THE DEAMINATION OF ISOTOPICALLY-LABELED BUTYLAMINES

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RAMON A. MOUNT
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This is to certify that the

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THE DEAMINATION OF

ISOTOPICALLY-LABELED BUTYLAMINES

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ABSTRACT

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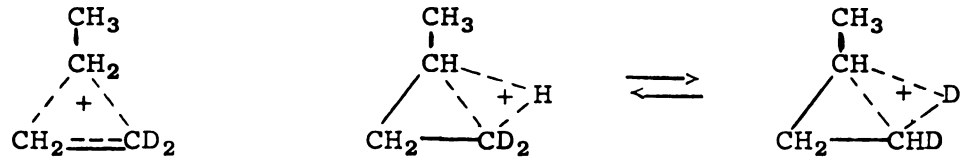
by Ramon A. Mount

The intermediacy of protonated cyclopropanes in the deamination of 1-propylamine has been ascertained by isotope-position rearrangement of the carbon skeleton and by formation of cyclopropane. Such intermediates have not been detected in the deamination of neopentylamine.

Aliphatic amines which are structurally intermediate between 1-propylamine and neopentylamine undergo rearrangements that have not been fully investigated. Thus, although a small amount of methylcyclopropane formation accompanies the deamination of 1-butylamine, 2-butylamine and isobutylamine, isotope-position rearrangement in these and similar systems is less documented. Accordingly, the present investigation was undertaken in order to assess the effects on deamination reactions of methyl substitution at C-1 and C-3 of the base 1-propyl model. To this end, isotopically-labeled 1- and 2-butylamines were prepared and deaminated under standard conditions. Analysis of product alcohols served as the basis for conclusions derived from this study.

Three labeled 1-butylamines, dideuterated at the 1-, 2- and 3-positions, respectively, gave 1-butanol and 2-butanol as the only alcoholic products. Mass spectral data showed that, in each case, the isotopic distribution of the 1-butanol formed was identical to that of the starting amine. This finding permits mechanistic pathways involving

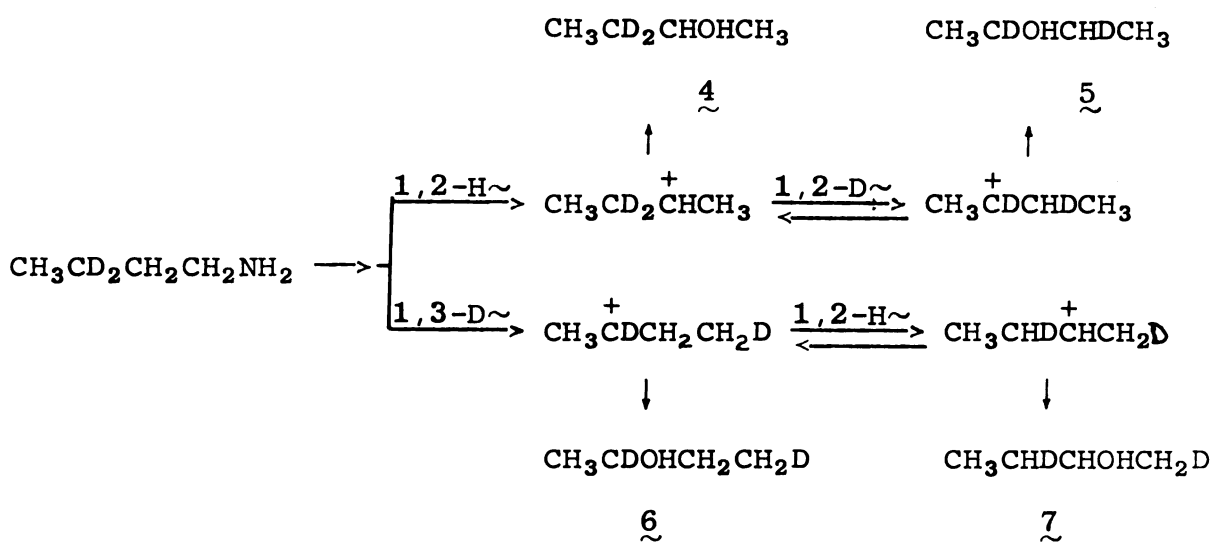
1,4-hydride shifts, 1,2-ethyl shifts and 1,3-methyl shifts to be excluded. Also, symmetrical bridged ions, such as 1, cannot be important in the formation of 1-butanol. Equilibration of protonated cyclopropanes such as 2 and 3,



1 2 3

with subsequent formation of 1-butanol, is likewise disallowed, as is any mechanism involving interconverting primary and secondary cations.

In each of the deaminations of the labeled 1-butylamines, about 75-81% of the 2-butanol formed was the result of a 1,2-hydride (or deuteride) shift followed by solvent capture of the resulting 2-butyl cation. Establishment of the mechanistic pathways(s) by which the remaining 2-butanol was produced was of interest, because of the possibility of a 1,3-hydride (or deuteride) shift occurring *via* carbon- or hydrogen-bridged intermediates (*e.g.*, 1-3). Mass spectral analysis of the 1-butyl-3,3-d_2 system (eq. 1), coupled with nmr data, permitted exclusion of mechanisms involving a nominal 1,3-hydrogen migration. By establishing that all of the product 2-butanols had deuteria only at C-2 and C-3, alcohols (6 and 7) arising from a 2-butyl cation formed by an initial 1,3-deuteride shift was ruled out. All of the detectable 2-butanol formed by deamination of



the labeled 1-butylamines was the result of one or more 1,2-hydride (or deuteride) shifts.

The deaminations of both 2-butyl-2-d-amine and 2-butyl-3,3-d_2-amine gave 2-butanol as the only alcohol. In these systems, also, only 1,2-hydrogen migrations were observed. Again, there were no 1,3-shifts and no interconverting primary and secondary cations. No evidence for bridged-ion intermediates was obtained.

It was also established that in the deamination of 1- and 2-butylamine (a) alcohol formation is irreversible; (b) alcohols are formed from unrearranged or rearranged carbonium ions that have precursors derived from the starting amines, not from other reaction products such as olefins; and (c) mechanisms involving diazoalkane or carbene formation are not significant.

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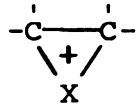
INTRODUCTION

Throughout the history of organic chemistry new and novel hypotheses have been advanced intended to help chemists rationalize and understand their experimental data. These new ideas often could be reported only by using new structural notation which frequently was the subject of test, modification, expansion and controversey to an extent equal to that of the theory being described.

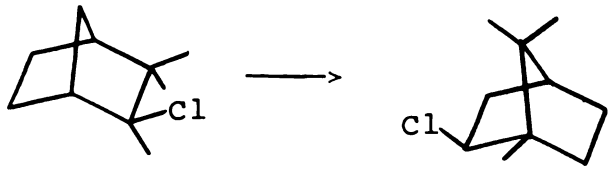
An example of such an idea, which has been in the process of development for thirty years, is shown by the bridged cationic species 1. Such notation was used as early as 1937



1

by Roberts and Kimball (1) to describe a bromine-ethylene, or bromonium, complex ion (1, X = Br).

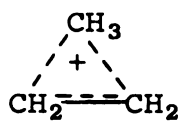
In 1938 Winstein and Lucas (2) used 1, X = Ag, to describe a resonance contributor of the silver-ethylene complex and suggested 1, X = H, as an important intermediate in the hydration of olefins. Moreover, Nevell, de Salas and Wilson (3) hypothesized a carbon-bridged ion (1, X = C) in 1939 to help explain the rearrangement of camphene hydrochloride (2) to isobornyl chloride (3).



2 3

Since these early days, the possibilities of existence of hydrogen- and carbon-bridged cationic species as true intermediates have been closely examined and vigorously debated (4).

The simplest system involving nonclassical carbon-bridging is that of a methyl-bridged ethylene, e.g., as represented by 4, which may be conceivably derived from

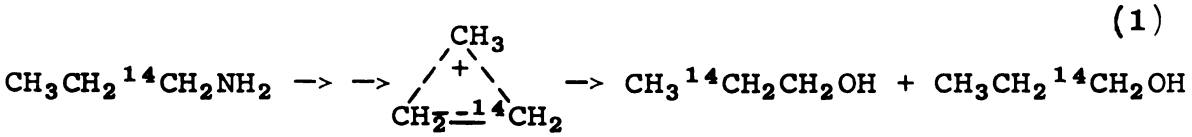


4

cyclopropane or 1-propyl systems. In 1953 Roberts and Halmann (5) reported evidence for the existence of 4. Deamination of 1-propyl-1-^{14}C-amine in aqueous perchloric acid led to, among other products, 1-propanol with only 91.5% of the carbon-14 label retained at C-1.

Since 1,2-hydride shifts were observed to occur to an extent of only 1.5% during the deamination of ethyl-1-^{14}C-amine (6), the 8.5% isotope-position rearranged product in the propyl system was attributed to sequence 1. This afforded

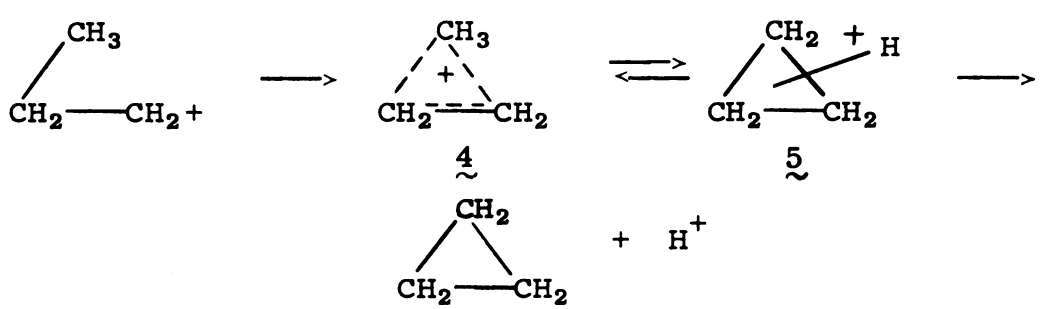
(1)



the label at C-2 in the rearranged 1-propanol, rather than at C-3, which would be the result of a 1,3-hydride shift prior to capture of the 1-propyl cation by solvent. Competing with this, of course, were mechanistic pathways leading to the formation of 2-propanol, propylene and unrearranged 1-propanol as well as nitrites and nitrates that are characteristically produced during deamination of aliphatic amines (7).

Thus an aliphatic carbon-bridged ion was judged important in the propyl system, though not as significant as an aronium bridge in the deamination of 2-phenylethylamine. The latter intermediate was reported (8,9) to be the precursor of 54% of the 2-phenylethanol produced, as opposed to a value of 17% in the propyl system (5).

The methyl-bridged ion $\underset{\sim}{4}$, and the related protonated cyclopropane $\underset{\sim}{5}$, were given roles as short-lived intermediates by Skell and Starer when they reported cyclopropane as a hydrocarbon product of the deamination of 1-propylamine (10).

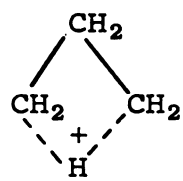


(2)

The protonated cyclopropane $\underset{\sim}{5}$ was suggested to be an intermediate in the formation of isotope-position rearranged

products as well as the cyclopropane, although these workers later explained (11) the reaction in terms of equilibrating 1-propyl cations.

Formation of cyclopropane was accommodated by a 1,3-ring closure by way of the ion 6.

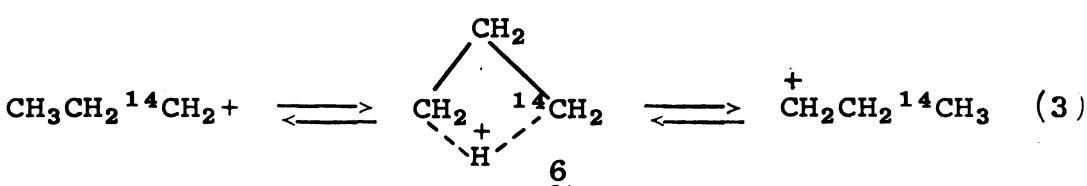


6

Results were also reported at that time which indicated that the carbenoid intermediate CH_3CH_2CH: was not involved in the "major pathway to cyclopropane".

Reutov and Shatkina (12) repeated the experiment of Roberts and Halmann with 1-propyl-1-^{14}C-amine. In contrast to the earlier work, in which it was concluded that the ^{14}C label moved to C-2 in the rearranged 1-propanol, Reutov and Shatkina reported that the ^{14}C label was exclusively at C-1 and C-3.

Two possible explanations were advanced, neither of which included nonclassical intermediates. The first involved 1,3-hydride migration, perhaps by way of 6.



(3)

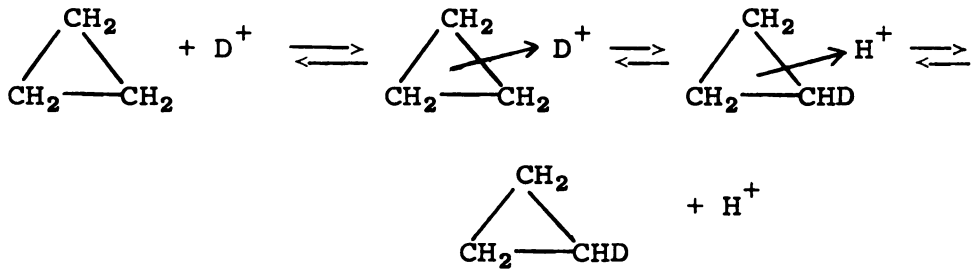
The second consisted of two successive 1,2-hydride shifts, the intermediate being a 2-propyl cation.

$$CH_3CH_2{}^{14}CH_2{}^{+} \rightleftharpoons CH_3\overset{+}{C}H{}^{14}CH_3 \rightleftharpoons \overset{+}{C}H_2CH_2{}^{14}CH_3 \qquad (4)$$

Sequence 4 was precluded by the results of Karabatsos and Orzech (13) concerning the deamination of 1-propyl-1,1,2,2-$\underline{d}_4$-amine, as no significant amount of protium was found to be incorporated at C-2. Their results agreed with a nominal 1,3-shift mechanism.

Reutov (14) also gave evidence for a 1,3-hydride shift mechanism with the deamination of 1-propyl-2-$\underline{t}$-amine. The 1-propanol product was reported to contain tritium only at C-2.

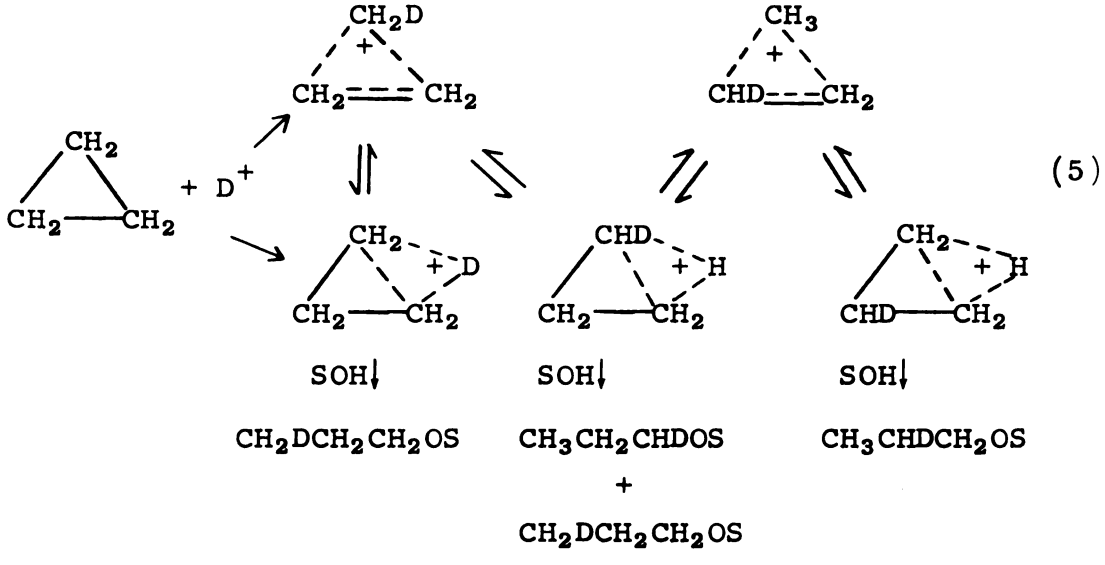
In 1963 Baird and Aboderin (15) reported new evidence accommodating the existence of protonated cyclopropanes as true intermediates. Treatment of cyclopropane with 7.5 $\underline{M}$ deuteriosulfuric acid gave significant amounts of monodeuerated and dideuterated cyclopropane, along with solvolysis products. Although a chain mechanism embracing classical ionic structures could not be excluded, a mechanism involving reversible formation of cyclopropane-H^+-π-complexes attractively rationalized the observations.



Results of a study of the solvolysis products were published in 1964 (16). The 1-propanol produced was found

to have an average deuterium distribution of 0.38, 0.17 and 0.46 deuterium atom in the 1-, 2-, and 3-positions, respectively. It was also observed that 1-propanol, 2-propanol and propylene were formed in relative amounts of 1:0.0027: 0.0005, in contrast to values of 1:4.6:4 obtained in the deamination of 1-propylamine (17).

These data precluded a mechanism involving equilibrating primary carbonium ions as the major solvolysis pathway. On the other hand, they could be fitted to a mechanism composed of equilibrating carbon- and hydrogen-bridged cations, which was also consistent with the observed formation of 1-propyl solvolysis products (sequence 5).



(5)

While the above scheme did not correlate with the results of Reutov and Shatkina, it could be used to interpret the findings of Aboderin and Baird (18) regarding the deamination of 1-propyl-3,3,3-$\underline{d}_3$-amine. The cyclopropane produced, isolated by gas chromatography and analyzed by mass spectrometry,

was found to consist of 43% $\underline{d_2}$- and 57% $\underline{d_3}$-species.

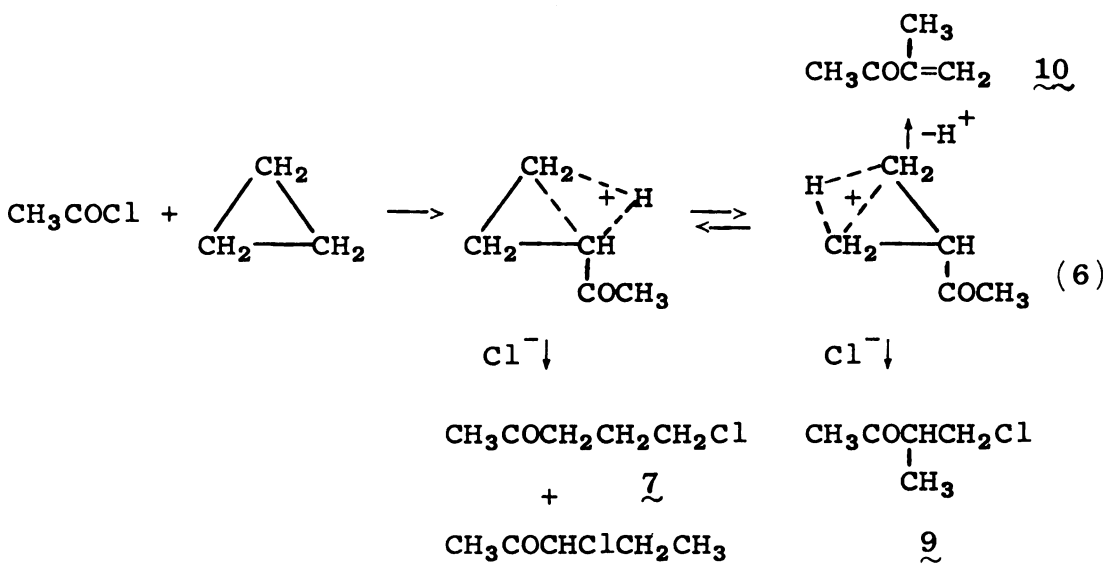
The high concentration of cyclopropane-$\underline{d_3}$ could not be rationalized by using equilibrating primary carbonium ions without invoking an unprecedented high k_H/k_D ratio. However, the results were explained by using a reasonable k_H/k_D (2.7 to 3.0) in conjunction with a mechanism involving formation of a hydrogen-bridged ion from a 1-propyl cation (or its immediate precursor) followed by equilibration with isomeric carbon-bridged ions.

Communications published in 1965 by Lee and coworkers and by Karabatsos, Orzech and Meyerson supported the conclusions of Baird and Aboderin. Lee, Kruger and Wong (19) examined the 1-propyl solvolysis product of the deamination of 1-propyl-2,2-$\underline{d_2}$-amine and 1-propyl-1-$\underline{t}$-amine. Regarding the former, nuclear magnetic resonance spectroscopy qualitatively indicated a protium increase at C-2. Approximately 3% of the 1-propanol from the tritiated amine was found to have tritium at C-2 and C-3, with roughly equal amounts at each position. Based on their finding 3-4% isotopic rearrangement from C-1 to C-2 and C-3, again in equal amounts, in the deamination of 1-propyl-1-^{14}C-amine, Lee and Kruger (20,21) concluded 4-6% of the 1-propanol formed had protonated cyclopropane precursor.

Karabatsos, Orzech and Meyerson concurred from results of their study (22) of the deamination of two isotopically-labeled 1-propylamines, dideuterated at C-1 and C-2, respectively. Their observations were in accord with a mechanism

involving equilibrating protonated cyclopropanes, not necessarily arising from methyl-bridged species.

Two other recent reports are relevant to the present discussion. Hart and Schlosberg (23) obtained the chloroketones 7, 8 and 9, along with the butenone 10, upon acetylation of cyclopropane with acetyl chloride and aluminum chloride. Intermediacy of protonated cyclopropanes accounted for the observations, as shown in eq. 6.

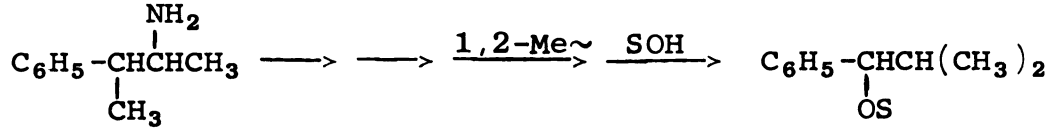


Deno and Lincoln (24) published similar observations concerning bromination of cyclopropane. In this instance, the products of the reaction were three isomeric dibromopropanes.

As the propyl system is the simplest in which isotope-position rearrangements can be observed, one may classify higher homologs as a 1-propyl system substituted at carbons 1, 2 and/or 3. For example, methyl substitution at C-1, C-2

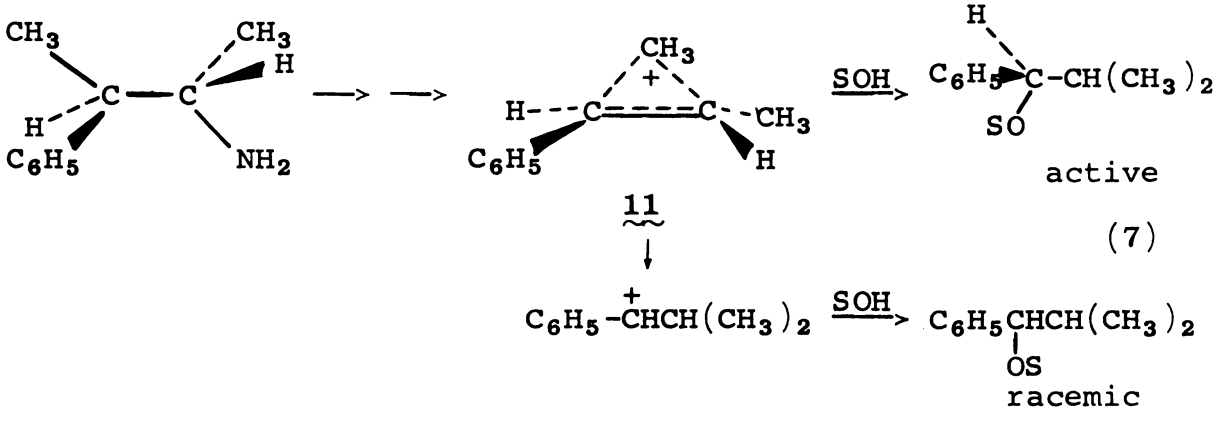
and C-3 yields the 2-butyl, isobutyl and 1-butyl systems, respectively.

In an important paper published in 1957, Cram and McCarty (25) reported the first experimental evidence directly implicating a bridged-alkyl species in a butyl system. These workers investigated the methyl-shift products of the deamination of threo- and erythro-3-phenyl-2-butylamine in glacial acetic acid.



On reduction of the acetates produced, 1-phenyl-2-methyl-1-propanol was obtained in amounts of 32% (of total alcohol formed) from threo-amine, 6% from erythro-amine. In the threo case, 16% of this alcohol was found to be optically active; in the erythro only 3%.

Cram and McCarty advanced a scheme (see sequence 7) that could account for the activity of the methyl-rearranged

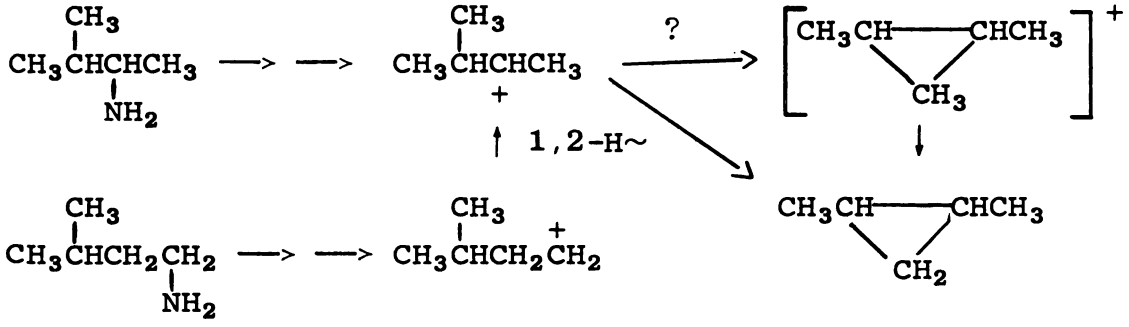


(7)

product. Its important feature was an asymmetric methyl-bridged cationic intermediate (11) that either was captured

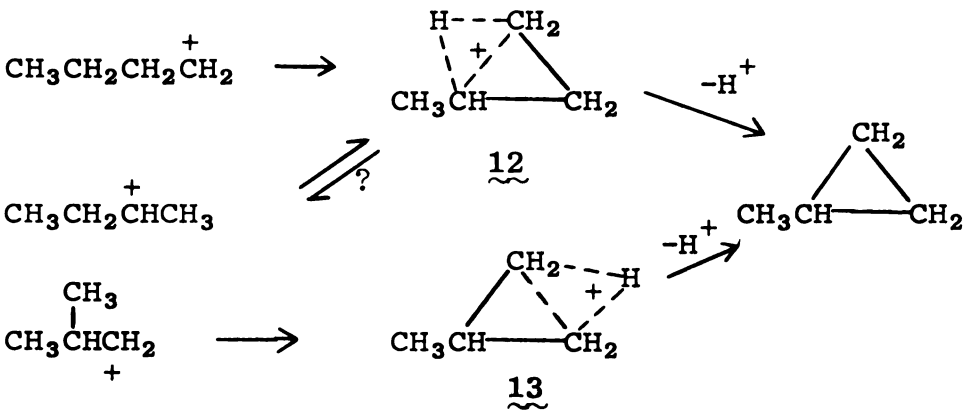
by solvent at C-1 to give active acetate, or opened up affording a symmetric 1-phenyl-2-methylpropyl cation that yielded racemic acetate. These authors acknowledged that another mechanism could be formulated in which the bridged ion 11 is a transitory intermediate. The difference in optical activity in the threo and erythro runs could be ascribed to different rates of capture of sterically different disolvated ions arising from the respective bridged transition states.

In 1960 Silver (26) disclosed more evidence supporting a cyclic cationic intermediate. Deamination of 3-methyl-2-butylamine in acetic acid gave a hydrocarbon fraction containing 5.6% cis- and 10.1% trans-1,2-dimethylcyclopropane.



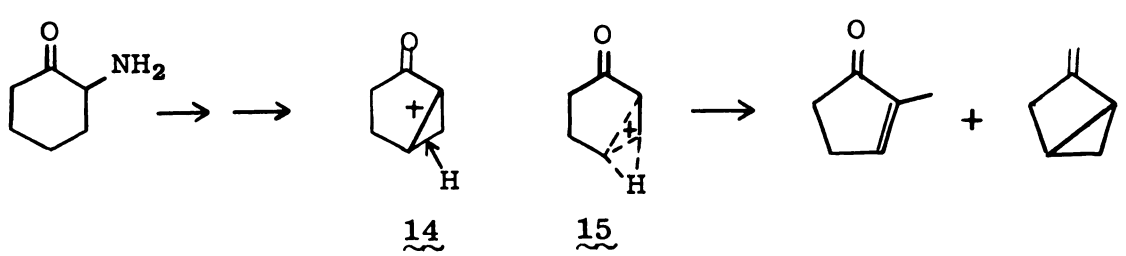
Interestingly, isoamylamine also afforded the 1,2-dimethylcyclopropanes (0.5% and 1%, respectively), but no 1,1-dimethylcyclopropane. Silver later preferred (27) to use classical carbonium ions to account for the open-chain hydrocarbons observed, and found it difficult to reconcile the dimethylcyclopropanes produced with results that indicated a lack of methyl-bridging in the propyl system (12,13).

More recently, Bayless, Mendicino and Friedman (28) communicated their finding methylcyclopropane, which was attributed to hydrogen-bridged intermediates (12 and 13), as a hydrocarbon product of the aprotic deamination of 1-butylamine, 2-butylamine and isobutylamine (see eq. 8).

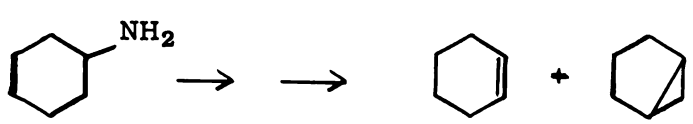


(8)

Protonated cyclopropanes have also been invoked in mechanisms of deaminations of alicyclic systems. Edwards and Lesage (29) suggested 14 and/or 15 as possible formulations for intermediates in the deaminative reaction of 2-aminocyclohexanone.



Similar reactions observed by these authors are shown below.



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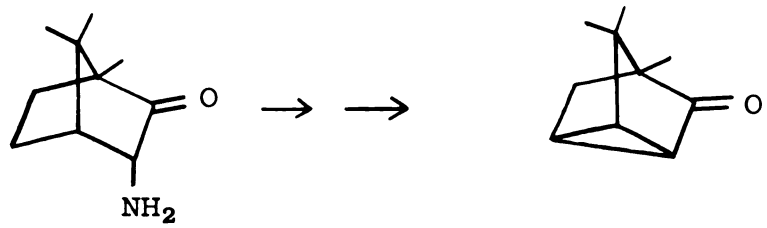

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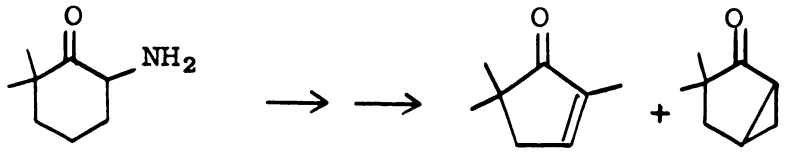
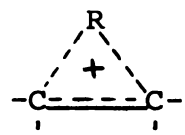


(Ref. 30)

Intermediacy of bridged-hydrogen or bridged-carbon ions in the rearrangement of strained systems (e.g., neopentyl or related systems) has not been the subject of the degree of controversy which characterized the less-substituted aliphatic systems.

Early work by Winstein and Marshall (31) and by Bartlett (32) on the solvolyses of neopentyl and tri-t-butyl derivatives, respectively, gave indications that alkyl participation (as in 16) was assisting the ionization process. However, Bartlett and Swain (33) again cautioned in 1955 that

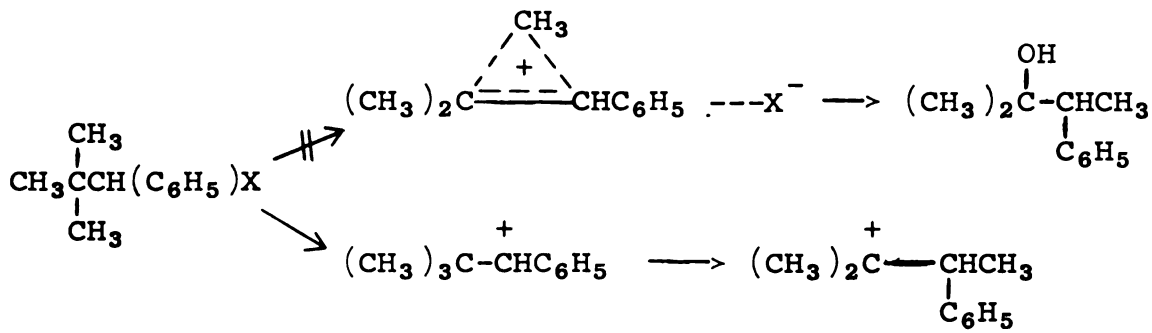


16

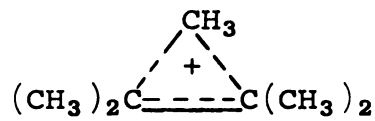
extreme reactivity of such highly branched derivatives might be due to relief of steric strain, as well as to participation.

Numerous searches for ions such as 16 were unsuccessful. For example, Winstein and Morse (34) found "no support for

bridged structures" in the rearrangement of α-phenylneopentyl derivatives. Brown and coworkers (35) showed that carbon-

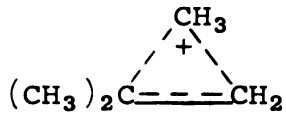


bridged intermediates did not play important roles in either the 2,2,3-trimethyl-3-pentyl or 2,3,3-trimethyl-2-pentyl systems in the chlorination of the respective alcohols or solvolysis of the chlorides. After studying rearrangement reactions of 2,3,3-trimethyl-2-chlorobutane-1-^{14}C, Roberts and Yancey (36) concluded that the nonclassical ion 17 was less stable than the classical ions and that the ion 17 represented an energy maximum. The investigation by Karabatsos



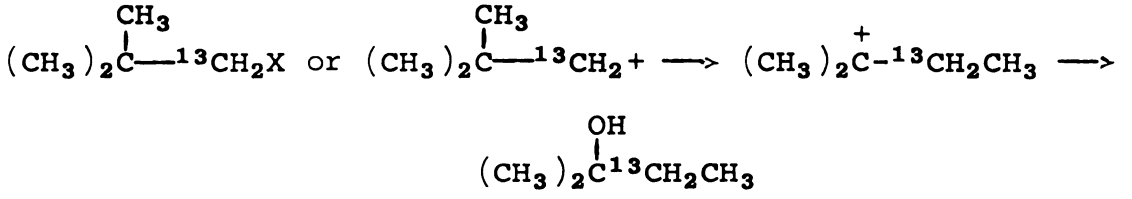
17

and Graham of the neopentyl-1-^{13}C system similarly proved that protonated cyclopropanes were not major intermediates in the rearrangement of that system (37). Silver (38), on finding that olefins produced during solvolyses of neopentyl and t-pentyl derivatives had a common precursor, excluded the intervention of a methyl-bridged carbonium ion such as 18. Finally, Karabatsos, Orzech and Meyerson (39) showed



18

that the neopentyl deaminative rearrangement took place with no detectable 1,3-hydride shifts and without the intermediacy of protonated cyclopropanes or hydrogen-bridged ions. Thus, deamination of neopentylamines labeled (with ^{13}C or CD_2) at C-1 led to t-pentyl alcohols with all of the label at C-3 of the t-pentyl alcohol.



From the forgoing discussion it is seen that intermediacy of bridged ions in reactions of 1-propyl derivatives is evidenced by isotope-position rearrangement of the carbon skeleton and by formation of cyclopropane. The latter is observed not only in deamination reactions, but also in the deoxideation of 1-propanol (10). Disubstitution of the 1-propyl system at C-2 gives, on the other hand, neopentyl-related derivatives that are characterized by not undergoing deamination reactions via bridged-ion intermediates. Moreover, cyclopropanes were not detected in the deamination of neopentylamine (10,26) or the deoxideation of neopentyl alcohol (10,40).

Aliphatic derivatives which are structurally intermediate

between 1-propyl and neopentyl undergo rearrangements which are less easily particularized. Thus, although a small amount of methylcyclopropane formation accompanies deamination of 1-butylamines, 2-butylamines and isobutylamines (28) and deoxideation of the respective alcohols (10,41), isotope-position rearrangement in these and similar systems is less documented. Accordingly, an investigation was undertaken, the object of which was to assess the effects on deamination reactions of methyl substitution at C-1 and C-3. To this end, isotopically-labeled 1- and 2-butylamines were prepared and deaminated under standard conditions. Analysis of product alcohols served as the basis for conclusions derived from this study.

RESULTS AND DISCUSSION

I. General

The primary objective of this study was to determine the relative importance of mechanistic pathways considered by previous investigators to have possible significance in the reactions of carbonium ions. Specificially, rearrangements of cations derived from the deaminations of 1- and 2-butylamines were examined in order to determine which, if any, of these pathways predominate and how they relate to reactions of similar aliphatic systems.

The perchloric acid salts of three 1-butylamines and two 2-butylamines, isotopically labeled with deuterium at various positions, were prepared for deamination. 1-Butyl-1,1-$\underline{d}_2$-amine was prepared directly from butyronitrile by reduction with lithium aluminum deuteride. 1-Butyl-2,2-$\underline{d}_2$-amine and 1-butyl-3,3-$\underline{d}_2$-amine resulted from lithium aluminum hydride reduction of the respective dideuterated nitriles, which were prepared by appropriate malonic ester syntheses shown in Figures 1 and 2 and described in detail in the EXPERIMENTAL.

Lithium aluminum deuteride reduction of 2-butanone oxime gave 2-butyl-2-$\underline{d}$-amine. Synthesis of 2-butyl-3,3-$\underline{d}_2$-amine was accomplished by way of 2-butanol-3,3-$\underline{d}_2$, as is schematically shown in Figure 3.

$$CH_2(COOEt)_2 \xrightarrow[OEt^-]{CH_3CH_2Br} CH_3CH_2CH(COOEt)_2 \xrightarrow{KOH} CH_3CH_2CH(COOH)_2$$

$$CH_3CH_2CH(COOH)_2 \xrightarrow[Exchange]{D_2O} CH_3CH_2CD(COOD)_2 \xrightarrow[-CO_2]{150^0} CH_3CH_2CD_2COOD$$

$$CH_3CH_2CD_2COOD \xrightarrow[2.NH_3]{1.SOCl_2} CH_3CH_2CD_2CONH_2 \xrightarrow[100^0]{SOCl_2} CH_3CH_2CD_2CN + H_2O$$

$$CH_3CH_2CD_2CN \xrightarrow[2.\ H_2O,\ OH^-]{1.\ LiAlH_4} CH_3CH_2CD_2CH_2NH_2$$

Figure 1. Synthesis of 1-butyl-2,2-$\underline{d}_2$-amine.

$$CH_2(COOEt)_2 \xrightarrow[OEt^-]{CH_3Br} CH_3CH(COOEt)_2 \xrightarrow{KOH} CH_3CH(COOH)_2$$

$$CH_3CH(COOH)_2 \xrightarrow[Exchange]{D_2O} CH_3CD(COOD)_2 \xrightarrow{140^0} CH_3CD_2COOD + CO_2$$

$$CH_3CD_2COOD \xrightarrow[2.H_2O,\ OH^-]{1.\ LiAlH_4} CH_3CD_2CH_2OH \xrightarrow[2.\ H_2O]{1.\ PBr_3} CH_3CD_2CH_2Br$$

$$CH_3CD_2CH_2Br \xrightarrow[aq.\ CH_3OH]{NaCN} CH_3CD_2CH_2CN \xrightarrow[2.H_2O,\ OH^-]{1.\ LiAlH_4} CH_3CD_2CH_2CH_2NH_2$$

Figure 2. Synthesis of 1-butyl-3,3-$\underline{d}_2$-amine.

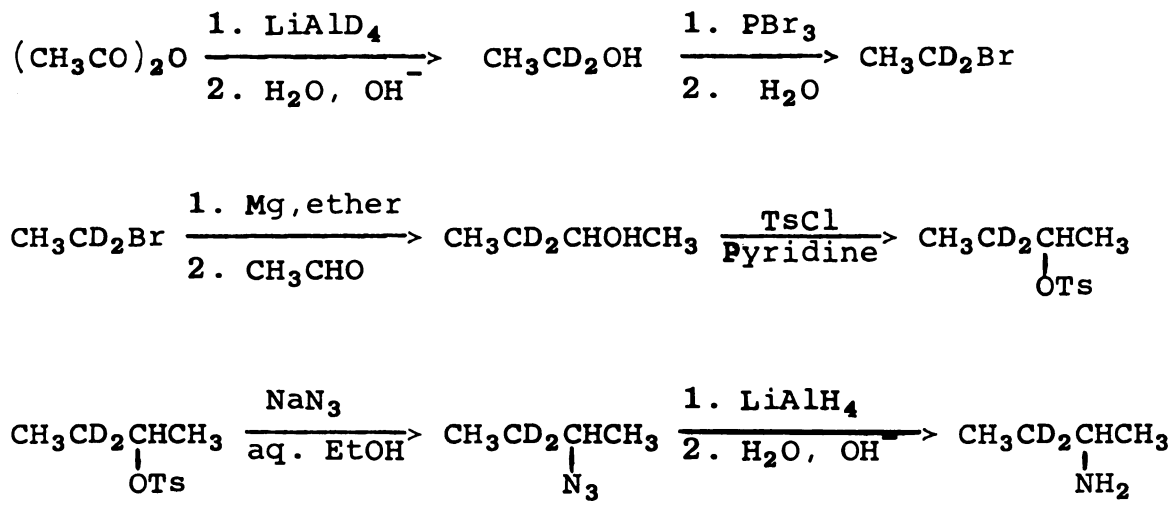


Figure 3. Synthesis of 2-butyl-3,3-$\underline{d}_2$-amine.

Deaminations of the perchlorates were carried out according to the procedure of Roberts and Halmann (5). The product alcohols arising from the 1-butylamines were collected and shown to be comprised only of 1- and 2-butanol, in agreement with earlier observations (7,42,43). The 2-butylamines afforded 2-butanol as the only alcoholic product, as previously noted (28).

Trimethylsilyl ether derivatives (44) of each alcohol were prepared, collected and analyzed by mass specrometry. In some cases alcohols, as well as the trimethylsilyl ether derivatives, were also analyzed by nuclear magnetic resonance (nmr) spectroscopy. Duplicate deaminations gave identical results.

II. Mass Spectral Data

Trimethylsilyl ethers of unlabeled 1- and 2-butanol were prepared. Mass spectral data of these compounds appear in Tables I and II.

Since the experimental approach of the problem depended on the assumption that the alcohols were irreversibly formed, it was imperative to demonstrate that the product alcohols were stable to the reaction medium. An authentic, deuterated alcohol, 2-butanol-2-d, was prepared and subjected to the experimental conditions. Mass spectral data of the trimethylsilyl ether derivatives of the authentic 2-butanol-2-d and of the 2-butanol isolated from the blank reaction are given in Tables III and IV. The spectra are identical.

Table I. Mass spectrum of $CH_3CH_2CH_2CH_2OSi(CH_3)_3$

M/e	Pk. Ht.	Mono.	
136	0.1	0.0	
135	0.7	0.6	
134	6.6	0.8	
133	99.9	-0.5	
132	284.0	-3.2	$(P - Me)^+$
131	2424.0	2423.0	99.6% at mass 131
130	2.0	1.1	
129	6.9	6.8	$(C_6H_{15}OSi)^+$
128	1.2	1.2	11.85, 4.13, 0.24
		Σ 2432.1	
106	1.1	0.1	
105	22.6	0.7	
104	55.7	0.3	$(P - Pr)^+$
103	567.0	562.5	88.2% at mass 103
102	36.9	33.7	
101	32.7	32.2	$(C_4H_7OSi)^+$
100	1.3	0.3	9.61, 3.86, 0.17
99	9.3	9.3	
		Σ 638.0	
147	14.0	Conc. HMDS = 0.28 vol. %	

Table II. Mass spectrum of $CH_3CH_2CH(CH_3)OSi(CH_3)_3$

M/e	Pk. Ht.	Mono.	
136	0.2	0.1	
135	0.7	--	
134	3.9	1.4	
133	33.6	-0.4	
132	78.7	-0.15	$(P - Me)^+$
131	660.0	640.9	98.8% at mass 131
130	3.0	2.2	
129	5.3	5.0	$(C_6H_{15}OSi)^+$
128	0.9	0.9	11.85, 4.13, 0.24
		Σ 649.0	
121	0.2	0.05	
120	3.9	0.3	
119	67.2	0.4	
118	177.9	-0.5	$(P - Et)^+$
117	1662.0	1656.1	98.9% at mass 117
116	5.9	3.3	
115	16.6	13.3	
114	0.6	0.1	$(C_5H_{13}OSi)^+$
113	3.3	2.0	10.72, 3.96, 0.21
		Σ 1674.8	
147	403.0	Conc. HMDS = 7.4 vol. %	

Table III. Mass spectrum of authentic $CH_3CH_2CD(CH_3)OSi(CH_3)_3$

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
136	0.1	0.1			
135	2.0	0.2			
134	29.0	-0.4			
133	85.8	1.6	98.8% of	1.6	0.2% $\underline{d}_2$
132	708.0	707.2	Σ = 712.0	707.2	99.3% $\underline{d}_1$
131	6.6	6.2		3.2	0.5% $\underline{d}_0$
130	2.1	1.7		712.0	
129	3.0	2.9			
128	1.0	1.0			
		Σ 720.6			

				$(P - Et)^+$ Mono.	$(P - Et)^+$ Dist'n.
121	3.9	0.1			
120	71.0	-0.2			
119	193.2	0.4	98.9% of	0.4	--
118	1794.0	1791.4	Σ = 1808.3	1791.4	99.1% $\underline{d}_1$
117	20.9	19.4		16.5	0.9% $\underline{d}_0$
116	12.9	12.6		1808.3	
115	2.8	2.7			
114	1.0	0.9			
113	1.0	1.0			
		Σ 1828.4			

147 3.0 Conc. HMDS = 0.06 vol. %

Table IV. Mass spectrum of $CH_3CH_2CH(CH_3)OSi(CH_3)_3$ from 2-butanol recovered from blank deamination with 2-butanol-2-d.

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
136	0.3	0.3			
135	2.0	0.2			
134	29.9	-0.5			
133	87.8	0.4	98.8% of	0.4	Trace
132	736.0	735.2	Σ = 738.4	735.2	99.6% d_1
131	6.3	6.0		2.8	0.4% d_0
130	2.0	1.6		738.4	
129	3.4	3.3			
128	0.9	0.9			
		Σ 747.4			
122	0.1	0.6			
121	4.3	0.4			
120	74.0	-0.3			
119	200.7	-1.1			
118	1878.0	1875.5	98.9% of	1875.5	99.2% d_1
117	19.6	18.1	Σ = 1889.9	14.4	0.8% d_2
116	13.4	13.1		1889.9	
115	2.6	2.5			
114	0.9	0.8			
113	0.9	0.9			
		Σ 1910.9			
147	1.0	Conc. HMDS = 0.02 vol. %			

In Tables V and VI, respectively, are shown the mass spectra of the derivatives of the 1- and 2-butanols isolated from the deamination product mixture of 1-butyl-1,1-$\underline{d}_2$-ammonium perchlorate. The mass spectra of authentic 1-butyl-1,1-$\underline{d}_2$ trimethylsilyl ether and 2-butyl-1,1-$\underline{d}_2$ trimethylsilyl ether are presented in Tables VII and VIII, respectively.

Trimethylsilyl ethers derived from 1- and 2-butanols resulting from the deamination of 1-butyl-2,2-$\underline{d}_2$-ammonium perchlorate were prepared and their mass spectra are shown in Tables IX and X. Tabulation of the mass spectrum of the ether of authentic 1-butanol-2,2-$\underline{d}_2$ is given in Table XI.

Mass spectra of the derivatives from 1- and 2-butanol collected from the deamination of 1-butyl-3,3-$\underline{d}_2$-ammonium perchlorate are detailed in Tables XII and XIII. The mass spectrum of authentic 1-butyl-3,3-$\underline{d}_2$ trimethylsilyl ether is shown in Table XIV.

The mass spectrum of the 2-butanol obtained by deaminating 2-butyl-2-$\underline{d}$-ammonium perchlorate is displayed in Table XV. Mass spectral data of authentic 2-butyl-2-$\underline{d}$ trimethylsilyl ether have already been given (Table III).

Tables XVI and XVII relate to the 2-butyl-3,3-$\underline{d}_2$ system. The former shows the mass spectrum of the ether of the 2-butanol obtained from the deamination while the latter details the mass spectrum of authentic 2-butyl-3,3-$\underline{d}_2$ trimethylsilyl ether.

Table V. Mass spectrum of $CH_3CH_2CH_2CH_2OSi(CH_3)_3$ from 1-butanol obtained from the deamination of 1-butyl-1,1-$\underline{d}_2$-ammonium perchlorate.

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
137	0.2	0.2			
136	5.1	0.1			
135	84.9	-1.7			
134	246.6	-3.2			
133	2100.0	2095.6	99.7% of	2095.6	98.3% $\underline{d}_2$
132	35.3	34.6	Σ = 2131.8	34.6	1.6% $\underline{d}_1$
131	5.7	5.1		1.6	0.1% $\underline{d}_0$
130	2.7	2.7		2131.8	
129	0.2	0.7			
		Σ 2138.2			

				$(P - Pr)^+$ Mono.	$(P - Pr)^+$ Dist'n.
107	17.3	0.0			
106	43.4	-0.9			
105	450.0	445.9	88.1% of	445.9	97.9% $\underline{d}_2$
104	37.4	35.6	Σ = 455.4	9.5	2.1% $\underline{d}_1$
103	16.2	15.0		455.4	
102	10.1	9.5			
101	5.1	4.6			
100	3.0	2.6			
99	3.7	3.7			
		Σ 516.9			

147 5.9 Conc. HMDS = 0.12 vol. %

Table VI. Mass spectrum of $CH_3CH_2CH(CH_3)OSi(CH_3)_3$ from 1-butanol obtained from the deamination of 1-butyl-1,1-$\underline{d_2}$-ammonium perchlorate.

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
136	1.3	0.0			
135	21.4	-0.2			
134	62.6	-0.1			
133	529.0	522.8	98.8% of	522.8	82.7% $\underline{d_2}$
132	23.0	10.3	Σ = 632.2	10.3	1.6% $\underline{d_1}$
131	107.1	105.5		99.1	15.7% $\underline{d_0}$
130	1.1	1.1		632.2	
129	0.2	0.2			
		Σ 639.9			
122	2.8	0.2			
121	49.2	0.2			
120	132.6	-1.7			
119	1254.0	1236.0	98.9% of	1236.0	75.6% $\underline{d_2}$
118	66.9	25.8	Σ = 1633.8	25.8	1.6% $\underline{d_1}$
117	382.0	381.1		372.0	22.8% $\underline{d_0}$
116	3.5	2.7		1633.8	
115	6.2	5.8			
114	0.5	0.5			
113	0.2	0.1			
		Σ 1652.0			
147	33.9	Conc. HMDS = 0.68 vol. %			

Table VII. Mass spectrum of authentic $CH_3CH_2CH_2CD_2OSi(CH_3)_3$

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
136	6.3	0.3			
135	100.8	-1.8			
134	292.0	-3.6			
133	2487.0	2481.9	99.6% of	2481.9	98.1% $\underline{d}_2$
132	38.8	36.6	Σ = 2529.7	36.6	1.5% $\underline{d}_1$
131	18.0	17.4		11.2	0.4% $\underline{d}_0$(?)
130	3.2	3.1		2529.7	
129	0.3	0.2			
128	0.7	0.7			
		Σ 2539.9			

M/e	Pk. Ht.	Mono.		$(P - Pr)^+$ Mono.	$(P - Pr)^+$ Dist'n.
108	0.8	-0.1			
107	20.5	0.1			
106	51.7	-0.7			
105	532.0	526.9	88.2% of	526.9	96.7% $\underline{d}_2$
104	46.8	44.3	Σ = 544.7	17.8	3.3% $\underline{d}_1$
103	22.6	21.1		544.7	
102	13.0	12.3			
101	6.2	5.8			
100	3.1	2.7			
99	4.5	4.5			
		Σ 617.6			

147 4.8 Conc. HMDS = 0.10 vol. %

Table VIII. Mass spectrum of authentic $CH_3CH_2CH(CHD_2)OSi(CH_3)_3$

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
136	1.1	0.0			
135	19.9	-0.4			
134	58.6	0.7			
133	489.0	481.8	98.8% of	481.8	77.4% $\underline{d}_2$
132	26.4	10.0	Σ = 622.2	10.0	1.6% $\underline{d}_1$
131	137.7	136.5		130.4	21.0% $\underline{d}_0$
130	1.2	1.1		622.2	
129	0.4	0.4			
		Σ 629.8			
122	3.8	0.3			
121	63.6	-0.5			
120	176.4	3.7			
119	1611.0	1607.1	98.9% of	1607.1	98.1% $\underline{d}_2$
118	33.1	32.1	Σ = 1638.7	31.6	1.9% $\underline{d}_1$
117	9.8	9.1		1638.7	
116	2.0	1.1			
115	7.2	7.0			
114	0.4	0.4			
113	0.2	0.1			
		Σ 1656.9			
147	23.0	Conc. HMDS = 0.49 vol. %			

Table IX. Mass spectrum of $CH_3CH_2CH_2CH_2OSi(CH_3)_3$ from 1-butanol obtained from the deamination of 1-butyl-2,2-$\underline{d}_2$-ammonium perchlorate.

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
137	0.2	0.1			
136	5.9	0.6			
135	89.0	-2.4			
134	260.7	-4.7			
133	2220.0	2209.4	99.6% of	2209.4	96.3% $\underline{d}_2$
132	86.6	85.9	Σ = 2293.8	84.4	3.7% $\underline{d}_1$
131	5.5	4.4		2293.8	
130	2.3	2.2			
129	0.3	0.2			
128	0.9	0.9			
		Σ 2303.0			

M/e	Pk. Ht.	Mono.		$(P - Pr)^+$ Mono.	$(P - Pr)^+$ Dist'n.
107	0.2	-0.1			
106	3.6	1.3			
105	22.8	3.3	88.2% of	3.3	0.9% $\underline{d}_2$
104	71.7	30.1	Σ =430.4	30.1	7.0% $\underline{d}_1$
103	430.0	428.5		397.0	92.2% $\underline{d}_0$
102	12.9	11.8		430.4	
101	10.0	9.6			
100	3.1	2.8			
99	1.9	1.9			
		Σ 488.0			

147 12.2 Conc. HMDS = 0.24 vol. %

Table X. Mass spectrum of $CH_3CH_2CH(CH_3)OSi(CH_3)_3$ from 2-butanol obtained from the deamination of 1-butyl-2,2-$\underline{d_2}$-ammonium perchlorate.

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
136	1.7	0.3			
135	24.0	-0.1			
134	73.0	-0.5			
133	590.0	573.6	98.8% of	573.6	81.0% $\underline{d_2}$
132	135.6	134.8	Σ = 708.4	134.8	19.0% $\underline{d_1}$
131	5.5	4.8		708.4	
130	2.6	2.5			
129	0.4	0.3			
128	1.0	1.0			
		Σ 717.0			
122	3.1	0.4			
121	51.4	0.3			
120	140.4	-1.1			
119	1311.0	1286.1	98.9% of	1286.1	72.0% $\underline{d_2}$
118	117.0	69.6	Σ = 1786.0	69.6	3.9% $\underline{d_1}$
117	440.0	439.0		430.3	24.1% $\underline{d_0}$
115	8.7	8.5		1786.0	
115	1.7	1.5			
114	1.0	1.0			
113	0.2	0.2			
		Σ 1805.9			
147	8.9	Conc. HMDS = 0.18 vol. %			

Table XI. Mass spectrum of authentic $CH_3CH_2CD_2CH_2OSi(CH_3)_3$

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
136	7.1	0.9			
135	105.0	2.0			
134	298.0	0.05			
133	2499.0	2490.3	99.6% of	2490.3	97.3% $\underline{d}_2$
132	70.2	68.6	Σ = 2560.2	68.6	2.7% $\underline{d}_1$
131	9.0	8.1		1.3	trace $\underline{d}_0$
130	2.5	2.4		2560.2	
129	1.0	1.0			
		Σ 2570.5			
				$(P - Pr)^+$	
106	2.9	-0.6		Mono.	Dist'n.
105	30.2	8.4	88.2% of	8.4	1.7% $\underline{d}_2$
104	81.0	34.7	Σ = 483.2	34.7	7.2% $\underline{d}_1$
103	478.0	476.3		440.1	91.1% $\underline{d}_0$
102	14.1	12.9		483.2	
101	11.2	10.8			
100	3.0	2.7			
99	2.0	2.0			
		Σ 547.8			
147	13.4	Conc. HMDS = 0.27 vol. %			

Table XII. Mass spectrum of $CH_3CH_2CH_2CH_2OSi(CH_3)_3$ from 1-butanol obtained from the deamination of 1-butyl-3,3-$\underline{d}_2$-ammonium perchlorate.

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
137	0.3	0.3			
136	5.5	0.2			
135	88.0	-3.7			
134	259.8	-6.8			
133	2226.0	2214.7	99.6% of	2214.7	95.7% $\underline{d}_2$
132	100.8	100.0	Σ = 2313.4	98.7	4.3% $\underline{d}_1$
131	6.4	5.7		2313.4	
130	1.2	1.1			
129	0.3	0.2			
128	1.0	1.0			
		Σ 2322.7			
				$(P - Pr)^+$ Mono.	$(P - Pr)^+$ Dist'n.
106	1.1	0.1			
105	20.2	0.9	88.2% of	0.9	0.2% $\underline{d}_2$
104	50.5	1.9	Σ = 493.6	1.9	0.4% $\underline{d}_1$
103	496.0	491.7		490.8	99.4% $\underline{d}_0$
102	38.3	35.8		493.6	
101	23.8	23.3			
100	3.8	3.4			
99	2.7	2.7			
		Σ 559.7			
147	13.0	Conc. HMDS = 0.25 vol. %			

Table XIII. Mass spectrum of $CH_3CH_2CH(CH_3)OSi(CH_3)_3$ from 2-butanol obtained from the deamination of 1-butyl-3,3-$\underline{d}_2$-ammonium perchlorate.

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
136	2.1	0.3			
135	30.9	-0.6			
134	89.7	-1.9			
133	766.0	761.9	98.8% of	761.9	96.3% $\underline{d}_2$
132	32.0	31.4	Σ = 791.5	29.6	3.7% $\underline{d}_1$
131	4.2	3.0		791.5	
130	3.2	3.1			
129	0.8	0.7			
128	1.0	1.0			
		Σ 801.1			
121	0.7	-0.1			
120	18.0	0.5		$(P - Et)^+$	
119	99.3	-0.3		Mono.	Dist'n.
118	526.0	361.2	98.9% of	361.2	19.2% $\underline{d}_1$
117	1536.0	1535.1	Σ = 1883.8	1522.6	80.8% $\underline{d}_0$
116	6.8	6.5		1883.8	
115	1.3	1.1			
114	0.9	0.9			
113	0.1	0.0			
		Σ 1904.8			
147	16.6	Conc. HMDS = 0.32 vol. %			

Table XIV. Mass spectrum of authentic $CH_3CD_2CH_2CH_2OSi(CH_3)_3$

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
137	0.2	0.2			
136	5.0	0.3			
135	80.0	-1.6			
134	233.1	-3.4			
133	1980.0	1970.8	99.6% of	1970.8	96.5% $\underline{d}_2$
132	73.7	72.9	Σ = 2043.1	72.3	3.5% $\underline{d}_1$
131	6.4	5.6		2043.1	
130	1.0	1.0			
129	0.2	0.1			
128	0.9	0.9			
		Σ 2051.3			
				$(P - Pr)^+$ Mono.	$(P - Pr)^+$ Dist'n.
106	0.8	-0.1			
105	18.3	1.4	88.2% of	1.4	0.3% $\underline{d}_2$
104	44.6	2.1	Σ = 431.6	2.1	0.5% $\underline{d}_1$
103	433.0	429.2		428.1	99.2% $\underline{d}_0$
102	33.7	31.6		431.6	
101	20.6	20.2			
100	3.0	2.7			
99	2.1	2.1			
		Σ 489.3			
147	14.4	Conc. HMDS = 0.29 vol. %			

Table XV. Mass spectrum of $CH_3CH_2CH(CH_3)OSi(CH_3)_3$ from 2-butanol obtained from the deamination of 2-butyl-2-d-ammonium perchlorate.

M/e	Pk. Ht.	Mono.		(P - Me)+ Mono.	(P - Me)+ Dist'n.
135	2.9	0.7			
134	26.9	2.2			
133	80.1	13.7	98.8% of	13.7	2.4% d_2(?)
132	558.0	557.0	Σ = 574.3	557.0	97.0% d_1
131	7.0	6.3		3.6	0.6% d_0
130	2.3	2.3		574.3	
129	2.0	2.0			
		Σ 581.3			
122	0.5	0.2			
121	4.9	0.8			
120	56.1	2.6			
119	171.0	28.3	98.9% of	28.3	1.9% d_2(?)
118	1284.0	1264.3	Σ = 1469.5	1264.3	86.1% d_1
117	181.5	180.2		176.9	12.0% d_0
116	10.4	10.2		1469.5	
115	1.9	1.7			
114	0.4	0.3			
113	0.8	0.8			
		Σ 1485.8			
147	7.0	Conc. HMDS = 0.15 vol. %			

(P - Et)+

Mono.	Dist'n.
28.3	1.9% d_2(?)
1264.3	86.1% d_1
176.9	12.0% d_0
1469.5	

Table XVI. Mass spectrum of $CH_3CH_2CH(CH_3)OSi(CH_3)_3$ from 2-butanol obtained from the deamination of 1-butyl-3,3-$\underline{d}_2$-ammonium perchlorate.

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
136	1.8	0.1			
135	28.0	-0.3			
134	81.9	-0.1			
133	690.0	678.8	98.8% of	687.8	97.5% $\underline{d}_2$
132	13.2	11.7	Σ = 705.6	11.7	1.6% $\underline{d}_1$
131	12.3	11.5		6.1	0.9% $\underline{d}_0$
130	2.0	1.9		705.6	
129	0.6	0.5			
128	0.8	0.8			
		Σ 714.2			
121	0.6	0.2		$(P - Et)^+$ Mono.	$(P - Et)^+$ Dist'n.
120	9.4	-0.2			
119	77.8	0.7	98.9% of	0.7	0.1% $\underline{d}_2$
118	327.0	159.1	Σ = 1667.8	159.1	9.5% $\underline{d}_1$
117	1518.0	1517.1		1508.0	90.4% $\underline{d}_0$
116	6.3	6.1		1667.8	
115	1.7	1.5			
114	1.2	1.1			
113	0.7	0.7			
		Σ 1686.3			
147	14.0	Conc. HMDS = 0.29 vol. %			

Table XVII. Mass spectrum of authentic $CH_3CD_2CH(CH_3)OSi(CH_3)_3$

M/e	Pk. Ht.	Mono.		$(P - Me)^+$ Mono.	$(P - Me)^+$ Dist'n.
136	2.1	0.1			
135	33.0	0.0			
134	94.8	-0.5			
133	801.0	798.4	98.8% of	798.4	97.4% $\underline{d}_2$
132	16.0	14.2	Σ = 819.6	14.2	1.7% $\underline{d}_1$
131	14.0	12.7		7.0	0.9% $\underline{d}_0$
130	2.5	2.3		819.6	
129	1.0	0.9			
128	1.1	1.1			
		Σ 829.6			

M/e	Pk. Ht.	Mono.		$(P - Et)^+$ Mono.	$(P - Et)^+$ Dist'n.
121	1.0	0.9			
120	4.7	0.4			
119	78.3	1.2	98.9% of	1.2	0.1% $\underline{d}_2$
118	209.7	1.3	Σ = 1932.5	1.3	0.1% $\underline{d}_1$
117	1941.0	1939.8		1930.0	99.8% $\underline{d}_0$
116	7.9	7.5		1932.5	
115	2.2	1.8			
114	1.8	1.7			
113	0.8	0.7			
		Σ 1954.0			

147 22.0 Conc. HMDS = 0.45 vol. %

III. 1-Butyl Systems

Although acknowledgment is made of formation of other (particularly hydrocarbon) products (7,28,43), the relevance of which to the present study is discussed later, this investigation was chiefly concerned with the alcohols produced. That these were formed irreversibly was illustrated by recovering 2-butanol-2-d unchanged after subjecting it to the reaction conditions. In Tables XVIII and XIX are compiled mass spectral isotopic distributions of the silyl ethers of all authentic and product 1- and 2-butanols, including the tested alcohol before and after the blank deamination.

Shown in Figure 4 are carbonium ion rearrangement mechanisms which have been considered by previous investigators in related systems. These, as applied to the 1-butyl model, include (a) 1,2-hydride shifts, (b) 1,3-hydride shifts, (c) 1,4-hydride shifts, (d) 1,2-ethyl shifts, (e) 1,3-methyl shifts and (f) involvement of bridged ions or protonated cyclopropanes. Of course, combinations of pathways would lead to other degrees of scrambling of the carbon or hydrogen atoms. Possible competition of reaction modes between carbonium ions in the system and precursors of carbonium ions, such as alkyl diazonium ions (42,45,46), also must be recognized.

Although Figure 4 depicts how, by reasonable mechanisms, a 1-butyl cation (or its precursor in the deamination of 1-butylamine) might be converted into derivatives of isotope-

Table XVIII. Results of mass spectral analyses of the trimethylsilyl ethers of authentic, deuterated alcohols.

	$CH_3CH_2CH_2CH_2OSi(CH_3)_3$		$CH_3CH_2CH(CH_3)OSi(CH_3)_3$	
	$(P-CH_3)^+$	$(P-C_3H_7)^+$	$(P-CH_3)^+$	$(P-C_2H_5)^+$
Authentic	98.1% $\underline{d}_2$	96.7% $\underline{d}_2$		
$CH_3CH_2CH_2CD_2OSi(CH_3)_3$	1.5% $\underline{d}_1$	3.3% $\underline{d}_1$		
	0.4% $\underline{d}_0$			
Authentic	97.3% $\underline{d}_2$	1.7% $\underline{d}_2$		
$CH_3CH_2CD_2CH_2OSi(CH_3)_3$	2.7% $\underline{d}_1$	7.2% $\underline{d}_1$		
	trace $\underline{d}_0$	91.1% $\underline{d}_0$		
Authentic	96.5% $\underline{d}_2$	0.3% $\underline{d}_2$		
$CH_3CD_2CH_2CH_2OSi(CH_3)_3$	3.5% $\underline{d}_1$	0.5% $\underline{d}_1$		
		99.2% $\underline{d}_0$		
Authentic			0.2% $\underline{d}_2$	
$CH_3CH_2CD(CH_3)OSi(CH_3)_3$			99.3% $\underline{d}_1$	99.1% $\underline{d}_1$
			0.5% $\underline{d}_0$	0.9% $\underline{d}_0$
Authentic			77.4% $\underline{d}_2$	98.1% $\underline{d}_2$
$CH_3CH_2CH(CHD_2)OSi(CH_3)_3$			1.6% $\underline{d}_1$	1.9% $\underline{d}_1$
			21.0% $\underline{d}_0$	
Authentic			97.4% $\underline{d}_2$	0.1% $\underline{d}_2$
$CH_3CD_2CH(CH_3)OSi(CH_3)_3$			1.7% $\underline{d}_1$	0.1% $\underline{d}_1$
			0.9% $\underline{d}_0$	99.8% $\underline{d}_0$

Table XIX. Results of mass spectral analyses of trimethylsilyl ethers of deamination product alcohols.

	$CH_3CH_2CH_2CH_2OSi(CH_3)_3$		$CH_3CH_2CH(CH_3)OSi(CH_3)_3$	
	$(P-CH_3)^+$	$(P-C_3H_7)^+$	$(P-CH_3)^+$	$(P-C_2H_5)^+$
From $CH_3CH_2CH_2CD_2NH_2$	98.3% $\underline{d}_2$	97.9% $\underline{d}_2$	82.7% $\underline{d}_2$	75.6% $\underline{d}_2$
	1.6% $\underline{d}_1$	2.1% $\underline{d}_1$	1.6% $\underline{d}_1$	1.6% $\underline{d}_1$
	0.1% $\underline{d}_0$		15.7% $\underline{d}_0$	22.8% $\underline{d}_0$
From $CH_3CH_2CD_2CH_2NH_2$	96.3% $\underline{d}_2$	0.8% $\underline{d}_2$	81.0% $\underline{d}_2$	72.0% $\underline{d}_2$
	3.7% $\underline{d}_1$	7.0% $\underline{d}_1$	19.0% $\underline{d}_1$	3.9% $\underline{d}_1$
		92.2% $\underline{d}_0$		24.1% $\underline{d}_0$
From $CH_3CD_2CH_2CH_2NH_2$	95.7% $\underline{d}_2$	0.2% $\underline{d}_2$	96.3% $\underline{d}_2$	
	4.3% $\underline{d}_1$	0.4% $\underline{d}_1$	3.7% $\underline{d}_1$	19.2% $\underline{d}_1$
		99.4% $\underline{d}_0$		80.8% $\underline{d}_0$
From $CH_3CH_2CD(CH_3)NH_2$			2.4% $\underline{d}_2$ (?)	1.9% $\underline{d}_2$ (?)
			97.0% $\underline{d}_1$	86.1% $\underline{d}_1$
			0.6% $\underline{d}_0$	12.0% $\underline{d}_0$
From $CH_3CD_2CH(CH_3)NH_2$			97.5% $\underline{d}_2$	0.1% $\underline{d}_2$
			1.6% $\underline{d}_1$	9.5% $\underline{d}_1$
			0.9% $\underline{d}_0$	90.4% $\underline{d}_0$
From blank deamination with $CH_3CH_2CD(CH_3)OH$	(No 1-butanol detected)		trace $\underline{d}_2$	
			99.6% $\underline{d}_1$	99.2% $\underline{d}_1$
			0.4% $\underline{d}_0$	0.8% $\underline{d}_0$

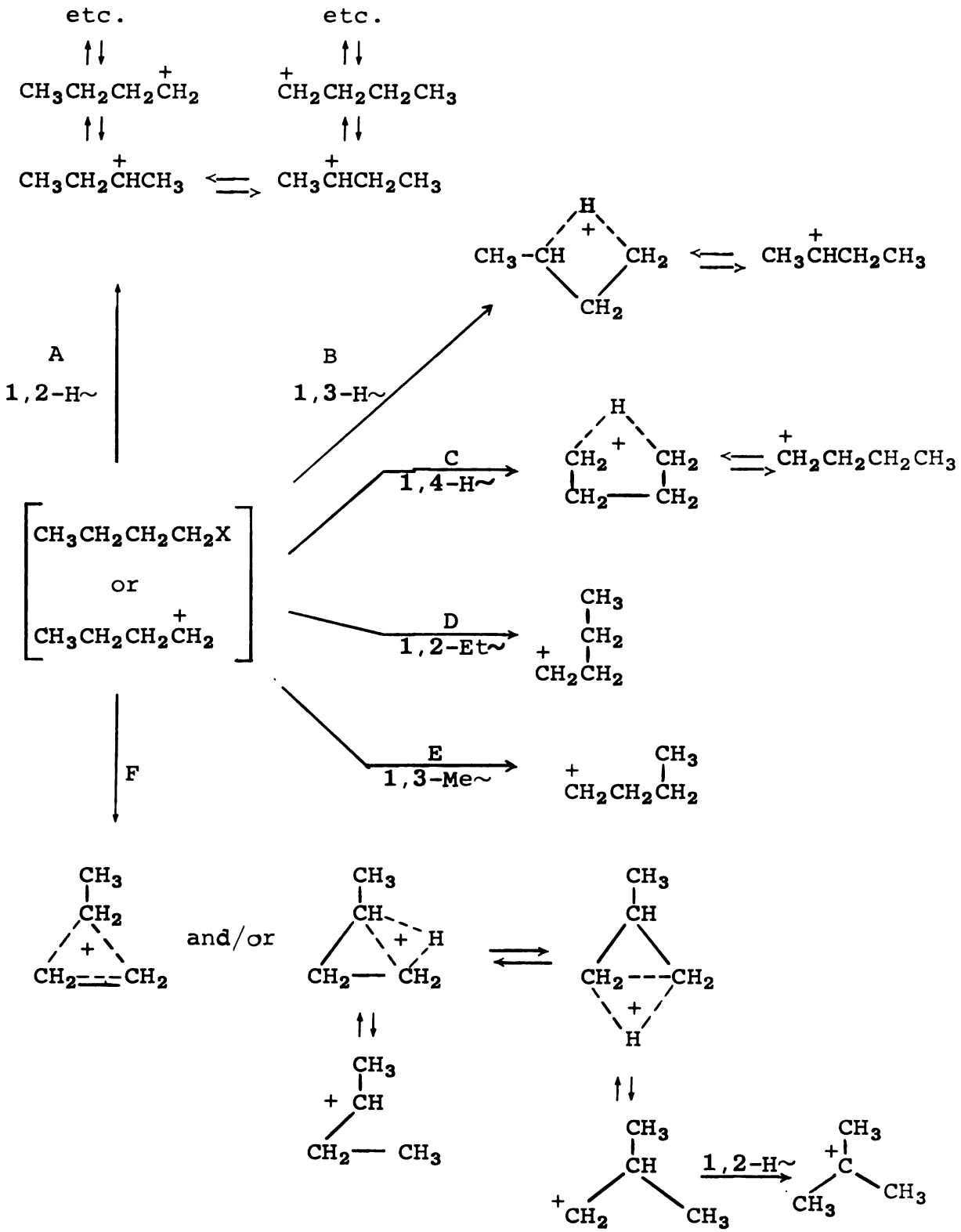


Figure 4. Possible rearrangement pathways of the 1-butyl cation.

position rearranged 1-butyl, 2-butyl, isobutyl, and even t-butyl (by way of isobutyl) functions, some of the pathways can be, and have been, excluded. Thus, the observation that isobutyl and t-butyl solvolysis products are not formed in the deamination of 1-butylamine (7,28,47) reduces the significance of mechanisms involving isobutyl and t-butyl cations as intermediates. Study of the isotopic distribution of the 1- and 2-butanols formed from the deamination of suitably labeled 1-butylamines allows exclusion of some other pathways of Figure 4.

A. 1-Butanol Formation

The 1-butanols were found to have isotopic distributions nearly identical to those of the amines from which they were respectively produced. In regard to the 1-butyl-1,1-d_2 system, this observation precludes the participation of rearrangements C, D and E (in Figure 4 and below) as significant in the production of 1-butanol. Streitweiser and Schaeffer (42) have shown 1,2-ethyl shifts to be absent in this system.

$$\left[\begin{array}{c} CH_3CH_2CH_2CD_2X \\ \text{or} \\ CH_3CH_2CH_2\overset{+}{C}D_2 \end{array}\right]$$

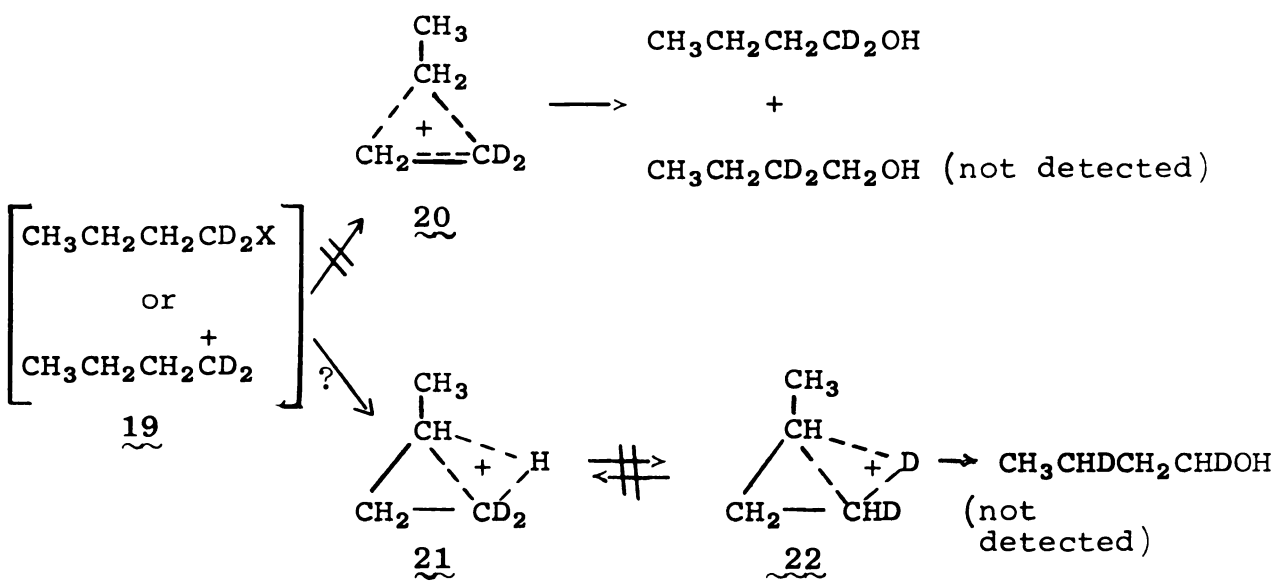
$$\xrightarrow[1,4\text{-H}\sim]{C} \overset{+}{C}H_2CH_2CH_2CHD_2 \rightarrow \overset{OH}{C}H_2CH_2CH_2CHD_2$$

$$\xrightarrow[1,2\text{-Et}\sim]{D} \overset{+}{C}H_2CD_2CH_2CH_3 \rightarrow \overset{OH}{C}H_2CD_2CH_2CH_3$$

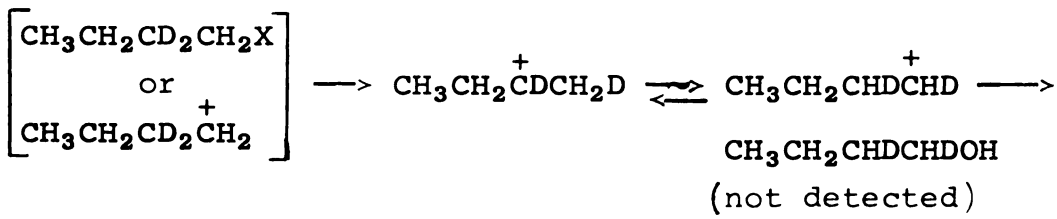
$$\xrightarrow[1,3\text{-Me}\sim]{E} CH_2CH_2CD_2CH_3 \rightarrow \overset{OH}{C}H_2CH_2CD_2CH_3$$

The fact that the ($P-CH_3$) ion $\underline{d_2}$ contribution of the ether of the 1-butanol equals that of the ether of authentic 1-butanol-1,1-$\underline{d_2}$ indicates that a mechanism involving diazoalkane or carbene formation can account for no more than 1% of the product alcohol (6,11,28,42,48).

Symmetrical bridged ions, such as 20, are excluded as



intermediates (in the formation of 1-butanol) as 1-butanol-2,2-$\underline{d_2}$ was not detected. Equilibration of ions such as 21 and 22 with subsequent formation of 1-butanol is likewise disallowed. Moreover, absence of deuterium scrambling in the 1-butanol resulting from the 1-butyl-1,1-$\underline{d_2}$ and 1-butyl-2,2-$\underline{d_2}$ runs disfavors any mechanism involving interconverting primary and secondary cations. This observation supports previous conclusions (5,13,49).



It can therefore be concluded that in the deamination of 1-butylamine, 1-butanol arises from displacement on a 1-butyl cation precursor by solvent and/or from capture by solvent of a 1-butyl cation. Strietweiser and Schaeffer (42) showed that at least 69 ± 7% of the 1-butyl-1-d-acetate obtained in the deamination of 1-butyl-1-d-amine in acetic acid resulted from displacement that inverts the configuration at C-1.

B. 2-Butanol Formation

From Table XIX, the isotopic compositions of the 2-butanols formed from 1-butyl-1,1-d_2-amine (98.4% d_2 and 1.6% d_1) may be calculated. These are corrected by removing the contribution of the singly deuterated amine and shown below. The d_0 ($P-C_2H_5$) ion is attributed solely to **24** with no contribution by $CH_3CHOHCHDCH_2D$ or $CH_3CHOHCD_2CH_3$, as mechanisms of interconverting primary and secondary cations have been excluded.

$$CH_3CH_2CH_2CD_2NH_2 \longrightarrow \underset{\textbf{23}}{CH_3CH_2\overset{OH}{\overset{|}{C}}HCHD_2} + \underset{\textbf{24}}{CH_3\overset{OH}{\overset{|}{C}}HCH_2CHD_2}$$

100% 77% 23%

It should be noted that the data of Table XIX indicate that the ($P-CH_3$) ion should be 22.8% d_2 if C-methyl fragmentation of the 2-butyl trimethylsilyl ether occurred exclusively and 98.4% d_2 if only Si-methyl cleavage occurred. Since the ($P-CH_3$) ion was observed to be 82.7%, the contribution of ($P-CH_3$) ion by loss from the trimethylsilyl group

is (82.7-22.8)/(98.4-22.8) x 100% = 79%, with 21% by loss from the 2-butyl group. The mass spectral data of the ether of authentic 2-butanol-1,1-$\underline{d_2}$ are in accord with the calculated values.

2-Butanol arising from 1-butyl-2,2-$\underline{d_2}$-amine (96.3% $\underline{d_2}$ and 3.7% $\underline{d_1}$) is calculated to be the following.

$$CH_3CH_2CD_2CH_2NH_2 \longrightarrow \underset{\underset{\underset{\underset{\underset{25}{\sim\sim}}}{}}{}}{CH_3CH_2\overset{\overset{OH}{|}}{C}DCH_2D} + CH_3\overset{\overset{OH}{|}}{C}HC_2H_3D_2$$

100% 75% 25%

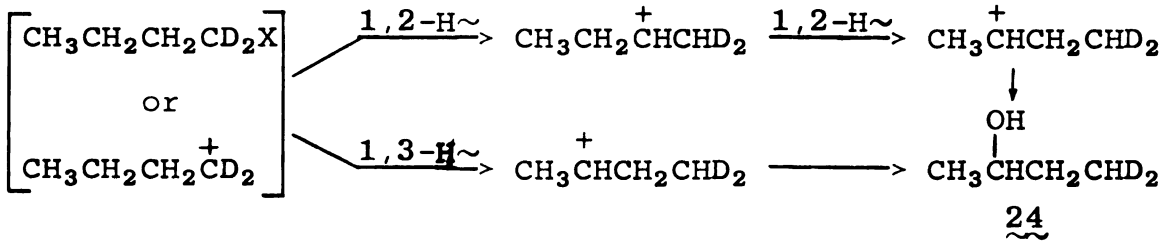
Finally, 1-butyl-3,3-$\underline{d_2}$-amine (95.7% $\underline{d_2}$ and 4.3% $\underline{d_1}$) afforded 2-butanol which, from the ($P-C_2H_5$) ion of its ether, is indicated to be as shown.

$$CH_3CD_2CH_2CH_2NH_2 \longrightarrow \underset{\underset{\underset{\underset{\underset{26}{\sim\sim}}}{}}{}}{CH_3CD_2\overset{\overset{OH}{|}}{C}HCH_3} + \underbrace{\underset{\underset{\underset{\underset{\underset{27}{\sim\sim}}}{}}{}}{CH_3\overset{\overset{OH}{|}}{C}DCHDCH_3} + \underset{\underset{\underset{\underset{\underset{28}{\sim\sim}}}{}}{}}{CH_3CHD\overset{\overset{OH}{|}}{C}HCH_2D}}$$

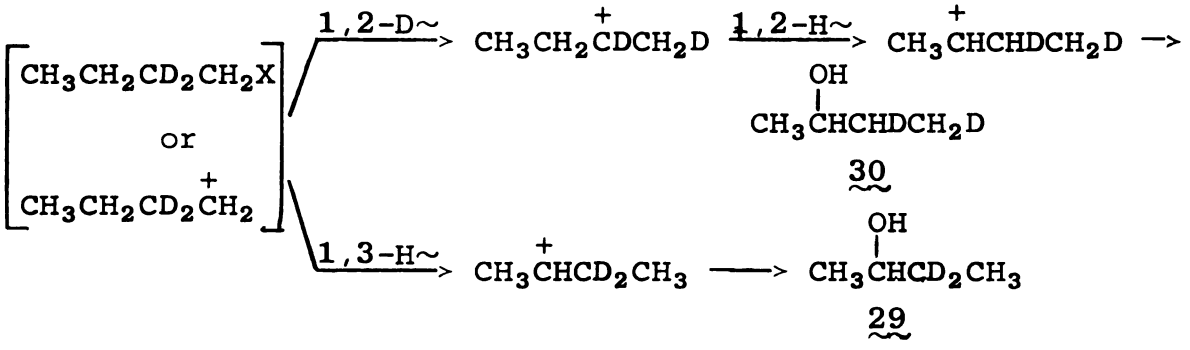
100% 81% 19%

It is possible to distinguish between mechanisms of formation of 2-butanol. From the distributions given above it is evident that the predominant path involves a 1,2-hydride (or deuteride) shift from C-2 to C-1 (rearrangement path A in Figure 4). The lesser amount(s) of 2-butanol may possibly be derived from (1) subsequent 1,2-hydride shifts of the newly formed 2-butyl cation or (2) nominal 1,3-hydride shifts (paths B or F) of the 1-butyl cation or its precursor.

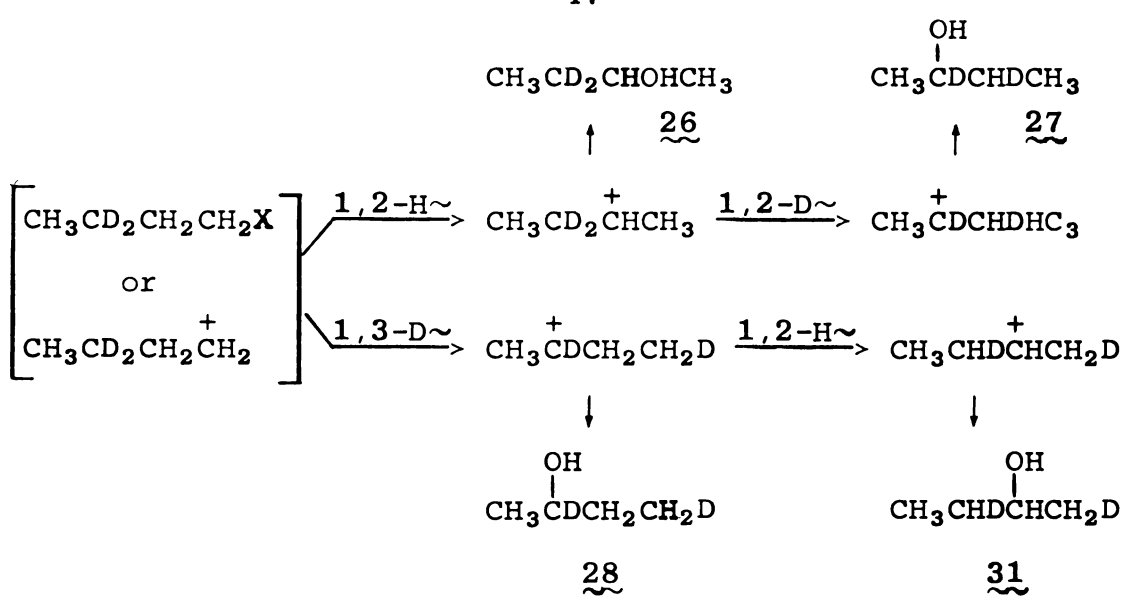
The alcohol 24 (from 1-butyl-1,1-d_2-amine) is consistent with both paths B and F of Figure 4, as well as a successive 1,2-shift mechanism.



Although different 2-butanols (29 and 30) are formed in the 1-butyl-2,2-d_2 system by the two proposed mechanisms, mass spectral data cannot distinguish them since the $(P-C_2H_5)$ ion of each would be a d_0 species, and the $(P-CH_3)$ ion a d_2 species.



Also, the $(P-C_2H_5)$ ion does not allow differentiation of the alternative (27 and 28) of the 1-butyl-3,3-d_2 model. The $(P-CH_3)$ ion in formation is more definitive, however, in combination with nmr data. If subsequent 1,2-hydride shifts in the 2-butyl cation compete successfully with solvent capture, alcohol 31 might also be expected as a significant product. That it is not, is supported by the observation that the $(P-CH_3)$ ion d_1 contribution of the 2-butanol (3.7%)



derived from the deamination is smaller than the $\underline{d_1}$ present in the starting material (4.3%).

Having established the absence of 31 (i.e., no deuterium at C-1), nmr permits differentiation of 28, which contains deuterium at C-4, and 27, which does not. Under the spectroscopic conditions used, the ratio of integrated signals of C-1 methyl (appearing at τ8.87) to C-4 methyl (at τ9.10) of the trimethylsilyl either of unlabeled 2-butanol was essentially the same as that for the ether of the derived 2-butanol (see Figure 5 and Table XX). As the predominant alcohol (26), arising from a single 1,2-hydride shift, also should contain no deuterium in either methyl group, equal ratios are indicative of all of the product 2-butanols having deuteria only at C-2 and C-3.

Since the only detectable 2-butanols produced from 1-butyl-3,3-$\underline{d_2}$-amine have been shown to be the alcohols 26 and 27, the 81:19 ratio of their concentrations is supported by careful integration of the nmr spectrum of the mixture

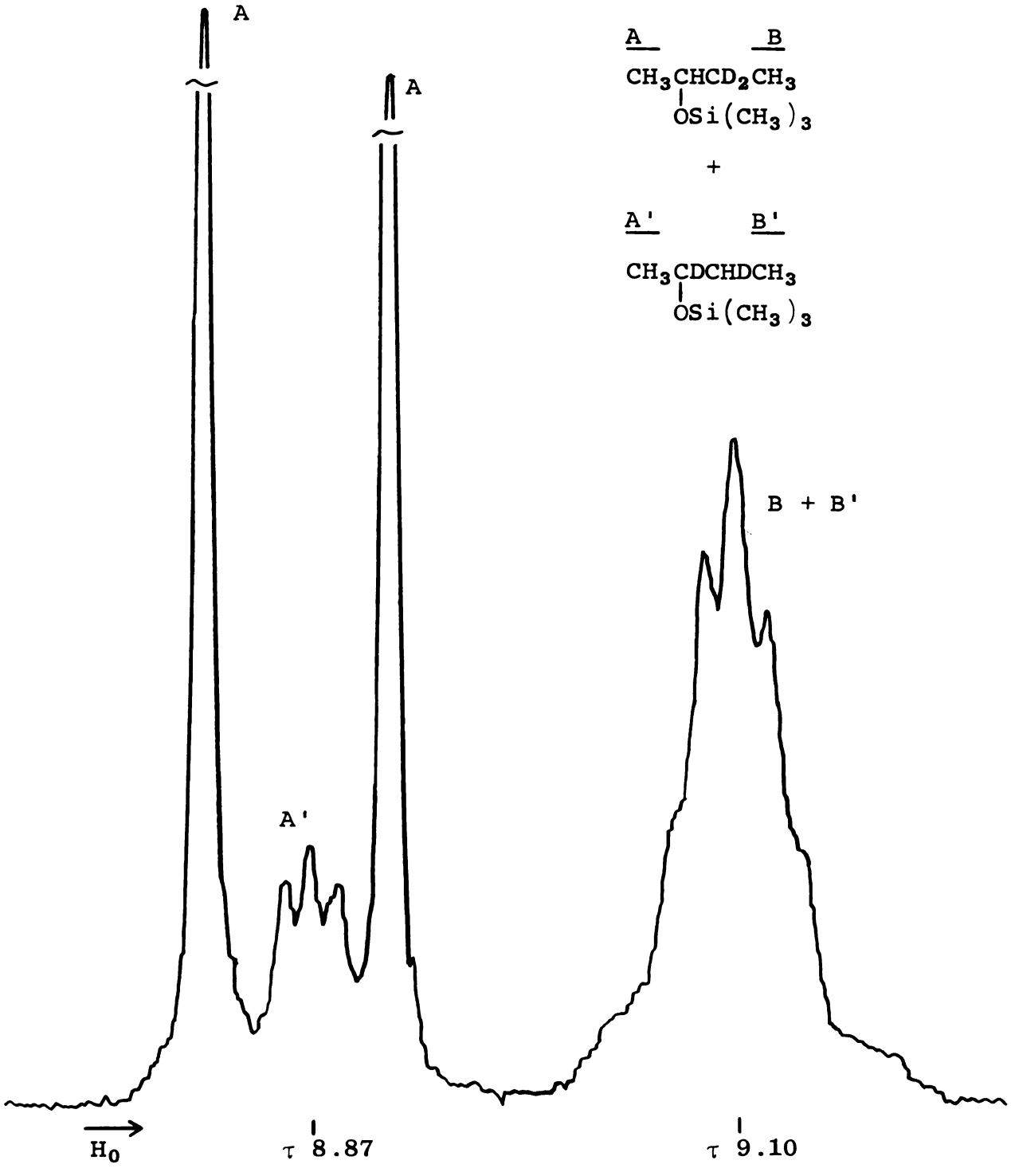


Figure 5. Methyl region of the nmr spectrum of the trimethylsilyl ether of the 2-butanol obtained from 1-butyl-3-3-$\underline{d_2}$-amine.

Table XX. Integrated nmr signals of methyl protons of the trimethylsilyl ethers of 2-butanol obtained from the deamination of 1-butyl-3,3-$\underline{d_2}$-ammonium perchlorate and of unlabeled 2-butanol.

Compound	Protons	τ	Signal Intensity	Ratio
$\underline{sec}$-$C_4H_7D_2OSi(CH_3)_3$	1-Methyl	8.86	7.1	1.08
	4-Methyl	9.10	6.6	1.00
$CH_3CH_2CH(CH_2)Si(CH_3)_3$	1-Methyl	8.86	7.8	1.07
	4-Methyl	9.10	7.3	1.00

Table XXI. Integrated nmr signals of various protons of the 2-butanol obtained from the deamination of 1-butyl-3,3-$\underline{d_2}$-ammonium perchlorate.

Proton(s)	τ	Signal Intensity	Ratio
Hydroxyl	5.23	16.1	1.00
Methine	6.35	13.1	0.81
1-Methyl triplet	8.87	1.7	0.19
1-Methyl doublet	8.86	7.2	0.81
1-Methyl total	--	8.9	1.00

(see Figure 6). Thus, the hydroxyl proton:methine proton ratio was found to be 1.0:0.81. Also, the 1-methyl groups of 26 and 27 gave a doublet (J = 6.0 cps) and triplet (J = 0.9 cps), respectively, whose integrated signal ratio was 0.81:0.19 (see Table XXI). The 4-methyl groups did not give absorptions sufficiently resolved to permit separate integration. Therefore, all 2-butanol produced in deaminative reactions of 1-butylamine is accounted for by a series of 1,2-hydride shifts. No evidence supporting bridged-ion intermediates or 1,3-hydride shifts was obtained.

IV. 2-Butyl Systems

Figure 7 illustrates some rearrangement mechanisms which a 2-butyl cation might be expected to undergo. Because 2-butanol is the only alcoholic product of the deamination of 2-butylamine (28), mechanisms involving formation of 1-butyl (paths A_2 and B, for example), isobutyl and t-butyl (path C) cations need not be considered as significant pathways.

From what has been observed regarding the behavior of 2-butyl cations in deamination reactions of 1-butylamine, partial scrambling of C-2 and C-3 hydrogens is expected through a series of reversible 1,2-shifts. Determination of whether or not more complex rearrangements occur, by means of bridged-ion intermediates, requires closer examination with the aid of isotopic labeling.

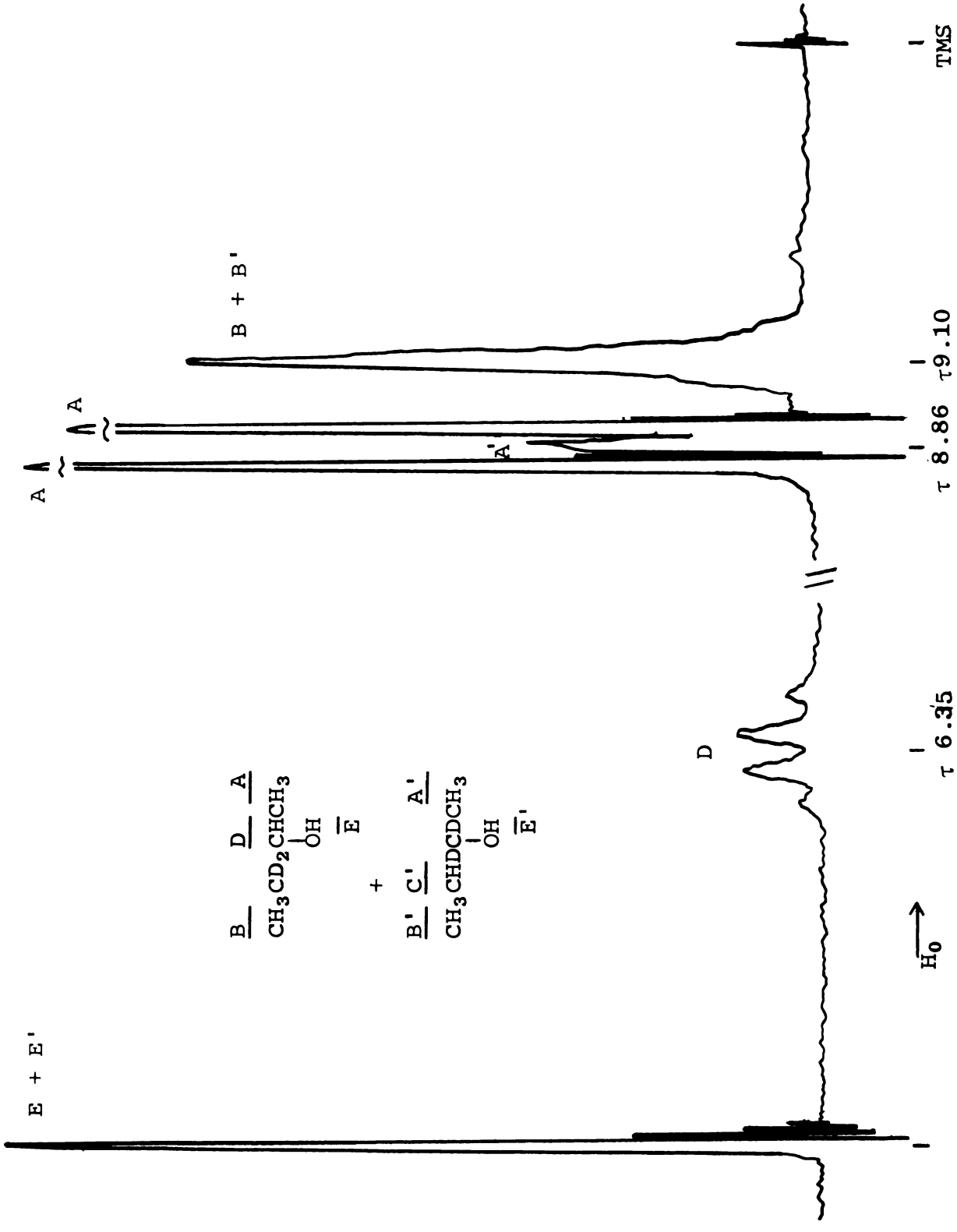


Figure 6. Nmr spectrum of the 2-butanol obtained from 1-butyl-3,3-$\underline{d}_2$-amine.

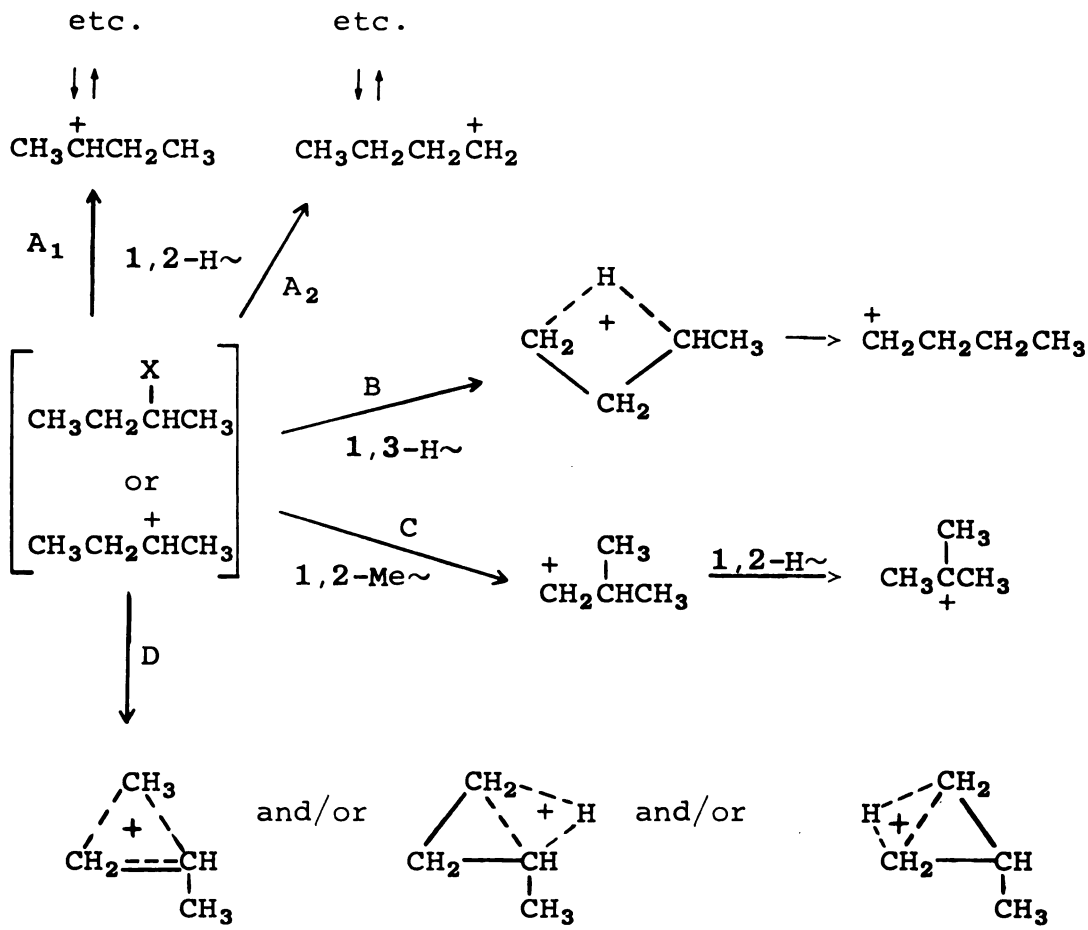
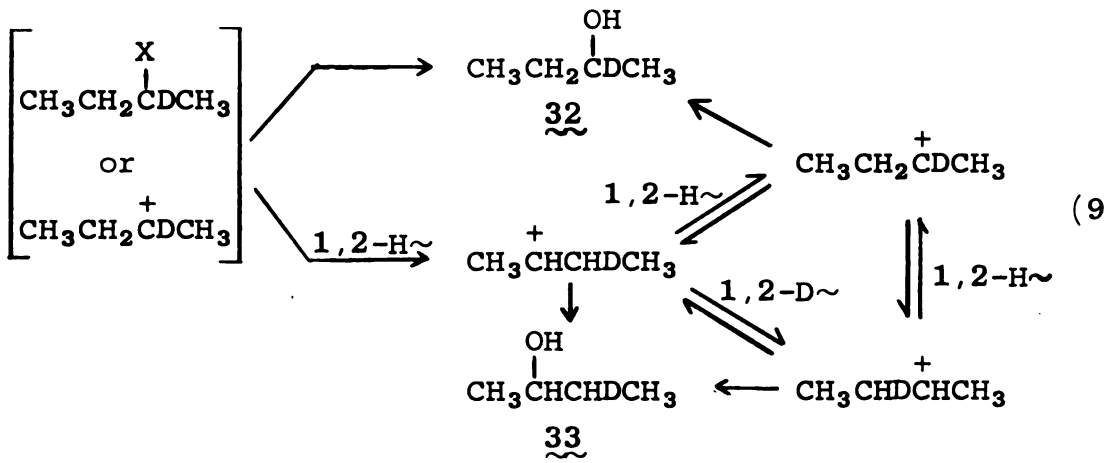


Figure 7. Possible rearrangement pathways of the 2-butyl cation.

2-Butyl-2-d System. If 1,2-hydride (or deuteride) shifts were the only detectable rearrangements taking place, the 2-butanol formed from 2-butyl-2-d-amine would be a mixture of the two alcohols 32 and 33, neither of which have deuterium in a methyl group (see sequence 9). Whether or not there was deuterium at C-1 or C-4 was established by using nmr and mass spectral data. The ratios of integrated signals of 1-methyl protons to 4-methyl protons (Figure 8)



(9)

was found to be the same for the derived 2-butanol product(s) as for standard, unlabeled 2-butanol (see Table XXII). Thus, any deuterium present in the methyl groups must be equally distributed between C-1 and C-4 of various 2-butanol molecules.

Since the ($P-CH_3$) ion of the product 2-butanol lost essentilly no deuterium [0.6% d_0; ($P-CH_3$) ion of authentic 2-butanol-2-d was 0.5% d_0](50), there could not have been a significant amount of deuterium migration into the 1-methyl group (of the final products). This implies no deuterium at C-4 since presumably the reversible sequence 10 would

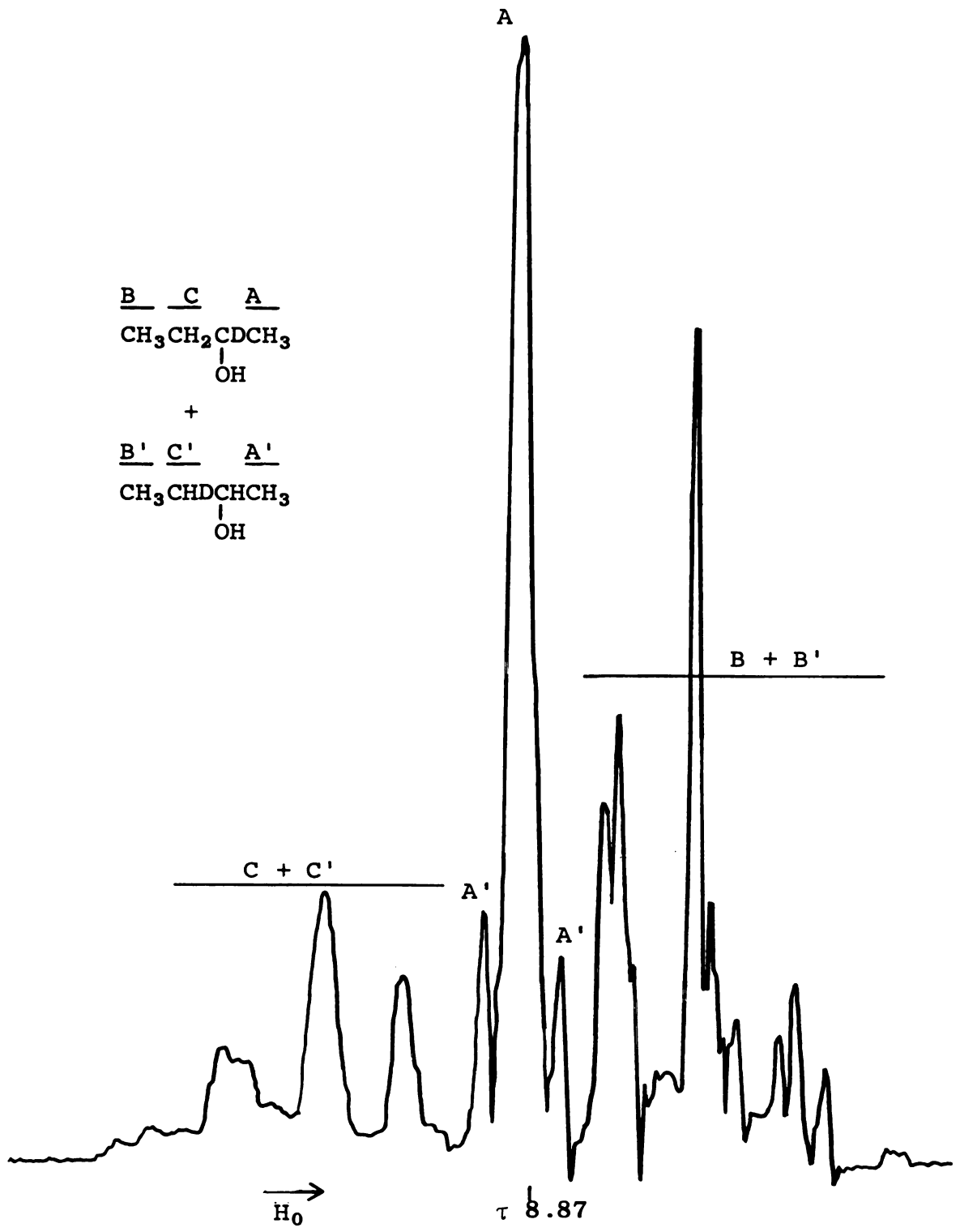
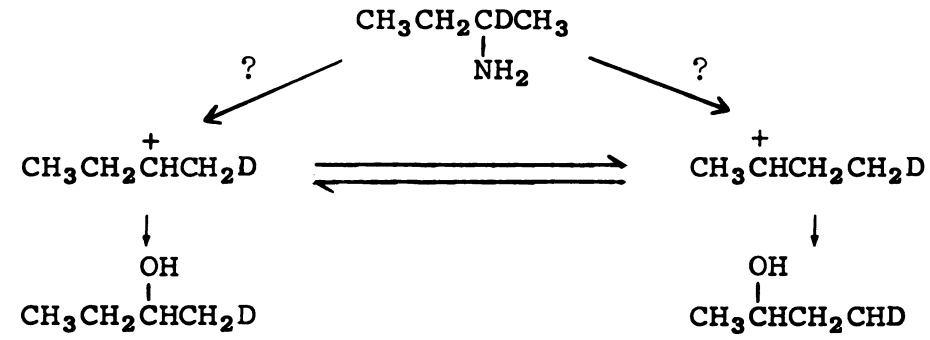


Figure 8. Methylene and methyl regions of the nmr spectrum of the 2-butanol obtained from 2-butyl-2-d-amine.

Table XXII. Integrated nmr signals of various protons of the 2-butanol obtained from the deamination of 2-butyl-2-d-ammonium perchlorate and of unlabeled 1-butanol.

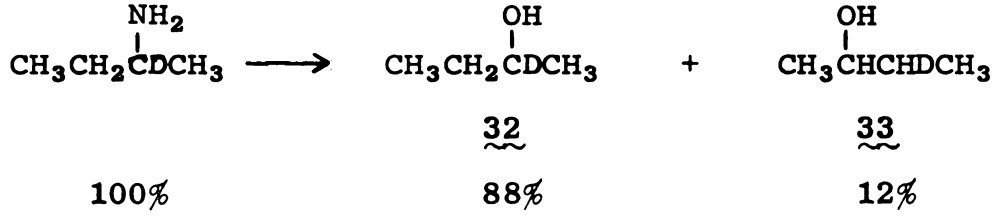
Compound	Protons	τ	Signal Intensity	Ratios
sec-C_4H_8DOH	1-Methyl triplet	8.87	6.5	0.87
	1-Methyl doublet	8.86	1.0	0.13
sec-C_4H_8DOH	1-Methyl total	8.87	7.5	0.99
	4-Methyl total	9.10	7.6	1.00
$CH_3CH_2CH(CH_3)OH$	1-Methyl total	8.87	8.5	0.99
	4-Methyl total	9.10	8.6	1.00

compete with solvent capture of either 2-butyl cation.



(10)

As there is no deuterium in the product alcohols other than at C-2 and C-3, the composition of the derived 2-butanol can be calculated from the ($P-C_2H_5$) ion.



Although less accurate, nmr data are in essential agreement. By comparing the integrated signal of the triplet (J = 0.9 cps) due to the 1-methyl protons of 32 to the total signal of 1-methyl protons, a concentration of 87 ± 3% is calculated. As Figure 9 illustrates, resolution is not complete between the triplet and the doublet (J = 6.2 cps), due to the 1-methyl group of 33.

2-Butyl-3,3-d_2 System. The expected similarities of this model and the 2-butyl-2-d system were verified experimentally. The ratios of protons at C-1 to those at C-4 were identical (Table XXIII) for derived 2-butanol and 2-butanol-d_0. That no deuterium migration to C-1 (of the

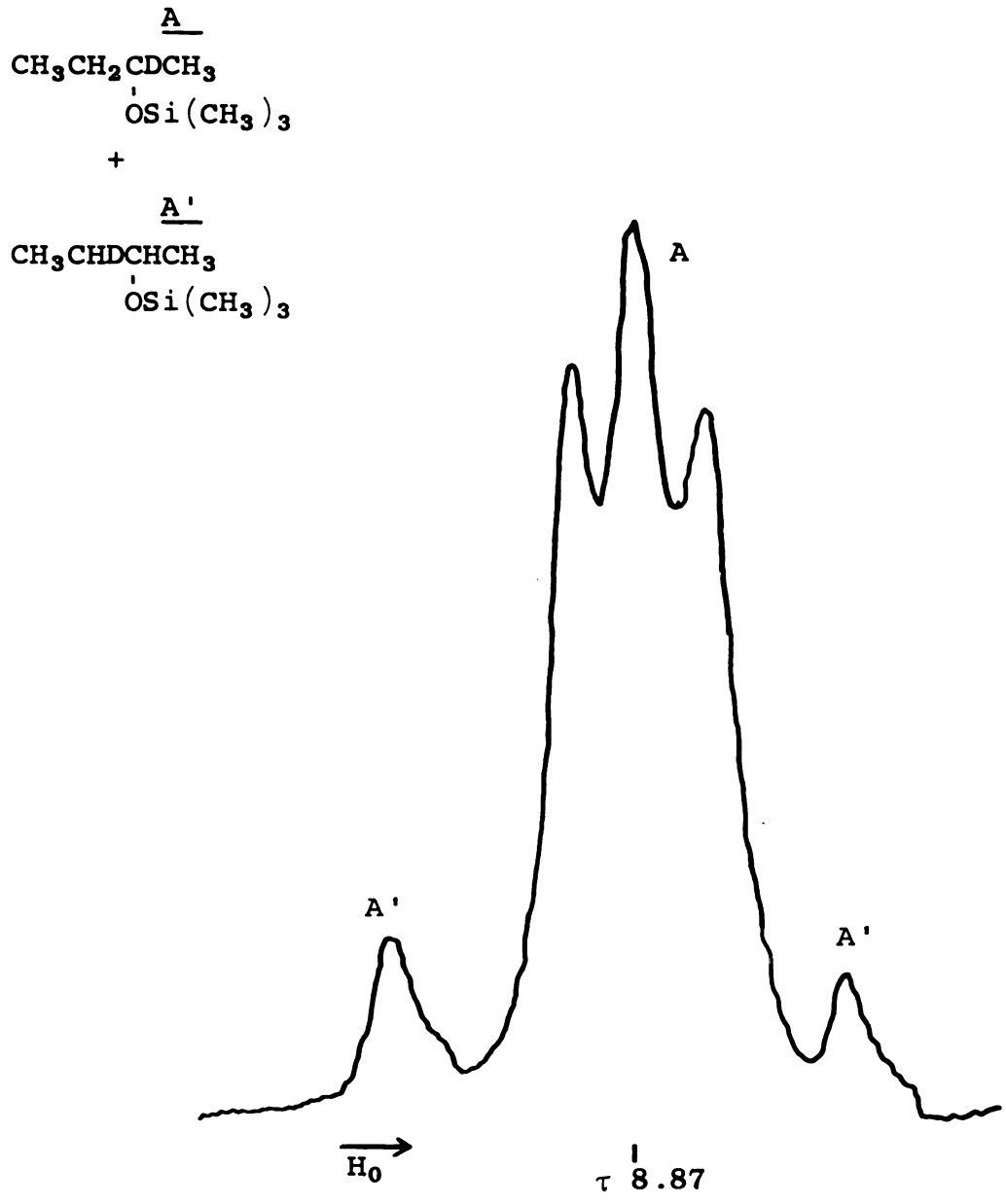
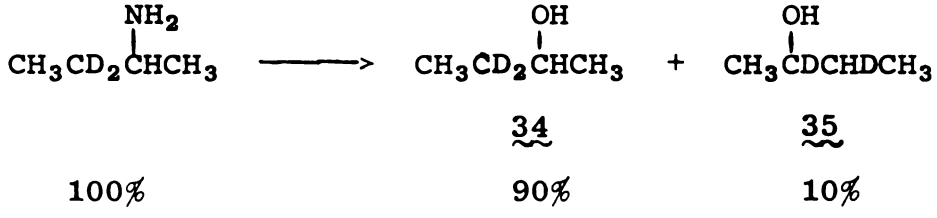


Figure 9. 1-Methyl region of the nmr spectrum of the trimethylsilyl ether of the 2-butanol obtained from 2-butyl-2-d-amine.

Table XXIII. Integrated nmr signals of various protons of the 2-butanol obtained from the deamination of 2-butyl-3,3-$\underline{d_2}$-ammonium perchlorate and of unlabeled 2-butanol.

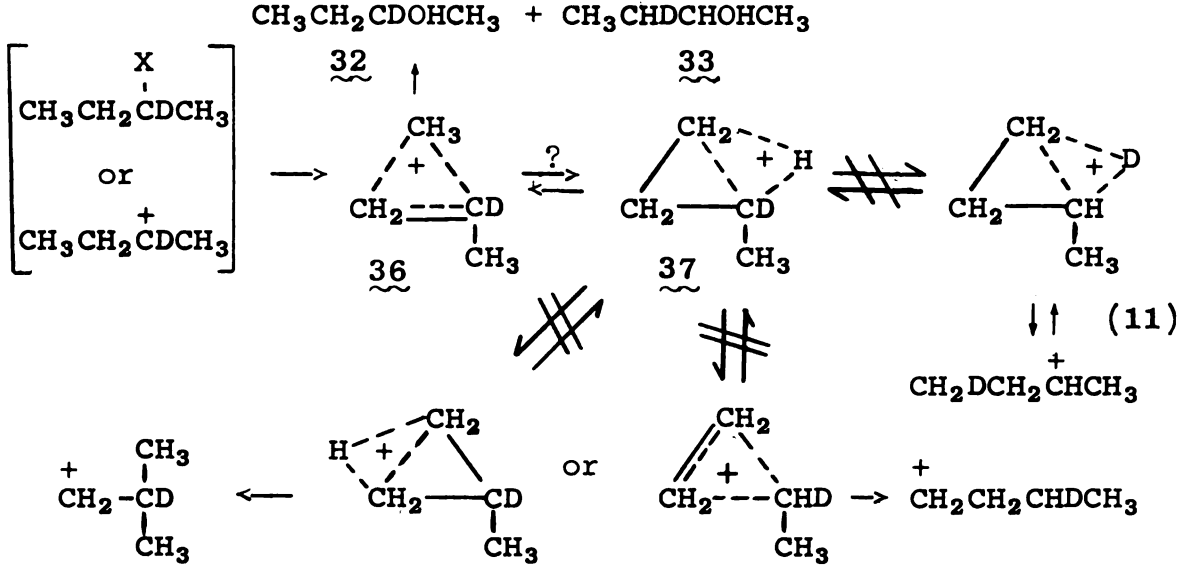
Compounds	Protons	τ	Signal Intensity	Ratios
$\underline{sec}$-$C_4H_7D_2OH$	1-Methyl triplet	8.87	0.8	0.11
	1-Methyl doublet	8.86	6.2	0.89
$\underline{sec}$-$C_4H_7D_2OH$	1-Methyl total	8.86	7.0	1.03
	4-Methyl total	9.10	6.8	1.00
$CH_3CH_2CH(CH_3)OH$	1-Methyl total	8.86	7.0	1.03
	4-Methyl total	9.10	6.8	1.00

alcohol) occurred was again indicated by the low $\underline{d}_0$ contribution of the ($P-CH_3$) ion [0.9% $\underline{d}_0$; ($P-CH_3$) ion of authentic 2-butyl-3,3-$\underline{d}_2$ trimethylsilyl ether was also 0.9% $\underline{d}_0$]. Therefore, the composition of alcohols is calculated from the ($P-C_2H_5$) ion to be the following:



Resolution of the nmr 1-methyl signals of 34 and 35 was again incomplete (Figure 10); however, concentration of 34 in the 2-butanol mixture is estimated by integration to be 89 ± 3%, in accord with mass spectral calculations.

The above observations concerning the 2-butyl systems do not exclude the possibility of formation of the bridged-methyl ion 36 (see eq. 11 regarding the 2-butyl-2-$\underline{d}$ system).



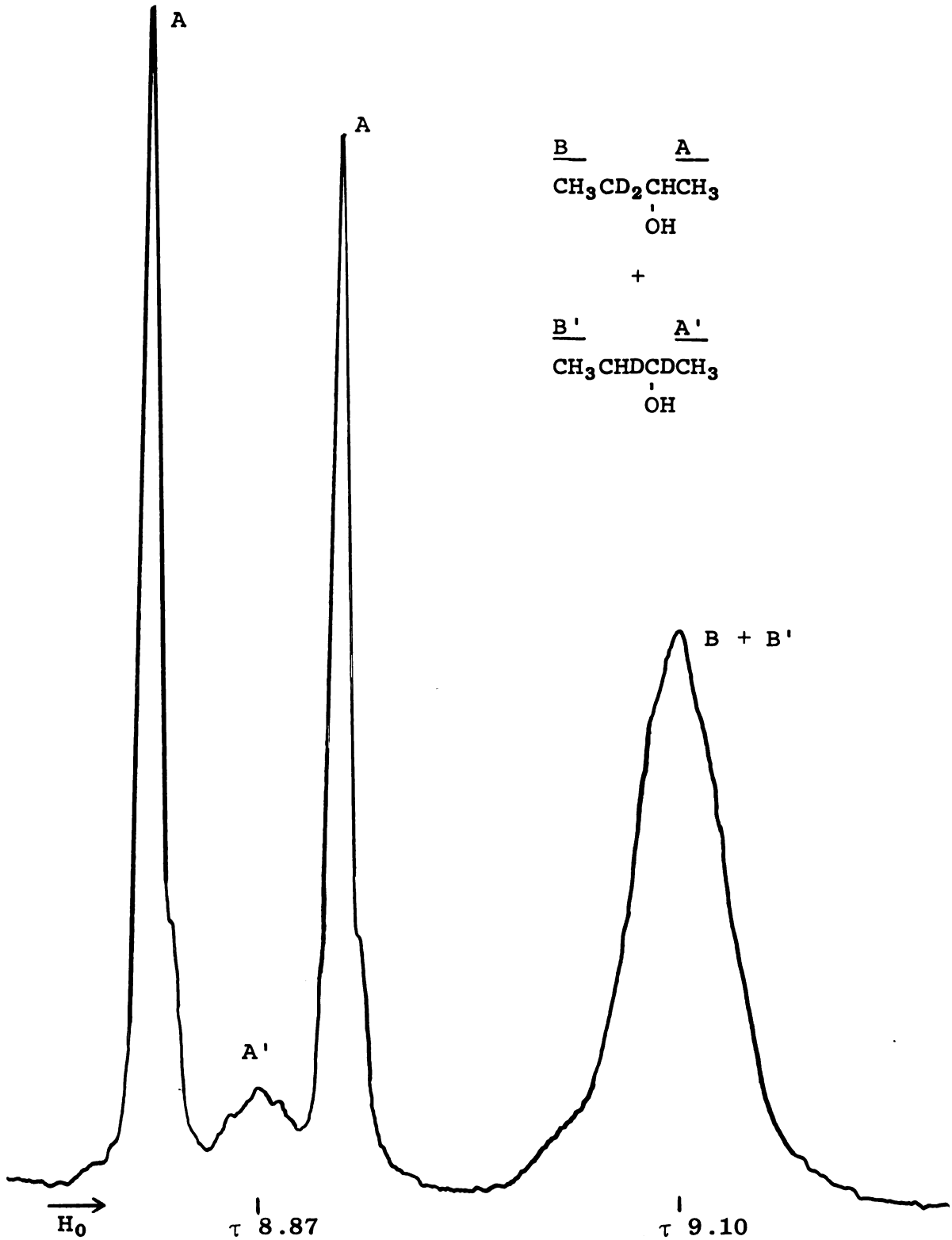
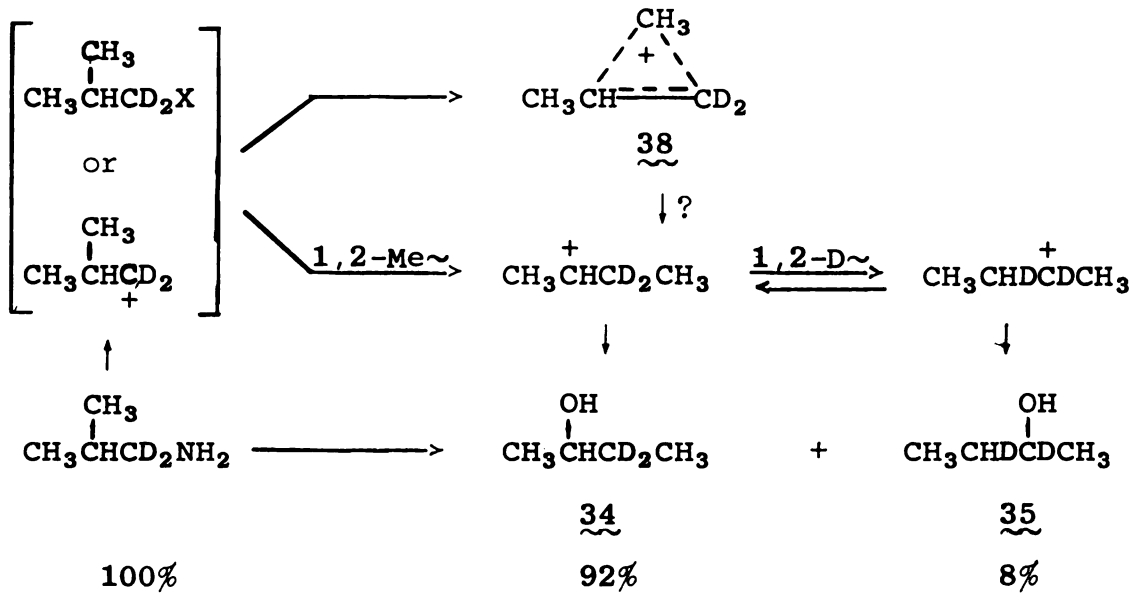


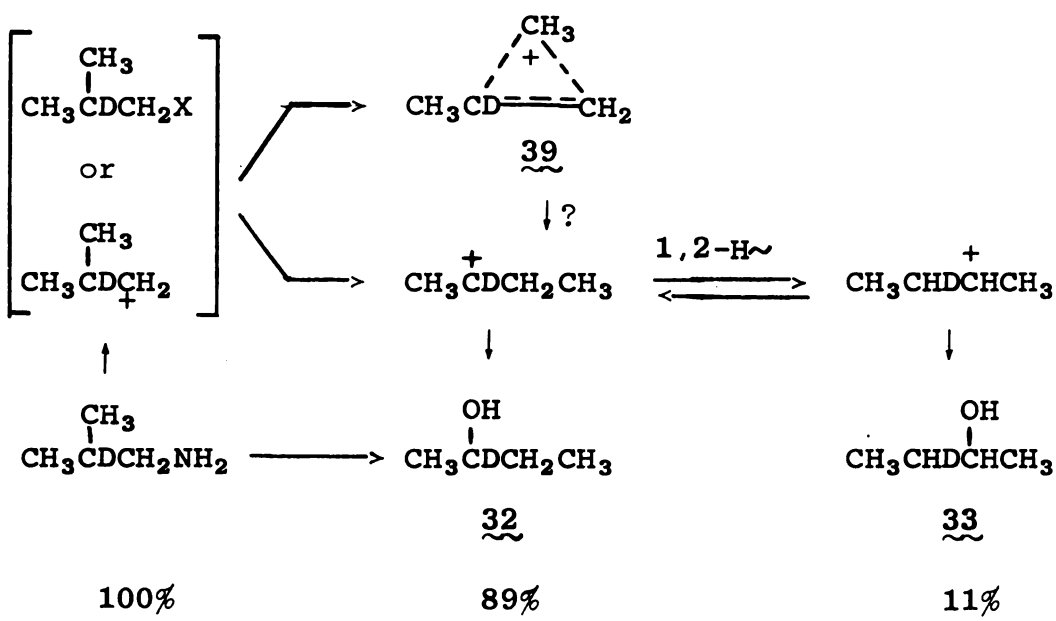
Figure 10. Methyl region of the nmr spectrum of the 2-butanol obtained from 2-butyl-3,3-$\underline{d}_2$-amine.

Indeed, observed (28,48) formation of methylcyclopropane strongly implicates a bridged-ion species of some kind. The absence of 1-butanol products casts doubt on involvement of protonated cyclopropane intermediates, such as 37, but the evidence is not prohibitive. Equilibration of 37 with other hydrogen- or alkyl-bridged intermediates can be considered unimportant, however, as 1-butanol, isobutyl alcohol and 2-butanol with deuterated methyl groups were not detected. Any 2-butanol produced from 36 would not be distinguishable from 32, formed by simple solvent capture of the original 2-butyl cation or displacement on its precursor, or from 33, formed by capture after a 1,2-hydride shift. It has been reported (51,52) that a displacement mechanism accounts for ca. 22% of the 2-butanol-2-d formed from 2-butyl-2-d-amine. Results of the 2-butyl-3,3-d_2 system are consistent. That a 1,2-shift competes less successfully with capture than in the 2-butyl-2-d system can be ascribed to an isotope effect that is discussed later.

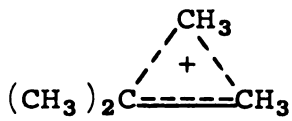
The data gathered from the deaminations of deuterated 1- and 2-butylamines correlate with those concerning the deamination of isobutylamine. It was demonstrated (53) that the alcohols 34 and 35 were the only 2-butanols formed from isobutyl-1,1-d_2-amine. The isobutyl alcohol formed was isotopically unrearranged. Thus, involvement of hydrogen-bridged intermediates was not substantiated, although 38 may be a possible representation for the precursor of methylcyclopropane (28), and perhaps for some of the alcohol 34 as well.



Similar results have been obtained from deamination of isobutyl-2-d-amine (54). In this case, also, the 2-butanol was formed solely by way of a 2-butyl cation which was the product of a 1,2-methyl shift. The data did not support the intermediacy of protonated cyclopropanes.



Any correlation of the results of this investigation with those of previous workers must reconcile the formation of hydrocarbons (7,42,43) with that of substitution products. As was noted earlier, intermediate protonated cyclopropanes (possibly edged-protonated, and equilbrating through methyl-bridged ions) satisfactorily accommodated the formation of cyclopropane and isotope-position rearranged 1-propanol (20,21,22). On the other hand, the ion 40 has not been detected, if present, and 41 has been ruled out as an intermediate in the deamination of neopentylamine (39).



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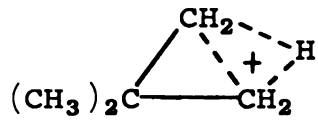

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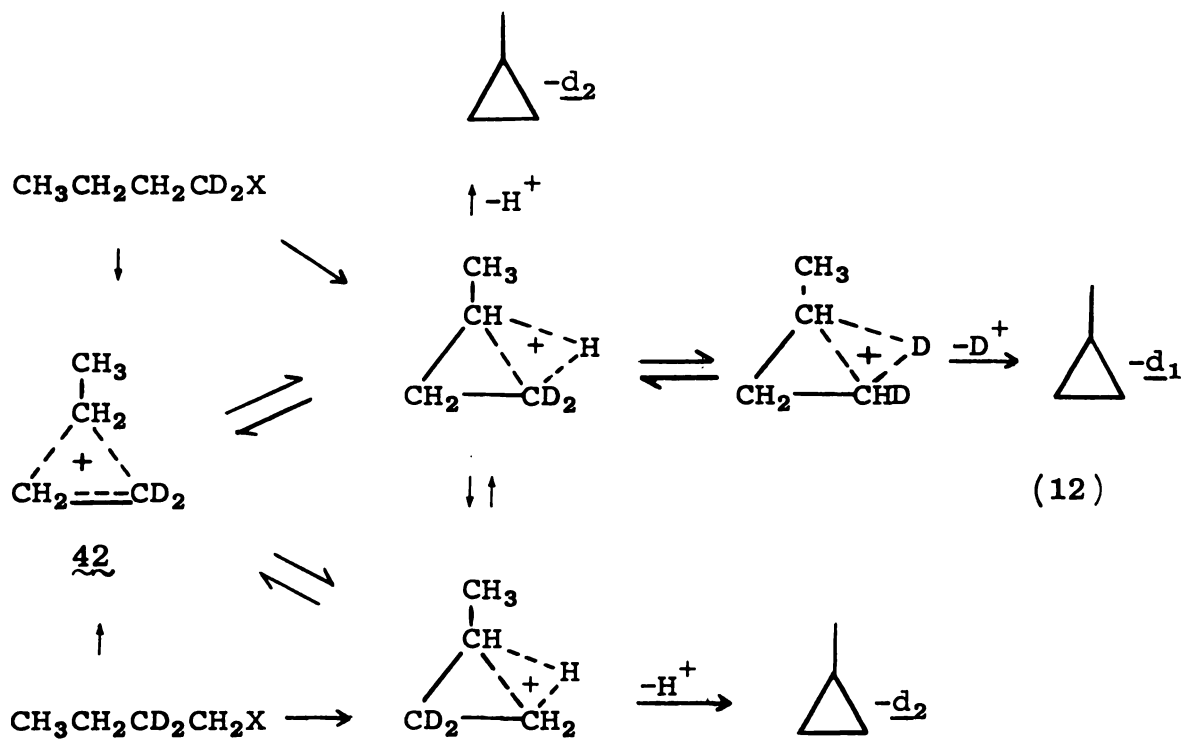
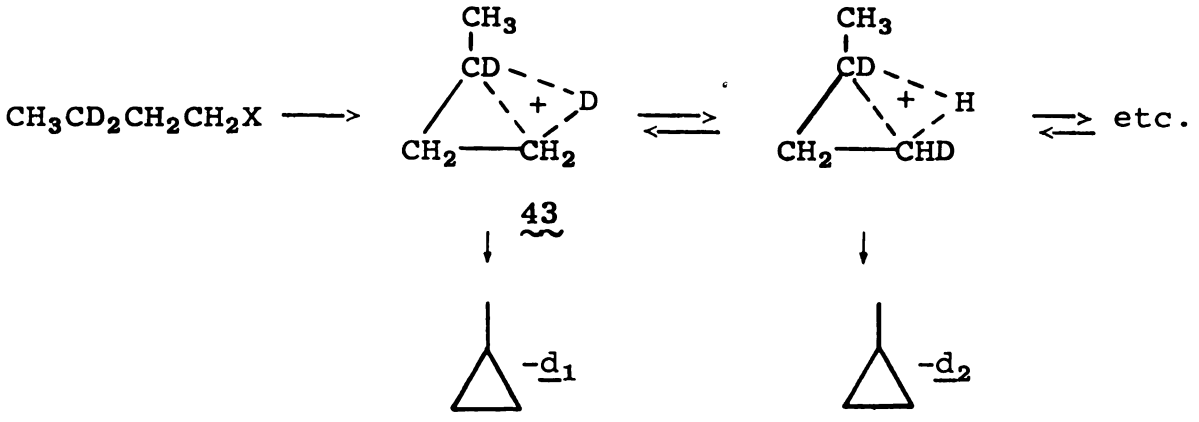
The butyl systems exhibit properties in deamination reactions that are intermediate between those of the propyl and the neopentyl systems. Methylcyclopropane has been characterized as a deamination product of 2-butylamine, isobutylamine and 1-butylamine in yields of 4%, 2.5% and 0.3% (28) of the hydrocarbon fraction, which was reported to be ca. 12% of the total product mixture in the 50% aqueous acetic acid deamination (55). Furthermore, isotopic analyses of methylcyclopropane obtained from the deamination of deuterated 1-butylamines in aqueous acetic acid have indicated (56) that a methyl-bridged ion (as 42 below) cannot be a sole precursor of the methylcyclopropane. Thus, the 1-butyl-1,1-d_2-amine gave 9% d_1- and 91% d_2-methylcyclopropane,

while values of 11% $\underline{d}_1$ and 89% $\underline{d}_2$ were obtained from the 1-butyl-2,2-$\underline{d}_2$ system. These data give credence to a mechanism involving equilibrating protonated cyclopropanes without, necessarily, the intervention of a methyl-bridged species (sequence 12). Such an equilibration would lead to



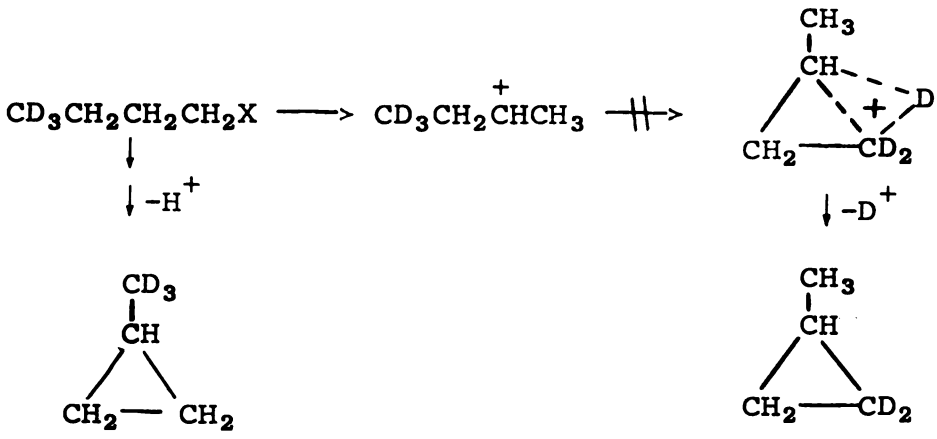
equal amounts of methylcyclopropane-$\underline{d}_1$ from 1-butyl-1,1-$\underline{d}_2$-amine and 1-butyl-2,2-$\underline{d}_2$-amine. The 9:1 ratio of $\underline{d}_2$- to $\underline{d}_1$-species might reflect not only the relative ease of H^+ to D^+ loss resulting from a statistical factor (4 H to 2 D) and an isotope effect after equilibration, but also competition between methylcyclopropane formation and species equilibration. This competition factor would explain the

results of 43% $\underline{d_1}$- and 57% $\underline{d_2}$-methylcyclopropane afforded by deamination of 1-butyl-3,3-$\underline{d_2}$-amine. Thus, the ion **43** would be the most important precursor of the cyclic product.

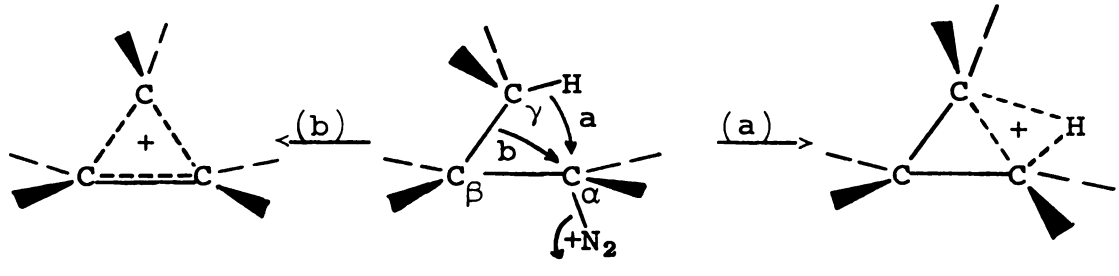


A similar phenomenon has been observed in the deamination of 1-propylamine (22) and in the formolysis of 1-propyl tosylate (57), in which cases solvent capture competes with the equilibration of the protonated cyclopropanes. Such equilibration before H^+ (or D^+) loss to give methylcyclopropane can account for the small difference detected (48) in deuterium distribution between methylcyclopropane and 1-butene in the aprotic deamination of isobutyl-1,1-$\underline{d_2}$-amine. In this instance, the olefin, which could not be formed with corresponding loss of deuterium, always contained slightly more deuterium than the methylcyclopropane, which could be produced with loss of deuterium by means of a series of equilibrations as depicted in eq. 12.

It was also disclosed (56) that 1-butyl-4,4,4-$\underline{d_3}$-amine gave only trideuterated methylcyclopropane. This finding indicates that a 2-butyl cation may not be the main precursor of the bridged species. If the bridged species were



formed at least 100 times faster from the cationic precursors (e.g., diazonium ions) than from the cations, then the much greater amounts of cyclic products produced from 2-butylamine (28) and 3-methyl-2-butylamine (26) than from 1-butylamine and isopentylamine, respectively, would be reasonable. An S_Ni-like mechanism, with the leaving group being internally displaced by (a) the bonding electrons of the γ-carbon and one of its hydrogens to lead to a protonated cyclopropane, or (b) by the electrons comprising the bond between C_β and C_γ to result in a carbon-bridged species, would accommodate the results. One might consider (a) and (b) to be pathways competing with each other as well as with



simple dissociation of the diazonium ion. Dissociation also would compete with concurrent migration or elimination of a function on C_β.

By using the 1-propyl system (no substitution on C_α, C_β, or C_γ) as a base, the protonated cyclopropane pathways for isobutyl (methyl on C_β) and 1-butyl (methyl on C_γ) would be less significant than the corresponding one for 1-propyl because of 1,2-eclipsed interactions between hydrogen and methyl in the latter systems. In the neopentyl system, the carbon-bridge route would be favored over the hydrogen-bridge route because the tertiary C_β can successfully stabilize the incipient positive charge. Indeed, it may do this so well that the bridged species may be merely a transition state in the conversion to a t-amyl cation (39).

By taking into account all of the available data, a scheme can be formulated which accommodates the results obtained from the deamination of 1-butylamine. It is illustrated in Figure 11. The dotted arrows represent pathways for which direct experimental evidence has not been obtained.

A mechanistic implication of Figure 11 is that the alcohols are not only irreversibly formed, but also that they are formed from unrearranged or rearranged carbonium ions that have precursors derived from the starting amines, not from other reaction products. That hydration of the olefins in not such a pathway will now be demonstrated.

The mass spectral data from the 1-butyl-2,2-d_2 system permit a check on the extent of sequence 13. The ($P-C_2H_5$) ion of 44 would be a d_1 species, whereas those of 25 and 30

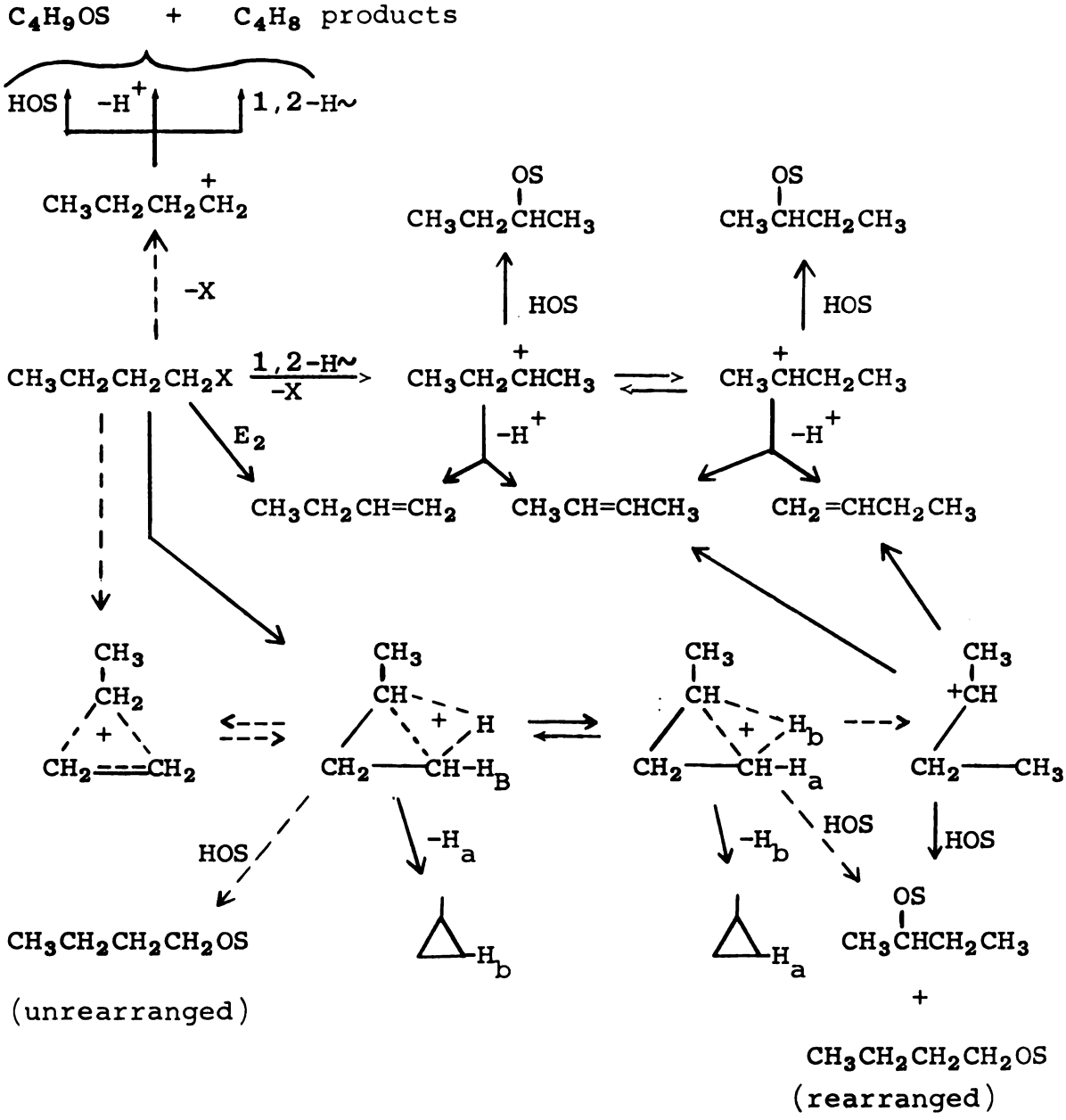
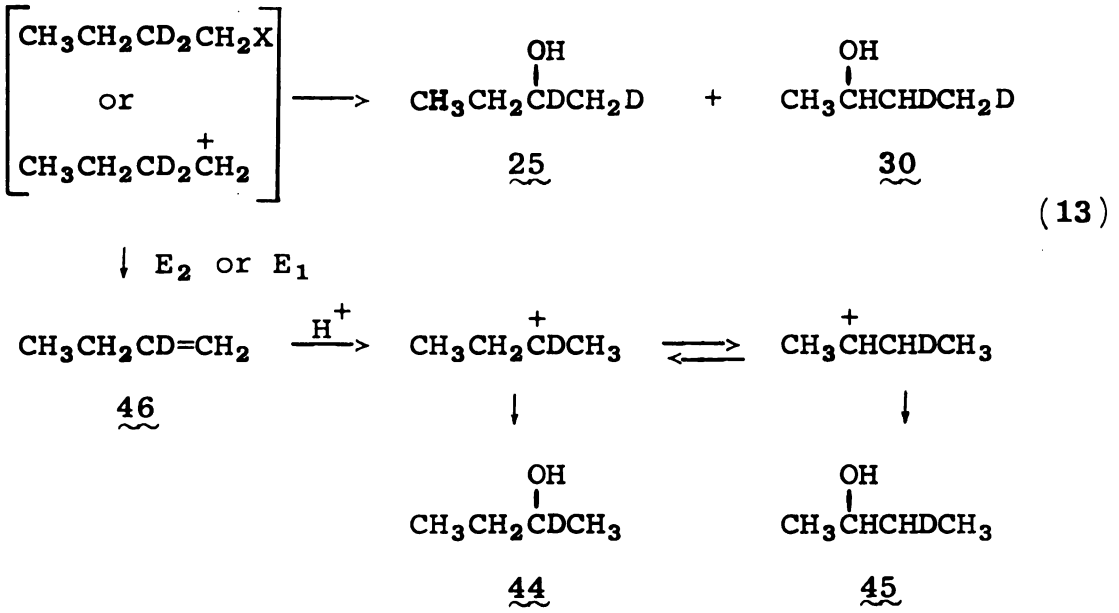
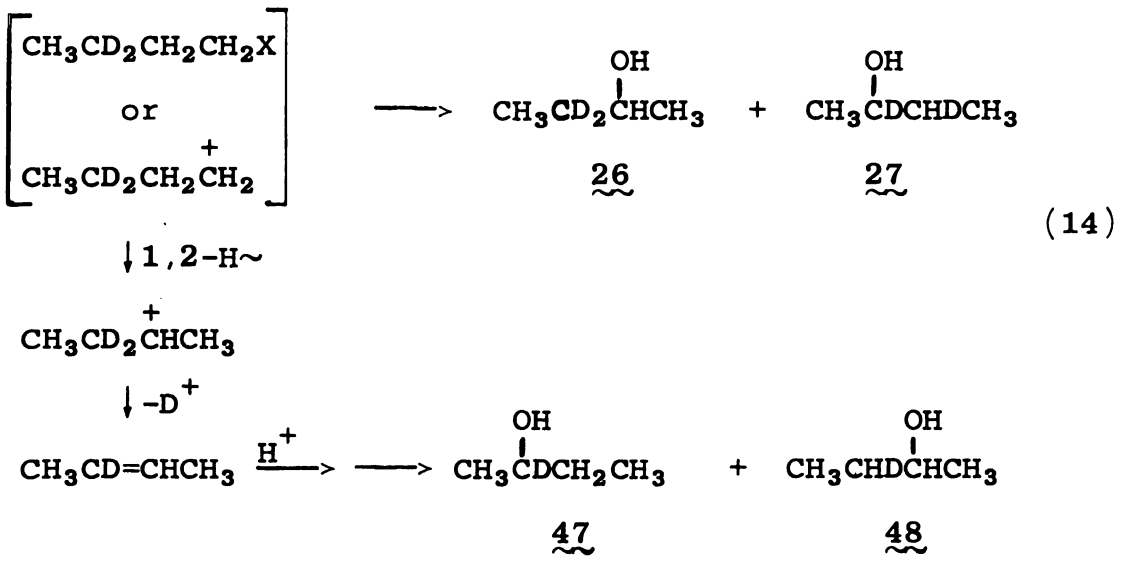


Figure 11. Proposed mechanisms of formation of the products of the deamination of 1-butylamine.



(13)

would be $\underset{\sim}{d_2}$ and $\underset{\sim}{d_0}$, respectively. Table XIX shows that the $\underset{\sim}{d_1}$ ($P-C_2H_5$) ion contribution of the product 2-butanol from 1-butyl-2,2-$\underset{\sim}{d_2}$-amine (which contained 3.7% amine) was 3.9%. Thus, alcohol $\underset{\sim}{44}$ is not a significant product. It can be likewise established that 2-butene is not a 2-butanol precursor (sequence 14). Alcohols $\underset{\sim}{47}$ and $\underset{\sim}{48}$ would produce



(14)

a $\underline{d}_1$ ($P-CH_3$) ion. As the experimental value of 3.7% $\underline{d}_1$ is less than the 4.3% present in the starting material, sequence 14 is excluded.

The unimportance of olefin hydration was not unexpected, as Karabatsos, Orzech and Meyerson (39) had shown that no t-amyl products arose by such a pathway in the deaminative rearrangement of neopentylamine. Also, Otvos and coworkers (58) had shown that isobutylene was converted only very slowly into carbonium ions in 96% sulfuric acid.

This investigation was not designed to yield specific information on the mechanism of deamination prior to the dissociation step, or even of the dissociation itself. However, the ratios of the various isotopically-distributed 2-butanols obtained in the deaminations of the 1-butyl, 2-butyl and isobutyl systems were found to be curiously different, and may be indicative of the characteristics of the dissociation and the steps immediately following it (42,59).

In Figure 12 is shown the 2-butanol formed from seven related butyl models. It should be noted that because the "second" 2-butyl cation formed can rearrange in competition with being captured by solvent, the analyzed ratios of alcohols are typical, but not exact, measures of the extent of the second 1,2-shift, relative to capture of the "first" 2-butyl cation by water.

Many of the differences in the ratios are readily interpreted as due to deuterium isotope effects. Thus IIIb

Case	2-Butanols	No.	Relative %
I $CH_3CH_2CH_2CD_2X$ $\xrightarrow{1,2\text{-H}\sim}$	$CH_3CH_2\overset{+}{C}HCHD_2 \rightarrow CH_3CH_2\overset{OH}{C}HCHD_2$	Ia	77
	$CH_3\overset{+}{C}HCH_2CHD_2 \rightarrow CH_3\overset{OH}{C}HCH_2CHD_2$	Ib	23
II $CH_3CH_2CD_2CH_2X$ $\xrightarrow{1,2\text{-D}\sim}$	$CH_3CH_2\overset{+}{C}DCH_2D \rightarrow CH_3CH_2\overset{OH}{C}DCH_2D$	IIa	75
	$CH_3\overset{+}{C}HCHDCH_2D \rightarrow CH_3\overset{OH}{C}HCHDCH_2D$	IIb	25
III $CH_3CD_2CH_2CH_2X$ $\xrightarrow{1,2\text{-H}\sim}$	$CH_3CD_2\overset{+}{C}HCH_3 \rightarrow CH_3CD_2\overset{OH}{C}HCH_3$	IIIa	81
	$CH_3\overset{+}{C}DCHDCH_3 \rightarrow CH_3CD_2\overset{OH}{C}HCH_3$	IIIb	19
IV $CH_3CH_2\underset{X}{C}DCH_3$ $\longrightarrow$	$CH_3CH_2\overset{+}{C}DCH_3 \rightarrow CH_3CH_2\overset{OH}{C}DCH_3$	IVa	88
	$CH_3\overset{+}{C}HCHDCH_3 \rightarrow CH_3\overset{OH}{C}HCHDCH_3$	IVb	12
V $CH_3CD_2\underset{X}{C}HCH_3$ $\longrightarrow$	$CH_3CD_2\overset{+}{C}HCH_3 \rightarrow CH_3CD_2\overset{OH}{C}HCH_3$	Va	90
	$CH_3\overset{+}{C}DCHDCH_3 \rightarrow CH_3\overset{OH}{C}DCHDCH_3$	Vb	10
VI $CH_3\underset{CH_3}{C}HCD_2X$ $\xrightarrow{1,2\text{-Me}\sim}$	$CH_3CD_2\overset{+}{C}HCH_3 \rightarrow CH_3CD_2\overset{OH}{C}HCH_3$	VIa	92
	$CH_3\overset{+}{C}DCHDCH_3 \rightarrow CH_3\overset{OH}{C}DCHDCH_3$	VIb	8
VII $CH_3\underset{CH_3}{C}DCH_2X$ $\xrightarrow{1,2\text{-Me}\sim}$	$CH_3CH_2\overset{+}{C}DCH_3 \rightarrow CH_3CH_2\overset{OH}{C}DCH_3$	VIIa	89
	$CH_3\overset{+}{C}HCHDCH_3 \rightarrow CH_3\overset{OH}{C}HCHDCH_3$	VIIb	11

Figure 12. Ratios of labeled 2-butanols obtained from the deaminations of deuterated 1-butylamine, 2-butylamine and isobutylamine.

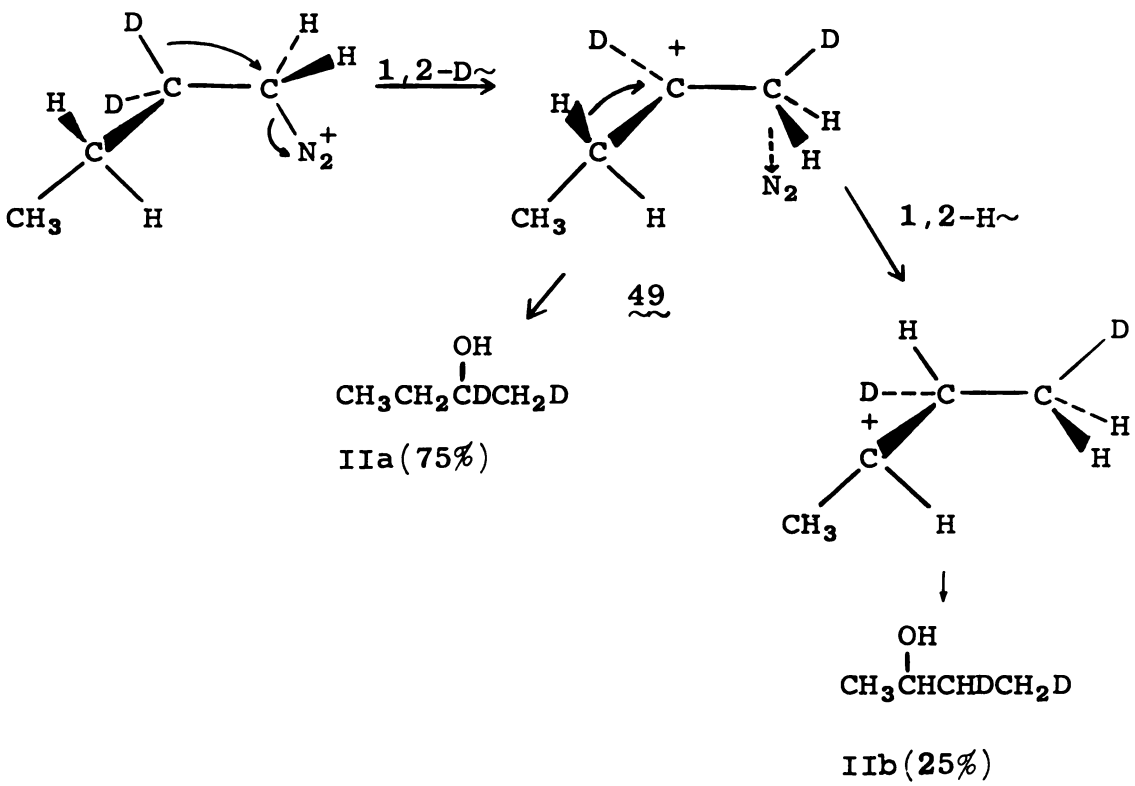
is expected to be formed to a lesser extent than Ib or IIb since the second 1,2-shift involves deuterium rather than protium and, consequently, would compete less successfully with solvent capture. For the same reason, Vb is less than IVb and VIb less than VIIb. Furthermore, IIb may have been detected in a slightly greater amount than Ib because of the less likelihood of the cation precursor of IIb undergoing a third 1,2-shift than that of Ib.

The finding that the ratios VIb/VIa and Vb/Va are smaller than the corresponding ratios IIb/IIa and IIIb/IIIa can be partially explained by direct displacement on the diazonium ion of IV and V, to lead to larger amounts of IVa and Va. Yet assuming a value of 22% (51) for the amount of 2-butanol arising by direct displacement (leading to IVa, for example, in case IV) the percent of IVb should have been 20-22%, not 12% as found. There are other differences in the values determined which are also less easily rationalized. For example, apparently similar 2-butyl cations are initially formed in cases III and VI (by a 1,2-hydride shift in case III and a 1,2-methyl shift in case VI). Yet a second 1,2-shift was more than twice as competitive in case III than in case VI. The same is true in cases II and VII.

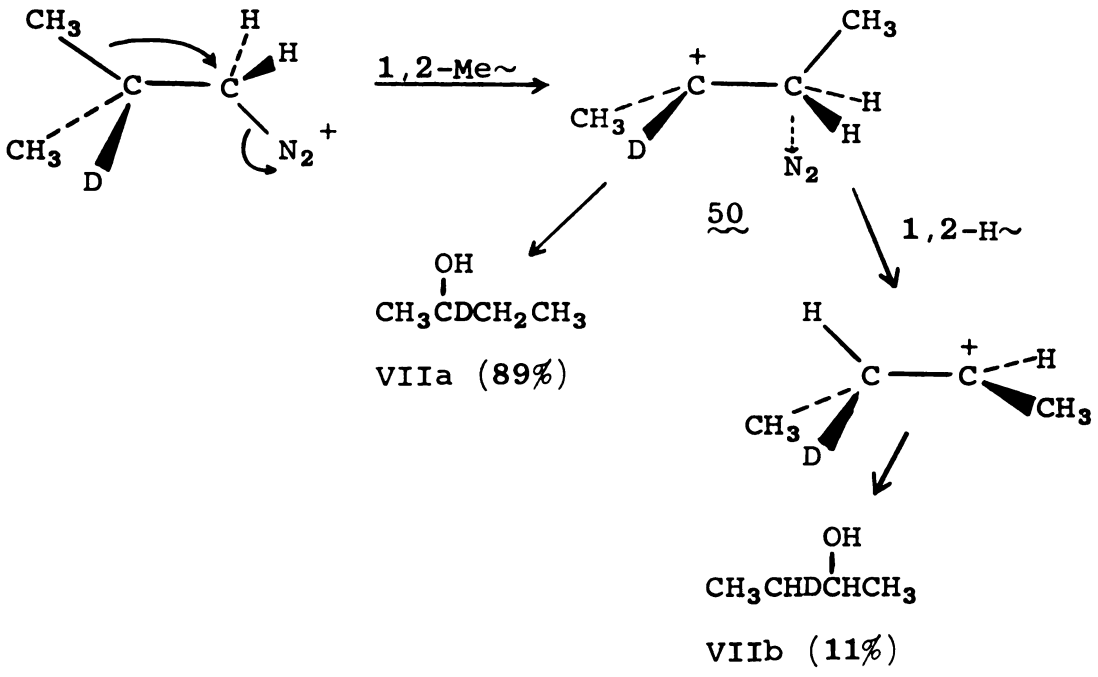
The aforementioned differences can be explained as follows. The low value obtained for IVb is most easily rationalized in terms of competing direct displacement on the diazonium ion and carbonium ion formation. Conceivably

the S_N2 pathway accounts for more than the 22% reported (51). A value of 40-45% displacement as a pathway to 2-butanol in the 2-butyl systems would make the 12% IVb comparable to 25% IIb.

The low amount of VIIb formed in the isobutyl-2-d case can be accounted for in terms of the stereochemistry of the first 2-butyl cation. The intially-formed 2-butyl cation (49) from the 1-butyl system can assume a geometry where a second 1,2-shift is favorable. A slightly different situation pertains to the isobutyl system. The



2-butyl cation (50) formed by the 1,2-methyl shift is not of appropriate conformation to facilitate a subsequent 1,2-hydride shift. Consequently, the required rotation about



the middle carbon-carbon bond may make the second 1,2-shift less competitive with solvent capture of the initially-formed 2-butyl cation (50).

V. Summary

The following points were brought out during the course of this investigation.

i. All of the 1-butanol produced in the deamination of 1-butylamine arises from displacement by solvent on a 1-butyl cation precursor (such as a diazonium ion) and/or from capture by solvent of an unrearranged 1-butyl cation.

ii. The mechanism by which 2-butanol is formed from 1-butylamine involves only 1,2-hydride shifts, with no significant contribution of a nominal 1,3-hydride shift.

iii. The only alcohol formed in the deamination of 2-butylamine is 2-butanol, which results from displacement by solvent on a 2-butyl cation precursor and from solvent capture of interconverting 2-butyl cations.

iv. The carbonium ions leading to the alcohols have precursors derived from the starting amines, not from olefins. Diazoalkanes or carbenes are not significant intermediates in the alcohol formation.

EXPERIMENTAL

I. General

Analytical vapor phase chromatography (v.p.c.) was performed on an F & M Model 700 or on an Aerograph Model A-90-P gas chromatograph. The latter instrument was also used for small-scale preparative v.p.c. Larger scale preparative work was done on a Perkin-Elmer Model 154 Vapor Fractometer.

Nuclear magnetic resonance spectra were taken on a Varian Model A-60, high resolution spectrometer.

II. Preparation of 1-Butyl-1,1-d_2-ammonium Perchlorate

To a stirred slurry of 4.0 g (0.095 mole) of lithium aluminum deuteride (Metal Hydrides, Inc.) in dry ether was slowly added an ethereal solution containing 6.6 g (0.096 mole) of butyronitrile. Stirring was continued at reflux for four hr after addition was complete. The ether phase obtained by filtration, after alkaline treatment of the reaction mixture, was combined with ether washings of the inorganic salts and neutralized with 71% perchloric acid. Removal of solvent at reduced pressure left white crystals which were washed with pentane and dried *in vacuo*, affording 15.2 g (yield, 90%) of 1-butyl-1,1-d_2-ammonium perchlorate, mp 186-188°.

III. Preparation of 1-Butyl-2,2-$\underline{d}_2$-ammonium Perchlorate

A. Preparation of Butyric-2,2-$\underline{d}_2$ acid-$\underline{d}$

To 1180 g of absolute ethanol in which 69 g (3.0 g-atoms) of sodium had been dissolved was added 480 g (3.0 moles) of diethyl malonate, followed by 343 g (3.15 moles) of bromoethane. The resulting mixture was neutral after 0.5 hr reflux. Rotary evaporation of the filtered alcoholic solution left a two-phase residue of sodium bromide, ethanol and diethyl ethylmalonate, which was extracted with ether. The ether extracts were combined and the solvent removed. Unreacted diethyl malonate was removed by shaking the product ester for one minute with 50 ml of cold, 20% sodium hydroxide solution. The yield of diethyl ethylmalonate was 535 g (95%).

The diester was hydrolyzed by adding it to a hot solution of 525 g of potassium hydroxide in 500 ml of water. Ethanol was removed continuously by a vacuum line. The mixture resulting from neutralization with concentrated hydrochloric acid was extracted several times with ether and ethyl acetate. Removal of solvent left 309 g of ethylmalonic acid, which was exchanged six times with deuterium oxide. Nmr indicated the absence of a methine proton. A portion of the ethylmalonic-2-$\underline{d}$ acid-$\underline{d}_2$ was decarboxylated by distillation at atmospheric pressure. About 41 g of butyric-2,2-$\underline{d}_2$ acid-$\underline{d}$ was obtained at 150-157^0.

B. Preparation of Butyronitrile-2,2-$\underline{d_2}$

To 36.0 g (0.40 mole) of butyric-2,2-$\underline{d_2}$ acid-$\underline{d}$ was added 50.7 g (0.43 mole) of thionyl chloride that had been purified by successive distillations from quinoline and linseed oil. After two hour reflux, the mixture was taken up in 500 ml dry ether and cooled. Ammonia was passed over the ethereal solution fo 1.5 hr. The butyramide-2,2-$\underline{d_2}$ was removed from the inorganic salts by Soxhlet extraction with benzene. After recrystallization from benzene, 24.0 g (yield, 68%) of product was obtaind.

Dehydration of 20.3 g (0.23 mole) of amide to butyronitrile-2,2-$\underline{d_2}$ was accomplished by refluxing it with 40.7 g (0.34 mole) of thionyl chloride at 100^0 for 3.5 hr. Addition of water (to hydrolyze excess thionyl chloride) to the mixture which was taken up in ether was followed by washing of the ether phase with saturated sodium bicarbonate solution and drying over anhydrous magnesium sulfate. After distillation, the yield was 11.2 g (70% from amide) of butyronitrile-2,2-$\underline{d_2}$.

C. Preparation of 1-Butyl-2,2-$\underline{d_2}$-ammonium Perchlorate

An ethereal solution containing 11.1 g (0.156 mole) of butyronitrile-2,2-$\underline{d_2}$ was slowly added to 6.1 g (0.16 mole) of lithium aluminum hydride in dry ether. The mixture was refluxed 3 hr and hydrolyzed with alkali. The ether layer was decanted, added to the ether washings of the inorganic

salts and neutralized with 71% perchloric acid. Removal of solvent at reduced pressure gave white crystals, which were washed with petroleum ether and dried in vacuo to give 17.9 g (yield, 65%) of 1-butyl-2,2-d_2-ammonium perchlorate, mp 192-193°.

IV. Preparation of 1-Butyl-3,3-d_2-ammonium Perchlorate

A. Preparation of Propionic-2,2-d_2 Acid-d

Method A. Bromomethane, generated by warming a mixture of 770 g of concentrated sulfuric acid, 908 g of sodium bromide and 600 g of methanol, was bubbled for 3.5 hr into a mixture of 1180 g absolute ethanol, 69 g (3.0 g-atoms) of sodium and 480 g (3.0 moles) of diethyl malonate. After an additional two-hour reflux period, ethanol was removed by rotary evaporation and the diethyl methylmalonate was extracted from the aqueous solution of the inorganic salts with ether. Removal of solvent, hydrolysis with hot potassium hydroxide solution and acidification with concentrated hydrochloric acid gave 251 g (yield, 71%) of methylmalonic acid. The product of six exchanges with deuterium oxide was decarboxylated by refluxing for 12 hr at 135°. Distillation (130-140°) gave 100 g of propionic-2,2-d_2 acid-d (yield, 43% from diethyl malonate).

Method B. Iodomethane (500 g, 3.52 moles) was added in a two-hour period to a mixture consisting of 79 g (3.44 g-atoms) of sodium dissolved in 1400 g of absolute ethanol.

After a 0.5 hr reflux period, most of the ethanol was removed by rotary evaporation. Extraction with ether, which was subsequently removed, yielded 610 g of wet diethyl methylmalonate, which included small amounts of unmethylated and dimethylated diesters as well. Basic hydrolysis, neutralization with hydrochloric acid, and exchange of the resulting diacid with deuterium oxide gave methylmalonic-2-d acid-$_2$, which was decarboxylated by refluxing at 140° for 50 hr. Distillation gave 164 g (yield, 62% from diethyl malonate) of propionic-2,2-d_2 acid-d.

B. Preparation of 1-Propanol-2,2-d_2

To a slurry of 61 g (1.6 moles) of lithium aluminum hydride in dry ether was added 96 g (1.25 moles) of propionic-2,2-d_2 acid-d. Alkaline hydrolysis of the mixture stirred at room temperature for 8 hr gave an ether phase which was decanted, dried over anhydrous sodium sulfate and distilled to give 49 g (yield, 85%) of 1-propanol-2,2-d_2.

C. Preparation of 1-Bromopropane-2,2-d_2

Method A. To 39.6 g (0.64 mole) of 1-propanol-2,2-d_2 was added 75.0 g (0.27 mole) of phosphorus tribromide at 0°. The mixture was stirred at room temperature for 18 hr. After adding 60 ml of water, the top (aqueous) layer was extracted with ether and the combined extracts were added to the lower layer. The ether phase was dried and distilled, giving 24 g (yield, 30%) of 1-bromopropane-2,2-d_2.

Method B. Twenty-seven grams (0.10 mole, 13% excess) of phosphorus tribromide was added in 50 min. to ice-cooled 1-propanol-2,2-d_2 (16.4 g, 0.264 mole). After stirring at room temperature for 22 hr, then at gentle reflux for 1 hr, 30 ml of water was added to the two-phase liquid mixture. The clear, lower (bromide) layer was separated and washed with water and saturated solutions of sodium chloride and sodium bicarbonate. The 1-bromopropane-2,2-d_2 (26 g, 80% yield) was purified by distillation at 68-69°.

D. Preparation of Butyronitrile-3,3-d_2

A solution of 20.0 g (0.16 mole) of 1-bromopropane-2,2-d_2 in 26 ml of methanol was added to 8.6 g (0.18 mole) of sodium cyanide dissolved in 11 ml of water. After refluxing 20.5 hr at 115°, the mixture was extracted continuously with ether for 40 hr. The ether phase was washed with solutions of hydrochloric acid, sodium bicarbonate and sodium chloride (which removed side-product isonitrile as well as methanol), dried and distilled, yielding 10 g (80%) of butyronitrile-3,3-d_2.

E. Preparation of 1-Butyl-3,3-d_2-ammonium Perchlorate

Butyronitrile-3,3-d_2 (5.41 g, 0.076 mole) in ether was slowly added to 3.6 g (0.095 mole) of lithium aluminum hydride in dry ether. The reaction mixture was stirred at reflux temperature for 4.5 hr, then at room temperature for 4 hr, and hydrolyzed with base. After standing overnight,

the ether phase and ether washings of the aqueous paste were combined and neutralized with 71% perchloric acid. White crystals of 1-butyl-3,3-$\underline{d}_2$-ammonium perchlorate, mp 189-191°, resulted from solvent removal and washing with petroleum ether. The yield was 11.8 g (89%).

V. Preparation of 2-Butyl-2-$\underline{d}$-ammonium Perchlorate

To a slurry of 4.9 g (0.12 mole) of lithium aluminum deuteride in dry di-$\underline{n}$-butyl ether was added 10.2 g (0.12 mole) of 2-butanone oxime in di-$\underline{n}$-butyl ether. After stirring for 5 hr at 150°, the brown product mixture was hydrolyzed with base. The decanted ethereal phase was dried and distilled to give a 4.5 g fraction, bp 65-70°, containing 85% 2-butyl-2-$\underline{d}$-amine (yield, 50%).

Neutralization with 3.4 ml 71% perchloric acid (0.061 mole) gave a slurry of perchlorate salt in di-$\underline{n}$-butyl ether. Because removal of solvent was difficult, the salt was dissolved in water and the organic materials were removed by extraction with ether. The resulting aqueous solution was then subjected to deamination conditions.

VI. Preparation of 2-Butyl-3,3-$\underline{d}_2$-ammonium Perchlorate

A. Preparation of Ethanol-1,1-$\underline{d}_2$

An ethereal solution of 30.4 g (0.298 mole) of acetic anhydride was slowly added to an ice-cooled slurry of 11.4 g (0.271 mole) of lithium aluminum deuteride in dry ether.

The mixture was refluxed for 8 hr, hydrolyzed with base, and stirred overnight. The ether phase was decanted and combined with the Soxhlet ether extracts of the inorganic salts. Distillation, after drying over anhydrous magnesium sulfate, gave 15.9 g (yield, 62%) of ethanol-1,1-$\underline{d_2}$.

B. Preparation of Bromoethane-1,1-$\underline{d_2}$

Phosphorus tribromide (34.9 g, 0.129 mole, 16% excess) was added dropwise to 15.9 g (0.332 mole) of ethanol-1,1-$\underline{d_2}$ at 0^0. The mixture was brought to room temperature and stirred for 45 hr. After refluxing gently for 45 min. and adding 35 ml of water, the mixture was transferred to a separatory funnel and the lower bromide layer drawn off. The yield of bromoethane-1,1-$\underline{d_2}$ was 22.2 g (60%).

C. Preparation of 1-Butanol-3,3-$\underline{d_2}$

To 24 g (0.22 mole) of magnesium turnings was added 22.2 g (0.20 mole) of bromoethane-1,1-$\underline{d_2}$ in dry ether. The resulting grey solution was refluxed for 0.5 hr and cooled. To it was added 9.70 g (0.20 mole) of acetaldehyde in ether. After refluxing for 1.5 hr and hydrolyzing with aqueous ammonium chloride, the mixture was separated into an ether phase and a slurry of inorganic salts. The salts were extracted thoroughly with ether. The ether phases were combined, dried, and distilled to give 8.2 g (yield, 54%) of 2-butanol-3,3-$\underline{d_2}$.

D. Preparation of 2-Butyl-3,3-d_2 p-toluenesulfonate

A mixture of 23.0 g (0.121 mole) of p-toluenesulfonyl chloride and 40 ml of pyridine was added slowly to 8.2 g (0.12 mole) of 1-butanol-3,3-d_2 in 20 ml of pyridine. The reaction mixture was maintained at -5^0, or below, during the addition and subsequent 0.5 hr period of stirring. After allowing to stand at -10^0 for 17 hr, the mixture was added to 50 ml of water and the organic materials were extracted with ether. Careful washing of the combined ether phases with aqueous solutions of hydrochloric acid (6 N) and sodium chloride was followed by removal of solvent by rotary evaporation. About 24.8 g of 2-butyl-3,3-d_2 p-toluenesulfonate (yield, 90%) was obtained.

E. Preparation of 2-Butyl-3,3-d_2-azide

A mixture of 11.0 g (0.169 mole) of sodium azide, 40 ml of water, and 100 ml of methanol was heated to 60^0. To it was added 14.8 g (0.108 mole) of 2-butyl-3,3-d_2 p-toluenesulfonate in 40 ml of methanol. Reflux was maintained during the addition and for another 16 hr. After cooling the product mixture to room temperature, 80 ml of water was added and the resulting mixture was taken up in ether. A solution consisting of 40 g of calcium chloride in 100 ml of water was added and the resulting phases were separated. The ether layer was combined with the ether extracts of the aqueous phase and dried over anhydrous magnesium sulfate. Because of its unstable properties the azide was not isolated.

F. Preparation of 2-Butyl-3,3-d_2-ammonium Perchlorate

The ethereal azide described above was added to a cold slurry of 5.0 g (0.13 mole) of lithium aluminum hydride in dry ether. After refluxing for 4 hr, the mixture was hydrolyzed with base and stirred overnight. The ether layer was decanted and combined with the ether washings of the inorganic salts. Neutralization with 71% perchloric acid and evaporation of solvent left a brown slurry containing ca. 3.1 g of 2-butyl-3,3-d_2-ammonium perchlorate (yield, 30% from 2-butyl-3,3-d_2 p-toluenesulfonate). The perchlorate salt was not isolated and purified, but was dissolved in water and the solution was extracted thoroughly with ether. After removing remaining traces of ether by heating on a steam bath for 5 min, the aqueous solution was subjected to deamination conditions.

VII. Preparation of Authentic, Deuterated Alcohols

A. Preparation of 1-Butanol-1,1-d_2

An ethereal solution containing 1.1 g (0.012 mole) of butyric acid was slowly added to a cold slurry of 0.41 g (0.0098 mole) of lithium aluminum deuteride in dry ether. After addition, the mixture was stirred at reflux for 4 hr and allowed to stand overnight. After alkaline hydrolysis the ether phase was dried over anhydrous magnesium sulfate and distilled to give 0.2 g of 1-butanol-1,1-d_2.

B. Preparation of 1-Butanol-2,2-d_2

To cold slurry of 1.35 g (0.036 mole) of lithium aluminum hydride in dry ether was slowly added 4.3 g (0.047 mole) of butyric-2,2-d_2 acid-d. After 12 hr of reflux and alkaline hydrolysis, the ether phase was decanted, dried, and distilled, affording 0.25 g of 1-butanol-2,2-d_2.

C. Preparation of 1-Butanol-3,3-d_2

A mixture of 0.80 g (0.011 mole) of butyronitrile-3,3-d_2, 5 ml of 85% phosphoric acid and 3 ml of 75% sulfuric acid was slowly heated to 165°, at which temperature it was refluxed for 1.5 hr. Extraction with ether of the mixture that was diluted with water afforded an ethereal solution of butyric-3,3-d_2 acid, which was dried and added to 0.43 g (0.11 mole) of lithium aluminum hydride in dry ether. Careful distillation of the decanted ether phase yielded 0.14 g of 1-butanol-3,3-d_2.

D. Preparation of 1-Butanol-2-d

To 0.94 g (0.022 mole) of lithium aluminum deuteride in dry ether was added a solution of 1.61 g (0.022 mole) of 1-butanone in ether. The mixture was refluxed for 6 hr, then allowed to stand overnight. After alkaline treatment, the ether phase was separated from the aqueous paste, dried and distilled. The yield of 2-butanol-2-d was 0.9 g.

VIII. Deamination of Butylammonium Perchlorates

A typical run consisted of placing 21.5 g (0.123 mole) of deuterated 1-butylammonium perchlorate, 15.4 g (0.109 mole) of 71% perchloric acid and 60 g of water in a 3-necked, 250 ml flask equipped with condenser, addition funnel, thermometer and magnetic stirrer. Sodium nitrite (17.7 g, 0.257 mole, Mallinckrodt) dissolved in 40 g of water was added dropwise over a two-hour period, during which the reaction temperature generally rose to 35-38°. After an additional three hours of stirring, the solution was salted out with sodium chloride and extracted with ether. The combined ether layers were washed with saturated solutions of sodium chloride and sodium bicarbonate. The ethereal solution, which usually remained straw yellow, was dried over anhydrous magnesium sulfate and distilled until a liquid residue of approximately 2 ml remained. This residue was fractionated on a preparative gas chromatograph, by using a nine-foot column of 25% Carbowax at 115°, which permitted collection of 1-butanol and 2-butanol either individually or together. If necessary, the alcohols were further purified by preparative gas chromatography at the above conditions.

Hexamethyldisilazane (Metallomer Laboratories) and alcohol (either pure or a mixture of 1- and 2-butanol), in a 1:2 molar ratio, respectively, were refluxed overnight with a drop of chlorotrimethylsilane. The trimethylsilyl

ethers were then separated, if necessary, and purified by gas chromatography on a 20-foot Carbowax column at 85°.

Deaminations of the 2-butylammonium perchlorates were carried out under the same conditions. Work up was also similar, the only difference being that the only alcohol detected (by analytical gas chromatography) was 2-butanol, which was collected and derivatized with hexamethyldisilazane as above.

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