

2. These compounds follow, with certain qualifications, the same qualitative differentiation previously found to exist between primary, secondary and tertiary amines of the aryl and aryl-alkyl types.

3. In di- and tribenzylamine both the  $3.3 \mu$  band and the  $3.5 \mu$  band have been resolved. The significance of this observation has been indicated.

4. A new band characteristic of the benzene nucleus has been located at  $5.1 \mu$ .

BALTIMORE, MARYLAND

[CONTRIBUTION No. 110 FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY,  
UNITED STATES DEPARTMENT OF AGRICULTURE]

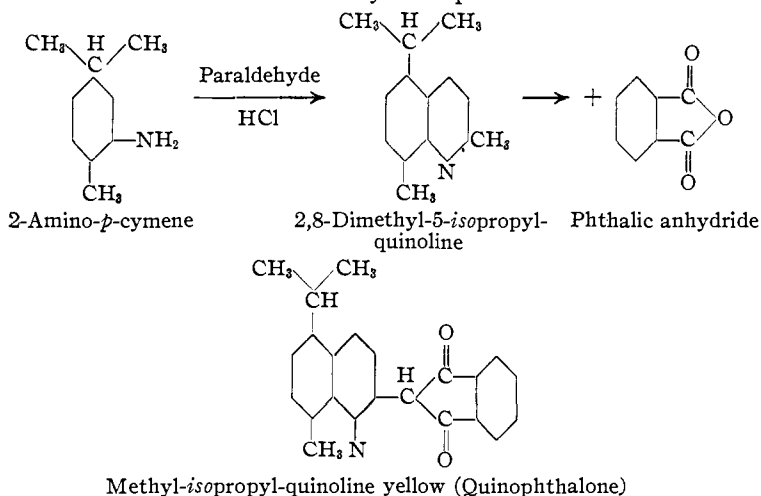
## THE PREPARATION AND PROPERTIES OF METHYL-ISOPROPYL-QUINOLINE YELLOW

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An investigation was undertaken for the purpose of ascertaining the effect of the methyl-*isopropyl* substitution on the absorption and fastness of quinoline yellow. The starting material for the preparation of the new dye was 2-amino-*p*-cymene. This amino compound was converted into 2,8-dimethyl-5-*isopropyl*-quinoline by the Doebner and Miller<sup>1</sup> modification of the Skraup synthesis. When condensed with phthalic anhydride this quinoline derivative yielded methyl-*isopropyl*-quinoline yellow. The reactions involved may be represented as follows:



### Experimental Part

**Methyl-*isopropyl*-quinoline yellow (2,8-Dimethyl-5-*isopropyl*-quinoline).**—Sixty-four g. of cyidine was added to 80 g. of concd. hydrochloric acid, and to this a solution of 60 g.

<sup>1</sup> Doebner and Miller, *Ber.*, **14**, 2814 (1881).

of paraldehyde in 30 g. of nitrocymene was added gradually. The flask containing this reaction mixture was refluxed on the water-bath for two hours. The reaction product was distilled in a current of steam to remove nitrocymene, and the residual solution was made alkaline and again distilled in a current of steam. The combined distillate containing the quinaldine base and unreacted cymidine was made acid with dil. sulfuric acid and concentrated on the steam bath to a volume of 3 liters. The concentrated solution was cooled to 5° and treated with a solution of sodium nitrite to diazotize the unreacted cymidine. The diazotized solution was allowed to stand for 15 minutes and then heated to boiling and maintained at this temperature for about one-half hour in order to convert the diazocymene into the corresponding phenol. This solution was distilled in a current of steam to remove the phenolic products, the residual liquid was made alkaline and the methyl-*isopropyl*-quinaldine was removed by continuing the steam distillation. An oil, which solidified on standing, separated from the distillate. This was extracted with ether, the ether solution was dried over anhydrous sodium sulfate, the ether was removed by distillation, and the residue was crystallized once from 95% alcohol and once from 60% alcohol. It was obtained as colorless, shiny plates; m. p., 78.2° (corr.); yield, 19.2 g., or 22.5%. This compound is insoluble in water and soluble in benzene, alcohol, ether, chloroform, carbon tetrachloride and acetone.

*Anal.*<sup>2</sup> Subs., 0.1371, 0.1609: CO<sub>2</sub>, 0.4236, 0.4976; H<sub>2</sub>O, 0.1045, 0.1219. Subs., 0.1007, 0.1167: 5.00 cc., 5.70 cc. of 0.1 *N* acid. Calcd. for C<sub>14</sub>H<sub>17</sub>N: C, 84.36; H, 8.60; N, 7.03. Found: C, 84.26, 84.33; H, 8.53, 8.48; N, 6.95, 6.84.

A molecular-weight determination was made by the boiling-point method, using benzene as the solvent.

*Mol. wt.* Subs., 0.2268: *W*, 14.1575;  $\Delta t$ , 0.212. Calcd. for C<sub>14</sub>H<sub>17</sub>N: mol. wt. 199.2. Found: 197.2.

The gold double salt was prepared from the hydrochloride in the usual manner. It separated as yellow, microscopic needles.

*Anal.* Subs., 0.2420, 0.3720: Au, 0.0888, 0.1376. Calcd. for C<sub>14</sub>H<sub>17</sub>N.HCl.AuCl<sub>3</sub>: Au, 36.57. Found: 36.69, 36.98.

**Methyl-*isopropyl*-quinoline Yellow (Methyl-*isopropyl*-quinophthalone).**—The method used for the preparation of this dye was similar to that employed by Jacobsen and Reimer<sup>3</sup> for the preparation of quinoline yellow. Twenty g. of methyl-*isopropyl*-quinaldine, 18 g. of phthalic anhydride and 5 g. of anhydrous zinc chloride were heated for four hours in an oil-bath maintained at 180–190°. The reaction product was washed with 95% alcohol and dissolved in hot glacial acetic acid. An equal volume of 95% alcohol was added, whereupon the dye separated as yellow needles. A second crystallization from the acetic acid-alcohol mixture yielded a pure product; m. p., 220.4° (corr.); yield, 20.2 g., or 61%. The compound is insoluble in water, very slightly soluble in ethyl alcohol, methyl alcohol and acetone, and soluble in acetic acid, benzene and carbon tetrachloride.

*Anal.* Subs., 0.1771, 0.2138: CO<sub>2</sub>, 0.5201, 0.6281; H<sub>2</sub>O, 0.0912, 0.1085. Subs., 0.1002, 0.1102: 2.90 cc., 3.20 cc. of 0.1 *N* acid. Calcd. for C<sub>22</sub>H<sub>19</sub>O<sub>2</sub>N: C, 80.21; H, 5.81; N, 4.25. Found: C, 80.08, 80.11; H, 5.76, 5.68; N, 4.05, 4.07.

The absorption<sup>4</sup> of methyl-*isopropyl*-quinoline yellow as measured with a Hilger

<sup>2</sup> The carbon and hydrogen determinations recorded in this paper were made by Mr. Raymond Hann of this Bureau.

<sup>3</sup> Jacobsen and Reimer, *Ber.*, **16**, 1082 (1883).

<sup>4</sup> The spectrophotometric measurements were made by Mr. W. C. Holmes of this Laboratory.

wave-length spectrometer provided with a Nutting photometer is recorded in the graph shown in Fig. 1 (Curve 1). A comparison with quinoline yellow itself failed to reveal any appreciable displacement in the absorption maximum through the methyl-*isopropyl* substitution.

**Sodium Methyl-*isopropyl*-quinoline Yellow Disulfonate.**—Ten g. of the dye and 40 g. of fuming sulfuric acid (containing 23% of sulfur trioxide) were heated together at 150° until complete sulfonation had taken place (about two hours). The reaction product, after cooling, was poured into ice water and neutralized with sodium carbonate solution. The dye was salted out with sodium chloride, filtered off and dried. It was obtained as a yellow powder which dissolved in water, yielding a greenish-yellow solution.

*Anal.* Subs., 0.1225, 0.1225: BaSO<sub>4</sub>, 0.1280, 0.1283. Calcd. for C<sub>22</sub>H<sub>17</sub>O<sub>2</sub>N·(SO<sub>3</sub>Na)<sub>2</sub>: S, 14.79. Found: 14.40, 14.43.

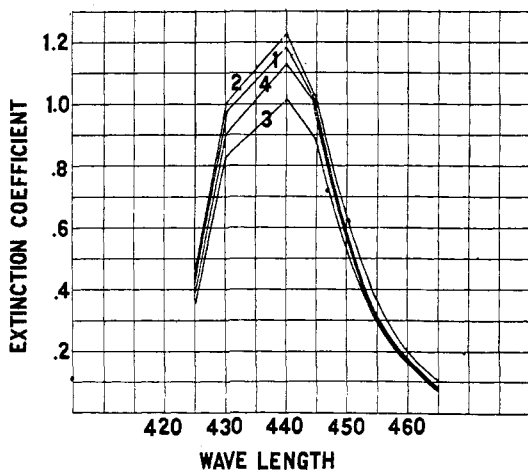


Fig. 1.—1, Methyl-*isopropyl*-quinoline yellow in 50% alcohol. 2, Quinoline yellow in 50% alcohol. 3, Sodium methyl-*isopropyl*-quinoline yellow disulfonate in water. 4, Sodium quinoline yellow disulfonate in water.

The concentration in each case is 0.025 g. per liter.

The absorption of this sulfo derivative as compared with that of the corresponding derivative from quinoline yellow (Quinoline Yellow S, color index No. 801) failed to show any appreciable displacement in the absorption maximum (Fig. 1, Curves 3 and 4).

From an acid bath the methyl-*isopropyl*-quinoline yellow disulfonate dyes silk and wool a greenish-yellow. No appreciable difference could be noted in the fastness of this dye as compared with that of the corresponding product from quinoline yellow (color index No. 801).

### Summary

2,8-Dimethyl-5-*isopropyl*-quinoline was prepared from 2-amino-*p*-cymene by the application of the Doebner and Miller synthesis. Condensed with phthalic anhydride, it gave methyl-*isopropyl*-quinoline yellow.

A comparison of the absorption of methyl-*isopropyl*-quinoline yellow with that of quinoline yellow failed to reveal any appreciable displacement in the absorption maximum through the methyl-*isopropyl* substitution.

The disulfo derivative of methyl-*isopropyl*-quinoline yellow dyes wool and silk a greenish-yellow. It is equal in fastness to the corresponding quinoline yellow derivative (Quinoline Yellow S).

The absorption of the disulfo derivative as compared with that of Quinoline Yellow S failed to indicate any appreciable difference in the absorption maximum through the methyl-*isopropyl* substitution.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARKANSAS]

## REACTIONS OF CARBON DISULFIDE. I.<sup>1</sup>

### With Ammonium Hydroxide

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Experiments in this Laboratory for the production of keto dithio acids<sup>1a</sup> have frequently called for the use of solutions of carbon disulfide in ammonium hydroxide. These were made up from concd. "ammonia water" and an excess of carbon disulfide, and allowed to stand in glass-stoppered bottles. Such solutions on standing a short time acquire a deep red color. While on mixing there is always considerable pressure of ammonia gas, the solutions show negative pressure after five or six days' standing.

In the literature the reaction of carbon disulfide and ammonia is reported as follows:<sup>2</sup>  $CS_2 + 2NH_3 \rightarrow NH_2-C \begin{array}{l} \diagup S \\ \diagdown S \end{array} -NH_4$ ;  $NH_2-C \begin{array}{l} \diagup S \\ \diagdown S \end{array} -NH_4 \rightarrow NH_4CNS + H_2S$ ;  $H_2S + 2NH_3 \rightarrow (NH_4)_2S$ . These equations are given for "alcoholic ammonia." Meyer and Jacobson's textbook<sup>3</sup> reports, "Alkoholisches Ammoniak wirkt leicht auf Schwefelkohlenstoff unter Bildung von dithiocarbamidsaurem Ammonium bzw. Rhodan-ammonium. Wässriges Ammoniak wirkt in gleicher Weise, aber langsamer." Another reference states that aqueous ammonia and carbon disulfide yield a mixture of ammonium trithiocarbonate and ammonium thiocyanate.<sup>4</sup>

The red color of the solution in hand would seem to give evidence of the presence of a trithiocarbonate, since it is known that soluble salts of trithiocarbonic acid yield red solutions.<sup>5</sup> Moreover, ammonium dithiocarbamate gives a practically colorless solution and ammonium poly-

<sup>1</sup> Paper No. 30, Journal Series, University of Arkansas.

<sup>1a</sup> *Science*, **58**, 494 (1923).

<sup>2</sup> Hofmann, *Jahresber.*, **1858**, 334.

<sup>3</sup> "Lehrbuch der Organischen Chemie," Veit and Co., Leipzig, **1913**, vol. 1, part 2, p. 1360.

<sup>4</sup> Zeise, from (a) Gmelin-Kraut, "Handbuch der anorganischen Chemie," Carl Winter, Heidelberg, **1911**, vol. 1, part 3, p. 789.

<sup>5</sup> *J. Chem. Soc.*, **89**, 1813 (1906); **119**, 41, 51 (1921).