Organic Ions in the Gas Phase. XVII. A Bicyclic Doubly Hydrogen-Bridged Transition State in Decomposition of 6-Substituted Alkanoic Acids and Esters

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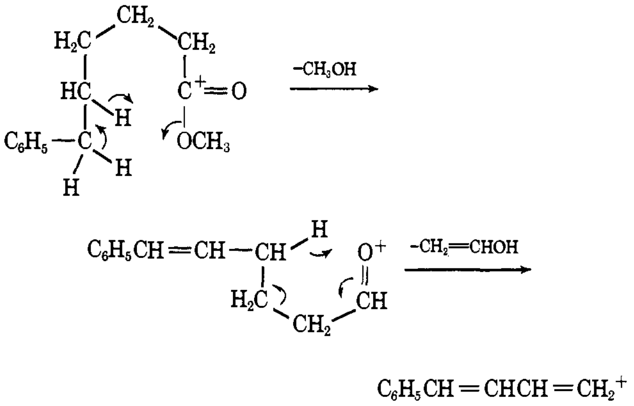
Abstract: Mass spectra of 6-phenylhexanoic acid and the derived methyl ester show not only the known rearrangement–dissociation processes associated with the phenyl and carbonyl groups, but also a previously unknown major competing reaction path. The latter path, which is energetically preferred, is apparently triggered by activation of a hydrogen atom on C-6. Deuterium-retention data for species labeled on C-6, C-5, and C-4 furnish evidence for the mechanism



By analogy, these findings support similar bicyclic hydrogen-bridged transition states that have been proposed to account for mass spectral features of alkyl isothiocyanates and cyanides.

The mass spectrum of a compound gives the distribution by mass of the products of decomposition by electron impact. The chemist's ability to deduce the structure of the original molecule from the spectrum depends on his knowledge of the underlying reactions, supplemented by speculation where the requisite knowledge is not available. Recent years have seen considerable effort devoted to increasing knowledge of the physical and chemical processes induced by electron impact, and thereby to reducing the extent to which reliance on speculation is necessary.[2] The present report, like earlier ones in this series, is intended as a contribution toward development of a systematic chemistry of gaseous ions.

Mass spectra of compounds containing either a phenyl[3] or a carbonyl group[4] show similar breakdown patterns, apparently directed by the functional group —scission of a bond once removed from the functional group accompanied by migration of a γ-hydrogen atom. With the original intent of examining the competition between these two reactions in a molecule that contains both groups so located that the same hydrogen atom is γ to both,[5] the spectra of 6-phenylhexanoic acid and the derived methyl ester were measured. In addition to the two expected reactions, the spectra revealed yet another major, and totally unexpected, rearrangement–dissociation path. The study reported here was carried out to clarify this third path.

The path is defined by intense peaks at the parent mass less 18 and less 62 units in the spectrum of 6-phenylhexanoic acid and at the parent mass less 32 and less 76 units in that of the methyl ester. Metastable peaks show that the two ions in each spectrum arise by successive steps in a single reaction sequence. The first step consists evidently of loss of H_2O from the acid or of CH_3OH from the ester, to give what is presumably a common product of mass 174. Only one reaction is known that seems able to account for loss of 44 mass units in the second step—loss of $CH_2{=}CHOH$ from an aldehyde.[4,6] Thus, the intermediate is most likely an unsaturated aldehyde with an available hydrogen atom on the carbon atom γ to the carbonyl group. Consideration of 6-phenylhexenal structures suggests the Δ^5-isomer as the most likely one. Conjugation of the double bond with the ring would tend to stabilize both the intermediate aldehyde and the resultant phenylbutadiene ion. Such stabilization should be even more pronounced in the ions than it would be in the neutral molecules because

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(1) (a) American Oil Co.; (b) National Research Council.

(2) See, for example, H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964.

(3) K. Biemann, "Mass Spectrometry. Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 122, and references cited therein.

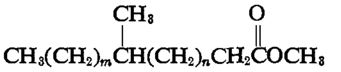
(4) S. Meyerson and J. D. McCollum, *Advan. Anal. Chem. Instrumentation*, 2, 179 (1963), and references cited therein.

(5) We are indebted to J. D. McCollum for suggesting this problem and for furnishing samples of 6-phenylhexanoic acid and methyl 6-phenylhexanoate for preliminary examination.

(6) J. A. Gilpin and F. W. McLafferty, *Anal. Chem.*, 29, 990 (1958).

of the progressive lowering of the ionization potential with extension of a conjugated π-electron system. Moreover, the second step would be assisted by allylic activation of the C–H bond to C-4. In the Δ^4-isomer, in contrast, this C–H bond would be deactivated by the adjacent double bond; the spectrum of 4-methylhept-6-en-3-one,[7] for example, shows no measurable yield of the rearrangement–dissociation product that would be expected to appear prominently in the absence of the double bond. Similarly, intensity of the $CH_2{=}C(OH)OCH_3^+$ ion—expressed as a fraction of total ion intensity—is nearly twice as great in the spectrum of methyl *trans*-5-hexenoate as in those of methyl *cis*- and *trans*-4-hexenoates.[8,9] Also pertinent by virtue of the close parallel between reactions of carbonyl compounds induced by ultraviolet light and by electron impact[4,10] is the observation that attempted photolysis of hex-5-en-2-one gives no more than possible traces of acetone and allene.[11]

A mass spectral study of methyl esters of methyl-branched alkanoic acids[12] reports a curious observation that seems to be closely related to the case in question. In the spectra of a large number of such esters

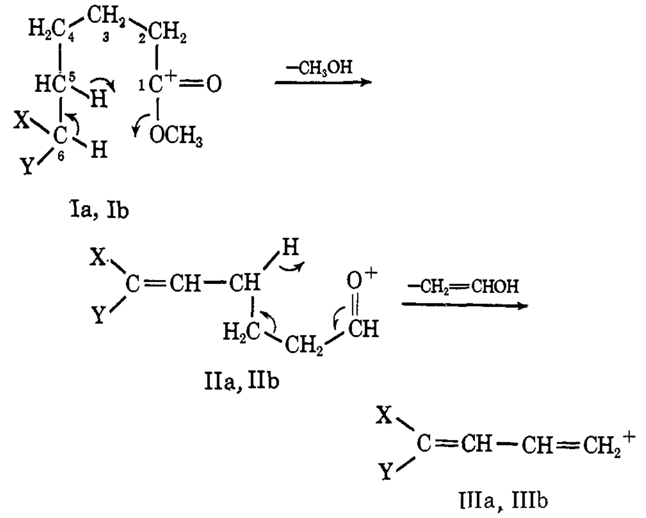


$$CH_3(CH_2)_m\overset{\overset{\displaystyle CH_3}{|}}{C}H(CH_2)_nCH_2\overset{\overset{\displaystyle O}{\|}}{C}OCH_3$$

the most intense even-mass peak occurs always at mass 74—corresponding to the $CH_2{=}C(OH)OCH_3^+$ ion—with but one exception. In the spectrum of methyl 6-methyloctadecanoate, the only ester studied that has a branch on C-6, the strongest peak occurs at the parent mass less 76 units. Spectra of methyl 5-methyl- and 7-methylalkanoates show small peaks at the parent mass less 76; when the methyl branch is in other positions, no such peak is observed at all. Evidently, the position of branching is critical for the reaction involved. A similar study of multiply branched methyl esters[13] yielded one more spectrum—of methyl 3,6-dimethyltetracosanoate—with an intense peak at the parent mass less 76 units, and one—of 2,4,6-trimethyltetracosanoate—with a small, possibly related peak at the parent mass less 90. Thus, three methyl esters are known that produce intense peaks at the parent mass less 76 units. The structures of all three would be expected to labilize the hydrogen atoms on C-6. Such labilization, or activation, at this apparently critical position may well be the common feature responsible for triggering the apparently common reaction sequence.

This line of reasoning suggested the mechanistic pathway shown in Scheme I. The driving force for the first step is furnished by the electron deficiency in the carbonyl group, assisted by the activated C–H bond to C-6, and, in Ib, the conjugation of the resulting double bond with the aromatic ring. The second step is assisted by allylic activation of the C–H bond to C-4 and by conjugation of the newly forming double bond with the π-electron system already present in II. A methyl branch on C-3, C-4, or C-6 would be retained in the product III, but one on C-2 would be lost in the second step. Thus, the product derived from a 3,6-dimethyl ester would have a mass 76 units less than that of the starting compound, and that from a 2,4,6-trimethyl ester, 90 units less, in accord with the observed spectra. Highly ordered bicyclic transition states similar to that proposed here have been suggested to account for the loss of SH from pentyl and higher alkyl isothiocyanates[14] and loss of olefin from hexyl and higher alkyl isothiocyanates[14] and from heptyl and higher alkyl cyanides.[15]

Scheme I



a, $X = CH_3$; $Y = C_nH_{2n+1}$
b, $X = C_6H_5$; $Y = H$

The proposed mechanism requires that a hydrogen atom from C-6 be lost in the first step and that one hydrogen atom each from C-6, C-5, and C-4 be lost in the over-all reaction I → III. Deuterium labeling permits a critical test of these predictions. A study was therefore undertaken of the spectra of 6-phenylhexanoic acid unlabeled, -6-*d*, -5-*d*$_2$, and -4-*d*$_2$, and the derived methyl esters. To assist interpretation, the spectra of phenylacetic, 3-phenylpropanoic, 4-phenylbutanoic, and 5-phenylpentanoic acids also were included.

Experimental Section

The synthetic route employed in preparing the labeled 6-phenylhexanoic acids was similar to that reported in a previous paper for labeled hexanols,[16] namely, lengthening of the carbon chain of the appropriate labeled intermediates by means of trimethylene oxide.[17] Thus, 6-phenylhexanoic acid-6-*d* was prepared by the following steps.

$$C_6H_5CH{=}CHCH_2OH \xrightarrow[2.\ D_2O]{1.\ LiAlH_4} C_6H_5CHDCH_2CH_2OH \xrightarrow{HBr}$$

$$C_6H_5CHDCH_2CH_2Br \xrightarrow{Mg} C_6H_5CHDCH_2CH_2MgBr \xrightarrow{\overline{CH_2CH_2CH_2O}}$$

$$C_6H_5CHD(CH_2)_4CH_2OH \xrightarrow{\text{tosyl chloride}} C_6H_5CHD(CH_2)_4CH_2OTos$$

$$\xrightarrow{Me_2SO} C_6H_5CHD(CH_2)_4CHO \xrightarrow{Ag_2O} C_6H_5CHD(CH_2)_4CO_2H$$

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[7] L. Ahlquist, R. Ryhage, E. Stenhagen, and E. von Sydow, *Arkiv Kemi*, **14**, 211 (1959).

[8] W. K. Rohwedder, A. F. Mabrouk, and E. Selke, *J. Phys. Chem.*, **69**, 1711 (1965).

[9] Occurrence of the $CH_2{=}C(OH)OCH_3^+$ ion in the spectra of the Δ^4-esters, as in those of methyl 2- and 3-hexenoates,[8] is most likely made possible by double-bond migration preceding decomposition of the parent ions.

[10] S. Meyerson, *J. Phys. Chem.*, **68**, 968 (1964).

[11] R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1960).

[12] R. Ryhage and E. Stenhagen, *Arkiv Kemi*, **15**, 291 (1960).

[13] R. Ryhage and E. Stenhagen, *ibid.*, **15**, 333 (1960).

[14] A. Kjaer, M. Ohasi, J. M. Wilson, and C. Djerassi, *Acta Chem. Scand.*, **17**, 2143 (1963).

[15] F. W. McLafferty, *Anal. Chem.*, **34**, 26 (1962).

[16] S. Meyerson and L. C. Leitch, *J. Am. Chem. Soc.*, **86**, 2555 (1964).

[17] S. Searles, *ibid.*, **73**, 124 (1951).

The labeled 3-phenylpropanol was prepared as described in Murray and Williams.[18] Yields were generally 80 to 90% in each step except in the chain extension, where it was only 50 to 60%. Approximate purity of the product was assessed by the neutralization equivalent, 194 (theoretical, 193). The 5-d_2 acid was prepared from ethyl phenylacetate by the following sequence.

$$C_6H_5CH_2CO_2R \xrightarrow{LiAlD_4} C_6H_5CH_2CD_2OH \xrightarrow{HBr} C_6H_5CH_2CD_2Br \xrightarrow{Mg}$$

$$C_6H_5CH_2CD_2MgBr \xrightarrow{\overline{CH_2CH_2CH_2O}} C_6H_5CH_2CD_2(CH_2)_3OH \xrightarrow{HBr}$$

$$C_6H_5CH_2CD_2(CH_2)_3Br \xrightarrow{Mg} C_6H_5CH_2CD_2(CH_2)_3MgBr \xrightarrow{CO_2} C_6H_5CH_2CD_2(CH_2)_3CO_2H$$

Here again the yields were high except for the chain-lengthening step. The 4-d_2 acid was prepared similarly from ethyl 3-phenylpropanoate.

$$C_6H_5CH_2CH_2CO_2R \xrightarrow{LiAlD_4} C_6H_5CH_2CH_2CD_2OH \xrightarrow{HBr}$$

$$C_6H_5CH_2CH_2CD_2Br \xrightarrow{Mg} C_6H_5CH_2CH_2CD_2MgBr \xrightarrow{\overline{CH_2CH_2CH_2O}}$$

$$C_6H_5CH_2CH_2CD_2(CH_2)_3OH \xrightarrow{\text{tosyl chloride}} C_6H_5CH_2CH_2CD_2(CH_2)_3\text{-}$$

$$OTos \xrightarrow{Me_2SO} C_6H_5CH_2CH_2CD_2CH_2CH_2CHO \xrightarrow{Ag_2O} C_6H_5CH_2CH_2CD_2CH_2CH_2CO_2H$$

The unlabeled acid was prepared by the same route as the 4-d_2, but with lithium aluminum hydride instead of deuteride.

The mass spectra of the 6-phenylhexanoic acids showed that removal of impurities was incomplete. However, the principal impurity, 3-phenylpropanoic acid, does not interfere in the mass spectral regions relevant to the main reaction path under study, so it was not a matter of great concern.

The acids were esterified by G. W. Powers with methanol and hydrochloric acid, and the esters were purified by D. K. Albert by preparative gas chromatography. The phenylacetic acid was kindly furnished by A. H. Sehon, of McGill University; the 3-phenylpropanoic and 4-phenylbutanoic acids were supplied by A. T. C. H. Tan, of McGill University. The 5-phenylpentanoic acid was Aldrich Chemical Co. material, twice recrystallized from hexane.

Mass spectra were measured with 70-v. electrons on a modified[19] Consolidated Model 21-103c instrument with the inlet system at 250°. Low-voltage spectra of the esters were measured at a series of ionizing voltages at 0.5-v. intervals, starting at 5.5 v. (nominal). For the low-voltage measurements, the repeller plates were maintained at an average potential of 3 v.; actual settings, adjusted for maximum ion current, were 3.50 v. on the inner repeller and 2.50 v. on the outer one.

Isotopic impurities of the labeled materials were estimated from the parent regions of the low-voltage spectra[20] (see Table I).

Table I

	Acids			Esters		
	6-d	5-d_2	4-d_2	6-d	5-d_2	4-d_2
Unlabeled, %	4.4	0.3	3.0	4.3	0.3	0.4
d_1, %	95.6	2.6	1.3	95.7	1.5	1.5
d_2, %	...	97.1	95.7	...	98.2	98.1

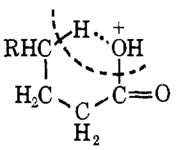
The excess unlabeled material found in the 4-d_2 acid over that in the derived ester is probably instrument background from incomplete pumpout of the unlabeled acid from the preceding run. The 70-v. spectrum of the 6-d ester was corrected for the isotopic impurity and for naturally occurring heavy isotopic contributions. Only the latter correction was made to the other spectra.

Results and Discussion

Table II shows partial spectra of ω-phenylalkanoic acids with 2 to 6 aliphatic carbon atoms. Facile loss of H_2O apparently requires an aliphatic chain of at least four carbon atoms, just as in primary alcohols.[16,21] The parallel suggests that loss of H_2O from acids, as from alcohols, occurs preferentially *via* a six-membered hydrogen-bridged cyclic intermediate or transition state.

Table II. Partial Spectra of ω-Phenylalkanoic Acids, $C_6H_5(CH_2)_nCOOH$

	Relative intensity				
Mass	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
Parent	100.0	100.0	100.0	100.0	100.0
Parent less 18	3.2	3.5	23.8	91.6	21.1
Parent less 62	3.0	0.2	7.9	9.7	168.9



Intensity at the parent mass less 62 units—corresponding to loss of H_2O and $CH_2{=}CHOH$—is substantial in only one of the spectra, that of 6-phenylhexanoic acid. Thus, a hydrogen atom on C-6 is apparently required for the two-step reaction sequence, as suggested by the parallel with methyl-branched methyl alkanoates.[12]

Partial spectra of the four isotopic species of 6-phenylhexanoic acid are shown in Table III. Although

Table III. Partial Spectra of 6-Phenylhexanoic Acids

		Relative intensity			
Mass	Ion[a]	Unlabeled	6-d	5-d_2	4-d_2
194		...	2.0	100.0	100.0
3		...	100.0	2.6	1.5
2	$C_{12}H_{16}O_2^+$	100.0	4.5	0.4	3.1
178		...	...	...	0.5
7		...	0.4	2.2	2.7
6		...	2.9	13.4	16.8
5		2.2	12.1	3.6	1.9
4	$C_{12}H_{14}O^+$	21.1	5.6	0.4	0.8
135		...	...	7.4	5.3
4		...	13.8	18.4	18.0
3		8.1	21.8	8.5	13.9
2		18.6	21.0	20.3	21.7
1		9.9	106.1	151.5	169.5
0	$C_{10}H_{10}^+$	168.9	86.1	16.9	21.1
129		6.4	5.6	2.7	4.2

Metastable peaks					
		Relative intensity			
Mass	Transition denoted	Unlabled	6-d	5-d_2	4-d_2
159.7	(194+)→(176+) + 18	...	...	0.84	0.95
158.7	(193+)→(175+) + 18	...	0.60	...	...
157.9	(194+)→(175+) + 19	...	...	0.17	...
157.7	(192+)→(174+) + 18	1.24	...	...	...
97.5	(176+)→(131+) + 45	...	...	0.30	0.43
97.1	(174+)→(130+) + 44	0.57	...	...	...

[a] Formulas are shown opposite masses of the appropriate unlabeled ions only.

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(18) A. Murray and D. L. Williams, "Organic Syntheses with Isotopes," Interscience Publishers, Inc., New York, N. Y., 1958, p. 1456.

(19) H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moeller, 7th Annual Meeting of the American Society for Testing Materials Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May 1959.

(20) D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, **72**, 5612 (1950).

(21) W. Benz and K. Biemann, *ibid.*, **86**, 2375 (1964).

Table IV. Isotopic Distributions of Fragment Ions from Labeled 6-Phenylhexanoic Acids

Ion	Mass	6-*d* 70 v.	6-*d* Low voltage[a]	5-d_2 70 v.	5-d_2 Low voltage[a]	4-d_2 70 v.	4-d_2 Low voltage[a]
$C_{12}H_{14}O^+$-d_0, %	174	32	27	2	1	4	2
-d_1, %	175	68	73	21	14	10	6
-d_2, %	176	..	..	77	85	86	92
$C_{10}H_{10}^+$-d_0, %	130	~40	50	..	5	..	10
-d_1, %	131	~60	50	Most	84	Most	82
-d_2, %	132	..	..	..	11	..	8

[a] Low-voltage results shown are derived from measurements close to the respective appearance potentials of the ions.

some uncertainty is unavoidable because of small isotopic impurities, unknown isotope effects, and—in the case of the $C_{10}H_{10}^+$ ion—interference from neighboring ions, one can make rough estimates of label retentions in fragment ions. These are shown in Table IV. Of the $C_{12}H_{14}O^+$ ions, corresponding to loss of H_2O, about 32% derived from the 6-*d* species, 21% from the 5-d_2, and 10% from the 4-d_2 have lost a deuterium atom. The material balance of 95%—(2 × 32) + 21 + 10—is gratifying and furnishes evidence that little or no hydrogen is lost from other positions. About 60% of the $C_{10}H_{10}^+$ ions from the 6-*d* acid retain the label (alternative assumptions[22] lead to estimates of 106.1/168.9 or 63% and 106.1/(106.1 + 86.1) or 55%), and the bulk of these ions from the two d_2 species retains one deuterium atom. Isotopic distributions measured at ionizing voltages close to the respective appearance potentials, also shown in Table IV, accord fairly well with the 70-v. data. The material balance for hydrogen lost as H_2O from C-6, C-5, and C-4 is only 74%, suggesting either greater isotope effects than in the 70-v. spectra or a proportionately greater loss of hydrogen from other positions. The observed 50% retention in $C_{10}H_{10}^+$ in the 6-*d* spectrum implies that one hydrogen atom has been lost from C-6 in all the molecules reacting by this path. To the extent that the discrepancy between the observed retention in $C_{12}H_{14}O^+$ and 50% is caused by an isotope effect, the second step must be subject to an almost exactly compensating effect—an unlikely looking possibility. Alternatively, to the extent that the discrepancy is caused by competing modes of H_2O loss involving hydrogen from positions other than C-6, the primary products so arising apparently do not contribute to $C_{10}H_{10}^+$ formation. The low-voltage spectra show further that over 80% of the $C_{10}H_{10}^+$ ions have lost one hydrogen atom each from C-5 and C-4, as required by the suggested mechanism.

Partial spectra of the methyl esters are shown in Table V, and isotopic distributions of the $C_{12}H_{14}O^+$ ions, estimated from the 70-v. spectra and also from measurements at ionizing voltages close to the respective appearance potentials, are shown in Table VI. The isotopic distributions are approximately independent of ionizing voltage, implying that each of the ions arises by either a single path or by two or more paths with essentially equal energy requirements.[23]

Table V. Partial Spectra of Methyl 6-Phenylhexanoates

Mass	Ion[a]	Relative intensity Unlabeled	6-*d*[b]	5-d_2	4-d_2
208		...	...	100.0	100.0
7		...	100.0	1.6	1.5
6	$C_{13}H_{18}O_2^+$	100.0	...	0.3	0.4
5		0.2	0.1	...	...
177		1.2	0.5	102.4	109.1
6		0.1	100.4	232	254
5		101.8	209	17.3	7.8
4	$C_{12}H_{14}O^+$	251	30.5	1.2	0.9
3		3.4	0.7	...	0.2
134		...	5.0	25.0	20.6
3		6.1	24.2	23.1	26.0
2		29.0	24.0	60.8	41.5
1		29.5	408	610	715
0	$C_{10}H_{10}^+$	696	272	42.8	34.3
129		20.0	12.5	7.0	7.8
8		11.7	5.6	3.2	4.0
94		0.8	2.8	29.3	3.4
3		2.9	181	254	145
2	$C_7H_8^+$	205	1275	370	162
1	$C_7H_7^+$	1475	214	1015	912
0		22.9	30.7	25.2	16.4
76		6.7	10.0	12.8	24.5
5		23.0	89.1	116.4	417
4	$C_8H_6O_2^+$	474	405	449	112.2
3		89.8	85.5	16.6	3.0

Metastable peaks

Mass	Transition denoted	Relative intensity Unlabeled	6-*d*[b]	5-d_2	4-d_2
148.9	$(208^+) \rightarrow (176^+) + 32$	...	...	3.5	3.5
148.0	$(207^+) \rightarrow (175^+) + 32$	...	3.2	...	...
147.0	$(206^+) \rightarrow (174^+) + 32$	3.6	...	...	...
98.1	$(175^+) \rightarrow (131^+) + 44$	...	1.8	...	...
97.5	$(176^+) \rightarrow (131^+) + 45$	...	...	2.1	1.8
97.1	$(174^+) \rightarrow (130^+) + 44$	2.3	0.8	...	...
91.0	$(93^+) \rightarrow (92^+) + 1$	...	1.4	...	...
90.0	$(92^+) \rightarrow (91^+) + 1$	2.0	...	0.7	...

[a] Formulas are shown opposite masses of the appropriate unlabeled ions only. [b] Corrected for contributions of unlabeled impurity.

The poor material balance for hydrogen loss from C-6, C-5, and C-4 derived from isotopic distributions of $C_{12}H_{14}O^+$—36% at 70 v., 40% at low voltage—implies more pronounced isotope effects or more extensive loss from C-3, C-2, and perhaps the phenyl ring than in the acid. The $C_{10}H_{10}^+$ data, in good agreement with the corresponding data for the labeled acids, imply loss of a deuterium atom in nearly half—40%—of the ions derived from the 6-*d* ester, in 86% of those from the 5-d_2 ester, and in 91% of those from the 4-d_2 ester.

Water is apparently lost from 6-phenylhexanoic acid, and CH_3OH from methyl 6-phenylhexanoate, in

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[22] H. M. Grubb and S. Meyerson, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p. 453.

[23] S. Meyerson, *J. Chem. Phys.*, **34**, 2046 (1961); S. Meyerson, T. D. Nevitt, and P. N. Rylander in "Advances in Mass Spectrometry," Vol. II, R. M. Elliott, Ed., Pergamon Press Inc., New York, N. Y., 1963, p. 313; S. Meyerson and H. Hart, *J. Am. Chem. Soc.*, **85**, 2358 (1963).

Table VI. Isotopic Distributions of Fragment Ions from Labeled Methyl 6-Phenylhexanoates

		6-*d*		5-d_2		4-d_2	
Ion	Mass	70 v.	Low voltage[a]	70 v.	Low voltage[a]	70 v.	Low voltage[a]
$C_{12}H_{14}O^+$-d_0, %	174	13	16	...	...	...	...
-d_1, %	5	87	84	7	6	3	2
-d_2, %	6	...	...	93	94	97	98
$C_{10}H_{10}^+$-d_0, %	130	40	41	6	6	4	3
-d_1, %	1	60	59	86	86	91	92
-d_2, %	2	...	...	8	8	5	5

[a] Low-voltage results shown are derived from measurements close to the respective appearance potentials of the ions.

Table VII. Low-Voltage Measurements on Unlabeled Methyl 6-Phenylhexanoate

		Peak height, arbitrary units					
Mass	Ion	5.5[a]	6.0[a]	6.5[a]	7.5[a]	8.0[a]	
206	$C_{13}H_{18}O_2^+$	3.8	11.2	21.7	33.3	45.0	56.3
174	$C_{12}H_{14}O^+$	4.2	16.9	41.6	74.0	111.0	147.0
130	$C_{10}H_{10}^+$	...	0.4	2.0	7.1	20.6	44.0
92	$C_7H_8^+$	...	...	...	0.5	0.8	1.8
74	$C_3H_6O_2^+$	...	...	...	...	1.3	4.1

[a] Ionizing volts (nominal).

multiple ways that differ but little in energy requirements. The contribution of 1,6-elimination is far greater than those of 1,5- and 1,4-; those of 1,3- and 1,2-elimination and processes involving ring hydrogen atoms are unknown. Despite the participation of alternative primary steps, isotopic distributions of $C_{10}H_{10}^+$ ions agree closely enough with prediction from the proposed mechanism to constitute strong supporting evidence for that mechanism. Thus, of the isomeric primary products, only that arising by 1,6-elimination apparently has the structure required for facile secondary loss of $CH_2{=}CHOH$.

The ability of this reaction path to compete effectively with the better known low-energy paths available can be rationalized in terms of energy requirements. The low-voltage measurements show that the path leading to products II and III requires substantially less energy than the paths leading to $C_7H_8^+$ and $C_3H_6O_2^+$ ions, the expected products of the known rearrangement–dissociation reactions directed by the phenyl and carbonyl groups, respectively. From the data shown in Table VII, differences between appearance potentials of the ionic products can be roughly estimated. Thus, $A(C_{10}H_{10}O^+) - A(C_{12}H_{14}O^+) > 0.5$ e.v.; $A(C_7H_8^+) - A(C_{10}H_{10}^+) \simeq 1$ e.v.; and $A(C_3H_6O_2^+) - A(C_7H_8^+) \simeq 0.5$ e.v.

Postscript. Labeling data on the $C_7H_8^+$ and $C_3H_6O_2^+$ ions are included in Table V. In neither case are the underlying reactions fully defined. The $C_7H_8^+$ peak is accompanied by an even more intense $C_7H_7^+$ peak, and how much of the $C_7H_7^+$ yield arises by loss of H from $C_7H_8^+$, by primary β-cleavage, and by other, unspecified paths is unknown. The high intensity at mass 93 in the 5-d_2 spectrum (due to $C_7H_8^+$-d_1 or $C_7H_7^+$-d_2 or both) requires the participation of such other, unspecified paths. The summation of intensities at masses 91, 92, and 93 in the 4-d_2 spectrum is markedly less than in any of the other spectra; the isotope effect thus revealed implies that a large part of the $C_7H_8^+$ and $C_7H_7^+$ ion yield arises by a path or paths involving cleavage of a C–H bond to C-4. Most of the $C_3H_6O_2^+$ ions clearly contain a hydrogen atom originally on C-4 but, equally clearly, hydrogen atoms from C-5 and C-6 have been incorporated in some of these ions. Thus, in response to the original question that prompted this study, available data establish only that both reactions persist in the face of competition from each other and from yet other paths.

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