



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.

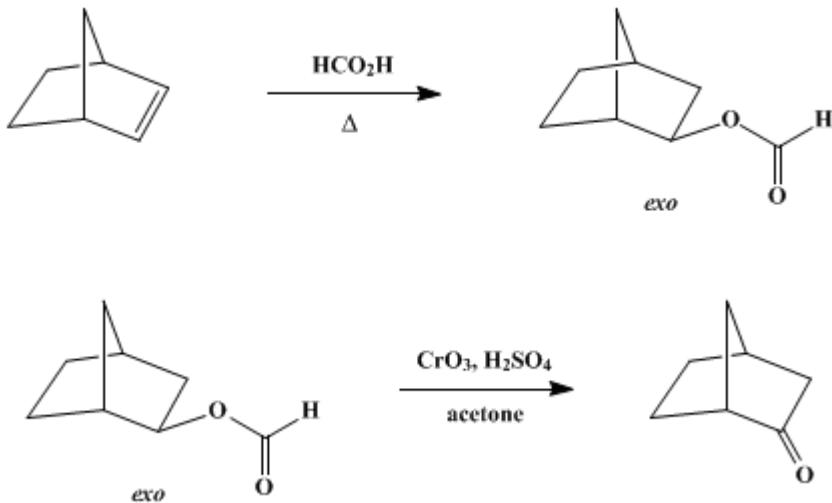
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.852 (1973); Vol. 42, p.79 (1962).

2-NORBORANONE

[Norcamphor]



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1. Procedure

A. *2-exo-Norbornyl formate*. Approximately 800 g. (17.44 moles) of 98–100% **formic acid** (Note 1) is added to 400 g. (4.25 moles) of nobornene (Note 2) in a 2-l. round-bottomed flask equipped with a condenser, and the mixture is boiled under reflux for 4 hours (Note 3). The dark solution is cooled and the flask arranged for distillation using a 30-cm. Vigreux column. The excess **formic acid** is removed under reduced pressure (b.p. 26–30°/21–30 mm.). Distillation of the residue then gives a forerun of about 100 ml. of a mixture of **formic acid** and ester followed by about 485 g. of *2-exo-norbornyl formate*, a colorless oil, b.p. 65–67°/14–16 mm. n_D^{25} 1.4594–1.4597. Another 55–65 g. of ester is obtained by adding water to the forerun, extracting with 30–60° petroleum ether, washing the extracts with dilute **sodium carbonate** solution, drying over **sodium sulfate**, and distilling. The total yield is 540–550 g. (90.5–92.5%) (Note 4).

B. *2-Norbornanone*. A solution of 510 g. (3.64 moles) of *2-exo-norbornyl formate* in 1.5 l. of reagent grade **acetone** is contained in a 5-l. three-necked flask equipped with a thermometer, stirrer, and dropping funnel containing 8*N* **chromic acid** solution (Note 5). The flask is cooled with an ice bath and the oxidant is added at a rate such that the reaction temperature is maintained at 20–30°. Approximately 1870 ml. of oxidant solution is required, completion of the reaction being shown by the persistence of the brownish orange color. A slight excess of oxidant is added, and the solution is stirred overnight at room temperature. Solid **sodium bisulfite** is added in portions to reduce the excess oxidant.

The reaction mixture is poured into a large separatory funnel. The dark green **chromic sulfate** sludge, which has formed during the course of the reaction, is separated either by decantation and washing or by drawing it off from the bottom of the funnel. The **acetone** solution is washed three times with 200–250 ml. portions of an aqueous saturated **potassium carbonate** solution and finally is dried over anhydrous **potassium carbonate**. The **acetone** is removed by distillation through a 30-cm. Vigreux column at atmospheric pressure; **benzene** may be added near the end to assist in the removal of water by azeotropic distillation. When it is observed that the distillation of solvent is complete and the considerably hotter vapors of product begin to ascend the column, the condenser is removed from the top and replaced by an adapter and collection flask immersed in ice water. The adapter is heated and maintained above 100° by a free flame until the product begins to distil (Note 6). 2-Norbornanone, 335–

350 g. (83–87%), distils at 170–173° and crystallizes immediately in the collection flask. The crystals melt at 90–91° (Note 7) and are sufficiently pure for most preparative purpose (Note 8).

2. Notes

1. Baker and Adamson 98–100% formic acid was used.
2. Prepared as described in *Org. Syntheses, Coll. Vol. 4*, 738 (1963).
3. Norbornene is not soluble in cold formic acid; initially there are two layers. As heat is applied to the flask, solution occurs and the reaction becomes quite exothermic. It is recommended that a splash trap be mounted at the top of the condenser and that an ice bath be nearby in case the refluxing becomes too rapid. *Caution! Formic acid causes severe burns!*
4. Quite pure 2-exo-norborneol, m.p. 127–128°, can be prepared by saponification of 2-exo-norbornyl formate in an aqueous ethanolic solution of potassium hydroxide. The product can be isolated in about 85% yield by distillation and boils at 178–179°.
5. The 8N chromic acid solution² is prepared by dissolving 534 g. of chromium trioxide in ice water, adding 444 ml. of conc. sulfuric acid carefully, and diluting to 2 l. with water.
6. The product solidifies readily. Care should be taken to prevent clogging of the adapter. Once begun, there is no difficulty if the distillation proceeds smoothly to completion.
7. The melting points given in the literature vary from 90–91° (Ref. ³) to 95.5° (Ref. ⁴). Pure 2-norbornanone, m.p. 97.2–98.0°, may be made by regeneration from its semicarbazone derivative, m.p. 196.5–197.6°.
8. Gas chromatographic analysis shows this material to have a purity of about 96%. Besides a small amount of water (up to 0.5%) there are two minor impurities. Neither 2-exo-norbornyl formate nor 2-exo-norbornyl is present, however. Oxidation of 2-exo-norbornanol with chromic acid, under a variety of conditions, gives 2-norbornanone contaminated with some starting material.

3. Discussion

2-Norbornanone is generally prepared from the Diels-Alder adduct of cyclopentadiene and vinyl acetate by hydrogenation, saponification, and oxidation with chromic acid in acetic acid solution.⁵ The present procedure, which gives higher over-all yields in fewer steps, makes use of the superior solvent, acetone, for mild chromic acid oxidations² and of the observation that formate esters of secondary alcohols can be oxidized directly to ketones.⁶

4. Merits of Preparation

2-Norbornanone is a useful starting material for various bicyclic derivatives of theoretical interest. The present procedure provides a convenient method for its preparation and illustrates a general method for the oxidation of formate esters to ketones.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 845

References and Notes

1. Department of Chemistry, Princeton University, Princeton, New Jersey.
 2. K. Bowden, I. M. Heibron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch, and G. W. Wood, *J. Chem. Soc.*, 2402 (1951).
 3. G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).
 4. G. Becker and W. A. Roth, *Ber.*, **67**, 627 (1934).
 5. K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1940).
 6. E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *J. Am. Chem. Soc.*, **81**, 6305 (1959).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

petroleum ether

nobornene

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

formic acid (64-18-6)

sodium bisulfite (7631-90-5)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

chromic acid (7738-94-5)

chromic sulfate (15244-38-9)

chromium trioxide (1333-82-0)

vinyl acetate (108-05-4)

CYCLOPENTADIENE (542-92-7)

Norbornene

2-Norbornanone,
Norcamphor (497-38-1)

2-exo-norbornyl (30967-37-4)

2-exo-Norbornyl formate (41498-71-9)

2-exo-norborneol,
2-exo-norbornanol (1632-68-4)