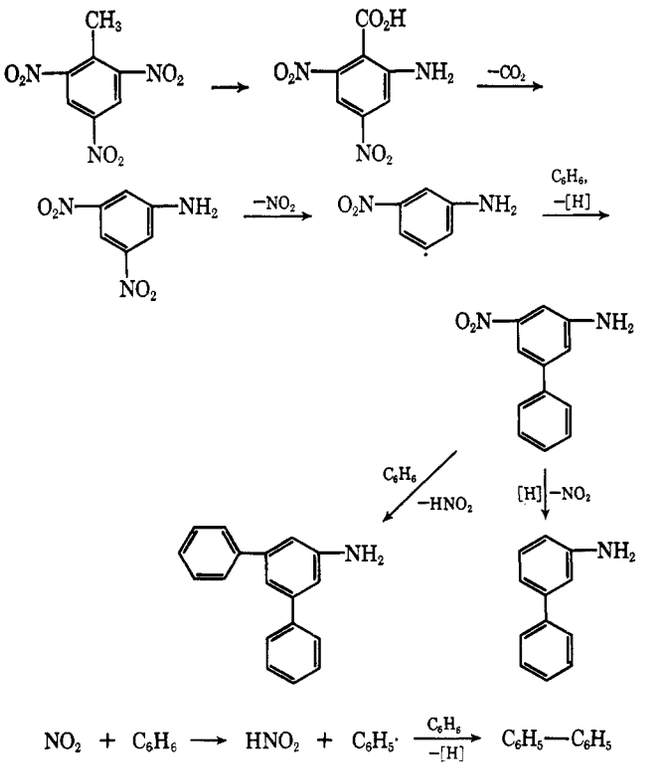
SCHEME II



$$NO_2 + C_6H_6 \longrightarrow HNO_2 + C_6H_5\cdot \xrightarrow[-[H]]{C_6H_6} C_6H_5{-}C_6H_5$$

Aminobiphenyl is present in appreciably greater amount than aniline. This may be because the radical from dinitroaniline must participate in two hydrogen abstractions rather than one as in the case of the aminobiphenyl radical.

With increasing temperature the products still containing nitro groups, dinitroaniline and nitroaminobiphenyl, decreased, as would be anticipated. Even at the lowest temperature, 400°, no trinitrotoluene apparently survived; it is therefore considerably less stable than *o*-nitrotoluene, 50% of which was recovered after 20 sec at 500°.

TABLE XI
PRODUCTS FROM 2,4,6-TRINITROTOLUENE WITH BENZENE AT VARIOUS TEMPERATURES[a]

Total weight of products, g	2.75	3.7	3.92	4.0
Temperature, °C	400°	450°	500°	550°
	Relative concn[b]			
Products				
Aniline	5	7	20	19
Biphenyl	100	100	100	100
Aminobiphenyl	13	29	29	27
Dinitroaniline	8	3	1	1
Nitroaminobiphenyl	2	3	0.4	0.3
Aminoterphenyl		3	5	6

[a] Conditions: 20-sec contact time, N_2 at 20 cc/min, moles of TNT:benzene 0.05:0.5. [b] Relative intensities in the low-voltage (7.5 V, uncorrected) mass spectrum normalized to biphenyl = 100.

The present work has shown a striking difference in the reactions of *o*-nitrotoluene and substituted *o*-nitrotoluenes from those of the *meta* and *para* isomers. We are pursuing this study further by examining the behavior of labeled and unlabeled *o*-nitroethylbenzene, *o*-nitrocumene, and *o*-nitro-*t*-butylbenzene at 600°.

Registry No.—Benzene, 71-43-2; benzene-d_6, 1076-43-3; chlorobenzene, 108-90-7; methanol, 67-56-1; *o*-nitrotoluene, 88-72-2; *m*-nitrotoluene, 99-08-1; *p*-nitrotoluene, 99-99-0; 2,4-dinitrotoluene, 121-14-2; 2,4,6-trinitrotoluene, 118-96-7.

Acid-Catalyzed Cleavage of 1-Methylnortricyclene[1]

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The preparation of 1-methylnortricyclene (**7**) was accomplished in good yield from 1-methyl-2-norbornanone *p*-toluenesulfonylhydrazone (**6**). The kinetic product from reaction of **7** with acetic acid was 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**), which was slowly converted into 1-methyl-2-*exo*-norbornyl acetate (**3**), and 2-*exo*-methyl-2-*endo*-norbornyl acetate (**10**) under the reaction conditions. Cleavage with acetic acid-O-*d* gave a mixture of **3**, **9**, and **10** containing up to five deuteriums per molecule. Treatment of the acetates with alumina, ozonolysis, and washing with aqueous alkali gave monodeuterated 2-norbornanone (**1**). The infrared spectrum of this material showed that the deuterium was 62 ± 3% 6-*endo* and 38 ± 3% 6-*exo*, demonstrating that cleavage of the cyclopropyl C–C bond by the electrophile, D^+, occurs with predominating retention of configuration. The results are accounted for in terms of a carbonium ion intermediate which can react by any of five paths; qualitative conclusions are presented on the way in which the intermediate partitions among these paths.

Studies of cleavage of the cyclopropane ring in tricyclo[2.2.1.$0^{2,6}$]heptanes with acetic acid have been concerned for the most part with the question of product distribution. In the case of unsymmetrically substituted tricyclo[2.2.1.$0^{2,6}$]heptanes, any one of three bonds may cleave, and each can add an unsymmetrical reagent like acetic acid with either of two modes of orientation. Thus, as many as six different products can be formed, neglecting stereochemistry. Compounds such as apocyclene[2] (3,3-dimethyltricyclo[2.2.1.$0^{2,6}$]heptane) and epicyclene[3] (3,3,4-trimethyltricyclo[2.2.1.$0^{2,6}$]heptane), which have hydrogens on all three cyclopropyl carbons, give mixtures of isomeric acetates on reaction with acetic acid. In contrast, derivatives of 1-methylnortricyclene (**7**) have been reported to be converted cleanly into substituted 1-methyl-2-norbornyl acetates;[4] 1-methylnortricy-

(1) This research was supported in part by a National Science Foundation Undergraduate Research Participation grant to the Department of Chemistry, Swarthmore College.

(2) S. S. Nametkin and Z. Alexandrova, *J. Russ. Phys. Chem. Soc.*, **57**, 395 (1926); S. S. Nametkin and Z. Alexandrova, *Ann.*, **467**, 191 (1928).

(3) S. S. Nametkin and L. Bryusova, *J. Russ. Phys. Chem. Soc.*, **62**, 333 (1930).

(4) S. Moycho and F. Zienkowski, *Ann.*, **340**, 17 (1905).

clene itself is a typical example, giving only 1-methyl-2-*exo*-norbornyl acetate (**3**).[5] However, 2-*endo*-methyl-2-*exo*-norbornyl acetates are now known to rearrange to 1-methyl-2-*exo*-norbornyl acetates under conditions considerably less vigorous than those employed for cyclopropyl ring cleavage.[6,7] The secondary acetates obtained may have been kinetic products; alternatively, tertiary acetates may have formed first and subsequently rearranged to the secondary isomers. No evidence has previously been presented on this point.

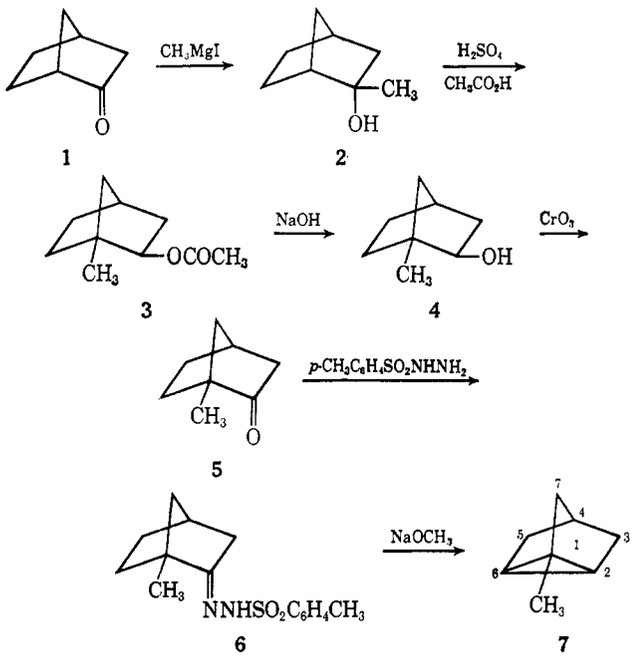
A second point of interest is the stereochemistry of addition of acetic acid to nortricyclene derivatives. Cleavage of nortricyclene by acetic acid-O-*d* occurs with complete lack of stereospecificity for the deuteration and complete *exo* specificity for the acetate, implying that the reaction proceeds through a carbon-bridged norbornyl cation (or the equivalent with respect to these experiments, an equilibrating pair of classical cations).[8] If there is a preferred stereochemistry for deuteration, in the unsubstituted norbornyl system it is unobservable because of the symmetry of the bridged ion. Introduction of a group other than hydrogen at the 1 position would destroy this symmetry and allow determination of the stereochemistry of deuteration.

Our investigation of acetic acid cleavage of 1-methylnortricyclene was undertaken to shed light on these two questions: (1) identification of the kinetic product of cleavage, and (2) determination of the preferred stereochemical course for the deuteration step.

Discussion and Results

Synthesis of 1-Methylnortricyclene.—2-Norbornanone (**1**) was converted into 1-methyl-2-norbornanone (**5**) by a series of known reactions (Scheme I).[9] Treatment of **1** with methylmagnesium iodide gave 2-*exo*-methyl-2-*endo*-norbornanol (**2**). Simultaneous rearrangement and acetylation of **2** with sulfuric acid in acetic acid yielded 1-methyl-2-*exo*-norbornyl acetate (**3**), which was saponified to the corresponding alcohol (**4**). Chromium trioxide oxidation of **4** gave 1-methyl-2-norbornanone (**5**). The *p*-toluenesulfonylhydrazone of **5** reacted with sodium methoxide in refluxing diglyme to give an 88% yield of 1-methylnortricyclene (**7**). Analysis by gas chromatography showed **7** to be 99% pure, and the infrared spectrum showed cyclopropyl C–H stretching absorption at 3055 cm^{-1} and characteristic 1-substituted nortricyclene absorption[10] at 849 and 785 cm^{-1}.

SCHEME I



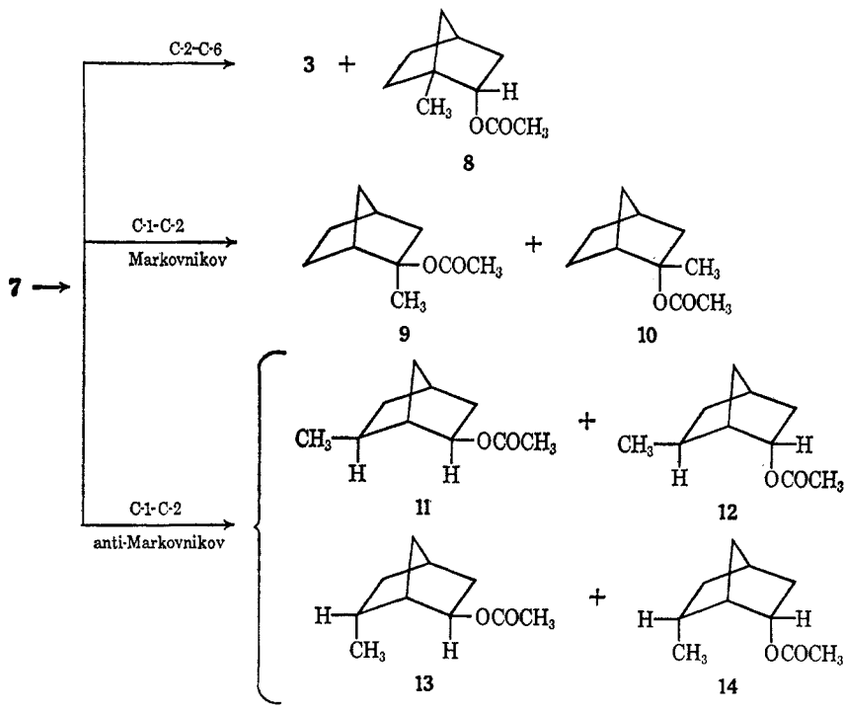
Ring Cleavage in Acetic Acid.—Addition of acetic acid to 1-methylnortricyclene (**7**) could lead to any of eight possible products (Scheme II). Cleavage of the C-2–C-6 bond would give 1-methyl-2-*exo*-norbornyl acetate (**3**) or its 2-*endo*-acetoxy epimer (**8**). Cleavage of the C-1–C-2 bond could occur by either of two orientation modes. Markovnikov addition would yield 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**) or its 2-*exo*-methyl-2-*endo*-acetoxy epimer (**10**). Anti-Markovnikov cleavage of this bond could give any of four 6-methyl-2-norbornyl acetates: 6-*exo*-methyl-2-*exo* acetate (**11**), 6-*exo*-methyl-2-*endo* acetate (**12**) 6-*endo*-methyl-2-*exo* acetate (**13**), or 6-*endo*-methyl-2-*endo* acetate (**14**).

The ring-cleavage experiments were carried out at 24.5 ± 0.1° in the presence of 0.005 *M* sulfuric acid. After 2 hr 1-methylnortricyclene (**7**) was 15 ± 5% converted into acetate. The product was isolated by pentane–water extraction and vacuum distillation. Comparison of the infrared (ir) spectrum of this material with spectra of acetates **3**, **8**, **9**, and **10** established that the cleavage product was 2-*endo*-methyl-2-*exo* norbornyl acetate (**9**) containing no detectable **3**, **8**, or **10**. Examination of spectra of artificial mixtures of **9** with **3**, with **8**, and with **10**, showed that as little as 2.5% of any one of these three isomers could have been detected with certainty. Thus, the kinetic product of acetic acid addition to **7** is pure or nearly pure tertiary *exo*-acetate (**9**), the product of C-1–C-2 cleavage and Markovnikov addition. The fact that only *exo* acetate is formed suggests that the reaction proceeds through a 2-norbornyl cation; these ions are well known to react with acetate from the *exo* side under conditions of kinetic control. Two other reactions which proceed by way of the same cation, acetolysis of 1-methyl-2-*exo*-norbornyl *p*-toluenesulfonate[11a] and nitrosative deamination of 2-*endo*-methyl-2-*exo*-norbornylamine in acetic acid,[11b] were reported to give **9** as the kinetic product.

When the cleavage reaction was continued for 42 hr, conversion of **7** into acetates was nearly complete. The ir spectrum of the product mixture revealed the presence of three acetates, 1-methyl-2-*exo*-norbornyl acetate (**3**), 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**), and 2-*exo*-methyl-2-*endo*-norbornyl acetate (**10**), and comparison of this spectrum with spectra of artificial mixtures of the three isomers indicated that the product consisted of 55 ± 5% the kinetic product,

(5) J. Paasivirta, *Suomen Kemistilehti*, **B33** (2), 57 (1960).
(6) H. Meerwein and K. van Emster, *Ber.*, **53**, 1815 (1920); **55**, 2500 (1922).
(7) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Amer. Chem. Soc.*, **89**, 2590 (1967).
(8) A. Nickon and J. H. Hammons, *ibid.*, **86**, 3322 (1964).
(9) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *ibid.*, **83**, 3986 (1961).
(10) H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959).
(11) (a) J. A. Berson, A. W. McRowe, and R. G. Bergman, *J. Amer. Chem. Soc.*, **89**, 2573 (1967); (b) S. Beckmann, R. Schaber, and R. Bamberger, *Ber.*, **87**, 997 (1954).

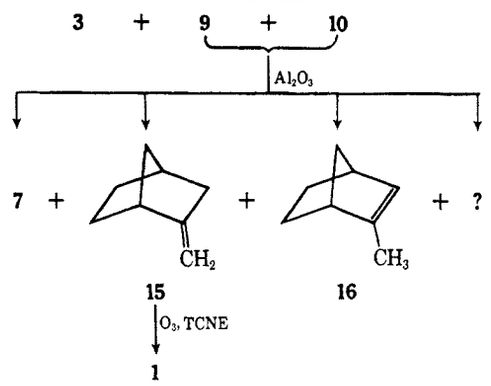
SCHEME II



9, 28 ± 5% 3, and 17 ± 5% 10;[12a] none of the secondary *endo* acetate 8 appeared to be present. The four 6-methyl-2-norbornyl acetates, 11, 12, 13, and 14, were not prepared and therefore could not be demonstrated with certainty to be absent from the reaction mixture. However, the superimposability of the infrared spectrum of the product on that of an artificial mixture of 3, 9, and 10 argues against the formation of any of these isomers, and this argument is supported by the gas chromatograph of the acetate mixture which showed that no substance of retention time longer than that for 9 was present.[12b]

Degradation of 2-*endo*-Methyl-2-*exo*-norbornyl Acetate to 2-Norbornanone.—The second purpose of our investigation was to determine the stereochemistry of the deuteration step in reaction of 1-methylnortricyclene (7) with acetic acid-O-*d*. No direct method was available for analysis of the stereochemistry of the deuterium at C-6 of 2-*endo*-methyl-2-*exo*-norbornyl acetate (9). A possible indirect method involved degradation of 6-deuterated 9 to 6-deuterated 2-norbornanone (1) and analysis of the stereochemistry of the deuterium by comparison of the ir spectrum of this compound with spectra of the known 6-*exo*-*d*- and 6-*endo*-*d*-2-norbornanone.[13] Our plan of attack was to separate 9 from 3 and 10 by chromatography and to convert 9 into 2-methylenenorbornane (15), which would be readily oxidized to 1 (see Scheme III). Chromatography of pure 3 on alumina of activity grade I let to recovery of unchanged 3. In contrast, 9 was cleanly converted into a mixture of four lower boiling compounds. The major component, which constituted

SCHEME III



56% of the mixture, was identified both by its ir spectrum and by vpc retention time as the desired alkene, 15. Two of the minor components had retention times identical with those of 7 and 2-methyl-2-norbornene (16); the remaining product was not identified. Chromatography of 10 gave some unchanged 10, together with the same four low-boiling compounds previously obtained from acetate 9; 15 constituted 49% of the more volatile fraction obtained from the *endo* acetate.

Ozonolysis of 15 in the usual way gave primarily oxidation products other than 1, but ozonolysis in the presence of an equimolar amount of tetracyanoethylene[14] resulted in successful conversion of 15 into 1; 1 was readily purified by sublimation.

In view of the fact that an adequate yield could be obtained from the ring cleavage only with reaction times long enough to produce substantial amounts of the thermodynamic products 3 and 10, it was necessary to decide in the later experiments with deuterated acetates whether to separate the acetate mixture before treatment with alumina or to chromatograph the mixture directly. Our decision was to subject the mixture

(12) (a) Analysis of this mixture by vapor phase chromatography was not satisfactory for two reasons. First, partial pyrolysis of 9 lowered the accuracy considerably; second, 3 and 10 were not resolved on any of our columns. (b) Acetates 3, 9, and 10 are known to have markedly shorter retention times on a triscyanoethoxypropane column than any of 13 isomeric methyl-2-norbornyl acetates, including 11 and 13; see ref 11a.

(13) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Amer. Chem. Soc.*, **85**, 3713 (1963).

(14) This method was reported for ozonolysis of camphene by R. Criegee and P. Günther, *Ber.*, **96**, 1564 (1963).

itself to chromatography. This choice was made for the following reasons. First, no anomalous results would be observed as a consequence of the presence of **3**, as this acetate was shown not to be converted into alkenes on alumina. Second, although **10** is partially converted into alkenes on alumina, there are sound reasons for thinking that the stereochemistry of the deuterium at C-6 in **10** would not be significantly different from that in the *exo* epimer **9**. As the arguments in the concluding section of the Discussion indicate, the stereochemistry of the deuterium at C-6 is determined when D^+ adds to **7** to form carbonium ion **17**, and it is unchanged by subsequent events. Acetate **10** is formed by *endo* attack of acetic acid on deuterated ion **17** after the deuteration step is complete. The possibility that *endo* acetate is formed from **7** by a completely different path involving different stereochemistry for the C-6 deuterium is ruled out by the facts that the protonation step is irreversible and that the amount of *endo* acetate in the kinetic product is too small to be detected.

The conversion of deuterated alkene **15** into 2-norbornanone (**1**) was also accomplished by direct ozonolysis of the four-component mixture produced by chromatography and not by isolation of pure **15** followed by ozonolysis. This approach is justified on the ground that none of the three minor components of the mixture would give **1** on ozonolysis.

Cleavage in Deuterated Acetic Acid. Deuterium Incorporation.—The acetic acid-O-*d* used in these experiments was prepared from distilled acetic anhydride and a slight excess of D_2O (99.77% D) and contained 0.5% water by Karl Fischer analysis. The ring cleavage mixture, consisting of 0.12 *M* 1-methylnortricyclene (**7**) and 0.0061 *M* sulfuric acid-d_2 in acetic acid-O-*d*, was maintained at 24.5 ± 0.1° for 39 hr. Work-up of the reaction mixture and fractional distillation of the recovered materials gave a small amount of a low-boiling fraction, shown by gas chromatography to contain 96% starting material and 4% 2-methylenebornane (**15**), and a large higher boiling fraction which consisted of 58 ± 5% 2-*endo*-methyl-2-*exo*-norbornyl acetate and 42 ± 5% isomeric acetates **3** and **10**.

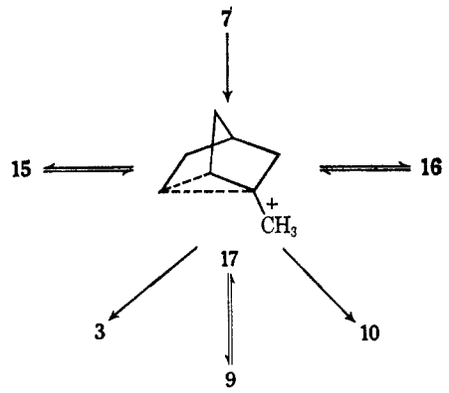
When a portion of the acetate fraction was converted into alcohols and analyzed by mass spectrometry, the alcohols were found to contain not just the one deuterium to be expected on the basis of simple addition of one molecule of acetic acid-O-*d* to **7**, but instead up to five deuterium atoms per molecule. Thus, the original objective of determination of the stereochemistry of the 6-deuterium could be accomplished only if the extra four deuterium atoms could be located and removed. Examination of the fragmentation patterns for the deuterated alcohols and for undeuterated 2-*endo*-methyl-2-*exo*-norbornanol (**18**) yielded useful information. A major fragmentation peak for **18** occurred at mass 111 (M − 15), corresponding to loss of the methyl group. For the deuterated sample the major peaks appeared at mass 112 and 113 (mono- and dideuterated ions), and the peaks at mass 114, 115, and 116 were barely greater than that calculated for natural isotopic abundance. Clearly three of the deuterated positions were in the methyl group.

This conclusion was confirmed by the results of degradation of the mixture of deuterated acetates to 2-norbornanone (**1**). Chromatography on alumina of activity grade I gave a mixture of four components (**7**, **15**, **16**, and the unidentified one) containing up to four deuterium atoms per molecule, and ozonolysis of the alkene mixture in the presence of tetracyanoethylene yielded 2-norbornanone (**1**) which was 96% composed of un-, mono-, and dideuterated molecules. Degradative removal of the methyl group of acetate **9**, then, was accompanied by loss of three deuterium atoms.

The fragmentation patterns of **1** and dideuterated **1** gave a clue as to the location of the remaining extra deuterium. The base peak for **1** appeared at mass 67. By analogy to the fragmentation of camphor, which loses ketene and a methyl radical to give a base peak at mass 95, attributed to an allylic dimethylcyclopentenyl cation,[15] we attribute the base peak of 2-norbornanone to an allylic cyclopentenyl cation formed by loss of ketene and a hydrogen atom from C-7. In our deuterated **1** the base peak appeared at mass 68. This result was consistent with the presence of one deuterium at C-6 and a second at C-3. Treatment of dideuterated **1** with methanolic aqueous alkali to remove enolizable deuterium gave a sample of **1** which was 83% mono- and 17% undeuterated, thus demonstrating that the last of the extra deuterium atoms had been incorporated in the 3 position of **9**.

These deuterium incorporation results are readily explained in terms of a bridged methylnorbornyl cation (**17**) or a pair of classical cations interconvertible by Wagner–Meerwein rearrangement (Scheme IV).

SCHEME IV



Deuteration of 1-methylnortricyclene (**7**) gives a cation (**17**) which is labeled at C-6. Loss of a proton from a carbon α to the charged site yields an alkene, which can add D^+ and regenerate the carbonium ion. Repeated loss of a proton from the methyl to form 2-methylenenorbornane (**15**), followed by addition of D^+ to the methylene carbon, results in introduction of three deuterium atoms into the methyl of the carbonium ion (**17**). Loss of a proton from C-3 yields 2-methyl-2-norbornene (**16**), which can regenerate the carbonium ion by addition of D^+ to C-3. As the 2-norbornanone from ozonolysis contained up to two deuterium atoms per molecule and as only one deuterium could be removed by treatment with alkali, evidently only one deuterium atom in acetate **9** was located at C-3. Therefore, proton loss and deuteration at C-3 are ap-

(15) D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966); D. R. Dimmel and J. Wolinsky, *ibid.*, **32**, 410 (1967).

parently highly stereoselective. Similar stereoselectivity has recently been reported in base-catalyzed deuteration of 2-norbornanone, camphor, and isofenchone,[16a] and in addition of deuterium chloride to norbornene in methylene chloride;[16b] nmr data indicated that *exo* deuteration was the preferred path in each case.

Rationalization of the incorporation of three extra deuterium atoms per molecule in terms of the intermediate formation of 2-methylenenorbornane (**15**) requires that **15** should react substantially faster than 1-methylnortricyclene (**7**) does under the cleavage conditions, and that it should give the same product distribution as **7**, namely, clean conversion into 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**).[17] In fact **15** reacted with a half-life approximately $^1/_{30}$ that of **7**, and, when the addition reaction was interrupted after about one half-life, the product was pure **9**. Further confirmation of the role of this alkene as an intermediate was obtained by actual isolation of a trace of it from a large-scale cleavage of 1-methylnortricyclene (**7**) in acetic acid-O-*d*. Fractional distillation of the product mixture permitted separation of the low-boiling alkene and starting material from acetates, and preparative gas chromatography yielded a small amount of pure alkene (**15**). The compound contained up to four deuterium atoms per molecule. The amount of material was too small to permit location of these deuteriums by degradation, but the ir spectrum provided evidence that up to two deuterium atoms per molecule were on the methylene carbon. The significant peaks were the following: 3055 (vinyl H stretch), 2305 and 2255 (vinyl D stretch), 2170 (alkyl D stretch), 1660, 1645, and 1630 (assigned to $C{=}CH_2$, $C{=}CHD$, and $C{=}CD_2$ stretch, respectively), 870 (vinyl H out-of-plane bend), and 800 cm^{-1} (possibly due to vinyl D out-of-plane bend). These results are all readily accounted for on the basis of reversible formation of 2-methylenenorbornane.

Examination of the stability of 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**) under the cleavage conditions gave the following results. After 40 hr **9** was more than 50% rearranged to 1-methyl-2-*exo*-norbornyl acetate (**3**) and 2-*exo*-methyl-2-*endo*-norbornyl acetate (**10**). When **9** was subjected to the cleavage conditions in acetic acid-O-*d* and the mixture of deuterated **9**, **3**, and **10** was converted into alcohols with lithium aluminum hydride, the alcohols contained up to four deuterium atoms per molecule. Clearly conversion of **9** into 2-methyl-2-norbornyl cation (**17**) does occur, and the cation can revert to **9**, incorporate deuterium by way of alkenes **15** and **16**, or undergo conversion into either of the two isomeric acetates, **3** and **10**. In contrast to the behavior of **9**, neither 1-methyl-2-*exo*-norbornyl acetate (**3**) nor 2-*exo*-methyl-2-*endo*-norbornyl acetate (**10**) was detectably rearranged after 170 hr, and **3** was shown to have incorporated no deuterium after 40 hr with acetic acid-O-*d*.[18] Apparently neither of these acetates reverts to cation **17** under these conditions.

The 2-methyl-2-norbornyl cation (**17**) can be converted into either of two alkenes and to any one of three acetates. The above observations, together with several additional experimental results, provide much information on the way in which the cation partitions among the five paths. Acetic acid-O-*d* treatment of 2-methylenenorbornane (**15**) converted it into acetate **9**, which gave 2-*endo*-methyl-2-*exo*-norbornanol (**18**) on reaction with lithium aluminum hydride; mass spectrometric analysis of the alcohol showed that it was 6.7% d_0, 84.4% d_1, and 8.9% d_2. As reversible formation of either alkene would lead to multiply deuterated acetate, the fact that **18** was only 8.9% multiply deuterated implies that carbonium ion **17** is converted into 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**) roughly ten times faster than it is to either of the alkenes. The rate ratio may in fact be much larger than ten, as the acetate **9** may be rapidly reconverted into the carbonium ion under these conditions; deuterium incorporation and rearrangement of **9** to the isomeric acetates **3** and **10** provide ways to measure a minimum rate for the reconversion, but no way to prove that the actual rate of reconversion is not very much faster than this minimum.[19]

Qualitative conclusions can also be drawn about the partition of cation **17** between alkene formation and combination with acetic acid to yield 1-methyl-2-*exo*-norbornyl acetate (**3**) and 2-*exo*-methyl-2-*endo*-norbornyl acetate (**10**). The extent of alkene formation can be estimated from deuteriumin corporation, and, because of the stability of acetates **3** and **10** in the reaction medium, the product distribution gives the total amount of conversion of the carbonium ion (**17**) into these acetates directly. In the acetate mixture from acetic acid-O-*d* cleavage of 1-methylnortricyclene (**7**) or from acetic acid-O-*d* treatment of 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**), the deuterium content of the deuterated positions approached a value corresponding to equilibrium with the solvent pool. Thus, conversion of the cation **17** into alkenes **15** and **16** must be fast compared with irreversible formation of acetates **3** and **10**.

Although conversion of 2-methyl-2-norbornyl carbonium ion (**17**) into 2-methylenenorbornane (**15**) and 2-methyl-2-norbornene (**16**) is clearly slow relative to formation of the tertiary *exo* acetate (**9**) and fast with respect to formation of the secondary *exo* or tertiary *endo* acetate (**3** or **10**), our results give no information as to whether the cation loses a proton more rapidly from the methyl, giving **15**, or from C-3, giving **16**. Unlike these alkenes, acetates **3** and **10** *are* stable in the reaction medium, and the way in which cation **17** partitions between the two paths can be readily evaluated from the product distribution. Isomerization of 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**) to 28 ± 5% 1-methyl-2-*exo*-norbornyl acetate (**3**) and 17 ± 5% 2-*exo*-methyl-2-*endo*-norbornyl acetate (**10**) indicates

(16) (a) A. F. Thomas and B. Willhalm, *Tetrahedron Lett.*, 1309 (1965); see also J. M. Jerkunica, S. Borcic, and D. E. Sunko, *ibid.*, 4465 (1965); (b) H. C. Brown and K. T. Liu, *J. Amer. Chem. Soc.*, **89**, 3900 (1967).

(17) The same conditions hold for 2-methyl-2-norbornene (**16**) if it is to be proposed as an intermediate. Preliminary experiments have shown that **16** [prepared as described by K. Alder and H. J. Ache, *Ber.*, **95**, 503 (1962)] is converted into pure **9** in acetic acid containing 0.005 *M* H_2SO_4 at 24.5 ± 0.1°; the reaction is approximately 100 times more rapid than cleavage of **7**.

(18) Deuterium incorporation in 2-*exo*-methyl-2-*endo*-norbornyl acetate (**10**) was not examined.

(19) Only observable changes can be used to measure the rate of conversion of 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**) into the carbonium ion, and there is no way to prove that the rate of the fastest observable process is the same as the actual rate of this conversion. Acetate **9** might be interconverted with the cation many times without any observable change. In this context, it would be interesting to study the rate of loss of ^{18}O from **9** labeled in the etherlike oxygen.

that acetate attacks **17** on the *exo* side of the secondary carbon 1.1–2.8 times faster than it attacks the *endo* side of the methyl-bearing carbon. The low accuracy of our ir analytical method does not permit more precise determination of the rate ratio. A sixth and final reaction of carbonium ion **17** which must be considered is loss of a proton from C-6 to regenerate 1-methylnortricyclene (**7**).[20] Two deuterium incorporation results show that this path does not compete successfully with the five observed reactions of the cation. First, the 2-norbornanone from acetic acid-O-*d* cleavage of **7** was cleanly monodeuterated at C-6. Second, 1-methylnortricyclene recovered from incomplete cleavage contained less than 0.2% monodeuterated molecules in excess of the natural abundance. Therefore, protonation of **7** is apparently irreversible under these conditions.

The Stereochemistry of Deuteration at C-6.—The monodeuterated 2-norbornanone (**1**) obtained from ring cleavage, degradation, and treatment with alkali, was used to investigate the stereochemistry of attack of D^+ on 1-methylnortricyclene (**7**). The ir spectrum of this sample, consisting of 17% 1-d_0 and 83% 1-d_1, was compared with spectra of known mixtures of 6-*exo*-*d*- and 6-*endo*-*d*-2-norbornanone.[21] It proved to be superimposable in all significant regions on a spectrum of a mixture of 12% **1**-d_0 and 88% **1**-d_1, the monodeuterated portion of which was 62.2% 6-*endo*-*d* and 37.8% 6-*exo*-*d*; the only detectable differences were in regions of strong absorption by undeuterated **1**. Mixtures composed of 6-*endo*-*d*- and 6-*exo*-*d*-2-norbornanone in the ratios 57.6:42.4 or 66.8:33.2 gave spectra which differed appreciably from that of the ketone derived from ring cleavage. The deuterium at C-6 in this ketone, therefore, is 62 ± 3% *endo* and 38 ± 3% *exo*.

We believe that these percentages accurately reflect the stereoselectivity of attack by D^+ on 1-methylnortricyclene (**7**). One way in which the apparent stereoselectivity could be lowered would be through repeated conversion of the carbonium ion back into **7**. Occurrence of this process is ruled out by the absence of deuterium in the recovered starting material; further confirmation comes from the fact that none of the **1** derived from acetic acid-O-*d* cleavage is doubly deuterated at C-6.

The second process which could lower the apparent stereoselectivity is 6,1- or 6,2-hydride shift. This step could occur in the cation during the cleavage reaction; the same cation may be formed in alumina in the chromatographic conversion of 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**) into alkenes **15** and **16**, and hydride shift may occur at this point. Examination of the consequences of each possible mode of 6,2 shift makes it possible to establish that the stereochemistry of the 6 deuterium in our compounds is not changed by rearrangements of this type. The unlikely process of 6,2 shift, which in this system converts a tertiary cation into a secondary one, would lead to 6-methyl-2-norbornyl acetates, none of which was found. A 6,1 shift of hydrogen would not reverse the stereochemistry of the 6 deuterium, but would give a 1-*d*-2-norbornanone after degradation. With respect to 6,1 shifts of deuterium, four types are conceivable: *exo,exo*, *endo,endo*, *exo,endo*, and *endo,exo*. Berson and Grubb recently presented evidence that the preferred path for 6,2 shift is the *endo,endo* one,[22] and the results of Benjamin and Collins provide support for this conclusion.[23] The direct conversion of optically active 2-*exo*-methyl-2-*endo*-norbornanol (**2**) into 1-methyl-2-*exo*-norbornyl acetate (**3**), which proceeds through the 2-methyl-2-norbornyl cation (**17**), is accompanied by substantial, though not complete, racemization;[9] presumably the racemization results from *endo,endo* 6,2-hydride shift in the cation. As our cleavage of 1-methylnortricyclene was run in the same medium and led to the same cationic intermediate, a significant amount of *endo,endo* 6,2 shift may have occurred in our experiments as well. Neither this process nor the corresponding *exo,exo* shift produces a stereochemical change, however. Only the stereochemically unfavorable process of *exo,endo* (or *endo,exo*) shift of deuterium would reverse the orientation of the 6 deuterium. If this process were a major one for the cation, 6,1 shift of hydrogen would also become a major process; the reaction product would be partially deuterated at C-1 and should lead to 2-norbornanone with deuterium at C-1. The spectrum of our 2-norbornanone from cleavage appeared to be the spectrum of a mixture of **1**-d_0, 6-*endo*-*d*-**1**, and 6-*exo*-*d*-**1**. There was no indication of the presence of a fourth component. For this reason we feel that no more than a minor amount of 6,1 shift of the *endo,exo* or *exo,endo* type could have occurred. The stereochemical purity of the 6 deuterium in our 2-norbornanone (**1**) is an accurate measure of the stereoselectivity of D^+ attack on 1-methylnortricyclene (**7**).

It is now evident that the stereochemical course of electrophilic substitution at saturated carbon can range from complete retention to complete inversion of configuration. In a number of cases of substitution with retention, it has been suggested that the initial step is formation of a bond between the attacking electrophile and the leaving group, and that the electrophilic substitution is a cyclic, internal process. Winstein and Traylor hypothesized that cleavage of di-4-camphylmercury by acetic acid, a reaction which cannot occur with inversion, occurs by formation of a bond from mercury to an oxygen of acetic acid, followed by intramolecular conversion into camphane and 4-camphylmercuric acetate.[24] Nickon, *et al.*, found that 1-hydroxynortricyclene and 1-acetoxynortricyclene undergo cleavage of the cyclopropyl ring in acetic acid-O-*d* to yield 6-*d*-2-norbornanone in which the deuterium is at least 90% *endo*.[13] Cram suggested that the high degree of retention at the electrophilic substitution site can be rationalized in terms of protonation of the hydroxyl oxygen, providing an internal electrophile for attack on the 6 carbon from the more accessible *endo* side.[25] The same argument can be used to account for the retention of configuration which has been observed in

(20) There are several other paths which the carbonium ion might take. Of these, loss of a proton to give 1-methyl-2-norbornene can be ruled out on the basis of the deuterium incorporation results. Various 3,2- and 6,2-hydride shifts either are ruled out by the evidence or are not required to explain the results.

(21) We are most grateful to Professor A. Nickon for supplying samples of 6-*endo*-*d*- and 6-*exo*-*d*-2-norbornanone; see ref 13.

(22) J. A. Berson and P. W. Grubb, *J. Amer. Chem. Soc.*, **87**, 4016 (1965).

(23) B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966).

(24) S. Winstein and T. G. Traylor, *ibid.*, **78**, 2597 (1956).

(25) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 115.

other acid-catalyzed cleavage reactions of cyclopropanols.[26,27] If this reasoning is correct, one might expect cyclopropane cleavage to take quite a different stereochemical course when no heteroatom substituents are present on the ring, and in fact LaLonde recently reported that sulfuric acid-d_2 in acetic acid-O-d cleaves the C-2–C-4 bond of *exo*-tricyclo[3.2.1.0^{2,4}]octane with essentially complete inversion for the deuteration step.[28] However, this hydrocarbon is not a typical case, as the authors point out, in that protonation with retention is subject to severe steric hindrance.

Interpretation of our stereochemical result is not complicated by the presence of a heteroatom substituent on the three-membered ring, but steric effects may well play a part. The methyl at C-1 hinders attack of a proton on C-6 from the C-1 side, whereas the hydrogen at C-2 is less of an obstacle to attack from the C-2 side; steric effects would favor electrophilic attack with inversion. Although the degree of stereoselectivity is low, the dominating path is the sterically unfavorable one of retention. Apparently the stereoelectronic preference for front-side attack is large enough to override the opposing steric hindrance by a small margin.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. Band positions are expressed in cm^{-1}. Gas chromatograms were done on an Aerograph Model A-90-P instrument, and the column used was 0.125 in. in diameter with tris-β-cyanoethoxypropane as the liquid phase, unless otherwise indicated. Mass spectra were run at the Chemistry Department of the University of Pennsylvania by Mr. Robert Graff on a Consolidated Electrodynamics Corp. Model 21-130 spectrometer, with an ionizing potential of 76 eV.

2-*exo*-Methyl-2-*endo*-norbornanol (**2**).—The alcohol **2** was prepared from 2-norbornanone (**1**, 490 g; Aldrich Chemical Co.) and methylmagnesium iodide by the procedure of Toivonen, *et al.*,[29] to yield 395 g (70%), bp 166–172°.

1-Methyl-2-*exo*-norbornyl Acetate (**3**).—Alcohol **2** (370 g) was rearranged and acetylated with sulfuric acid and acetic acid by the method of Toivonen, *et al.*,[29] to yield crude acetate **3**, 451 g (91%).

1-Methyl-2-*exo*-norbornanol (**4**).—This alcohol (**4**) was prepared by saponification of the corresponding acetate (**3**). A mixture of 207 g of **3**, 375 g of sodium hydroxide, 500 ml of water, and 2 l. of ethanol was refluxed for 16 hr on a steam bath. The solution was cooled and extracted with two 1-l. portions of pentane. The pentane layers were combined, washed with four 2-l. portions of water, and dried over magnesium sulfate and charcoal. Evaporation of the pentane through a Vigreux column left 118 g (76%) of crude **4**.

1-Methyl-2-norbornanone (**5**).—Oxidation of 236 g of alcohol **4** with chromium trioxide and sulfuric acid in acetone, by the method of Berson, *et al.*,[9] gave 120 g (52%) of ketone **5**, bp 168–175°.

1-Methyl-2-norbornanone *p*-Toluenesulfonylhydrazone (**6**).—A mixture of 109 g of ketone **5**, 170 g of *p*-toluenesulfonylhydrazine, 9 ml of acetic acid, and 900 ml of ethanol was refluxed for 90 min on a steam bath. The mixture was cooled at 0° overnight and filtered. The filter cake was washed with 300 ml of cold ethanol and dried to yield 205 g of **6**, mp 146.5–148.0°. Concentration of the mother liquor to 100 ml yielded an additional 28.5 g, mp 146.0–148.5° (total yield, 91%).

Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.61; H, 6.89. Found: C, 61.61; H, 6.88.

1-Methylnortricyclene (**7**).—A mixture of 54 g of **6**, 115 g of freshly prepared sodium methoxide, and 500 ml of dry diglyme was stirred and refluxed for 3 hr. The mixture was distilled to remove the low-boiling **7** and methanol, plus 25 ml of diglyme. An additional 58 g of **6** and 200 ml of diglyme were added to the reaction mixture, which was again refluxed for 3 hr. The product **7**, together with methanol and diglyme, was removed by distillation as before, and the two distillates were combined and extracted with pentane and water. The dried ($MgSO_4$) pentane extract was concentrated and fractionally distilled to give 36.5 g (88%) of **7**: bp 110–112°; n^{20}D 1.4516 (lit.[30] bp 114–114.5°; n^{20}D 1.4555); 99% homogeneous by vpc; ir (neat) 3055 (cyclopropyl H stretch) and 840, 785 cm^{-1} (lit.[10] 850, 785 cm^{-1}).

2-*endo*-Methyl-2-*exo*-norbornanol (**18**).—Reaction of alcohol **2** with HCl and treatment of the crude chloride with NaOH according to the procedure of Toivonen[29] gave alcohol **18**: mp 82.5–84.0° (lit.[29] mp 86°).

2-*endo*-Methyl-2-*exo*-norbornyl Acetate (**9**).—Alcohol **18** was acetylated with acetyl chloride and dimethylaniline in ether:[31] bp 95–98° (29 mm); n^{20}D 1.4606 [lit.[29] bp 93.4° (22 mm); n^{20}D 1.4610].

2-*exo*-Methyl-2-*endo*-norbornyl Acetate (**10**).—Acetylation[31] of alcohol **2** gave **10**: bp 106.0–106.5° (50 mm); n^{25}D 1.4575 [lit.[29] bp 88.5–89.0° (22 mm); n^{20}D 1.4587].

1-Methyl-2-*endo*-norbornyl Acetate (**8**).—Ketone **5** was reduced to 1-methyl-2-*endo*-norbornanol with lithium aluminum hydride as reported.[32] The alcohol was acetylated with acetic anhydride in pyridine: bp 91–93 (21 mm); n^{20}D 1.4554.

2-Norbornanemethanol.—Reaction of lithium aluminum hydride with methyl 2-norbornanecarboxylate (Aldrich Chemical Co.) in the usual way gave the alcohol in 91% yield: bp 106–108° (25 mm); n^{20}D 1.4884.

2-Methylenenorbornane (**15**).—2-Norbornanemethanol was converted into the methyl xanthate, which was pyrolyzed to give alkene **15**:[33] bp 120–121° (lit. bp 123°); ir (neat) 3065 (vinyl H stretch), 1665 (C=C stretch), and 874 cm^{-1} (*gem*-disubstituted alkene); 100% homogeneous by vpc.

Cleavage of 1-Methylnortricyclene (7) in Acetic Acid.—A solution of 2.0 g of **7** (99% pure) and 0.0052 *M* sulfuric acid in 20 ml of glacial acetic acid was kept at 24.5 ± 0.1° for 122 min. The solution was poured into 100 ml of pentane, and the pentane extract was washed with water and aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated. The relative absorptions of the pentane solution in the ir spectrum at 1745 (C=O) and 850 cm^{-1} (due to **7** only) indicated that the cleavage was 15 ± 5% complete. Bulb-to-bulb distillation gave 0.44 g (14%) of acetate, bp ~97–103° (22 mm). The ir spectrum of this product was superimposable in all regions with that of pure 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**) and differed markedly from the spectra of acetates **3**, **8**, and **10** in the fingerprint region. Solutions of the four acetates (200 mg of acetate in 10 ml of CS_2) were used to prepare artificial mixtures, and comparison of the ir spectra of these mixtures with that of the cleavage product **9** showed that the latter contained less than 2.5% **3**, **8**, or **10**.

A second cleavage run, with 0.5 g of **7** and 0.0052 *M* H_2SO_4 in 5 ml of glacial acetic acid, was continued at 24.5 ± 0.1° for 42 hr. Bulb-to-bulb distillation gave 0.45 g (59%) of acetate product, bp 100–104° (22 mm). The ir spectrum (CS_2) of this product was superimposable on that of a mixture of 55% acetate **9**, 28% 1-methyl-2-*exo*-norbornyl acetate (**3**), and 17% 2-*exo*-methyl-2-*endo*-norbornyl acetate (**10**).

Stability of Acetates 3 and 10 in H_2SO_4–HOAc.—A solution of 0.5 g of 1-methyl-2-*exo*-norbornyl acetate (**3**) and 0.0052 *M* H_2SO_4 in 5 ml of glacial acetic acid was kept at 24.5 ± 0.1° for 194 hr. The acetate was recovered and purified by the same method used for the cleavage experiments. The ir spectrum (CS_2) of the product was superimposable on that of pure **3**, and comparison with spectra of artificial mixtures of **3** with **10** showed that less than 5% **10** had been formed. 2-*exo*-Methyl-2-*endo*-norbornyl acetate (**10**) was treated with H_2SO_4 in acetic acid in the identical manner. The spectrum (CS_2) of the recovered acetate was superimposable on that of pure **10**, and the amount of **3** present was shown to be less than 5%.

Conversion of Acetates 9 and 10 into Alkene 15 on Alumina.—Chromatography of acetate **9** on Woelm basic alumina of activity

(26) P. S. Wharton and T. I. Bair, *J. Org. Chem.*, **31**, 2480 (1966).
(27) C. H. DePuy and F. W. Breitbeil, *J. Amer. Chem. Soc.*, **85**, 2176 (1963).
(28) R. T. LaLonde, J. Ding, and M. A. Tobias, *ibid.*, **89**, 6651 (1967).
(29) N. J. Toivonen, E. Siltanen, and K. Ojala, *Ann. Acad. Sci. Fennicae Ser. A II*, **64** (1955).
(30) M. Blanchard and J. E. Germain, *Compt. Rend.*, **254**, 3351 (1962).
(31) C. R. Hauser, B. E. Hudson, B. Abramovitch, and J. S. Shivers, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 142.
(32) S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956).
(33) O. Diels and K. Alder, *Ann.*, **470**, 62 (1929).

grade I gave a product which was eluted readily with 5% ether–95% pentane and which decolorized bromine. Vpc analysis on the Ucon column showed that the product mixture consisted of four components. The first three of these, constituting 2, 27, and 56% of the mixture, had retention times identical with those of 1-methylnortricyclene (**7**), 2-methyl-2-norbornene (**16**), and 2-methylenenorbornane (**15**), respectively; the fourth component (15%) was not identified. Chromatography of acetate **10** in the same manner led to recovery of the same four products in the proportions 9, 14, 49, and 28%, together with some unreacted **10**. Chromatography of acetate **3** gave no alkene; elution with 100% ether yielded unchanged **3** nearly quantitatively.

Ozonolysis of 2-Methylenenorbornane (15).—Alkene **15** was ozonolyzed in ethyl acetate in the presence of an equimolar amount of tetracyanoethylene, according to the procedure of Criegee and Gunther.[14] Fractional distillation up to 77° and vacuum distillation of the residue gave a brown semisolid, which was chromatographed on alumina. Concentration of the 20% ether–80% pentane fraction and sublimation of the residue gave pure 2-norbornanone (**1**): 100% homogeneous by vpc; ir (CS_2) identical with that of authentic **1**.

Acetic Acid-O-*d* from Acetic Anhydride.—Distilled acetic anhydride (953 ml, 10.1 mol, bp 138.5–140.0°) and deuterium oxide (210.6 g, 10.5 mol, 99.75% deuterium; E. Merck, Darmstadt) were stirred at room temperature for 163 hr, and the solution was dried over Na_2SO_4. Titration with Karl Fischer reagent[34] indicated the presence of 0.5% water.

Cleavage of 1-Methylnortricyclene (7) in Acetic Acid-*O-d*.—A solution of 26.4 g of **7** (99% pure) and 0.307 g of D_2SO_4 (0.00614 *M*) in 500 ml of acetic acid-O-*d* was kept at 24.5 ± 0.1° for 39 hr. The reaction mixture was poured into 1 l. of pentane, and the pentane extract was washed with 1 l. of water and 1 l. of aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated. Molecular distillation on a vacuum line gave a highly volatile fraction of 6.5 g, shown by vpc to consist of pentane, starting material (**7**), and a trace of **15**, plus a less volatile fraction of 27.5 g. The major fraction was distilled (12 mm) to give 21.75 g (53%) of deuterated acetates; vpc indicated that the mixture contained 58 ± 5% **9** and 42 ± 5% **3** and **10**. A portion of the mixture was converted into alcohols with $LiAlH_4$; the mass spectrum showed that the alcohols (mol wt 126) contained up to five deuteriums per molecule: 126 (15), 127 (40), 128 (65), 129 (90), 130 (100), 131 (60), and 132 (5).

Fractional distillation of the volatile 6.5-g fraction, followed by preparative vpc on a Ucon column of 0.25-in. diameter, gave unreacted starting material (**7**) plus 55 mg of a substance with retention time identical with that of alkene **15**. Each substance was 100% homogeneous by vpc. The mass spectrum of the recovered **7** showed that it had incorporated no deuterium: 105 (100) and 109 (9.0). Mass spectrometric analysis of the second component showed that it contained up to four deuteriums per molecule: 108 (100), 109 (40), 110 (46), 111 (53), 112 (36), and 113 (3.4).

Conversion of Deuterated Acetate Mixture into Alkenes.—Chromatography of 13.0 g of the deuterated acetate mixture from ring cleavage on 360 g of Woelm basic alumina of activity I and concentration of the pentane eluate through a fractionating column left a residue of 4.6 g. Distillation of this residue gave 2.7 g of product, bp 113–125°. The alkene mixture contained up to four deuteriums per molecule by mass spectrometric analysis: 108 (15), 109 (76), 110 (100), 111 (75), 112 (13), and 113 (2).

Ozonolysis of Deuterated Alkene Mixture.—The mixture (2.46 g) of deuterated **7**, **15**, **16**, and the unidentified component was ozonolyzed in the presence of tetracyanoethylene,[14] as described for undeuterated **15**. Concentration of the solution by fractional distillation gave a residue of 6 ml. Chromatography on 150 g of Woelm neutral alumina (activity I) with 2700 ml of 20% ether–80% pentane, concentration of the eluate by fractional distillation, and sublimation of the residue gave 2-norbornanone (**1**). Mass spectrometric analysis showed the product contained up to two deuteriums per molecule: 110 (34), 111 (100), 112 (81), 113 (14), and 114 (2.6).

A 500-mg portion of this sample was mixed with 11.0 ml of methanol, 1.1 g of KOH, and 5.0 ml of water, and the resulting solution was stirred for 100 hr at room temperature. The mixture was poured into 100 ml of pentane, and the pentane layer was washed twice with water, dried ($MgSO_4$), and concentrated. The residual **1** was purified by sublimation; mass spectrometric analysis showed it to be 17% undeuterated and 83% monodeuterated: 110 (29), 111 (100), and 112 (8.9).

Analysis of the Stereochemistry of the 6-Deuterium.—Samples of 6-*exo-d*-**1** and 6-*endo-d*-**1** were generously supplied by Professor A. Nickon.[35] The 6-*exo-d*-**1** was 89.7% monodeuterated and 10.3% undeuterated, and the deuterium was at least 90% *exo;* the 6-*endo-d*-**1** was 86.6% monodeuterated and 13.4% undeuterated, and the deuterium was at least 94.5% *endo*. Two standard solutions were prepared; one contained 198.8 mg of 6-*endo-d*-**1** in 10.0 ml of Spectrograde CS_2, and the other contained 205.1 mg of 6-*exo-d*-**1** in 10.0 ml. Artificial mixtures were prepared from these standard solutions with a 100-μl syringe, and their ir spectra were recorded in matched 0.5-mm KBr cells with CS_2 as a reference. Monodeuterated **1** (94 mg), from ozonolysis and alkaline removal of enolizable deuterium, was dissolved in 4.58 ml of CS_2, and the ir spectrum of the solution was recorded in the same way. This spectrum was superimposable in all significant regions on that of a mixture containing 6-*endo-d*-**1** and 6-*exo-d*-**1** in ratio 62.2:37.8; the only differences were in regions of strong absorption by undeuterated **1**, and could readily be accounted for on the basis of the slightly larger amount of undeuterated **1** in our product. Mixtures of 6-*endo-d*-**1** and 6-*exo-d*-**1** in the ratios 57.6:42.4 or 66.8:33.2 gave spectra which differed appreciably from that of our product.

Incorporation of Deuterium in Acetates 3 and 9.—A solution of 1.61 g of acetate **3** in 20 ml of acetic acid-O-*d* (99.7% deuterium) containing 0.0065 *M* H_2SO_4 was kept at 24.5 ± 0.1° for 40 hr. The reaction mixture was poured into pentane, and the pentane was washed with water and aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated. The acetate was purified by bulb-to-bulb distillation under vacuum. Conversion of the acetate into alcohol with $LiAlH_4$ and analysis by mass spectrometry showed that less than 2% monodeuterated **3** had been formed: 126 (100) and 127 (11.9).

Identical treatment of 1.07 g of acetate **9** in 13 ml of H_2SO_4–DOAc and treatment of the recovered acetates with $LiAlH_4$ gave a mixture of alcohols containing up to four deuteriums per molecule: mass spectrum 126 (25), 127 (35), 128 (70), 129 (100), 130 (70), and 131 (7).

Addition of Acetic Acid to 2-Methylenenorbornane (15).—A solution of 1.01 g of **15** in 10 ml of acetic acid containing 0.0052 *M* H_2SO_4 was kept at 24.5 ± 0.1°. Aliquots were withdrawn and poured into pentane, and the pentane was washed with water and aqueous $NaHCO_3$ and dried ($MgSO_4$). The progress of the reaction was followed by the disappearance of the ir peak (pentane) at 1665 cm^{-1} (C=C stretch) and the appearance of the 1745-cm^{-1} peak (C=O stretch) of the acetate. Reaction was virtually complete after 50 min, and the spectrum of the purified product was superimposable on that of acetate **9** and distinctly different from spectra of acetates **3**, **8**, and **10**.

Addition of Acetic Acid-O-*d* to 15.—A solution of 0.81 g of **15** in 10 ml of acetic acid-O-*d* containing 0.0065 *M* H_2SO_4 was kept at 24.5 ± 0.1° for 50 min. The usual work-up gave acetate which was converted into alcohol with $LiAlH_4$. Mass spectrometric analysis showed that the alcohol was mostly monodeuterated: 126 (20), 127 (100), 128 (21), 129 (2.1).

Registry No.—**2**, 3212-16-6; **3**, 17410-98-9; **5**, 10218-04-9; **6**, 13533-72-7; **7**, 4601-85-8; **8**, 17410-99-0; **9**, 17411-09-5; **10**, 17411-10-8; **15**, 497-35-8; 2-norbornanemethanol, 5240-72-2.

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(35) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **88**, 3354 (1966).