Thus the data obtained in this research make it possible to conclude that mass spectrometry is inapplicable for the determination of the position of the tautomeric equilibrium in compounds of this series.

EXPERIMENTAL

We described the synthesis of III, IV, X, XII, XIV, XV, XXII, and XXIV in [3]. Compounds VI, XI, and XVII-XX were synthesized by the method in [5]. The preparation of V and IX was accomplished by the method in [4], whereas the data in [6] (VII), [7] (VIII), [8] (II), [9] (XVI), [10] (XXI), and [11] (XXIII) were used for the preparation of the remaining compounds. Deuterium derivative XIII was obtained by two recrystallizations of XII from deuteromethanol.

The mass spectra were obtained with MKh-1303 and Varian MAT-44S spectrometers with direct introduction of the samples into the ion source at ionization energies of 50 and 70 eV, respectively.

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SYNTHESIS AND THERMAL DECOMPOSITION OF HALOALKOXY-sym-TRIAZINES.

7.* THERMAL DECOMPOSITION OF 2-DIALKYLAMINO-4-(2-CHLOROETHOXY)-6-METHOXYAMINO-sym-TRIAZINES

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and S. M. Saakyan

UDC 547.873'785.5.07

Two 2-dialkylamino-4-(2-chloroethoxy)-6-methoxyamino-sym-triazines were synthesized. It was established that when they are heated at 120°C, the 2-chloroethoxy group undergoes rearrangement with cyclization to give 2-dialkylamino-4-oxo-8-methoxy-6,7-dihydroimidazo[1,2-a]-sym-triazines, the structure of which was confirmed by data from the IR, PMR, and mass spectra.

Continuing our research on the thermal decomposition of 2-chloroethoxy derivatives of the sym-triazine series [1-5] we studied the specificity of the rearrangement-cyclization reaction in the case of 2-dialkylamino-4-(2-chloroethoxy)-6-methoxyamino-sym-triazines (IIa, b).

We established that, in contrast to the corresponding alkylamino derivatives, methoxyamino-sym-triazines are NH acids owing to the electronegative inductive effect of the methoxy group. In order to avoid the formation of salts due to the hydrogen atom of the methoxy-

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*See [6] for Communication 6.

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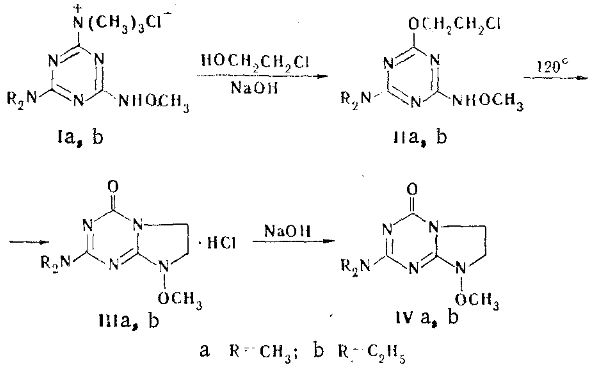
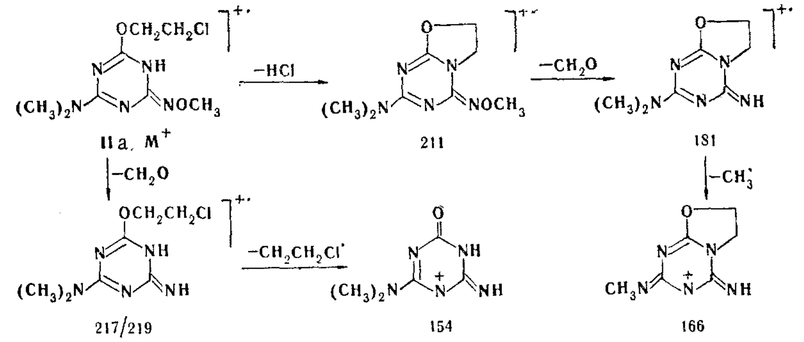
amino group, the preparation of IIa, b was accomplished in chloroform by means of dry sodium hydroxide.

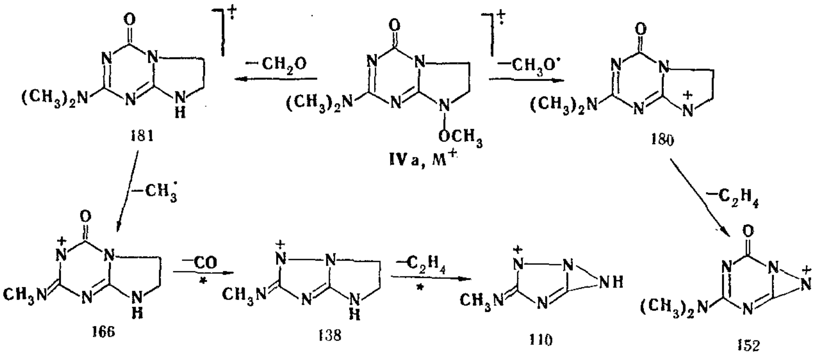


Compounds IIa, b upon brief heating at 120°C are converted to hydrochlorides IIIa, b which after treatment with alkali are converted to 2-dialkylamino-4-oxo-8-methoxy-6,7-dihydroimidazo[1,2-a]-sym-triazines IVa, b, as confirmed by the results of elementary analysis and IR, PMR, and mass-spectrometric data.

The IR spectra of IIa, b contain absorption bands of an NH group at 3200 cm^{-1}, and vibrations of the triazine ring are observed at 1550, 1570, and 1600 cm^{-1}; however, the absorption band of an NH group vanishes in the spectra of IVa, b, and an absorption band of a C=O group appears at 1690 cm^{-1}.

The molecular masses of IIa, b and IVa, b determined by mass spectrometry correspond to the calculated values (Table 1), and the principal fragmentation pathways confirm their structure:





A singlet of a methoxy group at 3.85 ppm is present in the PMR spectra of IVa, b and a symmetrical multiplet centered at 3.87 ppm (an AA'BB' system), which is characteristic for the methylene protons of the dihydroimidazoline ring, appears in the spectra of IIa, b instead of two triplets of a OCH_2CH_2Cl group.

TABLE 1. Mass Spectra of IIa, b and IVa, b*

Compound	m/e values (relative intensities of the ion peaks, %)
IIa	249 (8)/247 (22), 219 (15)/217 (46), 211 (100), 166 (66), 154 (80), 151 (34), 138 (50), 83 (52), 82 (85), 69 (86)
IIb	277 (6)/275 (16), 247 (7)/245 (21), 240 (85), 239 (49), 211 (100), 210 (44), 180 (44), 179 (40), 138 (41), 97 (30), 96 (54)
IVa	211 (100), 181 (40), 180 (70), 166 (20), 152 (58), 138 (18), 124 (38), 110 (16), 98 (87), 70 (82), 69 (42)
IVb	239 (43), 209 (32), 208 (100), 181 (12), 180 (54), 178 (22), 166 (22), 165 (12), 152 (20), 138 (12), 110 (11), 97 (32)

*The peaks of the molecular ions and the 10 most intense ions in the mass spectra are presented.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard. The mass spectra were obtained with an MKh-1303 spectrometer with direct introduction of the samples into the ionization region at an ionizing-electron energy of 50 eV. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates with acetone–hexane systems (1:1 or 1:2).

(2-Dialkylamino-6-methoxyamino-sym-triazin-4-yl)trimethylammonium Chlorides (Ia, b). These compounds were obtained by the method in [1]. Compound Ia, with mp 154-155°C (dec.), was obtained in 97% yield. Found: Cl 14.0; N 32.3%. $C_9H_{19}ClN_6O$. Calculated: Cl 13.5; N 32.0%. Compound Ib, with mp 157-159°C (dec.), was obtained in 70% yield. Found: Cl 12.5; N 28.7%. $C_{11}H_{23}ClN_6O$. Calculated: Cl 12.2; N 28.9%.

2-Dimethylamino-4-(2-chloroethoxy)-6-methoxyamino-sym-triazine (IIa). A 0.4-g (0.01 mole) sample of dry NaOH was added slowly in portions with stirring at 0-5°C to a mixture of 2.6 g (0.01 mole) of Ia, 3.2 g (0.04 mole) of ethylene chlorohydrin, and 10 ml of $CHCl_3$, and the mixture was maintained under these conditions for 1 h. It was then filtered, and the filtrate was evaporated. The residue was treated with water, and the mixture was filtered by suction filtration with a water aspirator to give 2.0 g (80%) of a product with mp 112-113°C (hexane). Found: Cl 14.5; N 28.5%. $C_8H_{14}ClN_5O_2$. Calculated: Cl 14.3; N 28.3%. R_f 0.58.

Compound IIb, with mp 105-106°C (hexane), was similarly obtained in 76% yield. Found: Cl 12.7; N 25.1%. $C_{10}H_{18}ClN_5O_2$. Calculated: Cl 12.9; N 25.4%. R_f 0.56.

2-Dimethylamino-4-oxo-8-methoxy-6,7-dihydroimidazo[1,2-a]-sym-triazine Hydrochloride (IIIa). A 2.5-g (0.01 mole) sample of IIa was heated at 120°C for 1 h, after which it was washed with ether and removed by filtration to give 2.4 g (96%) of IIIa with mp 187-188°C (dec.). Found: Cl 14.8; N 28.1%. $C_8H_{14}ClN_5O_2$. Calculated: Cl 14.3; N 28.3%.

Compound IIIb, with mp 127-129°C (dec.), was similarly obtained in 94% yield. Found: Cl 13.1; N 25.7%. $C_{10}H_{18}ClN_5O_2$. Calculated: Cl 12.9; N 25.4%.

2-Dimethylamino-4-oxo-8-methoxy-6,7-dihydroimidazo[1,2-a]-sym-triazine (IVa). A 0.5-g (0.012 mole) sample of sodium hydroxide was added to 2.5 g (0.01 mole) of IIIa in 2 ml of water (pH 3), the resulting solution (pH 8) was evaporated at 20-25°C, and the IVa was extracted with chloroform. Evaporation of the chloroform gave 1.6 g (75%) of a product with mp 70-72°C (toluene). Found: C 45.9; H 6.5; N 33.0%. $C_8H_{13}N_5O$. Calculated: C 45.5; H 6.2; N 33.2%. The product also had R_f 0.23.

Compound IVb, with mp 90-92°C (toluene), was similarly obtained in 74% yield. Found: C 50.6; H 7.3; N 29.6%. $C_{10}H_{17}N_5O$. Calculated: C 50.2; H 7.1; N 29.3%. The product also had R_f 0.63.

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REARRANGEMENTS IN THE HALOALKOXY(ALKYLTHIO, ALKYLAMINO)-sym-TRIAZINE SERIES.

5.* THERMOLYSIS OF 2-DIMETHYLAMINO-4-(2'-CHLOROETHOXY)-6-(1'-METHYL-2'-ACETYLHYDRAZINO)-sym-TRIAZINE

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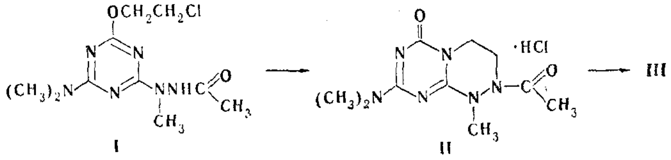
UDC 547.872'873:542.952

2-Dimethylamino-4-(2'-chloroethoxy)-6-(1'-methyl-2'-acetylhydrazino)-sym-triazine was synthesized, and it was shown that an unsymmetrical triazino-sym-triazine is formed during its thermolysis.

In [2] it was shown that the thermolysis of 2-(2'-chloroethoxy)-4-dialkylamino-6-alkylamino-sym-triazines, in contrast to the thermolysis of 4,6-bis(dialkylamino)-sym-triazines, proceeds regioselectively and exclusively at the exocyclic nitrogen atom of the alkylamino group.

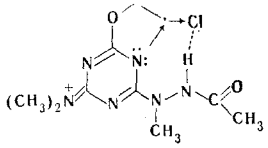
The aim of the present research was to study the effect of the hydrogen atom attached to the N_2 atom of the acetylhydrazino group on the pathway of the thermolysis of 2-dimethylamino-4-(2'-chloroethoxy)-6-(1'-methyl-2'-acetylhydrazino)-sym-triazine (I) and to obtain a condensed heterocycle with a sym-triazine fragment.



When I is heated, it undergoes intramolecular cyclization to give 1-methyl-2-acetyl-6-oxo-8-dimethylamino-1,2,3,4-tetrahydro-1,2,4-triazino[3,4-a]-sym-triazine hydrochloride (II), which is converted to the corresponding base (III) by the action of alkali.

The rearrangement could have proceeded with the formation of an intermediate N-2-chloroethyl derivative as a result of attack by the chloride ion on the $O—C_8$ bond of the oxazolidine ring [1] or directly without the participation of the chloride ion. Since the rearrangement takes place in water, in which the chloride ion is solvated and cannot participate in the process, the first possibility should be excluded.

The regioselectivity of the rearrangement is possibly explained by a hydrogen bond between the chlorine atom and the hydrogen atom of the hydrazino group, which lowers the energy of the C—Cl bond.



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*See [1] for Communication 4.

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