

mixture having a boiling range of 100–120° gave a main fraction which distilled at 113–116°; n_D^{25} 1.4055, d_4^{25} 0.9225. This material had a menthol-like odor and reacted with 2,4-dinitrophenylhydrazine reagent to give a derivative of m. p. 116° which analyzed correctly for the dinitrophenylhydrazone of γ -hydroxybutyraldehyde. Wilson¹⁶ reported this compound as melting at 116–117°.

Anal. Calcd. for $C_{10}H_{12}O_5N_4$: N, 20.9. Found: N, 21.1.

On the basis of this evidence and the close agreement of the calculated and found molecular refractivities (calcd. 30.99; found, 30.86), this product is believed to be 2-ethoxytetrahydrofuran.

The low-boiling (69–70°) fraction from the hydrogenation of I over copper chromite at 200° contained very little ethanol and had a higher refractive index (n_D^{25} 1.4268) than tetrahydrofuran. Treatment with bromine in chloroform indicated the presence of unsaturated material. Attempted hydrolysis with acid followed by treatment with carbonyl reagents gave no derivatives. No definite products were isolated.

Hydrogenation of (I) over palladium on barium sulfate gave appreciable amounts of materials boiling higher than the normal hydrogenation product II. Hydrolysis of 1 ml. of this material with 0.6 *N* hydrochloric acid followed

by treatment with 1 ml. of phenylhydrazine in 7 ml. of 15% acetic acid gave a small amount N-phenyldihydropyridazine (IX), m. p. 183–184°.¹⁰

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.9; H, 6.33; N, 17.7. Found: C, 75.8; H, 6.28; N, 17.7.

Summary

1. The preparation of 2,5-dialkoxytetrahydrofurans by catalytic hydrogenation of the corresponding dihydrofurans is described.

2. 2,5-Diethoxytetrahydrofuran is shown to be convertible to succinaldehyde, 1,4-butanediol, and, in low yield, to pyrrole and pyrrolidine.

3. Several 2-substituted-2,5-diethoxytetrahydrofurans were also prepared and characterized by conversion to derivatives of the corresponding 1,4-dicarbonyl compounds.

4. Some evidence is given to show that ethanol, tetrahydrofuran and 2-ethoxytetrahydrofuran are formed on hydrogenolysis of 2,5-diethoxy-2,5-dihydrofuran.

(16) C. L. Wilson, *J. Chem. Soc.*, 58 (1945).

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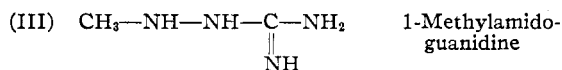
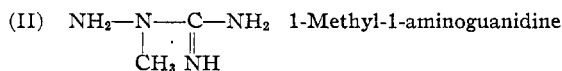
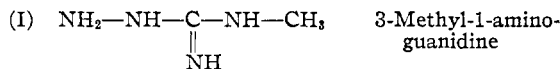
RECEIVED MAY 19, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

1-Methyl-1-aminoguanidine¹

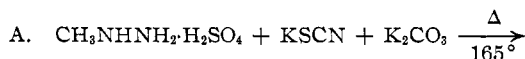
BY ALBERT H. GREER² AND G. B. L. SMITH³

In the course of the investigation of the preparation of the isomers of sulfanylmethylaminoguanidine it was found necessary to prepare the three possible structural isomers of methylaminoguanidine. These isomers can be assigned the structures



Isomer (I) has been reported in the literature.⁴ The present paper describes the preparation and character of Isomer (II) in the form of its sulfate salt. Isomer (III) is now under investigation.

Isomer (II) as its sulfate salt has been prepared according to two procedures

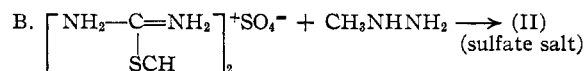
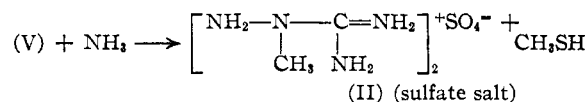
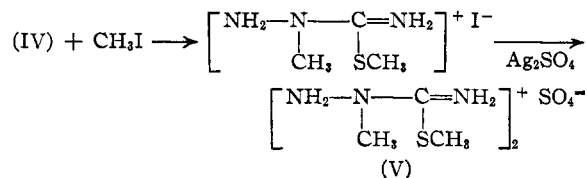
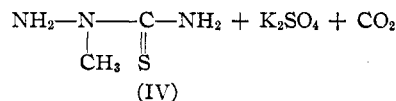


(1) Abstracted from part of the thesis submitted by Albert H. Greer to the Graduate Faculty in partial fulfillment of the Ph.D. degree in Chemistry, 1949.

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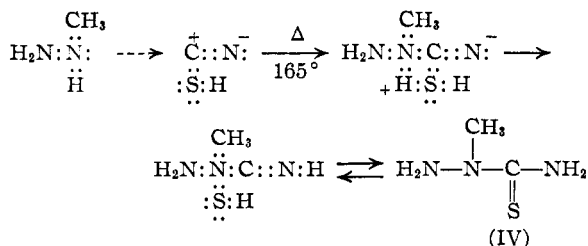
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(4) Kirsten and Smith, *THIS JOURNAL*, **58**, 800 (1936).



Evidence for the configuration of (IV) is given by the formation of a benzylidene derivative. According to the nature of the reaction⁵ this indicates that (IV) contains a primary hydrazine amino group. The reaction does not take place with the —NH_2 of the amide group. It is reasonable to assume that in the formation of (IV), the nitrogen atom adjacent to the methyl group of methylhydrazine is the more basic and it would appear that this reaction consists of a nucleophilic attack by methylhydrazine on the carbon atom of thiocyanic acid or thiocyanate anion

(5) Thiele and Bilian, *Ann.*, **302**, 299 (1898).



A benzylidene derivative was also obtained from (II). It can also be concluded that in the hydrazinolysis of S-methylthiourea sulfate by methylhydrazine, the nucleophilic center of methylhydrazine is on the nitrogen adjacent to the methyl group. If the beta nitrogen of methylhydrazine was the nucleophilic center then 1-methylamidoguanidine would have been the product of hydrazinolysis. However, since this compound does not contain a primary hydrazine amino group, no benzylidene derivative will be formed.

Experimental

Method A. 2-Methylthiosemicarbazide (IV).—The following procedure is an adaptation of the method used by Cattelain.⁶ Fifty-five grams (0.385 mole) of methylhydrazine sulfate was dissolved in 200 ml. of warm water and 29 g. of anhydrous potassium carbonate was slowly added to the solution with stirring. The solution was heated to reflux and 40 g. (0.41 mole) of potassium thiocyanate was added with stirring and reflux continued for fifteen minutes longer. Two hundred milliliters of boiling ethanol was added, the precipitated potassium sulfate filtered and the filtrate evaporated on the steam-bath to 5% of the original volume. The thick sirup was heated with vigorous stirring until the temperature reached 165° which was maintained for one minute. The evaporating dish was immediately chilled by an ice-water-bath, whereupon a yellow material solidified out. The crude product was dissolved in a minimum of boiling water, Norit added, the mixture filtered and the filtrate chilled. Upon cooling, long white needles separated to give 15 g. of product (38%), m. p. 183–184° dec. *Anal.* Calcd. for $\text{C}_2\text{H}_7\text{N}_3\text{S}$: S, 30.5. Found: S, 30.0. **Benzylidene derivative**, m. p. 170–172°. *Anal.* Calcd. for $\text{C}_9\text{H}_{11}\text{N}_3\text{S}$: S, 15.2. Found: S, 15.6.

S-Methyl-2-methylthiosemicarbazide Sulfate (V).—In a 250 ml. r. b. flask fitted with a reflux condenser were placed

19 g. (0.143 mole) of (IV), 150 ml. of dry isopropyl alcohol and 12 ml. of methyl iodide. The mixture was refluxed for forty-five minutes, the alcohol distilled on the steam-bath, and the residual thick oil dissolved in 300 ml. of water containing three drops of glacial acetic acid. Silver sulfate, 19.6 g. (0.07 mole) was added with stirring, and the mixture was stirred for an additional hour. The silver iodide was removed and the filtrate evaporated to dryness on the steam-bath. Crystallization of the residue from 90% ethanol gave 10 g. (43%) of long white needles, m. p. 138–140° dec. *Anal.* Calcd. for $(\text{C}_2\text{H}_5\text{N}_3)_2\cdot\text{H}_2\text{SO}_4$: S, 11.7. Found: S, 11.8.

1-Methyl-1-aminoguanidine Sulfate (II).—A 100 ml. r. b. flask was fitted with a condenser equipped with a gas venting tube to two gas scrubbers containing a 25% solution of sodium hydroxide. A solution containing 8.0 g. (0.051 mole) of (V) in 30 ml. of water and 4 ml. (0.05 mole) of concentrated ammonia water was added to the flask and refluxed for one hour. The solution was evaporated to dryness on the steam-bath and the residue was crystallized from 50% ethanol to give 3 g. (62%) of long white needles, m. p. 287–289° dec. *Anal.* Calcd. for $\text{C}_2\text{H}_5\text{N}_4\cdot\frac{1}{2}\text{H}_2\text{SO}_4$: S, 11.7. Found: S, 11.6.

Method B. 1-Methyl-1-aminoguanidine Sulfate (II).—Employing the same apparatus previously described, 34.5 g. (0.24 mole) of methylhydrazine sulfate was dissolved in 72 ml. of water, the solution neutralized to congo red paper with a measured volume of a 40% solution of potassium hydroxide and then an equivalent volume of this solution was added. The hydrazine solution was added to a suspension of 34.8 g. (0.12 mole) of S-methylthiourea sulfate in 60 ml. of water. The mixture was refluxed for forty-five minutes when no further methyl mercaptan was evolved. The liquid was evaporated to 25% of the original volume on the steam-bath, 100 ml. of boiling ethanol added, the precipitated potassium sulfate filtered and the filtrate chilled overnight. Nine grams (55%) of a white crystalline material was obtained, m. p. 293–293.5° dec. after several recrystallizations from 80% ethanol. A mixed melting point was made with the material obtained from Method A and showed no depression. *Anal.* Calcd. for $\text{C}_2\text{H}_5\text{N}_4\cdot\frac{1}{2}\text{H}_2\text{SO}_4$: S, 11.7; N, 40.09. Found: S, 11.5; N, 40.15.

Benzylidene derivative, m. p. 173–175°. *Anal.* Calcd. for $\text{C}_9\text{H}_{12}\text{N}_4$: N, 31.21. Found: N, 31.24.

Summary

A new isomer of methylaminoguanidine, 1-methyl-1-aminoguanidine has been described and characterized as its sulfate salt.

A possible mechanism for the formation of 2-methylthiosemicarbazide has been offered.

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RECEIVED AUGUST 3, 1949

(6) Cattelain, *Compt. rend.*, **209**, 799 (1939).