Characteristics of mass spectra of dichlorocarbene derivatives of isomeric dodecen-1-ols

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The m/z of characteristic ion of the mass spectra of the dichlorocarbene derivatives of dodecen-1-ols was used as a parameter to locate the position of double bond in these isomers by a new formula.

Keywords   Mass spectra, isomeric dodecen-1-ols, double bond

Introduction

It is well known that the position of a double bond affects the biological activities of insect sex pheromones. However, spectroscopic methods (IR, NMR and MS) can usually only give evidence for the existence of a double bond, but can not locate the position. Mass spectrometry of derivatives of unsaturated compounds has proven of diagnostic value in locating the position of a double bond, and the derivatization methods include ozonolysis, epoxidation, silylation, methoxymercuration and oxyselenation, etc. In a previous paper,[1] we reported a new formula for locating the double bond position in dodecenyl acetates based on mass spectral data of dimethyl disulfide derivatives. As an extension of our previous work, in this paper we investigate mass spectra of dichlorocarbene derivatives of dodecen-1-ols. The characteristics of chlorine isotopic clusters of the mass spectra can be utilized to calculate the position of a double bond in the original dodecen-1-ols by a new formula.

Experimental

NaOH (200 mg) and TEBAC (5 mg) were added to dodecen-1-ols (2.5 μL for each isomer) in 2 mL of chloroform. The mixture was stirred magnetically for 10 minutes and filtered to get the liquid phase. The mass spectra of the derivatives were recorded with a Finnigan-MAT GCQ gas chromatograph/mass spectrometer. Column temperature: 60°C (1 min) → 200°C (10°C/min); ion source temperature: 200°C; ionization energy: 70 eV (EI).

Results and discussion

The mass spectra of the dichlorocarbene derivatives of ten isomeric dodecen-1-ols show no evident molecular ions and the m/z of most base peaks are 55 or 67. There are four groups of fragment ions common to all the dodecen-1-ols with the differences only in their relative abundance, that is, $C_nH_{2n-5}^{\cdot+}$ (m/z 65, 79, 93, 107, 121), C_nH_{2n-3} or $C_nH_{2n-3}Cl_2^{\cdot+}$ (m/z 67, 81, 95, 109, 123, 137), $C_nH_{2n-1}^{\cdot+}$ (m/z 55, 69, 83, 97, 111, 125) and $C_nH_{2n-4}Cl^{\cdot+}$ (m/z 115, 129, 143, 157). The most striking feature of these mass spectra is that the chlorine isotopic clusters make two groups of fragment ions conspicuous (listed in Table 1). In Group I the intensity ratio of isotopic peaks ($116 + 14n$, $118 + 14n$ and $120 + 14n$) is about $3:3:1$, which indicates that there are three chlorine atoms in these fragments; and in Group II the intensity ratio of isotopic peaks ($250 - 14n$, $252 - 14n$ and $254 - 14n$) is about $9:6:1$, which indicates that there are two chlorine atoms in these fragments. The formation process is shown in Fig. 1.

$$CH_3(CH_2)_m \diagdown\!\!\!\!\!\diagup (CH_2)_n\overline{Cl}]^{\ddagger}$$

$$\begin{array}{c} -CH_3(CH_2)_mCH: \\ \end{array} \longrightarrow \;\; \begin{array}{c} Cl \\ Cl \end{array}\!\!\!\!>\!C\!=\!CH(CH_2)_n\overline{Cl}]^{\ddagger} \quad \text{I}$$

$$\begin{array}{c} -Cl(CH_2)_nCH: \\ \end{array} \longrightarrow \;\; \begin{array}{c} Cl \\ Cl \end{array}\!\!\!\!>\!C\!=\!CH(CH_2)_mCH_3]^{\ddagger} \quad \text{II}$$
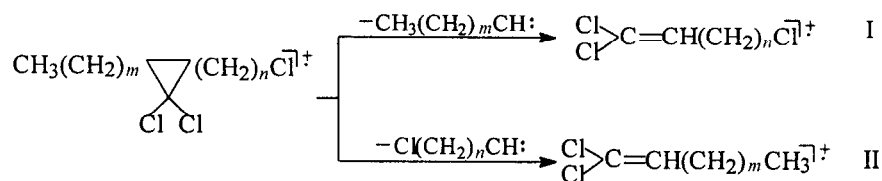
Fig. 1 Formation of the fragment ions of Group I and Group II.

The above two main fragmentation of the dichloro-cyclopropane ring can be described as follows: firstly, the loss of a $CH_3(CH_2)_mCH$: fragment by the cleavage of two carbon-carbon bonds of the dichlorocyclopropane ring due to high bond angle strain, and yielding ions containing three chlorine atoms (Group I ions); secondly, a loss of $Cl(CH_2)_nCH$: fragment by the dichlorocyclopropane breaking, so leading to ions containing two chlorine atoms (Group II ions). The position of the dichlorocyclopropane ring in the dichlorocarbene adduct is the same with the original double-bond position of dodecenols, so the two main fragmentation of the dichloro-cyclopropane ring give evidence about the position of double-bond in dodecenols. It is well know that the larg-

er the alkyl group, the more easily the loss. So preference for the loss of the largest alkyl fragment at a reactive site works when the ion fragmentation takes place. In many cases, the intensity of the resulting product ions is inversely proportional to their masses for loss of larger fragment.[2] When the position of the dichlorocyclopropane ring is 3,4,5,6, respectively, the larger alkyl fragment ($CH_3(CH_2)_mCH$:) is more easily lost. When the position of the dichlorocyclopropane ring is 7,8,9,10, respectively, the larger $CH(CH_2)_nCl$ fragment is more easily lost. The intensity of the two series of isotopic fragments of the derivatives of dodecen-1-ols in Table 1 is consistent with these empirical rules and the m/z of these fragments depend on the double-bond position.

Table 1 The two series of isotopic fragments of the derivatives of dodecen-1-ols

Compound	Group I	Group II
$\Delta^3 - C_{12} - OH$	158(54),160(60),162(22)	—
$\Delta^4 - C_{12} - OH$	172(61),174(59),176(18)	—
$\Delta^5 - C_{12} - OH$	186(40),188(41),190(13)	—
$\Delta^6 - C_{12} - OH$	200(12),202(13),204(4)	—
$\Delta^7 - C_{12} - OH$	—	152(12),154(7),156(1)
$\Delta^8 - C_{12} - OH$	—	138(32),140(21),142(4)
$\Delta^9 - C_{12} - OH$	—	124(41),126(25),128(5)
$\Delta^{10} - C_{12} - OH$	—	110(62),112(38),114(7)

—: There are no evident isotopic peaks.

According to the data in Table 1, a simple new formula is given to facilitate the rapid calculation of the position of original double bond in isomeric dodecen-1-ols:

For Group I: $\Delta n = (x - 116)/14$ (1)

For Group II: $\Delta n = (250 - y)/14$ (2)

Δn is the position of double bond and is only a positive integer, x represents m/z of the isotopes of lowest mass in Group I and y represents m/z of the iso-

topes of the lowest mass in Group II. 116 is the m/z of $Cl_2C = CHCl]^{+}$ minus 14, and 250 is the m/z of $Cl_2C = CH(CH_2)_8CH_3]^{+}$ plus 14.

For example, there are three ions (m/z 186, 188 and 190) of the chlorine isotopic cluster in mass spectrum of dichlorocarbene derivative of dodecenol. Δn can be calculated as follows:

$$\Delta n = (x - 116)/14 = (186 - 116)/14 = 5 \quad (3)$$

$$\Delta n = (250-y)/14 = (250 - 186)/14 = 4.6 \quad (4)$$

Because Δn should be a positive integer, the result of Eq. (4) is unreasonable, so Δn should be 5, which is consistent with the double-bond position of this compound.

The Δn values of other isomers of dodecenols are also calculated based on the formula (1) or (2), all Δn values are consistent with the original double-bond position in each isomer.

A major disadvantage of this method is that the fragment ions of Group I and Group II are too small to be recognized in Δ^2 and Δ^{11}-isomers , perhaps because the dichlorocarbene derivatization of Δ^2- and Δ^{11}-dodecen-1-ols was unsuccessful due to their inactivity.

In conclusion, the m/z of the characteristic chlorine isotopic clusters of mass spectra of dichlorocarbene derivatives made it rapid and convenient to locate the position of double bond in the initial $\Delta^3 \sim \Delta^{10}$-isomers of dodecen-1-ols. The reaction of dichlorocarbene derivatization is simple with high yields and there is no need to work under anhydrous conditions. It is very valuable if one is working with location of double-bond position in insect sex pheromone.

References

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