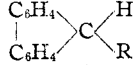
few additional experiments are therefore included in this note.

This interpretation shows that the dehydrogenation of certain 9-substituted fluorenes by unsaturated compounds involves a Michael condensation. In a recent paper on this subject,[2d] we reported the formation of condensation products which were either stable propane derivatives or unstable ones breaking up into their original or related components. In this study the condensations of unsaturated compounds with 9-substituted fluorenes containing a labile hydrogen in the substituent yield products, which undergo intramolecular oxidation-reduction. This mechanism not only explains the reactions presented in this paper and those reported previously,[3] but also serves as a basis for making the following predictions.[4] (1) Compounds of the type  $(C_6H_4)_2C(H)R$ where R is phenyl,[5] naphthyl, carbethoxy,[2b] dimethylamino and triphenyl methyl will condense with dibiphenylene-ethylene to form propane derivatives. Whether these condensates will be stable or undergo dismutation similar to tetrabromotribiphenylenepropane or dibiphenylene-phenylpropane[2d] will depend upon the relative electronegativities of the fluoroyl groups of the ethylene and of the addenda. (2) Other 9-substituted fluorenes which have a potentially labile hydrogen in the substituent such as, methylamino, ethylamino, anilino, methyl,[6] ethyl and benzyl will react with dibiphenylene-ethylene to form unstable intermediate products which will undergo intramolecular oxidation-reduction.

### Experimental

**Reaction of 9-Fluorenol with Dibiphenylene-ethylene in Ammonia.**—One gram of 9-fluorenol (excess) and 0.9 g. of dibiphenylene-ethylene in liquid ammonia reacted completely in three days at room temperature. The course of the reaction could be followed visually by the alteration of the red ethylene into the colorless ethane, both being only slightly soluble. On cooling the tube in liquid ammonia the fluorenone was also precipitated. The solvent was decanted and the insoluble portion was triturated with petroleum ether whereby 0.40 g. of fluorenone was extracted, m. p. and mixed m. p. with fluorenone 83°. The petroleum ether insoluble residue after crystallizing from benzene yielded 0.49 g. of dibiphenylene-ethane, m. p. and mixed m. p. 249°. The benzene-soluble fraction consisted of a mixture of the ethane, fluorenone and fluorenol. On recrystallizing the ammonia soluble fraction from benzene, 0.31 g. of fluorenol was obtained, m. p. 150°, mixed m. p. 152°.

The same reaction took place in absolute alcohol in the presence of sodium ethylate. From a reaction of 0.25 g. of fluorenol and 0.45 g. of dibiphenylene-ethylene were isolated 0.16 g. of fluorenone and 0.425 g. of dibiphenylene-ethane.

**Reaction of 9-Aminofluorene with Dibiphenylene-ethylene in Alcoholic Sodium Ethylate.**—An alcoholic solution of sodium ethylate containing 1 g. of dibiphenylene ethylene and 0.66 g. of 9-aminofluorene hydrochloride was allowed to react in a sealed tube at room temperature for a month. Practically quantitative yields of dibiphenylene-ethane and fluorylidene-imine were isolated and identified in a manner previously described.[3] This reaction could be obtained in a much shorter time at a higher temperature since the latter would favorably effect the solubility of the ethylene and rate of reaction.

**Reaction of 2,7-Dibromo-9-fluorenol with Azobenzene.**—A rapid reaction (one to two hours) took place at room temperature between 2 g. of 2,7-dibromo-9-fluorenol and 1 g. of azobenzene in an alcoholic solution of sodium ethylate, yielding 1.78 g. of 2,7-dibromofluorenone, m. p. and mixed m. p. 205°, and 0.80 g. of hydrazobenzene m. p. and mixed m. p. 124°. The latter was rearranged in dilute acid and the free benzidine was recrystallized from water, m. p. 126° and when mixed with an authentic specimen it melted at 127°. This reaction was also obtained in alcohol containing piperidine.

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[4] These ideas were developed after 1938, when my work on fluorene chemistry was terminated and I was, hitherto, not in a position to verify them.—L. A. P.

[5] Conant and Wheland, (*ibid.*, **54**, 1212 (1932)) reported that phenyl fluorene is somewhat more acidic than fluorene.

[6] The lability of the hydrogen on the methyl group was demonstrated by the reaction of 9-methyl-9-bromofluorene with ammonia yielding biphenylene-ethylene (Pinck and Hilbert, *ibid.*, **59**, 8 (1937)).

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## 5-Substituted Cinchomeronic Acids[1]

BY LESTER J. REED[2] AND WILLIAM SHIVE[3]

An investigation of the synthesis and properties of 5-substituted cinchomeronic acids was carried out in connection with the synthesis of 5-hydroxy-3,4-pyridinedimethanol, a homolog of pyridoxine.

Oxidation of 4-bromoisoquinoline which was readily obtained by direct bromination of isoquinoline afforded fair yields of 5-bromocinchomeronic acid. Esterification of this acid was effected readily with diazomethane, but all attempts to convert the methyl 5-bromocinchomeronate directly into 5-aminocinchomeronamide failed. However, conversion of 5-bromocinchomeronic acid into 5-aminocinchomeronic acid was accomplished in good yields with concentrated ammonium hydroxide in the presence of copper sulfate at elevated temperatures. Difficulties were encountered in the esterification of 5-aminocinchomeronic acid; so it was then transformed into 5-hydroxycinchomeronic acid by diazotization in concentrated sulfuric acid followed by decomposition of the diazonium salt in dilute sulfuric acid. The hydroxycinchomeronic acid was isolated as a monohydrate. The anhydrous form was obtained by drying under reduced pressure in the presence of phosphorus pentoxide; however, reversion to the monohydrate occurred rapidly when the anhydrous form was allowed to stand exposed to the atmosphere.

### Experimental

**4-Bromoisoquinoline.**—Isoquinoline was brominated by the method of Bergstrom and Rodda[4] and purified by a

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[1] From a thesis submitted by Lester J. Reed in partial fulfillment of the requirements for the degree of Bachelor of Science.

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[3] Present address: Department of Chemistry, University of Texas, Austin.

[4] Bergstrom and Rodda, THIS JOURNAL, **62**, 3030 (1940).

process similar to that of Craig and Cass.[5] The reaction mixture was made alkaline, and the crude bromoisoquinoline separated as a dark colored oil. The oily layer was removed, and the solution was extracted with ether. The combined extracts and crude material were dried over solid potassium hydroxide and fractionated through a Vigreux column at a reflux ratio of 8 to 1. By careful fractionation, a yield of 56.5% of relatively pure 4-bromoisoquinoline, m. p. 39–40°, was obtained without the necessity of recrystallization.

**5-Bromocinchomeronic Acid.**—Oxidation of 4-bromoisoquinoline to 5-bromocinchomeronic acid was accomplished with alkaline permanganate by a method analogous to that of Edinger and Bossung.[6] Purification by their method of precipitation of the lead salt afforded relatively pure samples, m. p. 236–237°; however, crude preparations contaminated with appreciable amounts of phthalic acid were more easily obtained by filtration of the oxidation mixture, acidification of the filtrate with hydrochloric acid, evaporation to dryness and removal of inorganic salts by leaching with cold water. For the preparation of 5-aminocinchomeronic acid, this crude product was satisfactory in that the phthalic acid was easily removed during the process.

**Methyl 5-Bromocinchomeronate.**—A relatively pure sample of 5-bromocinchomeronic acid (1.4 g.) was dissolved in 20 cc. of methanol. Excess (10%) diazomethane in ether was added slowly to the solution. The mixture was allowed to stand for thirty minutes before the ether and methanol were evaporated. A viscous yellow oil was obtained which solidified when cooled. Recrystallization from petroleum ether gave 0.97 g. (62%) of colorless prisms, m. p. 75.5–76.5°.

*Anal.* Calcd. for $C_9H_8BrNO_4$: Br, 29.16. Found: Br, 29.22.

**5-Aminocinchomeronic Acid.**—A solution of 103 g. of crude 5-bromocinchomeronic acid and 24 g. of copper sulfate in 240 cc. of concentrated ammonium hydroxide was heated in sealed tubes at 200° for thirty hours. The reaction mixture was filtered, evaporated to dryness and dissolved in 400 cc. of water. Most of the material dissolved when the solution was heated. Concentrated hydrochloric acid was added until the solution reached a *p*H of 2. Upon cooling, the solution deposited fine crystals of phthalic acid which was filtered and washed with a small portion of dilute hydrochloric acid. The amount of phthalic acid, 31.8 g., indicated that the crude 5-bromocinchomeronic acid contained approximately 30.9% phthalic acid. Concentrated ammonium hydroxide was added to the filtrate until a green precipitate formed. The mixture was heated and saturated with hydrogen sulfide and at the same time agitated vigorously. The precipitate from this treatment was suspended in 250 cc. of water and again treated with hydrogen sulfide in an analogous manner. The filtrates from both sulfide treatments were combined and cooled in an ice-bath. Most of the 5 aminocinchomeronic acid, 26.7 g., crystallized from the cooled solution. The filtrate from this product was evaporated to dryness, and the residue was redissolved in hot water and treated with copper acetate. The green copper salt of the amino acid was removed and suspended in 250 cc. of hot water and treated with hydrogen sulfide. After removal of the copper sulfide, the filtrate was cooled in an ice-bath to obtain an additional amount, 8.4 g., of the amino acid. The total yield after accounting for phthalic acid as in impurity was 66.6% of the theoretical.

5-Aminocinchomeronic acid is insoluble in most organic solvents, including ethanol, methanol, acetone, chloroform, dioxane, benzene and carbon tetrachloride. It is sparingly soluble in hot water. After repeated recrystallizations from pyridine, the amino acid melted at 223–224°.

*Anal.* Calcd. for $C_7H_6N_2O_4$: N, 15.38. Found: N, 15.35.

**5-Hydroxycinchomeronic Acid.**—A solution of nitrosylsulfuric acid was prepared by adding 0.9 g. of sodium nitrite slowly to 2 cc. of cold concentrated sulfuric acid. The nitrosylsulfuric acid was then diluted slowly at a low temperature with 1 cc. of cold water. A solution of 1.8 g. of 5-aminocinchomeronic acid in 4 cc. of concentrated sulfuric acid was added dropwise with vigorous agitation to the nitrosylsulfuric acid maintained at 2–4°. The reaction mixture was stirred for one hour at temperatures of 2–4° with gradual additions of small pieces of ice to liberate additional amounts of nitrous acid. The reaction mixture was then added slowly to 30 cc. of water maintained at 80°. After gas was no longer evolved, the solution was cooled and neutralized with a concentrated solution of 6.5 g. of sodium hydroxide and 2.9 g. of potassium hydroxide. The resulting solution, *p*H 3, deposited 0.75 g. of fine crystals of 5-hydroxycinchomeronic acid on cooling. An additional 0.15 g. of material was obtained by extracting with pyridine the residue from evaporation to dryness of the filtrate. The yield was 0.90 g. or 50% of the theoretical. Recrystallization from water and from methanol and drying under low pressure at 100° in the presence of phosphorus pentoxide gave colorless prisms, m. p. 243–244° with gas evolution.

*Anal.* Calcd. for $C_7H_5NO_5$: N, 7.65. Found: N, 7.86.

On standing in air the anhydrous form rapidly gained weight equivalent to one mole of water, and the melting point was lowered slightly, 237–238° with gas evolution.

*Anal.* Calcd. for $C_7H_5NO_5{\cdot}H_2O$: N, 6.96. Found: N, 6.88.

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[5] Craig and Cass, *ibid.*, **64**, 783 (1942); also Padbury and Lindwall, *ibid.*, **67**, 1268 (1945).

[6] Edinger and Bossung, *J. prakt. Chem.*, **43**, 190 (1891).

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## The Action of Cuprous Cyanide on *p*-Methoxybenzyl Chloride

BY STANLEY WAWZONEK AND HSIEN-LIANG HSU[1]

The action of sodium cyanide on *p*-methoxybenzyl chloride under the usual conditions gives a mixture of the benzyl alcohol and ethyl ether.[2] Modifications[2,3] of this method give at best a 43% yield of *p*-methoxybenzyl cyanide.

In an attempt to increase the yield of the nitrile, the reaction of cuprous cyanide on *p*-methoxybenzyl chloride was investigated. The products obtained under various conditions were tars. These results indicate that in the presence of cuprous cyanide, *p*-methoxybenzyl chloride polymerizes in a similar fashion to that observed with benzyl chloride in the presence of certain metals and metallic chlorides.[4] Benzyl chloride, however, behaved normally with cuprous cyanide under anhydrous conditions, giving a 71% yield of benzyl cyanide.

### Experimental

**Benzyl Cyanide.**—Freshly distilled benzyl chloride (63.2 g.) and dry cuprous cyanide (45 g.) were heated with

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[1] Abstracted from a thesis by Hsien-Liang Hsu presented to the Graduate College of the State University of Iowa, in partial fulfillment of the requirements for the M. S. degree, February, 1946.

[2] Lapine, *Bull. soc. chim.*, [5] **6**, 390 (1939).

[3] Shriner and Hull, *J. Org. Chem.*, **10**, 228 (1945).

[4] Shriner and Berger, *ibid.*, **6**, 305 (1941).