Organic
Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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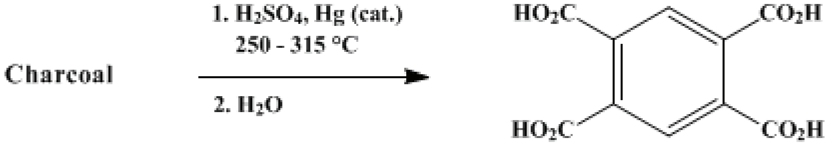
PYROMELLITIC ACID



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1. Procedure

In a 5-l. round-bottomed flask, set on a wire gauze in a hood and provided with a thermometer, are placed 100 g. of finely powdered pine or spruce charcoal (Note 1), 650 cc. of 82–88 per cent sulfuric acid (sp. gr. 1.76–1.80) (Note 2), and a small drop of mercury (Note 3). The mixture is heated with a small flame so that the temperature is raised to 250° during four hours. During another half hour the temperature is raised to 290°, when the acid begins to volatilize and the reaction mixture froths and expands greatly (Note 4). During the next hour the temperature is raised to 300°, and during the following hour to 315°. The mixture thickens somewhat, then much bubbling and spurting take place and fine white needles of pyromellitic anhydride begin to collect in the neck of the flask (Note 5). Fifty cubic centimeters of sulfuric acid is now added—the acid being poured in so as to rinse the walls of the flask; the syrupy reaction mixture is again heated to 250° for a few minutes and is transferred while still hot to a 1-l. tubulated retort (Note 6). The flask is rinsed with the minimum amount of water and the washings are added to the retort.

The material in the retort is heated with a free flame until the water present has distilled, then 30 g. of acid potassium sulfate is added and the distillation is continued. At first almost colorless sulfuric acid distils. As soon as crystals of pyromellitic anhydride appear, the receiver is replaced by one containing 50 cc. of water and the distillation is continued until nothing more passes over. The retort is then rinsed with 100 cc. of water and the rinsings are filtered and evaporated on the steam bath to 25 cc. (Note 7). The last distillate is also evaporated to 25 cc. On cooling, pyromellitic acid crystallizes. The product from both portions is collected on a suction funnel, using hardened filter paper, washed with two 10-cc. portions of ice water (Note 8), and recrystallized from four parts of boiling water. After drying at 105° the product (containing 2 moles of water of crystallization) melts at 271° (262° uncorr.). The yield is 6–8 g. (Note 9).

2. Notes

1. The yield of pyromellitic acid depends considerably on the kind of charcoal used. An experiment with ordinary willow charcoal gave none of the desired product.
2. The specific gravity of the acid used should not vary from the limits indicated.
3. A series of experiments has proved the helpful action of mercuric sulfate.
4. If the time for the first stage (temperature below 250°) is shortened, the frothing is greater at this point, and the final yield is lowered.
5. The end of the reaction can be readily detected by the bubbling and spurting which take the place of the quiet boiling. If the mixture is not fairly thick, less sulfuric acid should be used in the next run. If it is solid, more acid should be used.
6. The transfer to the retort must be made before the mixture solidifies. The best method of closing the tubulure of the retort (unless this consists of Pyrex glass) is by means of a glass stopper too small for the hole and wrapped with asbestos paper moistened with sodium silicate solution.
7. If much pyromellitic anhydride collects in the neck of the retort, it should be rinsed into a clean dish rather than into the receiver for the receiver contains considerable sulfuric acid.
8. In recovering pyromellitic acid from the mother liquor it is advisable first to remove the sulfuric acid by adding a slight excess of barium hydroxide and acidifying to Congo red with hydrochloric acid.

9. The anhydride of pyromellitic acid may be obtained by boiling the dry anhydrous acid with acetic anhydride.

3. Discussion

Pyromellitic acid may be obtained by the oxidation of benzene derivatives containing organic substituents in the 1-, 2-, 4-, and 5-positions: by the oxidation of durene with nitric acid;[1] by condensing benzene with diethylmalonyl chloride, reducing to the hydrocarbon, again condensing in the same way, and finally oxidizing the resulting tetraethylbenzodihydrindenedione; [2] by an analogous synthesis from *m*-xylene, involving condensation with acetyl chloride, reduction, and oxidation;[3] and by the oxidation of tetrahydro-5,6-benzindan-1-one.[4]

Mellitic acid can be decarboxylated to yield pyromellitic acid, either by the action of heat alone[5] or in the presence of sulfuric acid.[6]

The oxidation of wood charcoal by means of sulfuric acid leads to mellitic acid and its decarboxylation products;[7] nitric acid may also be employed.[8] Pyromellitic acid has also been obtained by the electrolytic oxidation of graphite in an alkaline medium.[9]

References and Notes

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4. Darzens and Levy, Compt. rend. **201**, 904 (1935).
5. Erdmann, Ann. **80**, 281 (1851); Baeyer, Ann. Suppl. **7**, 36 (1870).
6. Erdmann, Ann. **80**, 282 (1851); Silberrad, J. Chem. Soc. **89**, 1795 (1906).
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8. Silberrad, Ger. pat. 214,252 [Frdl. **9**, 173 (1908–10)]; Philippi and Rie, Ann. **428**, 287 (1922).
9. Bartoli and Papasogli, Gazz. chim. ital. **12**, 113 (1882); **13**, 37 (1883).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Congo red

tetraethylbenzodihydrindenedione

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

acetic anhydride (108-24-7)

acetyl chloride (75-36-5)

sodium silicate

nitric acid (7697-37-2)

mercury (7439-97-6)

barium hydroxide (17194-00-2)

mercuric sulfate (7783-35-9)

Durene (95-93-2)

Pyromellitic acid (89-05-4)

pyromellitic anhydride (89-32-7)

diethylmalonyl chloride (54505-72-5)

tetrahydro-5,6-benzindan-1-one

Mellitic acid (517-60-2)

m-xylene (108-38-3)