Solvolysis of *exo*- and *endo*-5,6-(*o*-Phenylene)- and -(1,8-naphthylene)-2-norbornyl Toluene-*p*-sulphonates

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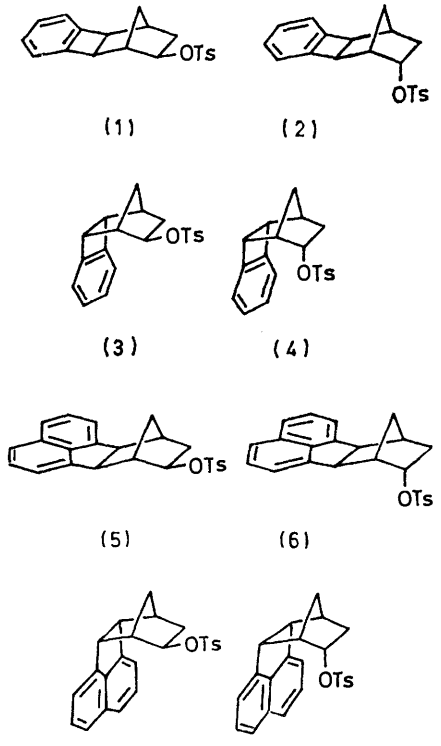
The rates and products of solvolysis of the toluene-*p*-sulphonates (1)—(8) in acetic acid and formic acid are reported and the nature of the solvolysis intermediates is discussed. A small amount of carbon–carbon bond participation cannot be excluded in the ionisation process in the solvolysis of compound (3), and 95% of the product is formed by migration of the C(1)–C(6) bond. Although a similar rearrangement occurs in the solvolysis of compound (7), no anchimeric assistance is observed in the ionisation, and the rate of solvolysis is determined by steric factors. The possibility of ion-pair return has been investigated in these reactions by comparison of rates of solvolysis with that of 1,2,2-trimethylpropyl *p*-bromobenzenesulphonate, which confirms the absence of carbon–carbon participation in the ionisation process of all but compound (3). Substantial steric inhibition to ionisation is found in the solvolysis of compounds (4) and (8) and the data are compared with those for other systems.

We have previously reported studies on the solvolyses of *exo*-5,6-*o*-arylene-2-norbornyl toluene-*p*-sulphonates.[1,2] Although these studies were initiated to obtain specific information on the behaviour of classical secondary carbonium ions in bicyclo[2,2,1] systems, the results were best explained in terms of weak carbon–carbon bond participation which, in acetic acid, did not affect the rate of solvolysis but did play some part in the control of product formation.[3] We now report rates and products of solvolysis of the toluene-*p*-sulphonates (1)—(8) in acetic and formic acids and discuss the factors



which determine their reactivity; these include both steric acceleration [4] and steric inhibition to ionisation.[5]

RESULTS AND DISCUSSION

Rate and products of solvolysis in acetic acid and formic acid were studied (Tables 1 and 2, Scheme 1).

TABLE 1

Solvolysis of toluene-*p*-sulphonates in acetic and in formic acid

Acetic acid	10^7k/s^{-1}		$\Delta H^{\ddagger}$/	$\Delta S^{\ddagger}$/cal
Substrate	75° [a]	100° [a]	kcal mol^{-1}	mol^{-1} K^{-1}
(1)	79·5	1429	29·1	+1·5
(2)	45·8	683	27·1	−5·2
(3)	2675 [b]			
(4)	1·2	25·0	30·6	−2·5
(5)	66·5	1250	29·5	+2·4
(6)	34·3	517	27·3	−5·5
(7)	385 [b]			
(8)		9·41		
exo-Norbornyl [b]	51,900		21·6	−7·2
endo-Norbornyl [b]	509	6330	25·8	−2·5

Formic acid	10^7k/s^{-1}			$\Delta H^{\ddagger}$/	$\Delta S^{\ddagger}$/cal
Substrate	25° [a]	50° [a]	75° [a]	kcal mol^{-1}	mol^{-1} K^{-1}
(1)	257	6700		24·3	+2·0
(2)	18·7	585		25·7	+1·6
(3)	6200 [b]				
(4)		25·7	641	28·1	+2·8
(5)	124	3787		25·5	+4·4
(6)	13·95	465		26·2	+1·5
(7)	440 [b]				
(8)		9·13	218·5	27·7	−0·5
endo-Norbornyl	246				

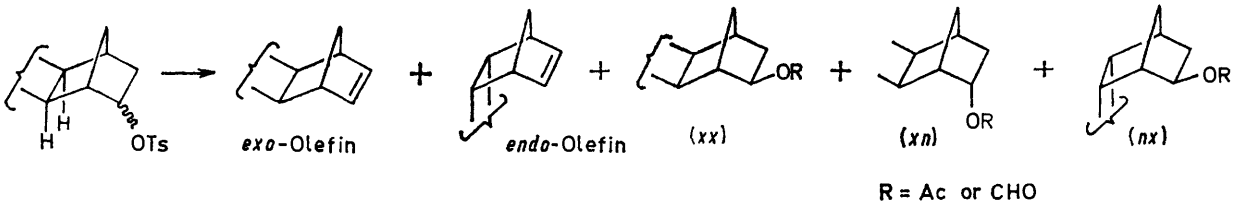
[a] Rates quoted as mean of two runs (error ±2%). [b] Mean of two runs (error ±4%).

The low *exo* : *endo* rate ratio for both pairs (1) and (2) and (5) and (6) confirms the important difference between the solvolysis of these systems and that of 2-norbornyl toluene-*p*-sulphonates.[6] Introduction of the 5,6-substituents as in compounds (1) and (5) also produces a large decrease in rate compared to that for *exo*-norbornyl toluene-*p*-sulphonate which is too large

[1] R. Baker and T. J. Mason, *J. Chem. Soc.* (*B*), 1971, 1144.
[2] R. Baker and J. Hudec, *Chem. Comm.*, 1967, 929.
[3] J. A. Bone and M. C. Whiting, *Chem. Comm.*, 1970, 115.
[4] H. C. Brown and R. S. Fletcher, *J. Amer. Chem. Soc.*, 1949, **71**, 1845; 1950, **72**, 1223; F. Brown, T. D. Davies, I. Dostrovsky, O. J. Evans, and E. D. Hughes, *Nature*, 1951, **167**, 987; P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, 1955, **77**, 2806.
[5] H. C. Brown, 'The Transition State,' *Chem. Soc. Special Publ.*, No. 6, 1962; H. C. Brown, *Chem. in Britain*, 1966, **2**, 199; H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Nat. Acad. Sci., U.S.A.*, 1966, **56**, 1653; H. C. Brown and W. J. Hammar, *J. Amer. Chem. Soc.*, 1967, **89**, 6378; H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *ibid.*, p. 6381; H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *ibid.*, 1967, **89**, 6380; H. C. Brown and D. L. Vander Jagt, *ibid.*, 1969, **91**, 6850.
[6] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, 1965, **87**, 375.

to be the result of the electron-withdrawing property of the benzene or naphthalene ring. A measure of this effect can be obtained by a comparison of the solvolysis rate of compounds (2) and (6) with that of *endo*-norbornyl toluene-*p*-sulphonate, giving factors of 14·8 and 11·1 at 75°, respectively. Consideration of the electron-withdrawing effect for compounds (1) and (5) still leaves a substantial difference between their rates of solvolysis and that of *exo*-norbornyl toluene-*p*-sulphonate, which is indicative of intermediates with different characteristics to that of the non-classical ion formed in solvolysis of the latter.[7]

The small increase in *exo* : *endo* rate ratio for the pair (1) and (2) with change in solvent from acetic to formic acid and the nature of the products of solvolysis have been previously explained in terms of weak carbon–carbon bond participation in the solvolysis of compound (1), which although not affecting the rate of solvolysis in acetic acid, does largely control product formation.[1] The changes in *exo* : *endo* rate ratio on changing the medium to formic acid were interpreted as resulting from an increase in the importance of carbon–carbon bond participation so that a k_Δ process [8] becomes more important in the solvolysis. These same conclusions also apply to the solvolysis of compound (5). Similarly, conclusions regarding the importance of a k_s process and absence of a k_Δ component in the solvolysis of compound (2), which does, however, lead to some rearranged product, also apply to the solvolysis of compound (6).[1] Scheme 2 summarises the most likely pathway for product formation in the solvolysis of compounds (1) and (5).



SCHEME 1 The terms (*xx*) *etc.* refer to the stereochemistry of the 5,6-substituent and the 2-substituent, in that order

TABLE 2

Products from solvolysis of toluene-*p*-sulphonates

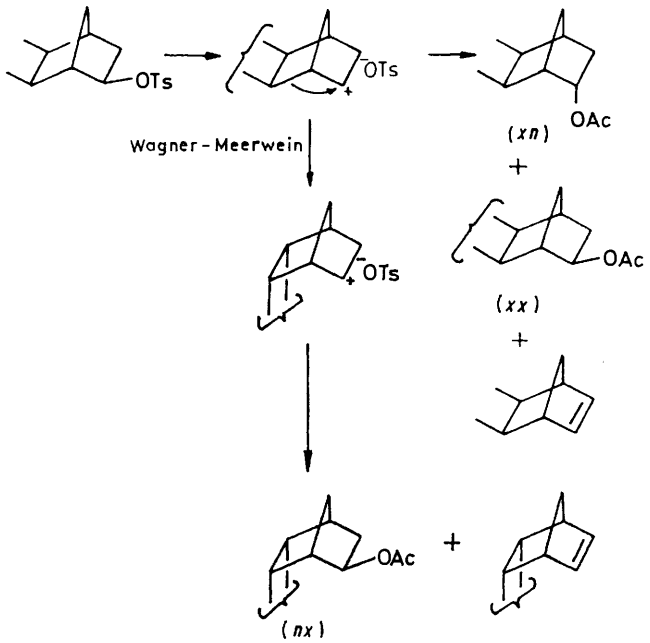
Acetic acid

	Products				
	Olefins		Acetates		
Substrate	*exo* *	*endo* *	*xx* *	*xn* *	*nx* *
(1)	8·5		87·5	<2·0	2·0
(2)	<1·0		98·0		1·0
(3)	6·3		86·7	<4·0	3·05
(4)	2·2	0·6	81·2		16·0
(5)	15·2	2·4	75·0	3·7	3·7
(6)	2·65		94·3	1·2	1·9
(7)	10·9	3·7	72·7	7·0	5·7
(8)	3·5	2·5	57·3	1·9	34·8

Formic acid

	Olefins	Formates	
Substrate	*exo* * + *endo* *	*xx* *	*nx* *
(1)	1·3	97·2	1·5
(2)		99·3	0·7
(3)	1·25	97·2	1·5
(4)		95·6	4·4
(5)	0·05	94·1	5·8
(6)		96·4	3·6
(7)		93·3	6·7
(8)		83·5	16·5

* See Scheme 1 for terminology.



SCHEME 2

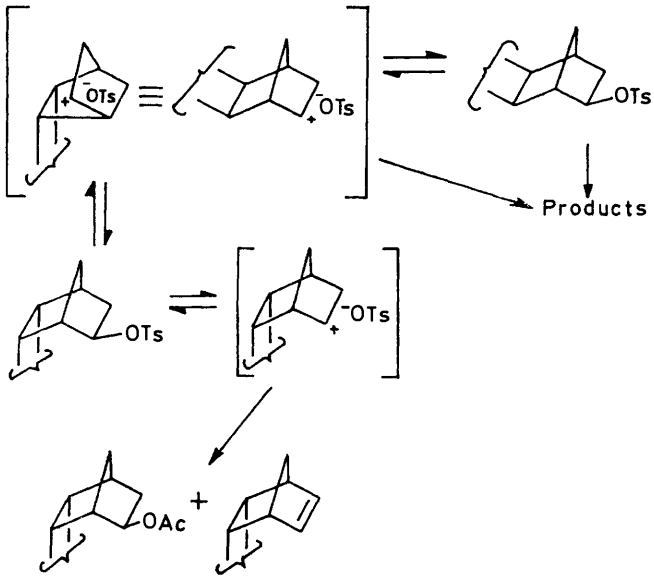
The predominant product, in both cases, is that with *exo*,*exo*-configuration (*xx*) indicating some control of product formation by the C(1)–C(6) bond. Only minor amounts of *exo*,*endo*- (*xn*) product are found, which is a consequence of both neighbouring carbon–carbon bond participation and solvent access being more difficult from the *endo*-side of the norbornyl systems. Small amounts of rearranged product (*nx*) are also formed, resulting from a Wagner–Meerwein rearrangement of the initially formed carbonium ion.

The situation in the solvolysis of compounds (3) and (7) is more complex. In both cases the products consist

[7] G. D. Sargent, *Quart. Rev.*, 1966, **20**, 301; B. Capon, *ibid.*, 1964, **18**, 45.

[8] C. J. Lancelot and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1969, **91**, 4291; C. J. Lancelot, J. J. Harper, and P. von R. Schleyer, *ibid.*, p. 4294; C. J. Lancelot and P. von R. Schleyer, *ibid.*, p. 4297.

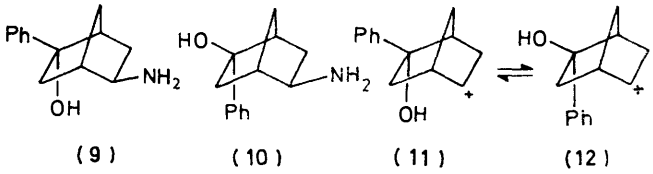
mainly of (*xx*)-acetate (or formate). Complex kinetics were found in the acetolysis of compound (3) in that the titrimetric rate constant decreased over the first 15—20% of the reaction to the rate observed for compound (1). Clearly the solvolysis involved a C(1)–C(6) Wagner–Meerwein shift which, by ion-pair return, gave the derivatives (1) and (6). The reaction subsequently observed was the solvolysis of these compounds. It was evident that the initial rate constant of 305×10^{-7} s^{-1} found for the solvolysis of compound (3) was only a minimum value for the ionisation. A better estimate of this rate constant was obtained from measurements of the rates of isomerisation in acetic and formic acids by following the rates of change in the intensity of the n.m.r. signals associated with the benzylic protons H-5 and H-6 during their rearrangement from *exo*- to *endo*-configuration. Again, the isomerisation rates (added to the solvolysis rates) can only be a minimum measure of the true ionisation rates since the initially formed ion-pair could collapse to unrearranged starting material as well as rearranged toluene-*p*-sulphonate. Taking the isomerisation rate as a measure of ionisation, compound (3) is 34 times more reactive than compound (1) in acetic acid at 75° and 24 times more reactive in formic acid at 25°. In contrast, again by considering



SCHEME 3

isomerisation rates, compound (7) appears to only be 6 times more reactive than compound (5) in acetic acid at 75° and 3·5 times more reactive in formic acid at 25°. Clearly the higher reactivity of compound (7) compared to (5) is caused by the decrease in non-bonded interaction between the *endo*-2-H and the *endo*-5,6-substituents on going from the ground state into the transition state. The greater reactivity of compound (3) compared to (1) may also be explained by this same effect and the larger differences may be explained by small distortions in the bicyclo[2,2,1] skeleton due to the 5,6-substituents,[9] but this question will be discussed again in the section on ion-pair return.

The products of solvolysis of both compounds (3) and (7) are predominantly rearranged (Table 2), and can be accounted for by Scheme 3. The relatively large amount of the *exo*-5,6-naphthylene-*endo*-acetate obtained in the acetolysis of compound (7) confirms the classical nature of the resulting carbonium ion formed as a result of Wagner–Meerwein shift of the C(1)–C(6) bond. It has, in fact, already been reported [10] that the interconversion of classical ions can take place in deaminations of the substituted norbornylamines (9) and (10) in acetic acid without the intervention of a



(9) (10) (11) (12)

degenerate non-classical ion, although the reaction differs from solvolysis in that the decomposition of the diazonium acetates produces an acetate counter-ion in close proximity to the norbornyl cation. Deaminations of compounds (9) and (10) produce initially the carbonium ions (11) and (12), respectively, which may then interconvert by C(1)–C(6) shift. In the solvolysis of the present series of compounds, although a small amount of carbon–carbon bond participation cannot be excluded, the carbonium ion formed on rearrangement must be classical in character (from the observation of *endo*-acetate product).

Ion-pair Return.—It is instructive to consider the question of ion-pair return for the reactions in acetic acid. Shiner compared the solvolysis rates of several secondary *p*-bromobenzenesulphonates with that of 1,2,2-trimethylpropyl *p*-bromobenzenesulphonate.[11] It was postulated that rate ratios higher than 0·1 indicated the dominance of some accelerating effect on ionisation, *e.g.* relief of steric strain, nucleophilic solvent attack, or neighbouring-group participation. Significant amongst these ratios was the value of 128 for *exo*-norbornyl *p*-bromobenzenesulphonate in acetic acid, which clearly indicated that for this substrate some large rate accelerating effect was in operation. If a factor of 3·46 is introduced to reflect more nearly the true ionisation rate,[12] the rate ratio becomes 440. This treatment of kinetic results was applied to a series of the toluene-*p*-sulphonates (Table 3); allowances were made for the inductive effects of the aromatic 5,6-substituents. The rate ratios obtained for the *exo*-5,6-substituent derivatives clearly illustrate (*a*) the absence of any significant acceleration to ionisation

[9] R. Baker and T. J. Mason, *J. Chem. Soc.* (*B*), 1971, 988.
[10] C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, 1970, **92**, 3182.
[11] V. J. Shiner, R. D. Fischer, and W. Dowd, *J. Amer. Chem. Soc.*, 1969, **91**, 7748.
[12] S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, 1952, **74**, 1152.

in the solvolysis of compounds (1) and (5) in acetic acid, and (*b*) the increase in the solvolysis rate ratios of these isomers on changing from acetic to formic acid compared with the corresponding rate ratio decrease for compounds (2) and (6). The conclusion from these observations must be that the change from acetic to formic acid results in a faster dissociation of ion-pairs from the *exo*-toluene-*p*-sulphonates in the less nucleophilic, more ionising solvent.

TABLE 3

Solvolysis rates of toluene-*p*-sulphonates [a] relative to that of 1,1,2-trimethylpropyl toluene-*p*-sulphonate [b,d,e]

Substrate	Solvent: Acetic acid at 75°	Solvent: Formic acid at 25°
(1)	0·69	1·40
(2)	0·40	0·10
(5)	0·77	0·91
(6)	0·40	0·10
(3)	23·20	33·80
(7)	4·45	3·22
exo-Norbornyl	140·0 [6,12]	
endo-Norbornyl	0·40 [6]	0·10 [d]
Cyclopentyl	4·25 [f]	3·10 [f]

[a] Allowing for inductive factors for the 5,6-*o*-phenylene and 5,6-(1,8-naphthalene) derivatives of 11·1 and 14·8, and 13·1 and 17·6 in acetic acid and formic acid, respectively. [b] Rates of solvolysis of 1,2,2-trimethylpropyl toluene-*p*-sulphonate, $12{\cdot}8 \times 10^{-5}$ s^{-1} in acetic acid at 75° and $2{\cdot}4 \times 10^{-4}$ s^{-1} in formic acid at 25°. [c] Calculated on the basis that the rate of solvolysis of toluene-*p*-sulphonate is 0·35 times that of rate of solvolysis of *p*-bromobenzenesulphonate. [d] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*. 1952, **74**, 1120. [e] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1956, **78**, 2780. [f] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 1127.

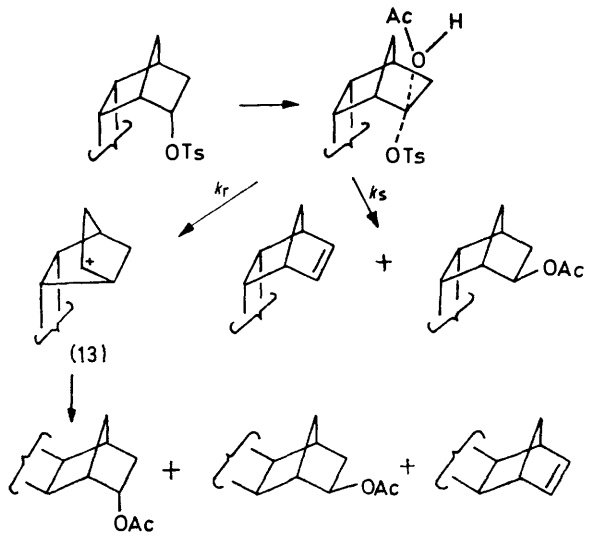
The rate ratios for compound (7) both in acetic and in formic acid are closely similar to the rate ratios for cyclopentyl toluene-*p*-sulphonate, so that it is unnecessary to invoke anchimeric assistance by the C(1)–C(6) bond to explain the ratios of 4·45 and 3·22 for the ionisation of compound (7) in acetic and in formic acid, respectively. For compound (3), however, rate ratios of 23·2 and 33·8 are found in acetic and in formic acid, respectively. Certainly, some of the acceleration to ionisation in the reaction of compound (3) could be explained in terms of steric acceleration resulting from the decrease in non-bonded interaction between the *endo*-2-H and the *endo*-5,6-substituent, but the result adds support to the earlier conclusion that some C(1)–C(6) bond participation cannot be excluded.

Steric Inhibition to Ionisation.—The very low rates of solvolysis of compounds (4) and (8) compared with compounds (2) and (6), respectively, provide evidence that the former pair exhibit considerable steric inhibition to ionisation.[5,13] The solvolysis rate ratios [(4) : (2)] and [(8) : (6)] are 0·0365 and 0·0182 in acetic acid at 100° and 0·044 and 0·0196 in formic acid at 50°, respectively (Table 1). Since back-side solvation is unhindered for all four derivatives the only explanation for these rate ratios must be that the *endo*-5,6-substituent provides considerable hindrance to the ionisation path of the leaving toluene-*p*-sulphonate group in both compounds (4) and (8) and results in an increase in the enthalpies of activation for the solvolysis of these isomers compared with those of compounds (1) and (5). For a true measure of the extent of steric inhibition to ionisation in these substrates it would be necessary to take into account their ground-state energies. Clearly, if compound (4) has greater non-bonded interactions in the ground state than compound (1), the energy barrier in going to the transition state will be smaller than if both substrates were identical in ground-state energy. One estimate of the ground-state energies can be obtained from the chromic acid oxidation rates of the parent alcohols.[9] The ground-state energy difference between the alcohols of compounds (4) and (1) has been estimated as 1·9 kcal mol^{-1},[9] and if this factor is applied to the toluene-*p*-sulphonates a solvolysis rate factor of 25 in favour of compound (4) can be predicted. From this it is evident that the true relative rate factor for steric inhibition to ionisation of compounds (4) and (1) is at least 1430 at 100° (observed rate factor $\times 25$). Unfortunately, this type of treatment cannot be applied for the solvolysis rate of compound (8) compared to (5) since the oxidation of the parent alcohol of compound (8) does not proceed with rate-limiting elimination [9] but the factor for steric inhibition to ionisation would be expected to be considerably larger than that for compound (4).

The solvolysis of both U-shaped substrates (4) and (8) must proceed with substantial solvent participation (k_s). Products from the acetolysis of these systems emphasise the difference between the ionisation in these and the *exo*-5,6-substituted *endo*-toluene-*p*-sulphonates (2) and (6). Owing to the considerable hindrance to ionisation in the former pair the solvent becomes more strongly associated with the *exo*-side of the developing carbonium ion than it does in the latter pair during solvolysis (Scheme 4). A point is reached in the displacement [ion (13)] at which the C(2)–OTs bond is sufficiently extended to cause considerable strain between the leaving group and the *endo*-5,6-substituent and is weakened to the point of collapse either by continued solvent displacement (k_s) or a Wagner–Meerwein shift (k_r) which displaces the attacking solvent molecule. The extent to which these two processes occur depends on the drive toward rearrangement (k_r route) which as has already been shown in the solvolysis of compound (3) compared to that of (7), is greater for the *endo*-*o*-phenylene group. Similarly, the acetolysis of compound (4) as compared to that of (8) gives less product which has retained the stereochemistry. The rate of acetolysis of the latter will be lower owing to the greater inhibition to ionisation of this substrate. The 1·9% of rearranged *endo*-acetate produced in the acetolysis of compound (8) arises from solvent attack on the rearranged carbonium ion (13). In formic acid less product will be formed by the k_s pathway because of the lower nucleophilicity of the medium compared with acetic acid, and for the reasons

[13] R. Baker and T. J. Mason, *Tetrahedron Letters*, 1969, 5013.

above the proportion of retained configuration product will be less from compound (4) than from (8).



SCHEME 4

Table 4 illustrates a series of U-shaped secondary derivatives with the relative degrees of steric inhibition to ionisation shown by the acetolysis rate ratios compared to *endo*-norbornyl toluene-*p*-sulphonate at 100°. From these results it is clear that both compounds (4) and (8) are exhibiting far greater inhibition to ionisation than compounds (14)—(16). An anomalous result is however obtained for the acetolysis rate of compound (17) at 25°. Rothberg [14] has postulated that for this substrate the strain in the molecule is sufficient to alter the leaving path of the toluene-*p*-sulphonate group so that strain is relieved in going from the ground state to the transition state and the rate of acetolysis is 22 times greater than that of *endo*-norbornyl toluene-*p*-sulphonate. In other words the high ground-state energy of the substrate is relieved at a very early stage in the ionisation so that the energy barrier to solvolysis is small compared to that in substrates exhibiting steric inhibition to ionisation.

EXPERIMENTAL

A Pye 104 chromatograph was employed for all g.l.c. analyses (glass columns, gas flow rate 60 ml min^{-1}). N.m.r. spectra were obtained with Varian A60 and HA100 instruments, with tetramethylsilane as internal standard and deuteriochloroform as solvent. The toluene-*p*-sulphonates (see Table 5) were prepared by standard techniques [15] from alcohols previously described.[9]

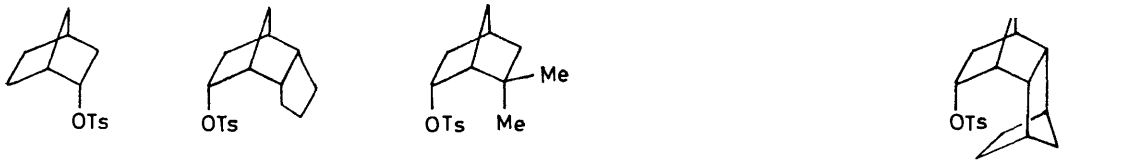
Kinetics.—The purification of the acetic and the formic acid and the technique for kinetic studies have been previously described.[16] The acetic acid was unbuffered but the formic acid contained sodium formate (0·017M).

The isomerisation [(3) ⟶ (1)] in acetic and in formic acid was followed by n.m.r. measurements involving changes in the integration of the signals corresponding to the benzylic protons at τ 6·45 and 6·95, respectively. Similarly for isomerisation [(7) ⟶ (5)] signals at τ 6·20 and 6·68 were observed.

Product Studies.—Products from both acetolysis and formolysis of the *o*-phenylene adducts were analysed, by g.l.c., in two parts. The olefinic fraction was determined on a column (10 ft × ⅛ in) of 10% polypropylene glycol adipate (PPGA) on Phase Sep. W 60—72 mesh at 150°. After reduction by lithium aluminium hydride the substitution products were converted into silyl ethers [17] and analysed on a column (5 ft × ¼ in) of 5% diethylene glycol succinate (DEGS) on Chromosorb W 100—120 mesh.

TABLE 4

Acetolysis rates of U-shaped toluene-*p*-sulphonates relative to *endo*-norbornyl toluene-*p*-sulphonate at 100°



	(14)	(15)	(16)	(4)	(8)	(17)
k_{rel}	1·00	0·19[a]	0·135[8]	0·037*	0·018*	22·0(at 25°)[14]

* Allowing for inductive factors of 9·3 and 12·1 for compounds (4) and (8) respectively.

[a] K. Takeuchi, T. Oshika, and Y. Koga, *Bull. Chem. Soc. Japan*, 1965, **38**, 1310.

TABLE 5

Compd.	M.p.	$\nu_{max.}$ (Nujol)/cm^{-1}
(1)	117–119°	670, 740, 770, 790, 880, 930, 1175, 1365, 1603
(2)	109—110	670, 760, 820, 880, 965, 1170, 1185, 1360, 1603
(3)	86—87	670, 730, 820, 880, 930, 960, 1175, 1185, 1365, 1603
(4)	82—83	670, 750, 830, 875, 970, 1170, 1180, 1190, 1355
(5)	117—118	670, 780, 880, 980, 1175, 1195, 1360, 1603
(6)	100—101	670, 780, 880, 970, 1175, 1185, 1360, 1603
(7)	166—167	670, 780, 885, 1165, 1175, 1185, 1360, 1603
(8)	122—123	670, 780, 810, 830, 845, 875, 885, 985, 1175, 1185, 1360, 1603

Acetolysis products from compounds (4)—(8) were analysed on a column (5 ft × ¼ in) 10% silicone gum

[14] I. Rothberg, *Chem. Comm.*, 1968, 268.
[15] R. S. Tipson, *J. Org. Chem.*, 1944, **9**, 235.
[16] S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1970, **70**, 821.
[17] T. Luukainen, W. J. A. Vanden Heuvel, E. O. A. Haahti, and E. C. Horning, *Biochim. Biophys. Acta*, 1961, **52**, 599.

rubber (XE60) on J and J Diatomite 100—120 mesh at 200°. The olefins were inseparable, as were the two acetates from compounds (5) and (6), but the overall percentages of substitution and elimination were determined. The retention times of the olefin from (5) and (6), the acetate from (7), and the acetate from (5) or (6) were 5·1, 28·2, and 31·8 min, respectively. The proportions of *exo*- and *endo*-olefins were determined on a column (5 ft × ¼ in) of 10% Versamid 900 on J and J Diatomite 100—120 mesh at 200°. The acetate products were separated on a column (10 ft × ⅛ in) of 1·8% cyclohexanedimethyl succinate (CDMS) on J and J Diatomite 60—72 mesh at 200°; retention times for the acetates from (7), (6), and (5) were 28·6, 34·2, and 38·4 min, respectively. Formolysis products were identified as silyl ethers [17] at 150° on the 5% diethylene glycol succinate column.

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