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.

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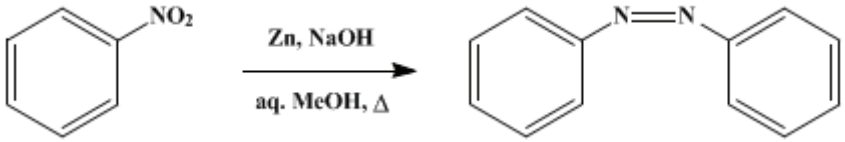
AZOBENZENE



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1. Procedure

A 5-l. three-necked round-bottomed flask, fitted with a mercury-sealed stirrer and a reflux condenser, is placed on a steam cone. In the flask are placed 250 g. (208 ml., 2 moles) of nitrobenzene, 2.5 l. of methanol, and a solution of 325 g. (8.1 moles) of sodium hydroxide (Note 1) in 750 ml. of distilled water. To the mixture is added 265 g. (4.1 moles) of zinc dust (Note 2), the stirrer is started, and the mixture is refluxed for 10 hours (Note 3). The mixture is filtered while hot, and the precipitate of sodium zincate is washed on the filter with a little warm methanol. All the methanol is distilled from the filtrate, the residue is chilled, and the crystalline azobenzene is filtered.

In order to remove zinc salts from the crude azobenzene, the latter is added to 500 ml. of 2% hydrochloric acid, the mixture is warmed to about 70° in order to melt the azobenzene and is stirred rapidly for about 5 minutes. Stirring is continued while the mixture is chilled to solidify the azobenzene. The product is filtered, washed well with water, and recrystallized from a mixture of 720 ml. of 95% ethanol and 60 ml. of water. The yield of azobenzene melting at 66–67.5° is 156–160 g. (84–86%).

2. Notes

1. This amount assumes 100% purity. The checkers used 342 g. of 95% sodium hydroxide.
2. This amount assumes 100% purity. The checkers used 288 g. of 92% zinc dust.
3. At the end of this time, the reddish mixture should be free from the odor of nitrobenzene. If it is not, refluxing is continued for 2–3 hours longer.

3. Discussion

Azobenzene has been prepared by many different methods, of which the following are representative. It may be obtained by the reduction of nitrobenzene with iron and acetic acid;[1] with sodium amalgam;[2] with alkali sulfides;[3] with cellulose,[4] molasses,[5] or dextrose[5] in alkaline solution; and by catalytic reduction.[6] The reduction with zinc and sodium hydroxide described here is a modification of Alexejew's method.[7] Azobenzene also results from the reduction of diazotized aniline with cuprous salts.[8] Aniline has been oxidized to azobenzene by air[9] and by potassium permanganate.[10] The condensation of nitrobenzene and aniline acetate also yields azobenzene.[11]

References and Notes

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10. Glaser, *Ann.*, **142**, 364 (1867).
11. Baeyer, *Ber.*, **7**, 1638 (1874).

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

sodium zincate

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

methanol (67-56-1)

aniline (62-53-3)

sodium hydroxide (1310-73-2)

iron (7439-89-6)

potassium permanganate (7722-64-7)

zinc (7440-66-6)

sodium (13966-32-0)

Nitrobenzene (98-95-3)

dextrose (492-62-6)

Azobenzene (103-33-3)

aniline acetate