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: $(RCOOR')^+$ → $(RCO_2H_2)^+$ + $(R' - 2H)\cdot$. 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).

Table I. Principal Peaks in Mass Spectra of Butyl Propionate (Figure 1) and Deuterated Analogs[a]

Compd.	Isotopic purity	M+	M − 29	M − 30	M − 43	M − 55	M − 56	M − 57	M − 59	M − 73	M − 74	M − 75
$C_2H_5CO_2CH_2CH_2CH_2CH_3$ (I)		130	101	100	87	75	74	73	71	57	56	55
$C_2H_5CO_2CD_2CH_2CH_2CH_3$ (II)	>99% d_2	132 (q)	103 (q)	100 (q)	89 (q)	75 (88%) 76 (12%)	74	73 (33%) 75 (67%)	71 (q)	57 59	57 (8%) 58 (92%)	55 56 57
$C_2H_5CO_2CH_2CD_2CH_2CH_3$ (III)	95% d_2 5% d_1	132 (q)	103 (q)	102 (q)	87 (q)	75 (19%) 76 (81%)	74	73 (33%) 75 (67%)	73 (q)	57 59	57 (58%) 58 (42%)	55 56 57
$C_2H_5CO_2CH_2CH_2CD_2CH_3$ (IV)	94% d_2 6% d_1	132	101 (35%) 103 (65%)	102 (q)	87 (q)	75 (22%) 76 (78%)	74	73 (33%) 75 (67%)	73 (q)	57 59	57 (42%) 58 (58%)	55 56 57
$C_2H_5CO_2CH_2CH_2CH_2CD_3$ (V)	82% d_3 12% d_2 6% d_0	133	101 (35%) 104 (65%)	103 (q)	87 (q)	75 (78%) 76 (22%)	74	73 (33%) 76 (67%)	74 (q)	57 60	59 (q)	55 57 58

[a] The symbol q denotes a quantitative transfer (95%). All numerical values are considered accurate to ±5% for peaks in excess of 20% relative abundance. Correction for isotopic contaminants and ^{13}C contributions have been made in all instances.

the ethoxy hydrogens occurs and an adequate mechanistic explanation has been presented.[11] In isopropyl esters, contrary to earlier conclusions,[10] both hydrogens seem to be derived largely from the two methyl groups.[11] Historically, the first deuterium-labeling studies[12] coupled with a concrete mechanistic proposal are due to McLafferty[8,12] who examined the mass spectra of sec-butyl acetate and its 2-d_1 and 3-d_1 analogs. He concluded that the β and γ hydrogens were principally involved and implied a concerted process that may be depicted in terms of the general expression a → b.[13]
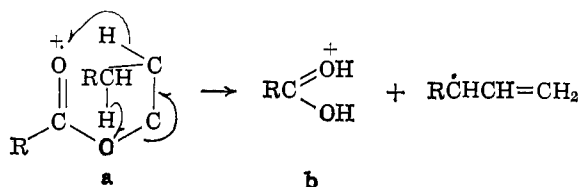
Biemann[14] has pointed out some of the uncertainties in basing generalizations for higher esters on the sec-butyl acetate example. First, only one hydrogen atom on any given carbon atom was replaced by deuterium, thus ignoring the known[15] operation of isotope effects in related hydrogen-transfer reactions. Second, only a three-carbon chain is available to test the effect of distance upon the hydrogen transfer. An additional disadvantage is that a branched alcohol was employed, which creates the complication of possible preference for a secondary hydrogen rather than a primary one from the β position.

McFadden and collaborators,[16] on the basis of certain deuterium-labeled butyl acetate and butyl propionate spectra, concluded that the first proton was abstracted specifically from the γ position with the second one being derived in a random manner from all the other possible positions. A serious objection to their conclusions is that they are based on results with 4-d_1- and 3-d_1-butyl acetates, thus ignoring any isotope ef-

fects,[15] and that no label in the β (C-2) position was available.

Still another conclusion was reached by Benz and Biemann,[17] who examined the mass spectra of n-pentyl acetate, together with its 2,2-d_2 and 3,3-d_2 analogs, as well as n-hexyl acetate and its 4,4-d_2 derivative. They observed that in the reaction (CH₃COOR)⁺ → (RH)⁺ + CH₃COOH, involving transfer of one hydrogen atom with formation of an "ionized olefin" and neutral acetic acid, 55% of this hydrogen is derived from the β (C-2) and 45% from the γ (C-3) positions. They conclude that, in the double hydrogen rearrangement leading to the protonated acetic acid ion, the first hydrogen atom is again derived from the β and γ positions with the second one being abstracted randomly.

In view of this diversity of conclusions bearing on the double hydrogen-transfer reaction, butyl propionate was selected as a typical aliphatic ester in which all the hydrogen atoms attached to any given carbon atom can be completely replaced by deuterium. This complete labeling was carried out on every carbon atom in the alcohol side chain. Furthermore, it was considered desirable to extend this approach to butyl benzoate, a typical ester of an aromatic acid, in order to determine whether the nature of the acyl fragment exerted any effect upon the double hydrogen transfer. Finally, the availability of the labeled butanols[18] prompted us to synthesize the appropriate dibutyl phthalates, which would permit a detailed examination of the mechanism governing the most significant peak in the mass spectra of all the phthalates other than dimethyl phthalates. It is in this order that the subsequent discussion will be presented.

Mass Spectrum of Butyl Propionate

The low-resolution mass spectrum of butyl propionate is reproduced in Figure 1, while the data for the most important peaks in the deuterated analogs II–V are summarized in Table I. The ion of mass m/e 75 corresponds to the charged product (protonated propionic acid) of the double hydrogen transfer under discussion, and its composition ($C_3H_7O_2^+$) was established by high-

(12) F. W. McLafferty and M. C. Hamming, Chem. Ind. (London), 1366 (1958); see also F. W. McLafferty, Anal. Chem., 31, 82 (1959).

(13) See ref. 5, p. 197, as well as F. W. McLafferty in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p. 147.

(14) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 125.

(15) D. H. Williams, H. Budzikiewicz, and C. Djerassi, J. Am. Chem. Soc., 86, 284 (1964).

(16) D. R. Black, W. H. McFadden, and J. W. Corse, J. Phys. Chem., 68, 1237 (1964).

(17) W. Benz and K. Biemann, J. Am. Chem. Soc., 86, 2375 (1964).

(18) A. M. Duffield, R. Beugelmans, H. Budzikiewicz, D. A. Lightner, D. H. Williams, and C. Djerassi, ibid., 87, 805 (1965), and references cited therein.
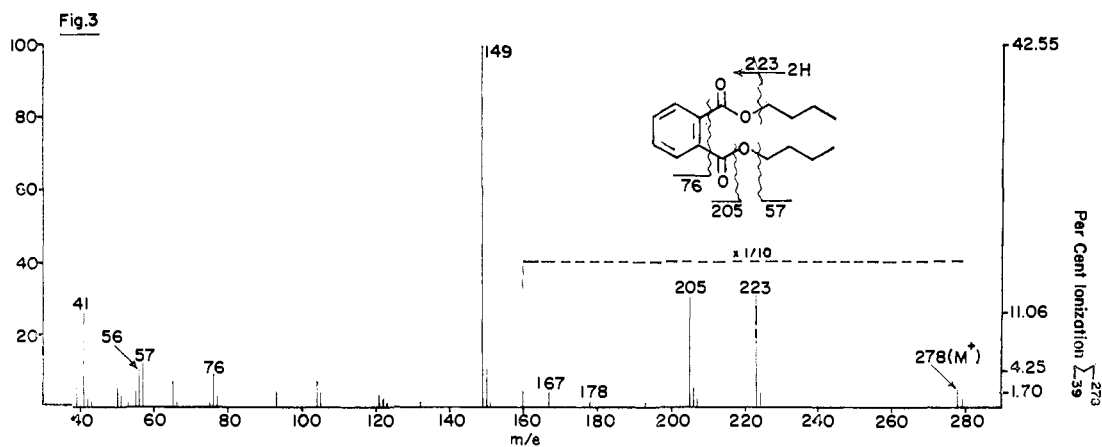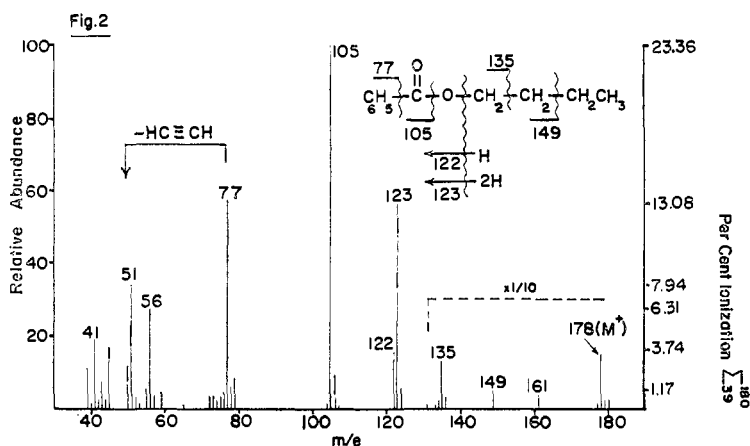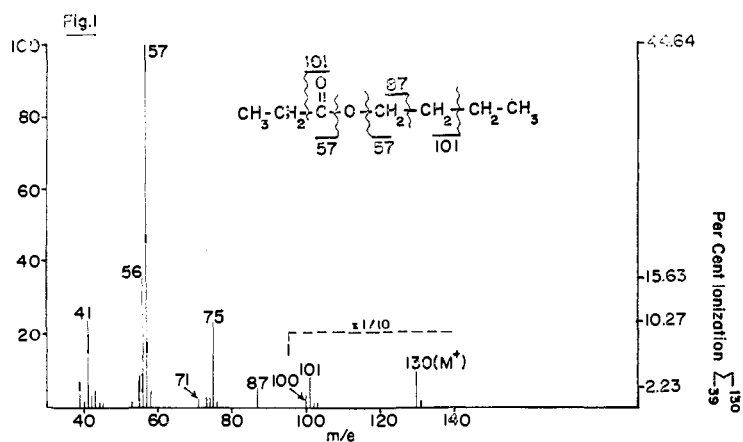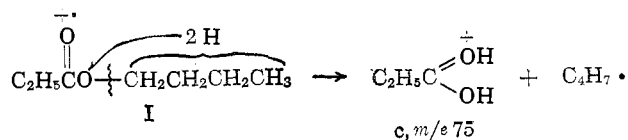
Figure 1. Mass spectrum of butyl propionate.
Figure 2. Mass spectrum of butyl benzoate.
Figure 3. Mass spectrum of dibutyl phthalate.

resolution mass measurements.[7,19] Formally, the process corresponds to

c, m/e 75

and by utilizing the quantitative data on the peak group m/e 71–77 collected in Table II, one arrives at the results

(19) All high-resolution mass measurements were performed by Dr. D. Becher on an A. E. I. MS-9 double-focussing mass spectrometer and, where comparison with the literature (ref. 7) was possible, the results were in agreement.

summarized in Table III. These account for 193% out of the required 200%, the difference presumably being due to an isotope effect, and show that while the two hydrogen atoms are predominantly transferred from the β and γ positions, a certain amount (12 and 22%, respectively) arises from the α- and δ-carbon atoms.

Before considering the mechanistic implications of these data, it is worthwhile to cover briefly the nature of the remaining peaks in the butyl propionate spectrum (Figure 1) starting from the high mass range. Qualitatively, they follow the major paths outlined by earlier workers,[6,12] and the principal reason for commenting upon them at all is that the labeled compounds (see Table I) offer quantitative information

Table II. Percentage of Total Ionization ($\Sigma_n{}^{77}$) of the Peak Group m/e 71–77 in the Spectra of Butyl Propionate (I) and Deuterated Analogs (II–V)

Compd. $C_2H_5CO_2CH_2$-$CH_2CH_2CH_3$	71	72	73	m/e^a 74	75	76	77
d_0 (I)	7		5	8	80		1
α-d_2 (II)	8		1	4	76	10	1
β-d_2 (III)			9	7	19	65	1
γ-d_2 (IV)			8	6	21	62	2
δ-d_3 (V)			2	14	63	21	1

^{a} These values have been corrected for isotopic contaminants and for ^{13}C contributions.

Table III. Source of Hydrogen Transferred to Protonated Carboxylic Acid in Mass Spectra of Butyl Propionate (m/e 75 in Figure 1) and Butyl Benzoate (m/e 123 in Figure 2)

Position	Butyl propionate, %	Butyl benzoate, %
α	12	12
β	81	71
γ	78	81
δ	22	18
	193	182^a

^{a} The appearance of small peaks at m/e 125 in the spectra of the γ- and δ-labeled butyl benzoates (Table V) indicates that two hydrogen atoms attached to the γ or δ carbon may be transferred to a small extent, thus raising the total migrating hydrogen which has been accounted for from 182 to 192%.

which on occasion is not available by any other means.

The m/e 101 peak by high-resolution mass measurements[19] has been shown to correspond to only one empirical species ($C_5H_9O_2{}^+$), but the labeling results (Table I) demonstrate that it arises to the extent of 65% through loss of an ethyl radical from the acyl group and to the extent of 35% from the butyl fragment. The m/e 100 species, though small, is mechanistically very interesting since it requires the occurrence of an alkyl rearrangement. McFadden and collaborators[16,20] first called attention to the fact that its formation involves the loss of the elements of formaldehyde, and we have confirmed this by high-resolution mass measurements[19] ($C_6H_{12}O^+$). Of the two most likely formulations (d or d'), we favor the former, because it offers the only rational explanation for the origin of the somewhat more intense peak at m/e 71 (see Figure 1). High-resolution mass spectrometry had already demonstrated[7] its composition as C_4H_7O, and the deuterium-labeling results (Table I) now show quite unambiguously that all but the α-carbon atom of the butyl group is retained in the m/e 71 species. Its formulation as e is very plausible, since it would then arise by the well-known[21] α fission of ethyl propyl ketone (d).

The m/e 87 species is the exclusive (see Table I and ref. 7) product (f) of α cleavage of a molecular ion in which the charge is retained on the alkoxy oxygen atom, while charge retention on the acyloxy oxygen atom results in α fission of the ester linkage with generation of the base peak (m/e 57, g) and a butoxy radical.

(20) See also W. H. McFadden, K. L. Stevens, S. Meyerson, G. J. Karabatsos, and C. E. Orzech, Jr., *J. Phys. Chem.*, **69**, 1742 (1965), who discuss the special case of neopentyl esters.

(21) A. G. Sharkey, J. L. Shultz, and R. A. Friedel, *Anal. Chem.*, **28**, 934 (1956).

$$d, m/e\ 100 \qquad e, m/e\ 71$$

$$d', m/e\ 100$$
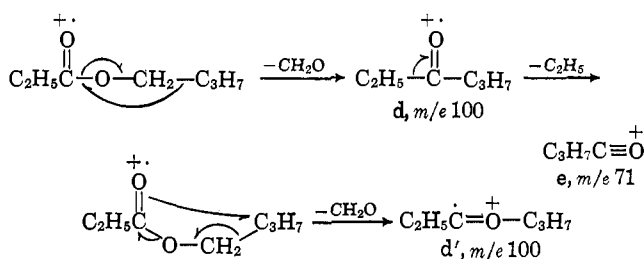
According to high-resolution[7,19] and deuterium-labeling (Table I) data, this process accounts for over 90% of the m/e 57 peak, the remainder being attributable to the less favored production of a butyl ion and a propionyloxy radical.

$$f, m/e\ 87$$
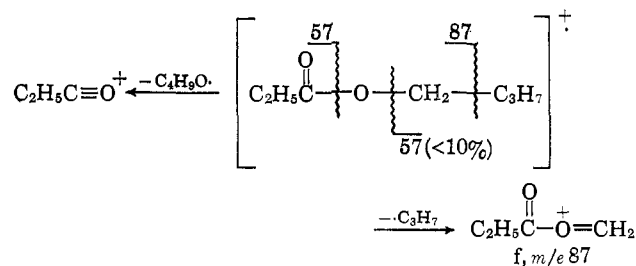
The peaks at m/e 73 and 74, though very small, can be assigned plausible structures and modes of formation because of the high-resolution[7,19] and deuterium-labeling data (Table I). The m/e 73 peak consists of a 1:2 mixture of two species, $C_3H_5O_2{}^+$ and $C_4H_9O^+$, derived from cleavage around the ether oxygen atom (see wavy lines in I) with charge retention on the oxygen atom. Such charge localization is clearly less favorable than charge retention on the other moiety (mass 57) and thus explains why the two components of the m/e 57 peak carry a much higher proportion of the ion current than the two m/e 73 species.


I
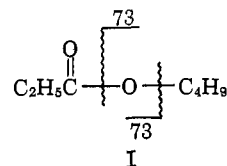
Two more peaks (at m/e 56 and 74) merit mention since they are both connected with the single hydrogen-transfer process, $(RCOOR')^{+} \rightarrow RCOOH + (RH)^{+}$, studied most recently by Benz and Biemann.[17] They, as well as earlier workers,[6] had already noticed that charge retention on the carboxylic acid fragment (m/e 74 in Figure 1) occurs to a very small extent, most of the ion current in this process being carried by the ionized olefin (m/e 56 in Figure 1). This is in accord with high-resolution mass measurements[7,19] which show that the m/e 56 species consists of C_4H_8 and C_3H_4O in a ratio of 20:1. Furthermore, the results with the labeled butyl propionates (Table I) indicate that 56% of the migrating hydrogen arises from the β and 44% from the γ position, which is in excellent agreement with the values (55 and 45%, respectively) deduced in the earlier study[17] with labeled pentyl and hexyl acetates. In view of the minuteness of the m/e 74 peak and the existence of adjacent ones, no calculations with respect to origin of transferred hydrogen could be performed.

Table IV. Principal Peaks in Mass Spectra of Butyl Benzoate (Figure 2) and Deuterated Analogs[a]

Compd.	Isotopic purity	M⁺	M − 29	M − 43	M − 55	M − 56	M − 73	M − 101	M − 122	M − 127
$C_6H_5CO_2CH_2CH_2CH_2CH_3$ (VI)		178	149	135	123	122	105	77	56	51
$C_6H_5CO_2CD_2CH_2CH_2CH_3$ (VII)	>99% d_2	180 (q)	151 (q)	137 (q)	124 (12%) 123 (88%)	122 (q)	105 (q)	77 (q)	58 (96%) 57 (4%)	51 (q)
$C_6H_5CO_2CH_2CD_2CH_2CH_3$ (VIII)	95% d_2 5% d_1	180 (q)	151 (q)	135 (q)	124 (71%) 123 (29%)	123 (78%) 122 (22%)	105 (q)	77 (q)	58 (75%) 57 (25%)	51 (q)
$C_6H_5CO_2CH_2CH_2CD_2CH_3$ (IX)	94% d_2 6% d_1	180	149 (q)	135 (q)	125 (4%) 124 (81%) 123 (15%)	122 (q)	105 (q)	77 (q)	58 (36%) 57 (64%)	51 (q)
$C_6H_5CO_2CH_2CH_2CH_2CD_3$ (X)	82% d_3 12% d_2 6% d_0	181	149 (q)	135 (q)	125 (1%) 124 (18%) 123 (81%)	122 (q)	105 (q)	77 (q)	59 (q)	51 (q)

[a] See footnote in Table I.

With the above information at hand, we can now consider the implications of the results collected in Table III on the mechanism of the double hydrogen rearrangement leading to the protonated propionic acid ion (m/e 75 in Figure 1). Three likely interpretations present themselves. (1) The concerted mechanism a → b involving transfer of the β and γ hydrogens does indeed predominate in straight-chain aliphatic esters to the extent of 70–80%, with the remainder coming indiscriminately from the remaining positions. (2) Again, predominant transfer (70–80%) of the β and γ hydrogens is assumed, except that the reaction proceeds in a stepwise manner (h → i → c and/or j → k → c).
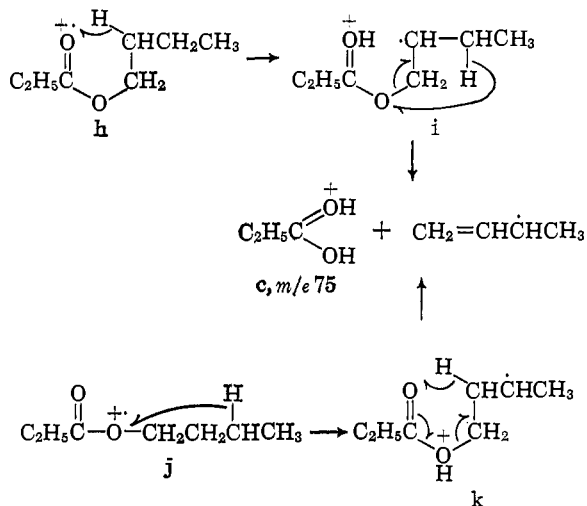

(3) As suggested by Benz and Biemann,[17] the first step follows the single hydrogen-transfer path, by hydrogen migrating to the extent of 55% from the β and 45% from the γ positions. If one subtracts these values from those collected in Table III for the double hydrogen transfer, one reaches the conclusion[17] that the second hydrogen atom originates to a certain extent from every carbon atom in the alcohol moiety: 12% α, 26% (81 − 55) β, 33% (78 − 45) γ, and 22% δ transfer. While certainly not excluded, we consider this third mechanism less likely for reasons discussed below in connection with the mass spectral behavior of butyl benzoate.

Mass Spectrum of Butyl Benzoate

Esters derived from aliphatic alcohols and aromatic acids, such as alkyl benzoates, have been studied in the past,[8,9,22] and a general similarity between their frag-

mentation pattern and that of esters derived from aliphatic acids was noted. This applies especially to the double hydrogen-transfer reaction with generation of the protonated acid ion, which has been discussed in the preceding section. In contrast to the plethora of papers[10-12,16,17,20] dealing with labeled aliphatic esters, nothing has so far been published on such studies with esters of an aromatic acid, and it is generally assumed[8] that the double hydrogen transfer proceeds by a similar mechanism. In order to determine whether the nature of the acyl residue affects this process, we have examined the mass spectrum (Figure 2) of butyl benzoate[8] and compared it (Table IV) with those of its deuterium-labeled analogs VII–X.

The peaks corresponding to m/e 149, 135, 105, 77, and 51 (loss of acetylene[23] from phenyl ion m/e 77) are represented schematically by wavy lines in structure VI and are self-explanatory. There remain only for consideration the peaks at m/e 123, 122, and 56, which pertain to the hydrogen-transfer processes typical of esters.
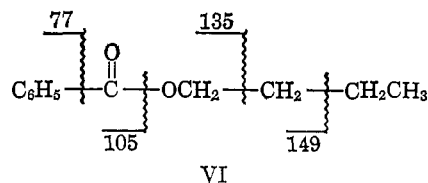
The m/e 122 and 56 peaks are related since they correspond to the alkyl–oxygen fission accompanied by the transfer of one hydrogen atom, the charge remaining either with the alkyl (m/e 56) or acyloxy (m/e 122) ion.
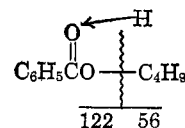
The much greater intensity of the benzoic acid fragment (m/e 122 in Figure 2) as compared to the propionic acid ion (m/e 74 in Figure 1) is noteworthy and indicates increased stabilization of the charge through the aromatic moiety. Even more striking are the differences (compare Tables I and IV) between butyl propionate and butyl benzoate with respect to the origin of the transferred hydrogen atom. In contrast to the 55 and 44% distribution between β and γ hydrogens leading to the olefin fragment in the aliphatic series

(22) T. Aczel and H. E. Lumpkin, Anal. Chem., 34, 33 (1962).
(23) See ref. 5, Chapter 9.

(see also ref. 17), in butyl benzoate only 25% of the transferred hydrogen originates from the β position and 64% from the γ position. Formally, the ionized C_4H_8 fragment (m/e 56) is the product of a McLafferty rearrangement (see arrows in VIa) with charge retention on the hydrocarbon. As shown by the hydrogen transfer values summarized in Table IV, no more than 25% can be formed by such a process with migration of the β-hydrogen atom. On the other hand, in butyl benzoate, contrary to the situation existing in butyl propionate (m/e 74 in Figure 1), a much larger portion of the ion current rests with the ionized carboxylic acid (m/e 122 in Figure 2), and this does originate to the extent of 78% (see Table IV) by a McLafferty rearrangement with transfer of the β-hydrogen atom. The data in Table V

Table V. Percentage of Total Ionization ($\Sigma_{122}{}^{125}$) of the Peak Group m/e 122-125 in the Spectra of Butyl Benzoate (VI) and Deuterated Analogs (VII-X)

Compd. $C_6H_5CO_2CH_2CH_2CH_2CH_3$ α β γ δ	122	123	124	125
d_0 (VI)	23	77		
α-d_2 (VII)	23	67	9	
β-d_2 (VIII)	5	40	55	
γ-d_2 (IX)	23	12	62	3
δ-d_3 (X)	23	62	14	1

[a] These values have been corrected for isotopic contaminants and for ^{13}C contributions.

indicate no movement of the m/e 122 peak in any of the other deuterated substrates, thus leaving the origin of 22% of transferred hydrogen unaccounted for. The only rational explanation is the operation of a considerable isotope effect in the McLafferty rearrangement of esters involving hydrogen migration from the alcohol portion of the molecule.


VIa
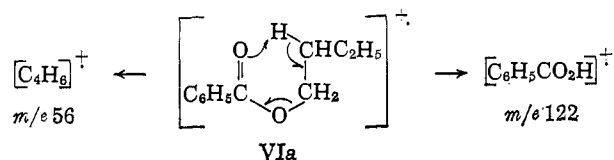
The per cent total ionization data for the peak group m/e 122-125 of butyl benzoate (VI) and its deuterated analogs VII-X are summarized in Table V, from which the per cent hydrogen transfer from each carbon atom can be calculated as listed in Table III. Inspection of that table shows that the double hydrogen-transfer reaction leading to the protonated carboxylic acid ion is not greatly affected by the nature of the acyl group, in contrast to the single hydrogen transfer leading to the olefin or the carboxylic acid ion. Of the three likely mechanisms for the double hydrogen transfer discussed in the preceding butyl propionate section, the third one (implying similar origins for one of the itinerant hydrogens in the single and the double hydrogen-transfer reactions) appears to us somewhat less plausible. The close quantitative similarity in the double hydrogen transfer for butyl propionate and butyl benzoate (Table III) would then require a similar correspondence for the single hydrogen-transfer step, which is not the case.

Mass Spectrum of Dibutyl Phthalate

By far the most intense ion in the mass spectra of all dialkyl phthalates[8,9] other than dimethyl phthalate is the one of mass 149, which carries nearly half of the total ionizing current (see Figure 3). While no deuterium labeling has as yet been performed among phthalates, all authors[8,9,24,25] agree on the formulation m for the m/e 149 species. Mechanistically, several paths leading to this ion have been proposed, and it is quite likely that more than one route is operative.

Both McLafferty[8] and Beynon[24] visualize the production of the m/e 149 species m through the intermediacy of the ion n (m/e 205 in the mass spectrum (Figure 3) of dibutyl phthalate), which would be formed by the usual alkoxy radical loss (see Figures 1 and 2) typical of esters. The intermediate n is then assumed[8] to undergo the typical "McLafferty rearrangement" (see arrows in n) with transfer of the β-hydrogen atom to yield the final product m, the sequence XI → n → m being indicated by the detection[9,24] of appropriate metastable peaks (marked by an asterisk in the flow sheet) in the dibutyl and diethyl phthalate spectra. Emery[9] and Biemann[25] on the other hand, assume that the first process is a double hydrogen rearrangement of the type discussed earlier in this paper with formation of the protonated carboxylic acid o (m/e 223 in Figure 3). In Biemann's view,[25] o undergoes a McLafferty rearrangement to p (see m/e 167 in Figure 3) followed by loss of water to m. Metastable ions for the steps o → p and p → m were recognized[25] in the mass spectrum of dioctyl phthalate. Emery,[9] working with dipropyl phthalate, proposed the sequences o → n → m and o → m on the basis of the appropriate metastable ions. The various reactions are summarized below using dibutyl phthalate as an example.
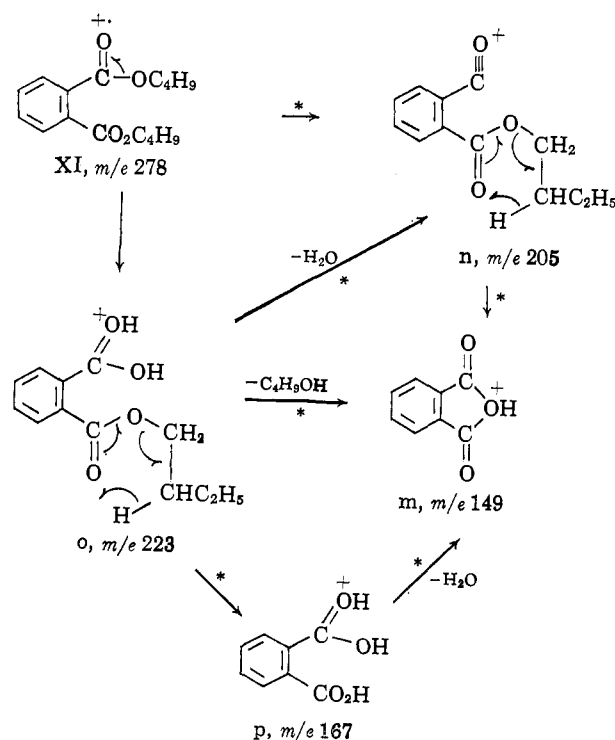
(24) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p. 377.
(25) Reference 14, pp. 170, 171.

Table VI. Metastable Peaks in Mass Spectra (Figure 3) of Dibutyl Phthalate Metastable Peak (m/e)

Obsd.	Calcd.	Transition
151.3 (small)	151.2	278 (XI) → 205 (n)
179.0	178.9	278 (XI) → 223 (o)
188.5	188.4	223 (o) → 205 (n)
Absent	125.1	223 (o) → 167 (p)
99.5	99.2	223 (o) → 149 (m)
108.5	108.3	205 (n) → 149 (m)
133.0	132.9	167 (p) → 149 (m)

effect discriminating against deuterium would also be expected to operate.

The general pattern of the hydrogen-transfer values summarized in the last column of Table VII is so reminiscent of the results encountered[28] in our laboratory for hydrogen transfers to triply bonded oxygen that we prefer to replace the expression n → m and o → p in the above flowsheet by n' → n'' → m and o' → o'' → p'.

Table VII. Principal Peaks in Mass Spectra of Dibutyl Phthalate and Deuterated Analogs[a]

Compd.	Isotopic purity	M^+	$M - 57^b$	$M - 73$	$M - 129$	Hydrogen transfer in m/e 149 peak, %
o-$C_6H_4(CO_2CH_2CH_2CH_2CH_3)_2$ (XI)	...	278	223	205	149	...
o-$C_6H_4(CO_2CD_2CH_2CH_2CH_3)_2$ (XII)	>99% d_2	282 (q)	226 (5%) 225 (95%)	207 (q)	150 (11%) 149 (88%)	11
o-$C_6H_4(CO_2CH_2CD_2CH_2CH_3)_2$ (XIII)	95% d_2 5% d_1	282 (q)	226 (52%) 225 (48%)	207 (q)	150 (30%) 149 (70%)	30
o-$C_6H_4(CO_2CH_2CH_2CD_2CH_3)_2$ (XIV)	94% d_2 6% d_1	282	226 (89%) 225 (11%)	207 (q)	150 (36%) 149 (64%)	36
o-$C_6H_4(CO_2CH_2CH_2CH_2CD_3)_2$ (XV)	91% d_3 6% d_2 3% d_0	282	227 (23%) 226 (77%)	208 (q)	150 (11%) 149 (89%)	11
					Total	88

[a] See footnote in Table I. [b] For further discussion of this very weak peak see p. 173 in ref. 3.

It should be noted that in none of these studies[8,9,24,25] was a metastable peak observed for the step XI → o nor were all of the metastable peaks recorded in the literature found in any one spectrum. Therefore, we repeated the measurement of the dibutyl phthalate spectrum under the most favorable conditions for metastable ion detection, namely with an Atlas CH-4 mass spectrometer in conjunction with a logarithmic transfer recorder.[26] The results are summarized in Table VI and demonstrate that all of the processes listed in the flow sheet are feasible[27] and that there are several routes to the m/e 149 species.
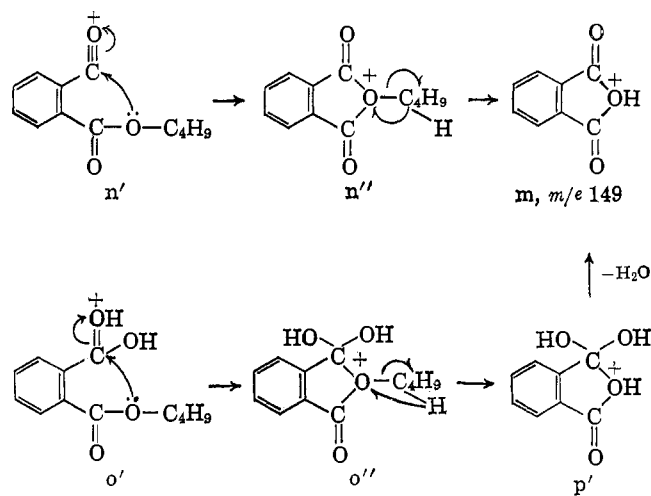
The shifts of the principal peaks in the spectra of the deuterated dibutyl phthalates are collected in Table VII. Of particular relevance to the present investigation is the origin of the migrating hydrogen implicated in the genesis of the key m/e 149 species (m). The results show that hydrogen can be abstracted from every carbon atom in the butyl chain with the γ-carbon atom (see XIV in Table VII) being the preferred locus. The originally postulated[8] sole intervention of the hydrogen atom from the β-carbon atom (XI → n → m) is thus excluded, and this also applies to the sequence XI → o → n → m. It is pertinent to note that the sum total of hydrogen transferred (last column in Table VII) as determined through deuterium labeling amounts only to 88%, but it should be remembered that intervention of steps o → m[9] or p → m[25] for any of the deuterated compounds (XII–XV) can lead to deuterium-free products if C_4H_9OD or D_2O rather than C_4H_9OH or H_2O is lost in the appropriate steps. In addition an isotope

(26) R. T. Aplin, H. Budzikiewicz, H. S. Horn, and J. Lederberg, Anal. Chem., 37, 776 (1965).
(27) No metastable peak for the transition o → p (see ref. 25) could be recognized (see Table VI), but the existence[25] of the subsequent step (p → m) was confirmed.

n'   n''   m, m/e 149

o'   o''   p'

Experimental Section

All mass spectra, except for the one used to construct Table VI, were obtained with a CEC Model 21-103C mass spectrometer using an all-glass inlet system heated to 200° with the isatron temperature at 250° and an ionizing energy of 70 e.v. We are indebted to Mr. John Smith for these measurements and to Dr. H. Budzikiewicz for assistance with some of the calculations. The various esters were prepared from the appropriate acid chloride and the labeled butanols[18,28] and purified by gas phase chromatography with a Wilkens Aerograph instrument. A phenyl diethanolamine succinate column (120–130°) was employed for the butyl propionate and butyl benzoate experiments, while an SE-30 column maintained at 210° was used for dibutyl phthalate.

(28) C. Djerassi and C. Fenselau, J. Am. Chem. Soc., 87, 5747 (1965).