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Mass Spectra of Seven Isomeric Hexen-1-ols

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Mass spectra of seven isomeric hexen-1-ols have been determined in order to detect any correlations between fragmentation patterns and molecular structure. The double bond isomers have proved to be easily recognizable by their different base peaks. The mass spectra of the corresponding *cis* and *trans* isomers are in general very similar. Some differences between the spectra of the geometric isomers of 2- and 3-hexen-1-ols exist, however, which are sufficient for qualitative analysis. Gas chromatographic retention times for the isomeric hexen-1-ols are given.

Mass spectrometric identification of volatile organic compounds has become very popular in recent decades and a large number of mass spectra are now available in published form. Although the saturated alcohols [1] have been investigated very thoroughly by mass spectrometry, no information is available on the mass spectra of unsaturated alcohols. Nor has much use been made of the mass spectrometer for distinguishing geometric isomers. McLafferty [2] has found that in the mass spectrum of *cis* 1,2-dichloroethylene the intensity of the rearranged Cl_2^+ ion is about 5 times greater than in the spectrum of the *trans* isomer, showing that there is a steric influence on the activation energy. Natalis [3] has observed that the ionized *cis* isomer of some 1,2-dialkyl substituted derivatives of cycloalkanes is less stable than the corresponding *trans* isomer. In disubstituted ethylene derivatives [4] (I) no difference in stability is observed between the *cis* and *trans* isomers if R_1 and R_2 are methyl, ethyl or isopropyl groups. If one of the radicals is the *tert.* butyl group, however, the abundance of the molecular ion is 10–20 % greater in the *trans* isomer, and if both radicals are *tert.* butyl groups the parent ion intensity is about 7 times stronger in the *trans* isomer.

$$R_1-CH=CH-R_2$$

I

In the present investigation the mass spectra of seven isomeric hexen-1-ols [5] were determined with a mass spectrometer (Modified CEC Model 21-401) under the following conditions: 70 V electrons, an ionizing current of 100 μA and ion source temperature of 250°C and a sample inlet system developed in this laboratory.[6] To ensure purity, the samples were first subjected to gas chromatography. The retention times of the various isomers are presented in Table 1.

The mass spectra of the isomeric hexen-1-ols (Fig. 1) to some extent resembles the spectra of saturated alcohols. Typical peaks corresponding to the loss of mass 18 (water) and the loss of mass 33 (water and a methyl group), and likewise the fragment at mass 31 ($^+CH_2OH$), are visible. In the 2-, 3-, and 4-hexen-1-ols the molecular ion is present in an intensity of 0.2—0.9 % of the total ionization, whilst in hex-5-en-1-ol and hexen-1-ol [1] the intensities are only 0.015 % and 0.011 %, respectively. This is a consequence of the stabilization effect of the double bond. Some differences are seen, however, in the mass spectra of the double bond isomers. All have different base peaks; for 2-, 3-, 4- and 5-hexen-1-ol the respective m/e's are 57, 41, 67, and 54. The formation of the peaks, such as m/e = 67, 57, 55, and 41, can only be interpreted as due to rearrangement of the molecular ion. The mass spectrum of hex-5-en-1-ol most nearly resembles the spectrum of the corresponding saturated alcohol,[1] which very readily loses the neutral fragment 46 (ethanol) and forms the ion m/e = 31 ($^+CH_2OH$) at the electron impact. In the spectra of the other isomers these peaks, m/e = 31 and 54, occur at a considerably lower intensity.

The formation of the peak at mass 41, which is very intense in the spectra of all the isomers, can be assumed to be due to simple cleavage of the 5-isomer. The resonance stabilization of this ion ($^+CH_2-CH=CH_2 \longleftrightarrow CH_2=CH-CH_2^+$) increases the probability of the fragmentation of a carbon-carbon bond β to a double bond.[7] In all the other isomers this fragment is brought about by a rearrangement process.

The peak at mass 57 ($C_4H_9^+$) is characteristic of hex-2-en-1-ols. It is a peak typical of alkanes, and is probably formed by the fragmentation of the molecular ion between the carbon atoms 2 and 3 after the shift of the double bond to the position 1,2.

Table 1. Retention times (in minutes) of seven isomeric hexen-1-ols.

Substance	Column a	Column b
cis Hex-2-en-1-ol	18.0	23.9
trans Hex-2-en-1-ol	17.5	23.2
cis Hex-3-en-1-ol	16.2	21.8
trans Hex-3-en-1-ol	12.5	19.9
cis Hex-4-en-1-ol	17.8	25.3
trans Hex-4-en-1-ol	17.5	23.5
Hex-5-en-1-ol	15.8	23.4

Column a: Polyethylene glycol-6000, Ø 6 mm, 300 cm, 150°C, with a N_2 flow of 30 ml/min.
Column b: Polyethylene glycol-1500, Ø 4.5 mm, 600 cm, 175°C, with a N_2 flow of 45 ml/min.

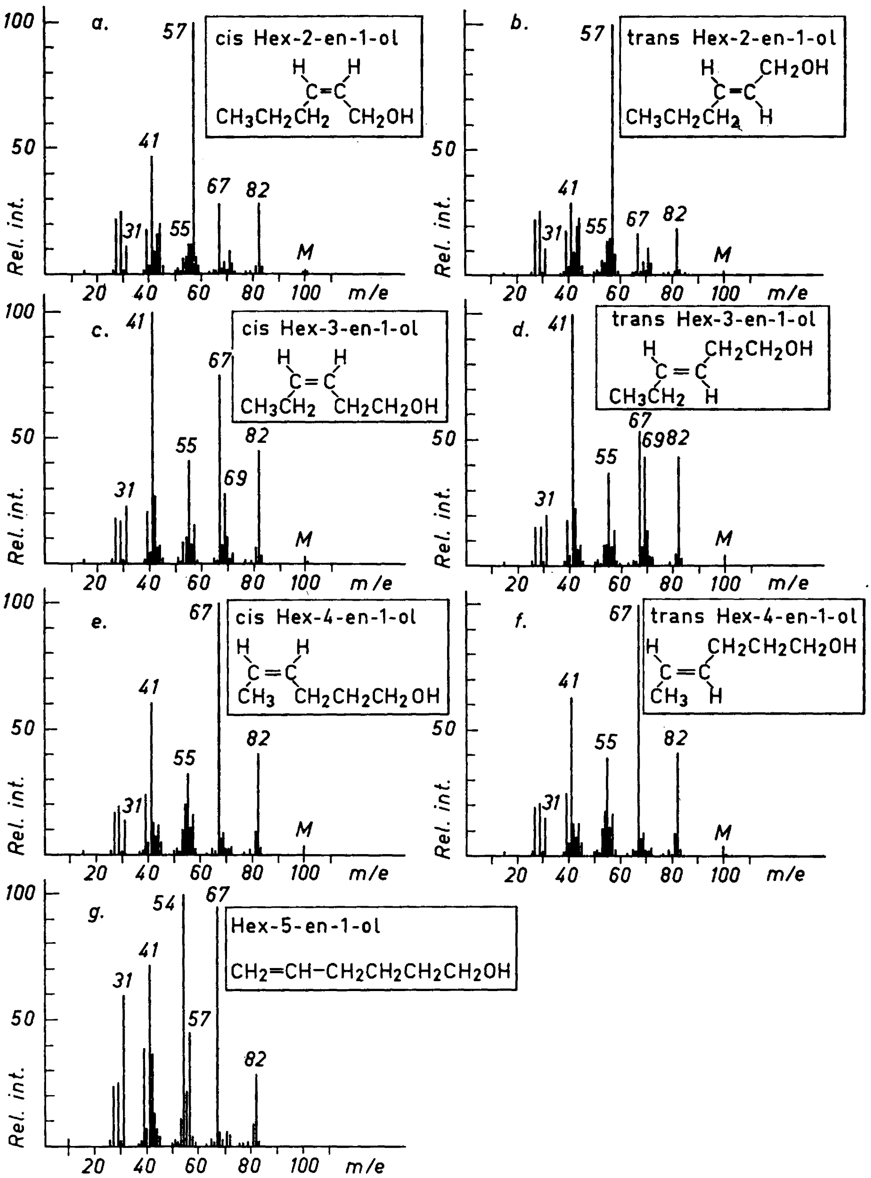
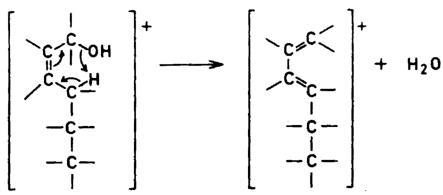


Fig. 1. Mass spectra of seven isomeric hexen-1-ols.

The mass spectra of the corresponding *cis* and *trans* isomers are very similar, as is to be expected. After the electron impact the molecular ion isomerizes very readily, so that differences between the geometrical configurations disappear. Small differences, however, are to be seen in the spectra of the geometric isomers of 2- and 3-hexen-1-ol. The peaks with $m/e = 41$, 67, and 82 appear in the spectrum of *cis* hex-2-en-1-ol in somewhat greater intensity than in the spectrum of the *trans* isomer. In the spectra of *cis* and *trans* hex-3-en-1-ol the intensity ratio of the peaks $m/e = 67$ and $m/e = 69$ is quite different.

The differences in the abundance of the molecular ion of *cis* and *trans* isomers are very small in comparison with the possible experimental errors. The parent peak seems to be somewhat more intense in the spectra of the *trans* isomers. This is a consequence of different rates of decomposition and may be due to the formation of a "cyclic intermediate" (II, for example by *cis* hex-2-en-1-ol) in the case of the *cis* isomer, sterically favouring the loss of water from the molecular ion.[7]



II III

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