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.

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.

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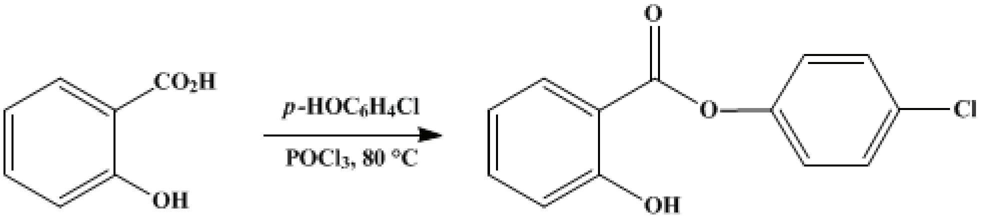
p-CHLOROPHENYL SALICYLATE

[Salicylic acid, *p*-chlorophenyl ester]



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Checked by R. T. Arnold and J. John Brezinski.

1. Procedure

To a mixture of 138.1 g. (1 mole) of salicyclic acid and 128.6 g. (1 mole) of *p*-chlorophenol in a 2-l. round-bottomed flask fitted with a thermometer reaching to the bottom of the flask and a reflux condenser with a drying tube (Note 1) is added 58.3 g. (0.38 mole) of phosphorus oxychloride. The mixture is heated with occasional swirling, and the temperature is maintained at 75–80°. At the end of 4 hours the reactants have been reduced to a molten mass, and this is poured slowly, with vigorous stirring, into a solution of 120 g. of sodium carbonate in 800 ml. of water. The precipitated ester is collected on a filter and washed with four 200-ml. portions of water. The yield of crude, air-dried, *p*-chlorophenyl salicylate is 174–189 g. (70–76%); m.p. 65–66°. Recrystallization from absolute ethanol yields 136–154 g. (55–62%) of pure product; m.p. 69.5–70.5°. A second crop may be obtained by concentration of the filtrate from the first crop or by the addition of water (Note 2).

2. Notes

1. It is advisable to attach the drying tube to a water trap[2] in order to prevent the escape of hydrogen chloride into the atmosphere.
2. The above method has been used in the preparation of other substituted phenyl salicylates to give the following yields of recrystallized products with the indicated melting points.

	Yield, (%)	M.P.
o-Chlorophenyl ester	67	52.0–52.4°
p-Nitrophenyl ester	53	151.5–151.9°
p-*tert*-Butylphenyl ester	42	63.0–63.4°
p-Phenylphenyl ester	66	109.2–109.6°
o-Phenylphenyl ester	70	89.2–89.5°

These esters, with the exception of the *p*-nitrophenyl derivative, can be recrystallized from absolute ethanol. The nitro compound is recrystallized from dioxane.

3. Discussion

Substituted phenyl salicylates can be prepared by heating salicylic acid and the appropriate phenol in the presence of phosphorus oxychloride,[3,4,5] phosphorus trichloride,[4,5] phosphorus pentachloride,[4,6] phosgene,[4] or thionyl chloride,[4] or by heating the phenol and salol.[7]

References and Notes

1. Polytechnic Institute of Brooklyn, Brooklyn, New York.
2. *Org. Syntheses Coll. Vol.* **1**, 97 (1941).
3. Seifert, *J. prakt. Chem.*, [2] **31**, 472 (1885); Nencki and Heyden, Ger. pats. 38,973 [*Ber.*, **20R**, 351 (1887)] and 43,713 [*Ber.*, **21R**, 554 (1888)]; Walther and Zipper, *J. prakt. Chem.*, [2] **91**, 399 (1915); Krauz and Remenec, *Collection Czechoslov. Chem. Communs.*, **1**, 610 (1929) [*C. A.*, **24**, 1365 (1930)]; Kolloff and Page, *J. Am. Chem. Soc.*, **60**, 948 (1938).
4. Nencki and Heyden, Ger. pat. 70,519 [*Ber.*, **26R**, 967 (1893)].
5. Harris and Christiansen, *J. Am. Pharm. Assoc.*, **24**, 553 (1935); U. S. pat. 2,141,172 [*C. A.*, **33**, 2655 (1939)].
6. Tozer and Smiles, *J. Chem. Soc.*, **1938**, 1897.
7. Cohn, *J. prakt. Chem.*, [2] **61**, 550 (1900).

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

salicyclic acid

salol

ethanol (64-17-5)

hydrogen chloride (7647-01-0)

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

sodium carbonate (497-19-8)

salicylic acid

Phosphorus Oxychloride (21295-50-1)

phosgene (75-44-5)

phosphorus trichloride (7719-12-2)

dioxane (123-91-1)

p-chlorophenol (106-48-9)

p-Chlorophenyl salicylate,
Salicylic acid, p-chlorophenyl ester (2944-58-3)

o--Chlorophenyl salicylate

p-Nitrophenyl salicylate

p-tert-Butylphenyl salicylate

p-Phenylphenyl salicylate

o-Phenylphenyl salicylate