Electron Ionization Mass Spectra of 3-Dimethylaminomethylcyclohexanol Derivatives

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The mass spectra of 3-dimethylaminomethylcyclohexanol derivatives (1-5) were measured under a direct inlet system by electron impact ionization, and their characteristic fragmentations are discussed. The characteristic ions in the mass spectra of 1-5 are the fragment ions at m/z 58, m/z 71, m/z 72, m/z 111 and m/z 156. The characteristic peak at m/z 58 is the base peak in the mass spectra of all compounds. The structure of this ion appears to be CH$_2$$^+$=N$^+$+(CH$_3$)$_2$. The cis-and trans-configurations of 1-5 can be identified by observing the peak intensities at m/z 71, m/z 72 and m/z 156 in the mass spectra and by observing the peak corresponding to loss of a hydrogen molecule from the m/z 84 ion in the ion kinetic energy (IKE) spectra.

1. Introduction

In connection with synthetic studies of aminoalcohols, the mass spectra of the 3-dimethylaminomethylcyclohexanol derivatives (1-5) in Fig. 1 have been examined.

Some papers have discussed the mass spectra of aminoalcohols. But the mass spectra of 3-dimethylaminomethylcyclohexanol derivatives have not been reported yet. Mass spectra of 1-5 show the characteristic ions. In addition, these compounds have cis-and trans-isomers. In an attempt to determine their configurations we examined their mass spectra and IKE spectra, and obtained important structural information.

2. Experimental

The mass spectra were recorded with a Hitachi RMU-7MG double focusing mass spectrometer, which was additionally equipped with an IKEES apparatus. The samples were introduced via the direct inlet system. The ionizing energy normally used was 70eV and partially was 20eV. The ion accelerating voltage was 3kV. Total electron emission current was 80 $\mu$A.

3-Dimethylaminomethylcyclohexanols were synthesized according to the procedure described in previous papers, and purified by fractionation under reduced pressure and by alumina column chromatography.

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**Cis-trans nomenclature refers to relative orientation of the R and the dimethylaminomethyl group.
The relative intensities of molecular ions were generally weak. This fact can be explained in terms of the easy formation of the ion at \( m/z 58 \). This ion is the base peak and the characteristic peak in the mass spectra of the all compounds possessing a dimethylaminomethyl group has a positive charge. Then, 3-isobutyl-1-phenylcyclohexanol which has an isobutyl group instead of a dimethylaminomethyl group was synthesized and its mass spectrum was measured (Fig.5). The mass spectrum of 3-isobutyl-1-phenylcyclohexanol gave a large number of fragment ions. But the peak corresponding to the ion at \( m/z 58 \) was not detected. The mass spectrum of this compound showed the peak corresponding to the presence of the fragmentations due to the hydroxyl group.

The molecular ion decomposes into the \( m/z 156 \) ion, \([C_{6}H_{16}NO]^+\), with elimination.

### Table I

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<th>Compound</th>
<th>N⁺</th>
<th>( m/z ) 156</th>
<th>( m/z ) 111</th>
<th>( m/z ) 84</th>
<th>( m/z ) 72</th>
<th>( m/z ) 71</th>
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<td></td>
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<td>( C_9H_{18}NO )</td>
<td>( C_7H_{11}NO )</td>
<td>( C_5H_{10}NO )</td>
<td>( C_4H_{10}N )</td>
<td>( C_4H_{9}N )</td>
<td>( C_3H_{8}N )</td>
<td>( C_3H_{2}O )</td>
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<td>-</td>
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The data in the table are the relative intensities.

Cis-trans nomenclature refers to the relative orientation of the R and the dimethylaminomethyl groups.
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Fig. 2  Mass spectrum of 4 at 20 eV.

Fig. 3  Mass spectrum of 5 at 20 eV.

Fig. 4  Fragmentation pathways of compounds 1-5.

Table II  Empirical Formula of the Principal Ions of 2 and 3.

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3-trans 213.2102 1.1 13 27 1 1
156.1386 -0.1 9 18 1 1
111.0844 3.5 7 11 0 1
84.0842 2.9 5 10 1 0
82.0689 3.3 5 8 1 0
72.0821 0.8 4 10 1 0
71.0754 2.0 4 9 1 0
58.0667 1.1 3 8 1 0
55.0187 0.4 3 3 0 1
44.0502 0.2 2 6 1 0

Fig. 5  Mass spectra of compound 5 and 3-isobutyl-1,1-phenylcyclohexanol.
of the alkyl radical. This intermediate ion at \( m/z \) 156 decomposes into the \( m/z \) 111 ion, \((C_3H_{11}O)^+\), which loss of a dimethylamine molecule. But these peaks at \( m/z \) 156 and \( m/z \) 111 cannot be observed in the mass spectrum for compound 5. Since compound 5 has the phenyl substituent, this is unable to give the fragment ions produced by \( \alpha \)-cleavage of the phenyl group. In addition, the intensity of the ion at \( m/z \) 156 in the mass spectra of the trans-isomers of 1-4 is more abundant than that of the corresponding cis-isomers. The differences of these peak intensities, due to orientation of the hydroxyl group, seem to be based on the stability of the molecule. Formation of the ion at \( m/z \) 156 may be explained by the fragmentation corresponding to the presence of the hydroxyl group of compounds 1-4. This fact shows that the oxygen atom in the hydroxyl group as well as the nitrogen atom in the dimethylaminomethyl group has a positive charge.

The ion at \( m/z \) 72, \((C_4H_{10}N)^+\), due to loss of \((R+C_3H_{11}O)^+\) from the molecular ion, was observed in the spectra of the cis-isomers of 1-5, but not in the case of the corresponding trans-isomers. On the other hand the ion at \( m/z \) 71, \((C_4H_{11}N)^+\), due to loss of \((R-C_3H_{11}N)\) from the molecular ion, was observed in the spectra of the trans-isomers of 1-4, but not in the case of the corresponding cis-isomers.

On the basis of these results presented above, the cis-trans configurations of the isomers can be identified with the peak intensities at \( m/z \) 71, \( m/z \) 72 and \( m/z \) 156. But these peak intensities are weak. Then, the configurations of these compounds were determined, using IKE spectra. The IKE spectra of isomers of compounds 3 and 5 are shown in Fig.6 and Fig.7.

The spectra of the isomers are similar to each other, but there is a minor distinction between them. In Fig.6 and Fig.7, the peak at 0.9760 E corresponding to the reaction \( m/z \) 84 \( \rightarrow \) \( m/z \) 82 by loss of a hydrogen molecule was observed. The peak corresponding to this reaction was only observed in the IKE

![Fig.6 IKE spectra of compound 3.](image_url)

![Fig.7 IKE spectra of compound 5.](image_url)

![Fig.8 Mass spectrum of trans-isomer of 3.](image_url)
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spectra of the trans-isomers of 3 and 5. The reaction in suppoed by the presence of the ion at \( m/z \) 84 and \( m/z \) 82 in the mass spectra (Fig.8) and by the presence of the metastable peak for this process. From these results, IKES spectra are a useful method for distinguishing the isomers.

4. Conclusion

Electron ionization mass spectra of 1-5 were determined. The cis-and trans-configurations are distinguishable by comparison of the peak intensities at \( m/z \) 71, \( m/z \) 72 and \( m/z \) 156 in the mass spectra. Furthermore, the correlation between the mass spectra and the stereochemistry also seem to be applicable to the elucidation of stereochemical problems of other derivatives or related compounds. These compounds show the common ion at \( m/z \) 58 which is formed from the dimethylaminomethyl group of 1-5. The compounds form the fragment ion corresponding to the loss of substituent in the fragmentations due to the presence of the hydroxyl group of 1-4. IKES were similar to each other. But the isomers can be distinguished from their counterparts by the difference in the peak intensities.

References

Keywords
Electron ionization mass spectra
Amino alcohols
3-Dimethylaminomethylcyclohexanol derivatives
Cis-trans isomers