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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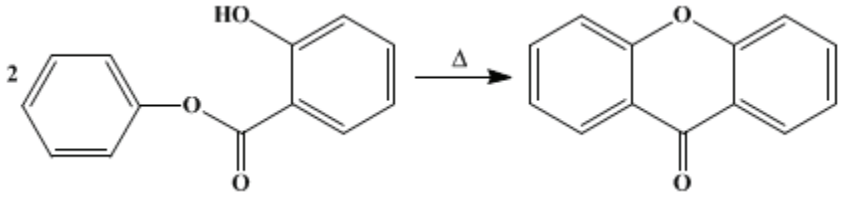
XANTHONE



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1. Procedure

Five hundred grams (2.34 moles) of phenyl salicylate is heated in a 1-l. special distilling flask having a wide (Note 1) side arm 20–25 cm. long, and fitted with two thermometers, one extending to the bottom of the flask, and the other just below the side arm. When the temperature of the liquid reaches 275–285°, phenol begins to distil. The heating is so regulated that the temperature of the vapor never exceeds 175° and preferably remains below 170° (Note 2). In this way the phenol distils at the rate of 5–10 drops per minute. The temperature of the liquid rises gradually (Note 3), and after six to seven hours reaches 350–355°. At this point the distillation of the phenol practically ceases; the weight of the distillate is 220–225 g.

The receiver is now changed, the lower thermometer is raised from the liquid (Note 4), and the contents of the flask distilled as rapidly as possible (Note 5). Heating is continued until the tarry residue begins to foam; towards the end of the distillation the color of the vapor becomes deep yellow with a greenish fluorescence. The distillate weighs 165–170 g.; it is poured while still molten into a cold dish and allowed to cool, ground in a mortar with 100 cc. of 5 per cent sodium hydroxide, and warmed on the steam bath for ten to fifteen minutes with 400 cc. of this solution. When cold, the xanthone is filtered off, washed free of alkali, and dried. A small amount of low-melting impurity is removed by boiling for ten to fifteen minutes with 250 cc. of methyl alcohol, cooling, filtering, and washing with the same solvent. A few grams can be recovered from the filtrate. The product melting at 170–172°, after softening slightly at 168–170°, weighs 141–145 g. (61–63 per cent of the theoretical amount). It is pure enough for the preparation of xanthydrol (p. 554). A purer product can be obtained by recrystallization from twenty parts of 95 per cent ethyl alcohol, from which it separates as pale yellow needles, melting at 173–174°.

2. Notes

1. The side arm should have an internal diameter of at least 10 mm. in order to minimize the danger of stoppage by solidified distillate. This danger occurs particularly when the higher-melting xanthone first begins to distil. No condenser is employed, the flask used as a receiver being cooled sufficiently by the air to condense all the vapors.
2. The regulation of temperature is difficult at first, but becomes easier after the first half-hour.
3. In consequence of this gradual rise in temperature, it is necessary to increase the size of the flame gradually.
4. Although the boiling point of xanthone is about 350°, the liquid in the flask reaches temperatures which would be dangerous to a mercury thermometer.
5. If a Pyrex flask is used, it is not only safe, but advisable, to remove the wire gauze and heat directly with the free flame. This permits the xanthone to be distilled rapidly and with a minimum loss.

3. Discussion

Xanthone can be prepared by heating phenyl salicylate[1] alone or with acetic anhydride;[2] by heating salicylic acid, phenol, and acetic anhydride;[3] and by warming *o*-phenoxybenzoic acid with concentrated

sulfuric acid[4] or phosphorus pentoxide;[5] by distilling *o*-phenoxybenzoyl chloride *in vacuo*;[6] and by heating aspirin[7] or *o*-hydroxybenzophenone.[8]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 554

References and Notes

1. Graebe, Ann. **254**, 279 (1889).
2. Perkin, Ber. **16**, 339 (1883).
3. Dhar, J. Chem. Soc. **117**, 1061 (1920).
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5. Knapp, J. prakt. Chem. **146**, 118 (1936).
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7. Spektor, Khim. Farm. Prom. **1933**, 195 [C. A. **28**, 575 (1934)].
8. Cullinane, Morgan, and Plummer, Rec. trav. chim. **56**, 631 (1937).

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

ethyl alcohol (64-17-5)

sulfuric acid (7664-93-9)

methyl alcohol (67-56-1)

acetic anhydride (108-24-7)

sodium hydroxide (1310-73-2)

phenol (108-95-2)

salicylic acid

Xanthone (90-47-1)

phenyl salicylate (118-55-8)

Xanthydrol (90-46-0)

aspirin (50-78-2)

phosphorus pentoxide (1314-56-3)

o-phenoxybenzoic acid (2243-42-7)

o-phenoxybenzoyl chloride

o-hydroxybenzophenone (117-99-7)