# A Transannular Hydride Shift in the Bicyclo[3,3,2]decane System

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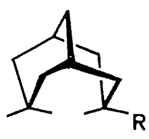
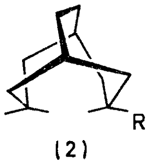
*Summary* Buffered acetolysis of *exo*-3-2,2,3,4,4-pentadeuteriobicyclo[3,3,2]decyl toluene-*p*-sulphonate is accompanied by 48% transannular hydride shift probably involving a specific C(7) to C(3) hydrogen migration.

A recent publication[1] has indicated a variety of factors which still require evaluation in terms of their influence on transannular hydride shifts in cationic reactions. In particular, the question of relative proximity of a CH group to a developing carbonium ion and the associated ring strain, is illustrated by the buffered acetolysis of cyclo-octyl bromobenzene-*p*-sulphonate, which is accompanied by 53% C(5) to C(1) transannular hydride shift,[2] whereas similar treatment of *exo*-3-bicyclo[3,3,1]nonyl toluene-*p*-sulphonate (**1**; R=OTs) results in only 5% of the related C(7) to C(3) shift.[3] If, in both these cases, this rearrangement occurs after the rate-determining step,[4] then an examination of models reveals the existence of several relatively strain-free conformations of the cyclo-octyl cation with a C(1)–C(5) interatomic distance of less than 2 Å, whereas the bridging C(9) methylene group imposes severe angle strain on any twin-chair conformation of the bicyclo[3,3,1]nonyl cation with a C(3)–C(7) separation less than 2·6Å. It was therefore of interest to examine the buffered acetolysis of *exo*-3-bicyclo[3,3,2]decyl toluene-*p*-sulphonate (**2**; R=OTs), since in the ground state twist-twin-chair form[5] of the corresponding cation, the *endo*-C(7) hydrogen atom is virtually equidistant from C(7) and C(3), *i.e.* the C(7)–C(3) interatomic distance is 2·1Å.

*exo*-3-Hydroxy-2,2,3,4,4-pentadeuteriobicyclo[3,3,2]decane was synthesised by the following route.[6] The tetradeuterio-ketone (**3**),[7] with 3·895 deuterium atoms per molecule,[8] was prepared by treatment of the corresponding 3-one with 0·1M-NaOD–dioxan.[9] Lithium aluminium deuteride reduction of (**3**) gave an inseparable mixture of the pentadeuterio-*exo*- and -*endo*-3-ols in the ratio of 2 : 3 which was converted into a mixture of the corresponding toluene-*p*-sulphonates and then treated with KOBu$^t$–Bu$^t$OH to afford 2,3,4,4-tetradeuteriobicyclo[3,3,2]dec-2-ene (**4**) as a highly volatile, crystalline solid. Subsequent deuterioboration[10] yielded a mixture of the pentadeuterio-*exo*-3- and *exo*-2-ols in the ratio 3 : 2, from which the required *exo*-3-isomer (**5**; R=OH) was isolated by preparative t.l.c.



(1)



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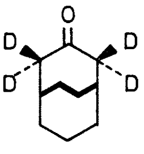

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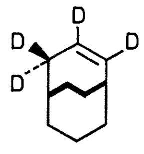

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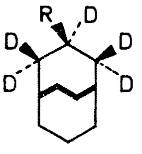

(5)

The corresponding pentadeuteriotoluene-*p*-sulphonate (**5**; R=OTs), 4·9 deuterium atoms per molecule, was solvolysed in sodium acetate buffered acetic acid at room temperature for 22 h, and the resultant products, a 94 : 6 mixture of the 2-ene and the epimeric 3-acetates, hydroborated, the *exo*-3-ol separated as before, and then oxidised with Jones reagent. This partially deuteriated 3-one was then treated with NaOH–aqueous dioxan under conditions known to exchange completely all four deuterium atoms, in (**3**). The resultant sample of 3-one contained 2·36 deuterium atoms per molecule and although these deuterium atoms could be located at any position except C(2), C(3), and C(4), since the solvolysis of (**2**; R=OTs)[5] gives no detectable amounts of 2- or 9-acetates,† it seems reasonable to equate the result with a specific C(7) to C(3) hydride shift. The above sequence was performed on a product mixture of 2-ene (94%) and 3-acetates (6%) and in the event of hydride migration occurring in the 3-acetates to the extent of 100% one can place a lower limit of 42% transannular hydride shift in the major product from solvolysis of (**5**; R=OTs).

If the transition-state geometry for this rearrangement requires a coplanar arrangement of the H–C(7)–H and $C^+$(3)H [as would seem likely in order to have maximum orbital overlap between the migrating *endo*-C(7) hydrogen atom and the vacant 2*p*-orbital of the 3-cation], this can only be achieved with a symmetrical twin-chair form of the 3-cation, in which the ethano-bridge is fully eclipsed.[5]‡

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† Limits of detection 0·2%.

‡ It should be pointed out that evidence has been presented for an untwisted ethano-bridge in the structurally related homoadamantane (ref. 11).

[1] E. N. Marvell, J. Seubert, D. Strumer, and W. Federici, *J. Org. Chem.*, 1970, **35**, 396.

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

[3] M. A. Eakin, J. Martin, and W. Parker, *Chem. Comm.*, 1968, 298.

[4] M. A. Eakin, J. Martin, W. Parker, C. Egan, and S. H. Graham, *Chem. Comm.*, 1968, 337.

[5] M. P. Doyle and W. Parker, *Chem. Comm.*, 1969, 319.

[6] This protracted sequence was necessitated by the finding that sodium–moist ether reduction of bicyclo[3,3,2]decan-3-one gave the *exo*- and *endo*-3-ols as an inseparable mixture in the ratio of 48 : 52, whereas similar treatment of bicyclo[3,3,1]nonan-3-one afforded the corresponding 3-ol mixture with an *exo* : *endo* ratio of 9 : 1; M. A. Eakin, Ph.D. Thesis, University of Glasgow, 1967.

[7] M. P. Doyle and W. Parker, *Tetrahedron Letters*, 1970, **12**, 945.

[8] Determined mass spectrometrically on an AEI*MS902 instrument and converted for isotope effects by the procedure described by K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, 1962.

[9] J. P. Schaefer and J. C. Lark, *J. Org. Chem.*, 1965, **30**, 1337.

[10] According to the method of J. Mazur M. Nassim, F. Sondheimer, and J. Wolfe, *J. Org. Chem.*, 1959, **24**, 1034, using lithium aluminium deuteride in place of lithium aluminium hydride.

[11] P. von R. Schleyer, E. Funke, and S. Liggero, *J. Amer. Chem. Soc.*, 1969, **91**, 3965.