The Effect of Large Steric Interactions on Solvolysis Rates of Rigid Cyclic Systems

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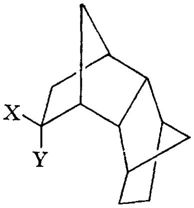
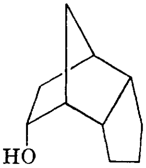
RECENT solvolysis studies of derivatives of the norbornyl ring system have shown that the rate of solvolysis of *endo*-2-tosylates have been decreased by *endo*-alkyl substituents at C-6.[1] This has been attributed to steric hindrance to ionization of the leaving group. This type of behaviour has also been found in other rigid ring systems in solvolysis[1a,2] and in S_N2 reactions.[3] We report here an example where alkyl substituents at C-6 have increased the rate of solvolysis.

Compound (II) was prepared from isodrin.[4] Chromic acid oxidation yielded the ketone (m.p. 91·5–92·0°) and its reduction with lithium aluminium hydride yielded (I), m.p. 87·5—88·0°. Oxidation of (I) gave a single ketone identical with the oxidation product of (II).

Table 1 lists the rates of acetolysis of tosylates of (I), *endo*-2-norbornyl, and *endo*-5,6-trimethylene-*endo*-2-norbornyl (III) alcohols along with carbonyl frequencies of the respective ketones. Table 2 shows the rate of chromic acid oxidation of the alcohols.



(I) X=H, Y=OH
(II) X=OH, Y=H



(III)

TABLE 1

Rate of acetolysis of tosylates at 25·0°

Tosylate	$k \times 10^9$ sec.$^{-1}$	Relative rate	Ketone frequency (cm.$^{-1}$)
(I)	1800	22	1743
endo-2-Norbornyl[a]	82·8	1·0	1751
(III)[b]	8·60	0·10	1743

[a] Ref. 1a, b. [b] Ref. 1a

TABLE 2

Rate of chromic acid oxidation of alcohols at 25·0° *in* 40% *aqueous acetic acid*[a]

Compound	$k_2 \times 10^3$ l.mole^{-1} sec.$^{-1}$	Relative rate
(I)	860	206
endo-Norbornyl ..	4·17	1·0
(III)	286	68·5

[a] Concentrations were 1·79 × 10^{-3}M in chromic acid and 2·68 × 10^{-3}M in alcohol.

The rate of chromic acid oxidation of bicyclic alcohols has been shown to be essentially independent of the inductive effect of alkyl groups at C-5 and C-6,[5] so that the very much greater rate of oxidation of (I) in comparison to *endo*-norbornyl serves to help substantiate the structure and also serves to indicate the much greater steric interactions on the hydroxy-group that must be present in (I). The data also indicate that (I) is more sterically crowded than (III), as can be seen by the use of Dreiding models.

The carbonyl frequency of the ketones of (I) and (III) are identical so that hybridization or angle strain differences as measured by the Foote and Schleyer correlation[6] cannot explain the differences in behaviour of the rates of acetolysis. Steric factors must be increasing the rate of acetolysis of (I) relative to *endo*-norbornyl and decreasing (III). The explanation may be that if ground-state strain is sufficiently large a path other than perpendicular to the resulting carbonium ion would result as the preferred path of the leaving group. Once this had occurred additional ground-state strain would increase the rate rather than decrease it.

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