MASS-SPECTROMETRIC INVESTIGATION OF HYDROCARBONS

Mass Spectra of the Diethyl Dithioacetals of 2,4 : 3,5-Di-O-benzylidene-D-xylose and 2,4 : 3,5-Di-O-benzylidene-D-ribose

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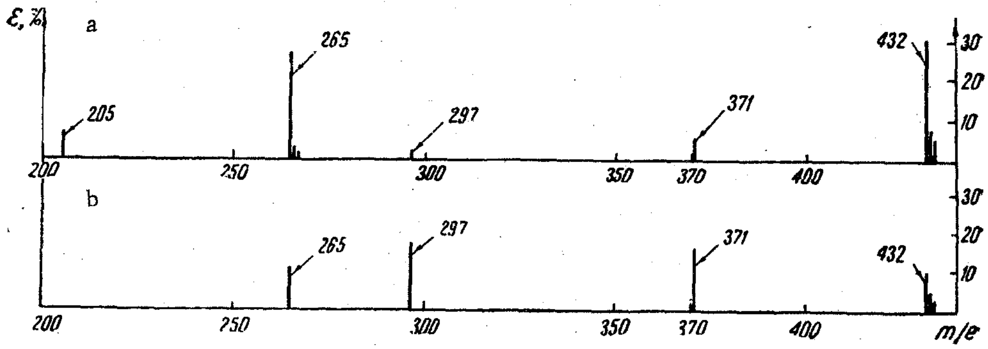
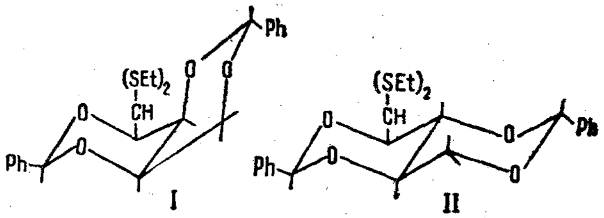
Attempts to use mass spectrometry to investigate stereochemical differences in the carbohydrate series have not so far given any positive results. From the data of Heyns and Scharmann [1], the differences in the mass spectra of the methyl ethers of the pentapyranoses are insufficiently large to permit the stereochemistry of any particular isomer to be deduced. Moreover, the authors do not give a satisfactory explanation of the differences observed. They mention only the fact that they exist, renouncing in principle the putting forward of conformational ideas in treating the mass spectra obtained.



Mass spectra of the diethyl dithioacetals of the 2,4:3,5-di-O-benzylidene derivatives of D-ribose (a) and D-xylose (b).

We have attempted to investigate the stereochemical differences in a number of carbohydrates with their alkylidene derivatives as examples, starting from the following considerations. Some alkylidene derivatives of carbohydrates, in particular the dibenzylidene derivatives of the diethyl dithioacetals of the pentoses, possess a rigid bicyclic system. The fragmentation of such systems may lead to marked differences in the mass spectra permitting their interpretation from the point of view of conformational ideas. For example, it is stated that there is a difference in the mass spectra of derivatives of cis- and trans-decalins [2].

As the first models for the investigation we selected a pair of epimers: the diethyl dithioacetal of 2,4: 3,5-di-O-benzylidene-D-xylose (I) and the diethyl dithioacetal of 2,4:3,5-O-benzylidene-D-ribose (II).

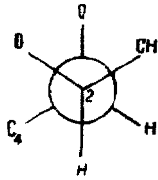


I

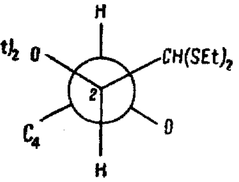
II

The high-molecular-weight region of the mass spectra of compounds (I) and (II) (figure) enabled their behavior under ionization conditions to be evaluated, and the peaks appearing in the mass spectra permit an evaluation of the structure of the molecule, i.e., they are characteristic. The non-characteristic peaks, e.g., those corresponding to benzaldehyde ions (m/e 106) or the diethyl dithioacetal group (m/e 135), are of no interest for interpreting the structure of compounds (I) and (II). Moreover, the fragmentation of the diethyl dithioacetal group agrees completely with that observed by de Jongh [3] and is included in a scheme which he proposed.

Compound (II) is considerably more volatile. This is easily explained by the assumption that the module has a less compact packing in the crystal. At the same time, compound (II) is more stable [its molecular peak is three times larger than the molecular peak of (I)], for which its structure is responsible. Being a trans compound, (II) does not undergo the interactions caused by the position of the diethyl dithioacetal group at C_1 and with respect to two of the oxygen atoms of the rings which can be well seen from Formulas (Ia) and (IIa):

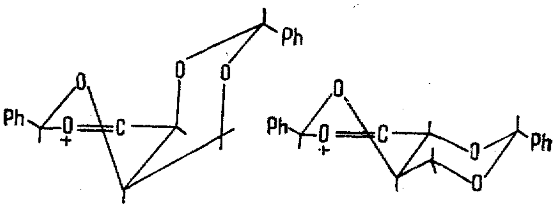


Ia



IIa

For the same reason, the ejection of the group concerned takes place considerably more easily in the case of (I) than that of (II) [the peak with m/e 297 in the spectrum of (I) is eight times larger than in the spectrum of (II)]. As a consequence of this ejection, an ion with a more planar structure and considerably weaker intramolecular interactions is formed. In the case of compound (II), however, a plane molecule is still further flattened, which leads to an increase in the angular strain and its conformation becomes less favorable. Consequently, the peak with m/e 297 in the spectrum of (II) is very small.



Ion with m/e 297 in the spectrum of (I)

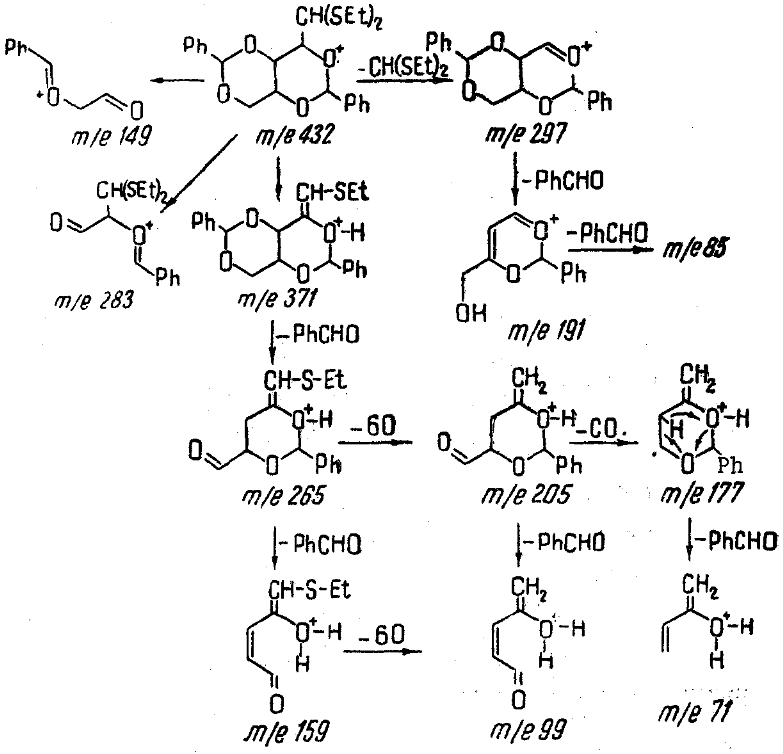
Ion with m/e 297 in the spectrum of (II)

A decrease in the intramolecular interaction can also explain the fact that the loss of 61 mass units in (I) is considerably greater than in (II) [the peak with m/e 371 in the mass spectrum of (I) is three times larger than in the mass spectrum of (II)].

Epimers	$\frac{m/e\ 371}{m/e\ 432}$		$\frac{m/e\ 297}{m/e\ 432}$		$\frac{m/e\ 265}{m/e\ 371}$	
	Temperature, °C					
	134	150	134	150	134	150
Diethyl dithioacetal of 2,4:3,5-di-O-benzylidene-D-xylose	1.25	1.05	1.37	0.8	0.86	0.93
Diethyl dithioacetal of 2,4:3,5-di-O-benzylidene-D-ribose	0.17	0.16	0.07	0.07	5.0	6.0

A more accurate idea of the relative ease of one rupture or another in compounds (I) and (II) is given by the table, in which the data of the mass spectra obtained at 134° and 150° C are given.

There are considerable differences in the intensities of some peaks in the low-molecular-weight region of the mass spectra (for example, the peaks with m/e 159, 151, 135, 111, 97, and others). However, even without a detailed review of the routes of fragmentation (scheme 1) the differences due to stereochemical factors can be seen sufficiently clearly and confirm the general features of the conformational ideas.



Scheme 1

Experimental

The mass spectra were obtained on a MKh-1303 instrument fitted with a system for introducing the sample directly into the ion source at temperatures of 134° and 150° C, with an ionization energy of 26 eV.

Summary

1. The mass spectra of the diethyl dithioacetals of 2,4: 3,5-di-O-benzylidene-D-xylose and 2,4:3,5-di-O-benzylidene-D-ribose have been studied.

2. The differences caused by stereochemical factors have been interpreted from the point of view of conformational ideas.

REFERENCES

1. K. Heyns and H. Scharmann, Tetrah., 21, 507, 1965.
2. V. I. Zaretskii et al., DAN SSSR, 158, 385, 1964.
3. Don de Jongh, J. Am. Chem. Soc., 86, 3149, 1964.

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