MASS-SPECTROMETRIC BEHAVIOR OF SOME CYANO-SUBSTITUTED 4-(β-CHLOROETHYLMERCAPTO)-sym-TRIAZINES

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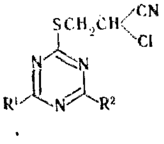
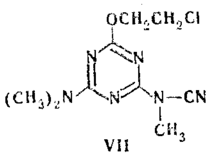
Intense $[M-Cl]^+$ and $[M-CH_2=CCNCl]^+$ ion peaks are characteristic for the mass spectra of 4-(β-chloro-β-cyanoethylmercapto)-sym-triazines. The introduction of monoalkylamino groups into the 2 and 6 positions of the heteroring does not lead to the development of $[M-HCl]^+$ ion peaks in the mass spectra or to a change in the characteristic fragmentation pathways.

We have previously shown that 2-dialkylamino-4-(β-chloroethylmercapto)-sym-triazines that contain dialkylamino or methylmercapto groups in the 6 position readily lose a chlorine atom or a molecule of vinyl chloride under electron impact [1-3], whereas the principal dissociative ionization process involves the elimination of a molecule of hydrogen chloride by the molecular ion when methoxyamino or cyanamino groups, which contain a labile hydrogen atom, are present in the 6 position [4, 5].

In order to ascertain the effect of a cyano group on the change in the fragmentation pathway we studied the mass-spectrometric fragmentation of sym-triazines I-VI, which contain a β-chloro-β-cyanoethylmercapto group in the 4 position. For comparison, we also used VII with a cyanomethylamino group in the 6 position.



I-VI



VII

I $R^1=R^2=N(CH_3)_2$; II $R^1=R^2=NHC_2H_5$; III $R^1=N(CH_3)_2$, $R^2=OCH_3$; IV $R^1=NHC_2H_5$, $R^2=OCH_3$; V $R^1=N(CH_3)_2$, $R^2=SCH_3$; VI $R^1=N(C_2H_5)_2$, $R^2=OCH_3$

The mass spectra of I-VII and the W_M values are presented in Table 1. It is apparent from the data in Table 1 that the stabilities of the molecular ions (the W_M values) of 2,6-diamino derivatives I, II, and VI are higher than the values for the remaining compounds. It also follows from the mass spectra presented in Table 1 that the above-mentioned characteristic type of fragmentation with elimination of a Cl radical (the F_1 ion in the scheme presented below) or a molecule of α-chloroacrylonitrile (the F_2 ion) is retained for the molecular ions of I-VI, regardless of the substituents in the 2 and 6 positions.

Similar processes also characterize the primary pathway of the dissociative ionization of VII. The F_2 ion peak is the maximum peak in the mass spectra of all of the compounds, including those that contain hydrogen-containing residues in the 2 or 6 position (II and IV). Peaks of $[M-HCl]^+$ ions, the formation of which is observed when the hydrogen atom of the substituent in the 6 position has acidic properties (greater lability), are completely absent in the mass spectra of these compounds, and this confirms the assumption expressed in [4].

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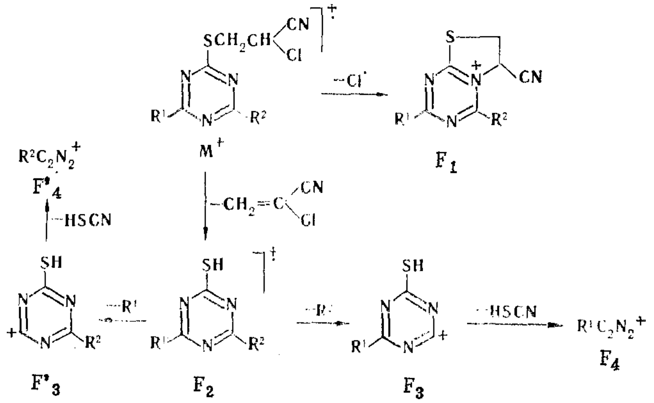
TABLE 1. Mass Spectra of I-VII

Compound	m/z values (relative intensities of the ion peaks in %) *
I	288 (22), 287 (12), 286 (70), 273 (7), 271 (18), 259 (3), 257 (10), 251 (85), 200 (10), 199 (100), 170 (20), 166 (20), 155 (74), 154 (16), 128 (12), 123 (6), 97 (8), 96 (86), 85 (6), 71 (28), 70 (16), 69 (12); $W_M = 14{,}8$
II	288 (20), 287 (11), 286 (60), 273 (6), 271 (19), 252 (18), 251 (77), 200 (8), 199 (100), 198 (32), 197 (13), 171 (40), 169 (38), 166 (15), 156 (12), 155 (52), 138 (6), 128 (17), 113 (22), 96 (44), 85 (30), 71 (38), 70 (16), 69 (36); $W_M = 12{,}0$
III	275 (6), 273 (16), 240 (6), 239 (12), 238 (70), 188 (6), 187 (10), 186 (100), 171 (18), 157 (13), 155 (7), 142 (22), 128 (8), 97 (8), 96 (34), 85 (14), 83 (25), 71 (12), 70 (8), 69 (26); $W_M = 4{,}2$
IV	275 (5), 273 (14), 260 (5), 258 (9), 240 (6), 239 (12), 238 (72), 188 (6), 187 (12), 186 (100), 185 (8), 171 (14), 158 (20), 155 (7), 142 (14), 128 (8), 123 (8), 113 (24), 96 (8), 85 (8), 71 (6), 69 (24); $W_M = 4{,}9$
V	291 (6), 289 (18), 276 (7), 274 (20), 254 (24), 216 (22), 206 (20), 204 (58), 203 (16), 202 (100), 158 (24), 155 (60), 123 (20), 110 (18), 99 (26), 98 (24), 97 (30), 96 (8), 85 (24), 83 (22), 71 (50), 70 (25), 69 (65); $W_M = 2{,}9$
VI	303 (22), 302 (18), 301 (86), 288 (36), 287 (22), 286 (85), 274 (38), 273 (24), 272 (100), 266 (40), 260 (10), 258 (25), 214 (50), 213 (65), 199 (20), 198 (14), 185 (60), 183 (14), 171 (24), 142 (44), 124 (24), 117 (30), 97 (14), 96 (12), 87 (30), 86 (20), 85 (18), 83 (25), 72 (40), 71 (10), 70 (10), 69 (50); $W_M = 11{,}6$
VII	244 (3), 242 (9), 207 (80), 206 (100), 192 (56), 191 (40), 181 (8), 180 (11), 179 (8), 178 (42), 177 (18), 166 (9), 165 (12), 164 (22), 163 (12), 152 (22), 151 (24), 139 (8), 138 (9), 137 (14), 136 (9), 124 (26), 123 (22), 98 (64), 97 (10), 96 (40), 85 (10), 83 (56), 82 (14), 71 (40), 70 (50), 69 (58)

*The ion peaks with intensities ⩾ 3% of the maximum intensity are presented.

The primary F_1 fragments that are formed are stable and do not undergo further fragmentation, whereas the F_2 ions lose substituent R^1 or R^2 entirely with subsequent elimination of a molecule of thiocyanic acid [in the case of VII ejection of isocyanic acid (the F_4 ion)]. Let us note that the preferred loss of the less electronegative substituent apparently takes place in the second stage; thus in the case of III, IV, and VI it is preferable that radical R^1 be lost, since $I'_{F_3}/I_{F_3} > 1$ (I are the intensities of the peaks of the corresponding ions), whereas in the case of V this value < 1.



It is characteristic that the current of the F_1—F_4 (F'_4) ions *in toto* constitutes 25-50% of the total ion current, which indicates the high selectivity of the fragmentation of the investigated compounds. It is interesting to note that competitive elimination of a cyano group (instead of a chlorine atom) by the molecular ions of I-VI is not observed.

Thus the elimination of a halogen atom and a molecule of chloroolefin is evidently a general fragmentation process for all 4-[β-haloalkyloxy(mercapto)]-sym-triazines and is a distinctive feature of the mass spectra of compounds with this type of structure.

EXPERIMENTAL

The mass spectra were obtained with an MKh-1303 spectrometer with direct introduction of the samples into the source at an ionizing-electron energy of 50 eV, an emission current of 100 mA, and an ionization chamber temperature of 110°C.

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OXIDATION OF 3,5-DISUBSTITUTED 6-METHYL-1,2,4-TRIAZINES

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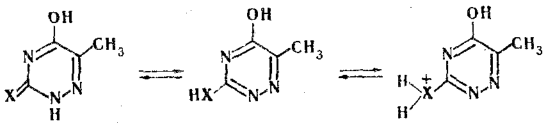
The corresponding substituted 1,2,4-triazine-6-carboxylic acids were obtained by oxidation of 3,5-disubstituted 6-methyl-1,2,4-triazines with hydrogen peroxide in an acidic medium. It is shown that the nature of the substituents does not affect the course of the process.

1,2,4-Triazine derivatives are finding ever increasing application as pesticides [1,2]. Carboxy-containing 1,2,4-triazines, which are the triazine analogs of nicotinic acid, which plays an important role in the metabolism of plants [3], are of interest from the point of view of their biological activity.

A general method for the production of aryl carboxylic acids is oxidation of the corresponding methyl derivatives [4]. However, their production by this method is difficult in the case of methyl-substituted 1,2,4-triazines. The oxidation of 3,5-diaryl-6-methyl-1,2,4-triazines with potassium permanganate in alkaline solution leads to the production of 3,5-diaryl-6-hydroxy-1,2,4-triazines, evidently as a consequence of decarboxylation of the probable intermediate, viz., the 3,5-diaryl-1,2,4-triazine-6-carboxylic acid.

We have carried out the oxidation of 3,5-dihydroxy-6-methyl-1,2,4-triazine (Ia), 3-thio-5-hydroxy-6-methyl-1,2,4-triazine (Ib), and 3-amino-5-hydroxy-6-methyl-1,2,4-triazine hydrochloride (Ic) with hydrogen peroxide in hydrochloric acid. The oxidation proceeds smoothly at 40-50°C. The reaction products were identified from the IR spectroscopic data and their elementary compositions. 3,5-Disubstituted-1,2,4-triazine-6-carboxylic acids were obtained in all cases. It should be noted that the character of the substituents in the 3 position does not have an appreciable effect on either the rate of oxidation or the yield of product. In view of the ability of hydroxy, mercapto, and amino groups to undergo oxidation even under relatively mild conditions, their inertness under the experimental conditions deserves discussion. A possible reason for the stability of the indicated groups may be their primary existence in tautomeric forms II (keto, thioxo, or imino), which are more resistant to oxidation than the III forms:



II III IV

X = O, S, NH

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