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# INVESTIGATIONS INTO FUNCTIONALLY SUBSTITUTED AZINES.
# 6.* REACTIONS OF N-POTASSIOCYANAMINO-sym-TRIAZINES WITH CHLORIDES OF CHLORALAMIDES

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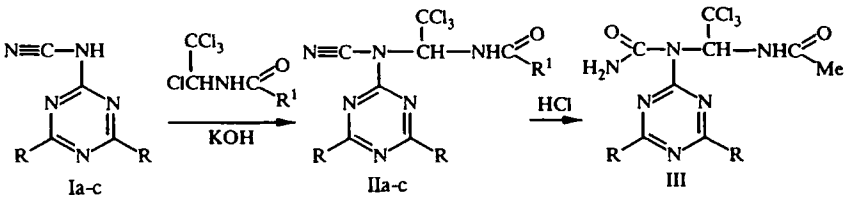
*Reaction of 2-N-potassiocyanamino-4,6-bisisopropyl(dimethylamino)-sym-triazines with acid 1,2,2,2-tetrachloroethylamides leads to the formation of 2-N-cyano-N-(1-acylamino-2,2,2-trichloroethyl)amino-4,6-bisisopropyl(dimethylamino)-sym-triazines. Reaction with 1-hydroxy(methoxy)-2,2,2-trichloroethylamides of chloroacetic acid leads to 2-(2-imino-4-oxooxazolidin-1-yl)-4,6-bis(dimethylamino)-sym-triazine and its 1-methoxy-2,2,2-trichloroethyl derivative substituted at the position 3 of the oxazolidine ring.*

In the search for new pesticides, we accomplished the syntheses of heterocyclic derivatives of chloral [1-8]. Interest is presented by the development of methods for the synthesis of N-sym-triazinyl-N-acylaminals of chloral since some chloralaminals containing the piperidine and morpholine rings are known to have high fungicidal activity [9]. We showed previously that cyanamino-sym-triazines are readily subjected to N-alkylation by alkyl halides and their functional derivatives [10-15]. The present paper presents results of the study of analogous reactions using derivatives of chloralamides containing a reactive chlorine atom.

The action of 1,2,2,2-tetrachloroethylamides of formic and acetic acids on 2-N-potassiocyanamino-4,6-bisdimethyl(isopropylamino)-sym-triazines (Ia-c) results in the formation of the expected aminals — 2-N-cyano-N-(1-acylamino-2,2,2-trichloroethyl)amino-4,6-bisdimethyl(isopropylamino)-sym-triazines (IIa-c). Compound (IIc) is not deacetylated in concentrated hydrochloric acid and, by reacting regioselectively at the cyano group, is converted to the urea derivative (III).




I, II a R = $NMe_2$, $R^1$ = Me; b R = *i*-$C_3H_7NH$, $R^1$ = H;
c R = *i*-$C_3H_7NH$, $R^1$ = Me

A somewhat unexpected result was found in the reaction of compound (Ia) with the 1-hydroxy-2,2,2-trichloroethylamide of chloroacetic acid leading to the formation of 2-(2-imino-4-oxooxazolidin-1-yl)-4,6-bisdimethylamino-sym-triazine (VI), previously described and synthesized by ammonolysis of the corresponding 2-N-cyano-N-methoxycarbonylmethylamino derivative [16]. Such a reaction path can be interpreted satisfactorily if it is considered that, instead of the open-chain cyanamino derivative (IV), the product (V) of its intramolecular imination is thereby formed; by the elimination of chloral, this is then stabilized as compound (VI). The reaction of the chloralamide having the methyl protection of the hydroxyl group,

*For Communication 5, see [1].

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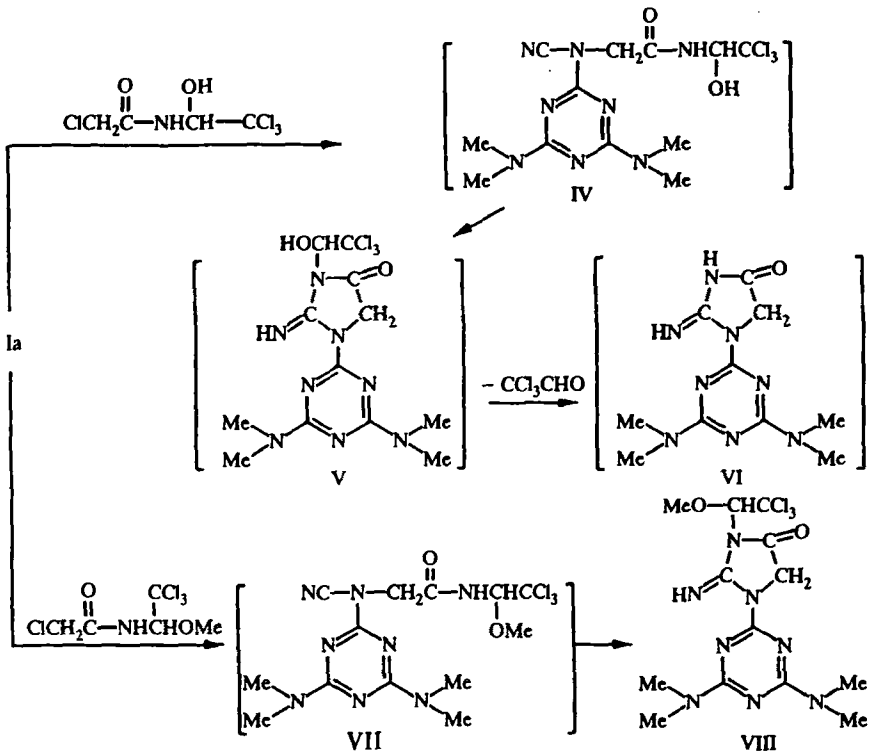
i.e., the 1-methoxy-2,2,2-trichloroethylamide of chloroacetic acid, with compound (Ia) results in the formation of the normal reaction product — 2-[2-imino-3-(1-methoxy-2,2,2-trichloroethyl)-4-oxoimidazolidin-1-yl]-4,6-bisdimethylamino-sym-triazine (VIII), probably via the intermediate (VII).



## EXPERIMENTAL

The IR spectra were taken on the UR-20 spectrometer using mineral oil. The PMR spectra were taken on the Varian T-60 instrument. The purity of the compounds was monitored by TLC using plates of Silufol UV-254 and the 1:2 or 2:3 solvent system of acetone–hexane; the developer was 2% $AgNO_3$ + 0.4% BFS + 4% citric acid.

**2-N-Cyano-N-(1-acetylamino-2,2,2-trichloroethyl)amino-4,6-bisdimethylamino-sym-triazine (IIa).** To the solution of 0.7 g (10 mmole) of 84% technical potassium hydroxide in 6 ml of water are added 2.1 g (10 mmole) of 2-cyanamino-4,6-bisdimethylamino-sym-triazine (Ia), and the mixture is stirred for 10-15 min at room temperature. The solution of 2.5 g (11 mmole) of 1,2,2,2-tetrachloroethylacetamide in 8-10 ml of acetone is added dropwise while cooling the mixture with ice. The mixture is stirred for 5-6 h prior to the addition of 10-15 ml of water and the filtration of the precipitated residue. The yield of 3 g (75%) of compound (IIa), with the mp 190-192°C (from acetone) and the $R_f$ 0.4, is obtained. The IR spectrum is as follows: 2220-2240 $cm^{-1}$ (C≡N), 1540 $cm^{-1}$, 1600 $cm^{-1}$ (C=C, C=N), 1650 $cm^{-1}$ (O=C–N), and 3340 $cm^{-1}$ (NH). The PMR spectrum (DMSO-$D_6$) is as follows: 2.03 ppm (3H, s, $COCH_3$), 3.09 ppm (12H, s, $NCH_3$), 7.6 ppm (1H, d, J = 10 Hz, CH), and 9.35 ppm (1H, d, NH). Found, %: N 28.7 and Cl 26.6. $C_{12}H_{17}Cl_3N_8O$. Calculated, %: N 28.3 and Cl 26.9.

**2-N-Cyano-N-(1-formylamino-2,2,2-trichloroethyl)amino-4,6-bisisopropylamino-sym-triazine (IIb).** By analogy with the synthesis of the triazine (IIa), 0.7 g (10 mmole) of 84% potassium hydroxide in 6 ml of water, 2.35 g (10 mmole) of 2-cyanamino-4,6-bisisopropylamino-sym-triazine, and 2.3 g (11 mmole) of 1,2,2,2-tetrachloroethylformamide in 8-10 ml of acetone yield 3.1 g (76%) of compound (IIb), with the mp 176-178°C and the $R_f$ 0.38. The IR spectrum is as follows: 2230 $cm^{-1}$ (C≡N), 1530 $cm^{-1}$, 1600 $cm^{-1}$ (C=C, C=N), 3310-3330 $cm^{-1}$ (NH), and 1660 $cm^{-1}$ (O=C–N). The PMR spectrum is as follows: 1.10 ppm (12H, d, $CH_3$), 4.00 ppm (2H, m, J = 6 Hz, CH), 7.40 ppm (2H, m, NH, CH), and 8.10 ppm (1H, broad s, COH). Found, %: N 27.02 and Cl 26.40. $C_{13}H_{19}Cl_3N_8O$. Calculated, %: N 27.35 and Cl 26.08.

**2-N-Cyano-N-(1-acetylamino-2,2,2-trichloroethyl)amino-4,6-bisisopropylamino-sym-triazine (IIc).** By analogy with the synthesis of the triazine (IIa), 0.7 g (10 mmole) of 84% technical potassium hydroxide in 6 ml of water, 2.35 g (10 mmole)

of 2-cyanamino-4,6-bisisopropylamino-sym-triazine, and 2.5 g (11 mmole) of 1,2,2,2-tetrachloroethylacetamide in 8-10 ml of acetone yield 3.3 g (75%) of compound (IIc), with the mp 100-102°C and the $R_f$ 0.3. The IR spectrum is as follows: 2250 $cm^{-1}$ (C≡N), 1530 $cm^{-1}$, 1600 $cm^{-1}$ (C=C, C=N), 3310-3330 $cm^{-1}$ (NH), and 1650 $cm^{-1}$ (O=C−N). The PMR spectrum (DMSO-$D_6$) is as follows: 1.1 ppm (12H, d, $CH_3$), 2.1 ppm (3H, s, $CH_3$), 4.2 ppm (2H, m, CH), 7.0 ppm (2H, d, NH), 6.0 ppm (1H, m, CH), and 9.15 ppm (1H, NH). Found, %: N 26.8 and Cl 24.1. $C_{14}H_{21}Cl_3N_8O$. Calculated, %: N 26.4 and Cl 25.1.

**N-(1-Acetylamino-2,2,2-trichloroethyl-N-4,6-bisisopropylamino-sym-triazin-2-yl)urea (III).** To 0.4 g (1 mmole) of 2-N-cyano-N-(1-acetylamino-2,2,2-trichloroethyl)amino-4,6-bisisopropylamino-sym-triazine are added 1.5 ml of concentrated HCl. The mixture is left at room temperature for 20 h. After the addition of 2.3 ml of water, the mixture is neutralized with $NaHCO_3$, and the crystals are filtered off. The yield of 0.35 g (79%) of compound (III), with the mp 123-125°C, is obtained. The IR spectrum is as follows: 1670 $cm^{-1}$ (O=C−NH), 3340-3400 $cm^{-1}$ (NH, $NH_2$), 1520 $cm^{-1}$, and 1610 $cm^{-1}$ (C=C, C=N). Found, %: N 25.3 and Cl 24.1. $C_{14}H_{23}Cl_3N_8O_2$. Calculated, %: N 26.32 and Cl 25.02.

**2-[2-Imino-3-(1-methoxy-2,2,2-trichloroethyl)-4-oxoimidazolidin-1-yl]-4,6-bisdimethylamino-sym-triazine(VIII).** To 2.5 g (10 mmole) of the potassium salt of cyanamino-sym-triazine in 10 ml of DMF are added 2.6 g (10 mmole) of 1-methoxy-2,2,2-trichloroethylchloroacetamide and 1 g of sodium iodide. The mixture is heated at 60-70°C for 8 h prior to the addition of water and filtration of the precipitated residue. The yield of 4.2 g (90%) of compound (VIII), with the mp 190-191°C, is obtained. The IR spectrum is as follows: 1720-1750 $cm^{-1}$ (C=O), 1780 $cm^{-1}$, 1790 $cm^{-1}$ (C=N), 3320-3430 $cm^{-1}$ (NH), and 1080-1100 $cm^{-1}$ (C−O−C). The PMR spectrum is as follows: 3.1 ppm (12H, s, $NCH_3$), 3.67 ppm (3H, s, $OCH_3$), 4.4 ppm (2H, s, $CH_2$), and 6.1 ppm (1H, s, CH). Found, %: N 26.5 and Cl 25.3. $C_{13}H_{19}Cl_3N_8O_2$. Calculated, %: N 26.32 and Cl 25.02.

The synthesis with the 1-hydroxy-2,2,2-trichloroethylamide of chloroacetic acid leads to compound (VI), the mp of which corresponds with the published data (348-350°C [16]), and which does not give a depression of the melting temperature in the mixed test with the known sample.

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