[Forty-third Contribution from the Color Laboratory of the Bureau of Chemistry.]

SYNTHESIS OF PHOTOSENSITIZING DYES (II), DICYANINE A.[1]

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The photosensitizing dyes (derived from quinoline) in use prior to 1919 were of 4 general types: isocyanines, *e. g.*, pinaverdol, sensitizing to green and yellow; cyanines and pinacyanols, both sensitizing to orange and red; and dicyanines, which extend the sensitiveness of the plate to, or even beyond 9000 Å. The dye of this last type which, from the point both of preparation and of use, we have found most satisfactory is that termed by the German manufacturers "Dicyanin A."

We have prepared this dye by the action of sodium methylate (or ethylate) in absolute methyl (or ethyl) alcoholic solution, in the presence of air, on 2,4-dimethyl-6-ethoxy-quinoline ethnitrate, obtained by the action of silver nitrate on the ethiodide of the same base. The base is prepared from *p*-phenetidine by condensation with paraldehyde and acetone.[2]

The corresponding dicyanine A iodide is more difficult to use in the plate-staining bath, but has somewhat better keeping qualities.

Preparation of 2,4-dimethyl-6-ethoxy-quinoline.—A mixture of 300 g. of acetone and 200 g. of paraldehyde, cooled on ice, is saturated with hydrogen chloride. After standing at 0° for 2 hours, the saturation is repeated, the mixture removed from the ice-bath and allowed to stand at room temperature for 20 hours. It is then added slowly to a solution of 300 g. of phenetidine in 600 g. of conc. hydrochloric acid (sp. gr. 1.2). The mixture, in a flask attached to a reflux condenser, is heated in a water-bath for 2 hours, then it is cooled, neutralized with a concentrated solution of sodium hydroxide, and extracted with ether. The ether extract is dried with anhydrous sodium sulfate, the ether removed by distillation and the residue distilled under reduced pressure. To the distillate is added an equal weight of acetic anhydride; this mixture is heated on a steam-bath for half an hour and poured into water. The phenacetine and unchanged anhydride are removed by filtration, the filtrate neutralized with a concentrated solution of sodium hydroxide, and extracted with ether; then the ether is removed and the residue distilled as before. The distillate is dissolved in twice its weight of conc. hydrochloric acid and a slight excess of sodium nitrate solution added at 0°. The solution is extracted with ether at 0°, and the extract discarded. The diazo-compounds are

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[1] The preparation of pinaverdol and pinacyanol has been described by L. E. Wise, E. Q. Adams, J. K. Stewart and C. H. Lund. *J. Ind. Eng. Chem.*, **11**, 460 (1919).

[2] The preparation of 2,4-dimethyl-quinoline is described by L. A. Mikeska, J. K. Stewart and Louis E. Wise. *J. Ind. Eng. Chem.*, **11**, 456 (1919).

destroyed by heating the solution on the steam-bath; the solution is neutralized with conc. sodium hydroxide solution and extracted with ether, the ether removed by distillation and the residue distilled under reduced pressure. The distillate is dissolved in its own weight of 95% alcohol, and an equal weight of alcohol containing about 10% in excess of the theoretical amount of sulfuric acid added. The precipitated sulfate is collected on a filter, washed with alcohol and then with ether. The base is recovered as before and recrystallized from petroleum ether. A yield of 75 g. of base boiling between 314° and 316° should be obtained.

A preparation made as above, except that the final purification was made by fractional distillation, gave in 4 analyses:

Calc. for $C_{13}H_{15}NO$: N, 6.96. Found: 6.96, 6.95, 6.97, 6.88.

Preparation of 2,4-dimethyl-6-ethoxy-quinoline Ethiodide.—To 10 g. of 2,4-dimethyl-6-ethoxy-quinoline is added an equal weight of ethyl iodide. The mixture in a flask attached to a reflux condenser is heated for 20 hours on the steam-bath. After it has cooled the solid reaction product is washed in the flask with ether. It is then recrystallized several times from boiling 95% alcohol. A yield of 10 g. should be obtained.

Calc. for $C_{15}H_{20}NOI$: N, 3.92. Found: Kjeldahl, 3.76, 3.71.

Preparation of Dicyanine A Nitrate (**A VI**).—A solution of 5.36 g. of 2,4-dimethyl-6-ethoxy-quinoline ethiodide (0.015 mol) in 25 cc. of absolute ethyl alcohol is slowly added to a solution of 2.55 g. of silver nitrate in 175 cc. of hot absolute ethyl alcohol. The precipitated silver iodide is removed by filtration. If the filtrate is found to contain silver, a slight excess of the ethiodide solution is added and the filtration repeated. The solution is concentrated to 60 cc., cooled to 10°, and air passed through it while a solution of sodium ethylate, prepared by dissolving 0.1725 g. of metallic sodium in 15 cc. of absolute ethyl alcohol, is added slowly. The aeration is continued for 16 hours, the precipitated sodium nitrate removed by filtration with the aid of suction, and the solution placed in a vacuum desiccator for 24 hours.

The grass-green crystals which separate are collected on a filter and washed with ice-cold ethyl alcohol, ethyl alcohol-ether, and finally, ether alone. The yield is about 0.15 g.

Preparation of Dicyanine A Iodide (**A IV**).—A solution of sodium methylate was prepared by dissolving 0.345 g. of metallic sodium in 30 cc. of absolute methyl alcohol. This sodium methylate was added slowly to a solution of 10.72 g. of 2,4-dimethyl-6-ethoxy-quinoline ethiodide (0.03 mol.) in 100 cc. of methyl alcohol, the mixture cooled to 10° and shaken continuously. The solution is then allowed to stand at room temperature in an open Erlenmeyer flask for 60 hours. The beetle-green crystals which separate are collected on a filter and washed with ice-cold methyl alcohol, then with methyl alcohol-ether mixture, and finally, with ether alone. The yield is about 0.25 g.

Summary.

Directions are given for the preparation of 2,4-dimethyl-6-ethoxy-quinoline from *p*-phenetidine; for the preparation of the ethiodide of this base, and, from it, the nitrate and iodide of Dicyanine A.

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TETRAMETHYL-QUINOLINES.

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Among the photosensitizing dyes prepared from quinoline derivatives, those which extend the sensitiveness of the photographic plate farthest into the infra-red are the dicyanines. They are prepared by treating with alkali the quaternary halides of 2,4-dimethyl-quinoline or its homologs. 2,4-Dimethyl-quinoline is obtained from aniline, acetone and paraldehyde by a condensation similar to the well-known Skraup synthesis. The substitution of toluidines for aniline in this reaction gives rise to derivatives of 2,4-dimethyl-quinoline with one methyl group in the benzene ring. As the dicyanine obtained from 2,4,6-trimethyl-quinoline seems to be somewhat superior to that obtained from 2,4-dimethyl-quinoline, a study of the effect of the introduction of another methyl group in the benzene ring was undertaken. To do this, xylidines were substituted for aniline in the synthesis. Since this reaction required an unsubstituted hydrogen in the *ortho* position to the amino group it is evident that it is inapplicable to *m*-2-xylidine. On the other hand, *o*-4-xylidine can theoretically yield 2 isomers, so that it should be possible to obtain 6 tetramethyl-quinolines from the 6 known xylidines.

A search of the literature has revealed that this reaction has been applied to *m*-4-xylidine by Levin and Riehm,[1] who obtained a tetramethyl-quinoline to which they assigned the alternative constitutions of 2,4,5,6- and 2,4,6,7-tetramethyl-quinolines, based on the erroneous assumption that *m*-4-xylidine is 1,2-dimethyl-4-aminobenzene. Since the name and structure applied to the xylidine used do not accord it was necessary to repeat their work in order to ascertain whether *m*-4-xylidine or *o*-4-xylidine was actually used. Levin and Riehm employed acetone alone in this condensation, whereas we used a mixture of acetone and paraldehyde. The melting point of the tetramethyl-quinoline obtained from *m*-4-xylidine agrees with that of the base obtained by Levin and Riehm, thus indicating that they used *m*-4-xylidine.

[1] J. Levin and P. Riehm, *Ber.*, 19, 1394 (1886).