together (provided they are of the same symmetry species). Although the methyl stretching frequencies are quite high compared to most other frequencies, they are even higher for CH_3 than CD_3, and might therefore couple less. For example, the lowest CH stretching frequency (symmetric) observed for N,N-dimethylaniline (2801 cm^{-1}) is much higher (by 1358 cm^{-1}) than the highest observed CH_3 symmetric bend (probably at 1443 cm^{-1}), compared to the difference (of 990 cm^{-1}) between the lowest CD stretching vibration (2054 cm^{-1}) and the highest symmetric CD_3 deformation (1064 cm^{-1}).

For the product cations (salts), the lowest CH stretch (2822 cm^{-1}) is 1406 cm^{-1} higher than the highest symmetric CH_3 bend at 1416 cm^{-1}, whereas the lowest CD stretching frequency (2080 cm^{-1}) is 1027 cm^{-1} higher than the CD_3 deformation mode at 1053 cm^{-1}.

It should also be noted that the ratios of the CH to CD stretching vibrations in both the reactants and products are substantially less (1.31–1.36) than the "ideal" value of 1.41 (observed when $\mu_H \simeq \mu_D/2$), indicating incorporation of zero-point differences into other normal modes.

Since the total effect of the changes in the methyl stretching frequencies on going from reactant to product is to produce a normal isotope effect, the observed inverse kinetic effect should therefore be due to increased bending force constants, or, in other words, to the steric effect.

Assignment B, which produces the most reasonable calculated isotope effect, shows a decrease for methyl deformations and rocking modes on going from reactant to product. In the absence of a more complete vibrational assignment, including the frequencies below 740 cm^{-1}, we cannot decide for certain whether assignment B is entirely reasonable and the observed decreases result from coupling with lower vibrations, or assignment B is in error. Though the analysis of the spectra is made more uncertain by such extensive coupling, we believe that eventually more reliable assignments based on further theoretical and experimental study can give a relatively simple answer in terms of valence force constant changes.

In analyzing the observed kinetic isotope effects, one cannot yet be certain whether the smaller effect for the phosphine than for the amine results from a decreased equilibrium effect for the phosphine, or from a more reactant-like transition state, or both.

Acknowledgments. Support of this work through Public Health Service Fellowship 5-Fl-GM-20,482 is gratefully acknowledged. The kindness of M. H. Lietzke[30] and of M. Wolfsberg[32] in supplying source decks, of W. De Forest, University of Pennsylvania Computer Center, in making modifications for our use, and of the University of Pennsylvania Computer Center, in supplying computer time, is also gratefully acknowledged.

Stereochemistry of Deuteron Attack of a Strained Bond in *exo*-Tricyclo[3.2.1.$0^{2,4}$]octane[1]

Robert T. LaLonde, Jan-yih Ding, and Michael A. Tobias[2]

Contribution from the Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210.

Received July 10, 1967.

Abstract: *exo*-Tricyclo[3.2.1.$0^{2,4}$]octane was treated with sulfuric acid-d_2 in acetic acid-d_1 solution to determine the stereochemistry of electrophilic attack on the C_2–C_4 bond. The principal product, *exo*(axial)-bicyclo[3.2.1]octan-2-ol-4-d_1 acetate was converted to the corresponding alcohol, ketone, and hydrocarbon. By taking the difference in shift values (per cent) for the two principal peaks (*m/e* 67 and 80) in the mass spectrum of the ketone, the percentage deuterium at C_4, the point of electrophilic attack, was determined to be 86%. The two principal fragmentation modes of bicyclo[3.2.1]octan-2-one was ascertained through mass spectral studies with labeled ketones. Examination of the hydrocarbon, bicyclo[3.2.1]octane-*exo*(axial)-, and -*endo*(equatorial)-2-d_1 in the C–D stretching region of the infrared revealed the identity of the hydrocarbon with the *exo*(axial) isomer. Therefore, it was concluded that deuteron attack on the C_2–C_4 bond must be "end on" and results in inversion of configuration.

Conceptually, there are two ideal ways by which a strained carbon–carbon bond might interact with an electrophile. In one of these, the electrophile and strained bond approach each other orthogonally. This mode of interaction results in retention of configuration at the carbon atom forming the new bond with the electrophile. In the other mode of interaction, the electrophile approaches the strained bond from along an extended axis joining the two carbon atoms; that is, the electrophile approaches the bond "end on" and interaction ultimately results in inversion of configuration at the carbon atom forming the new electrophile–carbon bond.

The steric mode of electrophilic attack of strained carbon–carbon bonds is a question which has received some attention in connection with studies of acid- and base-catalyzed transformations of cyclopropanols to aldehydes and ketones. DePuy[3] concludes on the

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(1) (a) Paper VII in a series dealing with carbon–carbon bond fission in cyclopropanes. (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this work.

(2) National Science Foundation Cooperative Fellow, 1963–1964.

(3) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Am. Chem. Soc.*, **88**, 3347 (1966).

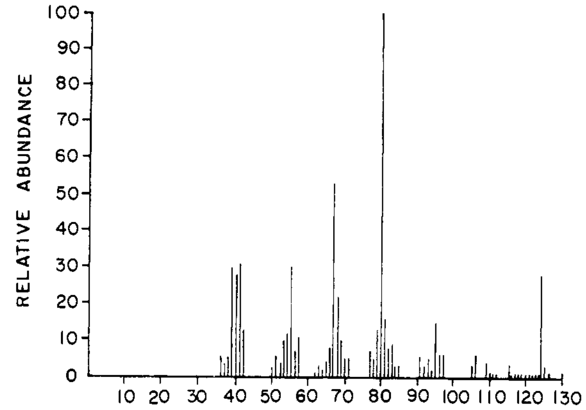
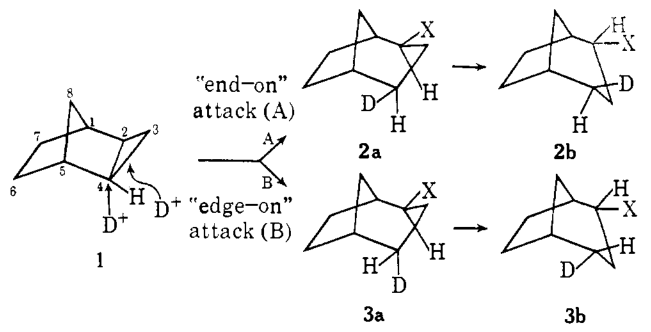


Figure 1. The mass spectrum of bicyclo[3.2.1]octan-2-one.

basis of stereochemical studies with optically active *cis*-1-methyl-2-phenylcyclopropanol that the acid-catalyzed conversion of this cyclopropanol to 4-phenyl-2-butanone occurs with retention of configuration. Nickon[4] and Wharton[5] also have observed retention of configuration accompanying acid-catalyzed conversion of ring-fused cyclopropanols and cyclopropyl acetates to aldehydes and ketones.

In light of demonstrated retention accompanying electrophilic fission of strained bonds, the question of whether inversion of configuration could be observed seemed an interesting one. To answer this question we chose to study the deuteron attack of *exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**1**) a substrate where "edge on"[6] attack on the C_2–C_4 bond of the three-membered ring would be hindered by the severe steric crowding within the concave, U-shaped environment of the *endo* face of the molecule. It appeared that for this particular substrate (**1**), what might normally be the less favorable mode of attack would become the major mode and a net stereochemical result of inversion of configuration then might be observed. This would be manifested in the formation of a bicyclo[3.2.1]octyl derivative, **2a**, possessing an equatorial deuterium atom at C_4 when in the boat conformation but an axial deuterium atom in the more favorable chair conformation, **2b**. Arguments[7] and experimental evidence[8] have been given for the conformational preference of the chair form of bicyclo[3.2.1]octanes substituted on the three-membered bridge. On the other hand, should deuteron attack of **1** occur with retention of configuration, the resulting bicyclo[3.2.1]octyl derivative **3b** should possess an equatorial deuterium atom in the more favorable chair conformation.



We had observed earlier[9] that treatment of **1** with acetic acid, 0.07 *N* in sulfuric acid, afforded (to the extent of 72%) products resulting from cleavage of the C_2–C_4 bond. Among these products the major one was *exo*(axial)-bicyclo[3.2.1]octan-2-ol acetate. Thus the substrate **1** seemed to be well suited for our purposes. This paper describes our attempts to determine the principal location and stereochemistry of the deuterium in the major product resulting from treatment of **1** with sulfuric acid-d_2 in acetic acid-d_1 solution.

Results

exo-Tricyclo[3.2.1.$0^{2,4}$]octane (**1**) was prepared by the method of Simmons.[10] That the methylene bridge of **1** is *exo* is based on the following two considerations. First, hydrogenation of **1** is reported[11] to afford nearly a quantitative yield of *exo*-2-methylnorbornane. Secondly, addition of a host of reactants are known to occur from the *exo* face of norbornene.[12] Treatment of **1** with acetic acid-d_1, 0.07–0.08 *N* in sulfuric acid-d_2, at 25° for 48–50 hr gave a mixture of acetates and olefins as previously reported.[9] These mixtures were converted to mixtures of olefins and alcohols with lithium aluminum hydride. The desired *exo*(axial)-bicyclo[3.2.1]octan-2-ol was separated from the mixture by vapor phase chromatography. Since the formation of *exo*(axial)-bicyclo[3.2.1]octan-2-ol from **1** involves a carbonium ion intermediate,[9] the scrambling of deuterium throughout the molecule by hydride shift was a possibility which needed checking. An attempt to ascertain the isotopic composition and position of deuterium in the alcohol was made by obtaining mass spectra of the alcohol and its α-naphthylurethan. However, both alcohol and urethan derivatives gave such small parent peaks, through elimination, that the spectral data were useless for our purposes. Consequently, the *exo*(axial)-bicyclo[3.2.1]octan-2-ol was oxidized to the corresponding ketone **4** and its mass spectrum was determined. The isotopic composition was 15% d_0 and 85% d_1. In addition to this mass spectrum, mass spectra of the unlabeled bicyclo[3.2.1]octan-2-one (**5**) and several deuterium-labeled bicyclo[3.2.1]octan-2-ones were obtained for the purpose of establishing the mode of fragmentation and ultimately determining the amount of deuterium at C_4 in the ketone originating from electrophilic bond rupture. The synthesis of labeled bicyclo[3.2.1]octan-2-ones, the mass spectral data, and the derived conclusion are presented in the section immediately following.

Mass Spectral Studies. The mass spectrum (Figure 1) of bicyclo[3.2.1]octan-2-one (**5**) reveals two major peaks of interest. These are m/e 80, the base peak

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(4) (a) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 3713 (1963); (b) A. Nickon, J. L. Lambert, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966).

(5) P. S. Wharton and T. I. Bair, *J. Org. Chem.*, 31, 2480 (1966).

(6) Attack in this manner is one possible mode of orthogonal approach. It corresponds to interaction in the region of the "banana bond" protruding downward from the C_2–C_4 bond axis.

(7) A. A. Youssef, M. E. Baum, and H. M. Walborsky, *J. Am. Chem. Soc.*, **81**, 4709 (1959).

(8) J. G. Durocher and H. Favre, *Can. J. Chem.*, **42**, 260 (1964).

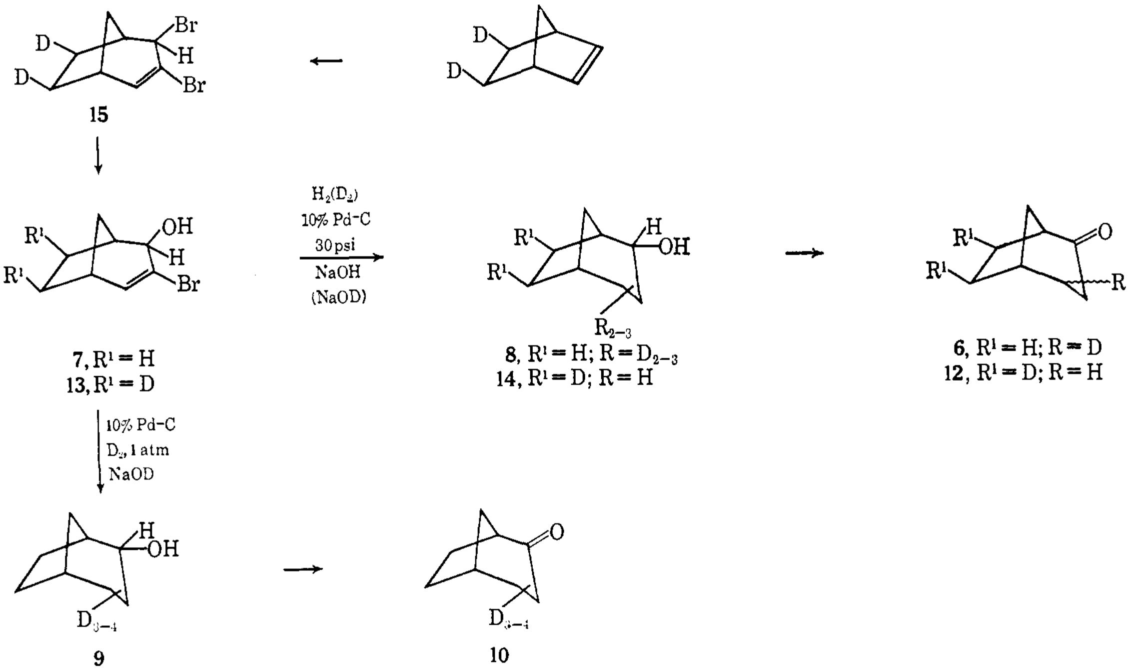
(9) R. T. LaLonde and J. J. Batelka, *Tetrahedron Letters*, 445 (1964).

(10) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(11) E. M. Milvitskaya and A. F. Plate, *Neftekhimiya*, 3, 188 (1963); *Chem. Abstr.*, **59**, 6272 (1963).

(12) For a leading reference, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 303.

Scheme I. The Synthesis of Deuterium-Labeled Bicyclo[3.2.1]-octan-2-ones



which corresponds to the loss of C_2H_4O, and *m/e* 67, which corresponds to the loss of C_3H_5O. The genesis of these ions was established from the study of the fragmentation patterns of the deuterium-labeled ketones.

The synthesis of bicyclo[3.2.1]octan-2-one-4-d_1 (**6**) was achieved starting with *exo*-3-bromobicyclo[3.2.1]-oct-3-en-2-ol (**7**)[13] which as shown previously for the corresponding chloro derivative could be converted to bicyclo[3.2.1]octan-*exo*-2-ol through catalytic hydrogenation.[14] Thus, catalytic deuteration of **7** in basic solution over palladium on charcoal at 30 psi afforded the deuterium-labeled, saturated alcohol **8**. This was oxidized and then back exchanged in basic solution to give bicyclo[3.2.1]octan-2-one-4-d_1 (**6**). The isotopic composition of this ketone, and all others, are given in Table I. When the synthesis was modified by lowering the deuterium pressure to one atmosphere, and the back-exchange step eliminated, a bicyclo-[3.2.1]octan-2-one (**10**) was produced which was tri- and tetradeuterated at C_3 and C_4. These syntheses are summarized graphically in Scheme I. Bicyclo-[3.2.1]octan-2-one-3,3-d_2 (**11**) was obtained by exchange of the unlabeled ketone in sodium methoxide–deuteriomethanol. Finally, bicyclo[3.2.1]octan-2-one-*exo*-6-*exo*-7-d_2 (**12**) was prepared from *exo*-3-bromobicyclo-[3.2.1]oct-3-en-2-ol-*exo*-6-*exo*-7-d_2 (**13**) through catalytic hydrogenation in basic solution at 1 atm and subsequent chromic acid oxidation. The deuterium label was introduced into the precursor **13** in the following manner. Incomplete catalytic deuteration of norbornadiene could be controlled to give a mixture of norbornane-d_4 and 2-norbornene-*exo*-5-*exo*-6-d_2 which was rich in the labeled olefin. The *exo* disposition of deuterium follows from the preferred addition[12] to the *exo* face of double bonds incorporated into the norbornane ring system. The mixture of deuterium labeled norbornene and norbornane was treated with bromoform and potassium *t*-butoxide in the manner prescribed[13,15] for the preparation of 3-*exo*-4-dibromobicyclo[3.2.1]oct-2-ene. The deuterium-labeled counterpart, **15**, was separated from the nonreacting norbornane-d_4 by distillation and then treated with silver nitrate in aqueous acetone to give the labeled unsaturated bromohydrin, **13**. This synthesis is also summarized in Scheme I.

The deuterium labeling results as summarized in Table I reveal that the base peak, *m/e* 80, is shifted in all cases except when the ketone is labeled at C_3. On the other hand, the peak at *m/e* 67 is shifted only when the ketone is labeled at C_6 and C_7. These observations point to two modes of cleavage as summarized in formula **16**. Significantly, the difference in these

Table I. Shifts[a] of the Two Major Peaks (*m/e*) in the Mass Spectra of Deuterated Bicyclo[3.2.1]octan-2-ones

Compd	Isotopic compn (%)	M^+	$M^+ - 44$ (%)	$M^+ - 57$ (%)
d_0, **5**	. . .	124	80	67
exo-4-d_1, **4**	d_0 (15)			
	d_1 (85)	125	81 (95)	67 (91)
				68 (9)
4-d_1, **6**	d_0 (8)			
	d_1 (88)	125	81 (100)	67 (100)
	d_2 (4)			
	d_1 (2)			
	d_2 (16)			
3,3,4-d_3, 3,4,4-d_3	d_3 (41)	127	81 (100)	67 (92)
3,3,4,4-d_4, **10**	d_4 (41)	128	82 (94)	
3,3-d_2, **11**	d_1 (10)			
	d_2 (88)	126	80 (95)	67 (88)
	d_3 (2)			
exo-6-*exo*-7-d_2, **12**	d_0 (12)			
	d_1 (6)			
	d_2 (82)	126	82 (100)	69 (98)

[a] Reported shifts are corrected for isotopic impurity as well as ^{13}C contributions.

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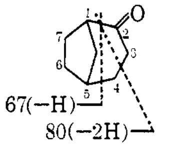
(13) C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *J. Am. Chem. Soc.*, **87**, 2183 (1965).

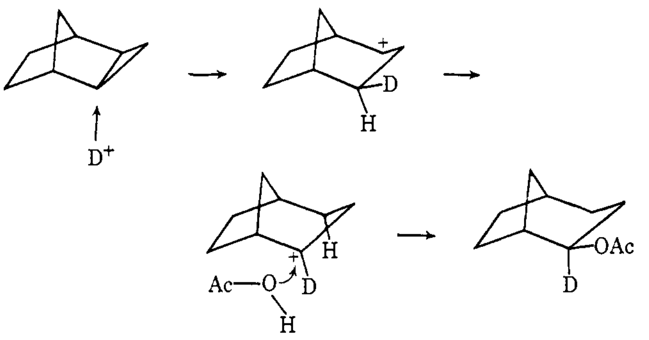
(14) E. Bergman, *J. Org. Chem.*, **28**, 2210 (1963).

(15) W. R. Moore, W. R. Moser, and J. E. LaPrade, *ibid.*, **28**, 2200 (1963).



16

two principal modes of cleavage in terms of carbon atoms involved is in the inclusion (*m/e* 80) or exclusion (*m/e* 67) of C_4, *the same carbon atom in the substrate* **1** *to undergo deuteron attack.* Therefore, by taking the difference in the shift values (per cent) for *m/e* 67 and *m/e* 80, the amount of deuterium located at C_4 can be determined.[16] This is 86%. Possibly some deuterium incorporated by deuteron attack of substrate **1** might be lost in the oxidation of *exo*-bicyclo[3.2.1]octan-2-ol to the corresponding ketone **4**. The loss would result if some deuterium were introduced at C_2 through a $C_2 \rightarrow C_4$ hydride shift occurring as depicted below. However, the loss of deuterium in this manner is not of major importance. A portion of the mixture of alcohols from the same bond rupture experiment was treated with *p*-toluenesulfonyl chloride and the resulting mixture of tosylates was treated with lithium aluminum hydride. Bicyclo[2.2.2]octane and bicyclo[3.2.1]octane were separated as a single fraction from the total mixture of hydrocarbons by vapor phase chromatography. The mass spectrum of this mixture of two bicycloalkanes revealed an isotopic composition of 15% d_0 and 85% d_1, the same isotopic composition as that exhibited by the ketone **4**. Therefore, little if any deuterium is removed through the oxidation process.



The cation formed initially from the electrophilic rupture of the C_2–C_4 bond of **1** should be much the same as the cation formed through the ring expansion route starting from the *exo*-2-norbornylcarbinyl system. Interestingly, the failure to observe a $C_2 \rightarrow C_4$ hydride shift in the bond rupture of **1** is consistent with Berson's observation[17] that no $C_2 \rightarrow C_4$ hydride shift occurs in the closely analogous cation derived from the *endo*-2-norbornylcarbinyl system.

Infrared Studies. Once it had been determined that at least 86% of the deuterium remained at the carbon atom attacked, the next problem to be considered was the stereochemistry of the C–D bond. A homogeneous sample of deuterium-labeled *exo*(axial)-bicyclo[3.2.1]octan-2-ol-4-d_1 from the bond rupture experiment was isolated by vapor phase and elution chromatography. The infrared spectrum of this material was carefully examined in the C–D stretching region of the infrared in order to ascertain the stereochemistry of the C–D bond. A study of the infrared spectrum of the corresponding hydrocarbon, bicyclo[3.2.1]octane-2-d_1, was deemed necessary since the presence of an *exo*(axial)-hydroxyl group at C_2 possibly could bring about anomalous spectral characteristics, especially if the C_4 deuterium atom were axial. Furthermore, the infrared studies of the deuterium-labeled hydrocarbon offered the advantage that comparison compounds containing only one asymmetric center need be synthesized. A homogeneous sample of the deuterium-labeled hydrocarbon was obtained in the following manner. A mixture of bicyclo[2.2.2]octanol and bicyclo[3.2.1]-octanol was isolated by vapor phase chromatography from the mixture of alcohols obtained from the bond rupture experiment. This material was oxidized to a mixture of ketones and then reduced by a modified Wolff–Kishner procedure[18] to a mixture of deuterium-labeled bicyclo[3.2.1]octane-2-d_1 and bicyclo[2.2.2]octane-2-d_1. The former was then separated from the mixture of two hydrocarbons by vapor phase chromatography and examined in the infrared spectra. The principal bands in the carbon–deuterium stretching region for both *exo*(axial)-bicyclo[3.2.1]octan-2-ol-4-d_1 and bicyclo[3.2.1]octane-2-d_1 are given in Table II.

Table II. Summary of the Infrared Carbon–Deuterium Bands of Deuterium-Labeled Derivatives of Bicyclo[3.2.1]octane

Compd	Principal absorption bands, cm^{-1}
exo(axial)-2-ol-4-d_1, **2b** (X = OH)	2121 (w), 2150 (s), 2164 (m)
-2-d_1, **2b** (X = H)	2119 (m), 2149 (s), 2158 (m), 2190 (m)
exo(axial)-2-d_1, **20**	2119 (m), 2148 (s), 2158 (m), 2190 (m)
endo(equatorial)-2-d_1, **22**	2110 (w), 2122 (w), 2152 (w), 2167 (s), 2173 (sh)
exo(axial)-2-d_1, **20**, and *endo*(equatorial)-2-d_1, **22**	2109 (w), 2118 (w), 2149 (s), 2167 (s)
2,2-d_2, **26**	2090 (s), 2148 (m), 2170 (w), 2187 (s)

The pertinent features of the spectra are reproduced in Figure 2. The observation that both alcohol and hydrocarbon exhibited their strongest band in the 2150-cm^{-1} region suggested that the orientation of the C–D bond in both compounds was axial rather than equatorial. This suggestion had its foundation in a few examples[19,20] of axial deuterium in cyclohexane systems exhibiting its strongest pattern near 2150 cm^{-1} and equatorial deuterium displaying its strongest absorption pattern at somewhat higher frequencies. However, to be certain of the infrared assignment, bicyclo[3.2.1]octane-*exo*(axial)- and -*endo*(equatorial)-2-d_1 were prepared for comparison purposes.

The acetolysis of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (**17**) proceeds through the bicyclo-[3.2.1]oct-2-en-3-yl cation (**18**) to give the *exo* isomer of bicyclo[3.2.1]oct-2-en-3-yl acetate (**19**) to the extent of 98%.[21] There are other examples of the very high preference for *exo* nucleophilic attack of the bicyclo-

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[16] This calculation is made on the assumption that *m/e* 80 and 67 are due entirely to the fragmentations given in formula **16** and that other possible modes giving the same *m/e* are not important. This assumption appears to be a reasonable one based on the very high shift values for all the deuterium-labeled ketones.

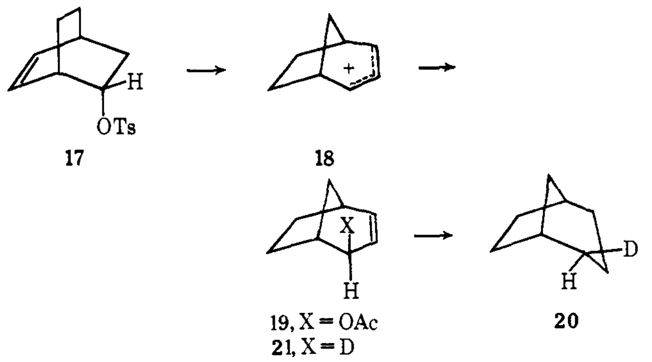
[17] J. A. Berson and D. Willner, *J. Am. Chem. Soc.*, **86**, 609 (1964).

[18] Huang-Minlon, *ibid.*, **68**, 2487 (1946).

[19] E. J. Corey, M. G. Howell, A. Boston, R. L. Young, and R. A. Sneen, *ibid.*, **78**, 5036 (1956).

[20] F. R. Jensen and L. H. Gale, *ibid.*, **82**, 145 (1960).

[21] H. L. Goering and D. L. Towns, *ibid.*, **85**, 2295 (1963).



17 18

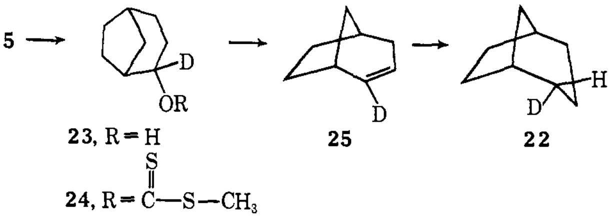
19, X = OAc 20

21, X = D

[3.2.1]oct-2-en-3-yl cation.[13,15,22–25] Therefore, we applied this solvolysis route in the synthesis of the *exo*-(axial)-2-d_1 hydrocarbon **20**. The tosylate **17** in a 65:35 (v/v) glyme–water medium was treated with sodium borodeuteride, according to the solvolytic conditions previously employed by Brown[26] for trapping carbonium ion intermediates. This procedure afforded deuterium-labeled bicyclo[3.2.1]oct-2-ene (**21**) (67.5%), *exo*-bicyclo[3.2.1]oct-3-en-2-ol (32.4%), and bicyclo[2.2.2]octene (0.1%). The desired olefin **21** could be removed from the reaction mixture as formed by sublimation. Further purification by vapor phase chromatography gave material containing 0.9 ± 0.1 atoms of deuterium as determined by nmr analysis. The same deuterium-labeled olefin prepared a second time by the same method showed an isotopic composition of 12% d_0 and 88% d_1 by mass spectral analysis. That the deuterium-labeled olefin was a bicyclo[3.2.1]-octene rather than a bicyclo[2.2.2]octene was evident from the nmr spectrum which showed two different vinyl signals, a broad triplet at τ 4.27 (1 H) and a doublet of doublets centered at τ 4.74 (1 H).

Transformation of the deuterium-labeled olefin **21** to the corresponding saturated hydrocarbon **20** was achieved through diimide hydrogenation. According to the mass spectrum, the isotopic composition was 24% d_0 and 76% d_1. The infrared spectrum of **20** (see Figure 2 and Table II) was identical in all respects with the spectrum of the deuterium-labeled hydrocarbon which originated from tricyclo[3.2.1.0^{2,4}]octane (**1**) in the bond rupture experiment.

Bicyclo[3.2.1]octane-*endo*(equatorial)-2-d_1 (**22**) was synthesized according to the scheme depicted below. Bicyclo[3.2.1]octan-2-one (**5**) was reduced with sodium borodeuteride to the mixture of alcohols **23**. This was converted to the methyl xanthate (**24**) which on pyrolysis gave bicyclo[3.2.1]oct-2-ene-2-d_1 (**25**). The nmr spectrum revealed only one vinyl proton while the mass spectrum showed an isotopic composition of 11% d_0, 85% d_1, and 4% d_2. Diimide hydrogenation of the olefin produced bicyclo[3.2.1]octane-*endo*(equatorial)-2-d_1 (**22**). According to the mass spectrum, the isotopic composition was 18% d_0, 78% d_1, and 4% d_2. The *endo* stereochemistry of the deuterium atom is based on the assumption that diimide will approach from the less hindered *exo* face. The assumption is based not only on the reported preference for *exo* attack of the bicyclo[3.2.1]oct-3-en-2-yl cation by nucleophiles[13,15,22–25] but also on examples of preferred allylic bromination,[27] hydrogenation,[28] and electrophilic attack[29] of the Δ^2 double bond from the *exo* face.



23, R = H

24, R = $\overset{\text{S}}{\overset{\|}{\text{C}}}$—S—CH$_3$

25 22

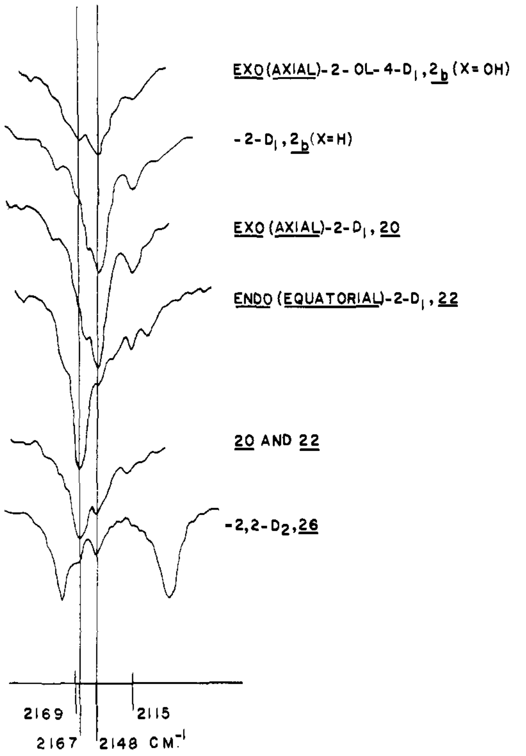


Figure 2. The infrared carbon–deuterium stretching bands of deuterated bicyclo[3.2.1]octanes.

The infrared spectrum of bicyclo[3.2.1]octane-*endo*-(equatorial)-2-d_1 (**22**) (see Table II and Figure 2) displays the strongest band in the carbon–deuterium stretching region at 2167 cm^{-1}, a higher frequency than the most intense band of the *exo*(axial) isomer **20**. Though the 2167- and 2148-cm^{-1} bands are located close to one another, they are still distinguishable in preparations containing both isomers. One such mixture of **20** and **22** was prepared from the tosylhydrazone of bicyclo[3.2.1]octan-2-one according to a variation[30] of the Wolff–Kishner procedure which involved lithium aluminum deuteride treatment followed by the addition of water. This procedure when applied to a steroidal ketone has been reported[31] to give a mixture of epimerically labeled steroidal hydrocarbons. It is apparent from the infrared spectrum (Figure 2) that isomerically labeled bicyclo[3.2.1]octanes

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(22) R. C. DeSelms and C. M. Combs, *J. Org. Chem.*, **28**, 2206 (1963).

(23) H. L. Goering and U. Mayer, *J. Am. Chem. Soc.*, **86**, 3753 (1964).

(24) C. W. Jefford and R. Medary, *Tetrahedron Letters*, 2069 (1966).

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(**20** and **22**) are afforded likewise by the reduction of bicyclo[3.2.1]octan-2-one.

Bicyclo[3.2.1]octane-2,2-d_2 (**26**) was produced from the tosylhydrazone of bicyclo[3.2.1]octan-2-one by the action of lithium aluminum deuteride and then deuterium oxide. The isotopic composition of **26** was 11% d_1, 86% d_2, and 4% d_3 as determined by mass spectral analysis. The effect of coupling symmetrical and unsymmetrical modes[32] of C–D stretching vibrations was observed in the infrared spectrum as two very intense bands which flanked the normal absorption positions of *exo* and *endo* C–D bands.

Discussion

The mass spectral studies of the labeled bicyclo[3.2.1]-octan-2-ones have demonstrated that 86% of the deuterium introduced through electrophilic bond rupture remains at the carbon atom attacked (C_4 of **4**). Furthermore, the absence of multiple labeling in the products originating from tricyclo[3.2.1.0^{2,4}]octane shows that deuterium and cyclopropyl hydrogens are not exchanged prior to the bond rupture step.

The stereochemistry of the deuterium atom at C_4 in the alcohol obtained from **1** must be *exo*(axial) on the basis of the infrared studies which demonstrate the presence of an *exo*(axial)-deuterium atom in the corresponding hydrocarbon. The isomeric purity of this hydrocarbon must be very nearly the same as the purity of the *exo*(axial) hydrocarbon (**20**) which was independently synthesized. This is evident from the identity of all features of the infrared spectra of these two hydrocarbon samples and especially when considered along with the distinctive characteristics of the *endo*(equatorial) hydrocarbon spectrum. The key step in the independent synthesis of the *exo*(axial) hydrocarbon was the introduction of *exo* deuterium through the preferential *exo*-deuteride attack of the bicyclo[3.2.1]oct-3-en-2-yl cation. If deuteride attack is as stereoselective as attack of the same cation by acetic acid,[21] then the independently synthesized comparison hydrocarbon, and therefore the hydrocarbon originating from the bond rupture experiment would contain close to 98% *exo*(axial)-deuterium. The least amount of *exo*(axial)-deuterium must be 85% since an infrared spectrum of a synthetic mixture containing 15% of the *endo*(equatorial) isomer gives a readily discernible shoulder at 2167 cm^{-1} not detectable in the spectrum of the hydrocarbon **2b** (X = H). Insufficient quantities of labeled hydrocarbons prevented further analysis. Accordingly, the predominant mode of deuteron attack of the C_2–C_4 bond of tricyclo[3.2.1.0^{2,4}]octane (**1**) is occurring "end on" (path A) with resulting inversion of configuration.

The variable stereochemistry of electrophilic substitutions involving base-generated carbanions[33] from compounds of different functionality is now beginning to become evident in other electrophilic substitutions such as those of alkylboronic acids[34,35] and organolithiums.[36] Emerging from these investigations is the suggestion[35] of the significant role of cyclic transition states in which leaving and entering groups are associated with an ionic ligand. At present it is not quite clear what influence the hydroxyl group of cyclopropanols has in determining the stereochemistry of electrophilic bond rupture. Possibly one such influence is that the basic hydroxyl group may function as a ligand to direct the entering electrophile to the center of highest electron density; this center would be the bent carbon–carbon bond. At the very least the hydroxyl group obviously functions in stabilizing the developing positive charge at the leaving α-carbon atom. On the other hand, the hydroxyl group may have no significant directive influence on the entering electrophile. Should this be the case, the electrophile, in the absence of any precluding steric factors, could simply interact orthogonally with the bent bond although the inversion pathway would be available. In this view, cyclopropanols would not be a special case and compared with our results from the presently described study with tricyclo[3.2.1.0^{2,4}]octane would again manifest that variable pathways are available in the electrophilic rupture of strained bonds as they are in other electrophilic substitutions.

Experimental Section[37]

The Addition of Acetic Acid-d_1 to *exo*-Tricyclo[3.2.1.0^{2,4}]octane (1). A sealed glass vessel containing 15.0 g (0.140 mole) of **1**,[10] 600 mg of sulfuric acid-d_2, and 170 ml of acetic acid-d_1 was maintained at 25° for 48 hr. The reaction mixture was poured into 200 ml of water, and the resulting solution was extracted continuously with pentane for 19 hr. The pentane solution was washed repeatedly with a saturated sodium bicarbonate solution until neutral, and then dried over magnesium sulfate. Pentane was removed by distillation through a 12-in. column, and the last trace of pentane was removed at reduced pressure. A light yellow oil, 17.4 g, was obtained. In a second experiment, 13.5 g of **1**, 581 mg of sulfuric acid-d_2, and 145 ml of acetic acid-d_1 was maintained at 25° for 50 hr. Processing the reaction mixture in the usual fashion gave 17.5 g of light yellow oil.

Hydrogenolysis of Acetates to Alcohols. The resulting ring-opening mixture (16.4 g) was placed in 50 ml of anhydrous ether and added dropwise to 3.0 g of lithium aluminum hydride in 100 ml of anhydrous ether. The resulting reaction mixture was stirred overnight and then processed in the usual manner. Ether was removed from the ether solution of products by distillation; the final trace of ether was removed at reduced pressure. The product (9.0 g), a colorless crystalline solid, melted at 125–132° after one sublimation.

Chromatographic Isolation of *exo*(axial)-Bicyclo[3.2.1]octan-2-ol-*exo*(axial)-4-d_1 (2b) (X = OH). An 18-mg sample of **2b** (X = OH) was cleanly separated from the mixture of alcohols by vapor phase chromatography which utilized an 11.5-ft, 25% glycerol-on-Celite column at 108°. The homogeneity of the alcohol was demonstrated by reinjection which resulted in a single symmetrical peak at 46.7 min. Principal features of the infrared spectrum in the C–D region are given in Figure 2. A second sample of the alcohol (50 mg) was separated from the mixture of alcohols by employing

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[37] Melting points were determined in sealed capillaries and are uncorrected. Atom % excess hydrogen was determined by J. Nemeth, Urbana, Ill. Elemental analyses were determined by Mrs. Marjorie Westerfield. Infrared spectra were measured in carbon tetrachloride solution using a Baird-Atomic infrared spectrometer. A lithium fluoride prism was employed to measure carbon–deuterium stretching frequencies and in these cases the absorption minimum at 2143 cm^{-1} and the maxima at 2115 and 2169 cm^{-1} of carbon monoxide were used as calibration standards. The nmr spectra were obtained from a Varian Model A60A spectrometer using tetramethylsilane (τ 10.00) and carbon tetrachloride or deuteriochloroform as solvents. Mass spectra were determined with a Perkin-Elmer-Hitachi RMU-6E mass spectrometer using a heated inlet system heated to less than 100° with the ionizing energy at 70 ev and the ionizing current at 80 μa. The mass spectra were determined by Dr. Richard E. Enrione and Mrs. Anna Willis, Department of Chemistry, Syracuse University.

a 15-ft, 20% glycerol-on-Chromosorb P column at 110°. After one sublimation, material melting at 189–192° was obtained. The infrared spectral characteristics were identical with those of the first sample. The mass spectrum of **2b** (X = OH) showed peaks at *m/e* 108 ($M^+ - 19$) and 109 ($M^+ - 18$) of nearly equal intensity.

Bicyclo[3.2.1]octan-2-one-*exo*(axial)-4-d_1 (4). A 50-mg sample of **2b** (X = OH) was placed in 0.2 ml of anhydrous glacial acetic acid. Chromium oxide, 40 mg (0.40 mmole) in 0.3 ml of glacial acetic acid and three microdrops of water were added. The resulting mixture was allowed to stand at 25° for 23 hr, then heated on a steam bath for 1 hr and finally poured into 10 ml of saturated sodium chloride solution. The resulting mixture was extracted repeatedly with pentane. The combined pentane extract was neutralized with saturated sodium bicarbonate solution, dried over magnesium sulfate, and filtered into a vial which afterward was loosely capped to allow slow, room temperature evaporation of the solvent. In this manner, 46 mg of crude bicyclo[3.2.1]octan-2-one-*exo*(axial)-4-d_1 was obtained which after sublimation melted at 122.5–125.0°, whose infrared spectrum displayed bands at 2136 (m), 2153 (s), and 2185 cm^{-1} (sh) and whose mass spectrum showed M^+ at *m/e* 125. The isotopic composition is given in Table I.

Conversion of Alcohols to Hydrocarbons. A sample of the same mixture of alcohols obtained from the bond rupture experiment and employed in the preparation of the ketone **4** was dissolved in 3 ml of anhydrous pyridine and converted to a oily mixture of tosylates with *p*-toluenesulfonyl chloride. The crude mixture of tosylates in anhydrous ether solution was heated to reflux for 2 days with an excess of lithium aluminum hydride. After processing the reaction mixture in the usual manner, a crude mixture of hydrocarbons was obtained from which deuterated bicyclo[3.2.1]octane and bicyclo[2.2.2]octane were isolated together as a crystalline solid by vapor phase chromatography employing a 10-ft Carbowax column at 90°. The mass spectrum of the hydrocarbon mixture showed M^+ at *m/e* 111 and an isotopic composition of 15% d_0 and 85% d_1.

Bicyclo[3.2.1]octane-*exo*(axial)-2-d_1 (2b) (X = H) from Bond Cleavage. Bicyclo[2.2.2]octan-2-ol-d_1 and *exo*(axial)-bicyclo[3.2.1]octan-2-ol-*exo*(axial)-4-d_1 **(2b)** (X = OH) were cleanly separated together from the mixture of alcohols originating from bond rupture by preparative vapor phase chromatography. Elution of this mixture of two alcohols with ether from a short column of alumina followed by sublimation yielded 439 mg of soft white crystals. Analysis for atom % excess hydrogen showed the mixture of two alcohols contained 0.93–0.94 atom of deuterium per molecule.

Anal. Calcd for $C_8H_{13}OD$: D, 7.14. Found: D, 6.67, 6.70.

Oxidation of a 410-mg sample of the mixture of two alcohols according to the chromic oxide procedure of Walborsky[7] afforded 237 mg of a mixture of ketones. This mixture was heated for 2 hr with 1.5 g of 85% hydrazine hydrate. After cooling to room temperature, 2.5 ml of 1,3-propanediol and 350 mg of potassium hydroxide were added, and the resulting mixture was slowly heated to 210° and then maintained at that temperature for 1 hr. After cooling, the reaction mixture was diluted with water, then extracted repeatedly with pentane. The combined pentane solution was washed with 10% hydrochloric acid and dried over calcium chloride. The solvent was removed through a 12-in. Vigreux column and the residue chromatographed on a column of alumina to obtain 168 mg of a mixture of hydrocarbons. Vapor phase chromatography employing an 11.5-ft, 20% Silicone 550-on-Celite column allowed the separation of 13 mg of bicyclo[3.2.1]octan-2-d_1 **(2b)** (X = H) from bicyclo[2.2.2]octane-2-d_1. The homogeneity of **2b** (X = H) was demonstrated by reinjection. Principal features of the infrared spectrum of **2b** (X = H) are given in Table II and Figure 2.

Bicyclo[3.2.1]octan-2-one (5). The ketone was prepared from *exo*-3-bromobicyclo[3.2.1]oct-3-en-2-ol **(7)**[13] in 44% yield according to the method of Bergman,[14] mp 121.5–123.5° (lit.[38] mp 123.0–126.5°), M^+ at *m/e* 124.

Bicyclo[3.2.1]octan-2-one-4-d_1 (6). The Bergman procedure, slightly modified, was again employed in the preparation of the deuterium-labeled ketone **6**. A solution of 450 mg of 3-bromo-*exo*-bicyclo[3.2.1]oct-3-en-2-ol in 10 ml of tetrahydrofuran and 10 ml of 1 *N* sodium deuterioxide in deuterium oxide was shaken with 500 mg of 10% palladium on charcoal under deuterium at 30 psi for 1.5 hr. The reaction mixture was diluted with deuterium oxide, saturated with sodium chloride, and extracted with ether. Evaporation of the ether at reduced pressure afforded 150 mg of the crude deuterium-labeled bicyclo[3.2.1]octanol. This sample of alcohol was oxidized to the corresponding ketone by the same procedure employed in the preparation of ketone **4**. The dry ether solution of **6** was then added to 1 ml of sodium methoxide in methanol. The resulting solution was allowed to stand at room temperature for 3 days. Processing this reaction mixture in the usual manner gave 10 mg of bicyclo[3.2.1]octan-2-one-4-d_1 **(6)**, M^+ at *m/e* 125; the isotopic purity is given in Table I.

Bicyclo[3.2.1]octan-2-one-3,4$_3$,4-*d* and Bicyclo[3.2.1]octan-2-one-3,3,4,4-d_4 (10). A solution of 1.327 g of *exo*-3-bromobicyclo-[3.2.1]oct-3-en-2-ol **(7)** in 20 ml of tetrahydrofuran and 20 ml of a 1 *N* sodium deuteroxide in deuterium oxide was shaken with 0.8 g of 10% palladium on charcoal under deuterium at 1 atm. Processing in the usual fashion produced 481 mg of a crystalline mixture of alcohols **9**, mp 140–141°.

A 30-mg sample of the above-described mixture of alcohols was oxidized by chromium oxide in a solution of 0.2 ml of acetic acid-d_1 and 0.002 ml of deuterium oxide. The resulting ketone, 27 mg, mp 118.0–119.5°, was isolated in the usual fashion. The mass spectral analysis showed M^+ at *m/e* 127 and 128. The isotopic composition is given in Table I.

Bicyclo[3.2.1]octan-2-one-*exo*-6-*exo*-7-d_2 (12). After a few trial runs it was found that the optimum conversion of norbornadiene to norborn-2-ene-*exo*-5-*exo*-6-d_2 could be realized by stopping the catalytic deuteration of the diene as soon as the diene was no longer detected by vapor phase chromatography. In this manner, 5.0 g of norbornadiene in 15 ml of pentane and 200 mg of 10% palladium on charcoal were shaken under deuterium at a pressure of 1 atm. The product was a mixture consisting of 70% norborn-2-ene-*exo*-5-*exo*-6-d_2 and 30% norbornane-d_4 according to vapor phase chromatography. The catalyst was removed by filtration, and the resulting pentane solution was used directly in the Bergman procedure[14] for the preparation of *exo*-3-bromobicyclo[3.2.1]oct-3-en-2-ol-*exo*-6-*exo*-7-d_2. Thus to the ice-cooled pentane solution of norborn-2-ene-*exo*-5-*exo*-6-d_2 and bicyclo[2.2.1]heptane-d_4 was added 15 g of potassium *t*-butoxide and then 33 g of bromoform (0.13 mole) in a dropwise manner. After the addition of bromoform was complete, the ice bath was removed, and the reaction mixture was allowed to come to room temperature. The solids were dissolved by the addition of water. The pentane layer was separated, washed with saturated sodium chloride, then dried. Removal of the solvent by distillation and fractionation of the resulting residue produced a yellow oil, bp 90–93° (6 mm), which was treated with silver nitrate in acetone, then hydrogenated to the alcohol **8** (100 mg, mp 189–191°), and finally oxidized; these last three steps were carried out in the manner described for the preparation of the other ketones labeled at C_4; 66 mg of bicyclo[3.2.1]-octan-2-one-*exo*-6-*exo*-7-d_2, mp 122–124°, M^+ at *m/e* 126, was obtained. The isotopic purity is given in Table I.

Bicyclo[3.2.1]octan-2-one-3,3-d_2 (11). A 210-mg sample of bicyclo[3.2.1]octan-2-one **(5)** in 15 ml of a 0.66% solution of sodium deuterioxide in deuteriomethanol was stirred at room temperature for 3 days then diluted with 30 ml of deuterium oxide. The resulting solution was saturated with sodium chloride and extracted with ether. The combined ether extract was dried. After removal of the ether by slow evaporation at room temperature, 100 mg (mp 124–126, M^+ at *m/e* 126) of colorless crystalline bicyclo[3.2.1]octan-2-one **(11)** was obtained. The infrared spectrum displayed C–D stretching bands at 2104 (m), 2129 (m), and 2220 cm^{-1} (s). The isotopic composition of the above-described sample of **11** is given in Table I.

Bicyclo[3.2.1]octane-*exo*-2-d_1 (20). *endo*-Bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfate **(17)** was prepared by the method of Goering.[39] A solution containing 1.7 g of this tosylate (10.2 mmoles), 2 g of sodium borodeuteride (48.0 mmoles), and 810 mg of sodium hydroxide (20.4 mmoles) in 20.4 ml of diglyme–water (65:35 v/v) was heated at 50° for 48 hr in a 50-ml flask the top of which was connected directly through a curved glass tube to a trap immersed in liquid air. As the reaction proceeded, bicyclo[3.2.1]oct-2-ene-*exo*-4-d_1 **(21)** sublimed onto the upper regions of the flask. The product was transferred to the trap by slightly reducing the pressure of the system. In this manner 260 mg of hydrocarbon was obtained. After purification by vapor phase chromatography the product melted at 35.0–36.0°; nmr peaks were at τ 4.27 (1 vinyl H, broad triplet), 4.75 (1 vinyl H, doublet of doublets), 7.5–7.9 (2 H, broad singlet), and 8.2–8.9 (multiplet). Calculation of the number

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[39] H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1391 (1961).

of deuterium atoms gave a value of 0.9 ± 0.1 based on the integral value of the τ 7.5–7.9 signal. The infrared spectrum of the olefin displayed C–D stretching bands at 2113 (s), 2140 (m), 2158 (sh), and 2173 cm^{-1} (w).

The solution remaining in the reaction flask was diluted with 100 ml of water, and the resulting solution was extracted repeatedly with small quantities of pentane. The combined pentane extract was washed with water then dried. Removal of the bulk of the pentane by careful distillation through a 12-in. Vigreux column gave a pentane residue which contained only a trace of bicyclo[3.2.1]oct-2-ene-*exo*-4-d_1 (**21**).

In another preparation of the olefin **21** a solution containing 2.0 g of the tosylate **17** (12.3 mmoles) and 0.52 g of sodium borodeuteride in 25 ml of glyme–deuterium oxide (65:35) in a sealed thick-walled glass tube was heated in an oil bath at 60–65° for 48 hr. The tube was opened with caution after cooling it in liquid air. The contents were diluted with a large quantity of water, and the resulting mixture was extracted repeatedly with ether. The combined extracts were dried. Removal of the ether by careful distillation gave 0.75 g of residue whose vapor phase chromatogram (4.5-ft Carbowax 20M at 90°) showed the presence of bicyclo[3.2.1]oct-2-ene-*exo*-(axial)-4-d_1 (**21**) (67.5%), bicyclo[2.2.2]octene-*d* (0.1%), and *exo*-bicyclo[3.2.1]oct-3-en-2-ol (32.4%). Preparative-scale vapor phase chromatography afforded a pure sample of **21**. The mass spectrum showed M$^+$ at m/e 109 and an isotopic composition of 12% d_0 and 88% d_1.

A 260-mg sample of bicyclo[3.2.1]oct-2-ene-*exo*-4-d_1 (2.4 mmoles), 930 mg of *p*-toluenesulfonylhydrazine, a small piece of sodium hydroxide, and 3.5 ml of anhydrous diglyme were sealed in a tube. The lower part of the tube was immersed in an oil bath at 130°. The product, bicyclo[3.2.1]octan-*exo*-2-d_1 (**20**), sublimed into the upper part of the tube as it was formed. The deuterated hydrocarbon was collected and sublimed once to obtain 53 mg of crystalline material. The principal features of the C–D infrared spectrum are given in Figure 2 and Table II. The mass spectrum showed M$^+$ at m/e 111 and an isotopic composition of 24% d_0 and 76% d_1.

Bicyclo[3.2.1]octane-*endo*-2-d_1 (22). To a solution of 2.1 g of sodium borodeuteride and sodium deuterioxide in methanol-d_1–deuterium oxide was added 5 g of bicyclo[3.2.1]octan-2-one in methanol-*d* in a dropwise fashion. The resulting mixture was stirred for 2 days at room temperature. The solution was diluted with water, acidified, saturated with salt, and extracted with ether. The combined ether extract was washed with water then dried. Removal of the ether by distillation gave 4.4 g of white crystalline bicyclo[3.2.1]octan-2-ol-2-d_1 (**23**) which when once sublimed melted at 180–183° and whose infrared spectrum showed a C–D band at 2115 cm^{-1} (s).

A 2.0-g sample of **23** (16 mmoles) and 2.4 g of sodium hydride (100 mmoles) in 100 ml of benzene were heated to reflux for 24 hr. Carbon disulfide, 7.6 g (100 mmoles), was added, and the resulting reaction mixture was heated to reflux for an additional 24 hr after which time the reaction mixture was cooled to room temperature. Methyl iodide, 7.1 g (50 mmoles), was added, and the resulting solution was heated to reflux for a third 24-hr period. After cooling, water was added, and the benzene layer was separated and dried. The bulk of the benzene was removed at the rotary evaporator. The residue, diluted with pentane, was passed through 10 g of neutral alumina in a 1-cm diameter column. The column was eluted with additional pentane. Removal of the pentane gave 4.0 g of crude methyl xanthate (**24**).

The above-described crude methyl xanthate in a small amount of pentane was added dropwise to a U tube which was heated at 210° in an oil bath. The pyrolysate was carried by a gentle flow of nitrogen into a cooled trap containing pentane. Bicyclo[3.2.1]oct-2-ene-2-d_1 (**25**) (M$^+$ at m/e 109; nmr peak τ 4.70 (1 vinyl H, broad singlet), 7.5–7.8 (multiplet), 7.9–8.8 (multiplet)) was separated from the pentane solution by vapor phase chromatography. The isotopic composition was 11% d_0, 85% d_1, and 4% d_2. The infrared showed a C–D band at 2255 cm^{-1}.

A 100-mg sample of olefin **25** (0.92 mmole), 930 mg of *p*-toluenesulfonylhydrazide (5.0 mmoles), and a small piece of sodium hydroxide in 3 ml of anhydrous diglyme were sealed in a thick-walled tube which was then heated in an oil bath at 130°. The crude product, 100 mg, was collected from the upper portion of the tube and was once sublimed to afford bicyclo[3.2.1]octane-*endo*-2-d_1 (**22**), mp 126–127°, M$^+$ at m/e 111. The isotopic purity was 18% d_0, 78% d_1, and 4% d_2. The principal features of the infrared spectrum are given in Table II and Figure 2.

Bicyclo[3.2.1]octane-*exo*- and -*endo*-2-d_1 (20 and 22). Bicyclo[3.2.1]octan-2-one, 1 g (8 mmoles), and 3 g of *p*-toluenesulfonylhydrazide (16 mmoles) were dissolved in 10 ml of methanol, and the resulting solution was refluxed 1.5 hr. A 2-g sample of crystalline precipitate was collected; mp 175–180° dec.

A 1-g sample of the above-described tosylhydrazone (3.5 mmoles) and 0.4 g of lithium aluminum deuteride (9.5 mmoles) in 10 ml of anhydrous dioxane was heated to gentle reflux for 1.5 hr. Water (1 ml) was added and then after 5 min, 5 ml of methanol containing a few microdrops of dilute hydrochloric acid. The resulting reaction mixture was allowed to reflux for 30 min. The reaction mixture was filtered and diluted with water and the resulting mixture was extracted repeatedly with pentane. The combined pentane extract was washed with saturated sodium chloride and dried. The bulk of the pentane was removed by careful distillation. According to a vapor phase chromatogram (11-ft Carbowax at 67°) the residue consisted of 85% of the labeled bicyclo[3.2.1]octanes **20** and **22** and 15% bicyclo[3.2.1]oct-2-ene. A mixture of **20** and **22** (100 mg) was isolated by preparative vapor phase chromatography. Principal features of the C–D region of the infrared spectrum are given in Figure 2 and Table II.

Bicyclo[3.2.1]octane-2,2-d_2 (26). The procedure employed was the same as that used to convert the tosylhydrazone of bicyclo[3.2.1]octanone to the mixture of monodeuterated hydrocarbons except that lithium aluminum deuteride (0.4 g, 9.5 mmoles), deuterium oxide (0.5 ml), and methanol-*d* (5.0 ml) were used as the reagents. The mass spectrum showed M$^+$ at m/e 112 and an isotopic purity of 11% d_1, 86% d_2, and 3% d_3. The principal features of the infrared spectrum in the C–D region are given in Figure 2 and Table II.

***exo*(axial)-Bicyclo[3.2.1]octan-2-ol α-Naphthylurethan.** α-Naphthyl isocyanate, 118 mg (0.70 mmole), and *exo*(axial)-bicyclo-[3.2.1]octan-2-ol, 88 mg (0.70 mmole), were mixed in a vial which was placed in a refrigerator for 24 hr. Recrystallization of the product from naphtha solvent gave the urethan, mp 124–126.5°; in the mass spectrum no peak was found above m/e 250.

Anal. Calcd for $C_{19}H_{21}O_2N$: N, 4.75. Found: N, 4.97.