Acid-catalysed Hydration of Norbornene at 250°

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Summary Hydration of norbornene at 250° in 10% DOAc-D₂O gives predominately exo- and endo-norborneols (65 35), which contain up to 104 deuterium atoms per molecule

The addition of deuterioprotic acids to norbornene at -78to 100° yields exclusively exo-norbornyl derivatives which contain only one deuterium atom per molecule and which undergo little scrambling with the tag distributed between the exo-2- and syn-7-positions ¹ Some incorporation of deuterium occurs when norbornene is heated at 130° in the medium SnCl₄/HCl/D₂O² Recently, Lee et al showed that isotopic scrambling accompanies acetolysis of 2-norbornyl derivatives and suggested that a study of the effect of temperature on the scrambling process would be worthwhile ³

As a continuation of our studies⁴ on the hydration of olefins at 250° in 10% HOAc–H₂O (10% DOAc–D₂O) as a route to perdeuterio-materials we have found that norbornene (1) in 10% CD₃CO₂D-D₂O at 250° yields primarily exo- and endo-norborneol (65:35), which contain up to



10.4 non-exchangeable atoms of deuterium per molecule Norbornyl acetate (3) and the di-norbornyl ether (6), \dagger as a mixture of stereoisomers, are also found The results of a preliminary study are listed in the Table

That the exchange is acid-catalysed is shown by entries IV and IX As shown in entries IV and V, strong acid lowers the yield of norborneols by forming intractable materials

			Rel % yield ^b							% Yield ^c	D/molecule ^d
Entrya	Substrate	Time (h)	(1)	(2)	(3)	(4)	(5)	(6)	Other	(4) + (5)	n'(4) + (5)
1	(1)	15	63 2		72	28 6			10	18	22
11	(1)	4	81	92	92	428	193	68	47	36	98
111 ^e	$(4) + (5)^{t}$	4									$10 \ 4$
1V	(1)	15	28	31	72	474	26 0	13	$2\ 2$	69	95
$\mathbf{v}^{\mathbf{g}}$	(1)	15	$15\ 4$			23 8	10 8	22 6	27 4	29	99
V1	(4)	15	07	13	80	610	$28\ 2$	04	04	79	98
V11	(2)	15	_							42	98
\mathbf{v}_{111}	(3)	15	08	05	$39\ 2$	37 3	167		$5\ 5$	51	$10\ 2$
1 X ^h	(1)	60	99 0				_				
x	(1)	120	12		92	$56\ 2$	20 9	74	51	80	10 1
X1	(1)	528	07	06	78	$23 \ 1$	$10\ 2$	47	530	10	99

Data for hydration of substrates at 250°

^a Typically a solution of (1) in 10% v/v $CH_aCO_2D-D_2O$ was de-gassed and heated in a sealed tube ^b Determined by g1c on 10 ft \times 1/8 in 10% SE-30 and 10% Carbowax on Chromosorb-W columns.

^c Determination by preparative glc and corrected for collection losses

^d Determined mass spectrometrically on the acetates at low voltage e Run in 10% CD₂CO₂D-D₂O

^t The norborneol from entry in containing 9.8 D/molecule was used in this run. ^g Run in 1% v/v HCl-D₂O ^h Run in D₂O only

 \dagger I r n m r, and m s data are consistent with the structure (6) N m r. shows that the stereoisomeric mixture is composed of 70% exo and 30% endo linkages

Entries vi, vii, and viii show that (2), (3), (4), and (5) also tend to the same mixture of products as is obtained from (1). Entries ii, iii, iv, and x show that the exchange is rapid and is essentially complete at 4 h, and that isotopic dilution through exchange of the methyl group in CH₃CO₂D reduces the total incorporation.

Eu(dpm)₃ analysis⁵ was used to establish the distribution in an exo-, endo-norborneol mixture (80:20) which contained 5.8 atoms of deuterium. The mixture was oxidized[‡] to norcamphor with Brown's reagent⁶ and the ketone was reduced with lithium aluminium hydride to deuteriated endo-norborneol. $Eu(dpm)_a$ analysis at mol = 0.6 at 100 MHz in CCl₄ established the following deuterium distribution. 1-H 0.5, 2-H 0.5-0.6,§ 3-H exo 0.5, 3-H endo 0.5, 4-H 0.5, 5-H exo 0.5, 5-H endo 0.5, 6-H exo 0.6, 6-H endo 0.6, 7-H syn 0.5, 7-H anti 0.5 (\pm 0.05) atoms of deuterium, respectively. Positional assignment of protons in endo-norborneol and [2H2]-exo-5,exo-6-endo-2-norborneol was established previously at mol = 0.62.

Certainly, the hydrogen-deuterium exchange occurs by protonation-deprotonation and/or addition-elimination of acetic or H₂O pathways in combination with 1,2 Wagner-Meerwein shifts, 2,6- and 2,3-hydrogen (deuterium) shifts, and 1,2- and 1,3-elimination of a proton (deuteron).

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‡ Control experiments show that exchange α to the carbonyl group is not significant. N. H. Werstiuk and R. Tailefer, unpublished data.

§ This is the difference between the deuterium content of the starting norborneol mixture (5.8) and that determined by Eu(dpm), analysis after oxidation and reduction $(5\cdot 2)$.

¶ At an Eu(dpm)₃/alcohol ratio (mol.) of 0.62 our analysis shows that 6-H exo and 4-H appear at δ 6.78 and 6.48, respectively downfield from Me₄Si. This does not agree with Paasivirta's assignments of δ 4.12 and 4.32 for 6-H exo and 4-H, respectively, obtained at mol. 0.33. Eu(dpm)₃ analysis on [²H₂]-exo-5,exo-6,endo-2-norborneol corroborated our assignments.⁷

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⁶ H. C. Brown and C. Cary, *J. Amer. Chem. Soc.*, **1961**, **83**, 2951. ⁷ N. H. Werstiuk and T. Kadai, unpublished results.