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.

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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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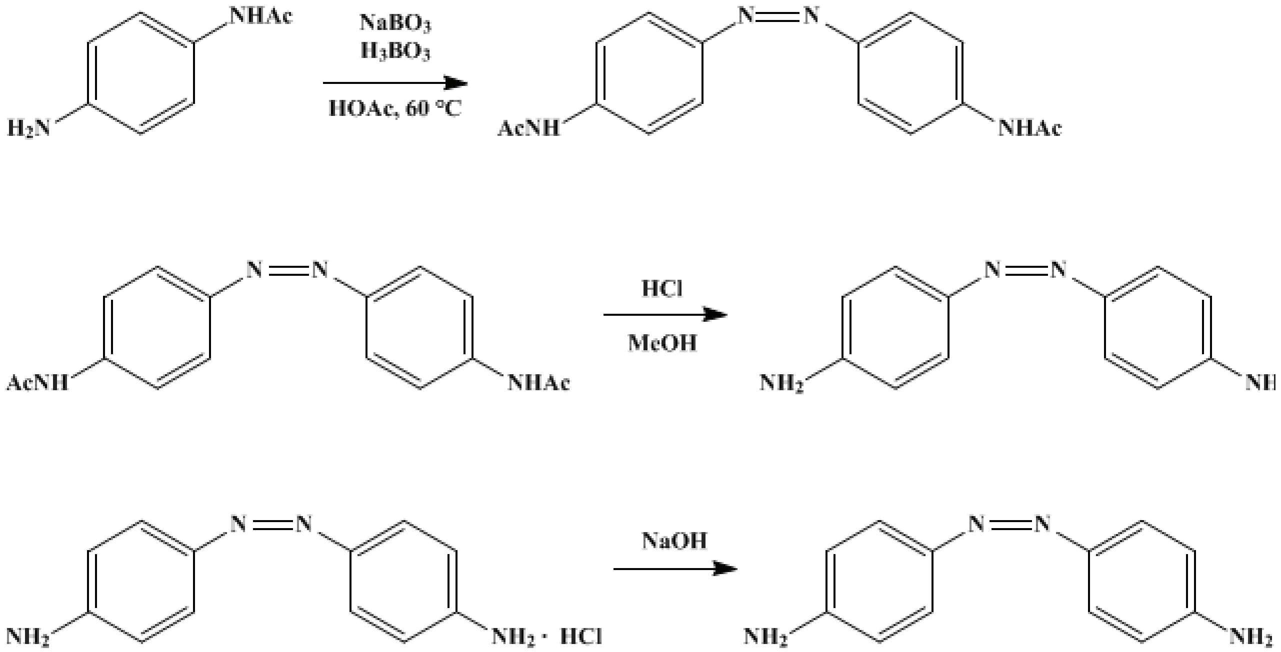
4,4'-DIAMINOAZOBENZENE

[Aniline, 4,4'-azodi-]



Submitted by Pasco Santurri, Frederick Robbins, and Robert Stubbings[1].
Checked by Max Tishler, Earl M. Chamberlin, and William Harrison.

1. Procedure

In a 1-l. three-necked round-bottomed flask equipped with an efficient stirrer, a reflux condenser, and a thermometer (Note 1) are placed 500 ml. of glacial acetic acid (Note 2), 29.0 g. (0.19 mole) of *p*-aminoacetanilide (Note 3), 40 g. (0.26 mole) of sodium perborate tetrahydrate, and 10 g. (0.16 mole) of boric acid. The mixture is heated with stirring to 50–60° and held at this temperature for 6 hours. Initially the solids dissolve but, after heating for approximately 40 minutes, the product begins to separate. At the end of the reaction period, the mixture is cooled to room temperature and the yellow product is collected on a Büchner funnel. It is washed with water until the washings are neutral to pH paper (Note 4) and then dried in an oven at 110°. The yield of 4,4'-bis(acetamido)azobenzene, m.p. 288–293° (dec.), is 16.5 g. (57.7%). It is used as such for the hydrolysis step (Note 5).

In a 500-ml. round-bottomed flask equipped with a reflux condenser and a magnetic stirrer (Note 6) are placed 150 ml. of methanol, 150 ml. of 6*N* hydrochloric acid, and the total yield of 4,4'-bis(acetamido)azobenzene. The mixture is heated under reflux for 1.5 hours. The reaction mixture is cooled and the violet solid collected on a Büchner funnel (Note 7). The damp product is suspended in 500 ml. of water in a 1-l. beaker equipped with a stirrer, and the mixture is slowly neutralized by the addition of 2.5*N* sodium hydroxide. In the course of the neutralization, the salt dissolves and the free base separates. The 4,4'-diaminoazobenzene is collected on a Büchner funnel, washed with water, and dried under reduced pressure. The yield of yellow product, m.p. 238–241° (dec.), is 11–12 g. The overall yield from *p*-aminoacetanilide is 52–56%.

2. Notes

1. The submitters carried out the reaction in a 1-l. beaker. The checkers found that considerable evaporation of acetic acid occurs when a beaker is used.
2. The use of dilute acetic acid decreases the yield.

3. Technical grade *p*-aminoacetanilide (m.p. 158–160°) obtained from Eastman Kodak Company (T-13) was used.
4. If the product is not washed well, the dried material will turn violet, indicating unreacted *p*-aminoacetanilide.
5. Witt and Kopetschni[2] report a melting point of 295–296° (dec.). This compound may be recrystallized from glacial acetic acid or ethanol.
6. The submitters did not stir the hydrolysis mixture. The checkers found that, if stirring was omitted, bumping occurred during the reflux period.
7. This product is probably the monohydrochloride salt. The dihydrochloride is reported to be red.[3]

3. Discussion

4,4'-Diaminoazobenzene was reported by Nietzki[4] to have been prepared by diazotizing *p*-nitroaniline and coupling the product with aniline. The resulting 4-nitrodiazoaminobenzene[5] is rearranged and the nitro group reduced. The submitters tried several times to carry out this procedure but were unsuccessful. 4,4'-Diaminoazobenzene has been prepared by the oxidation of *p*-nitroaniline with potassium persulfate[6] followed by the reduction of the nitro groups.[7]

The general method used by the submitters has been reported by others[8] for the preparation of other azo compounds.

4. Use of 4,4'-Diaminoazobenzene

The product is useful as a model compound for studies of the chemistry of derivatives of colored diamines. Specifically, the submitters used the compound for the preparation of colored diisocyanates.

References and Notes

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4. R. Nietzki, *Ber.*, **17**, 343 (1884).
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6. A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 1309 (1939).
7. J. N. Ashley, H. J. Barber, A. J. Ewins, G. Newbery, and A. D. H. Self, *J. Chem. Soc.*, 103 (1942).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

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)

potassium persulfate (7727-21-1)

boric acid (10043-35-3)

sodium perborate tetrahydrate (10486-00-7)

4-nitrodiazoaminobenzene

p-nitroaniline (100-01-6)

p-aminoacetanilide (122-80-5)

4,4'-Diaminoazobenzene,
Aniline, 4,4'-azodi- (538-41-0)

4,4'-bis(acetamido)azobenzene (15446-39-6)