Tetrahedron, 1967, Vol. 23, pp. 2893 to 2909. Pergamon Press Ltd. Printed in Northern Ireland

MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS—CXVII*

ALIPHATIC α,β-EPOXYKETONES

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(*Received in USA* 25 *August* 1966; *accepted for publication* 8 *November* 1966)

Abstract—The mass spectra of 11 α,β-epoxyketones are reported, and a number of characteristic fragmentation pathways are documented by a combination of high resolution mass measurements and deuterium labeling experiments. The predominant cleavage occurs between the CO group and the oxirane ring with charge retention on the former fragment. Cleavage of β-alkyl groups is also observed. Electron impact induced rearrangements of epoxyketones to dicarbonyl ions are discussed; and on the strength of direct comparisons with authentic dicarbonyl compounds, such transformations are not considered to be important. McLafferty rearrangements involving the CO group are not observed, but hydrogen transfer to the epoxide oxygen is significant.

INTRODUCTION

AN EXAMINATION of the mass spectra of a series of simple, aliphatic α,β-epoxyketones was undertaken primarily for two reasons. First, it provided an extension of recent studies by one of us concerning thermal and photochemical reactions of epoxyketones.[2,3] A comparison of these processes with electron impact induced reactions seemed particularly worthwhile, inasmuch as similarities between mass spectral fragmentation reactions and photochemical transformations have been observed[4] for several small ring compounds. Second, we hoped to uncover any unique conjugation effects by comparing the epoxyketone substrates with simple aliphatic ketones and epoxides. The course of electron impact induced fragmentation of ketones is well established,[5] and recent work from this laboratory[6] has illuminated the behavior of aliphatic epoxides.

The molecular ion of an α,β-epoxyketone is expected to have significant charge localization on oxygen; however in view of the very close electron impact ionization potentials reported for 1,2-propylene oxide[7] and acetone[8] (9·8 to 9·9 eV) a specific assignment cannot be made with confidence.

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* Paper CXVI, G. Schroll, H. J. Jakobsen, S.-O. Lawesson, P. Brown and C. Djerassi, *Arkiv Kemi*, **26**, 279 (1966).

[1] National Institutes of Health, Special Fellow, 1965–1966. Current address, Department of Chemistry, Michigan State University.

[2] C. K. Johnson, B. Dominy and W. Reusch, *J. Am. Chem. Soc.* **85**, 3894 (1963).

[3] W. Reusch, C. K. Johnson and J. A. Manner, *J. Am. Chem. Soc.* **88**, 2803 (1966).

[4] N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner and P. D. Angelo, *J. Am. Chem. Soc.* **87**, 4097 (1965).

[5] H. Budzikiewicz, C. Djerassi and D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds* Chap. 1 Holden Day, San Francisco (1964).

[6] P. Brown, J. Kossanyi and C. Djerassi, *Tetrahedron* Suppl. **8**, part I, 241 (1966).

[7] E. J. Gallegos and R. W. Kiser, *J. Am. Chem. Soc.* **83**, 773 (1961).

[8] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.* **20**, 1021 (1952).

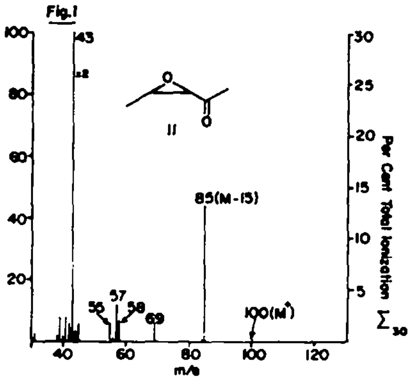


FIG. 1 Mass spectrum of 3,4-epoxy-2-pentanone (II), Atlas.

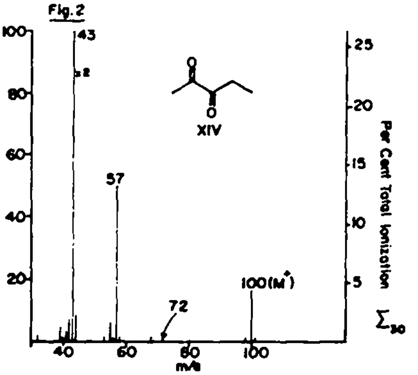


FIG. 2 Mass spectrum of 2,3-pentanedione (XIV), Atlas.

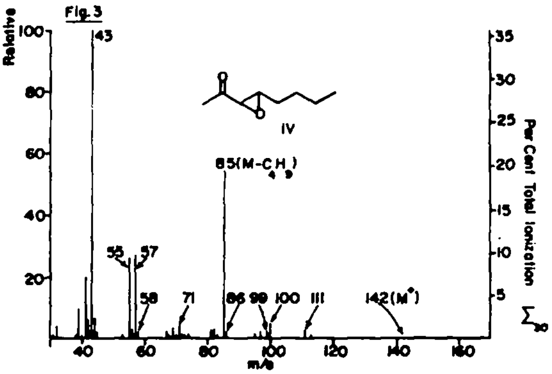


FIG. 3 Mass spectrum of 3,4-epoxy-2-octanone (IV), Atlas.

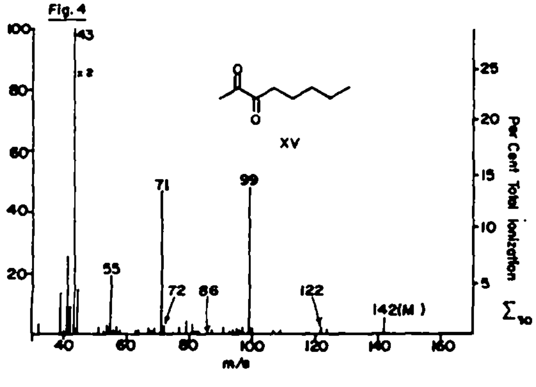


FIG. 4 Mass spectrum of 2,3-octanedione (XV), Atlas.

Fig.5

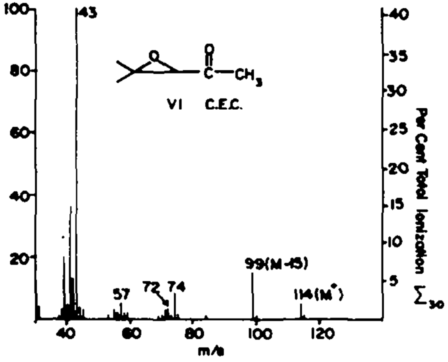


Fig. 5 Mass spectrum of 4-methyl-3,4-epoxy-2-pentanone (VI), C.E.C.

Fig.6

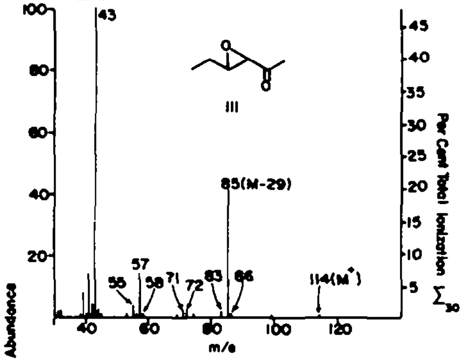


Fig. 6 Mass spectrum of 3,4-epoxy-2-hexanone (III), Atlas.

Fig 7

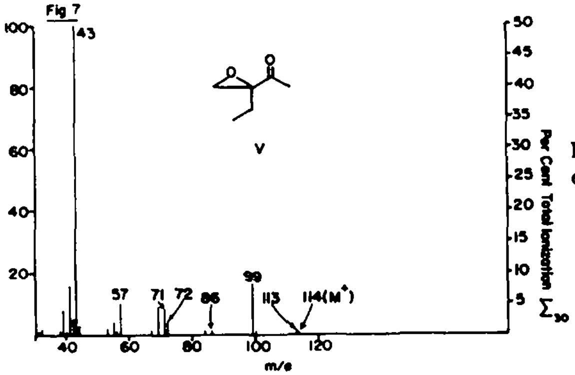


Fig. 7 Mass spectrum of 3-ethyl-3,4-epoxy-2-butanone (V), Atlas.

Fig 8

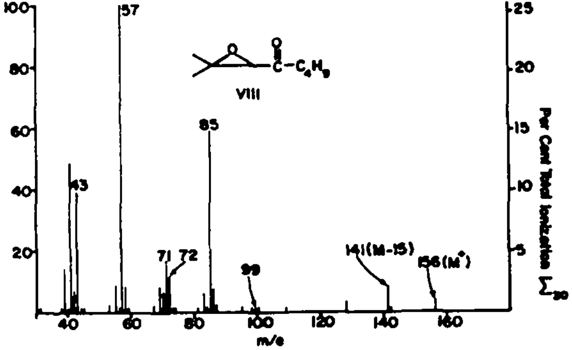


Fig. 8 Mass spectrum of 2-methyl-2,3-epoxy-4-octanone (VIII), Atlas.

Fig.9

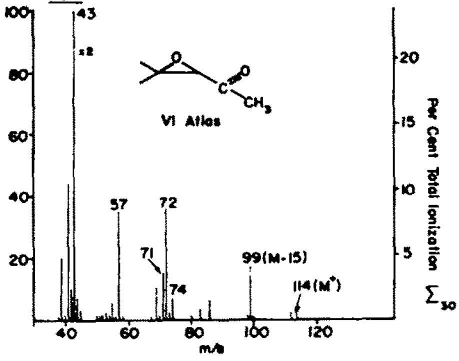


FIG. 9. Mass spectrum of 4-methyl-3,4-epoxy-2-pentanone (VI), Atlas.

Fig.10

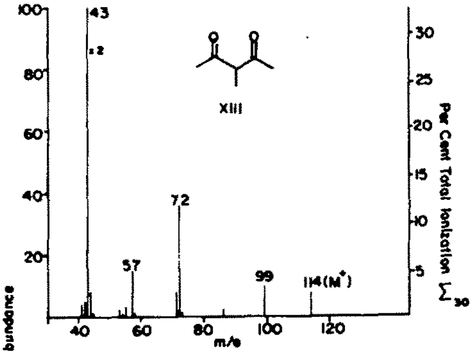


FIG. 10. Mass spectrum of 3-methyl-2,4-pentanedione (XIII), Atlas.

Fig.11

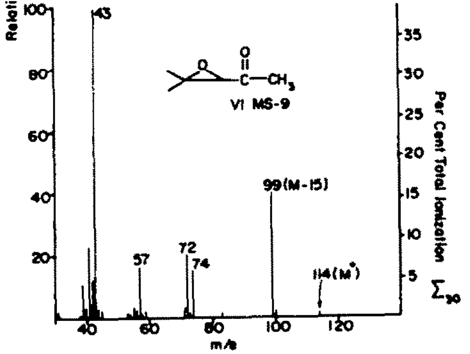


FIG. 11. Mass spectrum of 4-methyl-3,4-epoxy-2-pentanone (VI), MS-9.

Fig.12

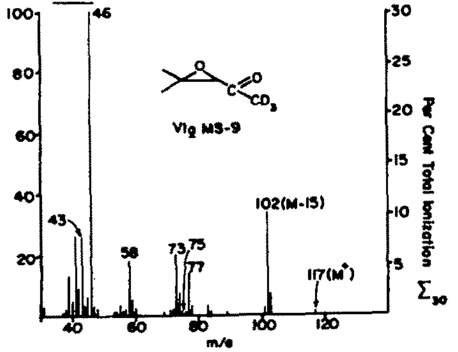
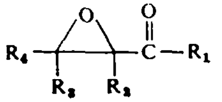


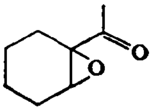
FIG. 12. Mass spectrum of 1,1,1-trideuterio-4-methyl-3,4-epoxy-2-pentanone (VIa), MS-9.

RESULTS AND DISCUSSION

The epoxyketones employed in this study were all prepared from the corresponding unsaturated ketones. Characterization was effected by IR and NMR spectroscopy. Since *trans* and *cis* dypnone oxide (IX and X) gave virtually identical mass spectra, the stereochemical purity of II, III and IV was not considered a vital factor. Actually, these compounds were assumed to be predominantly the *trans* isomers on the strength of the very small coupling constants observed for the vicinal oxirane hydrogen atoms.[9]



I $R_1 = Me$; $R_2, R_3, R_4 = H$
II $R_1, R_3 = Me$; $R_2, R_4 = H$
III $R_1 = Me$; $R_3 = Et$; $R_2R_4 = H$
IV $R_1 = Me$; $R_3 = Bu$; $R_2, R_4 = H$
V $R_1 = Me$; $R_2 = Et$; $R_3, R_4 = H$
VI $R_1, R_3, R_4 = Me$; $R_2 = H$
VIa $R_1 = CD_3$; $R_3, R_4 = Me$; $R_2 = H$
VII $R_1, R_2, R_3, R_4 = Me$
VIII $R_1 = Bu$; $R_3, R_4 = Me$; $R_2 = H$
IX $R_1, R_3 = Ph$; $R_4 = Me$; $R_2 = H$ (*trans*)
X $R_1, R_4 = Ph$; $R_3 = Me$; $R_2 = H$ (*cis*)



XI

A comparison of the spectra of selected epoxyketones (eg. Figs 5, 9 and 11) obtained with a C.E.C. Model 21-103 spectrometer, an A.E.I. MS-9 double focussing spectrometer and an Atlas CH-4 spectrometer disclosed only minor variations. In general, the Atlas spectra (eg. Figs 1, 3, 6–9) are characterized by small amounts of M-2 and M-16 peaks. These ions are usually absent in spectra (see Figs 5 and 11) from the other instruments. Most of the spectra reported in this paper are from the Atlas spectrometer.

Although cleavage of bonds leading to the oxirane ring was relatively unimportant in simple epoxides,[6] such fission with charge retention on the carbonyl oxygen atom is

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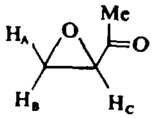
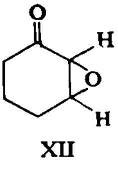
[9] C. A. Reilly and J. D. Swalen, *J. Chem. Phys.* 32, 1378 (1960) have analyzed the NMR spectrum of 3,4-epoxy-2-butanone (I) and report the following:



$$\left.\begin{array}{ll} J_{AB} & 5{\cdot}78 \\ J_{AC} & 1{\cdot}95 \\ J_{BC} & 5{\cdot}21 \end{array}\right\} \pm 0{\cdot}05 \text{ c/s}$$

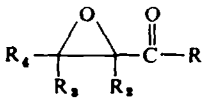
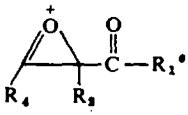
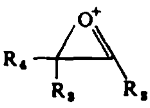
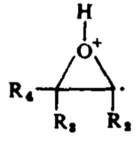
We have also observed a coupling of 4·0 c/s for the *cis* oxirane hydrogen atoms in XII. The corresponding coupling in II, III and IV is less than 2·0 c/s.



XII

the major fragmentation mode observed in the α,β-epoxyketones. This, and other characteristic fragmentations are summarized in Table 1. The formal structures written for certain fragment ions are simply a convenient means of representing common types of fission and do not necessarily indicate the actual ion structures.

TABLE 1. GENERAL FRAGMENTATION PROCESSES[a]

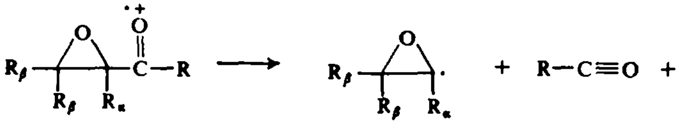
Epoxyketone	m/e (% Σ_{40})				
	M^+		$R_1-C\equiv O$ +		
I	86(10)	85(6)	43(51)	43	44(2·5)
II	100(<0·3)	85(14)	43(62)	57(3·8)	58(2·2)
III	114(<0·4)	85(20)	43(47)	71(1·0)	72(1·0)
IV	142(<0·1)	85(19)	43(32)	99(0·8)	100(0·1)
V	114(<0·1)	113(<0·1)	43(50)	71(4)	72(2)
VI	114(<0·2)	99(4·5)	43(43)	71(3·5)	72(8·5)
VII	128(<0·1)	113(5)	43(34)	85(7·5)	86(7)
VIII	156(0·8)	141(2)	85(15)	71(4·5)	72(2·8)
IX[b]	238(1·8)	223(0·8)	105(25)	133(0·5)	—
X[b]	238(1·8)	223(0·8)	105(28)	133(0·8)	—
XI	140(1·2)	139(0)	43(24)	97(4·5)	98(2·5)

[a] Underlined values are confirmed by high resolution measurements (Table 5).

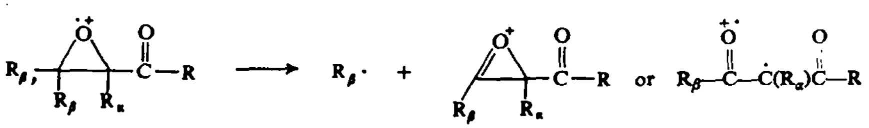
[b] Obtained by direct admission to a C.E.C. Model 21-103C mass spectrometer.

[c] For preferred representation of this α-fission ion see Eq. (2) in discussion.

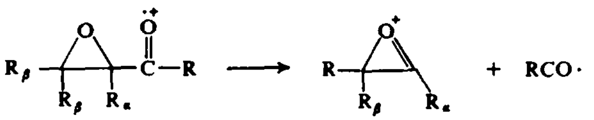
From the data in Table 1 it is evident that cleavage of the acyl group (Eq. 1) predominates and that loss of a β-alkyl substituent (Eq. 2) can be significant. This latter type of α-fission is an unfavored process in aliphatic epoxides[6] and it is likely that its comparative prevalence in epoxyketones (see III and IV in Table 1) is due to some stabilizing feature of the carbonyl group as expressed in the alternate representation of the fragment ion of Eq. (2).



(1)



(2)



(3)

When the acyl substituent is an acetyl group (eg. compounds I–VII and XI), the most abundant charged fragment is $C_2H_3O^+$ (m/e 43); a parallel cleavage in VIII produces the abundant C_5H_9O ion (m/e 85). The base peak at m/e 57 in the spectrum of VIII (Fig. 8) is largely C_4H_9 (see Table 5), part of which must be formed by decarbonylation of the *m/e* 85 ion (a broad metastable ion is formed at *m/e* 38–38·6). The preferred course of acyl cleavage is that illustrated in Eq. 1; however, the alternate charge disposition (Eq. 3) is also observed. The preference for charge retention on the carbonyl oxygen atom (Eq. 1) is reasonable in view of the known stability of acylium ion fragments[5] and oxirane radicals.[10]

The M-15 ions found in the spectra of compounds II, VI, VII and VIII (Table 1) are produced by loss of a β-Me radical (Eq. 2). Cleavage of the acetyl Me group, as an alternate route to these ions, was eliminated in the case of VI by examining the trideuterio analog VIa; the *m/e* 99 peak in VI moved completely to *m/e* 102 in the labeled compound (Fig. 12). In this regard it may be noted that loss of the Bu group from VIII with consequent formation of an ion of mass 99 (M-57) is a very minor process (ca. 0·25% Σ_{30}). This is a further indication that the genesis of the abundant ion of mass 57 in VIII is primarily by decarbonylation of its *m/e* 85 precursor.

The dypnone oxides IX and X showed surprisingly little M-15 and, as expected, no loss of a Ph group (M-78). Compounds having hydrogen at the β-position exhibit M-1 ions, but these are generally less abundant than the molecular ion. The strong M-15 ion (9% Σ_{30}) in I denotes cleavage of the acetyl Me groups, and together with the relatively abundant molecular ion (10% Σ_{30}) implies that only limited decomposition modes are available to this simple system. A similar loss of an acetyl Me group is probably responsible for the *m/e* 99 peak in V (Fig. 7), although cleavage of a Me group from the α-side chain cannot be ruled out. Finally, the absence of significant α-alkyl group elimination is apparent from a comparison of the mass spectra (Figs. 6 and 7) of III and V.

Rearrangement to carbonyl intermediates

Our earlier study of aliphatic epoxides[6] and an independent report[11] concerning aromatic epoxides have disclosed an apparent rearrangement of the epoxide molecular ion to an isomeric carbonyl species. A combination of high resolution mass measurements and deuterium labeling experiments demonstrated that certain fragment ions, characteristic of the carbonyl intermediates, were present in the epoxide spectra. Consequently, a complete discussion of the epoxyketone data must take into consideration the possibility of molecular ion rearrangement to isomeric dicarbonyl ions. Such a rearrangement could manifest itself in three ways (Eq. 4) all having precedent in condensed phase chemistry.[12] The rearrangement to *C* (Eq. 4) corresponds to the major photochemical transformation exhibited by α,β-epoxyketones.[2,13]

If the subject of electron impact rearrangement of epoxyketones to α- and β-diketones (i.e. *A*, *B* and *C*) is to be intelligently explored, it is necessary to know something about the mass spectra of these dicarbonyl compounds. The recently reported findings of Bowie *et al.*,[14] supplemented by our measurement of 3-methylpentane-2, 4-dione (XIII) provide a clear picture of β-diketone ion reactions. Thus, the most abundant ion from XIII (*m/e* 43, >95% C_2H_3O, 65% Σ_{30}) is produced by

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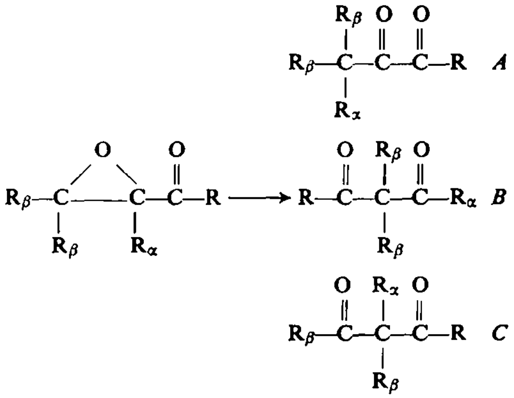
[10] C. Walling and P. S. Fredericks *J. Am. Chem. Soc.*, **84**, 3327 (1962).

[11] H. E. Audier, J. F. Dupin, M. Fétizon and Y. Hoppilliard, *Tetrahedron Letters* 2077 (1966).

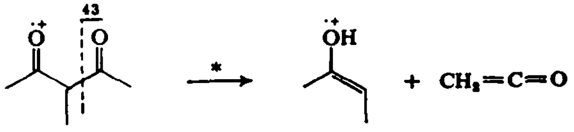
[12] R. Parker and N. Issacs, *Chem. Rev.* **59**, 737 (1959).

[13a] H. E. Zimmerman, B. R. Crowley, C. Y. Tseng and J. W. Wilson, *J. Am. Chem. Soc.* **86**, 947 (1964); [b] O. Jeger, K. Schaffner and H. Wehrli, *Pure and Appl. Chem.* **9**, 555 (1964).

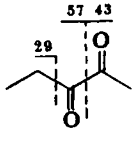


(4)

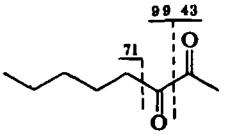
α-cleavage; and a McLafferty rearrangement, ejecting ketene as a neutral fragment, yields an ion (a) of mass 72 (12% Σ_{30}). The latter process is substantiated by a characteristic metastable ion at *m/e* 45·5.



XIII a (5)



XIV



XV

With the exception of biacetyl,[15] no previous mass spectral investigation of α-diketones has been reported; consequently, we determined the mass spectra (Figs 2 and 4) of XIV and XV. The fragmentation of these diketones is very simple, consisting predominantly of bond cleavage between the carbonyl groups. Both acyl groups appear as charged species which decarbonylate to alkyl ions (XV shows a metastable ion at *m/e* 51 for 99 → 71). No ions characteristic of McLafferty type rearrangements are observed in either XIV (i.e. *m/e* 72, Fig. 2) or XV (ie. *m/e* 72 and 86, Fig. 4).

Since rearrangement of epoxyketones II and IV to type *A* products would yield the α-diketones XIV and XV respectively, a comparison of the mass spectra of these compounds should be particularly instructive. Although II (Fig. 1) and XIV (Fig. 2) both exhibit the same base peak (*m/e* 43), the strong peaks at *m/e* 57 (13% Σ_{30}) and *m/e* 29 (17% Σ_{29}) in the latter compound and the abundant M-15 ion of mass 85 (13% Σ_{30}) in the former represent prominent differences. *Assuming that the α-diketone molecular ion produced by rearrangement of* II *is indistinguishable from that*

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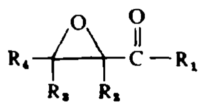
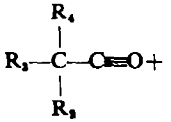
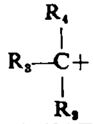
[14] J. H. Bowie, D. H. Williams, S. O. Lawesson and G. Schroll, *J. Org. Chem.* 31, 1384 (1966).

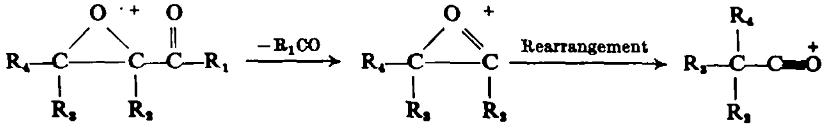
[15] *Catalog of Mass Spectral Data* Spectrum No. 782. American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.

TABLE 2. TYPE *A* α-DIKETONE REARRANGEMENT IONS[a]

Epoxyketone 	 *m/e* (% Σ_{30})	 *m/e* (% Σ_{30})
II	57(3·8)	29(6·0)
III	71(1·0)	43(2·0)
IV	99(0·8)	71(1·5)
V	71(4·0)	43(<0·1)
VI	71(3·5)	43(4·8)
VII	85(7·5)	57(4·8)
VIII	71(4·5)	43(3·5)
IX and X	133(0·5 to 0·8)	

[a] Underlined values are confirmed by high resolution measurements (Table 5).

formed by direct ionization of XIV, a simple calculation based on molecular ion intensities indicates that a maximum of 7% rearrangement could have occurred. Even though the quantitative aspects of these arguments may have doubtful merit, a consideration of the extent to which ions characteristic of α-diketones appear in the mass spectra of epoxyketones (Table 2) suggests that this rearrangement occurs only to a limited degree if at all. Furthermore, α-diketone intermediates are not uniquely required to explain these ions, and a rearrangement subsequent to acyl cleavage (Eq. 6) is equally feasible.



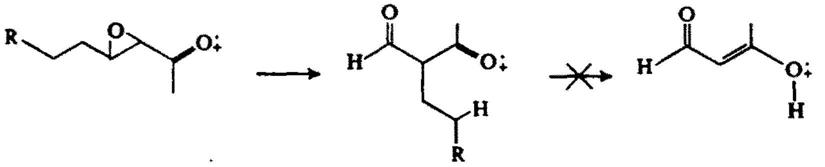
(6)

If a type *B* rearrangement makes a significant contribution to the mass spectra of epoxyketones bearing an α-hydrogen (ie. $R_2 = H$), the α-formylketone thus generated should give a strong CHO ion (*m/e* 29). This ion is found in every compound of this kind studied, but is usually rather weak (Table 3). Furthermore, the α-formylketone (XVI) derived from III and IV should exhibit a McLafferty rearrangement to an ion of mass 86 (Eq. 7). Such an ion is not observed in either compound. A similar rearrangement of V to the β-diketone XVII is consistent[14] with the *m/e* 57 (C_3H_5O, 5% Σ_{30}) and 29 (C_2H_5, 4·5% Σ_{29}) peaks observed in the mass spectrum (Fig. 7) of the

TABLE 3. FORMYL IONS FROM TYPE *B* β-DIKETONE REARRANGEMENT

Epoxyketone	CHO % Σ_{30} Atlas CH-4	A.E.I. MS-9
II	5·0	—
IV	1·2	0·6
VI	1·8	0·2
VIII	0·8	0·2
IX	—	0·2
X	—	0·1

former; but again the *m/e* 58 peak expected from a McLafferty rearrangement (Eq. 8) is not present.

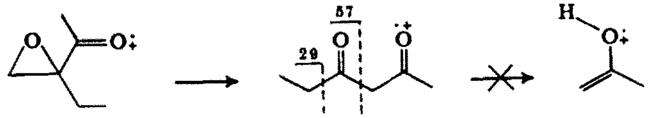


(7)

R = H: III
R = Et: IV

XVI

m/e 86



(8)

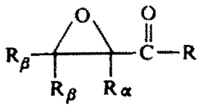
V

XVII

m/e 58

The third mode of epoxyketone rearrangement could generate a β-dicarbonyl species *C* (Eq. 4) the mass spectrum of which would be expected[14] to display peaks corresponding to fragment ions $R_\beta CO+$ and $R_\beta +$. Ions of this kind are indeed present in the mass spectra of epoxyketones (Table 4); however, considerable ambiguity is attached to interpretations of such data. For example, III and IV both exhibit metastable ions at *m/e* 38·2 and 14·7, which indicate the following transitions: *m/e* 85 → 57 → 29 (Eq. 9). High resolution measurements (Table 5) with IV demonstrate that the ion of mass 85 is >95% $C_4H_5O_2$ and that of mass 57 is 90% C_3H_5O, as required by the transformations proposed in Eq. 9. A parallel situation is found in compound VIa, where other routes to the ion of mass 43 (Eqs 10 and 11) are suggested by metastable ions at *m/e* 18·1 ($43^2/102$) and 25·3 ($43^2/73$)—these correspond to equivalent ions at *m/e* 18·7 ($43^2/99$) and 25·7 ($43^2/72$) in VI. Analogous ion transformations in VIII (ie. 141 → 43 and 72 → 43) are indicated by metastable ions at *m/e* 13·2 and 25·7. If, despite these alternatives, we assume that β-diketone intermediates (*C*) generate the characteristic fragment ions listed in Table 4, certain charged species unique to McLafferty rearrangement of these intermediates[14] should appear in the mass spectra of the epoxyketones. For example, diketones XVIII and

TABLE 4. TYPE *C* β-DIKETONE REARRANGEMENT IONS[a]

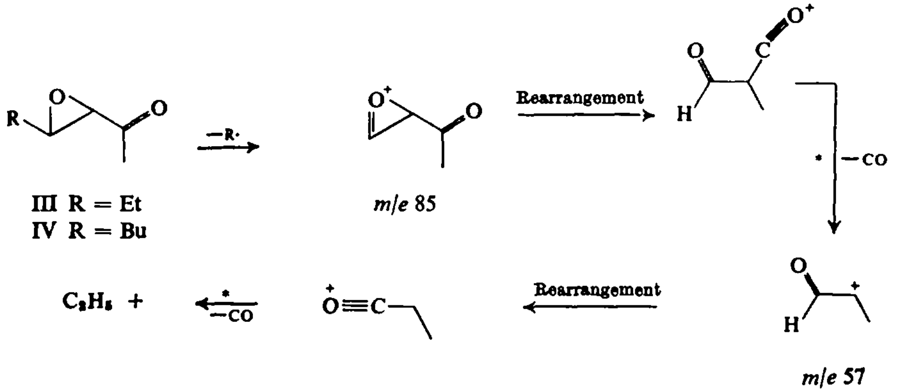
Epoxyketone	$R_\beta \overset{+}{\equiv} CO$	$R_\beta +$
	*m/e* (% Σ_{40})	*m/e* (% Σ_{40})
III	57(7·0)	$\underline{29}$(3·6)
IV	$\underline{85}$(<1)	$\underline{57}$(<1)
VIa	$\underline{43}$(6·5)	
VIII	$\underline{43}$(6·5)	
IX and X	$\underline{43}$(2·0)	

[a] Underlined values are confirmed by high resolution measurements (Table V).

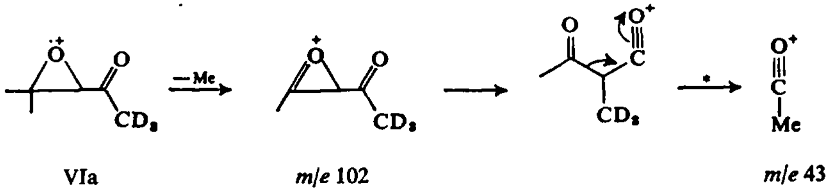
TABLE 5. HIGH RESOLUTION MEASUREMENTS

Compound	Ion (*m*/*e*)	Composition
II	58	C_3H_6O
II	57	C_3H_5O
II	43	C_2H_3O
II	42	C_2H_2O
II	41	75% C_3H_5, 25% C_2HO
II	29	55% C_2H_5, 45% CHO
III	43	95% C_2H_3O, 5% C_3H_7
III	29	60% C_2H_5, 40% CHO
IV	100	>90% $C_4H_8O_2$, <10% $C_6H_{12}O$
IV	85	>95% $C_4H_5O_2$, <5% C_5H_9O
IV	57	90% C_3H_5O, 10% C_4H_9
IV	55	75% C_4H_7, 25% C_3H_3O
IV	43	88% C_2H_3O, 12% C_3H_7
IV	29	80% C_2H_5, 20% CHO
V	71	C_4H_7O
V	69	C_4H_5O
V	57	C_3H_5O
V	55	85% C_4H_7, 15% C_3H_3O
V	43	C_2H_3O
V	41	C_3H_5
VI	74	$C_3H_6O_2$
VI	72	C_4H_8O
VI	57	>90% C_3H_5O, >10% C_4H_9
VI	43	90% C_2H_3O, 10% C_3H_7
VI	29	50% HCO, 50% C_2H_5
VII	86	$C_5H_{10}O$
VII	85	C_5H_9O
VII	59	C_3H_7O
VII	57	C_4H_9
VII	55	85% C_3H_3O, 15% C_4H_7
VII	43	>95% C_2H_3O, <5% C_3H_7
VII	41	C_3H_5
VIII	85	C_5H_9O
VIII	83	>95% C_5H_7O, <5% C_6H_{11}
VIII	71	C_4H_7O
VIII	57	90% C_4H_9, 10% C_3H_5O
VIII	55	65% C_4H_7, 35% C_3H_3O
VIII	43	65% C_2H_3O, 35% C_3H_7
VIII	41	C_3H_5
VIII	29	<90%, C_2H_5, <10% CHO
XI	112	60% $C_7H_{12}O$, 40% $C_6H_8O_2$
XI	109	C_7H_9O
XI	98	$C_6H_{10}O$
XI	97	>95% C_6H_9O, <5% $C_5H_5O_2$
XI	81	80% C_6H_9, 20% C_5H_5O
XI	70	C_4H_6O
XI	69	75% C_5H_9, 25% C_4H_5O
XI	55	70% C_3H_3O, 30% C_4H_7

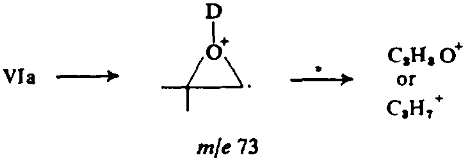
XIX from epoxyketones III and IV respectively would rearrange to an ion of mass 58 (Eq. 12); however, this fragment is not present in the spectrum (Fig. 6) of III and is of very low abundance (0·5% Σ_{30}) in IV (Fig. 3). Corresponding rearrangement ions from VIII (Fig. 8) and IX (or X) appear at mass 114 (ca. 0·1% Σ_{30}) and 196 (0·2% Σ_{30}) respectively.



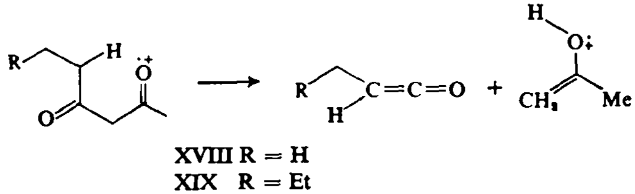
(9)



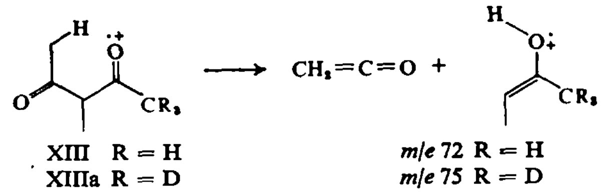
(10)



(11)



(12)

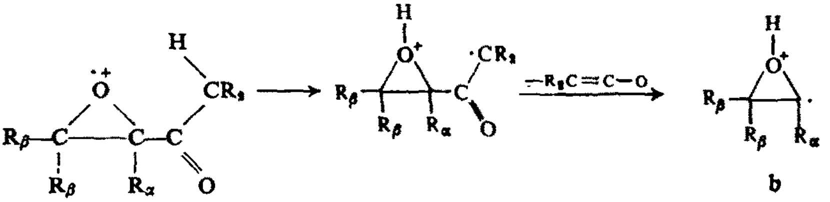


(13)

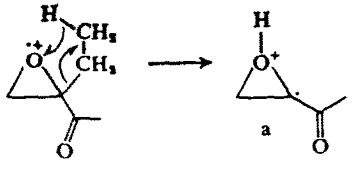
Since β-diketone XIII would be the product of a type C rearrangement (Eq. 4) of 4-methyl-3,4-epoxy-2-pentanone (VI), a comparison of the mass spectra of these compounds and the deuterium labeled analog VIa should be particularly meaningful. The m/e 72 ion from XIII is produced by the degenerate McLafferty rearrangement illustrated in Eq. 13 and has an abundance of 10% Σ_{30}. This same ion is found in the spectrum (Fig. 9) of VI, and proved to be C_4H_8O (7·5% Σ_{30}) by high resolution analysis (Table 5). In the labeled compound VIa the *m/e* 72 peak shifts (Fig. 12) predominantly to *m/e* 73 (6% Σ_{30}); and the extent to which a β-diketone intermediate XIIIa serves as its progenitor may be determined by measuring the *m/e* 75 peak that must be formed along with *m/e* 73 in the McLafferty rearrangement (Eq. 13). The very small amount of *m/e* 75 (0·2% Σ_{30}, corrected for *m/e* 74 isotope contribution) observed in the spectrum of VIa limits the β-diketone rearrangement to 4% or less. Thus, more than half the $C_2H_3O^+$ ion formed from VIa must be generated in some manner (eg. Eq. 10 and 11) that does not involve a β-diketone intermediate.

Hydrogen transfer reactions

In the epoxyketone substrates reported here the only hydrogen transfer consistently observed is that described in Eq. 14. Although several structures can be envisaged for the resulting ion (e.g. b), the essential features of the process are indicated by high resolution analysis (Table 5) of the *m/e* 58, 72, 86 and 98 peaks in II, VI, VII and XI respectively (see the last column in Table 1) and the shift of *m/e* 72 to 73 in VIa. It is instructive to compare this process with other five and 6-membered cyclic hydrogen transfers to electron deficient oxygen species. For example, the molecular ion from V can conceivably display several kinds of hydrogen transfer (eg. Eqs 14, 15 and 16). However, the M-28 ions (mass 86) produced by the latter two processes are of very low abundance (<0·5% Σ_{30}, see Fig. 7), indicating a preference for the loss of ketene rather than ethylene. A similar preference is seen in the decomposition of 3-ethylpentane-2,4-dione.[14] The inefficiency of the McLafferty transfer (Eq. 16) is perhaps due to the unfavourable location of the enolic double bond in d.

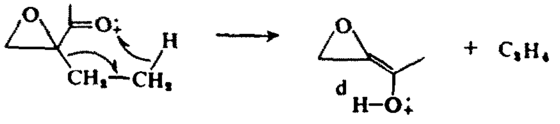


(14)



V *m/e* 86

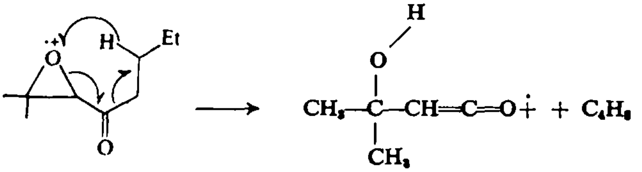
(15)



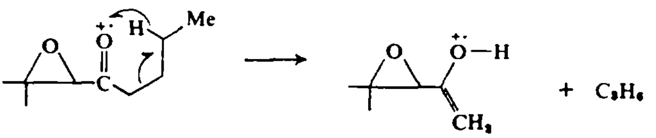
V *m/e* 86

(16)

The n-Bu group of VIII is a potential source for several hydrogen transfer reactions (Eqs. 14, 17 and 18); however, only the former (yielding an ion of mass 72) makes a significant contribution (2·8% Σ_{30}) to the mass spectrum (Fig. 8) of this compound. The analogous six membered cyclic transfer (Eq. 17) generates an ion of mass 100, which is only weakly observed (<0·3% Σ_{30}). Loss of a Me group from e would give the abundant *m/e* 85 species; however, high resolution measurement of the latter peak shows that no $C_4H_5O_2^+$ is present (Table 5). These results are in striking contrast with the relatively favorable "inside" McLafferty rearrangement reported[6] for 1-hexene oxide. The absence of a McLafferty rearrangement involving the CO group of VIII (Eq. 18) is particularly surprising in view of the important role which this process plays in saturated ketones.[5,16] Competition from other more facile decomposition modes (e.g. α-cleavage as in Table 1) is apparently responsible for the altered reactivity of conjugated CO and epoxide groups.

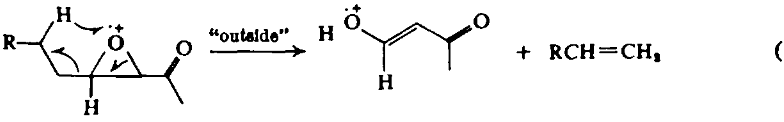


VIII e *m/e* 100 (17)



VIII f *m/e* 114 (18)

Hydrogen transfer from a β-alkyl substituent to the epoxide oxygen can proceed by either an "outside" (Eq. 19) or an "inside" (Eq. 20) mechanism.[6] The former would generate an *m/e* 86 peak from compounds III and IV, but the small amount of this ion



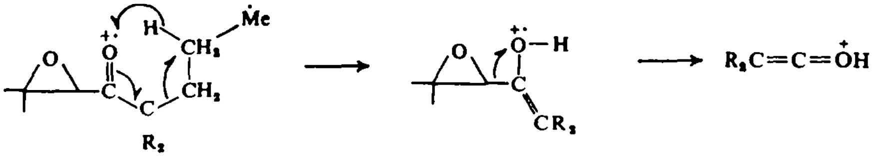
III R = H
IV R = Et

m/e 86 (19)

---

[16] The unlikely possibility that the McLafferty rearrangement ion f decomposes rapidly and quantitatively to an ion of mass 43 was eliminated by the observation that *m/e* 45 is an insignificant peak (0·6% Σ_{40}) in the spectrum of VIIIa.

i.e.

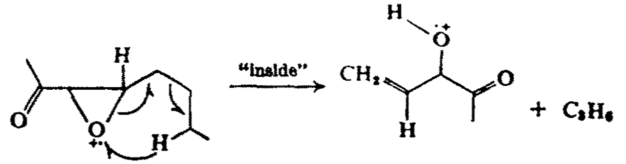


R₂
VIII R = H
VIIIa R = D

f

m/e 43 R = H
m/e 45 R = D

found in the corresponding mass spectra (Figs. 6 and 3) is in both cases an isotope satellite of the abundant *m/e* 85 species. The weak signal at *m/e* 100 (1·8% Σ_{30}) in the mass spectrum (Fig. 3) of IV could arise from either an "inside" epoxide rearrangement (Eq. 20) or the ubiquitous ketone ejection (Eq. 14). High resolution measurements reveal that this ion is >90% $C_5H_8O_2$ as required by the former rearrangement (20).

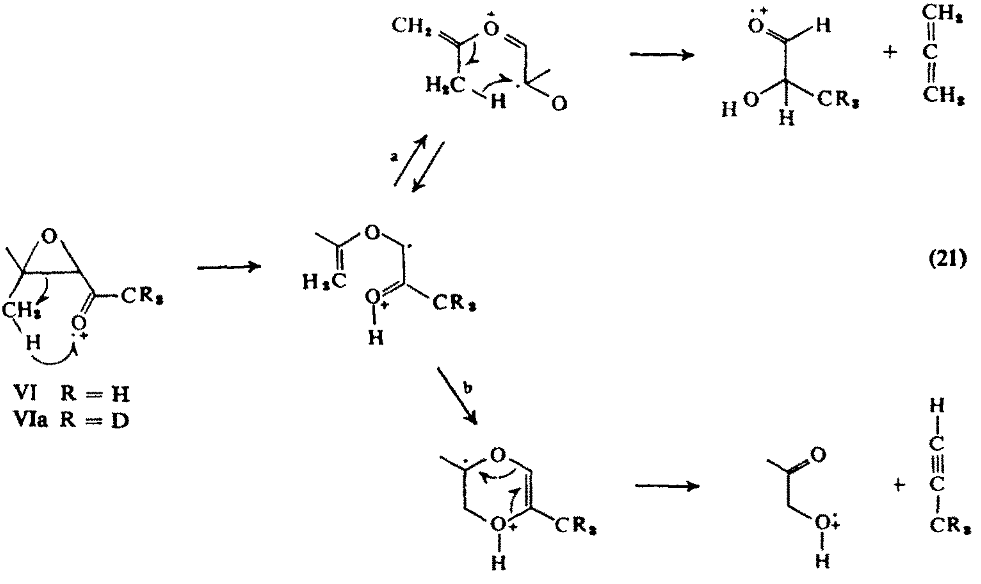


IV

m/e 100

(20)

Hydrogen transfer from a *β*-alkyl substituent to the carbonyl oxygen does not necessarily cause fragmentation of the molecular ion; consequently, only indirect evidence for such a transfer can be cited. A rearrangement ion of mass 74 in the mass spectrum of VI provides an example of such evidence. This ion is relatively weak in the Atlas spectrum (Fig. 9, 1·5% Σ_{30}), but is quite significant in the C.E.C. (Fig. 5) and MS-9 (Fig. 11) spectra (3·5 and 5·8% Σ_{30} respectively). A composition of $C_3H_6O_2$ was determined for the mass 74 ion by high resolution analysis. In VIa some of this peak remains at *m/e* 74 but the major portion shifts to *m/e* 77 (77/74 = 2·8). This species can be formed by transfer of two hydrogen atoms from the left hand part to the right hand part of the molecule (path a in Eq. 21), or by transfer of the acyl oxygen atom to the left hand part (path b in Eq. 21). Both processes appear to take place although the former is preferred according to the labeling results. In the mass spectrum of VII a homologous ion is observed at mass 88 (1·2% Σ_{30}), but *m/e* 74 is absent. The only other substrates that exhibit this rearrangement are the dypnone



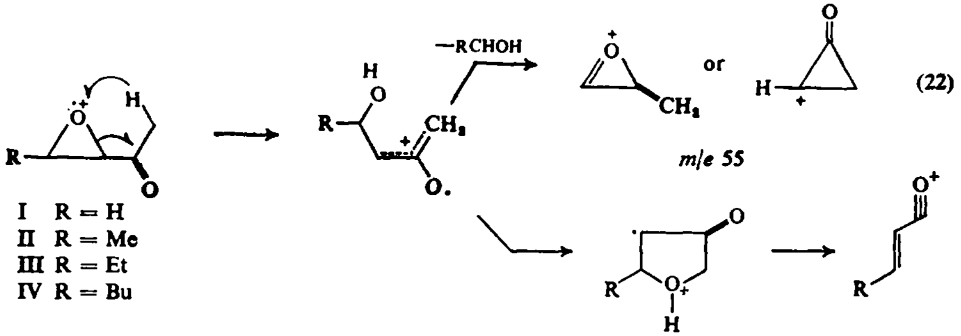
(21)

VI R = H
VIa R = D

oxides (IX and X) which show a weak ion of mass 136 (ca. 1·2% Σ_{40}). A corresponding hydrogen transfer is known to occur photochemically in IX.[13a]

Miscellaneous ions

The mass spectrum of 3,4-epoxy-2-butanone (I) contains a moderately abundant ion of mass 55 (8% Σ_{30}), which can only be C_3H_3O. This ion and its homologs are found at *m/e* 55 (2% Σ_{30}) and 69 (2% Σ_{30}) in II (Fig. 1), *m/e* 55 (1·7% Σ_{30}) and 83 (0·4% Σ_{30}) in III (Fig. 6) and *m/e* 55 (C_3H_3O is 2·3% Σ) and 111 (1% Σ_{30}) in IV (Fig. 3). A rationale for the genesis of these ions is given in Eq. 22. Also metastable ions at *m/e* 24·4, 36·4 and ca. 62 in II, III and IV respectively, suggest that carbon monoxide is easily lost from the *m/e* 69, 83 and 111 ions. A similar series of reactions (Eq. 23) would account for the ions of mass 109 (1·8% Σ_{30}, C_7H_9O) and 81 (2·4% Σ_{30}, C_6H_9) observed in XI.

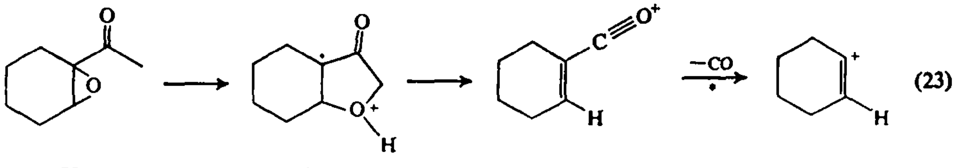


(22)

I R = H
II R = Me
III R = Et
IV R = Bu

m/e 55

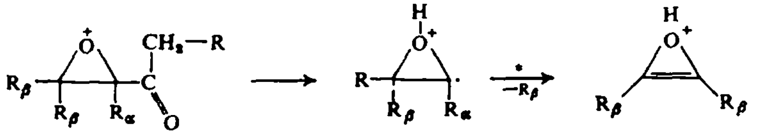
m/e 55 R = H
69 Me
83 Et
111 Bu



(23)

XI *m/e* 109 *m/e* 81

Loss of a β-substituent from the hydrogen transfer ion b is indicated by characteristic metastable ions in the mass spectra of II, III, VI, VII and VIII. Thus, a metastable ion at *m/e* 45·2 in the spectra (Figs. 9 and 8) of VI and VIII requires that an ion of mass 72 decompose to an *m/e* 57 species, as shown in Eq. 24. Isotopically



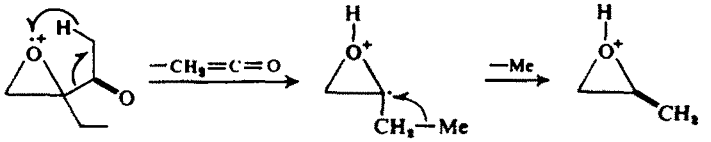
(24)

VI R = Rα = H, Rβ = Me
VIII R = Pr, Rα = H, Rβ = Me

m/e 72
b

m/e 57
VI C_3H_5O, 5·5% Σ
VIII C_3H_5O, 2·6% Σ

labeled derivatives (i.e. VIa and VIIIa) show the expected shifts (i.e. *m/e* 72 → 73 and *m/e* 57 → 58). The *m/e* 57 ion (5% Σ_{30}, C_3H_5O) present in the spectrum of V (Fig. 7) may be formed in a similar manner (Eq. 25).



V

(25)

EXPERIMENTAL

Low resolution mass spectra were obtained by Drs. Alan Duffield and John MacLeod, using an Atlas CH-4 spectrometer; by Mr. R. G. Ross, using an A.E.I. MS-9 double focussing spectrometer; and by Mr. N. S. Garcia, using a C.E.C. Model 21-103C mass spectrometer. High resolution measurements with the A.E.I. MS-9 instrument were secured by Mr. Ross. The inlet system in the Atlas and MS-9 instruments were heated to ca. 150°, and the all glass inlet of the C.E.C. spectrometer was held at 200°. Source temp varied from below 200° in the Atlas and MS-9 to ca. 250° in the C.E.C. spectrometer.

The unsaturated ketone precursors of the α,β-epoxyketones are all known compounds and were obtained either from commerical sources or by well defined synthetic routes. Epoxidation was generally effected by alkaline peroxide mixtures. In most cases a procedure similar to that described by Payne[17] was used; however, I, II and V were prepared according to the method of Yang and Finnegan.[18] Since 3,4-dimethyl-3-pentene-2-one was inert to the alkaline epoxidation mixtures, *m*-chloroperbenzoic acid was used in the synthesis of VII. The purity of the epoxyketone samples used in the mass spectral measurements was checked by VPC and TLC. In most cases IR and NMR spectra confirmed the structure. The α- and β-diketones were purified from commerical samples.

Isotopic labeling of VI was accomplished by allowing a homogeneous mixture of the epoxyketone and K_2CO_3aq in D_2O to remain at room temp for 2 days. The resulting orange soln was extracted with anhyd ether and the crude extract purified by VPC. The low resolution mass spectrum showed VIa to be 6% d_2, 81% d_3 and 12% d_4. A NMR spectrum of VIa revealed complete deuteration of the acetyl Me group.

Deuterium labeling of VIII was effected in a similar manner, but required the addition of methanol-d_1 to achieve a homogeneous reaction mixture. Analysis of the product was complicated because the molecular ion is very weak; however, a consideration of the *m/e* 87 peak indicated the composition to be 16·5% d_1, 80% d_2 and 3% d_3.

Acknowledgements—We thank Dr. Lois Durham and her staff for determining the NMR spectra. The purchase of an Atlas CH-4 spectrometer was made possible by Grant NsG 81-60 from NASA. Financial assistance by the National Institutes of Health (grant No. AM04257) is gratefully acknowledged.

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[18] N. C. Yang and R. A. Finnegan, *J. Am. Chem. Soc.* **80**, 5845 (1958).