Mass Spectrometric Studies of α, β-Epoxyketones

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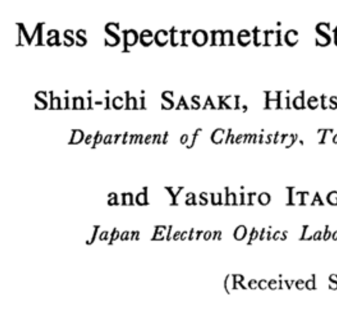
The mass spectra of epoxy compounds have already been published in some detail[1a–1d] and have proven to be of diagnostic use in the structure determination of natural compounds.[1a] We now extend our studies to several α, β-epoxyketones: chalcone oxide (1), monodeuterated chalcone oxide (2), 2, 3-benzochalcone oxide (3), 4-methoxychalcone oxide (4), 1, 2-epoxy-1-phenyl-3-butanone (5), 2, 3-epoxy-1-phenyl-1-butanone (6) and *cis*- and *trans*-dypnone oxide (7 and 8).



Scheme 1.

The characteristic peaks observed in the spectra of these compounds are listed in Table 1 in which R_k and R_e represent the aromatic or aliphatic group adjacent to the carbonyl and epoxide group, respectively. The fragmentation of epoxy compounds are summarized in Scheme 1.

α, β-Epoxyketones (1—6), excepting the two dypnone oxides (7 and 8), lose one hydrogen radical to give ion (a), and groups R_k and or R_e to form ions (b) and (c), respectively. The CO-epoxide bond is also cleaved to afford cations (d) and (e). For instance, chalcone oxide (1) produces rather weak peaks at *m/e* 223 (M-1)(a), *m/e* 147 (M-C_6H_5)(b) and/or (c), *m/e* 119 (M-C_6H_5CO) (e) and a base peak at *m/e* 105 (C_6H_5CO) (d) as shown in Scheme 2, which is similar to that encountered in aromatic epoxides.[1b]

Ions (f) and (g) obviously arise from the β-diketone forms produced by rearrangement; similar ions (h) owe their geneses to the rearranged α-diketone form. It should be noted that the peaks (f) and (g) are not present in dypnone oxides, in which rearrangement to a β-diketone is not possible because of the extra methyl group. Furthermore, the spectrum of chalcone oxide (1) closely resembles

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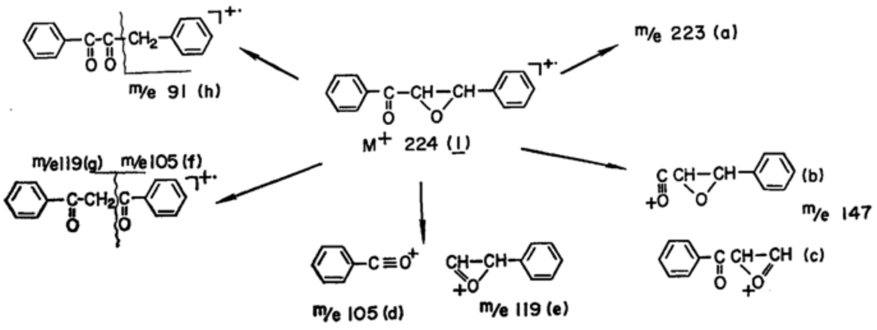
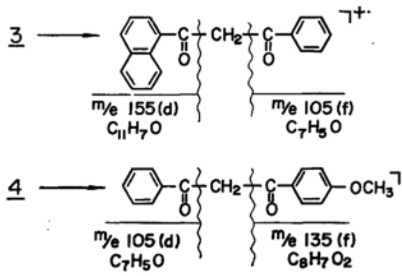
1) a) Y. Itagaki, T. Kurokawa, H. Moriyama, S. Sasaki and Y. Watanabe, *Chem. & Ind.*, **1965**, 1654; S. Sasaki, Y. Itagaki, H. Moriyama, K. Nakanishi, E. Watanabe and T. Aoyama, *Tetrahedron Letters*, **1966**, 623. b) E. H. Audier, J. F. Dupin, M. Fetizon and Y. Hoppilliard, *Tetrahedron Letters*, **1966**, 2077. c) N. S. Issacs, *Canad. J. Chem.*, **44**, 395 (1966). d) J. Baldas and Q. N. Porter, *Chem. Commn.*, **1966**, 571.

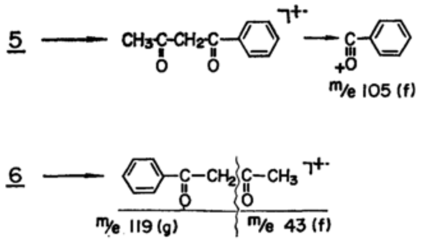

Scheme 2.

that of dibenzoylmethane[2] which corresponds to the rearranged β-diketone form. The formation of ions m/e 105 (f) and m/e 135 (f) in the mass spectra of (3) and (4), respectively, also support the occurence of the rearrangement mechanism. The composition of ions m/e 155 (d) and m/e 105 (f) of (3), and m/e 105 (d) and m/e 135 (f) of (4) was determined by high resolution mass spectrometry (Scheme 3).

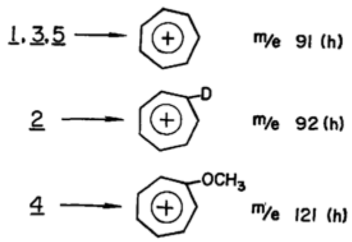

Scheme 3.

The ion m/e 105 decomposes further by successive elimination of carbon monoxide and acetylene to m/e 77 and m/e 51 as evidenced by appropriate metastable ions (m/e 56.5 and 33.8, respectively) in every case.

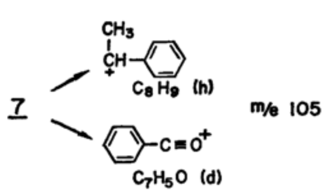
Compounds (5) and (6) carry alkyl groups, but their mass spectral fragmentations are almost identical with those of the chalcone oxides (1—4). The formation of ion m/e 105 (f) in (5), and ions m/e 43 (f) and 119 (g) in (6) are again due to hydrogen migration to form the corresponding β-diketones (Scheme 4).


Scheme 4.

The conversion of epoxyketones to α-diketones is observed in the spectra of (1—5), in which tropylium ions are found at m/e 91, 92, 91, 121 and 91, respectively (Scheme 5).


Scheme 5.

Similarly the *cis* and *trans* dypnone oxide (7 and 8), which give identical spectra, also rearrange to the corresponding α-diketone to give the ion (h) at m/e 105. The fact that the base peak at m/e 105 also involves the benzoyl ion (d) as well indicated by measurements of high resolution mass spectrometry (Scheme 6).


Scheme 6.

Finally, the spectra of α, β-epoxyketones (1—5, 7 and 8) show ions corresponding to the loss of HCO and CO from the molecular ion. For instance, the ions m/e 195 (M-CHO) and m/e 196 (M-CO) appear in the spectrum of chalcone oxide (1). The geneses of these peaks are accounted for by the repulsion of carbon monoxide[3] from the M-1 ion and carbon monoxide from the molecular ion.

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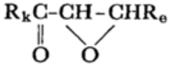
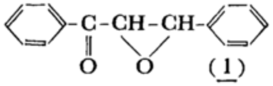
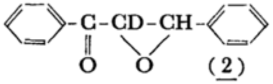
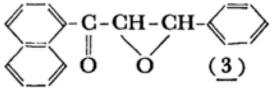
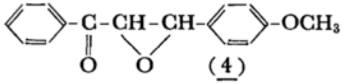
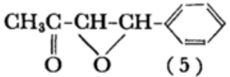
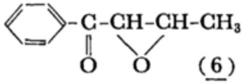
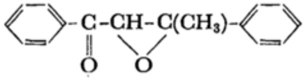
[2] J. H. Bowie, D. H. Williams, S.-O. Lawesson and G. Schroll, *J. Org. Chem.*, **31**, 1384 (1966).

[3] J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson and G. Schroll, *Chem. Commn.*, **1965**, 403.

TABLE 1. CHARACTERISTIC PEAKS OF α,β-EPOXYKETONES. Relative intensity % of the base peak are enclosed in parentheses

	M-1 (a)	M-R_k (b)	M-R_e (c)	$R_kC{\equiv}O^+$ (d)	M-$R_kC{\equiv}O$ (e)	$R_eC{\equiv}O^+$ (f)	M-$R_eC{\equiv}O$ (g)	$R_eCH_2^+$ (h)	M-CHO (i)	M-CO (j)
 (1)	223 (4)	147*1′ (2)	147*1′ (2)	105*2 (100)	119 (1)	105*2′ (100)	119 (1)	91 (13)	195 (2)	196 (1)
 (2)	M-H 224 (18) M-D 223 (8)	148*3 (3)	148*3′ (3)	105*4 (100)	120*5 (2)	105*4′ (100)	120*5′ (2)	92 (7)	196 (1)	197 (1)
 (3)	273 (11)	147 (2)	197 (2)	155 (97)	119 (3)	105 (32)	169 (3)	91 (12)	245 (2)	246 (2)
 (4)	253 (2)	177 (7)	—	105 (100)	149 (9)	135 (5)	— —	121 (50)	225 (1)	226 (3)
 (5)	161 (8)	147 (5)	85 (5)	43 (95)	—	105 (10)	—	91 (100)	133 (4)	134 (1)
 (6)	161 (16)	—	147 (12)	105 (100)	—	43 (5)	119 (1)	29 (9)	—	—
 trans (7), cis (8)	—	—	—	105*6 (100)	133 (2)	—	—	105*6′ (100)	209 (2)	210 (12)

The ions marked with *1 and *1′ have the same mass units and are most probably originated from different parts of the molecular ion. Then the same mass and intensity are listed in this table. The pairs of ions marked with *2, *2′; *3, *3′; *4, *4′; *5, *5′ and *6, *6′ are listed in this manner.

Experimental

All the samples were synthesized according to known procedures. For instance, 4-methoxychalcone oxide (4) was prepared by the epoxidation of 4-methoxychalcone with alkaline hydrogen peroxide.4) Monodeuterated chalcone oxide (2) was synthesized by the condensation of ω-d_3-acetophenone and benzaldehyde, following the epoxidation with hydrogen peroxide, mp 52—54°C.

Mass spectra were obtained with a Hitachi RMU-6D Mass Spectrometer, with an energy of 70 eV and an 80 μA ionizing current. The temperature of ion source was 250°C. High resolution mass spectra were determined with a JMS-OIS Mass Spectrometer. The temperature of ion source 130—150°C, ionizing voltage 25—40 eV, ion accl. volt. 7.5 kV, and exposure 3×10^{-11} coulomb.

Exact masses and compositions of ions

2, 3-Benzochalcone oxide (3)

m/e observed	*m/e* calculated	composition
155.048	155.049	$C_{11}H_7O$
105.033	105.034	C_7H_5O

4-Methoxychalcone oxide (4)

m/e observed	*m/e* calculated	composition
105.034	105.034	C_7H_5O
135.046	135.044	$C_8H_7O_2$

Dypnone oxide (7)

m/e observed	*m/e* calculated	composition
105.070	105.070	C_8H_9
105.033	105.034	C_7H_5O

The authors (S.S. and K. N.) are grateful to the Toyo Rayon Company for the grant to purchase the RMU-6D mass spectrometer.

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4) E. Weitz, A. Scheffer, *Ber.*, **54**, 2335, 2339 (1921).