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of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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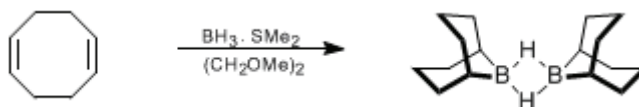
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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9-BORABICYCLO[3.3.1]NONANE DIMER

[9-Borabicyclo[3.3.1]nonane, dimer]



Submitted by John A. Soderquist¹ and Alvin Negron.
Checked by Daniel M. Berger and Larry E. Overman.

1. Procedure

CAUTION! The manipulation and handling of air-sensitive compounds requires the use of special techniques. While no difficulties have been encountered with the present procedures, the preparer should consult References ³ and ² prior to carrying out these syntheses.

A 2-L, three-necked, round-bottomed flask containing a magnetic stirring bar is fitted with a 250-mL addition funnel and a distillation assembly set for downward distillation to a 500-mL receiver flask. Rubber septa are used to isolate the system from atmospheric contact. Under a nitrogen purge, vented to an exhaust hood through a mercury bubbler, the entire system is thoroughly flame-dried (Note 1). After the 2-L flask is cooled to room temperature, it is charged with 500 mL of pure, dry 1,2-dimethoxyethane (Note 2) and 153 mL (1.53 mol) of borane-methyl sulfide complex (Note 3) employing a double-ended needle to effect the transfer. With a similar technique, 164 g (1.52 mol) of 1,5-cyclooctadiene (Note 4) is transferred to the addition funnel. To the stirred borane solution, 1,5-cyclooctadiene is added dropwise over ca. 1 hr to maintain a reaction temperature of 50–60°C during which time a small amount of dimethyl sulfide (bp 38°C) distills slowly from the reaction mixture. After the addition is completed, the addition funnel is replaced with a glass stopper and approximately 300 mL of the solution is distilled to reach a final distillation temperature of 85°C, indicating the complete removal of dimethyl sulfide from the reaction mixture (Note 5). If the distillate temperature does not reach 85°C, 150 mL of additional 1,2-dimethoxyethane is added and the distillation is continued until the distillate temperature reaches 85°C. The distillation assembly is replaced with a rubber septum and 1,2-dimethoxyethane is added to the reaction flask to bring the total liquid volume to 1 L. The mixture is warmed to effect the dissolution of the solid and allowed to cool very slowly to 0°C, which results in the formation of crystalline 9-borabicyclo[3.3.1]nonane (9-BBN) dimer. The supernatant liquid is decanted from the product using a double-ended needle and the 9-BBN dimer is dissolved in 1 L of fresh 1,2-dimethoxyethane. After the flask is cooled to 0°C, the supernatant liquid is removed as above and the large needles are dried under reduced pressure for 12 hr at 0.1 mm to give 158–165 g (85–89%) of product (mp 152–154°C, sealed capillary) (Note 6),(Note 7),(Note 8).

2. Notes

1. Alternatively, the apparatus can be dried for 4 hr at 150°C, assembled hot and purged with dry nitrogen.
2. 1,2-Dimethoxyethane, available from the Aldrich Chemical Company, Inc., was predried over calcium hydride and distilled from sodium/benzophenone prior to use. The solvent was used directly after purification or stored in an ampule bottle, available from the Aldrich Chemical Company, Inc., under a nitrogen atmosphere.
3. Borane-methyl sulfide complex, obtained from the Aldrich Chemical Company, Inc., was used directly without additional purification. However, titration of the reagent was carried out with glycerol as described³ to determine its actual molarity. Older samples of this reagent can be distilled under aspirator vacuum to obtain pure reagent.
4. 1,5-Cyclooctadiene, obtained from the Aldrich Chemical Company, Inc., was distilled under aspirator

pressure from lithium aluminum hydride prior to use.

5. Failure to remove the dimethyl sulfide from the reaction mixture increases the solubility of the 9BBN dimer and lowers the overall yield to ca. 65%.

6. The spectra of the product are as follows: ^1H NMR (300 MHz, C_6D_6) δ : 1.44–1.57 (m, 4 H), 1.58–1.74 (m, 12 H), 1.83–2.07 (m, 12 H). A standard HETCOR experiment revealed that protons on each of the methylene carbons were superimposed upon one another to give rise to these downfield multiplets; ^{13}C NMR (75 MHz, C_6D_6) δ : 20.2 (br, C-1,5), 24.3 (C-3,7), 33.6 (C-2,4,6,8); ^{11}B NMR (96 MHz, C_6D_6) δ : 28.

7. The 9-BBN dimer so prepared is reasonably air-stable so that exposure to the atmosphere for 1 month lowered the mp to ca. 146–151°C. Due to the potential for the formation of pyrophoric contaminants, it is recommended that 9-BBN be stored and handled under an inert atmosphere at all times.

8. Purification of commercial 9-BBN and other samples can be effected by recrystallization from 1,2-dimethoxyethane. Insoluble impurities can be removed from hot 1,2-dimethoxyethane solutions of 9BBN by decantation of the solution to a second dry flask. To prevent clogging of the double-ended needle during the transfer process it is important to keep the ends of needle below the liquid surfaces. We have found that the receiver vessel should be charged with a small quantity of fresh, hot 1,2-dimethoxyethane prior to decantation and that a portion of this material should be transferred under a positive pressure of nitrogen to the 9-BBN solution to warm initially the transfer needle. Subsequently, the hot 9-BBN solution can be transferred without difficulty.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

9-Borabicyclo[3.3.1]nonane (9-BBN) has been prepared by the thermal redistribution of 9-n-propyl-9-BBN,⁴ and the hydroboration of 1,5-cyclooctadiene with borane-tetrahydrofuran complex followed by thermal isomerization of the mixture of dialkylboranes at 65°C.⁵ Solutions of 9-BBN have been prepared from the hydroboration of 1,5-cyclooctadiene with borane-methyl sulfide in solvents other than THF.⁶ The present procedure involves the cyclic hydroboration of 1,5-cyclooctadiene with borane-methyl sulfide in 1,2-dimethoxyethane.⁷ Distillative removal of the dimethyl sulfide in this special solvent system provides a medium that gives high purity, large needles of crystalline 9-BBN dimer in excellent yield. The material can be handled in air for brief periods without measurable decomposition.

As a dialkylborane, 9-borabicyclo[3.3.1]nonane (9-BBN) is unrivaled in both stability and selectivity.⁸ It has been distilled (bp 195°C, 12 mm) and exhibits a strong characteristic IR absorption band at 1560 cm^{-1} (B-H-B) for the bridged dimeric structure.⁵ The crystal structure of 9-BBN dimer has been determined⁹ and the drawing above approximates the conformational features of this compound. The ^{13}C NMR properties of 9-BBN adducts have been studied extensively.¹⁰

Since the 9-methoxy derivative of 9-BBN is a common by-product of several reactions of 9-BBN,¹¹ its efficient conversion back to 9-BBN has been described.¹² Such a process enables one to recycle 9BBN in reactions which require its high regioselectivity in hydroboration reactions and the related organoborane conversions.

The selective transformations of 9-BBN are numerous and varied, with derivatives being readily prepared through both hydroboration and organometallic methodology.⁸ It has been used for the preparation of isomerically-pure boracycles,^{11,13} the highly enantioselective reduction of aldehydes and ketones,¹⁴ the preparation of new selective borohydride reducing agents,¹⁵ C-C bond-forming transformations,¹⁶ and radiopharmaceutical labeling.¹⁷ Its reactivity has made it the reagent of choice for many organoborane conversions.¹⁸ The stability and distinctive spectral properties of 9-BBN have provided the initial key information to unravel the details of hydroboration reactions.^{8,19}

This preparation is referenced from:

- Org. Syn. Coll. Vol. 9, 107

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

9-BBN

9-Borabicyclo[3.3.1]nonane dimer

9-Borabicyclo[3.3.1]nonane, dimer

9-borabicyclo[3.3.1]nonane (9-BBN) dimer

9-BBN dimer

9-Borabicyclo[3.3.1]nonane (9-BBN)

9-n-propyl-9-BBN

9-BB

glycerol (56-81-5)

nitrogen (7727-37-9)

Benzophenone (119-61-9)

sodium (13966-32-0)

borane (7440-42-8)

dimethyl sulfide (75-18-3)

THF (109-99-9)

lithium aluminum hydride (16853-85-3)

calcium hydride (7789-78-8)

1,2-dimethoxyethane (110-71-4)

1,5-cyclooctadiene

borane-tetrahydrofuran complex (14044-65-6)

borane-methyl sulfide complex,
borane-methyl sulfide (13292-87-0)

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