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# MASS SPECTROMETRIC DECOMPOSITION OF β-PHENYLOXIRANECARBOXYLIC ESTERS

O. S. Anisimova, V. V. Chistyakov, A. I. Bokanov,
V. I. Shvedov, and Yu. N. Sheinker

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The electron-impact mass spectra of the E- and Z-isomers of the α,β-methyl substituted esters of β-phenyloxiranecarboxylic acids have been studied.

Ethylene oxide derivatives, particularly the β-phenyloxiranecarboxylic acids and their esters, are interesting materials for study in connection with their structural features, tendency to isomerize, and unequivocal course of their addition reactions; this has been responsible for the study of this class of compounds by various chemical and spectral methods [1-4]. However, the oxiranecarboxylic acids have been insufficiently studied by mass spectrometry. Hitherto, the electron-impact mass spectra have been considered for a series of ethyl and tert-butyl esters of β-phenyloxiranecarboxylic acids [5, 6]. The authors of [5] proposed an interpretation of those spectra on the basis of rearrangements of the molecular ion (M^+) before decomposition, opening of the oxirane ring at the C—C and C—O bonds, and migration of the substituents located at the α- and β-carbons. However, the methods used in [5] to establish the decomposition sequence were extremely limited in scope, due to the absence at that time of the DADI procedure and defocusing in the first field-free space.

The present work presents a chromato-mass spectrometric study of the E-isomer of α-methyl-β-phenyloxiranecarboxylic acid E-I, and the E- and Z-isomers of the oxiranecarboxylic esters II-V:

E-isomers
I - V

Z-isomers
II - V
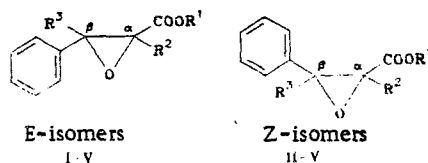
E-I R¹=R³=H, R²=CH₃; E-,Z-II R¹=C₂H₅, R²=CH₃, R³=H; E-,Z-III R¹=R²=CH₃;
R³=H; E-,Z-IV R¹=C₂H₅, R²=H, R³=CH₃; E-,Z-V R¹=C₂H₅, R²=R³=CH₃

0009-3122/86/2210-1058$12.50

TABLE 1. Electron-Impact Mass Spectra of Compounds I-V at 70 eV*

Com-pound	m/z (intensity, %)
E-I	134 (4), 133 (3), 132 (5), 108 (8), 107 (100), 105 (12). 104 (3), 103 (3), 91 (24), 90 (54), 89 (42), 80 (3), 79 (40), 78 (3), 76 (16), 72 (3), 65 (4), 54 (4), 63 (4)
E-II	136 (10), 135 (100), 133 (9), 132 (4), 108 (6), 107 (81), 105 (21), 103 (3), 91 (6), 90 (22), 89 (17), 79 (33), 77 (10), 43 (87)
Z-II	136 (10), 135 (100), 133 (7), 132 (3), 108 (5), 107 (65), 105 (14), 91 (4), 90 (18), 89 (14), 79 (21), 77 (8), 43 (86)
E-III	133 (5), 132 (3), 122 (9), 121 (100), 107 (3), 105 (12), 91 (5), 90 (23), 89 (16), 79 (6), 77 (13), 63 (5), 51 (6), 43 (23)
Z-III	133 (4), 122 (9), 121 (100), 107 (3), 105 (11), 91 (5), 90 (24), 89 (14), 79 (4), 77 (10), 63 (4), 51 (5), 43 (16)
E-IV	206 (4), 205 (6), 189 (5), 178 (8), 161 (5), 160 (14), 150 (3), 149 (10), 135 (6), 134 (6), 133 (51), 132 (100), 121 (14), 119 (3), 105 (72), 104 (62), 103 (61), 91 (6), 79 (19), 78 (36), 77 (46), 51 (12), 43 (54)
Z-IV	206 (3), 205 (5), 178 (4), 161 (4), 160 (11), 149 (14), 135 (6), 134 (4), 133 (30), 132 (100), 121 (13), 119 (3), 105 (54), 104 (63), 103 (5⁻), 91 (6), 79 (26), 78 (41), 77 (43), 51 (11), 43 (60)
E-V	219 (3), 174 (6), 149 (55), 147 (31), 146 (72), 132 (5), 131 (6), 121 (52), 119 (13), 105 (21), 104 (100), 103 (55), 91 (15), 78 (32), 77 (25), 51 (11), 43 (90)
Z-V	219 (4), 178 (5), 174 (7), 173 (3), 149 (59), 147 (39), 146 (92), 132 (8), 131 (9), 121 (61), 119 (15), 105 (23), 104 (100), 103 (66), 91 (20), 78 (47), 77 (39), 51 (13), 43 (88).

*Ion peaks with intensity ≥3% of maximum are shown.

In considering the data (Table 1) it must be noted first of all that the mass spectra of individual E- and Z-isomers show no stereoselectivity in the principal decomposition routes.
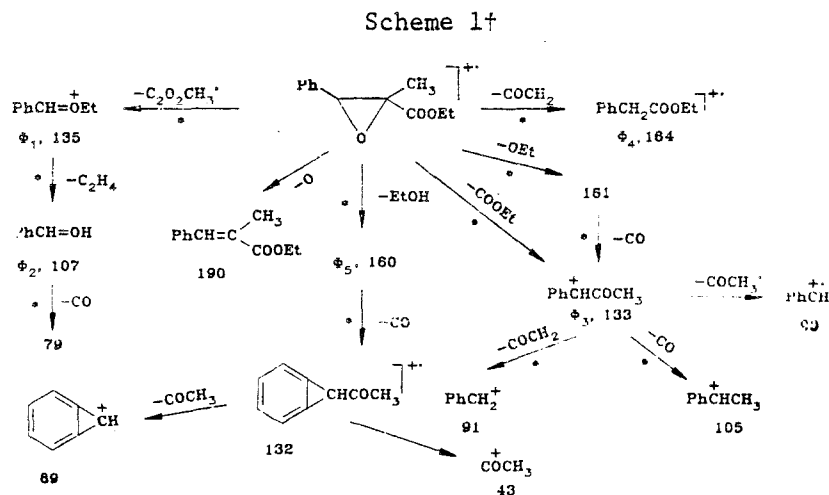
Scheme 1†

†In all cases in the schemes, the number characterizing the ion determines the m/z value.

The fragmentation sequence of the compounds was determined from the DADI spectra and by defocusing in the first field-free space. It was established that the decisive course of fragmentation of the α-methyl substituted compounds I-III is the formation of ion Φ_1 and its decomposition products (Scheme 1). $PhCR^3=OR^1$, the structure proposed for Φ_1 in [5], was confirmed by the dependence of the change in mass number on substituents R^1 and R^3 (Table 2, compounds I-V). Study of the mass spectra of esters E-II and Z-II in which the ester oxygen is replaced by isotope ^{18}O†† showed that Φ_1 contained an appreciable amount of tracer. This means that Φ_1 forms by the migration of alkoxy to the β-carbon followed by detachment of

††Mixtures of isomers E-, Z-III were obtained by transesterification with $C_2H_5{}^{18}OH$ in the presence of $C_2H_5{}^{18}ONa$.

1059

TABLE 2. m/z Values and Intensities of Characteristic Ions in Mass Spectra of Compounds I-V

Ion	E-I	E-II	Z-II	E-III	Z-III	E-IV	Z-IV	E-V	Z-V
M+	178 (1)	206 (1)	206 (1)	192 (1)	192 (1)	206 (4)	206 (3)	220 (1)	220 (2)
[M−H]+	—	—				205 (6)	205 (5)	219 (3)	219 (4)
Φ_1	107 (100)*	135 (100)	135 (100)	121 (100)	121 (100)	149 (10)	149 (14)	149 (55)	149 (59)
Φ_2		107 (81)	107 (65)	107 (3) R=CH₃	107 (3)	121 (14)	121 (13)	121 (52)	121 (61)
Φ_3	133 (3)	133 (9)	133 (7)	133 (5)	133 (4)	133 (51)	133 (30)	147 (31)	147 (39)
Φ_4	—	164 (1)	164 (1)	164 (1)	164 (1)	—	—	178 (2)	178 (5)
Φ_5	160 (1)	160 (1)	160 (1)	160 (1)	160 (1)	160 (14)	160 (11)	174 (6)	174 (7)
Φ_6	132 (5)	132 (4)	132 (3)	132 (3)	132 (2)	132 (100)	132 (100)	146 (72)	146 (92)
Φ_7	104 (3)	104 (2)	104 (1)	104 (1)	104 (1)	104 (62)	104 (63)	104 (100)	104 (100)

*For compound E-I (R = H), Φ_2 and Φ_1 are identical.

TABLE 3. Ion Peak Intensity
in Spectra of Isomeric Esters
E-, Z-II at 12 eV

Ion	Relative intensity, %	
	E-II	Z-II
M^+	7	9
$[M - O]^+$	39	40
Φ_4	21	23
Φ_1	100	100

$C_2O_2R^2$. The other decomposition paths for M^+ of compounds I-III are related to the stepwise detachment of the ester group (ion Φ_3) with elimination of an O atom,* R^1OH molecules (Φ_5), and $COCH_2$ (Φ_4), but the intensities of these peaks in the 70 eV spectra do not exceed 1% (Table 2). Scheme 1 shows as an example the steps in the decomposition of esters E-, Z-II.

It is important to note that according to our data the ion with mass number 105 forms only by decomposition of $[M - COOEt]^+$ (Φ_3) and apparently has the composition and structure shown in Scheme 1. Direct formation from M^+ of benzoyl cation with the same mass number was not observed. Analogously in the case of the β-methyl substituted esters E-, Z-IV, and V the molecule ion does not decompose to form acetyl cation.† These data indicate the absence of rearrangements related to the scission cleavage of C—C and C—O bonds or the mirgration of β-substituents to the α-carbon as presumed in [5]:

Scheme 2
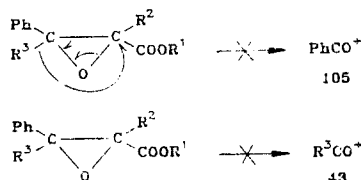
It is evident that the oxirane ring actually opens by electron-impact ionization before decomposition, but of the two C—O bonds the more polarized bond of oxygen with benzyl carbon (the β-carbon) is preferentially cleaved.†† This is indicated by the fact that all the subsequent rearrangements proceed by migration of groups from the α-carbon to the cationic center at the β-carbon (Scheme 3).

It should be noted that the rearrangements involving opening of the oxirane ring are very favored energetically; the peaks of the respective ions appear in the spectra even when the energy of the ionizing electrons is reduced, and the Φ_1 peak in the spectra of esters E- and Z-II at 12 eV remains maximal as before (Table 3). It is clear that the very ease of heterocycle opening under electron impact conditions causes the spectra of the E- and Z-isomers to coincide. As follows from Table 3, even at 12 eV energy the spectra of the E- and Z-isomers are practically the same.

It is known that the introduction of alkyl substituent at the β-carbon in β-phenyloxiranecarboxylic esters causes a rotation of the plane of the phenyl ring, due to the steric effect of the β-substituent [7]; this apparently creates conditions favorable for the elimination of the ortho-hydrogen atom. From the favorability of the subsequent detachment of a $COOC_2H_5$ group it can be presumed that the resulting $[M - H]^+$ ion has a bicyclic structure as shown in Scheme 4 for the β-methyl substituted esters E-, Z-IV and -V.

*Since the metastable transition that confirms detachment of oxygen from the molecule ion by dissociative ionization was not observed, the possible thermal nature of this process cannot be excluded.
†In the spectra of E-, Z-IV, and -V, acetyl cation forms only by detachment of a benzene molecule from Φ_2 (Scheme 4).
††Opening of the oxirane ring by cleavage of the C—C is less probable, because in this ring the C—O bond is more easily cleaved [1, 3].

Scheme 3
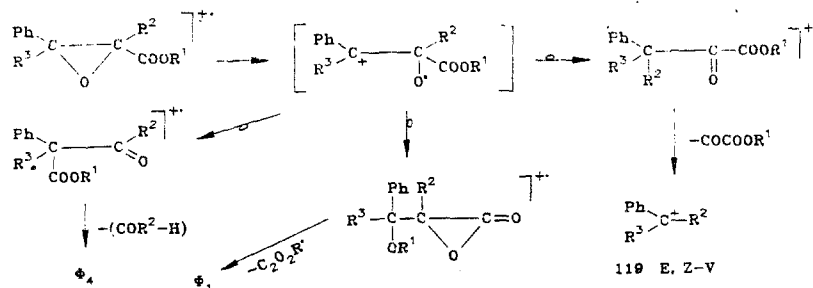
A comparison of the mass spectra of esters II-V shows the great effect of substituent location on the course of decomposition. In the spectra of E- and Z-IV (R^2 = H, R^3 = CH$_3$) the peak intensity of Φ_1 falls to 10-14%, whereas there is a sharp increase in intensity of the ions involved in elimination of a hydrogen M^+ and of those formed by stepwise detachment of ethoxycarbonyl. This decomposition route is decisive in the spectra of compounds E- and Z-IV (Table 2).

As shown by the spectra of compounds E- and Z-IV-D$_5$, in which all phenyl hydrogens are replaced by deuterium,* the $[M - H]^+$ ion forms exclusively by elimination of phenyl hydrogen. The elimination of an ethyl alcohol molecule that is typical of compounds E- and Z-IV (to form Φ_5) also goes to an appreciable extent with capture of a phenyl hydrogen. This is indicated by the 3:1 ratio of the peak intensities of ions, $I_{[M-C_2H_5OD]}^+/I_{[M-C_2H_5OH]}^+$.

The most intense peaks in the spectra of compounds E-, Z-IV and -V correspond to Φ_6 [M − HCOOC$_2$H$_5$]$^+$ and the products of the subsequent elimination therefrom of the species COR^2-H (Φ_7) and COR^2 (Φ_8).

Scheme 4
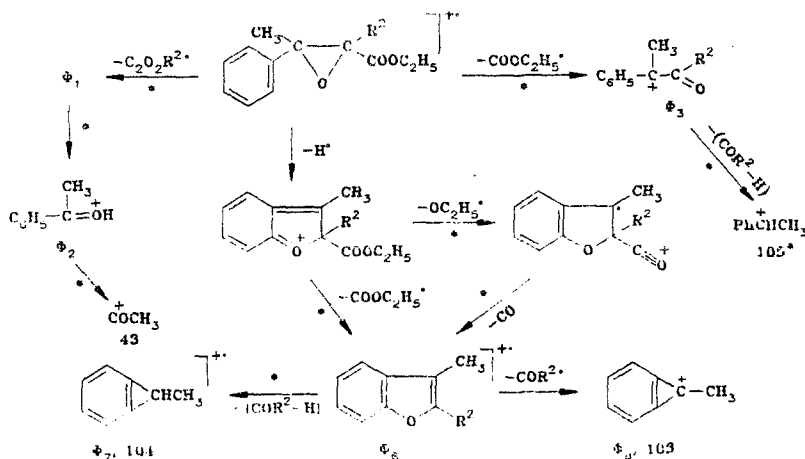
†According to the high resolution spectrum of ester E-IV the ion with mass number 105 has 89% of composition C$_3$H$_9$ [5].

As a result of the introduction of methyl groups at either the α- or β-positions of the oxirane, both decomposition routes in the spectra of ethers E- and Z-V (migration of ethoxy and elimination of ortho-hydrogen from the benzene ring) are of nearly equal probability (Table 2); i.e., the decomposition of β-phenyloxiranecarboxylic esters by electron impact depends to a substantial extent on the nature of the substitution in the oxirane ring.

*E- and Z-isomers of ester IV-D$_5$ were obtained from D$_5$-acetophenone under the usual conditions of the Darzens reaction [4].

EXPERIMENTAL

Electron impact mass spectra, DADI spectra, and defocusing spectra in the first field-free space were obtained on a Varian MAT-112. Electron ionization energies were 70 and 12 eV. Ionization chamber temperature was 180°. Samples were introduced into the mass spectrometer through a Varian Aerograph 1440 chromatograph. Column, 3% SE-30 on Chromosorb W (180 cm × 2 mm), He at 20 ml/min, T_{inj} = 220°, T_{sep} = 230°, T_{col} = 120-230° (10°/min).

Esters II-V were synthesized by the Darzens method [4], viz., the reaction of benzaldehyde or acetophenone with monochloroacetate or 2-bromopropionate esters. In all cases, esters were obtained as a 1:1 mixture of E- and Z-isomers. E- and Z-isomers were separated during mass spectral photography by introduction of the samples into the mass spectrometer through the chromatograph. Retention times: E-, Z-II 6'30" and 4'50"; E-, Z-III 5'20" and 3'50"; E-, Z-IV 7'50" and 5'00"; E-, Z-V 4'40" and 4'00", respectively.

Acid E-I was obtained by hydrolysis of the mixture of E- and Z-II esters [8].

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PHOTOCHEMISTRY OF UNSATURATED LACTONES.
2.* PHOTOANNELATION OF 2-ACETYL-3,4,4-TRIMETHYL-2-BUTEN-4-
OLIDE BY TERMINAL ALKYNES

A. A. Avetisyan, A. Kh. Margaryan, G. K. Nalbandyan,   UDC 547.314.217.1'728:514.14:
and T. V. Avetisyan   543.422'51

The photochemical cycloaddition of 2-acetyl-3,4,4-trimethyl-2-buten-4-olide to 1-heptyne and 1-chloro-2-propyne was carried out. The reaction gives isomeric cycloadducts of the "head to head" and "head to tail" types. The influence of solvent on the directivity of the reaction was investigated. The possibility was shown of using the cycloadducts obtained in the synthesis of difficulty available polyfunctionally substituted butanolides and heterocyclic compounds containing a spirocyclobutene fragment.

The use of α,β-unsaturated lactones in their photoannelation reaction by alkynes has been dealt with in only one paper by Japanese authors [2]. To broaden the field of application of this reaction, we studied the photocycloaddition of 2-acetyl-3,3,4-trimethyl-2-buten-4-olide (I) to 1-heptyne (IIa) and 1-chloro-2-propyne (IIb).

*For Communication 1, see [1].