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.

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.

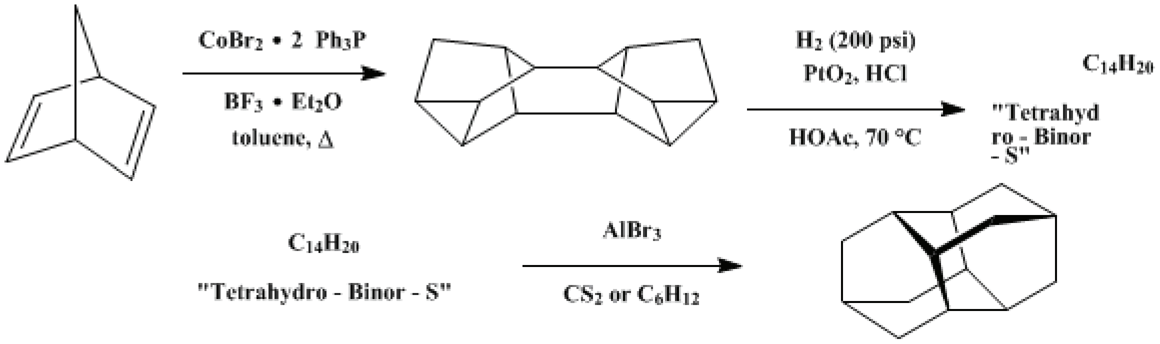
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.053.0030

Organic Syntheses, Coll. Vol. 6, p.378 (1988); Vol. 53, p.30 (1973).

DIAMANTANE: PENTACYCLO[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]TETRADECANE

[Butanetetraylnaphthalene, 3,5,1,7-[1,2,3,4]-decahydro-]



Submitted by Tamara M. Gund, Wilfried Thielecke, and Paul v. R. Schleyer[1].
Checked by H. Gurien, R. Regenye, and A. Brossi.

1. Procedure

A. *Binor-S.*[2] A 2-l., three-necked flask equipped with Teflon sleeves (Note 1), a thermometer, a condenser, a dropping funnel, and a mechanical stirrer is flushed with nitrogen and charged with 200 g. (2.18 moles) of freshly distilled norbornadiene (Note 2), 400 ml. of dry toluene, and 7.8 g. of cobalt bromide–triphenylphosphine catalyst (Note 3). While stirring at room temperature, 2.1 ml. of boron trifluoride diethyl etherate co-catalyst (Note 4) is added dropwise. The mixture is heated slowly to 105°, and the heating mantle is lowered. The ensuing exothermic reaction maintains the temperature at 105–110° for 15 minutes. When the temperature begins to fall, the mantle is raised, the mixture is brought to the reflux temperature, and stirring and refluxing are continued for 12 hours. The cooled mixture is diluted with 650 ml. of dichloromethane, transferred to a separatory funnel, and washed with three 650-ml. portions of water. The organic phase is dried over anhydrous magnesium sulfate, and the solvents are evaporated at reduced pressure. The residual crude material, 185–203 g., is distilled at 106–107° (1.5 mm.), giving 165–170 g. (82–85%) of Binor-S, which solidifies on cooling to a white solid, m.p. 59–63°.

B. *Tetrahydro-Binor-S*. Binor-S (135.0 g., 0.734 mole) is dissolved in 670 ml. of glacial acetic acid containing 5.7 ml. of concentrated hydrochloric acid. To this solution is added 1.0 g. of platinum oxide catalyst. The reaction mixture is hydrogenated at 200 p.s.i. hydrogen pressure and 70° for 3 hours, using a 1200-ml., glass-lined autoclave (Note 5). After cooling to room temperature, the catalyst is removed with suction filtration, and water (*ca.* 1.5 l.) is added to the filtrate until two layers form. The bottom layer, containing only tetrahydro-Binor-S, is removed, and the top layer, consisting of a mixture of acetic acid and water, is extracted with one 400 ml. and two 100-ml. portions of dichloromethane. The combined dichloromethane–tetrahydro-Binor-S layers are washed twice with 100 ml. of water, dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residual tetrahydro-Binor-S is purified by distillation under reduced pressure, b.p. 105–110° (1.5 mm.), giving 125–130 g. (90–94%) of colorless liquid (Note 6).

C. *Diamantane*. A 500-ml., three-necked flask, equipped with a reflux condenser, a drying tube, a magnetic stirring bar, and a dropping funnel is charged with 28 g. (0.11 mole) of fresh aluminum bromide and 100 ml. of cyclohexane (Note 7). The apparatus is flushed with hydrogen bromide gas (Note 8). When the aluminum bromide has dissolved, 100 g. (0.532 mole) of hydrogenated Binor-S is added dropwise to the rapidly stirred solution, and the reaction mixture refluxes for a short time without external heat. The course of the reaction is monitored by GC until no starting material remains (Note 9). Occasionally, an additional 5 g. portion of aluminum bromide, and application of external heat are needed to complete the reaction. The total reaction time is about 2–3 hours (Note 10). The hot cyclohexane layer is carefully decanted, and the aluminum bromide layer is extracted with five 200-ml. portions of hot cyclohexane. Diethyl ether (400 ml.) is added to the cooled cyclohexane extracts (Note 11), and the combined solvent fractions are washed with two 100-ml. portions of water and dried over anhydrous magnesium sulfate. Evaporation of the solvent leaves a semi-solid residue, which is partially dissolved in about 100 ml. of pentane. The undissolved white solid, diamantane, is collected by suction filtration. Additional diamantane is obtained by concentrating the pentane solution to a small volume and collecting the solid that precipitates. The total amount of diamantane obtained, after drying, is 60–62 g. (60–62%), m.p. 240–241° (closed tube) (Note 12). This product is sufficiently pure for most purposes, but it may be purified further by recrystallization from pentane, giving white crystals, m.p. 244.0–245.4°.

2. Notes

1. Teflon sleeves were used to keep the joints from freezing.
2. Once distilled, norbornadiene may be stored below 0°. Samples as old as 2 weeks were used successfully.
3. This catalyst[3] is prepared in quantitative yield by refluxing by 200 ml. benzene solution containing 10 g. (0.046 mole) of anhydrous cobalt dibromide and 24.4 g. (0.0931 mole) of triphenylphosphine. A color change is observed, and the blue-green solid that precipitates on cooling to room temperature is filtered and dried. This catalyst, stored in a dry atmosphere, appears to be active indefinitely.
4. Boron trifluoride etherate may be used without prior distillation only if fresh material is available. Care must be taken with this reagent because of fuming. The dimerization does not proceed without this co-catalyst.
5. At 70° Binor-S remains in solution, and the uptake of hydrogen is rapid. The checkers have observed that occasionally hydrogen uptake is incomplete, and an additional 1 g. of catalyst must be added to complete the absorption of hydrogen. The submitters carried out the hydrogenation in a large-scale Parr apparatus under three atmospheres of pressure with similar results.
6. After a small solvent-containing forefraction, which is discarded, essentially all of the material should distill in the indicated range, but occasionally material boiling as high as 130° (1.5 mm.) is obtained. This is included in the product.
7. Either carbon disulfide or cyclohexane may be used with comparable yields. The advantage of carbon disulfide is the greater solubility of diamantane. When extracting with cyclohexane, a boiling solution must be used to increase solubility. However, cyclohexane is less poisonous, does not have a foul odor, and gives a whiter product. Therefore, the use of carbon disulfide was not examined by the checkers. Use of dichloromethane has been reported[2] to lead to an 82% yield.
8. Flushing the apparatus with hydrogen bromide may not be necessary, especially for small-scale runs.
9. A Carbowax 20M or 1500 GC column at a temperature of 180° may be used. Diamantane has a shorter retention time than tetrahydro-Binor-S. The checkers used a 10% OV101 GCQ column, 100/120, at 200°; retention times are Binor-S, 11.5 minutes; tetrahydro-Binor-S, 7.6 minutes; diamantane, 6.2 minutes.
10. About 30 minutes after the addition of tetrahydro-Binor-S is complete, the reaction mixture begins to cool and external heat must be supplied to continue the refluxing and complete the reaction. If GC monitoring reveals that the rearrangement is proceeding slowly, an additional 0.5 g. of aluminum bromide is added and refluxing is continued until all the starting material is converted to product.
11. Addition of ether prevents crystallization of the diamantane from cooled cyclohexane.
12. The material obtained is pure by GC and ^{1}H NMR. The ^{1}H NMR spectrum of diamantane shows only a singlet at δ 1.68 ($CDCl_3$).[4] The pentane mother liquors contain a by-product. A comparable yield can be obtained using aluminum chloride in boiling dichloromethane, and the crude mixture at the end of the reaction need not, in some instances, be worked up before subsequent functionalization reactions are carried out.[2,5]

3. Discussion

Like adamantane,[6] diamantane (also known as congressane[4]), the second member of the diamond family, may also be prepared by aluminum halide-catalyzed isomerization. A variety of starting materials have been shown to give diamantane,[2,4,7,8] but the very best results are obtained by the present procedure[2,8] starting with Binor-S.[2,3,9] Diamantane may be converted to a variety of functionalized derivatives.[2,5,10,11] 4-Methyldiamantane may also be prepared by rearrangement.[10] The mechanisms of these transformations have been analyzed.[12]

References and Notes

1. Department of Chemistry, Princeton University, Princeton, New Jersey 08540. This work was supported by Grant GM-19134, National Institutes of Health, and by Hoffmann-La Roche Inc., Nutley, New Jersey 07110. [Present address: Institute für Organische Chemie, Universität Erlangen-Nürnberg, 8520 Erlangen, Federal Republic of Germany.]
2. T. Courtney, D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J. Chem. Soc., Perkin Trans. I*, 2691 (1972).
3. G. N. Schrauzer, R. K. Y. Ho, and G. Schlesinger, *Tetrahedron Lett.*, 543 (1970).
4. C. Cupas, P. v. R. Schleyer, and D. J. Trecker, *J. Am. Chem. Soc.*, **87**, 917 (1965).
5. D. Faulkner, R. A. Glendinning, D. E. Johnston, and M. A. McKervey, *Tetrahedron Lett.*, 1671 (1971).
6. P. v. R. Schleyer, M. M. Donaldson, R. D. Nicholas, and C. Cupas, *Org. Synth.*, **Coll. Vol. 5**, 16 (1973).
7. V. Z. Williams, Jr., P. v. R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *J. Am. Chem. Soc.*, **88**, 3862 (1966).
8. T. M. Gund, V. Z. Williams, Jr., E. Osawa, and P. v. R. Schleyer, *Tetrahedron Lett.*, 3877 (1970); T. M. Gund, E. Osawa, V. Z. Williams, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **39**, 2979 (1974).
9. G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Am. Chem. Soc.*, **88**, 4890 (1966).
10. T. M. Gund, M. Nomura, V. Z. Williams, Jr., and P. v. R. Schleyer, *Tetrahedron Lett.*, 4875 (1970); R. Hamilton, D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J. Chem. Soc. Chem.*, 1209 (1972); T. M. Gund, M. Nomura, and P. v. R. Schleyer, *J. Org. Chem.*, **39**, 2987 (1974).
11. T. M. Gund and P. v. R. Schleyer, *Tetrahedron Lett.*, 1583 (1971). T. M. Gund, P. v. R. Schleyer, G. D. Unruh, and G. J. Gleicher, *J. Org. Chem.*, **39**, 2995 (1974); F. Blaney, D. E. Johnston, M. A. McKervey, and J. J. Rooney, *Tetrahedron Lett.*, 99 (1975).
12. T. M. Gund, P. v. R. Schleyer, P. H. Gund, and W. T. Wipke, *J. Am. Chem. Soc.*, **97**, 743 (1975).

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

Diamantane

Binor-S

Tetrahydro-BINOR-S

DIAMANTANE: PENTACYCLO[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]TETRADECANE

congressane

4-Methyldiamantane

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

ether,
diethyl ether (60-29-7)

hydrogen (1333-74-0)

hydrogen bromide (10035-10-6)

nitrogen (7727-37-9)

platinum oxide

cyclohexane (110-82-7)

aluminum chloride (3495-54-3)

toluene (108-88-3)

carbon disulfide (75-15-0)

Pentane (109-66-0)

aluminum bromide

dichloromethane (75-09-2)

magnesium sulfate (7487-88-9)

boron trifluoride etherate,
boron trifluoride diethyl etherate (109-63-7)

Adamantane (281-23-2)

norbornadiene

triphenylphosphine (603-35-0)

Butanetetraylnaphthalene, 3,5,1,7-[1,2,3,4]-decahydro-

cobalt dibromide,
cobalt bromide (7789-43-7)

PENTACYCLO[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]TETRADECANE