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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 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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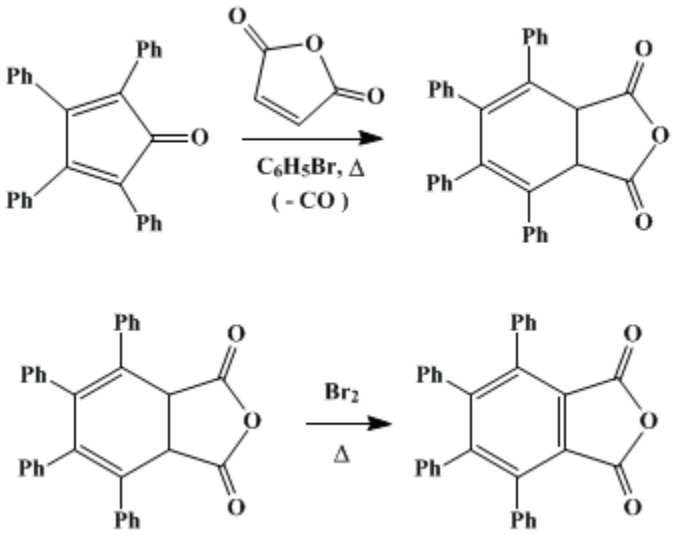
TETRAPHENYLPHTHALIC ANHYDRIDE

[Phthalic anhydride, tetraphenyl-]



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1. Procedure

An intimate mixture of 35 g. (0.094 mole) of tetraphenylcyclopentadienone (p. 806) and 9.3 g. (0.095 mole) of maleic anhydride is placed in a 200-ml. round-bottomed flask (Note 1), and to it is added 25 ml. of bromobenzene. After the mixture has been refluxed gently for 3.5 hours (Note 2), it is cooled (Note 3), a solution of 7 ml. of bromine in 10 ml. of bromobenzene is added through the condenser, and the flask is shaken until the reagents are thoroughly mixed. After the first exothermic reaction has subsided, the mixture is refluxed gently for 3 hours (Note 4). The flask is then immersed in a cooling bath and the temperature of the mixture is held at 0–10° for 2–3 hours. The mixture is filtered with suction, and the crystalline product is washed three times with 10-ml. portions of petroleum ether (b.p. 60–68°). After the product has been dried in the air, it weighs 37–38 g. (87–89%) and melts at 289–290°. It is light brown, but when pulverized it is almost colorless. The filtrate, when diluted with an equal volume of petroleum ether and cooled to 0–10°, yields an additional 2–3 g. of a less pure product which melts at 285–288°. The impure material may be purified by recrystallization from benzene, using 8–9 ml. of benzene per gram of solid (Note 5).

2. Notes

1. Ground-glass equipment is preferred; corks are attacked by the bromine used later.
2. The operation should be carried out in a hood because of the carbon monoxide evolved.
3. The tetraphenyldihydrophthalic anhydride may be isolated at this point in practically quantitative yields by cooling the mixture, filtering with suction, and washing the solid with three 10-ml. portions of petroleum ether (b.p. 60–68°). The yield is 41–42 g.; the product melts at 235–240°.
4. This operation should also be performed in a hood, or the top of the condenser should be connected to a suitable trap.
5. The crystallized product must be dried at 110° for 1–1.5 hours; otherwise benzene, possibly benzene of crystallization, will be retained by the solid indefinitely.

3. Discussion

Tetraphenylphthalic anhydride has been prepared by condensation of tetraphenylcyclopentadienone and maleic anhydride in nitrobenzene,[1] followed by dehydrogenation of the tetraphenyldihydrophthalic anhydride with sulfur.[2,3]

Tetraphenylphthalic anhydride has also been prepared by condensation of tetraphenylcyclopentadienone with chloromaleic anhydride;[4] and by oxidation of tetraphenylhydrindene with chromic acid[5] or oxidation of 7-carboxy-4,5,6,7-tetraphenyl-3*a*,4,7,7*a*-tetrahydroindene with potassium permanganate.[6]

References and Notes

1. Dilthey, Schommer, and Trosken, *Ber.*, **66**, 1627 (1933).
2. Dilthey, Thewalt, and Trosken, *Ber.*, **67**, 1959 (1934).
3. Allen and Sheps, *Can. J. Research*, **11**, 171 (1934).
4. Synerholm, *J. Am. Chem. Soc.*, **67**, 1229 (1945).
5. Grummitt, Klopper, and Blenkhorn, *J. Am. Chem. Soc.*, **64**, 604 (1942).
6. Allen, Jones, and VanAllan, *J. Am. Chem. Soc.*, **68**, 708 (1946).

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

petroleum ether

Benzene (71-43-2)

carbon monoxide (630-08-0)

potassium permanganate (7722-64-7)

bromine (7726-95-6)

sulfur (7704-34-9)

chromic acid (7738-94-5)

Nitrobenzene (98-95-3)

bromobenzene (108-86-1)

maleic anhydride (108-31-6)

Tetraphenylcyclopentadienone (479-33-4)

Tetraphenylphthalic anhydride,
Phthalic anhydride, tetraphenyl- (4741-53-1)

tetraphenyldihydrophthalic anhydride

chloromaleic anhydride

tetraphenylhydrindene

7-carboxy-4,5,6,7-tetraphenyl-3a,4,7,7a-tetrahydroindene