Summary.

The *n*-butyl ether of thioglycolic acid, $C_4H_9SCH_2COOH$, and some of its salts and derivatives have been studied. The following new compounds have been prepared. In each case R indicates the radical $C_4H_9SCH_2$.

RCOOH	$(RCO_2)_2Sr.1.5H_2O$
RCOCl	$(RCO_2)_2Ni.2H_2O$
$RCONH_2$	$(RCO_2)_2CO.2H_2O$
RCO_2CH_3	$(RCO_2)_2Zn.2H_2O$
$RCO_2C_2H_5$	$(RCO_2)_2Cd.H_2O$
$RCO_2C_4H_9$	$(RCO_2)_2Mn.H_2O$
$(RCO_2)_2Ba.0.5H_2O$	$(RCO_2)_2Cu.2H_2O$
$(RCO_2)_2Ca.0.5H_2O$	RCO_2Ag

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[FORTY-FOURTH CONTRIBUTION FROM THE COLOR LABORATORY, U. S. BUREAU OF CHEMISTRY.]

ISOCYANINE DYES FROM LEPIDINE AND ITS HOMOLOGS.

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The mixed alkyl halides[1] of quinoline[2] and lepidine[3] give with alcoholic alkalies blue dyes known as "cyanines;"[4] when quinaldine[5] replaces lepidine, pink "isocyanines"[6] are formed. In both cases the quinoline may be replaced by quinaldine so that the mixed alkyl halides of quinaldine and lepidine give with alcoholic alkalies a blue;[7] and alkyl halides of quinaldine only, a pink color.

From these and other data it has been concluded that "cyanine"[8] is a derivative of 4,4-diquinolyl-methane and "isocyanine" of 4,2-diquinolyl-methane. It needs hardly to be stated that the hydrogens (1) and (1′) must be replaced to permit the formation of dyes capable of existence in alkaline solution.

The formation of a dye with alkali and quinaldine alkyl halides alone is explained as a condensation of the 2-methyl and 4-hydrogen, respectively,

[1] It is now known that other quaternary addition compounds react similarly but the earliest dyes of all the types mentioned were halides.

[2] Benzene-substituted quinolines react similarly.

[3] *I. e.*, 4-methyl quinoline; benzene-substituted lepidines react similarly.

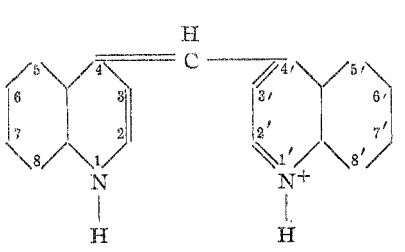
[4] C. Greville Williams, *Chem. News*, **1**, 15 (1860).

[5] *I. e.*, 2-methyl quinoline. Benzene-substituted quinaldines react similarly.

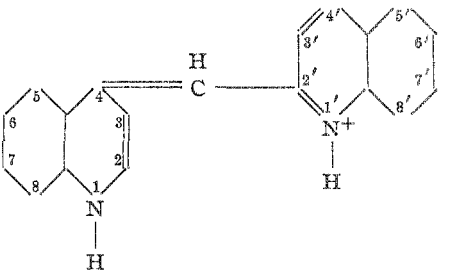
[6] Spalteholz, *Ber.*, **16**, 1849 (1883). Hoogewerff and V. Dorp, *Rec. trav. chim.* **2**, 28, 41 (1883); **2**, 317–26 (1883); **3**, 336–62 (1884).

[7] The results obtained with this combination appear to be nowhere recorded in the literature available to us; since the blue solution thus prepared is a mixture of at least 5 dyes, no one of which can be obtained crystalline, this omission is hardly to be wondered at.

[8] This nomenclature was first suggested by Hoogewerff and V. Dorp, *loc. cit.* A more detailed explanation, together with a more complete bibliography, will be given in a paper from this laboratory by L. E. Wise.



Cyanine(ion).



Iso-cyanine (ion).

of 2 molecules of the intermediate. If this explanation be correct, it should be possible to get a similar dye by the action of alkali on a lepidine alkyl halide by condensation of a 4-methyl and a 2-hydrogen. All the published accounts of dye formation from lepidine describe a blue or violet color. This is probably due to the presence of quinoline in the lepidine used, for lepidine made from cinchonine is certain to contain quinoline. Synthetic lepidine should contain no quinoline, but may contain quinaldine, and as mentioned above, this impurity likewise permits the production of a dye of the cyanine type. When lepidine ethiodide of sufficient purity is treated with alcoholic alkali in hot concentrated solution, the principal product is an *iso*-cyanine. In dilute solution or in the presence of formaldehyde other products result, which will be described in a later article. The isocyanine is presumably isomeric with that from quinaldine ethiodide, but is crystallographically[1] very different; its photosensitizing action is similar. Since other isocyanines possess greater photosensitizing power, these new isocyanines are interesting chiefly from the light which their existence throws on the nature of the isocyanine condensation; this type of dye can be formed alike from a 2-methyl and from a 4-methyl-quinoline alkyl halide, hence the only possible formulation of the reaction is as a 4,2′ condensation.

Preparation of Isocyanine from Lepidine Methiodide.—One hundredth of a mole (2.85 g.) of lepidine methiodide, was dissolved in 25 cc. methyl alcohol and the solution heated to boiling. 10 cc. of 0.5 *N* solution of sodium methylate (0.005 mole, equivalent to 0.115 g. of sodium) was gradually added to the boiling solution. Boiling was continued for a few minutes after the addition of the alkali, the flask loosely stoppered and the slightly concentrated solution allowed to cool very slowly. After 24 hours very fine bluish-black crystals separated. These were filtered off with suction, washed with ice-cold methyl alcohol, methyl alcohol-ether, and finally ether alone. The yield was about 0.8 g.

Preparation of Isocyanine from Tolu-lepidine Methiodide.—The same

[1] The crystallography of these 2 and of 2 other isomers is being studied by Dr. E. T. Wherry, of the Crystallography Laboratory of the Bureau of Chemistry.

procedure, starting with 2.99 g. of tolu-lepidine methiodide (1,4,6-trimethyl-quinolium iodide) gave 0.75 g. of a crystal felt with a bluish-green sheen.

Preparation of Isocyanine from Tolu-lepidine Ethiodide.—The same procedure, starting with 3.13 g. of tolu-lepidine ethiodide (1-ethyl-4,6-dimethyl-quinolinium iodide) gave 0.47 g. of a purplish-black powder, containing many crystals showing brassy and blue-green metallic reflections.

Preparation of Isocyanine from Lepidine Ethiodide.—Starting with 1.5 g. of lepidine ethiodide, the same procedure was followed (half the quantity of all reagents being used) except that the solution was concentrated to a volume of 5 cc. and allowed to stand for 2 weeks. The dye separated in blunt (apparently) square prisms, with a brass-like luster, and showing peculiarly mottled reflection colors. The yield was 0.16 g.

Preparation of Isocyanine from Tolu-lepidine Methnitrate.—A solution of 4.50 g. of tolu-lepidine methiodide in 40 cc. of methyl alcohol was added to a solution of 2.56 g. of silver nitrate in 80 cc. of methyl alcohol, and the precipitated silver iodide filtered off. As the solution gave a test for silver, a small amount of the solution of the intermediate was added, and the filtration repeated. The solution was concentrated to 50 cc. and 15 cc. of 0.5 *N* sodium methylate (0.1725 g. of sodium in 15 cc. of methyl alcohol) was added to the boiling solution, which was then concentrated to 25 cc. and allowed to cool very slowly. The blue-black crystals which separated were washed with ice-cold methyl alcohol, methyl alcohol-ether, and finally ether alone. The yield was 0.43 g.

Summary.

1. The quaternary addition products of sufficiently pure lepidine (or homologs of lepidine) give when treated with alcoholic alkalies in hot, concentrated solution, dyes of the isocyanine type, similar to, but not identical with, those given by the corresponding derivatives of quinaldine.

2. The preparation of 5 such dyes is described.

3. The formation of isocyanines from lepidine confirms the hypothesis, now generally accepted, that these dyes contain 2 quinoline nuclei attached to a central carbon atom in Positions 4 and 2 respectively.

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