

1-Boraadamantane Blows Its Top, Sometimes. The Mono- and Polyhomologation of 1-Boraadamantane

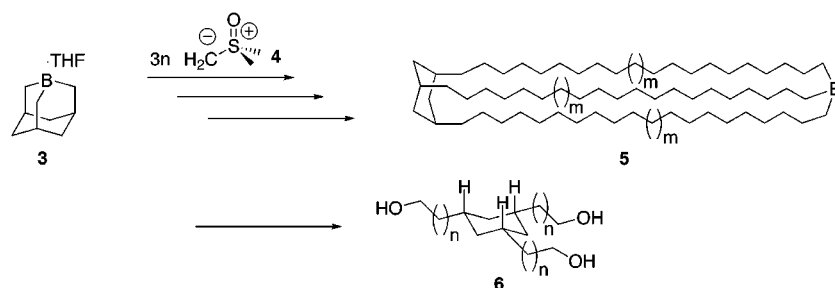
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ABSTRACT



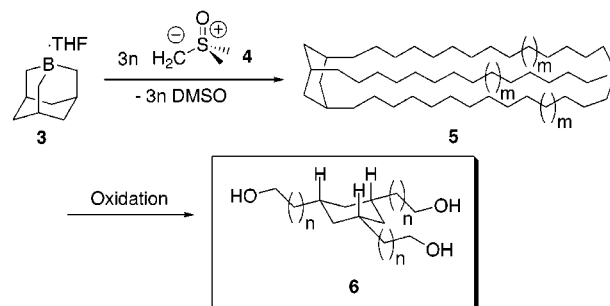
1-Boraadamantane-THF (**3**) reacts with 1 equiv of dimethylsulfoxonium methylide (**4**) to afford a *monohomologated* product. The polyhomologation of 1-boraadamantane-THF by ylide **4** followed by oxidative cleavage generates star polymethylene polymers incorporating a cyclohexane core. However, only *one-third* of the initiators lead to product formation, resulting in an observed degree of polymerization three times higher than expected. The polyhomologation of **3** was found to contain branch points after the fourth and fifth methylene insertions. At the branch points, the propagating species either terminate in tricyclic trialkylborane cages with collapsed, pyramidal inverted boron centers that are unreactive toward ylide or they continue in uninterrupted polymerization and eventually result in the formation of giant “tube-like” structures such as **5**.

Multiple homologations (polyhomologation) of cyclic and bicyclic organoboranes provide a novel route to oligomeric and polymeric boracyclanes and carbocyclics.¹ Applying the polyhomologation reaction² to *polycyclic* organoboranes offers an opportunity for the construction of “tube-like” organoboranes which may be elaborated to hydrocarbon star polymer architectures. 1-Boraadamantane-THF (**3**) was selected for study as a tricyclic alkylborane initiator to access a *three-armed* star polymethylene polymer, with the arms radiating from a cyclohexane core. In this strategy, trialkylborane **3** would serve as an initiator while dimethylsulfoxonium methylide (**4**) would serve as a methylene monomer source. One equivalent of DMSO would be expelled for each equivalent of ylide **4** consumed. The “tube-like” macropolycyclic organoborane (**5**) would be formed as the polymeric

product. The living nature of the polyhomologation reaction would allow control of the length of each wall of the “tube-like” **5**.³ Subsequent oxidation of **5** would give a regular star polymethylene polymer (**6**) (Scheme 1).

Thus, 1-boraadamantane-THF (**3**) was synthesized by the

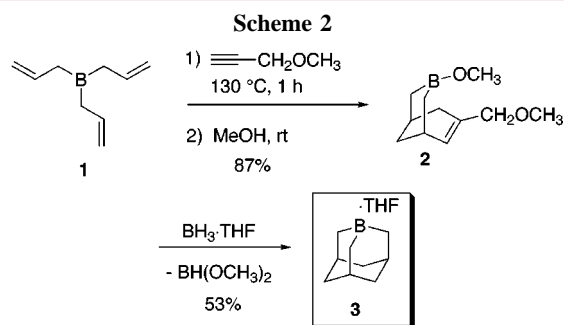
Scheme 1



(1) (a) Shea, K. J.; Lee, S. Y.; Busch, B. B. *J. Org. Chem.* **1998**, *63*, 5746. (b) Shea, K. J.; Busch, B. B.; Paz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1391.

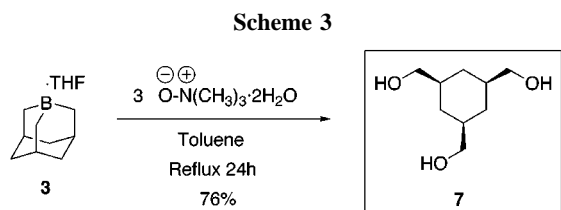
(2) Shea, K. J.; Walker, J. W.; Zhu, H.; Paz, M.; Greaves, J. *J. Am. Chem. Soc.* **1997**, *119*, 9049.

hydroboration of 3-methoxy-7-(methoxymethyl)-3-borabicyclo-[3.3.1]non-6-ene (**2**). This compound was prepared by the reaction of triallylborane (**1**) with methyl propargyl ether followed by methanolysis, according to the procedure of Mikhailov and co-workers (Scheme 2).⁴ Triallylborane (**1**)



was synthesized in 60% yield according to the method of Zakharkin and co-workers.⁵ Complex **3** was purified by vacuum sublimation, and its structure was confirmed by X-ray crystallography.

The polyhomologation reaction involves a two-step process consisting of addition of the nucleophilic ylide **4** to form an “ate” complex followed by a [1,2]-migration. Related migrations of bicyclic organoboranes proceed via an antiperiplanar transition state.⁶ To ensure the compatibility of the 1-boraadamantane core with addition–migration, we first examined its oxidation. Compound **3** is readily oxidized by trimethylene *N*-oxide dihydrate (TAO),⁷ giving the triol, *cis*-1,3,5-tris(hydroxy-methyl)cyclohexane (**7**), in 76% yield (Scheme 3).



The ^1H NMR spectrum of triol **7** in deuterium oxide includes a doublet at 3.36 ppm ($J = 6.3$ Hz), assigned to the hydroxymethylene protons of **7**. Also, the equatorial and axial methylene protons of the cyclohexane ring appear as a doublet at 1.67 ppm ($J = 12.0$ Hz) and a quartet at 0.50 ppm ($J = 12.3$ Hz), respectively.

(3) Shea, K. J. *Chem. Eur. J.* **2000**, *6*, 1113.

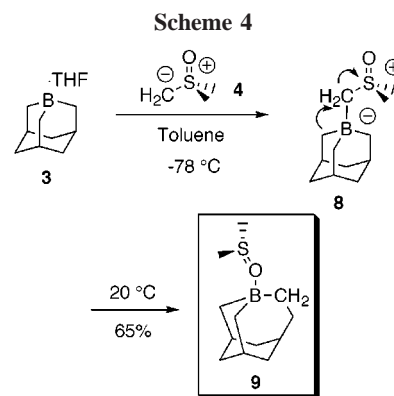
(4) (a) Mikhailov, B. M.; Baryshnikova, T. K.; Kiselev, V. G.; Shashkov, A. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, *28*, 2544. (b) Mikhailov, B. M.; Baryshnikova, T. K.; *Izv. Akad. Nauk SSSR, Ser. Khim. Nauk*, **1979**, *28*, 2541.

(5) Zakharkin, L. I.; Stanko, V. I. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1960**, 1896.

(6) Soderquist, J. A.; Najafi, M. R. *J. Org. Chem.* **1986**, *51*, 1330.

(7) Kabalka, G. W.; Hedgecock, H. C., Jr. *J. Org. Chem.* **1975**, *40*, 1776.

Monohomologation was achieved by slowly adding 1 equiv of ylide **4** to a solution of 1-boraadamantane·THF (**3**) in toluene at $-78\text{ }^\circ\text{C}$. The resulting white crystalline precipitate was filtered cold, washed with hexanes, and dried under vacuum (0.01 Torr, $-60\text{ }^\circ\text{C}$). Upon warming to room temperature under vacuum, the white crystalline solid rapidly melted, exothermically, forming a colorless liquid. The liquid crystallized upon cooling. These observations are consistent with the initial formation and isolation of a 1-boraadamantane·ylide complex (**8**) that subsequently undergoes a [1,2]-migration upon warming to room temperature. The expelled DMSO is captured to form 1-borahomoadamantane·DMSO (**9**) (Scheme 4).



Complex **9** sublimes (0.01 mmHg, $75\text{ }^\circ\text{C}$) and was isolated in 65% yield. The structure of **9** was confirmed by X-ray crystallography.

The *monohomologation* of 1-boraadamantane was previously achieved with trimethylamine methylide. The primary product, 1-borahomoadamantane·trimethylamine, proved difficult to separate from the *nonhomologated* 1-boraadamantane·trimethylamine formed as a byproduct of the reaction.⁸ *Monohomologation* of 1-boraadamantane by triphenylphosphine methylide could not be accomplished because of thermal decomposition prior to migratory insertion.⁹ Thus, the successful *monohomologation* of 1-boraadamantane depends not only on the facility with which the leaving group departs but also on the degree to which the ylide remains complexed to boron under a given set of conditions for [1,2]-migration. The *monohomologation* of 1-boraadamantane by dimethylsulfoxonium methylide (**4**) is a rather unique example, because it readily transpires from the solid state, but most importantly it demonstrates the controlled homologation of a trialkylborane¹⁰ by ylide **4**.

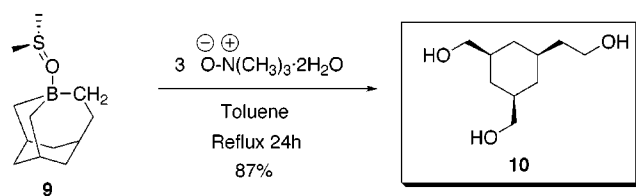
Compound **9** is readily oxidized with TAO, providing *cis*-1-hydroxyethyl-3,5-bis(hydroxymethyl)cyclohexane (**10**) in 87% yield after chromatography (Scheme 5).

(8) Mikhailov, B. M.; Govorov, N. N.; Angelyuk, Ya. A.; Kiselev, V. G.; Struchkova, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1980**, *29*, 1621.

(9) Mikhailov, B. M.; Gurskii, M. E.; Pershin, D. G. *J. Organomet. Chem.*, **1984**, *260*, 17.

(10) (a) Tufariello, J. J.; Lee, L. T. C. *J. Am. Chem. Soc.* **1966**, *88*, 4757. (b) Goddard, J.; Le Gall, T.; Mioskowski, C. *Org. Lett.* **2000**, *2*, 1455.

Scheme 5



1-Boraadamantane·THF (**3**) was then tested as an initiator for the polyhomologation reaction. Toluene solutions of ylide **4** were preheated to 80 °C and treated with an aliquot of a toluene solution of **3**. The ylide was rapidly consumed (5 min), and TAO was added to affect oxidation under reflux conditions. Removal of solvents followed by filtering and washing of the polymeric solids with methanol, water, and hexanes gave near quantitative crude yields of polymeric triol **6**. Purification by reprecipitation in toluene/acetonitrile afforded a purified white polymer in high yield.

The ^1H NMR spectra of the star polymer **6** (C_6D_6 , 78 °C) produced by these reactions have features consistent with the proposed assignment of a regular star architecture. There is a triplet at 3.38 ppm ($J = 6.4$ Hz) corresponding to terminal hydroxymethylene protons of **6**. Also, there is an apparent doublet at 1.85 ppm ($J = 12.2$ Hz) and a quartet at 0.59 ppm ($J = 11.8$ Hz) corresponding to the equatorial and axial methylene protons of the cyclohexane ring of **6** (Figure 1).

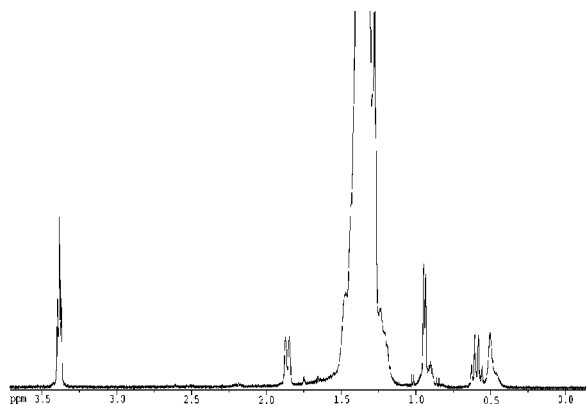


Figure 1. Representative ^1H NMR spectrum of polymeric triol **6** (C_6D_6 , 78 °C, 500 MHz). This spectrum depicts the polymeric product of trial 2 in Table 1.

The clear pseudo-symmetry of the equatorial and axial protons, as well as the multiplicity of the terminal hydroxymethylene groups, supports the conclusion that all three branches of the propagating species participate in migration to generate a star polymer.

The degree of polymerization (DP) was established by GPC and ^1H NMR end group analysis (Table 1). Reactions were run with initial ratios of ($1/3$)ylide:boraadamantane of

Table 1. Molecular Weight Data for Star Polymers **6**

| trial | DP ^a calcd | M_N^b | DP ^b | DP ^c | dead catalysts ^c | |
|-------|-----------------------|---------|-----------------|-----------------|-----------------------------|------------------|
| | | | | | (%) | PDI ^b |
| 1 | 25 | 2403 | 53 | 73 | 66 | 1.06 |
| 2 | 50 | 5595 | 129 | 148 | 66 | 1.09 |
| 3 | 69 | 10 542 | 246 | 190 | 63 | 1.08 |
| 4 | 138 | 19 613 | 462 | 345 | 60 | 1.08 |

^a The DP refers to n (Scheme 1). ^b Data refer to GPC in *o*-xylenes at 100 °C calibrated with linear polyethylene standards. ^c Data refer to ^1H NMR analysis end group analysis (i.e., the ratio of the terminal hydroxymethylene protons to the broad polymethylene peak of **6**).

25, 50, 69, and 138. These reactions should produce regular star polymers **6** with $n = 25, 50, 69,$ and $138,$ respectively (Scheme 1). In all cases, however, the DP by ^1H NMR end group analysis was consistently three times greater than the calculated DP.

While the GPC was calibrated with linear polyethylene standards, corrections for star topology should result in observed (GPC) molecular weights that are *lower* than the calculated molecular weight on the basis of stoichiometry.¹¹ Furthermore, previous examples of regular three-armed star polymethylene carbinol polymers resulted in polymers whose theoretical and observed molecular weights by GPC corresponded within 10%.³ Importantly, the PDI's of all trials in the present study are $<1.09,$ a result consistent with living polymerization.

Because extreme care was taken to quantitate the stoichiometric ratios of catalyst **3** to monomer **4**, it appeared that a significant fraction of propagating species terminated and did not result in polymer formation. This presented us with a mechanistic quandary. Following an apparent smooth initiation by **3**, approximately two-thirds of the propagating species must terminate (dead catalysts in Table 1) to account for the molecular weight discrepancy. The demise of these propagating species must be rather sudden, since competing termination reactions during the course of polymerization would result in a higher polydispersity.

Insight into this problem came from a polymerization conducted with an initial ($1/3$)ylide:boraadamantane ratio of 27. After oxidation and reprecipitation, polymer **6** was isolated in 93% yield. The polymer's DP was observed to be 100 by GPC with a polydispersity of 1.08. The *filtrate* from reprecipitation and washing of the polymer was found by TLC to contain a distribution of triols with R_f values similar to that of **10**. The triols were acetylated by heating with excess acetic anhydride at 100 °C, followed by purification by column chromatography.

The GC-chromatograph of the acetylated triols produced by the oxidation of terminated species revealed three components (Figure 2). The two species appearing at 20.9 and 21.7 min both have masses corresponding to a DP of 5 and account for 14 and 51% of the terminated species, respectively (MS-CI). The third component appearing at 22.4 min has a mass corresponding to a DP of 6 and accounts for

(11) Burchard, W. *Adv. Polym. Sci.* **1999**, *143*, 113.

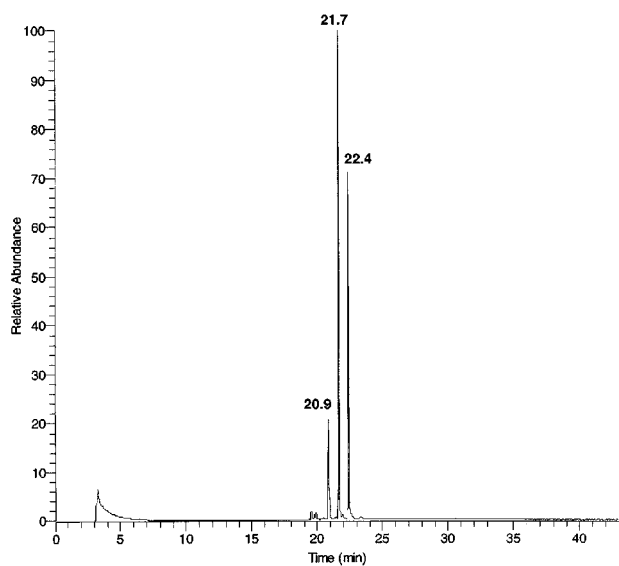


Figure 2. GC-chromatogram of acetylated triols produced by the oxidation of terminated species.

35% of the terminated species. The total mass of the acetylated triols accounts for 63% of the initiator used.

We now speculate that following the fourth and fifth methylene insertions the tricyclic organoboranes are presented with branch points in the path of polymerization. At these points, approximately 60–66% of the propagating species terminate by forming cage structures with collapsed, inverted pyramidal boron centers that are unreactive toward ylide. The remaining 34–40% of propagating species continue to polymerize via cage structures that remain reactive toward ylide and result in “tube-like” organoborane structures **5**. Preliminary results from molecular modeling

of the possible architectures and pathways of polymerization support this analysis and point to structures **11** and **12** as likely candidates for two of the terminated organoboranes with DP 5 (Figure 3).

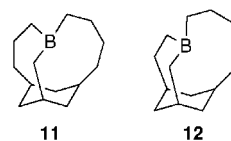


Figure 3. Possible candidates for two of the terminated organoboranes.

In conclusion, we have synthesized 1-borahomoadamantane·DMSO (**9**) by the controlled *monohomologation* of 1-boradamantane·THF (**3**) with dimethylsulfoxonium methylide (**4**). Also, we have demonstrated that **3** can be used as an initiator for polyhomologation, giving rise to “tube-like” trialkylborane structures **5**. The “tube-like” species **5** may be further elaborated by oxidation to regular star polymers **6**. Discrepancies between the calculated and observed molecular weight of **6** have led to the discovery of branch points in the early stages of polymerization in which approximately two-thirds of the propagating molecules terminate by the formation of unreactive tricyclic organoboranes. Molecular modeling offers insight into the possible candidates that result in the termination of the polymerization.

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