

REACTION CHROMATO-MASS SPECTROMETRY  
WHEN STUDYING CYCLOPROPANE COMPOUNDS

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The substantial interest displayed recently in cyclopropane compounds is due to the creation of new methods for their preparation, their application in synthetic studies, and their widespread occurrence in nature [1]. All of this necessitates the development of efficient and sensitive methods, which permit establishing the presence of the cyclopropane ring and its location in the molecule. Many difficulties are encountered when such a sensitive method as chromato-mass spectrometry is used to study cyclopropane compounds, since their mass spectra contain few criteria that characterize a three-membered ring, and frequently they are close to the spectra of the isomeric olefins [2].

We developed a very efficient and rapid method for the analysis of such compounds, which is based on the use of their transformations in a special pulse microreactor, which is located in the admission system of a chromato-mass spectrometer (LKV-2091 instrument). The principle of the method will be demonstrated on the example of the pure monosubstituted cyclopropanes: cyclo-C<sub>3</sub>H<sub>5</sub>-R (I)-(V), where R = n-C<sub>8</sub>H<sub>17</sub> (I); CH<sub>2</sub>CH<sub>2</sub>·CO<sub>2</sub>CH<sub>3</sub> (II); CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub> (III); CH<sub>2</sub>CH(CH<sub>3</sub>)CO<sub>2</sub>CH<sub>3</sub> (IV), and C<sub>6</sub>H<sub>5</sub> (V), whose synthesis was described in [3].

The mass spectra of these compounds contain noticeable M<sup>+</sup> peaks, and also a number of peaks that characterize the nature of the R substituent. The most intense peaks in the spectrum of (I) are those of the ions [M-C<sub>n</sub>H<sub>2n+1</sub>]<sup>+</sup> and [M-C<sub>n</sub>H<sub>2n</sub>]<sup>+</sup> (n ≥ 2), which are also typical for monoolefins. Very characteristic in the spectra of esters (II)-(IV) are the peaks of the ions [CHR<sup>1</sup>=C(OH)OR<sup>2</sup>] (m/z 74 when R<sup>1</sup>=H, R<sup>2</sup>=CH<sub>3</sub>; 88 when R<sup>1</sup>=H, R<sup>2</sup>=C<sub>2</sub>H<sub>5</sub>, and R<sup>1</sup>=R<sup>2</sup>=CH<sub>3</sub>) and [CH<sub>2</sub>CHR<sup>1</sup>CO<sub>2</sub>R<sup>2</sup>]<sup>+</sup> (m/z 87 when R<sup>1</sup>=H, R<sup>2</sup>=CH<sub>3</sub>; 101 when R<sup>1</sup>=H, R<sup>2</sup>=C<sub>2</sub>H<sub>5</sub>, and R<sup>1</sup>=R<sup>2</sup>=CH<sub>3</sub>), which are caused by the fragmentation of the R substituent. The mass spectrum of (V) is close to the spectra of indan and methylstyrene [4]. Peaks, caused by the presence of a three-membered ring, could not be observed for (I)-(V). Consequently, when studying the structure of such compounds it is convenient to use the method of reaction chromato-mass spectrometry developed by us.

For the chemical modification of compounds (I)-(V) we used the hydrogenolysis method, which proceeds easily in the gas phase and leads to a saturated aliphatic compounds. The hydrogenolysis of the cyclopropane compound (0.01-0.05 μliter) was run in a microreactor on a catalyst (20% Pt deposited on Chromaton W0.20 mm), which forms a column with a diameter of 2 mm and a height of 3-4 mm. In the chromatographic portion of the instrument we used a 3 × 3 mm column packed with 5% SE-30 deposited on Chromaton W. The chromatographing was run in either an H<sub>2</sub> or a D<sub>2</sub> stream, which serve both as a carrier gas and a reactant gas, at a flow rate of 20 ml/min. The microreactor contained a bypass system, which permitted recording the mass spectra of the starting compounds. It was installed either between the column of the chromatograph and the mass spectrometer or ahead of the column.

The use of the microreactor between the column and the mass spectrometer is especially effective when studying mixtures that contain cyclopropane compounds since each component, eluted after chromatographic separation, suffers chemical action. In this case, the chromatogram corresponds to the starting mixture, while the mass spectra correspond to the transformation products. When studying pure cyclopropane compounds it is most convenient to place the microreactor ahead of the chromatographic column, on which the hydrogenolysis products are then separated and can be subjected to the usual chromato-mass spectrometric analysis.

The hydrogenolysis of cyclopropanes (I)-(V) gives compounds of the (A) and (B) type, whose ratio depends predominantly on the nature of the R substituent [5].

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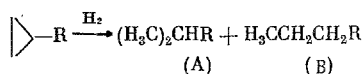
A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow; A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 5, pp. 1181-1184, May, 1983. Original article submitted October 1, 1982.

TABLE 1. Characteristic Peaks in Mass Spectra of Hydrogenolysis Products of Cyclopropanes (I)-(V) (m/z, in parentheses are given the intensities, in % of the maximum peak)

Compound	Structural formula	Ion		
		M <sup>+</sup>	[M-CH <sub>3</sub> ] <sup>+</sup>	other ions, common for isomers (A) and (B)
(IA)	(H <sub>3</sub> C) <sub>2</sub> CHC <sub>6</sub> H <sub>17</sub>	156(2)	141(6)	[M-C <sub>n</sub> H <sub>2n+1</sub> ] <sup>+</sup> (n ≥ 2)
(IB)	H <sub>3</sub> C(CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>17</sub>	156(7)	141(0)	
(IIA)	(H <sub>3</sub> C) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>3</sub>	130(0)	115(5)	[H <sub>2</sub> C=C(OH)OCH <sub>3</sub> ] <sup>+</sup>
(IIB)	H <sub>3</sub> C(CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub>	130(2)	115(1)	[CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub> ] <sup>+</sup>
(IIIA)	(H <sub>3</sub> C) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	144(1)	129(4)	[H <sub>2</sub> C=C(OH)OC <sub>2</sub> H <sub>5</sub> ] <sup>+</sup>
(IIIB)	H <sub>3</sub> C(CH <sub>2</sub> ) <sub>4</sub> COOC <sub>2</sub> H <sub>5</sub>	144(4)	129(2)	[CH <sub>2</sub> CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub> ] <sup>+</sup>
(IVA)	(H <sub>3</sub> C) <sub>2</sub> CHCH <sub>2</sub> CH(CH <sub>3</sub> )COOCH <sub>3</sub>	144(0)	129(3)	[CH(CH <sub>3</sub> )=C(OH)COOCH <sub>3</sub> ] <sup>+</sup>
(IVB)	H <sub>3</sub> C(CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>3</sub> )COOCH <sub>3</sub>	144(0)	129(2)	[CH <sub>2</sub> CH(CH <sub>3</sub> )COOCH <sub>3</sub> ] <sup>+</sup>
(VA)	(H <sub>3</sub> C) <sub>2</sub> CHC <sub>6</sub> H <sub>5</sub>	120(24)	105(100)	[C <sub>7</sub> H <sub>7</sub> ] <sup>+</sup> , [C <sub>6</sub> H <sub>5</sub> ] <sup>+</sup>
(VB)	H <sub>3</sub> C(CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	120(17)	105(3)	

TABLE 2. Ratio of Products (A) and (B), Formed during Hydrogenolysis of (I)-(V) on 20% Pt/Chromaton W at Various Temperatures

Starting compound	(A):(B) ratio		
	40°	100°	200°
(I)	92:8	93:7	92:8
(II)	93:7	94:6	94:6
(III)	94:6	94:6	93:7
(IV)	93:7	96:4	93:7
(V)	13:87	15:85	14:86



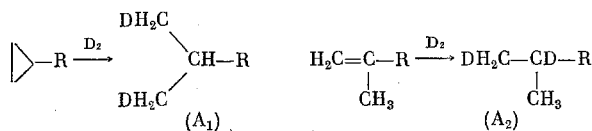
The mass spectra of these products have a set of diagnostic peaks, which permit establishing the nature of the R radical (Table 1). The isomeric products can reliably be assigned to either type (A) or (B) when their spectra are subjected to comparative analysis. This assignment is made on the basis that the stability of M<sup>+</sup> is much lower, while the probability of forming the [M-CH<sub>3</sub>]<sup>+</sup> ions via the ejection of a CH<sub>3</sub> radical from the site of branching is substantially higher for structures of the (A) type than for the (B) type. Actually, in the case of compounds (IA)-(IIIA) and (VA) the peaks of the [M-CH<sub>3</sub>]<sup>+</sup> ions are more intense than for compounds (IB)-(IIIB) and (VB). Compounds (IVA) and (IVB) are an exception, whose mass spectra show little difference in the intensities of the peaks of the [M-CH<sub>3</sub>]<sup>+</sup> ions. This is probably related to the fact that the molecule of the starting cyclopropane (IV) already has a CH<sub>3</sub> substituent, which for compounds (IVA) and (IVB) is responsible for forming a substantial portion of such ions.

The fact that both types of products (A) and (B) are formed in the hydrogenolysis of cyclopropanes (I)-(V), in which connection the (A) products predominate over the (B) products for (I)-(IV), while the reverse is true for (V), is in full agreement with the data given in [5]. In the temperature range 40-200°C the ratio of the products is actually constant (Table 2). It should be mentioned that the same ratio of compounds (A) and (B) was observed by us when using unsupported PtO<sub>2</sub> as the catalyst.

The formation of compounds of the (A) and (B) type during the hydrogenolysis of (I)-(V) is proof that a three-membered ring is present in the latter. These compounds can be distinguished in this way from the isomeric aliphatic olefins, which, as is known, are hydrogenated under the indicated catalytic conditions to a single product.

The above cited results were obtained by locating the microreactor ahead of the chromatograph column. Two problems arise when a system, containing the microreactor between the column and the mass spectrometer, is used. One of them is associated with the fact that the mass spectra, recorded under these conditions for (I)-(V), represent the sum of the spectra of products (A) and (B). However, the data given in Table 2 show that for these compounds one of the isomers is always formed in much greater amount than the other. Consequently, the recorded spectrum will actually correspond to the main product, which in this way is easily identified. But another problem arises here. For example, in the case of compounds (I)-(IV) the mass spectra, obtained under such conditions, are identical with the spectra of the pure (A) compounds, which at the same time can be formed from the H<sub>2</sub>C=C(CH<sub>3</sub>)R olefins. To differentiate the cyclopropane and olefin compounds

we proposed the use of deuterium as the carrier gas and the reactant gas. In this case the given types of compounds form dideutero derivatives with a different location of the label, which can be established via the mass spectrum



The hydrogenolysis of cyclopropanes in a  $D_2$  medium on catalysts of the platinum group includes the addition of  $D_2$  at the site of ring cleavage, associated with the exchange of H atoms by deuterium [6]. However, at 40–80° the deutero exchange is strongly suppressed and dideutero products ( $A_1$ ) are formed predominantly. In the mass spectra of such products, obtained from compounds (I)–(III) under the conditions of reaction chromatography-mass spectrometry, are observed only the peaks of the  $[M-\text{CH}_2\text{D}]^+$  ions and, as was to be expected, the peaks of the  $[M-\text{CH}_3]^+$  ions are completely absent. At the same time, the spectrum of the deuteration product ( $A_2$ ) of 2-methyl-1-pentene contains a doublet of the peaks of the  $[M-\text{CH}_3]^+$  and  $[M-\text{CH}_2\text{D}]^+$  ions of equal intensity.

As a result, the use of deuterium under the conditions of reaction chromatography-mass spectrometry permits reliably differentiating alkyl-substituted cyclopropanes and olefins.

### CONCLUSIONS

The use of hydrogenolysis microreactor in the admission system of chromatography-mass spectrometer in either an  $H_2$  or  $D_2$  stream permits establishing the structure of substituted cyclopropane compounds via the mass spectra of the transformation products.

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