REACTIONS OF DERIVATIVES OF AMINO- AND MERCAPTO-sym-TRIAZINES WITH ETHYLENEIMINE AND ETHYLENEDIAMINE

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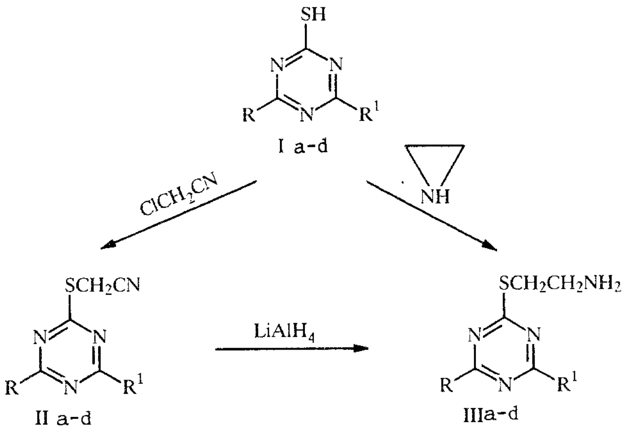
It was established that the action of ethyleneimine on mercapto- and cyanamino-sym-triazines gives 2-aminoethylthio- and iminoimidazolidinyl-sym-triazines. The latter are also obtained from salts of cyanamino-sym-triazines with ethylenediamine by heating. The 2-aminoethylthio derivatives were tosylated and phenylcarbamoylated.

The aim of this research was to study the reaction of derivatives of mercapto- and amino-sym-triazines with ethyleneimine and ethylenediamine, which led to the synthesis of 2-aminoethylamino(thio)-sym-triazines, which are of definite interest as possible herbicides and starting substances for the synthesis of new derivatives of sym-triazines.

It was found that amino-sym-triazines do not react with ethyleneimine either at room temperature or with heating, while mercapto-sym-triazines form the expected 2-aminoethylthio-sym-triazines IIIa-d. Compounds IIIa-d are also obtained by alternative synthesis by reduction of cyanomethylthio derivatives IIa-d, obtained by the action of chloroacetonitrile on the corresponding mercaptides.



Since mercapto-sym-triazines are SH acids [2, 3], one might have assumed that NH acids of the sym-triazine series, which, as we have previously demonstrated [4, 5], cyanamino-sym-triazines are, could or would react with ethylenediamine.

In fact, these compounds react readily with ethyleneimine; however, instead of the expected 2-aminoethyl derivatives, sym-triazines Va, b are formed. In the series of amino-, mercapto-, and cyanamino-sym-triazines only the latter react with ethylenediamine to give the corresponding salts VIa, b, which eliminate ammonia and are converted to Va, b when they are heated.

Armenian Agricultural Institute, Yerevan 375200. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 818-821, June, 1993. Original article submitted November 21, 1990.

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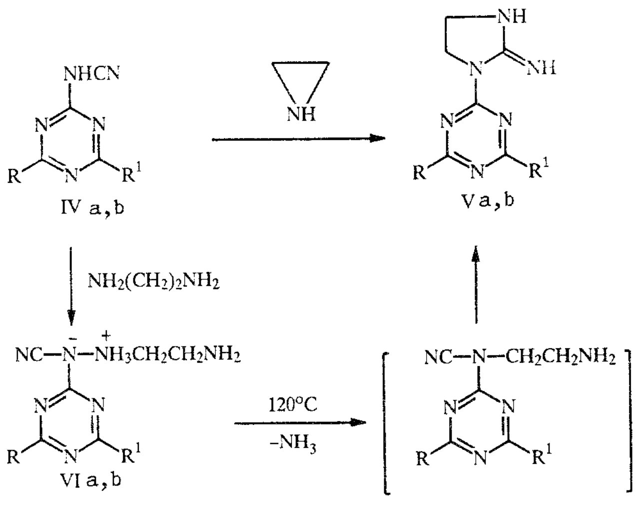
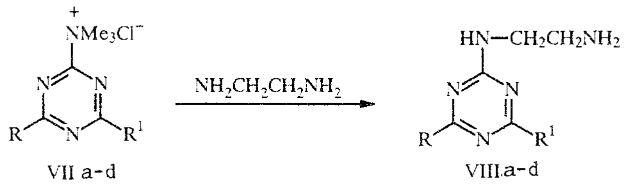
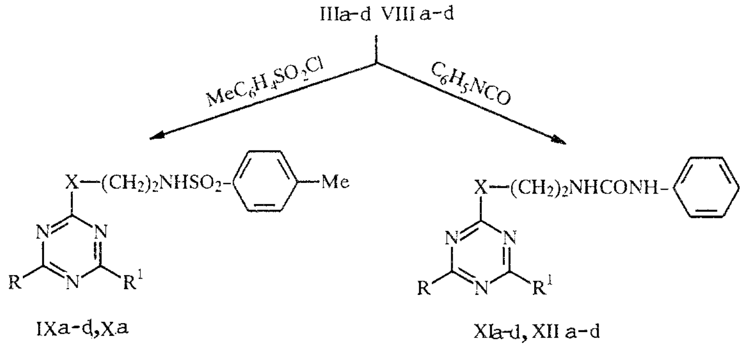


Ethylenediamine in this case behaves like a monoacidic base, and one amino group therefore generally remains unaffected, virtually excluding the formation of disubstituted derivatives, during the formation of the salts, as well as in the case of alkylation of the cyanamino-sym-triazines with ethyleneimine. The reaction of trimethyl-sym-triazinylammonium salts with ethylenediamine, as a result of which only 2-aminoethylamino-sym-triazines are obtained, also constitutes evidence in favor of a decrease in the reactivity of this group.



I—IIIa $R=R^1=NHC_2H_5$; b$R=NHC_2H_5$, $R^1=NHC_3H_7$-iso; c $R=R^1=NHC_3H_7$-iso: d $R=R^1=N(CH_3)_2$;
VII, VIIIa $R=R^1=N(CH_3)_2$; b$R=R^1=N(C_2H_5)_2$; c $R=R^1=NHC_2H_5$; d$R=C_2H_5NH$; $R^1=NHC_3H_7$- iso

Tosylation and phenylcarbamoylation were accomplished at the site of the free amino group.



IXa-d, XIa-d, X = S; Xa, XIIa-d X = NH

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ or d_6-acetone were recorded with a Varian T-60 spectrometer (60 MHz) with TMDS as the internal standard. The mass spectra were obtained with an MKh-1303 spectrometer; the

TABLE 1. 2-(2'-Aminoethylthio)-4,6-disubstituted sym-Triazines IIIa-d and 2-(2'-Aminoethylamino)-4,6-disubstituted sym-Triazines VIIIa-d

Compound	Empirical formula	mp, °C	R_f	Yield, %
IIIa	$C_9H_{18}N_6S$	95...96	0,36	93
IIIb	$C_{10}H_{20}N_6S$	80...82	0,43	95
IIIc	$C_{11}H_{22}N_6S$	52...55	0,40	95
IIId	$C_9H_{18}N_6S$	105...107	0,41	91
VIIIa	$C_9H_{19}N_7$	129...130	0,39	89
VIIIb	$C_{13}H_{27}N_7$	58...60	0,50	72
VIIIc	$C_9H_{19}N_7$	33...34	0,44	80
VIIId	$C_{10}H_{21}N_7$	48...50	0,33	70

TABLE 2. 2-(2'-Tolylsulfonamidoethylthio)-4,6-bis(substituted)-sym-triazines IXa-d and Xa

Compound	Empirical formula	mp, °C	R_f	Yield, %
IXa	$C_{16}H_{24}N_6O_2S_2$	86...87	0,35	78
IXb	$C_{17}H_{26}N_6O_2S_2$	52...54	0,40	75
IXc	$C_{18}H_{28}N_6O_2S_2$	63...65	0,55	70
IXd	$C_{16}H_{24}N_6O_2S_2$	167...169	0,50	70
Xa	$C_{17}H_{27}N_7O_2S_2$	140...142	0,43	94

samples were introduced directly into the source, and the ionizing-electron energy was 50 eV. Analysis by TLC was carried out on Silufol UV-254 plates.

The characteristics of the synthesized compounds are presented in Tables 1-3.

The results of elementary analysis for C, H, N, and S were in agreement with the calculated values.

2-(2'-Aminoethylthio)-4,6-bis(dimethylamino)-sym-triazine (IIId, $C_9H_{18}N_6S$). A. A 0.54-ml (0.02 mole) sample of ethyleneimine was added with cooling to a suspension of 2.0 g (0.01 mole) of Id in 15 ml of dioxane, and the reaction mixture was heated in an ampul for 5-6 h at 70-80°C. It was then filtered, and the dioxane was removed by fractional distillation in vacuo at 50-52°C (100 mm). The residue was treated with 10-15 ml of petroleum ether, and the product was isolated by suction filtration. The yield of the product, which had mp 108-110°C and R_f 0.41 [heptane–acetone (1:2)], was 2.2 g (91%). Found: M^+ 242. Calculated: M 242.35. PMR spectrum: 3.03 [12H, s, $(NMe_2)_2$] and 3.2-3.5 ppm (4H, m, CH_2CH_2).

B. Reduction was realized in accordance with the description presented in [5]. The product, which had mp 107-109°C and R_f 0.41, was obtained in 70% yield. The starting IIa-d were obtained in accordance with the description presented in [1].

2-(2'-Aminoethylamino)-4,6-bis(dimethylamino)-sym-triazine (VIIIa, $C_9H_{19}N_7$). A 2.6-g (0.01 mole) sample of VIIa was added with stirring and cooling to −5°C to 0°C to 10 ml of ethylenediamine, and the reaction mixture was maintained at 20°C for 24 h. The excess ethylenediamine was removed by fractional distillation in vacuo (30 mm) at 35-37°C, and the residue was extracted with 20 ml of absolute benzene. Evaporation gave 2 g (89%) of VIIIa with mp 129-130°C. PMR spectrum: 2.0 (2H, s, NH), 3.05 [12H, s, $(NMe_2)_2$], 3.4-4.0 (4H, m, CH_2CH_2), and 5.3 ppm (1H, broad s, NH).

Reaction of Cyanamino-sym-triazine IVa with Ethylenediamine (VIa, $C_{10}H_{21}N_9$). A mixture of 2.1 g (0.01 mole) of IVa and 2.4 g (0.04 mole) of ethylenediamine in 30 ml of dioxane was stirred for 24 h at 22°C. The precipitate was removed by filtration and washed with 30 ml of absolute ether to give 2.45 g (92%) of VIa with mp 155-157°C.

Compound VIb, with mp 62-65°C, was similarly obtained in 82% yield.

Iminoimidazolidinyl-sym-triazine (Va, $C_{10}H_{18}N_8$). A. A suspension of 2.1 g (0.01 mole) of IVa and 1 g (0.023 mole) of ethyleneimine in 20 ml of dioxane was heated in an ampul for 7 h at 70°C, after which it was filtered. The filtrate was washed with 10-15 ml of ether to give 1.85 g (74%) of Va with mp 240-242°C and R_f 0.42. IR spectrum: 1510, 1550 (conjugated C=N); 1680 (C=NH); 1160 cm^{-1} (NH). Found: M^+ 250.

TABLE3.N-Phenyl-N'-[4,6-bis(substituted)-sym-triazin-2-yl]mercaptoethylureasXIa-d and N-Phenyl-N'-[4,6-bis(substituted)-sym-triazin-2-yl]aminoethylureas (XIIa-d)

Compound	Empirical formula	mp, °C	R_f	Yield, %
XIa	$C_{16}H_{23}N_7OS$	103...105	0,43	89
XIb	$C_{17}H_{25}N_7OS$	134...136	0,40	83
XIc	$C_{18}H_{27}N_7OS$	68...70	0,46	89
XId	$C_{16}H_{23}N_7OS$	168...170	0,35	91
XIIa	$C_{16}H_{24}N_8O$	147...148	0,41	86
XIIb	$C_{20}H_{32}N_8O$	100...102	0,41	80
XIIc	$C_{16}H_{24}N_8O$	125...127	0,49	85
XIId	$C_{17}H_{26}N_8O$	58...60	0,47	78

B. A 2.67-g (0.01 mole) sample of VIa was refluxed for 8 h (until ammonia evolution ceased) in 15 ml of toluene, after which the mixture was filtered, treated with water, and filtered again. The yield of Va, which had mp 240-242°C, was 2.37 g (94%). Found: M^+ 250. Calculated: M 250.32.

Compound Vb, which had mp 198-200°C, was similarly obtained.

N-Phenyl-N'-[4,6-bis(dimethylamino)-sym-triazin-2-yl]mercaptoethylurea (XId, $C_{16}H_{23}N_7OS$). A mixture of 2.42 g (0.01 mole) of IIId and 1.19 g (0.01 mole) of freshly distilled phenyl isocyanate in 10 ml of absolute benzene in the presence of two drops of pyridine was allowed to stand at 20-25°C for 24 h. The precipitated XId was removed by filtration and washed with 5 ml of hexane to give 3.29 g (91%) of a product with mp 168-170°C and R_f 0.35 [acetone–hexane (1:1)]. PMR spectrum: 3.05 [12H, s, $(NMe_2)_2$], 3.6 (2H, t, NCH_2), 4.0 (2H, t, CH_2), 5.0 (1H, t, $NHCH_2$), 7.8 (1H, s, NHPh), and 6.9-7.4 ppm (5H, m, Ph).

2-(2'-Tolylsulfonamidoethylthio)-4,6-bis(dimethylamino)-sym-triazine (IXd, $C_{16}H_{24}N_6O_2S_2$). A 1.9-g (0.01 mole) sample of p-toluenesulfonyl chloride was added to a solution of 2.42 g (0.01 mole) of VIIId in 10 ml of acetone, after which 0.7 g (0.01 mole) of 84% potassium hydroxide in 3 ml of water was added dropwise with stirring and cooling to −5°C to 0°C. The reaction mixture was then allowed to stand for 20 h at 20-25°C, 20 ml of ice water was added, and IXd was removed by filtration. The yield of the product, which had mp 167-169°C and R_f 0.50 [acetone–hexane (4:5)], was 2.78 g (70%). PMR spectrum: 2.35 (3H, s, CH_3), 3.1 [12H, s, $(NMe_2)_2$], 3.1-3.4 (4H, m, CH_2CH_2), 6.3 (1H, broad s, NH), and 7.2-7.8 ppm (4H, m, Ar).

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