

## A Simple Procedure for Localisation of Ethylenic Bonds by Mass Spectrometry

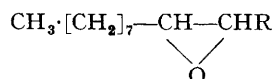
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THE difficulty of localising ethylenic bonds in various types of natural products by mass spectrometry has led to the use of introduced functional groups to locate the position of previous unsaturation.<sup>1-3</sup> However, these methods employed for aliphatic compounds suffer from various disadvantages. Either the relevant ions are of low abundance<sup>3</sup> or the method of functionalisation gives rise to a mixture of products.<sup>2</sup>

In an effort to find a simple method for locating ethylenic bonds, we have examined the fragmentation patterns of a number of epoxides derived from aliphatic and alicyclic<sup>4</sup> compounds. We now report a simple method for localising ethylenic bonds in aliphatic chains.

The epoxides (I—V) prepared by the action of perlauric acid on the appropriate olefin, were purified by preparative t.l.c. and admitted into the mass spectrometer by direct insertion. In contrast to the spectra of a number of low molecular-weight epoxides,<sup>5</sup> very intense



- (I) *cis*-R =  $[\text{CH}_2]_7 \cdot \text{CO}_2\text{Me}$   
 (II) *trans*-R =  $[\text{CH}_2]_7 \cdot \text{CO}_2\text{Me}$   
 (III) *cis*-R =  $[\text{CH}_2]_{11} \cdot \text{CO}_2\text{Me}$   
 (IV) *cis*-R =  $[\text{CH}_2]_{11} \cdot \text{CH}_2\text{OH}$   
 (V) *cis*-R =  $[\text{CH}_2]_{11} \cdot \text{CH}_3$

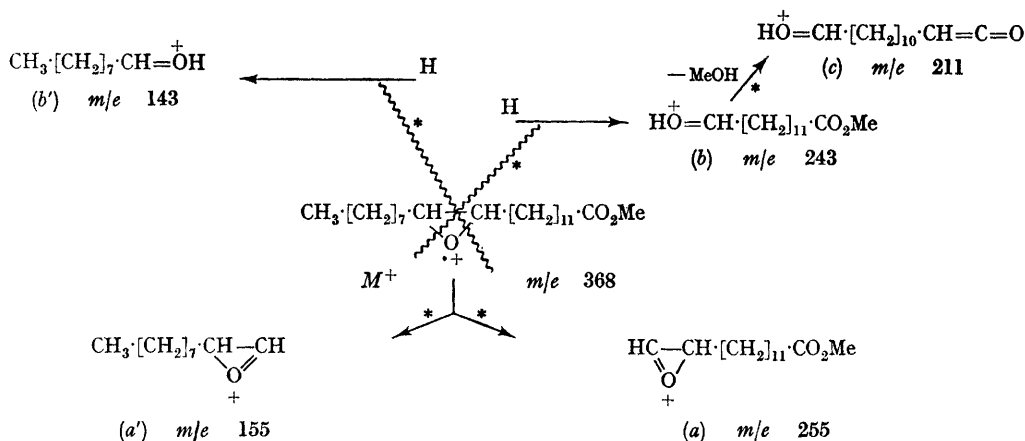
fragmentation occurs  $\alpha$  to the functional group to give the species (*a*) and (*a'*); in addition transannular fragmentation takes place with concomitant hydrogen transfer to give the prominent ions (*b*) and (*b'*) (Table) as shown for (III) in the Scheme. In the case of the esters (I—III) in addition to these ions, and the expected *m/e* 74 peak due to McLafferty's rearrangement, the species

TABLE

Major fragments in the spectra of some aliphatic epoxides

Compound	<i>M</i> <sup>+</sup>		<i>a</i>		<i>a'</i>		<i>b</i>		<i>b'</i>		<i>c</i>		Base peak <i>m/e</i>
	<i>m/e</i>	%	<i>m/e</i>	%	<i>m/e</i>	%	<i>m/e</i>	%	<i>m/e</i>	%	<i>m/e</i>	%	
(I)	312	2	199	32	155	33 <sup>‡</sup>	187	15	143	6	155	66 <sup>‡</sup>	155
(II)	312	2	199	35	155	33 <sup>‡</sup>	187	15	143	5	155	66 <sup>‡</sup>	155
(III)	368	3	255	31	155	32	243	13	143	20	211	25	55
(III)†	368	12	255	81	155	100	243	35	143	68	211	93	155
(IV)	340	3	227	36	155	37	215	4	143	6	—	—	55
(V)	324	18	211	96	155	91	199	9	143	12	—	—	69

† Ionising voltage nominally 16 ev. ‡ Composition determined by high-resolution measurements.



SCHEME

\* metastable peak observed

(b) loses methanol to give the fragment (c), 44 mass units below (a), which serves to identify the fragment containing the ester group.<sup>6</sup> Intensification of these oxygen-containing fragments were achieved by determining the spectra at low ionising voltage (e.g., III, Table). Only slight intensity differences

were observed in the spectra of the *cis/trans*-isomers (I) and (II). However these can be readily distinguished by their 100 Mc./sec. n.m.r. spectra. The *cis*-epoxide hydrogens give rise to a broad singlet at  $\tau$  7.12 and those of the *trans*-epoxide give a partially resolved triplet at  $\tau$  7.34.

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<sup>2</sup> H. E. Audier, S. Borg, M. Fétizon, P. Longevialle, and R. Toubiana, *Bull. Soc. chim. France*, 1964, 3034.

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