



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. 3, p.803 (1955); Vol. 21, p.105 (1941).

TETRANITROMETHANE

[Methane, tetranitro-]



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Checked by Nathan L. Drake and Ralph Mozingo.

1. Procedure

Caution! The product is toxic. The reaction should be carried out in a hood.

In a 250-ml. Erlenmeyer flask provided with a two-holed stopper which has a slit cut in one edge to serve as an air vent and which holds a thermometer, the bulb of which reaches almost to the bottom of the flask, is placed 31.5 g. (0.5 mole) of anhydrous [nitric acid](#) (Note 1). The flask is cooled below 10° in ice water, and 51 g. (0.5 mole) of [acetic anhydride](#) (Note 2) is slowly added from a buret through the second hole in the stopper in portions of about 0.5 ml. at a time. The temperature of the reaction mixture is never allowed to rise above 10° (Note 3). After about 5 ml. of the [acetic anhydride](#) has been added the reaction becomes less violent, and larger portions, increasing gradually from 1 to 5 ml., may be introduced at a time with constant shaking. After all the [acetic anhydride](#) has been added, the stopper and the thermometer are removed. The neck of the flask is wiped clean with a towel, and the flask is then covered with an inverted beaker and allowed to come up to room temperature in the original ice bath (Note 4).

The mixture is allowed to stand at room temperature for 7 days (Note 5), and the [tetranitromethane](#) is separated by pouring the mixture into 300 ml. of water in a 500-ml. round-bottomed flask and steam distilling (Note 6). The [tetranitromethane](#) passes over with the first 20 ml. of the distillate. The heavy product is separated from the upper layer of water, washed first with dilute alkali, finally with water, and dried over anhydrous [sodium sulfate](#). The yield of [tetranitromethane](#) is 14–16 g. (57–65%). *The product should not be distilled, as it may decompose with explosive violence.* [Tetranitromethane](#) must be kept out of contact with aromatic compounds except in *very small* test portions, since violently explosive reactions can occur (Note 7).

2. Notes

1. The anhydrous [nitric acid](#) (sp. gr. > 1.53) is most easily obtained by slowly distilling ordinary fuming [nitric acid](#) from its own bulk of concentrated [sulfuric acid](#). If ordinary concentrated [nitric acid](#) (sp. gr. 1.42) is used, it is advisable to distil twice from equal volumes of [sulfuric acid](#). A technical grade of fuming [nitric acid](#) having a specific gravity of 1.60 was found to give satisfactory yields when used without further treatment; but an equivalent amount of a weaker commercial acid, corresponding to 98% [nitric acid](#) by gravity, gave considerably lower yields. The use of more than the calculated amount of [nitric acid](#) decreases the yield of [tetranitromethane](#).
2. According to the submitter, the purity of [acetic anhydride](#) is not so important as that of the [nitric acid](#). Equivalent amounts of 99–100% and 94–95% [acetic anhydride](#) gave practically the same yield of [tetranitromethane](#).
3. If the flask is not cooled, the reaction proceeds more and more vigorously as the temperature rises and may, if unchecked, become violent.
4. If the flask is removed from the ice bath after the addition of the anhydride, and allowed to stand at room temperature, the reaction may become violent with great loss of product.
5. The yield is only 35% after 2 days and no greater than 65% after 10–15 days. If it should be necessary to obtain the product in shorter time, the reaction mixture may be allowed to stand at room temperature for 48 hours and then slowly heated to 70° during an interval of 3 hours and maintained at 70° for 1 hour longer before pouring into water. The yield of a run carried out in this way was,

according to the submitter, 40%.

6. It is most convenient to use a 50-ml. graduated separatory funnel as the receiver during the steam distillation, if it is desired to estimate roughly the yield of [tetranitromethane](#), the density of which is 1.65 at 15°.

7. [Tetranitromethane](#) is a valuable reagent for detecting the presence of double bonds, especially those which do not give the ordinary reactions of such linkages.¹

3. Discussion

The procedure described is essentially that of Chattaway.² [Tetranitromethane](#) has also been prepared by nitrating [nitroform](#),³ from [acetic anhydride](#) by the action of diacetylorthonitric acid,⁴ from iodopicrin and [silver nitrite](#),⁵ from [acetyl nitrate](#) by heating with [acetic anhydride](#) or glacial [acetic acid](#),⁶ from [nitrobenzene](#) by distilling with a mixture of [nitric acid](#) and fuming [sulfuric acid](#),⁷ by adding [acetic anhydride](#) to [nitrogen pentoxide](#) or a mixture of [nitrogen pentoxide](#) and [nitrogen peroxide](#),⁸ by the action of [acetic anhydride](#) on highly concentrated [nitric acid](#),⁹ from [toluene](#) by nitration,¹⁰ from [acetylene](#) by the action of [nitric acid](#),¹¹ from [nitrobenzene](#) and a mixture of nitric and fuming nitric acids,¹² and from [acetylene](#) and [ethylene](#) by the action of [nitric acid](#) in the presence of a catalyst.¹³

References and Notes

1. Meyer, H., *Analyse und Konstitutionsermittlung organischer Verbindungen*, 6th ed., p. 773, Julius Springer, Vienna, 1938; Ruzicka, Huyser, Pfeiffer, and Seidel, *Ann.*, **471**, 21 (1929).
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4. Pictet and Genequand, *Ber.*, **36**, 2225 (1903).
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6. Pictet and Khotinsky, *Compt. rend.*, **144**, 210 (1907); *Ber.*, **40**, 1163 (1907).
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10. Will, *Ber.*, **47**, 704 (1914).
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12. McKie, *J. Soc. Chem. Ind.*, **44**, 430T (1925).
13. McKie, *J. Chem. Soc.*, **1927**, 962.

Appendix

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

diacetylorthonitric acid

iodopicrin

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

[acetylene](#) (74-86-2)

[acetic acid](#) (64-19-7)

[acetic anhydride](#) (108-24-7)

nitric acid (7697-37-2)

sodium sulfate (7757-82-6)

toluene (108-88-3)

Nitrobenzene (98-95-3)

ethylene (9002-88-4)

silver nitrite (7783-99-5)

tetranitromethane,
Methane, tetranitro- (509-14-8)

nitrogen peroxide

nitrogen pentoxide

nitroform

acetyl nitrate (591-09-3)