dichloromethane as eluant to give the *alcohol* as a yellow oil (5.8 g, 25%), R_F 0.21, $\nu_{max.}$ (CCl_4) 3 505 (OH) and 1 294 and 1 132 cm^{-1} (SO_2), τ (CCl_4) 2.4 (5 H, m, Ph), 5.94 (1 H, q, *J* 7 Hz, C*H*MeOH), 6.47 (1 H, s, OH), 8.68 * and 8.94 * (each 3 H, s, CMe_2), and 8.91 (3 H, d, *J* 7 Hz, *Me*CHOH), *m/e* 228 (M^+, 0.7%), 184 (100), 143 (30), 125 (24), and 78 (25).

1,2-*Dimethyl*-2-*phenylsulphonylpropyl Toluene*-p-*sulphonate* (27).—The alcohol (26) (1.14 g) was esterified by the butyl-lithium method as above [(16) ⟶ (17)] to give the *tosylate* (1.2 g, 63%), m.p. 119.5—120.5°, R_F 0.26, $\nu_{max.}$ ($CHCl_3$) 1 358, 1 306, 1 175, and 1 134 cm^{-1} (SO_2), τ ($CDCl_3$) 2.4 (9 H, m, Ar), 6.02 (1 H, q, *J* 6 Hz, C*H*Me), 7.58 (3 H, s, *Me*Ar), 8.48 (3 H, d, *J* 6 Hz, CH*Me*), and 8.70 * and 8.83 * (each 3 H, s, CMe_2), *m/e* 382 (M^+, 0.1%), 241 (50), 156 (26), and 155 (100) (Found: C, 56.7; H, 5.8; S, 16.8. $C_{18}H_{22}O_5S_2$ requires C, 56.5; H, 5.8; S, 16.8%).

Trifluoroacetolysis of the Tosylate (27).—The usual procedure [4] with the tosylate (27) (161 mg), sodium trifluoroacetate (68 mg), and trifluoroacetic acid (8 ml) gave, after 7 days, a brown oil from which was separated by preparative t.l.c. (1 : 1 petrol–ether) 2-*methyl*-3-*phenylsulphonylbut*-1-*ene* (28) as a brown liquid (79 mg, 90%), R_F 0.31, $\nu_{max.}$ ($CHCl_3$) 1 642 (C=C) and 1 306 and 1 146 cm^{-1} (SO_2), τ ($CDCl_3$) 2.4 (5 H, m, Ph), 5.00 (1 H, q, *J* 1 Hz, C=CH), 5.27 (1 H, s, C=CH), 6.30 (1 H, q, *J* 6 Hz, C*H*Me), 8.18 (3 H, s, C=CMe), and 8.53 (3 H, d, *J* 6 Hz, C*H*Me), *m/e* 210 (M^+, 27%), 143 (27), and 69 (100) (Found: M^+, 210.0718. $C_{11}H_{14}O_2S$ requires *M*, 210.0714).

3-*Methyl*-3-*phenylsulphonylbutan*-2-*one* (29).—Jones' reagent [37] was prepared by adding concentrated sulphuric

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acid (15.3 ml), followed by water (50 ml), slowly to a stirred solution of chromium trioxide (17.5 g) in water (25 ml) at 0 °C. The oxidizing solution was added dropwise to a solution of the alcohol (26) (2.5 g) in acetone (50 ml) cooled in an ice-bath, until the orange colour persisted. Propan-2-ol was added to destroy the excess of oxidizing agent and the mixture was poured into water (100 ml), salted out (NaCl), and extracted with chloroform (4 × 50 ml). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow oil, which was purified on a silica column with dichloromethane as eluant and gave the ketone as an oil (1.6 g, 64%) which crystallized to a white solid, m.p. 48—51° (lit.,[38] 47—48°), R_F 0.23, $\nu_{max.}$ (CCl_4) 1 714 (CO) and 1 323 and 1 147 cm^{-1} (SO), τ (CCl_4) 2.5 (5 H, m, Ph), 7.58 (3 H, s, MeCO), and 8.57 (6 H, s, CMe_2), *m/e* 226 (M^+, 35%), 184 (100), 125 (28), 85 (61), and 78 (81).

3-*Methyl*-3-*phenylsulphonyl*[1,1,1-$^2H_3$]*butan*-2-*one*, [$^2H_3$]-(29).—The ketone (29) (250 mg) was added to a mixture of deuterium oxide (5 ml), anhydrous dioxan (5 ml), and potassium carbonate (1 g) and the mixture was heated to 50 °C for 3 h. It was poured into chloroform (50 ml) and the solution washed with water (2 × 50 ml) and dried ($MgSO_4$). Evaporation gave the *deuteriated ketone* as a colourless oil (251 mg, 100%), R_F 0.23, $\nu_{max.}$ (CCl_4) 1 711 (CO) and 1 323 and 1 144 (SO_2) cm^{-1}, τ (CCl_4) 2.4 (5 H, m, Ph) and 8.56 (6 H, s, CMe_2), *m/e* 229 (M^+ 83%), 185 (100), 125 (92), 88 (83), 77 (83), and 60 (79).

3-*Methyl*-3-*phenylsulphonyl*[1,1,1-$^2H_3$]*butan*-2-*ol*, [$^2H_3$]-(26).—The deuteriated ketone [$^2H_3$]-(29) (250 mg) was stirred with lithium borohydride (22 mg) in dry tetrahydrofuran (10 ml) for 10 min. Saturated ammonium chloride solution was added and the mixture extracted with chloroform (3 × 25 ml). The extracts were dried (Na_2SO_4) and evaporated to give a yellow oil (248 mg, 99%), R_F 0.28, $\nu_{max.}$ (CCl_4) 3 505 (OH) and 1 302 and 1 132 cm^{-1} (SO_2), τ (CCl_4) 2.4 (5 H, m, Ph), 5.98 (1 H, s, $CHCD_3$), 6.53 (1 H, s, OH), and 8.71 * and 8.94 * (each 3 H, s, CMe_2), *m/e* 231 (M^+, 1%), 184 (100), 143 (19), 125 (21), 90 (89), and 78 (87). The *toluene*-p-*sulphonate* [$^2H_3$]-(27), prepared as above [(16) ⟶ (17)] had m.p. 117—119°, R_F 0.26, $\nu_{max.}$ ($CHCl_3$) 1 371, 1 309, 1 174, and 1 135 cm^{-1} (SO_2), τ ($CDCl_3$) 2.4 (9 H, m, Ar), 5.04 (1 H, s, $CHCD_3$), 7.58 (3 H, s, *Me*Ar), and 8.69 * and 8.81 * (each 3 H, s, CMe_2), *m/e* 244 (48%), 156 (25), 155 (73), 91 (100), and 72 (70).

Trifluoroacetolysis of the Tosylate [$^2H_3$]-(27).—A procedure similar to that for trifluoroacetolysis of (27) gave 2-*methyl*-3-*phenylsulphonyl*[4,4,4-$^2H_3$]*but*-1-*ene* [$^2H_3$]-(28) as a yellow oil, R_F 0.31, $\nu_{max.}$ ($CHCl_3$) 1 644 (C=C) and 1 311 and 1 152 cm^{-1} (SO_2), τ ($CDCl_3$) 2.4 (5 H, m, Ph), 4.99 (1 H, q, *J* 1 Hz, C=CH_2), 5.26 (1 H, s, C=CH_2), 6.28 (1 H, s, $CHCD_3$), and 8.16 (3 H, s, MeC=C).

(2RS)-3-*Methyl*-3-[(RS)-*phenylsulphinyl*]*butan*-2-*ol* (31).—Isopropyl phenyl sulphoxide (30) (prepared by oxidation of the sulphide [36] with sodium periodate [39]) (3.37 g) in dry tetrahydrofuran (80 ml) saturated with lithium bromide was treated with butyl-lithium (12.7 ml of 1.6M-solution in hexane) at −65 °C in a nitrogen atmosphere. After 0.5 h, acetaldehyde (0.9 g) was added dropwise. After 1 h at −65 °C, the mixture was allowed to warm to room temperature, poured into water, and extracted with dichloromethane (4 × 30 ml). The extracts were dried (Na_2SO_4) and evaporated to give an oil which gave white crystals (1.40 g, 33%) on trituration with ether. The (2*RS*,*SRS*) *alcohol*, recrystallized from di-isopropyl ether, had m.p. 138—140°, R_F 0.17, $\nu_{max.}$ ($CHCl_3$) 3 370 (OH) and 1 010 cm^{-1} (SO), τ ($CDCl_3$) 2.5 (5 H, m, Ph), 5.47 (1 H, s, OH), 5.95 (1 H, q, *J* 7 Hz, C*H*MeOH), 8.62 * and 9.14 * (each 3 H, s, CMe_2), and 8.86 (3 H, d, *J* 7 Hz, *Me*CH), *m/e* 151 (30%), 126 (100), and 87 (30) (Found: C, 62.4; H, 7.3; S, 15.2. $C_{11}H_{16}O_2S$ requires C, 62.3; H, 7.6; S, 15.1%).

(1RS)-1,2-*Dimethyl*-2-[(RS)-*phenylsulphinyl*]*propyl Toluene*-p-*sulphonate* (32).—The butyl-lithium method [see (16) ⟶ (17)] was used, with the (2*RS*,*SRS*)-alcohol (312 mg), butyl-lithium (1.0 ml of 1.5M-solution in hexane) and tosyl chloride (285 mg). The *tosylate* (386 mg, 70%) had m.p. 101—104°, R_F 0.22, $\nu_{max.}$ ($CHCl_3$) 1 367, 1 176 (SO_2), and 1 042 cm^{-1} (SO), τ ($CDCl_3$) 2.17 and 2.69 (4 H, ABq, *J* 8 Hz, Ar), 2.54 (5 H, s, Ph), 5.08 (1 H, q, *J* 6 Hz, C*H*Me), 7.58 (3 H, s, *Me*Ar), 8.50 (3 H, d, *J* 6 Hz, *Me*CH), and 9.03 * and 9.09 * (each 3 H, s, CMe_2), *m/e* 218 (31%), 172 (100), 126 (100), 107 (62), 91 (100), and 89 (51) (Found: C, 59.0; H, 5.9; S, 17.4. $C_{18}H_{22}O_4S_2$ requires C, 59.0; H, 6.0; S, 17.5%).

Formolysis of the Tosylate (32).—The usual procedure [4] with the sulphinyl tosylate (32) (115 mg) and formic acid (3 ml) gave, after 1.5 h at 55 °C, a brownish oil which consisted of a single diastereoisomer of 2-*methyl*-3-*phenylsulphinylbut*-1-*ene* (33), R_F 0.38, τ ($CDCl_3$) 2.5 (5 H, m, Ph), 4.98 (1 H, q, *J* 1 Hz, C=CH_2), 5.25 (1 H, s, C=CH_2), 6.54 (1 H, q, *J* 7 Hz, C*H*Me), 8.22 (3 H, d, *J* 1 Hz, MeC=C), and 8.79 (3 H, d, *J* 7 Hz, *Me*CH). After 7 weeks at −15 °C, the oil was found to be a mixture of diastereoisomers which were purified by preparative t.l.c. (they were inseparable), yielding a colourless oil (46 mg, 74%), R_F 0.38, $\nu_{max.}$ ($CHCl_3$) 1 639 (C=C) and 1 021 cm^{-1} (SO); n.m.r. showed a 2 : 3 mixture of the above diastereoisomers with τ ($CDCl_3$) 2.5 (5 H, m, Ph), 4.98 (1 H, q, *J* 1.5 Hz, C=CH_2), 5.15 (1 H, s, C=CH_2), 6.81 (1 H, q, *J* 7 Hz, C*H*Me), 8.27 (3 H, d, *J* 1.5 Hz, MeC=C), and 8.63 (3 H, d, *J* 7 Hz, *Me*CH); *m/e* 194 (M^+, 3%), 126 (31), 78 (41), 69 (100), and 41 (100) (Found: C, 67.9; H, 7.3; S, 16.3. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.3; S, 16.5%). The reaction mixtures from formolysis at 35 °C and acetolysis at 75 °C both showed this same mixture of diastereoisomers.

1-(1-*Phenylthiocyclohexyl*)*ethanone*.—(Phenylthio)acetone [40] (3.58 g, 21.5 mmol) was added to a slurry of petrol-washed sodium hydride (1.03 g, 43 mmol) in dry tetrahydrofuran (30 ml) with vigorous stirring in a nitrogen atmosphere. When hydrogen evolution had ceased, 1,5-dibromopentane (5.06 g, 22 mmol) in anhydrous dimethylformamide (30 ml) was added. After 3 days, the mixture was poured into ammonium chloride solution (150 ml) and extracted with chloroform (4 × 40 ml). Drying (Na_2SO_4) the extracts and evaporation gave a brown oil, which was distilled through a Vigreux column to yield the *oxosulphide* (1.75 g, 35%), b.p. 135—139° at 0.2 mmHg, R_F 0.51 ,$\nu_{max.}$ (film) 1 697 cm^{-1} (CO), τ ($CDCl_3$) 2.76 (5 H, s, Ph), 7.68 (3 H, s, MeCO), and 8.0—8.8 (10 H, m, methylene envelope). Reduction of this ketone (0.40 g) with sodium borohydride (19 mg) in 80% ethanol (40 ml) gave 1-(1-*phenylthiocyclohexyl*)*ethanol* (0.38 g, 94%), R_F 0.42, $\nu_{max.}$ (film) 3 470 cm^{-1} (OH), τ ($CDCl_3$) 2.3—2.8 (5 H, m, Ph), 6.49 (1 H, q, *J* 7 Hz, C*H*MeOH), 6.97br (1 H, s, OH), 7.9—9.0 (10 H, m, methylene envelope), and 8.83 (3 H, d, *J* 7 Hz, CH*Me*OH), *m/e* 236 (M^+, 13%), 191 (43), 110 (71), 109 (100), and 45 (73).

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Oxidation of 1-(1-*Phenylthiocyclohexyl*)*ethanone with Periodate*.—The oxo-sulphide (1.7 g) and sodium periodate (1.6 g) were stirred in 40% aqueous methanol (40 ml) for 24 h. The mixture was filtered through a glass wool plug to remove sodium iodate and the solution extracted with chloroform (4 × 25 ml). The extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give a yellow oil (1.5 g) which consisted of about 90% of 1-(1-*phenylsulphinylcyclohexyl*)*ethanone* (38), R_F 0.30, $\nu_{max.}$ (film) 1 695 (CO) and 1 020 cm^{-1} (SO), τ ($CDCl_3$) 2.53 (5 H, s, Ph), 7.79 (3 H, s, MeCO), and 8.1—8.9 (10 H, m, methylene envelope), and about 10% of acetylcyclohexene, R_F 0.56, $\nu_{max.}$ (film) 1 666 (CO) and 1 630 cm^{-1} (C=C), τ ($CDCl_3$) 3.1 (1 H, m, C=CH), 7.74 (3 H, s, COMe), and 8.2—8.5 (8 H, m, methylene envelope). Heating the neat mixture at 100 °C for 1 h caused total conversion of (38) into acetylcyclohexene. Reduction of the initial mixture (1.22 g) with sodium borohydride produced a mixture from which three compounds were separated by preparative t.l.c. They were 1-(1-phenylthiocyclohexyl)ethanol (see above) (0.13 g), R_F 0.42, and the two diastereoisomers of 1-(1-phenylsulphinylcyclohexyl)-ethanol (39) (see below), isomer A (0.42 g), R_F 0.32, and isomer B (0.17 g), R_F 0.22.

1-(1-*Phenylsulphinylcyclohexyl*)*ethanol* (39).—(a) *By oxidation of* 1-(1-*phenylthiocyclohexyl*)*ethanol*. The hydroxy-sulphide (0.37 g) and sodium periodate [39] (0.38 g) gave a mixture of diastereoisomers of the *hydroxy-sulphoxide* which were separated by preparative t.l.c., yielding isomer A (0.19 g, 48%), m.p. 95—96.5°, R_F 0.32, $\nu_{max.}$ ($CHCl_3$) 3 380 (OH) and 1 000 cm^{-1} (SO), τ ($CDCl_3$) 2.2—2.5 (5 H, m, Ph), 4.66br (1 H, s, OH), 5.89 (1 H, dq, *J* 6.5, 2 Hz, C*H*MeOH), 7.4—8.8 (10 H, m, methylene envelope), and 8.85 (3 H, d, *J* 6.5 Hz, *Me*CH), *m/e* 252 (M^+, 0.05%), 126 (62), 109 (100), and 83 (69) (Found: C, 66.4; H, 8.0; S, 13.0. $C_{14}H_{20}O_2S$ requires C, 66.6; H, 8.0; S, 12.7%); isomer B (0.15 g, 38%), R_F 0.22, $\nu_{max.}$ (film) 3 360 (OH) and 1 010 cm^{-1} (SO), τ ($CDCl_3$) 2.2—2.5 (5 H, m, Ph), 5.93 (1 H, dq, *J* 5, 6.5 Hz, C*H*MeOH), 6.99 (1 H, d, *J* 5 Hz, CHO*H*), 8.1—8.6 (10 H, m, methylene envelope), and 8.71 (3 H, d, *J* 6.5 Hz, *Me*CH), *m/e* 252 (M^+, 0.6%), 127 (70), 126 (75), 109 (100), and 78 (69).

(b) *By alkylation of cyclohexyl phenyl sulphoxide*. Cyclohexyl phenyl sulphoxide [41] (prepared by oxidation with periodate [39] of the sulphide [42]) (0.58 g) in dry tetrahydrofuran (45 ml) and tetramethylethylenediamine (5 ml) was treated with butyl-lithium (1.6 ml of 1.8M-solution in hexane) at −70 °C under a nitrogen atmosphere. After 1 h stirring, anhydrous lithium bromide (0.5 g) was added, followed by acetaldehyde (0.13 g) in dry tetrahydrofuran (10 ml). The solution was stirred for 1 h, then allowed to warm to room temperature and quenched with ammonium chloride solution (50 ml). Extraction with chloroform (4 × 30 ml), drying (Na_2SO_4) the extracts, evaporation, and preparative t.l.c. gave isomer B of (39) (0.16 g, 22%), R_F 0.22, and a mixture (0.58 g), R_F 0.32, of isomer A of (39) and cyclohexyl phenyl sulphoxide. This mixture was stirred in 98% formic acid (2 ml) for 16 h. The *formate* of the alcohol (39) (isomer A) was produced, R_F 0.28, τ ($CDCl_3$) 2.07 (1 H, s, OCHO), 2.3—2.7 (5 H, m, Ph), 4.57 (1 H, q, *J* 6.5 Hz, C*H*Me), 8.3br (10 H, s, methylene envelope), and 8.83 (3 H, d, *J* 6.5 Hz, *Me*CH), and was purified by preparative t.l.c. and saponified by stirring with potassium carbonate in aqueous acetonitrile to give pure isomer A of (39), which was recrystallised from di-isopropyl either; yield 0.18 g, 25% overall, m.p. 95—96.5°, R_F 0.32.

1-(1-*Phenylsulphinylcyclohexyl*)*ethyl Toluene*-p-*sulphonate* (40).—The tosylate was made from isomer A of the alcohol (39) by the butyl-lithium method [see (16) ⟶ (17)] as a white solid (63%), m.p. 88—89°, R_F 0.27, $\nu_{max.}$ ($CHCl_3$) 1 350, 1 170 (SO_2), and 1 003 cm^{-1} (SO), τ [$(CD_3)_2CO$] 2.33 and 2.74 (4 H, ABq, *J* 9.5 Hz, Me*Ar*), 2.53 (5 H, s, Ph), 5.01 (1 H, q, *J* 6.5 Hz, C*H*Me), 7.52 (3 H, s, *Me*Ar), 8.0—8.7 (10 H, m, methylene envelope), and 8.82 (3 H, d, *J* 6.5 Hz, *Me*CH), *m/e* 218 (100), 109 (34), 91 (29), and 79 (31) (Found: C, 62.0; H, 6.6. $C_{21}H_{26}O_4S_2$ requires C, 62.0; H, 6.5%).

1-(1-*Phenylsulphinylethyl*)*cyclohexene* (41).—Solvolysis of the tosylate (40) (82 mg) with sodium formate (76 mg) in formic acid (0.5 ml) in an n.m.r. tube at 35 °C gave one diastereoisomer (isomer A; see below) of the olefin (41), with a half-life of about 10 min. After 50 min, the mixture was worked up in the usual manner,[4] and was found to be a 1 : 2 mixture of diastereoisomers (A and B) which were purified by preparative t.l.c. to give a colourless oil (37 mg, 78%), R_F 0.37, $\nu_{max.}$ (film) 1 657 (C=C) and 1 038 cm^{-1} (SO), τ ($CDCl_3$) 2.6 (5 H, m, Ph), 4.6 (1 H, m, C=CH), 6.69^A and 6.99^B (1 H, each q, *J* 7 Hz, C*H*Me), 7.9—8.8 (8 H, m, methylene envelope), and 8.65^B and 8.86^A (3 H, each d, *J* 7 Hz, *Me*CH), *m/e* 218 (3%), 126 (22), 110 (81), 109 (100), and 79 (63) (Found: *m/e*, 218.1127. $C_{14}H_{18}S$ requires *M*, 218.1128).

2-*Methyl*-3-*phenylsulphinylbutan*-2-*ol* (43).—This alcohol was prepared in a similar way [43] to the alcohol (31), from ethyl phenyl sulphoxide (0.74 g), butyl-lithium (3.9 ml of 1.2M-solution in hexane), and anhydrous acetone (0.28 g) in dry tetrahydrofuran (30 ml). The product was recrystallized from ethyl acetate as a single diastereoisomer of (43) (0.21 g, 21%), m.p. 127.5—128°, R_F 0.23, $\nu_{max.}$ ($CHCl_3$) 3 590, 3 390 (OH), and 1 024 cm^{-1} (SO), τ ($CDCl_3$) 2.52 (5 H. s, Ph), 7.47 (1 H, q, *J* 7 Hz, C*H*Me), 7.57 (1 H, s, OH), 8.46 * and 8.55 * (each 3 H, s, CMe_2), and 8.96 (3 H, d, *J* 7 Hz, *Me*CH), *m/e* 212 (M^+, 3.7%), 126 (98), 87 (76), 78 (61), and 43 (100) (Found: C, 62.2; H, 7.7; S, 14.9. $C_{11}H_{16}O_2S$ requires C, 62.2; H, 7.6; S, 15.1%). The alcohol decomposed in formic and trifluoroacetic acids without producing the alkene (33).

Solvolysis Rate Determinations.—The reactions were performed in n.m.r. tubes, constant temperature being maintained (±1 °C) by a thermostatted water- or oil-bath. The approximate rate of each solvolysis was found by following either the decay of the C*H*OTs n.m.r. signal or the appearance of the olefinic proton signals, in each case with correction for a constant value of the sum of a starting material and product integral.

[6/634 *Received*, 2*nd April*, 1976]

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