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SYNTHESIS AND THERMAL DECOMPOSITION OF HALOALKOXY-sym-TRIAZINES.
6.* SYNTHESIS AND THERMOLYSIS OF 2-(2-CHLOROETHOXY)-4-N-METHYL-N-CYANOAMINO-6-DIALKYLAMINO-syn-TRIAZINES

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2-(2-Chloroethoxy)-4-N-methyl-N-cyanoamino-6-dialkylamino-sym-triazines were synthesized. It was established that thermolysis of the indicated compounds in xylene is accompanied by dechloroalkylation; however, it takes place at the site of both the dialkylamino and alkylcyanoamino groups to give a mixture of two imidazo-sym-triazines. The structures of the latter were confirmed by data from the IR, PMR, and mass spectra.

It has been shown [1] that the thermolysis of 2-(2-chloroethoxy)-4,6-bis(dialkylamino)-sym-triazines proceeds unambiguously to give 2-dialkylamino-4-oxo-8-alkyl-6,7-dihydroimidazo[1,2-a]-sym-triazines.

The aim of the present research was to study the specificity of the analogous reaction in the case of 2-(2-chloroethoxy)-4-N-methyl-N-cyanoamino-6-dialkylamino-sym-triazines, the rearrangement-cyclization of which may proceed with the elimination of both alkyl chlorides and cyanogen chloride.

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*See [4] for Communication 5.

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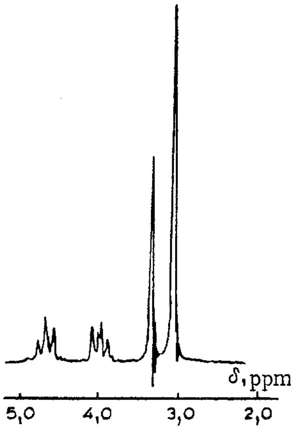


Fig. 1

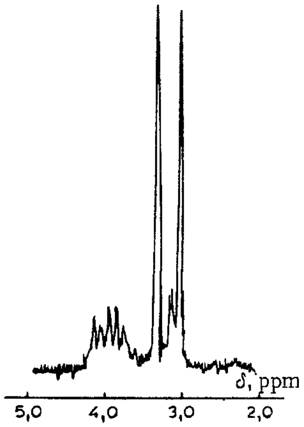
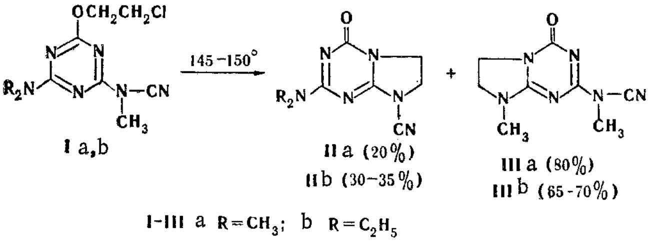


Fig. 2

Fig. 1. PMR spectrum of Ia.

Fig. 2. PMR spectrum of the products of thermolysis of Ia (IIa and IIIa).



It was established that the thermolysis of Ia,b in xylene at 145-150°C does not involve the cyano group and is accompanied by dechloroalkylation at the site of both the dialkylamino and methylcyanoamino groups, which leads to the formation of a mixture of two imidazo-sym-triazines (IIa,b and IIIa,b). The structures of the latter were confirmed by data from the IR, PMR, and mass spectra.

The absorption bands of a C–O group vanish in the IR spectra of II and III, while an absorption band of a C=O group appears at 1695 cm^{-1}; ring vibrations show up at 1540 and 1620 cm^{-1}, and absorption bands of a C≡N group appear at 2240 and 2250 cm^{-1}.

The PMR spectrum of Ia, in which the singlet signals of $N(CH)_2$ [sic] and $N-CH_3$ groups appear at 3.0 and 3.25 ppm, respectively, and triplet signals of protons of methylene groups are observed at 3.9 (CH_2Cl) and 4.62 ppm (CH_2O), is presented in Fig. 1.

The PMR spectrum of a mixture of IIa and IIIa, in which two peaks of singlet absorption with identical intensities are observed at 3.05 and 3.35 ppm, is presented in Fig. 3; the observed pattern is possible only in the case of realization of structure IIIa. The weak-intensity absorption bands at 3.1 and 4.12 ppm were assigned to the dimethylamino group and to the protons of cyclic methylene grups of IIa. A quantitative estimate of the singlet intensities of the signals indicates relative percentages of the IIa and IIIa forms of 20% and 80%, respectively.

A similar pattern is observed in the thermolysis of Ib. The signals of the ethyl groups of IIb and IIIb differ somewhat with respect to their chemical shifts but are of equal intensity, the relative percentages of IIb and IIIb should therefore be ∿30-35% and ∿65-70%, respectively.

An analysis of the mass spectra of the products of thermolysis of Ia (Fig. 3) and a study of the fragmentation scheme convince us that the presence in the mass spectrum of peaks of ions of the a_1 (m/e 98), a_2 (m/e 70), and a_3 (m/e 83) type, on the one hand, and of peaks of a'_1 (m/e 109), a'_2 (m/e 81), and a'_3 (m/e 94) ions, on the other, which differ by 11 mass

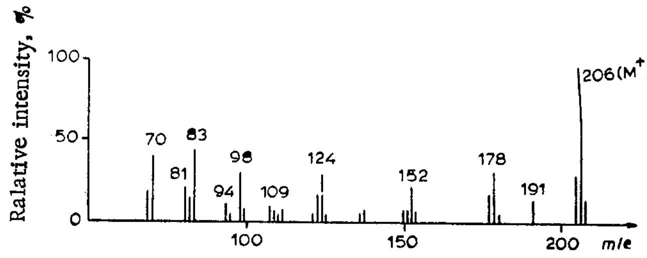
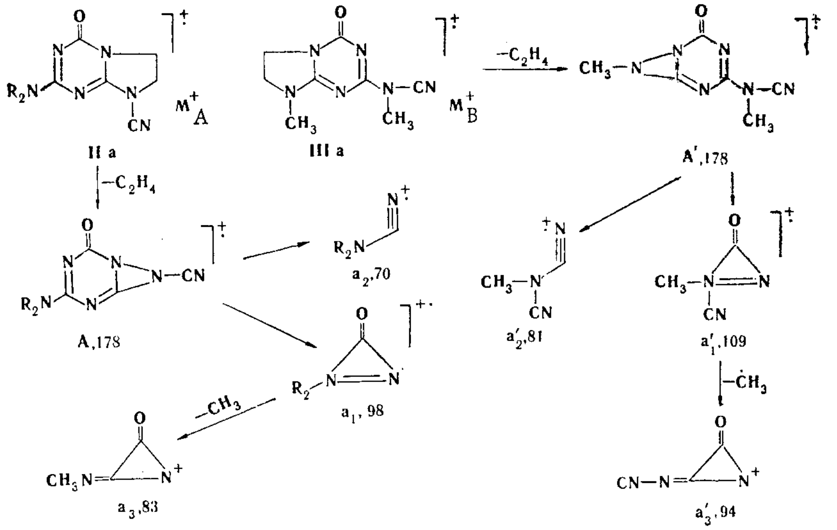


Fig. 3. Mass spectrum of the products of thermolysis of Ia (IIa and IIIa).

units (amu) (the difference in mass between the CH_3, and CN radicals) indicates that a CH_3 radical from both the dimethylamino and N-methylcyanoamino groups is included in the composition of the eliminated CH_3Cl molecule.



A dimethylamino group is completely or partially retained in ions of the a type, which confirms the IIa structure, an N-methylcyanoamino group, which confirms the IIIa structure, is retained in ions of the a' type.

Two peaks that differ by 14 amu (m/e 234 and 220), which correspond to the molecular ions of imidazo-sym-triazines IIb (234) and IIIb (220), are present in the mass spectrum of the products of thermolysis of Ib in the high-mass-number region.

Compounds IIIa and IIIb are formed in higher yields than IIa and IIb. This should evidently be explained by the smaller degree of orderliness of the alkyl groups of the dialkylamino fragment of starting Ia,b as compared with N-methyl-N-cyanoamino group, in which the methyl group is in a more ordered state. Dechloroalkylation therefore proceeds more readily at the site of the dialkylamino group.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of solutions in deuteropyridine (Ia,b) and $CDCl_3$ (II and III) were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard. The mass spectra were measured with an MKh-1303 spectrometer with direct introduction of the samples into the ionization region at an ionizing-electron energy of 30 eV and temperatures that were 20-30°C below the melting points of the investigated substances. Thin-layer chromatography was carried out on Silufol UV-254 plates in an acetone—hexane system (1:2).

2-(2-Chloroethyl)-4-N-methyl-N-cyanoamine-6-dialkylamino-sym-triazines (Ia,b). These compounds were obtained by the method that we developed in [1]. Compound Ia, with mp 127-129°C (by dissolving in ether and evaporation), was obtained in 88% yield. Found: Cl 14.2; N 32.3%. $C_9H_{13}ClN_6O$. Calculated: Cl 13.8; N 32.7%. R_f 0.64. Compound I, with mp 56-58°C, was obtained in 81% yield. Found: Cl 12.5; N 29.1%. $C_{11}H_{23}Cl_6O$. Calculated: Cl 12.2; N 28.9%. R_f 0.59.

Thermolysis of 2-(2-Chloroethoxy)-4-N-methyl-N-cyanoamino-6-dimethylamino-sym-triazine. A suspension of 2.6 g (0.01 mole) of Ia in 6 ml of xylene was heated at 145-150°C for 15 h, after which the xylene was decanted, and the precipitate was triturated with ether and removed by filtration to give 1.9 g (92%) of a mixture of 2-dimethyl-amino-4-oxo-8-cyano- (IIa) and 2-N-methyl-N-cyanoamino-4-oxo-8-methyl-6,7-dihydroimidazo [1,2-a]-sym-triazines (IIIa). Found: C 46.0; H 4.6; N 40.5%. $C_8H_{10}N_6O$. Calculated: C 46.6; H 4.9; N 40.8%. R_f 0.31 and 0.37. Mass spectrum: M^+ 206.

The thermolysis of Ib was carried out similarly. Workup gave a mixture of 2-diethylamino-4-oxo-8-cyano- (IIb) and 2-N-methyl-N-cyanoamino-4-oxo-8-ethyl-6,7-dihydroimidazo [1,2-a]-sym-triazine (IIIb) with mp 90-112°C and R_f 0.63 and 0.80. Mass spectrum: M^+ 234 and 220.

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