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

Properties

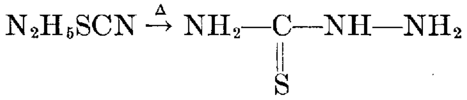
This compound melts with decomposition at 232°, is relatively nonhygroscopic, and is difficultly soluble in cold water and dilute acids. However, it dissolves to the extent of 4.72 g./100 g. of water at 65°. A saturated aqueous solution hydrolyzes to a noticeable extent at 65°.

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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ml. of water in a 2-l. beaker. A solution of 145 g. of barium thiocyanate 2-hydrate (0.5 mol) in 500 ml. of water is added to the solution of hydrazinium sulfate. The barium sulfate precipitate is stirred thoroughly and is then digested on a steam bath for 2 hours or more before filtering. For quick removal of the barium sulfate precipitate, the slurry is filtered by suction through a mat of filter-paper pulp between two pieces of filter paper,* using a fairly large (14-cm.) Büchner funnel. The clear, or only slightly cloudy, filtrate is then evaporated in a large evaporating dish on a steam bath until the total volume has been reduced to about 200 ml. At this point it may be necessary to filter the solution again. The clear solution is then transferred to a round-bottomed flask fitted with a thermometer well. The solution is boiled until its temperature reaches 110°. A reflux condenser is then attached to the flask, and the solution is maintained at the boiling point for 30 minutes. Upon cooling, a mass of crystals separates; these are removed by filtration. The filtrate is returned to the flask, and the refluxing at 100° is repeated. Five fractions of crystals are obtained from the solution in this manner. The crude thiosemicarbazide is purified by recrystallization from 50% ethanol. The yield of recrystallized material varies from 40 to 50% of theory, depending on the completeness of the conversion of the salt to product.†

Properties

Pure thiosemicarbazide is a white crystalline mass, which is very soluble in water and in ethanol. The reported melting point of the material is 181°, but this is not a reliable criterion of purity. The melting point appears to depend on the kind of crystal obtained by recrystallization. The crystals obtained range from those of micro size to long

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* Whatman ashless tablets are recommended.

† The checkers have pointed out that the synthesis can be simplified, though with some loss of yield and purity, by simple evaporation of the filtered solution of hydrazine thiocyanate to a volume of 75 ml., or until a yellow precipitate begins to form.

needles or large plates. They melt in the range 170 to 181°, and all give identical x-ray diffraction patterns. A qualitative test for the presence of the thiocyanate ion, using iron(III) chloride in acid solution, showed that all were about equally pure. A variety of transitions can be observed to take place during the process of melting.

Reference

1. Freund and Schander: *Ber.*, **29**, 2500 (1896).

13. IODOTRICHLOROSILANE AND DIIODODICHLOROSILANE

$$HSiCl_3 + I_2 \rightarrow SiICl_3 + HI$$
$$SiICl_3 + HI \rightarrow SiI_2Cl_2 + HCl$$

Submitted by Robert West* and Eugene G. Rochow*
Checked by C. A. Burkhard†

Various methods have been used to obtain equilibrium mixtures of the iodochlorides of silicon. These include passing a mixture of silicon tetrachloride and hydrogen iodide through a hot tube[1] or an electric discharge,[2] passing iodine monochloride over silicon at dull red heat,[1] and treating silicon tetrachloride with fused potassium iodide.[3] Although Besson mentioned that iodotrichlorosilane could be prepared from trichlorosilane and iodine in a Carius tube,[1] the conditions and yield data were not published. This reaction is more safely carried out in a pressure vessel, as described below.

Procedure

The reaction is carried out in a steel bomb of approximately 1 l. capacity, fitted with a thermocouple or thermometer, and equipped for rocking. The vessel should be capable of withstanding at least 2000 p.s.i. It is charged with 254 g. of iodine (1.0 mol) and 169 g. of trichlorosilane

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