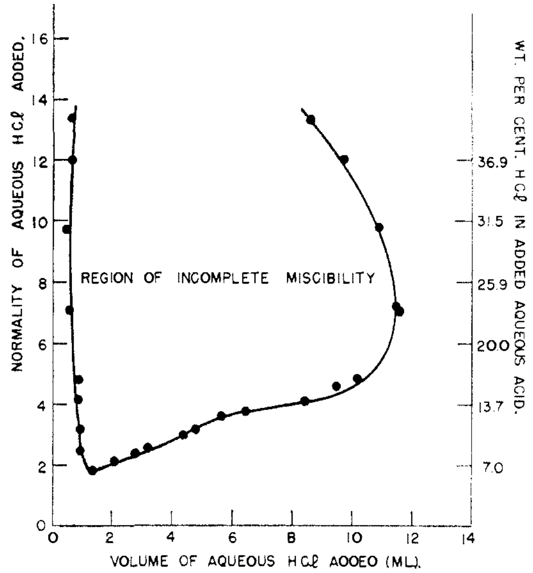

Fig. 4.—Solubility of aqueous hydrochloric acid of various concentrations on 25 ml. of 1,4-dioxane at 25.0°.

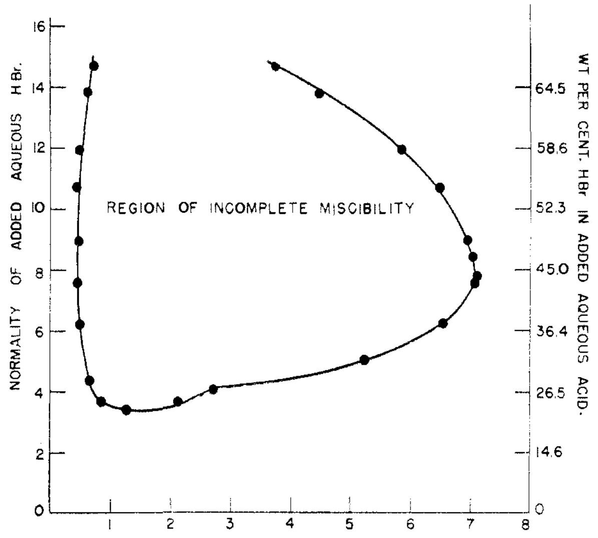

Fig. 5.—Solubility of aqueous hydrobromic acid of various concentrations in 25.0 ml. of 1,4-dioxane at 25.0°.

less than 1.87 N and hydrobromic acid solutions less than 3.64 N are completely miscible with 1,4-dioxane.

Acknowledgment.—The authors are indebted to Dr. S. W. Kantor, for supplying some of the purified dioxane employed in this study, and to Mr. L. B. Bronk for analysis of some of the aqueous hydrogen chloride samples.

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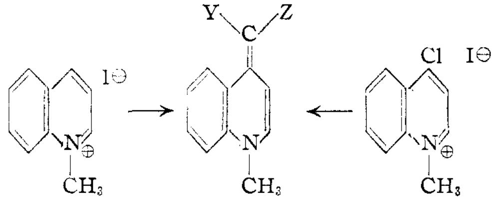
Reactions of Quinolinium Compounds with Malononitrile and Ethyl Cyanoacetate

BY NELSON J. LEONARD AND ROBERT L. FOSTER

Our finding[1] that the product resulting from the condensation of 1-methylquinolinium iodide (I) with nitromethane in the presence of base is 1-methyl-4-nitromethylenequinolane (IIa), a correction of the structure suggested earlier by Kaufmann,[2] prompted the investigation of the reaction of 1-methylquinolinium iodide with other active methylene compounds. Malononitrile and ethyl cyanoacetate, of activity commensurate with that of nitromethane, have now been found to undergo reaction with quinolinium compounds to give similar condensation products (II). The reaction is related to that used for the preparation of dyes of the cyanine and isocyanine type,[3] which possess 4,α-unsaturation.



I II III

a, Y = H; Z = NO_2;
b, Y = CN; Z = CN;
c, Y = CN; Z = COOEt

Combination of 1-methylquinolinium iodide (I) with malononitrile in ethanolic sodium ethoxide gave a yellow product, m.p. 291.5–292.5°, in low yield. The analysis was correct for its formulation as 1-methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline (IIb), analogous to the established structure of the product (IIa) from nitromethane. The infrared absorption spectrum was also consistent with structure IIb. This structure was established unequivocally by the synthesis, in quantitative yield, of 1-methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline from 1-methyl-4-chloroquinolinium iodide (III) and malononitrile in alkaline solution. The products from the two reactions were identical. The device of comparing products obtained from 1-alkylquinolinium iodide with those from either the 4-chloro- or 4-iodo-1-alkylquinolinium iodide[4,5] has been useful for proving 4-substitution in the isocyanine dyes.

Malononitrile reacted with 1,2-dimethylquinolinium iodide in the presence of sodium ethoxide to produce 1,2-dimethyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline in 34% yield. The structure of the product as the 2-methyl derivative of IIb was assigned on the basis of homology and effective blocking of the 2-position from attack by the malononitrile anion. The condensation of 1-methylquinolinium iodide with ethyl cyanoacetate gave 1-methyl-4-(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline (IIc), the structure of which was assigned on the basis of elemental analysis, analogy with the preceding examples, and similarity of the infrared spectrum with that of IIb. Similarly, 1,2-dimethylquinolinium iodide and ethyl cyanoacetate yielded 1,2-dimethyl-4-

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(1) N. J. Leonard, H. A. DeWalt, Jr., and G. W. Leubner, THIS JOURNAL, **73**, 3325 (1951).

(2) A. Kaufmann, German Patent 250,154, July 15, 1912; *Frdl.*, **10**, 1317 (1910–1912).

(3) F. M. Hamer, *Quart. Revs.*, **4**, 327 (1950); M. Q. Doja, *Chem. Revs.*, **11**, 273 (1932); E. C. Franklin and F. W. Bergstrom, *ibid.*, **35**, 77 (1944).

(4) A. Kaufmann and E. Vonderwahl, *Ber.*, **45**, 1404 (1912).

(5) F. M. Hamer, *J. Chem. Soc.*, 1008 (1939).

(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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(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

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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.

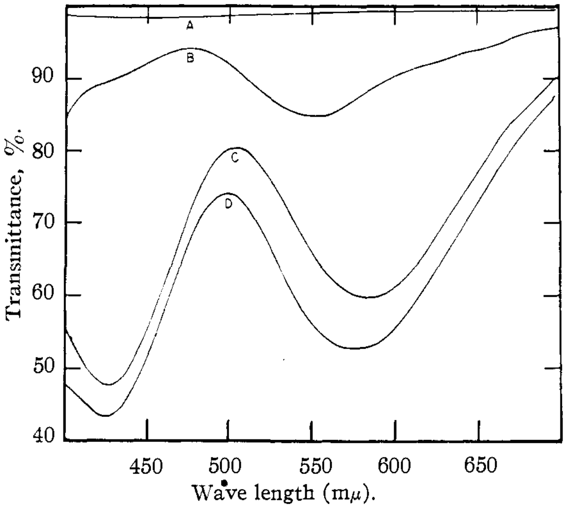

Fig. 1.—Absorption spectra: A, 0.0025 SSA *vs.* H_2O blank; B, 1:1 Cr(III)/SSA total molarity = 0.005 *vs.* Cr(III) blank (0.0025 *M*); C, Cr(III) (0.0025 *M*) *vs.* H_2O blank; D, 1:1 Cr(III)/SSA total molarity = 0.005 *vs.* H_2O blank.

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).