*p*H 3.5. The *p*H at which the color change to green first appeared decreased as the concentration of sulfosalicylic acid was increased. These *p*H effects indicate that complex formation probably involves the $^{-}OOCC_6H_3OHSO_3^{-}$ ion. The second dissociation constant[2] for the acid is in the range $1.5\text{–}3.2 \times 10^{-3}$. Thus in the *p*H range 3–5, the second dissociation is from 60 to virtually 100% complete.

The extent of complex formation decreased somewhat with increased temperature. Heating from 23 to 32°, for example, decreased the intensity of color.

Addition of excess sulfosalicylic acid increased the color intensity, with the maximum absorption shifting slightly toward longer wave lengths. With a 1:3 ratio of chromium(III) to sulfosalicylic acid, the peak occurred at 570 mμ. Small increases in absorption were also observable in the region of 430 and 630 mμ.

The Job method of continuous variations[3] was employed to determine the composition of the complex at a *p*H 5.0. The four wave lengths indicated by the previous discussion were used: 430, 630, 550 and 570 mμ. Typical data are shown graphically in Fig. 2, at 550, 570 and 630 mμ. The data at 430 mμ were inconclusive because of the relatively large corrections which had to be made for absorption by the chromium(III).

The optical density data recorded on Fig. 2 are values of $\bar{D}$, which is the observed optical density of the particular mixture minus the absorption which the chromium(III) and sulfosalicylic acid would show had no reaction occurred. A plot of $\bar{D}$ against mole fraction of chromium(III) should exhibit a maximum value of $\bar{D}$ corresponding to the mole ratio in which the reagents combine to form the complex.

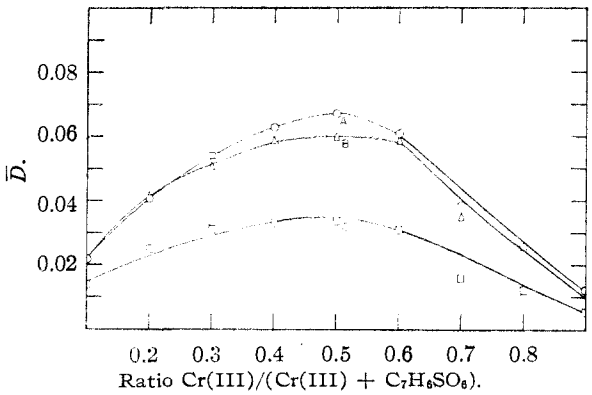

Fig. 2.—Method of continuous variations: A, 550 mμ; B, 570 mμ; C, 630 mμ.

The peaks which occur at a mole fraction of 0.5 correspond to a 1:1 mole ratio of the two components in the complex. Since the data at 570 mμ still indicate a 1:1 complex with only a small shift toward higher ratios, it may be concluded that, although other complexes may be present in the system, they occur in low enough relative concentrations to make their detection by the present methods uncertain.

The experimental errors, arising particularly from the relatively large corrections necessary for absorption by the chromium(III) nitrate, make it impractical to use the spectrophotometric technique for studies of the structure of the complex. It is notable, however, that the color effects, etc., with the sulfosalicylic acid resemble closely those reported with sulfate.[4]

The experimental difficulties also make infeasible calculations of the extinction coefficient of the complex and the equilibrium constant for its formation. Approximate evaluation of these by the methods already outlined[1] indicates that the extinction coefficient for the complex is approximately 40 at 550 mμ and that the equilibrium constant for formation of the complex from chromium(III) and sulfosalicylate ions is of the order of magnitude of 10^{-3}.

Experimental

Materials.—Chromium(III) nitrate stock solutions were prepared by dissolving accurately weighed quantities of the monohydrate in water at 25°. The concentration was checked by gravimetric analysis as chromium(III) oxide.

Sulfosalicylic acid and sodium hydroxide were prepared as described earlier.[1] Sodium nitrate solution was prepared by dissolving a weighed quantity of the salt in water.

Absorption measurements were made with a Beckman DU type spectrophotometer and a General Electric Hardy Recording Spectrophotometer.

In the preparation of all solutions at constant *p*H, the chromium(III) nitrate and sulfosalicylic acid were added in such amounts as to give the desired final concentration. A relatively large excess of sodium nitrate was then introduced to maintain a constant final ionic strength of 0.30. Water was added to the mixture to a point only several cubic centimeters short of the required volume. Acid or base was then added to adjust the solution to the desired *p*H before diluting to the final volume with water.

(2) C. V. Banks and James H. Patterson, *ibid.*, **73**, 3062 (1951). See also footnote 1.

(3) P. Job, *Ann. Chim.*, **11**, 97 (1936); *cf.* Vosburgh and Cooper, THIS JOURNAL, **63**, 436 (1941).

(4) *Cf.* for example: Graham, *Am. Chem. J.*, **48**, 187 (1912); Colson, *Ann. chim. phys.*, [8] **12**, 433 (1907).

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A Curarimimetic Analog of Decamethylene Ditrimethylammonium (C_{10})[1]

BY F. W. SCHUELER AND CALVIN HANNA

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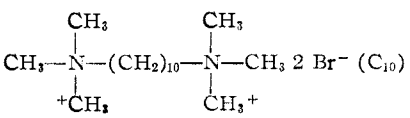
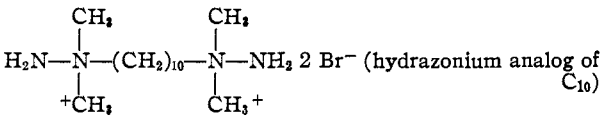
In a previous communication,[2] the synthesis and pharmacological properties of several hydrazonium analogs related to acetylcholine and tetraethylammonium have been reported. The present communication extends these previous studies to the synthesis of a new curarimimetric analog of C_{10} obtained through the quaternarization of unsymmetrical dimethylhydrazine with decamethylene dibromide.



(1) This research was supported by a grant from the United States Public Health Service.

(2) F. W. Schueler and Calvin Hanna, *Arch. intern. pharmacodynamie*, **88**, 351 (1951).



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.[3] 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.[4] Preparation of the hydrazonium analog of C_{10} 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.[5]

The LD_{50} for mice of the hydrazonium C_{10}-analog is 26 mg. per kg. and the head drop dose (HDD) for rabbits 2.9 mg. per kg. The ratio of the LD_{50} for mice to the HDD for rabbits is, therefore, of the same order as C_{10}.

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-(dimethylhydrazonium) Dibromide.—In 10 ml. of dry ether are mixed 3.0 g. (0.01 mole) of pure decamethylene dibromide[4] 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 $C_{14}H_{36}N_4Br_2$: N, 16.22. Found: N, 15.88.

Unsymmetrical dialkylhydrazines react with alkyl bromides and iodides to form "onium" ion on the alkyl substituted nitrogen.[6] In the case of the hydrazonium C_{10}-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-(dimethylhydrazonium) dibromide since no tertiary amine could be isolated from solution (A).

(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.

(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_2Cl_2 and Ammonia

BY LIES NIJSSEN AND WILLIAM N. LIPSCOMB

RECEIVED JANUARY 14, 1952

The formation of the mercury(II) compounds $Hg_2NCl\cdot H_2O$ (chloride of Millon's base), $HgNH_2Cl$ (infusible precipitate) and $Hg(NH_3)_2Cl_2$ (fusible precipitate) has been demonstrated[1–4] in reactions among ammonia, ammonium chloride and mercury(I) chloride. The claim[4] of an intermediate Hg_2O has now been disproved.[1] Extensive evidence for the existence of the mercury(I) analogs of these three mercury(II) compounds has been presented by Gleditsch and Egidius.[2,3] In the present study we have repeated these chemical preparations[3] 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[2,3] our conclusions are completely different.

The diffraction pattern attributed by Gleditsch and Egidius[2] to Hg_2NH_2Cl corresponds with our pattern of $Hg_2NCl\cdot H_2O$. The diffraction pattern given by Egidius[3] for $Hg_2(NH_3)_2Cl_2$ is that of a mixture of $Hg(NH_3)_2Cl_2$ and Hg_2Cl_2. The pattern[3] of Hg_2NH_2Cl is actually that of $HgNH_2Cl$ and is different from that given in an earlier paper[2] for Hg_2NH_2Cl. The pattern given[3] for $Hg_4NCl(H_2O)_x$ is actually that of $Hg_2NCl\cdot H_2O$, and we have been unable to identify the pattern given[3] by Egidius for $Hg_2NCl\cdot H_2O$, 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).