

Synthesis:

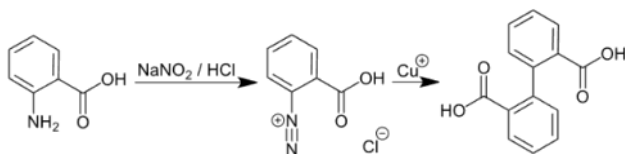
(a) Diazotization of anthranilic acid

A) Diazotization of Anthranilic Acid.—Fifty grams (0.365 mole) of anthranilic acid (m.p. 143–144°) is ground in a mortar with 150 cc. of water and 92 cc. of concentrated hydrochloric acid (sp. gr. 1.19). The suspension is transferred to a 1-l. round-bottomed flask which is equipped with a mechanical stirrer. The flask is surrounded by an ice bath. When the contents have cooled to 0–5°, a solution of 26.3 g. (0.38 mole) of sodium nitrite in 350 cc. of water is added from a dropping funnel during thirty minutes. The resulting diazonium solution is kept at a temperature below 5° and, unless it is entirely clear, is filtered by suction through a chilled Büchner funnel immediately before use.

(B) Preparation of the Reducing Agent.—One hundred and twenty-six grams (0.505 mole) of hydrated cupric sulfate is dissolved in 500 cc. of water in a 2-l. beaker and 210 cc. of concentrated ammonium hydroxide (sp. gr. 0.90) is added. The solution is then cooled to 10°. A solution of 42 g. (0.256 mole) of commercial hydroxylammonium sulfate (Note 1) in 120 cc. of water is prepared and cooled to 10°; to this latter solution there is added 85 cc. of 6 N sodium hydroxide solution, and the resulting solution of hydroxylamine is then filtered by suction if not clear. The hydroxylamine solution is immediately added to the ammoniacal cupric sulfate solution with hand stirring. Reduction occurs at once; a gas is evolved during the process, and the solution becomes pale blue in color. If this solution is not to be used at once it should be protected from the air.

(C) Synthesis of Diphenic Acid.—The reducing solution in the 2-l. beaker is surrounded by an ice bath so that the temperature of the solution is kept at about 10°. The beaker is fitted with a mechanical stirrer. The stem of a 100-cc. cylindrical dropping funnel is fitted with a glass tube which dips well below the surface of the solution and is bent upward at the end and constricted so that the opening is about 2 mm. (Note 2). An 80- to 90-cc. portion of the diazonium solution is placed in the dropping funnel and added at the rate of about 10 cc. per minute (Note 3). The remainder of the diazonium solution is added at the same rate and stirring is continued for five minutes longer. The solution is then rapidly heated to boiling and carefully acidified with 250 cc. of concentrated hydrochloric acid (Note 4). Diphenic acid precipitates as light brown crystals. After the solution has stood overnight the solid is removed by filtration and washed free of mother liquor while on the filter with about 50 cc. of cold water. When dried, the product melts at 222–227° (corr.) and weighs 39–40 g. (88–91 per cent of the theoretical amount).

The crude product is suspended in 200 cc. of water, and 40 g. of solid sodium bicarbonate is added. The resulting solution is filtered by gravity, then boiled with 0.1 g. of Norite. The mixture is filtered and the yellowish-brown filtrate is acidified while still hot with an excess of 6 N hydrochloric acid. The DOI:10.15227/orgsyn.007.0030precipitated diphenic acid is collected on a filter and washed with 40 cc. of cold water. When dried at 100° the product melts at 225–228° and weighs 32–37 g. **(72–84 per cent of the theoretical amount).**
It is a light cream color



(b) Oxidation of phenanthrene

A. MATERIALS

Commercial phenanthrene, which was obtained by a local market, 30% H₂O₂ (A.R) and glacial acetic acid (A.R) were used for oxidation of phenanthrene to 2,2'-diphenic acid

1) Oxidation of Phenanthrene

Oxidation

In a four-necked flask, which provided with a stirrer, thermometer, fractional column and dropping funnel, phenanthrene, glacial acetic acid and benzene were

proportionally introduced, and the mixture was heated to boil. Then 30% H₂O₂ was gradually added drop by drop for 3h~12h. The water was continuously distilled off in the form of the azeotropic mixture with benzene during the reactions. The conversion of phenanthrene by oxidation into diphenic acid

Recovery of phenanthrene, acetic acid and solvent

After the reaction was completed, acetic acid and the solvent benzene, which could be repeatedly used for making 2,2'-diphenic acid, distilled off under reduced pressure. Then 10% of sodium hydroxide was added in the residue. The undissolved materials, which contained

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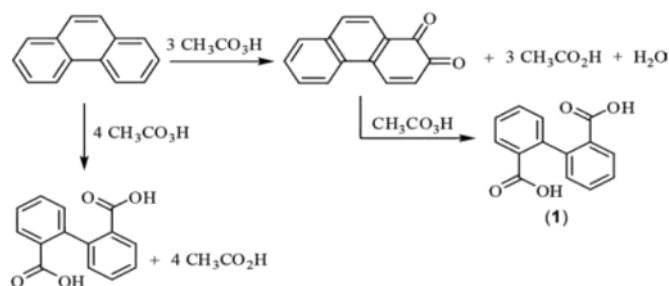
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mainly un-reacted phenanthrene and could be used again for oxidation of phenanthrene, were separated by filtration, whereas diphenic acid as a salt, which was formed by reaction of diphenic acid with sodium hydroxide, was dissolved in the filtrate.

Separation of diphenic acid

Finally, the filtrate was acidified with concentrated hydrochloric acid, diphenic acid precipitated in crystalline form and the diphenic acid was obtained by filtration. Neutralization by adding base and acidifying by adding acid was repeated several times till the products of purer diphenic acid were obtained



Through repeated experiments under the optimum conditions, the **yields** of diphenic acid could reach 60~67%, the **purity** of diphenic acid prepared was 96~98%, and the melting point of the products was 232 ~ 233°C.