



The replacement of a single nitrogen methyl group in the trimethylammonium series by an amino group of similar dimensions makes this type of analog of theoretical as well as practical interest in the field of pharmacological activity and chemical constitution.

A synthesis of unsymmetrical dimethylhydrazine through the reduction of nitrosodimethylamine using lithium aluminum hydride has already been reported.<sup>3</sup> During the present research it was found expedient to prepare decamethylene dibromide starting with ethyl sebacate using lithium aluminum hydride. The preparation of decamethylene dibromide from the glycol makes use of a method essentially similar to that outlined by McEwen.<sup>4</sup> Preparation of the hydrazoneium analog of C<sub>10</sub> is given in the experimental section and requires no special comment. A preliminary report upon the pharmacological properties of this material have been detailed elsewhere.<sup>5</sup>

The LD<sub>50</sub> for mice of the hydrazoneium C<sub>10</sub>-analog is 26 mg. per kg. and the head drop dose (HDD) for rabbits 2.9 mg. per kg. The ratio of the LD<sub>50</sub> for mice to the HDD for rabbits is, therefore, of the same order as C<sub>10</sub>.

#### Experimental

**Decamethylene Glycol.**—To a slurry of 4 g. of lithium aluminum hydride in 350 ml. of dry tetrahydrofuran contained in a 1-liter 3-necked flask under reflux and vigorous stirring was added 26 g. (0.1 mole) of dry diethyl sebacate in 200 ml. of tetrahydrofuran. The addition requires 45 to 60 minutes but the time of addition may be shorter than that given above but care should be exercised in order to avoid excessive refluxing of the solvent. At the completion of the addition of the diethyl sebacate the flask contents are allowed to stand until cool (about 30 minutes). Anhydrous ethyl acetate is used to destroy any excess reagent, lumps are broken up with a stirring rod and the mixture decomposed with about 500 ml. of dilute hydrochloric acid after which the mixture is cooled. The oily layer is separated, washed twice with 100-ml. portions of cool water and finally chilled to a white solid. If the washings are likewise chilled together with the hydrochloric acid layer a further small quantity of white solid is obtained. The collected solid is washed twice with 100-ml. portions of cold water by filtration. The product represents an 80% yield of decamethylene glycol which is white if the initial reagents are pure. It melts at 71.5° (cor.) and corresponds without further purification in quality to the purified material obtained through sodium alcohol reduction.

**Decamethylene Di-(dimethylhydrazoneium) Dibromide.**—In 10 ml. of dry ether are mixed 3.0 g. (0.01 mole) of pure decamethylene dibromide<sup>4</sup> and 1.2 g. (0.02 mole) of dry unsymmetrical dimethylhydrazine. The mixture is allowed to stand at room temperature in a stoppered bottle for one week. At the end of this time, 3.2 g. (98% of the theory) of a non-hygroscopic white solid is obtained after filtration and washing with small portions of dry ether; m.p. 114–115.5° (cor.). *Anal.* Calcd. for C<sub>14</sub>H<sub>32</sub>N<sub>4</sub>Br<sub>2</sub>: N, 16.22. Found: N, 15.88.

Unsymmetrical dialkylhydrazines react with alkyl bromides and iodides to form "onium" ion on the alkyl sub-

stituted nitrogen.<sup>6</sup> In the case of the hydrazoneium C<sub>10</sub>-analog a marked change in the curarimimetic activity would result depending on whether the compound was an "onium" bromide or an amino hydrobromide.

To 0.5 g. of the above product was added 50 ml. of cold 30% sodium hydroxide. No oil separated out and no ammoniacal odor could be detected. This solution (A) was extracted with six 50-ml. portions of ether. The combined ether extracts were evaporated to dryness and the residue (B) was extracted with 100 ml. of absolute ether. The ether was treated with dry hydrobromic acid and no crystals formed even on slow evaporation to 5 ml. The residue (B) gave a positive test for sodium ions and the aqueous solutions were alkaline. The alkaline solution (A) was allowed to remain in an uncovered beaker for 26 days during which time crystals formed over the top of the solution. In this solid, oily drops formed which were mechanically separated giving 0.12 g. of an oily semi-solid. This oil was soluble in a drop of water and on treatment with 20 ml. of a satd. sodium bromide solution no organic compound could be separated by fractional crystallization. These results would indicate that the compound prepared above is decamethylene di-(dimethylhydrazoneium) dibromide since no tertiary amine could be isolated from solution (A).

(6) Renauf, *Ber.*, **13**, 2172 (1880); Wieland and Schamberg, *ibid.*, **53**, 1333 (1920); Westphal, *ibid.*, **74B**, 759, 1365 (1941).

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### On the Question of Mercury(I) Intermediates in Reactions between Hg<sub>2</sub>Cl<sub>2</sub> and Ammonia

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The formation of the mercury(II) compounds Hg<sub>2</sub>NCl·H<sub>2</sub>O (chloride of Millon's base), HgNH<sub>2</sub>Cl (infusible precipitate) and Hg(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (fusible precipitate) has been demonstrated<sup>1–4</sup> in reactions among ammonia, ammonium chloride and mercury(I) chloride. The claim<sup>4</sup> of an intermediate Hg<sub>2</sub>O has now been disproved.<sup>1</sup> Extensive evidence for the existence of the mercury(I) analogs of these three mercury(II) compounds has been presented by Gleditsch and Egidius.<sup>2,3</sup> In the present study we have repeated these chemical preparations<sup>3</sup> and have taken X-ray diffraction patterns with a standard General Electric XRD-3 unit. While our diffraction patterns agree favorably with those of the earlier papers<sup>2,3</sup> our conclusions are completely different.

The diffraction pattern attributed by Gleditsch and Egidius<sup>2</sup> to Hg<sub>2</sub>NH<sub>2</sub>Cl corresponds with our pattern of Hg<sub>2</sub>NCl·H<sub>2</sub>O. The diffraction pattern given by Egidius<sup>3</sup> for Hg<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> is that of a mixture of Hg(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and Hg<sub>2</sub>Cl<sub>2</sub>. The pattern<sup>3</sup> of Hg<sub>2</sub>NH<sub>2</sub>Cl is actually that of HgNH<sub>2</sub>Cl and is different from that given in an earlier paper<sup>2</sup> for Hg<sub>2</sub>NH<sub>2</sub>Cl. The pattern given<sup>3</sup> for Hg<sub>4</sub>NCl·(H<sub>2</sub>O)<sub>x</sub> is actually that of Hg<sub>2</sub>NCl·H<sub>2</sub>O, and we have been unable to identify the pattern given<sup>3</sup> by Egidius for Hg<sub>2</sub>NCl·H<sub>2</sub>O, but unfortunately the method of preparation is not given. The struc-

(1) S. D. Arora, W. N. Lipscomb and M. C. Sneed, *THIS JOURNAL*, **73**, 1015 (1951).

(2) E. Gleditsch and T. F. Egidius, *Compt. rend.*, **202**, 574 (1936); *Z. anorg. Chem.*, **226**, 265 (1936); *ibid.*, **228**, 249 (1936).

(3) T. F. Egidius, *ibid.*, **240**, 97 (1938).

(4) H. Freche and M. C. Sneed, *THIS JOURNAL*, **60**, 518 (1938).

(3) F. W. Schueler and Calvin Hanna, *THIS JOURNAL*, **73**, 4996 (1951).

(4) W. L. McEwen, *Org. Syntheses*, **20**, 24 (1940).

(5) Calvin Hanna and F. W. Schueler, Abstracted in the Proceedings of the Society for Pharmacology and Experimental Therapeutics, Omaha Meeting, 1951.

ture determinations of  $\text{Hg}_2\text{NCl}\cdot\text{H}_2\text{O}$ ,<sup>5</sup>  $\text{HgNH}_2\text{Cl}^6$  and  $\text{Hg}(\text{NH}_3)_2\text{Cl}_2^7$  provide conclusive evidence that these are really mercury(II) compounds. Thus the investigations of Gleditsch and Egidius do not prove the existence of mercury(I) intermediates in these reactions.

In addition, we have found no mercury(I) intermediates in investigations over the full ranges of concentrations of aqueous solutions, whether diffraction patterns are taken of wet or dry precipitates.

An interesting change occurs in the precipitates at the early stages of the reaction. When wet or immediately after drying,  $\text{Hg}_2\text{Cl}_2$  may not be observed, but gradually appears on standing, sometimes rapidly, and sometimes after a day or so. We believe that this phenomenon is due to the presence of Hg and other reaction products formed at the surface of  $\text{Hg}_2\text{Cl}_2$  crystals, which are therefore obscured from the relatively non-penetrating  $\text{CuK}\alpha$  radiation. Subsequent agglomeration and evaporation of the Hg thus makes these crystals of  $\text{Hg}_2\text{Cl}_2$  available for diffraction.

The chloride of Millon's base appears to show also a crystalline modification which is a very slight distortion of the cubic form previously reported.<sup>6</sup> The (222) reflection shows splitting into two nearly equal components  $0.6^\circ$  apart on the diffraction pattern. This split reflection becomes single on conversion to the base by treatment with 20% aqueous KOH, and becomes split again when the base is reconverted to the chloride in 20% aqueous KCl. The nature of this distortion has not been ascertained, partly because the particle size broadening of the reflections makes the details of the pattern obscure, especially at higher scattering angles. The variations of this small distortion may be related to the degree of hydration of this compound, or to the degree of substitution of  $\text{OH}^-$  for  $\text{Cl}^-$ .

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(5) W. N. Lipscomb, *Acta Cryst.*, **4**, 156 (1951).

(6) W. N. Lipscomb, *ibid.*, **4**, 266 (1951).

(7) C. H. MacGillivray and J. M. Bijvoet, *Z. Kristall.*, **94**, 231 (1936).

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### The Reaction of Sodium Tungsten Bronze with Molybdenum(VI) Oxide. The Sodium Molybdenum Bronze<sup>1</sup>

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Sodium tungsten bronze easily dissolves tungsten(VI) oxide at elevated temperatures, forming solid solutions.<sup>2</sup> It was expected that molybdenum(VI) oxide, which is very similar in its properties to tungsten(VI) oxide, would also form solid solutions with the sodium tungsten bronze. The pur-

pose of this paper is to describe the reactions that occurred during the heating of a mixture of the two compounds just mentioned.

Closely related to the reactivity of molybdenum(VI) oxide with sodium tungsten bronze is the preparation and existence of alkali molybdenum bronzes. Sodium molybdenum bronze was first mentioned by Stavenhagen and Engels,<sup>3</sup> who obtained the bronze, by the electrolytic decomposition of fused sodium molybdate in the form of a dark bluish-grayish, or reddish-violet powder, having the properties of the bronzes. Later the lithium, sodium and potassium molybdenum bronzes were prepared by Canneri,<sup>4</sup> using the same method and with a small yield. However, the next year Burgers and van Liempt<sup>5</sup> showed that the bronzes mentioned by Canneri were mixtures consisting of molybdenum(IV) oxide and molybdenum blue. Finally, according to Magnéli, only molybdenum oxides were obtained by Hägg in similar experiments.<sup>6</sup>

An attempt was made to prepare sodium molybdenum bronze by a method described previously.<sup>2</sup>

#### Experimental

The materials for the experiments were sodium tungsten bronzes containing 10 and 22% by weight tungsten(VI) oxide,<sup>2</sup> dry molybdenum(VI) oxide and sodium molybdate. The molybdenum metal used was an electrolytically produced powder.

Calculated amounts of these reagents were weighed, intimately mixed, and ground. Then the mixtures were put in porcelain crucibles with a copper lid and heated in a furnace which could be evacuated. Or else the mixtures were put into quartz glass bulbs, evacuated, sealed off, and heated at different temperatures between 450 and 1000°.

The reaction products were well washed with water.<sup>2</sup> The composition of all water soluble and insoluble compounds were identified by their X-ray diffraction patterns. The corresponding compounds for the identification were synthesized (e.g.,  $\text{Na}_2\text{WO}_4(\text{MoO}_3)_x$ ,  $x < 1$ ). All reagents used were of the highest purity obtainable.

#### Results and Discussion

**Sodium Tungsten Bronze and Molybdenum(VI) Oxide.**—Qualitative tests showed that a reaction proceeds between these two substances, because the mixture turns deep blue when heated. Samples of sodium bronze (with 10% tungsten(VI) oxide) containing 5, 10, 15, 20 and 30% by weight of molybdenum(VI) oxide were prepared and heated for two hours at 800°. This resulted in there still being a bronze in the first four cases, but with a lattice parameter which rapidly decreased from 3.8436 kX. to 3.8310 kX. as the molybdenum(VI) oxide content was increased. However, the appearance of strange lines in the patterns of samples even with 5% molybdenum(VI) oxide testified that no equilibrium was reached during the heating and that a chemical reaction occurred. The strange lines belonged to the powder pattern of molybdenum(IV) oxide. Hence, the following reactions occur during heating in a vacuum, assuming that reaction (1) represents the equilibrium of the sodium bronze at elevated temperatures as shown previously<sup>2</sup>

(3) A. Stavenhagen and E. Engels, *Ber.*, **28**, 2281 (1895).

(4) C. Canneri, *Gazz. chim. ital.*, **60**, 113 (1930).

(5) W. G. Burgers and J. A. M. van Liempt, *Z. anorg. Chem.*, **202**, 325 (1931).

(6) A. Magnéli, *N. Acta Reg. Sc. Upsalienis*, **14**, No. 8, 16 (1949).

(1) Excerpt from a thesis submitted by K. K. Irani to the Graduate School of the University of Missouri, School of Mines and Metallurgy, in partial fulfillment of the requirements for a Master's Degree.

(2) M. E. Straumanis, *This Journal*, **71**, 679 (1949).