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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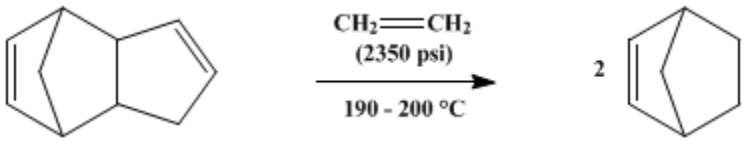
Organic Syntheses, Coll. Vol. 4, p.738 (1963); Vol. 37, p.65 (1957).

NORBORNYLENE

[2-Norbornene]



Submitted by J. Meinwald and N. J. Hudak[1].
Checked by J. D. Roberts, C. M. Sharts, and W. G. Woods.

1. Procedure

A 1-l. steel bomb is charged with 200 g. (1.5 moles) of dicyclopentadiene (Note 1). The bomb is flushed with ethylene (Note 2) and then filled while shaking to an initial pressure of 800–900 p.s.i. at 25°. Shaking is continued as the bomb is slowly heated (Note 3) to 190–200° and maintained at this temperature for 7 hours (Note 4). At the end of this period, the reaction vessel is cooled and vented, and the crude product is transferred to a simple distillation apparatus (Note 5). A fraction boiling between 93° and 100° is collected, yield 162–202 g. (57–71%, based on dicyclopentadiene) (Note 6). The norbornylene may be redistilled with negligible losses to give a final product, b.p. 94–97°/740 mm., m.p. 44–44.5° (sealed capillary).

2. Notes

1. The dicyclopentadiene used by the submitters was supplied by the Enjay Company. No preliminary purification is required. Technical (85%) dicyclopentadiene has been found by the checkers to give 54–56% yields of norbornylene without preliminary purification.
2. C.P. grade ethylene was obtained from the Matheson Company.
3. To avoid complications due to the exothermic nature of this reaction,[2] a rate of heating of about 50° per hour was adopted (cf. (Note 6)).
4. Near 180°, the maximum pressure (about 2350 p.s.i.) is developed.
5. In spite of the low melting point of norbornylene, the product has a remarkable tendency to crystallize. Care should therefore be taken to prevent premature solidification of the distillate. A short-path, air-cooled assembly using rather wide-diameter tubing is convenient for this purpose.
6. The submitters report the same yields using a 3-l. bomb and 3.68 moles of dicyclopentadiene. Larger-scale preparations may necessitate special control procedures.

3. Discussion

The procedure described above is essentially that of Thomas.[2] Norbornylene has also been prepared by the addition of ethylene to monomeric cyclopentadiene[3] (p. 238), by dehydration of β-norborneol with phosphorus pentoxide,[4] and by dehydrohalogenation of norbornyl chloride or bromide using quinoline.[4,5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 852
- Org. Syn. Coll. Vol. 6, 142

References and Notes

1. Cornell University, Ithaca, New York.

2. Thomas, *Ind. Eng. Chem.*, **36**, 310 (1944); Thomas and Universal Oil Products, U. S. pat. 2,340,908 [*C. A.*, **38**, 4273 (1944)].
3. Joshel and Butz, *J. Am. Chem. Soc.*, **63**, 3350 (1941).
4. Komppa and Beckmann, *Ann.*, **512**, 175 (1934).
5. Alder and Rickert, *Ann.*, **543**, 10 (1940).

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

β-norborneol

norbornyl chloride or bromide

ethylene (9002-88-4)

Quinoline (91-22-5)

CYCLOPENTADIENE (542-92-7)

dicyclopentadiene (77-73-6)

Norbornylene (498-66-8)

2-Norbornene

phosphorus pentoxide (1314-56-3)