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Studies in the Cyanine Dye Series. IX. 4,4'-Pyridocyanines and 4-Pyrido-4'cyanines

By R. H. Sprague and L. G. S. BROOKER

Dyes of the 4,4'-pyridocyanine type (I) have



not been described hitherto, but theoretically might be formed by the condensation of 4-iodopyridine alkyl iodides with γ -picoline quaternary salts. We have accordingly made attempts to prepare the methiodide and ethiodide of 4-iodopyridine by heating 4-chloropyridine with the appropriate alkyl iodide. From the now readily available 4-hydroxypyridine,¹ the 4-chloro compound was prepared by the method of Koenigs and Kinne,² but this is known to be very unstable³ (as is also the 4-bromo compound⁴) and attempts to prepare 4-iodopyridine methiodide or ethiodide by the method outlined gave only tarry decomposition products. By carefully treating 4-chloropyridine with methyl iodide at 0° , 4-chloropyridine methiodide was obtained and could be used to prepare dyes, but with ethyl iodide the results were less satisfactory, the solid product of the reaction rapidly deteriorating in air with tar formation.

In an alternative method 4-phenylmercaptopyridine hydrochloride was formed very smoothly by treating 4-chloropyridine with phenyl mercaptan, and from the free base the methiodide and ethiodide were prepared. These quaternary salts are quite stable, and the ethiodide condensed readily with γ -picoline etho-p-toluenesulfonate with elimination of phenyl mercaptan to give 1,1'-diethyl-4,4'-pyridocyanine (I) which was isolated as the perchlorate. In methyl alcoholic solution this dye has a single absorption band with its maximum at 5050 Å. (Fig. 1A). 1,1'-Dimethyl-4,4'-pyridocyanine perchlorate, obtained either from 4-chloro- or 4-phenylmercaptopyridine methiodide, gave an absorption curve very similar to that of the 1,1'-diethyl dye but with its maximum at 5025 Å.

The two new 4,4'pyridocyanines are both very good photographic sensitizers. They give smooth

- (2) Koenigs and Kinne, ibid., 54, 1357 (1921).
- (3) Haitinger and Lieben, Monatsh., 6, 315 (1885).
- (4) Wibaut, Overhoff and Geldof, Rec. trav. chim., 54, 807 (1935).

bands out to about 5900 Å. with maxima at about 5300 Å. and the plates are clean and free from fog.

Two dyes of a second new type, 1,1'-dimethyland 1,1'-diethyl-4-pyrido-4'-cyanine perchlo-



rates (II) were prepared by condensing together the appropriate quaternary salts of 4-phenylmercaptopyridine and of lepidine in the presence of triethylamine, and the first of these was also made by condensing 4-chloropyridine methiodide with lepidine methiodide. The absorption curve of the 1,1'-diethyl dye (Fig. 1B) has its maximum at 5300 Å. The curve of the 1,1'-dimethyl dye is very similar, but its maximum is at 5285 Å.



Fig. 1.—Absorption curves: A, 1,1'-diethyl-4,4'pyridocyanine perchlorate; B, 1,1'-diethyl-4-pyrido-4'-cyanine perchlorate.

The two dyes sensitize very similarly, the effect of either extending to about 6200 Å. with principal and secondary maxima at 5450 Å. and 5050 Å., respectively, but when the 1,1'-diethyl dye is used in higher concentrations it shows a tendency to fog which is lacking in the 1,1'-dimethyl dye.

⁽¹⁾ Koenigs and Greiner, Ber., 64, 1049 (1931).

Alternative names of a type recommended by Dr. F. Richter, editor of Beilstein's "Handbuch," are given for each new dye.

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Experimental

4-Chloropyridine Methiodide.—4-Chloropyridine (16 g., 1 mol.) and excess of methyl iodide (67 g., 4 mols.) were chilled separately to 0° , mixed and allowed to stand together in the dark at 0° for four days. The methiodide separated as a yellow solid, m. p. $152-155^{\circ}$ dec. (25.6 g.; 80% yield) which was sufficiently pure for the dye condensations. A portion was purified for analysis by dissolving in acetone (260 cc. per g.), adding an equal volume of ether to promote crystallization. After two such treatments the almost colorless crystals had m. p. $161-163^{\circ}$, dec.

Anal. Calcd. for C_6H_7CIIN : I, 49.58. Found: I, 49.87.

This salt is quite stable when pure. A specimen kept for a year and a half showed no deterioration. Found: I, 49.68.

4-Phenylmercaptopyridine.—4-Chloropyridine (15.5 g., 1 mol.) was added to phenyl mercaptan (22 g., 1 mol.) cooled in a freezing mixture. The reaction was very vigorous and the whole set to a solid mass which was heated at 100° for a further ten minutes. The hydrochloride was washed with ether and the base liberated with ammonia, extracted with ether and purified by distillation; yield 66% of colorless oil, b. p. 128-129°(2 mm.).

Anal. Calcd. for C₁₁H_☉NS: C, 70.55; H, 4.85. Found: C, 70.17; H, 4.94.

4-Phenylmercaptopyridine Methiodide.—The base (3.4 g., 1 mol.) and methyl iodide (6.6 g., 2 mols.) were refluxed gently for one-half hour (vigorous initial reaction). The solid which separated on chilling was washed with absolute ether and dried *in vacuo;* yield 3.4 g. (57%) of colorless crystals m. p. $174-176^{\circ}$, dec.

Anal. Caled. for C₁₂H₁₂INS: I, 38.57. Found: I, 38.79.

4-Phenylmercaptopyridine ethiodide was obtained similarly, the reactants being heated in a sealed tube at 100° for seventeen hours; yield 99% of ether-washed product, being 80% after recrystallization from acetone. The colorless crystals had m. p. 178–180°, dec.

Anal. Calcd. for $C_{18}H_{14}INS$: C, 45.46; H, 4.11. Found: C, 45.38; H, 4.05.

1,1'-Dimethyl-4,4'-pyridocyanine Perchlorate or bis-(1-Methyl-4-pyridine)-methinecyanine Perchlorate.— γ -Picoline metho-*p*-toluenesulfonate⁵ (6.9 g., 1 mol.), 4chloropyridine methiodide (6.4 g., 1 mol.), *n*-propyl alcohol (15 cc.) and triethylamine (5.8 g., 2.2 mols.) were heated at 100° for one-half hour. The dye was precipitated by the addition of ether and the tarry residue, dissolved in hot water (10 cc.), and treated with a concentrated solution of sodium perchlorate (3.5 g.); yield of crude dye 76%. After two recrystallizations from methyl alcohol (300 cc. per g.) the m. p. remained constant at $263-265^\circ$, dec., but even after further recrystallizations it proved difficult to get consistent analytical results for carbon and hydrogen and so in a fresh experiment the dye was converted into the picrate by treatment with picric acid. The picrate formed reddish needles with greenish reflex and had m. p. $231-232^\circ$, dec. Analysis showed that two molecules of the dye picrate were combined with a molecule of picric acid.

Anal. Calcd. for $C_{44}H_{37}N_{13}O_{21}$: C, 48.73; H, 3.44; N, 16.81. Found: C, 48.62; H, 3.83; N, 16.66.

In the alternative method of preparation γ -picoline metho-*p*-toluenesulfonate (5.6 g., 1 mol.), 4-phenylmercaptopyridine methiodide (6.6 g., 1 mol.), *n*-propyl alcohol (30 cc.) and triethylamine (6.3 g., 3.3 mols.) were refluxed together for ninety minutes. Dye iodide separated on cooling (yield 14%) and was dissolved in the minimum quantity of hot methyl alcohol and converted into the perchlorate. After two recrystallizations the specimen was identical with the perchlorate obtained by the other method (appearance, mixed m. p.). The dye perchlorate forms reddish-brown needles with a greenish reflex.

1,1'-Diethyl-4,4'-pyridocyanine Perchlorate or bis-(1-Ethyl-4-pyridine)-methinecyanine Perchlorate.— γ -Picoline etho-*p*-toluenesulfonate⁵ (17.6 g., 3 mols., *i. e.*, 200% excess), 4-phenylmercaptopyridine ethiodide (8 g., 1 mol.), *n*-propyl alcohol (15 cc.) and triethylamine (4.2 g. 2.2 mols.) were refluxed for ninety minutes. The dye was precipitated by adding ether and sodium perchlorate solution (2.5 g. in 3 cc. of water) was added to the residue. Dye separated after concentrating somewhat and washing with ether and acetone removed colorless material. The dye (yield 21%) was finally purified by two recrystallizations from a mixture of acetone and water (yield 8%). The beautiful brownish-orange needles with a bright greenish-golden reflex had m. p. 196–198°, dec.

Anal. Calcd. for $C_{15}H_{19}ClN_2O_4$: C, 55.12; H, 5.86. Found: C, 55.19; H, 5.51.

1,1'-Dimethyl-4-pyrido-4'-cyanine Perchlorate or (1-Methyl - 4 - pyridine) - (1 - methyl - 4 - quinoline) - methinecyanine Perchlorate.—Lepidine methiodide (2.85 g., 1 mol.), 4-chloropyridine methiodide (2.55 g., 1 mol.), *n*propyl alcohol (15 cc.) and triethylamine (2.1 g., 2.1 mols.) were heated at 100° for one-half hour. After conversion to the perchlorate the yield of dye was 65% and this was twice recrystallized from methyl alcohol (350 cc. per g.) (yield 26%) when it was obtained as reddish crystals with bright metallic reflex, m. p. 220-221°, dec.

Anal. Caled. for $C_{17}H_{17}CIN_2O_4$: C, 58.51; H, 4.92. Found: C, 58.30; H, 4.86.

By the second method lepidine methiodide (2.85 g., 1 mol.), 4-phenylmercaptopyridine methiodide (3.3 g., 1 mol.), *n*-propyl alcohol (20 cc.) and triethylamine (1.05 g., 1 mol.) were heated at 100° for forty-five minutes. After conversion to perchlorate the yield was 46% and one recrystallization (yield 36%) gave a product identical with that obtained above (appearance, mixed m. p.). Found: C, 58.25; H, 4.82.

1,1'-Diethyl-4-pyrido-4'-cyanine Perchlorate or (1-Ethyl - 4 - pyridine) - (1 - ethyl - 4 - quinoline) - methinecyanine Perchlorate.--4-Phenyl mercaptopyridine ethio-

⁽⁵⁾ Brooker and Keyes, THIS JOURNAL, 57, 2488 (1935).

dide (3.5 g., 1 mol.), lepidine ethiodide (3 g., 1 mol.), triethylamine (1.05 g., 1 mol.) and *n*-propyl alcohol (20 cc.) were refluxed for forty-five minutes. The dye was precipitated by adding ether and the residue treated with sodium perchlorate solution; yield 23%. After two recrystallizations from methyl alcohol (70 cc. per g.) (yield 16%) the beautiful beetle-green tablets melted at 172–174°, dec.

Anal. Calcd. for C₁₉H₂₁ClN₂O₄: C, 60.52; H, 5.62. Found: C, 60.51; H, 5.70.

Summary

1. 4-Chloropyridine is known to be unstable and attempts to convert it into 4-iodopyridine alkiodide by heating with methyl or ethyl iodide were unsuccessful. At 0° , however, addition of methyl iodide yields 4-chloropyridine methiodide which is stable. 2. 4-Chloropyridine methiodide is reactive and condensation with γ -picoline metho-p-toluenesulfonate yielded 1,1'-dimethyl-4,4'-pyridocyanine (isolated as the perchlorate); it also yielded a 4-pyrido-4'-cyanine.

3. 4-Chloropyridine reacts with phenyl mercaptan to give 4-phenylmercaptopyridine hydrochloride. The alkiodides of the free base condense with quaternary salts of γ -picoline and of lepidine with elimination of phenyl mercaptan to give 1,1'-dialkyl-4,4'-pyridocyanines and 1,1'dialkyl-4-pyrido-4'-cyanines.

4. The 1,1'-dialky1-4,4'-pyridocyanine perchlorates are strong photographic sensitizers. Rochester, N. Y. Received November 1, 1937

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The Mercuration and Arsenation of Benzothienone

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The metallation of thiophene and of its alkyl and halogen derivatives has been studied extensively. Mercuration is readily accomplished by reaction at room temperature of thiophene or its derivatives with an alcoholic solution of mercuric chloride buffered with sodium acetate. The presence of so-called meta directing groups seems to inhibit mercuration. With the exception of 2chloromercuri-5-thenoic acid¹ metallic derivatives of this group were hitherto unknown. Steinkopf² reports the failure of 2-nitrothiophene to be mercurated under the above conditions and in this Laboratory it has been shown that benzothienone or phenyl thienyl ketone is not mercurated under the same conditions.

Mercuration.—Under more stringent conditions benzothienone formed a monomercurial, a dimercurial and a double compound consisting of one mole of a monomercurial with one mole of a dimercurial.

The monomercurial, 2-chloromercuri-5-benzothienone, formed almost quantitatively when benzothienone was refluxed with a mixture of equivalent amounts of mercuric chloride and mercuric acetate in glacial acetic acid solution.

 $RH + HgCl_2 + Hg(OAc)_2 = 2R - HgCl + 2HOAc$

Proof of structure was accomplished by convert-

ing the mercurial into the corresponding iodo compound, which was shown by means of a mixed melting point to be identical with a sample of 2-iodo-5-benzothienone prepared from 2-iodothiophene and benzoyl chloride by the Friedel-Crafts reaction.

The double compound consisting of one mole of 2-acetoxymercuri-5-benzothienone and one mole of 2,3-diacetoxymercuri-5-benzothienone was formed by fusion of benzothienone with mercuric acetate.

$$2RH + 3Hg(OAc)_2 = R - HgOAc \cdot R' = (HgOAc)_2 + 3HOAc$$

Analysis indicated a ratio of two atoms of sulfur to three atoms of mercury. Cleavage with iodine and potassium iodide gave a gummy mixture from which 2-iodo-5-benzothienone was isolated by prolonged fractional crystallization, proving the presence and identity of the monomercurial.

A dimercurial was obtained from the double compound by refluxing with excess mercuric acetate in methyl cellosolve solution.

$$\mathbf{R} - \mathbf{HgOAc} \cdot \mathbf{R'} = (\mathbf{HgOAc})_2 + \mathbf{Hg(OAc)}_2 =$$

 $2R' = (HgOAc)_2 + HOAc$

Cleavage of the dimercurial with iodine and potassium iodide gave a diiodide which was a viscous, gummy oil. The position taken by the second entering substituent could not be anticipated, but by analogy with the mercuration of

⁽¹⁾ Steinkopf, Ann., 413, 330-3 (1917).

⁽²⁾ Steinkopf and Bauermeister, *ibid.*, **403**, 50-72 (1914); Steinkopf, Augestad-Jensen and Donat, *ibid.*, **430**, 78-112 (1922).