Acetolysis of 3,4-Benzotricyclo[4,2,1,$0^{2,5}$]non-3-en-7-yl Toluene-*p*-sulphonates

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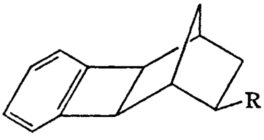
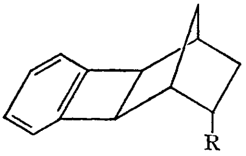
The nature of the norbornyl cation has been extensively investigated.[1] Our aim was to study the importance of nonbonded interactions, steric inhibition to ionisation, and dipole effects in the solvolysis of bicyclic systems.

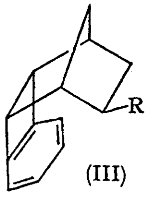
The experimental data, summarised in the Table, suggest that compounds (I)—(IV)† solvolyse through classical intermediates.

Comparison of the ratio of the rates of (I) and (II) (1·7) with the *exo*/*endo*-ratio for the norbornyl system[2] (107)‡, and the fact that the rate of solvolysis of *exo*-norbornyl toluene-*p*-sulphonate (V) is 650 times faster than (I) supports the contention that the *exo*-norbornyl cation is non-classical. Comparison of (II) with (VI) indicates that the benzo-group accounts for a ten-fold inductive deceleration in the rate of solvolysis; a similar effect is assumed for (I), (III), and (IV). There remains a rate factor of 65 between (V) and (I) which is probably a measure of the participation by the 1,6 bond in the solvolysis of *exo*-norbornyl toluene-*p*-sulphonate. Similarly, it is evident that (III) solvolyses through a classical intermediate.

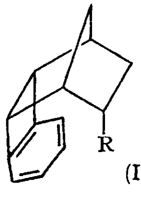


(I)





(III)



(IV)

($R=O\cdot SO_2\cdot C_6H_4\cdot Me\text{-}p$)

The marked change in character of the intermediates in the solvolyses from norbornyl to the substituted norbornyl derivatives may be due to

TABLE

Toluene-*p*-sulphonate	10^7k (sec.$^{-1}$) 75·0°[a]	10^7k (sec.$^{-1}$) 100·0°[a]	$\Delta H‡$ (kcal.)	$\Delta S‡$ (e.u.)
(I)	79·5	1429	29·1	+1·5
(II)	45·8	683	27·1	−5·2
(III)	305[b]	3340[b]	24·0	−10·6
(IV)	1·20	25·0	30·6	−2·5
exo-Norbornyl[2] (V)	51,900	—	21·6	−7·2
endo-Norbornyl[2] (VI)	509	6330	25·8	−2·5

[a] Rates quoted are the mean of two runs, accuracy ± 2%.

[b] Initial rates. Rate constant after 15% reaction was identical to (I).

the fact that conversion of (I) and (III) into transition states leading to non-classical intermediates would result in increased nonbonded interactions and distortion effects.[2,3]

The larger rate of (III) compared to (I) is probably due to a decrease in the nonbonded interactions between the *endo*-5,6-substituent and the *endo*-2-hydrogen in formation of the transition state in the solvolysis of (III). From earlier work[4] it is apparent that this small rate difference of (III) and (I) is unlikely to be attributed to neighbouring group participation of the phenyl group. The rate ratio of 61 between (IV) and (I) is a measure of the steric inhibition to ionisation in the solvolysis of (IV). If allowance is made for the higher ground-state energy of (IV) the existence of an even larger decelerating effect is apparent. Brown[5] has argued that these considerations should lead to a rate factor of 100 favouring *endo*-5,6-trimethylene-*endo*-2-norbornyl over *endo*-norbornyl toluene-*p*-sulphonate. If a similar factor is applied for (IV) a rate factor of 6100 is obtained for steric inhibition to ionisation. No evidence was obtained that dipole interactions affect the rates of solvolysis to any marked degree.

The reaction product in the solvolyses of (I)—(IV), in acetic acid buffered with an excess of sodium acetate, was identified as (I; R = OAc) (v.p.c., i.r. spectra, and mixed melting point). No *endo*-substituted products could be identified. Control experiments showed that under the solvolysis conditions, (III; R = OAc) did not rearrange to form (I; R = OAc). The formation of (I; R = OAc) from the solvolysis of (III; R = OAc) was expected since a rapid rearrangement of (III) to (I) occurs under the solvolysing conditions, the rate of (III) could only be obtained by measuring initial rates of solvolysis. The formation of (I; R = OAc) from (IV) must involve a Wagner–Meerwein rearrangement of the intermediate cation.

The stereochemistry of the product, (I; R = OAc), which we observe in these systems, supports the argument[5] that *exo*-substitution cannot be used as a criterion for the non-classical nature of ions.

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† Compounds (I) and (II) were prepared by hydroboration of the corresponding olefins (H. E. Simmonds, *J. Amer. Chem. Soc.*, 1961, **83**, 1657; M. P. Cava and M. J. Mitchell, *ibid.*, 1959, **81**, 5409) and (II) and (IV) by oxidation followed by reduction. Satisfactory analyses were obtained for the toluene-*p*-sulphonates.

‡ ref. 2, comparison of rates at 75°.

[1] G. D. Sargent, *Quart. Rev.*, 1966, **20**, 301.

[2] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, 1965, **87**, 375.

[3] M. M. Donaldson, Ph.D. Thesis, Princeton University, 1958; (*Diss. Abs.*, 1961, **22**, 738).

[4] P. D. Bartlett and R. Barnes, 12th National Organic Chemistry Symposium, American Chemical Society, Denver, Colorado, June, 1951, Abstracts, pp. 4–7.

[5] H. C. Brown, *Chem. and Eng. News*, 1967, **45**, No. **7**, 87.