Preparation and Solvolysis of *trans,trans,trans*-Tricyclo[7.3.1.$0^{5,13}$]tridecan-3-yl Toluene-*p*-sulphonates in Acetic Acid and Aqueous Hexafluoropropan-2-ol. The Role of Non-chair Conformers and the Question of Internal Return in the Limiting S_N1 Solvolytic Mechanism

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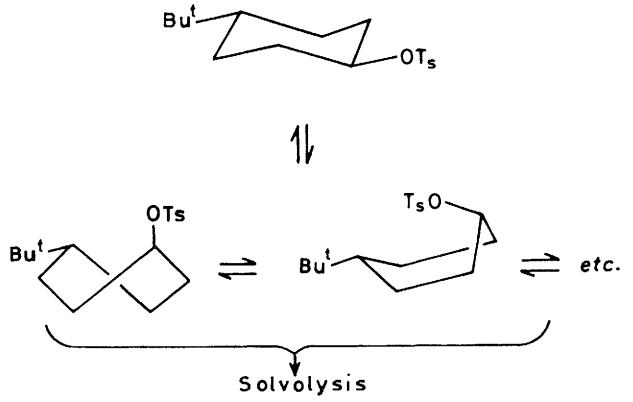
Details are reported of a general synthesis of the epimeric *trans,trans,trans*-tricyclo[7.3.1.$0^{5,13}$]tridecan-3-ols and the corresponding toluene-*p*-sulphonates, (**5a** and **b**). Both compounds react in buffered acetic acid slightly more slowly than simpler unbridged axial and equatorial cyclohexyl toluene-*p*-sulphonates, but the axial:equatorial epimeric rate ratio is very similar at 3.4:1 (50 °C) and is quite different from the divergent values obtained for bridged systems. The epimeric rate ratio is even smaller in 97:3 (w/w) hexafluoropropan-2-ol–water (97HFIP), 1:1 at 25 °C, and the equatorial compound is estimated to be the more reactive in this medium below *ca.* 6 °C. Remarkably, the standard enthalpy of activation for solvolysis in 97HFIP is lower for the equatorial than the axial isomer. These results, the role of non-chair conformers for the equatorially substituted isomer, and the nature of the rate-determining step in the limiting S_N1 solvolytic mechanism generally are discussed.

Knowledge, let alone understanding, of the relationship between reactivity and stereochemistry of cyclohexane compounds is far from complete. The principal difficulty arises from the conformational freedom of simple six-membered rings which allows interconversion of axial and equatorial substituents by ring inversion at rates much faster than the rates of most chemical reactions. The problem was first addressed by employing a remote t-butyl group which was believed to act as a conformational lock but which would not otherwise interfere with the reaction centre.[1] More recent kinetic[2,3] and product analytical studies[4] on 4-t-butylcyclohexyl arenesulphonates have shown that, whereas the *cis*-isomer (**1a**) may react from its ground-state conformation with an unambiguously axial nucleofuge, the *trans*-isomer (**1b**) reacts predominantly, if not exclusively, through less stable but more reactive non-chair, flexible conformers (Scheme 1). Consequently, we still know



Scheme 1.

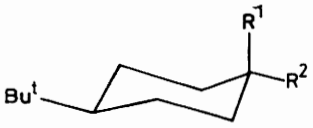
very little about the true reactivity of unambiguously equatorial nucleofuges in solvolytic reactions of simple cyclohexane substrates.

Other attempts to restrict the conformational freedom of cyclohexanes have involved adding a second ring to give decalins (**2**),[5,6] and bridging to give, for example, bicyclo-[3.2.1]octanes (**3**).[7,8] It appears that decalins such as (**2b**) are still sufficiently flexible to allow reactions to proceed through non-ground-state conformers,[4-6] and the six-membered ring of bicyclo-octanes is distorted from regular cyclohexane geometry (and therefore strained) to such an extent that these compounds are unsuitable as models for simple unbridged cyclohexanes.[8-10] Adamantane and its derivatives (**4**) have no conformational freedom and are relatively strain-free.[10] However, a substituent X at C-2 of (**4**) is axial to one six-membered ring and, at the same time, equatorial to another. Moreover, the branching at C-1 and -3 allows carbon–carbon hyperconjugation in a solvolytic reaction involving a leaving group at C-2 and hence the carbocationic intermediate is not simple.[11]

The requirement, then, is a cyclohexane with restricted conformational freedom, but one which is free of substituents close to the reaction site, and without the strain associated with the ground-state deformations of bridged systems. Molecular models and force-field calculations suggested that the all-*trans*-fused tricyclo[7.3.1.$0^{5,13}$]tridecane system (**5**) in its all-chair conformational ground state is not more strained than cyclohexane itself,[12-15] whereas any other conformation corresponding to an energy minimum such as (**6**) is at least 30 kJ mol^{-1} more strained. The diastereoisomeric toluene-*p*-sulphonates (**5a, b**) derived from the corresponding alcohols (**5c, d**) were chosen, therefore, as our first solvolytic substrates based upon this aesthetically pleasing carbocyclic system.[16]

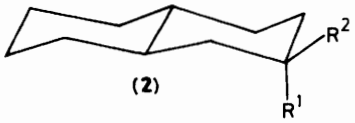
The parent hydrocarbon (**5e**), its stereoisomers, and various simple substituted and unsaturated derivatives are known, but no general versatile synthesis, particularly of 3-substituted compounds, had been reported at the beginning of our study. Of the four possible ring geometries of tricyclo[7.3.1.$0^{5,13}$]-tridecane, derivatives of the all-*trans*,[17-20] the all-*cis*,[19-21] and the *cis,cis,trans*[19-21] systems (**5**), (**7**), and (**8**) are known. The all-*trans* configuration occurs naturally in sponges as diterpenoid isocyanides and formamides whose structures were established by *X*-ray crystallographic and n.m.r. studies.[17] Unsaturated analogues occur naturally as phenalenones and have been reviewed recently.[22]

One obvious entry to the tricyclic system (**5**) is to append a three-carbon residue to an α-decalone and then cyclize it onto the aromatic ring. Compound (**9a**) was first made in modest yield by this route, anhydrous hydrogen fluoride being more effective



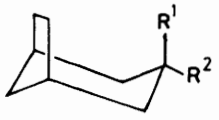
(1)

a; R^1 = OTs, R^2 = H
b; R^1 = H, R^2 = OTs
c; R^1 = NH_2, R^2 = H
d; R^1 = H, R^2 = NH_2



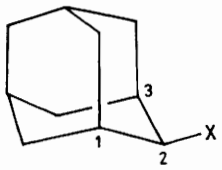
(2)

a; R^1 = OTs, R^2 = H
b; R^1 = H, R^2 = OTs

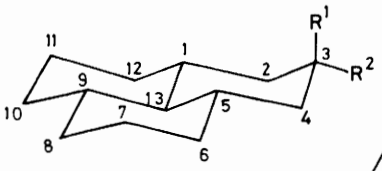


(3)

a; R^1 = OTs, R^2 = H
b; R^1 = H, R^2 = OTs
c; R^1 = NH_2, R^2 = H
d; R^1 = H, R^2 = NH_2

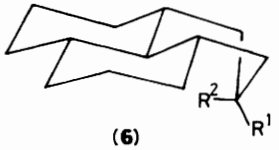


(4)



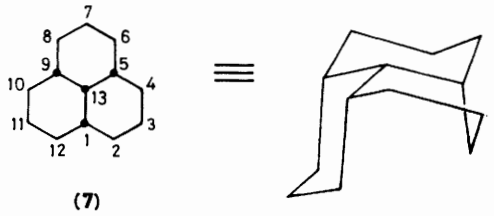
(5)

a; R^1 = OTs, R^2 = H
b; R^1 = H, R^2 = OTs
c; R^1 = OH, R^2 = H
d; R^1 = H, R^2 = OH
e; R^1 = R^2 = H
f; R^1 R^2 = O

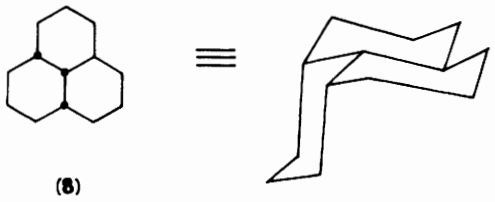


(6)

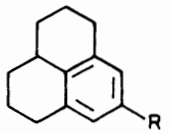
a; R^1 = H, R^2 = OTs
b; R^1 = R^2 = H



(7)

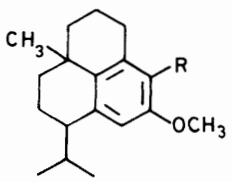


(8)



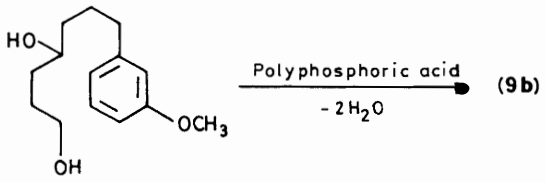
(9)

a: R = H
b: R = OCH_3



(11)

R = H, Pr^i



(10)

Scheme 2.

Results

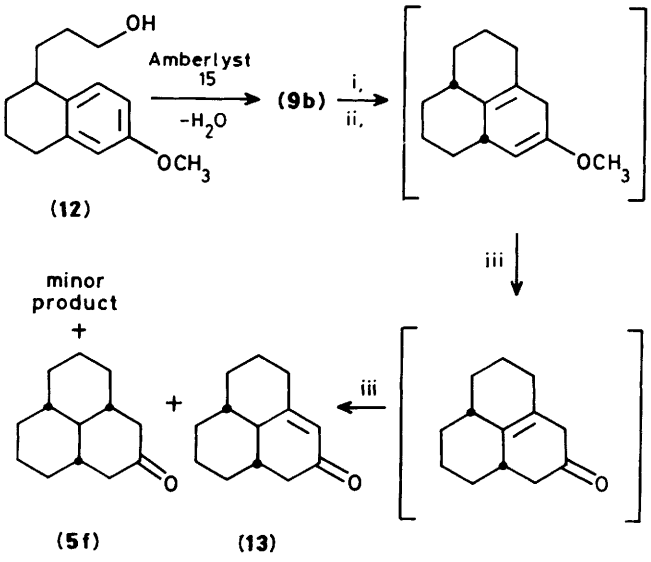
Preparations.—Our synthesis of (**5a**, **b**) started from the methoxy-substituted compound (**9b**) which was prepared by an improved method of cyclization of (**12**).[24,30] A polymer-supported acid resin (Amberlyst 15) in refluxing light petroleum gave a cleaner sample in better yield than polyphosphoric acid and without the hazard associated with anhydrous hydrogen fluoride. A modification to the Wilds and Nelson[31] procedure for the Birch reduction[32] of (**9b**) followed by hydrolysis gave 43% of the enone (**13**), 16% of a saturated ketone by over-reduction, and *ca.* 2% of an isomer of (**13**). The hydrolytic step involved a number of intermediates and had to be monitored carefully by g.l.c. since the yield of (**13**) decreased if the reaction was left too long. None of the intermediates in the conversion of (**9b**) into (**13**) were characterized, but on the basis of the accepted mechanisms[32] and by analogy with the reaction of the very closely related 2-methoxytetrahydronaphthalene itself,[31] the route in Scheme 3 seems probable. The structure of the enone (**13**) was proposed on the basis of analytical data ($C_{13}H_{18}O$), n.m.r. (single vinylic signal δ 5.75) and i.r. ($\bar{\nu}_{max.}$ 1 650 cm^{-1}) evidence, and was confirmed by *X*-ray crystallography.[33] The very minor product (*ca.* 2%) was also identified as $C_{13}H_{18}O$ by mass spectrometry and had a 60 MHz n.m.r. spectrum very similar to that of the enone (**13**) (vinylic signal δ 5.75) and a very similar αβ-unsaturated carbonyl band in the i.r. ($\bar{\nu}_{max.}$ 1 665 cm^{-1}). It remains unidentified but is almost certainly a stereoisomer of (**13**).

The enone (**13**) was reduced by dissolving metals to give two products in proportions determined by the precise experimental conditions.[34] One is the same saturated ketone that had been obtained as a by-product in the Birch reduction and hydrolysis of the arene (**9b**) (see above), the other is an alcohol. The

Table 1. ^{13}C N.m.r. data for compounds (**5c**, **d**, and **f**)[a]

Carbon	Chemical shift δ (p.p.m.) (multiplicity)[b]		
	(**5c**)	(**5d**)	(**5f**)
3	66.92 (d)	69.86 (d)	210.23 (s)
2,4	40.55 (t)	43.50 (t)	49.01 (t)
1,5	34.71 (d)	39.78 (d)	42.41 (d)
6,12	34.22 (t)	34.16 (t)	34.60 (t)
7,11	25.93 (t)	25.96 (t)	25.85 (t)
8,10	34.06 (t)	34.02 (t)	33.86 (t)
9	41.21 (d)	41.46 (d)	41.80 (d)
13	53.38 (d)	52.61 (d)	52.17 (d)

[a] In $CDCl_3$ solution, 80 MHz, chemical shifts are downfield from Me_4Si. [b] Multiplicity of the partially decoupled signals.



Scheme 3. *Reagents:* i, Li–NH_3–THF, −78 °C; ii, EtOH–NH_4Cl–water; iii, water–THF–H_2SO_4

ketone ($C_{13}H_{20}O$; $\bar{\nu}_{max.}$ 1 715 cm^{-1}) had only eight lines in its ^{13}C n.m.r. spectrum (Table 1) which, together with its mode of formation from (**13**), requires structure (**5f**). The assignments of the ^{13}C signals due to the carbonyl carbon (C-3), the two carbons flanking the carbonyl (C-2, -4), and the central carbon (C-13) are based upon the observed multiplicities of the partially decoupled spectrum and the chemical shifts of the equivalent carbons in 4-t-butylcyclohexanone.[35] The assignments for the tertiary carbons C-1, -5 and C-9 are based upon the relative intensities of the doublets at δ 42.42 and 41.80 p.p.m., the former being twice that of the latter. The assignments of the three remaining triplets are more tentative.

The alcohol ($C_{13}H_{22}O$) also had only eight lines in its ^{13}C n.m.r. spectrum (Table 1) and gave the ketone (**5f**) upon oxidation.[36] Its ^1H n.m.r. spectrum included a one-hydrogen multiplet at δ 3.65 of 20 Hz peak width at half-height. This is characteristic of equatorial cyclohexanols[7,37] and confirms structure (**5d**) for this alcohol.

The same alcohol and an isomer were obtained from ketone (**5f**) in the ratio 4:1 and 1:6.5 upon reduction with lithium aluminium hydride and lithium tri-s-butylborohydride, respectively. As expected, the second alcohol also showed only eight lines in the ^{13}C n.m.r. spectrum (Table 1), and a one-hydrogen multiplet in its ^1H n.m.r. spectrum at δ 4.10, peak width at half-height only 6.35 Hz which confirm it as (**5c**) with an axial hydroxy group.[7,35,37] The selectivity of (**5f**) towards these different reducing agents is in accord with results from other systems.[8,38]

The toluene-*p*-sulphonates (**5a**, **b**) were made by the Tipson procedure[39] and their spectroscopic data were fully in agreement with the structural assignments.

Rates of Solvolysis.—Buffered acetic acid and 97:3 (w/w) hexafluoropropan-2-ol–water (97HFIP) were used as solvolytic media. The former has been used over many years and allows ready comparison of the results of our new system with those of very many other compounds.[40] It is only weakly ionizing and modestly nucleophilic. The latter is typical of a number of media relatively new in use; it is highly ionizing and only very weakly nucleophilic.[3,41] Sodium acetate in the one and water in the other act as bases to prevent toluene-*p*-sulphonic acid causing any complicating secondary reactions. Our methodology and instrumentation have already been described.[3,8,42] No deviations from strict first-order kinetics were detected, nor was there any sign of curvature in the four Eyring plots. Rate constants for acetolysis of (**5a** and **b**) between 66 and 91 °C were reported in our preliminary communication[43] and are included in Table 2 along with the new results for reaction of (**5a** and **b**) and (**1a** and **b**)[3] in 97HFIP.

Discussion

Compound (**5b**) with the ground-state equatorial leaving group is less reactive in buffered acetic acid than (**1b**),[1] (**2b**),[5] and *cis,cis*-3,5-di-t-butylcyclohexyl toluene-*p*-sulphonate[44] as had been expected. However, the epimer (**5a**) is also less reactive than the corresponding axially substituted cyclohexyl toluene-*p*-sulphonates.[1,5,44] Consequently, the acetolysis rate ratio (**5a**):(**5b**) is not larger, as we had anticipated, than that for other unbridged cyclohexyl epimeric pairs, but very similar. The same differences between ground-state axial and equatorial substrates appear to exist for (**5a** and **b**) as for the other pairs, and the new tricyclic system of fused cyclohexane rings has failed to shed new light on the original problem. Either (**5b**) and the other equatorially substituted cyclohexyl analogues react directly in their ground-state conformation[1] as some have maintained[7,45] or (**5b**) is not appreciably less able to react through a non-chair form. The former possibility leaves too great a body of experimental work, both kinetic and product analytical, quite inexplicable. In particular it cannot account for the product fall-out from, for example, the solvolysis of (**1a**, **b**)[4] and bicyclo[3.2.1]octan-3-yl toluene-*p*-sulphonates (**3a**, **b**):[8a] predominant elimination, unrearranged substitution with inversion of configuration, and substantial product *via* 1,2-hydride shift, all in relative amounts very similar from both *cis* and *trans* (*endo* and *exo*) substrates. This is in marked contrast to the outcome of the deamination of the correspondingly substituted cyclohexylamines (**1c**, **d**) and (**3c**, **d**), another reaction type which proceeds through carbonium ions but whose product analysis is strongly characteristic of the ground-state stereochemistry of the amino group.[46] Further, a mechanism for equatorial tosylate solvolysis from the ground-state conformation cannot adequately account for the secondary deuterium kinetic isotope effects.[2,3,8b] It appears, therefore, that the tricyclic system still does not render non-chair forms sufficiently inaccessible for the rate of acetolysis of (**5b**) to be selectively retarded.

Nevertheless, comparison of the epimeric rate ratio (**5a**):(**5b**) with those of the others included in Table 2 of our preliminary report[43] brings into sharper focus the systematic difference between unbridged cyclohexanes on the one hand, and the bridged compounds on the other. In particular, the anomalously high reactivity of the bicyclo[3.3.1]nonane system[47] is still in need of an explanation.

Table 2. Rate constants[a] and activation parameters[b] for solvolysis of (**1a** and **b**) and (**5a** and **b**)

Compound	Solvent	Temperature[d] (°C)	$10^6k/s^{-1}$	$\Delta H^{\circ\ddagger}$/ kJ mol^{-1}	$\Delta S^{\circ\ddagger}$/ J K^{-1} mol^{-1}
(**5a**)	ACOH[c]	91.25	209 ± 1	112	−8
		80.30	64.3 ± 0.3		
		67.91	15.4 ± 0.1		
		50.00	1.62[e]		
		25.00	0.0447[e]		
(**5b**)	AcOH[c]	91.28	78.9 ± 1.4	118	−1
		75.93	13.7 ± 0.1		
		66.14	4.08 ± 0.03		
		50.00	0.481[e]		
		25.00	0.0111[e]		
(**5a**)	97HFIP[f]	53.56	630 ± 2	81	−58
		45.67	278 ± 2		
		35.84	106 ± 1		
		25.38	33.6 ± 0.2		
		50.00	439[e]		
		25.00	32.1[e]		
(**5b**)	97HFIP[f]	53.71	487 ± 3	77	−73
		45.67	233 ± 1		
		35.84	91.7 ± 0.3		
		25.38	29.8 ± 0.1		
		50.00	350[e]		
		25.00	29.0[e]		
(**1a**)[g]	97HFIP[f]	51.78	842 ± 3	80	−60
		40.83	300 ± 2		
		24.78	53.8 ± 0.3		
		50.00	720[e]		
		25.00	55.5[e]		
(**1b**)[g]	97HFIP[f]	53.34	300 ± 3	84	−56
		43.12	131[h]		
		29.55	25.2 ± 0.2		
		50.00	232[e]		
		25.00	15.7[e]		

[a] Rate constants quoted are mean values of duplicate parallel runs and quoted errors are equal to or greater than the difference between the mean and the upper and lower measured values. Standard deviations on individual rate constants measured by our previously described method were normally <0.5%.[3,8,42,49] [b] Estimated errors, ⩽ 3 kJ mol^{-1} and ⩽ 7 J K^{-1} mol^{-1} in $\Delta H^{\circ\ddagger}$ and $\Delta S^{\circ\ddagger}$. [c] CH_3CO_2H, 0.05M in CH_3CO_2Na. [d] Standard deviation on the temperature, which was measured throughout each run, between 0.02 and 0.08 °C depending upon the length of the run. [e] Estimated from results at other temperatures using Eyring plots; correlation coefficients between 0.99$_6$ and 0.999999. [f] 97:3 (w/w) Hexafluoropropan-2-ol–water. [g] We thank Dr. J. T. Thompson who measured the rates for (**1a** and **b**). [h] Single measurement.

In 97HFIP, the results are even more surprising, but we do not have as large a body of other results available for comparison. At 25 °C, the axial compound is only marginally the more reactive, (**5a**):(**5b**) = 1.1, and insofar as the standard enthalpies of activation are different, that for (**5b**), the equatorial epimer, is the lower. This is unexpected by any mechanism; furthermore, because the standard entropy of activation for (**5b**) is even more negative than that for (**5a**), we have the remarkable result that the compound with the ground-state equatorial tosylate reacts *faster* at temperatures not far below ambient ($k_{(5b)} \geqslant k_{(5a)}$ when $T \leqslant 6$ °C). We were aware of no precedent for this finding, and measured the activation parameters for (**1a** and **b**) in 97HFIP for comparison. As indicated by the results in Table 2, they are normal in this respect.

Although our results do not contribute further to the proof that equatorial cyclohexyl tosylates react *via* non-chair conformers, they do bear positively upon another matter of current controversy: the question of whether or not initial ionization of simple secondary alkyl arenesulphonates is necessarily rate determining (irreversible) in limiting solvolysis in highly ionizing media.

The *minimum* enthalpy difference between the stable conformer (**5b**) and a non-chair form (**6a**), a value which is unlikely to be very solvent-dependent, is the difference between the chair and twist-boat conformers of cyclohexane itself, *ca.* 20—25 kJ mol^{-1};[13,14,48] a value calculated by molecular mechanics for the difference between (**5e**) and (**6b**) is somewhat higher, *ca.* 30 kJ mol^{-1}.[13,14] Subtracting the smallest of this range of possibilities from our experimental value of $\Delta H^{\circ\ddagger}$ 77 kJ mol^{-1} for the solvolysis of (**5b**) in 97HFIP, the rate-determining step of which almost certainly involves ionization,[3,8] gives an estimated *maximum* value of *ca.* 57 kJ mol^{-1} for the enthalpy of activation for ionization of the unstable reactive conformer (**6a**). This is appreciably less than our experimental value of $\Delta H^{\circ\ddagger}$ 81 kJ mol^{-1} for the *solvolysis* of the epimer (**5a**) in 97HFIP from its ground-state conformation by an amount well outside the possible uncertainties in the quantities involved.

In view of the similarity between the reaction sites of the chair form of (**5a**) and the non-chair form of (**5b**), *i.e.* (**6a**), a difference of >20 kJ mol^{-1} in their standard enthalpies of activation for ionization in 97HFIP is unreasonable. We regard this as quantitative evidence that ionization alone of (**5a**) cannot be the rate-determining step of its limiting solvolysis; ionization must be reversible and followed by a subsequent rate-determining step as shown in the Figure.[3,8,49,50] [The difference in standard enthalpies of formation of (**5a** and **b**) is unlikely to be more than about 8 kJ mol^{-1},[1,51] and this value is used to include (**5a** and **b**) in the common composite standard enthalpy reaction profile of the Figure.] In other words, the enthalpy of ionization of (**5a**) is augmented by the enthalpy of activation of a subsequent step of the initially formed intimate ion-pair to give a value of 81 kJ mol^{-1} for the overall solvolytic enthalpy of activation of (**5a**) in

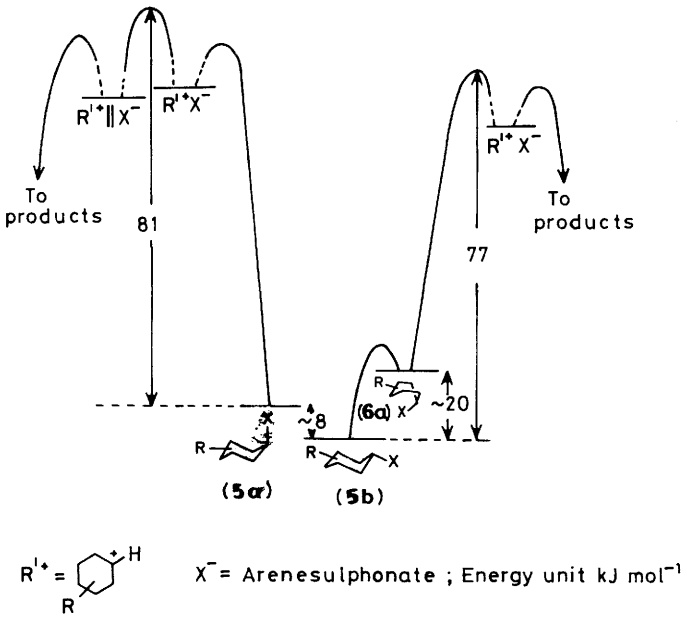


Figure. Standard molar enthalpy reaction profiles for the limiting solvolysis of epimeric cyclohexyl toluene-*p*-sulphonates (**5a** and **b**) in 97:3 hexafluoropropan-2-ol–water

97HFIP. And this is numerically similar to the overall solvolytic enthalpy of activation of (**5b**), 77 kJ mol^{-1}, which, in turn, is the sum of the enthalpy of the initial conformational conversion of (**5b**) into (**6a**) plus the enthalpy of activation for ionization of (**6a**).

Other current mechanisms for the limiting solvolysis of simple conformationally mobile cyclohexyl arenesulphonates which deny either internal return of intimate ion-pairs in some cases[52] or reaction of (initially) equatorial leaving groups *via* non-chair conformers[4,5] are quite incompatible with at least one aspect of what is, by now, a substantial body of direct experimental evidence.

Experimental

General features of our synthetic procedures have already been described.[24] Kieselgel GF254 (Merck) was used for all medium-pressure column chromatography, elution being with ether–light petroleum mixtures under nitrogen at 10 lb in^{-2}; g.l.c. analyses were carried out using a Perkin-Elmer F30 gas chromatograph fitted with a 50 ft SCOT Carbowax 20M column at 160 °C and nitrogen as carrier gas.

2,3,3a,4,5,6-*Hexahydro*-8-*methoxy*-1H-*phenalene* (**9b**).—A solution of compound (**12**)[24,30] (1.49 g, 6.77 mmol) in light petroleum (30 cm^3) containing Amberlyst 15 (Rohm and Haas Company; 1.5 g) was stirred and heated to 110 °C under a reflux condenser fitted with a Dean and Stark water trap for 10 h. The mixture was cooled, filtered, and the catalyst was washed with ether (3 × 25 cm^3). The ether–light petroleum solution was evaporated under reduced pressure to leave a pale yellow oil which was purified by medium-pressure chromatography, the elution being with ether–light petroleum (1:1), and detection by t.l.c. The product (1.15 g, 5.69 mmol, 84%) was identical with an earlier sample prepared using the polyphosphoric acid method.[24]

trans,trans-*Tricyclo*[7.3.1.0^{5,13}]*tridec*-1-*en*-3-*one* (**13**).[33]—Dry ammonia (*ca.* 90 cm^3 as liquid) was condensed into a three-necked flask containing a solution of (**9b**) (0.60 g, 3.00 mmol) in absolute tetrahydrofuran (20 cm^3) at −78 °C. Lithium wire (0.60 g, 86 mmol) was cut into pieces and added to the magnetically stirred reaction. After 15 min at −78 °C, the CO_2–acetone cooling bath was removed, then, after a further 20 min, dry ethanol (1.5 cm^3, 26 mmol) was added over 5 min. At 5 min intervals, more ethanol (20 cm^3) to quench the residual blue colour, then ammonium chloride (1.0 g, 19 mmol), and finally diethyl ether (30 cm^3) and water (30 cm^3) were added, and the mixture was allowed to come to room temperature as the ammonia evaporated. The two phases were separated and the aqueous phase was extracted with more ether. The combined ether phase was dried (Na_2SO_4), treated with charcoal, filtered, and evaporated under reduced pressure. The residue was dissolved in tetrahydrofuran (40 cm^3) and aqueous sulphuric acid (1M; 20 cm^3) and stirred at room temperature. Portions were withdrawn, partitioned between ether and aqueous sodium hydrogencarbonate, and analysed by g.l.c. When the concentration of (**13**) appeared maximal, the reaction mixture was made alkaline, and worked up in the usual way; g.l.c. analysis of the crude mixture indicated (**13**) and (**5f**) in the approximate ratio 3:1. Compound (**13**) was isolated by medium-pressure chromatography (0.245 g, 1.29 mmol, 43%), m.p. (from ether–pentane at low temperatures) 122—122.5 °C; δ($CDCl_3$) 5.75 (1 H, s) and 0.8—2.6 (17 H, m); $\bar{\nu}$(KBr) 2 900, 2 840, 1 650 (s), 1 605 (w), 1 440, 1 270, 1 240, 890, and 820 cm^{-1} (Found: $M^{+\cdot}$, 190.1345. $C_{13}H_{18}O$ requires M, 190.1357).

Compound (**5f**) was isolated from the combined residues of several reactions and was shown to be identical with the material obtained by further reduction of (**13**) and by oxidation of (**5d**) (see below). An as yet unidentified stereoisomer of (**13**) was also isolated in low yield (*ca.* 2%) from combined residues, m.p. (from pentane) 113—114 °C; δ($CDCl_3$) 5.75 (1 H, s) and 1.0—2.5 (17 H, m); $\bar{\nu}$(KBr) 2 920, 2 880, 2 850, 1 665 (s), 1 615 (w), 1 445, 1 260, and 930 cm^{-1} (Found: $M^{+\cdot}$, 190.1369. $C_{13}H_{18}O$ requires M, 190.1357).

Reduction of Enone (**13**).—(a)[31,32] Ammonia (*ca.* 70 cm^3 as liquid) was distilled into a cooled (−78 °C), stirred solution of compound (**13**) (0.280 g, 1.47 mmol) in absolute tetrahydrofuran (35 cm^3). Lithium pellets (1.40 g, 243 mmol) were added and the stirring was continued for 75 min before ethanol (20 cm^3) was added over 5 min followed by water (25 cm^3). After the mixture had attained room temperature, it was extracted with ether (3 × 30 cm^3) in the normal way. Medium-pressure chromatography allowed isolation of ketone (**5f**) (60 mg, 0.31 mmol, 21%), m.p. (sublimed 75—100 °C at 12 Torr) 29—31 °C; $\bar{\nu}$ (liquid film) 2 920, 2 850, 1 715 (s), 1 445, and 1 260 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 0.7—2.5 (m); δ_C 210.23 (s), 52.17 (d), 49.01 (t), 42.41 (d), 41.80 (d), 34.60 (t), 33.86 (t), and 25.85 p.p.m. (t) (Found: $M^{+\cdot}$, 192.1508. $C_{13}H_{20}O$ requires M, 192.1514), and alcohol (**5d**) (180 mg, 0.928 mmol, 63%), m.p. (from pentane–ether) 90—91 °C; $\bar{\nu}$(KBr) 3 050—3 600, 2 910, 2 850, 1 450, 1 440, 1 050, 1 045, 1 025, and 960 cm^{-1}; δ_H (80 MHz; $CDCl_3$) 3.65 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz) and 0.7—2.1 (21 H, m); δ_C 69.86 (d), 52.61 (d), 43.50 (t), 41.46 (d), 39.78 (d), 34.16 (t), 34.02 (t), and 25.96 p.p.m. (t) (Found: $M^{+\cdot}$, 194.1672. $C_{13}H_{22}O$ requires M, 194.1671).

(b)[31,32] Ammonia (*ca.* 100 cm^3 of liquid) was distilled into a cooled (−78 °C), stirred solution of compound (**13**) (200 mg, 1.05 mmol) in absolute ether (40 cm^3). Lithium wire (0.24 g, 34 mmol) was added then, after only 10 min, the temperature was allowed to rise to *ca.* −33 °C before the reaction was quenched by the addition of ammonium chloride (1.0 g, 18.7 mmol) followed by water (20 cm^3) and ether (30 cm^3). The mixture was allowed to attain room temperature and was then worked-up in the normal way. Medium-pressure column chromatography allowed isolation of ketone (**5f**) (85 mg, 0.44 mmol, 42%) and alcohol (**5d**) (70 mg, 0.36 mmol, 34%).

(c)[34] Ethylamine (*ca.* 20 cm^3) was distilled from lithium into a two-necked flask cooled to −78 °C, fitted with a silica gel guard tube, and containing lithium wire (0.125 g, 18 mmol). This mixture was magnetically stirred for 30 min then a solution of enone (**13**) (64 mg, 0.34 mmol) and t-butyl alcohol (320 mg, 4.3 mmol) in absolute tetrahydrofuran (5 cm^3) was added over 1 h through a septum. The mixture was stirred for a further 30 min, then water (3 cm^3) was added, and it was then allowed to come to room temperature. The mixture was extracted between more water (3 cm^3) and ether (3 × 20 cm^3). The combined ether phase was dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The residual oil (45 mg) was analysed by g.l.c. and shown to comprise ketone (**5f**), alcohol (**5d**), and unchanged enone (**13**) in the ratio 94:4:2.

Reduction of trans,trans,trans-*Tricyclo*[7.3.1.$0^{5,13}$]-*tridecan*-3-*one* (**5f**).—(a) A solution of lithium tri-s-butylborohydride[38] in tetrahydrofuran (L-Selectride, Aldrich Chemical Company; 1 mol dm^{-3}; 2.0 cm^3) was injected through a septum into a stirred solution of compound (**5f**) (94 mg, 0.49 mmol) in absolute ether (12 cm^3) under nitrogen. After 2 h, the reaction was quenched with water (2 cm^3) and aqueous sulphuric acid (1M; 10 cm^3), and worked up and chromatographed in the normal way to give (**5c**) (80 mg, 0.41 mmol, 84%), m.p. (sublimed 100 °C at 12 Torr) 104.5—107.5 °C; $\bar{\nu}$(KBr) 3 100—3 600, 2 905, 2 840, 1 440, 1 160, 1 010, 950, 905, and 830 cm^{-1}; δ_H (80 MHz; $CDCl_3$) 4.12 (1 H, m, $W_{\frac{1}{2}}$ 6.35 Hz) and 0.7—1.9 (21 H, m); δ_C (80 MHz; $CDCl_3$) 66.92 (d), 53.38 (d), 41.21 (d), 40.55 (t), 34.71 (d), 34.22 (t), 34.06 (t), and 25.93 p.p.m. (t) (Found: $M^{+\bullet}$, 194.1678. $C_{13}H_{22}O$ requires *M*, 194.1671), and a smaller amount of (**5d**) (12 mg, 0.062 mmol, 12%), identical with the alcohol obtained as the major product upon lithium–ammonia reduction of enone (**13**).

(b) Lithium aluminium hydride (10 mg, 0.26 mmol) was cautiously added to a stirred solution of ketone (**5f**) (22 mg, 0.115 mmol) in ether (10 cm^3). The reaction was quenched several hours later by the cautious addition of water (1 cm^3) followed by aqueous sulphuric acid (1 mol dm^{-3}; 5 cm^3). The mixture was then worked up in the normal way and the crude crystalline product was chromatographed to yield (**5d**) (17 mg, 0.088 mmol, 76%) and (**5c**) (4 mg, 0.021 mmol, 18%).

Toluene-p-*sulphonates* (**5a** *and* **b**).—Compound (**5a**) was made by the Tipson method[39] as previously described[3,8] from alcohol (**5c**) (83%), m.p. (from ether–pentane at low temperature) 84—86 °C; $\bar{\nu}$(KBr) 2 910, 2 850, 1 600, 1 445, 1 350, 1 190, 1 175, 1 155, 1 095, 935, 905, 870, 830, 815, 695, 650, 570, and 555 cm^{-1}; δ_H (80 MHz; $CDCl_3$) 7.80, 7.33 (4 H, ABq, *J ca.* 8 Hz), 4.80 (1 H, m, $W_{\frac{1}{2}}$ 6.9 Hz), 2.45 (3 H, s), and 0.6—2.0 (20 H, m). Another crystalline form could be formed by a higher temperature recrystallization, m.p. 112.5—115.5 °C, which had identical n.m.r., i.r. and mass spectra, but which gave a mixed m.p. of 84—86 °C with the lower melting polymorph. Compound (**5b**) was made in the same way from (**5d**) (94%), m.p. (from ether–pentane at low temperature) 107—109 °C; $\bar{\nu}$(KBr) 2 920, 2 850, 1 600, 1 360, 1 350, 1 190, 1 175, 940, 920, 865, 845, 820, 665, 580, 550, and 530 cm^{-1}; δ_H (80 MHz; $CDCl_3$) 7.80, 7.30 (4 H, ABq, *J ca.* 8 Hz), 4.2—4.7 (1 H, m), 2.47 (3 H, s), and 0.7—2.1 (20 H, m).

Oxidation of (**5d**).—A sample of alcohol (**5d**) obtained as the minor product from the lithium–ammonia reduction of enone (**13**) (see above) was oxidized by the two-phase Brown and Garg method[36] to give ketone (**5f**) identical by g.l.c. with the samples obtained (i) as a minor product in the lithium–ammonia reduction-hydrolysis sequence from the aromatic compound (**9b**), and (ii) as the major product in the lithium–ammonia reduction of enone (**13**).

Solvolytic Media.—Acetic acid was distilled from acetic anhydride then fractionally distilled twice; it was made up to 0.05 mol dm^{-3} in anhydrous sodium acetate (AnalaR grade). Hexafluoropropan-2-ol was twice distilled and made up to 97:3 by weight with distilled water.

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