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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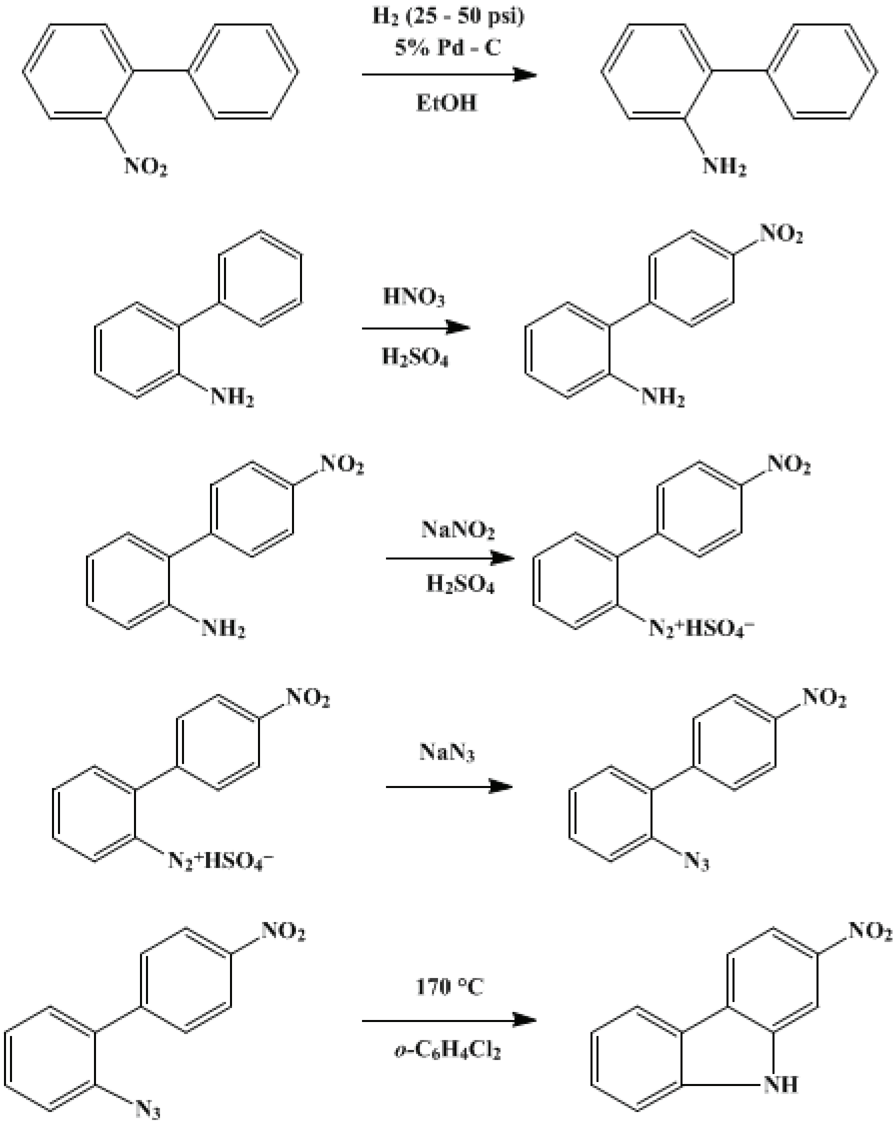
2-NITROCARBAZOLE

[Carbazole, 2-nitro]



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1. Procedure

A. *o-Aminobiphenyl*. A Parr bottle is charged with 60 g. (0.30 mole) of *o*-nitrobiphenyl (Note 1), 3 g. of 5% palladium-on-carbon catalyst (Note 2), and 200 ml. of 95% ethanol. The mixture is shaken with hydrogen under 25–50 p.s.i. until the gas is no longer absorbed (about 70 minutes), the catalyst is filtered from the hot solution and washed with 20 ml. of ethanol, and the filtrates are poured in a thin stream into 1 l. of ice water contained in a 2-l. Erlenmeyer flask (Note 3). After standing for 20 minutes the white solid is filtered with suction, pressed to remove excess water, and allowed to dry in air. The yield of essentially pure *o*-aminobiphenyl is 48–51 g. (94–100%), m.p. 43–45.5°.

B. *o-Amino-p'-nitrobiphenyl*. Concentrated sulfuric acid (400 ml.) is placed in a 1-l. round-bottomed flask fitted with a mechanical stirrer and a thermometer. Stirring is begun, and 45.0 g. (0.27 mole) of powdered *o*-aminobiphenyl is added all at once through a powder funnel. When the amine has dissolved, the flask is placed in an ice-salt bath and its contents cooled to a temperature between 0° and −5°. A mixture of 30 ml. of concentrated sulfuric acid and 11.0 ml. of fuming nitric acid (density 1.5) is then added dropwise from a separatory funnel while the temperature is kept below 0°. The addition requires about an hour, and stirring is continued 45 minutes longer. The liquid is poured onto 1.5 kg. of ice in a 4-l. beaker and treated carefully until neutral with a solution of 580 g. (14.5 moles) of sodium hydroxide in 1.5 l. of water cooled to room temperature. The resultant hot suspension of product is allowed to cool nearly to room temperature, filtered with suction, and the orange solid is washed with 500 ml. of water. The crude material is pressed free of excess water and recrystallized from 850–1000 ml. of 95% ethanol (Note 4), giving 32–42 g. (56–74%) of orange needles, m.p. 156–158.5°.

C. *o-Azido-p′-nitrobiphenyl*. Water (100 ml.) is placed in a 1-l. round-bottomed flask equipped with a thermometer and an efficient mechanical stirrer. With stirring, 30 ml. of concentrated sulfuric acid is added, followed by 32.1 g. (0.15 mole) of recrystallized *o*-amino-*p′*-nitrobiphenyl. When all the amine has been converted to the white sulfate, 50 ml. more of water is added and the suspension is cooled to 0–5° in an ice-salt bath. A solution of 11 g. (0.16 mole) of sodium nitrite in 30 ml. of water is added dropwise over a period of 15 minutes (Note 5), and the mixture is stirred for 45 minutes longer. A thick precipitate of the sparingly soluble diazonium salt may have separated from the initially clear solution by this time. With strong stirring, a solution of 12 g. (0.17 mole) of sodium azide in 40 ml. of water is run in (Note 6), and stirring is continued for 40 minutes longer. The thick white solid is filtered with suction and washed with 200 ml. of water. After pressing free of excess water, the material is allowed to dry in air in a dark place. The yield of gray-white azide is 35.5–36 g. (99–100%), m.p. 91.5–92.5° (Note 7).

D. *2-Nitrocarbazole*. In a 2-l. round-bottomed flask fitted with a mechanical stirrer, a thermometer, and a short air condenser are placed 35.5 g. (0.15 mole) of powdered *o*-azido-*p′*-nitrobiphenyl and 1 l. of *o*-dichlorobenzene (Note 8). The stirred mixture is heated above 170° for 1 hour by means of a heating mantle, allowed to cool to room temperature, and chilled in a refrigerator (5°) for several hours. The crude product is filtered with suction, washed with 40 ml. of light petroleum, and sucked dry on the filter. There results 26–28 g. of yellow-brown crystals, m.p. 171.5–174°. The filtrate is distilled under aspirator pressure to a volume of 150–200 ml. and chilled as before, to yield an additional 2–3 g., m.p. 171–174°. The total yield is 28–30 g. (89–96%). The combined crops are dissolved in 400–450 ml. of boiling 95% ethanol with 3–4 g. of Norit® to remove impurities and filtered through a preheated Büchner funnel. The filtrate on cooling deposits bright yellow needles of product, which are filtered after standing at 5° for several hours. This crop weighs 23–25 g., m.p. 174–175.5°. Concentration of the mother liquor to a small volume (50–70 ml.) and chilling gives a second crop of lesser purity, 1–2 g., m.p. 172–175°. The total yield of recrystallized material is 24–26.5 g. (77–85%), and the overall yield from *o*-nitrobiphenyl is 40–63%.

2. Notes

1. An Eastman Kodak technical grade of *o*-nitrobiphenyl was used by the submitters. This is no longer available, and the checkers used the material supplied by K and K Laboratories. Both *o*-amino- and *o*-nitrobiphenyl are available from the Aldrich Chemical Company.
2. The Baker Co. catalyst was used.
3. This carcinogen is more easily handled in a flask than in a beaker. Contact with the skin obviously should be avoided.
4. Recrystallization is best accomplished by adding the compound to boiling ethanol and filtering. Prolonged heating should be avoided, as the substance gradually decomposes in hot solvent.
5. The sodium nitrite solution must be added carefully in order to avoid loss of material due to vigorous foaming.
6. This operation should be carried out in a hood to avoid the unpleasant effects of exposure to hydrogen azide vapors.
7. The compound may be recrystallized from a large volume of ethanol, but no increase in yield was noted using recrystallized material in the next step.
8. Eastman Kodak *o*-dichlorobenzene of 95% purity was used. Olefin-free kerosene or decalin may be substituted for the solvent, keeping the reaction temperature between 170° and 190°.

3. Discussion

o-Aminobiphenyl has been prepared by the reduction of the corresponding nitro compound with zinc and acetic acid,[2] zinc and hydrochloric acid,[3] iron and hydrochloric acid,[4] sodium bisulfite under pressure,[5] or hydrazine and palladium;[6] by the Hofmann reaction on *o*-phenylbenzamide;[7] and by pyrolysis of diazoaminobenzene.[8,9]

o-Amino-*p*'-nitrobiphenyl has been made by the nitration of *o*-aminobiphenyl with ethyl nitrate;[10] by hydrolysis of the corresponding acetamide derivative;[11,12] and by partial reduction of *o*, *p*'-dinitrobiphenyl with sodium bisulfite under pressure.[5]

2-Nitrocarbazole has been prepared by the dehydrogenation of 2-nitro-1,2,3,4-tetrahydrocarbazole with chloranil,[13] by the deamination of 2-nitro-3-aminocarbazole,[14] and by the thermal decomposition of *o*-azido-*p*'-nitrobiphenyl.[15] The procedure given here is a slight modification of the last-mentioned method.

4. Merits of the Preparation

The decomposition of *o*-azidobiphenyls is a convenient and general synthesis for a variety of carbazoles in good yield,[15] especially those not available through direct substitution of carbazole itself. Many of the required intermediates can be prepared from *o*-aminobiphenyl by substitution reactions. The method is also applicable to the preparation of analogs of the carbazole system in which a heterocyclic ring replaces a benzene ring, to the preparation of indoles, and to certain analogous aliphatic systems.

References and Notes

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

palladium-on-carbon

light petroleum

o-amino- and o-nitrobiphenyl

chloranil

o-azidobiphenyls

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

iron (7439-89-6)

nitric acid (7697-37-2)

sodium nitrite (7632-00-0)

sodium bisulfite (7631-90-5)

zinc (7440-66-6)

palladium (7440-05-3)

hydrazine (302-01-2)

sodium azide (26628-22-8)

carbazole (86-74-8)

Diazoaminobenzene (136-35-6)

ethyl nitrate (625-58-1)

decalin (91-17-8)

hydrogen azide

o-Aminobiphenyl (90-41-5)

2-Nitrocarbazole,

Carbazole, 2-nitro (14191-22-1)

2-nitro-1,2,3,4-tetrahydrocarbazole

2-nitro-3-aminocarbazole

o-dichlorobenzene (95-50-1)

o, p'-dinitrobiphenyl

o-nitrobiphenyl (86-00-0)

o-phenylbenzamide

o-Azido-p'-nitrobiphenyl (14191-25-4)

o-Amino-p'-nitrobiphenyl (6272-52-2)