

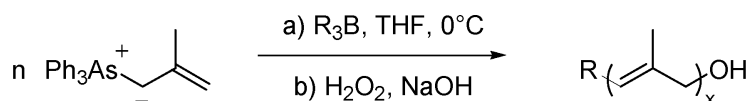
Communication

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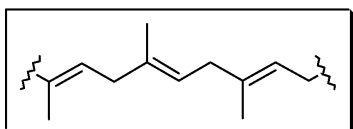
J. Am. Chem. Soc., **2003**, 125 (31), 9242-9243 • DOI: 10.1021/ja035792m • Publication Date (Web): 12 July 2003

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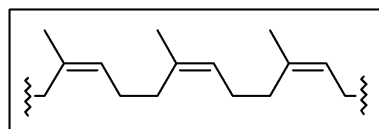


n = molar ratio of arsonium ylide to boron compound

New polymer:



Natural rubber:



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Chain Elongations by Three Carbon Atoms at a Time in the Boron-Catalyzed Polymerization of Methallyltriphenylarsonium Ylide

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It is of great interest to develop methods that can provide access to new polymeric structures, which could lead to useful applications for which known polymers are not suitable. In this report, we describe the boron compound-catalyzed polymerization of methallyltriphenylarsonium ylide **1**. In contrast with the well-known polymerization of alkenes, which proceeds by successive elongations of *two atoms* in a carbon chain, the polymerization described in the present work proceeds by successive elongations of *three carbon atoms at a time*.

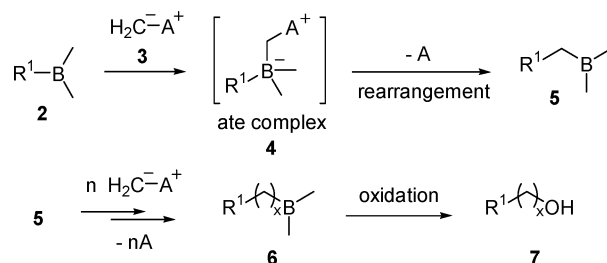
Boron compounds have been used as catalysts in the polymerization of diazomethane and other diazoalcanes.¹ Several reports of formation of oligomers in reactions of nucleophilic species having an α -leaving group with boron compounds have been published.^{2–4} However, until the recent studies of Shea and colleagues on the boron compound-catalyzed preparation of polymethylene and ethylene-propylene copolymers from sulfur ylides,^{5–7} such a method of polymerization was neglected. These reactions are thought to proceed as depicted in Scheme 1. Reaction of boron compound **2** with nucleophile **3** produces ate complex **4**, which rearranges, with loss of the leaving group A, to another boron compound **5**. The overall transformation from **2** to **5** corresponds to the insertion of a methylene group in a carbon–boron bond. If excess nucleophile is present, a polymerization may occur, leading to boron-containing polymer **6**, which can then be oxidized to the polymeric alcohol **7**.

The reaction of ylide **1** in the presence of trialkylboranes did not lead to polymers substituted on every carbon atom, but rather to polymers **8**, in which the chain has been elongated by three carbon atoms at a time. Polymers of varying degrees of polymerization were obtained by using varying ratios of ylide **1** to boron compound (Table 1).⁸ However, the degrees of polymerization were larger than expected from these ratios.

A representative ¹H NMR spectrum of polymer **8** is shown in Figure 1. Comparison of the ¹³C NMR chemical shifts observed in compound **8** and in the closely related polymers *cis*-polyisoprene and *trans*-polyisoprene (in particular those of the methyl groups) indicates that the double bonds are *E*-configured.⁹

The formation of polymer **8** can be explained as described in Scheme 2. Ate complex **9** initially produced from ylide **1** and boron compound **2** rearranges, with loss of triphenylarsine, to allylic borane **10**. The latter undergoes a [1,3] sigmatropic (or boratropic) rearrangement that leads to isomeric allylic borane **11**. Several cycles of reaction with ylide **1** eventually afford a polymeric boron compound, which is then oxidized to alcohol **8**. A [1,3] sigmatropic rearrangement is involved in each cycle.

Scheme 1. Polymerization of a Nucleophile Having an α -Leaving Group in the Presence of a Boron Compound^a



^a A = leaving group such as N₂, Me₂S(O).

Table 1. Preparation of Polymer **8** by Polymerization of Ylide **1** Catalyzed by Trialkylboranes Followed by Oxidative Treatment

entry	boron compound	<i>n</i> ^a	yield (%)	DP ^b
1	Bu ₃ B	9	89	12
2	Bu ₃ B	20	81	26
3	Et ₃ B	100	61	75

^a Molar ratio of ylide to boron compound. ^b Degree of polymerization, determined from ¹H NMR spectra integrations.

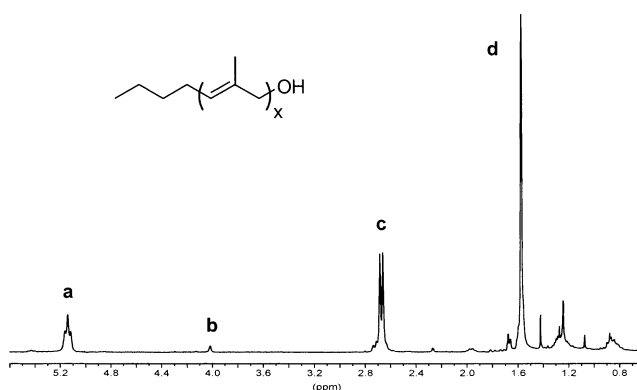


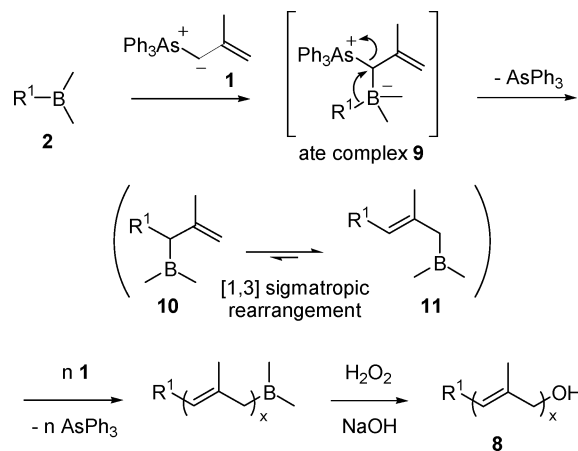
Figure 1. ¹H NMR spectrum (300 MHz, CDCl₃) of compound **8** (R = Bu; DP = 26). Spectral assignments of typical protons: (a) ethylenic proton; (b) CH₂O; (c) bis-allylic methylene proton; (d) methyl group.

Allylic boron compounds are prone to undergo a boratropic rearrangement, which involves an interaction between the double bond and the vacant orbital on the boron atom.¹⁰ This process is fast in allylic organoboranes, which are strong Lewis acids. In particular, NMR studies have shown that tris(methallyl)borane rearranged rapidly.¹¹ It is highly probable that any intermediate such

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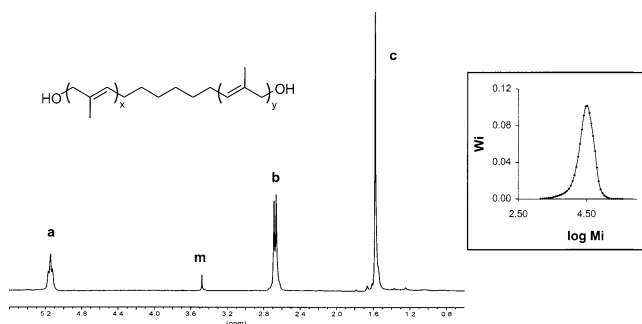
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Scheme 2. Mechanism of the Polymerization of Ylide 1**Table 2.** Preparation of Polymer **13** by Polymerization of Ylide **1** Catalyzed by *B*-Thexylborepane Followed by Oxidative Treatment

entry	n^a	DP ^b	yield (%)	M_w^c	M_n^c	M_w/M_n^c
1	10	425	81	33 570	23 040	1.46
2	50	490	74	39 600	26 470	1.50

^a Molar ratio of ylide to boron compound. ^b Degree of polymerization, determined from M_n . ^c M_w (weight-averaged molecular weights) and M_n (number-averaged molecular weights) determined versus polystyrene standards.

**Figure 2.** ¹H NMR spectrum (300 MHz, CDCl₃) of compound **13** (DP = 425). Spectral assignments of typical protons: (a) ethylenic proton; (b) bis-allylic methylene proton; (c) methyl group; (m) residual peak of methanol. Inset: SEC trace of compound **13** (versus polystyrene standards).

as **10**, which is obtained from ate complex **9**, will rearrange rapidly to **11**. In this compound, the boron atom is in a much less hindered position, and the double bond is in a more stabilized position; hence, **11** is certainly very favored.

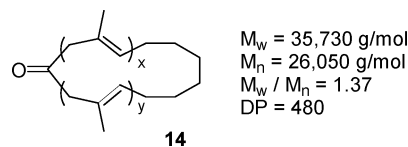
It should be noted that triphenylarsine oxide, formed during the oxidative treatment, is easily separated from the polymer either by chromatography or by precipitation of the polymer upon addition of methanol.

The polymerization of ylide **1** (10 or 50 equiv) in the presence of 1 equiv of *B*-thexylborepane **12**,^{12,13} a cyclic triorganoborane, was also evaluated (Table 2). After oxidation with alkaline hydrogen peroxide and purification, polymeric diol **13** was obtained. Its

structure was characterized by ¹³C NMR (four peaks, $\delta = 15.9$, 38.0, 122.1, 135.5 ppm), ¹H NMR, and size exclusion chromatography (Figure 2).

In both cases, the degree of polymerization of the polymer obtained was much larger than expected on the basis of the ratio of ylide to boron compound. This implies that only a small portion of borane **12** actually reacted with ylide **1**. It can be reasoned that **12** is much less reactive than the cyclic, allylic boranes obtained from this first reaction and from later reactions.

Polymeric, cyclic ketones were also prepared from **12**.¹³ Thus, **12** was treated with **1** (10 equiv) under the conditions described above, and then the mixture was treated with NaCN (2 equiv) and (CF₃CO)₂O (2.2 equiv) for 5 h from -78 °C to room temperature. After alkaline hydrogen peroxide oxidation, workup, and purification, polymeric ketone **14** was isolated as a white solid (yield 43%).



The SEC and the NMR spectra were in good accordance with the previously obtained polymers. The ketone function was characterized as its 2,4-dinitrophenylhydrazine adduct, the UV spectrum of which comprised a band typical of the corresponding hydrazone at $\lambda = 372$ nm.^{14,15}

In conclusion, the reaction of methallyltriphenylarsonium ylide **1** with boron compounds produces, via successive chain elongations of three carbon atoms at a time, new linear polymers arranged with regularity. In these polymers, methyl-substituted double bonds are separated by one methylene group, whereas in polyisoprene (rubber), such bonds are separated by two methylene groups. The method also allows the preparation of cyclic, polymeric ketones.

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JA035792M