



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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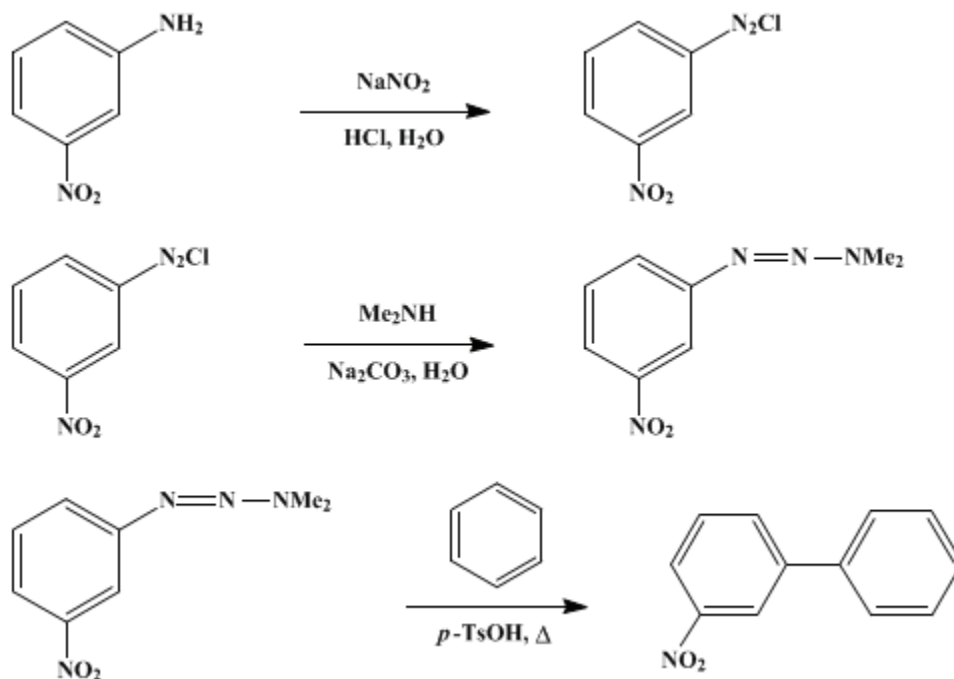
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.718 (1963); Vol. 33, p.56 (1953).

m-NITROBIPHENYL

[Biphenyl, 3-nitro-]



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1. Procedure

A. *1-(m-Nitrophenyl)-3,3-dimethyltriazene*. To a 3-l. three-necked flask containing 276 g. (2 moles) of technical grade *m*-nitroaniline (Note 1) are added 250 ml. of concentrated hydrochloric acid and 500 ml. of hot water. The contents of the flask are heated to about 85° to dissolve the *m*-nitroaniline; then 550 ml. of concentrated hydrochloric acid is added, and the solution is cooled rapidly. A stirrer, a thermometer, and a long-stemmed dropping funnel are attached to the flask, and its contents are then cooled to -3 to -5° by means of a salt-ice bath. A solution of 144 g. (2.09 moles) of sodium nitrite in 350 ml. of water is added dropwise under the surface of the acid solution while it is being stirred. The rate of addition is regulated (Note 2) so that the temperature does not rise above 0°. The stirring is continued for 15–20 minutes after the sodium nitrite solution has been added; then a solution of 8–10 g. of urea in 25 ml. of water is added during about 15 minutes (foaming), and the stirring is discontinued. The diazonium salt solution must be kept cold while the next step is proceeding.

Two and one-half liters of water in a 3-gal. crock is stirred vigorously with a mechanical stirrer, and 870 g. (7 moles) of pulverized sodium carbonate monohydrate (Note 3) is added portionwise (Note 4). Crushed ice is added to the sodium carbonate suspension until the temperature is lowered to 10°; then 423 g. (2.35 moles) of 25% dimethylamine solution (Note 5) is added. The ice-cold *m*-nitrobenzenediazonium chloride solution is added over a period of 25–35 minutes under the surface of the vigorously stirred dimethylamine solution by means of a dropping funnel (Note 6) while the temperature is maintained at about 10° by the addition of ice. The solution is stirred for 15–20 minutes after the addition is complete. The crude yellow triazene is removed by filtration on a large Büchner funnel. The cake is washed twice by removal and thorough mixing with 2–2.5 l. of water. After the second washing the cake is pressed as dry as possible, then removed and dissolved in 1.8–2.0 l. of boiling 95% ethanol contained in a 4-l. flask under a reflux condenser. The triazene is allowed to crystallize as the ethanol is cooled in water, then removed by filtration, and washed with two 200-ml.

portions of 95% ethanol. After drying in air at room temperature, the yield of 1-(*m*-nitrophenyl)-3,3-dimethyltriazene is 348–365 g. (89–94%), m.p. 100.8–101.5°.

B. *m*-Nitrobiphenyl. To a 5-l. three-necked flask equipped with a sealed mechanical stirrer, a dropping funnel, and a reflux condenser are added 116.4 g. (0.6 mole) of 1-(*m*-nitrophenyl)-3,3-dimethyltriazene and 2.5 l. of benzene. The benzene solution is heated to maintain refluxing and stirred vigorously while a solution of 148 g. (0.8 mole) of 94% toluenesulfonic acid (Note 7) in 750 ml. of benzene is added dropwise (Note 8) over a period of 4–4.5 hours. The refluxing is continued for 1–1.5 hours (Note 9) after the toluenesulfonic acid has been added. The solution is allowed to cool somewhat, 800 ml. of water is added cautiously with stirring through the separatory funnel, and then the water layer is removed. The benzene layer is extracted twice with 500-ml. portions of water, then three times with 500-ml. portions of 5% sodium hydroxide solution, and finally with a 500-ml. portion of water. The benzene solution is shaken with 30–40 g. of anhydrous calcium chloride to remove most of the water. The benzene is removed by distillation by dripping it into a 500-ml. Claisen flask which is heated sufficiently to maintain a rapid rate of distillation. After most of the benzene is removed, the residue is transferred to a 125-ml. Claisen flask. The low-boiling material is removed at a pressure of 20–30 mm. up to a bath temperature of 135–140°. The residue is then distilled at 0.1 mm. pressure. After a fore-run of nitrobenzene (2–5 ml.), the *m*-nitrobiphenyl is distilled (Note 10) at 115–118° at 0.1 mm. while the bath temperature is maintained at 155–160°. The yield of the crude yellow oil is 50–60 g. (42–50%) (Note 11). For purification, the substance is dissolved in 50 ml. of hot methanol. Upon cooling, two layers separate. Crystallization is induced by scratching the inner surface with a glass rod. When the crystalline mass is cold, the yellow solid is removed by filtration and washed with two 30-ml. portions of cold methanol. After drying in air, the yield of *m*-nitrobiphenyl is 40–50 g. (34–42%), m.p. 58.5–59.5°.

2. Notes

1. E. I. du Pont de Nemours and Company technical product, m.p. 111–112°, was used.
2. The time required for the addition varies from 1.5 to 2 hours.
3. There must be an excess of sodium carbonate to prevent the troublesome frothing caused by the liberation of carbon dioxide near the end of the coupling reaction.
4. The addition must be regulated so as to prevent the formation of large chunks of sodium carbonate decahydrate.
5. Obtained from Eastman Organic Chemicals Department, Distillation Products Industries, Rochester, New York.
6. Small portions are added to the separatory funnel while the main portion is kept in the ice bath.
7. Monsanto Chemical Company anhydrous toluenesulfonic acid, which is about 80% of the *para* isomer, was used.
8. Some toluenesulfonic acid hydrate which does not dissolve in benzene must be pushed through the stem of the funnel by means of a wire or a thin glass rod.
9. The evolution of nitrogen gas may be followed by attaching a bubble counter containing kerosene to the top of the reflux condenser. Generally, the evolution of nitrogen is complete within an hour.
10. The *m*-nitrobiphenyl has a tendency to crystallize in the side arm of the Claisen flask. Arrangements must be made to keep the side arm sufficiently warm to prevent crystallization.
11. After the oil has congealed to a solid, the substance melts at 53–57°.

3. Discussion

The procedure described for the preparation of 1-(*m*-nitrophenyl)-3,3-dimethyltriazene is the method of Elks and Hey,² and the preparation of *m*-nitrobiphenyl is also a modification of their procedure. The other principal methods for the preparation of *m*-nitrobiphenyl are the decomposition of *N*-nitroso-*m*-nitroacetanilide in benzene³ and the decomposition of alkaline *m*-nitrobenzenediazohydroxide in benzene.⁴ Other methods that have been reported include the decomposition of potassium *m*-nitrobenzenediazotate in benzene with acetyl chloride,⁵ the decomposition of *m*-nitrobenzoyl peroxide in boiling benzene,⁶ the decomposition of benzenediazonium borofluoride in nitrobenzene⁷ at 70°, and the reduction of 4-(3'-nitrophenyl)-benzenediazonium acid sulfate in boiling ethanol.⁸

References and Notes

1. Indiana University, Bloomington, Indiana.
 2. Elks and Hey, *J. Chem. Soc.*, **1943**, 441.
 3. Bachmann and Hoffman, in Adams, *Organic Reactions*, Vol. 2, p. 249, John Wiley & Sons, 1944.
 4. Gomberg and Bachmann, *J. Am. Chem. Soc.*, **46**, 2339 (1924); Blakey and Scarborough, *J. Chem. Soc.*, **1927**, 3000; Elks, Haworth, and Hey, *J. Chem. Soc.*, **1940**, 1284.
 5. Jacobsen and Loeb, *Ber.*, **36**, 4082 (1903).
 6. Hey and Walker, *J. Chem. Soc.*, **1948**, 2213.
 7. Nesmeyanov and Makarova, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **1947**, 213 [*C. A.*, **42**, 5441*a* (1948)].
 8. Fichter and Sulzberger, *Ber.*, **37**, 878 (1904).
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Appendix

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

potassium m-nitrobenzenediazotate

4-(3'-nitrophenyl)-benzenediazonium acid sulfate

ethanol (64-17-5)

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methanol (67-56-1)

sodium hydroxide (1310-73-2)

acetyl chloride (75-36-5)

sodium carbonate (497-19-8)

nitrogen (7727-37-9)

sodium nitrite (7632-00-0)

carbon dioxide (124-38-9)

Nitrobenzene (98-95-3)

urea (57-13-6)

nitroaniline

sodium carbonate decahydrate (6132-02-1)

dimethylamine (124-40-3)

benzenediazonium borofluoride

toluenesulfonic acid (88-20-0)

Biphenyl, 3-nitro-,
m-Nitrobiphenyl (2113-58-8)

sodium carbonate monohydrate (5968-11-6)

toluenesulfonic acid hydrate

m-nitroaniline (99-09-2)

m-nitrobenzoyl peroxide

m-nitrobenzenediazonium chloride

1-(m-Nitrophenyl)-3,3-dimethyltriazene (20241-06-9)

N-nitroso-m-nitroacetanilide

m-nitrobenzenediazohydroxide