



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.

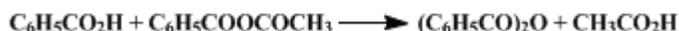
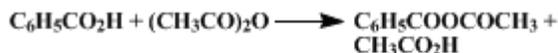
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

Organic Syntheses, Coll. Vol. 1, p.91 (1941); Vol. 3, p.21 (1923).

BENZOIC ANHYDRIDE



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1. Procedure

In a 5-l. flask, provided with a two-holed stopper fitted with a 90-cm. fractionating column¹ and a dropping funnel, are placed 1500 g. (12.3 moles) of **benzoic acid**, 1500 g. (1390 cc., 14.7 moles) of **acetic anhydride** (or an equivalent quantity of 95 per cent **acetic anhydride**), and 1 cc. of sirupy **phosphoric acid**. The mixture is very slowly distilled, at such a rate that the temperature of the vapor at the head of the column does not exceed 120° (**Note 1**). When 250 cc. of distillate has been collected, 250 g. of **acetic anhydride** is added, and distillation is continued. This process is again repeated, so that in all 2000 g. (1850 cc., 19.6 moles) of **acetic anhydride** has been taken. Fractionation is then continued, fractions which distil respectively below 120°, at 120–130°, and at 130–140° being collected. Heating is continued until the temperature of the reaction mixture in the flask reaches 270°.

The residue is fractionally distilled under reduced pressure, resulting in the collection of fractions which boil respectively below 165°, at 165–210°, and at 210–220°, all under 19–20 mm. pressure (**Note 2**). The lower fractions are mixed with the fraction which boils at 120–130°, and distilled as before after the addition of one drop of **phosphoric acid**, when a further quantity of material boiling at 210–222° /20 mm. is obtained. This fraction, amounting to 1100–1200 g., consists of crude **benzoic anhydride**. The lower-boiling fractions may be redistilled until they become too small to justify further work.

The fraction which boils at 120–130° under atmospheric pressure is redistilled, yielding further quantities of **acetic acid** (below 120°) and **acetic anhydride** (130–140°).

The crude **benzoic anhydride** (which is apt to supercool without crystallizing) contains a small proportion of an oily impurity which causes the product to turn yellow on standing; it is recrystallized by dissolving in **benzene** (50 cc. for each 100 g.) then adding just enough petroleum ether to cause a cloudiness (about 100 cc. is required) and chilling, when the pure anhydride separates in perfectly colorless and odorless crystals melting at 43°. The first crop amounts to about 50 per cent of the crude material taken; the mother liquors are freed of solvent by distillation on the water bath, and the residue distilled under reduced pressure, when a further quantity of pure material can be obtained by recrystallizing the distillate boiling at 210–220° /19 mm. If this process is repeated until the mother liquor becomes too small in amount to redistil satisfactorily, the yield of pure **benzoic anhydride** melting at 43° amounts to 1000–1030 g. (72–74 per cent of the theoretical amount) (**Note 3**). It is generally more convenient to distil the mother liquors only once or possibly twice, under which conditions a somewhat lower yield is obtained. The remaining mother liquors may then be mixed with a subsequent preparation.

2. Notes

1. As it is probable that the equilibria between the two acids and the three anhydrides are established in reactions of relatively low velocity, the distillation must be carried on very slowly, in spite of the catalytic action of the **phosphoric acid**. The intermediate fractions contain the mixed anhydride, detectable by its odor, which resembles that of **acetophenone**.

2. Owing to the high boiling point of the end-product, the second stage must be conducted under reduced pressure. The temperatures indicated depend, of course, upon the pressure under which the distillation is carried out, and allowances will have to be made for pressures differing materially from 20 mm.

3. Although the yield is by no means quantitative, the only reason why it should not be made nearly so by continual redistillation of the various fractions in presence of the catalyst lies in the length of time required for the process. This, however, could be avoided if a large number of runs were to be made, when the intermediate fractions could be worked over repeatedly with each subsequent batch, until practically nothing but [acetic acid](#) and [benzoic anhydride](#) remain.

3. Discussion

[Benzoic anhydride](#) can be prepared from [benzoyl chloride](#) and [benzoic acid](#);² from [benzoyl chloride](#) and [lead nitrate](#),³ or potassium pyrosulfite,⁴ or [sodium carbonate](#);⁵ from [benzotrichloride](#) and [sulfuric acid](#);⁶ from [benzoic acid](#) and [acetic anhydride](#);⁷ from [benzoic acid](#) and [phosphorus](#) in [benzene](#) solution by shaking with air or [oxygen](#);⁸ and from [diphenyldichloromethane](#) and [sodium benzoate](#).⁹ Numerous patented procedures have been described for preparing [benzoic anhydride](#) from salts of [benzoic acid](#) and inorganic acid chlorides and inorganic acid anhydrides. Some of these would be more suitable for the commercial preparation of [benzoic anhydride](#), but the procedure described is satisfactory for the laboratory.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 560](#)
- [Org. Syn. Coll. Vol. 3, 28](#)

References and Notes

1. Clarke and Rahrs, *Ind. Eng. Chem.* **15**, 349 (1923).
2. Monsanto Chemical Co., U. S. pat. 1,948,342 [*C. A.* **28**, 2730 (1934)].
3. Lachowitz, *Ber.* **17**, 1282 (1884).
4. Gazopulos, *Praktika Akad. Athenon* **6**, 154 (1931) [*C. A.* **26**, 4318 (1932)].
5. Errera, *Gazz. chim. ital.* **22** (I), 215 (1892); Deninger, *J. prakt. Chem.* (2) **50**, 479 (1894).
6. Jenssen, *Ger. pat.* 6,685 [*Frld.* **1**, 24 (1877-87)]; Payman and Hall, *Brit. pat.* 280,373 [*C. A.* **22**, 2951 (1928)].
7. Autenrieth, *Ber.* **34**, 184 (1901); Autenrieth and Thomae, *Ber.* **57**, 431 (1924); van der Haar, *Rec. trav. chim.* **47**, 321 (1928).
8. Rankov, *Ann. univ. Sofia, II, Faculté phys.-math., Livre 2*, **33**, 221 (1937) [*C. A.* **32**, 3335 (1938)].
9. Evlampiev, *J. Gen. Chem. (U.S.S.R.)* **7**, 2934 (1937) [*C. A.* **32**, 5377 (1938)].

Appendix

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

potassium pyrosulfite

[sulfuric acid](#) (7664-93-9)

[acetic acid](#) (64-19-7)

[Benzene](#) (71-43-2)

[acetic anhydride](#) (108-24-7)

sodium carbonate (497-19-8)
PHOSPHORUS (7723-14-0)
oxygen (7782-44-7)
Benzoic acid (65-85-0)
Acetophenone (98-86-2)
benzoyl chloride (98-88-4)
Benzoic anhydride (93-97-0)
phosphoric acid (7664-38-2)
lead nitrate (10099-74-8)
benzotrichloride (98-07-7)
diphenyldichloromethane (2051-90-3)
sodium benzoate (532-32-1)