

Calc. for $C_{13}H_{22}NO_2Ag$: Ag, 32.53. Found: 32.83.

The specific gravity of the di-*iso*-amylcyano-acetic acid *iso*-amyl ester was 0.9074 at 22°. The total amount of this ester obtained from the product of the reaction was 21.5 g., or 70.3% of the whole.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF
WISCONSIN.]

THE PREPARATION OF 9(10)-PHENANTHRIDONE FROM PHENANTHRENE.

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An attempt was made to prepare a compound similar to the vat dye indanthrene red-violet, 2RN, by the following series of transformations: phenanthrene \rightarrow phenanthraquinone \rightarrow diphenic acid \rightarrow diphenic anhydride \rightarrow diphenamic acid \rightarrow 1-amino-10-carboxyl-diphenyl and the condensation of this compound with α -chloro-anthraquinone. In attempting to convert the diphenamic acid into 1-amino-10-carboxyl-diphenyl by Hofmann's reaction, 9(10)-phenanthridone was obtained instead of the desired amino acid. The 9(10)-phenanthridone was then condensed with α -chloro-anthraquinone.

Experimental Part.

Phenanthraquinone.—The method used in this oxidation is a modification of the one used by Anschutz and Schultz.¹ One hundred g. of "commercial phenanthrene," supposedly 80% pure, was ground to a very fine powder. This was added with constant stirring to an oxidizing solution, contained in a 12-inch evaporating dish, consisting of 1500 cc. of water, 500 cc. of 96% sulfuric acid and 300 g. of potassium dichromate. When the first brisk reaction had ceased an additional 300 g. of dichromate was added. After being slowly heated to the boiling point the solution was cooled and an equal volume of water added. After standing a few hours the mixture was filtered through glass wool (or asbestos) in a Büchner funnel. The yellow precipitate was washed until the wash water came through colorless. The product was suspended in 500 cc. of conc. sulfuric acid for 12 hours in order to remove resins and other acid-soluble impurities. A liter of water was then added in order to decrease the solubility of the phenanthraquinone,² the solution heated to boiling and filtered as before. After thoroughly washing the precipitate with water it was washed with a liter of saturated sodium carbonate solution to re-

¹ Anschutz and Schultz, *Ann.*, 196, 37 (1878).

² *J. Chem. Soc.*, 115, 850 (1919)

move the diphenic acid and resins, and then with ether to remove the unoxidized hydrocarbons. In order to separate the phenanthraquinone from the anthraquinone the product was placed in 2 liters of hot saturated sodium hydrogen sulfite solution and the whole heated to boiling. The undissolved anthraquinone was filtered off and the filtrate was acidified by adding it to an equal volume of a dilute solution of sulfuric acid containing about 50 g. of dichromate per liter. The finely divided, yellow phenanthraquinone so obtained was filtered off and washed thoroughly. The results of 3 characteristic experiments are given below.

	I. G.	II. G.	III. G.
Anthraquinone.....	31.2	30.1	34.7
Hydrocarbons.....	7.8	2.6	3.2
Diphenic acid and resins.....	1.0	1.3	2.0
Phenanthraquinone.....	45.5	46.1	47.5
Yield of phenanthraquinone.....	53.1%	53.1%	50.2%

In calculating the yields of phenanthraquinone the weight of anthracene corresponding to the amount of anthraquinone obtained is subtracted from the weight of crude hydrocarbons used. The melting point of the phenanthraquinone was 203° (205°).

Diphenic Acid.—The rather indefinite directions of Schmitz¹ as interpreted by us gave only about 20% yields of the acid. By a modified method diphenic acid melting at 228° (227°) was obtained in 53% yield. Fifty g. of phenanthraquinone, 200 g. of potassium dichromate, 300 g. of sulfuric acid and 500 cc. of water were mixed, kept at 100° and stirred frequently for 6 hours. The mixture was then cooled, filtered, and the precipitate washed with water. The diphenic acid was separated from the unchanged quinone by extraction with a liter of a saturated solution of sodium carbonate. The diphenic acid was then obtained by precipitation with hydrochloric acid.

Diphenic Anhydride.—The method of Traube and Aubin² was used. A mixture of 25 g. of diphenic acid and 75 cc. of acetic anhydride was heated at 120° for an hour under a reflux condenser. Traube and Aubin recommend only half this amount of acetic anhydride. On cooling, the diphenic anhydride crystallized in colorless needles. The acetic anhydride was removed by washing the crystals with acetic acid. The yield was 20.8 g., or 92.3%; m. p. 212°.

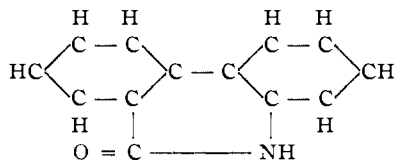
Diphenamic Acid.—The method of Traube and Aubin³ was used. Twenty g. of diphenic anhydride and 40 cc. of ammonium hydroxide (sp. gr. 0.90) were boiled under a reflux condenser for half an hour. The diphenamic acid was precipitated from this solution in white crystals by the addition of hydrochloric acid. The yield was 97%; m. p. 190°.

¹ Schmitz, *Ann.*, **193**, 116 (1878).

² Traube and Aubin, *ibid.*, **247**, 263 (1888).

³ *Loc. cit.*, p. 269.

9(10)-Phenanthridone.—Twenty-five g. of diphenamic acid (0.1 mol) was dissolved in 100 cc. of 10% sodium hydroxide solution, and to it was added, slowly but immediately, 5.1 cc. (0.1 mol) of bromine dissolved in 140 cc. of 10% sodium hydroxide solution. After the mixture had stood for a half hour, 5 cc. of a concentrated solution of sodium hydrogen sulfite was added to reduce the excess of hypobromite. Forty cc. of 37% hydrochloric acid was added slowly and the bulky white precipitate filtered off and washed thoroughly with water. The yield was 94%. The compound melted at 291° after being recrystallized from alcohol. It is insoluble in hot or cold water, in hot or cold conc. or dil. hydrochloric acid, in alkali solutions and in ether. It is soluble in acetic acid, conc. nitric acid, hot alcohol and hot nitrobenzene. A Kjeldahl determination showed the nitrogen content to be from 7.15 to 7.23%. This agrees with the nitrogen content of 9(10)-phenanthridone (7.18%)



and is considerably higher than the nitrogen content of the amino carboxylic acid which was sought (6.57%), (1) $\text{COOH}\text{C}_6\text{H}_4 - \text{C}_6\text{H}_4.\text{NH}_2$ (10).

Attempts were made to condense the phenanthridone with α -chloro-anthraquinone, using boiling nitrobenzene as a solvent and finely divided copper in the presence of sodium carbonate or acetate as a catalyst. Two products were obtained. One of them consisted of white crystals melting at 82° and containing 11.8% nitrogen. The other was a brick-red powder which gave a red color in alkaline solution and a yellow in acid solution. This product when reduced in an alkaline solution, using zinc and calcium hydroxide, gave a beautiful red color which faded on standing and imparted no color to cotton fabrics. Work upon the purification and properties of these and other condensation products of 9(10)-phenanthridone is being continued.

Summary.

Modified methods are described for preparing phenanthraquinone, diphenic acid, diphenic anhydride and diphenamic acid. The yields obtained are given.

A method for the preparation of 9(10)-phenanthradone from diphenamic acid is described.

A compound of apparently no tinctorial value was obtained by the condensation of the phenanthridone with α -chloro-anthraquinone.