Solvolytic Behaviour of *cis*- and *trans*-[5-$^2H_1$]Cyclo-octyl *p*-Bromobenzenesulphonate—a Stereospecific, Remote ε-Deuterium Isotope Effect

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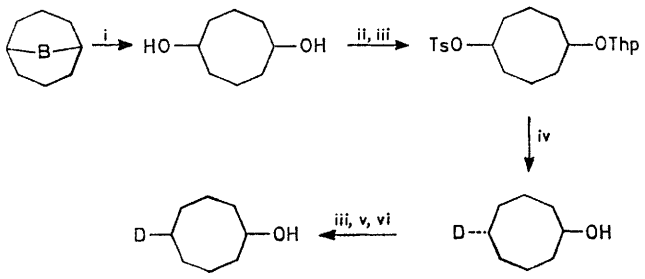
cis- and *trans*-5-Deuteriocyclo-octyl *p*-bromobenzenesulphonates have been prepared and their kinetic isotope effects and extent of transannular (C-5 ⟶ C-1) hydride shift have been determined for buffered acetolysis. The *trans*-isomer shows a significant effect (k_H/k_D = 1.12) and there is a 10 : 1 preference for *trans*-5-hydride migration.

THE occurrence of intramolecular 1,*n*-hydrogen shifts ($n > 3$) in heterolytic [1a] and homolytic [1b] reactions is now well established in aliphatic, alicyclic, and bridged-ring systems. In particular the rates of solvolysis of medium-sized ring halides and arenesulphonates are greater than those of cyclohexyl and alicyclic models, and the reactions are accompanied by transannular hydride shifts (particularly 1,5) to an extent dependent on the ring size and substitution pattern.[2] Marvell[3] has pointed out that as yet the relative importance in these rearrangements of such factors as proximity of the C–H bond to the cationic centre, strain on the ring, and hindrance to reaction with solvent is not clear; indeed the question of whether sequential ion formation, rearrangement, and solvent reaction is required or whether partially or fully concerted processes are possible has not been unequivocally answered.

The current view is that such rate enhancement should be attributed primarily to *I*-strain [4] relief in the formation of the intermediate cation with little, if any, participation of the migrating hydride ion in the rate-determining step. It has been argued [4,5] that if anchimeric assistance is involved a kinetic isotope effect should be observed on replacement of the migrating hydrogen atom by deuterium and, in addition, the α-deuterium isotope effect would be significantly depressed in the solvolysis. Values of 1.08 for k_H/k_{D_4} in 5,5,6,6-tetradeuteriocyclodecyl tosylate [6] and 1.21 for $k_H/k_{D_{10}}$ in 3,3,4,4,5,5,6,6,7,7-decadeuteriocyclo-octyl tosylate [7] have been reported and taken † to support the *I*-strain explanation, even although in the former case the deuterium label was introduced by *catalytic* deuteriation of an acetylenic precursor, a process known in many cases to result in positional scrambling of the label. Certainly remote kinetic isotope effects associated with such solvolysis appear to be small; however, in the light of the data available,[8] one might expect in the absence of some transannular interaction either no effect or an *inverse* effect of *ca.* 1—2% per deuterium atom. Hence the above data for multi-labelled substrates can, at best, only provide an *average* k_H/k_D value and certainly cannot pinpoint any stereo- or positional specificity.



(II) (I)

SCHEME Reagents: i, NaOH–H_2O_2 (ref. 9); ii, dihydropyran–H^+; iii, *p*-$MeC_6H_4{\cdot}SO_2Cl$–C_5H_5N (ref. 10); iv, $LiBDEt_3$ (ref. 11); v, $Bu_4N^+OAc^-$ (ref. 12); vi, $LiAlH_4$. Thp = tetrahydropyranyl

RESULTS

With these points in mind, we prepared *trans*- (I) and *cis*- (II) [5-$^2H_1$]cyclo-octanol by the route shown in the Scheme.

† This technique of employing a multideuteriated derivative (k_H/k_{D_n}) followed by extrapolation or factorisation to arrive at a k_H/k_D value is not uncommon: for example, S. Winstein and R. L. Hansen (*J. Amer. Chem. Soc.*, 1960, **82**, 6206) quote k_H/k_D = 1.24 for the buffered acetolysis of a decahydrodimethanonaphthalene system which involves a 1,5-hydride shift. The figure was obtained from the corresponding octadeuterio-derivative.

[1] (*a*) J. L. Fry and G. I. Karabatsos in 'Carbonium Ions,' vol. II, eds. G. Olah and P. von R. Schleyer, Wiley–Interscience, New York, 1970; see also D. M. Bronwen and A. A. Kiffen, *Rec. Trav. chim.*, 1973, **92**, 906; Q. Branca and D. Arigoni, *Chimia* (*Switz.*), 1969, **23**, 189; R. S. Atkinson and R. H. Green, *J.C.S. Perkin I*, 1974, 394; R. S. Atkinson, *Chem. Comm.*, 1969, 735; T. H. Cohen, C. H. McMullen, and K. Smith, *J. Amer. Chem. Soc.*, 1968, **90**, 6866; Y. Pepin, H. P. Husson, and P. Potier, *Tetrahedron Letters*, 1975, 493; J. K. Kim, J. K. Pau, and M. C. Caserio, *J.C.S., Chem. Comm.*, 1974, 121; M. Saunders and J. J. Stofko, jun., (*J. Amer. Chem. Soc.*, 1973, **95**, 252) have employed low temperature ^1H n.m.r. studies of superacid-derived cations to obtain values of 8.5 kcal mol^{-1} for 1,3-, 12—13 kcal mol^{-1} for 1,4-, and 6.7 kcal mol^{-1} for 1,5-hydride shifts; (*b*) J. Y. Nedelec and D. Lefont, *Tetrahedron Letters*, 1972, 5073; S. Milosavljevic, D. Jeremic, and M. L. Mihailovic, *Tetrahedron*, 1973, **29**, 3547 and references cited therein.

[2] V. Prelog and J. G. Traynham in 'Molecular Rearrangements,' Part I, ed. P. de Mayo, Interscience, 1963, p. 593; A. C. Cope, M. M. Martin and M. A. McKervey, *Quart. Rev.*, 1966, **20**, 119; J. Sicher, *Progr. Stereochem.*, 1962, **3**, 202.

[3] E. N. Marvell, J. Seubert, D. Sturman, and W. Federici, *J. Org. Chem.*, 1970, **35**, 396.

[4] H. C. Brown and K. Ichikawa, *Tetrahedron*, 1957, **1**, 221 and the review articles cited in ref. 2.

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[6] V. Prelog and S. Borcic, unpublished results, quoted by V. Prelog, Proceedings of XVIth I.U.P.A.C. Congress, Paris, 1957, p. 261.

[7] A. A. Roberts and C. B. Anderson, *Tetrahedron Letters*, 1969, 3883.

[8] (*a*) V. J. Shiner, jun., in 'Isotope Effects in Chemical Reactions,' A.C.S. Monograph No. 167, ed. C. J. Collins and N. S. Bowman, 1970, ch. 2, pp. 151—155; (*b*) D. E. Sunko and S. Borcic, *ibid.*, ch. 3, p. 172; for a particularly appropriate example in γ-effects see B. L. Murr, A. Nickon, T. D. Swartz, and N. H. Werstivk, *J. Amer. Chem. Soc.*, 1967, **89**, 1730; J. M. Jerkunika, S. Borcic, and D. E. Sunko, *ibid.*, p. 1732.

[9] H. C. Brown, E. F. Knights, and C. G. Scouter, *J. Amer. Chem. Soc.*, 1974, **96**, 7765.

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[12] S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron*, 1966, **22**, (Suppl. 8), 621; R. Baker, J. Hudec, and K. L. Rabone, *J. Chem. Soc.* (*C*), 1969, 1605; B. L. Murr and J. A. Conkling, *J. Amer. Chem. Soc.*, 1970, **92**, 3462.

Both products ran concurrently with authentic cyclo-octanol in g.l.c. analysis and showed i.r. and ^{1}H n.m.r. spectral properties consistent with their gross structures. Analysis of C–D stretching vibrations has been used to determine the orientation of deuterium substituents in cyclohexane systems,[13] and recently a ^{1}H n.m.r. study with use of a lanthanide shift reagent has helped to locate and determine the extent of deuterium labelling in certain cyclohexanols.[14] Use of Eu(dpm)$_3$ with (II) in carbon tetrachloride gave an expanded ^{1}H n.m.r. spectrum in which signals assigned to the α-, β-(*cis* and *trans*), and γ-(*cis* and *trans*) protons were well resolved. Unfortunately the signals due to the five δ- and ε-protons positions could not be separated even with large concentrations of the shift reagent. Hence, for the moment the stereochemical assignments in this work rest on the mode of synthesis, which employs highly stereoselective reactions, although Wiseman's [13] recent use of ^{2}H n.m.r. to distinguish *cis*- and *trans*-1-t-butyl[4-^{2}H$_1$]cyclohexane may yet provide the desired spectroscopic confirmation.

TABLE 1

Kinetic isotope effects, in deuteriated cyclo-octyl bromobenzenesulphonates in 0.02M-NaOAc–HOAc at *ca.* 36 °C

Bromobenzenesulphonate	No. of runs	k_H/k_D * (mean and standard deviation)
[1-^{2}H$_1$]Cyclo-octyl	5	1.178 ± 0.009
trans-[5-^{2}H$_1$]Cyclo-octyl	4	1.124 ± 0.008
cis-[5-^{2}H$_1$]Cyclo-octyl	5	1.044 ± 0.010

* Corrected for incomplete deteriation.

TABLE 2

Analysis of acetate product *

Substrate bromobenzenesulphonate	Product acetate (%) [1-^{2}H$_1$]Cyclo-octyl	[5-^{2}H$_1$]Cyclo-octyl
[1-^{2}H$_1$]Cyclo-octyl	50.6	49.4 [a,c]
trans-[5-^{2}H$_1$]Cyclo-octyl	4.2	95.8 [b,c]
cis-[5-^{2}H$_1$]Cyclo-octyl	40	60 [b,c]

[a] By 90 MHz ^{1}H n.m.r. of recovered acetate. [b] By conversion of acetate into corresponding ketone and mass spectral determination of ^{2}H$_1$ incorporation. [c] Corrected for incomplete ^{2}H$_1$ labelling in substrate.

* Cyclo-octene (72%) and cyclo-octyl acetate (28%) are produced from the buffered acetolysis of cyclo-octyl bromobenzenesulphonate at 35 °C and are stable to the reaction conditions. ^{1}H N.m.r. analysis of the cyclo-octyl acetate formed from solvolysis of [1-^{2}H$_1$]cyclo-octyl bromobenzenesulphonate showed it to contain 49.4% of the [1-^{1}H]-isomer.

The buffered acetolyses were monitored spectrophotometrically [15] in paired runs with the all-protium isomer and the results are shown in Table 1. The acetate products were recovered from the solvolyses and analysed by either ^{1}H n.m.r. spectroscopy or conversion into the corresponding ketones and mass spectrometry.*

* Deuteriated cyclo-octanols were analysed by mass spectrometry either as the corresponding trimethylsilyl ethers or as the corresponding cyclo-octanone. We are grateful to the P.C.M.U. (Harwell) and the Glenochil Research Station, Distillers Company Ltd., for mass spectral facilities.

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DISCUSSION

The kinetics of solvolysis of the deuteriated substrates could be complicated by internal return, *e.g.* in the case of *trans*- and *cis*-[5-^{2}H$_1$]cyclo-octyl *p*-bromobenzenesulphonates it has been established (see later) that it is predominantly the *trans*-5-substituent which migrates. Thus rearrangement by internal return of the *cis*-[5-^{2}H$_1$]-isomer generates the [α-^{2}H$_1$]-bromobenzenesulphonate, and the observed k_H/k_D value is expected to be slightly greater than the true value. In this context the *trans*-[5-^{2}H$_1$]-case is uncomplicated, as rearrangements by *trans*-5-migration and internal return are equivalent.

Roberts and Anderson [7] investigated this phenomenon by monitoring the acetolysis of [α-^{2}H$_1$]cyclo-octyl tosylate by ^{1}H n.m.r. and estimated that, at $t_{\frac{1}{2}}$, as much as 20% of the remaining tosylate had rearranged. We have repeated the experiment with [α-^{2}H$_1$]cyclo-octyl bromobenzenesulphonate in 1M-NaOAc–HOAc and find that the amount of rearranged material in the remaining bromobenzenesulphonate rises in *ca.* $t_{\frac{1}{2}}$ to an approximately constant amount of 5—6%. This is not enough to cause a detectable deviation from the good first-order fit observed, and should only slightly depress the observed value of k_H/k_D from the true value. Hence, the observed α-kinetic isotope effect, $k_H/k_D = 1.18$, for cyclo-octyl bromobenzenesulphonate is within the range [16] usually associated with systems undergoing solvolysis devoid of neighbouring group participation and substitution by deuterium of the *cis*-hydrogen atom at C-5 has little, if any, effect on the reaction rate ($k_H/k_D = 1.04$).

On the other hand the ionization taking place at C-1 *of cyclo-octyl bromobenzenesulphonate obviously induces a significant change in the vibrational force constants associated with the* trans-*hydrogen atom at* C-5, $k_H/k_D = 1.12$. It is notable that more than half the total effect detected by Roberts and Anderson [7] for the [^{2}H$_{10}$]cyclo-octyl tosylate ($k_H/k_D = 1.21$) is associated with this position. Murr and Donnelly have discussed [17] the influence of ion-pair intervention on secondary isotope effects in solvolytic processes. Consideration of the relationships derived by these authors, together with the low amounts of internal return observed in the acetolysis of cyclo-octyl bromobenzenesulphonate, leads us to conclude that our observed solvolytic isotope effects are to be associated mainly with the primary ionization step and not with any ion-pair partitioning phenomenon.

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[16] A. Streitwieser, R. H. Jagow, R. C. Fahey, and S. Susuki, *J. Amer. Chem. Soc.*, 1958, **80**, 2326; S. Seltzer, *ibid.*, 1961, **83**, 2625; V. J. Shiner, jun., M. W. Rapp, E. A. Halevi, and M. Wolfsberg, *ibid.*, 1968, **90**, 7171; A. Streitwieser and G. A. Dafforn, *Tetrahedron Letters*, 1969, 1263; J. M. Harris, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 2551; V. J. Shiner, jun., and R. D. Fisher, *ibid.*, p. 2553.

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If one chooses to regard the acetolysis of cyclo-octyl *p*-bromobenzenesulphonate as composed of two independent, competing solvolytic processes,[18] *viz.* anchimerically unassisted (k_S) and anchimerically hydrogen-assisted (k_S), then the formula (i) can be applied where

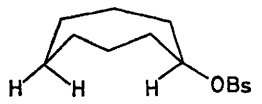
$$I = I_\Delta[(1 + k_\Delta/k_S)/(k_\Delta/k_S + I_\Delta/I_S)] \qquad \text{(i)}$$

I, I_Δ, and I_S are isotope factors on total, anchimerically assisted, and solvent-assisted processes. If a purely primary isotope effect is assumed (*i.e.* $I_S = 1$) and an $I_\Delta = 2$ is chosen in the range found for intramolecular and intermolecular hydride shifts [18-21] then a value of k_Δ/k_S may be extracted, and consequently F_Δ, the fraction of the reaction which proceeds by anchimerically assisted process, may be calculated to be *ca.* 22%. It is to be emphasized, however, that there is no satisfactory estimate of I_Δ, and indeed F_Δ is not particularly sensitive to increases in the assumed value of I_Δ; *e.g.* with $I_\Delta = 3$, $F_\Delta = 18\%$, but as $I_\Delta \longrightarrow I$ F_Δ rises rapidly, *i.e.* at $I_\Delta = 1.5$, $F_\Delta = 51\%$.

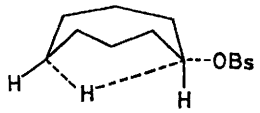
Alternatively the solvolysis could be envisaged as a single pathway with the observed k_H/k_D for (I) brosylate considered as a *secondary effect.*[22]

To paraphrase Shiner,[23] there are five possible interactions that could take place between the reacting centre and the *trans*-5-hydrogen atom: (i) the developing cation could exert a through-bond inductive effect on the ε-C–H bond; (ii) the developing vacant orbital on C-1 might overlap directly with the ε-C–H bond (a hyperconjugative effect); (iii) the departing bromobenzenesulphonate anion and the accompanying spatial rearrangements might release some non-bonded repulsion; (iv) there may be specific interactions between a ε-hydrogen atom and adjacent solvent molecules * enhanced by the polar character of the transition state; and (v) the carbon–bromobenzenesulphonate dipole produced in the transition state may influence the ε-H by a direct field effect. Hyperconjugation [25] appears to be the currently preferred interpretation for such effects although doubtless a case could be made [26] for the strain-release argument.

It is clear that the transition state geometry for this reaction must place C-1 and C-5 in close proximity, and when this is taken in conjunction with recent n.m.r. studies on the conformational preference of cyclo-octanone [27] and monosubstituted cyclo-octanes [28] it is tempting to envisage the solvolysis proceeding from a boat-chair ground state (III) (which allows close approach of C-1 and the *trans*-C-5 position) to the corresponding boat-chair transition state (IV). However in order to reconcile Cope's finding that buffered acetolysis of [1,2,2,8,8-$^2H_5$]cyclo-octyl bromobenzenesulphonate is accompanied by 53% transannular C-5 ⟶ C-1 hydride shift [29] (in both the olefin and acetate products) with the low k_H/k_D for (I) brosylate (see above) it is necessary to add the rider that most of the hydride shift takes place at the intimate and/or solvent separated ion-pair stage(s).[30]



(III)



(IV)

Although there is a well-established *trans*-5 stereochemical dependence on the extent of hydride migration in the solvolysis of 5-substituted cyclo-octanes,[31] this had not been established for cyclo-octyl bromobenzenesulphonate itself and so the deuteriated cyclo-octyl acetate samples produced from both (I) and (II) bromobenzenesulphonates were converted into cyclo-octanone by reduction with lithium aluminium hydride and subsequent Jones oxidation; † the resultant trace incorporation is shown in Table 2. It is clear that the percentage deuterium retained (95.8%) in the cyclo-octanone derived from (I) brosylate is a composite figure

* Solvent effects on β-secondary kinetic isotope effects are known to be small [24] but there is no evidence that this would be true for the cyclo-octyl system. Indeed a change to solvent systems of lower nucleophility might well allow hyperconjugative overlap from the *trans*-5-H to play a more significant role.

† Control experiments established that this sequence does not result in any deuterium loss.

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[27] F. A. L. Anet, Abstracts, Twentieth National Organic Chemistry Symposium of the American Chemical Society, Burlington, Vermont, 1967, p. 87; F. A. L. Anet, M. St. Jacques, and P. M. Henrichs, *Intra-Sci. Chem. Reports*, 1970, **4**, 251; F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 1347.

[28] F. A. L. Anet and M. St. Jacques, *J. Amer. Chem. Soc.*, 1966, 2585, 2586; J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *ibid.*, 1969, **91**, 1386.

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which reflects the extent of reaction without rearrangement *and* with *trans* C-5 ^{2}H-shift, whereas the percentage deuterium loss (4.2%) in the ketone is a direct measure of *cis*-5-hydride shift.

Conversely the percentage of [$^2H_1$]cyclo-octanone (40%) from (II) bromobenzenesulphonate reflects the *trans*-5-H shift whereas the [$^2H_1$]cyclo-octanone figure (60%) is a consequence of no rearrangement added to a *cis*-5-^{2}H shift. Whether or not one argues that the presence of a C-5 deuterium atom exerts an α-secondary kinetic isotope effect [17] on the migration of the other C-5 hydrogen atom, it is clear that there is a 10 : 1 migration preference for the *trans*-5-hydride. In a study of a related cyclo-octyl system, Traynham [30] has demonstrated that such transannular hydride migrations occur to nearly the same extent in both the intimate and solvent-separated ion pairs, but it remains to be established whether the above stereoselectivity is operative at both intermediate stages, or, for example, whether the migration at the intimate ion-pair stage is stereospecifically *trans*-5-H.

There are three additional aspects of the mechanism of these rearrangements which warrant further examination: (i) the stereochemistry of the substitution processes which occur at the site of hydride *departure*, *e.g.* the stereochemistry of the 3,2-hydride shift/solvent capture process associated with the solvolysis of 2-cyclohexyl-1-methylpropyl tosylate involves the solvent molecule reacting at the tertiary centre *from the same side* as the departing hydride; [21] (ii) the sensitivity of the above remote isotope effect to solvent [24] and substituent effects; theoretical arguments and experimental data have been presented [32] in support of the view that k_H/k_D values for hydride transfer should be markedly less sensitive to substituents than proton transfer processes; (iii) the relationship between extent of hydride migration and/or participation and orbital alignment of the developing carbocation and the transannular C–H bond; stereoelectronic effects on 1,2-hydride shifts and associated hyperconjugation are well established [33] but the situation as regards the transition state for inter- and transannular intra-hydride shifts is more confused. A linear arrangement ($\overset{\delta+}{C}\cdots\overset{\delta-}{H}\cdots\overset{\delta+}{C}$) has been suggested on the basis of the facility of hydride transfer between triarylmethyl cations [34] whereas a triangular array has been proposed to accommodate low k_H/k_D values and a similarity with aliphatic electrophilic substitution reactions.[35] We expect to comment on some of these problems in a future communication.

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EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 157G or 457G spectrophotometer. N.m.r. spectra were determined for solutions in carbon tetrachloride with a Perkin-Elmer R32 spectrometer (90 MHz) with tetramethylsilane as an internal standard. The mass spectra were determined on an MS902 (P.C.M.U., Harwell) or an RMU-7 instrument (Glenochil). Analytical g.l.c. was performed with a Perkin–Elmer F11 with either a 2 m × $\frac{1}{8}$ in stainless steel column [packings 5% FFAP and 2½% OV-1 Silicone on Chromosorb-G (80—100 mesh)] at 150 °C (carrier gas nitrogen; inlet pressure, 20 lb in^{-2}) or a 50 m capillary column with TCEP stationary phase. Light petroleum refers to the fraction of b.p. 40—60°. Silica-gel GF_{254} was employed for both analytical and preparative t.l.c.

cis-Cyclo-octane-1,5-diol was prepared from 9-BBN by the literature method.[11]

[1-$^2H_1$]Cyclo-octanol was prepared by reduction of cyclo-octanone with lithium aluminium deuteride. ^{1}H N.m.r. showed the alcohol to be at least 97% α-$^2H_1$.

trans-[5-$^2H_1$]*Cyclo-octanol* (I).—A solution of *cis*-cyclo-octane-1,5-diol (1.04 g, 0.008 mol) toluene-*p*-sulphonic acid (50 mg), and dihydropyran (0.8 g) in anhydrous tetrahydrofuran (10 ml) was heated briefly to reflux and set aside overnight (t.l.c. showed two spots, neither of which corresponded to starting diol). After removal of solvent the residual oil was dissolved in dry pyridine (20 ml); the solution was cooled to 0 °C, treated with recrystallised toluene-*p*-sulphonyl chloride (3.0 g), set aside overnight, and then worked up in the usual manner to give a clear viscous oil (3.3 g) which showed no OH or C=O i.r. bands. This mixture of bistetrahydropyranyl ether and monotosylate monotetrahydropyranyl ether was dissolved in anhydrous tetrahydrofuran (5 ml) and treated with a solution of lithium triethylborodeuteride (10 ml; 1M) in tetrahydrofuran. The mixture was heated under reflux overnight, cooled, quenched with water, treated with alkaline hydrogen peroxide, and extracted with light petroleum. Removal of the solvent left a clear oil (1.38 g) which was dissolved in methanol, treated with concentrated hydrochloric acid (2 drops), and set aside overnight. This mixture was treated with aqueous sodium hydrogen carbonate and thoroughly extracted with light petroleum; the combined extracts were washed with water, dried, and evaporated to give a mixture of *trans*-[$^2H_1$]cyclo-octanol and *cis*-cyclo-octane-1,5-diol as a clear oil which was easily separated by preparative t.l.c. (developing solvent diethyl ether). Kugelrohr distillation then gave the *trans*-[$^2H_1$]cyclo-octanol (0.12 g), pure by t.l.c. and g.l.c. analysis (FFAP, TCEP, and OV-1 stationary phases); δ_H (CCl_4) 1.55 (7 H, unresolved), 3.1 (1 H, s), and 3.65 (1 H, m), $\nu_{max.}$ (CCl_4) 3 610, 3 350, 2 900, 2 180, 1 470, 1 450, 1 360, 1 120, 1 080, 1 050, 980, 950, and 920 cm^{-1}. The mass spectrum of the corresponding trimethylsilyl ether showed the sample to contain 76% [$^2H_1$]-material whereas the corresponding ketone [Jones oxidation of (I)] had 83%.

cis-[5-$^2H_1$]*Cyclo-octanol* (II).—The *trans*-alcohol (I) was converted into the toluene-*p*-sulphonate by the Tipson procedure [10] and purified by low-temperature crystallisation from light petroleum. This tosylate [(II) tosylate] (0.32 g)

[34] N. Deno, G. Saines, and M. Spangler, *J. Amer. Chem. Soc.*, 1962, **84**, 3295.

[35] E. S. Lewis and M. C. R. Symons, *Quart. Rev.*, 1958, **12**, 230; M. F. Hawthorne and E. S. Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 4296.

was then dissolved in anhydrous benzene (2 ml), treated with a solution of tetrabutylammonium acetate (0.6 g) in benzene (5 ml), and heated under reflux for 2 h. The cooled mixture was then washed with water, dried, and evaporated, and the residual oil was distilled (Kugelrohr; 15 mmHg) to give *cis*-[5-$^2H_1$]cyclo-octyl acetate (0.12 g), pure by g.l.c. (FFAP stationary phase). Brief treatment of this acetate with lithium aluminium hydride in the usual manner gave *cis*-[5-$^2H_1$]cyclo-octanol (0.074 g), pure by t.l.c. and g.l.c. (FFAP and OV-1 stationary phases), 91% [$^2H_1$]-material by mass spectrometric analysis of the corresponding trimethylsilyl ether and 90% by mass spectrometry of the corresponding ketone; δ_H (CCl_4) 1.55 (7 H, m, unresolved), 3.4 (1 H, s), and 3.65 (1 H, m); $\nu_{max.}$ (CCl_4) 3 610, 3 350, 2 960, 2 170, 1 570, 1 550, 1 365, 1 055, 990, 920, and 890 cm^{-1}.

cis- *and* trans-[5-$^2H_1$]*Cyclo-octyl* p-*Bromobenzenesulphonates*.—These were prepared by the Tipson procedure [10] and purified by low-temperature recrystallisation from pentane.

Product Analyses.—The appropriate bromobenzenesulphonate (*ca.* 70 mg) was dissolved in buffered acetic acid (5 ml; HOAc 0.1M in NaOAc + 1% Ac_2O) and kept in a sealed flask at 35 °C for at least 30 half-lives (48 h). The mixture was then poured into water (20 ml) and thoroughly extracted with pentane. The combined extracts were then washed with water (2 × 10 ml) and saturated aqueous sodium hydrogen carbonate and dried, and the solvent was carefully removed (Vigreux column). The oily residue (olefin + acetate) was then dissolved in dry ether (5 ml) and treated with lithium aluminium hydride (2 h; room temperature); the mixture was then quenched with saturated aqueous sodium sulphate and the ether layer was separated and dried. The solvent was carefully removed and the residual oil was dissolved in light petroleum and adsorbed on a short column of silica gel. Elution with the same solvent gave the olefin fraction; further elution with ether gave the alcohol, which was subsequently treated with Jones reagent at 0 °C and the resultant cyclo-octanone was isolated by preparative t.l.c.

In the case of [1-$^2H_1$]cyclo-octyl bromobenzenesulphonate the acetate product was isolated by the above procedure and the % hydride shift was determined by ^1H n.m.r. (integration of the C*H*OAc signal relative to CH_3CO_2R).

Kinetic Measurements.—Buffered acetic acid (2 ml; HOAc–0.02M-NaOAc) was placed in each of three 1 cm u.v. cells which were then placed in the thermostatted block of a Gilford 2400 u.v. spectrophotometer and allowed to equilibrate to 35 °C for at least 1 h. The appropriate [$^2H_1$]-bromobenzenesulphonate (1 μl) was then added to one of the cells and cyclo-octyl bromobenzenesulphonate (1 μl) was added to another (a syringe was used; the bromobenzenesulphonate melts on warming with the hand); the cells were shaken for 1 s and then the solvolytically induced change in absorbance at 273 nm was monitored as a function of time. Points from the resultant curves were employed in a local version of the LETAGROP programme to give the rate data recorded (Table 3); all gave good first-order kinetics with an accuracy of ±0.5%.

TABLE 3

Solvolysis of cyclo-octyl and [5-$^2H_1$]cyclo-octyl bromobenzenesulphonates; paired runs in 0.2M-NaOAc–HOAc

Temp. (°C) (±0.1°)	Cyclo-octyl bromobenzenesulphonate $k \times 10^2$/min^{-1}	[1-$^2H_1$] Cyclo-octyl bromobenzenesulphonate $k \times 10^2$/min^{-1}	k_H/k_D
36.1	2.335 (±0.016)	2.013 (±0.009)	1.160
36.2	2.365 (±0.010)	2.009 (±0.010)	1.177
36.2	2.376 (±0.009)	2.006 (±0.007)	1.184
36.2	2.359 (±0.016)	2.012 (±0.009)	1.172
35.8	2.331 (±0.008)	2.001 (±0.009)	1.165

k_H/k_D (mean and standard deviation) = 1.172 ± 0.009; corrected for 97% $^2H_1$ k_H/k_D = 1.178 ± 0.009.

	Cyclo-octyl bromobenzenesulphonate	*trans*-[5-$^2H_1$] Cyclo-octyl bromobenzenesulphonate	
36.2	2.374 (±0.017)	2.162 (±0.017)	1.098
35.8	2.295 (±0.014)	2.105 (±0.017)	1.090
36.2	2.374 (±0.009)	2.140 (±0.010)	1.109
36.3	2.445 (±0.014)	2.214 (±0.009)	1.105

k_H/k_D (mean and standard deviation) = 1.101 ± 0.008; corrected for 83% $^2H_1$ k_H/k_D = 1.124 ±0.008.

	Cyclo-octyl bromobenzenesulphonate	*cis*-[5-$^2H_1$] Cyclo-octyl bromobenzenesulphonate	
36.8	2.563 (±0.009)	2.425 (±0.013)	1.057
36.8	2.544 (±0.009)	2.459 (±0.007)	1.035
36.8	2.584 (±0.008)	2.487 (±0.013)	1.039
36.8	2.574 (±0.012)	2.497 (±0.012)	1.031
36.8	2.594 (±0.007)	2.511 (±0.022)	1.033
Mean and standard deviation	2.572 (±0.019)	2.475 (±0.034)	

k_H/k_D (mean and standard deviation) = 1.039 ± 0.010; corrected for 90% $^2H_1$ k_H/k_D = 1.044 ± 0.010.

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