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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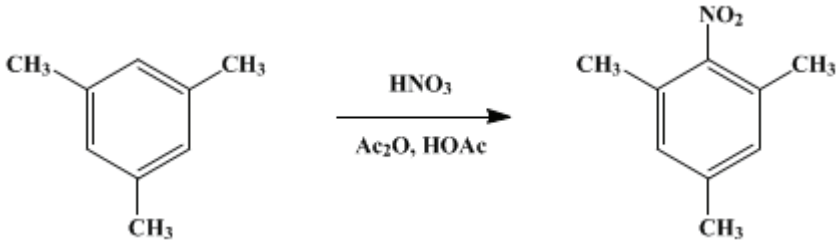
Organic Syntheses, Coll. Vol. 2, p.449 (1943); Vol. 14, p.68 (1934).

NITROMESITYLENE

[Mesitylene, 2-nitro-]



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1. Procedure

In a 500-cc. three-necked, round-bottomed flask, provided with a mechanical stirrer, a dropping funnel, and a thermometer well, are placed 40 g. (0.333 mole) of mesitylene (Org. Syn. Coll. Vol. I, **1941**, 341) and 60 g. (55.5 cc.) of acetic anhydride (Note 1). The flask is placed in a bath of ice and water, and the reaction mixture is cooled below 10°. A solution of 31.5 g. (20.8 cc., 0.5 mole) of fuming nitric acid (sp. gr. 1.51) in 20 g. (19.1 cc.) of glacial acetic acid and 20 g. (18.5 cc.) of acetic anhydride (Note 2) is added, with stirring, over a period of forty minutes, the temperature being kept between 15° and 20°.

When the addition of the nitric acid solution is complete, the reaction mixture is removed from the ice bath and allowed to stand at room temperature for two hours. The flask is then warmed, with shaking, to 50° on a water bath (Note 3) and maintained at that temperature for ten minutes. The cooled reactants are then poured slowly into 800 cc. of ice water and well stirred. About 40 g. of sodium chloride is added, and the aqueous layer is decanted and extracted with 200–250 cc. of a commercial grade of ether. The ethereal extract is added to the residual nitromesitylene, and this ethereal solution is washed with three or four 30-cc. portions of a 10–15 per cent sodium hydroxide solution until the water extract is distinctly alkaline. The ether is then distilled from a steam bath. The residue, after the addition of about 150 cc. of 10 per cent sodium hydroxide solution, is steam-distilled until a test sample of the distillate is clear and free of oil drops. The steam distillation requires about three hours, during which time 1.5 l. of distillate is collected. The nitromesitylene settles to the bottom of the distillate. The water is decanted through a filter paper, and the residue is dissolved in 30 cc. of ether. The filter paper, if it contains any solid particles, is washed with 10 cc. of ether, and the two fractions are combined and placed in a 150-cc. distilling flask with a water-cooled receiver. After removal of the ether on a steam bath, the yellow residue is distilled with a free flame. All but 0.5 to 1.5 g. of material distils at 243–250°, and the distillate, which weighs 47 g., solidifies on cooling. The yellow crystalline product is purified by dissolving in 25 cc. of commercial methyl alcohol and cooling with stirring in a bath of ice and salt. The crystals are then filtered on a small Büchner funnel and washed twice with 5-cc. portions of cold methyl alcohol. From the wash alcohol, by exactly the same procedure, there is obtained 6–8 g. of crude crystals boiling at 243–249°. This material yields on crystallization 4 g. of pure nitromesitylene. The pure nitromesitylene, which has a light yellow color, melts at 43–44°. The yield is 41–42 g. (74–76 per cent of the theoretical amount).

2. Notes

1. A commercial grade of 85 per cent acetic anhydride is of sufficient purity.
2. The nitric acid is added with care to the acetic acid-acetic anhydride solution, the temperature being kept below 20° by means of a bath of ice and salt. An **explosive** reaction will take place if the nitric acid is added too rapidly.

3. A higher temperature is not advisable.

3. Discussion

Nitromesitylene has been prepared by the direct nitration of mesitylene with concentrated nitric acid;[1] by the action of benzoyl nitrate on mesitylene in carbon tetrachloride at low temperature;[2] and from dinitromesitylene by reduction of one nitro group and replacement of the resulting amino group by hydrogen.[3]

References and Notes

1. Fittig and Storer, Ann. **147**, 1 (1868); Biedermann and Ledoux, Ber. **8**, 58 (1875); Schultz, ibid. **17**, 477 (1884); Bamberger and Rising, ibid. **33**, 3625 (1900).
2. Francis, ibid. **39**, 3801 (1906).
3. Ladenburg, ibid. **7**, 1135 (1874).

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

acetic acid (64-19-7)

methyl alcohol (67-56-1)

ether (60-29-7)

acetic anhydride (108-24-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

sodium chloride (7647-14-5)

carbon tetrachloride (56-23-5)

Mesitylene (108-67-8)

Nitromesitylene

Mesitylene, 2-nitro- (603-71-4)

benzoyl nitrate

dinitromesitylene