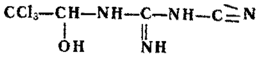
CONDENSATION OF DICYANDIAMIDE WITH CHLORAL HYDRATE

V. V. Dovlatyan, T. Z. Papoyan,
and G. K. Tarkhanyan

UDC 547.86:542.953

A substituted 1,3,5-oxadiazine derivative that exists in two tautomeric forms was obtained by reaction of dicyandiamide with chloral hydrate. The structure of the product was established on the basis of its IR spectrum and chemical transformations.

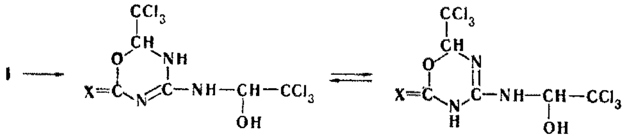
From the data available in the literature [1] it follows that dicyandiamide reacts with chloral (present in a slight excess) to give monochloraldicyandiamide (I).



$$CCl_3-\underset{OH}{\underset{|}{CH}}-NH-\underset{NH}{\underset{\|}{C}}-NH-C\equiv N$$

In addition, there is some indication that when a considerable excess of chloral is present, the reaction mixture undergoes resinification, and the corresponding dichloraldicyandiamide, the formation of which should have been expected in analogy with dichloralurea [2], cannot be obtained. We were unable to reproduce the synthesis of I. A mixture, which melted at 80-100°C, was formed as a result of the reaction.

We were able to select conditions under which the reaction of chloral hydrate with dicyandiamide gives unsubstituted 1,3,5-oxadiazine, which exists in two tautomeric forms, in good yield; the absorption band of a C≡N group is absent in the IR spectrum of the product.



IIa,IIIa IIb,IIIb

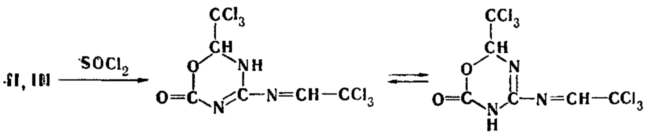
II X=NH; III X=O

The absorption band characteristic for a conjugated system of C=N—C=N bonds at 1538-1572 cm^{-1} provides evidence in favor of structure IIa, and the absorption band at 1638 cm^{-1} indicates the presence of an unconjugated C=N bond, i.e., it constitutes evidence in favor of structure IIb. The IR spectrum of II also contains absorption bands at 1698-1705 (C=NH) and 3272-3400 cm^{-1} (OH).

The presence of an imino group in II was confirmed by the formation of the corresponding hydroxy derivatives (III) from it by treatment with hydrochloric acid. The absorption band of a C=NH bond (1698-1705 cm^{-1}) vanishes in the IR spectrum of oxo compound III, and characteristic vibrations of a C=O group (1728-1731 cm^{-1}) appear.

In an attempt to synthesize chloro derivatives of II and III we obtained identical dehydration products. Consequently, in the case of II hydrolytic cleavage of the imino group occurs along with dehydration, and this leads to IV in both cases.

Armenian Agricultural Institute, Erevan. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 473-474, April, 1975. Original article submitted May 21, 1974.



IVa IVb

In the IR spectra of IV the absorption band of a OH group at 3272-3400 cm^{-1} vanishes with the appearance of an absorption band at 1504-1510 cm^{-1}, which is characteristic for a conjugated C=N—C=N—C=O system.

EXPERIMENTAL METHOD

The IR spectra of mineral-oil suspensions of the compounds were recorded with an IKS-14 spectrometer.

2-Trichloromethyl-4-(α-hydroxy-β-trichloroethylamino)-6-imino-1,3,5-oxadiazine (II). A mixture of 2.52 g (0.03 mole) of dicyandiamide, 10.75 g (0.065 mole) of chloral hydrate, and 60 ml of CCl_4 was heated to 70° with vigorous stirring. The reaction mixture dissolved after heating for 20 min, after which a precipitate formed. Heating was continued for 3 h, after which the precipitate was removed by filtration and washed with hot water to give 10.5 g (89.3%) of a product with mp 173° (dec.). Found %: Cl 56.2; N 15.1. $C_6H_6Cl_6N_4O_2$. Calculated %: Cl 56.2; N 14.8.

2-Trichloromethyl-4-(α-hydroxy-β-trichloroethylamino)-6-oxo-1,2,3,5-oxadiazine (III). A 1-g sample of II was dissolved in 10 ml of 15% HCl, and the solution was allowed to stand overnight. The resulting precipitate was removed by filtration and washed several times with water to give 0.95 g (95%) of a product with mp 150-152° (dec.). Found %: Cl 55.9; N 10.9. $C_6H_5Cl_6N_3O_3$. Calculated %: Cl 56.0; N 11.0.

2-Trichloromethyl-4-(β-trichloroethylimino)-6-oxo-1,3,5-oxadiazine (IV). A) 1.2-g (0.01 mole) sample of thionyl chloride was added to 1.89 g (0.005 mole) of II in 30 ml of dry CCl_4, after which the mixture was stirred and heated on a water bath. After 10-15 min, the solid dissolved, and a precipitate formed again. Heating was continued for 5 h, after which the precipitate was removed by filtration, washed with carbon tetrachloride, treated with water, and removed by filtration to give 1.5 g (83.3%) of a product with mp 242-243° (dec.). Found %: Cl 59.0; N 11.9. $C_6H_3Cl_6N_3O_2$. Calculated %: Cl 58.8; N 11.6.

B) A 1.2-g (0.01 mole) sample of thionyl chloride was added to 1.9 g (0.005 mole) of III in 30 ml of dry CCl_4, after which the mixture was stirred and heated on a water bath for 5-6 h. The resulting precipitate was removed by filtration, washed with carbon tetrachloride, treated with water, and removed by filtration to give 1.7 g (88.8%) of a product with mp 245° (dec.).

No melting-point depression was observed for a mixture of the products obtained by methods A and B.

LITERATURE CITED

1. A. E. Kretov and G. V. Tikhonov, Zh. Obshch. Khim., 34, 2429 (1964).
2. N. N. Mel'nikov, Yu. A. Beskakov, and M. E. Kuperman, Organic Insectofungicides and Herbicides [in Russian], Goskhimizdat, Moscow (1958), p. 266.