Carbonium Ions. XI. Deamination of 1-Aminopropane and the Question of Protonated Cyclopropane *vs.* the 1-Propyl Cation

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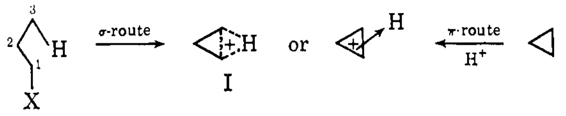
Abstract: The aqueous acid deaminations of 1-aminopropane-1,1-d_2, -2,2-d_2, -3,3,3-d_2, and -1-^{13}C led to 1-propanols that were about 4% isotope-position rearranged and to 2-propanols that were exclusively isotope-position unrearranged, *i.e.*, having arisen from a nominally irreversible 1,2-hydride shift. The percentage of 1-propanols with one deuterium atom at the α-carbon was the same from either the 1,1-d_2- or the 2,2-d_2-labeled amine; that with two deuterium atoms at the α-carbon was about the same from either the 2,2-d_2 or the 3,3,3-d_3 amine. The results have been interpreted in terms of edge-protonated cyclopropane intermediates that account for about 6% of the over-all yield of product. The mechanism of edge-protonated cyclopropane equilibration is pictured as occurring by a "pseudorotation," or equivalent process, about the carbon-carbon bond, that leads to simultaneous carbon-carbon and hydrogen-hydrogen scrambling, with the carbon-carbon scrambling being more extensive than the hydrogen-hydrogen. It is estimated that this process is about 5-10 times faster than capture of the protonated cyclopropane by water to give 1-propanol. Under the deamination conditions the edge-protonated cyclopropanes leak neither to the 1-propyl nor to the 2-propyl cation.

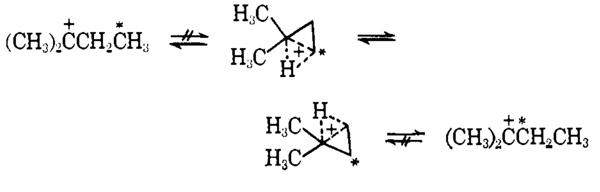
In recent years we have channeled a major part of our research effort toward the solution of various problems associated with carbonium ions and their rearrangements. We have focused attention on such subjects as the significance of bimolecular reactions and Wagner-Meerwein shifts (hydride and alkyl) of orders higher than 1,2 as mechanistic paths in carbonium ion rearrangements of acyclic systems, and on the intermediacy of primary carbonium ions and protonated cyclopropanes in such rearrangements. In this and subsequent publications we wish to address ourselves in more detail to the role that protonated cyclopropanes play in carbonium ion rearrangements of simple acyclic systems.[2a]

Protonated cyclopropanes may arise either by the "σ route" or by the "π route,"[2b] as depicted in eq 1. We have taken the "σ route"[3] and concentrated our efforts toward establishing: (a) whether the edge-protonated cyclopropane I (twofold axis of symmetry) or the face-protonated cyclopropane II (threefold axis of symmetry) best describes the structure of the intermediate species; (b) whether the methyl-bridged ion III intervenes as an intermediate and, if so, whether it precedes or follows either I or II; (c) how X and reaction conditions affect the extent of protonated cyclopropane intervention; and (d) how alkyl substitution at C-2 and C-3 of the 1-propyl system affects the relative stabilities of protonated cyclopropanes and their classical counterparts. Having established that the rearrangement pictured in eq 2 does not occur, we have chosen systems where C-1 is unsubstituted (primary). This choice was dictated not only by the fact that the rearrangement shown in eq 2 did not occur, but also by the reasonable expectation that the unstable primary carbonium ions (or their precursors) would be much more prone to lead to protonated cyclopropanes than would the significantly more stable secondary and tertiary analogs.



(1)

III



(2)

We will start with the unsubstituted propyl system by discussing the deamination of 1-aminopropane in this paper[4] and the reactions of 1-propyl bromide and tosylate in the next.

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[1] Research and Development Department, American Oil Company, Whiting, Ind.

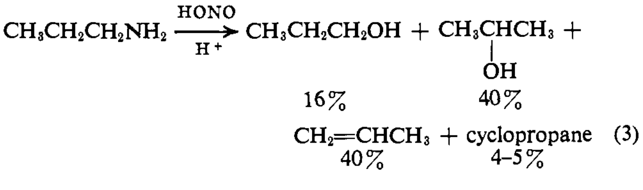
[2] (a) For relevant studies on bicyclic systems see: J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Amer. Chem. Soc.*, **76**, 4501 (1954); J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956); S. Winstein and D. Tifan, *ibid.*, **74**, 1154 (1952); A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965); J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965); A. Nickon and N. H. Werstink, *ibid.*, **89**, 3915, 3917 (1967); C. J. Collins and B. M. Benjamin, *ibid.*, **89**, 1652 (1967); B. M. Benjamin, B. W. Ponder, and C. J. Collins, *ibid.*, **88**, 1558 (1966); C. J. Collins and M. H. Lietzke, *ibid.*, **89**, 6565 (1967); C. C. Lee and J. K. Kruger, *Tetrahedron*, **23**, 2539 (1967); (b) for the notation "σ route" and "π route" to nonclassical carbonium ions see S. Winstein and P. Carter, *J. Amer. Chem. Soc.*, **83**, 4485 (1961). The term "Δ-route" has been recently suggested by A. Nickon and G. D. Pandit, *Tetrahedron Lett.*, **33**, 3663 (1968), for paths involving the electrophilic opening of three-membered rings.

[3] For studies by the "π route" see: (a) R. L. Baird and A. A. Aboderin, *ibid.*, **4**, 235 (1963); (b) R. L. Baird and A. A. Aboderin, *J. Amer. Chem. Soc.*, **86**, 252, 2300 (1964); (c) H. Hart and R. H. Schlosberg, *ibid.*, **88**, 5030 (1966); (d) N. C. Deno and D. R. Lincoln, *ibid.*, **88**, 5357 (1966); (e) G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968); (f) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968); (g) C. C. Lee, W. Koo-Ying Chwang, and Kwok-Ming Wan, *ibid.*, **90**, 3778 (1968).

[4] Part of this work appeared in G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, **87**, 4394 (1965).

Results

The deamination of 1-aminopropane gave 1-propanol, 2-propanol, propene, and cyclopropane in overall product yields of 60–70%. The remaining percentage was found to be unreacted 1-aminopropane. On the basis of this and previous studies,[5–7] the approximate product distribution may be roughly estimated as follows (eq 3)



$$CH_3CH_2CH_2NH_2 \xrightarrow[H^+]{HONO} \underset{16\%}{CH_3CH_2CH_2OH} + \underset{40\%}{CH_3\underset{OH}{\underset{|}{C}}HCH_3} + \underset{40\%}{CH_2{=}CHCH_3} + \underset{4\text{–}5\%}{\text{cyclopropane}} \qquad (3)$$

The alcohol product from the deamination of 2-aminopropane was exclusively 2-propanol (less than 0.2% 1-propanol, as judged by gas chromatography).

The propanols obtained from the various deaminations were separated by gas chromatography and converted to the trimethylsilyl ether derivatives for mass spectral analysis, so as to obtain the distribution of molecules containing various numbers of labels—that is, an isotopic analysis—and to determine the location of labels in the molecules.

The label in a molecule can be located only if the relevant decomposition paths are known and if the various parts of the molecule do not lose identity before decomposition. We have used the parent less-methyl region of the mass spectrum of the trimethylsilyl ether derivative of 1-propanol to obtain an isotopic analysis, and the parent less-ethyl region to locate the labels in the molecule. To secure accurate analysis, unlabeled, known position-labeled, and reaction product samples were run consecutively.

A. Mass Spectral Analysis of the Trimethylsilyl Ether Derivatives of 1-Propanols-1,1-d_2. In Table I are summarized the label distributions in the parent less-methyl and parent less-ethyl ion fragments of the trimethylsilyl ether derivatives of 1-propanols-1,1-d_2. Entries 1, 2, and 3 are those of samples synthesized by reduction of appropriate precursors (propionic anhydride and propionyl chloride) with lithium aluminum deuteride. The remaining entries are those of samples from product 1-propanols obtained from the deamination of various 1-aminopropanes-1,1-d_2; one sample of 1-aminopropane-1,1-d_2 was used in entries 4 and 6, another in entry 5, and a third in 7 and 8. Duplicate mass spectral analyses agreed to ±0.1%.

From inspection of the parent less-methyl and parent less-ethyl label distributions in entries 1, 2, and 3, it can be concluded that about 0.5% d_1 and 0.1% d_0 of the parent less-ethyl ion arise from sources other than primary loss of the ethyl group from the propyl system. To put it more simply, a sample of a trimethylsilyl ether of 1-propanol-1,1-d_2 containing 100% d_2 molecules would give a parent less-ethyl ion distribution of 99.4% d_2, 0.5% d_1, and 0.1% d_0. In calculating the label distribution in the product 1-propanols, we must, therefore, subtract 0.5 and 0.1 units from the percentage d_1 and d_0 values, respectively. We judge these values to be correct to ±0.1 unit. That the parent less-methyl ion arises exclusively by loss of methyl from the trimethylsilyl group can be concluded from the following results: mass spectral analysis of the parent ion of the benzoate of 1-propanol-3-^{13}C, synthesized by reaction of methyl-^{13}C-magnesium iodide with ethylene oxide, gave 19.7% ^{13}C and 80.3% ^{12}C. The parent less-methyl ion of the trimethylsilyl ether of the same alcohol gave 19.8% ^{13}C and 80.2% ^{12}C. Similarly, parent-ion analysis of the benzoate of 1-propanol-1-^{13}C, prepared by reduction of propionic-1-^{13}C acid with lithium aluminum hydride, gave 30.6% ^{13}C and 69.4% ^{12}C. The parent less-methyl ion of the trimethylsilyl ether of the same alcohol also gave 30.6% ^{13}C and 69.4% ^{12}C. Although we did not examine the 1-propanol-2-^{13}C derivative, the results (discussed later) from 1-propanol-2,2-d_2 rule out any contribution to the parent less-methyl ion from C-2 of the propyl group.

Table I. Label Distributions[a] in the Trimethylsilyl Ether Derivatives of 1-Propanols-1,1-d_2

		Parent less-methyl, %			Parent less-ethyl, %		
No.	Compound	d_2	d_1	d_0	d_2	d_1	d_0
1	$CH_3CH_2CD_2OSi(CH_3)_3$[b]	98.8	1.2	0.0	98.3	1.6	0.1
2	$CH_3CH_2CD_2OSi(CH_3)_3$[b]	99.0	1.0	0.0	98.3	1.6	0.1
3	$CH_3CH_2CD_2OSi(CH_3)_3$[c]	88.4	11.5	0.1	87.7	12.0	0.3
4	C–C–C–OSi$(CH_3)_3$[d]	98.0	2.0	0.0	95.4	2.8	1.8
5	C–C–C–OSi$(CH_3)_3$[e]	96.4	3.6	0.0	91.6	4.9	3.5
6	C–C–C–OSi$(CH_3)_3$[e]	98.0	2.0	0.0	93.6	3.2	3.2
7	C–C–C–OSi$(CH_3)_3$[f]	98.2	1.8	0.0	93.7	3.2	3.1
8	C–C–C–OSi$(CH_3)_3$[f]	98.2	1.8	0.0	93.3	3.4	3.4

[a] Calculated from 70-V mass spectra. [b] Derivatives of 1-propanol samples synthesized by reduction of propionic anhydride with lithium aluminum deuteride. [c] Derivative of 1-propanol synthesized by reduction of propionyl chloride with lithium aluminum deuteride. [d] Derivative of 1-propanol obtained from the deamination at −10 to 0° of 1-aminopropane-1,1-d_2. [e] Derivatives of 1-propanol samples obtained from the deamination at 40° of two different samples of 1-aminopropane-1,1-d_2. [f] Derivatives of 1-propanol samples obtained from two different deaminations at 60° of 1-aminopropane-1,1-d_2.

The objective of the mass spectral analysis was to accurately establish the label distribution in the 1-propanol products obtained from the deamination of specifically position-labeled 1-aminopropanes. To illustrate our procedure, we will discuss in detail the results in entry 5. The 96.4% d_2 and 3.6% d_1 parent less-methyl distribution corresponds to the isotopic composition of the product 1-propanol, *i.e.*, 96.4% doubly labeled and 3.6% singly labeled molecules. The parent less-ethyl ion distribution of 91.6% d_2, 4.9% d_1, and 3.5% d_0, when corrected by 0.5 d_1 and 0.1 d_0 units, becomes 92.2% d_2, 4.4% d_1, and 3.4% d_0 and corresponds to the isotopic composition of the α-methylene group of 1-propanol, *i.e.*, 92.2%-CD_2OH, 4.4%-CHDOH, and 3.4%-CH_2OH. Although the doubly labeled fragment arises exclusively from the doubly labeled molecules, the singly labeled and unlabeled fragments arise from both the doubly labeled and the singly labeled (3.6%) molecules. Since about 95% of the product alcohol is isotope-position unrearranged, the contribution of the singly labeled molecules to d_1 and d_0 ought to be about 3.4 d_1 and 0.2 d_0. The doubly labeled 1-propanol molecules have, therefore, the following label distribution: 92.2% C_2H_5-CD_2OH, 1.0% C_2H_4D-CHDOH, and 3.2% $C_2H_3D_2$-CH_2OH. Normalization makes these

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(5) P. S. Skell and I. Starer, *J. Amer. Chem. Soc.*, **82**, 2971 (1960).

(6) F. C. Whitmore and R. S. Thrope, *ibid.*, **63**, 1118 (1941).

(7) G. J. Karabatsos and C. E. Orzech, Jr., *ibid.*, **84**, 2823 (1962).

values 95.7%, 1.0%, and 3.3%, respectively. The results presented in Table I may thus be summarized as shown in Chart I.

Chart I

$$\underset{100\%\ d_2}{CH_3CH_2CD_2NH_2} \longrightarrow \underset{\text{I}'}{C_2H_5\text{–}CD_2OH} + \underset{\text{II}'}{C_2H_4D\text{–}CHDOH} + \underset{\text{III}'}{C_2H_3D_2\text{–}CH_2OH}$$

	I′ %	II′ %	III′ %
$\xrightarrow{-10\text{ to }0^\circ}$	97.8	0.6	1.6
$\xrightarrow{40^\circ}$	95.7	1.0	3.3
$\xrightarrow{40^\circ}$	96.2	0.8	3.1
$\xrightarrow{60^\circ}$	96.0	1.0	3.0
$\xrightarrow{60^\circ}$	95.5	1.2	3.3

To assess the extent of protium–deuterium exchange between substrate and solvent during the reaction, we converted the 1-aminopropanes used in 5 and 6 to the diacetamide derivatives and subjected the latter to mass spectral analysis. Their parent less-methyl ions had the following composition: 96.6% d_2 and 3.4% d_1 (entry 5) and 97.8% d_2 and 2.2% d_1 (entry 6). The good agreement between these values and the corresponding ones of the parent less-methyl ions of the trimethylsilyl ether derivatives (Table I) excludes any such exchange.

B. Mass Spectral Analysis of the Trimethylsilyl Ether Derivatives of 1-Propanols-2,2-d_2. In Table II are summarized the label distributions in the parent less-methyl and parent less-ethyl ion fragments of the trimethylsilyl ether derivatives of 1-propanols-2,2-d_2. Entries 1 and 2 refer to 1-propanol samples synthesized by reduction of propionic-2,2-d_2 acids with lithium aluminum hydride. Entry 3 gives the distribution of the derivative of the 1-propanol obtained from the deamination at 40° of 1-aminopropane-2,2-d_2. Entries 5 and 6 also correspond to product alcohols from deaminations at 40 and 60°, respectively. Entry 4 refers to the same alcohol as in 2; it was run consecutively with samples 5 and 6 and its isotopic distribution (parent less-ethyl) was used to correct the label distribution in the parent less-ethyl ion of these two samples. The results, after correction and normalization, are summarized as shown in Chart II.

Table II. Label Distributions[a] in the Trimethylsilyl Ether Derivatives of 1-Propanols-2,2-d_2

		Parent less-methyl, %			Parent less-ethyl, %		
No.	Compound	d_2	d_1	d_0	d_2	d_1	d_0
1	$CH_3CD_2CH_2OSi(CH_3)_3$[b]	98.4	1.6	0.0	0.3	0.2	99.5
2	$CH_3CD_2CH_2OSi(CH_3)_3$[b]	98.0	2.0	0.0	0.2	0.3	99.5
3	C–C–C–OSi$(CH_3)_3$[c]	98.0	2.0	0.0	1.4	1.1	97.5
4	$CH_3CD_2CH_2OSi(CH_3)_3$[d]	98.4	1.6	0.0	0.6	0.3	99.1
5	C–C–C–OSi$(CH_3)_3$[e]	98.0	2.0	0.0	1.9	1.5	96.6
6	C–C–C–OSi$(CH_3)_3$[f]	98.0	2.0	0.0	1.8	1.6	96.6

[a] Calculated from 70-V mass spectra. [b] Derivatives of 1-propanol samples synthesized by reduction of propionic-2,2-d_2 acid with lithium aluminum hydride. [c] Derivative of 1-propanol obtained from the deamination at 40° of 1-aminopropane-2,2-d_2. [d] Derivative of 1-propanol same as in *b;* this sample was analyzed at the same time as samples in 5 and 6. [e] Derivative of 1-propanol obtained from the deamination at 40° of 1-aminopropane-2,2-d_2. [f] Derivative of 1-propanol obtained from the deamination at 60° of 1-aminopropane-2,2-d_2.

Chart II

$$\underset{100\%\ d_2}{CH_3CD_2CH_2NH_2} \longrightarrow \underset{\text{I}'}{C_2H_5\text{–}CD_2OH} + \underset{\text{II}'}{C_2H_4D\text{–}CHDOH} + \underset{\text{III}'}{C_2H_3D_2\text{–}CH_2OH}$$

	I′ %	II′ %	III′ %
$\xrightarrow{40^\circ}$	1.1	0.9	97.9
$\xrightarrow{40^\circ}$	1.3	1.2	97.4
$\xrightarrow{60^\circ}$	1.2	1.3	97.5

Again, the good agreement in the parent less-methyl label distribution between authentically synthesized 1-propanol-2,2-d_2 samples and product 1-propanol samples obtained from the deamination of 1-aminopropanes-2,2-d_2 excludes any protium–deuterium exchange between substrate and solvent during the reaction.

C. Mass Spectral Analysis of the Trimethylsilyl Ether Derivatives of 1-Propanols-3,3,3-d_3. In Table III are summarized the label distributions in the parent less-methyl and parent less-ethyl ions of the trimethylsilyl derivatives of 1-propanols-3,3,3-d_3. Entries 1 and 3 are of samples prepared by reduction of propionic-3,3,3-d_3 acid with lithium aluminum hydride. Entries 2 and 4 are of the product alcohols from the deamination of 1-aminopropane-3,3,3-d_3 (prepared from the same sample of propionic acid used to synthesize the alcohols in 1 and 3) at 40 and 60°, respectively. Entries 1 and 2 were run consecutively; so were 3 and 4. The corrected and normalized results are summarized as shown in Chart III.

Chart III

$$\underset{100\%\ d_3}{CD_3CH_2CH_2NH_2} \longrightarrow \underset{\text{I}''}{C_2H_4D\text{–}CD_2OH} + \underset{\text{II}''}{C_2H_3D_2\text{–}CHDOH} + \underset{\text{III}''}{C_2H_2D_3\text{–}CH_2OH}$$

	I″ %	II″ %	III″ %
$\xrightarrow{40^\circ}$	1.0	1.2	97.8
$\xrightarrow{60^\circ}$	1.2	1.6	96.2

As with the previous cases, the results again exclude any protium–deuterium exchange between substrate and solvent during the reaction.

D. Mass Spectral Analysis of the Trimethylsilyl Ether Derivatives of 1-Propanols-1-^{13}C. The trimethylsilyl ether derivative of 1-propanol-1-^{13}C, synthesized by reduction of propionic-1-^{13}C acid with lithium aluminum hydride, gave parent less-methyl 30.6% ^{13}C and parent less-ethyl 30.8% ^{13}C. That of the product 1-propanol from the deamination of 1-aminopropane-1-^{13}C (synthesized from the same acid samples as the authentic alcohol) gave parent less-methyl 30.5% ^{13}C and parent-less-ethyl 29.8% ^{13}C. The corrected and normalized results, therefore, become

$$\underset{100\%\ ^{13}C}{CH_3CH_2\text{–}^{13}CH_2NH_2} \longrightarrow \underset{97\%}{CH_3CH_2\text{–}^{13}CH_2OH} + \underset{3\%}{\overbrace{CH_3CH_2}^{13}\text{–}CH_2OH}$$

E. Mass Spectral Analysis of the Trimethylsilyl Ether Derivatives of 2-Propanols. In Table IV are

Table III. Label Distributions[a] in the Trimethylsilyl Ether Derivatives of 1-Propanols-3,3,3-d_3

		Parent less-methyl, %				Parent less-ethyl, %			
No.	Compound	d_3	d_2	d_1	d_0	d_3	d_2	d_1	d_0
1	$CD_3CH_2CH_2OSi(CH_3)_3$[b]	97.5	1.9	0.6	0.0	0.0	2.2	3.0	94.8
2	C-C-C-$OSi(CH_3)_3$[c]	97.2	2.0	0.8	0.0	0.0	3.2	4.2	92.6
3	$CD_3CH_2CH_2OSi(CH_3)_3$[d]	97.4	1.9	0.7	0.0	0.0	0.4	3.3	96.3
4	C-C-C-$OSi(CH_3)_3$[e]	97.4	1.9	0.7	0.0	0.0	1.6	4.9	93.5

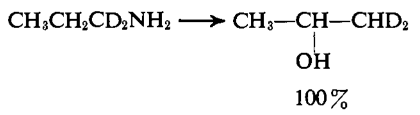
[a] Calculated from 70-V mass spectra. [b] Derivative of 1-propanol synthesized by reduction of propionic-3,3,3-d_3 acid with lithium aluminum hydride. [c] Derivative of 1-propanol obtained from the deamination at 40° of 1-aminopropane-3,3,3-d_3. Samples 1 and 2 were run consecutively. [d] Derivative of 1-propanol synthesized as in *b*. [e] Derivative of 1-propanol obtained from the deamination at 60° of 1-aminopropane-3,3,3-d_3. Samples 3 and 4 were run consecutively.

Table IV. Label Distributions[a] in the Trimethylsilyl Ether Derivatives of 2-Propanols

		Parent less-methyl, %		
No.	Compound	d_2	d_1	d_0
1	$CHD_2\overset{\overset{CH_3}{\vert}}{C}HOSi(CH_3)_3$[b]	84.5	1.8	13.7
2	$C-\overset{\overset{C}{\vert}}{C}-OSi(CH_3)_3$[c]	84.3	2.0	13.7
3	$C-\overset{\overset{C}{\vert}}{C}-OSi(CH_3)_3$[d]	84.5	1.9	13.6
4	$C-\overset{\overset{C}{\vert}}{C}-OSi(CH_3)_3$[e]	82.4	3.6	14.0

[a] Calculated from 70-V mass spectra. [b] Derivative of 2-propanol that was synthesized by reaction of methyl-d_2-magnesium iodide (98.4% d_2 and 1.6% d_1) with acetaldehyde. [c] Derivative of 2-propanol obtained from deamination at 40° of 1-aminopropane-1,1-d_2 (98.2% d_2 and 1.8% d_1, entry 7 in Table I). [d] Derivative of 2-propanol obtained from the deamination at 60° of 1-aminopropane-1,1-d_2 (98.2% d_2 and 1.8% d_1, entry 8 in Table I). [e] Derivative of 2-propanol obtained from the deamination at 40° of 1-aminopropane-1,1-d_2 (96.4% d_2 and 3.6% d_1, entry 5 in Table I).

summarized the label distributions in the parent less-methyl ion of the trimethylsilyl ether derivatives of isotopically labeled 2-propanols. Entry 1 is that of 2-propanol prepared by the reaction of methyl-d_2-magnesium iodide (98.4% d_2 and 1.6% d_1) with acetaldehyde. This ion, therefore, arises 27.4% by loss of methyl from the isopropyl group and 72.6% by loss from the trimethylsilyl group. Entries 2 and 3 are those of product 2-propanols from the reactions of 1-aminopropane-1,1-d_2, whose isotopic composition was 98.2% d_2 and 1.8% d_1 (7 and 8 in Table I). Entry 4 is that of the product 2-propanol from the reaction of 1-aminopropane-1,1-d_2, whose isotopic composition was 96.4% d_2 and 3.6% d_2 (5 in Table I). From the data it can be concluded that the 2-propanol product is completely isotope-position unrearranged, *i.e.*, exclusively the isotopic species expected from a nominally *irreversible* 1,2-hydride shift, as shown

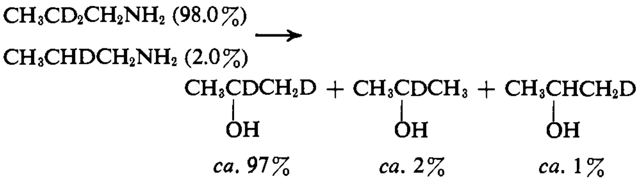


$$CH_3CH_2CD_2NH_2 \longrightarrow CH_3-\underset{\underset{OH}{\vert}}{CH}-CHD_2$$

100%

Further support of this conclusion is provided by mass spectral analysis of the trimethylsilyl ether of 2-propanol obtained from the deamination of 1-aminopropane-1-^{13}C. Mass spectral analysis of the trimethylsilyl ether of 2-propanol synthesized by the reaction of methyl-^{13}C-magnesium iodide with acetaldehyde—whose isotopic purity was 19.7% ^{13}C by parent-ion analysis of its benzoate, and 19.8% ^{13}C by analysis of the trimethylsilyl ether of 1-propanol synthesized from the same methyl-^{13}C-magnesium iodide with ethylene oxide—gave 17.0% ^{13}C and 83.0% ^{12}C. The parent less-methyl ion, therefore, arises 27.4–28.3% by loss of methyl from the isopropyl group and 72.6–71.7% by loss from the trimethylsilyl group. The parent less-methyl ion of the trimethylsilyl ether of the 2-propanol product obtained from the deamination of 1-aminopropane-1-^{13}C (30.5% ^{13}C and 69.5% ^{12}C) was 25.8% ^{13}C and 74.2% ^{12}C. Had any ^{13}C label been present at C-2 of the 2-propanol product, the parent less-methyl ion should have given more than 26.2% ^{13}C. Since it is less, 25.8%, the 2-propanol has all the ^{13}C label at C-1, none at C-2.

Mass spectral analysis of the trimethylsilyl ether derivatives of the product 2-propanols from the deaminations of 1-aminopropane-2,2-d_2, whose composition was 98.0% d_2 and 2.0% d_1 (see entries 5 and 6 in Table II), gave parent less-methyl 83.7% d_2 and 16.3% d_1. These results shed no further light on the question of whether the 2-propanol is isotope-position unrearranged, because the isotopic purity of the 2-propanols formed in the deamination would be different than the 98.0% d_2 and 2.0% d_1 of the starting amine, as a result of the k_H/k_D effect of the 1,2-hydride shift that gives rise to them. Although this k_H/k_D cannot be accurately determined, it can be estimated from the results, as follows: assuming that 27.4% of the parent less-methyl ion arises by loss of methyl from the isopropyl group, we calculate from the 83.7% d_2 that 13.2% d_1 arises from doubly labeled 2-propanol (presumably, solely 2-propanol-1,2-d_2). The remaining 3.1% d_1, therefore, arises from singly-labeled 2-propanol (2-propanol-2-*d* and 2-propanol-1-*d*). Since no d_0 fragment was detected, the 2-propanol-1-*d* should comprise not much more than 1%. The results may, thus, be roughly estimated as



$$\begin{array}{l} CH_3CD_2CH_2NH_2\ (98.0\%) \\ CH_3CHDCH_2NH_2\ (2.0\%) \end{array} \longrightarrow$$

$$CH_3\underset{\underset{OH}{\vert}}{C}DCH_2D + CH_3\underset{\underset{OH}{\vert}}{C}DCH_3 + CH_3\underset{\underset{OH}{\vert}}{C}HCH_2D$$

ca. 97% *ca.* 2% *ca.* 1%

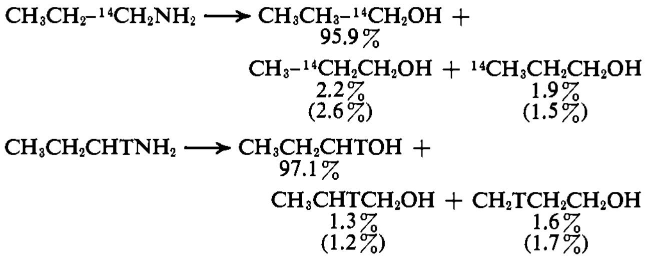
From these, k_H/k_D appears to be about 1.5–2.0.

Discussion

Any mechanistic interpretation of the formation of isotope-position rearranged 1-propanol must be based, at least, on the following observations: (1) over 95%

of the 1-propanol product is isotope-position unrearranged, *i.e.*, 1-propanol with the label at the same position as the precursor 1-aminopropane. (2) Approximately the same amount of 1-propanol with one deuterium at the α-carbon (species II′) is obtained from either the 1,1-d_2 or the 2,2-d_2-labeled 1-aminopropane. (3) About the same amount of 1-propanol with two deuterium atoms at the α-carbon is obtained from either the 2,2-d_2- or the 3,3,3-d_3-labeled 1-aminopropane. These observations require that the 1-propanol be formed by at least two paths; one that leads to isotope-position unrearranged 1-propanol and one that leads to isotope-position rearranged. The latter path effectively equilibrates all three carbon atoms of the propyl system. In accord with this conclusion is the finding[8] that the 1-propanol product obtained from the deamination of 1-aminopropane-1-^{14}C is about 96% isotope-position unrearranged with the 4% rearranged label about equally distributed—within experimental error—between C-2 and C-3, and the corresponding 1-propanol from the deamination of 1-aminopropane-1-*t* is about 97% isotope-position unrearranged with the 3% rearranged label again about equally distributed between C-2 and C-3, as shown in Chart IV.

Chart IV



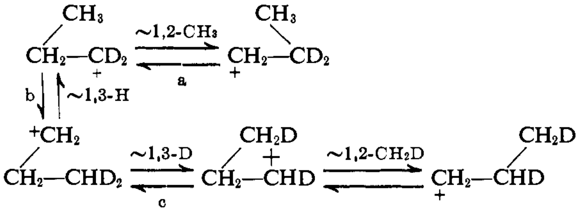
$$CH_3CH_2\text{–}{}^{14}CH_2NH_2 \longrightarrow \underset{95.9\%}{CH_3CH_3\text{–}{}^{14}CH_2OH} + \underset{\substack{2.2\% \\ (2.6\%)}}{CH_3\text{–}{}^{14}CH_2CH_2OH} + \underset{\substack{1.9\% \\ (1.5\%)}}{{}^{14}CH_3CH_2CH_2OH}$$

$$CH_3CH_2CHTNH_2 \longrightarrow \underset{97.1\%}{CH_3CH_2CHTOH} + \underset{\substack{1.3\% \\ (1.2\%)}}{CH_3CHTCH_2OH} + \underset{\substack{1.6\% \\ (1.7\%)}}{CH_2TCH_2CH_2OH}$$

Before embarking on a discussion of the nature of the intermediates responsible for the formation of the isotope-position rearranged 1-propanol, the following comment should be made regarding the path responsible for the rearrangement. Although this path equilibrates the three carbon atoms of the 1-propyl system, it does not completely equilibrate the hydrogens of the system. Had such complete equilibration occurred prior to the formation of the isotope-position rearranged 1-propanol, the ratio of I′:II′:III′ species arising from this path would be 1:10:10 from either the 1,1-d_2 or the 2,2-d_2 aminopropane, and 1:4:2 from the 3,3,3-d_3 aminopropane. The ratio II′:III′ is about 1:3, instead of 1:1, from the reactions of 1-aminopropane-1,1-d_2; the ratio I′:II′ is about 1:1, instead of 1:10, from the reactions of 1-aminopropane-2,2-d_2, and about 1:1, instead of 1:4, from the reactions of 1-aminopropane-3,3,3-d_3.

Consideration of Classical Carbonium Ion Mechanisms. Reversible intramolecular 1,2-hydride shifts involving the 1-propyl and 2-propyl cations are ruled out as the mechanistic path responsible for the formation of the isotope-position rearranged 1-propanol. Not only do they fail to account for the observed carbon scrambling, but they also are in conflict with the fact that the 2-propanol product is completely isotope-position unrearranged. The results also exclude reversible 1,3-hydride shifts as the only source of the rearranged 1-propanol. Such shifts alone equilibrate only the one and three carbon atoms and their hydrogens. The results may, however, be explained in terms of classical carbonium ions, if both 1,2-methyl and 1,3-hydride shifts are invoked, as illustrated in Chart V.

Chart V



For this mechanism to be correct, the results require the following to be true. 1. The reversible 1,2-methyl shifts, a, occur at least five times faster than capture of the 1-propyl cation by water. This condition is required by the fact that the isotope-position rearranged 1-propanol comes from a path that has nearly equilibrated the C-1 and C-2 atoms.

2. The 1,3-hydride and deuteride shifts, b and c, must also be faster than capture of the 1-propyl cation by water. This condition is required by the fact that carbons 2 and 3 have nearly equilibrated prior to the formation of the isotope-position rearranged 1-propanol.

3. The isotope-position unrearranged 1-propanol, which comprises about 95% of the 1-propanol fraction, does not arise from the 1-propyl cation invoked in statements 1 and 2.

4. The 1-propyl cation responsible for the isotope-position rearranged 1-propanol is not an intermediate along the path to 2-propanol. If it were, the 2-propanol product would be isotope-position rearranged.

5. The 1,2-hydride shift converting the 1-propyl cation invoked in statements 1 and 2 to the 2-propyl cation is much slower than capture of 1-propyl cation by water. If not, part of the 2-propanol product would be isotope-position rearranged.

We consider these restrictions demanded by the classical carbonium ion mechanism unrealistic on the grounds of the following arguments. A. For statements 1, 2, and 5 to be true, the primary-to-primary carbonium ion rearrangement, either by a 1,2-methyl or a 1,3-hydride shift, would have to be much faster than the corresponding primary-to-secondary rearrangement. Although the accuracy of our measurements does not permit a quantitative evaluation of the free energy difference between these rearrangements, the results of Baird and Aboderin,[3b] if interpreted in similar terms, would require that the primary-to-primary rearrangement be favored over the primary-to-secondary by at least 3 kcal/mol. To justify such an explanation, one must invoke conformational control of product formation, as pictured below.

If the 1,2-methyl shift (step a) is much faster than rotation about the carbon (sp^2)-carbon(sp^3) bond (step b), then the 2-propanol would be isotope-position unrearranged and the objections raised about the primary-to-primary rearrangement being much faster than the primary-to-secondary would be invalidated. Such conformational control of product formation has been invoked in several deamination reactions.[9] However,

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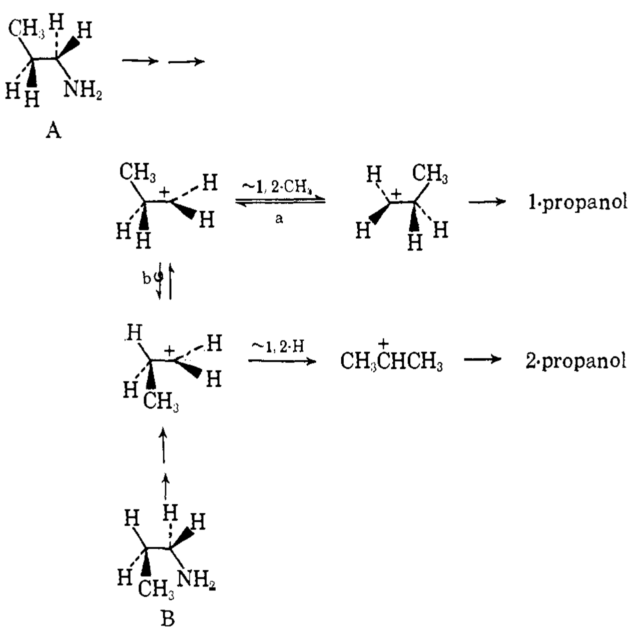
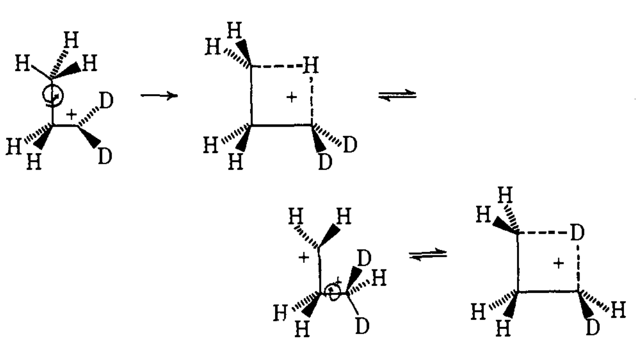
[8] C. C. Lee, J. E. Kruger, and E. W. C. Wong, *J. Amer. Chem. Soc.*, **87**, 3985 (1965); C. C. Lee and J. E. Kruger, *ibid.*, **87**, 3986 (1965).

[9] (a) D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957); (b) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *ibid.*, **83**, 3654 (1961);

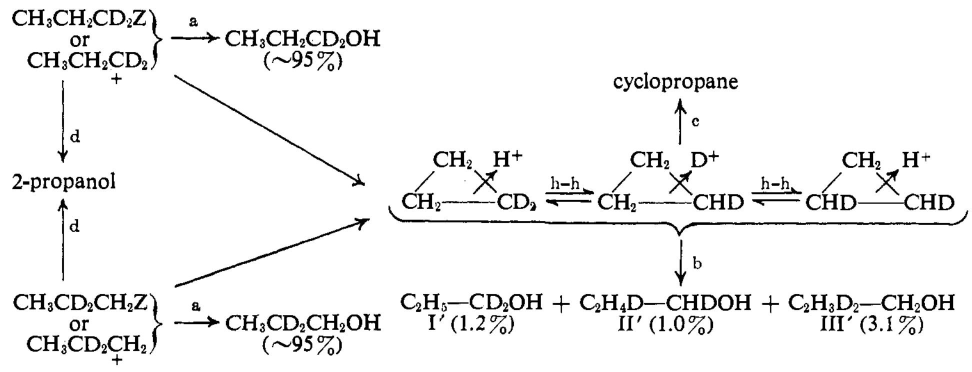


the major reaction products (about 80%) are 2-propanol and propene. These two products should arise



from conformation B, which in turn would require that conformation B be appreciably more stable than A. Such a conclusion is unreasonable. Furthermore, the interpretation of the results also requires that the 1,3-hydride shift be faster than rotation about the carbon(sp^2)-carbon(sp^3) bond (step b). Let us now examine the details of the 1,3-hydride shift, as shown above.

Scheme I



In the process of these reversible shifts, rotation about the carbon(sp^3)-carbon(sp^3) bond is required. To accept the argument, therefore, in support of the classical carbonium ion mechanism, one must also accept that the rotational barrier about the sp^2–sp^3 bond is much higher than about the sp^3–sp^3 bond. Yet, all the available evidence in the literature shows the reverse. For example, whereas the barrier to rotation of ethane is 2.8 kcal/mol, those of acetaldehyde[10] and propene[11] are 1.5 kcal/mol and 2.0 kcal/mol, respectively. Furthermore, the barrier to rotation about the sp^2–sp^3 bond of the 1-propyl radical is only 0.5 kcal/mol.[12] In the cases where such conformational control is significant, the substituents on the relevant carbon atoms are bulky and the rotation barriers are probably higher than, or competitive with, the activation energies for the rearrangements.

B. A second, equally significant, argument against the classical carbonium ion mechanism is the finding that the 1-butanol[13] and 1-pentanol[14] obtained from the deamination of various labeled 1-aminobutanes and 1-aminopentanes are exclusively (more than 99.9%) isotope-position unrearranged. It is unreasonable to suggest that the ratio of the nonrearranging–rearranging path is about 95:5 in the 1-propyl system and greater than 999:1 in the 1-alkyl systems.

On the basis of these arguments, we therefore reject the classical carbonium ion mechanism as the path responsible for the isotope-position rearranged 1-propanol.

Protonated Cyclopropane Mechanisms. Two reasonable mechanistic schemes involving protonated cyclopropanes as intermediates along the path of formation of isotope-position rearranged 1-propanol can be envisaged that are in accord with the data obtained from the deamination reaction. The first involves face protonation; the second, edge protonation.

1. Face-Protonated Cyclopropanes. Scheme I rationalizes the results in terms of face-protonated cyclopropanes. For illustrative purposes we have used the 1,1-d_2- and the 2,2-d_2-aminopropanes. About 95% of the 1-propanol arises from a direct nonrearranging path a—either from the 1-propyl cation or a suitable precursor—and about 5% from the protonated cyclopropane. Cyclopropane also arises from the protonated cyclopropane path,[3b] whereas the 2-propanol arises from some

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(c) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Amer. Chem. Soc.*, **79**, 6160 (1957); (d) D. J. Cram and M. R. V. Sahyun, *ibid.*, **85**, 1257 (1963); (e) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, **86**, 1994 (1964).

[10] R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *J. Chem. Phys.*, **26**, 1695 (1957).

[11] D. R. Herschbach and L. C. Krishner, *ibid.*, **28**, 728 (1958).

[12] R. H. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963); R. W. Fessenden, *J. Chim. Phys.*, **61**, 1570 (1964).

[13] G. J. Karabatsos, R. A. Mount, D. O. Ricketer, and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 5651 (1966).

[14] G. J. Karabatsos and M. Anad, unpublished results.

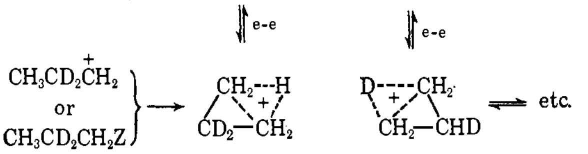
other direct path, d. Since propene derived from labeled 1-aminopropanes has not been analyzed, there is no basis for judging how much of it arises from the protonated cyclopropane intermediate and how much from other paths. On the assumption that it does not arise from the protonated cyclopropane, the protonated cyclopropane intermediate is responsible for about 6% of the over-all product.

The face-protonated cyclopropane mechanism is consistent with the results. For example, it accommodates the equivalence of the three carbon atoms of the 1-propyl group. The only requirement made on it is that the hydrogen–hydrogen exchange, path h–h, be competitive with nucleophilic attack by water on the protonated cyclopropane to yield cyclopropane and 1-propanol. The ratio c:b is about 6:1.

The validity of a face-protonated cyclopropane intermediate may, however, be questioned on several grounds, *other* than the deamination results. For example, whereas it predicts equal label distribution between carbons two and three of the recovered 1-propyl bromide from the reaction of 1-propyl-1-^{13}C bromide with aluminum bromide, twice as much[15] carbon-13 was found at C-3 as at C-2. Similarly, whereas it predicts that the solvolysis in deuteriosulfuric acid of cyclopropane to 1-propyl derivatives would lead to equal amounts of deuterium at C-1 and C-2 in these derivatives, 38% was found[3b] at C-1 and only 17% at C-2. Finally, theoretical calculations[16] on the relative stabilities of edge-protonated *vs.* corner-protonated (methyl-bridged) and face-protonated cyclopropanes lead to the conclusion that the edge protonated ought to be more stable than the corner protonated, which in turn is more stable than the face-protonated and classical 1-propyl cation. On the basis of these arguments an alternative mechanism to the one involving face-protonated cyclopropanes must be proposed.

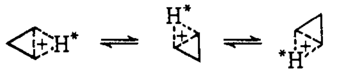
2. Edge-Protonated Cyclopropanes. The available results can be accommodated in terms of Scheme II,

Scheme II



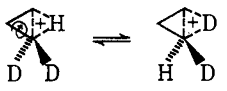
which differs from Scheme I only in the nature of the protonated cyclopropane. In view of the equivalence of the three carbon atoms of the propyl group prior to the formation of 1-propanol, the edge–edge equilibration, e–e, between protonated cyclopropanes must be faster than attack of nucleophile to lead to 1-propanol and cyclopropane. On the other hand, the proton–deuterium scrambling, h–h, must be slower than edge–edge equilibration and competitive with nucleophilic attack on the protonated cyclopropane.

Several questions now arise with respect to the details of the edge–edge and hydrogen–hydrogen equilibration. For example, (1) are the edge-protonated cyclopropanes the only intermediates involved, or are other intermediates, such as methyl-bridged (corner-protonated cyclopropane) ions, also present? If so, do they precede or follow the formation of the edge-protonated cyclopropane? (2) Are there two distinct paths, one leading to edge–edge equilibration where the same hydrogen is involved (eq 4), and the other to hydrogen–hydrogen



(4)

equilibration by some "pseudorotation" process (eq 5),[4b] or is a single process responsible for both edge–



(5)

edge and hydrogen–hydrogen equilibration?

The path depicted in eq 4 is unrealistic, as there is no good way to move the same hydrogen around the edges of cyclopropane without deprotonating the species. If eq 5 correctly depicted the mechanism of hydrogen–hydrogen equilibration, with some other path edge–edge equilibrating the species, then 5 would have to be slower than the edge–edge equilibrating path. We propose a mechanism, in effect a refinement and extension of the Baird–Wiberg mechanism,[3b] that is both reasonable and economical. This mechanism is shown in Scheme III in terms of the edge-protonated cyclopropanes from the 1,1-d_2 and the 2,2-d_2 1-propyl systems.

Let us start with VI, the edge-protonated cyclopropane from the 1-propyl-1,1-d_2 system. This species may be converted through A and A″ (either transition states or intermediates) only to the corresponding species VII and VIII. This process may be visualized as a 60° "pseudorotation" about the 1–2 and 2–3 carbon–carbon bond which might occur before, after, or concurrently with electron redistribution. The main difference between this mechanism and the Baird–Wiberg[3b] is that conversion of VI to VI′ (hydrogen–hydrogen equilibration) is not direct as pictured in eq 5, but is preceded by an edge–edge equilibration (VI → VII → VI′). This choice is dictated by the fact that, whereas hydrogen–hydrogen scrambling is far from complete, carbon–carbon scrambling is—within experimental error of the measurements—complete. The relative extents of carbon–carbon and hydrogen–hydrogen scrambling will depend on the relative rates of k_1 and k_2 (k_2 containing a nucleophile concentration term). Two extreme cases can be envisaged for a reaction proceeding by such a mechanism. If the rate of equilibration of the various edge-protonated cyclopropanes is large compared with the rate of capture of these species by a nucleophile, *i.e.*, $k_1 \gg k_2$, then all three carbon atoms of the propyl group will become equivalent and the amount of isotope-position isomerization observed in the products will approach a statistical value. Such a process is indistinguishable from the one that involves a symmetrical face-protonated cyclopropane. On the other hand, if the rate of nucleophilic capture of the edge-protonated cyclopropane species is rapid compared with the rate of equilibration, *i.e.*, $k_2 \gg k_1$, then the products that are

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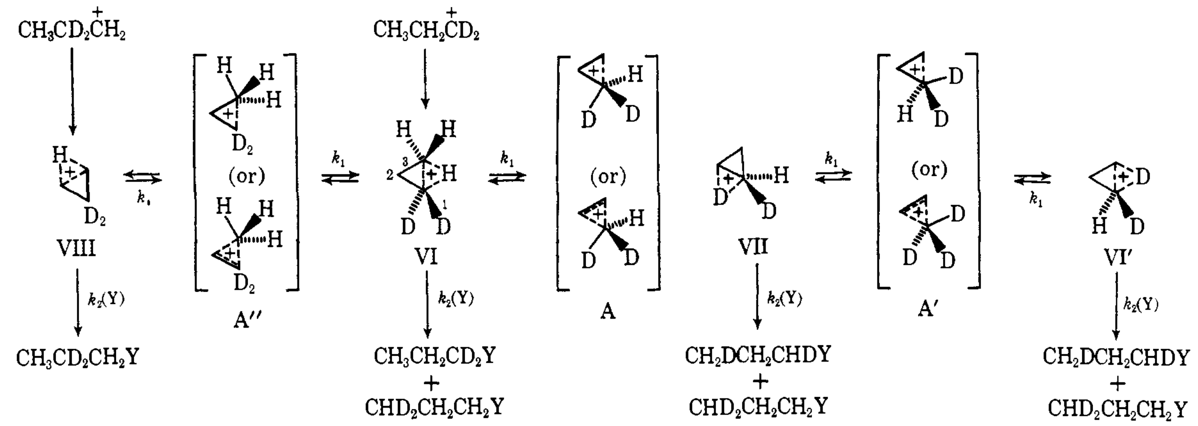
[15] G. J. Karabatsos, J. L. Fry, and S. Meyerson, *Tetrahedron Lett.*, **38**, 3735 (1967).

[16] (a) R. Hoffman, *J. Chem. Phys.*, **40**, 2480 (1964); (b) S. Ehrenson, *J. Amer. Chem. Soc.*, **86**, 847 (1964); (c) J. D. Petke and J. L. Whitten, *ibid.*, **90**, 3338 (1968).

Scheme III

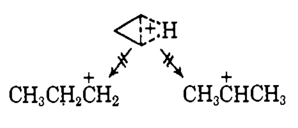


formed will appear to have arisen through a process involving a direct 1,3-hydride shift between two isotopically isomeric primary ions.

The deamination reaction falls in the category $k_1 \gg k_2$. A ratio of about 5–10 : 1 is fairly consistent with the results, *i.e.*, practically complete carbon–carbon scrambling, or hydrogen–hydrogen scrambling when only one hydrogen is labeled, but incomplete hydrogen–hydrogen scrambling, when two or three deuterium atoms are present in the propyl system. The advantage, therefore, of doubly over singly labeling in probing deeper into the nature of the mechanism of protonated cyclopropane equilibration is quite evident. The $k_1 \colon k_2$ ratio is somewhat smaller in the solvolysis of cyclopropane in deuteriosulfuric acid,[3b] and probably in the reaction of 1-propyl bromide with aluminum bromide,[17] but still greater than one. Apparently, the reverse may be true, $k_2 \gg k_1$, in the deoxidation reaction of alcohols[18] and in the reaction of 1-chloropropane with zinc chloride and hydrochloric acid.[19]

The question of whether the conversion of one edge-protonated cyclopropane to another proceeds through an intermediate methyl-bridged ion or through a transition state resembling it, is impossible to decide. Neither our results, nor those of Lee and coworkers, are sufficiently accurate to unambiguously resolve this question.

The results do not permit an evaluation of the relative stabilities of the propyl cations, 1-propyl, 2-propyl, and edge-protonated cyclopropane. From the fact that the 2-propanol is completely isotope-position unrearranged, we conclude that the protonated cyclopropane



leaks neither to the 2-propyl, nor to the 1-propyl cation. The relative stabilities ought to be 2-propyl > protonated cyclopropane > 1-propyl. The failure of the protonated cyclopropane to leak to the 2-propyl cation results from an energy of activation for the rearrangement that is greater than that for capture of the protonated cyclopropane by a nucleophile.

Experimental Section

Preparation of Labeled Compounds. All labeled compounds used in this study were prepared by established procedures. The labeled 1-aminopropanes were synthesized from the corresponding nitriles by reduction with lithium aluminum hydride or deuteride. The following is a typical procedure: to 13.3 g (0.35 mol) of lithium aluminum hydride in 250 ml of ether was added dropwise 14.24 g (0.25 mol) of propionitrile-2,2-d_2 in 50 ml of ether. The mixture was refluxed on a steam bath for 3 hr, cooled, hydrolyzed with 100 ml of water, and distilled into 35.8 g (0.25 mol) of 70% aqueous perchloric acid to convert the amine to its salt. Most of the liquid was removed under low vacuum. The wet solid that remained in the flask was recrystallized from a mixture of 1-heptanol–hexane to yield 25.73 g (75.2%) of 1-propylammonium-2,2-d_2 perchlorate.

The propionitrile-2,2-d_2 was synthesized as follows: methylmalonic acid was converted to methylmalonic acid-α-d-carboxyl-d_2 by repeated exchange with deuterium oxide at 55°. The trideuterio-acid was converted to propionic-α,α-d_2 acid by distillation at atmospheric pressure. The acid was converted to the acid chloride with thionyl chloride, the chloride was converted to the amide with anhydrous ammonia, and the amide to the nitrile with thionyl chloride.

The 1-aminopropane-1,1-d_2 was prepared by reduction of propionitrile with lithium aluminum deuteride. The 1-aminopropane-3,3,3-d_3 was prepared from the corresponding nitrile, which was in turn synthesized from propionic-3,3,3-d_3 acid.

Deamination of 1-Aminopropanes. The following is a typical procedure of the deamination of 1-aminopropanes. To 9.52 g (0.06 mol) of 1-propylammonium-1,1-d_2 perchlorate dissolved in 10 ml of water and 7.15 g (0.05 mol) of 70% perchloric acid was added dropwise, with constant stirring, over a 1-hr period, a solution of 8.80 g (0.127 mol) of sodium nitrite in 15 ml of water. The reaction mixture was distilled into a receiver cooled in ice. When approximately $^2/_3$ of the solution was distilled over, the distillation was discontinued and the distillate was saturated with potassium fluoride and extracted with 50-ml portions of ether. Fractional distillation of the dried ether yielded 1.56 g of a mixture of 1- and 2-propanols.

Preparation of Trimethylsilyl Ether Derivatives. The trimethylsilyl ether derivatives of the alcohols were prepared according to the procedure of Langer, Connell, and Wender.[20] About 0.1–0.5 g of the alcohol was refluxed on a steam bath for 2 hr with hexamethyldisilazane (1 : 0.5 molar ratio) and one drop of trimethylchlorosilane. Gas chromatography was then used to directly separate the derivatives from the reaction mixture.

Mass Spectral Analysis. Mass spectral analysis of the isotopically labeled trimethylsilyl ethers was done with 70-V electrons

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[17] G. J. Karabatsos, J. L. Fry, and S. Meyerson, *J. Amer. Chem. Soc.*, **92**, 614 (1970).

[18] P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962); P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962).

[19] O. A. Reutov and T. N. Shatkina, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 195 (1963); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 180 (1963).

[20] S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

on a Consolidated Model 21-103C instrument. Isotopic compositions of the propyl benzoates were derived from low-voltage measurements on the molecular ions.[21]

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[21] D. P. Stevenson and C. D. Wagner, *J. Amer. Chem. Soc.*, 72, 5612 (1950).

Acknowledgment. We thank the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for generous support of the research carried out at Michigan State University.

Carbonium Ions. XII. Reaction Paths in the Isomerization of Bromopropanes with Aluminum Bromide[1a]

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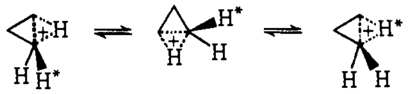
Abstract: The reactions of 1-bromopropane-1,1-d_2, -2,2-d_2, and -1-^{13}C with aluminum bromide, in 6:1 mol:mol ratios, at 0° for 5–6 min, yield mixtures of 1-bromopropane and 2-bromopropane. The recovered 1-bromopropanes show extensive hydrogen–hydrogen and carbon–carbon scrambling. The 2-bromopropanes are mainly isotope-position unrearranged, *i.e.*, they have arisen primarily from a nominally irreversible 1,2-hydride shift. The paths producing isotope-position rearranged 1-bromopropanes are shown to be reversible 1,2-hydride shifts and protonated cyclopropane intermediates. The results, however, do not firmly rule out 1,2-methyl shifts as an alternative to protonated cyclopropanes. Bimolecular reactions, elimination–addition reactions, and intermolecular hydride transfers do not occur under such reaction conditions. At longer reaction times, when the concentration of 2-bromopropane is large, intermolecular hydride transfers do occur. They were detected by the formation of propane and by isotopic analysis of the products. The rearrangement of 2-bromopropane to 1-bromopropane occurs by two paths—an intramolecular 1,2-hydride shift, which is the major path, and an intermolecular hydride transfer.

The question of the intermediacy of protonated cyclopropanes in carbonium ion reactions has recently received a good deal of attention, both theoretical[2] and experimental.[3] Up to now, however, most of the experimental evidence for the intervention of such species by the "σ route" has been restricted to reactions of a somewhat esoteric nature, such as amine deaminations,[3a] alcohol deoxidations,[4] or treatment of substrate with highly acidic media.[5] It is somewhat difficult to relate and extrapolate these findings to reactions more commonly encountered in organic chemistry, either because of the nature of the intermediate carbonium ions (vibrationally excited) in these reactions,[3a,4] or because of the nature of the reaction environment.[5] Because of this, we chose to study the propyl system under more common conditions, in order to ascertain whether protonated cyclopropanes intervene in these reactions. If so, we hoped to test the mechanism suggested[3a] for carbon–carbon and hydrogen–hydrogen scrambling (eq 1), *i.e.*, that a single process is responsible for both scramblings, and to ascertain whether or not the methyl-bridged ion I can be excluded at least as an intermediate preceding the formation of the edge-protonated cyclopropane.



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We report here our results and conclusions from the reactions of bromopropanes with aluminum bromide, and from the solvolysis of 1-propyl tosylate in aqueous 99% formic acid. As an adjunct to these reactions, we report also the results from the solvolysis of bromopropanes in water.

Results

I. Reaction of Aluminum Bromide with Unlabeled Bromopropanes. When either 1-bromopropane or 2-bromopropane was treated with aluminum bromide (5.8:1 molar ratio of bromopropane to aluminum bromide) at 0°, an equilibrium mixture was obtained that consisted of 6 ± 0.5% 1-bromopropane and 94 ± 0.5% 2-bromopropane.[6] The equilibrium was attained within 10–12 min when approached from the side of 1-bromopropane and within 6–7 min when approached from the side of 2-bromopropane. When the reaction of

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(1) (a) Part of this work was published as a preliminary communication: G. J. Karabatsos, J. L. Fry, and S. Meyerson, *Tetrahedron Lett.*, 38, 3735 (1967); (b) Research and Development Department, American Oil Company, Whiting, Ind.

(2) (a) J. D. Petke and J. L. Whitten, *J. Amer. Chem. Soc.*, 90, 3338 (1968); (b) R. H. Hoffmann, *J. Chem. Phys.*, 40, 2480 (1964); (c) S. Ehrenson, *J. Amer. Chem. Soc.*, 86, 847 (1964).

(3) For a discussion with leading references see (a) G. J. Karabatsos, C. E. Orzech, Jr., J. L. Fry, and S. Meyerson, *ibid.*, 92, 606 (1970), and (b) C. C. Lee and L. Gruber, *ibid.*, 90, 3775 (1968).

(4) P. S. Skell and I. Starer, *ibid.*, 81, 4117 (1959); *ibid.*, 82, 2971 (1960); however, see also *ibid.*, 84, 3962 (1962).

(5) G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, 90, 3882 (1968).

(6) The equilibration of the two bromopropanes by the action of aluminum bromide on the neat liquid has been reported by W. Gerrard, H. R. Hudson, and W. S. Murphy, *J. Chem. Soc.*, 2314 (1964). For a review see W. Gerrard and H. R. Hudson, *Chem. Rev.*, 65, 697 (1965).