



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.

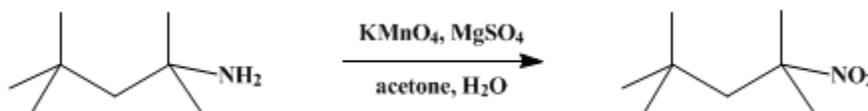
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 5, p.845 (1973); Vol. 43, p.87 (1963).*

## 4-NITRO-2,2,4-TRIMETHYLPENTANE

[Pentane, 2,2,4-trimethyl-4-nitro-]



Submitted by Nathan Kornblum and Willard J. Jones<sup>1</sup>.  
Checked by William G. Dauben and Paul R. Resnick.

### 1. Procedure

A solution of 25.8 g. (0.20 mole) of 4-amino-2,2,4-trimethylpentane (*tert*-octylamine) (Note 1) in 500 ml. of C.P. acetone is placed in a 1-l. three-necked flask equipped with a "Tru-Bore" stirrer and a thermometer and is diluted with a solution of 30 g. of magnesium sulfate (Note 2) in 125 ml. of water. Potassium permanganate (190 g., 1.20 moles) is added to the well-stirred reaction mixture in small portions over a period of about 30 minutes (Note 3). During the addition the temperature of the mixture is maintained at 25–30° (Note 4), and the mixture is stirred for an additional 48 hours at this same temperature (Note 5). The reaction mixture is stirred under water-aspirator vacuum at an internal temperature of about 30° until most of the acetone is removed (Note 6). The resulting viscous mixture is steam-distilled; approximately 500 ml. of water and a pale-blue organic layer are collected. The distillate is extracted with pentane, the extract is dried over anhydrous sodium sulfate, and the pentane is removed by distillation at atmospheric pressure. The residue is distilled through a column (Note 7) at reduced pressure to give 22–26 g. (69–82%) of colorless 4-nitro-2,2,4-trimethylpentane, b.p. 53–54°/3 mm.,  $n_D^{28}$  1.4314, m.p. 23.5–23.7°.

### 2. Notes

1. The *tert*-octylamine employed was redistilled commercial-grade material, b.p. 140°/760 mm.,  $n_D^{20}$  1.4240.
2. The magnesium sulfate was purified dried powder of J. T. Baker Chemical Co. This is approximately 70% magnesium sulfate and 30% water.
3. Good agitation prevents the permanganate from caking on the bottom of the flask. The formation of a cake results in local overheating and consumption of the permanganate as mentioned in (Note 4).
4. If a constant-temperature bath is not available, a bucket of water, initially at 25°, serves to dissipate the heat of reaction. At higher temperatures the potassium permanganate is rapidly consumed, presumably by reaction with the acetone.
5. At the end of the reaction time there was no unreacted amine as shown by the following test: A 10-ml. aliquot was filtered through "Supercel" to remove the manganese dioxide, and the filtrate was added to a mixture of 25 ml. of benzene and 25 ml. of water. Extraction of the benzene layer with 10% hydrochloric acid, followed by the addition of sodium hydroxide, gave no oil layer or characteristic odor of the free amine.
6. If agitation becomes difficult during the concentration, 100 ml. of water can be added to give a more fluid mixture.
7. A 60-cm. × 1-cm. externally heated column packed with 4-mm. glass helices and equipped with a total-reflux variable take-off head was used.

### 3. Discussion

The procedure described is that of Kornblum, Clutter, and Jones.<sup>2</sup> 4-Nitro-2,2,4-trimethylpentane has been prepared previously, in low yield, by allowing isoöctane to react with concentrated nitric acid in a sealed tube at elevated temperature.<sup>3</sup>

#### 4. Merits of the Preparation

This is a general method of preparing trialkylnitromethanes from the corresponding (trialkylmethyl) amines.<sup>2,4</sup> Table I lists seven prepared in this way. The procedure is simple and reliable, and the yields of product are high. Other methods give mixtures of products and low yields of nitro compounds and are inconvenient to perform.

TABLE I SYNTHESIS OF  
TRIALKYLNITROMETHANES, R<sub>3</sub>CNO<sub>2</sub>

Nitro Compound	Yield, %
2-Nitro-2-methylpropane	83
2-Nitro-2,3-dimethylbutane	71
2-Nitro-2,4-dimethylpentane	82
1-Nitro-1-methylcyclopentane	72
1-Nitro-1-methylcyclohexane	73
1-Nitro-1,4-dimethylcyclohexane	70
1,8-Dinitro- <i>p</i> -methane	61

<sup>a</sup> This oxidation was carried out in water.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 355
- Org. Syn. Coll. Vol. 6, 803

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#### References and Notes

1. Department of Chemistry, Purdue University, West Lafayette, Indiana. This research was supported by the United States Air Force under Contract No. AF 18(600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.
2. N. Kornblum, R. J. Clutter, and W. J. Jones, *J. Am. Chem. Soc.*, **78**, 4003 (1956).
3. S. S. Nametkin and K. S. Zabrodina, *Doklady Akad. Nauk SSSR*, **75**, 395 (1950) [*C.A.*, **45**, 6998 (1951)].
4. N. Kornblum, *Org. Reactions*, **12**, 115 (1962).

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

1,8-Dinitro-*p*-methane

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

potassium permanganate (7722-64-7)

sodium sulfate (7757-82-6)

acetone (67-64-1)

manganese dioxide (1313-13-9)

Pentane (109-66-0)

magnesium sulfate (7487-88-9)

1-Nitro-1-methylcyclohexane

4-Nitro-2,2,4-trimethylpentane,  
Pentane, 2,2,4-trimethyl-4-nitro- (5342-78-9)

4-amino-2,2,4-trimethylpentane (107-45-9)

2-Nitro-2-methylpropane (594-70-7)

2-Nitro-2,3-dimethylbutane

2-Nitro-2,4-dimethylpentane

1-Nitro-1-methylcyclopentane (30168-50-4)

1-Nitro-1,4-dimethylcyclohexane

tert-octylamine