the residual oil distilled at 200 mm. pressure. Unchanged aniline remaining in the distillate is removed by diazotizing¹ in hydrochloric acid and heating the solution. The acid solution is then rendered alkaline, the supernatant quinoline extracted with ether, the ether solution dried, the ether removed, and the residual oil distilled at atmospheric pressure. Quinoline thus obtained boils at 238° (uncorrected). The yield is 65 per cent of the calculated amount, based upon the weight of aniline taken.

Calculated for C_9H_7N : N = 10.86 per cent. Found: N = 10.73 per cent, 10.69 per cent.

ture of 120 g. of paraldehyde and 200 g. of acetone is saturated with dry hydrochloric acid and allowed to stand for 24 hrs., care being taken to exclude moisture. The mixture is then slowly added to 200 g. of aniline dissolved in 400 g. of hydrochloric acid, and the syrup finally heated during 1 hr. (in a water bath) under a return condenser. On rendering alkaline, a yellow oil separates from the solution. The oil is extracted with ether, and the ether evaporated. The residue, without further purification, is dissolved in an equal weight of hydrochloric acid and diazotized. Here again precautions are taken to remove nitroso compounds by extraction of the *cold* acid solution with ether. The aqueous solution is rendered alkaline and the yellow oil extracted with ether. The usual procedure is followed in the final purification of the 2,4-dimethylquinoline. The compound, which is obtained in 25 to 30 per cent yield, based upon the weight of aniline taken, boils at 260–264° (uncorrected) under ordinary pressure.

Calculated for $C_{11}H_{11}N$: N = 8.92 per cent. Found: N = 8.78 per cent, 8.73 per cent.²

The above procedure is very much simpler and far more rapid than that outlined by v. Bayer.³

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INTERMEDIATES USED IN THE PREPARATION OF PHOTSENSITIZING DYES. II—QUATERNARY HALIDES

By CARL H. LUND AND LOUIS E. WISE
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The second step in the synthesis of photosensitizing dyes is the formation of quaternary iodides from the bases described in the preceding paper. These compounds result from the direct addition of methyl, ethyl or other alkyl iodide to the quinoline base. Many of these addition products have been described in the literature, but there is too little available information on the best conditions for the preparation of these compounds.

¹ No special precautions are necessary. Tetrahydroquinoline is not present.

² Our thanks are due to Messrs. Jenkins and Ellis, of the Nitrogen Laboratory of the Bureau of Chemistry, for the analytical data given in this paper.

³ *Loc. cit.*

We therefore undertook a systematic study of the synthesis of the quaternary iodides with a view to establishing the simplest conditions which would give satisfactory yields of the pure compounds. Our many experiments need not be described in detail. After carrying out the addition reaction under varying conditions—in pressure flasks, in flasks under reflux condensers, with and without the use of various solvents, and with varying amounts of the components—we find that it is best to use equimolecular amounts of the alkyl iodide and the base and to carry out the reaction in a round bottom flask surmounted by a worm condenser. The flask should never be filled beyond one-third¹ of its capacity.

Depending on the nature of the base used, the reaction may proceed spontaneously and violently (as in the case of quinoline methiodide) or it may require external heating (as in the case of quinaldine ethiodide). The presence of an α -methyl group in the molecule appears to decrease the rate of reaction.

The product is usually obtained in the form of a solid cake, which may be gradually dissolved by treatment with hot alcohol. The iodide crystallizes from the alcoholic solution on cooling. In general, the yields of the quaternary halide are satisfactory, varying from 60 to 80 per cent of the theoretical. We have found, however, that small amounts of impurities in the reagents may decrease these yields very materially.

All the quaternary halides are crystalline compounds of a more or less pronounced yellow color. Many of them melt with decomposition. All of them are water-soluble and ionize in solution. The iodine content of any quaternary base may be rapidly and accurately determined by a slight modification of the Volhard method. This method served a useful purpose in permitting us to judge the purity of our products.

From the standpoint of the producer of photosensitizing dyes the following quaternary halides are perhaps the most important: quinoline methiodide and ethiodide, quinaldine ethiodide, toluquinaldine methiodide, and 2,4-dimethylquinoline ethiodide. We have prepared relatively large amounts of these compounds and small amounts of a few other analogous iodides, all of which are described in the experimental part.

EXPERIMENTAL

QUINOLINE METHIODIDE—When small amounts of this product—less than 100 g.—are required, the following procedure is convenient: Equimolecular amounts of methyl iodide and quinoline are mixed in a round bottom flask, and allowed to stand at *room temperature* under a reflux condenser. The mixture gradually becomes warm and crystals begin to appear in the flask. Since the reaction is exothermic, the mixture finally reaches a temperature at which the methyl iodide boils vigorously. When this point is reached the flask must be cooled in an ice bath to keep the reaction from proceeding too violently. After a

¹ This simple precaution is necessary. Well-annealed flasks filled half full frequently cracked during the course of the reaction.

yellow cake of the methiodide has formed, the flask is immersed in a hot water bath and heated for several hours to insure a complete reaction. The solid cake in the flask is then covered with 95 per cent alcohol and the heating continued until the methiodide has dissolved. On cooling and stirring, a crop of small, bright yellow crystals is obtained which are shown to be quinoline methiodide, monohydrate, $C_9H_7.CH_3I.H_2O$. In the recrystallization of the crude methiodide it is necessary to use enough 95 per cent alcohol to insure the presence of sufficient water to form this monohydrate, otherwise a mixture of the monohydrate and anhydrous methiodide (melting 90° to 120°) is obtained and recrystallization is required. The monohydrate melts at 70° to 71° (uncorrected). The melting point recorded by Marckwald and Meyer¹ is 72° . The yield varies from 70 to 80 per cent of the theoretical.

Calculated for $C_9H_7.CH_3I.H_2O$: I = 43.91 per cent. Found: I = 43.93 per cent.

By allowing the monohydrate to stand for several days over sulfuric acid *in vacuo*, complete dehydration takes place. The melting point of the dehydrated compound is 131° to 133° (uncorrected). Marckwald and Meyer² give 133° as the melting point of the anhydrous compound.

Calculated for $C_9H_7N.CH_3I$: I = 46.82 per cent. Found: I = 46.66 per cent.

In the preparation of larger amounts of quinoline methiodide, it is expedient to modify the above method since it becomes almost impossible to control the reaction by cooling with an ice bath (as described). The following modification is used: Methyl iodide is heated to boiling in a flask connected by means of a two-hole stopper, with a reflux worm condenser and with a dropping funnel. The source of heat is then removed and the quinoline added through the dropping funnel at such a rate that moderate refluxing of methyl iodide is maintained. After all the quinoline has been added, the mixture is allowed to cool. From this point on the procedure is identical with that outlined above.

QUINOLINE ETHIODIDE—The procedure is very similar to that used in the formation of the methiodide. In this case initial heating on the steam bath is required to start the reaction after the components have been mixed. The reaction then proceeds with such violence that the flask must be removed from the bath and rapidly cooled. The crude cake is recrystallized from 95 per cent alcohol, and anhydrous quinoline ethiodide is obtained in the form of bright yellow crystals melting at 155° to 157° (uncorrected). Miethe and Book³ give a melting point of 156° to 157° . The yield varies from 75 to 85 per cent of the theoretical.

Calculated for $C_9H_7N.C_2H_5I$: I = 44.53 per cent. Found: I = 44.35 per cent.

QUINALDINE METHIODIDE—Only small quantities of this compound were prepared and we have made no systematic study of the conditions for obtaining the best yields. The methiodide on recrystallization

from 95 per cent alcohol is obtained in the form of lemon-colored needles which melt at 190° (uncorrected). Döbner and Miller¹ give a melting point of 195° .

Calculated for $C_{10}H_9N.CH_3I$: I = 44.53 per cent. Found: I = 44.40 per cent.

QUINALDINE ETHIODIDE—Equimolecular amounts of quinaldine and ethyl iodide are mixed in a flask which is then connected with a reflux condenser. The mixture is heated on a steam bath for 18 to 20 hrs. The crude cake thus obtained is then heated under a reflux condenser with just enough 95 per cent alcohol to cause complete solution. (This requires about 8 parts by weight of alcohol to 1 part of the crude ethiodide.) On cooling, the alcoholic solution deposits quinaldine ethiodide in the form of coarse, straw-colored or brown needles, decomposing at 231° to 234° (uncorrected). Miethe and Book² who previously prepared this compound give the melting point as 234° – 235° .

Calculated for $C_{10}H_9N.C_2H_5I$: I = 42.44 per cent. Found: I = 42.30 per cent, 42.20 per cent.

The yield of ethiodide was 70 to 80 per cent of the theoretical. When the alcoholic mother liquors from the first crop of crystals are concentrated to one-tenth of their initial volume, a second crop of the ethiodide is obtained. This represents only about 5 per cent of the theoretical yield, and the crystals are so impure that they require further purification.

The procedure outlined above proved very satisfactory, and we found no difficulty in preparing several kilograms of the ethiodide by this method.

Attempts to shorten the procedure met with little success. When the initial time of heating on the steam bath was decreased to 10 hrs., the reaction did not go to completion, and yield of ethiodide was materially decreased. Similarly no advantage was gained by carrying out the reaction at a higher temperature (150°). In this case we also obtained a 70 to 80 per cent yield.

p-TOLUQUINALDINE METHIODIDE—Equimolecular amounts of *p*-toluquinaldine and methyl iodide are heated together under a reflux condenser for several hours. The crude cake is recrystallized from 95 per cent alcohol. The ethiodide is obtained in the form of fine, pale yellow, fluffy needles, decomposing at 246° – 247° (uncorrected). Möller³ gives the melting point as 236° – 237° . The compound was dried at 120° before it was analyzed.

Calculated for $C_{11}H_{11}N.MeI$: I = 42.44 per cent. Found: I = 42.14 per cent, 41.94 per cent.

The yield obtained varies from 65 to 75 per cent of the calculated amount.

p-TOLUQUINALDINE ETHIODIDE—Equimolecular quantities of *p*-toluquinaldine and ethyl iodide are heated together on the steam bath under a reflux condenser for about 18 hrs. The resulting solid cake is recrystallized from alcohol in the usual manner. The ethiodide forms granular, yellow crystals decomposing at 213° – 216° (uncorrected). The yield varies from 65 to 70 per cent of the theoretical. Bing,⁴ who previously

¹ Ber., 33 (1900), 1884.

² Loc. cit.

³ Ber., 37 (1904), 2009.

¹ Ber., 16 (1883), 2468.

² Loc. cit.

³ Ann., 242 (1887), 311.

⁴ "Ueber einige neue Isocyanine u. deren Einwirkung auf Bromsilbergelatine," Techn. Studien, 2 (1914), 12.

prepared this compound, obtained a 34 per cent yield of the ethiodide, which melted at 217° .

Calculated for $C_{12}H_{11}N.EtI$: I = 40.54 per cent. Found: I = 40.08 per cent.

2,4-DIMETHYLQUINOLINE ETHIODIDE—A mixture of equimolecular parts of 2,4-dimethylquinoline and ethyl iodide is permitted to stand at room temperature over night and then heated under reflux condenser on steam bath for 5 to 6 hrs. The product, when recrystallized from alcohol, yields granular, yellow crystals, m. p. $223-225^{\circ}$ (uncorrected). Beyer¹ gives the melting point as 214° . The yield is about 50 per cent of the theoretical.

Calculated for $C_{12}H_{11}N.EtI$: I = 40.54 per cent. Found: I = 40.17 per cent.

DETERMINATION OF IODINE—The analytical procedure for the determination of iodine in quaternary bases is as follows: A weighed sample (about 0.3 g.) of the iodide is transferred to a 500 cc. heavy walled bottle (provided with a ground-in glass stopper). The halide is dissolved in 200 cc. of water, and 5 cc. of 50 per cent nitric acid (free from halogens and oxides of nitrogen) are added to the mixture. A standardized 0.05 *N* silver nitrate solution is then gradually run into the mixture, which is vigorously shaken after the addition of each 5 cc. of the solution. When an excess of silver nitrate is present 3 cc. of a saturated ferric-ammonium alum solution (indicator) are added and the mixture is again thoroughly shaken. The precipitated silver halide need not be removed by filtration. The excess of silver nitrate is then titrated with 0.07 *N* ammonium thiocyanate solution. The first permanent (salmon) pink coloration in the solution marks the end-point of the titration. The percentage of iodine is calculated by the usual method.

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SYNTHESIS OF PHOTOSENSITIZING DYES²

PINAVERDOL AND PINACYANOL

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The photosensitizing dyes that have gained the ascendancy in panchromatic plate manufacture are two derivatives of quinoline, termed, "pinaverdol" and "pinacyanol" by the German dye manufacturers. Since 1916, these dyes have also been produced by British manufacturing chemists under the names "sensitol green" and "sensitol red," respectively. We have made more than fifteen dyes of this general type.³ A study of their absorption spectra, together with the results of photosensitizing experiments carried out under the direction of Drs. Merrill and Burns, of the Bureau of Standards, and by Mr. H. A. Piper, of the Chemical Section of the Science and Research Department of Aircraft Production, has

shown the identity with the above-named German and British products of two of our dyes, which we have termed, respectively, "Pv. I" and "Pc. IX."

Pinaverdol is prepared from a mixture of the methiodides¹ of toluquinaldine and quinoline by the action of alkali and air. The probable constitution² is best represented by the formula:

Pinacyanol is prepared from a mixture of the ethiodides¹ of quinaldine and quinoline, by the action of formaldehyde and alkali. The constitution of this dye is still in doubt, but from present indications it is problematical whether the quinoline ethiodide actually enters into the reaction. If it does not, the formula² of the dye becomes

When pinacyanol is treated with an excess of silver chloride under proper conditions, it is quantitatively converted into the corresponding chloride (Pc. XII). The greater solubility of this chloride renders it more suitable than pinacyanol (iodide) for use in bathing plates.

In the synthesis of these dyes we have been guided largely by the German patents³ which give good descriptions of the methods of preparation, but which fail to emphasize a few necessary precautions. The details of our own procedure for the preparation of Pv. I and Pc. IX and XII and absorption curves of the dyes are given in the following experimental part:

EXPERIMENTAL

PV. I (PINAVERDOL OR SENSITOL GREEN)—Fourteen grams of *p*-toluquinaldine methiodide and 25.8 g. of anhydrous quinoline methiodide are dissolved in 400 cc. 95 per cent alcohol. The solution is heated to boiling and 77 cc. of 0.7 *N* alcoholic potassium hydroxide (= 3.0 g. of potassium hydroxide) are gradually added from a burette. The mixture is maintained at its boiling point for 5 min. after the addition of the alkali is complete. Fifty cubic centimeters of alcohol are then added, and the crimson-colored solution is permitted to cool slowly. A blue-black, granular, crystalline mass is deposited. The crystals are filtered and dried. The weight of the crude dye is about 5.5 g. (about 25 per cent of the theoretical). The product is pulverized, the powder introduced into an extraction thimble and extracted with ether in a Soxhlet apparatus, until the extract is no longer

¹ *J. prakt. Chem.*, [2] **38** (1886), 406.

² The work on photography formerly carried on in connection with the Chemical Section of the Science and Research Department of the Bureau of Aircraft Production is now being completed by the Color Laboratory, Bureau of Chemistry, Washington, D. C.

³ Wise and Adams, *This Journal*, **10** (1918), 801.

⁴ Cf. preceding article.

⁵ The mechanism of the formation of these dyes has been discussed in an earlier communication from this Laboratory (Wise and Adams, *Loc. cit.*).

⁶ Pinaverdol, D. R. P. No. 167,159, Example 1 (1903); Pinacyanol, D. R. P. No. 172,118, Example 1 (1905).