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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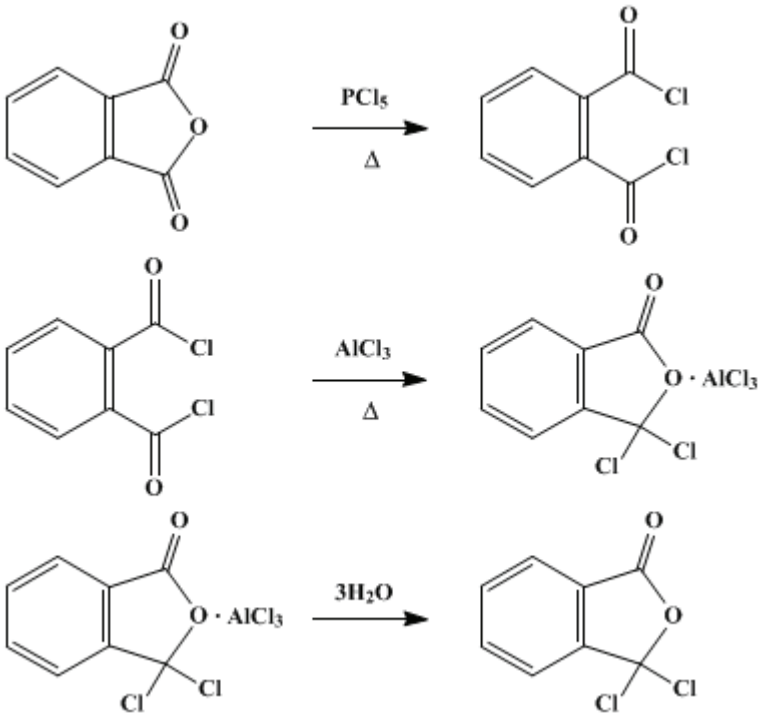
SYMMETRICAL AND UNSYMMETRICAL *o*-PHTHALYL CHLORIDES



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1. Procedure

(*A*) *Symmetrical o-Phthalyl Chloride*.—A mixture of 148 g. (1 mole) of phthalic anhydride (Note 1) and 220 g. (1.06 moles) of phosphorus pentachloride (Note 2) is placed in a 500-cc. Claisen flask. The flask is equipped with a reflux condenser, the upper end of which is provided with a calcium chloride tube, and the side arm of the flask is closed with a cork. The flask is inclined slightly so that any phosphorus oxychloride which collects in the stoppered side arm will run back into the flask. After heating in an oil bath at 150° for twelve hours, the air condenser and the stopper in the end of the side arm are removed, and the flask is connected to a water-cooled condenser. The temperature is then raised gradually to 250°, during which time most of the phosphorus oxychloride distils into a receiver. The liquid residue is distilled under reduced pressure; at first a small quantity of phosphorus oxychloride distils, and then the *sym. o*-phthalyl chloride distils at 131–133°/9–10 mm. The product thus obtained contains a small amount of phthalic anhydride; it solidifies on cooling in an ice-salt mixture and melts at 11–12° (Note 3). The yield is 187 g. (92 per cent of the theoretical amount).

(*B*) *Unsymmetrical o-Phthalyl Chloride*.—A mixture of 105 g. of the symmetrical *o*-phthalyl chloride and 75 g. of finely ground aluminum chloride (Note 4) is heated on a steam bath for eight to ten hours, with exclusion of moisture. The mixture should be stirred frequently until all the powder has dissolved. Upon cooling there is formed a hard mass which is broken into small pieces while still warm. When thoroughly cool, it is triturated with pieces of ice in a mortar, working with small amounts at a time. The white sediment which results is collected on a Büchner funnel and dissolved immediately in about 300 cc. of warm benzene (40–50°). The benzene solution is separated from the small aqueous layer, dried over calcium chloride for eight hours, and filtered. The benzene is distilled under reduced pressure by heating in a water bath at 30–40°. The crystalline residue is extracted in a Soxhlet apparatus with petroleum ether (b.p. 20–40°) until the residue in the thimble consists of practically pure phthalic

anhydride (Note 5). The petroleum ether is distilled from the extract, and the crude unsymmetrical phthalyl chloride is purified by fractional crystallization from petroleum ether (b.p. 20–50°). The purified chloride melts at 87–89°. The melting point is not sharp because the unsymmetrical compound begins to revert to the symmetrical isomer. The yield of pure unsymmetrical phthalyl chloride is about 76 g. (72 per cent of the theoretical amount) and is dependent on the quality of the aluminum chloride used.

2. Notes

1. A good grade of sublimed phthalic anhydride should be used (m.p. 128–129°). If this cannot be obtained the ordinary phthalic anhydride can be purified by sublimation.
2. The phosphorus pentachloride should be freed of any phosphorus trichloride or oxychloride present. This may be done by placing the pentachloride in a flask connected to an ice-cooled receiver and heating on a water bath. The pressure in the apparatus is reduced as much as possible by means of a water pump. A calcium chloride tube should be inserted between the pump and the receiver.
3. Pure symmetrical *o*-phthalyl chloride cannot be obtained, even by recrystallization from carbon tetrachloride. A product melting at 16° may be obtained by distilling the unsymmetrical phthalyl chloride at atmospheric pressure.
4. A good quality of aluminum chloride must be used. If this is not available, it may be prepared by heating dried aluminum granules in a current of pure, dry hydrogen chloride. The gas is dried thoroughly by passing it through a tube containing phosphorus pentoxide spread on glass wool. Access of moisture to the aluminum chloride while weighing and pulverizing should be avoided as far as possible.
5. The extraction requires from eight to ten hours. The residue should be practically pure phthalic anhydride (m.p. 126°).

3. Discussion

Symmetrical *o*-phthalyl chloride has been prepared by heating phthalic anhydride with phosphorus pentachloride,[1] thionyl chloride, or benzotrichloride. With the last two reagents a small amount of zinc chloride is used as a catalyst.[2]

Attempts have been made to prepare pure symmetrical *o*-phthalyl chloride by repeatedly heating the crude chloride, still containing phthalic acid, with small amounts of phosphorus pentachloride.[3]

Conversion of the symmetrical chloride into the unsymmetrical isomer can also be effected by heating with tin tetrachloride.[4] The yield, however, is not satisfactory.

References and Notes

1. Claus and Hoch, Ber. **19**, 1187 (1886).
2. Kyrides, J. Am. Chem. Soc. **59**, 206 (1937).
3. Brühl, Ann. **235**, 13 (1886).
4. Csányi, Ber. **52**, 1792 (1919).

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

unsymmetrical phthalyl chloride

o-PHTHALYL CHLORIDES

SYMMETRICAL AND UNSYMMETRICAL o-PHTHALYL CHLORIDES

Symmetrical o-Phthalyl Chloride

sym. o-phthalyl chloride

Unsymmetrical o-Phthalyl Chloride

calcium chloride (10043-52-4)

hydrogen chloride (7647-01-0)

Benzene (71-43-2)

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

carbon tetrachloride (56-23-5)

aluminum (7429-90-5)

phthalic anhydride (85-44-9)

Phosphorus Oxychloride (21295-50-1)

aluminum chloride (3495-54-3)

benzotrichloride (98-07-7)

phosphorus trichloride (7719-12-2)

zinc chloride (7646-85-7)

phthalic acid (88-99-3)

tin tetrachloride (7646-78-8)

phosphorus pentoxide (1314-56-3)