Organic Syntheses

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.

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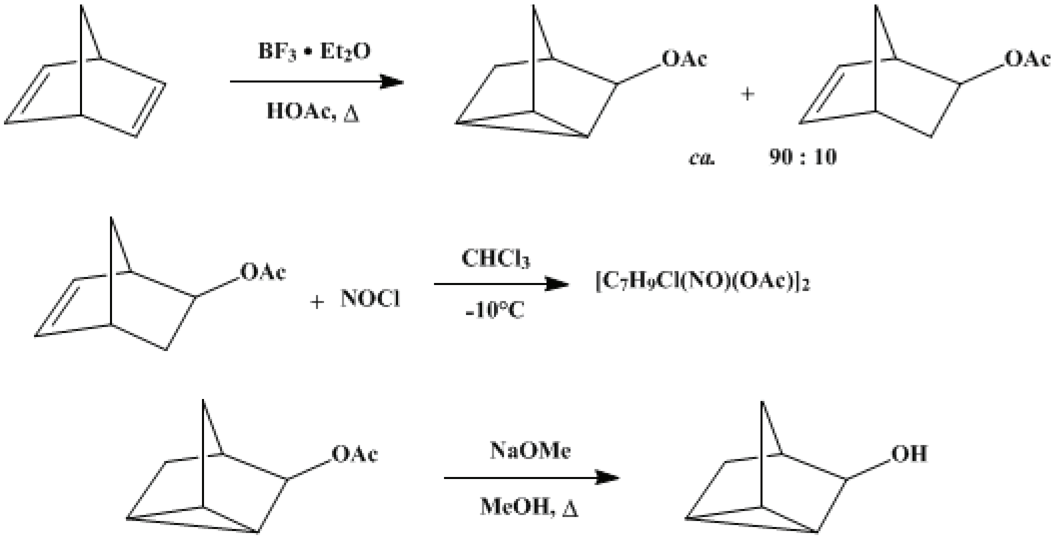
NORTRICYCLANOL

[Tricyclo[2.2.1.$0^{2,6}$]heptan-3-ol]



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1. Procedure

A. *Nortricyclyl acetate*. A mixture of 156 g. (1.70 moles) of bicyclo[2.2.1]hepta-2,5-diene (Note 1), 105 g. (100 ml., 1.75 moles) of glacial acetic acid, and 3 ml. of boron trifluoride etherate (Note 2) is placed in a 500-ml. flask attached to a condenser equipped with a drying tube. The mixture is heated on a steam bath for 6 hours, cooled to room temperature, and diluted with 250 ml. of ether. The ethereal solution is washed successively with two 50-ml. portions of 3*N* ammonia and 50 ml. of water and dried over magnesium sulfate. The ether is removed by distillation through a short column of glass helices, and the dark residue is distilled under reduced pressure to give about 200 g. of a mixture of nortricyclyl acetate and bicyclo[2.2.1]hepta-5-en-2-yl acetate as a colorless liquid, b.p. 85–95° (15 mm.) (Note 3).

The acetate mixture is dissolved in 500 ml. of chloroform (analytical reagent grade) in a 2-l. Erlenmeyer flask equipped with a thermometer and a gas-inlet tube and located in a good hood. *Caution! All operations using nitrosyl chloride should be performed in a good hood.* The solution is cooled to −10° in an ice-salt bath, and nitrosyl chloride (Note 4) is bubbled into the solution with swirling at −10° ± 3° until the color of the solution changes through bright green to a brownish green that indicates excess nitrosyl chloride. A white precipitate begins to form at this point. There is added 500 ml. of 30–60° petroleum ether, and the mixture is cooled at −10° ± 3° for an additional 15 minutes. The precipitated nitrosyl chloride adduct (Note 5) is collected by suction filtration *(Caution! Hood)*. The filtrate is washed successively with two 200-ml. portions of saturated sodium carbonate solution and 500 ml. of saturated sodium chloride and dried over magnesium sulfate. The solvent is removed through a short column of glass helices, and the dark residue is distilled under reduced pressure *(Caution! (Note 6))* to give 132–167 g. (52–66%) of nortricyclyl acetate as a faintly green liquid, b.p. 83–85° (13 mm.), n^{25}D 1.4673–1.4681 (Note 7).

B. *Nortricyclanol*. The nortricyclyl acetate obtained above is added to a solution of 0.5 g. of sodium in 500 ml. of anhydrous methanol (analytical grade reagent). The solution is heated on a steam bath, and the methanol is slowly distilled through a short column packed with glass helices (Note 8). The residue is cooled, diluted with 250 ml. of 30–60° petroleum ether, and the solution is washed with two 50-ml. portions of water and dried over magnesium sulfate. The solvent is removed by distillation through a short column packed with glass helices, finally at 25° and water-pump pressure. The crude product, which solidifies on cooling, is sublimed at 80° (2 mm.) to yield 84–107 g. (45–57% based on bicycloheptadiene; (Note 9)) of nortricyclanol, m.p. 108–110°. It is pure enough for most purposes. A slightly purer product is obtained by resublimation (Note 10).

2. Notes

1. Bicycloheptadiene supplied by Shell Chemical Corporation can usually be used without purification. If the material is cloudy or contains a precipitate, it should be distilled before being used.
2. The purified grade of Eastman Organic Chemicals is satisfactory. After the procedure had been checked, the submitters found that the use of only 1 ml. of this reagent gave the specified yield more consistently.
3. The exact proportion of unsaturated acetate varies slightly but is typically 10–15% as determined by vapor-phase chromatography.
4. Nitrosyl chloride from the Matheson Company is satisfactory.
5. The adduct may be recrystallized from chloroform to give a white crystalline product, m.p. 152–153°.
6. The hot residue decomposes vigorously with the evolution of irritating gases when opened to the atmosphere. Consequently, the distillation flask should be cooled to room temperature before breaking the vacuum.
7. Vapor-phase chromatographic analysis of this product showed less than 1% of isomeric material.
8. The checkers used a 1.3-cm. × 25-cm. column of helices and removed the solvent over a period of about 5 hours.
9. The yield of nortricyclanol from nortricyclyl acetate is 82–95%.
10. Vapor-phase chromatography shows no detectable impurities under conditions where <1% of isomeric material would be easily visible. A melting point of 108–109° has been reported.[2]

3. Discussion

The addition of carboxylic acids to bicyclo[2.2.1]hepta-2,5-diene has been described by several authors;[3] [4] [5] [6] the method described here is a modification of these procedures. Nortricyclanol has been prepared by the hydration of bicyclo[2.2.1]hepta-2,5-diene[7] and the solvolysis of nortricyclyl[2] and bicyclo[2.2.1]hept-2-en-5-yl[8] halides, as well as by the saponification[3], [9] and transesterification[5] of the corresponding esters. The described conversion of the acetate to the alcohol is patterned after a similar procedure of Hall.[5]

4. Merits of the Preparation

The present preparation affords high-purity nortricyclanol in good yield without the necessity of tedious purification. It illustrates a convenient way to convert olefins to alcohols and to remove olefinic impurities from alcohols. Nortricyclanol is of current interest in studies of highly strained ring systems. It is readily oxidized to nortricyclanone.[10]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 310
- Org. Syn. Coll. Vol. 5, 866
- Org. Syn. Coll. Vol. 8, 350

References and Notes

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

petroleum ether

Nortricyclyl acetate

Nortricyclanol

Nortricyclanone

acetic acid (64-19-7)

ammonia (7664-41-7)

methanol (67-56-1)

ether (60-29-7)

chloroform (67-66-3)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

sodium (13966-32-0)

nitrosyl chloride (2696-92-6)

magnesium sulfate (7487-88-9)

boron trifluoride etherate (109-63-7)

bicyclo[2.2.1]hepta-2,5-diene

Tricyclo[2.2.1.$0^{2,6}$]heptan-3-ol (695-04-5)

bicyclo[2.2.1]hepta-5-en-2-yl acetate

bicycloheptadiene