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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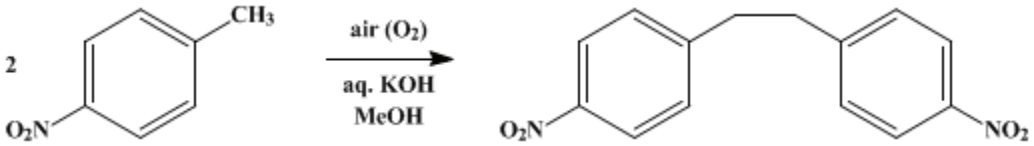
p,p'-DINITROBIBENZYL

[Bibenzyl, 4,4'-dinitro-]



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1. Procedure

In a 3-l. three-necked flask equipped with a mechanical stirrer and an inlet tube extending to the bottom of the flask is placed 2 l. of 30% methanolic potassium hydroxide (Note 1). The flask is immersed in an ice bath, and, when the solution has cooled to 10°, 100 g. (0.73 mole) of *p*-nitrotoluene (Note 2) is added to the flask. Vigorous stirring is begun, and a rapid stream of air from a compressed-air source is passed through the inlet tube. After 3 hours the ice bath is removed and the passage of air through the mixture is continued with uninterrupted, vigorous stirring for an additional 5 hours. The reaction mixture is immediately filtered with suction (Note 3), and the solid, while still on the filter, is washed with 2 l. of boiling water followed by 300 ml. of 95% ethanol at room temperature. The product is allowed to dry thoroughly in air and then is dissolved in a minimum quantity of boiling benzene (Note 4). The hot solution is filtered to remove a small amount of insoluble red-orange material and is allowed to cool. The *p,p'*-dinitrobibenzyl crystallizes as orange needles, m.p. 178–180°. The yield is 73–75 g. (74–76%). A second recrystallization from benzene gives yellow needles, m.p. 179–180°.

2. Notes

1. Thirty per cent methanolic potassium hydroxide may be prepared by dissolving 680 g. of C.P. (minimum 85%) potassium hydroxide pellets in 2 l. of methanol.
2. A good grade of *p*-nitrotoluene, m.p. 51–52°, such as supplied by the Eastman Kodak Company, was used.
3. A double layer of ordinary filter paper is satisfactory for this filtration.
4. Two to three liters of benzene is required. The checkers found the use of a heated funnel to be advantageous.

3. Discussion

p,p'-Dinitrobibenzyl has been prepared by the nitration of bibenzyl;[2] by the action of alkaline zinc chloride on *p*-nitrobenzyl chloride;[3] by the action of alkali on *p*-nitrotoluene;[4] by the oxidation of α,α-bis(*p*-nitrobenzyl) hydrazine with mercuric oxide;[5] and by the present method.[6] The course of the oxygen absorption in the latter reaction has been followed kinetically.[7]

References and Notes

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2. Rinkenbach and Aaronson, *J. Am. Chem. Soc.*, **52**, 5040 (1930); Tsekhanskii, *Izvest. Vysshykh Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, **1958**, No. 4, 61 [*C. A.*, **53**, 6150 (1959)].
3. Roser, *Ann.*, **238**, 363 (1887).
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6. Fuson and House, *J. Am. Chem.-Soc.*, **75**, 1325 (1953).

7. Tsuruta, Nagatomi, and Furukawa, *Bull. Inst. Chem. Research, Kyoto Univ.*, **30**, 46 (1952) [*C. A.*, **48**, 11369 (1954)].

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

methanolic potassium hydroxide

α,α-bis(p-nitrobenzyl) hydrazine

ethanol (64-17-5)

Benzene (71-43-2)

methanol (67-56-1)

oxygen (7782-44-7)

mercuric oxide (21908-53-2)

potassium hydroxide (1310-58-3)

zinc chloride (7646-85-7)

bibenzyl (103-29-7)

p-nitrotoluene (99-99-0)

p-nitrobenzyl chloride (100-14-1)

p,p'-DINITROBIBENZYL,
Bibenzyl, 4,4'-dinitro- (736-30-1)