isopropyl alcohol, butyl bromide (2 g.) was added, and the mixture was heated under reflux for 2–5 hr. before isolating the desired ether by gas phase chromatography (column temperature 25°). The labeled butyl bromides were synthesized by the earlier described procedure.[21] d_6-Acetone (Nuclear Research Chemicals, Inc., Orlando, Fla.) was reduced with lithium aluminum hydride to the corresponding d_6-isopropyl alcohol, which was then converted to IX.

Isopropyl n-Pentyl Ether (X) and Labeled Analogs XI–XV. The same procedure was employed as described for the lower homolog IV except that *n*-pentyl bromide was substituted. The 3,3-d_2- and 4,4-d_2-pentyl bromide syntheses have already been described[21] and the 1,1-d_2-analog was obtained by lithium aluminum deuteride reduction of valeric acid followed by treatment with 48% hydrobromic acid in concentrated sulfuric acid. 2,2-d_2-Pentyl bromide was prepared from the appropriately labeled butyl bromide[21] by carbonation of the Grignard reagent followed by lithium aluminum hydride reduction and transformation into the bromide. 5,5,5-d_3-Pentyl bromide was synthesized from 2,2,2-d_3-acetic acid (Calbiochem, Los Angeles) which was reduced with lithium aluminum hydride. The labeled ethanol was converted to 2,2,2-d_3-ethyl bromide, the Grignard reagent of which was condensed with ethylene oxide by the procedure[21] used to synthesize 4,4-d_2-pentyl bromide. 4,4,4-d_3-Butanol was treated with 48% hydrobromic acid in concentrated sulfuric acid and the resulting butyl bromide was transformed into 5,5,5-d_3-pentyl bromide as described for 2,2-d_2-pentyl bromide.

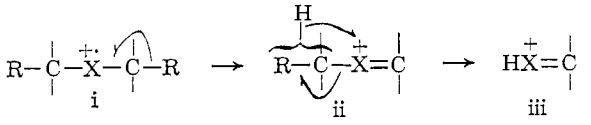
Ethyl 4,4-d_2-n-Hexyl Ether. 2,2-d_2-Butyl bromide was transformed into the Grignard reagent and the latter was treated with ethylene oxide in the manner described earlier[21] for pentyl bromide. The resulting hexyl alcohol was transformed into the bromide and then heated under reflux with sodium ethoxide in ethanol.

Mass Spectrometry in Structural and Stereochemical Problems. LXXXV.[1] The Nature of the Cyclic Transition State in Hydrogen Rearrangements of Aliphatic Amines[2,3]

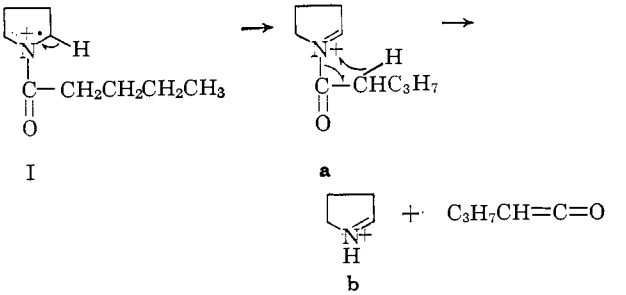
Carl Djerassi and Catherine Fenselau

Contribution from the Department of Chemistry, Stanford University, Stanford, California. *Received July 6, 1965*

The two most significant peaks in the mass spectra of aliphatic amines (X = NH or NR) are usually associated with α-cleavage (i → ii) and subsequent hydrogen rearrangement (ii → iii) with production of an immonium ion (iii, X = NH or NR) and expulsion of an olefin fragment. The hydrogen migration has been assumed to proceed through a four-membered cyclic transition state in amines (X = NH or NR) as well as ethers (X = O). However, recent work[1] with deuterium-labeled ethers has demonstrated that three-, five-, and six-membered rings are also feasible, and it is for that reason that the mass spectra of deuteriated N-methyl-N-isopropyl-n-butyl-, and -n-pentylamine were examined. The results demonstrate that, just as in ethers,[1] transition states involving three-, four-, five-, and six-membered rings can operate in the hydrogen-transfer step but that the nature of the heteroatom (X = O vs. X = N) does exert some effect as judged by quantitative differences between ethers and amines.



Four-membered transition states in mass spectrometric rearrangement processes are not well established, especially when there exist alternate paths proceeding through larger ring intermediates, notably six-membered ones. One authenticated case[4] is the loss of propylketene from the M − 1 species **a** of N-valerylpyrrolidine (I) where the hydrogen transfer to the immonium ion **b** was established by deuterium labeling to proceed to the extent of nearly 75% through a four-membered, cyclic transition state.



One of the most plausible, four-membered transition states which has been implicated[5] for hydrogen rearrangements involves the well-known elimination of an

(1) Paper LXXXIV: C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, 87, 5747 (1965).

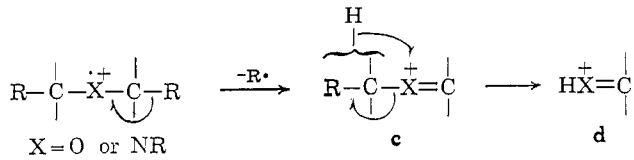
(2) Taken in part from the Ph.D. Thesis of C. F., Stanford University, 1965.

(3) Financial support (Grants No. GM-11309 and AM-04257) by the National Institutes of Health of the U. S. Public Health Service is gratefully acknowledged. The purchase of the Atlas CH-4 mass spectrometer was made possible through NASA Grant NsG 81-60. C. F. wishes to thank the Computation Center, Stanford University, for a Student Time Grant.

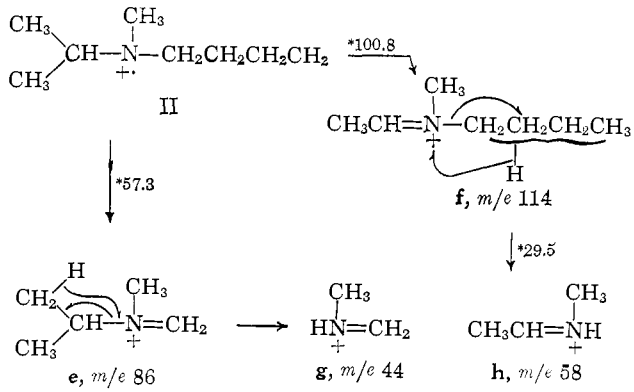
(4) A. M. Duffield and C. Djerassi, *J. Am. Chem. Soc.*, in press.

(5) R. S. Gohlke and F. W. McLafferty, *Anal. Chem.*, 34, 1281 (1962).

olefin (or its equivalent) from the ubiquitous α-cleavage product (**c**) of amines and ethers with transfer of a hydrogen to the heteroatom (**c** → **d**). Contrary to the original postulates,[6] which have been widely accepted,[7,8] we have shown[1] by means of deuterium labeling in ethers (X = O) that there exists no special preference for a four-membered cyclic transition state in this particular rearrangement when additional sites for hydrogen detachment are available.



Our results with ethers[1] thus cast doubt on the assumption[6,7] that four-membered rings operate in the analogous hydrogen rearrangement process of amines and, since the nature of cyclic transition states forms an important part of the ground rules dealing with the interpretation of mass spectrometric fragmentation processes,[9,10] studies were undertaken with appropriately labeled amines. Since the ether studies[1] were performed with isopropyl *n*-butyl ether, N-methyl-N-isopropyl-N-*n*-butylamine (II) was selected for labeling so as to permit as direct a comparison as possible with the analogous ethers.[1] The 70 e.v. spectrum of the unlabeled amine II is reproduced in Figure 1, while the shifts of the principal peaks in the spectra of the deuterated analogs III–VIII are summarized in Table I. The spectrum is relatively simple and is dominated by four fragment ions. Two of these are the expected α-cleavage products **e** (*m/e* 86) and **f** (*m/e* 114), the loss of the methyl group arising exclusively from the isopropyl moiety as demonstrated by the peak shifts in Table I. It is pertinent to note that elimination of the bulkier substituent leading to the ion **e** of mass 86 is preferred over the loss of a smaller (methyl) radical from a secondary carbon, while in the ether counterpart, isopropyl *n*-butyl ether,[1] these two factors essentially counterbalance each other. The peaks at *m/e* 58 and 44 correspond to the further decomposition



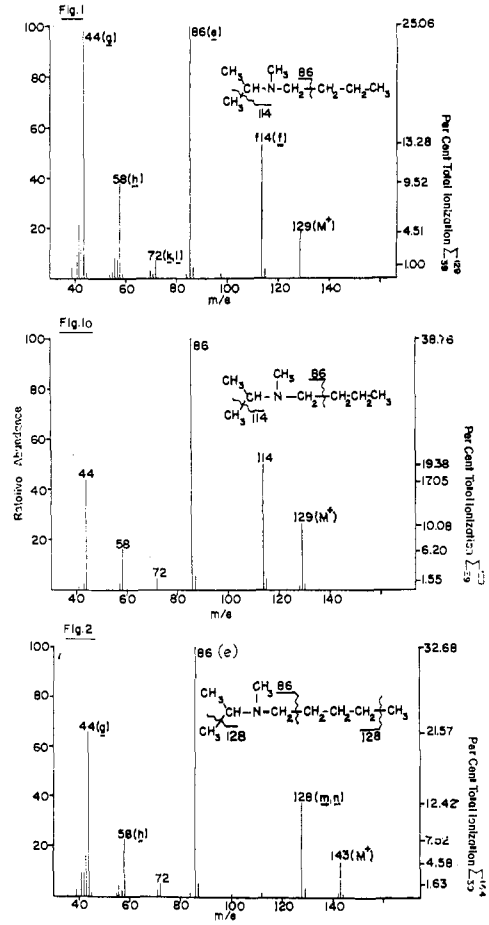


Figure 1. Mass spectrum (70 e.v.) of N-methyl-N-isopropyl-N-*n*-butylamine (II).
Figure 1a. Mass spectrum (15 e.v.) of N-methyl-N-isopropyl-N-*n*-butylamine (II).
Figure 2. Mass spectrum (70 e.v.) of N-methyl-N-isopropyl-N-*n*-pentylamine (IX).

products of **e** and **f** accompanied by the hydrogen transfer which prompted the present study. This particular sequence of events was supported by the detection of the appropriate metastable peaks.[11]

The ion of mass 44 arises by a hydrogen transfer from the *m/e* 86 progenitor **e**, and the labeling results indicate (Table I) that this reaction proceeds almost exclusively through a four-membered cyclic transition state by migration of an isopropyl methyl hydrogen atom. As noted elsewhere,[12] such an observation is not of great significance as far as generalizations on the operation of four-membered transition states are concerned, since larger membered alternatives are not possible. In order to examine this point, consideration has to be given to the origin of the hydrogen atom transferred in the genesis of the *m/e* 58 peak. A comparison of the relevant data (Table I) of the deuterated derivatives III and IV shows that 96% of the peak may be represented by structure **h**, while in 4% both the α- and β-carbon atoms of the butyl chain are still retained. This second and minor component is thus best repre-

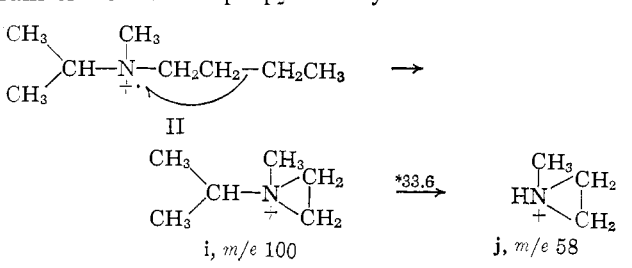
(6) F. W. McLafferty, *J. Am. Chem. Soc.*, 29, 1782 (1957).
(7) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 116.
(8) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p. 363.
(9) F. W. McLafferty in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, pp. 331–340.
(10) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964.
(11) All metastable peaks were determined with the use of a logarithmic transfer recorder described by R. T. Aplin, H. Budzikiewicz, H. S. Horn, and J. Lederberg, *Anal. Chem.*, 37, 776 (1965). For the sake of simplicity, all observed values for metastable peaks are presented with asterisked values above the arrows corresponding to the appropriate transitions.
(12) Reference 10, pp. 52 and 67.

Table I. Principal Mass Spectral Peaks in N-Methyl-N-isopropyl-N-*n*-butylamine (Figure 1) and Deuterated Analogs[a]

Compd.	Isotopic purity	M+	M − 15	M − 43	M − 57	M − 71	M − 85
$(CH_3)_2CHN(CH_3)CH_2CH_2CH_2CH_3$ (II)	...	129	114	86	72	58	44
$(CH_3)_2CHN(CH_3)CD_2CH_2CH_2CH_3$ (III)	96% d_2 4% d_1	131	116 (q)	88 (q)	74 (67%) 72 (33%)	60 (4%) 59 (10–25%)[c] 58 (71–86%)	46 (q)
$(CH_3)_2CHN(CH_3)CH_2CD_2CH_2CH_3$ (IV)	97% d_2 3% d_1	131	116 (q)	86 (q)	74 (13%) 73 (21%) 72 (66%)	60 (4%) 59 (20–24%) 58 (72–76%)	44 (q)
$(CH_3)_2CHN(CH_3)CH_2CH_2CD_2CH_3$ (V)	91% d_2 4% d_1 5% d_0	131	116 (q)	86 (q)	73 (55%)[b] 72 (45%)	59 (22%)[d] 58 (78%)	44 (q)
$(CH_3)_2CHN(CH_3)CH_2CH_2CH_2CD_3$ (VI)	96% d_3 4% d_2	132	117 (q)	86 (q)	73 (8%) 72 (92%)	59 (16%)[e] 58 (84%)	44 (q)
$(CH_3)_2CHN(CD_2H)CH_2CH_2CH_2CH_3$ (VII)	99% d_2	131	116 (q)	88 (q)	74 (q)	60 (q)	46 (q)
$(CD_3)_2CHN(CH_3)CH_2CH_2CH_2CH_3$ (VIII)	86% d_6 14% d_5	135	117 (q)	92 (q)	78 (37%) 75 (63%)	61 (92%)	45 (q)

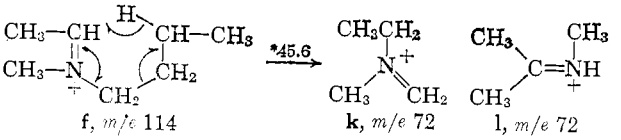
[a] The symbol q denotes a quantitative transfer (>95%). Correction for isotopic contaminants and ^{13}C contributions have been made in all instances. An uncertainty of ±5% is estimated in the calculations on all peaks of greater than 20% relative abundance. [b] At 15 e.v. virtually all of the peak moves to *m/e* 73. [c] At 15 e.v. 21% of the peak moves to *m/e* 59. [d] At 15 e.v. 25% of the peak moves to *m/e* 59. [e] At 15 e.v. 15% of the peak moves to *m/e* 59.

sented by structure **j** and may be visualized as arising from a β-cleavage product (**i**, *m/e* 100) by hydrogen transfer from the isopropyl moiety.



The per cent hydrogen transfer values from the butyl chain in the production of ion **h** are collected in Table I and demonstrate that, qualitatively, amines and ethers[1] behave similarly in that three-, four-, five-, and six-membered rings are possible and that, contrary to the situation in certain amides,[4] there exists no preference for a four-membered cyclic transition state. The reason that a relatively wide range had to be given for the per cent transfer from any given position is due to the existence of small peaks in the *m/e* 54–57 range, which by high-resolution mass spectrometry[13] were shown to be largely of dual origin (*m/e* 54 = C_4H_6 and C_3H_4N; *m/e* 55 = C_4H_7 and C_3H_5N; *m/e* 56 = C_3H_6N; and *m/e* 57 = C_4H_9 and C_3H_7N). Since the shifts of these peaks upon deuteration could not be predicted, an element of uncertainty is introduced into the calculations, which is reflected by the ranges listed in the M − 71 column of Table I.

One additional peak, though small, merits discussion since its nature could be unravelled through inspection of the peak shifts (Table I) in the spectra of the various deuterated analogs. All of the species of mass 72 must contain the N-methyl function, since the peak is moved quantitatively to *m/e* 74 in the spectrum of VII. Approximately 65% of the *m/e* 72 peak must correspond to species which retain one of the isopropyl methyl groups (*m/e* 75 peak in VIII) and the α-methylene group of the butyl substituent (*m/e* 74 in III). Structure **k** can thus be assigned to this major contributor (*ca.* 65%) of the *m/e* 72 peak, and its predominant formation through a McLafferty rearrangement of the α-fission product **f** with transfer of the γ-hydrogen atom is substantiated by the shift to *m/e* 73 in the spectrum of V.



The smaller portion of the *m/e* 72 peak retains all six methyl hydrogen atoms of the isopropyl group (see shift to *m/e* 78 in VIII) and hence is probably best depicted in terms of structure **l**.

The mass spectrum of N-methyl-N-isopropyl-N-*n*-butylamine (II) measured at 15 e.v. is reproduced in Figure 1a, and it will be noted that only quantitative changes ensue, the most striking one being the reduction in intensity of the *m/e* 44 peak and the virtual disappearance of some of the minor fragment ions below *m/e* 60.

By comparing the mass spectra of deuterated isopropyl *n*-butyl and isopropyl *n*-pentyl ethers, it was possible to demonstrate[1] a preference for hydrogen migration from a methylene as compared to a methyl group. In spite of the greater uncertainty in calculating accurately the per cent hydrogen transferred from each carbon atom in the butyl group of the amine II (*vide supra*), it was considered of interest to prepare the next higher homolog, N-methyl-N-isopropyl-N-*n*-pentylamine (IX) and to compare its mass spectrum (Figure 2) with those (see Table II) of its analogs labeled with deuterium in the pentyl side chain (X–XIV). The origin of the *m/e* 86 (**e**) and *m/e* 44 (**g**) peaks does not require any further comment since it is identical with that discussed above in terms of the lower homolog II. Of interest is the observation (see M − 15 column in Table II) that while 97% of the M − 15 species does indeed correspond to the expected α-fission product **m**, a small (3%) but significant portion is due to loss of the terminal methyl group from the pentyl side chain, while no such loss (see VI in Table I) occurred from the

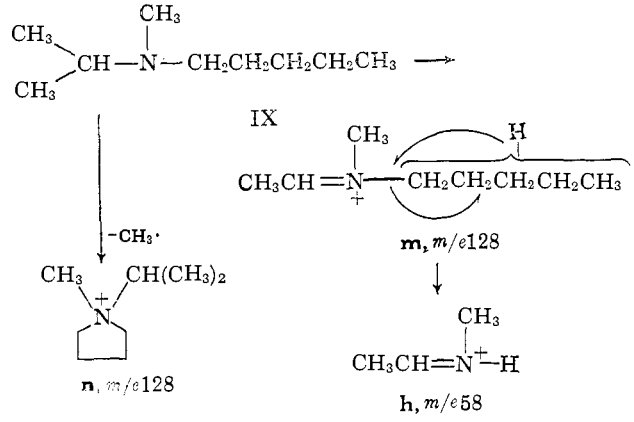
(13) These measurements were performed by Drs. L. Dolejs and D. A. Lightner with an AEI MS-9 double-focussing mass spectrometer.

Table II. Principal Mass Spectral Peaks in N-Methyl-N-isopropyl-N-*n*-pentylamine (Figure 2) and Deuterated Analogs[a]

Compd. R = $(CH_3)_2CHN(CH_3)$	Isotopic purity	M^+	M − 15	M − 57	M − 85	M − 99
$RCH_2CH_2CH_2CH_2CH_3$ (IX)	...	143	128	86	58	44 (q)
$RCD_2CH_2CH_2CH_2CH_3$ (X)	98% d_2	145	130 (q)	88 (q)	60 (4%) 59 (14–17%) 58 (79–82%)	46 (q)
$RCH_2CD_2CH_2CH_2CH_3$ (XI)	76% d_2 21% d_1	145	130 (q)	86 (q)	60 (4%) 59 (21–25%) 58 (71–75%)	44 (q)
$RCH_2CH_2CD_2CH_2CH_3$ (XII)	92% d_2 6% d_1 2% d_0	145	130 (q)	86 (q)	59 (19%) 58 (81%)	44 (q)
$RCH_2CH_2CH_2CD_2CH_3$ (XIII)	94% d_2 6% d_1	145	130 (q)	86 (q)	59 (19%) 58 (81%)	44 (q)
$RCH_2CH_2CH_2CH_2CD_3$ (XIV)	83% d_3 4% d_2 2% d_1 11% d_0	146	131 (97%) 128 (3%)	86 (q)	59 (6%) 58 (94%)	44 (q)

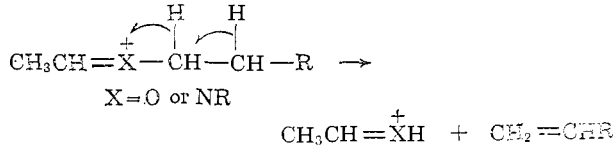
[a] See footnote *a* in Table I.

butyl group. This is a reflection of the stabilizing influence of a five-membered ring (**n**) and on the basis of other amine mass spectra[5,14] it can be predicted that an even larger proportion of the M − 15 species will be derived from the terminus of a hexyl side chain due to stabilization through a six-membered ring.



Hydrogen migration in the M − 15 ion **m** will lead again to species **h**, and the hydrogen transfer values in the M − 85 column of Table II should be contrasted with those (M − 71 column in Table I) of the butyl analog II. Particularly noteworthy is the fact that nearly equal transfer occurs from the δ-carbon atom in either the butyl (17% in VI, Table I) or pentyl (20% in XIII, Table II) analogs, thus showing that the pronounced preference for abstraction of a methylene hydrogen as compared to one from a methyl group demonstrated in ethers[1] does not apply to amines. The other quantitative differences in the origin of the itinerant hydrogen between ethers and amines are not so pronounced except for the somewhat greater prevalence in the latter of transfer from the α-carbon atom. Formally, such hydrogen migration from the α-position implies the generally unfavorable fission of two bonds connected to one carbon atom with the generation of a carbene, but this reaction can also be visualized as proceeding by additional hydrogen rearrangement within the alkyl group, the following sequence being a typical example.

(14) Reference 10, p. 65.



Experimental Section[15]

N-Methyl-N-isopropyl-N-n-butylamine (II) and Labeled Analogs III–VIII. Ethereal solutions of butyryl chloride and N-methyl-N-isopropylamine were mixed and stirred at room temperature overnight. After washing with water and drying, the ether was removed and N-methyl-N-isopropylbutyramide was distilled, b.p. 196–197°, column temperature 175° in gas chromatography.

Anal. Calcd. for $C_8H_{17}NO$: C, 67.09; H, 11.96. Found: C, 66.90; H, 11.92.

The amide was reduced by heating under reflux for 15 hr. with lithium aluminum hydride in tetrahydrofuran and the analytical sample of the amine (II) was purified by distillation (b.p. 138°) and gas phase chromatography (column temperature 100°).

Anal. Calcd. for $C_8H_{19}N$: C, 74.34; H, 14.82. Found: C, 74.23; H, 14.93.

The analog labeled in the α-position of the butyl side chain (III) was prepared by substituting lithium aluminum deuteride for the hydride in the above described reduction of the amide, while the remaining butyl-labeled derivatives IV, V, and VI were prepared from the appropriately labeled butyric acids. The 2,2-d_2 and 3,3-d_2 labeled acids were obtained according to the literature directions.[16] 4,4,4-d_3-Butyric acid was prepared from 2,2,2-d_3-acetic acid, which was reduced to the alcohol with lithium aluminum hydride. 2,2,2-d_3-Ethyl bromide was obtained on treatment of the

(15) All mass spectra were measured with an Atlas CH-4 mass spectrometer equipped with an AN-4 ion source (temperature 60°) and a logarithmic transfer recorder.[11] Unless specified otherwise, the ionizing energy was maintained at 70 e.v. We are indebted to Drs. R. T. Aplin and H. Budzikiewicz for the measurements and for advice in the numerous calculations. All amines were purified by gas phase chromatography using a Wilkens Aerograph instrument equipped with a polybutylene glycol column.

(16) A. M. Duffield, R. Beugelmans, H. Budzikiewicz, D. A. Lightner, D. H. Williams, and C. Djerassi, *J. Am. Chem. Soc.*, 87, 805 (1965).

alcohol with 48% hydrobromic acid in concentrated sulfuric acid, and was converted to butyric acid by a malonic ester synthesis.

Two deuterium atoms were introduced into the methyl group (VII) by reduction of N-isopropyl-N-butylformamide with lithium aluminum deuteride. The formamide was obtained from the reaction[17] of chloral and N-isopropyl-N-butylamine. The d_6-analog VIII was prepared by reduction of N-methyl-N-d_6-isopropylbutyramide with lithium aluminum hydride. To obtain the labeled tertiary amide, N-methylbutyramide was stirred under reflux in tetrahydrofuran with sodium hydride for 14 hr. d_6-Isopropyl bromide, obtained from d_6-isopropyl alcohol,[1] was added and the mixture was heated under reflux for 5 hr. N-Methyl-N-d_6-isopropylbutyramide was separated from unreacted N-methylbutyramide by preparative gas phase chromatography.

(17) F. F. Blicke and C. J. Lu, *J. Am. Chem. Soc.*, 74, 3933 (1952).

N-Methyl-N-isopropyl-N-n-pentylamine (IX) and Labeled Analogs X–XIV. The synthesis of the unlabeled amine IX was effected in the same manner as described for the lower homolog II except that valeryl chloride was employed in the first step. The amine boiled at 165–166° and could be purified by gas phase chromatography either on a polybutylene glycol (100°) or phenyl diethanolamine succinate (90°) column.

Anal. Calcd. for $C_9H_{21}N$: C, 75.44; H, 14.77. Found: C, 75.60; H, 14.90.

The α-labeled derivative X was prepared by lithium aluminum deuteride reduction of N-methyl-N-isopropylvaleramide, while analogs XI, XII, and XIV were obtained by the use of the appropriately labeled valeric acids, which in turn were synthesized by carbonation of the labeled[16] butylmagnesium bromides. 4,4-d_2-Valeric acid, required in the preparation of the amine XIII, was obtained by a malonic ester synthesis with 2,2-d_2-propyl bromide.[16]

Mass Spectrometry in Structural and Stereochemical Problems. LXXXVI.[1] The Hydrogen-Transfer Reactions in Butyl Propionate, Benzoate, and Phthalate[2,3]

Carl Djerassi and Catherine Fenselau

Contribution from the Department of Chemistry, Stanford University, Stanford, California. *Received July 29, 1965*

One of the most characteristic electron impact induced fragmentation processes of higher esters (i.e., larger than methyl) is the loss of the alkyl residue from the ester moiety together with transfer of two hydrogen atoms to produce the protonated carboxylic acid ion. Conflicting conclusions concerning the nature of this double hydrogen-transfer reaction are recorded in the literature. It is for this reason that butyl propionate and butyl benzoate, two typical examples of aliphatic and aromatic esters, were studied together with their deuterium-labeled analogs. While the itinerant hydrogen atoms were found to originate from every possible carbon atom, those attached to the β and γ positions were by far the most important ones. Mechanistic conclusions bearing on this and other fragmentation reactions of higher esters, typified by butyl esters, are discussed. Through the use of deuterium-labeled dibutyl phthalates it was possible to shed additional light on the course of the most significant fragmentation reaction of phthalates (other than dimethyl phthalate) which gives rise to an intense peak at m/e 149. Contrary to earlier assumptions in the literature, the hydrogen-transfer reaction implicated in the genesis of this important ion is not specific but rather involves hydrogen from every carbon atom in the butyl side chain.

(1) Paper LXXXV: C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, 87, 5752 (1965).

(2) Financial support from the National Institutes of Health (Grants No. CA-07195 and AM-04257) of the U. S. Public Health Service is gratefully acknowledged.

(3) Taken in part from the Ph.D. Thesis of C. F., Stanford University, 1965 where all of the original mass spectra were reproduced.

Introduction

Most of the fragmentation reactions of methyl esters in the mass spectrometer occur in the acyl rather than alcohol portion of the molecule.[4,5] In ethyl and higher esters, which in the aliphatic series have been studied by both low[6] and high[7] resolution, bond cleavages involving the alcohol moiety become more prevalent. One of the mechanistically most intriguing and at the same time most diagnostic reactions of such higher esters[6] is the loss of the alkyl fragment from the alcohol portion with transfer of two hydrogen atoms to produce the protonated carboxylic acid ion: $(RCOOR')^+ \rightarrow (RCO_2H_2)^+ + (R' - 2H)\cdot$. This process was found[8,9] to be equally prevalent in higher esters of aromatic acids and in the aliphatic series has been the subject of extensive mechanistic scrutiny using deuterium-labeled substrates in order to determine the origin of the two departing hydrogen atoms.

In aliphatic ethyl esters,[10,11] complete scrambling of

(4) For review see R. Ryhage and E. Stenhagen in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 9.

(5) For review see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 1.

(6) A. G. Sharkey, Jr., J. L. Shultz, and R. A. Friedel, *Anal. Chem.*, 31, 87 (1959); R. Ryhage and E. Stenhagen, *Arkiv Kemi*, 14, 483 (1959).

(7) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Anal. Chem.*, 33, 221 (1961).

(8) F. W. McLafferty and R. S. Gohlke, *ibid.*, 31, 2076 (1959).

(9) E. M. Emery, *ibid.*, 32, 1495 (1960).

(10) E. W. Godbole and P. Kebarle, *Trans. Faraday Soc.*, 58, 1897 (1962).

(11) A. G. Harrison and E. G. Jones, *Can. J. Chem.*, 43, 960 (1965).