Acid-catalysed Hydration of Norbornene at 250°

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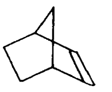
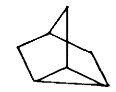
Summary Hydration of norbornene at 250° in 10% DOAc–D_2O gives predominately *exo*- and *endo*-norborneols (65 35), which contain up to 10 4 deuterium atoms per molecule


(1)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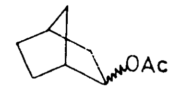
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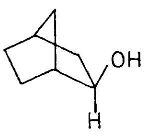
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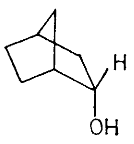
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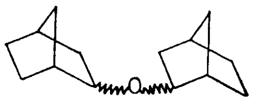
(6)

The addition of deuterioprotic acids to norbornene at −78 to 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 $SnCl_4/HCl/D_2O$ [2] 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 studies[4] on the hydration of olefins at 250° in 10% HOAc–H_2O (10% DOAc–D_2O) as a route to perdeuterio-materials we have found that norbornene (1) in 10% CD_3CO_2D–D_2O 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),† 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

Data for hydration of substrates at 250°

Entry[a]	Substrate	Time (h)	Rel % yield[b] (1)	(2)	(3)	(4)	(5)	(6)	Other	% Yield[c] (4) + (5)	D/molecule[d] in (4) + (5)
i	(1)	1 5	63 2		7 2	28 6		—	1 0	18	2 2
ii	(1)	4	8 1	9 2	9 2	42 8	19 3	6 8	4 7	36	9 8
iii[e]	(4) + (5)[f]	4	—	—	—	—	—	—	—	—	10 4
iv	(1)	15	2 8	3 1	7 2	47 4	26 0	1 3	2 2	69	9 5
v[g]	(1)	15	15 4	—	—	23 8	10 8	22 6	27 4	29	9 9
vi	(4)	15	0 7	1 3	8 0	61 0	28 2	0 4	0 4	79	9 8
vii	(2)	15	—	—	—	—	—	—	—	42	9 8
viii	(3)	15	0 8	0 5	39 2	37 3	16 7	—	5 5	51	10 2
ix[h]	(1)	60	99 0	—	—	—	—	—	—	—	—
x	(1)	120	1 2	—	9 2	56 2	20 9	7 4	5 1	80	10 1
xi	(1)	528	0 7	0 6	7 8	23 1	10 2	4 7	53 0	10	9 9

[a] Typicallv a solution of (1) in 10% v/v CH_3CO_2D–D_2O was de-gassed and heated in a sealed tube

[b] Determined by g l c on 10 ft × 1/8 in 10% SE-30 and 10% Carbowax on Chromosorb-W columns.

[c] Determination by preparative g l c and corrected for collection losses

[d] Determined mass spectrometrically on the acetates at low voltage

[e] Run in 10% CD_3CO_2D–D_2O

[f] The norborneol from entry ii containing 9 8 D/molecule was used in this run.

[g] Run in 1% v/v HCl–D_2O

[h] Run in D_2O only

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† 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 CH_3CO_2D reduces the total incorporation.

Eu(dpm)$_3$ analysis[5] 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 reagent[6] and the ketone was reduced with lithium aluminium hydride to deuteriated *endo*-norborneol. Eu(dpm)$_3$ analysis at mol = 0·6 at 100 MHz in CCl_4 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 (±0·05) atoms of deuterium, respectively. Positional assignment of protons in *endo*-norborneol and [$^2H_2$]-*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 H_2O 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)$_3$ analysis after oxidation and reduction (5·2).

¶ 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 Me_4Si. 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 [$^2H_2$]-*exo*-5,*exo*-6,*endo*-2-norborneol corroborated our assignments.[7]

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[7] N. H. Werstiuk and T. Kadai, unpublished results.