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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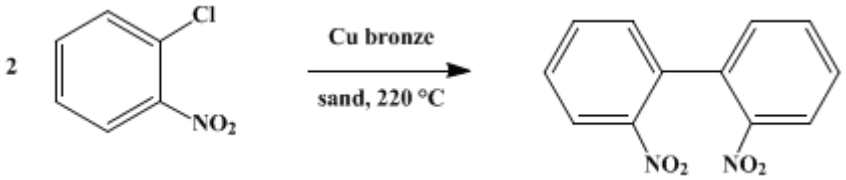
2,2'-DINITROBIPHENYL

[Biphenyl, 2,2'-dinitro-]



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1. Procedure

In a 1-l. flask equipped with a mechanical stirrer are placed 200 g. (1.27 moles) of *o*-chloronitrobenzene and 300 g. of clean dry sand. The mixture is heated in an oil bath to 215–225°, and then 200 g. of copper bronze (Note 1) is slowly added, the addition requiring about 1.2 hours (Note 2). The temperature is kept at 215–225° for 1.5 hours longer, the stirring being continued throughout. The mixture is poured while hot into a beaker containing 300–500 g. of sand and is then stirred until small clumps are formed; upon cooling, these are broken up in a mortar (Note 3). The mixture is boiled 10 minutes with two 1.5-l. portions of ethanol and removed by filtration each time. The filtrates are cooled in an ice bath, and the 2,2'-dinitrobiphenyl is collected on a filter (Note 4). A second crop is obtained by concentrating the filtrate. The product is dissolved in hot ethanol (Note 5), and the solution is treated with Norit, filtered, and cooled in an ice bath. The solid is recrystallized from hot ethanol and is obtained as pure, yellow crystals melting at 123.5–124.5° (cor). The yield is 80–95 g. (52–61%).

2. Notes

1. Ordinary copper bronze does not always give satisfactory results in the Ullmann reaction. More uniform results are obtained if the copper bronze is prepared as suggested by Kleiderer and Adams.[1] The copper bronze is treated with 2 l. of a 2% solution of iodine in acetone for 5–10 minutes. The product is then collected on a Büchner funnel, removed, washed by stirring into a slurry with 1 l. of a 1:1 solution of concentrated hydrochloric acid in acetone, and again filtered. The copper iodide dissolves, and the copper bronze remaining is separated by filtration and washed with acetone. It is then dried in a vacuum desiccator. It should be used immediately.
2. The temperature of the mixture must not be allowed to rise much above 240° or reduction of the nitro groups will occur and carbazole will be formed.
3. The reaction mixture should not be allowed to cool in the flask, as it will set to a hard mass; it is almost impossible to remove this from the flask.
4. If the first two extractions with ethanol do not yield about 90 g. of crude product, a third extraction of the sand and residue is well worth while (the yield of impure product was never less than 90 g. when this procedure was carried out).
5. If the impure material is recrystallized from the minimum amount of ethanol, the suction funnel will become rapidly plugged during filtration with consequent loss of time and material. Two liters of alcohol per 100 g. of 2,2'-dinitrobiphenyl is preferable. All filtrates were reduced to a small volume, and the crude material obtained was recrystallized twice, using Norit. (This amounted to about 10% of the total yield.)

3. Discussion

2,2'-Dinitrobiphenyl has been prepared by the action of copper on *o*-chloronitrobenzene, on *o*-bromonitrobenzene,[2,3] and on diazotized *o*-nitroaniline.[4]

References and Notes

1. Kleiderer and Adams, *J. Am. Chem. Soc.*, **55**, 4225 (1933).
2. Ullman and Bielecki, *Ber.*, **34**, 2174 (1901).
3. Mascarelli and Gatti, *Gazz. chim. ital.*, **67**, 807 (1937)
4. Niementowski, *Ber.*, **34**, 3325 (1901).

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

copper bronze

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

copper (7440-50-8)

iodine (7553-56-2)

acetone (67-64-1)

Norit (7782-42-5)

Biphenyl (92-52-4)

o-bromonitrobenzene (577-19-5)

o-chloronitrobenzene (88-73-3)

carbazole (86-74-8)

copper iodide (7681-65-4)

o-NITROANILINE (88-74-4)

2,2'-DINITROBIPHENYL (2436-96-6)