



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.

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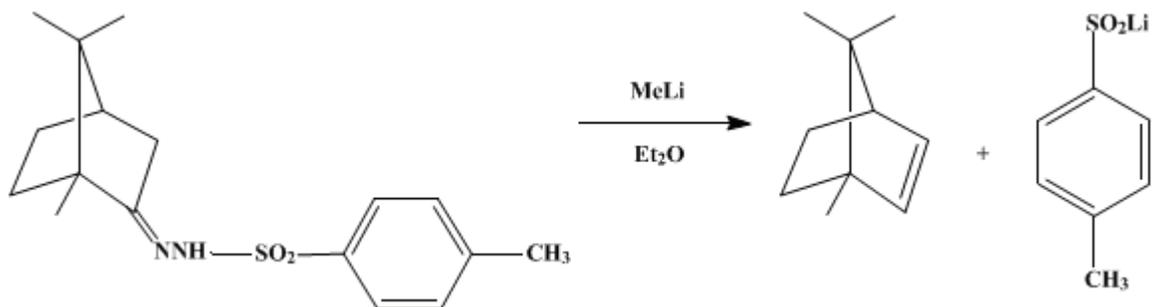
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.172 (1988); Vol. 51, p.66 (1971).

2-BORNENE

[1,7,7-Trimethylbicyclo[2.2.1]hept-2-ene]



Submitted by Robert H. Shapiro¹ and J. H. Duncan.
Checked by Robert Czarny and Robert E. Ireland.

1. Procedure

A dry, 1-l., three-necked flask equipped with a reflux condenser protected with a calcium sulfate drying tube, a 250-ml., pressure-equalizing dropping funnel, and a magnetic stirring bar is charged with 32 g. (0.10 mole) of **camphor tosylhydrazone** (Note 1) and 400 ml. of dry **diethyl ether** (Note 2). The flask is immersed in a cold-water bath (20–25°), and the contents are stirred magnetically. About 50 ml. of dry **ether** is placed in the dropping funnel, and the addition rate is set at 2–3 ml./minute (Note 3). After this addition 150 ml. of 1.6 N (0.24 mole) **methyl lithium** (Note 4) in **ether** is added to the dropping funnel and dropped into the reaction flask over 1 hour (Note 5), while the cooling bath temperature is maintained at 20–25°. The yellow-orange solution is stirred for 8–9 hours, during which time **lithium p-toluenesulfonate** precipitates and the solution develops a deep red-orange color. A small amount of water is carefully added to destroy excess **methyl lithium** before an additional 200 ml. is added. The layers are separated, the organic phase is washed with four 250-ml. portions of water, and the combined aqueous phases are shaken twice with 100-ml. portions of **ether**. After drying the combined ethereal extracts over anhydrous **sodium sulfate**, the volume of the solution is reduced to 50–60 ml. by distillation of the **ether** through a 25-cm. Vigreux column with gentle boiling on a steam bath. After 100 ml. of distilled **pentane** (Note 6) is added to the orange solution, the solvent is again gently boiled away, reducing the volume to 30–50 ml. The addition and removal of **pentane** is repeated two additional times to assure the complete removal of **ether**, and the final volume of the solution of **2-bornene** is reduced to 30–40 ml. The solution is added to an 80 × 5 cm. chromatography column packed with 500 g. of **alumina** (Note 7), and the product is eluted with 750 ml. of **pentane**. After concentration of the eluate by distillation of the solvent through a Vigreux column, the residue is transferred to a 50-ml. flask and distilled through a U-tube with the aid of an oil bath and a heating lamp (Note 8). After collecting a forerun (**pentane** and **2-bornene**), 8.5–8.8 g. (63–65%) of **2-bornene**, m.p. 110–111° (lit.^{2,3,4}, 109–110°), is collected as colorless crystals in a cooled flask (Note 9). GC analysis⁵ shows this product to be 98–99% pure, containing no **camphene** or **tricyclene** (Note 10).

2. Notes

- Camphor tosylhydrazone**⁶ is prepared in the following manner. To a 1-l., one-necked, round-bottomed flask are added 44 g. (0.24 mole) of *p*-toluenesulfonylhydrazide [*Org. Synth.*, **Coll. Vol. 5**, 1055 (1973)], 31.6 g. (0.208 mole) of **camphor**, and 300 ml. of 95% **ethanol**. One milliliter of concentrated **hydrochloric acid** is added, the flask is fitted with a reflux condenser, and the solution is heated under reflux for 2 hours. The resulting solution is cooled in an ice bath; colorless needles are collected by suction filtration and dried in air (Note 11). Recrystallization from **ethanol** yields 50 g. (73%) of pure **camphor tosylhydrazone**, m.p. 163–164°.
- Anhydrous **ether** available from Mallinckrodt Chemical Works can be used without further drying.

3. This prevents clogging of the funnel during the subsequent addition of [methyllithium](#) solution.
4. [Methyllithium](#) available from either Foote Mineral Company or Alfa Inorganics, Inc., can be used without further purification. The checkers used 137 ml. of a 1.85 M solution.
5. During the first half of the addition each drop of [methyllithium](#) solution produces a yellow color that quickly disappears. The solution turns yellow during the second half of the addition and slowly becomes more intensely colored until it reaches red-orange near the end of the reaction period.
6. Since the solvent is never completely removed at any time prior to final distillation of the product, the accumulation of higher boiling hydrocarbons results if petroleum ether is used. As a result the forerun of the final distillation will be larger, and the yield of [2-bornene](#) will be reduced. The [pentane](#) was distilled to assure the removal of any higher boiling impurities.
7. Neutral, reagent grade [aluminum oxide](#) available from Merck & Co., Inc., was used by the checkers.
8. When the temperature of the bath reaches 140–143°, the heating lamp is turned directly on the U-tube, and the receiver is changed to collect the [2-bornene](#).
9. The yield of the product is greatly reduced if the receiver is not cooled. A 2-propanol–dry ice bath was used.
10. On a 180 cm. × 32 mm. GC column containing 10% Apiezon L on Chromosorb P at 60° a synthetic mixture of [2-bornene](#) (10.3 minutes), [tricyclene](#) (12.3 minutes), and [camphene](#) (15.5 minutes) was readily resolvable.
11. The product has m.p. 161–163° and can be used without further purification.

3. Discussion

[2-Bornene](#) has been prepared from the reaction of [2-bromobornane-3-carboxylic acid](#) with aqueous [sodium hydrogen carbonate](#),⁷ by pyrolysis of isoborneol methyl xanthate,⁸ and by the β -elimination of [hydrogen chloride](#) from [bornyl chloride](#) with sodium alkoxides in various solvents.^{2,3,4}

This procedure appears to be general for the preparation, without rearrangement, of lesser substituted olefins. [2-Methylcyclohexanone tosylhydrazone](#) gives [3-methylcyclohexene](#) (98% yield by GC analysis).⁹ [Cholestan-6-one tosylhydrazone](#) gives [cholest-6-ene](#) (95% isolated yield), [androstan-17-one tosylhydrazone](#) gives [androst-16-ene](#) (91% isolated yield),⁹ and [phenylacetone tosylhydrazone](#) gives [allylbenzene](#) (70% yield by GC analysis, accompanied by the substitution product [isobutylbenzene](#) in 30% yield). Advantages of this procedure include its simplicity and the availability of carbonyl compounds as precursors. The reaction proceeds smoothly but more slowly at –25° and can be employed with heat-sensitive or volatile compounds in ordinary laboratory equipment.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 7, 77](#)

References and Notes

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

alumina

isoborneol methyl xanthate

ethanol (64-17-5)

hydrogen chloride,
hydrochloric acid (7647-01-0)

ether,
diethyl ether (60-29-7)

sodium hydrogen carbonate (144-55-8)

sodium sulfate (7757-82-6)

Pentane (109-66-0)

aluminum oxide (1344-28-1)

camphor (21368-68-3)

Methylithium (917-54-4)

allylbenzene (300-57-2)

2-Bornene,
1,7,7-Trimethylbicyclo[2.2.1]hept-2-ene (464-17-5)

camphor tosylhydrazone (10224-32-5)

camphene (565-00-4)

tricyclene (508-32-7)

2-bromobornane-3-carboxylic acid

bornyl chloride (464-41-5)

2-Methylcyclohexanone tosylhydrazone

3-Methylcyclohexene (591-48-0)

Cholestan-6-one tosylhydrazone

cholest-6-ene

androstan-17-one tosylhydrazone

androst-16-ene

phenylacetone tosylhydrazone

isobutylbenzene (538-93-2)

p-Toluenesulfonylhydrazide (1576-35-8)

lithium p-toluenesulfinate