



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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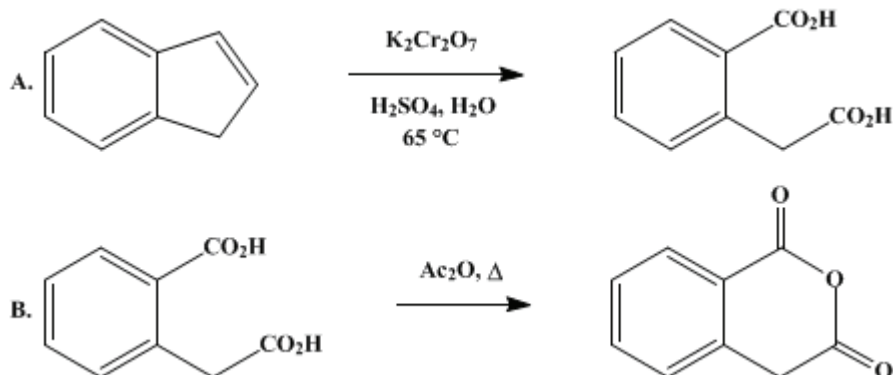
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.449 (1955); Vol. 29, p.49 (1949).

HOMOPHTHALIC ACID AND ANHYDRIDE

[Phenylacetic acid, *o*-carboxy-, and 1,3-Isochromandione]



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1. Procedure

A. *Homophthalic acid.* A solution of 243 g. (0.83 mole) of technical potassium dichromate in 3.6 l. of water and 1330 g. (725 ml., 13 moles) of concentrated sulfuric acid is prepared in a 5-l. three-necked flask fitted with a sealed mechanical stirrer, a thermometer, a 100-ml. dropping funnel, and a reflux condenser. The mixture is warmed to 65°, and 72 g. (72 ml., 0.56 mole) of technical 90% indene (Note 1) is added dropwise from the dropping funnel. The temperature must be kept at 65 ± 2°, and cooling by a water bath is necessary during the addition. After the addition is complete the mixture is stirred for 2 hours at 65 ± 2° (Note 2). At the end of this period the mixture is cooled with stirring to 20–25° and then further cooled in an ice-salt bath for 5 hours at 0°. The homophthalic acid which separates is collected on a 10-cm. Büchner funnel with the aid of suction, then washed with two 75-ml. portions of ice-cold 1% sulfuric acid and once with 75 ml. of ice water (Note 3). The precipitate is then dissolved in 215 ml. of 10% sodium hydroxide solution, and the resulting solution is extracted with two 50-ml. portions of benzene (Note 4), which are discarded. The aqueous solution is added to 160 ml. of 33% sulfuric acid with vigorous stirring, and the mixture is chilled in an ice-salt bath for 2–3 hours. The homophthalic acid is collected on a 10-cm. Büchner funnel with the aid of suction, washed with three 25-ml. portions of ice water, and pressed and sucked as dry as possible. The acid is transferred to a 500-ml. distilling flask, 300 ml. of benzene is added, and the mixture is distilled from a steam bath until about 250 ml. of distillate (benzene and water) has been collected (Note 5). The slurry of acid and benzene is filtered with the aid of suction through a 10-cm. Büchner funnel, and the product is spread out on a porous plate to allow the last traces of benzene to evaporate. The yield of white crystals of homophthalic acid, melting at 180–181° (Note 6), amounts to 67–77 g. (66–77% calculated on the basis of 90% indene content of the commercial indene) (Note 7).

B. *Homophthalic anhydride.* A mixture of 60 g. (0.33 mole) of dry homophthalic acid and 33.7 g. (31 ml., 0.33 mole) of acetic anhydride in a 200-ml. round-bottomed flask fitted to a reflux condenser by a ground-glass joint is refluxed for 2 hours. The mixture is cooled to about 10° for 30 minutes, and the solid anhydride is collected on a Büchner funnel with the aid of suction. It is washed with 10 ml. of glacial acetic acid and pressed, and as much of the solvent as possible is removed by suction. The product is spread out on a porous plate for several hours (Note 8); it amounts to 46–47.5 g (85–88%) of white crystals melting at 140–141° (Note 9).

2. Notes

1. Indene of approximately 90% purity may be obtained from the Koppers Company, Pittsburgh,

Pennsylvania, or United Gas Improvement Company, Philadelphia, Pennsylvania. The practical grade of the same purity from the Eastman Kodak Company may also be used. If the material is dark colored, it should be redistilled and the fraction boiling from 180° to 182° should be used.

2. It is important to control the temperature of this oxidation. If the oxidation is carried out at the reflux temperature, the yield of purified acid drops to about 52–54%.

3. **Homophthalic acid** possesses an appreciable solubility in water (about 1.6 g. per 100 ml. at 20°); hence it is necessary to cool the solutions and wash liquids to obtain good yields.

4. This extraction removes about 7–8 g. of oily alkali-insoluble products.

5. This azeotropic distillation is the quickest method for drying **homophthalic acid**. The acid turns dark colored if dried in an oven at 110°. It may be dried over anhydrous **calcium chloride** in a vacuum desiccator for 24–36 hours; it melts at 180–181°.

6. The melting point depends on the rate of heating. When the melting-point tube was placed in the bath preheated to 170°, the acid melted at 180–181°. When the heating was started at room temperature, the observed melting point was 172–174°.

7. If **phthalide** is available, an alternative procedure via *o*-carboxyphenylacetonitrile may be preferred for the preparation of **homophthalic acid** [*Org. Syntheses*, **22**, 61 (1942)].

8. Drying in an oven causes some loss because the anhydride sublimes.

9. If all the **acetic acid** is not removed the product melts lower, *ca.* 138–139°.

3. Discussion

Homophthalic acid has been prepared from **naphthalene**¹ or **tetralin**² via phthalonic acid; by hydrolysis of *o*-cyanobenzylcyanide;³ by oxidation of **β -indanone** with alkaline **permanganate** solution;⁴ from **α -indanone** by **chromic acid** oxidation,⁵ by nitrosation, Beckmann rearrangement, and hydrolysis,⁶ or by nitrosation, hydrolysis, and **hydrogen peroxide** oxidation;⁷ from *o*-toluic acid by bromination of the acid chloride followed by treatment with **ethanol** and **sodium cyanide** and hydrolysis with 50% **sulfuric acid**;⁸ from **indene** by oxidation with chromic and sulfuric acid;⁹ and from *o*-acetylbenzoic acid by Willgerodt reaction with **morpholine** and **sulfur** followed by hydrolysis of the dimorpholide.¹⁰ The oxidation of **indene** by alkaline **permanganate** produces **homophthalic acid**¹¹ and **phthalic acid**;¹² oxidation with **chromic acid** leads to a purer product.¹³ The hydrolysis of *o*-carboxyphenylacetonitrile yields **homophthalic acid**.¹⁴

The procedure described here is a modification of that described by Meyer and Vittenet⁹ and Whitmore and Cooney.¹⁵

Homophthalic anhydride has been obtained by heating the acid alone,¹ and by refluxing with **acetyl chloride**¹⁴ or with **acetic anhydride**.¹⁶

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 5*, 612

References and Notes

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

phthalonic acid

HOMOPHTHALIC ACID AND ANHYDRIDE

chromic and sulfuric acid

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

acetic anhydride (108-24-7)

sodium hydroxide (1310-73-2)

acetyl chloride (75-36-5)

sodium cyanide (143-33-9)

sulfur (7704-34-9)

chromic acid (7738-94-5)

Naphthalene (91-20-3)

hydrogen peroxide (7722-84-1)

permanganate

potassium dichromate (7778-50-9)

phthalic acid (88-99-3)

Tetralin (119-64-2)

α -indanone (83-33-0)

indene (95-13-6)

Phthalide (87-41-2)

Homophthalic acid,
Phenylacetic acid, o-carboxy- (89-51-0)

1,3-Isochromandione,
Homophthalic anhydride (703-59-3)

β -indanone (615-13-4)

morpholine (110-91-8)

o-Toluic acid (118-90-1)

o-CARBOXYPHENYLACETONITRILE (6627-91-4)

o-cyanobenzylcyanide (3759-28-2)

o-acetylbenzoic acid (577-56-0)