Electron Impact Behavior of β-Peroxylactones[1]

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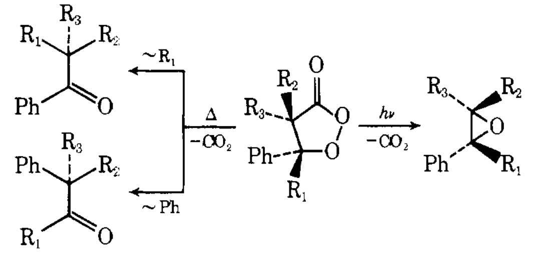
Mass spectral study of a series of β-peroxylactones with α-alkyl and β-alkyl or β-phenyl substitution and deuterium labeling was undertaken. By means of metastable ion mass spectra (MIMS), five primary fragmentation processes have been identified, consisting of loss of carbon trioxide, α-lactone, β-alkyl radical, hydroperoxy radical, and carbon dioxide. Except for the β-peroxylactones with β-benzyl substitution, for which the decarboxylation route is the major fragmentation process, the peroxide bond is strengthened on ionization and decarboxylation is significantly suppressed in comparison with photolysis and thermolysis. In all cases studied, employing MIMS, isotopic labeling, and high resolution, the M − CO_2 ions are epoxide-like in structure, as confirmed by their subsequent fragmentations. For example, the β-phenyl migration outweighs the β-alkyl migration. Thus, it is concluded that the electron impact behavior of β-peroxylacetones parallels the photolytic behavior of the compounds. However, in one case the M − CO_2 ion is not the result of a direct decarboxylation, but rather it is produced stepwise by first expelling a carbon monoxide, followed by deoxygenation.

A number of examples have been reported[3] demonstrating a correlation between mass spectral and photochemical behavior of organic compounds. We have observed an unusual energy-dependent decomposition in the thermo- and photodecarboxylation of β-peroxylactones. Thus, while thermolysis[4a] affords predominantly rearrangement ketones (alkyl and phenyl migration), photolysis[4b] leads principally to epoxides (eq 1). It was, therefore, of interest to investigate the electron-impact behavior of β-peroxylactones in order to assess whether the M − CO_2 fragment ion possesses an epoxide-like (photolysis) or a ketone-like (thermolysis) structure. This is particularly relevant since it has been shown[5] that cyclic carbonates, which are structurally isomeric with β-peroxylactones, fragment on electron impact into epoxide-like M − CO_2 ions. We report here our mass spectral study of β-peroxylactones **1–8**, by employing various techniques suitable for a double focusing instrument.



(1)

	1	2	3	4	5	6	7	8
R_1	CH_3	CH_3	CD_3	C_2H_5	i-C_3H_7	$C_6H_5CH_2$	Ph	$C_6H_5CH_2$
R_2	H	D	H	H	H	H	CH_3	CH_3
R_3	H	D	H	H	H	H	H	H

Extensive use of metastable ions has been made since it provides valuable information on ion fragmentation pathways and for ion structure determination.[6] In a decoupled mode operation, a metastable ion not only can be tremendously improved in terms of its intensity, but it also can be continuously scanned to afford either a metastable ion mass spectrum (MIMS) or an ion kinetic energy spectrum (IKES).[7,8] From a MIMS precursors of an ion can be unequivocally identified. Utilization of such metastable transitions, therefore, can provide useful clues for ion structure elucidation. Metastable ion characteristics also show that kinetic energy release in a fragmentation is dependent on the structure of the ion.[9,10]

In addition, the deuterium labeling technique was applied in this study to define the general geometry of the eliminative fragmentations and rearrangement reactions.[11] We also employed high-resolution mass spectrometry to differentiate ions of same nominal mass but different elemental compositions.[12]

Experimental Section

Materials. The β-peroxylactones were prepared according to the published procedures.[13] The deuterated β-peroxylactones **2** and **3** were kindly supplied by Mr. O. Cueto and a complete account of their synthesis and physical and spectral properties is forthcoming.

Spectra. All mass spectra were recorded on a Du Pont 21-492 B double focusing mass spectrometer, equipped with a cooled probe system and MIMS and IKES capabilities. The instrument was operated at 70 eV ionizing electron energy, 2000 eV ion accelerating potential (3.1 kV for high-resolution mass spectrometry), 500 μA ionizing electron emission current, source temperature 20 ± 2 °C, source pressure 1×10^{-5} Torr, and analyzer pressure 1×10^{-6} Torr.

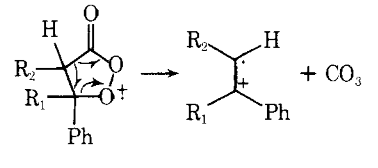
Samples were loaded via a glass capillary tube into the probe and cooled with Freon (R) while being inserted into the ion source. This procedure was followed in order to assure that no thermodecomposition occurred since β-peroxylactones are known to decompose at elevated temperature.[4a]

The IKES and MIMS were recorded on a Hewlett-Packard Model 7001 A X-Y Recorder. The MIMS were recorded by scanning the ion accelerating potential, holding the electric sector voltage constant.

Resolving power as high as 3000 was achieved readily by tuning up the ion source and reducing the β-slit width. Benzaldehyde and *p*-xylene were used as controls in assessing the resolution, showing a doublet at *m/e* 106 (M/AM-2900). For determination of the energy scale in the MIMS, a standard (*n*-decane) was used in the prerun. This exercise was also useful for possible ghost peak identification.

Results and Discussion

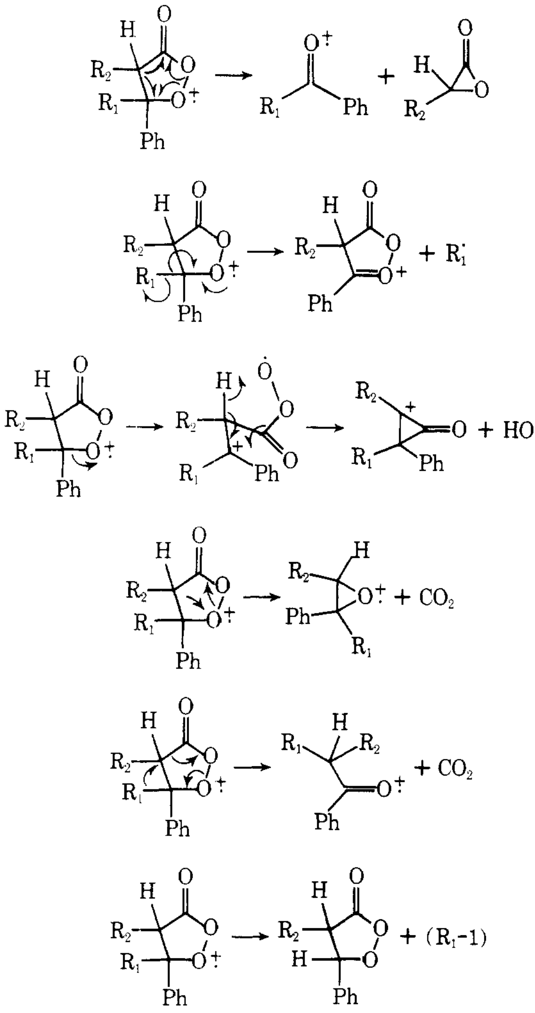
The mass spectra of the β-peroxylactones **1–8** are given in Table I. Except for β-peroxylactone **6**, molecular ions are all present; in some cases such as **2–4** they are abundant. The base peak corresponds to the *m/e* 105 ion ($C_6H_5CO^+$) for all but β-peroxylactone **4**. Contrary to the photolysis and thermolysis, decarboxylation of the molecular ion is greatly decreased. As expected, the fragmentation of the ionized β-peroxylactones in the gas phase is more complex than the decomposition of the neutral molecules in the liquid phase. For example, five major molecular fragmentations have been identified based on the MIMS data (eq 2 and Table II). The effect of substit-



(2a)

Table I. Ions (*m/e*) and Their Relative Abundances (%) of β-Peroxylactones

1		2		3		4		5		6		7		8	
m/e	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%
178	13	180	20	181	25	192	32	206	8	210	20	254	2	268	0.1
163	8	179	6	180	5	163	50	104	15	196	1	210	15	224	16
145	10	178	6	163	14	162	23	163	29	194	0.5	194	4	209	2
134	12	165	14	148	15	148	1	162	57	164	1	182	25	196	0.5
120	28	164	4	137	12	134	3	131	10	163	1	178	1	177	2
119	5	146	11	136	6	132	8	121	8	121	4	163	7	135	14
118	40	145	4	135	4	131	4	120	18	119	12	118	25	108	10
117	13	136	8	134	5	121	15	148	1	108	11	117	25	107	10
106	10	135	4	123	23	117	19	147	2	107	8	116	24	106	13
105	100	121	8	122	6	115	6	146	3	106	10	105	100	105	100
104	5	120	54	121	55	105	34	105	100	105	100	91	15	91	17
103	20	119	25	120	30	92	11	91	85	104	5	77	53	79	13
91	25	118	15	119	10	91	100	78	30	92	6	65	8	78	7
78	15	106	30	118	8	78	23	77	80	91	38	63	5	77	47
77	74	105	100	109	6	77	42	65	12	79	13	51	30	65	4
65	10	104	10	108	45	65	10	51	30	78	10	50	8	63	2
63	7	103	10	106	16	51	25	50	9	77	55	43	5	51	17
51	30	93	20	105	100	39	7	43	90	65	7	39	13	50	5
50	10	92	11	104	5			39	20	63	4			43	2
43	20	91	9	103	13					51	18			39	4
39	15	78	22	95	13					50	7				
		77	88	93	8					43	5				
		65	13	92	7					39	6				
		65	10	91	25										
		63	10	79	13										
		51	35	78	20										
		50	18	77	82										
				66	10										
				65	10										
				51	36										
				50	15										



(2b)

(2c)

(2d)

(2e)

(2e′)

(2f)

uents on the fragmentation patterns is summarized in Table III. Apparently, the α-methyl and β-benzyl substituents greatly modify the fragmentation pathways, either by stabilization of the substituents on the product ions or through the availability of a decomposition process requiring low activation energy. The detailed account of each of the five characteristic fragmentations follows.

Loss of Carbon Trioxide (Eq 2a). While direct loss of a CO_3 from $M\cdot^+$ has been confirmed by MIMS for β-peroxylactones **2**, **3**, and **6**, for the β-peroxylactones **4** and **7** the $M - CO_3$ fragments arise from an $M - CO_2$ ion by further loss of an oxygen atom (vide infra). From Table III, the β-benzyl group substantially affects the $M - CO_3$ ion abundance. The $M - CO_3$ ion subsequently decomposes via typical mass spectral patterns observed for alkenes, e.g., loss of a neutral alkyl or phenyl radical, as evidenced in the MIMS.

Loss of α-Lactone (Eq 2b). Loss of an α-lactone from $M\cdot^+$ is most evident for β-peroxylactone **7**. The driving force lies in the stabilization of the product benzophenone radical cation by the phenyl groups which subsequently decomposes according to its characteristic fragmentation pattern.

Loss of β-Alkyl Radical (Eq 2c). Theoretically, the relative abundance of M − R ion should follow the order of the stability of β-alkyl radical, i.e., $C_6H_5CH_2$ > *i*-Pr > Et > Me. Furthermore, the same β substituents may also kinetically favor reaction pathways such as M → $M - CO_2$ or M → M − (α-lactone). Consequently, the β-peroxylactones **6–8** show reduced $M - R_1$ abundance.

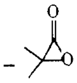
The MIMS reveal that $M - R_1$ ions undergo the subsequent fragmentations illustrated in eq 3. To distinguish between paths a and b (eq 3), the kinetic energy release, as measured from the metastable peak width, was determined for the cations produced in path a and b, and for the phenyl cation which is produced in path d from $M - R_1$. The kinetic energy release was estimated to be 2.5 times smaller for the phenyl cation than for the cation produced in path a or b. This

Table II. Metastable Ion Mass Spectra (MIMS) of Major Ions of β-Peroxylactones

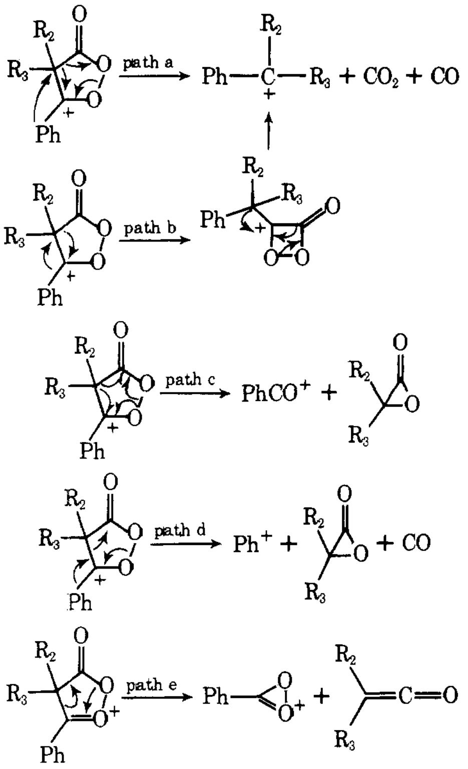
1 (M 178)			2 (M 180)			3 (M 181)			4 (M 192)			5 (M 206)			6 (M 254)			7 (M 254)			8 (M 268)		
m/e	P[a]	NL[a]	*m/e*	P[a]	NL[a]	*m/e*	P[a]	NL[a]	*m/e*	P[a]	NL[a]	*m/e*	P[a]	NL[a]	*m/e*	P[a]	NL[a]	*m/e*	P[a]	NL[a]	*m/e*	P[a]	NL[a]
163	178	CH_3	165	180	CH_3	163	181	CD_3	175	192	OH	163	206	C_3H_7	210	254[d]	CO_2	210	254[d]	CO_2	224	268	CO_2
145	178	O_2H	146	180	O_2D	148	181	O_2H	164	192	CO	162[c]	206	C_3H_8	196	254[d]	$C_2H_2O_2$	194	210	O	209	224	CH_3
134	178[d]	CO_2	136	180[d]	CO_2	137	181[d]	CO_2	159	192	O_2H	162[c]	206	CO_2	194	254[d]	CO_3	182	254	$C_3H_4O_2$	196	224	C_2H_4
120	178[d]	$C_2H_2O_2$	120	180[d]	$C_2D_2O_2$	123	181	$C_2H_2O_2$	163	192	C_2H_5	148	206[d]	$C_2H_2O_2$	181	210[d]	CHO	117	210	C_6H_5O	181	209	CO
118	178[d]	CO_3	120	180	CO_3	121	181	CO_3	162	192	C_2H_6	146	206[d]	CO_3	163	254[d]	C_7H_7		194	C_6H_5		224	C_2H_3O
117	145	CO					163	C_2H_2O	134	192[d]	$C_2H_2O_2$	147	162	CH_3	162	254	C_7H_8	116	117	H	178	268	C_7H_6
105	120	CH_3	105	120	CH_3	120	148	CO	148	164	O	131	147	O	121	162	C_2HO	115	194	C_6H_7	177	268	C_7H_7
	134	CHO		134	C_2H_3D	108	137	CHO	147	164	OH	121	163	C_2H_2O	120	210	C_7H_6	105	182	C_6H_5	135	224	C_7H_5
	134	C_2H_5		136	$C_2H_3D_2$	105	121	CD_2		175	CO	120	162	C_3H_6	119	210	C_7H_7		210	C_8H_9		240	C_7H_5O
	178	*e*		146	C_3H_3D		123	CD_3		148	H	119	146	C_2H_3	105	120	CH_3		210	C_7H_5O		268	*e*
103	118	CH_3		165	$C_2D_2O_2$		137	$C_2H_2D_3$		192	*e*	105	162	C_2HO_2		121	O	91	117	C_2H_2	134	128	CO_2
	105	H_2		180	*e*		147	C_2DO	132	148	O		162	C_4H_9		145	C_2O	77	105	CO	119	224	C_8H_9
91	118	C_2H_3	93	120	C_2H_3		163	$C_2H_2O_2$		160	CO		148	C_3H_7		163	$C_2H_2O_2$		105	C_2H_4	105	224	C_8H_7O
	163	C_2O_3		136	C_2H_3O		181	*e*		192	*e*		146	C_3H_5		196	C_7H_7					224	C_9H_{11}
	178	*e*		165	C_2O_3	103	121	CD_3	131	132	H		120	CH_3		210	C_8H_9					209	C_8H_8
77	105	CO		180	*e*	91	121	C_2D_3		147	O		206	*e*	103	194	C_7H_7					196	C_7H_7
	103	C_2H_2	77	120	$C_3H_3D_2$		137	C_2D_3O		159	CO	103	119	CH_4	91	119	CO					178	$C_3H_5O_2$
	163	$C_3H_2O_3$		105	CO		163	C_2O_3	121	162	C_2HO	91	119	C_2H_4		163	C_2O_3					134	C_2H_5
	178	*e*		165	$C_3D_2O_3$		181	*e*	120	148	C_2H_4		131	C_3H_4		181	C_7H_6					134	CHO
				180	*e*	77	105	CO	117	132	CH_3		146	C_4H_7		210	C_8H_7O					268	*e*
							103	C_2H_2	105	120	CH_3		163	C_2O_3	77	105	CO				91	119	CO
							148	C_4HD_3O		134	C_2H_5	77	105	CO		103	C_2H_3					224	C_9H_9O
							163	$C_3H_2O_3$		147	C_3H_6		103	C_2H_2		120	C_2H_3O				77	105	CO
							181	*e*		148	C_3H_7		120	C_2H_3O		162	C_3HO_3					196	C_8H_7O
										163	$C_2H_2O_2$		163	$C_3H_2O_3$								177	$C_4H_4O_3$
										192	*e*		78	H									
									103	132	C_2H_5												
									91	117	C_2H_2												
										131	C_3H_4												
										163	C_2O_3												
										192	*e*												
										78	H												
										103	C_2H_2												
										105	CO												
										121	CO_2												
										163	$C_3H_2O_3$												
										192													

[a] P = precursor; NL = neutral loss. [b] High resolution of 120 ion shows a doublet, corresponding to $C_9H_8D_2$ and C_8H_8O, with an intensity ratio of 1:3. [c] According to high resolution, 162 ion also shows a doublet which correspond to $M - CO_2$ and $M - C_3H_8$, with an intensity ratio of 1:15. [d] Precursor not observed. [e] Not assigned; may have more than one step fragmentation.

Table III. Molecular Ion Fragmentations of β-Peroxylactones 1–8[a]

Compd	M − CO_3	M − 	M − R_1	M − O_2H	M − CO_2
1	21	48	21	6	4
2	16	48	21	8	7
3	7	47	27	12	7
4	13	7	79		1
5	6	4	70		20
6	1	9	9		81
7	6	60			34
8		38	2		60

[a] Normalized data taken from 15-eV spectra. In those cases in which abundant secondary ions are still present in the 15-eV spectra, corrections were made to convert the secondary ion abundance into pertinent primary ions, based on MIMS.

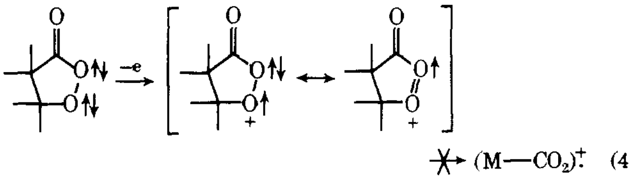


(3)

suggests that the latter cation is formed via a rearranged M − R_1 precursor (path b) rather than M − R_1 directly (path a). Loss of alkane from β-peroxylactones **4** and **5** and elimination of C_7H_6 and C_6H_4 neutrals from β-peroxylactones **6** and **7** are also observed (eq 2f).

Loss of Hydroperoxy Radical (Eq 2d). On the basis of deuterium labeled β-peroxylactones **2** and **3** and the MIMS for the M − O_2H ion, it is shown that the hydrogen is abstracted from the α carbon (Table III). As indicated in eq 2d, the reaction proceeds via a five-membered ring transition state. Although other hydrogen atoms are available for abstraction, e.g., from the α-methyl substituent in β-peroxylactones **6** and **8** (1,3 elimination), or from the β-methyl group (1,4 elimination) in β-peroxylactone **1**, the 1,2 elimination (eq 2d) is preferred.

Loss of Carbon Dioxide (Eq 2e). A prerequisite for decarboxylation is peroxide bond rupture. The minor M − CO_2 fragments observed in the spectra of β-peroxylactones **1–5** suggest that the peroxide bond is strengthened on ionization (eq 4). However, α-methyl and β-$C_6H_5CH_2$ substitution change the fragmentation pattern to favor the decarboxylation reaction. The structural assignment of the M − CO_2 ion is scrutinized according to eq 5.



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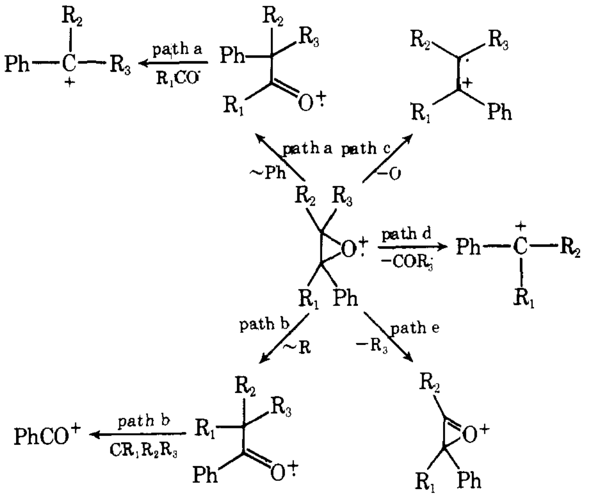


(5)

The skeletal rearrangements, path 5a (Ph migration) and path 5b (R migration), are well established for epoxides.[5,14] However, such evidence is circumstantial and can only support but not prove the epoxide structure of the decarboxylated product ion, M − CO_2. Pertinent information for ion structure identification has been provided through the fragmentations depicted in paths 5c–e, which bespeak an epoxide-like structure for the M − CO_2 ion. Thus, for β-peroxylactone **1** the metastable transition 134 → 105 was observed, which arose either by fragmentation of the M − CO_2 ion via path d (loss of HCO) or via path b from the rearranged M − CO_2 ion (loss of C_2H_5). Indeed, high-resolution data confirm that the 105 ion is a doublet, consisting of the $C_8H_9^+$ and $C_7H_5O^+$ fragments. Also the 106 ion, derived from β-peroxylactone **2**, consists of an analogous C_8H_8D and $C_6C^{13}H_5O$ doublet. Furthermore, from the MIMS of the 106 ion it is concluded that it arises via the consecutive decompositions

$$136 \xrightarrow{-D} 134 \xrightarrow{-CO} 106$$

confirming that the M − CO_2 fragment has an epoxide-like structure.

β-Peroxylactone **2** has also been useful in establishing the migratory aptitude of the phenyl group (path a) and the methyl group (path b) in eq 5. From Table II, the 93 ion arises from the 120, 165, and 136 ions as precursors, while the 105 ion arises from the 120, 134, 136, 145, 165, and 180 ions as precursors. Accordingly, the ion intensity of mass 136 relative to the sum of that of the masses 120, 136, and 165 is a measure of phenyl migration, while the ion intensity of mass 136 relative to the sum of that of the masses 120, 134, 136, 145, 165, and 180 measures the degree of methyl migration. The quotient of these two relative intensity ratios provides an estimate for the methyl to phenyl migratory aptitude, of course keeping in mind that ion intensity data derived from the MIMS gives only approximate values.[15] Our data reveal that phenyl migration outweighs methyl migration by threefold. For the other β-peroxylacetones it is also observed that phenyl migration is preferred over alkyl migration. Again this bears out epoxide-like behavior as established in the mass spectral fragmentations of epoxides.[14] This migratory aptitude is, however, contrary to the thermal chemistry of β-peroxylactones, in which alkyl migration predominates over phenyl migration,[4a] but coincides with their photochemistry.[4b]

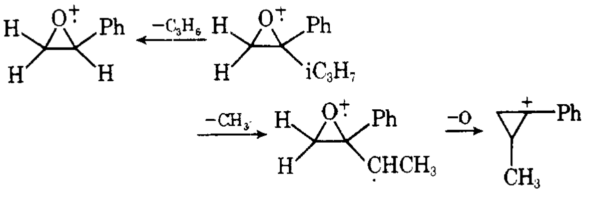
One convincing piece of structural information concerning the M − CO_2 ion comes from β-peroxylactone **3**, in which the abundant 108 ion ($C_6H_5CHCD_3$) derives from eliminating a CHO group from the M − CO_2 ion (Tables II and III and eq 5d). Such a reaction pathway is most characteristic of an epoxide-like M − CO_2 ion.[14]

For β-peroxylactone **4** the M − CO_2 ion (148) is comprised of a complex pathway consisting of decarbonylation, followed by deoxygenation:

$$M \xrightarrow{-CO} M - 28 \xrightarrow{-O} M - 44$$

These two steps clearly discount decarboxylation as a source for the M − 44 ion (eq 2e) and render a ketone-like structure for the final M − 44 ion unlikely. Also subsequent deoxygenation of the M − 44 ion, leading to the 132 ion, further supports an epoxide-like structure for the M − CO_2 ion.

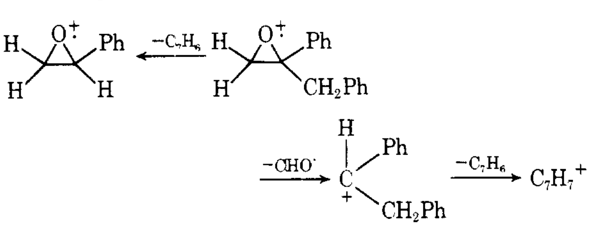
The M − CO_2 ion derived from β-peroxylactone **5** subsequently decomposes according to eq 6. This is indicative of a fragmentation pattern characteristic of an ionized epoxide.



(6)

Decarboxylation becomes the major pathway for the β-peroxylactones **6–8** on electron impact. All the M − CO_2 ions undergo typical epoxide-like decomposition patterns, as corroborated by their respective MIMS's (eq 7–9).

In conclusion, electron impact behavior of β-peroxylactones parallels their photochemistry in that an epoxide-like M − CO_2 fragment intervenes. Of course, efficient cooling of the sampling probe is mandatory in avoiding thermal decomposition of the β-peroxylactones prior to electron impact. Unlike the photolysis, decarboxylation is not necessarily the major process on electron impact and depends greatly on the substituent pattern of the β-peroxylactone.



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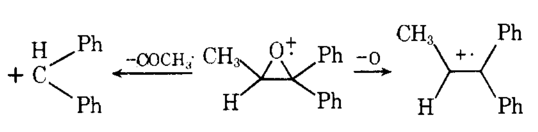

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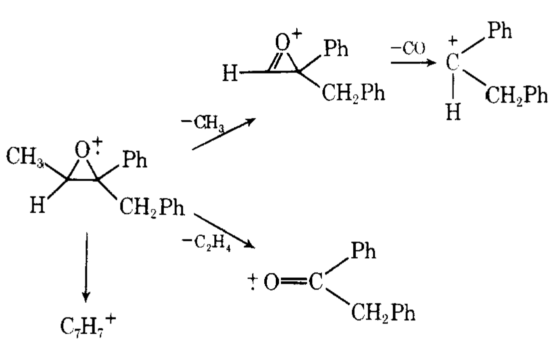

(9)

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Registry No.—**1**, 6782-11-2; **2**, 60909-10-6; **3**, 60909-11-7; **4**, 23002-41-7; **5**, 23002-43-9; **6**, 23002-42-8; **7**, 60909-12-8; **8**, 35394-04-8.

References and Notes

(1) Part 44 in the Cyclic Peroxide series.

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