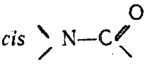
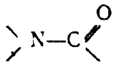
g (2 mmole) of freshly distilled benzoyl chloride; the mixture was stirred for 4 h at ca. 20°C, basified with NaOH solution, and extracted with chloroform. The extract was dried over magnesium sulfate. After solvent evaporation there was obtained 0.3 g (60%) of yellow crystals, mp 187-189°C (from a mixture of heptane and ethyl acetate). IR spectrum: 1618 (*cis*  $>N-C\overset{O}{\lessdot}$), 1593 cm^{-1} (*trans*  $>N-C\overset{O}{\lessdot}$) . PMR spectrum: 6.55 (1H, t, J = 2.6 Hz, 2-H) 5.77 (1H, m, J = 2.6 Hz, 3-H), 5.11 (1H, br g, J = 6.5 Hz, 4-H), 3.95 (1H, br d, J = 13.2 Hz, 6e-H), 3.37 (1H, dd, J = 13.2, 4.2, 2.8 Hz, 7-H), 1.31 (3H, d, J = 6.6 Hz, 4-CH_3), 1.09 (3H, d, J = 6.8 Hz, 7-CH_3). Found: C 75,6, H 7.2, N 10.7%. M^+ 254. $C_{16}H_{18}N_2O$. Calculated: C 75.6, H 7.1, N 11.0%. M 254.

LITERATURE CITED

1. B. A. Trofimov, A. S. Agavin, A. I. Mikhaleva, G. A. Kalabin, and E. G. Chebotareva, Zh. Org. Khim., 9, 2205 (1973).
2. L. X. Yakhontov, Usp. Khim., 49, 840 (1980).
3. B. A. Trofimov, S. E. Korostova, A. I. Mikhaleva, L. N. Sobenina, V. V. Shcherbakov, and M. V. Sigalov, Khim. Geterotsikl. Soedin., No. 2, 276 (1983).
4. A. I. Mikhaleva, N- VinylPyrroles [in Russian], Nauka, Moscow (1984), p. 14.
5. T. N. Borisova, N. D. Sergeeva, A. A. Espenbetov, D. S. Yufit, A. V. Varlamov, I. V. Eliseeva, and N. S. Prostatkov, Khim. Geterotsikl. Soedin., No. 9, 1200 (1986).

SYNTHESIS AND THERMAL DECOMPOSITION OF HALOGENALKOXY(THIO)-sym -TRIAZINES.

12.* SYNTHESIS AND CERTAIN TRANSFORMATIONS OF 2-DIALKYLAMINO-4-OXO-6-CYANODIHYDROTHIAZOLO-sym-TRIAZINES

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2-(2-Chloro-2-cyanoethylthio)-sym-triazines were synthesized by reacting mercapto-sym-triazines with 2,3-dichloropropionitrile in the presence of alkali and with 2-chloroacrylonitrile. Their rearrangement—cyclization leads to 2-dialkylamino-4-oxo-6-cyano-dihydrothiazolo-sym-triazones.

It has already been shown that 2-(2-chloroethylthio)-4-methoxy-6-dialkylamino- and also 2-(2-chloroethoxy)-4-methylthio -6-dialkylamino-sym-triazines rearrange during thermolysis into dihydrothiazolo-sym-triazines [1, 2].

The aim of the present work was to establish the path of the above reaction using as examples isomeric chlorocyanoethyl derivatives, whose cyclization would lead to cyanodihydrothiazolo-sym-triazines. They are not only of interest as physiologically active compounds, but can also serve as convenient starting compounds for the synthesis of new functionally substituted dihydrothiazolo-sym-triazines.

The above chlorocyanoethylthio derivatives can be obtained by reacting mercapto-sym-triazines with 2,3-dichloropropionitrile in the presence of alkali and by their chlorocyanoethylation by 2-chloroacrylonitrile. It was found that in both cases not isomeric, but identical compounds, 2-(2-chloro-2-cyanoethylthio)-sym-triazines, are obtained. Bearing in mind the pronounced tendency of 2,3-dichloropropionitrile to undergo dehydrochlorination reactions by the action of alkaline reagents [3], it can be assumed that in the reaction of mercapto-sym-triazines with this halogenonitrile in the presence of an alkali, first a dehydrochlorina-

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*For communication 11, see [7].

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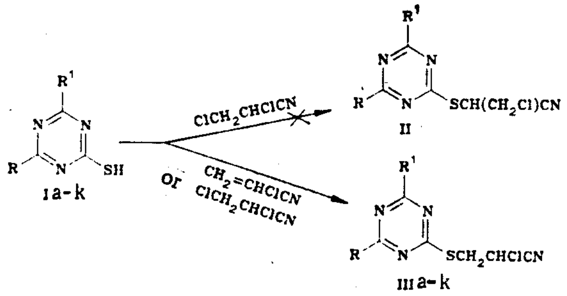
TABLE 1. Characteristics of Synthesized Compounds

Compound	mp, °C	R_f	Found, %			Empirical formula	Calculated, %			Yield, %
			Cl	N	S		Cl	N	S	
IIIa	110–112	0,45	13,1	25,7	11,9	$C_9H_{12}ClN_5OS$	12,9	25,6	11,7	86
IIIb	51–53	0,32	12,0	23,1	10,9	$C_{11}H_{16}ClN_5OS$	11,8	23,2	10,6	79
IIIc	115–117	0,41	13,2	25,2	11,5	$C_9H_{12}ClN_5OS$	12,9	25,6	11,7	81
IIId	92–93	0,46	12,4	24,4	22,3	$C_9H_{12}ClN_5S_2$	12,3	24,2	22,1	82
IIIe	54–56	0,39	11,3	22,2	20,4	$C_{11}H_{16}ClN_5S_2$	11,2	22,0	20,2	83
IIIf	118–119	0,40	12,4	24,5	22,0	$C_9H_{12}ClN_5S_2$	12,3	24,2	22,1	80
IIIg	85–86	0,30	12,1	29,5	11,3	$C_{10}H_{15}ClN_6S$	12,4	29,3	11,2	86
IIIh	51–52	0,50	10,5	24,7	9,1	$C_{14}H_{23}ClN_6S$	10,4	24,5	9,3	86
IIIi	109–111	0,32	12,5	29,0	11,5	$C_{10}H_{15}ClN_6S$	12,4	29,3	11,2	86
IIIj	90–92	0,48	11,6	28,1	11,0	$C_{11}H_{17}ClN_6S$	11,8	28,0	10,6	82
IIIk	75–77	0,44	11,5	26,5	10,3	$C_{12}H_{19}ClN_6S$	11,3	26,7	10,2	64

tion, and then by the action of the 2-chloroacrylonitrile formed, the chlorocyanoethylation of the initial mercapto deviative takes place.

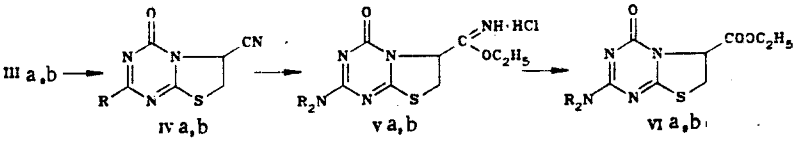


I, IIIa-c R=OCH_3, d-f R=SCH_3; a,d R'=$N(CH_3)_2$, b,e R'=$N(C_2H_5)_2$, c,f R'=NHC_2H_5; g R=R'=$N(CH_3)_2$; h R=R'=$N(C_2H_5)_2$, i R=R'=NHC_2H_5, j R=NHC_2H_5, R'=NHC_3H_7-*i*, k R=R'=NHC_3H_7-*i*

Compounds IIIa-k thus obtained cyclize during thermolysis to form cyanodihydrothiazolo-sym-triazines (IVa, b).

In contrast to 4-methoxy-6-dialkylamino derivatives, the corresponding alkylamino derivatives possibly react during thermolysis in different directions, which makes the isolation of the individual rearrangement products difficult.

By the action of ethanol and hydrogen chloride on suspensions of cyanodihydrothiazolo-sym-triazines in ether under Pinner reaction conditions, the hydrochlorides of iminoethyl ethers Va, b are obtained, which are decomposed by an aqueous solution of sodium bicarbonate into esters VIa, b.



IV–VI a R=CH_3; b R=C_2H_5

EXPERIMENTAL

The IR spectra were run on a UR-20 spectrophotometer in mineral oil, the PMR spectra on a Varian T-60 spectrometer (60 MHz) in deuteropyridine, using TMS as internal standard. The mass spectra were obtained on an MX-1303 spectrometer with direct introduction of the sample to the source, at an energy of ionizing electrons of 50 eV [4, 5]. The TLC was carried out on Silufol UV-254 plates in a 1:1 acetone–hexane system, with development by iodine vapors.

2-(2-Chloro-2-cyanoethylthio)-4-methoxy(methylthio,amino)-6-alkyl(dialkyl)amino-sym-triazines (IIIa-k). A 1-g portion (11 mmoles) of 2-chloropropionitrile is added dropwise, with cooling to 0°C and stirring, to a suspension of 0.01 mole of the corresponding 2-mercaptotriazine Ia-k [6] in 20 ml of water, and after 15 min, 0.44 g (11 moles) of NaOH in 2 ml of water is added. The reaction mixture is stirred for 1 h and the product is filtered, washed with water, and recrystallized from a 1:1 hexane-benzene mixture. Compounds IIIe and h are extracted with ether, and after drying the extract over $MgSO_4$, the solvent is distilled, and the residue treated with petroleum ether. The characteristics of compounds IIIa-k are given in Table 1.

Thermolysis of Compounds IIIa, b. A suspension of 2.7 g (0.01 mole of compound IIIa in 5 ml of absolute toluene is boiled for 5 h. Toluene is distilled off, the residue is treated with 25 ml of absolute ether, and compound IVa is filtered. Yield, 2.1 g (94%), mp 190-192°C. IR spectrum: 1610-1530 (C=N), 1705 (C=O conj), 2250 cm^{-1} (C≡N). PMR spectrum: 2.95 and 2.90 [6H, two s, $N(CH_3)_2$]; 3.6-4.3 (2H, m, SCH_2); 6.2 ppm (1H, d, d, CH). Found: N 31.6, S 14.8%. M 223 (mass-spectrometrically. $C_8H_9N_5OS$. Calculated: N 31.4, S 14.3%. M 223.26. R 0.53.

Compound IVb was obtained in a similar way in a yield of 83% mp 144-145°C. IR spectrum 1580, 1545, 1530 (C=N), 1697 (C=O), 2250 cm^{-1} (C≡N). PMR spectrum: 1.03-1.1 [6H], two triplets, methyl protons of $N(C_2H_5)_2$, 3.44-3.51 ([4H, two q, methylene protons of $N(C_2H_5)_2$]; 3.72-4.33 (2H, m. SCH_2); 6.28 ppm (1H, f, d, d, CH). Found: N 27.5, S 13.0%. M 251. $C_{10}H_{13}N_5OS$. Calculated: N 27.9, S 12.7, M 251.32. R_f 0.41.

Hydrochlorides of Iminoethyl Ethers (Va, b). A current of dry hydrogen chloride is passed to saturation through a suspension of 5 mmoles of compound IVa, b and 0.28 g (6 mmoles) of absolute ethanol in 10 ml of absolute ether. The mixture is allowed to stand overnight at 0°C, the compounds Va, b are filtered and thoroughly washed with 30 ml of absolute ether. Thus compound Va [yield 86%, T_{dec} 218-219°C. Found: Cl 11.9, N 23.1%. $C_{10}H_{16}ClN_5O_2S$. Calculated: Cl 11.6, N 22.9%] and Vb [yield 82%, T_{dec} 99-100°C. Found: Cl 11.0, N 20.8%. $C_{12}H_{20}ClN_5O_2S$. Calculated: Cl 10.6, N 21.0%] are obtained.

Ethyl Esters (VIab). A solution of 5 mmoles of compounds Va, b in 5 ml of water is neutralized by sodium bicarbonate to pH 7. Compounds VIa, b are filtered and washed with 5 ml of water. Compounds VIa [yield 80%, mp 175-176°C. Found: N 20.9, S 12.3%. $C_{10}H_{14}N_4O_3S$. Calculated: N 20.7, S 11.9%] and VIb [yield 79%, mp 155-156°C. Found: 19.2, S 10.4%. $C_{12}H_{18}N_4O_3S$. Calculated: N 18.8, S 10.7%] are obtained.

LITERATURE CITED

1. V. V. Dovlatyan, K. A. Éliazyan, S. M. Saakyan, and R. G. Mirzoyan, Khim. Geterotsikl. Soedin., No. 9, 1275 (1981).
2. V. V. Dovlatyan, A. V. Dovlatyan, K. A. Éliazyan, and R. G. Mirzoyan, Khim. Geterotsikl. Soedin., No. 10, 1420 (1977).
3. H. Brintzinger, K. Pfannsteil, H. Koddenbusch. Angew. Chem., 60, 311 (1948).
4. R. G. Mirzoyan, S. M. Saakyan, P. B. Terent'ev, K. A. Éliazyan, and V. V. Dovlatyan, Khim. Geterotsikl. Soedin., No. 9, 1268 (1982).
5. R. G. Mirzoyan, S. M. Saakyan, M. P. Demirchyan, P. B. Terent'ev, V. V. Dovlatyan, and A. V. Dovlatyan, Khim. Geterotsikl. Soedin., No. 1, 124 (1982).
6. French Patent No. 1339236; Chem. Abstr., 60, 2985 (1963).