The Solvolytic Behaviour of *exo*-7-Methylbicyclo[3,3,1]nonane *exo*- and *endo*-3-Toluene-*p*-sulphonates

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THE small transannular hybride shift found[1] in the major product from buffered acetolysis of *exo*-bicyclo[3,3,1]nonane 3-toluene-*p*-sulphonate (tosylate) prompted an investigation of the behaviour of the corresponding *exo*-7-methylbicyclo[3,3,1]-nonane *exo*- and *endo*-3-derivatives (I and II; R=OTs) under kinetically controlled solvolytic conditions.[2]

The *exo*-isomer [(I; R=OTs) $k_1 = 9{\cdot}25 \times 10^{-5}$ sec.$^{-1}$ at 25°] is slightly more reactive towards buffered acetolysis than the corresponding *nor*-methyl compounds[3] ($k_1 = 5{\cdot}78 \times 10^{-5}$ sec.$^{-1}$) and the product distribution (Table) shows 55% transannular rearrangement†

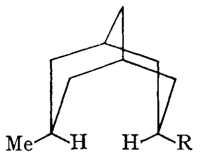
TABLE

Starting material	Buffered acetolysis products* (%) (X)	(XI)	(I+II; R=OAc)
(I; R = OTs)	44	55	1
(II; R = OTs)	80	17	3

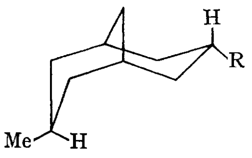
* Solvolyses at 25°; the three products were stable to the reaction conditions.

That a significant amount of C(7)—C(3) hydride shift occurs under kinetic control raises the possibility of synchronous transfer during ionisation *i.e.* the products could arise from interaction of the solvent with a bridged intermediate (III). If transfer of the hydride ion were concerted with the ionisation step then the monodeuteriated derivative (IV; R=OTs) would be expected to show significant rate retardation[4] compared with (I; R=OTs).

Treatment of (V; R=H)[5] with concentrated sulphuric acid[6] gave a methyl ketone identical in all respects with an authentic sample of *exo*-7-methylbicyclo[3,3,1]nonan-3-one (VI; R=H). The corresponding rearrangement of (V; R=D) gave the specifically labelled ketone (VI; R=D) where the deuterium position was confirmed by the ¹H n.m.r. spectrum. The conversion of (VI; R=D) into (IV; R=OTs) was achieved by standard procedures and its rate constant for buffere



(I)



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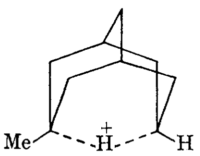

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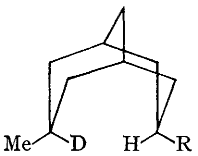
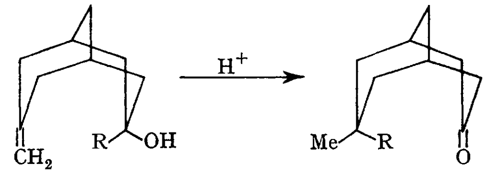
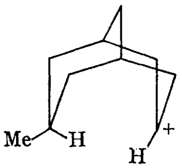


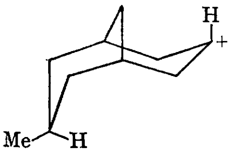
(IV)



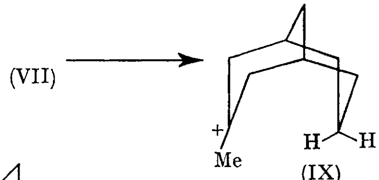
(V) (VI)



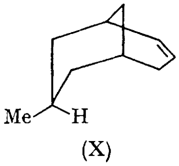
(VII)



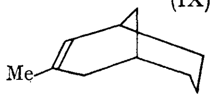
(VIII)



(IX)



(X)



(XI)

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† Treatment of *exo*-7-methylbicyclo[3,3,1]non-2-ene with refluxing formic acid gave 3-methylbicyclo[3,3,1]non-2-ene (93%) and *exo*-7-methylbicyclo[3,3,1]non-2-ene (7%), ref. 2a.

acetolysis ($k_1 = 9{\cdot}25 \times 10^{-5}$ sec.$^{-1}$ at 25°) was identical with that of (I; R=OTs); both sets of kinetic measurements being performed simultaneously.

Thus in the absence of a detectable isotope effect it must be assumed that transannular hydride shift occurs after the rate-determining step. There is some evidence[7] to support a boat–chair ground-state conformation for (II; R=OTs) and considerable evidence[8] pointing to the twin-chair conformation for (I;R=OTs). If both (I and II; R=OTs) react *via* classical 3-cations, then one explanation for the difference in hydride shift detected in the products from (I and II; R=OTs, Table), would be that solvolysis of (I; R=OTs) proceeds *via* the chair–chair cation (VII), whereas (II; R=OTs) reacts as the chair-boat cation (VIII) and the conformational flip from (VIII) to (VII) is slow relative to product formation.

The small amount of C(7)—C(3) hydride shift found in the solvolysis of *exo*-3-bicyclo[3,3,1]nonyl toluene-*p*-sulphonate has been ascribed[1] to a severe increase in angle strain associated with the approach of C(7) to the C(3) cation. This additional strain is not present in the corresponding C(5) to C(1) movement in the cyclo-octyl cation where a specific 1,5-hydride shift (50%) is observed.[10] The situation is markedly altered in the *exo*-7-methyl-3-*exo*-cation (VII) where a secondary cation is related to tertiary cation *via* a hydride shift (VII) — (IX).

Similar relative cationic stabilities can account for the more pronounced 1,5-shift (90%) observed in the acetolysis of *cis*-5-methylcyclo-octyl toluene-*p*-sulphonate[11] as compared with the cyclo-octyl case, although, here again, the much lower percentage shift in the corresponding *trans*-compound (10%) requires explanation. A kinetic examination of suitably deuteriated cyclo-octyl derivatives is now in progress to aid in deciding between concerted ionisation involving hydride shift (*e.g.* in the cyclo-octyl and *cis*-5-methylcyclo-octyl cases) and pathways involving classical carbonium ions.

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[1] M. A. Eakin, J. Martin, and W. Parker, in the press.

[2] Equilibration of the 7-methylbicyclo[3,2,1]nonyl-3- and 7-methylbicyclo[3,3,1]nonyl-7-carbonium ions with strong acid has been reported; (a) R. A. Appleton and S. H. Graham, *Chem. Comm.*, 1965, 297; for a related case see (b) H. Dugas, R. A. Ellison, Z. Valenta, K. Wiesner, and C. M. Wong, *Tetrahedron Letters*, 1965, 1279; (*c*) R. A. Appleton, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, 1967, **23**, 805.

[3] J. P. Schaefer and C. A. Flegal, *J. Amer. Chem. Soc.*, **89**, 5729, and ref. 1.

[4] S. Winstein and R. L. Hansen, *J. Amer. Chem. Soc.*, 1960, **82**, 6206 (*cf.* S. Borcic and V. Prelog, *Helv. Chim. Acta*, 1958, **41**, 199).

[5] M. A. Eakin, J. Martin, and W. Parker, *Chem. Comm.*, 1965, 206.

[6] W. A. Ayer and K. Piers, *Chem. Comm.*, 1965, 541.

[7] (a) W. D. K. Macrosson, J. Martin, and W. Parker, *Tetrahedron Letters*, 1965, 2589; C. Y. Chen and R. J. W. Le Fèvre, *J. Chem. Soc.* (*B*), 1966, 539.

[8] (a) W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 1964, 57; (b) W. A. C. Brown, J. Martin and G. A. Sim, *J. Chem. Soc.*, 1965, 1844; (c) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1964, **47**, 695. (d) I. Laszlo, *Rec. Trav. Chim.*, 1965, **84**, 251.

[9] A. C. Cope and D. M. Gale, *J. Amer. Chem. Soc.*, 1963, **85**, 3743.

[10] A. C. Cope and D. M. Gale, *J. Amer. Chem. Soc.*, 1963, **85**, 3747.