

*Anal.* Calcd. for  $C_{27}H_{40}O_2N_2$ : C, 76.4; H, 9.5; N, 6.6. Found: C, 76.5; H, 9.5; N, 6.8.

**Disemicarbazone of Chlorogenone.**—A mixture of 500 mg. of chlorogenone, 1 g. of semicarbazide hydrochloride, 1.2 g. of sodium acetate, 5 cc. of 95% ethanol and 5 cc. of water was refluxed on the steam-bath for one hour. The solution was then cooled and the white solid collected and crystallized from ethanol to give a product which darkened at 250° but did not melt at 290°.

*Anal.* Calcd. for  $C_{29}H_{46}O_4N_6$ : C, 64.2; H, 8.5. Found: C, 64.4; H, 8.7.

### Summary

The nuclear hydroxyl groups of chlorogenin are shown to be at the 3,6-positions rather than at the 3,12-positions as postulated by Noller.

Evidence is given in support of the *allo*-configuration at C-5.

STATE COLLEGE, PENNA. RECEIVED DECEMBER 3, 1939

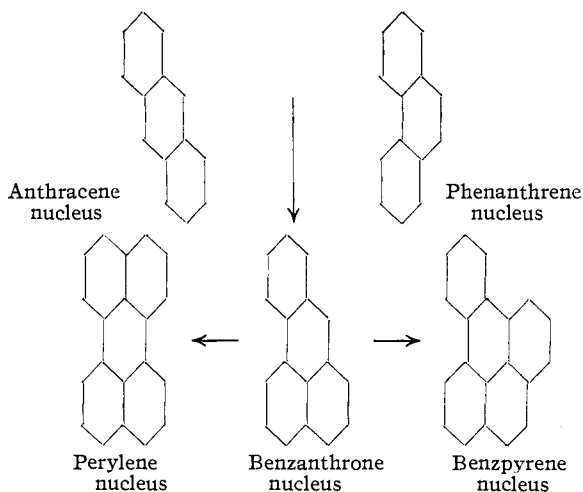
[CONTRIBUTION FROM THE JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND COMPANY]

## Hydrofluoric Acid as a Condensing Agent. I

BY WILLIAM S. CALCOTT, JOHN M. TINKER AND VIKTOR WEINMAYR

The preparation of benzanthrone from anthraquinone and its reduction products and from phenanthrene by a "*peri*" synthesis is well known.<sup>1</sup> The condensation of these compounds with acrolein (formed from glycerol in the course of the reaction) takes place in the presence of acid condensing agents, especially sulfuric acid.

In the literature there is no record of the use of a *peri* synthesis to add two additional benz rings to anthraquinone, reduced anthraquinone or phenanthrene; nor that a further *peri* synthesis could be effected using benzanthrone or a reduction product of benzanthrone. If such a *peri* condensation would take place, one should obtain a perylene or benzpyrene or both from anthraquinone, benzanthrone, or phenanthrene. The following formulas serve to illustrate the possible condensations schematically.



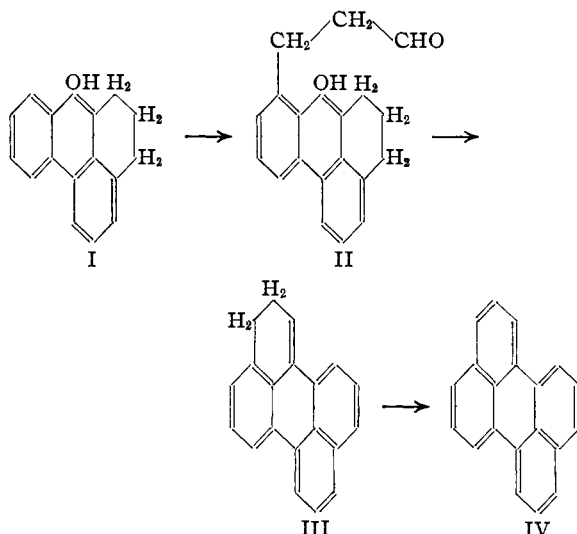
(1) O. Bally, *Ber.*, **38**, 194 (1905); O. Bally and R. Scholl, *ibid.*, **44**, 1660 (1911); R. Scholl and H. K. Meyer, *ibid.*, **69**, 154 (1936).

We have found that these reactions outlined above could be performed if essentially anhydrous hydrofluoric acid were used as the condensing agent. Thus we obtained perylene from phenanthrene and from 1,10-trimethylene-9-hydroxyphenanthrene, which is a reduction product of benzanthrone, and 4,5-benzpyrene from 9,10-dihydroanthracene. Acenaphthene gave a product showing a very characteristic brilliant green color in sulfuric acid. *peri*-Naphthindone was obtained from  $\alpha$ - and  $\beta$ -naphthol. Acrolein was used in all cases instead of glycerol.

High or non-fusible products were usually obtained as by-products. These substances could not be purified readily for identification and were probably higher condensation products. Undoubtedly conditions could be worked out under which these side reactions could be retarded and higher yields of pure products could be obtained.

We do not know what intermediate steps are involved in these condensations. The final products of the condensation are partially hydrogenated compounds from which perylene and benzpyrene are obtained by dehydrogenation. Presumably a nuclear alkylation takes place first, because we have found anhydrous hydrofluoric acid to be an excellent alkylating agent. Thus, 1,10-trimethylene-9-hydroxyphenanthrene (I) may first yield compound (II), which by loss of water is transformed by ring closure to a hydrogenated perylene (III). Perylene (IV) is finally obtained by dehydrogenation.

It appears, therefore, that hydrofluoric acid is a more suitable condensing agent than sulfuric acid. When preparing benzanthrone from anthraquinone with glycerol in sulfuric acid, it is



necessary to use temperatures above 100°. The condensations to be described are usually run at 20° or lower. A further advantage of hydrofluoric acid over sulfuric acid in these condensations is the absence of side reactions such as sulfonation, reduction, or oxidation.

### Experimental

The experiments were carried out in a forged steel or stainless steel vessel which was provided with tightly fitting cover, agitator, thermometer well and a charging hole. The charging hole was covered with a loosely fitting plug during the condensation but no special precautions were taken to avoid absorption of moisture from the air.

**Perylene from 1,10-Trimethylene-9-hydroxyphenanthrene.**—Commercial anhydrous hydrofluoric acid (500 g.) was weighed into the reaction vessel with the temperature at 10–15°. Acrolein (67 g.) and 1,10-trimethylene-9-hydroxyphenanthrene (117 g.) (m. p. 145–146°, lit. 150–151°) were added over a period of about one hour at a uniform rate. The charge was agitated at 10–15° overnight. From time to time during the first few hours of the condensation, samples were taken and dissolved in concentrated sulfuric acid. The initial orange color of benzanthrone soon changed to brown, then to purple. At the end of the condensation a sample in sulfuric acid was green for an instant, turning to blue and deep purple, a color change characteristic of perylene.

The reaction mass poured on ice, the precipitate was filtered, washed until free of acid, digested with hot dilute aqueous ammonia, washed again and dried. A mixture of hydrogenated perylenes and other condensation products (142 g., m. r. 250–300°) forming a light brown powder was obtained. The crude product was dehydrogenated by heating with mercury, and purified by distilling with mercury vapor, following H. Decker's method.<sup>3</sup>

The distillate was separated from the mercury by dissolving the hydrocarbon in benzene. The benzene was

evaporated and the residue crystallized from solvent naphtha. Perylene (22 g., m. p. 266°, lit. 264–265°) was isolated. Its identity was established by a mixed melting point with an authentic sample of perylene, by its typical color change in sulfuric acid, and by oxidation to 3,10-perylenequinone, which shows a typical color as a vat and in sulfuric acid.

Dehydrogenation by heating and distilling with mercury was more efficient than dehydrogenation by a zinc dust distillation or by sulfur in quinoline, but perylene was obtained from the crude condensation product by any of these methods.

**Perylene from Phenanthrene.**—Acrolein (25 g.) was added at 3–5° over a period of twenty minutes to a solution of phenanthrene (40 g.) in anhydrous hydrofluoric acid (360 g.). A test sample removed when part of the acrolein had been added showed an orange color with the fluorescence characteristic of benzanthrone compounds in sulfuric acid. A granular precipitate formed in the acid shortly after the addition of the acrolein was finished. The charge was agitated at 0–5° for forty-five minutes and then poured onto ice. The precipitate was filtered, washed acid free, washed with dilute caustic and water, and dried. A greenish-yellow solid (45 g.), which dissolved in concentrated sulfuric acid with a red-brown color that changed to purple after a short time was obtained. An aliquot of this product was distilled with mercury, the distillate extracted with benzene, and the residue left after the evaporation of the benzene digested with a small amount of acetone to dissolve oily impurities. The difficultly soluble perylene (about 1 g.) was filtered and crystallized from toluene. Its identity was established by melting point, mixed melting point with an authentic sample, and by its color reaction in sulfuric acid.

**4,5-Benzpyrene from 9,10-Dihydroanthracene.**—Acrolein (27 g.) was added at 5–10° within one hour to a solution of 9,10-dihydroanthracene (39.6 g.) in anhydrous hydrofluoric acid (200 g.). After a few grams of acrolein had been added, a sample of the condensation mass dissolved in concentrated sulfuric acid showed a color very similar to that of benzanthrone. The condensation mass was agitated at 15–20° for about twenty hours, then poured on ice, filtered, washed with dilute sodium hydroxide and hot water. A brown product (57 g., m. p. 140–180°) was obtained, which dissolved in sulfuric acid with a red-brown color and a slight red fluorescence, in organic solvents with a yellow color and a dull green fluorescence. The crude product was quite soluble in most organic solvents, but could not be crystallized readily. The crude product (20 g.) was distilled with mercury and the benzene extract of the distillate was concentrated until crystallization set in. The crystals were filtered, washed with petroleum ether and dried. This crude 4,5-benzpyrene (3 g.) was recrystallized twice from glacial acetic acid, giving 1 g. of greenish-yellow crystals (m. p. 166–168°). The product dissolved in sulfuric acid with practically no color, showing at first an orange fluorescence that soon changed to purple and finally to a faint red. A picrate melting from 223–225° was obtained. The material regenerated from the picrate melted at 169–170°. Although

(2) E. Clar and Fr. Furnari, *Ber.*, **65**, 1420 (1932).

(3) H. Decker, *ibid.*, **67**, 1636 (1934).

(4) H. Scholl, Chr. Seer and R. Weitzenböck, *ibid.*, **43**, 2202 (1910).

these data are not quite in agreement with those given in the literature for 4,5-benzpyrene<sup>6</sup> (m. p. 178–179°, picrate 229–230°), we believe that the structure is correct.

**peri-Naphthindone from  $\alpha$ -Naphthol.**— $\alpha$ -Naphthol (72 g.) and acrolein (56 g.) were added simultaneously, within forty minutes, to anhydrous hydrofluoric acid (530 g.) at 15–20°. A sample of the condensation mass soon showed the bright green fluorescence in sulfuric acid, characteristic for *peri*-naphthindone. A precipitate formed in the hydrofluoric acid, while the reaction mass was agitated overnight. The condensation mass was poured onto ice, and the suspension filtered and washed. A brown powder (105 g.) was obtained, which was soluble in sulfuric acid with a yellow color and a strong green fluorescence. Fifty grams of this product was extracted with 500 cc. of boiling dichlorobenzene. The solvent extract was steam distilled to remove the solvent. *peri*-Naphthindone crystallized from the water layer (4000 cc.) in light yellow crystals. Much tarry matter also was obtained. The *peri*-naphthindone was identified by its melting point (151°), mixed melting point with a sample prepared according to German Patent 283,066, by its color and fluorescence in sulfuric acid. Similarly, *peri*-naphthindone was obtained from  $\beta$ -naphthol.

**Condensation of Acenaphthene with Acrolein.**—Acrolein (28 g.) and acenaphthene (30.8 g.) were added to an-

(5) J. W. Cook, C. L. Hewett and I. Hieger, *J. Chem. Soc.*, 395 (1933).

hydrous hydrofluoric acid (370 g.) at 15–18° in ten minutes, and this solution was agitated for one hour at 10–15°. Acenaphthene showed no coloration in sulfuric acid, but the condensation product which formed as soon as acrolein was added dissolved in sulfuric acid with a brilliant green color. A finely divided precipitate formed while the charge was agitated at 15–20° for one hour. The reaction product isolated (51 g., light brown powder) after decomposition with ice had no melting point, dissolved in sulfuric acid with brilliant green color, and was only sparingly soluble in organic solvents with yellow color, and without appreciable fluorescence. A low melting product was isolated by extraction in a Soxhlet apparatus but could not be crystallized or identified.

### Summary

“*Peri*” condensations which are not possible in sulfuric acid were performed in anhydrous hydrofluoric acid. “*Peri*” condensations obtained in sulfuric acid also could be performed in hydrofluoric acid. Perylene was obtained from phenanthrene and 1,10-trimethylene-9-hydroxyphenanthrene, 4,5-benzpyrene from 9,10-dihydroanthracene, and *peri*-naphthindone from  $\alpha$ - and  $\beta$ -naphthol.

WILMINGTON, DEL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## Dibenzofuran. IX. Metalation of Some Derivatives\*

BY HENRY GILMAN, LEE C. CHENEY AND H. B. WILLIS

### Introduction

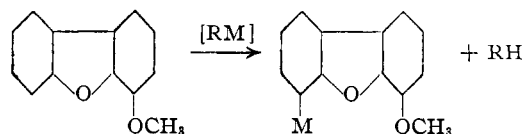
Metalation of dibenzofuran by a wide variety of metalating agents has given invariably a product having the metal in the 4-position, or ortho to the ether linkage.<sup>1</sup> Also, dimetalation has involved the positions ortho to the ether linkage to give 4,6-dimetalated dibenzofurans.<sup>1b</sup> It was shown subsequently that metalation of a variety of other ethers took place in an ortho position.<sup>2</sup>

Several substituted dibenzofurans have been metalated. With 4-methyldibenzofuran and with 4-methoxydibenzofuran, the metal enters the 6-position when *n*-butylsodium is used as the metalating agent.<sup>1b</sup>

(\*) Paper VIII, Gilman, Van Ess and Hayes, *THIS JOURNAL*, **61**, 643 (1939).

(1) (a) Gilman and Young, *ibid.*, **56**, 1415 (1934); (b) Gilman and Young, *ibid.*, **57**, 1121 (1935).

(2) (a) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) Gilman and Bradley, *THIS JOURNAL*, **60**, 2333 (1938); (c) Wittig, Pockels and Dröge, *Ber.*, **71**, 1903 (1938); (d) Gilman, Langham and Jacoby, *THIS JOURNAL*, **61**, 106 (1939); (e) Gilman and Bebb, *ibid.*, **61**, 109 (1939).



The first dibenzofuran derivative whose metalation did not involve an available 4- or 6-position was 2-methoxydibenzofuran.<sup>2c</sup> Two products were characterized in this case: a 1-metalated- and a 3-metalated-2-methoxydibenzofuran.

Later, we had need of large quantities of 4-hydroxy-6-methoxydibenzofuran and intended to prepare it by metalation of 4-methoxydibenzofuran with *n*-butyllithium followed by oxidation of the metalation product. However, after oxidation two isomeric hydroxy-4-methoxy-dibenzofurans were isolated. One of these was the expected 4-hydroxy-6-methoxydibenzofuran and the other was shown to be 3-hydroxy-4-methoxydibenzofuran by a diazo reaction on 3-amino-4-methoxydibenzofuran, the synthesis of