(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline. Diethyl malonate, ethyl acetoacetate,[2] ethyl phenylacetate and acetonitrile failed to yield products analogous to II under similar reaction conditions.

Experimental[6]

Reaction of 1-Methylquinolinium Iodide with Malononitrile.—To a mixture of 13.6 g. (0.05 mole) of 1-methylquinolinium iodide, m.p. 146°, 3.3 g. (0.05 mole) of malononitrile and 100 ml. of absolute ethanol, cooled in an ice-bath, was added with vigorous stirring a solution prepared from 2.3 g. (0.10 gram atom) of sodium in 50 ml. of absolute ethanol. The stirring was continued for 3 hours, and then the mixture was allowed to stand overnight. The product was isolated by filtration. Two recrystallizations from absolute ethanol gave 1.1 g. (10%) of material crystallizing as fine yellow filaments, m.p. 291.5–292.5°.

Anal. Calcd. for $C_{13}H_9N_3$: C, 75.35; H, 4.38; N, 20.28. Found: C, 75.12; H, 4.17; N, 20.30.

The infrared spectrum showed strong absorption in the nitrile region, at 2197 and 2176 cm.$^{-1}$, and indicative of conjugation with the nitrile groups, also a band at 1625 cm.$^{-1}$ and a double band at 1619–1620 cm.$^{-1}$.

1-Methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline (IIb).—1-Methyl-4-chloroquinolinium iodide, prepared by heating 4-chloroquinoline[7] under reflux with excess methyl iodide,[5] was recrystallized from ethanol as yellow needles, m.p. 204–206°. A mixture of 1.3 g. (0.004 mole) of 1-methyl-4-chloroquinolinium iodide, 0.3 g. (0.004 mole) of malononitrile and 75 ml. of absolute ethanol was cooled in an ice-bath. A solution of sodium ethoxide prepared from 0.1 g. (0.004 gram atom) of sodium and 50 ml. of absolute ethanol was added with vigorous stirring. The reaction appeared to take place immediately but stirring was continued for 8 hours to ensure completeness of reaction. The product was collected by filtration, and the yield was quantitative. Two recrystallizations from ethanol gave yellow filaments, m.p. 291.5–292°, which did not depress the melting point of the $C_{13}H_9N_3$ product obtained from 1-methylquinolinium iodide and malononitrile. The infrared spectra were also identical.

Reaction of 1,2-Dimethylquinolinium Iodide with Malononitrile. 1,2-Dimethyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline.—To a mixture of 14.2 g. (0.05 mole) of 1,2-dimethylquinolinium iodide, m.p. 195–196°, 3.3 g. (0.05 mole) of malononitrile, and 100 ml. of absolute ethanol, cooled in an ice-bath, was added with vigorous stirring a solution prepared from 1.2 g. (0.05 gram atom) of sodium in 50 ml. of absolute ethanol. Stirring was continued for 4 hours and the reaction mixture was allowed to stand at 25° for an additional 4 hours. The product was isolated by filtration and was recrystallized from absolute ethanol as yellow needles, m.p. 267.5–268°; yield 3.8 g. (34%).

Anal. Calcd. for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 18.99. Found: C, 76.16; H, 5.26; N, 19.14.

1-Methyl-4-(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline (IIc).—This compound was obtained from equimolar quantities of 1-methylquinolinium iodide, ethyl cyanoacetate and sodium ethoxide, following the same directions as those given in the preceding paragraph. The product was isolated as yellow needles from ethanol, m.p. 181.5–182.5°; yield 2.9 g. (23%).

Anal. Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.84; H, 5.55; N, 11.02. Found: C, 70.86; H, 5.66; N, 11.10.

The infrared spectrum showed strong absorption at 2189 cm.$^{-1}$, indicative of nitrile, and 1671 cm.$^{-1}$, indicative of carbonyl, as well as bands at 1624 and 1617 cm.$^{-1}$, similar to those exhibited by IIb.

1,2-Dimethyl-4-(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline.—This compound was prepared by the same method, using equimolar quantities of 1,2-dimethylquinolinium iodide, ethyl cyanoacetate and sodium ethoxide. The product was recrystallized from acetone as yellow needles, m.p. 172.5–173.5°.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.32; H, 6.20; N, 10.25.

Reactions of 1-Methylquinolinium Iodide with Other Active Methylene Compounds.—The reactions of 1-methylquinolinium iodide with diethyl malonate, acetonitrile and ethyl phenylacetate in ethanol with sodium ethoxide failed to produce any isolable condensation product. The reaction of 1-methylquinolinium iodide with ethyl acetoacetate in aqueous sodium hydroxide solution failed to produce the condensation product described by Kaufmann.[2] When sodium ethoxide in ethanol was used, the same result was obtained.

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RECEIVED DECEMBER 17, 1951

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[6] Melting points are corrected. The authors are indebted to Miss Elizabeth M. Petersen for determination of the infrared absorption spectra and to Miss Emily Davis, Mrs. Jean Fortney and Mrs. Katherine Pih for the microanalyses.

[7] B. Riegel, G. R. Lappin, B. H. Adelson, R. I. Jackson, C. J. Albisetti, Jr., R. M. Dodson and R. H. Baker, THIS JOURNAL, **68**, 1264 (1946).

Spectrophotometric Studies of Complex Formation with Sulfosalicylic Acid. V. With Chromium(III)

BY ALFRED M. LIEBMAN AND ROBBIN C. ANDERSON

RECEIVED NOVEMBER 23, 1951

The reaction of chromium(III) with sulfosalicylic acid has been studied as part of a series of investigations on complex formation in solution between sulfosalicylic acid and ions of various elements.[1]

Figure 1 shows, for comparison, the absorption spectrum of an equimolar mixture of chromium(III) nitrate and sulfosalicylic acid and those for corresponding solutions of each separately. Curve B shows the net difference in transmittance when the absorption curve for the mixture was determined using the chromium(III) as a blank. It is evident that some colored product is formed, with a maximum in absorption at 550 mμ. It was also found that the presence of sulfosalicylic acid increased materially the pH at which precipitation of chromium(III) hydroxide could occur.

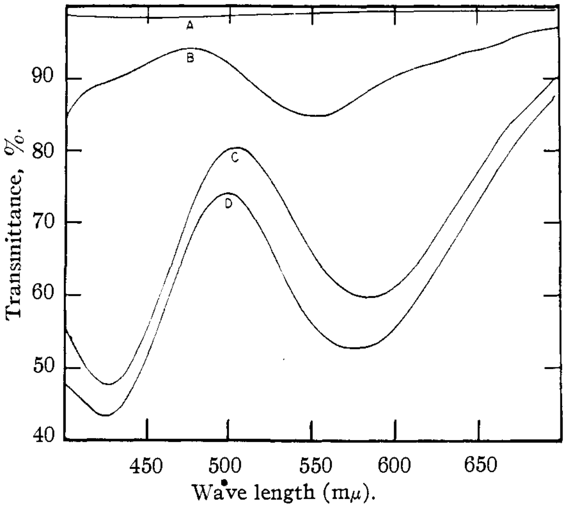

Fig. 1.—Absorption spectra: A, 0.0025 SSA *vs.* H_2O blank; B, 1:1 Cr(III)/SSA total molarity = 0.005 *vs.* Cr(III) blank (0.0025 *M*); C, Cr(III) (0.0025 *M*) *vs.* H_2O blank; D, 1:1 Cr(III)/SSA total molarity = 0.005 *vs.* H_2O blank.

Measurements in solutions of different pH values showed maximum color intensities in the range of

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[1] R. T. Foley and R. C. Anderson, THIS JOURNAL, **70**, 1195 (1948); **71**, 909 (1949); **72**, 5609 (1950); S. E. Turner and R. C. Anderson, *ibid.*, **71**, 912 (1949).

pH 3.5. The pH at which the color change to green first appeared decreased as the concentration of sulfosalicylic acid was increased. These pH 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 $1.5–3.2 \times 10^{-3}$. Thus in the pH 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 pH 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.

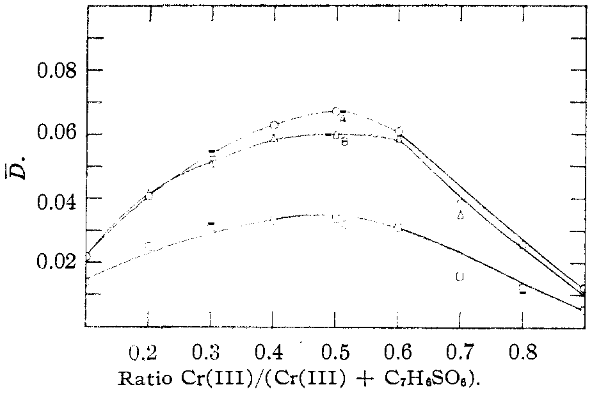

Fig. 2.—Method of continuous variations: A, 550 mμ; B, 570 mμ; C, 630 mμ.

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 pH, 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 pH before diluting to the final volume with water.

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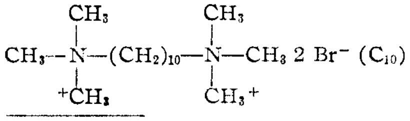
A Curarimimetic Analog of Decamethylene Ditrimethylammonium (C_{10})[1]

BY F. W. SCHUELER AND CALVIN HANNA

RECEIVED SEPTEMBER 10, 1951

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.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle {}^{+}CH_3}{N}}-(CH_2)_{10}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3{}^{+}}{N}}-CH_3\ 2\,Br^{-}\ (C_{10})$$

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[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).