A Transannular 2,6-Hydride Shift in the Bicyclo[3,3,1]nonane System

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Summary The relative base-catalysed incorporation of deuterium into *exo*- and *endo*-6-hydroxybicyclo[3,3,1]nonan-2-one points to an intramolecular transannular 6,2-hydride shift occurring stereospecifically in the *exo*-isomer.

BICYCLO[3,3,1]NONAN-2-ONE has been shown[1] to incorporate up to three deuterium atoms (at C-1,C-3, and C-3) when treated with sodium in D_2O–dioxan. Similar treatment† of *exo*-6-hydroxybicyclo[3,3,1]nonan-2-one‡ (**1**) gave the corresponding deuterio-ketol, with a percentage

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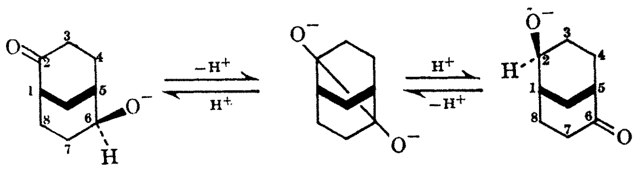
† An isolation procedure was adopted which ensured that ROD was converted to ROH prior to mass spectral examination.

‡ All new compounds gave analytical and spectral data consistent with their structure.

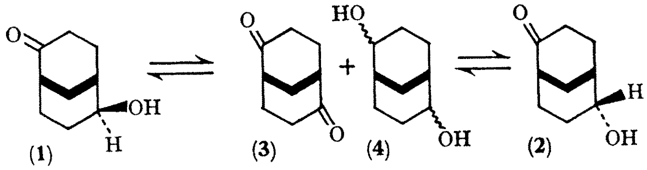
deuterium distribution of $[^2H_0]$ 0·4; $[^2H_1]$ 0·9; $[^2H_2]$ 1·1; $[^2H_3]$ 2·8; $[^2H_4]$ 9·2; $[^2H_5]$29·8; $[^2H_6]$ 55·2; $[^2H_7]$ 0·5; (average $[^2H_{5\cdot34}]$) whereas the deuteriated ketol† prepared from the *endo*-6-epimer (**2**) had an incorporation pattern of $[^2H_0]$ 1·5; $[^2H_1]$ 3·0; $[^2H_2]$ 19·3; $[^2H_3]$ 79·6; $[^2H_4]$ 0·8 (average $[^2H_{2\cdot74}]$). Oxidation of the deuteriated ketol (**1**) and subsequent treatment with NaOH–H_2O–dioxan gave the 2,6-dione (**3**) with only the natural deuterium abundance. Hence a mechanistic pathway must be available to (**1**) which exposes the hydrogen atoms on C-5 and C-7 to the deuterium exchange process in addition to those at C-1 and C-3.

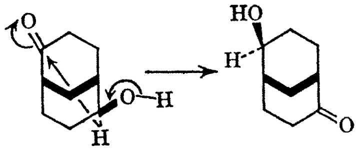
The presence of a carbinyl proton signal (1H, s, $\tau = 6{\cdot}04$) in the ¹H m.r. spectrum of the deuteriated form of (**1**) coupled with the lack of any appreciable amount of $[^2H_7]$ species precludes the operation of a homoenolisation process (Scheme 1).



A bimolecular redox mechanism (Scheme 2) can also be discounted since the *exo*-ketol (**1**) is not converted into (**2**) under the experimental conditions and no trace of (**1**) or (**2**) could be detected from a control experiment involving an equimolar mixture of the dione (**3**)[3] and diol (**4**).[3]

These facts are consistent with a stereospecific base-induced transannular 2,6-hydride shift[4] occurring in (**1**) in addition to the normal keto-enol exchange process (Scheme 3).





The transition state for this intramolecular rearrangement must involve a twin twist–boat conformation[5] of the bicyclo[3,3,1]nonane framework.

(*Received, September 10th,* 1969; *Com.* 1369.)

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[1] J. P. Schaefer and J. C. Lark, *J. Org. Chem.*, 1965, **30**, 1337; E. N. Marvell, G. P. Gleicher, D. Strumer, and K. Salisbury, *ibid.*, 1968, **33**, 3393 and references cited therein.

[2] Determined mass spectrometrically on an A.E.I./M.S.902 instrument and converted for isotope effects by the procedure described by K. Biemann, "Mass Spectrometry," McGraw-Hill, 1962.

[3] J. P. Schaefer and L. M. Honig, *J. Org. Chem.*, 1968, **33**, 2655.

[4] For related base-induced transannular hydride shifts see (a) W. Acklin and V. Prelog, *Helv. Chim. Acta*, 1959, **42**, 1239; (b) P. T. Lansbury and F. D. Saeva, *J. Amer. Chem. Soc.*, 1967, **89**, 1890 and references cited therein.

[5] This conformation was recently invoked to rationalise the formation of bicyclo[3,3,1]non-1-ene from base treatment of the mesylate of *endo*-2-hydroxybicyclo[3,3,1]nonane-1-carboxylic acid (J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, 1967, **89**, 5965); and the $NaBH_4$ reduction of the dione (3) to the *exo*-2, *endo*-6-glycol (4) (ref. 4).