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Transannular Hydride Shifts in Bicyclic Systems

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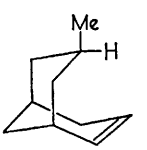
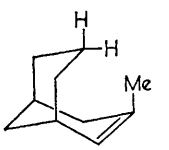
Evidence has been accumulating that the bicyclo-[3,3,1]nonane ring system exists as a twin-chair.[1-4] Measurements by Brown, Martin, and Sim,[4] which agree with those of Dobler and Dunitz,[3] give the separation between C–3 and C–7 as 3·06 Å, with a probable separation of 1·7 Å between the two *endo*-hydrogen atoms of the C–3 and C–7 methylenes. Some strain is present in the molecule since the average bond angles at positions 2, 3, 4, 6, 7, and 8 is 114°; this strain will be relieved when C–3 becomes trigonal as in a carbonium ion, and the situation is analogous to that which exists in medium-sized rings. This suggests that transannular hydride shifts might be observed in the bicyclic system similar to those which have been investigated by the schools of Cope and of Prelog.[5] We now report the first demonstration of such a shift.

7β-Methylbicylo[3,3,1]nonene[6] (I) and 3-methylenebicyclo[3,3,1]nonane[6] were converted by boiling formic acid into the same equilibrium mixture, consisting of 3-methylbicyclo[3,3,1]-nonene (II) (*ca.* 93%) and (I) (*ca.* 7%: analyses by p.m.r.[7] spectra and g.l.c. over tritolyl phosphate on deactivated celite). The structure of the new hydrocarbon (II), indicated by the absorption of the mixture at 3003 and 817 cm.$^{-1}$ and at τ 4·62 (doublet, one olefinic proton) and 8·32 (singlet, allylic methyl group), was confirmed by hydrogenation of the mixture to 3α-methylbicyclo[3,3,1]-nonane[6] (86·5%) and the 3β-epimer (13·5%). A sample of 3-methylenebicyclononane rearranged into the same equilibrium mixture of (I) (7·2%) and (II) (92·8%) when set aside for some months.

Similar hydride transfer is involved in the rearrangement[8] of 1-methylcyclo-octene to 5-methylcyclo-octene (2·5%) in formic acid, and the dehydration of 1-methylcyclo-octanol to 1-methyl-cyclo-octene (73%) and 5-methylcyclo-octene (6·3%).



(I)



(II)

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[1] M. W. J. Pumphrey and M. J. T. Robinson, I.U.P.A.C. Congress, July, 1963.
[2] W. A. C. Brown, K. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 1964, 57.
[3] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1964, **47**, 695.
[4] W. A. C. Brown, J. Martin and G. A. Sim, *J. Chem. Soc.*, 1965, 1844.
[5] For review see J. Sicher in "Progress in Stereochemistry," Ed. P. B. D. de la Mare and W. Klyne, Butterworths, London, 1962, Vol. 3, pp 243—246.
[6] R. A. Appleton and S. H. Graham, to be published.
[7] For which we thank Dr. D. A. Wilson, Cardiff.
[8] S. H. Graham and C. F. Mathews, unpublished work.

The following paper was originally published in Chem. Comm., 1965, 197. *Unfortunately, errors in the diagrams were such as to render the paper unintelligible. We are therefore reproducing the whole paper with revised diagrams.*