B. A mixture of 0.224 g (1 mmole) of compound (I) and 1 ml (10 mmole) of triethylamine was boiled in 10 ml of absolute ethanol until the spot of compound (I) on the chromatogram had disappeared (about 12 h). The mixture was evaporated to dryness under vacuum, and the residue was extracted with hot hexane and filtered. On cooling the chromatographically pure compound (II) separated from the hexane solution; mp 86-88°C. The yield was 0.19 g (85%).

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SYNTHESIS AND THERMAL DECOMPOSITION OF HALOGENOALKOXY-, HALOGENOALKYLTHIO-, AND HALOGENOALKOXYAMINO-SYM-TRIAZINES

13.* SYNTHESIS AND THERMOLYSIS OF 4,6-DISUBSTITUTED 2-(2-CHLOROETHOXY)- AND 2-(2-CHLOROETHYLAMINO)-SYM-TRIAZINES

K. A. Éliazyan, A. M. Akopyan, V. A. Pivazyan, A. G. Akopyan, and V. V. Dovlatyan

4-Amino-, 4-methoxy-, 4-methylthio-, 4-alkylamino-, and 4-dialkylamino-6-alkyl(dialkyl)amino-2-(2-chloroethoxy)-sym-triazines and the corresponding 2-(2-chloroethylamino)-sym-triazines were obtained. Their cyclization led to the sym-triazinium chlorides or imidazo-sym-triazines.

In the development of the applications of the rearrangement—cyclization of chloroalkoxy- and chloroalkylthio-sym-triazines [1-5] it seemed of interest to study the reactions of 4-amino-6-dialkylamino-2-(2-chloroethoxy)-sym-triazines, which could lead to tetrahydroimidazo-sym-triazines-. (See scheme at the top of the next page.)

The initial chlorides (Ia, b) were obtained earlier [2] from the corresponding quaternary ammonium salts and ethylene chlorohydrin. However, instead of the expected hydrochlorides (IIa, b), thermolysis of compounds (Ia, b) gave the isomeric quaternary salts (IVa, b) (oxazolo-sym-triazinium chlorides), which did not change even under more drastic thermolysis conditions.

*For Communication 12, see [1].

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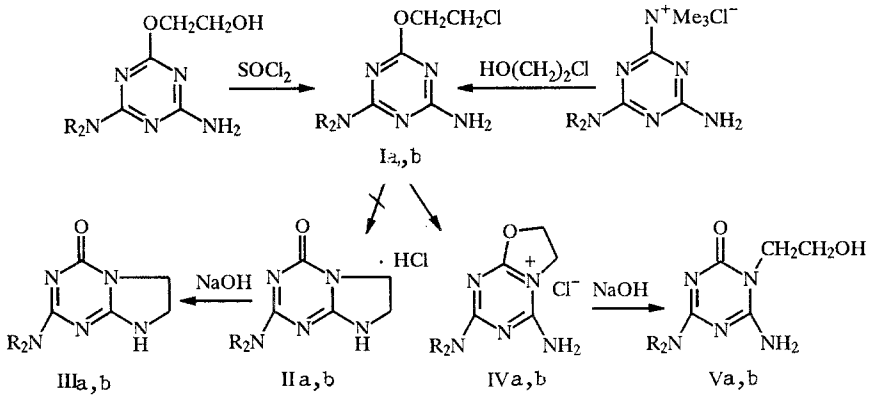
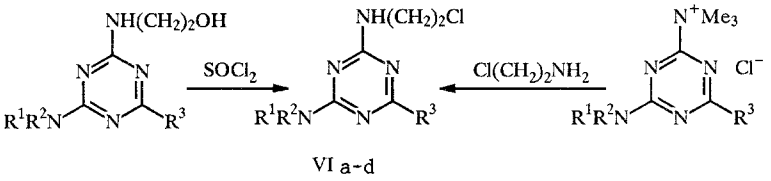


I-Va: R=Me; b R=Et

Thus, it was possible for the first time to isolate the fully stable quaternary salt (IV) (the intermediate rearrangement—cyclization product), whereas the analogous salts that we isolated earlier were extremely unstable [2,3]. Apart from the spectral data, the structure of the obtained compounds was also confirmed by their transformation into 1-(2-hydroxyethyl)-sym-triazinones (Va, b) by the action of alkali.

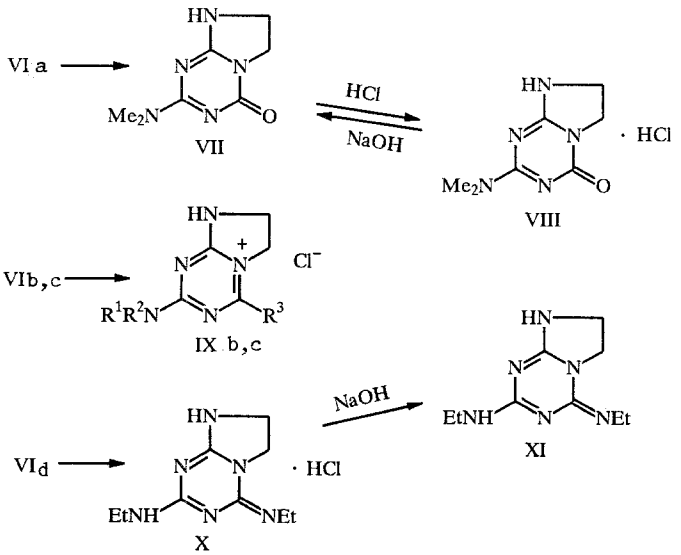
The synthesis of compound (IIIa, b) could be approached by a different path, i.e., by the rearrangement of 6-dialkylamino-4-methoxy-2-(2-chloroethylamino)-sym-triazines (VIa-d). The latter are produced either from 4,6-disubstituted 2-(2-hydroxyethylamino)-sym-triazines [6] or by the reaction of ammonium salts of the triazine series with chloroethylamine in chloroform.



VI a-d

VIa $R^1=R^2=Me$, $R^3=OMe$; b $R^1=R^2=Me$, $R^3=NMe_2$; c $R^1=R^2=Me$, $R^3=SMe$; $R^1=H$, $R^2=Et$, $R^3=NHEt$

The thermolysis of compounds (VIa-d) takes place in different ways, depending on the substituent in the triazine ring. Thus, compound (VIa) eliminated methyl chloride with the formation of the oxoimidazo-sym-triazine (VII), the hydrochloride of which (VIII) was not identical with (IVa). In the case of the thermolysis of compounds (VIb, c) the stable quaternary salts (IXb, c) are formed, while compound (VId) is transformed into the hydrochloride of imidazo-sym-triazine (X), which is converted into compound (XI) by the action of alkali.



EXPERIMENTAL

The IR spectra were recorded in Vaseline oil on a UR-20 instrument. The PMR spectra were recorded on a Varian T-60 spectrometer with TMS or HMDS as internal standard. The mass spectra were obtained on an MX-1303 instrument with direct injection at 50 eV. The purity of the substances was monitored by TLC on Silufol UV-254 plates.

4-Amino-6-dialkylamino-2-(2-chloroethoxy)-sym-triazines (Ia, b). The compounds were obtained by the previously described method [2]. The yield of compound (Ia) ($C_7H_{12}ClN_5O$) was 80%; mp 105-106°C, R_f 0.46 (1:2 heptane—acetone). The yield of compound (Ib) ($C_9H_{16}ClN_5O$) was 75%; mp 95-96°C, R_f 0.52.

Oxazolo-sym-triazinium chlorides (IVa, b). A suspension of 0.01 mole of the compound (Ia, b) in 10 ml of absolute toluene was boiled for 3 h. Compounds (IVa, b) were filtered from the hot mixture and washed with absolute ether. Compound (IVa) ($C_7H_{12}ClN_5O$), mp 186-187°C (decomp.), [M − Cl] 181/182, yield 97%. Compound (IVb) ($C_9H_{16}ClN_5O$), mp 169-170°C (decomp.). PMR spectrum (in D_2O), 1.2 (6H, t, CH_3), 3.60-3.65 (2H each, q, N—CH_2), 4.4 (2H, m, 6-H), 5.0 ppm (2H, m, 2-H); [M − Cl] 210, yield 96%.

6-Amino-4-dialkylamino-1-(2-hydroxyethyl)-sym-triazin-2-ones (Va, b). To a solution of 0.01 mole of the compound (IVa, b) in 15 ml of water we added 4 g (0.01 mole) of sodium hydroxide in 5 ml of water. The mixture was stirred at 20°C for 6 h, and the products were filtered off. Compound (Va) ($C_7H_{13}N_5O_2$), mp 235-236°C, R_f 0.54 (1:1 heptane—acetone). IR spectrum: 1640, 1660 (C=N), 1705 (C=O), 3180 (OH), 3340 cm^{-1} NH_2. PMR spectrum ($CDCl_3$ + CD_3OD): 3.14 and 3.9 [3H each, s, $N(CH_3)_2$], 4.0 ppm (4H, m, NCH_2CH_2O). M^+ 199. Yield 80%. Compound (Vb) ($C_9H_{17}N_5O_2$), mp 149-150°C, R_f 0.47 (1:1 heptane—acetone). PMR spectrum ($CDCl_3$ + CD_3OD): 1.18 (6H, t, CH_3), 3.58 (4H, q, 4-CH_2), 3.95 ppm (4H, m, NCH_2CH_2O). The yield was 95%.

2-Amino-4-methoxy-6-(2-chloroethylamino)-sym-triazines (VIa-d). A. To 10 ml of thionyl chloride at 0°C, while stirring, we added in portions 0.01 mole of 4,6-disubstituted 2-(2-hydroxyethylamino)-sym-triazine. The reaction mixture was kept at 20°C for 24 h. The excess of thionyl chloride was distilled under vacuum, the residue was washed with petroleum ether, and the mixture was decanted. A 10-ml portion of water was added, and the solution was neutralized to pH 8-9 with 10% sodium hydroxide solution. The precipitate of compounds (VIa-d) was filtered off.

The yield of compound (VIa) ($C_8H_{14}ClN_5O$) was 90%; mp 125-127°C, R_f 0.50 (4:5 heptane—acetone). The yield of compound (VIb) ($C_9H_{17}ClN_6$) was 60%; mp 58-60°C, R_f 0.45 (4:5 heptane—acetone). The yield of compound (VIc) ($C_8H_{11}ClN_5S$) was 80%; mp 123-133°C, R_f 0.46 (4:5 heptane—acetone). The yield of compound (VId) ($C_9H_{17}ClN_6$) was 91%, and the product formed a thick syrup; R_f 0.48 (4:5 heptane—acetone).

B. To 3.2 g (0.04 mole) of 2-chloroethylamine in 20 ml of dry chloroform we added in portions 0.01 mole of the quaternary ammonium salt and then 0.4 g (0.01 mole) of powdered sodium hydroxide. The mixture was stirred at 20°C for 4-5 h, and the sodium chloride was filtered off. The filtrate was evaporated, and compounds (VIa-d) were isolated after treatment of the dry residue with water.

Thermolysis of Compounds (VIa-d). A suspension of 0.01 mole of the compound (VIa-d) in 20 ml of xylene or toluene was boiled for 1-2 h. The reaction product was filtered off and washed with absolute ether.

Compound (VIa) gave 5,6-dihydro-2-dimethylaminoimidazo[1,2-a]-sym-triazin-8-one (VII) ($C_7H_{11}N_5O$); M^+ 181, R_f 0.54 (10:5:3 hexane—acetone—acetic acid).

Compound (VIIb) gave 5,6-dihydro-2,8-bis(dimethylamino)imidazo[1,2-a]-sym-triazinium chloride (IXb) ($C_9H_{17}ClN_6$); mp 150-152°C (decomp.), R_f 0.44 (10:5:4 hexane—acetone—water). PMR spectrum (deuterochloroform + pyridine-D_5): 3.0 [6H, s, 2-$N(CH_3)_2$], 3.1 and 3.2 [3H each, s, 4-$N(CH_3)_2$], 3.7 (2H, m, 6-H), 4.6 ppm (2H, m, 5-H). [M − Cl] 209. The yield was 97%.

Compound (VIc) gave 5,6-dihydro-2-dimethylamino-8-(methylthio)imidazo[1,2-a]-sym-triazinium chloride (IXc) ($C_8H_{14}ClN_5S$); mp 197-198°C, R_f 0.51 (10:5:4 acetone—hexane—water). PMR spectrum (deuterochloroform + tetradeuteromethanol): 2.6 (3H, s, SCH_3), 3.1 and 3.2 [3H each, s, $N(CH_3)_2$], 4.2 ppm (4H, m, CH_2CH_2), [M − Cl] 212. The yield was 80%.

Compound (VId) gave 2,8-dihydro-2-ethylamino-4-ethylimino-4H,6H-imidazo[1,2-a]-sym-triazine hydrochloride (X) ($C_9H_{16}N_6 \cdot HCl$); mp > 270°C. PMR spectrum (deuterochloroform + pyridine-D_5): 1.05 and 1.1 (6H, t, CH_3), 3.35 (4H, q, 2′- and 8′-CH_2), 3.7 (4H, s, 5- and 6-H), [M − HCl] 208. The yield was 97%.

After treatment with an equivalent amount of sodium hydroxide in water compound (XI) was isolated; mp 122-124°C. The yield was 93%.

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REACTION OF ALKENYNYLAMINES WITH 2-AMINORESORCINOL AS A METHOD FOR THE SYNTHESIS OF 2-(2-ALKENYL)-4-HYDROXYBENZOXAZOLES

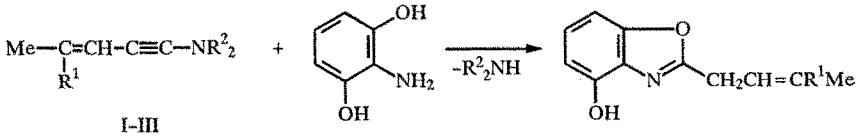
M. V. Kormer, S. E. Tolchinskii, and I. A. Maretina

The reaction of 1-diethylamino-(4-methyl)-3-penten-1-ynes with 2-aminoresorcinol leads to the formation of 2-(2-alkenyl)-4-hydroxybenzoxazoles.

A considerable number of papers (e.g., [1,2]) have been devoted to the synthesis of benzoxazoles. Earlier we developed methods for the production of heterocycles of the benzoxazole [3], 1,3-benzodioxole [4], and benzimidazole [5] series by the reaction of 1-dialkylamino-(4-methyl)-3-penten-1-ynes with bifunctional aromatic compounds. A special feature of the reaction is that it takes place by twofold attack at the $C_{(1)}$ carbon atom of the acetylene bond with the formation of condensed heterocycles containing an unconjugated unsaturated fragment at the second position of the ring. By monitoring the reaction between 1-diethylamino-4-methyl-3-penten-1-yne and o-aminophenol it was noticed that the reaction begins at the hydroxy group [3].

It could be supposed that if derivatives of dihydroxyaniline, containing amino and hydroxy groups in the ortho position to each other, were used instead of o-aminophenol the hydroxyl derivatives of benzoxazole would be obtained in the reaction with ynamines. However, investigation of the reaction showed that the reaction only took place with the unambiguous formation of the 2-(2-alkenyl)-4-hydroxybenzoxazoles in the case of 2-aminoresorcinol, whereas 2-amino-4-hydroxyphenol and 3-amino-2-hydroxyphenol gave a complex mixture of reactions of cyclic and noncyclic structure involving one and both hydroxy groups.

In the case of 2-aminoresorcinol, the molecule of which is strictly symmetrical, after addition at the triple bond the reaction can only develop with the participation of the amino group. After the elimination of the dialkylamine the 2-(3-methyl)-2-butenyl-4-hydroxybenzoxazoles (V, VI) are formed.



I R^1=H, R^2=Et; II R^1=Me, R^2=Et; III R^1=Me, R^2=Pr; V R^1=H; VI R^1=Me

Saint Petersburg Technological Institute, Saint Petersburg 198013.

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