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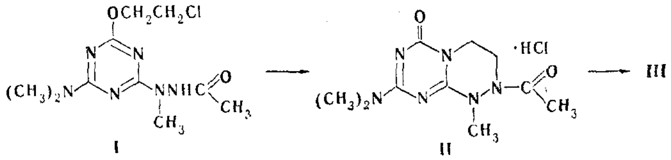
2-Dimethylamino-4-(2'-chloroethoxy)-6-(1'-methyl-2'-acetylhydrazino)-sym-triazine was synthesized, and it was shown that an unsymmetrical triazino-sym-triazine is formed during its thermolysis.

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.

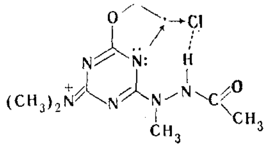
The aim of the present research was to study the effect of the hydrogen atom attached to the N_2 atom of the acetylhydrazino group on the pathway of the thermolysis of 2-dimethylamino-4-(2'-chloroethoxy)-6-(1'-methyl-2'-acetylhydrazino)-sym-triazine (I) and to obtain a condensed heterocycle with a sym-triazine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

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in $CDCl_3$ (for I, with tetramethylsilane as the internal standard) and D_2O (for II and III) were recorded with a Varian T-60 spectrometer. The mass spectra were recorded with an MKh-1303 spectrometer with direct introduction of the samples at an ionizing-electron 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 (5:5:1) and development with a mixture of 2% $AgNO_3$, 0.4% bromphenol blue, and 4% citric acid.

2-Dimethylamino-4-(2'-chloroethoxy)-6-(1'-methyl-2'-acetylhydrazino)-sym-triazine (I). A 0.4-g (0.01 mole) sample of 10% NaOH was added dropwise with stirring at −7°C to a mixture of 3.0 g (0.01 mole) of [2-dimethylamino-6-(1'-methyl-2'-acetylhydrazino)-sym-triazin-4-yl]-trimethylammonium chloride and 3.2 g (0.04 mole) of ethylene chlorohydrin, and the mixture was allowed to stand overnight. Ice water (30 ml) was then added, and the resulting precipitate was removed by filtration to give 2.3 g (80%) of a product with mp 86-88°C (from ether). IR spectrum: 1700 (C=O); 1065, 1080, 1160, and 1185 cm^{-1} (C—O—C). PMR spectrum: 2.05 (s, CH_3C), 3.35 (s, NCH_3), 3.1 [s, $N(CH_3)_2$], 4.73 (t, OCH_2), and 3.75 ppm (t, $ClCH_2$). The product also had R_f 0.48. Found: Cl 12.5; N 28.7%; M^+ 288. $C_{10}H_{17}ClN_6O_2$. Calculated: Cl 12.3; N 29.0%; M 288.

1-Methyl-2-acetyl-6-oxo-8-dimethylamino-1,2,3,4-tetrahydro-1,2,3-triazino[3,4-a]-sym-triazine Hydrochloride (II). A suspension of 2.9 g (0.01 mole) of I in 10 ml of absolute benzene was heated at 80°C for 3 h, and the resulting precipitate was removed by filtration to give 2.7 g (92%) of a product that decomposed at 172°C. IR spectrum: 1685 and 1700 cm^{-1} (C=O). PMR spectrum: 2.20 (s, CH_3C), 2.45 (s, NCH_3), 3.2 [s, $N(CH_3)_2$], 4.58 (t, NCH_2), and 4.8 ppm (t, NCH_2). The product also had R_f 0.35. Found: Cl 12.1; N 29.4%; M^+ 288. $C_{10}H_{17}ClN_6O_2$. Calculated: Cl 12.3; N 29.1%; M 288.

1-Methyl-2-acetyl-6-oxo-8-dimethylamino-1,2,3,4-tetrahydro-1,2,4-triazino[3,4-a]-sym-triazine (III). A 0.4-g (0.01 mole) sample of a 40% solution of NaOH was added slowly to a solution of 2.9 g (0.01 mole) of II in 5 ml of water, and the mixture was then evaporated to dryness. Ethanol (10 ml) was added to the residue, and the precipitate was removed by filtration. The ethanol was removed by distillation, 10 ml of xylene was added to the residue, and the mixture was heated at 140°C for 2 h. The precipitate was removed by filtration and washed with absolute ether to give 2.1 g (80%) of a product with mp 193-194°C. IR spectrum: 1672, 1732 (C=O); 1545, 1635 cm^{-1} (stretching vibrations of the triazine ring). PMR spectrum: 1.80 (s, CH_3C), 2.4 (s, NCH_3), 3.0 [s, $N(CH_3)_2$], 2.8 (t, NCH_2), and 3.8 ppm (t, NCH_2). The product also had R_f 0.36. Found: C 47.3; H 6.0; N 33.1%; M^+ 252. $C_{10}H_{16}N_6O_2$. Calculated: C 47.6; H 6.3; N 33.3%; M 252.

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