



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.

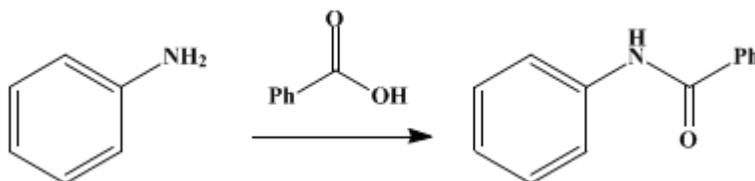
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.82 (1941); Vol. 7, p.6 (1927).

BENZANILIDE



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1. Procedure

In a 3-l. round-bottomed flask are placed 750 g. (8.1 moles) of [aniline](#) ([Note 1](#)) and 1 kg. (8.2 moles) of [benzoic acid](#). When about two-thirds of the [benzoic acid](#) is in the flask the mixture is melted to make room for the rest. The flask is placed in a large oil bath and connected to a condenser for distillation. The temperature of the oil is raised quickly to 180–190°, at which point distillation starts. The bath is held at this temperature until practically no more [aniline](#) and water distil (about two hours), and then the temperature is slowly raised to 225° and maintained at this temperature until no further distillation takes place (one to two hours). The oil bath is now removed and the contents of the flask are allowed to cool below 180° and 550 g. (5.9 moles) of [aniline](#) is added. The distillations at 190° and 225° are repeated (about six hours). The hot mixture is poured into two 20-cm. evaporating dishes (Hood) and is allowed to cool. The crude product weighs 1600–2000 g., depending on the amount of [aniline](#) retained.

The purplish-gray solid is ground ([Note 2](#)) in a large mortar and is poured with vigorous stirring into a 12-l. (3-gallon) crock containing 6 l. of approximately normal [hydrochloric acid](#) (5.5 l. of water and 500 cc. of concentrated [hydrochloric acid](#)). The stirring is continued for one hour after all the [benzanilide](#) has been added, and then the solid is filtered on a 20-cm. Büchner funnel. The process of stirring with acid and filtering is repeated twice to remove the excess of [aniline](#). The solid is stirred for two hours with 6 l. of water and is filtered. It is stirred for one hour with 6 l. of normal [sodium hydroxide](#) solution to remove the excess of [benzoic acid](#) and is then filtered. The stirring with alkali and filtering is repeated. The solid is next stirred for two hours with 7 l. of water and is filtered, sucked dry, and air-dried overnight on paper.

After drying on paper the purplish solid is dried to constant weight in three 20-cm. evaporating dishes at 90–100° (about two days) and is then repowdered. The product is light purplish-gray and weighs 1270–1325 g. (80–84 per cent of the theoretical amount). It melts at 157–160°. The product is pure enough for use in the preparation of *p*-dimethylaminobenzophenone ([p. 217](#)) and for most synthetic purposes. When 100 g. of [benzanilide](#) is dissolved in 750 cc. of hot [alcohol](#) ([Note 3](#)) and the solution is boiled with about 10 g. of [decolorizing carbon](#) ([Norite](#)), filtered, and cooled at 10° overnight, 80–86 g. of an almost colorless product melting at 160–161° separates. A second crystallization from alcohol using [decolorizing carbon](#) gives a white product with approximately the same loss in the mother liquors as in the first crystallization.

2. Notes

1. The ordinary "pure" [aniline](#) of commerce gives as good yields and as pure a product as redistilled [aniline](#).
2. The [benzanilide](#) must be finely ground in order that [aniline](#) and [benzoic acid](#) may be completely extracted.
3. Very little of the solid fails to go into solution. The hot solution must be filtered rapidly as the [benzanilide](#) crystallizes easily.

3. Discussion

Benzanilide can be prepared by the treatment of aniline with benzoyl chloride,¹ benzoic anhydride,² or benzoic acid.³ Benzanilide has also been prepared from benzamide, aniline, and boron fluoride.⁴ The method described in the procedure is essentially that of Nägeli.³

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 217
- Org. Syn. Coll. Vol. 4, 383

References and Notes

1. Gerhardt, Ann. **60**, 311 (1846); Dehn and Ball, J. Am. Chem. Soc. **36**, 2096 (1914).
 2. Meyer and Sundmacher, Ber. **32**, 2123 (1899).
 3. Hübner, Ann. **208**, 291 (1881); Nägeli, Bull. soc. chim. (3) **11**, 892 (1894).
 4. Sowa and Nieuwland, J. Am. Chem. Soc. **59**, 1202 (1937).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

alcohol (64-17-5)

hydrochloric acid (7647-01-0)

aniline (62-53-3)

sodium hydroxide (1310-73-2)

Benzoic acid (65-85-0)

Benzanilide (93-98-1)

decolorizing carbon (Norite),
carbon (7782-42-5)

benzoyl chloride (98-88-4)

Benzoic anhydride (93-97-0)

benzamide (55-21-0)

boron fluoride (7637-07-2)

p-Dimethylaminobenzophenone (530-44-9)