# MASS-SPECTRAL INVESTIGATION OF SOME ALKYL- AND DIALKYLAMINO-SUBSTITUTED OXAZOLINO- AND THIAZOLINO-sym-TRIAZINES

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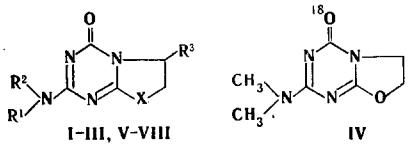
The mass spectra of eight alkyl- and dialkylamino-substituted oxazolino- and thiazolino-sym-triazines were investigated. It is shown that prior to fragmentation with opening of the oxazoline ring, the excited molecular ions of oxazolino-sym-triazines undergo rearrangement to N-vinyl-substituted sym-triazinols. The dissociative ionization of thiazolino-sym-triazines is primarily due to cleavage of the bonds in the thiazoline ring.

We have previously [1] studied the mass spectra of O- and N-(β-chloroethyl)-substituted sym-triazines. In a continuation of our investigation of biologically active derivatives of sym-triazines in the present research we studied the mass spectra of alkyl- and dialkylamino-substituted oxazolino- and thiazolino-sym-triazines (I-VIII), which were obtained by thermolysis of O- and N-(β-chloroethyl)-substituted sym-triazines [2-4].

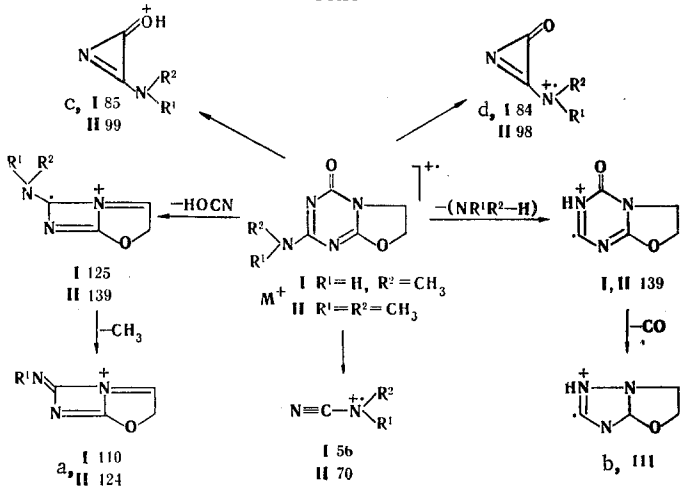


I-III, V-VIII IV

I $R^1=R^3=H$, $R^2=CH_3$, X=O; II $R^1=R^2=CH_3$, $R^3=H$, X=O; III $R^1=R^2=C_2H_5$, $R^3=H$, X=O, V $R^1=R^2=CH_3$, $R^3=H$, X=S; VI $R^1=R^2=C_2H_5$, $R^3=CN$, X=S; VII $R^1=R^2=CH_3$, $R^3=CN$, X=S; VIII $R^1=R^2=C_2H_5$, $R^3=CN$, X=S

One might have expected that the principal processes in the mass-spectrometric fragmentation of oxazolino-sym-triazines I-IV would be due to cleavage of the tetrahydrooxazole ring, which is sensitive to electron impact. However, in a joint examination of the mass spectra of

Scheme 1

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I-IV and data from the high-resolution mass spectrum of II we did not detect ions due to the elimination of particles that contain the elements of only the oxaxoline ring in any of the stages of the fragmentation.

As shown in Scheme 1, the primary pathways of the fragmentation of I and II are due to cleavage of the bonds in the side substituent and in the triazine ring. The compositions of ions a-d were established on the basis of data from the high-resolution spectrum of II, and the sequence of the fragmentation reactions was confirmed by the corresponding metastable transitions.

The dissociative ionization of diethylamine derivative III in the primary stages of fragmentation is primarily associated with fragmentation of the diethylamino group. The peaks of the ions with masses 195, 182, 181, and 167 (see Table 1), which correspond to the elimination of $CH_3$, $C_2H_4$, and $C_2H_5$ and, successively, $C_2H_4$ and $CH_3$ particles from the diethylamino substituent, are the most intense peaks in the spectrum of III. Cleavage of the triazine ring with the formation of ions of the a, b, and c type from the $[M - C_2H_4]^+$ ion with m/z 182* is suppressed, and the corresponding peaks with masses 139, 154, and 99 therefore have very low intensities (no more than 10% of the maximum peak).

Thus the dissociative ionization of oxazolino-sym-triazines I-III is due to destruction of the bonds in the side substituent and in the triazine ring. Elimination of particles that contain the elements of only the oxazoline ring is not observed.

This unusual behavior of I-III under electron impact can be understood if it is assumed that excited molecular ions ($[M^+]$) undergo rearrangement with opening of the oxazoline ring. To confirm our assumptions we investigated the mass spectrum of IV with an $^{18}O$ label in the carbonyl group of the triazine ring. Calculation of the $^{18}O/^{16}O$ isotope ratio in the fragment ions that contain one oxygen atom shows that prior to fragmentation, the oxazoline ring actually opens up to give molecular ions with the structures of N-vinyl-substituted sym-triazines ($M_1^+$ and $M_2^+$) (Scheme 2).

According to the data from the high-resolution mass spectrum of II, only ions with masses 124 (ion a), 111 (ion b), 99 (ion c), and 98 (ion d) contain one oxygen atom (Schemes 1 and 2). If it is assumed that these ions are formed from unopened form $M^+$, ions a and b should not contain an oxygen label, since they are formed in the elimination of HOCN and CO molecules that contain an $^{18}O$ label. Ions c and d, on the other hand, should retain the oxygen label completely. In fact, all of the ions indicated above contain an oxygen label, and, more importantly, the isotope ratio in these ions differs appreciably from the isotope ratio in $M^+$. The isotope ratio in $M^+$ is 1.27, as compared with 0.78, 0.43, 0.33, and 0.39, respectively, in ions a-d. This appreciable change in the initial isotope ratio in the ions indicated above constitutes evidence that they are actually formed from both forms $M_1^+$ and $M_2^+$ in the elimination of particles that contain or do not contain an $^{18}O$ label (Scheme 2).

An alternative mechanism for the formation of the ions indicated above with such values of the isotope ratio from unopened form $M^+$ is an extremely unlikely process, since the cleavage of two bonds in the oxazoline ring with the ejection of at least $CH_2O$ or $C_2H_4$ particles is much more favorable than the elimination of NCOH and CO molecules (the formation of a and b ions), which require cleavage of no less than four bonds in both the oxazoline and triazine rings (Scheme 1). Processes involving the elimination of particles that contain or do not contain an oxygen label (Scheme 2) become equally likely only after opening of the oxazoline ring, and this is the reason for the change in the initial isotope ratio in ions a and b, as well as in ions c and d.

Indirect evidence for opening of the oxazoline ring prior to fragmentation of $M^+$ is provided by the principles of the fragmentation of thiazolino-sym-triazines V-VIII, the dissociative ionization of which differs radically from the fragmentation of oxazolino-sym-triazines, despite the fact that they have similar structures. Whereas in the case of oxazolino-sym-triazines ions formed as a result of cleavage of the oxazoline ring were not detected in any of the fragmentation steps, in the case of V-VIII the principal fragmentation pathways are due to cleavage of the bonds in the thiazoline ring (Scheme 3).

The elementary composition of the ions presented in Scheme 3 was determined in the case of V by precise measurement of their masses. It is apparent from Scheme 3 that $M^+$ in the case

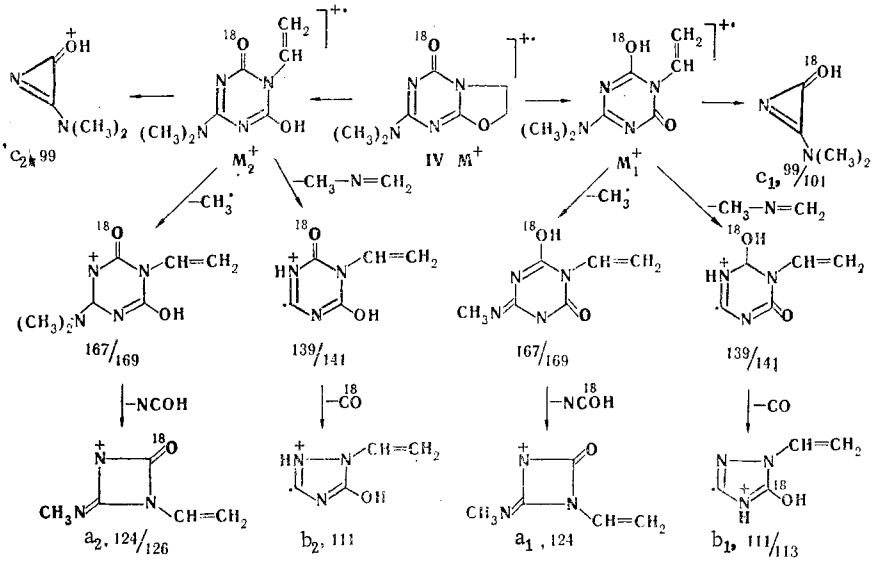
*Here and subsequently in the text and in the schemes, the numbers that characterize the ions are the mass-to-charge ratios (m/z).

TABLE 1. Mass Spectra of I-VIII

| Compound | m/z values (relative intensities of the ion peaks, %)* |
|---|---|
| I | 169 (15), 168 (100), 167 (14), 140 (12), 139 (42), 128 (10), 126 (36), 125 (10), 124 (7), 123 (6), 113 (5), 112 (30), 111 (48), 110 (16), 109 (10), 99 (44), 98 (7), 97 (30), 96 (10), 95 (26), 85 (22), 84 (52), 83 (64), 82 (18), 81 (34), 71 (48), 70 (20), 69 (42), 56 (30) |
| II | 183 (16), 182 (100), 181 (20), 168 (10), 167 (40), 154 (6), 153 (32), 140 (10), 139 (7), 124 (10), 123 (3), 112 (10), 111 (30), 99 (30), 98 (20), 85 (5), 83 (25), 81 (8), 71 (15), 70 (45), 69 (24) |
| III | 211 (18), 210 (83), 196 (7), 195 (50), 182 (35), 181 (100), 168 (12), 167 (70), 155 (3), 154 (8), 153 (6), 141 (10), 140 (7), 139 (9), 124 (12), 113 (22), 112 (27), 99 (9), 98 (8), 97 (8), 95 (15), 85 (10), 83 (9), 71 (20), 70 (26), 69 (22) |
| IV | 185 (10), 184 (100), 183 (20), 182 (85), 170 (4), 169 (50), 167 (42), 155 (35), 153 (32), 142 (24), 141 (13), 140 (26), 139 (10), 126 (18), 125 (4), 124 (20), 113 (20), 112 (17), 111 (49), 101 (13), 100 (14), 99 (40), 98 (22), 85 (22), 84 (6), 83 (44), 81 (15), 72 (17), 71 (16), 70 (54), 69 (32) |
| V | 200 (4), 199 (9), 198 (100), 197 (8), 183 (35), 170 (12), 169 (27), 165 (4), 156 (4), 155 (6), 154 (4), 152 (8), 151 (4), 140 (8), 139 (62), 127 (7), 124 (7), 115 (13), 98 (22), 83 (23), 71 (12), 70 (34), 69 (24) |
| VI | 228 (4), 227 (18), 226 (82), 225 (10), 211 (28), 199 (8), 198 (26), 197 (100), 196 (14), 183 (37), 169 (4), 170 (4), 167 (7), 129 (21), 128 (20), 98 (6), 97 (23), 95 (10), 71 (7), 70 (12), 69 (9) |
| VII | 225 (8), 224 (17), 223 (100), 222 (7), 208 (14), 197 (3), 194 (9), 190 (6), 177 (16), 170 (14), 169 (6), 165 (54), 156 (6), 140 (6), 139 (11), 124 (5), 112 (10), 98 (19), 95 (6), 84 (4), 83 (15), 82 (5), 70 (26), 69 (18) |
| VIII | 253 (3), 252 (8), 251 (63), 236 (26), 225 (6), 224 (7), 223 (14), 222 (100), 208 (22), 198 (28), 195 (4), 194 (6), 193 (11), 183 (4), 179 (10); 170 (16), 165 (4), 156 (3), 155 (4), 154 (14), 153 (10), 152 (8), 140 (7), 139 (4), 128 (4), 127 (6), 126 (7), 125 (4), 113 (5), 112 (12), 111 (7), 99 (4), 98 (15), 97 (26), 96 (6), 95 (28), 94 (13), 86 (6), 85 (10), 84 (11), 83 (17), 82 (5), 81 (5), 72 (11), 71 (16), 70 (6), 69 (47) |

*The peaks of ions with intensities ≥3% are presented.

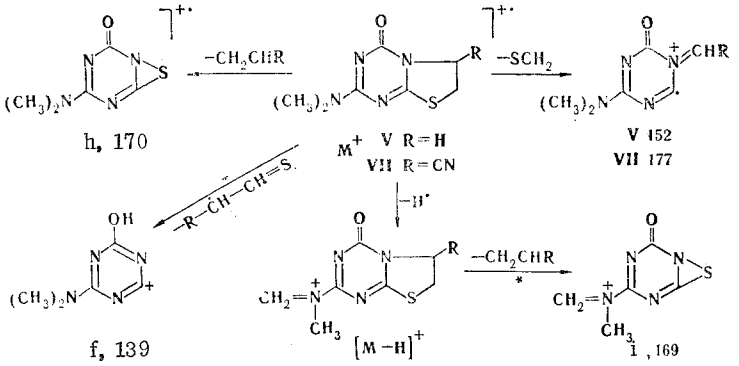
Scheme 2



of V in the primary stages of fragmentation eliminates $C_2H_3R$ and $SCH_2$ fragments to give ions h and g with masses 170 and 152, respectively. The most intense peak in the spectrum of V is the peak of the ion with m/z 139, which, as demonstrated by the corresponding metastable peak, is formed from $M^+$ by elimination of an R–CH–CH=S radical. Fragmentation of the thiazoline ring is also observed in the second step of dissociative ionization (the formation of ions with m/z 156 and 169). The introduction of a cyano group in the thiazoline ring does not substantially change the overall pattern of the fragmentation but does have an appreciable effect on the relative intensities of the fragment ions (see Table 1).

As in the case of diethylamino-substituted oxazolino-sym-triazine III, the dissociative ionization of VI and VIII is due to fragmentation of the diethylamino group to give $[M - CH_3]^+$,

Scheme 3




$[M - C_2H_4]^+$, $[M - C_2H_5]^+$, and $[M - C_2H_4, -CH_3]^+$ ions, the peaks of which have the highest intensities in the spectra. The fragmentation of both the thiazoline and triazine rings is suppressed substantially.

Thus, as a result of our investigation of the mass spectra of I-VIII, we have established that, prior to fragmentation, excited molecular ions of oxazolino-sym-triazines I-IV undergo rearrangement with opening of the oxazoline ring to give N-vinyl-substituted sym-triazinols. The dissociative ionization of thiazolino-sym-triazines in the primary and secondary stages of the fragmentation is primarily due to cleavage of the bonds in the thiazoline ring.

The fragmentation principles found in this research can be used in the establishment of the structures of related compounds by mass spectrometry.

## EXPERIMENTAL

The mass spectra were obtained with an MKh-1303 spectrometer with direct introduction of the samples into the ionization region at an ionizing voltage of 50 eV and at temperatures 20-30°C lower than the melting points of the samples. The elementary compositions of the principal ions in the mass spectra of II and V were determined with a Jeol IMS-01-SG-2 high-resolution spectrometer (Japan).

## LITERATURE CITED


1. R. G. Mirzoyan, S. M. Saakyan, A. V. Dovlatyan, and V. V. Dovlatyan, Arm. Khim. Zh., 32, 874 (1979).
2. V. V. Dovlatyan, K. A. Éliazyan, and A. V. Dovlatyan, Khim. Geterotsikl. Soedin., No. 7, 989 (1977).
3. V. V. Dovlatyan, A. V. Dovlatyan, K. A. Éliazyan, and R. G. Mirzoyan, Khim. Geterotsikl. Soedin., No. 10, 1420 (1977).
4. V. V. Dovlatyan and A. V. Dovlatyan, Khim. Geterotsikl. Soedin., No. 1, 124 (1979).