



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.

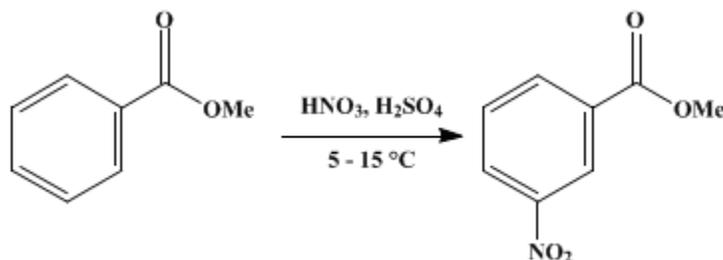
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.372 (1941); Vol. 3, p.71 (1923).

METHYL *m*-NITROBENZOATE

[Benzoic acid, *m*-nitro-, methyl ester]



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1. Procedure

Into a 2-l. round-bottomed flask fitted with a mechanical stirrer are placed 400 cc. of concentrated [sulfuric acid](#) cooled to 0° and 204 g. (1.5 moles) of pure [methyl benzoate](#) ([Note 1](#)). The mixture is cooled by means of an ice bath to 0–10° and then, with stirring, there is added gradually, by means of a dropping funnel, a mixture of 125 cc. (1.96 moles) of concentrated [nitric acid](#) (sp. gr. 1.42) and 125 cc. of concentrated [sulfuric acid](#). During the addition of the nitrating acid, which requires about one hour, the temperature of the reaction mixture should be kept within the range 5–15° ([Note 2](#)).

After the [nitric acid](#) has been added, stirring is continued for fifteen minutes longer; the mixture is then poured upon 1300 g. of cracked ice. The crude [methyl *m*-nitrobenzoate](#) separates as a solid and is filtered off by means of suction and washed with water. The product is placed in a flask and agitated with 200 cc. of ice-cold [methyl alcohol](#) in order to remove a small amount of *o*-nitrobenzoic ester and other impurities that are present. The cooled mixture is then filtered by means of suction, washed with another 100-cc. portion of cold [methyl alcohol](#) ([Note 3](#)), and the solid dried. The yield is 220–230 g. (81–85 per cent of the theoretical amount) ([Note 4](#)) of an almost colorless product melting at 74–76°. In order to obtain a product of maximum purity, which melts at 78°, it is advisable to recrystallize the ester from an equal weight of [methyl alcohol](#).

2. Notes

1. It is necessary that the [methyl benzoate](#) should be of high purity and dissolve in [sulfuric acid](#) without color. Commercial [methyl benzoate](#) which does not meet the latter specification may give yields about 10 per cent lower. Directions for the preparation of [methyl benzoate](#) are given in *Org. Syn.* **10**, 51, [Note 13](#).
2. The nitration of [methyl benzoate](#) runs unusually smoothly, but it is essential to keep the temperature within the specified limits, otherwise the yield falls; at 50°, 193 g. of solid product is obtained, while at 70° the yield falls to 130 g.
3. On diluting the methyl alcoholic filtrate with water, 10–20 cc. of oil separates; more of this oil is formed by nitrating at higher temperatures, amounting to 57 cc. at 50° and 100 cc. at 70°. The oil consists not merely of [methyl *o*-nitrobenzoate](#) with some of the meta compound but contains also traces of dinitrobenzoic ester and nitrophenolic compounds. Unchanged [methyl benzoate](#) does not appear to be present.
4. The nitration method is also adaptable to the preparation of [ethyl *m*-nitrobenzoate](#). The yield is, however, slightly lower, owing to the greater solubility of the ethyl ester.

3. Discussion

[Methyl *m*-nitrobenzoate](#) can be prepared by the esterification of [m-nitrobenzoic acid](#);¹ this method

is, however, obviously much less satisfactory than nitration of [methyl benzoate](#). Nitration by means of fuming [nitric acid](#) can also be applied to [methyl benzoate](#),² but the use of the ordinary nitration mixture of concentrated [sulfuric acid](#) and concentrated [nitric acid](#) is more satisfactory. Treatment of [ω-trichloro-*m*-nitroacetophenone](#) with [methyl alcohol](#) and [sodium methoxide](#) also furnishes [methyl *m*-nitrobenzoate](#).³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 391](#)

References and Notes

1. Chancel, Ann. **72**, 275 (1849).
 2. Taverne, Rec. trav. chim. **17**, 97, 100 (1898).
 3. Houben and Fischer, Ber. **64**, 2639 (1931).
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Appendix

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

[sulfuric acid](#) (7664-93-9)

[methyl alcohol](#) (67-56-1)

[nitric acid](#) (7697-37-2)

[sodium methoxide](#) (124-41-4)

[methyl benzoate](#) (93-58-3)

[*m*-Nitrobenzoic acid](#) (121-92-6)

[Methyl *m*-nitrobenzoate,
Benzoic acid, *m*-nitro-, methyl ester](#) (618-95-1)

[methyl *o*-nitrobenzoate](#) (606-27-9)

[Ethyl *m*-nitrobenzoate](#) (618-98-4)

[ω-trichloro-*m*-nitroacetophenone](#)