



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](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.

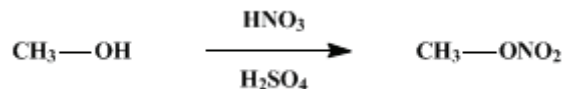
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.*

*Organic Syntheses, Coll. Vol. 2, p.412 (1943); Vol. 19, p.64 (1939).*

## METHYL NITRATE



Submitted by Alvin P. Black and Frank H. Babers.  
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### 1. Procedure

In a flask cooled in an ice bath are mixed 425 g. (300 cc., 4.7 moles) of c.p. nitrous-free, concentrated **nitric acid** (sp. gr. 1.42) (**Note 1**) and 550 g. (300 cc.) of c.p. concentrated **sulfuric acid** (sp. gr. 1.84). In a second flask, also cooled in an ice bath, 92 g. (50 cc.) of c.p. concentrated **sulfuric acid** is added to 119 g. (150 cc., 3.7 moles) of pure **methyl alcohol** (**Note 2**) while the temperature is maintained below 10°.

One-third of the cold nitric-sulfuric mixture is placed in each of three 500-cc. Erlenmeyer flasks (**Note 3**), and each portion is treated separately with one-third of the methyl alcohol-sulfuric acid mixture, with constant shaking and thorough mixing (**Note 4**). The temperature is allowed to rise fairly rapidly to 40° and kept at this point by external cooling. During the addition of the methyl alcohol-sulfuric acid, most of the ester separates as an almost colorless oily layer above the acid. The time required for completion of the reaction is two to three minutes for each flask. The reaction mixtures are allowed to stand in the cold for an additional fifteen minutes but not longer. The lower layer of spent acid is separated promptly and poured at once into a large volume of cold water (about 1 l. for each portion) to avoid decomposition which quickly ensues with copious evolution of nitrous fumes.

The combined ester layers are washed with two 25-cc. portions of ice-cold salt solution (sp. gr. 1.17) (**Note 5**). A small quantity (8–10 drops) of concentrated **sodium hydroxide** solution is added to the second wash liquid until it has a faintly alkaline reaction to litmus. The ester is washed free of alkali with ice-cold salt solution and finally washed with two 15-cc. portions of ice water (**Note 6**). The product is treated with 10–15 g. of anhydrous **calcium chloride** and allowed to stand with occasional shaking for an hour at 0°. It is then decanted onto a fresh 5-g. portion of the drying agent and after standing for one-half hour is filtered. The crude ester without further purification (**Note 7**) may be used directly for most synthetic purposes, such as the preparation of **phenylnitromethane** (p. 512). The yield is 190–230 g. (66–80 per cent of the theoretical amount). *The crude ester should be used promptly and not stored.*

### 2. Notes

1. Colored specimens of **nitric acid** may be treated with a small quantity of **urea** (about 1–2 g. per 100 cc.), but this is unnecessary unless the acid is appreciably colored.
2. Commercial synthetic **methanol** of high grade was used without further purification. This material is believed to be superior to wood alcohol for this preparation.
3. It should be noted that volume contractions occur in mixing the reagents. The total volume of the mixed acids is about 585 cc. (instead of 600 cc.), and that of the **methyl alcohol-sulfuric acid** is about 182 cc. (instead of 200 cc.).
4. *The treatment of methyl alcohol with a mixture of concentrated nitric and sulfuric acids is not without elements of danger, and adequate precautionary measures should be taken.* However, the submitters report that more than one hundred preparations were carried out without a single explosion or violent decomposition.
5. This corresponds to a 22 per cent solution of **sodium chloride**. This particular solution was found to give satisfactory separations and obviate emulsions.
6. Traces of acid remaining in the ester facilitate decomposition, and violent explosions may occur if such specimens are heated.

7. [Methyl nitrate](#) may be distilled if adequate precautions are taken. The ester must not be heated suddenly and must not contain any free acid. *Distillation is not recommended*, as the crude ester (after washing and drying) gives as good yields as the distilled product in most synthetic reactions. The loss in distillation is small, and the pure material distils at 64.5–65°. *The residue in the distilling flask must not be superheated.*

### 3. Discussion

[Methyl nitrate](#) has been prepared by distilling a [methyl alcohol-nitric acid](#) mixture to which [methyl alcohol-sulfuric acid](#) is added dropwise,<sup>1</sup> and by the use of dilute [nitric acid](#) in a procedure otherwise similar to that given above.<sup>2</sup> Neither of these methods is satisfactory, and explosions occur frequently.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 512](#)

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### References and Notes

1. Lea, *Am. J. Sci.* (2) **33**, 227 (1862) (*Chem. Zentr.* **1862**, 602).
2. Delépine, *Bull. soc. chim.* (3) **13**, 1044 (1895).

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### Appendix

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

[calcium chloride](#) (10043-52-4)

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

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

[sodium hydroxide](#) (1310-73-2)

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

[sodium chloride](#) (7647-14-5)

[urea](#) (57-13-6)

[Methyl nitrate](#) (598-58-3)

[Phenylnitromethane](#) (622-42-4)