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.

WASHINGTON, D. C.

TETRAMETHYL-QUINOLINES.

BY LOUIS A. MIKESKA AND ELLIOT Q. ADAMS.

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).

Symmetrical xylidine, obtained from mesitylene according to the method described by Haller and Adams[1] was used in the synthesis of 2,4,5,7-tetramethyl-quinoline; and *p*-xylidine served as an intermediate in the preparation of the corresponding 2,4,5,8-tetramethyl derivative.

The work on 2,4,7,8-, 2,4,5,6- and 2,4,6,7-tetramethyl-quinoline will be begun as soon as the necessary *o*-xylidines can be obtained in pure state.

The 3 tetramethyl-quinolines so far isolated[2] are obtained by the general procedure described below.

Experimental Part.

A mixture of 30 g. of acetone and 20 g. of paraldehyde is saturated with dry hydrogen chloride at 0° and is allowed to stand for 18 hours at room temperature. The reaction mixture is then poured into a solution of 27 g. of xylidine in 54 g. of conc. hydrochloric acid. The reaction begins at once with slight evolution of heat and is completed by heating for 1 to 2 hours on a water-bath under a return condenser. The dark brown mass is next neutralized with conc. sodium hydroxide solution, whereupon a brown oil is obtained, which is separated from the mother liquor by extraction with ether. The ether extract is dried with sodium sulfate, the ether removed, and the residue distilled under reduced pressure. In order to remove the unchanged xylidine the distillate is heated on a water-bath for 2 hours with an equal weight of acetic anhydride and is then poured into several volumes of cold water. The acetxylid is thus precipitated and removed by filtration, the filtrate treated with an excess of alkali to regenerate the base which separates in the form of an oil but solidifies on cooling and stirring. For 2,4,5,7- and 2,4,6,8-tetramethyl-quinolines the yield at this stage of purity is about 22 to 25 g. For 2,4,5,8-tetramethyl-quinoline the yield is somewhat less. The last traces of unchanged xylidine, together with small amounts of the corresponding tetrahydro-quinolines, are removed from the acid solution by diazotization with sodium nitrite. The nitroso tetrahydro-quinolines are removed by extracting the acid solution with ether, the diazonium salts are decomposed by heating and the quinoline bases are regenerated by treating with excess of alkali. The free base is then recrystallized from petroleum ether. 2,4,5,7- and 2,4,6,8-, tetramethyl-quinoline are readily obtained in the form of snow-white crystals melting at 59° and 86° respectively. It is somewhat more difficult to purify the corresponding 2,4,5,8-tetramethyl derivative which melts at 131°.

Summary.

1. The only 2,4-dimethyl-benzene-dimethyl-quinoline hitherto described, was incorrectly named by Levin and Riehm, who prepared it.

[1] H. L. Haller and E. Q. Adams, THIS JOURNAL, **42**, 1840–2 (1920).

[2] As the senior author has left the Color Laboratory, it has been thought best to publish the work completed to date.

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.

WASHINGTON, D. C.

THE PREPARATION OF LEPIDINE AND RELATED BASES.

By LOUIS A. MIKESKA.

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-

[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