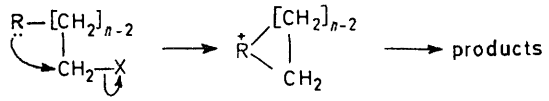
1,4-Carbonyl Participation in Solvolysis of Alkyl Toluene-*p*-sulphonates

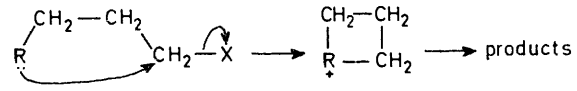
By **Philip K. G. Hodgson** and **Stuart Warren,*** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

2,2-Dimethyl-3-oxo-3-phenylpropyl toluene-*p*-sulphonate (tosylate) and some related 3-oxoalkyl tosylates are solvolysed in buffered carboxylic acid solvents by 1,4-carbonyl participation to give unrearranged carboxylate esters. The reactions are too fast to be direct displacements, and do not occur in similar compounds which lack the carbonyl group. Secondary alkyl tosylates in the same series also react by 1,4-carbonyl participation but the intermediate cation fragments, as well as reacting with solvent to give unrearranged products.

THE efficiency of neighbouring group participation [1] varies with the ring size of the cyclic intermediate (2). 1,3-Participation (1; $n = 3$) is thermodynamically unfavourable as the intermediate (2; $n = 3$) has a strained three-membered ring, but it can be so favourable kinetically that it is often observed.[2] The very common 1,5- and 1,6-participations [1] are favoured both kinetically and thermodynamically but 1,4-participation (1; $n = 4$) requires an unfavourable conformation of the reagent (3) and has a strained intermediate (4), and is therefore *un*favourable both kinetically and thermodynamically.

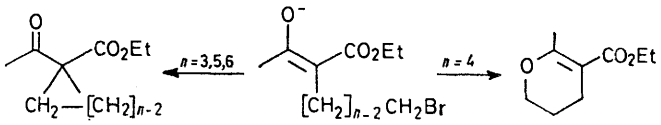


(1) (2)



(3) (4)

Thus Perkin found [3] that in the reaction of ethyl acetoacetate with dihalides in base, the three-, five-, and six-membered carbocyclic compounds (5; $n = 3$, 5, and 6) were formed easily from the enolate ions (6; $n = 3$, 5, and 6) but the enolate ion (6; $n = 4$) preferred to react by 1,6-oxygen participation rather than give a four-membered ring.



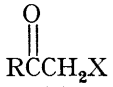
(5) (6)

Participation by the carbonyl group of esters and by carboxylate ions [1,4] is well known, but participation by the carbonyl groups of aldehydes and ketones has not been so well studied. There is no doubt that 1,5- and 1,6-participation is as efficient in these systems as in others [5] but studies on participation through the formation of smaller rings are complicated by a number of factors.

Phenacyl derivatives (7; R = Ph) are solvolysed neither by carbonyl nor by aryl participation,[6] and though there is one reaction [7] which could be interpreted in this way, it is doubtful whether 1,3-carbonyl participation will ever be observed as compounds (7) react so extremely rapidly by a direct displacement mechanism (S_N2),[8] the carbonyl group accelerating the reaction by some 10^4—10^5 over that of the corresponding alkyl halides.[9,10] Some workers [10] have reported that this

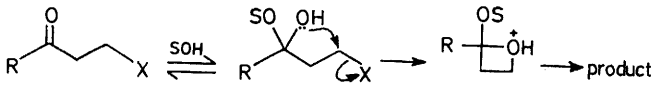
[1] A. Streitwieser, 'Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962, pp. 103—156.
[2] C. J. M. Stirling, *J. Chem. Educ.*, 1973, **95**, 844.
[3] W. H. Perkin, *J. Chem. Soc.*, 1929, 1347.
[4] B. Capon, *Quart. Rev.*, 1964, **18**, 45.
[5] G. Baddeley, E. K. Baylis, B. G. Heaton, and J. W. Rasburn, *Proc. Chem. Soc.*, 1961, 451; H. R. Ward and P. D. Sherman, *J. Amer. Chem. Soc.*, 1967, **89**, 4222; 1968, **90**, 3812; C. U. Pittman and S. P. McManus, *Chem. Comm.*, 1968, 1479; G. C. Levy and S. Winstein, *J. Amer. Chem. Soc.*, 1968, **90**, 3574; D. M. Brouwer, *Rec. Trav. chim.*, 1969, **88**, 530.
[6] D. J. Pasto, K. Garves, and M. P. Serve, *J. Org. Chem.*, 1967, **32**, 774.
[7] T. Masuike, N. Furukawa, and S. Oae, *Bull. Chem. Soc. Japan*, 1971, **44**, 448.
[8] C. A. Bunton, 'Nucleophilic Substitution at a Saturated Carbon Atom,' Elsevier, Amsterdam, 1963, p. 35.
[9] J. B. Conant, W. R. Kirner, and R. E. Hussey, *J. Amer. Chem. Soc.*, 1925, **47**, 488.
[10] F. G. Bordwell and W. T. Brannen, *J. Amer. Chem. Soc.*, 1964, **86**, 4645.

effect extends to the 3-oxo-derivatives (8), though the largest rate acceleration reported is only *ca.* 50-fold.



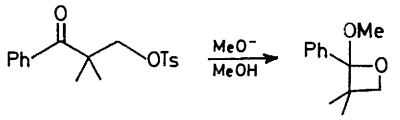
(7)

In many media, a further problem is that participation may be not by the carbonyl group itself, but by some adduct (9) such as an acetal.[11] In basic solution there is no doubt that this pathway is followed, thanks to the



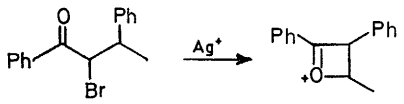
(8) (9)

extensive work of Nerdel and Weyerstahl,[12] who have even isolated [13] the intermediate (10) in one such reaction.



(10)

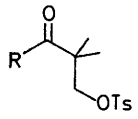
Nevertheless, it did seem likely that 1,4-carbonyl participation would eventually be observed. There are a number of published examples of 1,4-oxygen participation by alcohols,[14] alkoxides,[15] acetals,[11,16] and peroxides [17] while 1,4-carboxylate participation is actually preferred to 1,3 in some instances.[18] Intermediates [*e.g.* (11)] very similar to those required for 1,4-carbonyl participation, have been detected in the attempted formation of α-carbonyl cations from α-halogeno-ketones and silver ion.[19]



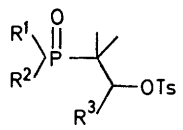
(11)

Previous attempts to detect 1,4-carbonyl participation [20,21] have used kinetic methods on β-halogeno-ketones reacting with metal ions, and have produced ambiguous results: the halogeno-ketone (8; R = Ph, X = Br) reacts [20] *slower* (×0·3) than Bu^{n}Br with mercuric ion, but the halogeno-ketone (8; R = Ph, X = Cl) reacts *faster* (×7·9) than Bu^{n}Cl with silver ion.[21] These rate factors are in any case too small to be significant. In addition, the halogeno-ketones (8) can enolise, and this would presumably accelerate the reaction.

We now describe [22] unambiguous examples of 1,4-carbonyl participation in the solvolysis of 3-oxoalkyl toluene-*p*-sulphonates (tosylates) (12)—(14) bearing *gem*-dimethyl groups to prevent enolisation. Our interest in these molecules arose from our work on the analogous phosphorus compounds (15) in which we had



(12) R = Ph
(13) R = Ar
(14) R = Me



(15)

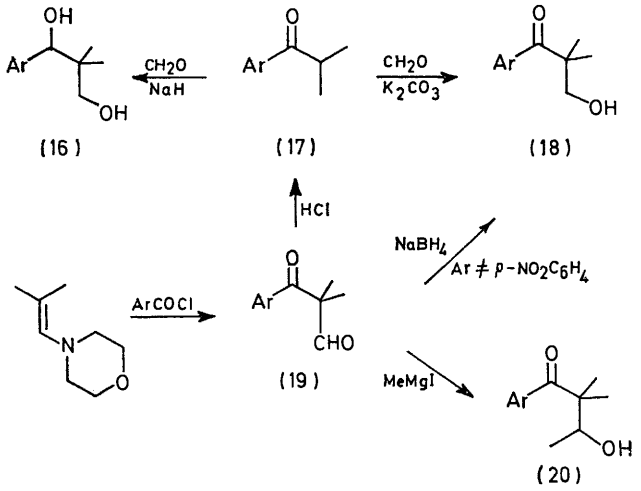
shown [23] that rearrangement occurred if R^1 = R^2 = Ph or R^1 = Ph, R^2 = Me, but that fragmentation occurred if R^1 = R^2 = OEt. We have since extended this work to other electronegative substituents [24] in place of R^{1}R^{2}PO, among which the acetyl and benzoyl compounds (12)—(14) provide so far the only examples of a third reaction pathway, 1,4-participation.

Synthesis of Hydroxy-ketones (18) *and* (20).—Addition of formaldehyde to 1-aryl-2-methylpropanones (17) under strongly basic conditions gives only the diols (16) by a Cannizzaro reaction.[25] The hydroxy-ketones (18) were prepared either by the same condensation catalysed by a weaker base [26] (K_2CO_3) or by selective reduction of the keto-aldehydes (19). These are readily available from the acylation of isobutyraldehyde enamine.[27] Both ketone and aldehyde groups are hindered in (19) but reduction, reaction with MeMgI, and acid-catalysed β-dicarbonyl cleavage [27] all occur with selective nucleophilic attack at the aldehyde group. Only when Ar = *p*-$NO_2C_6H_4$ does the keto-group become more easily reduced than the aldehyde.

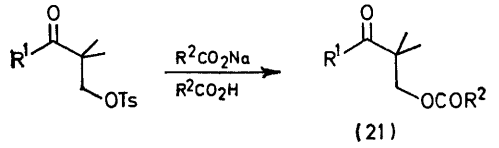
Solvolysis of Tosylates (12)—(14).—Solvolysis of the tosylates (12)—(14) in buffered acetic, formic, or trifluoroacetic acid gave as the only products the unrearranged esters (21; R^2 = Me, H, or CF_3). This is

[11] P. G. Gassman and J. L. Marshall, *Tetrahedron Letters*, 1968, 2429, 2433.
[12] K. Zabel, P. Weyerstahl, H. Marschall, and F. Nerdel, *Chem. Ber.*, 1972, **105**, 1053 gives references to earlier work.
[13] F. Nerdel, P. Wyerstahl, and K. Lucas, *Tetrahedron Letters*, 1968, 5751.
[14] S. Winstein and C. R. Lindegren, Abstracts 123rd Amer. Chem. Soc. Meeting, Los Angeles, 1953, p. 30M; H. W. Heine, A. D. Miller, W. H. Barton, and R. W. Greiner, *J. Amer. Chem. Soc.*, 1953, **75**, 4778.
[15] R. B. Clayton, H. B. Henbest, and M. Smith, *J. Chem. Soc.*, 1957, 1982; H. B. Henbest and B. B. Millward, *ibid.*, 1960, 3575; G. Schneider and I. Weisz-Vincze, *Chem. Comm.*, 1968, 1030.
[16] R. Baker and J. C. Salter, *J.C.S. Perkin II*, 1973, 150.
[17] W. H. Richardson, J. W. Peters, and W. P. Konopka, *Tetrahedron Letters*, 1966, 5531; W. H. Richardson and V. F. Hodge, *J. Amer. Chem. Soc.*, 1971, **93**, 3996.
[18] Ref. 1, p. 117; C. A. Kingsbury, *J. Org. Chem.*, 1968, **33**, 3247.
[19] D. Baudry and M. Charpentier-Morize, *Tetrahedron Letters*, 1972, 2561.
[20] S. Oae, *J. Amer. Chem. Soc.*, 1956, **78**, 4030.
[21] D. J. Pasto and M. P. Serve, *J. Amer. Chem. Soc.*, 1965, **87**, 1515.
[22] Preliminary communication, P. Hodgson and S. Warren, *J.C.S. Chem. Comm.*, 1973, 756.
[23] P. F. Cann, D. Howells, and S. Warren, *J.C.S. Perkin II*, 1972, 304; F. Allen, O. Kennard, L. Nassimbeni, R. Shepherd, and S. Warren, *ibid.*, 1974, 1530.
[24] P. Hodgson, R. Shepherd, and S. Warren, *J.C.S. Chem. Comm.*, 1974, 633.
[25] M. N. Tilichenko, *Zhur. Priklady Khim.*, 1956, **29**, 274 (*Chem. Abs.*, 1956, **50**, 13,838d).
[26] R. C. Fuson, W. E. Ross, and C. H. McKeever, *J. Amer. Chem. Soc.*, 1938, **60**, 2935.
[27] T. Inukai and R. Yoshizawa, *J. Org. Chem.*, 1967, **32**, 404.

remarkable enough since neopentyl compounds give unrearranged products only under special conditions



(good nucleophile, dipolar aprotic solvent) [28] far removed from those used here (poor nucleophile, protic solvent). Even more remarkable is that the rates of these reactions



in trifluoroacetic acid are about the same as those of the neopentyl rearrangement reactions (22; R = Me) or of the solvolysis of the rather closer models (22; R = $ArCH_2$) which give products from methyl and benzyl rearrangement and no unrearranged products at all.[29]

It is difficult to estimate accurately what the rate constant (k_s) for the direct displacement reaction of neopentyl tosylate would be under these conditions since it does not occur,[30] but by extrapolation from other solvents,[23] we estimate that k_s for neopentyl tosylate is *ca.* 10^7 smaller than k_Δ in trifluoroacetic acid, and

TABLE 1

Rates of solvolysis of tosylates $RCMe_2{\cdot}CH_2OTs$

R	k_{obs}/s^{-1} at 75° CF_3CO_2H	HCO_2H	CH_3CO_2H
MeCO (14)	$1{\cdot}1 \times 10^{-6}$	$5{\cdot}5 \times 10^{-7}$	*a*
PhCO (12)	$1{\cdot}8 \times 10^{-4}$	$4{\cdot}0 \times 10^{-5}$	$2{\cdot}1 \times 10^{-6}$
p-$MeOC_6H_4CO$	$5{\cdot}4 \times 10^{-4}$	$3{\cdot}5 \times 10^{-4}$	$1{\cdot}2 \times 10^{-5}$
p $NO_2C_6H_4CO$	$7{\cdot}6 \times 10^{-6}$	$>4 \times 10^{-3}$	$8{\cdot}2 \times 10^{-6}$
Me(k_Δ)[30]	$1{\cdot}1 \times 10^{-4}$	$1{\cdot}9 \times 10^{-5}$	$7{\cdot}7 \times 10^{-8}$
Me (k_s) [b]	$2{\cdot}3 \times 10^{-11}$	8×10^{-11}	$6{\cdot}1 \times 10^{-11}$

[a] No reaction was detected after 24 days. [b] Estimated [23] from data in ref. 30.

therefore *ca.* 10^5—10^8 smaller than the rates of our reactions (Table 1). The oxoalkyl tosylates ought to show *smaller* k_s values than neopentyl tosylate because they are more crowded and have electronegative substituents.[31] These reactions are therefore *at least*

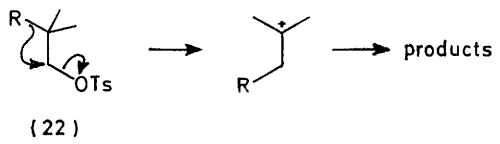


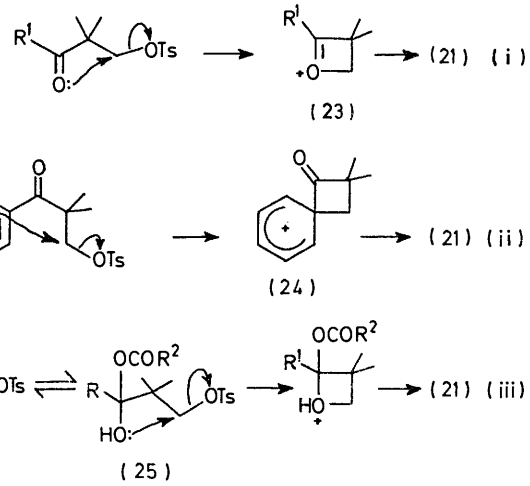
TABLE 2

Thermodynamic data for solvolysis of tosylates $RCMe_2{\cdot}CH_2OTs$ in trifluoroacetic acid

R	PhCO	*p*-MeO_6H_4CO	*p*-$NO_2C_6H_4CO$
k_{obs} (35°)/s^{-1}	$2{\cdot}6 \times 10^{-6}$	$1{\cdot}4 \times 10^{-5}$	
k_{obs} (50°)/s^{-1}	$1{\cdot}6 \times 10^{-5}$	$7{\cdot}4 \times 10^{-5}$	$4{\cdot}3 \times 10^{-7}$
k_{obs} (60°)/s^{-1}			$1{\cdot}6 \times 10^{-6}$
k_{obs} (75°)/s^{-1}	$1{\cdot}8 \times 10^{-4}$	$5{\cdot}4 \times 10^{-4}$	$7{\cdot}6 \times 10^{-6}$ [c]
$\Delta H^\ddagger$/kcal mol^{-1}	21	18	24
$\Delta S^\ddagger$/cal mol^{-1} K^{-1}	−15	−21	−13

[c] 10^5—10^8 faster than the direct displacement reaction and must occur by some form of participation.

There are three reasonable explanations of this: (i) 1,4-carbonyl participation, (ii) 1,4-aryl participation, or (iii) 1,4-oxygen participation by adduct (25). We believe that neither explanation (ii) nor (iii) can account adequately for our results in trifluoroacetic acid, but



that mechanism (iii) does occur to some extent in formic and acetic acids.

1,4-Aryl participation (ii) is unlikely on several grounds. It does not occur in systems specially designed to show it [32] and in our compounds (12) and (13), the restraints on conformation imposed by the conjugation between the carbonyl group and the aromatic ring mean that it is almost impossible for the *p* orbitals of the aromatic ring to approach the CH_2OTs group in a productive way. Finally, the ring is not very nucleophilic, again because of conjugation with the carbonyl group.

[28] B. Stephenson, G. Solladié, and H. S. Mosher, *J. Amer. Chem. Soc.*, 1972, **94**, 4184; P. H. Anderson, B. Stephenson, and H. S. Mosher, *ibid.*, 1974, **96**, 3171.

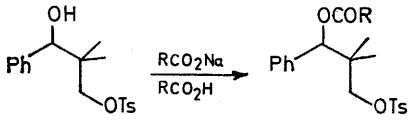
[29] J. R. Owen and W. H. Saunders, *J. Amer. Chem. Soc.*, 1966, **88**, 5809.

[30] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 1120; I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, 1969, **91**, 5635.

[31] S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 828.

[32] S. Winstein and R. F. Heck, *J. Org. Chem.*, 1972, **37**, 825.

In any case, the monotosylate (26), easily prepared from the diol (16; Ar = Ph), is solvolysed in carboxylic acids to give the esters (27). These are presumably S_N1 reactions *via* a stable secondary benzyl cation. The esters (27) do not lose tosylate under the conditions of our solvolyses for *at least four half-lives* of the oxoalkyl tosylates (12) in the same solvents. The carbonyl group is therefore essential for the participation reaction, and mechanisms which could operate equally

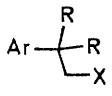


(26) (27)

well with the esters (27), such as direct displacement or aryl participation, are ruled out.

Participation by a carbonyl adduct (25) cannot be dismissed so easily. Acetals can certainly react by this mechanism,[11,16] 1,4-hydroxyl participation is known in other cases,[14] and there are none of the stereoelectronic problems associated with 1,4-carbonyl participation. Against this must be set the weak nucleophilicity of our solvents for the carbonyl group and the instability and presumably low concentrations of the adducts (25). The hydroxy-group in the monotosylate (26) does not react in this way, but this is not good evidence as it is rapidly converted into the ester (27) under the solvolysis conditions.

We must therefore turn to the effects of the *para*-substituents MeO, H, and NO_2 in the tosylates (13) to distinguish between mechanisms (i) and (iii). The acetolysis of benzyl tosylates with electron-donating substituents gives [33] a Hammett plot (against σ^+) with a ρ value of $-5{\cdot}7$. This reflects the large amount of positive charge in the transition state and means that the *p*-methoxy-compound reacts *ca.* 10^5 times faster than the unsubstituted compound. Surprisingly, in the acetolysis of compounds (28) which react by 1,3-aryl participation, ρ is much smaller,[34] being only $-2{\cdot}5$ to



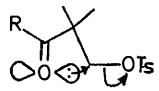
(28) R = H, Me; X = OTs, OBs

-3, giving *p*-MeO : H rate ratios of *ca.* 10^2. In 1,5- and 1,6-aryl participation,[32] this ratio drops even further to 2—3. Thus, even in reactions in which a positive charge develops on the ring itself, ρ may be small; indeed this seems to be characteristic of participation reactions.

Participation by an adduct (25) would be expected to give the reverse order of reactivities (positive ρ) for substituents in the aromatic ring. The rate-determining step itself, the participation, would show a very small dependence on substituent, but the concentration of the adduct (25), which would be small and therefore important, would be increased by electronegative substituents in the ring. In formic acid, we have a clear-cut case of this mechanism for the *p*-nitro-compound (13; Ar = *p*-$NO_2C_6H_4$) which reacts faster than either the unsubstituted compound (12) or the *p*-methoxy-compound. In acetic acid, too, the *p*-nitro-compound reacts faster than the unsubstituted compound. But the *p*-methoxy-compound reacts faster than the unsubstituted compound in both formic and acetic acids, while in trifluoroacetic acid, the solvent least able to form an adduct, the order of reactivity is clearly not compatible with adduct formation but is that expected for carbonyl participation. In any case, mechanism (iii) is ruled out by the very low reactivity of the acetyl compound (14) as it would form an adduct more easily than any of the aromatic compounds except the *p*-nitro-compound.

We suggest, therefore, that in trifluoroacetic acid, all the compounds (12)—(14) react by 1,4-carbonyl participation, and that this mechanism is also followed by compounds (13; Ar = *p*-$MeOC_6H_4$) and (14) in the other solvents while (13; Ar = *p*-$NO_2C_6H_4$) reacts by mechanism (iii) in formic and acetic acids. The unsubstituted benzoyl compound (12) may react by either mechanism (i) or (iii) in these two acids.

It would be incorrect to assign exact quantitative significance to the results in trifluoroacetic acid (whether the rates follow σ or σ^+ for example) because both methoxy- and nitro-groups form hydrogen bonds with this solvent.[35] The small dependence on substituent effects is characteristic of participation reactions and cannot be used to make deductions about the exact nature of the process. It has been suggested,[21] for example, that it is the *p*-like lone pair on the carbonyl oxygen atom which participates (29), rather than the π-bond itself. Certainly, this would remove some of the



(29)

difficulty of 1,4-participation as one of the 90° angles would already be established.

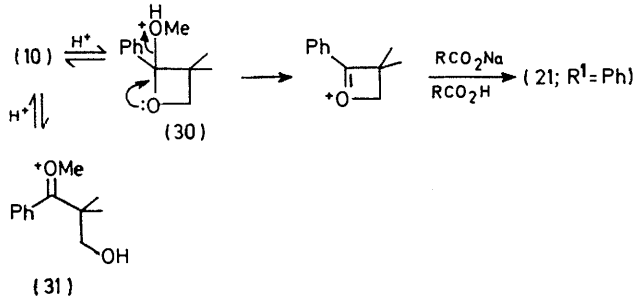
Though hydrogen bonding may make detailed quantitative comparisons invalid, it does not disturb the general quantitative analysis. All those compounds which we suggest react by 1,4-carbonyl participation are solvolysed fastest in trifluoroacetic acid, slower in formic, and slowest in acetic acid; the ionising order, and the reverse of the nucleophilicity order. This same order is found for the benzoyl compound (12) which suggests that this too reacts by the same mechanism. Only the *p*-nitro-compound shows a different order.

[33] A. Streitwieser, H. A. Hammond, R. H. Jagow, R. M. Williams, R. G. Jesaitis, C. J. Chang, and R. Wolf, *J. Amer. Chem. Soc.*, 1970, **92**, 5141.

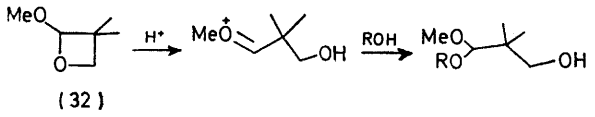
[34] J. M. Harris, F. L. Schadt, P. von R. Schleyer, and C. J. Lancelot, *J. Amer. Chem. Soc.*, 1969, **91**, 7508. For a review, see 'Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley–Interscience, New York, 1972, vol. III, p. 1370.

[35] F. L. Schadt and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 7860.

Results of Other Experiments.—The cation (30) is probably also an intermediate in the solvolysis of the oxetan acetal (10) under the same conditions. The reaction is much faster than the solvolysis of the tosylate (12) but the products are the same. Protonation and opening of the oxetan ring to give the alternative

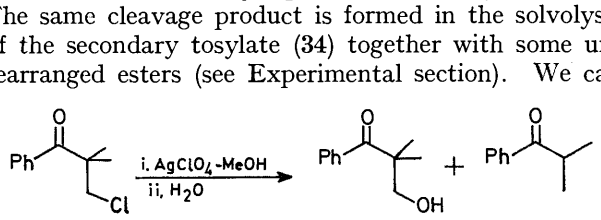


intermediate (31) are presumably reversible and so the reaction occurs by protonation and loss of the methoxy-group. It is expected that a compound closer in structure to the intermediate (30) should react faster, especially if it already contains the unstable four-membered ring. The hydrolysis of acetal (32) goes by a different mechanism.[36] Nucleophiles, such as alcohols, attack not the methylene group as in the solvolysis of acetal (10) but the carbon atom derived from the carbonyl group forming acyclic acetal products.[36] The

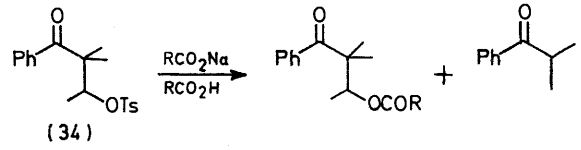


phenyl group would stabilise both intermediates (30) and (31) by conjugation but this is evidently more effective in the less stable intermediate (30) since the ester products (21) cannot be formed from intermediate (31).

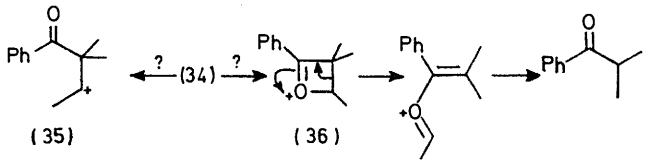
The halogeno-ketone (33), formed from tosylate (12) by direct displacement in the dipolar aprotic solvent dimethyl sulphoxide, also gives some unrearranged products on treatment with silver perchlorate in methanol, but the major product is isobutyrophenone. The same cleavage product is formed in the solvolysis of the secondary tosylate (34) together with some unrearranged esters (see Experimental section). We can



make no useful deductions about the rates of these reactions, which are much greater than those of the primary tosylate (12), in view of the uncertainty surrounding the mechanism of the solvolysis of pinacolyl compounds.[37] It is difficult to see how the cleavage



product could arise from the cation (35) but it could very easily be formed from the cyclic cation (36), the intermediate in the 1,4-carbonyl participation reaction. A similar reaction occurs [19] in the analogous cation (11). The cation (30) does not fragment this way presumably because attack of solvent is easier and the product of fragmentation would be a primary cation.



EXPERIMENTAL

I.r. spectra were taken on a Perkin-Elmer 257, n.m.r. spectra on Perkin-Elmer R12B or Varian HA 100, mass spectra on an A.E.I. MS9, and u.v. spectra on a Unicam SP 800B machine. T.l.c. was run on silica gel 60 F_{254} eluted with acetone (30%)–light petroleum (b.p. 60—80°) (70%). Petrol refers to light petroleum (b.p. 60—80°). N.m.r. peaks marked with an asterisk are diastereotopic.

2,2-Dimethyl-1-phenylpropane-1,3-diol (16).—A solution of 2-methyl-1-phenylpropanone (2 g) in anhydrous tetrahydrofuran (20 ml) was added slowly to a boiling, stirred mixture of sodium hydride [0·44 g; from 0·87 g 50% suspension in oil, washed with petrol (2 × 10 ml)] and paraformaldehyde (0·42 g) in tetrahydrofuran (15 ml). The mixture was boiled under reflux for 15 h, cooled, and poured into water. The aqueous layer was extracted with dichloromethane (3 × 50 ml) and the combined organic layers were washed with brine and dried ($MgSO_4$). Evaporation and recrystallisation from hexane gave the pale yellow diol (1·1 g, 44%), m.p. 78—79° (lit.,[25] 76—78°), R_F 0·13, $\nu_{max.}$ ($CHCl_3$) 3585 (OH) cm^{-1}, $\lambda_{max.}$ 219 nm (ε 2800), τ ($CDCl_3$) 2·78 (5H, s, Ph), 5·43 (1H, s, C*H*OH), 6·54 (2H, s, CH_2OH), 6·91br (1H, s, OH), 7·13br (1H, s, OH), 9·20 (3H, s, CMe_2*), and 9·22 (3H, s, CMe_2*).

3-Hydroxy-2,2-dimethyl-3-phenylpropyl Toluene-p-sulphonate (26).—This procedure [38] is typical of the method used to prepare the tosylates used in this work. Toluene-*p*-sulphonyl chloride (1·24 g, 0·006 mol; purified by the method of Pelletier [39]) was added in small quantities to an ice-cold solution of the diol (16) (0·54 g, 0·003 mol) in anhydrous pyridine (50 ml) in a glass-stoppered conical flask. The brown solution was kept at 0° for 24 h then poured onto crushed ice (100 g), and the resulting oil was extracted with ether (3 × 50 ml). The combined extracts were washed with dilute hydrochloric acid (2 × 100 ml) and water (2 × 100 ml) and dried (K_2CO_3–Na_2SO_4). Evaporation gave a red oil which crystallised on trituration

[36] R. F. Atkinson and T. C. Bruice, *J. Amer. Chem. Soc.*, 1974, **96**, 819.

[37] T. W. Bentley, S. H. Liggero, M. A. Imhoff, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 1970; A. Pross and R. Koren, *Tetrahedron Letters*, 1974, 1949.

[38] L. F. Fieser and M. Fieser, ' Reagents for Organic Synthesis,' Wiley, New York, 1967, p. 1180.

[39] S. W. Pelletier, *Chem. and Ind.*, 1953, 1034.

with petrol. Recrystallisation from petrol using a low temperature technique [38] gave the monotosylate (26) (0·43 g, 43%), m.p. 78—81° (lit.,[40] 82·5—83°), R_F 0·16, $\nu_{max.}$ (CCl_4) 3615 (OH) and 1190 (SO) cm^{-1}, $\lambda_{max.}$ 227 nm (ε 9700), τ (CCl_4) 2·20—2·76 (9H, m, ArH), 5·46 (1H, s, C*H*OH), 5·88 (1H, d, *J* 9·6 Hz, CH_2OTs*), 6·45 (1H, d, *J* 9·6 Hz, CH_2OTs*), 7·56 (3H, s, ArCH_3), 8·20 (1H, s, OH), 9·17 (3H, s, CMe_2*), and 9·21 (3H, s, CMe_2*).

Trifluoroacetolysis of Monotosylate (26).—This trifluoroacetolysis procedure is typical of all solvolyses used to isolate products. Sodium trifluoroacetate (102 mg, 0·78 mmol), dissolved in freshly distilled trifluoroacetic acid (10 ml) was added to the tosylate (26) (167 mg, 0·5 mmol) and the solution heated to 75°. When the reaction was complete (t.l.c.), the solution was allowed to cool and poured into ice–water (75 ml). The mixture was extracted with ether (3 × 25 ml), the combined extracts were washed with water (50 ml) and 10% sodium hydrogen carbonate solution (4 × 50 ml) and dried ($MgSO_4$). Evaporation, and recrystallisation from petrol using a low temperature technique [38] gave 2,2-*dimethyl*-3-*phenyl*-3-*trifluoroacetoxypropyl toluene*-p-*sulphonate* (27; R = CF_3) (168 mg, 79%), m.p. 113—114°, R_F 0·28, $\nu_{max.}$ (CCl_4) 1795 ($COCF_3$) and 1175 (SO) cm^{-1}, $\lambda_{max.}$ 226 nm (ε 6900), τ (CCl_4) 2·19) 2·19—2·77 (9H, m, ArH), 4·30 (1H, s, CHO_2CCF_3), 6·30 (2H, AB system, *J* 8 Hz, CH_2OTs*), 7·54 (3H, s, Ar*Me*), 9·00 (3H, s, CMe_2*), and 9·06 (3H, s, CMe_2*), *m/e* 430 (M^+, 0·1%), 227 (35), 203 (100), 155 (100), 91 (100), and 55 (33) (Found: C, 56·2; H, 5·2; F, 13·2; S, 7·5. $C_{20}H_{21}O_5F_3S$ requires C, 55·8; H, 4·9; F, 13·3; S, 7·4%).

Acetolysis of Monotosylate (26).—The solvolysis was carried out in the usual way with anhydrous sodium acetate (51 mg, 0·6 mmol), the tosylate (26) (167 mg, 0·5 mmol), and glacial acetic acid (10 ml). The product contained five compounds (t.l.c.), separated by preparative t.l.c. (1 : 4 acetone–petrol) to give starting material and the major product 3-*acetoxy*-2,2-*dimethyl*-3-*phenylpropyl toluene*-p-*sulphonate* (27; R = CH_3) as a liquid which slowly crystallised. Recrystallisation from petrol gave a white solid (39 mg, 23%), m.p. 108—109°, R_F 0·22, $\nu_{max.}$ (CCl_4) 1740 (ester C=O) and 1175 (SO) cm^{-1}, τ (CCl_4) 2·25—2·88 (9H, m, ArH), 4·51 (1H, s, C*H*OAc), 5·06 (1H, d, *J* 9·6 Hz, CH_2OTs*), 6·35 (1H, d, *J* 9·6 Hz, CH_2OTs*), 7·58 (3H, s, Ar*Me*), 8·09 (3H, s, CH_3CO), 9·09 (3H, s, CMe_2*), and 9·15 (3H, s, CMe_2*), *m/e* 321 (45%), 215 (53), 155 (100), 149 (34), 107 (35), and 85 (47) (Found: C, 63·9; H, 6·6; S, 8·4. $C_{20}H_{24}O_5S$ requires C, 63·8; H, 6·4; S, 8·5%).

3-*Hydroxy*-2,2-*dimethyl*-1-*phenylpropanone* (18; Ar = Ph).—This compound was prepared [26] as a liquid, b.p. 102·5—104° at 0·1 mmHg (lit.,[26] 152—153° at 12 mmHg), R_F 0·25, $\nu_{max.}$ (CCl_4) 3430 (OH) and 1676 (CO) cm^{-1}, $\lambda_{max.}$ 241 nm (ε 8000), τ (CCl_4) 2·17—2·70 (5H, m, Ph), 6·34 (2H, s, CH_2OH), 7·26br (1H, s, OH), and 8·64 (6H, s, Me_2). The toluene-*p*-sulphonate (12) had m.p. 69—70° (lit.,[26] 71—71·5°), R_F 0·22, $\nu_{max.}$ (CCl_4) 1678 (CO) and 1179 (SO) cm^{-1}, $\lambda_{max.}$ 228 nm (ε 25,000), τ (CCl_4) 2·2—2·8 (9H, m, Ar), 5·95 (2H, s, CH_2OTs), 7·56 (3H, s, Ar*Me*), and 8·66 (6H, s, CMe_2).

Trifluoroacetolysis of Tosylate (12).—The usual trifluoroacetolysis procedure gave 2,2-*dimethyl*-1-*phenyl*-3-*trifluoroacetoxypropanone* (21; R^1 = Ph, R^2 = CF_3) (92%) as a liquid, b.p. (bath) 60—70° at 0·001 mmHg, R_F 0·4, $\nu_{max.}$ (CCl_4) 1785 (CF_3CO_2) and 1678 (PhCO) cm^{-1}, $\lambda_{max.}$ 239 nm (ε 5500), τ (CCl_4) 2·3—2·8 (5H, m, Ph), 5·56 (2H, s, CH_2OCOCF_3), and 8·58 (6H, s, CMe_2), *m/e* 274 (M^+, 0·5%), 148 (10), 123 (27), 107 (9), 105 (100), and 77 (28) (Found: M^+, 274·0828. $C_{13}H_{13}O_3F_3$ requires *M*, 274·0817).

Formolysis of Tosylate (12).—Solvolysis of the tosylate (12) (332 mg) by the standard procedure in anhydrous formic acid (10 ml) containing sodium formate (85 mg) gave a yellow oil. Preparative t.l.c. developed in 1 : 4 acetone–petrol gave 2,2-*dimethyl*-3-*oxo*-3-*phenylpropyl formate* (21; R^1 = Ph, R^2 = H) (176 mg, 85%) as an oil, b.p. 65—70° (bath) at 0·001 mmHg, R_F 0·35, $\nu_{max.}$ (CCl_4) 1728 (HCO) and 1680 (PhCO) cm^{-1}, $\lambda_{max.}$ 239 nm (ε 7000), τ (CCl_4) 2·3—2·7 (5H, m, Ph), 2·08 (1H, s, CHO), 5·71 (2H, s, CH_2O), and 8·63 (6H, s, CMe_2), *m/e* 146 (10%), 106 (8), 105 (100), 77 (35), 51 (12), and 44 (17) (Found: C, 70·0; H, 6·9. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

Acetolysis of the Tosylate (12).—Solvolysis of the tosylate (12) (332 mg) by the standard procedure in acetic acid (10 ml) containing anhydrous sodium acetate (103 mg) gave an oil. Preparative t.l.c. developed in 1 : 4 acetone–petrol gave 3-acetoxy-2,2-dimethyl-1-phenylpropanone (21; R^1 = Ph, R^2 = CH_3) (181 mg, 82%) as an oil, b.p. 80—90° at 0·01 mmHg (lit.,[41] 155·5—156·5° at 11 mmHg), R_F 0·38, $\nu_{max.}$ (CCl_4) 1735 (MeCO) and 1678 (PhCO) cm^{-1}, $\lambda_{max.}$ 240 nm (ε 5200), τ (CCl_4) 2·3—2·7 (5H, m, Ph), 5·82 (2H, s, CH_2O), 8·06 (3H, s, MeCO), and 8·67 (6H, s, Me_2C).

3-*Chloro*-2,2-*dimethyl*-1-*phenylpropanone* (33).—The hydroxy-ketone (18; Ar = Ph) (700 mg) and thionyl chloride (15 ml) were heated under reflux for 18 h. Removal of the excess of thionyl chloride and distillation gave the chloro-ketone (33) (523 mg), b.p. 110—115° at 0·25 mmHg (lit.,[40] 100—102° at 0·1 mmHg), R_F 0·44, $\nu_{max.}$ (CCl_4) 1677 (PhCO) and 700 (CCl) cm^{-1}, $\lambda_{max.}$ 241 nm (ε 6600), τ (CCl_4) 2·3—2·7 (5H, m, Ph), 6·30 (2H, s, CH_2Cl), and 8·59 (6H, s, CMe_2).

Reaction of the Tosylate (12) *with Chloride Ion*.—The tosylate (12) (226 mg) in anhydrous dimethyl sulphoxide (7 ml) was stirred with anhydrous KCl (66 mg) for 14 h at 50°. The mixture was allowed to cool, poured into ice–water, and extracted with ether (4 × 15 ml). The extracts were washed with water (2 × 30 ml) and dried (Na_2SO_4). Evaporation of solvent and preparative t.l.c. gave the chloro-ketone (33).

Silver Ion-catalysed Solvolysis of the Chloro-ketone (33).—The chloro-ketone (33) (393 mg) and anhydrous silver perchlorate (621 mg) were heated under reflux in methanol (10 ml). After the normal aqueous work up, preparative t.l.c. gave the hydroxy-ketone (18; Ar = Ph) (76 mg) and 2-methyl-1-phenylpropanone (180 mg), R_F = 0·55.

Formolysis and Trifluoroacetolysis of 2-*Methoxy*-3,3-*dimethyl*-2-*phenyloxetan* (10).—The usual solvolysis procedure on the oxetan [42] (10) gave 2,2-dimethyl-3-oxo-3-phenylpropyl formate (21; R^1 = Ph, R^2 = H) (99%) and 2,2-dimethyl-1-phenyl-3-trifluoroacetoxypropanone (21; R^1 = Ph, R^2 = CF_3) (73%) respectively.

2,2-*Dimethyl*-3-p-*methoxyphenyl*- (19; Ar = *p*-$MeOC_6H_4$) *and* 2,2-*Dimethyl*-3-p-*nitrophenyl*-3-*oxopropanal* (19; Ar = *p*-$NO_2C_6H_4$).—These were prepared [27] by the reaction of the appropriate acid chloride with the morpholine enamine [43] of isobutyraldehyde.

[40] F. Nerdel and U. Kretzschmar, *Annalen*, 1965, **688**, 61.
[41] E. E. Blaise and I. Harman, *Ann. Chim.* (*France*), 1911, [8], **23**, 524.
[42] F. Nerdel and H. Kressin, *Annalen*, 1967, **707**, 1.
[43] E. Benzing, *Angew. Chem.*, 1959, **71**, 521.

3-*Hydroxy*-1-p-*methoxyphenyl*-2,2-*dimethylpropanone* (18; Ar = *p*-$MeOC_6H_4$).—Sodium borohydride (0·72 g) in methanol (100 ml) was added to a solution of the formyl ketone (19; Ar = *p*-$MeOC_6H_4$) (15 g) in methanol (400 ml) at 0°. After 100 min the mixture was poured into concentrated brine (100 ml) and extracted with ether (4 × 200 ml). The combined ether layers were washed with saturated sodium carbonate solution (400 ml) and water (400 ml) and dried (Na_2SO_4). Evaporation of the solvent and distillation gave the hydroxy-ketone (18; Ar = *p*-$MeOC_6H_4$) (13·5 g, 93%), b.p. 138—142° at 0·1 mmHg (lit.,[44] 156—160° at 0·3 mmHg), R_F 0·17, $\nu_{max.}$ (CCl_4) 3570 (OH) and 1660 (ArCO) cm^{-1}, $\lambda_{max.}$ 273 nm (ε 11,000), τ (CCl_4) 2·1—3·2 (4H, m, ArH), 6·16 (3H, s, OMe), 6·49 (2H, s, CH_2OH), 7·44br (1H, s, OH), and 8·63 (6H, s, CMe_2). The *toluene*-p-*sulphonate* (13; R = *p*-$MeOC_6H_4$), m.p. 72—73°, had R_F 0·26; $\nu_{max.}$ (CCl_4) 1677 (ArCO) and 1194 (SO) cm^{-1}, $\lambda_{max.}$ 224 nm (ε 17,500), τ (CCl_4) 2·3—3·3 (8H, m, ArH), τ ($CDCl_3$) 1·5—2·5 (4H, m, ArH), 5·20br (1H, s, C*H*OH), 6·41br (3H, s, CH_2OH and CHO*H*), 7·61br (1H, s, CH_2OH), and 9·13 (6H, s, CMe_2), *m/e* 225 (M^+, 0·4%), 153 (12), 136 (14), 106 (12), 56 (100), and 55 (17) (Found: C, 58·5; H, 6·5; N, 6·5. $C_{11}H_{15}NO_4$ requires C, 58·7; H, 6·7; N, 6·2%).

The major product was a yellow oil which slowly solidified after distillation to give the *hydroxy-ketone* (18; Ar = *p*-$NO_2C_6H_4$), m.p. 35—36°, $\nu_{max.}$ (CCl_4) 3623 (OH), 1677 (ArCO), and 1527 and 1352 (NO_2) cm^{-1}, $\lambda_{max.}$ 263 nm (ε 10,000), τ (CCl_4) 1·5—2·5 (4H, m, ArH), 6·40 (2H, s, CH_2O), 7·57br (1H, s, OH), and 8·73 (6H, s, CMe_2), *m/e* 223 (M^+, 1%), 150 (27), 104 (23), and 56 (100) (Found: C, 59·0; H, 5·9; N, 6·5. $C_{11}H_{13}NO_4$ requires C, 59·2; H, 5·8; N, 6·3%). The *toluene*-p-*sulphonate* (13; R = *p*-$NO_2C_6H_4$) had m.p. 118—119°, R_F 0·20, $\nu_{max.}$ ($CHCl_3$) 1693 (ArCO), 1522 and 1356 (NO_2), and 1176 (SO) cm^{-1}, $\lambda_{max.}$ 265 nm (ε 13,300), τ ($CDCl_3$) 1·5—2·7 (8H, m, ArH),

TABLE 3

Characterisation of carboxylic esters (21) *p*-$XC_6H_4CO{\cdot}CMe_2{\cdot}CH_2O{\cdot}COR^2$

			ν (cm⁻¹)			τ Values					λmax.				Found (%)			Required (%)		
X	R^2	M.p. (°C)	Ester	Ketone	Other	ArH	R^2	CH_2	CMe_2	Other	(nm)	ε	R_F	M^+ (%)	C	H	N	C	H	N
H	CF_3	Liq.	1785	1678		2·3—2·8		5·56	8·58		239	5500	0·40	274 (0·5)	*M*+ 274·0828 [a]			*M* 274·0817 [a]		
H	H	Liq.	1728	1680		2·3—2·7	2·08	5·71	8·63		239	7000	0·35		70·0	6·9		69·6	6·8	
H	CH_3	Liq.	1735	1678		2·3—2·7	8·06	5·82	8·67		240	5200	0·38		[b]			[b]		
OMe	CF_3	Liq.	1792	1676		2·0—3·5		5·53	8·54	6·15 [c]	272	11,800	0·40	304 (20)	*M*+ 304·0927 [a]			*M* 304·0921 [a]		
OMe	H	Liq.	1734	1677		2·0—3·5	2·03	5·67	8·61	6·17 [c]	271	12,100	0·35	236 (2)	66·0	6·6		66·1	6·8	
OMe	CH_3	53—56	1748	1675		2·0—3·5	8·07	5·82	8·67	6·23 [c]	270	11,300	0·31	250 (2)	67·0	7·0		67·2	7·2	
NO_2	CF_3	Liq.	1797	1694	1528 [d] 1354	1·5—2·5		5·54	8·59		261	11,100	0·32	319 (9)	*M*+ 319·0682 [a]			*M* 319·0666 [a]		
NO_2	H	Liq.	1737	1693	1527 [d] 1352	1·5—2·5	2·04	5·72	8·63		261	11,600	0·25		57·5	5·4	5·3	57·4	5·2	5·6
NO_2	CH_3	67—68	1756	1693	1524 [d] 1352	1·5—2·5	7·96	5·75	8·64		262	11,300	0·34	265 (1)	58·6	5·6	5·1	58·9	5·7	5·3

[a] High resolution mass spectrum. [b] Known compound.[43] [c] 3H, s, ArO*Me*. [d] NO_2 sym. and antisym. stretch.

5·98 (2H, s, CH_2OTs), 6·21 (3H, s, OMe), 7·58 (3H, s, Ar*Me*), and 8·64 (6H, s, CMe_2), *m/e* 362 (M^+, 2%), 136 (48), 135 (100), 92 (33), 91 (48), and 83 (35) (Found: C, 62·7; H, 6·2; S, 8·7. $C_{19}H_{22}O_4S$ requires C, 63·0; H, 6·1; S, 8·8%).

Borohydride Reduction of 2,2-*Dimethyl*-3-p-*nitrophenyl*-3-*oxopropanal* (19; Ar = *p*-$NO_2C_6H_4$).—The same procedure on the nitro-compound (180 mg) gave 2,2-dimethyl-3-hydroxy-3-*p*-nitrophenylpropanal (35 mg, 19%) and 2,2-dimethyl-3-*p*-nitrophenylpropane-1,3-diol (26 mg, 14%).

3-*Hydroxy*-2,2-*dimethyl*-1-p-*nitrophenylpropanone* (18; Ar = *p*-$NO_2C_6H_4$) *and* 2,2-*Dimethyl*-1-p-*nitrophenylpropane*-1,3-*diol* (16; Ar = *p*-$NO_2C_6H_4$).—2-Methyl-2-*p*-nitrophenylpropanone (6·2 g) (from the acid-catalysed deformylation of 2,2-dimethyl-3-*p*-nitrophenyl-3-oxopropanal),[27] potassium carbonate (0·47 g), and paraformaldehyde (1·1 g) were stirred in methanol for 5 days. The yellow solution was poured into water (200 ml), acidified with 50% hydrochloric acid, and extracted with benzene (4 × 30 ml). The combined extracts were washed with water (150 ml) and dried ($MgSO_4$). Evaporation of the benzene and column chromatography on silica gel using 9 : 1 petrol–ethyl acetate as eluant gave starting material, R_F 0·45 (1·9 g), a major product, R_F 0·25, and a minor product, R_F 0·18.

The minor product was recrystallised from carbon tetrachloride to give white needles (0·68 g) of the *diol* (16; Ar = *p*-$NO_2C_6H_4$), m.p. 96—98°, $\nu_{max.}$ ($CHCl_3$) 3595 (OH) and 1513 and 1357 (NO_2) cm^{-1}, $\lambda_{max.}$ 276 nm (ε 9900),

[44] T. I. Temnikova and N. A. Oshueva, *Zhur. obshchei Khim.*, 1963, **33**, 1403 (*Chem. Abs.*, 1963, **59**, 11,314).

5·88 (2H, s, CH_2OTs), 7·54 (3H, s, Ar*Me*), and 8·66 (6H, s, CMe_2), *m/e* 377 (M^+, 2%), 155 (72), 150 (100), 91 (47), and 56 (65) (Found: C, 57·1; H, 5·2; N, 3·6; S, 8·6. $C_{18}H_{19}NO_6S$ requires C, 57·3; H, 5·0; N, 3·7; S, 8·5%).

Solvolyses of the p-*Methoxy- and* p-*Nitro-compounds* (13; R = *p*-$MeOC_6H_4$ *and* *p*-$NO_2C_6H_4$).—These tosylates were solvolysed in the usual way, the products being in each case the corresponding carboxylic esters. Data for the products are given in Table 3 alongside those for the unsubstituted compounds.

Ethyl 2,2-*Dimethyl*-3-*oxobutanoate*.—Redistilled ethyl acetoacetate (64 g) in sodium-dried ether (250 ml) was added slowly to an efficiently stirred suspension of sodium hydride (13 g; from 23 g of a 60% suspension in oil, washed with petrol) in ether (1 l). The mixture was heated under reflux and methyl iodide (78 g) added dropwise. After 2·5 h under reflux, the mixture was allowed to cool to room temperature, and methyl iodide (78 g) was slowly added. The mixture was again heated under reflux while a slurry of sodium hydride (13 g; as before) in ether (200 ml) was added in small portions. After a further 3 h under reflux, the mixture was cooled, water (500 ml) and ether (500 ml) were added, and the layers separated. The aqueous layer was extracted with ether (2 × 250 ml), and the combined ether layers were washed with water (500 ml) and dried ($MgSO_4$). Removal of solvent and distillation gave the dimethylated ester (55 g, 70%), b.p. 75—77° at 16 mmHg (lit.,[45] 72—73° at 14 mmHg), R_F 0·50, $\nu_{max.}$ (CCl_4)

[45] K. Folkers and H. Adkins, *J. Amer. Chem. Soc.*, 1931, **53**, 1416.

1745 (ester CO) and 1720 (ketone CO) cm^{-1}, τ (CCl_4) 5·86 (2H, q, *J* 7·2 Hz, OCH_2Me), 7·94 (3H, s, MeCO), 8·71 (6H, s, CMe_2), and 8·74 (3H, t, *J* 7·2 Hz, OCH_2Me).

2-(1-*Ethoxycarbonyl*-1-*methylethyl*)-2-*methyl*-1,3-*dioxolan*. —The above ester (31·6 g), ethylene glycol (15 g), toluene-*p*-sulphonic acid (60 mg), and benzene (50 ml) were heated under reflux in a Dean–Stark apparatus.[46] After 6 h, water (4·8 ml) had been collected, and the solution was allowed to cool. Ether (200 ml) was added and the ethereal solution was washed with water (2 × 100 ml) and saturated sodium hydrogen carbonate solution (100 ml), and dried (Na_2SO_4). Evaporation and distillation gave the dioxolan ester (32 g, 70%), b.p. 109—110° at 16 mmHg (lit.,[47] 110° at 17 mmHg), R_F 0·49, $\nu_{max.}$ (CCl_4) 1728 (ester C=O), τ (CCl_4) 5·96 (2H, q, *J* 9·6 Hz, OCH_2Me), 6·14 (4H, s, OCH_2CH_2O), 8·77 (3H, t, *J* 9·6 Hz, OCH_2Me), 8·73 (3H, s, CMe), and 8·84 (6H, s, CMe_2).

2-(1,1-*Dimethyl*-2-*hydroxyethyl*)-2-*methyl*-1,3-*dioxolan*.— The dioxolan ester (22·8 g) in ether (100 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (3·8 g) in ether (100 ml) at such a rate that the ether gently boiled (2 h). The mixture was stirred for a further 2 h, water (20 ml) was added dropwise, and the mixture was filtered through a sinter. The precipitate was washed thoroughly with ether. The filtrate and washings were washed with water (250 ml) and dried (Na_2SO_4). Evaporation and distillation gave the dioxolan alcohol (11·8 g, 74%), b.p. 106—108° at 17 mmHg (lit.,[48] 100—102° at 5—6 mmHg), R_F 0·29, $\nu_{max.}$ (CCl_4) 3530 (OH), τ (CCl_4) 6·10 (4H, s, OCH_2CH_2O), 6·66 (2H, s, CH_2OH), 7·20br (1H, s, OH), 8·79 (3H, s, CMe), and 9·07 (6H, s,CMe_2).

4-*Hydroxy*-3,3-*dimethylbutan*-2-*one*.—The dioxolan alcohol (8 g), methanol (20 ml), water (10 ml), and concentrated hydrochloric acid (0·25 ml) were boiled under reflux for 3 h. The solvents were removed by distillation, and the residue dissolved in ether (100 ml). The solution was washed with sodium hydrogen carbonate solution (2 × 100 ml) and dried (Na_2SO_4). Evaporation and distillation gave the hydroxy-ketone (2·4 g, 41%), b.p. 91—92° at 24 mmHg (lit.,[49] 85° at 15 mmHg), R_F 0·20. The toluene-*p*-sulphonate (14) had m.p. 52—53·5° (lit.,[50] 54·5—55·5°), R_F 0·26. Both compounds had i.r. and n.m.r. spectra identical with those reported.[50]

Trifluoroacetolysis of the Tosylate (14).—The usual trifluoroacetolysis procedure gave a yellow oil which, after preparative t.l.c. and distillation gave colourless 3,3-dimethyl-4-trifluoroacetoxybutan-2-one (50%), b.p. 30—40° at 0·01 mmHg (lit.,[50] 28—30° at 0·01 mmHg), R_F 0·33, identified by its i.r. and n.m.r. spectra.[50]

3-*Hydroxy*-2,2-*dimethyl*-1-*phenylbutanone* (20; Ar = Ph). —A solution of methylmagnesium iodide, from magnesium (0·97 g) and methyl iodide (5·68 g), in anhydrous ether (100 ml) was transferred [51] through a glass wool filter into a solution of 2,2-dimethyl-3-phenyl-3-oxopropanal [27] (19; Ar = Ph) (7·04 g) in anhydrous ether (200 ml) at −5°. The mixture was allowed to warm to room temperature, stirred for 19 h, and poured onto crushed ice (300 g). The salts were dissolved in the minimum amount of 15% sulphuric acid, and the ether layer was separated. The aqueous layer was washed with ether (4 × 100 ml) and the combined ether extracts were washed with water (250 ml) and dried (Na_2SO_4 and K_2CO_3). The solvent was evaporated off, and the residual oil chromatographed on a column of 100—200 mesh silica (200 g) eluted with 80% petrol–20% ether. The main impurities were fast running and the major component after evaporation of solvent and distillation was the *hydroxy-ketone* (20; Ar = Ph) (3·9 g, 64%), b.p. 104—104·5° at 0·01 mmHg, R_F 0·29, $\nu_{max.}$ (CCl_4) 3490 (OH) and 1667 (CO) cm^{-1}, $\lambda_{max.}$ (EtOH) 238 nm (ε 8900), τ (CCl_4) 2·32—2·72 (5H, m, Ph), 5·99 (1H, q, *J* 6·0 Hz, MeC*H*OH), 7·53br (1H, s, OH), 8·72 (3H, s, CMe_2*), 8·74 (3H, s, CMe_2*), and 8·88 (3H, d, *J* 6·0 Hz, *Me*CH), *m/e* 192 (M^+, 0·1%), 148 (16), 105 (100), and 77 (31) (Found: C, 75·2; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%).

1,2,2-*Trimethyl*-3-*oxo*-3-*phenylpropyl Toluene*-p-*sulphonate* (34).—The hydroxy-ketone (20; Ar = Ph) (0·77 g) in anhydrous pyridine (40 ml) was cooled to 0° and tosyl chloride (1·66 g) added with stirring. The mixture was allowed to warm and was kept at room temperature for 3 days. The solution was worked up as usual to give the *toluene*-p-*sulphonate* (34) (0·62 g, 41%) as an oil which was crystallised from petrol at low temperature but melted below room temperature. It had R_F 0·33, $\nu_{max.}$ (CCl_4) 1678 (CO), 1192, and 1181 (SO) cm^{-1}, $\lambda_{max.}$

TABLE 4

Products of the solvolysis of the secondary tosylate (34)

$$PhC(:O)\cdot CMe_2\cdot CH(OTs)Me \xrightarrow[RCO_2H]{RCO_2Na} PhC(:O)\cdot CMe_2H + PhC(:O)\cdot CMe_2\cdot CH(OH)Me + PhC(:O)\cdot CMe_2\cdot CH(O_2CR)Me$$

(34) A B C

Characterisation of products C

R	Yield (%) A	B	C	ν (cm^{-1}) Ester	Ketone	Other	$\lambda_{max.}$ (nm)	ε	τ Values Ar	MeC*H*	*Me*CH	CMe_2 [a]	R	R_F	Found (%) C	H	Reqd. (%) C	H
										(*J*/Hz)	(*J*/Hz)							
CF_3	70		30	1791	1683	1227 [b] 1178			2·3—1·7	4·37 (6·6)	8·70 (6·6)	8·65 8·67		0·57				
H	30		70	1732	1682		240	8800	2·3—2·7	4·42 (6·0)	8·80 (6·0)	8·66 8·71	2·11	0·41	69·7	7·1	70·9	7·3
CH_3	24	32	44	1741	1679		239	5200	2·35—2·8	4·61 (6·0)	8·87 (6·0)	8·72 8·74	8·10	0·43	71·5	7·6	71·8	7·7

[a] Diastereotopic. [b] CF stretch.

[46] Method of E. Buchta and G. Wolfrum, *Annalen*, 1953, **580**, 132.

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[51] Method of N. L. Drake and G. B. Cooke, *Org. Synth.*, Coll Vol. II, 1943, p. 406.

(EtOH) 228 nm (ε 17,000), τ (CCl_4) 2·26—2·87 (9H, m, ArH), 4·86 (1H, q, *J* 6·0 Hz, MeC*H*OTs), 7·59 (3H, s, Ar*Me*), 8·71 (3H, s, CMe_2*), 8·76 (3H, s, CMe_2*), and 8·83 (3H, d, *J* 6·0 Hz, *Me*CH), *m/e* 105 (100%) and 70 (31) (Found: C, 65·9; H, 6·4; S, 9·5. $C_{19}H_{22}O_4S$ requires C, 65·9; H, 6·4; S, 8·3%).

Solvolysis of the Secondary Tosylate (34).—This compound was solvolysed in the usual way. The products are described in Table 4.

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