The High-temperature Hydration of Norbornadiene[1]

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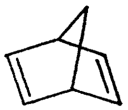
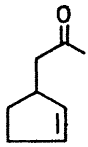
Summary The high-temperature hydration of norbornadiene at 250° in 10% HOAc–H_2O initially yields norbornenols, nortricyclanol, and norbornanediols which are gradually converted into cyclopent-2- and -3-ene-acetaldehydes, cyclohex-3-enecarboxaldehyde, and norcamphor.


(1)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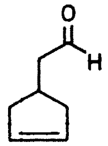
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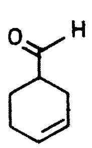
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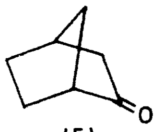
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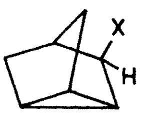
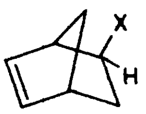

(6) a; X = OMe
b; X = OAc


(7) a; X = OMe
b; X = OAc

The acid-catalysed additions of methanol and acetic acid[2] to norbornadiene (1) at 25→230° yield a mixture of (6a), (7a) and (6b), (7b), respectively. Norbornadiene, in acetic acid–BF_3, yields a mixture of norbornyl diacetates.[3]

We have found that the hydration of (1) in 10% HOAc–H_2O at 250° *initially* yields norbornenols, nortricyclanol, and norbornanediols, which are gradually converted into (2), (3), (4), and (5). The results of a preliminary study are shown in the Table.

That the reaction is acid-catalysed is shown by entries i and v. Entries i and iv clearly show that (1) rapidly gives norbornenols, nortricyclanol, and norbornanediols, which are converted into (2), (3), (4), and (5) *via* rearrangement[4] and cleavage processes.[5] The preparation of (4), (5) and especially (2) and (3)[6] in one step from (1) and aqueous acetic acid is remarkable. When nortricyclanol is heated in 10% HOAc–H_2O at 250° (2), (3), (4), and (5)[7] are formed.

Norcamphor is most likely formed (a) *via* enols produced by 1,2- and 1,3-eliminations of a proton or H_2O and (b) from appropriate hydroxy-substituted cations by a 2,3- or 2,6-hydrogen shift.[4] Cleavage of a 1,6- or a 1,7-bond in suitable hydroxy-cations would yield the aldehydes.[5]

Data for the hydration of norbornadiene at 250°

Entry[a]	Time (h)	Rel. % yield[b] (2) + (3)	(4)	(5)	Diols	Other[c]	% Yield[d] (2)+(3)+(4)	(5)	D/molecule[e] (2)+(3)	(4)	(5)
i	0·5	4	3	8	55	30					
ii	1·5	15	18	40	20	7					
iii	3	17	19	45	15	4					
iv	9·5	14	17	54	14	1	21	33	2·5	2·6	2·4
v[f]	10	norbornadiene + polymer									

[a] Typically, a solution of (1) in 10% (v/v) HOAc–H_2O or 10% (v/v) DOAc–D_2O was de-gassed and heated in a sealed tube.

[b] The relative percent yields were determined by g.l.c. on $\frac{1}{8}$ in. × 10 ft. 10% SE-30 and 10% Carbowax on Chromosorb W columns.

[c] The norbornenols and nortricyclanol are included here.

[d] The yields were determined by preparative g.l.c. Each is corrected for collection losses.

[e] The enolizable deuterium in (2), (3), and (4) was washed out by three injections through a $\frac{3}{8}$ in. × 10 ft. 5% KOH + 20% Carbowax column maintained at 170°. (5) was treated three times with a KOH–MeOH-H_2O solution.

[f] The reaction was run in H_2O only.

When (1) is heated in deuteriated medium (entry iv), (2) and (3) combined, (4), and (5) contain 2·5, 2·6, and 2·4 nonenolizable deuterium atoms, each a composite of up to $^2H_6$-species. Control experiments have shown that (a) >95% of the deuterium must be incorporated into (2), (3), and (4), prior to cleavage and (b) deuterium is not incorporated into (5)† *via* acid-catalysed homoenolization[8] or some other mechanism which involves HOAc–AcO^-. That is, the hydrogens are exchanged prior to formation of the final products by a protonation–deprotonation pathway‡ which includes as steps 1,2-Wagner–Meerwein shifts, 2,6- and 2,3-hydrogen shifts and 1,2- and 1,3-eliminations of a proton.

We thank the National Research Council of Canada and the Department of University Affairs (Ontario) for financial support.

(*Received, September 28th*, 1970; *Com.* 1653.)

† Camphenilone also incorporates no deuterium on treatment with 10% DOAc–D_2O or 10% CF_3CO_2D–D_2O at 250° for 120 h.

‡ Interestingly, when norbornene is heated in 10% DOAc–D_2O at 250° for 15 h, the resulting *exo*-2-, *endo*-2-norborneol mixture (80 : 20) contains 8·3 deuterium atoms per molecule, a composite of up to $^2H_{11}$ species. Experiments with other substrates are presently under way to determine whether or not these conditions are useful generally to prepare perdeuterio-materials.

[1] Presented in part at the Joint Meeting of the American Chemical Society and Chemical Institute of Canada, Toronto, May, 1970.

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