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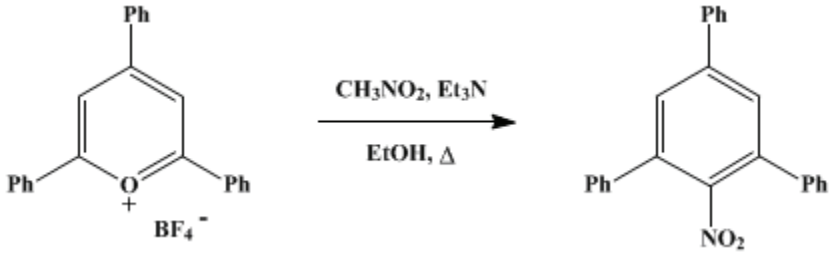
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.049.0114

Organic Syntheses, Coll. Vol. 5, p.1128 (1973); Vol. 49, p.114 (1969).

2,4,6-TRIPHENYLNITROBENZENE

[Benzene, 2-nitro-1,3,5-triphenyl-]



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Checked by Saul Cherkofsky and Richard E. Benson.

1. Procedure

In a 1-l. three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel are placed 119 g. (0.30 mole) of 2,4,6-triphenylpyrylium tetrafluoroborate (Note 1), 21 ml. (24 g., 0.39 mole) of nitromethane (Note 2), and 350 ml. of absolute ethanol (Note 3). Triethylamine (70 ml., 51 g.) (Note 4) is added rapidly from the dropping funnel to the well-stirred suspension. The reaction mixture becomes reddish brown immediately, and the solid dissolves. After all the triethylamine has been added, the mixture is heated under reflux for 3 hours, cooled, and allowed to stand overnight in a refrigerator. The crystalline product that separates is collected on a Buchner funnel and washed with two 50-ml. portions of ice-cold methanol. The product (75–80 g.; m.p. 142–144°) is recrystallized from 200–250 ml. of glacial acetic acid to yield 70–75 g. (67–71%) of 2,4,6-triphenylnitrobenzene as slightly yellow crystals, m.p. 144–145° (Note 5).

2. Notes

1. The preparation of 2,4,6-triphenylpyrylium tetrafluoroborate is described on p. 1135.
2. Nitromethane is dried over anhydrous calcium sulfate (Drierite) or calcium chloride for 1 day and distilled; the fraction with b.p. 101.5–102.5° is used.
3. Commercial absolute ethanol is used without additional drying.
4. Triethylamine is dried over sodium hydroxide pellets and distilled; the fraction with b.p. 89.5–90° is used.
5. The n.m.r. spectrum ($CDCl_3$) shows singlets at 7.45 p.p.m. (15 H) and 7.65 p.p.m. (2 H) (downfield from internal tetramethylsilane reference).

3. Discussion

2,4,6-Triphenylnitrobenzene may be prepared by direct nitration of 1,3,5-triphenylbenzene[2,3,4] and by the reaction of 2,4,6-triphenylpyrylium tetrafluoroborate with nitromethane.[5] The present procedure is an adaptation of the latter method.

This procedure illustrates a general method for converting substituted pyrylium salts to nitrobenzene derivatives. The reaction has been the subject of several reviews.[6,7,8] The yields are generally high, and under these conditions only a single product is formed, in contrast to the nitration of 1,3,5-triphenylbenzene. The preparation of 2,4,6-triphenylnitrobenzene from the corresponding pyrylium salt eliminates isomer separation problems, which are encountered when the direct nitration procedure is used. Also, labeled compounds can readily be prepared by this method.[9]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 1130

References and Notes

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8. K. Dimroth, W. Krafft, and K. H. Wolf, in T. Urbánski, "Nitro Compounds," Pergamon Press, Oxford, 1964, p. 361 [*Tetrahedron*, **20, Suppl. 1**, 361 (1964)].
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

calcium sulfate (Drierite)

ethanol (64-17-5)

calcium chloride (10043-52-4)

acetic acid (64-19-7)

methanol (67-56-1)

sodium hydroxide pellets (1310-73-2)

Nitromethane (75-52-5)

triethylamine (121-44-8)

2,4,6-Triphenylnitrobenzene,
Benzene, 2-nitro-1,3,5-triphenyl- (10368-47-5)

2,4,6-Triphenylpyrylium tetrafluoroborate (448-61-3)

1,3,5-triphenylbenzene (612-71-5)