

dry hydrogen chloride (92 g.). After the mixture had stood for three days at room temperature, the solid which had separated was collected on a filter, washed with ether and dried *in vacuo* over barium oxide. The yield was 66.5 g. or 83% of the amount expected from a quantitative reaction. The salt can be prepared from acetovanilnitrile but the yields are variable and often low (27-64%). When well washed with ether and completely freed of hydrogen chloride, the salt obtained directly from the reaction was found to be of high purity. Recrystallization can be carried out from boiling 90% aqueous acetone. The white microcrystals melt between 140 and 150° with decomposition depending upon the rate of heating.

*Anal.* Calcd. for  $C_{12}H_{13}O_3NCl$ : Cl, 13.56. Found: Cl, 13.56, 13.35.

**Vanillic Acid Amide.**—Vanillic acid *n*-butyl amido ester chloride (43.4 g.) was heated in a Claisen flask through which a stream of nitrogen was flowing. When the heating bath temperature reached 140-145° the decomposition began and continued smoothly while the external temperature was raised to 160-170°. *n*-Butyl chloride (12.9 g., b. p. 78°) was gradually produced. Absence of bubbling in the melt indicated the reaction had ceased. The contents of the flask was crystallized from ethanol and from water. The reaction yielded 26.5 g. of white needles m. p. 153-154°, 95% of the vanillic acid amide expected from a quantitative reaction. The yield of *n*-butyl chloride was 83.5%.

*Anal.* Calcd. for  $C_8H_9O_3N$ : N, 8.34. Found: N, 8.33, 8.34.

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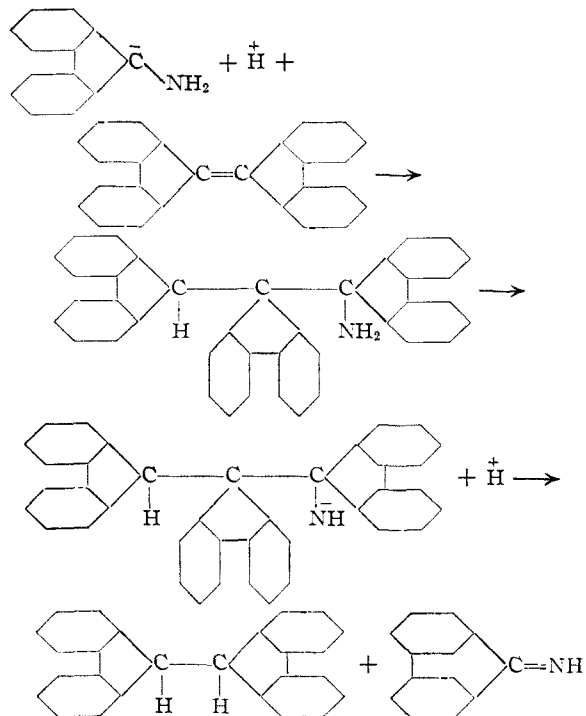
## The Dehydrogenation of 9-Aminofluorene and Fluorenol by Unsaturated Compounds. A Michael Condensation

BY LOUIS A. PINCK AND GUIDO E. HILBERT<sup>1</sup>

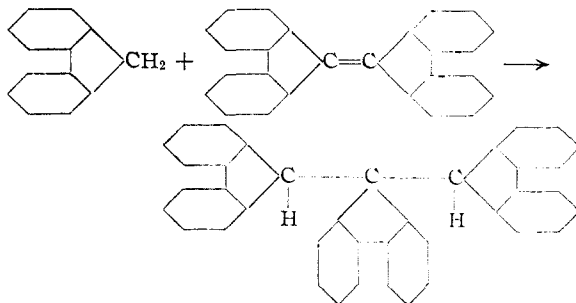
In retrospect of several studies reported by Pinck and Hilbert<sup>2</sup> dealing with reactions of fluorene, 9-substituted fluorenes and dibiphenylene-ethylene in liquid ammonia and in other alkaline media, the following conclusions are obtained: (1) In an alkaline medium fluorene dissociates into a fluoryl ion and a proton. (2) The lability of the hydrogen atom at the 9 position in 9-aminofluorene is greater than that of the hydrogen atom in the amino group; this of course presupposes that the amino hydrogen is also labile. Its corollary is that the hydrogen atom at the 9 position in 9-fluorenol has a greater lability than the hydrogen in the hydroxy group. (3) The great reactivity of the double bond in dibiphenylene-ethylene suggests that its electronic configuration is more like that of the ethylenic linkage with an adjacent carbonyl group than that of the normal type in ethylene.

On basis of these deductions we are now in a position to postulate a likely reaction mechanism for the dehydrogenation of 9-aminofluorene by dibiphenylene-ethylene and other reactive un-

saturated compounds.<sup>3</sup> Starting with ionized 9-aminofluorene the mechanism may be presented by the following equations



1-aminotribiphenylene-propane is assumed to be an unstable intermediate. Its formation and structure, however, are analogous to those of the stable tribiphenylene-propane.<sup>2d</sup>



The proposed mechanism not only illustrates the reaction *per se* but also serves as a general pattern for similar types of dehydrogenation. For example 9-fluorenol should undergo dehydrogenation in a manner similar to 9-aminofluorene. Furthermore this mechanism should apply to other unsaturated compounds previously cited,<sup>3</sup> which are capable of serving as hydrogen acceptors. Finally these reactions should occur in other alkaline media besides liquid ammonia. These deductions have been confirmed experimentally. Since reactions of 9-aminofluorene with dibiphenylene-ethylene, benzalfluorene, indigo, methylene blue and azobenzene in liquid ammonia had been previously reported, only a

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(2) Pinck and Hilbert, *THIS JOURNAL*, (a) **57**, 2398 (1935); (b) **68**, 377 (1946); (c) **68**, 867 (1946), (d) **68**, 2014 (1946).

(3) Pinck and Hilbert, *ibid.*, **54**, 710 (1932).

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,<sup>2d</sup> 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,<sup>3</sup> but also serves as a basis for making the following predictions.<sup>4</sup> (1) Compounds of the

type  $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C} \\ | \\ \text{C}_6\text{H}_4 \end{array} \begin{array}{c} \diagup \text{H} \\ \diagdown \text{R} \end{array}$  where R is phenyl,<sup>5</sup> naphthyl,

carbethoxy,<sup>2b</sup> dimethylamino and triphenyl methyl will condense with dibiphenylene-ethylene to form propane derivatives. Whether these condensates will be stable or undergo dismutation similar to tetrabromotribiphenylene-propane or dibiphenylene-phenylpropane<sup>2d</sup> 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,<sup>6</sup> 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

(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-bromo-9-fluorene with ammonia yielding biphenylene-ethylene (Pinck and Hilbert, *ibid.*, **69**, 8 (1937)).

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.<sup>3</sup> 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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### 5-Substituted Cinchomeronic Acids<sup>1</sup>

BY LESTER J. REED<sup>2</sup> AND WILLIAM SHIVE<sup>3</sup>

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-bromocinchomerionate 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<sup>4</sup> and purified by a

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