5. The structure of a base occurring in California kerosene stock as 2,3,8-trimethylquinoline is established, and its synthesis effected.

6. The preparation of 3,8-dimethyl- from 2,3,8-trimethylquinoline through a series of reactions, with the structure of the 3,8-dimethylquinoline confirmed by synthesis, is described.

7. This investigation reveals in Edeleanu residues from refining California crude petroleum distillate a vast wealth of nitrogen bases, probably in the main hydro-aromatic and in *greater amount* volatile, non-basic nitrogen compounds. For the separation of the latter methods remain to be developed. Although there is a practically inexhaustible potential supply of material for research in this field, anything like an intensive investigation of petroleum nitrogen will involve a great amount of labor and expense.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE PREPARATION OF SEMICARBAZIDE

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RECEIVED NOVEMBER 18, 1929 PUBLISHED MARCH 6, 1930

Semicarbazide in the form of its compounds has been used extensively in various organic reactions, but no simple method for the preparation of the free base has, as yet, been reported in the literature. The action of liquid ammonia upon certain hydrazine[1] and hydroxylamine[2] salts, in particular the sulfates, has afforded a convenient and expeditious means for the preparation of these bases, suggesting that this reaction might also be applied to semicarbazide. It was found that semicarbazide sulfate would react with liquid ammonia to give the free base in excellent yields. This method is both rapid and convenient and one which is highly desirable in view of the fact that semicarbazide undergoes decomposition rapidly and must, therefore, be prepared fresh. The reaction proceeds in accordance with the equation

$$NH_2CON_2H_3{\cdot}H_2SO_4 + 2NH_3 = NH_2CON_2H_3 + (NH_4)_2SO_4$$

The ammonium sulfate settles out as an insoluble precipitate from which the liquid ammonia solution of semicarbazide may readily be decanted. The ammonia may be removed by evaporation and the semicarbazide purified by recrystallization from absolute ethanol.

An alternative method employed by the author for preparing the free base involves the action of barium hydroxide upon the sulfate. An excess of barium hydroxide must be avoided since alkalies induce hydrolysis of semicarbazide. After removal of the precipitated barium sulfate, the

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[1] Browne and Welsh, THIS JOURNAL, **33**, 1728 (1911).

[2] Browne and Audrieth, unpublished investigations.

filtrate is concentrated by vacuum evaporation at temperatures below 60°. Evaporation of an aqueous solution of semicarbazide at the boiling point under ordinary atmospheric pressure results in a decided decrease in yields due to decomposition of the substance with formation of hydrazine and hydrazidicarbamide.[3]

Of the new methods outlined above for the preparation of semicarbazide from its sulfate, the first is much to be preferred since it is not only faster, but gives much better yields. Attempts to prepare free guanidine and aminoguanidine by treatment of the corresponding sulfates with liquid ammonia were unsuccessful, suggesting that possibly only those anhydrobases less basic than ammonia are susceptible to ammonolysis. Treatment of methylhydrazine sulfate with liquid ammonia has been employed by the author for the preparation of liquid ammonia solutions of methylhydrazine, although examination of the residues indicates that this reaction does not go to completion.

Experimental

Preparation of Semicarbazide by Ammonolysis of Semicarbazide Sulfate.—Five grams of the sulfate was added gradually to 40 cc. of liquid ammonia. The solution was agitated for a short time and the precipitate then allowed to settle. The clear supernatant liquid was removed by decantation and the residue washed with additional liquid ammonia. Upon evaporation of the ammonia, the solid residue was dissolved in hot absolute ethanol, which on cooling yielded 2 g. of semicarbazide, m. p. 96°, corresponding to a 93% yield.

Preparation of Semicarbazide by Treatment of the Sulfate with Barium Hydroxide.—A concentrated solution of the sulfate (17.3 g.) was treated with an aqueous solution of barium hydroxide and the excess of the latter removed by the addition of the requisite amount of dilute sulfuric acid. After removal of the precipitated barium sulfate, the solution was concentrated at reduced pressure below 60° and the crystalline residue extracted with hot ethanol. Six grams of the free base, corresponding to an 80% yield, was obtained.

Summary

Free semicarbazide may be prepared rapidly and conveniently by the ammonolysis of semicarbazide sulfate. An alternative method involves the action of barium hydroxide upon the same salt.

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[3] Curtius and Heidenreich, *Ber.*, **27**, 57 (1894).