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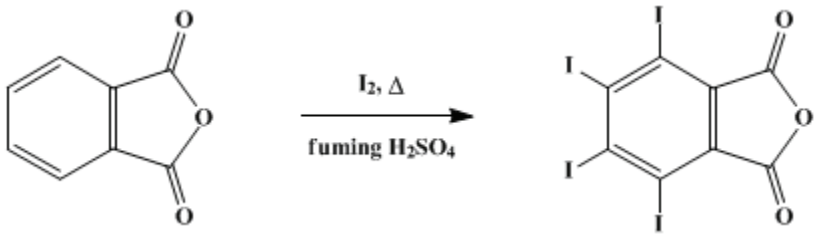
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.027.0078

Organic Syntheses, Coll. Vol. 3, p.796 (1955); Vol. 27, p.78 (1947).

TETRAIODOPHTHALIC ANHYDRIDE

[Phthalic anhydride, tetraiodo-]



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1. Procedure

In a 3-l. three-necked flask with ground-glass joints are placed 148 g. (1.0 mole) of phthalic anhydride, 324 g. (60% of the total of 2.12 moles to be added) of iodine, and 600 ml. of 60% fuming sulfuric acid. The flask, fitted with an air condenser 90–100 cm. in length (Note 1), is arranged for heating by a water bath. A tube leads from the condenser to a gas trap.

The temperature of the water bath is raised cautiously to 45–50°, at which point the reaction begins (Note 2). Heating is continued until visible reaction has almost completely stopped. During this time (Note 3), the temperature has been raised gradually to 65°. The flask is then cooled by flooding the bath with ice water, and a second portion, 162 g. (30% of the total), of iodine is added. The flask is heated again at 65° until the reaction ceases. After cooling as before, the last portion, 54 g. (10% of the total), of iodine is added.

When reaction at 65° has ceased and the flask has been cooled, the condenser is removed, and the flask is arranged for heating on an oil bath in a well-ventilated area (Note 4). The temperature of the bath is raised to 175° and maintained at 170–180° until the evolution of sulfur trioxide and iodine fumes has slowed considerably (about 2 hours at 170°). The flask is allowed to cool to about 60° before the contents are poured into a beaker, which is allowed to stand overnight at room temperature.

The solid is filtered by suction on a glass filter cloth and is washed with two 100-ml. portions of concentrated sulfuric acid and then with three 200-ml. portions of water (Note 5). The light-yellow crystalline material is then transferred to a 3-l. beaker where it is stirred for 30 minutes with a solution of 20 g. of sodium bisulfite in 1.5 l. of water to remove the last traces of iodine. The heavy solid is allowed to settle to the bottom of the beaker, and the bisulfite solution is poured off. The crystals are washed with three 1-l. portions of water, each portion being decanted as before (Note 6), and then are transferred to a funnel. The product is washed with an additional 1-l. portion of water and two 200-ml. portions of acetone and dried in an oven at 60°. The product amounts to 520–535 g. (80–82% based on the phthalic anhydride) (Note 7) and (Note 8) and melts at 327–328° (Note 9).

2. Notes

1. A water-cooled condenser maintained at 20–25° may be used.
2. Temporary cooling by cold water may be necessary to keep the reaction in check. It must be closely watched at this stage.
3. The lengths of the periods of heating are approximately 5, 3, and 1 hour, respectively. In a run of one-half the size described, the checkers found the periods required to be about 4, 1.5, and 1 hour, respectively.
4. This operation is carried on most conveniently out-of-doors. For the 0.5-mole run, the checkers fitted the flask to the gas trap with a U-tube of 2-cm. bore, having a ground-glass joint for the connection to

the flask. The large-diameter tube permitted the operation to be carried out in a hood with no danger of clogging of the apparatus by sublimed iodine.
5. This method of working up the product is superior to the usual one of pouring on ice in that a purer material is obtained and a difficult recrystallization is thus avoided.
6. Some impurities tend to float and are removed with the wash water.
7. It was observed that sunlight or illumination by a Photoflood lamp tended to make the reaction more vigorous but did not produce any significant increase in yield.
8. Yields of the same order were obtained starting with 0.5, 1.0, and 10.0 moles of phthalic anhydride. In the runs with 10.0 moles of phthalic anhydride, a greater excess of iodine was found necessary; i.e., the weights of iodine added were 3240 g., 1620 g., 540 g., 500 g., 300 g. The lengths of the heating periods were approximately 72, 48, 24, 24, and 12 hours, respectively.
9. The melting point may vary from 325° to 332° but usually falls within a 2° range. No suitable solvent for recrystallization has been found. The recrystallized product always has a lower melting point than the original material.

3. Discussion

The method given is the only satisfactory one so far reported.[1,2,3,4,5]

References and Notes

1. Juvalta, Ger. pat. 50,177 [*Frdl.*, **2**, 94 (1887–1890)].
2. Rupp, *Ber.*, **29**, 1634 (1896).
3. Pratt and Shupp, *J. Am. Chem. Soc.*, **40**, 254 (1918).
4. Perkins and Quimba, *Am. J. Pharm.*, **106**, 467 (1934).
5. Twiss and Heinzelmann, *J. Org. Chem.*, **15**, 496 (1950).

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

sulfuric acid (7664-93-9)

sulfur trioxide (7446-11-9)

sodium bisulfite (7631-90-5)

phthalic anhydride (85-44-9)

iodine (7553-56-2)

acetone (67-64-1)

Tetraiodophthalic anhydride,
Phthalic anhydride, tetraiodo- (632-80-4)