**Registry No.** 1a, 621-22-7; 4, 78870-34-5; 5, 26243-62-9; 6, 78870-35-6; 7, 78870-36-7; 8, 78870-37-8.

## A Simple, Remarkably Efficient Route to High Purity, Crystalline 9-Borabicyclo[3.3.1]nonane (9-BBN) Dimer

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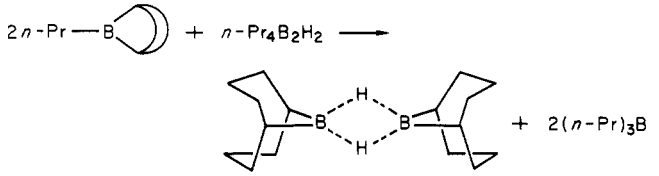
9-Borabicyclo[3.3.1]nonane (9-BBN) is a stable, crystalline dialkylborane, which, owing to its remarkable selectivity, has found wide application in organic synthesis.[1] We report a new, highly efficient preparation of crystalline 9-BBN dimer in high yield and purity from the cyclic hydroboration of 1,5-cyclooctadiene with borane–methyl sulfide complex, using 1,2-dimethoxyethane (monoglyme) as the reaction solvent. The product obtained under these conditions is resistant to decomposition in air and is indefinitely stable under a nitrogen atmosphere at room temperature. This development also makes possible the purification of 9-BBN from commercial and other sources to give a high purity, stable product.

First isolated and characterized by Köster,[2] 9-BBN dimer (1) was obtained from the thermal redistribution of *B*-*n*-propyl-9-BBN.

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However, since the preparation of the *B*-alkyl-9-BBN derivative was itself a two-step process,[3] a more attractive route to 9-BBN was found by Knights and Brown, involving the cyclic hydroboration of 1,5-cyclooctadiene with borane–tetrahydrofuran complex.[4]


A 70:30 mixture of the isomeric 9-borabicyclo[3.3.1]- and [4.2.1]nonanes were formed in the initial cyclic hydroboration step. However, simply heating the mixture at reflux temperature effected equilibration of the boranes to give 1 exclusively. This procedure gives a microcrystalline product of mp 142 °C in ca. 65% yield. Further purification of this material by vacuum sublimation increases the melting point to 152–155 °C.[5]

While this approach is a particularly convenient method for the preparation of 9-BBN, it suffers from several practical difficulties which diminish the yield and purity of the crystalline product actually obtained. For one, the choice of $BH_3$·THF as the reagent used for the initial hydroboration necessarily requires that THF be used as the reaction solvent. However, 9-BBN is significantly soluble in this medium, presumably due, at least in part, to the presence of an equilibrium concentration (ca. 14%) (see Table I) of a 9-BBN·THF complex (2).

$$\underset{1}{(\text{9-BBN})_2} \overset{\text{THF}}{\rightleftharpoons} \underset{2}{2\,\text{9-BBN·THF}}$$

Further, the microcrystalline product (1) obtained from THF solvent occasionally contains minor amounts of impurities which render the material pyrophoric.

Studies on the hydroboration of 1,5-cyclooctadiene using borane–methyl sulfide complex had revealed that this reagent could be used to prepare solutions of 9-BBN in solvents other than THF.[6] Of such solvents, the relatively low solubility of 9-BBN in diglyme[1] suggested that polyoxygenated ethers might provide an ideal reaction solvent to obtain the desired crystalline material.

The solubility of 9-BBN was measured in various solvents at 0 and 25 °C, and these results are summarized in Table II.

After investigating several solvent systems we found that monoglyme provided a superior reaction medium in that large crystals of 9-BBN dimer could be obtained in excellent yield (88%) and high purity (mp 153–155 °C). The high-purity crystalline 9-BBN dimer obtained from re-

**Table I. Complexation of 9-BBN with Basic Solvents**

| base | % complex | $^{11}$B chemical shift[a] ($J_{^{11}B-H}$) |
|---|---|---|
| THF | 14 | 13.9 (~90 Hz) |
| $S(CH_3)_2$ | 46 | 3.9 (107 Hz) |
| $NC_5H_5$[b] | 100 | -0.7 (88 Hz) |

[a] Chemical shifts are reported in parts per million with $BF_3$·$O(CH_2CH_3)_2$ ($\delta$ = 0.00 ppm) as an external standard. Absorbances due to dimeric 9-BBN were observed at 28 ppm for the first two entries. The percent complexation was calculated from the relative peak areas from complexed vs. dimeric 9-BBN. [b] $CDCl_3$ was used as solvent in this case. Excess pyridine showed no measurable effect on the chemical shift of the boron resonance.

**Table II. Molar Solubility of Dimeric 9-BBN in Representative Solvents[a]**

| solvent | temperature 0 °C | temperature 25 °C |
|---|---|---|
| monoglyme | 0.01 | 0.07 |
| diglyme | <0.01 | 0.04 |
| 1,4-dioxane | 0.03[b] | 0.07 |
| 1,3-dioxolane | <0.01 | 0.04[c] |
| diethyl ether | 0.09 | 0.18 |
| tetrahydrofuran | 0.12 | 0.29 |
| dichloromethane | 0.11 | 0.28 |
| chloroform | 0.21 | 0.50 |
| carbon tetrachloride | 0.15 | 0.36 |
| pentane | 0.13 | 0.23 |
| hexane | 0.11 | 0.25 |
| benzene | 0.19[d] | 0.36 |
| cyclohexane | 0.03[e] | 0.08 |
| toluene | 0.14 | 0.33 |
| dimethyl sulfide | | 0.60[f] |

[a] Values determined by hydride analysis.[14] [b] 15 °C. [c] Some chemical change in 9-BBN was observed in this solvent. [d] 4.4 °C. [e] 7 °C. [f] Value taken from ref 1.

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crystallization from monoglyme solvent has already found a number of useful applications in organic chemistry. These applications include the regiospecific, quantitative hydroboration of alkenylsilanes,[7] the preparation of molecular addition compounds,[8] detailed kinetic studies on the hydroboration reaction[9] as well as provide the basis for the commercial preparation of the reagent.[10]

Thus with this new route to high-purity 9-BBN dimer the fascinating chemistry of this most remarkable reagent can be more conveniently and efficiently explored.

## Experimental Section

All manipulations were carried out under a nitrogen atmosphere, using oven-dried glassware (4 h, at 110 °C). Monoglyme and 1,5-cyclooctadiene were distilled from lithium aluminum hydride prior to use. Borane–methyl sulfide complex (Aldrich-Boranes) was used without prior purification. The $^{11}B$ NMR spectra were obtained on a Varian FT-80A instrument.

**9-Borabicyclo[3.3.1]nonane (1).** A 2-L round-bottom flask containing a magnetic stirring bar and surmounted by an addition funnel and a distillation assembly was charged, under a nitrogen atmosphere, with 1,2-dimethoxyethane (monoglyme, 500 mL) and borane–methyl sulfide complex (153 mL, 1.53 mol), using a double-ended needle. The addition funnel was similarly charged with 1,5-cyclooctadiene (164 g, 1.52 mol). To the stirred borane solution 1,5-COD was added dropwise over ca. 1 h (reaction temperature, 50–60 °C) during which time, dimethyl sulfide (bp 38 °C) distills slowly from the reaction mixture. After the addition was complete, approximately 300 mL of the solution was distilled to reach a distillation temperature of 83–85 °C, which indicated the removal of the dimethyl sulfide from the reaction mixture.[11] The distillation assembly was replaced with a rubber septum and monoglyme was added to bring the volume to ca. 1 L. The mixture was allowed to cool slowly to 0 °C, which results in the formation of crystalline (needles) 9-BBN.[12] The supernatant liquid was decanted with a double-ended needle and the residue was dissolved in fresh monoglyme (1 L). After cooling slowly to 0 °C, the supernatant liquid was removed as above, and the large needles were dried in vacuo (60 °C for 16 h, at 100 μmHg) to give 162 g (88%) of product mp 153–155 °C, sealed capillary).[13]

**Solubility Determination.** With purified reagent-grade solvents, saturated solutions of 9-BBN dimer were allowed to equilibrate for several hours in a constant temperature bath. Aliquots were hydrolyzed in a 50:50 methanol–tetrahydrofuran mixture, and the hydride molarity was determined from the corrected volume of hydrogen evolved.[14] The values so determined for dimeric 9-BBN are presented in Table II.

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**Registry No.** 1, 21205-91-4; borane methyl sulfide, 13292-87-0; 1,5-cyclooctadiene, 111-78-4; 9-BBN·THF, 76422-63-4; 9-BBN·S-$(CH_3)_2$, 64045-91-6; 9-BBN·$NC_5H_5$, 64045-95-0.

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(11) Failure to remove the dimethyl sulfide lowers the overall yield to ca. 65%. The high solubility 9-BBN in dimethyl sulfide (see Table II), which is likely to be due to the formation of 9-BBN·$SMe_2$ (see Table I), probably accounts for this yield diminution.
(12) These crystals can be dried as described to give 91% of product (mp 152–154 °C).
(13) The 9-BBN so prepared is reasonably air stable so that exposure to the atmosphere for 1 month lowered the melting point to 146–151 °C. We were unable to detect any significant (<2%) loss of hydride activity or selectivity for the exposed sample.
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# 1-Substituted Benzocyclobutenes via Parham Cyclialkylation[1]

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The discovery that certain 1-substituted benzocyclobutenes can undergo intramolecular cycloaddition through isomerization to a derivative of *o*-quinodimethane was one of the important synthetic advances of the past decade.[2] While such cycloadditions frequently occur stereospecifically and in excellent yield, the preparation of the desired 1-substituted benzocyclobutenes (**4**) has frequently been less satisfactory. Of the many[2] available, the most versatile preparative scheme for **4** has involved a Bunnett[3] cyclization of an *o*-halodihydrocinnamonitrile (**1** → **2**, Scheme I) followed either by elaboration of the nitrile group[4,5] or by alkylation[6,7] at the tertiary carbon α to it (**2** → **3**) with subsequent reductive decyanation (**3** → **4**).

The purpose of the present preliminary investigation was to determine whether the Parham cyclialkylation[8-10] reaction might offer a useful alternate route to 1-substituted benzocyclobutenes. For the preparation of the requisite model dihalides **8**, (2-bromophenyl)acetonitrile (**5**)[11] appeared to be a convenient starting material, since it was known that at −100 °C it reacts with butyllithium selectively by hydrogen–lithium exchange.[11] Further, Kaiser and Hauser[12] had shown that the anion derived from phenylacetonitrile in essentially this way could be monoalkylated in good yield.[13] Good results were obtained in the alkylation of **5** (75–92%) by using benzyl bromide, 1-bromobutane, or 5-bromo-1-butene.

The usual route from (2-bromophenyl)acetonitrile (**5**) to 2-(*o*-bromophenyl)ethanol (**7**, R = H) is via hydrolysis of the nitrile to the (2-bromophenyl)acetic acid, followed by reduction.[16] The alkylated nitriles **6** proved so difficult to hydrolyze that it was found more effective to reduce

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