was used for the synthesis of dihydroxymethyl-1,2,3-triazole (X). The principal constants of the substances obtained are presented in Table 1.

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REARRANGEMENTS IN THE HALOALKOXY(THIO,AMINO)-sym-TRIAZINE SERIES.

10. SYNTHESIS AND REARRANGEMENT OF 2-DIMETHYLAMINO-4-(2-ACYLHYDRAZINO)-6,7-DIHYDROOXAZOLO[3,2-a]-sym-TRIAZINES

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2-Dimethylamino-4-(2-acetylhydrazino)- and 4-(2-benzoyl)hydrazino-6,7-dihydrooxazolo[3,2-a]-sym-triazines were synthesized. It was established that when these compounds are heated, they undergo rearrangement to the corresponding 2-dimethylamino-6,7-dihydroimidazo[2,1-a]-sym-triazines. Deacylation of the latter gives the N-amino derivative.

We have shown [1] that 2-(2-chloroethoxy)-4-dialkylamino-6-(1-methyl-2-acethylhydrazino)-sym-triazine undergoes intramolecular cyclization to give a substituted triazinotriazine derivative when it is heated.

It was of interest to study a similar reaction in the case of 2-dimethylamino-4-(2-chloroethoxy)-6-(2-acylhydrazino)-sym-triazine, which, inasmuch as it has labile hydrogen atoms in the α and β positions of the hydrazine fragment, may form both an oxazolo- or imidazotriazine and a triazinotriazine in the case of thermolysis.

We established that the reaction of quaternary salt Ia with ethylene chlorohydrin in the presence of alkali at low temperature gives, instead of the expected 2-chloroethoxy derivative, dihydrooxazolo-sym-triazine IIa, which upon heating (200°C) undergoes rearrangement to dihydroimidazo-sym-triazine IIIa.

Compound Ib reacts with ethylene chlorohydrin in the presence of alkali at low temperatures to give a mixture of dihydrooxazolo- and dihydroimidazo-sym-triazines in a ratio of 4:3. When this mixture is heated in xylene, the dihydrooxazolotriazine is converted to the more stable dihydroimidazotriazine IIIb.

Strongly hygroscopic amine IV, which was identified in the form of Schiff base V, is formed in the deacylation of IIIa, b.

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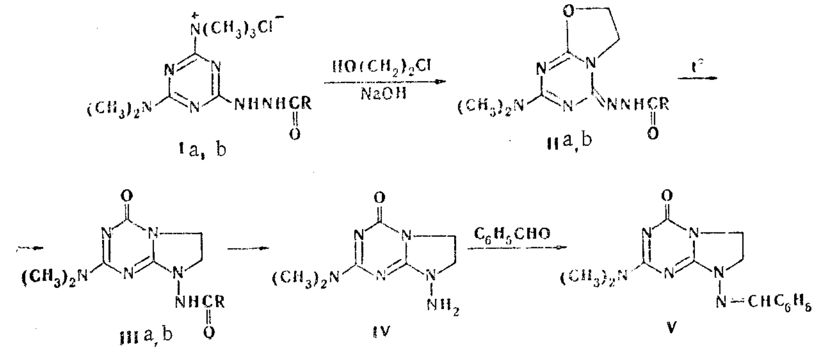
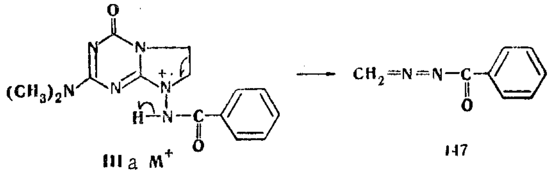


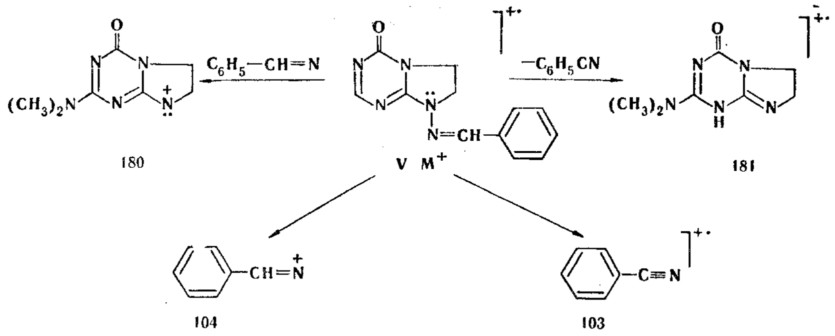
Ia R=C$_6$H$_5$, b R=CH$_3$

Signals of protons of N-methyl groups (3.1 ppm) and of the benzene ring (7.3-8.0 ppm) and two triplet signals at 4.2 and 4.7 ppm, which are related, respectively, to $N-CH_2$ and $O-CH_2$ groups, are observed in the PMR spectrum of IIa. The two triplet signals vanish in the spectrum of IIIa, and a narrow multiplet centered at 4.0 ppm appears in place of them; this is due to a rearrangement process, since in the spectrum of product IIIa the chemical shifts of the ring methylene groups should be close. A similar pattern is observed in the PMR spectra of IIb and IIIb.

The structures of IIa, b, IIIa, and V are also confirmed by their mass spectra (Table 1). The molecular masses of IIa, IIIa, IIb, and IIIb determined by mass spectrometry correspond to the calculated values (M = 300 and 238 amu, respectively). The mass spectra of triazines IIa and IIIa differ substantially. In addition to the change in the relative intensities of some of the peaks of the common fragment ions, one should point out the increase in the stability of the molecular ion (W_M) on passing from IIa (W_M = 14) to IIIa (W_M = 34). In addition, in contrast to IIa, the mass spectrum of IIIa contains an ion peak with m/z 147,* the formation of which is associated with fragmentation of the dihydroimidazole ring with migration of a hydrogen atom to the uncharged fragment:



The mass spectrum of V contains, in addition to the maximum molecular-ion peak with M 284, which corresponds to the calculated value, a number of characteristic peaks of fragment ions, the origin of which confirms the structure of V and, consequently, the structure of amino derivative IV:



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 CD_3OD + $CDCl_3$ were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard. The mass

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

TABLE 1. Mass Spectra of IIa, IIIa, and V*

Compound	m/z values (relative intensities of the ion peaks, %)
IIa	301 (14), 300 (40), 285 (8), 186 (11), 181 (18), 180 (12), 167 (17), 166 (9), 152 (14), 151 (7), 139 (14), 138 (16), 137 (6), 121 (24), 104 (15), 105 (100), 88 (22), 77 (40)
IIIa	301 (24), 300 (100), 299 (14), 285 (20), 271 (7), 196 (6), 191 (7), 182 (10), 180 (25), 166 (7), 152 (16), 147 (8), 139 (6), 138 (12), 121 (14), 106 (12), 105 (84), 98 (20), 77 (10)
V	285 (20), 284 (100), 283 (12), 269 (24), 241 (6), 213 (10), 182 (12), 181 (90), 180 (78), 179 (12), 178 (13), 167 (14), 166 (38), 153 (15), 152 (51), 151 (12), 139 (14), 138 (34), 137 (16), 125 (17), 124 (36), 123 (13), 122 (20), 111 (20), 110 (24), 109 (25), 105 (78), 104 (74), 103 (80), 98 (90), 97 (23), 91 (30), 85 (22), 84 (16), 83 (50), 82 (20), 81 (44), 77 (70), 76 (40), 70 (94), 69 (90)

*The ion peaks with intensities greater than 5% of the maximum peak are presented.

spectra were recorded with an MKh-1303 spectrometer with direct introduction of the samples into the ionization region at an ionization energy of 50 eV. The individuality of the substances was monitored by thin-layer chromatography (TLC) on Silufol UV-254 with elution by acetone—hexane—water (10:10:1) and development with 2% $AgNO_3$ + 0.4% Bromphenol blue + 4% citric acid.

2-Dimethylamino-4-(2-benzoylhydrazono)-6,7-dihydrooxazolo[3,2-a]-sym-triazine (IIa). A 0.4-g (0.01 mole) sample of NaOH was added at —8°C to a mixture of 3.5 g (0.01 mole) of 2-dimethylamino-4-chloro-6-(2-benzoylhydrazino)-sym-triazine trimethylammonium salt (Ia) and 3.2 g (0.04 mole) of ethylene chlorohydrin, and the mixture was stirred for 30 min and allowed to stand overnight. Water (20 ml) was added, and the precipitate was removed by filtration and washed with acetone to give 1.5 g (40%) of a product with mp 187-188°C. IR spectrum: 1660 (C=O) and 3340 cm^{-1} (N—H). PMR spectrum: 3.1 (s, N—CH_3), 7.3-8.0 (s, C_6H_5), 4.2 (t, N—CH_2), and 4.7 ppm (t, O—CH_2). The product had R_f 0.37. Found: N 27.75%; M^+ 300. $C_{14}H_{16}N_6O_2$. Calculated: N 28.0%; M 300.

2-Dimethylamino-4-oxo-8-benzamido-6,7-dihydroimidazo[2,1-a]-sym-triazine (IIIa). A 3-g (0.01 mole) sample of IIa was heated at 200°C for 30 min, after which the residue was worked up to give a product with mp 242-243°C in quantitative yield. IR spectrum: 1660 (C=O), 1605 (C=N), and 3330 cm^{-1} (NH). The product had R_f 0.58. Found: N 28.3%; M^+ 300. $C_{14}H_{16}N_6O_2$. Calculated: N 28.0%; M 300.

2-Dimethylamino-4-oxo-8-acetamido-4-oxo-8-acetamido-6,7-dihydroimidazo[2,1-a]-sym-triazine (IIIb). A) A 0.4-g (0.01 mole) sample of NaOH (pulverized) was added in portions at —8°C to a mixture of 2-dimethylamino-4-chloro-6-(2-acetylhydrazino)-sym-triazine trimethylammonium salt (Ib), 3.2 g (0.04 mole) of ethylene chlorohydrin, 10 ml of chloroform, and 1 ml of water, and the mixture was stirred for 1 h and allowed to stand overnight. The chloroform was evaporated, 10 ml of water was added to the residue, and the mixture was neutralized with $NaHCO_3$. The next day, the precipitated 2-dimethylamino-4-(2-acethylhydrazino)-6,7-dihydrooxazolo[3,2-a]-sym-triazine (IIb) was removed by filtration to give 1 g (40%) of a product with mp 178-180°C. IR spectrum: 1660 (C=O), 3320 (NH), and 1620 cm^{-1} (C=N). PMR spectrum: 3.15 (s, N—CH_3), 2.1 (s, $COCH_3$), 4.25 (t, N—CH_2), and 4.75 ppm (t, OCH_2). The product had R_f 0.28. Found: C 45.4; H 5.8; N 35.5%; M^+ 238. $C_9H_{14}N_6O_2$. Calculated: C 45.7; H 5.9; N 35.3%; M 238. The filtrate was evaporated to dryness, and IIIb was extracted with ethanol to give 0.7 g (30%) of a product with mp 236-238°C. IR spectrum: 1670 (C=O) and 3325 cm^{-1} (NH). PMR spectrum: 3.07 (s, N—CH_2), 2.1 (s, $COCH_3$), and 3.8-4.15 ppm (—CH_2CH_2—). The product had R_f 0.18. Found: C 45.35; H 5.7; N 35.6%; M^+ 238. $C_9H_{14}N_6O_2$. Calculated: C 45.7; H 5.9; N 35.9%; M 238. Compound IIIb was also obtained by heating IIb in xylene at 140°C for 2 h. The yield was quantitative.

B) A 0.4-g (0.01 mole) sample of NaOH (pulverized) was added in portions at —8°C to a mixture of 2.9 g (0.01 mole) of Ib, 3.2 g (0.04 mole) of ethylene chlorohydrin, 10 ml of chloroform, and 1 ml of water, and the mixture was stirred for 1 h. The chloroform was evaporated, and the excess ethylene chlorohydrin was extracted with ether. Xylene (10 ml) was added to the residue, and the mixture was refluxed for 2 h. The precipitate was removed by filtration and dissolved in water, and the solution was neutralized with $NaHCO_3$

and evaporated. The product was extracted with ethanol, the ethanol was removed by distillation, and the residue was washed with chloroform to give 2 g (85%) of IIIb with mp 236-238°C.

2-Dimethylamino-4-oxo-8-amino-6,7-dihydroimidazo[2,1-a]-sym-triazine (IV). A 0.04-mole sample of 10% HCl was added to a mixture of 0.01 mole of IIIa or IIIb and 10 ml of water, and the mixture was refluxed for 6 h. It was then extracted with chloroform, and the aqueous layer was neutralized with $NaHCO_3$. The solution was evaporated to dryness, and the product was extracted with ethanol. The ethanol was removed by distillation to give strongly hygroscopic amine IV, with mp 173-175°C (dec.), in 70% yield. Found: N 42.4%. $C_7H_{23}N_6O$. Calculated: N 42.8%.

2-Dimethylamino-4-oxo-8-benzylideneamino-6,7-dihydroimidazo[2,1-a]-sym-triazine (V). Without additional purification, 0.3 g (1.5 mmole) of amine IV was dissolved in water, and 0.6 ml of 10% HCl and 0.2 g (1.8 mmole) of benzaldehyde were added. The precipitated Schiff base was removed by filtration to give 0.3 g (70%) of a product with mp 290°C. Found: N 28.4%. $C_{14}H_{16}N_6O$. Calculated: N 28.19%.

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