# Carbonium Ions. XV. The Deamination of Deuterium-Labeled 1-Pentyl and 1-Hexylamines. Protonated Cyclopropanes and Intramolecular 1,2-Hydride Shifts

Gerasimos J. Karabatsos, Mona Anand, Donald O. Rickter, and Seymour Meyerson

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan, and the Research and Development Department, American Oil Company, Whiting, Indiana. Received July 2, 1969

Abstract: The aqueous acid deaminations of 1-pentyl-1,1-d_2-, -2,2-d_2-, and -3,3-d_2-amine gave mixtures of pentanols, consisting of about 60% 1-pentanol, 30–35% 2-pentanol, and 5–10% 3-pentanol. Mass spectral analysis of the trimethylsilyl ether derivatives of the product 1-pentanols showed that these alcohols were exclusively isotope-position unrearranged, i.e., they had the labels at the same carbon as the starting amines. Similarly, mass spectral analysis of the trimethylsilyl ether derivative of the 1-hexanol obtained from the deamination of 1-hexyl-1,1-d_2-amine showed that this alcohol was exclusively isotope-position unrearranged. Mass spectral analysis of the trimethylsilyl ether derivatives of the secondary alcohols revealed that these alcohols were extensively isotope-position rearranged. The results have been interpreted in terms of reversible 1,2-hydride shifts with no 1,2-alkyl, or 1,3-, 1,4-, 1,5- or 1,6-hydride shifts. The secondary carbonium ion formed from the normal alkyl system undergoes only two detectable 1,2-hydride shifts, the substitution product arising from a third shift contributing less than 0.1% to the yield of secondary alcohols. These intramolecular 1,2-hydride shifts are subject to strong conformational control, they exhibit k_H/k_D isotope effects of about 1.2–1.4, and they occur faster in the smaller alkyl than in the larger systems. The last conclusion seems best interpreted in terms of different amounts of excess vibrational energy in the carbon–hydrogen bond of the migrating hydrogen.

The protonated cyclopropane I has been shown not to intervene in formation of the 1- and 2-butanols obtained from the aqueous acid deamination of isotopically labeled 1-butylamines.[1]
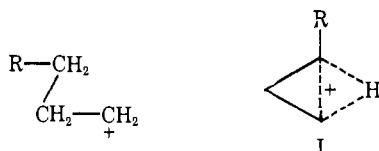
This paper reports results from the deamination of labeled 1-pentyl- and 1-hexylamines, which we studied with the following objectives. 1. Corroboration of the results obtained and conclusions drawn from the deamination of 1-butylamines with regard to the intermediacy of protonated cyclopropanes. 2. Assessment of the extent to which intramolecular 1,5-hydride shifts may occur in the system (II), as such shifts in simple, acyclic systems are rare. The only authenti-
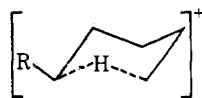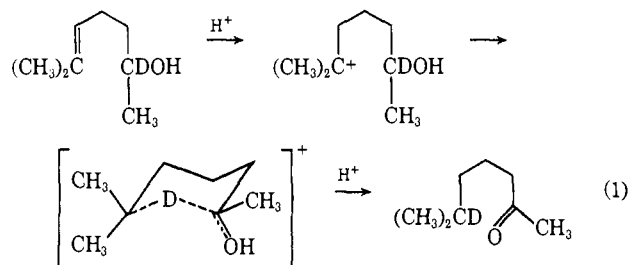
II, R = H, CH₃

cated case of such a shift, other than those involving monocyclic,[2] polycyclic,[3] and partly aromatic[4] systems,

is the acid-catalyzed conversion of some enols to ketones,[5] as illustrated by sequence 1. 3. Evaluation of

the relative rates of 1,2-hydride shifts interconverting secondary carbonium ions, and the factors influencing such shifts.

Results

Deamination of 1-Pentylamines. The deamination of 1-pentylamines with sodium nitrite in aqueous perchloric acid gave olefins (about 30%), 1-pentanol, 2-pentanol, 3-pentanol, and small amounts of the corresponding nitrites, nitrates, and nitroalkanes. The proportions of the three alcohols are summarized in Table I. The primary-to-secondary ratios were deter-

Table I. Alcohol Ratios from the Deamination of 1-Pentylamines

Amine	1-Pentanol: 2 + 3- pentanol	2-Pentanol: 3- pentanol
CH₃CH₂CH₂CH₂CD₂NH₂	1.38	4.35
CH₃CH₂CH₂CD₂CH₂NH₂	1.50	4.13
CH₃CH₂CD₂CH₂CH₂NH₂	1.29	6.35

(1) G. J. Karabatsos, R. A. Mount, D. O. Ricketer, and S. Meyerson, J. Amer. Chem. Soc., 92, 1248 (1970).

(2) For recent reviews see: A. C. Cope, M. M. Martin, and M. A. McKervey, Quart. Rev. (London), 20, 119 (1966); V. Prelog and J. G. Traynham in "Molecular Rearrangements," Vol. I, Part 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 593–615.

(3) R. C. Cookson and E. Crundwell, Chem. Ind. (London), 703 (1959); S. Winstein and R. L. Hansen, J. Amer. Chem. Soc., 82, 6206 (1960); G. Ourisson, Proc. Chem. Soc., 274 (1964); D. Hemlinger and G. Ourisson, Amer. Chem., 686, 19 (1965); R. A. Appleton and S. H. Graham, Chem. Commun., 297 (1965); R. A. Appleton, J. R. Dixon, J. M. Evans, and S. H. Graham, Tetrahedron, 23, 805 (1967).

(4) R. L. Letsinger and P. T. Lansbury, J. Amer. Chem. Soc., 81, 935 (1959); T. Cohen, R. M. Moran, Jr., and G. Sowinski, J. Org. Chem., 26, 1 (1961).

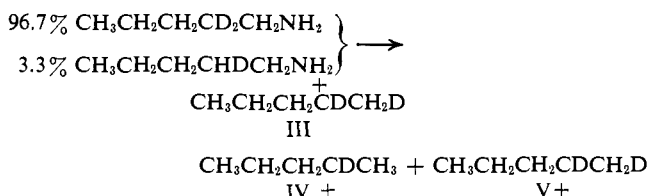(5) R. K. Hill and R. M. Carlson, J. Amer. Chem. Soc., 87, 2772 (1965).

Table II. Label Distributions[a] in the Trimethylsilyl Ethers of 1-Pentanols and 1-Hexanols

No.	Compound	Parent − methyl, %			Parent − butyl, %		
		d_2	d_1	d_0	d_2	d_1	d_0
1	$CH_3CH_2CH_2CH_2CD_2OSi(CH_3)_3$[b]	98.2	1.7	0.1	94.0	3.3	2.7
2	$CCCCCOSi(CH_3)_3$[c]	97.3	2.0	0.7	93.4	3.6	3.0
3	$CH_3CH_2CH_2CD_2CH_2OSi(CH_3)_3$[d]	97.3	2.4	0.3	1.2	1.8	97.0
4	$CCCCCOSi(CH_3)_3$[e]	96.5	3.3	0.2	1.3	1.8	96.9
5	$CH_3CH_2CD_2CH_2CH_2OSi(CH_3)_3$[f]	97.6	2.0	0.4	0.3	0.2	99.5
6	$CCCCCOSi(CH_3)_3$[g]	97.9	2.0	0.1	0.3	0.4	99.3
7	$CH_3CH_2CH_2CH_2CH_2CD_2OSi(CH_3)_3$[h]	98.2	1.6	0.2	95.4[j]	2.7	1.9
8	$CCCCCCOSi(CH_3)_3$[i]	97.0	2.9	0.1	93.9[j]	4.2	1.9

[a] Calculated from 70-V mass spectra. [b] Derivative of 1-pentanol-1,1-d_2 prepared by reduction of pentanoic acid with lithium aluminum deuteride. [c] Derivative of 1-pentanol from the deamination of 1-pentyl-1,1-d_2-amine. [d] Derivative of 1-pentanol-2,2-d_2 prepared by reduction of pentanoic-2,2-d_2 acid with lithium aluminum hydride. [e] Derivative of 1-pentanol from the deamination of 1-pentyl-2,2-d_2-amine. [f] Derivative of 1-pentanol-3,3-d_2 prepared by reduction of pentanoic-3,3-d_2 acid with lithium aluminum hydride. [g] Derivative of 1-pentanol from the deamination of 1-pentyl-3,3-d_2-amine. [h] Derivative of 1-hexanol-1,1-d_2 prepared by reduction of hexanoic acid with lithium aluminum deuteride. [i] Derivative of 1-hexanol from the deamination of 1-hexyl-1,1-d_2-amine. [j] Parent − pentyl ions.

Table III. Label Distributions[a] in the Trimethylsilyl Ethers of 2- and 3-Pentanols

No.	Compound	Parent − methyl, %			Parent − ethyl, %			Parent − propyl, %		
		d_2	d_1	d_0	d_2	d_1	d_0	d_2	d_1	d_0
1	$CH_3CH_2CH_2CD(CH_3)OSi(CH_3)_3$[b]	0.0	99.1	0.9				0.0	99.3	0.7
2	$(CH_3CH_2)_2CDOSi(CH_3)_3$[c]	0.0	96.7	3.3	0.0	93.7	6.3			
3	2- + 3-pentanol-Si(CH_3)_3[d]	78.5	1.8	19.7	49.4	1.3	49.3	91.8	2.5	5.7
4	2- + 3-pentanol-Si(CH_3)_3[e]	76.1	23.9	0.0	50.4	1.9	47.7	90.8	4.7	4.4
5	2- + 3-pentanol-Si(CH_3)_3[f]	98.5	1.5	0.0	48.2	48.3	3.3	0.0	1.0	99.0

[a] Calculated from 70-V mass spectra. [b] Derivative of the alcohol prepared by reduction of 2-pentanone with lithium aluminum deuteride. [c] Derivative of the alcohol prepared by reduction of 3-pentanone with lithium aluminum deuteride. [d] Derivative of the mixture of 2- and 3-pentanols obtained from the deamination of 1-pentyl-1,1-d_2-amine. [e] Derivative of the mixture of 2- and 3-pentanols obtained from the deamination of 1-pentyl-2,2-d_2-amine. [f] Derivative of the mixture of 2- and 3-pentanols obtained from the deamination of 1-pentyl-3,3-d_2-amine.

mined by gas chromatography and the 2- to 3-pentanol ratios by mass spectrometry and by gas chromatography. The corresponding 2-hexanol:3-hexanol ratio from the deamination of 1-hexyl-1,1-d_2-amine was found by mass spectrometry to be 5.

The alcohols were converted to the trimethylsilyl ether derivatives for mass spectral analysis.

Mass Spectral Analysis of 1-Pentanols and 1-Hexanols. In Table II are summarized the label distributions in the parent − methyl and parent − butyl ions of the trimethylsilyl ethers of various 1-pentanols along with those (entries **7** and **8**) of the parent − methyl and parent − pentyl ions of the trimethylsilyl ethers of authentic 1-hexanol-1,1-d_2 and 1-hexanol obtained from the deamination of 1-hexyl-1,1-d_2-amine. In all cases the primary alcohol product is exclusively isotope-position unrearranged, i.e., it has the label at the same position as the starting amine, as shown below

$$CH_3CH_2CH_2CH_2CD_2NH_2 \longrightarrow CH_3CH_2CH_2CH_2CD_2OH$$
$$100\% \ d_2 \qquad\qquad 100\% \ d_2$$

$$CH_3CH_2CH_2CH_2CH_2CD_2NH_2 \longrightarrow CH_3CH_2CH_2CH_2CH_2CD_2OH$$
$$100\% \ d_2 \qquad\qquad 100\% \ d_2$$

On the assumption that the parent − methyl ion arises solely by loss of methyl from the trimethylsilyl group, the parent − methyl label distribution constitutes an isotopic analysis of the alcohol. The label distributions of the parent − butyl ions of the authentic alcohols (entries **1, 3, 5**) show that this ion does not arise solely by primary loss of the butyl radical from the pentyl group. Thus, the label distribution of the parent − butyl ion of **1** is not identical with that of the parent − methyl. Instead, the d_1 and d_0 contents of the parent

− butyl ion yields are higher by 1.6% and 2.6%, respectively. The same is true—1.6% d_1 and 2.3% d_0—in case **2**.

Mass Spectral Analysis of 2- and 3-Pentanols. Because clean chromatographic separation of the 2- and 3-pentanols, or their trimethylsilyl ether derivatives, could not be accomplished readily, the two alcohols were collected together and their trimethylsilyl ethers were analyzed as a mixture. In Table III are summarized the label distributions in the parent − methyl, parent − ethyl, and parent − propyl ions of these mixtures, along with those of the derivatives of authentic 2-pentanol-2-d_1 and 3-pentanol-3-d_1. The parent − propyl ions are derived almost solely from the 2-pentanol derivatives and the parent − ethyl almost solely from the 3-pentanol derivatives. We have used these label distributions to estimate the per cent of each isotopic species present in the mixture. In so doing, we assumed that the alcohols did not arise by 1,3- or 1,4-hydride shifts. In view of the absence of 1,3 shifts in the deamination of 1-butylamine,[1] this assumption seems reasonable.

On the assumption that the 2-pentanol isotopic species arise from 1,2-hydride shifts interconverting secondary carbonium ions, the percentages of these alcohols can be estimated from the label distributions in the parent − methyl and parent − propyl ions. From entry **3** it can be concluded that the parent − methyl ion of the ether of 2-pentanol arises about 21.3% [19.7 × 100/(98 − 5.7)] by loss from the 2-pentyl group and 78.7% loss from the trimethylsilyl group.[6] These

(6) In this calculation, we are ignoring the 3-pentanol contributions to parent − methyl intensity, perhaps 5–10% of the total. The 3-pen-

Table IV. Isotopic Composition of 2- and 3-Pentanols from the Deamination of 1-Pentylamines

Amine	2- and 3-pentanols

$CH_3CH_2CH_2CH_2CD_2NH_2 \rightarrow CH_3CH_2CH_2CHCHD_2 + CH_3CH_2CHCH_2CHD_2 + CH_3CHCH_2CH_2CHD_2$

                  |OH |OH |OH

100% d_2 77.3%   18.7%   4.0%

$CH_3CH_2CH_2CD_2CH_2NH_2 \rightarrow CH_3CH_2CH_2CDCH_2D + CH_3CH_2CHCHDCH_2D \} + CH_3CHCH_2CHDCH_2D + CH_3CH_2CHDCHCH_2D$

                  |OH |OH |OH |OH

100% d_2 76.9%   +   } 19.5%   2.7%   0.9%

$CH_3CH_2CDCH_2CH_2D$

              |OH

$CH_3CH_2CD_2CH_2CH_2NH_2 \rightarrow CH_3CH_2CD_2CHCH_3 \} + CH_3CH_2CDCHDCH_3 + CH_3CH_2CHDCDCH_3$

                  |OH |OH |OH

100% d_2 +   } 85.6%   13.6%   0.8%

$CH_3CHCHDCHDCH_3$

              |OH

values are similar to the 21 and 79% observed for the loss of methyl from the trimethylsilyl ether of 2-butanol.[1]

Two serious difficulties arise in the calculation of the isotopic species of the 2-pentanols: (1) the possibility that some of the parent—propyl ions might arise *via* processes other than primary loss of the propyl group and (2) assessment of the isotopic purity—that is, per cent of doubly, singly, and unlabeled molecules—of the product 2-pentanols, especially in case **4**. For example, the isotopic purity of the starting amine from which this alcohol was obtained was about 96.7% d_2 and 3.3% d_1 (entry **4**, Table II). However, because of a k_H/k_D effect in the hydride shift, the initial 2-pentyl cations, III, IV, and

96.7% $CH_3CH_2CH_2CD_2CH_2NH_2$ $\}$ $\longrightarrow$
3.3% $CH_3CH_2CH_2CHDCH_2NH_2$ $\}$

$\overset{+}{CH_3CH_2CH_2CDCH_2D}$
III

$CH_3CH_2CH_2CDCH_3 + CH_3CH_2CH_2CDCH_2D$
     IV +   V+

V, are presumably not formed in the ratios 97.7% III and 3.3% (IV + V). The values that we have summarized in Table IV, therefore, are based on the assumption that the parent — propyl ion arises exclusively by primary loss of a propyl group, and that the k_H/k_D effect is about 1.3. The value 1.3 was chosen to agree with those calculated for the butyl systems.[1]

The mixture of 2- and 3-hexanols obtained from the deamination of 1-hexyl-1,1-d_2-amine was found by gas chromatography to be 83.3% 2-hexanol and 16.7% 3-hexanol. Their trimethylsilyl ether derivatives (mixture) were subjected to mass spectral analysis and gave the following results: parent — methyl, 75.5% d_2, 2.0% d_1, and 22.5% d_0; parent — ethyl, 4.1% d_2, 0.8% d_1, and 95.1% d_0; parent — propyl, 93.6% d_2, 4.9% d_1, and 1.5% d_0; and parent — butyl, 97.1% d_2 and 2.9% d_1. The parent — butyl ion arises almost solely from the 2-hexanol derivative, and the parent — ethyl and parent — propyl almost solely from the 3-hexanol

tanol contributions to the parent — propyl intensity is of the order of 0.1% of the total in all cases, and so can be safely ignored. Corrections for 3-amyl contribution to $[M - CH_3]^+$ intensity would lead to 22.5–23.7% instead of 21.3%.

derivative. If these values are treated in a fashion analogous to that by which were treated the results from the 2- and 3-pentanol derivatives, they give the following

$CH_3CH_2CH_2CH_2CH_2CD_2NH_2 \longrightarrow CH_3CH_2CH_2CH_2CHCD_2 +$
      100% d_2 |OH

                                           83.1%

$CH_3CH_2CH_2CHCH_2CHD_2 + CH_3CH_2CHCH_2CH_2CHD_2$
        |OH |OH
     15.9%   1.0%
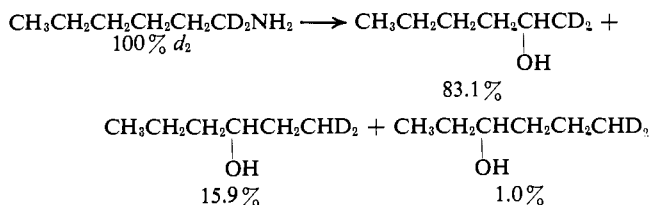
From the finding that the label distribution in the parent — butyl ion contains 0 per cent d_0, species VI must be absent.

$CH_3CHCH_2CH_2CH_2CHD_2$
     |OH
       VI
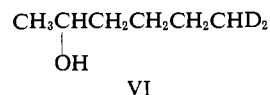
Discussion

The failure to detect any isotope-position rearranged primary alcohols rules out 1,2-alkyl shifts, 1,5-hydride (pentyl system), and 1,6-hydride (hexyl system) shifts. The absence of VI also mitigates against the occurrence of 1,5-hydride shifts as in II (R = methyl). The occurrence of such a shift in the treatment of the enols[5] with acid (sequence 1), but not in the deamination of 1-hexylamine, must be ascribed to the greater stability (tertiary carbonium ion) and longevity of the carbonium ion generated in the sulfuric acid, and to the greater driving force for the 1,5-hydride shift as a result of stabilization by the hydroxyl group of the positive charge generated at the migration origin. It is becoming more and more clear that the criteria that are of prime importance in determining the facility of hydride shifts of orders higher than 1,2 and 1,3 in relatively reactive carbonium ions are, in addition to steric and torsional effects, the proximity of the migrating hydrogen to the carbon bearing the positive charge and, concomitantly, a favorable geometrical arrangement that meets the stereoelectronic requirements of the transition state for such a hydride shift by allowing a maximum overlap of electrons from the migrating hydrogen into the empty p orbital of the migration
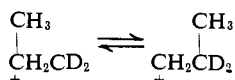
VII

cyclopropane path by alkyl substitution at C-3 of the 1-propyl system is, again, best rationalized in terms of the two eclipsing 1,2-hydrogen–alkyl interactions (VII), which destabilize the protonated cyclopropane—and, by inference increase the energy of activation needed to form it—sufficiently to make its formation less competitive with 1,2-hydride shifts and collapse of the cation to products by reaction with nucleophiles.

Intramolecular 1,2-Hydride Shifts and Isotope Effects. As was observed in the interconversion of the 2-butyl cations,[1] the intramolecular 1,2-hydride shifts inter-

terminus. It follows then that higher order shifts will be more prevalent in systems in which the potential migration origin and terminus are closely constrained, such as in cyclic systems,[2,3] rather than in the con-

Scheme I
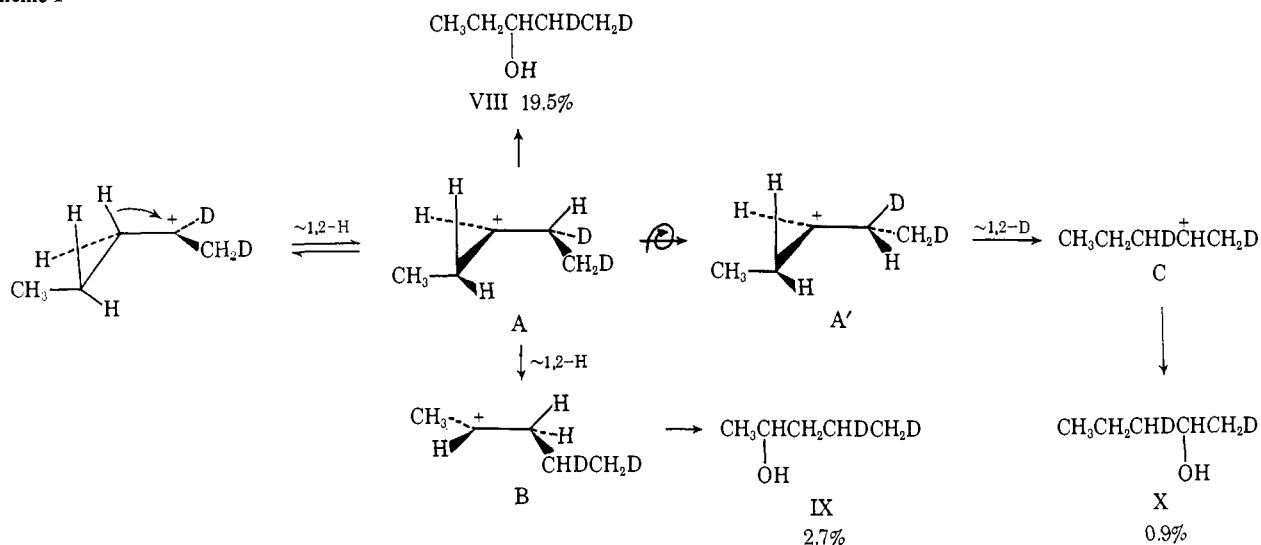
formationally flexible acyclic systems. The rate of carbon–carbon bond rotation required to position properly the hydrogen for transfer is simply too slow compared to the rate of conversion of a primary carbonium ion to a secondary or tertiary, or to the rate of nucleophilic capture of this cation. These arguments should apply not only to primary carbonium ions, but to secondary as well.[7]

Protonated Cyclopropanes. The absence of any isotope-position rearranged 1-pentanol and 1-hexanol from the deamination of their corresponding deuterium-labeled amines again rules out protonated cyclopropanes as intermediates in these systems and corroborates the results obtained and conclusions drawn from the deamination of 1-butylamine.[1] It furthermore supports, indirectly, the protonated cyclopropane mechanism proposed to explain the formation of cyclopropane and isotope-position rearranged 1-propanol in the deamination of 1-propylamine, rather than the alternative classical carbonium ion mechanism,[8] which demands that the 1,2-methyl shift, shown below, be five–ten times faster than capture of the 1-propyl cation by water.

As pointed out in our discussion of the 1-butyl system,[1] we see no reason why this 1,2-alkyl shift would now become five–ten times slower than capture of the cation by water when the group is ethyl, propyl, or butyl instead of methyl. The suppression of the protonated

(7) See also M. C. Whiting, *Chem. Brit.*, **2**, 482 (1966).
(8) G. J. Karabatsos, C. E. Orzech, Jr., J. L. Fry, and S. Meyerson, *J. Amer. Chem. Soc.*, **92**, 606 (1970).

converting various secondary pentyl cations exhibit k_H/k_D isotope effects of about 1.3–1.4. For example, the ratio of 2-pentanol to 3-pentanol is smaller from the deamination of 1-pentyl-3,3-d_2-amine than from the other amines (Table IV).

The low concentrations of the last products (Table IV) in the deamination of 1-pentyl-2,2-d_2-amine and 1-pentyl-3,3-d_2-amine confirm the conclusions drawn from the deamination of 1-butylamine[1] with regard to conformational control of the 1,2-hydride shifts. For example, let us consider the last two products from the deamination of the 2,2-d_2-amine (Scheme I). The 2.7% concentration of IX is three times higher than that of X (0.9%). Since the intramolecular k_H/k_D is only about 1.2–1.4, this difference cannot be ascribed solely to an intramolecular isotope effect. One reasonable source contributing to this large difference is the requirement that for carbonium ion A to be converted to C, which is the precursor of X, it must be converted first by rotation about the carbon–carbon bond to A′. No such process is needed to precede the conversion of A to B, as the migrating hydrogen is in a position fulfilling the stereoelectronic requirements of the rearrangement.

In summary, the following similarities and dissimilarities can be discerned among the products obtained from the deamination of 1-alkylamines.

1. The percentages of olefins obtained in the aqueous perchloric acid deaminations of 1-butyl, 1-pentyl-, and 1-hexylamine are about the same, 30 ± 5%, in all cases. The same percentage, about 30%, was also obtained from the deamination of 1-octylamine in acetic acid.[7]

2. In all four systems the ratios of primary substitution product (RCH_2Y) to the sum of the secondary

Table V. Secondary Substitution Products from the Deamination of 1-Alkylamines[a]

No.	Amine	Primary cation	Nucleophilic substitution products[b]		
1	1-Butyl[c]	$CCCC^+$ ⟶	CCC^+C →(~1,2-H)→	CC^+CC →(~1,2-H)→	CCC^+C
			↓ A, ca. 72%	↓ B, 23.2%	↓ C, ca. 5%
2	1-Pentyl[d]	$CCCCC^+$ ⟶	$CCCC^+C$ →(~1,2-H)→	CCC^+CC →(~1,2-H)→	CC^+CCC
			↓ A, 77.3%	↓ B, 18.7%	↓ C, 4.0%
3	1-Hexyl[d]	$CCCCCC^+$ ⟶	$CCCCC^+C$ →(~1,2-H)→	$CCCC^+CC$ →(~1,2-H)→	CCC^+CCC
			↓ A, 83.1%	↓ B, 15.9%	↓ C, 1.0%
4	1-Octyl[e]	$CCCCCCCC^+$ ⟶	$CCCCCCC^+C$ →(~1,2-H)→	$CCCCCC^+CC$ →(~1,2-H)→	$CCCCC^+CCC$
			↓ A, 86.1%	↓ B, 13.0%	↓ C, 0,9%

[a] The deaminations of **1, 2,** and **3** were carried out in aqueous acid (perchloric); that of **4,** ref 1, in acetic acid. [b] Products from **1, 2,** and **3** are the alcohols (the small amounts of the various nitrogen-substituted products, nitrites, nitrates, and nitroalkanes had about the same ratio as the alcohols). The products from **4** are the acetates.[8] [c] From ref 1. [d] From present work. [e] From ref 8.

substitution products are similar, varying from about 57:43 to 68:32. In the case of 1-propylamine this ratio is reversed, about 35:65.

These facts suggest that the relative rates by which the initially formed primary carbonium ions rearrange to secondary, react with nucleophiles to give substitution products, and collapse to olefins by nucleophilic attack on the α-hydrogens, are essentially independent of the length of the carbon chain, provided this chain has more than three carbon atoms. An attractive explanation of these observations can be formulated by invoking conformational control of rearrangement and product formation; i.e., the interconversion between conformers A and B by rotation about the sp²–sp³ bond is of the same magnitude or slower than the reaction paths available to them, when R is ethyl, propyl,
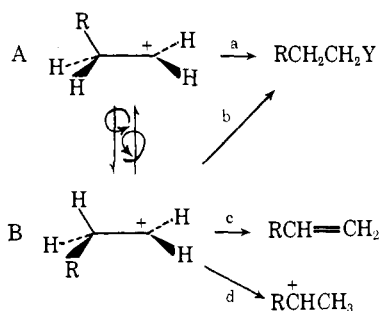
or hexyl. When R is methyl, the rotational barrier may be sufficiently low to allow extensive conformational equilibration to occur; thus, the results from the deamination of 1-propylamine, rather than those from the other amines, might be more representative of the relative rates of the various reaction paths.

3. The only major differences in the nature of the products formed in the deamination of 1-butyl-, 1-pentyl-, 1-hexyl-, and 1-octylamine are found in the ratios of the various secondary substitution products. This point is made clear by inspection of the data summarized in Table V. The ratios A:(B + C), i.e., those of the substitution products from the "initially" formed

(by 1,2-hydride shifts of the primary cations) secondary carbonium ions to those arising from carbonium ions formed by subsequent 1,2-hydride shifts, increases as the alkyl chain length of the substrate increases. They are: 77:28,[9] 77:23, 83:17, and 86:14 from the deaminations of the 1-butyl-, 1-pentyl-, 1-hexyl- and 1-octylamine, respectively. There are two reasonable explanations to account for the observed results.

A. The relative rates of nucleophilic capture vs. 1,2-hydride shift for each carbonium ion may be constant, but the rates of elimination to give olefins may be different for each cation. For example, whereas the rate of elimination from the 3-octyl cation might be appreciably faster than that from the 2-octyl cation, the rate of elimination from the "second" 2-butyl cation might be comparable to that from the "first." In order to be consistent with the results, the relative rate ratios of elimination from first:second:third secondary cations must decrease in going from the 1-butyl system to the 1-octyl system. This explanation must be rejected on the grounds that the relative ratios of products A, B, and C from the deaminations of 1-hexylamine and 1-octylamine decrease exactly as one would expect from three equilibrating carbonium ions whose relative rate ratios substitution:rearrangement:elimination are similar. Consonant with this statement are also the observations that VI is absent (<0.1%) from the deamination of 1-hexyl-1,1-d₂-amine, i.e., only two 1,2-hydride shifts interconverting secondary carbonium ions are detectable, and that the overall yields of olefins are about the same from all four systems.
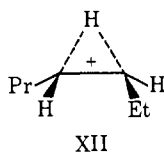
B. The relative rate ratios of substitution vs. 1,2-hydride shift are different for carbonium ions generated from different alkyl systems and increase with increase in the size of the alkyl chain. This might be brought

(9) The value 5% for C was estimated from the 1-butyl-2,2-d₂-amine. The value for C[CH₃CHDCH(OH)CH₂D] was 1.3%. However, the second rearrangement of the 2-butyl system leading to CH₃CHDC⁺HC-H₂D is conformationally controlled and subject to an isotope effect. We have, therefore, estimated the overall amount from the second rearrangement by assuming that this rearrangement is similar to that of the 1-pentyl system (see results from deamination of 1-pentyl-1,1-d₂-amine, Table IV).

about in three possible ways: (i) same rates of substitution but different rates of 1,2-hydride shifts, (ii) different rates of substitution but same rates of 1,2-hydride shifts, and (iii) different rates for both substitution and 1,2-hydride shift. We prefer the first of these, on the reasonable assumption that capture of these carbonium ions by solvent is diffusion controlled and, therefore, proceeds at the same rate for all four systems. If so, we are faced with the problem of explaining why the 1,2-hydride shift converting a 2-butyl cation to another one is faster than that converting a 2-pentyl to a 3-pentyl, which is faster than that converting a 2-hexyl to a 3-hexyl, and which, in turn, is faster than that converting a 2-octyl to a 3-octyl. We can suggest two possible explanations for this. 1.

XI
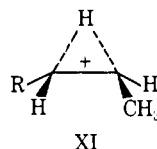
As R increases from methyl to ethyl to propyl to pentyl (XI), the corresponding energies of activation for the 1,2-hydride shift also increase because of increased R↔H vicinal nonbonded interactions. We do not particularly favor this interpretation, as the same effect should have been operative in the conversion of the 3-octyl to the 4-octyl cation (XII), thus making this conversion slower than that of the 2-octyl to the 3-octyl.

XII

However, as pointed out, the concentrations of A, B, and C (Table V, entry 4) suggest that the relative rate ratios of substitution–rearrangement for the three octyl cations are the same.

2. The carbonium ions generated from the four alkyl systems differ in the amount of excess vibrational energy that is located in each bond, i.e., the energy in the carbon–hydrogen bond involved in the rearrangement of the 2-butyl cation is higher than that in the corresponding bond of the 2-octyl cation because the latter cation is able to distribute its excess energy among more bonds. We find this interpretation attractive and preferable to the one that requires different degrees of solvation for these carbonium ions. We see no good reason why the 2-octyl cation should be better solvated and react faster with water than the 2-butyl cation. If such a difference in reactivity were to exist, it should favor the 2-butyl rather than the 2-octyl.

If the above interpretation is correct, then one would expect that, as the alkyl chain becomes progressively larger, the extent of the 1,2-hydride shift of the secondary carbonium ions generated from the deamination of primary amines would approach that of the secondary carbonium ions generates under normal solvolytic reactions of the corresponding primary compounds in the same solvents. This point remains to be tested.

Finally, the results argue against the intervention of path a, i.e., of a 2-substituted product by concerted 1,2-hydride shift and nucleophilic attack at C-2, to any great extent. Had it been so, the amount of A (Table V) with respect to B and C would have been much larger than experimentally found.
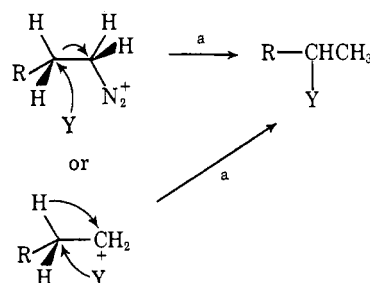
Experimental Section

Preparation of Trimethylsilyl Ethers. Trimethylsilyl ethers of the alcohols were prepared by adding a drop of trimethylchlorosilane to a 2:1 molar mixture of alcohol and hexamethyldisilazane in a small flask that was fitted with a water-cooled condenser attached to a drying tube. The mixture was heated on a steam bath overnight. The silyl ethers were collected by vapor phase chromatography using a 20 ft × ¹/₄ in. 20% Carbowax 20M on 60–80 Chromosorb W column.

Preparation of 1-Pentyl-1,1-d_2-ammonium Perchlorate. Lithium aluminum deuteride (0.12 mol) was placed in 250 ml of anhydrous ether in a 500-ml three-necked flask equipped with a water-cooled condenser fitted with a drying tube, a Teflon bladed Tru-bore stirrer, and an addition funnel with equalizing arm. A solution of 0.12 mol of valeronitrile in 30 ml of anhydrous ether was added dropwise at 0° to the rapidly stirred slurry of lithium aluminum deuteride in ether. The mixture was refluxed for 3 hr on a steam bath and stirred at room temperature for an additional 3 hr. It was then hydrolyzed at 0° by adding 8 ml of water, 5 ml of 20% sodium hydroxide solution, and, finally, 10 ml of water. After decanting the supernatant ether solution, the white inorganic solid was stirred three times with 15-ml portions of ether. The ether extract was mixed and dried over anhydrous magnesium sulfate. After neutralization of the ethereal solution with 71% perchloric acid and evaporation of the ether and water on a rotary evaporator at 80°, crystals of 1-pentyl-1,1-d_2-ammonium perchlorate were obtained. The crystals were washed with petroleum ether and dried in vacuo to yield 16.5 g of 1-pentyl-1,1-d_2-ammonium perchlorate.

Preparation of 1-Pentyl-2,2-d_2-ammonium Perchlorate. This perchlorate was prepared by reduction of valeronitrile-2,2-d_2 with lithium aluminum hydride and subsequent treatment of the amine as described above (preparation of 1,1-d_2 compound). The valeronitrile was prepared by established procedures: propylmalonic acid was converted to propylmalonic-2-d_1 acid-d_2 by repeated exchange with deuterium oxide. The acid was converted to pentanoic-2,2-d_2 acid-d_1 by decarboxylation at 140°. Conversion of the acid to the acid chloride with thionyl chloride, of the acid chloride to the amide with sodium hydroxide, and of the amide to the nitrile with thionyl chloride was effected in overall 35% yield.

Preparation of 1-Pentyl-3,3-d_2-ammonium Perchlorate. This perchlorate was prepared by reduction of valeronitrile-3,3-d_2 with lithium aluminum hydride and subsequent treatment of the amine as described above (preparation of 1,1-d_2 compound). The nitrile was prepared by the following sequence: 1-butanol-2,2-d_2 to 1-butyl-2,2-d_2 bromide to pentanoic-3,3-d_2 acid to acid chloride to amide to nitrile.

All other labeled compounds used in this study were also prepared by well-established standard procedures.

Deamination of 1-pentyl- and 1-hexylamines was carried out according to the procedure of Roberts and Halmann.[10] The reaction temperature was generally 35–40°. Product alcohols were extracted from the aqueous mixture with ether; then, after solvent removal, they were collected by preparative gas chromatography

(10) J. D. Roberts and M. Halmann, J. Amer. Chem. Soc., 75, 5759 (1953).

through a 6-ft column of 25% Carbowax 20M on 60–80 Chromosorb W.

Mass Spectral Analysis. Mass spectral analysis of the isotopically labeled compounds was done with 70-V electrons with a Consolidated Model 21-103C spectrometer. Source and inlet temperatures were both 250°.

Weak Bases in Strong Acids. III.[1] Heats of Ionization of Amines in Fluorosulfuric and Sulfuric Acids. A New General Basicity Scale[2]

Edward M. Arnett, Roderic P. Quirk, and John J. Burke[3]

Contribution from the Department of Chemistry, University of Pittsburgh, and Mellon Institute, Pittsburgh, Pennsylvania 15213. Received August 9, 1969

Abstract: Some inherent difficulties in determining the pK_a's of weak organic bases by acidity function methods are examined. The heat of protonation in an appropriate strong acid is proposed as an alternative criterion of base strength. As a test of this proposition, enthalpies of protonation for 35 amines, both aliphatic and aromatic, have been measured calorimetrically at 25° in pure fluorosulfuric acid and concentrated sulfuric acid. A good linear correlation between these enthalpies and the pK_a values of the corresponding conjugate acids in water is found spanning a range of 40 kcal/mole in enthalpy and 22 pK_a units. The correlation coefficient is 0.992. The significance of enthalpy-free energy correlations is discussed. Such diverse types of compounds as primary, secondary, and tertiary aromatic and aliphatic amines, pyridines, cyclopropenones, nitroaromatics, phosphine oxides, and acid chlorides fit the ΔH–pK_a correlation and it is used to estimate the pK_a's (± 0.7) of alcohols, ethers, water, and triphenylamine.

The transfer of protons from Bronsted acids to basic molecules in solution is probably the most important and general reaction in chemistry.[4] All organic compounds are acids or bases (or both) and their ability to undergo proton transfer is an important criterion of their reactivity. Accurate measurements of proton transfer thermodynamics are, therefore, of fundamental chemical interest. They are also essential for the detailed kinetic interpretation of acid- and base-catalyzed reactions which, in turn, comprise the largest single class of reaction mechanisms in organic and biological chemistry.[5]

The aqueous pH scale is the traditional standard of reference for determination of pK_a's of acid–base equilibria.[6] However, less than a half-dozen of the hundred-odd functional groups commonly encountered in organic chemistry ordinarily give measurable protolysis in the pH range of proton activity, although it has

been known for years that most of them are completely protonated in concentrated sulfuric acid.[7] Hammett's suggestion[8] that the pH range be extended to strong aqueous sulfuric acid solutions through an indicator-based acidity function was, therefore, a reasonable approach to the quantitative comparison of weak bases. Despite three decades of effort by many ingenious experimenters, the strengths of most classes of weak organic bases are poorly defined. The refined acidity function developed by Jorgenson and Hartter[9] for primary aniline indicators has not proven to be generally applicable to other families of bases in concentrated aqueous acid solutions. Its failure has been demonstrated for tertiary aromatic amines,[10] pyrroles,[11] indoles,[12] azulenes,[13] esters,[14] amides,[15] ketones,[16] alde-

(1) Previous paper in this series: E. M. Arnett and J. J. Burke, *J. Am. Chem. Soc.*, **88**, 4308 (1966).

(2) Supported by N. S. F. Grant GP-6550X and NIH Grant GM-10872.

(3) Taken in part from the thesis of J. J. Burke, University of Pittsburgh, 1966.

(4) Although approximately 1000 papers dealing with the strengths of weak bases have been published, we have cited only recent or very relevant papers and reviews.

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