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The Synthesis of Three Monodeuterionorbornanes, and the Stereochemistry of Acid-Catalyzed Cleavage of Nortricyclene¹

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This paper describes the synthesis and characterization of 1-deuterionorbornane (4), *exo*-deuterionorbornane (7), and *endo*-deuterionorbornane (14), and their use in a stereochemical study of ring cleavage of nortricyclene (1). Reduction of 1-chloronorbornane (3) with sodium and methanol-*d* gave 4. Treatment of the *p*-bromobenzenesulfonate of *endo*-norborneol with lithium aluminum deuteride gave 7, which also was the principal product on similar reduction of either *endo*- or *exo*-chloronorbornane. Reaction of norbornan-2-one with lithium aluminum deuteride gave 2-*exo-d-2-endo*-norborneol (12), which was converted to its *p*-bromobenzenesulfonate and reduced with lithium aluminum hydride to *endo-d*-norbornane (14), believed to contain a small proportion (<10%) of the 1-*d*- isomer 4. Cleavage of nortricyclene with deuterium chloride in methylene chloride gave *exo*-norbornyl chloride, whose mass spectrum revealed appreciable multiple deuteration. In contrast, cleavage with sulfuric acid-*d*₂ in acetic acid-*d* gave *exo*-norbornyl acetate with less than 3% of multiply deuterated species. Under conditions chosen to avoid rearrangements, the deuterio-*exo*-acetate was transformed to deuterionorbornane by reduction to the alcohol with lithium aluminum hydride, oxidation to the ketone with chromium trioxide, and Wolff-Kishner reduction. Quantitative infrared analysis of the deuterionorbornane revealed an *exo:endo* deuterium ratio of 1:1.08; a small amount of 1-*d*-norbornane was also indicated. The complete lack of stereospecificity for the electrophile (D⁺) and the complete *exo* specificity for the nucleophile (acetate) signify conversion of nortricyclene, by acid, to the carbon-bridged norbornylcarbonium ion. The results exclude hydrogen-bridged ions as the principal solvolytic intermediates.

Although electrophilic cleavage of cyclopropane rings was recognized in the 19th century,² mechanistic studies have dealt mainly with the effect of substitution on the position and direction of ring opening.³ Information has become available on the acid-catalyzed fission of fused-ring cyclopropanes,⁴ and the behavior of compounds containing the bicyclo[4.1.0]heptane system has been both likened^{4c} and contrasted^{4d} to that of cyclohexene 1,2-oxides. In unsymmetrically alkylated cyclopropanes the proton usually attacks the least substituted center and ruptures the bond that leads to the better carbonium ion (Markownikow rule).^{3,5} Exceptions to Markownikow cleavage have been observed with fused bicyclic^{4a,b,e} systems, and may exist in monocyclic⁶ systems. Apparent exceptions are common in fused tricyclic molecules⁷; an example relevant to the present work is the reported conversion of tricyclene to isobornyl acetate rather than to the acetate of camphene hydrate on cleavage with sulfuric acid in acetic acid.^{7a} However, in view of the known propensity of camphene hydrate esters to rearrange to isobornyl esters,^{8a} the final product may have arisen

(1) (a) Taken from the Ph.D. Dissertation of J. H. Hammons. The Johns Hopkins University, 1962. The results were presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963. A preliminary account of the synthetic work has been published (ref. 10); (b) Du Pont Teaching Fellow 1959-1960, Esso Fellow (1960-1961), Koppers Fellow (Summer, 1961).

(2) (a) R. Fittig and F. Roder, *Ann.*, **227**, 13 (1885); (b) A. Baeyer, *Chem. Ber.*, **18**, 2277 (1885); (c) G. Gustavson, *J. prakt. Chem.*, [2] **36**, 300, (1887).

(3) For recent reviews see (a) R. Breslow, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Part I, Chapter 4; (b) P. de Mayo, *Perfumery Essent. Oil Record*, **49**, 238 (1958).

(4) (a) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957); (b) R. T. LaLonde, and L. S. Forney, *J. Am. Chem. Soc.*, **85**, 3767 (1963); (c) R. T. LaLonde and M. A. Tobias, *ibid.*, **85**, 3771 (1963); (d) R. C. Cookson, D. P. G. Hamon, and J. Hudec, *J. Chem. Soc.*, 5782 (1963); (e) for an interesting example in a fused tricyclic system, see R. T. LaLonde and J. J. Batelka, *Tetrahedron Letters*, 445 (1964).

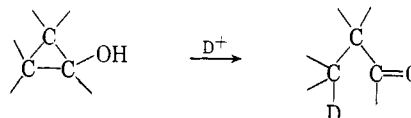
(5) (a) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1954, Chapter 3; (b) R. A. Raphael, "Chemistry of Carbon Compounds," Vol. II^a, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1953, p. 26.

(6) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **44**, 165 (1912); *Chem. Abstr.*, **6**, 1431 (1912).

(7) (a) S. Moycho and F. Zienkowski, *Ann.*, **340**, 17 (1905); (b) G. Komppa and R. H. Roschier, *ibid.*, **470**, 129, 154 (1929); (c) E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *J. Am. Chem. Soc.*, **81**, 6305 (1959); (d) J. Paasivirta, *Skomen Kemi.*, **33B**, No. 2, 57 (1960).

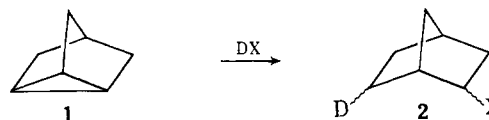
from ions capable of equilibrating the two ring systems.^{8b}

On the question of stereochemistry, present evidence indicates that the nucleophilic portion of the cleaving agent prefers to attack carbon by inversion of configuration if such attack accompanies rupture of the cyclopropane bond.^{4b,c,e} The only stereochemical



studies on the electrophilic attachment of the proton have involved ring opening of homoenols (eq. I).^{9,10} With two different homoenolic systems protonation with D⁺ in acid media proved stereospecific and was shown in the one case,¹⁰ and suggested in the other,⁹ to proceed with predominant retention of configuration.

This paper describes the synthesis of three monodeuterionorbornanes and their use in a stereochemical study of acid-catalyzed cleavage of tricyclo[2.2.1.0^{2,6}]heptane (nortricyclene, 1). This hydrocarbon has an axis of threefold symmetry and all the cyclopropyl carbons are equivalent. Fission of any of the cyclopropyl bonds with an unsymmetrical reagent (*e.g.*,



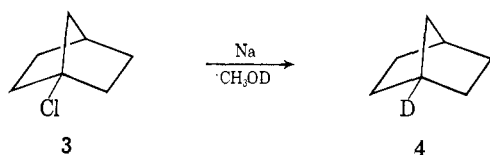
DX) would produce a 2,6-disubstituted norbornane (2), in which the electrophile (D) and nucleophile (X) can each have an *endo* or *exo* configuration. The stereochemical outcome for each moiety would provide information on the intermediates involved in the derivation of the bicyclo[2.2.1]heptane system.

(8) (a) H. Meerwein and K. van Emster, *Chem. Ber.*, **53**, 1815 (1920); **55**, 2500 (1922); (b) for other possible examples see A. Bhati, *Perfumery Essent. Oil Record*, **53**, 15 (1962).

(9) C. H. DePuy and F. W. Breitbeil, *J. Am. Chem. Soc.*, **85**, 2176 (1963).

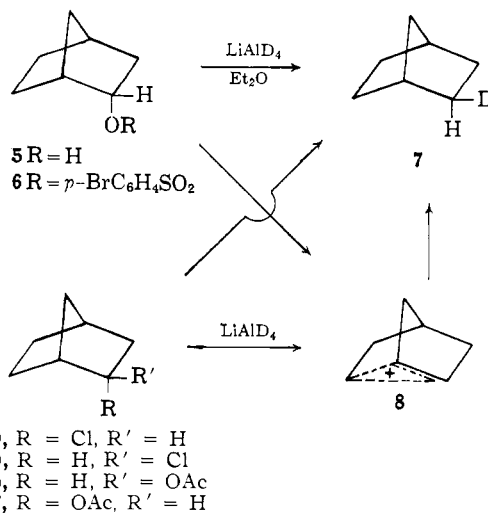
(10) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *ibid.*, **85**, 3713 (1963).

Synthesis of Monodeuterionbornanes.—1-Deuterionbornane (4) was prepared from the known 1-chloronbornane (3)¹¹ by reduction with sodium in



methanol-*d*. Analysis for deuterium by a combustion-infrared method indicated 0.96 D,¹² and mass spectrometry showed it was 96.5% monodeuterated. The infrared spectrum of 4 shows the C-D stretching band at 2200 cm.⁻¹ and a distinguishing fingerprint peak at 726 cm.⁻¹. There were no bands in regions where *exo-d*-norbornane, *endo-d*-norbornane, norbornene, and nortricyclene have specific absorption, and gas chromatography indicated a purity of 98.5%. In the n.m.r. spectrum the bridgehead hydrogen gave a peak at 2.22 δ , and the remaining hydrogens appeared as overlapping multiplets dominated by peaks at 1.40 and 1.21 δ . The intensity ratio of the 2.22 peak to the remainder was 1:10.8 (theoretical ratio 1:10).¹³

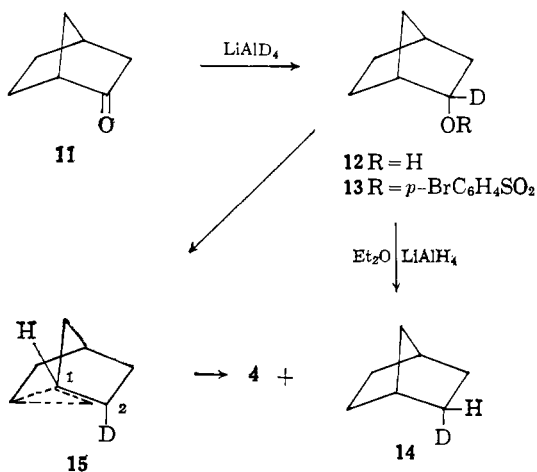
exo-Deuterionbornane (7) was obtained by prolonged reflux of *endo*-norbornyl *p*-bromobenzenesulfonate (6) with lithium aluminum deuteride in diethyl ether. If this reduction proceeded by direct displacement, the product would have an *exo*-deuterium, because concerted reductions with lithium aluminum hydride (and deuteride) at saturated carbons are known to occur with inversion of configuration.¹⁴ Alternatively, the *endo*-brosylate 6 might ionize and then rearrange to the nonclassical norbornyl ion 8.^{15,16} This ion is known to terminate with nucleophiles to give *exo*-substituted norbornanes exclusively, and combination with deuteride should likewise give *exo-d*-norbornane (7). As both pathways predict the same stereochemical result, the product 7 should be free of contamination by its *endo* epimer. After purification, 7 showed one peak on gas chromatography, and in the infrared spectrum it had C-D absorption at 2170 (shoulder at 2190) cm.⁻¹ and distinguishing fingerprint bands at 858 and 781 cm.⁻¹. The spectrum lacked absorption in regions specific to 1-*d*-norbornane, *endo-d*-norbornane, norbornane, norbornene, and nortricyclene. In the n.m.r. the intensity ratio for the bridgehead proton signal (2.22 δ) to the remaining protons was 1:4.4 (theory 1:4.5).¹⁷ Deuterium assay



indicated 0.95 D (by combustion-infrared) and 97.5% monodeuterionbornane by mass spectral analysis.

We also attempted reduction of *endo*-chloronorbornane (9) and *exo*-chloronorbornane (10) with lithium aluminum deuteride in bis(2-ethoxyethyl) ether. Infrared spectra showed that the crude product in each case was largely (if not exclusively) *exo-d*-norbornane (7). The *exo-d*-configuration could result from the *endo*-chloride 9 either by direct displacement or by an ionization mechanism (*via* 8) as discussed earlier for the case of the *endo*-brosylate 6. To account reasonably for the conversion of *exo*-chloride 10 to *exo-d*-norbornane (*i.e.*, net retention of configuration) we presume prior ionization to the nonclassical ion 8 followed by attack of lithium aluminum deuteride from the *exo* side. Nucleophilic replacement of *exo* substituents by net retention of configuration is typical of norbornyl systems.¹⁶

In our route to *endo-d*-norbornane (14) we treated norbornan-2-one (11) with lithium aluminum deuteride and obtained 2-*exo-d*-2-*endo*-norborneol (12).



(11) (a) W. P. Whelan, Dissertation, Columbia University, 1953; (b) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).

(12) All deuterium analyses refer to atoms per molecule in excess of natural abundance. See Experimental for the analytical methods.

(13) In norbornane this intensity ratio was 1:5.1 (theory 1:5.0).

(14) (a) E. L. Eiel, *J. Am. Chem. Soc.*, **71**, 3970 (1949); (b) E. R. Alexander, *ibid.*, **72**, 3796 (1950); (c) M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, *Bull. soc. chim. France*, **5**, 1042 (1952); (d) G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.*, **22**, 479 (1957).

(15) A pair of rapidly equilibrating classical norbornyl ions could be stereochemically equivalent to the symmetrical nonclassical ion, but the latter is used throughout this paper, partly for economy. For a discussion see H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p. 140.

(16) For a recent critical review see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Part I, Chapter 3.

(17) While our work was in progress, H. C. Brown and K. J. Murray [*J. Org. Chem.*, **26**, 631 (1961)] reported the preparation of *exo-d*-norbornane by reaction sequences that involved hydroboration and deuteriodoration of norbornene. Their assignment of deuterium configuration was based on

these n.m.r. assignments in norbornane: bridgehead protons are at lowest field (*cf.* our 2.22 δ); *exo* protons near 1.40 δ ; *endo* protons near 1.21 δ . They likened the *exo* and *endo* hydrogens to *equatorial* and *axial* hydrogens (respectively) in cyclohexane rings where it was known that equatorial hydrogens ordinarily appear at lower fields than corresponding axial ones. In our deuterionbornanes the decrease in intensities at 2.22, 1.40, and 1.21 δ for 1-*d*-, *exo-d*-, and *endo-d*-norbornanes, respectively, confirm Brown and Murray's assignments. However, overlap between the signals near 1.40 and 1.21 δ prevented us from using individual intensities in these two regions for quantitative assay of stereochemical purity. Professor Brown kindly sent us a sample of their *exo-d*-norbornane and we found its infrared spectrum corresponded to that of our *exo-d*-norbornane in all essential respects.

This alcohol was converted to the corresponding brosylate **13** and treated with lithium aluminum hydride. If the reduction occurred by a direct, rear displacement, the product would be *endo-d*-norbornane (**14**). However if, instead, the ester ionized to give (indirectly) the carbon-bridged ion **15**, then a mixture of *1-d*-norbornane (**4**) and *endo-d*-norbornane would result, corresponding to termination of ion **15** at C-1 and C-2, respectively.¹⁸ The deuterionorbornane obtained in the experiment had 0.98 D (combustion-infrared method) and was 98.5% monolabeled (mass spectrum). It exhibited one peak on gas chromatography and its infrared spectrum showed C–D absorption at 2185 cm.⁻¹ (shoulder at 2160) and characteristic fingerprint peaks at 840 and 790 cm.⁻¹. Although the spectrum gave no indication of contamination by *exo-d*-norbornane, norbornane, norbornene, or nortricyclene, there was very weak absorption at 726 cm.⁻¹ where *1-d*-norbornane has a prominent peak. In the n.m.r. the intensity ratio of the bridgehead protons (2.22 δ) to the remaining protons was 1:4.5. The theoretical ratio for *endo-d*-norbornane is 1:4.5, and for an equal mixture of *endo-d*- and *1-d*-norbornane it is 1:6.33. Consideration of the accuracy limits of our n.m.r. intensities together with the weak infrared absorption at 726 cm.⁻¹ raised the possibility that our *endo-d*-norbornane **14** might contain a small proportion of the *1-d*- isomer. In recent studies on homoketonization we obtained *endo-d*-norbornane by another route in which the possibility of contamination by the *1-d*- isomer did not arise.¹⁰ The infrared spectrum of *endo-d*-norbornane from this alternative route had a *minimum* at 726 cm.⁻¹ and established that absorption at this position is not characteristic of the *endo-d*- isomer. Consequently, in our *endo-d* product **14** obtained from **13** we attribute the weak band at 726 cm.⁻¹ to the presence of the *1-d*- isomer **4** (estimated to be <10%). Evidently reduction of the *endo*-brosylate proceeded largely by direct displacement (**13** \rightarrow **14**) although the ionization mechanism (*via* **15**) participated to a minor extent. Similar considerations would presumably hold for the reduction of **6** \rightarrow **7** although in that case the stereochemical outcome was unaffected.

Ring Cleavage in Protonic Media.—As a prelude to studies in deuterated media we treated nortricyclene with sulfuric acid (0.08 *M*) in acetic acid at room temperature. The product was *exo*-norbornyl acetate (**16**) containing no detectable amount (<5%) of the *endo* isomer **17** as shown by infrared spectroscopic comparison with authentic samples and with artificial mixtures prepared from them. *endo*-Norbornyl acetate (**17**) is known to be stable to reaction conditions more vigorous than ours.¹⁹ To establish that the *exo*-acetate **16** experiences no Wagner–Meerwein rearrangements or 6,2-hydrogen shifts subsequent to its formation, we subjected optically active *exo*-norbornyl acetate²⁰ to the reaction conditions and observed no detectable racemization. When nortricyclene was treated with hydrogen chloride in methylene chloride at room temperature the product was identified by infrared comparisons with authentic samples as *exo*-norbornyl chloride (**10**)

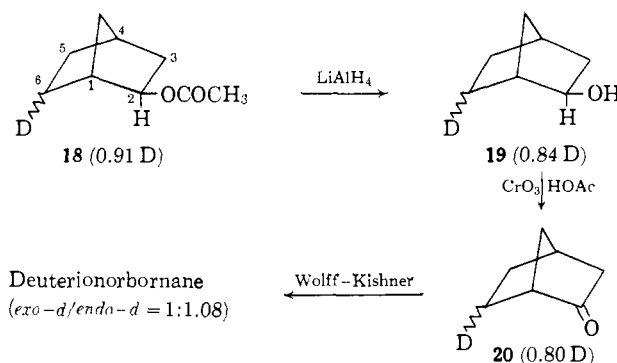
(18) Except for any isotope effect created by the deuterium at C-2, ion **15** should lead to a 1:1 mixture of **4** and **14**.

(19) (a) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147 (1952); (b) *ibid.*, **74**, 1154 (1952).

(20) Sample kindly provided by Professor K. Mislow [K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962)].

with no detectable amount (<3.5%) of *endo*-norbornyl chloride (**9**). Authentic *endo*-chloride was shown to be stable under the reaction conditions. Consequently, under both sets of ring-cleavage conditions the final attachment of the nucleophiles occurred with inversion of configuration.

Ring Cleavage in Deuterated Media.—Treatment of nortricyclene at room temperature in deuterioacetic acid (DOAc) with deuteriosulfuric acid (D_2SO_4 , 0.14 *M*) gave *exo*-norbornyl acetate that contained deuterium at C-6 (**18**). The acetoxy group was removed from the molecule by a three-step sequence that preserved the configurational integrity at C-6. In the first step the *exo*-acetate **18** was treated with lithium aluminum hydride, and the derived alcohol **19** was worked up in alkaline medium to avoid rearrangements. Oxidation to the corresponding deuterioketone **20** was accomplished with chromium trioxide in acetic acid under conditions known not to induce skeletal change or 6,2-hydrogen shift.²¹ Finally, Wolff–Kishner reduction converted **20** to deuterionorbornane. The possibility that deuterium



at C-6 is lost or scrambled by homoenolization during Wolff–Kishner reduction has been ruled out in other studies of 6-deuterionorbornan-2-one systems.¹⁰ The accompanying formulas summarize the transformations as well as the deuterium results from combustion analysis of **18**, **19**, and **20**.²² The mass spectrum of **20** indicated that less than 3% of the molecules were multiply labeled.²³ Quantitative infrared analysis with the aid of known mixtures of *exo-d*- and *endo-d*-norbornane (**7** and **14**) showed that the *exo*:*endo* ratio of deuterium in the derived deuterionorbornane was close to unity (1:1.08 \pm 0.15).²⁴ The spectrum also disclosed very

(21) Winstein and Trifan (ref. 19a) showed that whereas optically active *exo*-norborneol was racemized in acetic acid containing *p*-toluenesulfonic acid, the alcohol was stable when the strong acid was excluded. J. A. Berson, *et al.* [*ibid.*, **83**, 3986 (1961)], found that even in the presence of sulfuric acid, optically active 1-methyl-2-*exo*-norborneol was oxidized by chromium trioxide in aqueous acetone to 1-methylnorbornan-2-one without rearrangement and without racemization (by 6,2-hydrogen shift).

(22) The deuterium value shown for **18** was obtained by the combustion-infrared method and those of **19** and **20** were by the combustion-falling drop method. If the slight deuterium loss that attends removal of the acetate group is real and not attributable to experimental error, it would indicate that some deuterium had been incorporated into the enolizable methyl hydrogens. Possible loss of deuterium on oxidation of **19** to **20** is of interest since it would reveal if any label is present at the alcoholic carbon C-2 and/or at C-3, which becomes an enolizable site in the ketone **20**. The values for **19** and **20** appear to be within experimental error of each other. Additional assays of **19** and **20** by the combustion-infrared method and of **20** by mass spectrometry are given in the Experimental.

(23) That the deuterium in **20** is at least largely at C-6 was supported by its infrared spectrum, which showed (in carbon tetrachloride) no bands other than those expected in this solvent for a mixture of norbornan-2-one, 6-*endo-d*-norbornan-2-one, and 6-*exo-d*-norbornan-2-one. Spectra of the last two compounds became available recently (ref. 10).

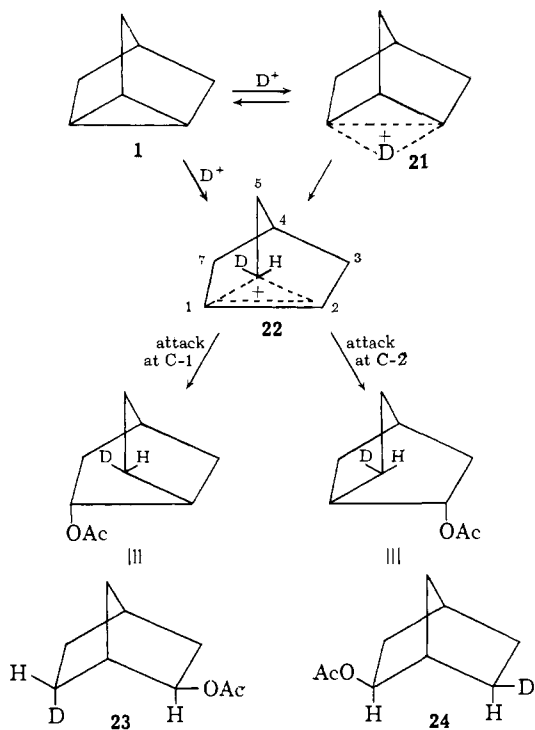
(24) Our *endo-d*-norbornane contains some *1-d*-norbornane, but because

weak absorption at 726 cm^{-1} suggestive of 1-*d*-norbornane, but the amount present was too small to estimate quantitatively.²⁵

Cleavage of nortricycylene with deuterium chloride in methylene chloride gave *exo*-norbornyl chloride, whose mass spectrum revealed appreciable multiple deuteration, *viz.* 21.5% no D, 52% 1D, 22.5% 2D, 4% 3D (total 1.09D). To confirm this multiple deuterium entry we removed the chlorine by conversion to the Grignard reagent followed by hydrolysis. The hydrocarbon derived from this procedure contained small amounts of impurities (nortricycylene and norbornene) and the mass spectral deuterium distribution was 21% no D, 53% 1D, 21% 2D, 5% 3D (total 1.10D) in satisfactory agreement with the results from the parent chloride.

Discussion

Although repeated treatment of nortricycylene with deuterium chloride gave only *exo*-norbornyl chloride, the presence of di- and trideuterated species indicates the intervention of reactions other than simple ring cleavage. The extra deuterium could have entered by exchange of cyclopropyl hydrogens prior to ring opening²⁶ or by the formation of a deuterionorbornene followed by addition of deuterium chloride. This deuterionorbornene could arise by isomerization of nortricycylene or by elimination of hydrogen chloride from the derived *exo*-norbornyl chloride.²⁷



the amount could not be specified we considered the *endo* isomer to be pure in the gravimetric preparation of the known mixtures. In the analysis of an unknown, this procedure would bias the assay in favor of the *endo* isomer. For example, if our *endo-d*-norbornane contained 6% 1-*d*-norbornane, a 1:1 mixture of *exo-d* : *endo-d*-norbornane would be assayed as 1:1.06 by our method. Consequently the slight preference for *endo* indicated by the experimental value 1:1.08 may not be real.

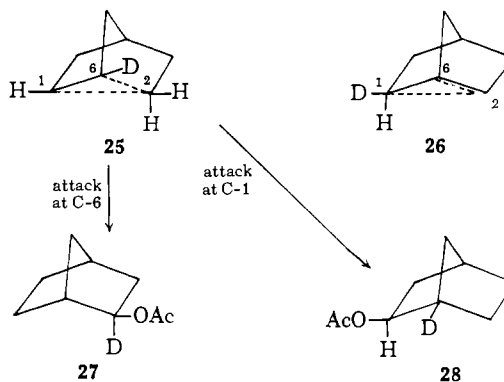
(25) The presence of nondeuterated norbornane (*ca.* 20%) was evident from the infrared spectrum but did not interfere appreciably in the assay of the *exo-d*:*endo-d* ratio.

(26) Compare the introduction of deuterium into cyclopropane [R. L. Baird and A. Aboderin, *Tetrahedron Letters*, 235 (1963)].

(27) Compare the equilibration of camphene hydrochloride, camphene, and isobornyl chloride in the presence of hydrogen chloride (ref. 8).

In contrast, ring rupture in acetic acid-*d* led to minor multiple labeling (<3%) and therefore deuterium enters during ring opening and not prior or subsequent to it. Since the derived *exo*-acetate is stable to further rearrangement, the deuterium stereochemistry is determined by events that precede covalent capture of the nucleophile. The complete selectivity of nucleophilic termination by inversion of configuration together with the virtually equal *exo*:*endo* distribution of the electrophile (D) suggests that nortricycylene is converted to the carbon-bridged norbornyl ion 22.¹⁵ Whatever is the steric course of any preceding step, cation 22 would be expected to unite with nucleophile at C-1 and C-2 to produce the *exo*-acetates 23 and 24 in equal amount (neglecting isotope effects). The bridged cation 22 evidently does not return appreciably to the neutral tricyclic system (or to norbornene) because proton loss would compete with deuterium loss and provide a means for eventual entry of more than one deuterium. Our results do not rule out formation of other ions (classical or not) prior to the generation of 22 but would impose restrictions on their behavior. For example, if a reversibly formed deuterium-bridged species such as 21 (or its equivalent) precedes cation 22 then the rearrangement 21 \rightarrow 22 must be essentially irreversible; otherwise multiple deuterium entry could result.²⁸

Reactions of nonclassical norbornyl cations can sometimes be accompanied by rearrangements that involve net migration of hydrogens from C-6 to C-1 and C-2.¹⁶ These so-called 6,2-hydrogen shifts would transform ion 22 into the related ions 25 and 26 according to whether



H or D migrates, respectively. Ion 26 differs from 22 only in the identity of the carbon atoms and would not be detected in our experiments. On the other hand, ion 25 would produce the *exo*-acetates 27 and 28 by termination at C-6 and C-1. If we neglect isotope effects and assume D and H migrations are equally probable in the 6,2-shifts, then every four migrations would produce one molecule of 27 and one of 28. In a C^{14} tracer study of the solvolysis of *exo*-norbornyl brosylate in acetic acid, Roberts, Lee, and Saunders found 30% of observable 6,2-shift.^{29a} If our system behaved comparably,

(28) For papers dealing with the question of protonated cyclopropanes in various reactions see ref. 19a and (a) P. S. Skell, I. Starer, and A. P. Krapcho, *J. Am. Chem. Soc.*, **82**, 5257 (1960); P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962); P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962); (b) M. S. Silver, *ibid.*, **82**, 2971 (1960); (c) G. J. Karabatsos and J. D. Graham, *ibid.*, **82**, 5250 (1960); G. J. Karabatsos and C. E. Orzech, Jr., *ibid.*, **84**, 2838 (1962); (d) O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 237 (1962); (e) O. E. Edwards and M. Lesage, *Can. J. Chem.*, **41**, 1592 (1963); (f) C. N. Pillai and H. Pines, *J. Am. Chem. Soc.*, **83**, 3274 (1961).

(29) (a) These shifts can also be formulated in terms of a nortricyclonium ion participating to the extent of about 45% [J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **76**, 4501 (1954)]. (b) The 30% of 6,2-shift observed by Roberts, *et al.*, and the 7.5% of 27 and 28 we could expect, are maximum

27 and 28 could each constitute about 7.5%^{29b} of the total deuterio-*exo*-acetate, and the presence of 27 would be revealed by deuterium loss in the oxidation of alcohol 19 to the ketone 20. Unfortunately, the deuterium analyses were not sensitive enough to detect, reliably, deuterium differences of this magnitude. The second consequence of 6,2-shifts would be the formation of 28 and, from it, ultimately 1-*d*-norbornane. Our deuterio-norbornane showed very weak absorption at 726 cm.⁻¹ where authentic 1-*d*-norbornane has a characteristic band. This result lends some support to the incursion of 6,2-shifts and thereby to the formation of carbon-bridged ions.

Baird and Aboderin^{30a} studied the ring opening of cyclopropane in 8.4 *M* deuteriosulfuric acid. To account for the deuterium distribution in the derived 1-propanol they postulated interconversion among carbon-bridged and hydrogen-bridged ions and concluded that solvolytic ring opening occurred primarily with the latter species. In our nortricyclene-D₂SO₄ system the three hydrogen- (and deuterium-) bridged ions formally derivable are 21, 29, and 30. Nucleophilic attack from the sides opposite to that of the delocalized bonds would produce *exo*-norbornyl acetate with a different deuterium distribution from each ion; *viz.*, 21 → 23; 29 → 24 + 27; 30 → 28. If isotope effects are neglected, the product from these hydrogen-bridged ions would



contain at least twice as much 6-*endo*-deuterium as 6-*exo*-deuterium; in addition, the amounts of 2-*endo-d-2-exo*-norbornyl acetate (27) and 6-*exo-d-2-exo*-norbornyl acetate (24) would be equal. These expectations are not borne out by our experimental results, and we conclude that the hydrogen-bridged species 21, 29, and 30 are not the principal acceptors of nucleophile in this system.^{30b} However, our method is not sensitive enough to reveal whether or not such species played minor roles.

Experimental³¹

1-Chloronorbornane was obtained from norbornan-2-one (Aldrich Chemical Co.) as described by Whelan^{11a}; b.p. 68–71° at 54

figures, which might well be corrected downward to accommodate ion-pair internal return in their system.

(30) (a) R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964). (b) This conclusion agrees with the suggestion made by Baird and Aboderin that hydrogen-bridged species might not be important in systems where carbon-bridged ions are specially favored.

(31) Melting points were taken in Pyrex capillaries, are corrected, and are rounded to the nearest 0.5°. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Band positions are expressed in cm.⁻¹. Indices of refraction were taken on an Abbe type refractometer (Bausch and Lomb Co., Model 56). Fractional distillations were performed on a Todd Co. apparatus with columns packed with glass helices. The spinning band column (Nester and Faust Co.) was 18 in. and had a stainless steel spinning band. Except where otherwise specified, this column was used only to remove the bulk of low-boiling solvent, and the reaction product was not distilled but was recovered as the pot residue. All sublimations were performed at about 60°. In sublimations from sodium the compound was placed in the sublimator, was covered with slices of freshly cut sodium, and was sublimed well below the melting point of sodium. Alumina Co. of America alumina was used for chromatography. N.m.r. spectra were recorded (in deuteriochloroform) by Dr. E. Warnhoff (University of Southern California) and also through the courtesy of Mr. L. Johnson (Varian Associates, Inc.) on a Model A60 spectrometer equipped with an area integrator. Band positions (δ) are expressed in p.p.m. downfield from internal tetramethylsilane. Mass spec-

tra were recorded on a Consolidated Electrodynamics Corp. Model 21-103c spectrometer by Mr. J. Sanders. Gas chromatography was performed on a Perkin-Elmer Model 154 fractometer. Deuterium analyses are expressed as atoms per molecule in excess of natural abundance.

mm. (reported^{11b} b.p. 81–85° at 87 mm.). Our product gave no precipitate with alcoholic silver nitrate after 2 hr., whereas both *exo*- and *endo*-norbornyl chloride gave copious precipitates within 5 min.

Norbornane.—Reduction of 1-chloronorbornane with sodium in methanol (in place of ethanol as reported^{11a}) gave norbornane, m.p. 83–86° after sublimation at atmospheric pressure from sodium. The same hydrocarbon (m.p. 87–88.5°) was obtained by hydrogenation of norbornene in ethyl acetate with a platinum catalyst according to a reported procedure.³² The reported m.p. is 87.8–88.3°. In the n.m.r. the relative intensity of the peak from the bridgehead hydrogens (2.22 δ) to the remaining hydrogens was 1:5.1 (theory 1:5.0). The infrared spectrum (CS₂) shows bands at 887, 870, and a specially characteristic strong band at 816 cm.⁻¹.

1-Deuterionorbornane.—The reduction was carried out in a drybox. 1-Chloronorbornane (1.30 g.) in deuteriomethanol (10 g., 99% CH₃OD, Merck Sharp and Dohme of Canada) was gently refluxed in an assembly connected at the top of the condenser to a Dry Ice trap. Sodium (2.5 g.) was added over a period of 1 hr., and the solution was refluxed 1 hr. longer, then cooled to room temperature. The solid that had collected in the condenser and in the trap was scraped out and sublimed twice from sodium at 1 atmosphere; 0.21 g. (21.6%), m.p. 84.5–85.5°. Gas chromatography on silicone and didecyl phthalate columns showed 1.5% of an impurity with the same retention time as that of the starting chloronorbornane. The infrared spectrum (in CCl₄) showed absorption at 2200, and (in CS₂) at 726 cm.⁻¹, where norbornane, *exo-d*-norbornane, and *endo-d*-norbornane show no absorption. No bands appeared between 909–833 cm.⁻¹ where the last three compounds each have at least two prominent peaks. Triplicate deuterium analyses by the combustion-infrared method gave 0.94, 0.97, and 0.97 D; the mass spectrum indicated 2% no D, 96.5% 1D, 1.5% 2D. In the n.m.r. spectrum the relative intensity of the bridgehead proton (2.22 δ) to the remaining protons was 1:10.8 (theory 1:10).

endo-Norborneol.—A solution of norbornan-2-one (25 g.) in dry ether (100 ml.) was added slowly to lithium aluminum hydride (18 g.) dissolved in 200 ml. of dry ether. After 45 min. reflux, the excess of hydride was decomposed by careful addition of water (30 ml.), followed by 5% hydrochloric acid. The water layer was separated and extracted with ether (100 ml.) and the combined ether layers yielded 18.5 g. of *endo*-norborneol, m.p. 144–148° (reported^{19a} m.p. 152–153°), contaminated with a little of the *exo* isomer.³⁴

endo-Norbornyl *p*-Bromobenzenesulfonate was prepared from *endo*-norborneol (m.p. 144–148°) as reported³⁵; m.p. 61–62° after recrystallization to constant m.p. from petroleum ether (b.p. 45–55°). The reported m.p. is 60–61.7°. We observed a significant m.p. depression when 3% of *exo* ester was mixed with the pure *endo* ester.

exo-Deuterionorbornane.—The following conditions were developed first by the use of lithium aluminum hydride and then applied to the preparation of the deuteriohydrocarbon. A solution of lithium aluminum deuteride (10.0 g., minimum 95% D, Metal Hydrides, Inc.) and *endo*-norbornyl *p*-bromobenzenesulfonate (23 g., m.p. 61–62°) in ether (2 l., dried by distillation from lithium aluminum hydride) was stirred and refluxed 12 days. The bulk of the ether was distilled from the mixture through a Todd fractionating column and the residue was concentrated further by distillation of ether through a spinning band column. The residue, still containing some ether, was dissolved in glacial acetic acid (15 ml.) and 8 drops of concentrated sulfuric acid was added (to convert any norbornene and nortricyclene to norbornyl acetate from which the product could be separated more easily). After 2 days at room temperature the mixture was poured into water (100 ml.) and extracted twice with pentane. The combined pentane layers were washed three times with water, dried with sodium sulfate, and filtered through a

tra were recorded on a Consolidated Electrodynamics Corp. Model 21-103c spectrometer by Mr. J. Sanders. Gas chromatography was performed on a Perkin-Elmer Model 154 fractometer. Deuterium analyses are expressed as atoms per molecule in excess of natural abundance.

(32) J. D. Roberts, L. Urbaneck, and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 3049 (1949).

(33) P. von R. Schleyer, *ibid.*, **80**, 1700 (1958).

(34) P. Hirsjarvi, *Suomen Kemi.*, **29B**, 138 (1956); *Chem. Abstr.*, **51**, 5004e (1957).

(35) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952).

column of alumina. The pentane solution was fractionally distilled through a spinning band column and the *exo-d*-norbornane fraction solidified in the condenser. This solid, 1.54 g. (22.8%), was gas chromatographically pure (didecyl phthalate column) and had m.p. 86.5–87°, ν (CCl₄) 2170 (shoulder at 2190), ν (CS₂) 858, 781 cm.⁻¹. There was no absorption at 840 (*endo-d*-norbornane), 816 (norbornane), 800 (nortricyclene), or 706 cm.⁻¹ (norbornene). Deuterium assay (combustion-infrared method) gave 0.93, 0.96 D; the mass spectrum indicated 2.5% no D, 97.5% 1D. The n.m.r. spectrum had a peak at 2.22 δ (bridgehead hydrogens) and overlapping bands dominated by peaks at 1.40 (*exo*-hydrogens) and 1.21 δ (*endo*- and C-7 hydrogens).¹⁷ The intensity ratio of the 2.22 δ peak to the remainder was 1:4.4 (theory 1:4.5).

2-*exo*-Deuterio-2-*endo*-norborneol.—A solution of lithium aluminum deuteride (5.0 g., minimum 95% D) and norbornan-2-one (26.0 g.) in dry ether (600 ml.) was stirred overnight at room temperature. Water (40 ml.) was cautiously added followed by 5% hydrochloric acid. The water layer was separated and extracted with more ether (150 ml.). The combined ether layers yielded 25.5 g. (95.5%) of crude 2-*exo-d*-2-*endo*-norborneol (m.p. 144–147°). A sample was sublimed (m.p. 145–147°) and analyzed for deuterium; 0.91, 0.92 D (combustion-infrared method).

2-*exo*-Deuterio-2-*endo*-norbornyl *p*-Bromobenzenesulfonate.—The procedure was the same as that used to prepare *endo*-norbornyl *p*-bromobenzenesulfonate except that 2-*exo-d*-2-*endo*-norborneol (m.p. 144–147°) was used. After recrystallization to constant melting point from petroleum ether the product had m.p. 60.5–61.5°.

***endo*-Deuterionorbornane** was prepared by the procedure used to obtain *exo-d*-norbornane, except that 2-*exo-d*-2-*endo*-norbornyl *p*-bromobenzenesulfonate (41 g., m.p. 60.5–61.5°) was used in place of *endo*-norbornyl *p*-bromobenzenesulfonate, and lithium aluminum hydride (20 g.) was used in place of lithium aluminum deuteride. The solid *endo-d*-norbornane obtained from the distillation through a spinning band column had m.p. 85.5–86.5° and was gas chromatographically pure (didecyl phthalate column). Loss of some product by accidental spillage prevented determination of yield. In the n.m.r. the intensity ratio of bridgehead protons (2.22 δ) to the remainder was 1:4.5 \pm 0.3 (theory 1:4.5). Deuterium analyses (combustion-infrared method) gave 1.01, 0.97, 0.99, 0.97, 0.94, and 1.00 D; the mass spectrum indicated 1% no D, 98.5% 1D, 0.5% 2D. The infrared spectrum (CCl₄) showed a band at 2185 (shoulder at 2160) and (CS₂) no absorption at 858 (*exo-d*-norbornane), 816 (norbornane), 800 (nortricyclene), or 706 cm.⁻¹ (norbornene). There was very weak absorption at 726 and, because *endo-d*-norbornane prepared by a different route¹⁹ exhibits a minimum at this position, we attribute the weak 726 cm.⁻¹ band to the presence of some (>10%) 1-*d*-norbornane.

***endo*-Norbornyl Chloride.**—*endo*-Dehydronorbornyl chloride was prepared (from vinyl chloride and cyclopentadiene) and hydrogenated by the method of Roberts and Bennett.³⁶ Our crude *endo*-norbornyl chloride (m.p. 25–27°, lit.³⁶ 34–36°) showed weak infrared absorption at 877 and 836 cm.⁻¹ where *exo*-norbornyl chloride has strong bands, and undoubtedly contained some of the *exo* isomer.

Reduction of *endo*-Norbornyl Chloride with Lithium Aluminum Deuteride.—A solution of the crude *endo*-chloride (1.0 g.) and lithium aluminum deuteride (0.5 g.) in bis(2-ethoxyethyl) ether (10 ml.) was stirred at 105° for 2 days. The crude *d*-norbornane that collected in the condenser had m.p. 81–83°; ν (CCl₄) 2175 and a shoulder at 2190 cm.⁻¹; ν (CS₂) 895, 880, 858, and 781 cm.⁻¹. All these bands are present in the spectrum of *exo-d*-norbornane. There was no absorption (in CS₂) at 888, 840, and 790 cm.⁻¹ where *endo-d*-norbornane has bands and we conclude that the crude product is chiefly, if not entirely, *exo-d*-norbornane.

Norbornene, prepared from ethylene and cyclopentadiene as reported,³⁷ had m.p. 45–46°, b.p. 95–96°, ν (CS₂) 706 cm.⁻¹; lit. m.p. 44–46°, b.p. 95–96°.

***exo*-Norbornyl Chloride.**—Hydrogen chloride was added to norbornene as reported³⁸; b.p. 51.5–52.5° (11 mm.), n^{25}_D 1.4840. The published constants are b.p. 52° (11 mm.), n^{20}_D 1.4849.

Reduction of *exo*-Norbornyl Chloride with Lithium Aluminum Deuteride.—A solution of *exo*-chloride (1.0 g.) and lithium aluminum deuteride (0.5 g.) in bis(2-ethoxyethyl) ether was stirred

at 105° for 2 days. The crude *d*-norbornane that collected in the condenser (0.24 g., 33%) had m.p. 81–83°. The infrared spectrum (in CCl₄) exhibited the bands characteristic of *exo-d*-norbornane (2175, shoulder at 2190, 895, 880, and 858 cm.⁻¹) and lacked bands at 888 and 840 characteristic of *endo-d*-norbornane. On this basis the crude hydrocarbon appeared to be largely, if not entirely, *exo-d*-norbornane.

Nortricyclene.—The procedure of Schleyer³³ was used to isomerize norbornene to nortricyclene with titanium dioxide and silica-alumina catalysts; m.p. 58°, ν (CS₂) 800 cm.⁻¹.

Addition of Hydrogen Chloride to Nortricyclene.—Reagent grade methylene chloride (25 ml.) was saturated with hydrogen chloride gas from a cylinder. Nortricyclene (1.29 g., containing 2% norbornene by gas chromatography on didecyl phthalate) was added and the solution was stirred 4 days at room temperature in a stoppered flask. The solvent was evaporated (on a steam bath) and was replaced by pentane (25 ml.), which was also evaporated. The residue was chromatographed on alumina and eluted with pentane to give 1.62 g. (97.6%) of oil. Comparison of its infrared spectrum with spectra of *exo*- and *endo*-norbornyl chloride and of artificial mixtures of the two isomers showed that the oil was *exo*-norbornyl chloride with no detectable *endo* isomer (less than 3.5%). An artificial mixture of 32% *endo*-norbornyl chloride and 68% *exo*-norbornyl chloride was subjected to the conditions of the ring opening reaction and was recovered. The infrared spectrum indicated that the composition of the mixture had not changed detectably.

Addition of Deuterium Chloride to Nortricyclene.—Deuterium chloride gas was generated from phosphorus trichloride and deuterium oxide as reported,³⁹ and passed through a Dry Ice trap. The gas was bubbled through a stirred solution of nortricyclene (5.5 g., containing 0.5% norbornene) in methylene chloride (300 ml., previously rinsed with 1 ml. of deuterium oxide), and the solution was stirred at room temperature for 1 week in a stoppered flask. The solvent was evaporated and replaced by pentane (100 ml.), which was also evaporated. The residue in fresh pentane was chromatographed on alumina. The pentane eluate was evaporated and yielded 6.36 g. (82.7%) of deuterio-*exo*-norbornyl chloride. Gas chromatography showed the presence of 3–4% of pentane. The mass spectral deuterium distribution in the *exo*-chloride was 21.5% no D, 52% 1D, 22.5% 2D, 4% 3D (total 1.09D).

Conversion of Deuterio-*exo*-norbornyl Chloride to Deuterio-norbornane.—Oven-dried magnesium turnings (0.55 g.) were placed in a dry flask with 80 ml. of ether (dried by distillation from lithium aluminum hydride) and Seaford grade nitrogen was bubbled through the ether for 10 min. Deuterio-*exo*-norbornyl chloride (2.63 g.) was added, along with several drops of methyl iodide. The flask was flushed with nitrogen, then stoppered, and the mixture was stirred 5.5 hr., after which only traces of magnesium remained. Careful addition of water and then 4% hydrochloric acid caused the ether to boil rapidly and gave a clear two-phase system. The ether layer was dried with sodium sulfate and distilled off through a spinning band column. Preparative gas chromatography⁴⁰ of the residual oil (3–4 ml.) yielded 0.60 g. (31%) of *d*-norbornane, which had m.p. 82–84.5° after sublimation from sodium at atmospheric pressure. The infrared spectrum (CS₂) showed bands characteristic of *exo-d*- and *endo-d*-norbornane, and norbornene; small amounts of nortricyclene (5–8%) and norbornene were also indicated. Analysis (by combustion-infrared) gave 1.01 and 1.02 D; the mass spectrum showed 21% no D, 53% 1D, 21% 2D, 5% 3D (total 1.10D).

***exo*-Norbornyl Acetate.**—*exo*-Norborneol (m.p. 124.5–125.5°, Aldrich Chemical Co.; reported⁴¹ m.p. 127–128°) was acetylated with acetic anhydride as reported¹⁹; n^{23}_D 1.4571, n^{25}_D 1.4549 (interpolated n^{25}_D 1.4565, lit.¹⁹ n^{25}_D 1.4565).

Stability of Optically Active *exo*-Norbornyl Acetate.—Optically active *exo*-norbornyl acetate³⁰ (0.2287 g.) in 2 ml. of a solution of 0.148 M sulfuric acid in acetic acid exhibited $[\alpha]_D +6.59 \pm 0.04^\circ$ at room temperature (23.5°). After 10 hr. at this temperature the optical rotation was $[\alpha]_D +6.63 \pm 0.04^\circ$.

***endo*-Norbornyl Acetate.**—Acetylation of *endo*-norborneol (m.p. 148–149.5°; contains a little *exo* isomer) in acetic anhydride as reported^{19a} gave the acetate, n^{23}_D 1.4588. Our com-

(39) D. H. R. Barton and P. de Mayo, *J. Chem. Soc.*, 2178 (1953).

(40) Conducted on an F and M Model 21 fractometer adapted with four 2-ft. lengths of stainless steel tubing (1 in. diameter) joined in series by short U-shaped pieces of 0.25 in. tubing. The packing was di-*n*-decyl phthalate on firebrick.

(41) G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).

(36) J. D. Roberts and W. Bennett, *J. Am. Chem. Soc.*, **76**, 4623 (1954).

(37) L. M. Joshel and L. W. Butz, *ibid.*, **63**, 3350 (1941).

(38) L. Schmerling, *ibid.*, **68**, 195 (1946).

pound gave a single peak on gas chromatography (silicone column) but, as we expect our *endo*-acetate to contain a little of the *exo*-isomer, apparently these two were not resolved on this column.

Cleavage of Nortricyclene. (a) **With Sulfuric Acid in Acetic Acid.**—A solution of sulfuric acid in glacial acetic acid (0.24 g. in 30 ml., 0.08 *M*) was combined with nortricyclene (2.00 g., m.p. 57–58°, 1% norbornene by gas chromatography) and stirred 24 hr. at room temperature. After dilution with water (100 ml.) and extraction with pentane the combined pentane layers were washed twice with sodium carbonate solution, then were dried with sodium sulfate. Evaporation left 2.97 g. (90.5%) of oil, n_D^{20} 1.4570. Comparison of its infrared spectrum with spectra of *exo*- and *endo*-norbornyl acetate and of artificial mixtures of the two isomers showed that the product was the *exo* isomer containing no detectable *endo* isomer (less than 5%).

(b) **With Deuteriosulfuric Acid in Deuterioacetic Acid.**—A 50-ml. solution of deuterioacetic acid ($\text{CH}_3\text{CO}_2\text{D}$, 98% D) that was 1.13 *M* in nortricyclene (5.30 g., m.p. 57.5–58°, 99% pure by gas chromatography on didecyl phthalate) and 0.136 *M* in deuteriosulfuric acid (D_2SO_4 , 0.68 g.) was stirred 10 hr. at room temperature. (Aliquots removed at periods up to 8 hr. still contained some unchanged nortricyclene.) The solution was diluted with water (250 ml.), was neutralized with sodium carbonate, and was extracted twice with pentane. The combined pentane layers were washed twice with aqueous sodium bicarbonate, were dried with sodium sulfate, and were concentrated with a spinning band column. The residual oil in fresh pentane was filtered through a column of alumina and, after the eluate was concentrated in a spinning band column, the last traces of pentane were removed on the steam bath and left 6.89 g. (79.3%, 83.9% corrected for aliquot withdrawal) of 6-deuterio-2-*exo*-norbornyl acetate. Deuterium assay by the combustion-infrared method gave 0.91, 0.91, 0.91, and 0.91 D.

The following sequence involving conversion to the alcohol, oxidation to the ketone, and reduction to the hydrocarbon was developed first with the corresponding nondeuterated compounds.

6-Deuterio-2-*exo*-norborneol.—A solution of 6-deuterio-2-*exo*-norbornyl acetate (6.80 g.) in dry ether (20 ml.) was added slowly to a stirred solution of lithium aluminum hydride (7.1 g.) in dry ether (200 ml.). After 16 hr. additional stirring at room temperature the excess of hydride was decomposed by successive addition of water (7.1 ml.), 15% sodium hydroxide (7.1 ml.) and water (21.3 ml.) according to the general method of Micovic and Mihailovic.⁴² The resulting mixture was extracted three times with ether. The combined ether layers were washed with water and dried with sodium sulfate. Evaporation left the crude 6-deuterio-2-*exo*-norborneol (3.81 g., 77%), m.p. 122.5–124.5°, raised to m.p. 126–127° on vacuum sublimation; reported for *exo*-norborneol, m.p. 127–128°. Deuterium analyses by the combustion-infrared method⁴³ gave 0.84 and 0.84 D; the combustion-infrared method gave 0.74, 0.76, 0.77, and 0.77 D. Assay by mass spectrometry was attempted, but quantitative analysis of the mass pattern did not prove feasible.

6-Deuterionorbornan-2-one.—To a solution of chromium trioxide (2.55 g.) in glacial acetic acid (20 ml.) was added 6-deuterio-2-*exo*-norborneol (3.42 g., m.p. 122.5–124.5°). The temperature of the mixture was kept at 40° for 30 min. and then at 50° for 30 min. Water (100 ml.) was added and the mixture was extracted twice with pentane. The combined pentane layers were washed with water and dried with sodium sulfate. On removal of the solvent with a spinning band column, the deuterio-ketone remained as a crude solid (1.23 g., 49.2%), which had m.p. 92.5–94° after one sublimation at atmospheric pressure (reported for norbornan-2-one, m.p. 93–94°,⁴⁴ 109–110°²¹). Deuterium analyses gave 0.80 and 0.80 D (combustion-falling drop⁴⁵), and 0.79, 0.80, 0.84 D (combustion-infrared). The mass spectrum indicated 17.5% no D, 89% 1D, and 2.5% 2D (total 0.85D).

(42) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(43) Performed by J. Nemeth, University of Illinois, Urbana, Ill.

(44) S. V. Hintikka and G. Komppa, *Ann. Acad. Sci. Fennicae*, **A10**, No. 22, 1 (1918); *Chem. Abstr.*, **13**, 2863 (1919).

2-Deuterionorbornane by Wolff-Kishner Reduction.⁴⁶—A mixture of 6-deuterionorbornan-2-one (1.2 g.), potassium hydroxide pellets (1.26 g.), 95% hydrazine hydrate (1.6 ml.), and triethylene glycol (8 ml.) was refluxed 4 hr. The solid deuterionorbornane that collected in the condenser was scraped out and sublimed at atmospheric pressure from sodium to give 0.23 g. (21.7%), m.p. 81–83° (lit.³³ m.p. 87.8–88.3°). To ensure removal of vestigial water and hydrazine prior to infrared analysis, a solution of the product in carbon disulfide was dried with calcium chloride and filtered. In addition to bands characteristic of *exo*- and *endo*-deuterionorbornane, the infrared spectrum (CS_2) indicated 20–25% norbornane (816 cm^{-1}) and possibly 3–4% of nortricyclene (based on absorbance at 800 cm^{-1}). There was very weak absorption at 726 cm^{-1} (characteristic of 1-deuterionorbornane), but its intensity was too low to be estimated quantitatively. Quantitative comparisons of several scans of the spectrum with those of *endo*- and *exo*-deuterionorbornane and of artificial mixtures of the two isomers indicated that the *exo:endo* ratio in the 2-deuterionorbornane from reduction was 1:1.08 \pm 0.15.

Deuterium Analyses. (a) **By Mass Spectrometry.**—Because of their volatility, our compounds were amenable to direct mass spectral analysis. Assay by this method depends on comparison of the relative heights of peaks corresponding to the parent ions of the labeled and unlabeled molecules. The method is valid provided that the labeled molecules fragment substantially in the same way and to the same extent as do the unlabeled analogs; otherwise the experimental deuterium values can be higher or lower than the true values. That this requirement was met by our deuterionorbornanes and by the deuterionorbornan-2-one is shown by the good agreement for values of total deuterium obtained by mass spectrometry and by the combustion-infrared method. In the mass analyses appropriate correction factors were applied for the natural abundances of heavy isotopes⁴⁶; the mass spectra of the corresponding unlabeled compounds were run to establish correction factors for relevant fragmentations (*e.g.*, those involving loss of one or two hydrogens).

(b) **By the Combustion-Infrared Method.**—The general technique was similar to that reported by Jones and MacKenzie⁴⁷ with modifications. It consisted of appropriate dilution of the labeled compound (either with the unlabeled analog or with a pure *n*-alkane of similar volatility⁴⁸), combustion in a train similar to those used for conventional microanalyses, collection of the derived water, and quantitative analysis of the O–D band intensity at *ca.* 2500 cm^{-1} in its infrared spectrum. Full details of the technique are available⁴⁹ and will be published elsewhere.

(c) **Combustion-Falling Drop Method.**—This method of assay, performed for us,⁴³ requires combustion of the organic compound and determination of the relative density of the derived water from its descent in a column of liquid immiscible with water.

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(45) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(46) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, Appendix I, p. 486.

(47) R. N. Jones and M. A. MacKenzie, *Talanta*, **3**, No. 4, 356 (1960).

(48) *exo*-Norborneol was the diluent for its deuterated analog and also for 2-*exo-d-2-endo*-norborneol; *exo*-norbornyl acetate was diluent for its labeled analog. Deuterionorbornanes were diluted with *n*-heptane (Fisher Co., Spectro Grade) or *n*-octane (Phillips Petroleum Co., pure grade) and the deuterionorbornan-2-one was diluted with *n*-decane (Phillips Petroleum Co., pure grade).

(49) J. L. Lambert, S. J., Ph.D. Dissertation, The Johns Hopkins University, 1963.