2. The synthesis of 2,4,6,8-, of 2,4,5,7-, and 2,4,5,8-tetramethyl-quinoline is described, and the properties of these bases noted.

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[FORTY-FIFTH CONTRIBUTION FROM THE COLOR LABORATORY OF THE BUREAU OF CHEMISTRY.]

THE PREPARATION OF LEPIDINE AND RELATED BASES.

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The first of the cyanine dyes was prepared by Williams,[1] from what we now know to have been a mixture of lepidine and quinoline, by treatment first with amyl iodide and then with alcoholic potash. The importance of lepidine as a source of cyanine has been considerably diminished by the introduction of pinacyanol, derived from the more easily obtained quinaldine,[2] possessing the same sensitizing properties as cyanine, and obtained in considerably better yield. The recent discovery that from the alkyl halides of lepidine and related bases can be obtained, not only a number of hitherto unknown dyes of the isocyanine (or pinaverdol) type, but also dyes of a new type,[3] possessing interesting and useful sensitizing properties in the infra-red, renders the preparation of pure lepidine in good yield again a matter of importance.

Several different methods for the preparation of lepidine are quoted in Beilstein's "Handbook," but without exception they are difficult to carry out and disappointing in yield and purity of product. The following procedure has been found to give a fair yield of pure lepidine.

Preparation of Lepidine.—A mixture of 300 g. of acetone and 300 g. of 40% formaldehyde is cooled in ice and saturated with hydrogen chloride. After standing overnight at room temperature, it is cooled and saturated with hydrogen chloride as before, and again allowed to stand overnight. It is then slowly added to a cooled mixture of 300 g. of aniline and 600 g. of hydrochloric acid (sp. gr. 1.2). The mixture is heated on a water-bath for 3 hours, under a reflux condenser. After cooling it is neutralized with conc. sodium hydroxide solution and extracted with ether. The extract is dried over sodium sulfate, the ether distilled off and the residue distilled under reduced pressure. To the distillate is added an equal weight of acetic anhydride, and the mixture is heated on the steam-bath half an hour and then poured into water. The acetanilide and unchanged anhydride are filtered off, and the lepidine recovered by neutral-

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[1] C. Greville Williams, *Chem. News*, 1, 15 (1860).

[2] By treatment with formaldehyde and alcoholic alkali, with exclusion of air. Cf. L. E Wise, E. Q. Adams, J. K. Stewart and C. H. Lund, THIS JOURNAL, 11, 460 (1919).

[3] Kryptocyanines. E. Q. Adams and H. L. Haller, will be published later

izing, extracting and distilling as before. Traces of acetanilide may be removed at this point by dissolving the lepidine in petroleum ether, filtering, and distilling off the solvent. The lepidine is dissolved in 1.5 times its own weight of hydrochloric acid (sp. gr. 1.2) and cooled. A slight excess of sodium nitrite is added and the cold solution extracted with ether (to remove nitroso-tetrahydro-lepidine). The solution is boiled to decompose the diazo-compound and the phenol formed removed by extracting the acid solution with ether. The lepidine is recovered by neutralizing, extracting and distilling as before. It is then dissolved in an equal weight of 95% alcohol, and twice as much alcohol containing a 10% excess of sulfuric acid is added. After cooling the sulfate is filtered off, washed with cold alcohol and then ether. From the snow-white sulfate the lepidine is recovered as before. A yield of 20 g. of lepidine boiling at 262° (atmospheric pressure) may be expected.

Preparation of *p*-Tolu-lepidine.—When the aniline is replaced by an equal weight of *p*-toluidine, the same procedure gives *p*-tolu-lepidine (*i. e.*, 4,6-dimethyl-quinoline).

Preparation of *p*-Ethoxy-lepidine.—When the aniline is replaced by an equal weight of *p*-phenetidine, the same procedure gives *p*-ethoxy-lepidine (*i. e.*, 4-methyl-6-ethoxy-quinoline). The product, being solid, may be recrystallized from petroleum ether. It then melts at 77°.

Calc. for $C_{12}H_{13}NO$: N, 7.48. Found: (Kjeldahl) 7.40, 7.32, 7.33.

The base gave an ethiodide melting at 187° (uncorr.).

The preparation of other related bases will be discussed in articles shortly to appear on trimethyl- and tetramethyl-quinolines.

Summary.

Recent developments in the field of photosensitizing dyes have brought lepidine and related bases again into prominence.

A procedure is given for the preparation of lepidine, *p*-tolu-lepidine and *p*-ethoxy-lepidine.

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