A MASS-SPECTROMETRIC STUDY OF INSECT PHEROMONES.

II. EPOXY COMPOUNDS

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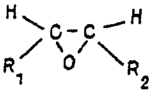
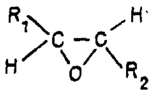
The mass spectra of epoxy compounds have been studied and the positions of the epoxy rings and their configurations have been shown.

Epoxy compounds are some of those found most frequently as components of pheromones of various species of insects [1-3]. In order to elucidate the possibility of the mass spectrometry of metastable ions in the investigation of such compounds, we have studied the mass spectra and the spectra obtained by the direct analysis of daughter ions (DADI) and by metastable defocusing (MD) of the M^+ ions and of key fragments of the (Z)-7,8-epoxy compounds (I)-(V) and the (E)- compound (VI).



I-V



VI

I. $R_1=(CH_3)_2CH(CH_2)_4$, $R_2=C_7H_{15}$
II. $R_1=(CH_3)_2CH(CH_2)_4$, $R_2=C_8H_{17}$
III. $R_1=C_6H_{13}$, $R_2=C_{10}H_{21}$
IV. $R_1=(CH_3)_2CH(CH_2)_3$, $R_2=C_{10}H_{21}$
V. $R_1=(CH_3)_2CH(CH_2)_4$, $P_2=C_{10}H_{21}$
VI. $R_1=(CH_3)_2CH(CH_2)_4$, $R_2=C_{10}H_{21}$

Characteristic for the mass spectra of these compounds are low intensities (3-5%) of the peaks of the molecular ions. The main directions of breakdown of the M^+ ion of an epoxy compound are: a) breakdown of the alkyl chains; b) breakdown of the epoxide ring; and c) cleavage of the α-bonds in relation to the epoxide oxygen. In each type of breakdown the formation of two types of ions is possible – not containing oxygen (ions of types a, b, c, and d) and oxygen-containing (ions of types a', b', c', and d'). The appearance of these ions is of great importance in determining the structures of epoxy compounds.

The oxygen-containing ions may, in their turn have the structures of oxonium ions (a', b') or of aldehydes (c', d').

The difference between the m/z values for the oxonium ions and M^+ always bears information on the position of the epoxide bridge in the molecule. This information can also be confirmed by the m/z values of the ions of types c' and d'.

In the mass spectra of compounds (I)-(VI) the intensities of the oxygen-free fragments in the high-mass region are low (3-10%). In the mass spectrum of compound (V), in the molecule of which there are two isomeric hydrocarbon radicals (heptyl and isoheptyl) attached to carbon atoms of the epoxide ring, the oxygen-containing and oxygen-free fragments have the same m/z value. This leads to an increase in the intensity of the peaks of these fragments.

As one of the possible explanations it may be suggested that the oxonium ions a' and b' with the same m/z value of 155 undergo rearrangement processes during which neutral alkenes are ejected from them with the formation of a number of oxonium ions the stabilities of which are greatest at low m/z values. A comparison of the intensities of the peaks of the a' and b' fragments (19 and 8%, respectively) in the mass spectra of epoxides (I)-(VI) has shown that the intensity is always greater for the heavy fragment [3].

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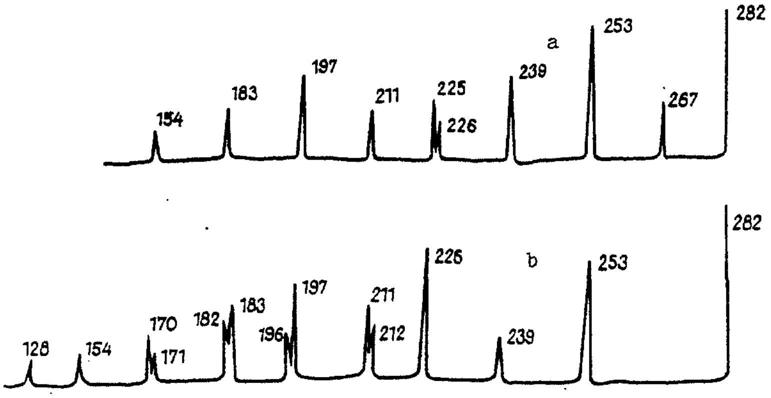


Fig. 1. DADI spectra of the M^+ ions of the isomeric compounds (V) (a) and (VI) (b).

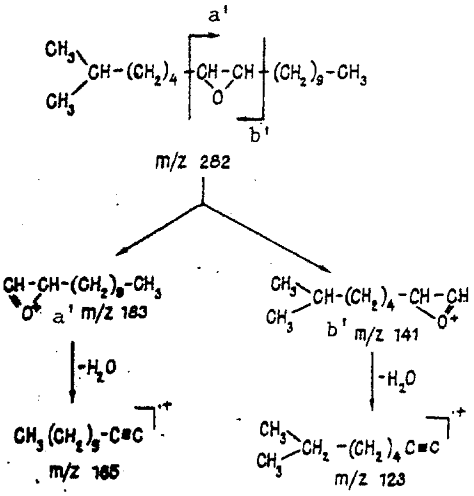
Compounds (V) and (VI) are isomers with respect to the confirmation of the hydrogen atoms in the epoxide ring (in the first, the cis-, and in the second, the trans-configuration). Such stereochemical differences do not usually appear in ordinary electron-impact mass spectra. In them, the intensities of the peaks of both the molecular and the other key fragments are practically identical. Definite differences are observed in a comparison of the DADI spectra of their molecular ions (Fig. 1a, b).

In the DADI spectrum of M^+ for (V) (Fig. 1a) there is a peak of an ion with m/z 267 corresponding to the splitting out of a methyl radical, while in the DADI spectrum of M^+ for the trans- isomer there is the peak of an ion with m/z 253 (splitting out of an ethyl radical) [4, 5]. These spectra contain peaks of ions with the same m/z values, such as 239, 226, 211, 197, and 183. But the intensities of the peaks of each of these ions in the spectra under comparison differ considerably. The greatest difference in the DADI spectrum of M^+ for the trans- isomer (Fig. 1b) consists in the appearance in it of numerous peaks split into doublets (212, 211; 197, 196; 183, 182; 171, 170) showing the occurrence of rearrangement processes competing with ordinary breakdown.

In the DADI spectrum of M^+ for the cis- isomer (Z)-2-methyl-7,8-epoxyoctadecane (Fig. 1a), only one doublet is observed, with m/z values of 225 and 226, corresponding to the splitting out of a propyl radical and of a propylene molecule. In both spectra, as the bonds undergoing cleavage approach the epoxide ring, the intensity of the resulting fragments diminishes.

Some of the key fragments appearing in the mass spectra of cis- and trans-2-methyl-7,8-epoxyoctadecanes are fragments of types a' with m/z 183 and b' with m/z 141 (Scheme 1). It is difficult to assume that in ions of types a and b the original configurations of the hydrogen atoms in the epoxide rings are retained. The DADI spectra of these ions should give definite information on this. It might be expected that on the formation of these ions the conformational state of the hydrogen atoms of the epoxide ring is averaged, and this should be shown in a greater similarity of their DADI spectra. Contrary to expectations, definite difference are observed in the DADI spectra of these pairs of ions (Fig. 2a, b). These are the presence in the DADI spectrum of the fragment with m/s 183 formed from compound (V) of peaks of ions with m/z 154 and 155 that are absent from the DADI spectrum of the corresponding ion formed from M^+ for (VI), and also the appearance of an ion with m/z 141 in the spectrum of the latter and its absence from the spectrum of the former. Otherwise, these spectra are similar. They have the same set of peaks of doublet ions with m/z 125, 126; 112, 113; and 97, 98, and of singlets with m/z 71. In each spectrum, the peak of anion with m/z 165 corresponding to the elimination of a water molecule has the maximum intensity. The formation of this ion is extremely characteristic. One of the probable explanations of the splitting out of a water molecule from the a' ion is the disruption of the epoxide ring with the formation of a triple bond in the terminal part of the fragment, as is shown in Scheme 1.

It must be mentioned that in the DADI spectrum of the fragment with m/z 183 of substance (V) the number of doublet peaks increases in comparison with the DADI spectrum of its molecular ion. A comparison of the DADI spectra of ions of type b' with m/z 141 from the isomers (V) and (VI) also shows differences and similarities.



Scheme 1. Scheme of the fragmentation of M^+ for (V) and (VI).

Characteristic for these spectra are the maximum intensity of the peak of the ion with m/z 123 (elimination of water) and the breakdown of the alkyl chain with the ejection of neutral molecules of alkenes (propene, isobutene, and isopentene).

In the high-resolution mass spectra of substances (V) and (VI) the peak of the ion with m/z 141 is split, giving a doublet with accurate m/z values of 141.1270 (found), 141.1275 (calculated), and 141.1532 (found), 141.1643 (calculated), which correspond to elementary compositions for the ions of $C_9H_{17}O$ and $C_{10}H_{21}$, respectively, the intensity of the oxygen-containing component of the doublet being three times higher [6, 7].

Other key fragments in the mass spectra of the epoxides that we have studied are fragments of types c' and d' (Scheme 2) containing oxygen atoms. The formation of these ions resembles the ozonolysis reaction, leading to the appearance of two aldehyde molecules. The

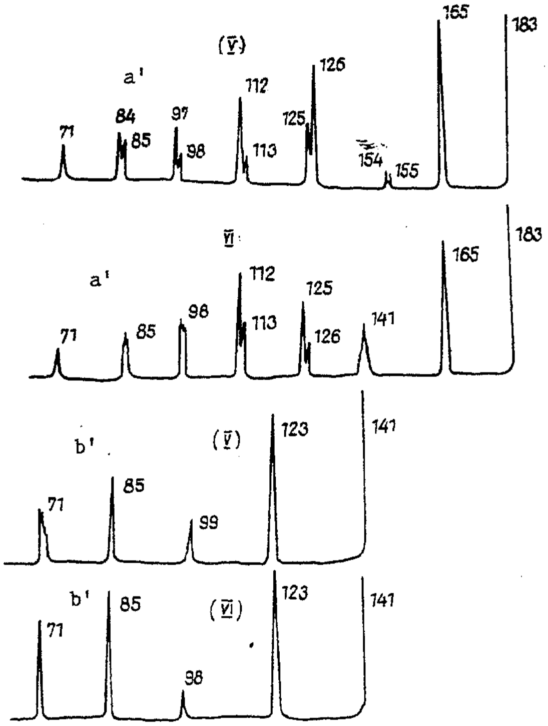
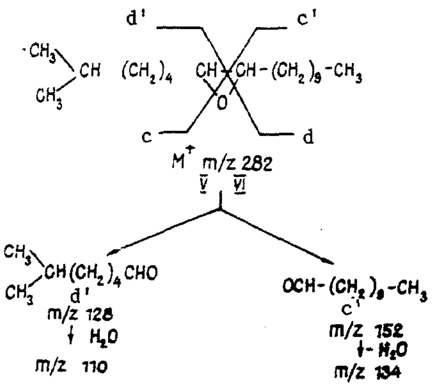


Fig. 2. DADI spectra of fragments a' and b' from compounds (V) and (VI).



Scheme 2

position of the double bond in the initial olefin is usually determined from the nature of the aldehydes obtained in this reaction. As already mentioned, fragments of types c' and d' are formed through the breakdown of the epoxide ring in both directions – from the side of the smaller R_1 radical (d') and from the side of the larger R_2 radical (c') (Scheme 2).

The main direction of fragmentation of metastable ions of types c' and d' is the elimination of a molecule of water from each of them, and this is reflected in their DADI spectra. In them, the maximum intensity is possessed by the peak of the dehydration ion (M – 18) with m/z 110. As an illustration of this, Fig. 3 gives the DADI spectrum of the ion with m/z from compound (VI).

The metastable defocusing spectra of ions of type c' with m/z 152, which are characteristic for compounds (V) and (VI), likewise differ by the number of peaks appearing in them and by their intensities (Fig. 4b).

As can be seen from the spectra given, the precursors of fragment c' of compound (V), the cis- isomer (Fig. 4a), are ions with m/z 170, 194, 207, 209, 263, and 282 (M^+).

As parents of fragment c' for the trans- isomer (VI) (Fig. 4b) appear ions with m/z 170, 208, 265, and 282 ($M^{\cdot}$). Judging from their intensities all these ions participate in equal degree in the formation of fragment c'. In the case of the cis- isomer the main source of appearance of fragment c' is the molecular ion with m/z 282.

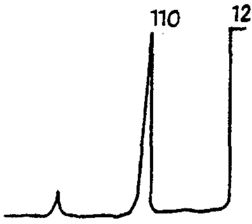


Fig. 3

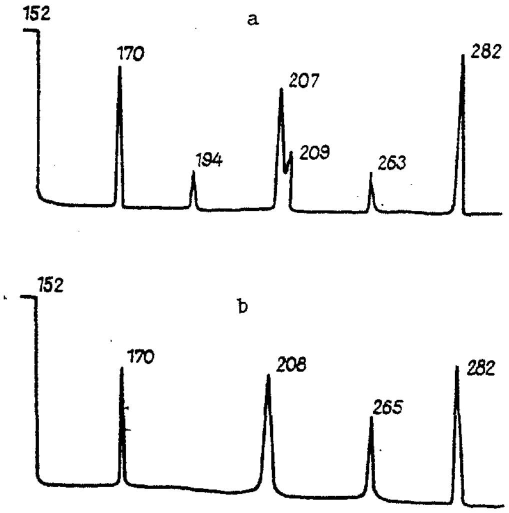


Fig. 4

Fig. 3. DADI spectra of the ions c' and d' formed from the M^+ ions of (V) and (VI).

Fig. 4. Metastable defocusing spectra of fragments of type c' with m/z 152 formed from the M^+ ions of (V) and (VI).

EXPERIMENTAL

The spectra were taken on a Varian MAT-311 instrument at an energy of the ionizing electrons of 70 eV, an accelerating voltage of 3 kV, and an evaporator temperature of 25-30°C. In the DADI spectra the mass of each daughter ion was calculated from the formula

$$m_2 = m_1 \frac{E_1}{E_0},$$

where m_1 is the mass of the mother ion; m_2 is the mass of the daughter ion; E_0 is the initial strength of the electric field; and E_1 is the electric field strength at which m_2 is recorded.

In the MD spectra, the mass number of the maternal ion was determined from the formula

$$m_1 = m_2 \frac{V_1}{V_0},$$

where V_0 is the initial value of the accelerating voltage at which the daughter ion m_2 was recorded; and V_1 is the value of the accelerating voltage at which the maternal ion m_1 was recorded.

The values of E_1 and E_0 and of V_1 and V_0 were determined by means of a digital voltmeter with an accuracy of ±0.5 V.

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