



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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.712 (1955); Vol. 25, p.87 (1945).

***p*-PHENYLAZOBENZOYL CHLORIDE**

[Benzoyl chloride, *p*-phenylazo-]



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1. Procedure

Fifty grams (0.22 mole) of recrystallized *p*-phenylazobenzoic acid (p. 711) (Note 1) and 50 g. (0.47 mole) of anhydrous sodium carbonate (Note 2) are placed in a 1-l. flask and thoroughly mixed by shaking. To this mixture is added 250 ml. (3.5 moles) of thionyl chloride (Note 3); a reflux condenser with a drying tube is fitted to the flask, and the mixture is refluxed for 1.5 hours (Note 4). A condenser is set for distillation, and as much as possible of the thionyl chloride is distilled on a steam bath (Note 5).

The acid chloride is dissolved by refluxing with 500 ml. of 90–100° ligroin, and the hot solution is decanted from the sodium carbonate onto a fluted filter. This process is repeated with three 150-ml. portions of ligroin. The combined filtrates are concentrated to 500 ml., filtered if necessary, and cooled to 0°. The acid chloride is collected on a Büchner funnel and pressed as dry as possible. It is washed twice with 30–60° petroleum ether and stored in a vacuum desiccator over phosphorus pentoxide and paraffin shavings (Note 6). The yield of orange-red crystals melting at 94.5–95.5° is 48 g. (89%).

2. Notes

1. The checkers found that 50 g. of unrecrystallized acid gave 45 g. of acid chloride melting at 92–94°. When this was recrystallized from 90–100° petroleum ether (10 ml. per g.), 41.5 g. of orange-red crystals melting at 94.5–95.5° was obtained. The over-all yield of pure acid chloride on the basis of unrecrystallized acid is the same. The use of unrecrystallized acid has an advantage in that the volume of solvent required for recrystallization of the acid chloride is much less than for the acid.
2. The use of sodium carbonate is unusual. It is claimed that the sodium carbonate prevents decomposition and tar formation during the reaction.
3. The checkers used Eastman Kodak Company's best grade of thionyl chloride.
4. Refluxing should be carried out under a hood or in an apparatus provided with a gas trap.
5. About 170 ml. of good thionyl chloride can be recovered.
6. The acid chloride holds the petroleum ether tenaciously. About a week is required for complete removal of the petroleum ether.

3. Discussion

p-Phenylazobenzoyl chloride (azoyl chloride) has been prepared by the action of thionyl chloride on the acid.^{1,2} The method used is a modification of that of Ladenburg, Fernholz, and Wallis.²

References and Notes

1. Reich, *Biochem. J.*, **33**, 1001 (1939).
2. Ladenburg, Fernholz, and Wallis, *J. Org. Chem.*, **3**, 294 (1938).

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

ligroin

petroleum ether

azoyl chloride

thionyl chloride (7719-09-7)

sodium carbonate (497-19-8)

phosphorus pentoxide (1314-56-3)

p-Phenylazobenzoic acid (1562-93-2)

p-Phenylazobenzoyl chloride,
Benzoyl chloride, p-phenylazo- (104-24-5)