



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.

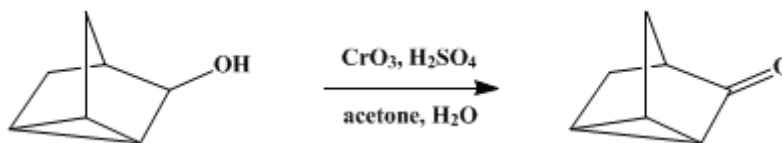
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.866 (1973); Vol. 45, p.77 (1965).

NORTRICYCLANONE

[Tricyclo[2.2.1.0^{2,6}]heptan-3-one]



Submitted by J. Meinwald, J. Crandall, and W. E. Hymans¹.

Checked by J. R. Roland and B. C. McKusick.

1. Procedure

The oxidation reagent is prepared by dissolving 70 g. (0.70 mole) of **chromium trioxide** in 100 ml. of water in a 500-ml. beaker. The beaker is immersed in an ice bath, and 112 g. (61 ml., 1.10 moles) of concentrated (18*M*) **sulfuric acid** followed by 200 ml. of water is added cautiously with manual stirring. The solution is cooled to 0–5°.

A solution of 110 g. (1.00 mole) of nortricyclanol (**Note 1**) in 600 ml. of **acetone** (analytical reagent grade) is cooled to 0–5° in a 2-l. three-necked flask immersed in an ice bath and equipped with an efficient mechanical stirrer, a thermometer, and a dropping funnel with a pressure-equalizing arm. The cooled oxidation reagent prepared above is poured into the dropping funnel, and the reagent is added with vigorous stirring, at a rate to maintain the temperature of the reaction mixture at about 20°. The stirring is continued for 3 hours after the addition is completed.

Sodium bisulfite is added in small portions until the brown color of **chromic acid** is gone from the upper layer of the two-phase mixture. The top layer is decanted, and the dense, green, lower layer is extracted with 200 ml. of 30–60° petroleum ether. Combination of this extract with the original upper layer causes a separation into two phases. The lower phase is drawn off and added to the original lower phase, which is then extracted with three 200-ml. portions of 30–60° petroleum ether (**Note 2**). The extracts are combined, washed successively with two 50-ml. portions of saturated **sodium chloride**, two 50-ml. portions of saturated **sodium bicarbonate** solution, and 50 ml. of saturated **sodium chloride** solution, and dried over **magnesium sulfate**. The solvent is removed by distillation through a short column containing glass helices, and the residue is distilled under reduced pressure to give 85–95 g. (79–88%) of nortricyclanonone, b.p. 103–105° (77 mm.), *n*²⁶_D 1.4873 (**Note 3**) and (**Note 4**).

2. Notes

1. The preparation of nortricyclanol is described in this volume, p. 863. The crude, unsublimed nortricyclanol is a satisfactory starting material.
2. Sufficient time between extraction and separation of layers must be allowed, for the organic layer separates slowly from the thick aqueous phase.
3. The product was shown to contain <1% of the starting material and no other detectable impurity by vapor-phase chromatographic analysis.
4. The reported² properties of this material are b.p. 78–79° (24 mm.), *n*²⁵_D 1.4878.

3. Discussion

Nortricyclanonone has been prepared by oxidation of nortricyclanol using **chromic acid** in **acetic acid**^{2,3} and using a modified Oppenauer reaction.⁴ The present procedure is based on the Jones modification⁵ of **chromic acid** oxidations.

4. Merits of the Preparation

This preparation illustrates a general and convenient way of oxidizing secondary alcohols to ketones. The novel feature of the reaction is represented by [acetone](#) solvent which affects markedly the properties of the oxidizing agent. The reaction is very rapid (if not instantaneous), and the yields are high, the reagent rarely attacking unsaturated centers. The procedure is applicable to acetylenic carbinols, allyl and other unsaturated alcohols, and saturated carbinols. The main limitation is the low solvent power of [acetone](#). Another example of the Jones oxidation is given on [p. 310](#) of this volume.

An attractive alternative to the Jones oxidation is oxidation with [chromic acid](#) in the two-phase system, water-[ether](#), the details of which were reported recently;⁶ however, this method has not been applied to the preparation of nortricyclanol.

The preparation illustrates the utility of the reaction in preparing the highly strained and reactive nortricyclanol, a compound of current interest in studies of strained ring systems.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 863](#)
- [Org. Syn. Coll. Vol. 6, 1033](#)

References and Notes

1. Department of Chemistry, Cornell University, Ithaca, New York.
 2. H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).
 3. J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950); H. Krieger, *Suomen Kemistilehti*, **32B**, 109 (1959).
 4. K. Alder, F. H. Flock, and H. Wirtz, *Ber.*, **91**, 609 (1958).
 5. R. G. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, *J. Chem. Soc.*, 457 (1953).
 6. H. C. Brown, C. P. Garg, and K.-T. Liu, *J. Org. Chem.*, **36**, 387 (1971).
-

Appendix

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

petroleum ether

Nortricyclanol

Nortricyclanolone

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

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

[ether](#) (60-29-7)

[sodium bicarbonate](#) (144-55-8)

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

[sodium bisulfite](#) (7631-90-5)

acetone (67-64-1)

chromic acid (7738-94-5)

magnesium sulfate (7487-88-9)

chromium trioxide (1333-82-0)

Tricyclo[2.2.1.0^{2,6}]heptan-3-one (695-05-6)