Substitution Reactions in Cyclic Systems: S_N2 Reactions of Some Cyclopentyl Toluene-*p*-sulphonates

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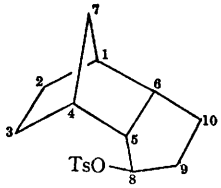
THE effect of increased steric interactions by alkyl groups on the leaving group in S_N2 reactions has been studied in cyclohexyl systems and the results showed that increased interaction neither decreases nor increases the rate very markedly.[1] This is in direct contrast to solvolysis reactions in these systems where the rate is increased by larger non-bonded steric interactions.[2] We are interested in the steric effects in S_N2 substitution reactions in cyclopentyl systems. The decrease in the rate of solvolysis of *endo*-5,6-trimethylene-*endo*-9-norbornyl (I) and *endo*-5,6-trimethylene-*endo*-8-norbornyl toluene-*p*-sulphonate (II) as ground-state steric interactions increase[3] prompted an investigation of the S_N2 reactivity of these compounds.



(II)

TABLE

*Second-order rate constants for reaction of toluene-*p*-sulphonates with potassium iodide*[a] *in anhydrous acetone at* 25·0°

Tosylate	$k_2 \times 10^7$ (l. mole^{-1}sec.$^{-1}$)	Relative rate
Cyclopentyl	3470[b]	857
(I)	430[b]	106
(II)	4·05[c]	1·00

[a] Runs were 0·100M in tosylate and 0·0200M in iodide;
[b] Average deviations were less than 5% between runs;
[c] Calculated from data at other temperatures.

The S_N2 character of the reaction was established thus: the kinetics were clearly second-order; also on another run, cyclopentyl toluene-*p*-sulphonate was run at 10 times the concentration of iodide to give very clearly pseudo-first-order and not zero-order kinetics. A slow *E*2 elimination with rapid addition of hydrogen iodide to the olefin formed was excluded as a possibility because the iodide isolated from reaction of (I) [in 60% yield after chromatography on alumina with pentane] had less than 0·5% of iodide at the 8-position determined by v.p.c.; while the iodide from (II) [in 55% yield after chromatography on alumina] had only 5% of its iodide at the 9-position Attack of hydrogen iodide on the olefin should give a mixture. As an example, the reaction of olefin with trichloroacetic acid gives after hydrolysis a mixture of alcohols with 55% of *exo*-8-alcohol and 45% of *exo*-9-alcohol. The iodide from (I) showed only a single peak in the v.p.c. Elemental analysis and i.r. and n.m.r. spectral data were completely compatible with *endo*-5,6-trimethylene-*exo*-9-norbornyl iodide. Reduction with zinc and hydrogen chloride in acetic acid gave only a single compound, whose v.p.c. retention time and i.r. spectrum after preparative v.p.c. were identical with tetrahydrodicyclopentadiene, proving no skeletal rearrangements had taken place. The iodide from (II) had 5% of unknown material but reduction also gave only tetrahydrodicyclopentadiene. Spectral data of the iodide were completely compatible with *endo*-5,6-trimethylene-*exo*-8-norbornyl iodide.

The rate of reaction with iodide of (II) compared with cyclopentyl toluene-*p*-sulphonate is extremely slow. As in the solvolyses in this system, we believe that the very slow rate can be explained as a combination of two effects. Steric interactions increase in the transition state as the toluene-*p*-sulphate group approaches the *endo*-3-hydrogen, and also torsional interactions may not be relieved as can occur in cyclopentyl toluene-*p*-sulphonate, which could result if the 9-methylene group is flexed down. This is very likely to relieve non-bonded interaction of the *endo*-8- and -10-substituents with *endo*-2- and -3-hydrogens. As the entering and leaving group become co-linear in the usual S_N2 transition state[4] the *exo*-8-hydrogen becomes co-planar with the remaining atoms decreasing the dihedral angle with the *exo*-5- and *exo*-9-hydrogens increasing the torsional interactions.[5] It is interesting that both solvolysis and S_N2 reactions of (II) are in direct contrast to chromic-acid oxidation, where the rate of oxidation is speeded by increasing ground-state interactions.[6]

The reaction of (I) with iodide is not as fast as cyclopentyl, because there may be some torsional and steric interactions not relieved, but the difference is not large.

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