

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Phenanthrene Derivatives. VI. The Preparation of 1-, 2- and 3-Phenanthryl Halides

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During the sixty-four years that have elapsed since the discovery of phenanthrene only one mono-halogen derivative, other than the 9-phenanthryl halides, has been prepared. This is not due to lack of effort, for numerous attempts have been made to obtain these compounds. An extensive study of the halogenation of phenanthrene and of phenanthrene derivatives was undertaken by Sandqvist² who succeeded in obtaining 3-chlorophenanthrene from 3-phenanthrene-sulfonic acid. The attempts at the total synthesis of the phenanthryl halides met with no more success. Pschorr³ applied his method of synthesis to the preparation of 1- and 3-bromophenanthrene but the attempt failed in the last step of the process. Berger⁴ likewise was unable to prepare 2-bromophenanthrene by a similar procedure. Nylen,⁵ somewhat more successful, obtained a small amount of 3-chlorophenanthrene by the Pschorr synthesis.

The idea of preparing the phenanthryl halides through the diazo reaction was first conceived by Schmidt⁶ but he abandoned the investigation because of the difficulty of obtaining the phenanthryl amines. Werner and Kunz⁷ reported that 3-aminophenanthrene could not be diazotized. Although Schmidt⁸ reported the successful diazotization of this amine, he did not state the yield of the coupling product obtained with β -naphthol, and his method of diazotization is laborious. In view of these results no attempt was made in the present investigation to use the ordinary methods of diazotization. Instead, we resorted to the method of de Milt and van Zandt⁹ which was developed recently for the diazotization of weakly basic and insoluble amines. Using their procedure we were able to diazotize 1-, 2- and 3-amino-phenanthrenes successfully.

Although the iodophenanthrenes were obtained by treating the phenanthrene diazonium sulfates with potassium iodide, the Sandmeyer reaction proved to be unsatisfactory for the preparation of the chloro- and bromophenanthrenes. These halides were obtained by using the procedure of Schwechten,¹⁰ which involves the intermediate formation and subsequent decomposition of a complex formed by interaction of the diazonium compound and mercuric halide and potassium halide. In Table I are presented the yields and properties of the phenanthryl halides that were prepared. By heating the aqueous solutions of the diazonium salts the corresponding 1-, 2- and 3-phenanthrols were obtained. We are now engaged in the preparation of the 4-phenanthryl halides and are also investigating other methods of preparation.

Experimental Part

Preparation of Chlorophenanthrenes and Bromophenanthrenes.—The 1-, 2- and 3-aminophenanthrenes¹¹ were all diazotized in exactly the same manner. One and five-tenths grams of sodium nitrite was added with stirring to a cold mixture of 7.5 cc. of water and 15 cc. of concentrated sulfuric acid. The mixture was then heated with stirring on a steam-bath until a clear solution of nitrosylsulfuric acid was obtained. This solution was cooled to 0° and stirred mechanically as a solution of 1.93 g. (0.01 mole) of aminophenanthrene (1-, 2- or 3-isomer) in 10 cc. of pyridine was added drop by drop in the course of an hour. After addition was complete the mixture was stirred for one hour longer; it was then diluted to a volume of 200 cc. by addition of ice and water and treated with a solution of 1 g. of urea in 25 cc. of water in order to destroy the excess of nitrous acid. After the solution had been stirred at 0° for another hour, the diazonium salt solution was ready for reaction.

To the yellow solution of the phenanthrene diazonium sulfate from 1.93 g. of aminophenanthrene was added a solution of 11 g. of mercuric chloride and 11 g. of potassium chloride in 50 cc. of water. The mixture was allowed to stand in the cold for an hour in order that the deeply colored (yellow, orange or orange-red) precipitate of the double salt which formed could coagulate. The precipitate was filtered off, washed with water and air-dried for twelve to twenty hours. The dry double salt (6 g.) was intimately mixed with 12 g. of potassium chloride and the mixture was heated cautiously in a 50-cc. distilling flask with a free flame, keeping the temperature just high

(1) From part of the Ph.D. dissertation of Charlotte H. Boatner.

(2) Sandqvist, *Ann.*, **369**, 104 (1909).

(3) Pschorr, *Ber.*, **39**, 3106 (1906).

(4) Berger, *J. prakt. Chem.*, **133**, 331 (1932).

(5) Nylen, *Ber.*, **53**, 198 (1920).

(6) Schmidt, *ibid.*, **12**, 1153 (1879).

(7) Werner and Kunz, *ibid.*, **34**, 2524 (1901).

(8) Schmidt, *ibid.*, **34**, 3531 (1901).

(9) De Milt and van Zandt, *THIS JOURNAL*, **58**, 2044 (1936). In a private communication, Professor de Milt informed us that she had secured quantitative diazotization of some 3-aminophenanthrene which we had sent her.

(10) Schwechten, *Ber.*, **65**, 1605 (1932).

(11) Bachmann and Boatner, *THIS JOURNAL*, **58**, 2097 (1936).

TABLE I

PHENANTHRYL HALIDES

All of the compounds were obtained as colorless crystals by recrystallization from alcohol.

Compound	Cryst. form	M. p., °C.	Yield, %	Formula	Analyses, % Calcd.	Found
1-Chlorophenanthrene	Plates	120-120.5	41	C ₁₄ H ₉ Cl	Cl 16.7	16.7
2-Chlorophenanthrene	Plates	85.5-86	42			16.7
3-Chlorophenanthrene	Needles	80.5-81.5 ^a	48			16.9
1-Bromophenanthrene	Needles ^b	109.5-110	72	C ₁₄ H ₉ Br	Br 31.1	30.6
2-Bromophenanthrene	Plates	95-96	70			31.2
3-Bromophenanthrene	Needles	83-84	70			31.1
1-Iodophenanthrene	Fine needles	112.5-113	53	C ₁₄ H ₉ I	I 41.8	41.0
2-Iodophenanthrene	Prisms	116-116.5	47			40.9
3-Iodophenanthrene	Stout needles	83.5-84	47			41.8

^a Nylen⁵ reported a melting point of 80-81° for the product obtained by the Pschorr synthesis. Sandqvist³ reported the two values, 70.5-71 and 81°, for the product prepared by interaction of 3-phenanthrenesulfonyl chloride and phosphorus pentachloride. ^b The compound also crystallizes in the form of plates.

enough for evolution of nitrogen to take place. When no more nitrogen was evolved, the chlorophenanthrene was distilled from the mixture under reduced pressure (4 mm.). The distillate was extracted with benzene in order to remove inorganic salts, the benzene solution was boiled with charcoal, filtered and evaporated and the residue of chlorophenanthrene was then recrystallized from alcohol. All of the halides are readily soluble in benzene and in acetone but only slightly soluble in cold alcohol.

The bromophenanthrenes were prepared in a similar manner. For larger runs the procedure was modified somewhat. Thus, the double salt (63 g.), which was obtained by addition of a solution of 55 g. of mercuric bromide and 55 g. of potassium bromide in 200 cc. of water to the diazonium salt solution from 9.65 g. of 2-aminophenanthrene, was mixed with twice its weight of potassium bromide, and the mixture was then heated cautiously in an evaporating dish on a sand-bath until evolution of nitrogen had ceased. The reaction product was digested with hot water, the residue was taken up in benzene, the filtered benzene solution was evaporated and the residue of 2-bromophenanthrene was purified by distillation, b. p. 185° (4 mm.), followed by recrystallization from alcohol; yield 9.0 g.

Preparation of Iodophenanthrenes.—A pale yellow precipitate was formed on addition of 10 g. of potassium iodide in 25 cc. of water to the diazonium salt solution from 9.65 g. of 3-aminophenanthrene (or its 1- or 2-isomer). After standing overnight at room temperature the reaction

mixture was heated at 100° until no more nitrogen was evolved. The precipitate which had formed was filtered from the cooled solution and dissolved in benzene; the benzene solution was washed with a solution of sodium bisulfite and with water and then evaporated to dryness. The residue of 3-iodophenanthrene was purified by distillation, b. p. 190° (4 mm.), followed by recrystallization from alcohol; yield 7.2 g. By using the procedure involving the intermediate formation and subsequent decomposition of a double salt with mercury iodide and potassium iodide a 31% yield of 3-iodophenanthrene was obtained.

Preparation of Phenanthrols.—The phenanthrene diazonium sulfate solution from 1.93 g. of aminophenanthrene was diluted to a volume of 400 cc. and heated at 100° until decomposition was complete. The precipitate of phenanthrol was filtered off and purified through its water-soluble potassium salt. The yields were: 1-phenanthrol, 11%; 2-phenanthrol, 40%; 3-phenanthrol, 39%. The properties of the compounds agreed with those described in the literature.

Summary

By means of the diazo reaction 1-, 2- and 3-chlorophenanthrene, 1-, 2- and 3-bromophenanthrene, 1-, 2- and 3-iodophenanthrene and 1-, 2- and 3-phenanthrol have been prepared.

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