

2-Chlorophenylsulfonyl Isocyanate (VII). A 4.11-g (214 mmole) sample of sulfonamide X was dissolved in 35 ml of chlorobenzene, and traces of water were removed by azeotropic distillation. The mixture was cooled to 100°C, 0.85 g (8.6 mmole) of n-butyl isocyanate was added, the mixture was heated to the boiling point, and 5 g (50 mmole) of phosgene was passed into it in the course of 1 h. The n-butyl isocyanate and solvent were then removed by distillation, and the product was distilled in vacuo to give 4 g (86%) of isocyanate VII with bp 160-164°C (14 mm). Mass spectrum: 217 (20) [M]<sup>+</sup>, 175 (54) [M - NCO]<sup>+</sup>, 111 (100) [M - SO<sub>2</sub>NCO]<sup>+</sup>.

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#### CONDENSATION OF ETHANOLAMINE WITH CHLORO-sym-TRIAZINES

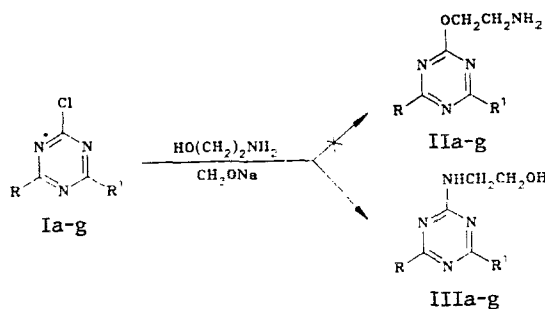
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2,2-Aminoethoxy-sym-triazines have been synthesized by reduction of cyanomethoxy-sym-triazines or by the reaction of sodium 2-aminoethoxide with quaternary ammonium salts of sym-triazines. Their structures have been established by PMR and mass spectral examination.

There are conflicting literature reports concerning the structure of the products of reaction of chloro-sym-triazines I with ethanolamine. Thus, according to [1], the indicated reaction in ethanolamine medium in the presence of an equimolar amount of sodium methoxide leads to the 2-aminoethoxy derivatives (II).

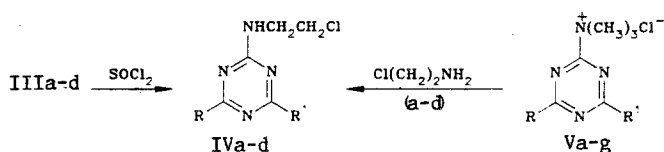
By contrast, other authors [2, 3] consider that the compounds obtained are the 2-hydroxyethylamines III.



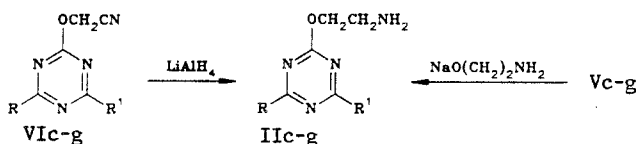
I-III a R=OCH<sub>3</sub>, b R=SCH<sub>3</sub>, c R=N(CH<sub>2</sub>)<sub>2</sub>, d, e R=NHC<sub>6</sub>H<sub>5</sub>, f R=NHC<sub>3</sub>H<sub>7</sub>-iso, g R=N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>; a-c R<sup>1</sup>=N(CH<sub>3</sub>)<sub>2</sub>, d R<sup>1</sup>=NHC<sub>2</sub>H<sub>5</sub>, e, f R<sup>1</sup>=NHC<sub>3</sub>H<sub>7</sub>-iso, g R<sup>1</sup>=N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>

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With the aim of determining the true structure of these compounds we have repeated their synthesis according to the literature. Independently of the method of synthesis we have found the products to be the 2-hydroxyethylamino-sym-triazines (IIIa-g). When treated with thionyl chloride IIIa-d are converted to the corresponding 2-chloroethylamino-sym-triazines. The structure of the latter was confirmed by an independent synthesis from the triazinyl quaternary ammonium salts [4] with chloroethylamine in chloroform, also at room temperature.



The data given in [1] was also unambiguously disproved by the following result: reduction of the cyanomethoxy-sym-triazines [5], previously obtained by us, gave the 2-aminoethoxy-sym-triazines which were not identical to those described in the quoted patent.



The structures of IIc-g and IIIc-g were confirmed by PMR and mass spectral data. For IIc, g ( $R=R^1 = \text{N(CH}_3)_2$  or  $\text{N(C}_2\text{H}_5)_2$ ) the triplet NMR signals for the  $\text{OCH}_2$  and  $\text{NCH}_2$  protons appeared at 4.32 and 3.05 ppm, the former chemical shift showing that the corresponding methyleneoxy group was linked to the triazine ring. By contrast, compounds IIIc-e, g showed methylene group proton signals as a multiplet in the region 3.4-3.9 ppm (in IIIId,e,g obscured by the quadruplet signal of the  $\text{NCH}_2$  group of the ethylamino substituents) thus confirming their 2-hydroxyethyl structure.

Mass spectrometry also gives unambiguous evidence for II and III. The first stages of molecular ion dissociation for IIc are fission of  $\gamma$ - and  $\beta$ -exocyclic bonds to eliminate OH and  $\text{CH}_2\text{OH}$  or  $\text{NH}_2$ ,  $\text{CH}_2\text{NH}_2$ , and  $\text{NC}_2\text{H}_5$  (with loss of an acrylic alcohol molecule via a McLafferty rearrangement).

On this basis it is clear that 2-aminoethoxy-sym-triazines have been characterized for the first time. Thanks to the presence of the primary amino group these compounds can be used as starting materials for the synthesis of novel, physiologically active species.

#### EXPERIMENTAL

PMR Spectra were recorded on a Varian T-60 (60 MHz) instrument in  $\text{CDCl}_3$  with TMS internal standard. Mass spectra were obtained on an MX-1303 spectrometer at an ionization energy of 50 eV with direct introduction of the sample into the source. TLC Analysis was performed on Silufol UV-254 plates using hexane-acetone-water 10:5:4 (compounds IIa-g) or heptane-acetone (IVa-d).

Parameters for these compounds are given in Table 1. Elemental analytical data was in agreement with that calculated.

2,2'-Hydroxyethylamino-4,6-bisdiethylamino-sym-triazine (IIIg,  $\text{C}_{13}\text{H}_{26}\text{N}_6\text{O}$ ) [1] was obtained from sodium (1.15 g, 50 mmole), methanol (40 ml), ethanolamine (39.6 g, 650 mmole) and the sym-triazine Ig (13.6 g, 52 mmole) in 9.8 g yield (70%) with bp  $153^\circ\text{C}$  (0.01 mm Hg), mp  $70-71^\circ\text{C}$  (lit. data  $71-73^\circ\text{C}$ ),  $R_f$  0.41 (acetone-heptane 1:1), and  $M^+$  (found = 282, calculated = 282.39). PMR Spectrum: 1.2 (12H, t,  $\text{CH}_3\text{CH}_2$ ); 3.6 (8H, q,  $\text{CH}_2\text{CH}_3$ ); 3.4-3.9 (4H, m,  $\text{NCH}_2\text{CH}_2\text{O}$ ) 4.9 and 5.3 ppm (each 1H, br s, OH and NH). The parameters for IIIa-f are given in Table 1.

2,2'-Aminoethoxy-4,6-bisdiethylamino-sym-triazine (IIg,  $\text{C}_{13}\text{H}_{26}\text{N}_6\text{O}$ ) [6]. A solution of 2-cyanomethoxy-4,6-bisdiethylamino-sym-triazine (2.8 g, 10 mmole) in absolute ether (20-25 ml) was added dropwise with stirring to a solution of lithium aluminum hydride (0.38 g, 10 mmole) in absolute ether (10 ml) at  $-10$  to  $-5^\circ\text{C}$ . The mixture was stirred for 1 h at  $0^\circ\text{C}$ , cooled to  $-5^\circ\text{C}$ , and water (0.4 ml), NaOH solution (15%, 3.8 ml) and then water (2 ml) were added successively. Stirring was continued for 30 min at  $0^\circ\text{C}$ , the solid was filtered off and washed

TABLE 1. 2,2'-Aminoethoxy- (IIc-f) and 2,2'-Hydroxyethylamino-sym-Triazines (IIIa-f).\*

Compound	Empirical formula	mp, °C	R <sub>f</sub>	Yield %
IIc	C <sub>9</sub> H <sub>18</sub> N <sub>6</sub> O	viscous syrup	0.42	70
IId	C <sub>9</sub> H <sub>18</sub> N <sub>6</sub> O	117...119	0.50	90
IIe	C <sub>10</sub> H <sub>20</sub> N <sub>6</sub> O	70...72	0.38	83
IIf	C <sub>11</sub> H <sub>22</sub> N <sub>6</sub> O	58...60	0.41	84
IIIa	C <sub>8</sub> H <sub>15</sub> N <sub>6</sub> O <sub>2</sub>	109...111	0.40	76
IIIb	C <sub>8</sub> H <sub>15</sub> N <sub>6</sub> OS	150...152	0.32	73
IIIc	C <sub>9</sub> H <sub>18</sub> N <sub>6</sub> O	113...115	0.48	78
IIId	C <sub>9</sub> H <sub>18</sub> N <sub>6</sub> O	88...90	0.35	70
IIIe	C <sub>10</sub> H <sub>20</sub> N <sub>6</sub> O	75...76	0.32	75
IIIf	C <sub>11</sub> H <sub>22</sub> N <sub>6</sub> O	88...89	0.43	76

\*Mass spectrum, m/z (Relative I, %): IIc 226 (18), 210 (66), 195 (50), 183 (100), 167 (90), 152 (50), 138 (30), 124 (20), 114 (20), 96 (20); IIIc 226 (44), 211 (24), 195 (100), 182 (94), 167 (38), 153 (26), 138 (30), 96 (20).

with ether (10-15 ml). The ether layer was dried (MgSO<sub>4</sub>) and solvent evaporated off to give IIg (2.2 g, 78%) as a viscous oil with  $n_D^{20}$  1.5240,  $d_4^{20}$  1.0868 (in agreement with data in [2]), and R<sub>f</sub> 0.47 (hexane-acetone-water 10:5:4). Found: M<sup>+</sup> 282. Calculated: M 292.39. PMR Spectrum: 1.2 (12H, t, CH<sub>3</sub>CH<sub>2</sub>); 2.0 (2H, s, NH<sub>2</sub>); 3.05 (2H, m, CH<sub>2</sub>NH<sub>2</sub>); 3.58 (8H, q, CH<sub>2</sub>CH<sub>3</sub>); 4.32 ppm (2H, t, OCH<sub>2</sub>).

B. Sodium aminoethoxide was prepared from sodium (0.23 g, 10 mmole) in ethanolamine (3 ml), washed twice with 5 ml aliquots of dioxane and decanted. After addition of dioxane (10 ml), cooling to 10°C and stirring, compound Vg (3.2 g, 10 mmole) was added and the mixture was stirred at 20°C for 24 h. The dioxane was distilled off (45°C, 50 mm) and the residue treated with water (5 ml). The oily layer was extracted with chloroform, dried (MgSO<sub>4</sub>), and solvent distilled off to give IIg (2.1 g, 74.5%) as a viscous syrup with  $n_D^{20}$  1.5241,  $d_4^{20}$  1.0867. The product was identical to that prepared in A (PMR and mass spectra).

2,2'-Chloroethylamino-4,6-bisdimethylamino-sym-triazine (IVc, C<sub>9</sub>H<sub>17</sub>ClN<sub>6</sub>). A. Compound IIIc (2.26 g, 10 mmole) was added portionwise with stirring to thionyl chloride (10 ml) at 0°C and the reaction mixture was held for 24 h at 20°C. Excess thionyl chloride was distilled off and the residue was washed with petroleum ether and decanted. After addition of water (10 ml) the solution was neutralized (10% NaOH) to pH 8-9 and the precipitated solid filtered off to give IVc (1.45 g, 60%) with mp 58-60°C. Found: M<sup>+</sup> 244/246. Calculated: M 244.73.

B. 2-Chloroethylamine (3.2 g, 40 mmole) was obtained with stirring at 0°C from the hydrochloride (4.64 g, 40 mmole) and NaOH (1.6 g, 40 mmole) in dry chloroform (20 ml). Compound Vc (2.6 g, 10 mmole) and the powdered NaOH (0.4 g, 10 mmole) were added and the mixture stirred at 20°C for 4-5 h. NaCl was filtered off and the filtrate was evaporated and the dry residue was treated with water. IVc was filtered off (1.6 g, 65%) with mp 58-60°C. The melting point of a sample mixed with that from method A was not depressed.

Compound IVa (C<sub>8</sub>H<sub>14</sub>ClN<sub>5</sub>O, yield 90%, mp 125-127°C, R<sub>f</sub> 0.5), IVc (C<sub>8</sub>H<sub>14</sub>ClN<sub>5</sub>, yield 80%, mp 132-133°C, R<sub>f</sub> 0.46) and IVd (C<sub>9</sub>H<sub>17</sub>ClN<sub>6</sub>, yield 91%, viscous syrup, R<sub>f</sub> 0.45) were obtained similarly.

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