

boxylic acid chloride in 250 cc. of dry benzene and 50 cc. of ether at 0°. The mixture was slowly brought to 35–40° and kept at that temperature overnight. The crude ketone was subjected to thorough steam distillation from an alkaline medium and then extracted with ether–benzene, distilled at the oil pump, and crystallized from ether–petroleum ether; colorless needles, m. p. 108–110°; 12.3 g. (56% yield, 10 g. of fluorene-1-carboxylic acid being recovered from the alkaline solution).

The ketone is very readily soluble in benzene, moderately soluble in ether, and sparingly soluble in alcohol. Recrystallized from benzene–ether it formed slender needles, m. p. 113–114°.

Anal. Calcd. for $C_{24}H_{16}O$: C, 89.97; H, 5.04. Found: C, 90.02; H, 5.15.

15,16-Benz-dehydrocholanthrene (IX).—Four grams of the above ketone was heated for twenty-five minutes at 415° under nitrogen and the product was distilled in vacuum and crystallized once from benzene; yield, 2.25 g. (60%) of orange-red material, m. p. 177°. Purification by chromatographic adsorption was more tedious and wasteful than with sulfuric acid and gave no better material. On shaking a dilute benzene solution of the hydrocarbon with small portions of sulfuric acid until the acid acquired only a yellow color, the extraneous red material was removed with little loss of product. The purified hydrocarbon crystallized from benzene, in which it is only moderately soluble, as bright yellow, cottony needles, m. p. 181–181.3° corr.

Anal. Calcd. for $C_{24}H_{14}$: C, 95.33; H, 4.67. Found: C, 95.23; H, 4.98.

The *picrate* crystallizes from benzene as small, brick-red needles, m. p. 174.5–175.5°, corr.

Anal. Calcd. for $C_{30}H_{17}O_7N_3$: N, 7.91. Found: N, 8.22.

1-(β -Naphthoyl)-fluorene was the chief product of the reaction of 14.5 g. of fluorene-1-carboxylic acid chloride with 9 g. of naphthalene, and 9.2 g. of aluminum chloride in 300 cc. of tetrachloroethane, the mixture being initially at 5–10°, then at room temperature. The crude ketone was heated with acetone and alkali in order to hydrolyze unchanged acid chloride, 3.9 g. of acid being recovered after distilling the solvent and extracting the ketone with ether–benzene. After distillation *in vacuo*, one crystallization from benzene–ligroin gave 8 g. of the nearly pure β -ketone, m. p. 145–150°; total yield, 12.5 g. (84%). After several crystallizations of the first crop from benzene–ether the substance formed clusters of pale yellow needles, m. p. 159–162°. The compound is considerably less soluble than the α -isomer.

Anal. Calcd. for $C_{24}H_{16}O$: C, 89.97; H, 5.04. Found: C, 89.97; H, 5.25.

1',2'-Naphtho-1,2-fluoranthene (X).—The pyrolysis of the above ketone proceeded as in the case of the α -isomer, but the hydrocarbon, which is considerably more soluble than IX, is best purified with the use of an adsorption tower. It crystallized from benzene–ether in the form of flat, golden yellow needles, m. p. 178–179°, corr.

Anal. Calcd. for $C_{24}H_{14}$: C, 95.33; H, 4.67. Found: C, 95.25; H, 5.04.

The *picrate* crystallizes from benzene in the form of crimson needles melting at 181–182° corr.

Anal. Calcd. for $C_{30}H_{17}O_7N_3$: N, 7.91. Found: N, 8.16.

Summary

Cholanthrene and three additional hydrocarbons of the 1,2-benzanthracene series have been prepared by the modified Elbs synthesis.

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Halogenation of Phenolsulfonic Acids in Nitrobenzene

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The replacement of sulfonic acid groups of phenols with nitro groups or halogen takes place with rapidity in the presence of aqueous acid.^{2,3} If, however, the reaction is carried on in alkaline solution this group is rendered stable and serves as an effective blocking agent.^{4,5}

Fuming sulfuric acid has been used with more or less success in the preparation of 2-nitroresor-

cinol⁶ and to protect the four and six positions of *m*-cresol during nitration.^{7,8} Good yields of 2-bromo-*m*-cresol⁹ and 2-chloro-*m*-cresol¹⁰ were obtained in this Laboratory by brominating or chlorinating *m*-cresol directly with one mole of halogen in four volumes of fuming sulfuric acid and then removing the sulfonic acid groups by hydrolysis with superheated steam at 180–200°.

Numerous attempts to adapt this method to the preparation of 2,6-dibromophenol and 2-

(1) Presented in partial fulfillment of the requirements for the Ph.D. degree.

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(5) Huston and Ballard, "Organic Syntheses," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1934.

(6) Kaufman and DePay, *Ber.*, **37**, 725 (1904).

(7) Gibson, *J. Chem. Soc.*, **123**, 1269 (1923).

(8) Hodgson and Beard, *ibid.*, **127**, 498 (1925).

(9) Huston and Peterson, *THIS JOURNAL*, **55**, 3880 (1933).

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bromophenol failed to give satisfactory yields of either compound but indicated that the halogenation might take place as desired if carried out in an inert anhydrous solvent. Accordingly a number of runs were made in various solvents including petroleum ether, gasoline, kerosene and nitrobenzene. It was found that freshly distilled nitrobenzene was very well suited to the purpose and the following procedure was developed which gave excellent yields of 2,6-dibromophenol. Slight modification gave satisfactory yields of 2-bromophenol, 2,6-dichlorophenol or 2-chlorophenol.

2,6-Dibromophenol and 2-Bromophenol.—A mixture of 31.3 g. (one-third mole) of phenol and 50 g. of concentrated sulfuric acid (d. 1.84) was heated with stirring at 100–110° for two hours on an oil-bath. It was cooled and 100 g. of freshly distilled nitrobenzene added. Cooling was continued while 15 g. of fuming sulfuric acid (49%) was added at such a rate that the temperature did not rise above 10°. One hundred seven grams (two-thirds mole) of bromine and 50 g. of nitrobenzene was added dropwise over a period of two hours and stirring was continued for an hour to complete bromination. One liter of water, in which 5–10 g. of sodium bisulfite had been dissolved, was added. The water and reaction mixture was thoroughly stirred for fifteen minutes to facilitate extraction of the brominated phenol sulfonic acids. For the most part, the tribromophenol remained in the nitrobenzene. This was drawn off by means of a separating funnel and the solution of sulfonic acids was evaporated from a 2-liter flask, suitably equipped for steam distillation, on an oil-bath maintained at 200°. The distillate obtained during the evaporation contained a small amount of nitrobenzene and was discarded. When the temperature of the sulfonic acid solution reached 115°, steam, superheated in a copper coil, was passed through it. The temperature of the oil-bath was maintained at 200, while the temperature of the contents of the flask continued to rise to 175–180° during hydrolysis. The brominated phenols were extracted from the distillate with ether and the phenol residue, after evaporation of the ether, was distilled under reduced pressure (4 mm.) from a modified Claisen flask having a 35 cm. column. Under these conditions a 10.4% yield of 2-bromophenol boiling at 55–60° (4 mm.)—190–191° (740 mm.)—and a 72.7% yield of 2,6-dibromophenol (m. p. 55–56°) boiling at 80–90° (4 mm.)—255–256° (740 mm.)—were obtained. Increasing amounts of sulfuric acid used in succeeding runs gave increasing amounts of 2-bromophenol and decreasing amounts of 2,6-dibromophenol. With 95 g. of sulfuric acid a minimum yield of 9.5% of 2,6-dibromophenol and a maximum yield of 46.5% of 2-bromophenol were obtained. Gradual reduction of bromine as the amount of sulfuric acid was increased did not change the yields.

2,6-Dichlorophenol, 2-Chlorophenol.—Reactants were used in the same quantities and under the same conditions as in the preparation of bromo derivatives except that 200 g. of nitrobenzene was used and the nitrobenzene solution of sulfonic acids was maintained at 55° while chlorine was passed in until no further reaction took place. A number

of runs made with increasing amounts of sulfuric acid, gave increasing amounts of 2-chlorophenol and decreasing amounts of 2,6-dichlorophenol. The use of 68 g. of sulfuric acid gave a maximum yield of 70.3% of 2,6-dichlorophenol (m. p. 66–67°) boiling at 80–85° (4 mm.)—219–220° (740 mm.)—and a minimum yield of 17% of 2-chlorophenol boiling at 50–55° (4 mm.)—177–178° (740 mm.). Minimum yields of 24% of 2,6-dichlorophenol and maximum yields of 72% of 2-chlorophenol were obtained when 100 g. of sulfuric acid was used.

Anal. Calcd. for $C_6H_4OCl_2$: Cl, 43.5. Found: Cl, 43.4.

6-Bromo-*o*-cresol.—Bromination of 36 g. of *o*-cresol at 5–10°, using 55 g. of concentrated sulfuric acid, 100 g. of nitrobenzene and 60 g. of bromine in 50 g. of nitrobenzene, gave a 60% yield of crude 6-bromo-*o*-cresol boiling at 55–65° (4 mm.) which contained about 8% *o*-cresol. When redistilled through a 90-cm. column (surrounded by an evacuated jacket) a pure product was obtained, b. p. 206–207° (740 mm.).

Anal. Calcd. for C_7H_7OBr : Br, 42.77. Found: Br, 42.3.

A small amount of 4,6-dibromo-*o*-cresol (13%), which boiled at 105° (4 mm.), was obtained.

6-Chloro-*o*-cresol.—Thirty-six grams of *o*-cresol chlorinated at 55°, using 60 g. of concentrated sulfuric acid and 200 g. of nitrobenzene, yielded 30% of 6-chloro-*o*-cresol boiling at 45–50° (4 mm.)—188–189° (740 mm.)—and 12% of 4,6-dichloro-*o*-cresol boiling at 73–78° (4 mm.).

2-Bromo-*m*-cresol, 4-Bromo-*m*-cresol and 2,6-Dibromo-*m*-cresol.—Several runs were carried out using 36 g. of *m*-cresol, 36 g. of concentrated sulfuric acid¹¹ and other reagents in the amounts given in the procedure for bromophenols. It was found necessary to brominate at 55–60° to prevent precipitation of the sulfonic acids before the reaction was completed. Two fractions were obtained. The first, boiling at 60–70° (4 mm.)—214–215° (743 mm.)—was identified as 2-bromo-*m*-cresol. (6-Bromo-*m*-cresol, which boils at approximately the same temperature, was probably present but was not isolated.) It was obtained in an average yield of 7% and solidified on standing in the receiver. When crystallized rapidly from a small amount of petroleum ether it formed a sheaf of tetragonal crystals. Slower crystallization from a greater amount of solvent gave large solid prisms, m. p. 61–62°.⁹

Anal. Calcd. for C_7H_7OBr : Br, 42.77. Found: Br, 42.4.

The second fraction boiling at 102–105° (4 mm.) also solidified in the receiver. However, toward the end of the distillation a small amount of material came over at about the same temperature which did not solidify. (This mixture was assumed to contain 4-bromo- and 2,4-dibromo-*m*-cresol¹² which have boiling points very near that of 2,6-dibromo-*m*-cresol.) The solid fraction was obtained in about 23% yield and was shown by analysis and the following series of reactions to be 2,6-dibromo-*m*-cresol. It crystallized from petroleum ether in clusters of needles which melted at 36.5–37.5° and formed a *p*-toluenesulfonyl ester¹³ melting at 131–132°.

(11) Claus and Krauss *Ber.*, **20**, 3089 (1887).

(12) Huston and Hutchinson, *THIS JOURNAL*, **54**, 1505 (1932).

(13) Einhorn and Holland, *Ann.*, **301**, 95 (1898).

Anal. Calcd. for $C_7H_6OBr_2$: Br, 60.15. Found: Br, 59.7.

Proof of Structure of 2,6-Dibromo-*m*-cresol.—Pure 4-nitro-*m*-cresol prepared by the method of Staedel and Kolb¹⁴ was brominated with two moles of bromine in glacial acetic acid and the resulting 2,6-dibromo-4-nitro-*m*-cresol was reduced by means of stannous chloride and hydrochloric acid.¹⁵ The hydrochloride of 2,6-dibromo-4-amino-*m*-cresol was diazotized by the procedure of Bigelow, Johnson and Sanborn¹⁶ and an unsuccessful attempt was made to prepare 2,6-dibromo-*m*-cresol by reducing the diazonium group with alcohol in the presence of finely divided copper. The first fraction obtained by the steam distillation of the reaction mixture remained an oil, while subsequent fractions solidified in the receiver and were shown by analysis to be 2,6-dibromo-4-chloro-*m*-cresol. Recrystallization from petroleum ether gave needle clusters melting at 68.5–69.5°. Analysis of the liquid fraction coming over in the first stages of the steam distillation for halogen indicated a mixture of 2,6-dibromo-*m*-cresol and 2,6-dibromo-4-chloro-*m*-cresol. Direct chlorination of this fraction in chloroform, after repeated attempts to purify it had failed, gave 2,6-dibromo-4-chloro-*m*-cresol melting at 68.5–69.5°. The *p*-toluene sulfonyl ester¹⁸ recrystallized from alcohol melted at 108–109°.

Conclusive proof of the structure of the 2,6-dibromo-*m*-cresol was obtained by chlorinating it directly in chloroform to the 2,6-dibromo-4-chloro-*m*-cresol, which was also prepared by the bromination of 4-chloro-*m*-cresol with two moles of bromine. In all cases the identity of the products was checked by melting point, ester formation and analysis.

An attempt to prepare 2-bromo- and 6-bromo-*m*-cresol was made by brominating 36 g. of *m*-cresol (one-third mole) and 36 g. of concentrated sulfuric acid in nitrobenzene at 5–10°. However, the reaction was found to yield a mixture of 25 g. (40%) of 2-bromo-*m*-cresol boiling at 60–65° (4 mm.) and 5 g. (8%) of 4-bromo-*m*-cresol boiling at 103–104° (4 mm.). The latter compound formed a mass of very fine needles when recrystallized from petroleum ether which melted at 58.5–59.5°. Its *p*-toluene sulfonyl ester¹⁸ melted at 112–113°. Recrystallization of 4-bromo-*m*-cresol, prepared by Huston and Hutchinson¹² from the same solvent, gave the same melting point and its *p*-toluene sulfonyl ester also melted at 112–113°. To further prove the structure of this (higher) fraction, 4-nitro-*m*-cresol was reduced by tin and hydrobromic acid in alcoholic solution and the hydrobromide diazotized in hydrobromic acid solution. Replacement of the diazonium group with bromine by the Sandmeyer reaction¹⁷ yielded

4-bromo-*m*-cresol, which was identified by the melting point and that of its *p*-toluene sulfonyl ester.

2-Chloro-*m*-cresol, 2,4-Dichloro-*m*-cresol and 2,6-Dichloro-*m*-cresol.—Adaptation of the method to the chlorination of *m*-cresol gave 2-chloro-*m*-cresol (m. p. 49–50°) boiling at 53–57° (4 mm.)—195–196° (740 mm.)—2,4-dichloro-*m*-cresol (m. p. 58–59°) boiling at 75–80° (4 mm.)—235–236° (745 mm.)—and 2,6-dichlorophenol boiling at 80–85° (4 mm.)—239.5–240.5° (745 mm.). The presence of 2,4-dichloro- and 2,6-dichloro-*m*-cresol in the same reaction is not surprising since Haworth and Lapworth¹⁸ report a mixture of the 4 and 6 sulfonic acids of *m*-cresol when it is sulfonated at 100–120°.

The structure of 2,4-dichloro-*m*-cresol was proved by brominating it in chloroform to the corresponding 2,4-dichloro-6-bromo-*m*-cresol (m. p. 58–59°), which was also prepared by chlorinating 6-bromo-*m*-cresol in chloroform. In order to prepare this in a pure state 6-nitro-*m*-cresol¹⁹ was reduced²⁰ and the resulting amino group was diazotized and replaced by bromine.¹⁸ It boiled at 70–73° (4 mm.)—210–212° (745 mm.)—and solidified upon standing in the receiver. When crystallized from petroleum ether it melted at 38.5–39.5°.

Similarly, the structure of 2,6-dichloro-*m*-cresol was proved by brominating it to 2,6-dichloro-4-bromo-*m*-cresol²¹ (m. p. 64–65°), which was also prepared by chlorinating 4-bromo-*m*-cresol directly.

Summary

1. Bromination of *p*-phenol sulfonic acid in anhydrous nitrobenzene gave excellent yields of 2,6-dibromo- and 2-bromophenol.
2. Chlorination of *p*-phenol sulfonic acids under similar conditions gave 2,6-dichloro and 2-chlorophenol.
3. Bromination or chlorination of the *p*-sulfonic acid of *o*-cresol in anhydrous nitrobenzene gave 6-bromo-*o*-cresol or 6-chloro-*o*-cresol.
4. Bromination or chlorination of the 4- and 6-sulfonic acids of *m*-cresol in anhydrous nitrobenzene gave 2-bromo-*m*-cresol, 2,6-dibromo-*m*-cresol and 4-bromo-*m*-cresol or 2-chloro-*m*-cresol, 2,4-dichloro-*m*-cresol and 2,6-dichloro-*m*-cresol.
5. Sulfonic acid groups on the benzene ring of phenol and phenol derivatives were shown to be stable toward halogenation in the presence of acid if carried out in an inert *anhydrous* solvent.

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