REARRANGEMENTS IN HALOALKOXY(THIO, AMINO)-sym-TRIAZINES

II.* THERMOLYSIS OF 2-METHOXY-4-(2-CHLOROETHOXY)-6-DIALKYLAMINO-sym-TRIAZINES

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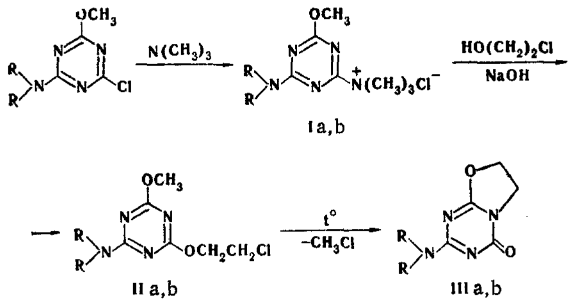
The reaction of [2-methoxy-6-dialkylamino-sym-triazin-4-yl]trimethylammonium chlorides with ethylene chlorohydrin gives 2-methoxy-4-(2-chloroethoxy)-6-dialkylamino-sym-triazones, which eliminate CH_3Cl when they are heated to give 2-dialkylamino-4-oxo-4,5,6,7-tetrahydro-oxazolo[3,2-a]-sym-triazines. Data from the UV, IR, PMR, and mass spectra are presented.

It has been previously shown that 2-(2-chloroethoxy)-4,6-bis(dialkylamino)-sym-triazines undergo dechloroalkylation when they are heated and rearranged to dihydroimidazo-sym-triazines [1]. It seemed of interest to investigate an analogous reaction in the case of 2-methoxy-4-(2-chloroethoxy)-6-dialkylamino-sym-triazines, as a result of the thermolysis of which one might have expected the formation of both imidazolo- and oxazolo-sym-triazines.

2-Methoxy-4-(2-chloroethoxy)-6-dialkylamino-sym-triazines (IIa,b) were obtained by the action of ethylene chlorohydrin in the presence of alkali at low temperatures on quaternary ammonium salts of the I type:



I-III a R=CH_3; b R=C_2H_5

Whereas 2-(2-chloroethoxy)-4,6-bis(dialkylamino)-sym-triazines split out alkyl chlorides when they are heated, CH_3Cl is evolved in the case of IIa,b. This process was confirmed by the mass spectra of III (Fig. 1, spectra b and c).

As compared with the PMR spectrum of IIa (Fig. 2, spectrum a), the PMR spectrum of IIIa (Fig. 2, spectrum b) does not contain the singlet of an OCH_3 group at 3.82 ppm, and CH_3Cl is consequently formed from the methoxy group also during thermolysis of IIa. The two triplets of the OCH_2CH_2Cl group in the spectra of IIa,b are converted to a symmetrical multiplet centered at 4.41 ppm, which is characteristic for an AA'BB' system.

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* See [1] for communication I.

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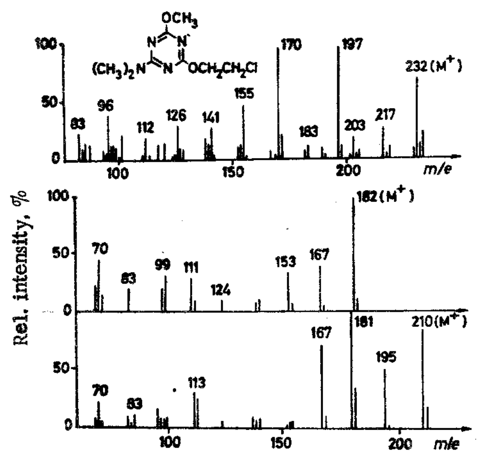


Fig. 1. Mass spectra: a) IIa; b) IIIa; c) IIIb.

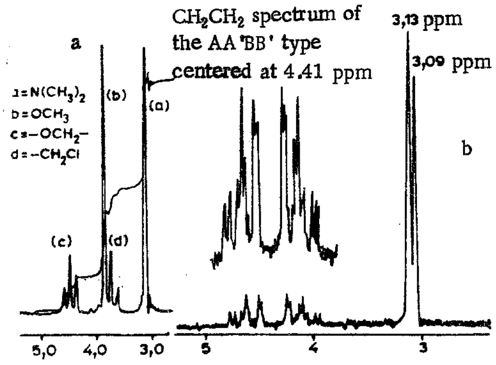
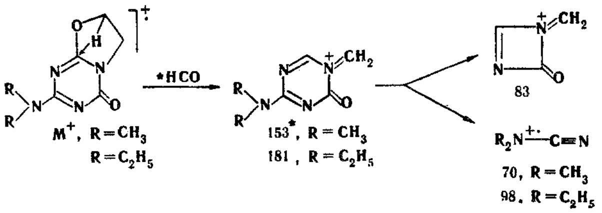


Fig. 2. PMR spectra: a) IIa; b) IIIa.

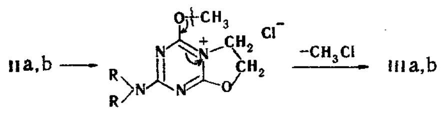
This means that the OCH_2CH_2 group in IIIa,b is incorporated in a fixed (i.e., cyclic) system. The intense absorption characteristic for a conjugated C=O group appears in the IR spectra on passing from IIa,b to their thermolysis products.

The information above provides a basis for the assumption that the products of decomposition of IIa,b are 2-dialkylamino-4-oxo-4,5,6,7-tetrahydrooxazolo[3,2-a]-sym-triazines (IIIa,b). The mass spectra of IIIa,b (Fig. 1, spectra b and c) contain some peaks of fragment ions, the origin of which can be explained by proceeding from the presence of an oxazolidine ring.

The presence of two singlets of an alkylamino group, which merge as the temperature rises, in the PMR spectrum of IIIa (Fig. 2, spectrum b) is explained by hindered rotation about the C–N bond due to conjugation of the p electrons of the exocyclic nitrogen atom with the sym-triazine ring. The free energies of activation ($\Delta G^{\neq}$) and the rate constants (k) for rotation about the C–N bond, calculated, respectively, from the Eyring and Gutowsky–Holm [2] equations, in which the difference ($\Delta\nu$) in the chemical shifts of the signals of the $N\langle^{R}_{R}$ groups was measured at temperatures ~60°C below the coalescence temperature (T_C), are presented in Table 1.



The driving force in the investigated reaction is evidently isomerization of IIa,b to intramolecular quaternary ammonium salts, which eliminate methyl chloride to give the final compounds:



It was shown by recording the PMR spectra of 2-chloro-4-methoxy-6-dialkylamino-sym-triazines at various temperatures (20–100°C) that methoxy-sym-triazines do not isomerize to N-methyl derivatives at moderate temperatures (the signal of the protons of the OCH_3 group did not change), whereas IIa,b undergo rearrangement when they are refluxed in n-heptane or when they are allowed to stand for a long time; the alternative mechanism for rearrangement

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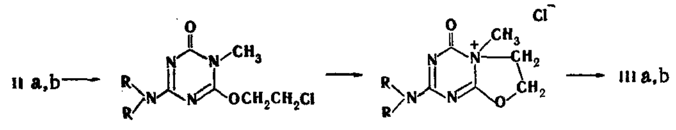
* Here and subsequently, the m/e values are presented for all of the ion peaks.

TABLE 1. Kinetic Parameters for Rotation about the C—N Bond

Compound		$\Delta\nu$, Hz	T_c, °C	k, sec^{-1}	$\Delta G^{\neq}_{C-N}$, kcal/mole
IIIa		2,7	42	12,0	17,0
IIIb	CH_2	7,0	65	31,1	17,5
	CH_3	4,1	62	18,2	17,7



is therefore impossible.

EXPERIMENTAL

The UV spectra of ethanol solutions of the compounds were recorded with a Specord spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were obtained with a UR-10 spectrometer. The PMR spectra of CCl_4 (IIa,b), $CDCl_3$ (IIIa), and deuteropyridine (IIIb) solutions of the compounds were recorded with Varian T-60 and JEOL C-60 spectrometers with tetramethylsilane as the internal standard. The temperature was determined with respect to ethylene glycol. The accuracy in the determinations was as follows: $T_C = 1°C$, $\Delta\nu = 0.1$ Hz, and $\Delta G^{\neq} = 0.3$–0.4 kcal/mole. The mass spectra were recorded with an MKh-1303 spectrometer with direct introduction of the samples into the ionization region at an ionizing-electron energy of 30 eV and at temperatures 20° below the melting points of the investigated compounds. The compounds were chromatographed on activity II aluminum oxide in an acetone–hexane system, and the chromatograms were developed with 2% $AgNO_3$ solution and examined in UV light.

[2-Methoxy-6-dimethylamino-sym-triazin-4-yl]trimethylammonium Chloride (Ia). A solution of 6.5 g (0.11 mole) of trimethylamine in 30 ml of absolute benzene was added with stirring and cooling to 5° to a solution of 18.9 g (0.1 mole) of 2-methoxy-4-chloro-6-dimethylamino-sym-triazine in 100 ml of absolute benzene, after which the mixture was allowed to stand overnight. The precipitate was removed by filtration, washed with absolute alcohol, and dried in a vacuum desiccator to give 23 g (94%) of a product with mp 124-126° (dec.). Found: Cl 14.2; N 28.2%. $C_9H_{18}ClN_5O$. Calculated: Cl 14.3; N 28.3%.

A similar procedure was used to obtain Ib, with mp 125-127°C (dec.), in 84% yield. Found: Cl 12.6; N 25.6%. $C_{11}H_{22}ClN_5O$. Calculated: Cl 12.9; N 25.4%.

2-Methoxy-4-(2-chloroethoxy)-6-dimethylamino-sym-triazine (IIa). A total of 4.0 g (0.1 mole) of 10% aqueous sodium hydroxide solution was added slowly with stirring at 0-5° to a mixture of 24.8 g (0.1 mole) of Ia and 32.2 g (0.4 mole) of ethylene chlorohydrin, after which the mixture was maintained under these conditions for 1-1.5 h. Ice water (60 ml) was then added, and the resulting precipitate was removed by filtration to give 21.6 g (93%) of IIa with mp 56-57°. UV spectrum: λ_{max} 231 nm (log ε 4.56). IR spectrum: 1599 and 1541 cm^{-1} (ring stretching vibrations). The product had R_f 0.67. Found: Cl 15.5; N 24.1%. $C_8H_{13}ClN_4O_2$. Calculated: Cl 15.3; N 24.1%.

A similar procedure was used to obtain IIb as a viscous syrup in 87% yield. UV spectrum: λ_{max} 233 nm (log ε 4.61). IR spectrum: 1593 and 1537 cm^{-1} (ring stretching vibrations). The product had R_f 0.53. Found: Cl 13.9; N 21.9%. $C_{10}H_{17}ClN_4O_2$. Calculated: Cl 13.6; N 21.5%.

2-Dimethylamino-4-oxo-4,5,6,7-tetrahydrooxazolo[3,2-a]-sym-triazine (IIIa). A suspension of 2.3 g (0.01 mole) of IIa in 6 ml of toluene was heated at 140° for 5 h. Methyl chloride, which was identified in the form of the S-methylisothiuronium chloride (mp 58-60°) [3] formed by absorption by an acetone solution of thiourea, began to evolve vigorously at 123-130°. At the end of the reaction, the contents of the flask were cooled to room temperature and filtered to give 1.7 g (93%) of IIIa with mp 180-181° (from octane). UV spectrum: λ_{max} 236 nm (log ε 4.71). IR spectrum: 1691 (C=O); 1636, 1569, and 1504 cm^{-1} (triazine ring stretching vibrations). PMR spectrum, δ: 3.11 d (CH_3), 4.41 m $(CH_2)_2$ ppm. The product had R_f 0.4. Found: C 46.6; H 5.9; N 30.5%. $C_7H_{10}N_4O_2$. Calculated: C 46.2; H 5.5; N 30.8%.

A similar procedure was used to prepare IIIb, with mp 128-130° (from octane), in 90% yield. UV spectrum: λ_{max} 238 nm (log ε 4.63). IR spectrum: 1698 (C=O); 1634, 1543, and 1496 cm^{-1} (triazine ring stretching vibrations). PMR spectrum, δ: 0.99 and 0.93 ppm (triplets of methylidyne protons, see Table 1), 3.39

[superimposition of $N(CH_2CH_3)_2$ quartets; J = $\Delta\nu$, see Table 1], and 4.25 ppm (dihydrooxazolidine ring protons). The product had R_f 0.7. Found: C 51.8; H 7.1; N 27.0%. $C_9H_{14}N_4O_2$. Calculated: C 51.4; H 6.7; N 26.7%.

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