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INVESTIGATIONS INTO FUNCTIONALLY SUBSTITUTED AZINES.

7.* A NEW APPROACH TO THE SYNTHESIS OF 2-(2-AMINOETHOXY)-sym-TRIAZINE

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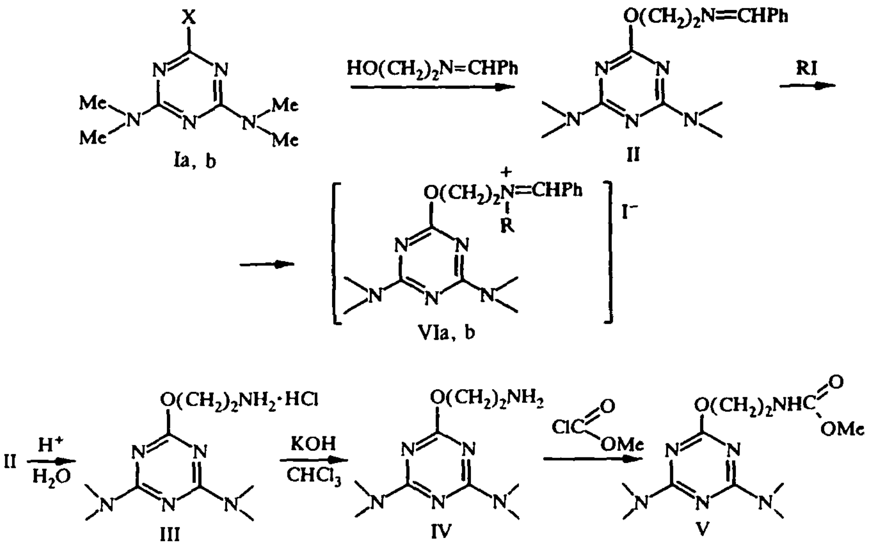
A new approach to the synthesis of 2-(2-aminoethoxy)-sym-triazine, based on the isolation and hydrolysis of benzylidenaminoethoxy-sym-triazine, was developed.

Methods of isolation and some conversions of 2-(2-aminoethoxy)-sym-triazines were described previously [2, 3]. The present paper presents a new effective and convenient method for the synthesis of compounds of this series. The method derives from the fact that a derivative of ethanolamine reacts with the chloro-sym-triazine (Ia) or the trimethyl-sym-triazinylammonium chloride (Ib) as the N-benzal derivative, and not as the sodium aminoethoxide. The protection of the amino group of ethanolamine by benzaldehyde suppresses side reactions and guarantees high yields of the intermediate benzal derivative (II), identified as the quaternary immonium salts — the alkyl iodides (VIa,b).

In an acidic medium, compound (II) is readily converted, in good yield, to the 2-(2-aminoethoxy)-sym-triazine hydrochloride (III), which reacts with dry potassium hydroxide in chloroform to give the free base (IV). Compounds (III) and (IV) are identical with samples of compounds obtained previously [2]. Compound (IV) was also identified in the form of the 2-(2-methoxycarbonylaminoethoxy) derivative (V).



I a X = Cl, b X = $\overset{+}{N}Me_3Cl$; VI a R = Me, b R = Et

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*For Communication 6, see [1].

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EXPERIMENTAL

The PMR spectra were taken on the Varian T-60 instrument (60 MHz) using $CDCl_3$ or acetone-D_6; the internal standard was HMDS or TMS. The mass spectra were obtained on the MX-1303 spectrometer by the method of the direct introduction of the sample at the source; the energy of the ionizing electrons was 50 eV. The TLC was performed on plates of Silufol UV-254.

2-(2-Benzylidenaminoethoxy)-4,6-bisdimethylamino-sym-triazine (II). A. To 0.01 mole of the sodium salt of benzylidenethanolamine, obtained from 1.5 g (0.01 mole) of benzylidenethanolamine [5] and 0.42 g (0.01 mole) of NaOH powder in 10 ml of $CHCl_3$, are added, in portions at 0°C, 2.6 g (0.01 mole) of 4,6-bisdimethylamino-sym-triazinyl-2-trimethylammonium chloride (Ib) [4]. The mixture is stirred for 1.5 h at 20°C and for 1 h at 40°C. The NaCl which separated out is filtered, and the filtrate is evaporated. The residue is treated with 5 ml of water, and the precipitated residue of compound (II) is filtered off *in vacuo*. The yield is 3 g (95%), and the mp is 92-93°C. The PMR spectrum is as follows: 3.05 ppm [12H, s, $(NMe_2)_2$], 3.6 ppm (2H, t, NCH_2), 4.4 ppm (2H, t, OCH_2), 8.4 ppm (1H, s, N=CH), and 7.2-7.85 ppm (5H, m, Ph). Found, %: C 60.7, H 7.1, and N 26.8. $C_{16}H_{23}N_6O$. Calculated, %: C 61.0, H 7.3, and N 26.7.

B. The mixture of 2.0 g (0.01 mole) of 2-chloro-4,6-bisdimethylamino-sym-triazine (Ia), 1.5 g (0.01 mole) of benzylidenethanolamine, 0.84 g (0.012 mole) of 84% KOH, and 0.12 g of TEBAC in 10 ml of dioxane is heated for 12 h at 100-110°C. The dioxane is distilled off, and the residue is treated with 10 ml of water. Compound (II) is filtered. The yield is 2.6 g (82%), and the mp is 93-94°C.

The methiodide (VIa) has the mp 178-180°C (decomp.), and the ethiodide (VIb) has the mp 72-74°C (decomp.).

2-(2-Aminoethoxy)-4,6-bisdimethylamino-sym-triazine Hydrochloride (III). The mixture of 2.6 g (0.083 mole) of compound (I), 1 ml of 36% HCl, and 2 ml of water is maintained for 48 h at 20°C. The benzaldehyde is extracted with ether, and the aqueous layer is evaporated. The residue is rubbed with ether prior to the filtration of the isolated compound (III). The yield is 1.9 g (88%), and the mp is 148-150°C (decomp.). Found, %: Cl 13.3 and N 31.7. $C_9H_{19}ClN_6O$. Calculated, %: Cl 13.5 and N 32.0.

2-(2-Aminoethoxy)-4,6-bisdimethylamino-sym-triazine (IV). The mixture of 2.6 g (0.01 mole) of compound (III) and 0.7 g (0.01 mole) of 84% KOH (powder) in 10 ml of $CHCl_3$ is stirred for 2 h at 15-20°C. The mixture is filtered from the KCl, and the filtrate is evaporated. The residue is rubbed with petroleum ether prior to the filtration of the isolated compound (VI). The yield is 1.5 g (66%). The mp is 98-100°C. The PMR spectrum is as follows: 2.0 ppm (2H, s, NH_2), 3.05 ppm (2H, m, CH_2NH_2), 3.1 ppm [12H, s, $(NMe_2)_2$], and 4.32 ppm (2H, t, OCH_2). Found, %: C 46.8, H 7.2, and N 29.4. $C_9H_{18}N_6O$. Calculated, %: C 46.5, H 7.0, and N 29.6.

2-(2-Methoxycarbonylaminoethoxy)-4,6-bisdimethylamino-sym-triazine (V). To 2.3 g (0.01 mole) of compound (IV) in 10 ml of $CHCl_3$ is added, in portions at −5-0°C, 0.95 g (0.01 mole) of methyl chloroformate, and then 0.7 g (0.01 mole) of 84% KOH (powder). The reaction mixture is maintained for 24 h at 15-20°C. The $CHCl_3$ is evaporated, and the residue is treated with water prior to the filtration of compound (V). The yield is 2.0 g (70%). The mp is 96-98°C, and the R_f is 0.47 (the 1:2 mixture of acetone−hexane). The IR spectrum is as follows: 1500 cm^{-1}, 1590 cm^{-1} (C=N), 1720 cm^{-1} (C=O), and 3290 cm^{-1} (NH). The M^+ is 284. Found, %: C 46.8, H 7.3, and N 29.8. $C_{11}H_{20}N_6O_3$. Calculated, %: C 46.5, H 7.1, and N 29.6.

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