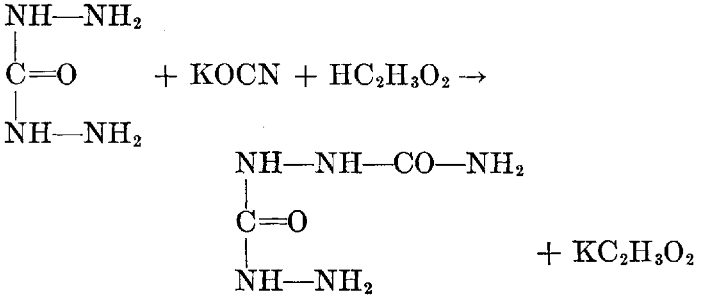
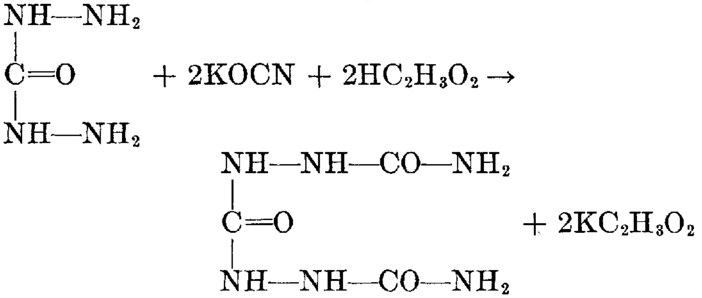
Inorganic Syntheses, Volume IV
Edited by John C. Bailar, Jr.

11. CYANATE CONDENSATION PRODUCTS OF CARBOHYDRAZIDE



$$\begin{array}{l}\mathrm{NH{-}NH_2}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH{-}NH_2}\end{array} + \mathrm{KOCN} + \mathrm{HC_2H_3O_2} \rightarrow \begin{array}{l}\mathrm{NH{-}NH{-}CO{-}NH_2}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH{-}NH_2}\end{array} + \mathrm{KC_2H_3O_2} \qquad (A)$$



$$\begin{array}{l}\mathrm{NH{-}NH_2}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH{-}NH_2}\end{array} + 2\mathrm{KOCN} + 2\mathrm{HC_2H_3O_2} \rightarrow \begin{array}{l}\mathrm{NH{-}NH{-}CO{-}NH_2}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH{-}NH{-}CO{-}NH_2}\end{array} + 2\mathrm{KC_2H_3O_2} \qquad (B)$$

SUBMITTED BY L. F. AUDRIETH* AND ELIZABETH B. MOHR*

Many hydrazine derivatives condense readily with potassium cyanate to give *N*-substituted semicarbazides. Carbohydrazide reacts with 1 or 2 mols of potassium cyanate to form carbohydrazide-*N*-carboxamide or carbohydrazide-*N*,*N*′-dicarboxamide.

A. CARBOHYDRAZIDE-*N*-CARBOXAMIDE

CHECKED BY SAMUEL HELF† AND K. G. OTTOSON†

This compound was first isolated as a secondary reaction product in the formation of diaminoguanidine hydrobromide and guanazine from the reaction of cyanogen bromide

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† Chemical Research Laboratory, Picatinny Arsenal, Dover, N.J.

with 2 mols of hydrazine.[1] Pellizzari and Roncagliolo[2] prepared carbohydrazide-*N*-carboxamide in good yield by the dropwise addition of glacial acetic acid to an equimolar mixture of carbohydrazide and potassium cyanate until the permanent disappearance of the phenolphthalein color. This procedure has been improved to give better yields and a more nearly pure and uniform product.

Procedure

The reaction is carried out in a 2-l. beaker above which is suspended a 500-ml. dropping funnel for slow addition of the cyanate solution. A mechanical stirrer is employed to agitate the mixture throughout the reaction and digestion processes.

Ninety-nine grams of carbohydrazide (1.10 mols) is dissolved in a solution containing 120 g. of glacial acetic acid (2.00 mols) and 1000 ml. of water. To this, a solution of 81 g. of potassium cyanate (1.00 mol) in 350 ml. water is added dropwise over a period of about 2 hours. The mixture is digested at room temperature for 5 hours. The precipitate is then removed by filtration and washed very thoroughly with water, alcohol, and ether. The dry product weighs approximately 115 g. (86%) and melts with decomposition at 227 to 228°.

Properties

Carbohydrazide-*N*-carboxamide is a white, nonhygroscopic, crystalline substance which is insoluble in water and in alcohol and other organic solvents. It is soluble in mineral-acid solutions, from which it may be reprecipitated by the addition of ammonia; however, it dissolves in sodium hydroxide with decomposition.

This compound reduces Fehling solution and ammoniacal silver nitrate readily. It is quite stable for long periods of time at 110°. When heated for 1 hour at 226°, it cyclizes to form urazine (synthesis 9). It condenses with aldehydes and ketones; the hydrochloride reacts with additional potassium cyanate to give carbohydrazide-*N*,*N*′-dicarboxamide.

B. CARBOHYDRAZIDE-*N*,*N*′-DICARBOXAMIDE

CHECKED BY C. F. DIETER* AND K. G. OTTOSON*

Pellizzari and Roncagliolo[2] prepared this compound by reaction of carbohydrazide in dilute acetic acid with 2 mols of potassium cyanate and also by condensation of carbohydrazide-*N*-carboxamide hydrochloride with 1 mol of cyanate. The former procedure does not give a pure product, probably because of the preferential formation of the less soluble carbohydrazide-*N*-carboxamide. The latter reacts with hydrochloric acid to form the hydrochloride, which is water-soluble. Prior condensation of carbohydrazide to form the *N*-carboxamide is advantageous, since the hydrochloride of this compound will undergo further reaction with cyanate to give the desired product by precipitation from water. When the procedure outlined below is followed, it is not necessary to recrystallize the carbohydrazide-*N*,*N*′-dicarboxamide unless an extremely pure material is desired.

Procedure

Thirteen and three-tenths grams of carbohydrazide-*N*-carboxamide (0.10 mol) is dissolved in a solution of 9.2 ml. of 12 *M* hydrochloric acid (0.11 mol) in 100 ml. of water. The resulting solution is filtered, if necessary, and to it is added a solution of 8.9 g. of potassium cyanate (0.11 mol) dissolved in 100 ml. of water. After a short time, precipitation begins. The resulting suspension is digested at room temperature for 5 hours with constant stirring. The crystals are filtered and washed with water, alcohol, and ether. The yield of carbohydrazide-*N*,*N*′-dicarboxamide thus obtained weighs about 15.0 g. (85%). A small sample melts with decomposition at 225°, or at 232° when heated rapidly.

If a material of greater purity is desired, the product may

* Chemical Research Laboratory, Picatinny Arsenal, Dover, N.J.

be recrystallized from 125 ml. of hot 3% hydrochloric acid solution. The recovery of purified carbohydrazide-*N*,*N'*-dicarboxamide is about 50%.

Properties

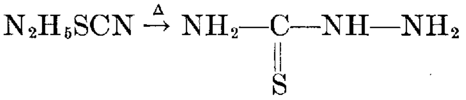
This compound melts with decomposition at 232°, is relatively nonhygroscopic, and is difficultly soluble in cold water and dilute acids. However, it dissolves to the extent of 4.72 g./100 g. of water at 65°. A saturated aqueous solution hydrolyzes to a noticeable extent at 65°.

References

1. PELLIZZARI and CANTONI: *Gazz. chim. ital.*, **35**, I, 291 (1905).
2. PELLIZZARI and RONCAGLIOLO: *ibid.*, **37**, I, 434 (1907).

12. THIOSEMICARBAZIDE

$$(N_2H_5)_2SO_4 + Ba(SCN)_2 \rightarrow BaSO_4 + 2N_2H_5SCN$$



$$N_2H_5SCN \xrightarrow{\Delta} NH_2\text{—}\underset{\underset{S}{\|}}{C}\text{—}NH\text{—}NH_2$$

SUBMITTED BY JOHN J. PITHA* AND JOHN P. OLATTA*
CHECKED BY EUGENE LIEBER,† S. H. PATINKIN,† AND R. D. PRATT†

Directions for the preparation of thiosemicarbazide as given in the literature[1] are lacking in detail, and so a good yield of the desired material in pure form is not assured. The procedure described here is a modification of that described by Freund[1] with emphasis on the temperature of conversion of hydrazinium thiocyanate to thiosemicarbazide. Thiosemicarbazide is a useful intermediate in the preparation of guanidine derivatives, which are of interest because of their high nitrogen content.

Procedure

A solution of 27.5 ml. of concentrated sulfuric acid (0.5 mol) in 500 ml. of water is added slowly, with stirring, to a solution of 59 g. of 85% hydrazine hydrate (1 mol) in 500

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* Michigan State College, East Lansing, Mich.
† Illinois Institute of Technology, Chicago, Ill.