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.

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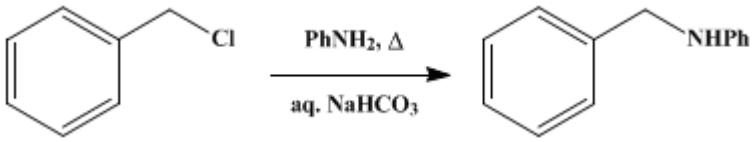
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.008.0038

Organic Syntheses, Coll. Vol. 1, p.102 (1941); Vol. 8, p.38 (1928).

BENZYLANILINE

[Benzylamine, N-phenyl-]



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1. Procedure

A 1500-cc. flask is fitted with a reflux condenser, a mechanical stirrer, and a 200-cc. separatory funnel. In the flask are placed 372 g. (4 moles) of aniline (Note 1), 105 g. (1.25 moles) of sodium bicarbonate (Note 2), and 100 cc. of water. The flask and contents are then heated on a steam bath to 90–95°, and 127 g. (115 cc., 1 mole) of benzyl chloride (Note 3) is run in slowly from the separatory funnel, vigorous agitation being maintained. The addition of benzyl chloride should take not less than one and one-half to two hours, and the reaction is complete in four hours.

The mixture is then cooled, filtered with suction, the layers of water and organic liquid separated, and the latter washed with saturated salt solution (Note 4). The amines are then dried by shaking with about 20 g. of anhydrous sodium sulfate, and again filtered with suction. The excess of aniline is removed by distillation under reduced pressure (Note 5) using a modified Claisen flask with a fractionating side arm (p. 130). The aniline distils at 81° /12 mm., and then the temperature rises quickly to the boiling point of benzylaniline, 180° /12 mm. or 190° /16 mm. When the temperature has risen to within about 5° of the boiling point of the benzylaniline, the receiver is again changed and the benzylaniline collected from 170–200° /12 mm., practically all boiling at 178–180° /12 mm. (Note 6).

The aniline recovered amounts to 250–260 g. (89–92 per cent of the theoretical amount), and the yield of benzylaniline is 155–160 g. (85–87 per cent of the theoretical amount based on the benzyl chloride). The product solidifies on cooling and melts at 33–36°. It is practically colorless and sufficiently pure for most synthetic purposes. A pure compound melting at 36° may be obtained by crystallizing the product from about 100 cc. of ligroin (b.p. 85–90°). The solution is cooled in a freezing mixture to cause crystallization, the crystals filtered with suction, washed with a little cold ligroin, pressed, and dried. The recovery is about 90 per cent of the original product.

2. Notes

1. Benzylaniline reacts with benzyl chloride to form dibenzylaniline. If the proportion of aniline used is less than that given, the yield of benzylaniline is lowered, and separation rendered more difficult.
2. Sodium bicarbonate is used on account of its high purity and convenience in handling. An equivalent amount of the normal carbonate may be substituted, but reagents of stronger basicity increase the proportion of high-boiling by-products.
3. The benzyl chloride should be freshly distilled and collected at 176–178°.
4. Saturated salt solution is used here in preference to water, as separation of the liquids is more rapid and clean.
5. The aniline may also be quite satisfactorily removed by distillation under atmospheric pressure, using an efficient fractionating column, the distillation being interrupted when the thermometer in the still-head registers 235°.
6. Benzylaniline distils without appreciable decomposition at atmospheric pressure at 298–300°. It assumes, however, a yellow color, and separation from any higher-boiling impurities is more difficult than when distillation is carried out under reduced pressure.

3. Discussion

Benzylaniline can be prepared from aniline and benzyl chloride by heating at 160° in a reaction which may be violent and always leads to mixtures;[1] at low temperatures with an excess of aniline;[2] and in a sodium carbonate solution.[3] It can also be prepared by the reduction of benzalaniline with sodium and alcohol,[4] and by the reductive alkylation of nitrobenzene or aniline with benzaldehyde, hydrogen, and a catalyst in the presence of sodium acetate.[5]

References and Notes

1. Fleischer, Ann. **138**, 225 (1866); Nolan and Clapham, J. Soc. Chem. Ind. **44**, 220T (1925).
2. Ullmann, "Enzyklopädie der technischen Chemie," Urban and Schwarzenberg, Berlin, **I**, 445 (1914); Desai, J. Indian Inst. Sci. **7**, 235 (1924) [C. A. **19**, 2645 (1925)].
3. Gomberg and Buchler, J. Am. Chem. Soc. **42**, 2059 (1920).
4. Fischer, Ann. **241**, 330 (1887).
5. Emerson and Walters, J. Am. Chem. Soc. **60**, 2023 (1938); Emerson and Mohrman, ibid. **62**, 69 (1940).

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

ligroin

alcohol (64-17-5)

sodium acetate (127-09-3)

aniline (62-53-3)

hydrogen (1333-74-0)

sodium bicarbonate (144-55-8)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

benzaldehyde (100-52-7)

Benzalaniline (538-51-2)

sodium (13966-32-0)

Benzylaniline,
Benzylamine, N-phenyl- (103-32-2)

benzyl chloride (100-44-7)

dibenzylaniline (91-73-6)

Nitrobenzene (98-95-3)