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# THREE-DIMENSIONAL STRUCTURES AND CHEMICAL-IONIZATION MASS SPECTRA OF ISOMERIC OXIMES OF 2-SUBSTITUTED 3-QUINUCLIDONES

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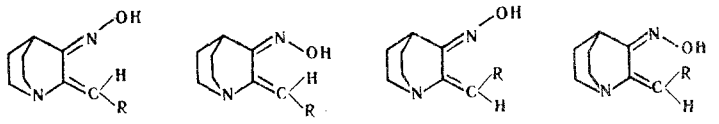
The chemical-ionization (CI; isobutane and ammonia as the reactant gases) mass spectra of 2-arylmethylene-3-quinuclidone oximes, which can exist in syn-cis, anti-cis, and syn-trans isomeric forms, were studied. A significant difference in the CI spectra of the cis and trans isomers, which makes it possible to unambiguously determine the configuration of the substituent in the 2 position, was established. It was found that the CI spectra of the syn and anti isomers differ substantially with respect to the ratios of the intensities of the $MH^+$ and $[MH - CH_4]^+$ ion peaks ($I_{MH^+}/I_{[MH - CH_4]^+}$), and this makes it possible to identify the syn and anti isomers by comparison of their individual CI spectra. The spatial configurations of 2-furyl- and 2-thienylmethylene-3-quinuclidones were established on the basis of the principles found.

The three-dimensional structures of 2-arylmethylene-3-quinuclidone oximes, for which existence in four isomeric forms is possible owing to cis-trans and syn-anti isomerism, were established in [1] by NMR spectroscopy and electron-impact (EI) mass spectrometry:



syn-cis anti-cis syn-trans anti-trans

However, the formation of an anti-trans isomer was not observed in a single case, evidently because of pronounced steric hindrance, and three geometrical isomers, viz., syn-cis, anti-cis, and syn-trans, are primarily realized.

Chromatographic mass-spectrometric analysis makes it possible to reliably distinguish the cis and trans isomers from the relative retention times and the characteristic differences observed in the EI mass spectra. However, a necessary condition for the successful performance of this sort of analysis is a comparative study of a pair of geometrical isomers in each case. In the analysis of only one isomer neither data on the retention times nor the EI mass spectra make it possible to obtain unambiguous information regarding its stereo-

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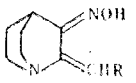
0009-3122/83/1910-1099$07.50  

TABLE 1



I–VIII

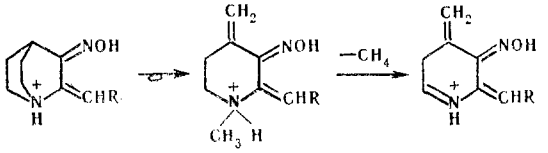
| R | Isomers |
|---|---|
| $C_6H_5$ | Three individually isolated isomers: syn-cis (I), anti-cis (II), and syn-trans (III) |
| p-$C_6H_4NO_2$ | Two individually isolated isomers: syn-cis (IV) and syn-trans (V) |
| 2-Furyl | Mixture* of two isomers (VI and VII) |
| 2-Thienyl | One individual isomer (VIII) |

*According to PMR spectroscopic data [2].

chemistry. One also cannot identify the syn and anti isomers by means of chromatographic mass spectrometry because of their identical chromatographic mobilities and the identical character of their EI mass spectra.

We found that it was possible to solve all of these problems by means of chemical-ionization (CI; the reactant gases were ammonia and isobutane) mass spectrometry. The CI mass spectra were obtained for the 2-aryl(hetaryl)methylene-substituted 3-quinuclidone oximes indicated in Table 1. Compounds I-V, the structures of which were previously established [1], were used as model compounds for the determination of the characteristic features of each of the isomers.

A comparison of the CI mass spectra obtained with different reactant gases (Table 2) showed that replacement of one reactant gas by another does not lead to substantial changes in the spectra and is manifested only in the appearance of low-intensity ($I_{rel}$ < 2%) peaks of [M + 57] and [M + 43] cluster ions in the case of isobutane, as well as in a certain degree of redistribution of the relative intensities of the individual peaks. The spectra are determined by fragmentation of the protonated molecular ion ($MH^+$). The presence of an intense peak of an $[MH - CH_4]^+$ ion, the formation of which can be explained by primary protonation of the nodal nitrogen atom, which facilitates the subsequent fragmentation of the bonds in the quinuclidine ring, is characteristic for all of the compounds:



This sort of peak is not observed in the CI mass spectra of aromatic and aliphatic amines [3].

The introduction of a nitro group in the para position of the aryl substituent leads to the appearance in the spectra of IV and V of peaks due to detachment of a nitro group from the protonated molecular ion; in the case of ionization with ammonia as the reactant gas the $[MH - NO_2]^+$ ion peaks are the maximum peaks in the spectra. It is interesting to note that in the EI mass spectra the fragmentation of the IV and V molecules, which involves the elimination of a nitro group, is suppressed substantially.

A comparative analysis of the spectra of I-III, IV, and V showed (Table 2) that there is a great difference in the fragmentation of the geometrical isomers. An intense peak of an $[MH - H_2O]^+$ ion, which is of low intensity in the spectra of cis isomers I, II, and IV, is observed in the spectra of trans isomers III and V. One of the possible mechanisms of this work of elimination, which involves the formation of an ion with a (2,3-quinolino)-quinuclidine structure in the case of a trans orientation of the aryl substituent, was previously described in an examination of the EI mass spectra of these compounds [1]. Another possible mechanism, which involves the successive elimination of a hydrogen atom from the quinuclidine ring and a hydroxyl radical from the oxime group in the case of protonation of the nodal nitrogen atom, is less likely, since in this case it is difficult to explain why the indicated pathway is markedly suppressed for the cis isomers. However, it

TABLE 2. Relative Intensities of the Peaks of the Characteristic Ions in the CI Mass Spectra of I-VIII

| Reactant gas | Fragments | Compound | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | I | II | III | IV | V | VI+VII | VIII |
| $i$-$C_4H_{10}$ | $MH^+$ | 7 | 22 | 24 | 34 | 72 | | 100 |
| | $[MH-CH_4]^+$ | 100 | 100 | 62 | 29 | 100 | | 40 |
| | $[MH-OH]^+$ | 9 | 20 | 12 | 15 | 18 | | 6 |
| | $[MH-H_2O]^+$ | 17 | 15 | 100 | 14 | 81 | | 66 |
| | $[MH-NO_2]^+$ | — | — | — | 24 | 24 | | — |
| $NH_3$ | $MH^+$ | 19 | 84 | 34 | 6 | 14 | 25 | 31 |
| | $[MH-CH_4]^+$ | 100 | 100 | 74 | 8 | 50 | 100 | 100 |
| | $[MH-OH]^+$ | 3 | 3 | 6 | — | 1 | 1 | 12 |
| | $[MH-H_2O]^+$ | 6 | 6 | 100 | 1 | 34 | 5 | 63 |
| | $[MH-NO_2]^+$ | — | — | — | 100 | 100 | — | — |

should be noted that in this case one cannot exclude the probability of detachment of $H_2O$ as a consequence of competitive protonation of the oxygen atom of the oxime group in the case of the trans isomers. Unfortunately, we did not obtain an unambiguous solution to the problem of the mechanism of the process because of the absence of deuterium-labeled reactant gas.

The elucidated characteristic peculiarities of the fragmentation of the cis and trans isomers under chemical-ionization conditions make it possible to draw unambiguous conclusions regarding the structures of VI-VIII. The presence of an intense $[MH - H_2O]^+$ ion peak in the spectrum of isomer VIII indicates a trans orientation of the thienyl group. The furyl residue in VI and VII is evidently cis-oriented (as indicated by the low intensity of the $[MH - H_2O]^+$ ion peak, which corresponds to fragmentation of the trans isomer), and the sample that, which, according to the NMR data, is a mixture of isomers, is evidently a mixture of syn-cis and anti-cis isomers.

As regards the difference in the spectra of the syn and anti isomers, in an examination of I and II, which were isolated individually, one sees a substantial difference in the ratios of the intensities of the peaks of the $MH^+$ and $[MH - CH_4]^+$ ions ($I_{MH^+}/I_{[MH - CH_4]^+}$); this ratio is greater by a factor of approximately three in the spectrum of the anti isomer. Thus the observed effect makes it possible to distinguish the syn and anti isomers of oximes from the CI spectra when one compares their individual spectra.

The observed increase in the relative intensity of the protonated molecular ion in the case of the anti isomer can probably be explained by partial protonation of the exocyclic nitrogen atom. The decrease in the percentage of molecules that are protonated at the nodal nitrogen atom should, of course, be reflected in a decrease in the probability of elimination of a molecule of methane from the $MH^+$ ion.

Thus the use of chemical-ionization mass spectrometry makes it possible to obtain reliable criteria for the determination of the three-dimensional structures of isomeric 2-aryl(hetaryl)methylene-3-quinuclidone oximes even in the absence of isolated (in the individual state) pairs of geometrical isomers of each compound.

## EXPERIMENTAL

The chemical-ionization mass spectra were obtained with a Varian MAT-212 mass spectrometer with direct introduction of the samples into the ion source; the ionizing voltage was 200 eV, and the reactant gases were isobutane and ammonia.

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