SYNTHESIS AND THERMAL DECOMPOSITION OF HALOALKOXY-sym-TRIAZINES.

8.* SYNTHESIS AND THERMAL DECOMPOSITION OF 2-METHOXY(METHYLTHIO)-4-(2-CHLOROETHYLTHIO)-6-DIALKYLAMINO-sym-TRIAZINES

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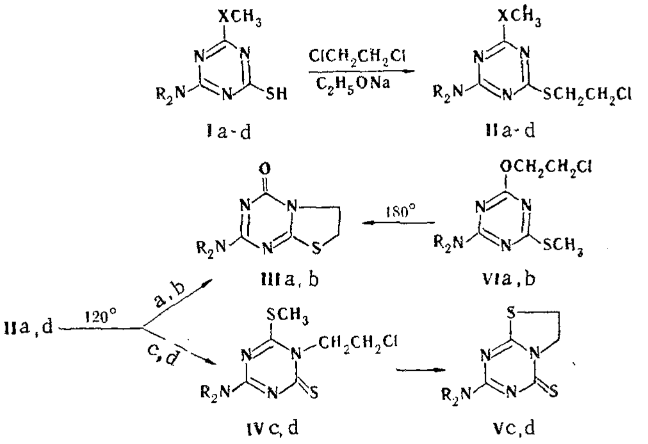
New 2-chloroethylthio derivatives of sym-triazine were obtained by the reaction of mercapto-sym-triazines and dichloroethane. It was established that these chlorides undergo cyclization to give 2-dialkylamino-4-oxo(thioxo)-4,5,6,7-tetrahydrothiazolo[1,2-a]-sym-triazines, the structure of which was confirmed by PMR and mass-spectral data, at moderate temperatures.

In the present research, which is a continuation of earlier studies of the thermolysis of haloalkoxy-sym-triazines [1-5], we studied the thermal decomposition of 2-methoxy(methylthio)-4-(2-chloroethylthio)-6-dialkylamino-sym-triazines (IIa-d), which were synthesized by the action of 1,2-dichloroethane on mercapto-sym-triazines (Ia-d).



a $R=CH_3$, $X=O$; b $R=C_2H_5$, $X=O$; c $R=CH_3$, $X=S$; d $R=C_2H_5$, $X=S$

When IIa-d are heated in refluxing toluene, they undergo intramolecular cyclization with the elimination of methyl chloride to give thiazolo-sym-triazine derivatives (IIIa, b and Vc, d).

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*See [7] for Communication 7.

TABLE 1. Characteristic Ion Peaks in the Mass Spectra of II, IV, and V

Compound	m/e values (intensities of the peaks, %)
IIc	266 (2), 264 (6), 229 (33), 202 (100), 155 (70), 139 (10), 96 (66), 71 (55), 70 (25)
IId	294 (12), 292 (26), 277 (24), 263 (45), 258 (26), 257 (46), 249 (16), 242 (22), 230 (100), 229 (52), 201 (26), 197 (20), 155 (18)
IVc	266 (0,7), 264 (2), 214 (100), 213 (20), 198 (14), 181 (48), 172 (12), 155 (20), 114 (15), 99 (18)
Vc	216 (10), 215 (14), 214 (100), 213 (15), 182 (10), 181 (60), 155 (18), 154 (15), 140 (16), 114 (18), 99 (28), 96 (30)
Vd	244 (12), 243 (14), 242 (100), 214 (15), 213 (52), 209 (30), 197 (32), 183 (16), 129 (24), 128 (24), 85 (26)

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TABLE 2. Characteristics of the Synthesized Compounds

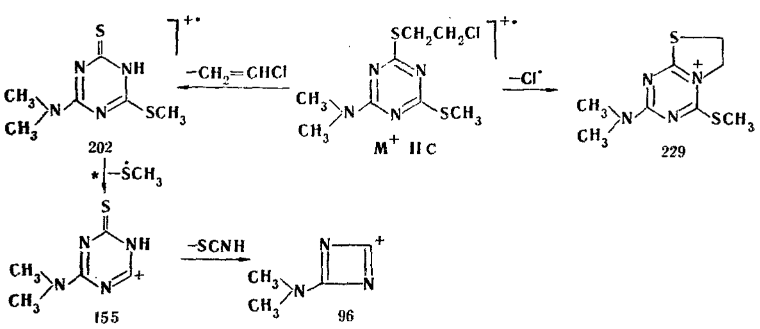
Compound	mp, °C	R_f	Found, %			Empirical formula	Calculated, %			Yield, %
			Cl	N	S		Cl	N	S	
IIa	70—71	0,63	14,6	22,3	13,3	$C_8H_{13}ClN_4OS$	14,3	22,5	12,9	81
IIb	Oil [a]	0,44	13,1	20,0	11,4	$C_{10}H_{17}ClN_4OS$	12,8	20,3	11,6	83
IIc	60—61	0,54	13,6	21,4	24,6	$C_8H_{13}ClN_4S_2$	13,4	21,2	24,2	93
IId	Oil [b]	0,39	12,4	19,0	21,7	$C_{10}H_{17}ClN_4S_2$	12,1	19,1	21,9	95

[a] This compound had n_D^{20} 1.5530 and d_4^{20} 1.0985. [b] This compound had n_D^{20} 1.5740 and d_4^{20} 1.2074.

It should be pointed out that IIc, d in contrast to IIa, b and the previously obtained 2-methoxy-4-(2-chloroethoxy)-6-dialkylamino-sym-triazines [4], are very easily converted by brief heating in toluene to IVc, d, which are then converted to Vc, d.

The structures of II-V were confirmed by a study of their mass spectra (see Table 1). The fragmentation of II under electron impact proceeds via the scheme established in [6]. A chlorine atom and a $CH_2{=}CHCl$ molecule are eliminated in the first step of the dissociative ionization of IIc to give ions with masses 229 and 202, respectively. The $[M - C_2H_3Cl]^+$ ion then subsequently loses an SCH_3 radical and an S=CNH molecule.

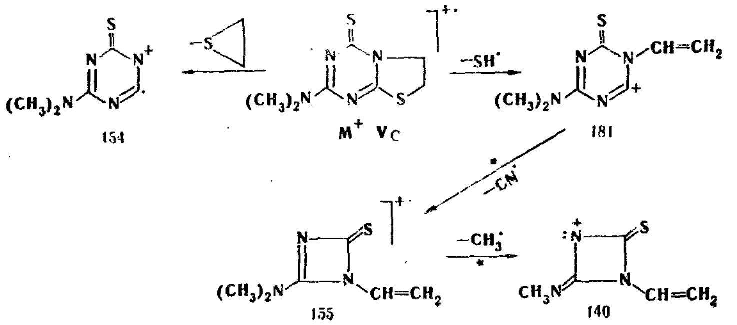
Scheme 1



Two multiplets centered at 3.8 and 3.4 ppm (an AA'BB' system) are observed in the PMR spectrum of IIc, in addition to singlet signals of $N{-}CH_3$ and SCH_3 groups.

The mass spectrum of IVc differs markedly from the spectrum of triazine IIc, in which the maximum peak is the $[M - CH_3Cl]^+$ pseudomolecular ion peak, the subsequent fragmentation of which is realized via the pathways that are characteristic for product Vc (see Scheme 2). The PMR spectrum of IVc contains, in addition to the multiplets observed for triazine IIc, two triplet signals at 4.83 and 4.0 ppm, which correspond to $N{-}CH_2$ and $ClCH_2$ groups.

Scheme 2



The dissociative ionization of Vc in the first steps of fragmentation is due to cleavage of a bond in the thiazoline ring (Scheme 2). Intense peaks of $[M - SH]^+$ (181),* $[M - SH - CN]^+$ (155), and $[M - SH, - CN, - CH_3]^+$ (140) ions are observed in the mass spectrum of Vc, along with molecular-ion peaks, which have the maximum intensity.

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*The numbers in the text and in the schemes are the m/e values of the ions.

Two triplets at 4.8 and 3.35 ppm, which are due to the protons of two methylene groups attached to the nitrogen and sulfur atoms, appear in the PMR spectrum of Vc, whereas the signal of the protons of the SCH_3 group observed in the spectrum of IVc vanishes.

The mass spectra of IIIa, b are identical to the mass spectra of the previously investigated 2-dialkylamino-4-oxothiazolino-sym-triazines [3].

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard. 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 50 eV. The systems for thin-layer chromatography (TLC) on Silufol UV-254 plates were CCl_4–acetone (4:1) (IIa-d) and acetone–hexane–CH_3COOH (16:3:1) (IIIa, b and IVc, d).

Compounds IIa-d. A 0.01-mole sample of Ia-d was added to 0.01 mole of sodium ethoxide obtained from 0.23 g (0.01 mole) of sodium and 9 ml of absolute ethanol, and the mixture was stirred for 15 min. Half of the alcohol was removed by distillation, 4 g (0.04 mole) of 1,2-dichloroethane was added, and the mixture was heated at 50-60°C for 3 h. It was then filtered, and the filtrate was evaporated to give IIa-d (see Table 2).

Compound IIIa. A 2.5-g (0.01 mole) sample of IIa was heated in 8 ml of toluene at 120°C for 8 h, and the precipitated crystals were removed by filtration to give 1.8 g (90%) of IIIa with mp 218-220°C. No melting-point depression was observed for a mixture with the thermolysis product obtained from VIa [3]. Found: C 42.6; H 5.3; S 15.8%. $C_7H_{10}N_4OS$. Calculated: C 42.3; H 5.0; S 16.1%. R_f 0.47.

The following compounds were similarly obtained. Compound IIIb, with mp 131-133°C, was obtained in 84% yield and was found to be identical to the substance obtained by thermolysis of triazine VIb with respect to a mixed-melting-point determination. Found: C 47.5; H 6.4; S 14.4%. $C_9H_{14}N_4OS$. Calculated: C 47.7; H 6.1; S 14.1%. R_f 0.64. Compound Vc, with mp 195-196°C, was obtained in 90% yield. Found: C 39.0; H 4.5; S 29.4%. $C_7H_{10}N_4S_2$. Calculated: C 39.3; H 4.7; S 29.9%. R_f 0.44. Compound Vd, with mp 172-174,C, was obtained in 85% yield. Found: C 44.9; H 6.0; S 26.8%. $C_9H_{14}N_4S_2$. Calculated: C 44.6; H 5.8; S 26.4%. R_f 0.33.

Compound IVc. A solution of 2.6 g (0.01 mole) of IIc in 10 ml of toluene was heated at 120°C for 15 min, after which the precipitate was removed by filtration to give 2.3 g (89%) of a product with mp 122-124°C (dec.). Found: Cl 13.1; N 21.3; S 12.2%. $C_8H_{13}ClN_4S_2$. Calculated: Cl 13.4; N 21.2; S 12.1%. R_f 0.34.

The same method was used to obtain IVd, with mp 80-82°C (dec.), in 82% yield. Found: Cl 11.9; N 19.4; S 11.1%. $C_{10}H_{17}ClN_4S_2$. Calculated: Cl 12.1; N 19.1; S 10.9%. R_f 0.31.

LITERATURE CITED

1. V. V. Dovlatyan, K. A. Éliazyan, and L. G. Agadzhanyan, Khim. Geterotsikl. Soedin., No. 2, 262 (1977).
2. V. V. Dovlatyan, K. A. Éliazyan, and A. V. Dovlatyan, Khim. Geterotsikl. Soedin., No. 7, 989 (1977).
3. V. V. Dovlatyan, K. A. Éliazyan, A. V. Dovlatyan, and R. G. Mirzoyan, Khim. Geterotsikl. Soedin., No. 10, 1420 (1977).
4. V. V. Dovlatyan and A. V. Dovlatyan, Khim. Geterotsikl. Soedin., No. 1, 124 (1979).
5. V. V. Dovlatyan and A. V. Dovlatyan, Khim. Geterotsikl. Soedin., No. 3, 411 (1980).
6. R. G. Mirzoyan, S. A. Saakyan, M. P. Demirchyan, A. V. Dovlatyan, and V. V. Dovlatyan, Armyansk. Khim. Zh., 32, 874 (1979).
7. V. V. Dovlatyan, V. A. Pivazyan, K. A. Éliazyan, R. G. Mirzoyan, and S. M. Saakyan, Khim. Geterotsikl. Soedin., No. 8, 1122 (1981).