

piperidine,<sup>1</sup> were tested for anti-pneumococcal activity in mice through the kindness of the Merck Institute for Therapeutic Research, Rahway, New Jersey. Under the experimental conditions these compounds showed little activity in comparison with sulfapyridine.

**N<sup>4</sup>-Acetylsulfanilylpyrrolidine.**—Acetylsulfanilyl chloride (11.7 g., 0.05 mole) was added in several portions to a solution of 8.5 g. (0.12 mole) of pyrrolidine in 40 cc. of dioxane and the resulting solution was allowed to stand overnight. Cold water (200 cc.) was added and the precipitate which formed was filtered and washed with cold water. The crude product (12.5 g.) was treated with decolorizing charcoal and recrystallized from 50% alcohol, yielding 10.3 g. (77%) of tiny colorless plates and needles of m. p. 179° (cor.).

*Anal.* Calcd. for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>S: N, 10.44. Found: N, 10.5.

**Sulfanilylpyrrolidine.**—Five grams of N<sup>4</sup>-acetylsulfanilylpyrrolidine was refluxed for one-half hour with 60 cc. of 12% hydrochloric acid. The solution was cooled and 20% sodium hydroxide solution was added with cooling and stirring to slight basicity. The resulting precipitate (4.0 g.) was recrystallized from 50% alcohol as slightly yellowish feathery crystals and from acetone–benzene as small plates of m. p. 167.5–168° (cor.). The yield of pure product was 3.3 g. (79%).

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>S: N, 12.38. Found: N, 12.4.

**N<sup>4</sup>-Acetylsulfanilylpyrroline.**—Five grams (0.021 mole) of acetylsulfanilyl chloride was added in portions to a cold solution of 1.5 g. (0.022 mole) of pyrroline and 5 cc. of pyridine in 25 cc. of acetone. The reddish colored solution was heated to boiling and allowed to stand for four hours at room temperature. The product was precipitated by the addition of 300 cc. of cold water and recrystallized from 50% alcohol, using decolorizing charcoal, as fine white needles of m. p. 201–202° (cor.); yield, 3.2 g. (57%).

*Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>S: N, 10.52. Found: N, 10.4.

**Sulfanilylpyrroline.**—N<sup>4</sup>-Acetylsulfanilylpyrroline (2.3 g.) was refluxed one-half hour with 20 cc. of 12% hydrochloric acid. The hydrolyzed product was precipitated by the addition of 20% sodium hydroxide solution with cooling. The crude material was recrystallized from 50% alcohol and from acetone–benzene as small white prisms of m. p. 176–177° (cor.). The yield of pure product was 1.3 g. (67%).

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>S: N, 12.49. Found: N, 12.6.

Attempts to prepare N<sup>4</sup>-acetylsulfanilylpyrrole, using pyrrole–pyridine mixtures or the potassium derivative of pyrrole and acetylsulfanilyl chloride, were unsuccessful.

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(1) Goldyrev and Postovskii, *J. Applied Chem.* (U. S. S. R.), **11**, 316 (1938); *C. A.*, **32**, 5800 (1938).

## Dehydration of 9-Fluorenylcarbinol: a New Synthesis of Phenanthrene

BY WELDON G. BROWN AND BENNIE BLUESTEIN

It may be anticipated that the hitherto unknown 9-fluorenylcarbinol<sup>1</sup> would undergo a Wagner rearrangement on dehydration by acids to yield phenanthrene. Analogous reactions of  $\beta$ , $\beta$ -diarylethanol, which yield stilbene derivatives, are known,<sup>2</sup> and the formation of 9,10-diphenylphenanthrene<sup>3</sup> from 9-phenyl-10-benzoylfluorene on reduction with hydriodic acid and phosphorus may be similarly interpreted. However, Courtot,<sup>1b</sup> in his extensive studies of the dehydration of fulvanols, appears not to have encountered this type of rearrangement. Thus it is stated that the methyl and ethyl homologs of 9-fluorenylcarbinol yield methyl- and ethyldibenzofulvene, respectively, rather than methyl- and ethylphenanthrene which would be the rearrangement products.

The synthesis of 9-fluorenylcarbinol has now been accomplished by reduction of 9-formylfluorene with aluminum isopropoxide. On treatment, in boiling xylene solution, with phosphorus pentoxide it loses water to form phenanthrene in practically quantitative yield.

This synthesis offers some promise for the synthesis of phenanthrene derivatives, and of higher angular hydrocarbons, and we are now working in this direction.

### Experimental

**9-Fluorenylcarbinol.**—Ten grams of 9-formylfluorene<sup>4</sup> in 30 cc. of ether was added to a mixture containing 16 g. of aluminum isopropoxide and 32 cc. of isopropyl alcohol. Ether and acetone were removed by slow distillation through a Vigreux column, the bath being maintained at 60–70° for four hours; 63 cc. of 15% sulfuric acid was added to the residue, precipitating a light yellow solid which was collected and extracted with hot alcohol. After precipitation from the alcohol extract by the addition of water it was recrystallized several times from high boiling ligroin as long needles, colorless, m. p. 99.5–100.0°; yield 5 g.

*Anal.* Calcd. for C<sub>14</sub>H<sub>12</sub>O: C, 85.68; H, 6.17. Found: C, 85.54; H, 6.36.

**9-Fluorenylcarbinol-3,5-dinitrobenzoate.**—M. p. 212°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>: N, 7.18. Found: N, 7.46.

(1) For previous attempts at the synthesis of this alcohol, see (a) Sieglitz and Jassay, *Ber.*, **55**, 2032 (1922); (b) Courtot, *Ann. chim.*, (9) **4**, 157 (1915).

(2) Ramart and Amagat, *ibid.*, (10) **8**, 263 (1927).

(3) Werner and Grob, *Ber.*, **37**, 2887 (1904).

(4) Prepared by the condensation of fluorene and methyl formate according to Wislicenus and Waldmüller, *ibid.*, **42**, 785 (1909).

**Dehydration of 9-Fluorenylcarbinol.**—One gram of 9-fluorenylcarbinol in 10 cc. of xylene, refluxed with phosphorus pentoxide for thirty minutes, yielded, after evaporation of the xylene at room temperature, nearly 1 g. of yellow solid. On recrystallizing twice from alcohol it was obtained in colorless plates, m. p. 97°. No change in m. p. resulted when the substance was sublimed in vacuum.

*Anal.* Calcd. for  $C_{14}H_{10}$ : C, 94.34; H, 5.66. Found: C, 94.27; H, 5.90.

This product formed a picrate, m. p. 144° (lit., phenanthrene picrate, m. p. 145°).

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### Oxidation of the Hydroxybiphenyls

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Substitution in *o*- and *m*-hydroxybiphenyl leads to isomers whose orientation must be established. While in one such study<sup>1</sup> in this Laboratory structure was established by a second synthesis of the new compound, this common method is not always available. It has been long known<sup>2</sup> that upon oxidation certain halogenated biphenyls yield benzoic or substituted benzoic acids, thus indicating the position of substituents. Although a systematic study<sup>3</sup> of polyhalogenated biphenyls has been reported, oxidation of the hydroxybiphenyls has been neglected. The formation of benzoic acid by the oxidation of a substituted hydroxybiphenyl would indicate the ring entered by the substituent, while formation of a substituted hydroxybenzoic acid would orient groups entering the ring containing the phenolic group. The present investigation represents a preliminary study of the conditions necessary for the formation of benzoic and hydroxybenzoic acids from the hydroxybiphenyls.

The method of oxidation followed is a modification of the use of chromic anhydride in acetic acid solution.<sup>4</sup> After standardizing the procedure by a study of the oxidation of biphenyl a study was made of the oxidation products from *o*-, *m*- and *p*-hydroxybiphenyl, 3-bromo-4-hydroxybiphenyl, 3,5-dibromo-4-hydroxybiphenyl and 3,5-dinitro-2-hydroxybiphenyl. In all of these cases benzoic acid and a small amount of unchanged starting material were the only substances isolated. Yields were low and differences

insufficient to establish influences due to groups and their positions in the ring.

The phenolic ring in the hydroxybiphenyls may be protected against complete oxidation in two ways, namely, by the steric effect of nitro groups in the diortho positions, and by the protective influence of a heavy ester group. 3,5-Dinitro-4-hydroxybiphenyl yields 3,5-dinitro-4-hydroxybenzoic acid, while in the case of 3-nitro-4-hydroxybiphenyl no benzoic acid and only a trace of the corresponding hydroxybenzoic acid could be isolated. When 2-hydroxybiphenyl was converted into the benzenesulfonate<sup>5</sup> and submitted to oxidation the only product isolated was benzenesulfonylsalicylic acid. This ester was readily transformed into salicylic acid.

### Procedure

**Benzoic Acid from Biphenyl.**—Thirty-five grams of chromic anhydride in 32 cc. of 37.5% acetic acid was added drop by drop with vigorous mechanical stirring and occasional warming over a period of thirty minutes to a hot solution of 5 g. of biphenyl in 50 cc. of glacial acetic acid. The reaction mixture was refluxed gently with stirring for two hours. The flame was removed, 6 cc. of acetaldehyde in 15 cc. of glacial acetic acid added, and gentle refluxing continued for an additional fifteen minutes; 50 cc. of water and 50 cc. of saturated salt solution was then added. The reaction mixture was extracted three times with ether, the ether distilled off and the residue made basic with concd. ammonium hydroxide. Solution in alcohol followed by dilution with water led to the recovery of 0.43 g. of unchanged biphenyl. The filtrate from the addition of ammonium hydroxide was acidified with concd. hydrochloric acid, boiled with Norit, filtered and cooled. The product gave 0.26 g. of benzoic acid upon recrystallization from water. An additional 0.20 g. was obtained by ether extraction of the filtrates. A second ether extract of the reaction mixture gave 0.32 g. of benzoic acid. Steam distillation of the reaction mixture (400 cc. of distillate) gave a small amount of impure acid. A second steam distillation, which was concentrated after making it alkaline, gave 0.55 g. of the acid. A final ether extraction of the reaction mixture yielded 0.21 g. more of the acid. The total weight of benzoic acid obtained from 5 g. of biphenyl was 1.54 g. or 38.88%. The addition of concd. hydrochloric acid to the reaction mixture gave a low yield, 5.7% of *m*-chlorobenzoic acid. When the oxidation was repeated with very slight modifications the yields of benzoic acid were as follows: from *o*-, *m*-, and *p*-hydroxybiphenyl 17.2%, 10% and 11.2%, respectively. 3-Bromo-4-hydroxybiphenyl, 3,5-dibromo-4-hydroxybiphenyl and 3,5-dinitro-2-hydroxybiphenyl gave 14.3%, 16.67% and 16.4% of benzoic acid. 3,5-Dinitro-4-hydroxybiphenyl gave a 5.0% yield of 3,5-dinitro-4-hydroxybenzoic acid and upon oxidation the benzene sulfonate of 2-hydroxybiphenyl gave 16.35% yield of benzenesulfonylsalicylic acid. The hydrolytic trans-

(1) Colbert, Meigs and Jenkins, *THIS JOURNAL*, **59**, 1122 (1937).

(2) Schultz, *Ann.*, **174**, 206 (1874).

(3) Case, *THIS JOURNAL*, **61**, 3487 (1939).

(4) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Inc., Boston, Mass., 1935, p. 230.

(5) Hazlet, *THIS JOURNAL*, **59**, 287 (1937).