Secondary Kinetic Isotope Effects and the Intervention of Non-classical Ions in the Solvolysis of *endo*-Bicyclo[3.2.1]octan-2-yl Toluene-*p*-sulphonate

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1,2-Dideuterio-*endo*-bicyclo[3.2.1]octan-2-yl toluene-*p*-sulphonate has been prepared and the secondary deuterium kinetic isotope effect has been measured in buffered formic acid (k^{H}/k^{D} = 1.154 at 29.9°) and in 80% aqueous ethanol (k^{H}/k^{D} = 1.116 at 64.4°). These low values are in accordance with a mechanism involving extensive bridging in the solvolytic transition state. The products of the formolysis reaction are also reported.

THE investigation of the solvolysis of *endo*-bicyclo[3.2.1]-octan-2-yl toluene-*p*-sulphonate (1a) by Goering and Fickes [1,2] established that this compound is comparable to *exo*-norborn-2-yl *p*-bromobenzenesulphonate [3] (2a) in important respects. Both chiral esters undergo solvolysis to give completely racemic products, and the rate of loss of optical activity k_{α} in both cases is faster than the rate of formation of products k_{t}. It has been convincingly argued that the racemization of the esters

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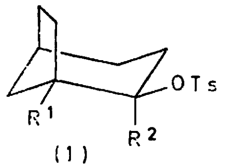
[1] H. L. Goering and G. N. Fickes, *J. Amer. Chem. Soc.*, 1968, **90**, 2848.

[2] H. L. Goering and G. N. Fickes, *J. Amer. Chem. Soc.*, 1968, **90**, 2856.

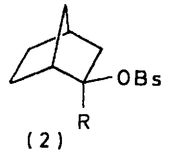
[3] S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, 1952, **74**, 1154.

involves internal return from achiral, intimate ion pairs concurrent with, but faster than, subsequent product-forming reactions of these intermediates. The proposed mechanism for the solvolysis of (1) is shown in Scheme 1 and includes the bridged intermediate cation (3) for which $k_{-1} > k_2$. The absence of a $LiClO_4$ special salt effect showed [1] that there is no significant external return from solvent separated ion pairs, consequently k_{-2} is negligible compared with k_3. Excluded from Scheme 1 are the routes by which the small amounts of *exo*-bicyclo[3.2.1]- and bicyclo[2.2.2]-octan-2-yl derivatives are produced,[2] as this aspect is not germane to the present investigation.



(1)

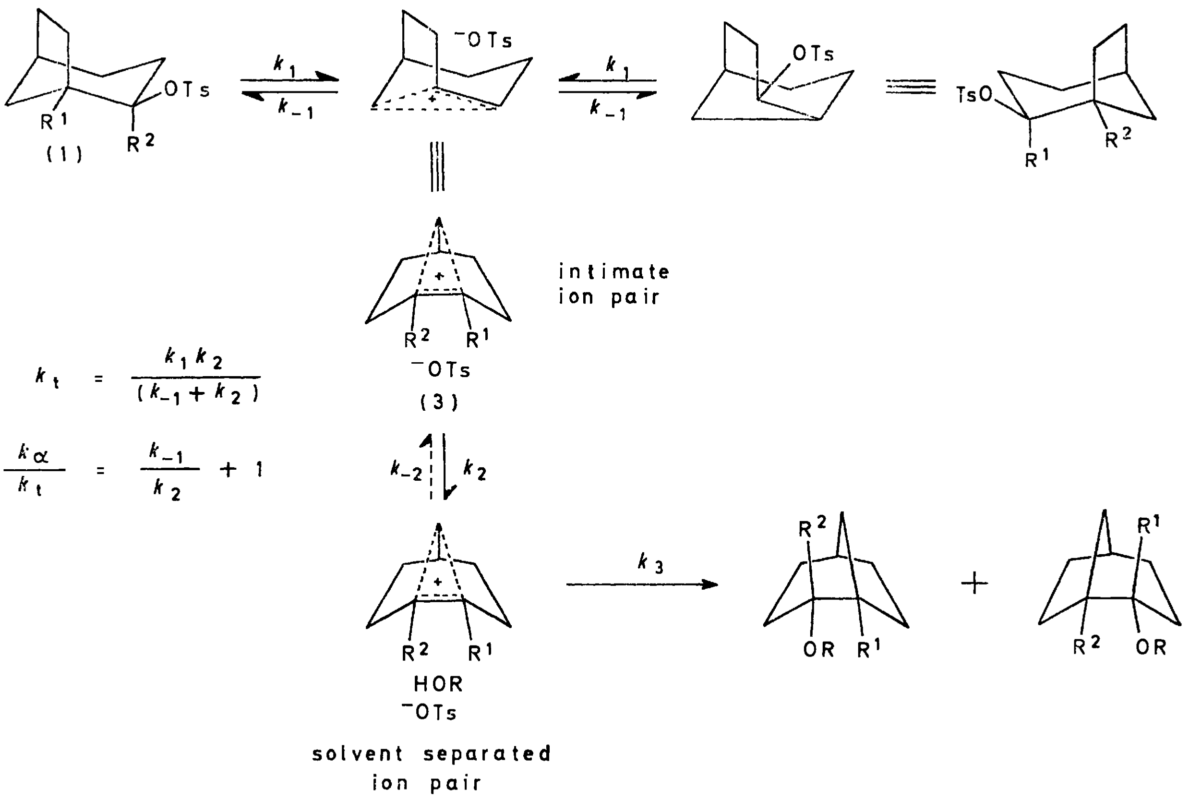
a; $R^1 = R^2 = {}^1H$
b; $R^1 = {}^1H, R^2 = {}^2H$
c; $R^1 = R^2 = {}^2H$



(2)

a; $R = {}^1H$
b; $R = {}^2H$

$Ts = SO_2C_6H_4Me$-*p*
$Bs = SO_2C_6H_4Br$-*p*

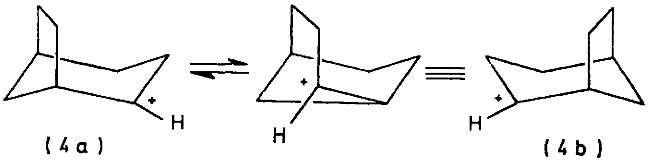


$$k_t = \frac{k_1 k_2}{(k_{-1} + k_2)}$$

$$\frac{k_\alpha}{k_t} = \frac{k_{-1}}{k_2} + 1$$

Scheme 1

An alternative mechanism, in which a rapidly interconverting pair of enantiomeric classical cations (4a) ⇌ (4b) is the intermediate source of achirality rather than a single bridged cation, would also account for the published stereochemical results for the solvolysis of *endo*-bicyclo[3.2.1]octan-2-yl tosylate. This interpretation has not been debated with the vigour of the analogous case of the *exo*-norborn-2-yl system,[4] but it is the resolution of this question which is the burden of this report.



(4a) (4b)

It has been established that nucleophilically unassisted solvolyses of secondary alkyl arenesulphonates have high secondary α-deuterium kinetic isotope effects (α-k.i.e. *ca.* 1.22 at 25°).[5] Furthermore, the magnitude of the effect appears to depend only upon mechanism for a given leaving group and is not especially affected by the nature of the solvent or by the structure of the secondary alkyl group.[5a] Nucleophilic assistance reduces α-k.i.e. regardless of whether it is intramolecular [5b] (neighbouring group participation) or bimolecular [5a] (S_N2). If anchimeric assistance is provided by electronic delocalization at the transition state with little, if any, bridging, it has been argued [5b] that there will be hardly any reduction in α-k.i.e. and that only when bridging is extensive at the

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[4] (*a*) G. D. Sargent, *Quart. Rev.*, 1966, **20**, 301; (*b*) H. C. Brown, *Chem. Soc. Special Publ.*, 1962, **16**, 140; *Accounts Chem. Res.*, 1973, **6**, 377; F. K. Fong, *J. Amer. Chem. Soc.*, 1974, **96**, 7638; (*c*) S. E. Scheppele, *Chem. Comm.*, 1971, 592.

transition state will α-k.i.e. be appreciably reduced. A corollary of such a non-linear relationship between α-k.i.e. and the extent of bridging is that a modestly reduced α-k.i.e. in an anchimerically assisted unimolecular solvolysis reaction may be evidence of quite extensive bridging in the solvolytic transition state.

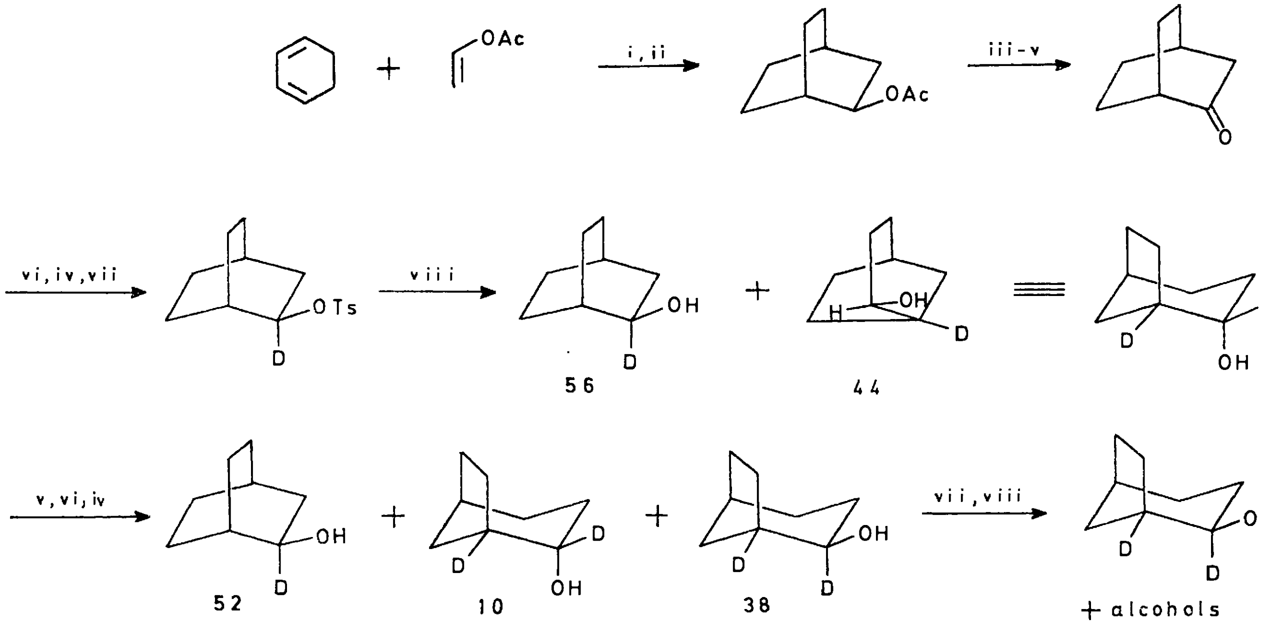
Goering and Fickes [1] showed that the solvolysis of (1) is anchimerically assisted. Bridging, *i.e.* increased proximity of the rear-side C-8 methylene group to the C-2 carbon to which the leaving group was bonded, would modify the bending vibrations of the hydrogen (deuterium) at C-2 in a way which would attenuate α-k.i.e.[5]

Similarly, it was thought that measurement of α-k.i.e. would resolve the question of whether or not there is bridging in the solvolysis of *exo*-norborn-2-yl brosylate (2).[6]

Unfortunately the precision of such measurements has not been high and values for the α-k.i.e. of (2) range from 1.11 [6,7] to 1.21 [5b,8] for acetolysis at 25°. A principal cause of the imprecision (and an alternative explanation for the low value if it proves to be accurate) is that internal return scrambles the *endo*-deuterium at C-2 and the bridgehead hydrogen at C-1 of the unsolvolysed arenesulphonate (2).

In the present investigation, I have circumvented this scrambling problem by stereospecifically incorporating two deuterium atoms into the substrate to give (1c). As illustrated in Scheme 1, internal return of racemic (1c), whether by interconverting classical ions or *via* a single non-classical ion, simply causes a degenerate rearrangement.

The preparation of (1c) is outlined in Scheme 2 and comprises known reactions.



SCHEME 2 Reagents: i, heat; ii, H_2–cat.; iii, $LiAlH_4$; iv, H^+; v, oxid.; vi, $LiAlD_4$; vii, TsCl–C_5H_5N; viii, H_2O

Regardless of whether the skeletal rearrangement of bicyclo[2.2.2]octan-2-yl tosylate [9,10] is *via* interconverting isomeric classical ions, or through a bridged non-classical ion,[4a] the deuterium (at C-2 of the unrearranged material) should be exclusively at C-1 of the rearranged product in the absence of hydride shift processes.

Goering and Fickes [1] had been able to purify *endo*-bicyclo[3.2.1]octan-2-yl tosylate by selectively solvolysing minor contaminating amounts of more reactive isomeric tosylates.[11] After precise experimental conditions had been established by preliminary work on undeuteriated materials,* this technique was exploited in the present study. Mass spectral analysis of (1c)

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* The perprotio-compound (1a) was made by lithium aluminium hydride reduction of purportedly pure commercial bicyclo-[3.2.1]octan-2-one. However, besides the expected *exo*- and *endo*-bicyclo[3.2.1]octan-2-ols [12] there was always a yield (*ca.* 15%) of bicyclo[2.2.2]octan-2-ol. The same result was obtained regardless of changes in experimental conditions and also when sodium borohydride was used. The conclusion must be that the commercial bicyclo[3.2.1]octan-2-one contained *ca.* 15% of bicyclo[2.2.2]octanone. I found no g.l.c. conditions capable of resolving these two ketones (an authentic sample of bicyclo-[2.2.2]octanone was available). Consequently compound (1a) was also purified by the method of selective solvolysis of the contaminating tosylates.

[5] 'Isotope Effects in Chemical Reactions,' eds. C. J. Collins and N. S. Bowman, A. Chem. Soc. Monograph 167, Van Nostrand, New York, 1970; (*a*) V. J. Shiner, ch. 2; (*b*) D. E. Sunko and S. Borcic, ch. 3; (*c*) S. E. Scheppele, *Chem. Rev.*, 1972, **72**, 511.

[6] C. C. Lee and E. W. C. Wong, *J. Amer. Chem. Soc.*, 1964, **86**, 2752; *Canad. J. Chem.*, 1965, **43**, 2254.

[7] B. L. Murr and J. A. Conkling, *J. Amer. Chem. Soc.*, 1970, **92**, 3462.

[8] K. Humski, R. Malojcic, S. Borcic, and D. E. Sunko, *J. Amer. Chem. Soc.*, 1970, **92**, 6534.

[9] H. L. Goering and M. F. Sloan, *J. Amer. Chem. Soc.*, 1961, **83**, 1397; H. L. Goering and G. N. Fickes, *ibid.*, 1968, **90**, 2862.

[10] R. S. Tipson, *J. Org. Chem.*, 1944, **9**, 235.

[11] H. L. Goering and M. F. Sloan, *J. Amer. Chem. Soc.*, 1961, **83**, 1992.

[12] A. A. Youssef, M. E. Baum, and H. M. Walborsky, *J. Amer. Chem. Soc.*, 1959, **81**, 4709.

showed 93% $^2H_2$, 6% $^2H_1$, and 1% $^2H_0$. The n.m.r. spectrum of (1a), the perprotio-analogue,* showed broad but resolved signals due to C-1 and C-5 bridgehead hydrogens at τ 7.7 and 7.9 and a complex multiplet at 5.5—5.8 due to the C-2 hydrogen. The signals at τ 7.7 and 5.5—5.8 were completely absent in the n.m.r. spectrum of (1c).

In addition, the n.m.r. spectrum of the sublimed alcoholic product of hydrolysis of (1c) was compared with the analogous spectrum of the product of hydrolysis of (1a). The product from the perprotio-compound, very largely *endo*-bicyclo[3.2.1]octan-2-ol,[2] gave a spectrum with multiplets at τ 6.3—6.6 and 7.75—8.05 in the ratio 1 : 2 due to hydrogens at C-2 and the bridgeheads respectively. The spectrum of the hydrolysis product of (1c) showed no trace of a signal below τ 7.7 (<0.02H) and a multiplet at 7.75—8.05 which integrated for 1 H only. This spectral evidence corroborates the evidence of the synthesis; the structure of the dideuteriated tosylate is unambiguously (1c) as shown. The good agreement of the product analyses from hydrolysis of (1a) and (1c) with those reported by Goering and Fickes [2] and the uncomplicated first-order kinetics of (1a and c) demonstrate the absence of significant alcoholic or tosylate impurities.

RESULTS AND DISCUSSION

Compounds (1a and c) were solvolysed in 80% aqueous ethanol (80E) and anhydrous formic acid (0.16M in sodium formate). The results are shown in Table 1 and compared with other results in Table 2.

TABLE 1

Rates and secondary kinetic isotope effect for solvolysis of (1) [a]

	80E (64.40 ± 0.04°)		$HCO_2H–Na^+HCO_3^-$ (29.9 ± 0.1°)	
	$10^4k^H/min^{-1}$	k^H/k_D	$10^3k^H/min^{-1}$	k^H/k_D
(1a,c)	72.67 (±0.54)	1.116 (±0.002)	61.63 (±0.76)	1.154 (±0.008)

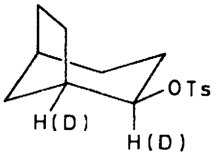
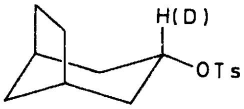
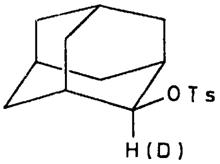
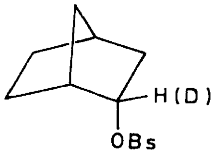
[a] Compounds (1a and c) were solvolysed simultaneously in the same cell compartment and the rates were measured spectrophotometrically (272 nm). The temperature stability during the time of a kinetic run was shown to be better than ±0.04° at 64.4° and ±0.01° at 29.9°. For aqueous ethanolysis two or three runs were done on each of three pairs of solutions; for the formolyses, seven pairs of freshly made up solutions were used. Good first-order kinetics were observed for six half-lives; the rate constants and standard deviations (which were always <1%) were computed by a non-linear least squares program. The quoted rate constants are means of eight and seven values, and the isotope effects are means of six and seven ratios respectively. The errors quoted are the standard errors. I thank Dr. R. L. Tranter of this department for help with the computing.

The kinetic isotope effects for (1c) are distinctly lower than the values for the model compounds and lower than would be expected for an α-k.i.e. in the absence of any neighbouring group involvement.[5] Although the intermediacy of (4a) $\rightleftharpoons$ (4b) could account for the stereochemical results,[2] the ion pair separations involving (4a and b) must proceed *via* parallel, enantiomeric transition states which involve essentially classical cations. Such a mechanism cannot account for the presently reported solvolytic kinetic isotope effects.

The similarity between the α-k.i.e. results for the model compounds undergoing unassisted solvolyses reflects Shiner's view that the structure of the alkyl group has very little effect within a given mechanism. In particular, the results for *endo*-norborn-2-yl brosylate show that the norbornane skeleton is not a cause of any anomaly, and 2-adamantyl tosylate, which has a structural resemblance to (1) shows no unanticipated effect. The low k.i.e. of (1c) cannot therefore be reasonably ascribed to any unique geometrical property of the compound.

TABLE 2

Comparison of kinetic isotope effects for (1) with analogues

Compound	80E (T/°C)	HCO_2H (T/°C)
	1.116 (64.4°)	1.154 (29.9°)
	1.178 (55.0°) [a]	1.20 (24.8°) [a]
	1.149 (99.8°) [b]	1.26 (25°) [b,c]
	1.193 (55°) [d]	1.22 (30.2°) [e]

[a] M. Banks and H. Maskill, unpublished results. [b] Ref. 14. [c] Value for trifluoroacetolysis. [d] Ref. 7. [e] Ref. 6.

It has been suggested that an α-k.i.e. is maximal for a given substrate when the rate-determining step is the conversion of one sort of ion pair into another, and that if the initial ionization were rate-determining α-k.i.e. would be somewhat lower [5a,13] (*ca.* 1.15 at 25°). Only when α-k.i.e. is much closer to unity is the incursion of an S_N2 process reported to be significant. If this interpretation is correct, and it is not a universally accepted view,[14] then the present results could simply be due to a mechanism in which k_1 is rate determining rather than

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* See footnote on p. 1852.

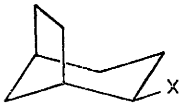
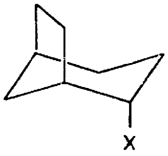
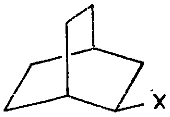
[13] (*a*) V. J. Shiner and R. D. Fisher, *J. Amer. Chem. Soc.*, 1971, **93**, 2553; (*b*) V. J. Shiner, S. R. Hartshorn, and P. C. Vogel, *J. Org. Chem.*, 1973, **38**, 3604.

[14] J. M. Harris, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 2551.

k_2, the latter being the rate-limiting step in the mechanisms of the model compounds. However, Goering and Fickes [1] showed that for (1a) $k_{-1}/k_2 \approx 2.1$ in 80% aqueous acetone and $\approx$4.5 in buffered acetic acid. In view of the similarities between these solvents and those presently used,[15] and the similarities between the product analyses reported by Goering and Fickes [2] and the present results for formolysis (Table 3), it seems improbable that in both aqueous ethanol and buffered anhydrous formic acid the initial ionization is the slowest step.

TABLE 3

Products from solvolysis of (1)

Product	Solvent Buffered CH_3CO_2H (49°) [a]	 Buffered 80A (49°) [a]	 Buffered HCO_2H (30°) [b]
	89.4	94.9	96.1
	6.6	4.1	2.2
	4.0	1.0	1.7
Hydrocarbon	0	0	<0.3 [c]

[a] Ref. 2. [b] Normalized averages of two analyses from each of two solvolyses using pentadecane and undecane as internal calibrants. Chromatogram peak areas were measured planimetrically. The unnormalized total analyses (93—99%) were not significantly less than complete. [c] Bicyclo[2.2.2]octene, <0.02%; bicyclo[3.2.1]oct-2-ene, <0.2%.

The deuterium at the C-1 bridgehead in (1c), whilst obviating the scrambling problem, may be thought to introduce an extra, complicating kinetic effect. It has been shown, however, that β-deuterium kinetic isotope effects in solvolytic reactions are conformation dependent,[4c,16] so the β-deuterium k.i.e. upon the ionization of (1c) should be nil, or small and rate retarding, if the reaction involves ionization to a classical cation. In this event,the composite k.i.e. for (1) is wholly, or almost wholly, attributable to the α-deuterium and the β-deuterium does not account for the lowness of the value. However, the work which led to the conclusion that the β-deuterium kinetic effect depends upon the dihedral angle between the β-deuterium bond and the developing vacant orbital, was on systems which did not involve non-classical ions. They may therefore be improper analogues in an investigation which is concerned with the possible intermediacy of non-classical ions. If there is extensive bridging in the ionization of (1c) there could well be a kinetic isotope effect of the β-deuterium and this would be rate retarding, *i.e.* a normal secondary deuterium kinetic isotope effect. Murr and Conkling [17] have suggested that this β-k.i.e. may be higher than 5% in the case of *exo*-norborn-2-yl brosylate. Without being able to estimate confidently the magnitude of this effect for (1c) it is sufficient to note that, assuming the effects of α- and β-deuterium atoms are cumulative,[18] a rate-retarding contribution to the composite k.i.e. by the β-deuterium requires that the α-deuterium kinetic isotope effect is less than the composite value, and even further decreased from the value expected of a system reacting without nucleophilic assistance. A positive contribution from the β-deuterium, therefore, strengthens the case for the intermediacy of bridged non-classical ions and only in the improbable event of a substantial inverse β-k.i.e. unprecedented in solvolytic reactions, can the bridgehead deuterium in (1c) render the results ambiguously interpretable.

It follows from Scheme 1 that equation (1) applies in

$$\frac{k^{H}{}_{t}}{k^{D}{}_{t}} = \frac{k^{H}{}_{1}}{k^{D}{}_{1}} \times \frac{k^{H}{}_{2}}{k^{D}{}_{2}} \times \left\{\frac{k^{D}{}_{-1} + k^{D}{}_{2}}{k^{H}{}_{-1} + k^{H}{}_{2}}\right\} \qquad (1)$$

which $k^{H}{}_{t}/k^{D}{}_{t}$ = solvolytic (titrimetric) kinetic isotope effect, k.i.e.$_{t}$, $k^{H}{}_{1}/k^{D}{}_{1}$ = ionization kinetic isotope effect, (k.i.e.$_{i}$) and $k^{H}{}_{2}(k^{D}{}_{-1} + k^{D}{}_{2})/{}_{4}k^{D}{}_{2}(k^{H}{}_{-1} + k^{H}{}_{2})$ = partitioning isotope effect (p.i.e.) [19] defined by equation (2). Since

$$\text{p.i.e.} = \left\{\frac{\dfrac{k^{H}{}_{2}}{k^{H}{}_{-1}} + \dfrac{k^{H}{}_{2}}{k^{H}{}_{-1}} \Big/ \dfrac{k^{D}{}_{2}}{k^{D}{}_{-1}}}{\dfrac{k^{H}{}_{2}}{k^{H}{}_{-1}} + 1}\right\} \qquad (2)$$

k_2/k_{-1} may be obtained from the ratio of polarimetric to solvolytic rate constants, the determination of p.i.e. is in principle possible. It would require the polarimetric rates for protio- and deuterio- compounds to a higher degree of precision than is commonly practicable and has not been achieved in the present investigation. The significance of this dissection is as follows. If the p.i.e. is reduced from the probable value of *ca.* 1·10 [20] for a reaction of a simple secondary alkyl arenesulphonate to *ca.* 1.00 for (1c), then k.i.e.$_{i} \approx$ k.i.e.$_{t}$ and the present results are not significantly different from values expected of an

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[15] S. Winstein and K. Schreiber, *J. Amer. Chem. Soc.*, 1952, **74**, 2165; A. F. Diaz, I. Lazdins, and S. Winstein, *ibid.*, 1968, **90**, 1904.

[16] V. J. Shiner, jun., and J. S. Humphreys, *J. Amer. Chem. Soc.*, 1963, **85**, 2416; V. J. Shiner, jun., B. L. Murr, and G. Heinemann, *ibid.*, p. 2413.

[17] B. L. Murr and J. A. Conkling, *J. Amer. Chem. Soc.*, 1970, **92**, 3464.

[18] V. J. Shiner, jun., and J. O. Stoffer, *J. Amer. Chem. Soc.*, 1970, **92**, 3191.

[19] B. L. Murr and M. F. Donnelly, *J. Amer. Chem. Soc.*, 1970, **92**, 6686.

[20] B. L. Murr and M. F. Donnelly, *J. Amer. Chem. Soc.*, 1970, **92**, 6688.

unassisted ionization. The bridging in this case occurs after the initial ionization and depresses only the p.i.e. If on the other hand $1{\cdot}10 >$ p.i.e. > 1.00 and k.i.e.$_i <$ k.i.e.$_t$ then not only does the transition state for the conversion of the intimate ion pair into the solvent separated ion pair involve a bridged cation but the bridging starts before the formation of the intimate ion pair *i.e.* at the transition state for ionization.

EXPERIMENTAL

Analytical g.l.c. was done on a Perkin-Elmer F11 gas chromatograph using 50 ft S.C.O.T. columns (Carbowax 20M at 60° for hydrocarbons and DEGS at 120° for alcohols) with an inlet splitter and nitrogen (20 p.s.i.) as carrier gas. The 90 MHz n.m.r. spectra were recorded at Stirling on a Perkin-Elmer R32 instrument and mass spectra were recorded by P.C.M.U., Harwell. Rates were recorded automatically on a Unicam SP 500 series 2 u.v. spectrophotometer fitted with a thermostatted cell compartment and an SP 505 program controller coupled to an SP 22 recorder.

Preparation of endo-*Bicyclo*[3.2.1]*octan*-2-*yl Toluene*-p-*sulphonate* (1a).—The mixture of *exo*- and *endo*-bicyclo-[3.2.1]octan-2-ols and bicyclo[2.2.2]octan-2-ol (21 : 64 : 15; 0.66 g, 5.2 mmol), obtained by reduction of impure commercial bicyclo[3.2.1]octan-2-one with lithium aluminium hydride, was dissolved in a solution of pyridine (2.0 cm^3) and recrystallized toluene-*p*-sulphonyl chloride (1.03 g; 5.41 mmol). The solution was kept at 0° for 4.5 days then was hydrolysed at 49° in 80% aqueous acetone (300 cm^3) for 30.0 h. The cooled solution was evaporated down to *ca.* 200 cm^3 below 10°, then extracted three times with ether. The ether solutions were successively washed with ice-cold dilute hydrochloric acid and aqueous sodium hydrogen carbonate solution. The combined ether solution was dried (K_2CO_3), filtered, and evaporated to dryness at room temperature, finally at 5 Torr for 30 min. The residue was fractionally recrystallized to constant m.p. from ether–light petroleum (b.p. 30—40°) at low temperature, m.p. 78—79° (lit.,[9] 80.1—80.8°), τ 2.30 and 2.75 (4 H AB q,), 5.5—5.8 (1 H, m), 7.56 (3 H, s), 7.7 (1 H, m), 7.9 (1 H, m), and 8.0—8.9 (10 H, m), $\tilde{\nu}_{max.}$ (KBr) 2 940, 2 860, 1 596m, 1 450m, 1 345, 1 174, 1 100, 930, 879m, 854, 834m, 820, 736w, 664, and 560 cm^{-1}.

Bicyclo[2.2.2]*octan*-2-*ol*.—The adduct of cyclohexa-1,3-diene and vinyl acetate was catalytically hydrogenated then reduced with lithium aluminium hydride in the usual manner.[9] A sample of the crude product (which contained less than 0.3% acetate by g.l.c.) was sublimed at 90—100° and 14 Torr, m.p. 219—220° (lit.,[9] 220.9—222.2°), τ 6.15 (1 H, complex d), 7.8 (1 H, s, removed by ^2H_2O), and 7.9—8.9 (12 H, m), and the remainder was oxidized directly.

Bicyclo[2.2.2]*octanone*.—The method of Brown and Garg [21] was used to oxidize bicyclo[2.2.2]octan-2-ol. The product, which contained <0.3% alcohol by g.l.c., was sublimed twice (60—100° at 30 Torr) to give an impure waxy solid (58% based upon cyclohexadiene).

[2-^{2}H]*Bicyclo*[2.2.2]*octan*-2-*ol*.— Bicyclo[2.2.2]octanone was reduced in the usual manner with lithium aluminium deuteride and the crude product (containing *ca.* 0.4% ketone) was sublimed at 14 Torr (91%), m.p. 220—221°, τ 7.5 (1 H, s, removed by ^2H_2O) and 7.9—8.9 (12 H, m). Mass spectral analysis of the trimethylsilyl ether showed the presence of only the monodeuteriated compound.

Preparation and Hydrolysis of [2-^{2}H]*Bicyclo*[2.2.2]*octan*-2-*yl Tosylate*.—A solution of the deuteriated alcohol (2.50 g, 0.0197 mol), recrystallized toluene-*p*-sulphonyl chloride (5.72 g, 0.0300 mol), and pyridine (8.00 g, 0.10 mol) was kept at 0° in a stoppered flask for 6 days. To the product mixture were added water (200 cm^3) and acetone (270 cm^3) and the solution was gently heated under reflux for 48 h. The reflux condenser was replaced by a Hempel column and the solution was fractionally distilled until almost all the acetone had been removed. The aqueous residue was cooled and extracted three times with ether and each extract was separately washed with aqueous sodium carbonate, twice with dilute hydrochloric acid, and finally with brine. The combined ether phase which contained [2-^{2}H]bicyclo-[2.2.2]octan-2-ol and *exo*-[1-^{2}H]bicyclo[3.2.1]octan-2-ol in the ratio 56 : 44, was dried (Na_2SO_4), filtered, fractionally distilled, and finally evaporated to leave a crystalline solid (2.18 g, 87%).

1,2-*Dideuterio*-endo-*bicyclo*[3.2.1]*octan*-2-*yl Tosylate* (1c).—A mixture of [2-^{2}H]bicyclo[2.2.2]octan-2-ol and *exo*-[1-^{2}H]bicyclo[3.2.1]octan-2-ol (0.66 g, 5.2 mmol) was oxidized by the two-phase method [21] to give a mixture of the two corresponding ketones (shown by g.l.c. to contain <0.2% of the alcohols). The ether solution of these was reduced with lithium aluminium deuteride (200 mg, 4.76 mmol) in the usual manner to give *exo*- and *endo*-[1,2-$^2H_2$]-bicyclo[3.2.1]octan-2-ol, and [2-^{2}H]bicyclo[2.2.2]octan-2-ol in the ratio 10 : 38 : 52. After being sublimed (14 Torr), the mixture of alcohols (0.55 g, 83%) was converted into the corresponding mixture of tosylates in the usual manner.[12] The mixed tosylates were then selectively hydrolysed as described above. The product was evaporated at 5 Torr and the residue was fractionally recrystallized from ether–light petroleum (b.p. 30—40°) five times to constant m.p. 77—78°, 93% $^2H_2$, 6% $^2H_1$, 1% $^2H_0$ by mass spectroscopy, τ 2.30 and 2.75 (4 H, ABq), 7.57 (3 H, s), 7.9 (1 H, m), and 8.1—8.9 (10 H, m), $\tilde{\nu}_{max.}$ (KBr) 2 940, 2 860, 2 170w, 1 596m, 1 450m, 1 347, 1 340, 1 178, 1 145w, 1 100m, 1 059m, 1 041m, 928, 920, 860, 820, 795m, 664, and 558 cm^{-1}.

Formolysis of Compound (1a).—Compound (1a) (accurately, *ca.* 21 mg), n-pentadecane (redistilled; accurately, *ca.* 25 mg), and n-undecane (redistilled; accurately, *ca.* 5 mg) were vigorously shaken in a stoppered flask with anhydrous formic acid 0.16M in sodium formate (3.50 cm^3) until the ester (but not the hydrocarbons) dissolved. The flask was maintained at 30° for 4 h then was cooled to 0°. The mixture was extracted between ether (10 cm^3) and an excess of cold aqueous sodium hydroxide. The separated ether solution was dried (K_2CO_3) and reduced with lithium aluminium hydride and worked-up in the usual manner. The unevaporated solution of products in ether was analysed directly by g.l.c. using the pentadecane as internal calibrant for the alcohols and the undecane for the hydrocarbons * (see Table 3).

Hydrolysis of Compounds (1a *and* c).—*endo*-Bicyclo-[3.2.1]octan-2-yl tosylate (*ca.* 40 mg) was dissolved in 80% aqueous acetone (5 cm^3) containing pyridine (50 mg) and

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* The molar response factors of bicyclo-octanols and -octenes with pentadecane and undecane respectively were measured by Mrs. R. M. Banks who also demonstrated that the products of formolysis of (1) are stable to the reaction and work-up procedures.

[21] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1961, **83**, 2952.

the solution was heated in a sealed vial at 100° for 48 h. The acetone was evaporated and the aqueous residue was acidified and extracted three times with pentane. Each extract was washed with aqueous sodium hydrogen carbonate and brine. The combined extracts were analysed by g.l.c. The results from (1a and c) were the same within experimental error (*endo*- and *exo*-bicyclo[3.2.1]octan-2-ols and bicyclo[2.2.2]octan-2-ol in relative amounts 93 : 5 : 2) and in agreement with the results previously reported [2] (see Table 3). The ether solution was dried (K_2CO_3), filtered, and fractionally distilled using a Hempel column. The n.m.r. spectrum of the sublimed (14 Torr) product from (1a) showed signals at τ 6.3—6.6 (1 H, m), 7.9 (2 H, m), and 8.0—8.8 (10 H, m); that of the sublimed (14 Torr) product from (1c) showed signals at 7.9 (1 H, m) and 8.0—8.8 (10 H, m).

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