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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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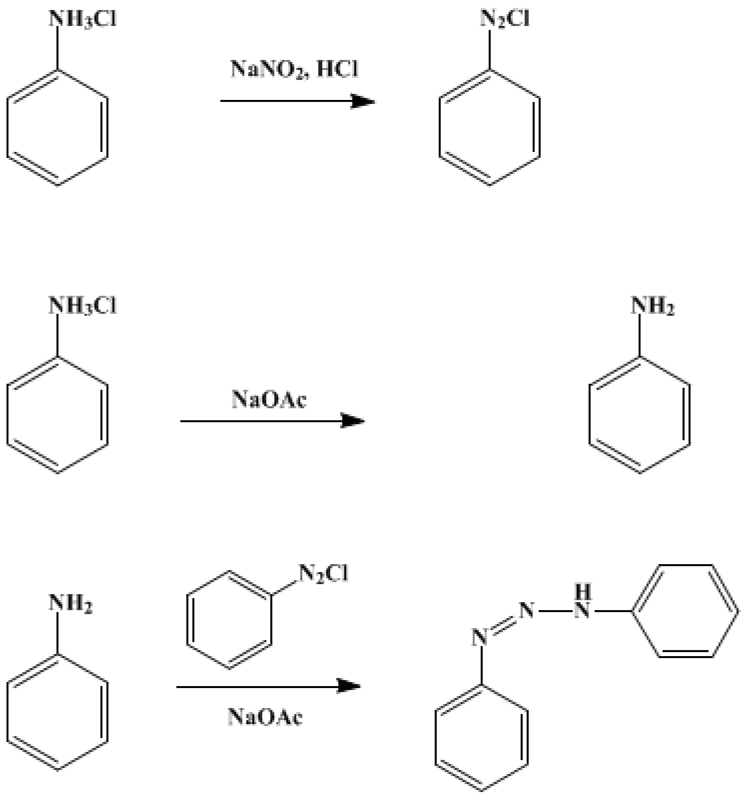
DIAZOAMINOBENZENE

[Triazene, 1,3-diphenyl-]



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1. Procedure

In a 5-l. flask fitted with a mechanical stirrer and a dropping funnel are placed 1 kg. of cracked ice, 1.5 l. of water, 279 g. (3 moles) of a technical grade of aniline, and 458 g. (388 cc., 4.5 moles) of concentrated hydrochloric acid (sp. gr. 1.18). The stirrer is started, and a solution of 109 g. (1.5 moles) of 95 per cent sodium nitrite in 250 cc. of water is added over a period of fifteen minutes. The reaction mixture is then stirred for fifteen minutes, and a solution of 422 g. (3.1 moles) of crystalline sodium acetate dissolved in 800 cc. of water is added over a period of five minutes. A yellow precipitate of diazoaminobenzene begins to form at once. Stirring is continued for forty-five minutes, keeping the temperature below 20° (Note 1). The yellow diazoaminobenzene is filtered on a 19-cm. Büchner funnel (Note 2), washed with 5 l. of cold water, and then sucked as dry as possible and spread out on a sheet of paper to dry (Note 3). The product thus obtained is dissolved in 4 l. of boiling ligroin (b.p. 60–90°) (Note 4), filtered, and allowed to cool to room temperature and stand overnight. When crystallization is complete, the yellow crystals are filtered on a 19-cm. Büchner funnel, washed with 500 cc. of cold ligroin (b.p. 60–90°), and dried at room temperature. The yield of yellow crystals melting at 92–94° is 242–251 g. (82–85 per cent of the theoretical amount) (Note 5). If a product of greater purity is desired, the diazoaminobenzene is dissolved in 4 l. of boiling ligroin (b.p. 60–90°) and crystallized as before. The recrystallized diazoaminobenzene weighs 204–218 g. (69–73 per cent of the theoretical amount) and melts at 94–96° (Note 6) and (Note 7).

2. Notes

1. The temperature noted is not known to be the maximum temperature at which the reaction may be run.
2. A centrifuge of suitable size is preferable.
3. A rubber dam is fitted over the top of the Büchner funnel and held in place by rubber bands in order to remove as much of the water as possible.
4. Prolonged heating of the diazoaminobenzene with ligroin causes decomposition. For this reason it is well to heat the ligroin to boiling before it is added to the product to be crystallized. Solution is effected as rapidly as possible. If the crude diazoaminobenzene is not dry, a layer of water will separate at the bottom of the flask. This should be removed as completely as possible before filtering the hot ligroin solution.
5. An additional crop of crystals weighing 20–25 g. and melting at 79–83° can be obtained by evaporating the mother liquors to 1 l. and chilling in an ice bath.
6. The size of the run may be halved; a run with half quantities gave 125 g. of product.
7. Pure diazoaminobenzene is described as faintly yellow needles melting at 100°. A procedure for the purification of diazoaminobenzene and other aminoazo compounds has been described by Dwyer.[1]

3. Discussion

Diazoaminobenzene has been prepared by the action of sodium nitrite on aniline sulfate;[2] by the action of sodium nitrite on aniline hydrochloride;[3] by the action of sodium nitrite and sodium acetate on aniline hydrochloride;[4] by the action of ammonium nitrate and hydrogen sulfide on aniline hydrochloride in the presence of iron;[5] by the action of sodium nitrite and potassium chromate or dichromate on aniline;[6] and from aniline and amyl nitrite.[7]

Diazoaminobenzene has also been prepared by the action of nitrous acid gas on aniline in alcohol;[8] by the action of silver nitrite on aniline hydrochloride;[9] and together with phenylurea by the action of nitrosophenylurea on aniline in methyl alcohol.[10] Niementowski and Roszkowski[11] have reported studies on the diazotization of aniline, aniline hydrochloride, and aniline sulfate with sodium nitrite and silver nitrite. The procedure described is adapted from that of Fischer.[4]

References and Notes

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

ligroin

potassium chromate or dichromate

hydrochloric acid (7647-01-0)

methyl alcohol (67-56-1)

sodium acetate (127-09-3)

aniline (62-53-3)

iron (7439-89-6)

hydrogen sulfide (7783-06-4)

aniline hydrochloride (142-04-1)

sodium nitrite (7632-00-0)

nitrous acid (7782-77-6)

amyl nitrite (463-04-7)

ammonium nitrate

Phenylurea (64-10-8)

aniline sulfate

Diazoaminobenzene,
Triazene, 1,3-diphenyl- (136-35-6)

silver nitrite (7783-99-5)

nitrosophenylurea