

Boron-mediated polymerization of ylides derived from allylic arsonium salts: influence of the double bond substitution on the outcome†

Régis Mondière,^a Jean-Philippe Goddard,^a Mickaël Huiban,^a Géraldine Carrot,^b Thierry Le Gall^{*a} and Charles Mioskowski^{*ac}

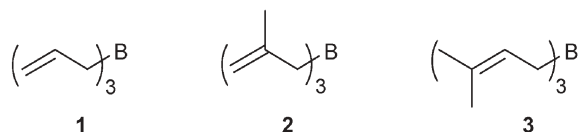
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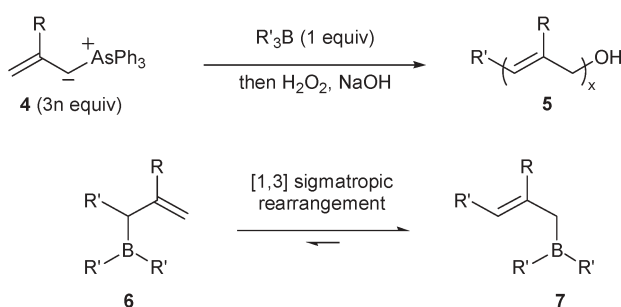
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New oligomers or polymers are prepared by polymerization of arsonium ylides in the presence of boron compounds.

The [1,3] sigmatropic rearrangement of allylic boron compounds has been the subject of several studies.^{1,2} The rate of the rearrangement depends on the substituents on boron and on the double bond. Thus, triallylborane **1** and trimethylallylborane **2** rearrange much more easily than triprenylborane **3**.³



We recently reported the polymerization of arsonium ylides **4**, in which the double bond is substituted in the 2-position by an alkyl group (R = methyl, ethyl, hexyl), in the presence of boron compounds (Scheme 1).^{4,5} The polymers **5** obtained resulted from successive chain elongations of three carbon atoms at a time. Each elongation cycle involves a [1,3] sigmatropic rearrangement of an allylic boron compound such as **6** leading to a favored isomer **7**, in which the boron atom is in a less crowded environment.



Scheme 1 Mechanism for the formation of a skipped polyene by boron-catalyzed polymerization of 2-substituted allylic arsonium ylides.

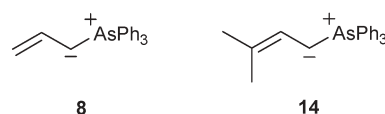
^aCEA-Saclay, Service de Marquage Moléculaire et de Chimie Bioorganique, Bât. 547, 91191 Gif-sur-Yvette, France. E-mail: thierry.legall@cea.fr; Fax: (+33) 1-6908-7991; Tel: (+33) 1-6908-7105

^bCEA-Saclay, Laboratoire Léon Brillouin CEA-CNRS, 91191 Gif-sur-Yvette, France

^cLaboratoire de Synthèse Bioorganique, UMR CNRS 7514, Faculté de Pharmacie, Université Louis Pasteur, 74 route du Rhin, B.P. 24, 67401 Illkirch, France. E-mail: mioskowski@aspirine.u-strasbg.fr; Fax: (+33) 3-9024-4306; Tel: (+33) 3-9024-4297

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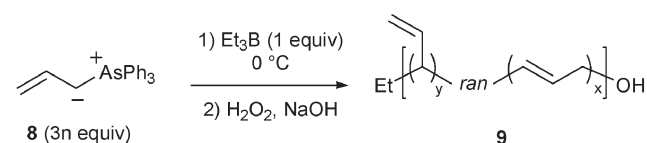
In this Communication, we report the boron-mediated polymerization of the arsonium ylides **8**, in which the double bond is not substituted, and **14**, in which the double bond is substituted by two methyl groups at the 3-position. The double bond substitution pattern in these ylides caused a striking impact on the polymerization outcome, and resulted in the formation of new polymeric materials.



Polymerization of ylide **8**, derived from allyltriphenylarsonium tetrafluoroborate,⁶ in the presence of Et₃B was carried out using initial molar ratios of ylide to Et₃B, *n* = 15, 30, 60 (corresponding to theoretical degrees of polymerization DP_{calcd} = 5, 10, 20, respectively). Addition of Et₃B to a bright red THF solution of ylide **8** at 0 °C led to an instantaneous discoloration, indicating the consumption of the ylide. After oxidative treatment and chromatography, oligomeric alcohols **9** were isolated in 56–84% yield (Table 1).

The oligomers were characterized by NMR and by size exclusion chromatography (SEC). The degree of polymerization, calculated using both techniques, was only slightly higher than expected from the initial ratios of ylide to boron compound employed in these reactions. The polydispersity indices (PDI) of the oligomers were very low. This may indicate a controlled process in the polymerization, although this would have to be confirmed in reactions leading to polymers having higher degrees of polymerization.

Table 1 Preparation of oligomer **9**



Entry	DP _{calcd} ^a	DP _{NMR} ^b	DP _{SEC} ^c	M _n ^c	PDI ^c	x/y ^d ratio	Yield (%)
1	5	7.7	5.8	277	1.14	2.1/1	84
2	10	13.0	14.3	620	1.10	2.4/1	56
3	20	23.1	20.6	871	1.09	1.9/1	61

^a Calculated from the initial molar ratio of ylide to boron compound. ^b Degree of polymerization, determined from ¹H NMR. ^c M_n, PDI, DP_{SEC} determined from SEC. ^d Ratio of propenylene to propenylidene moieties determined from ¹H NMR.

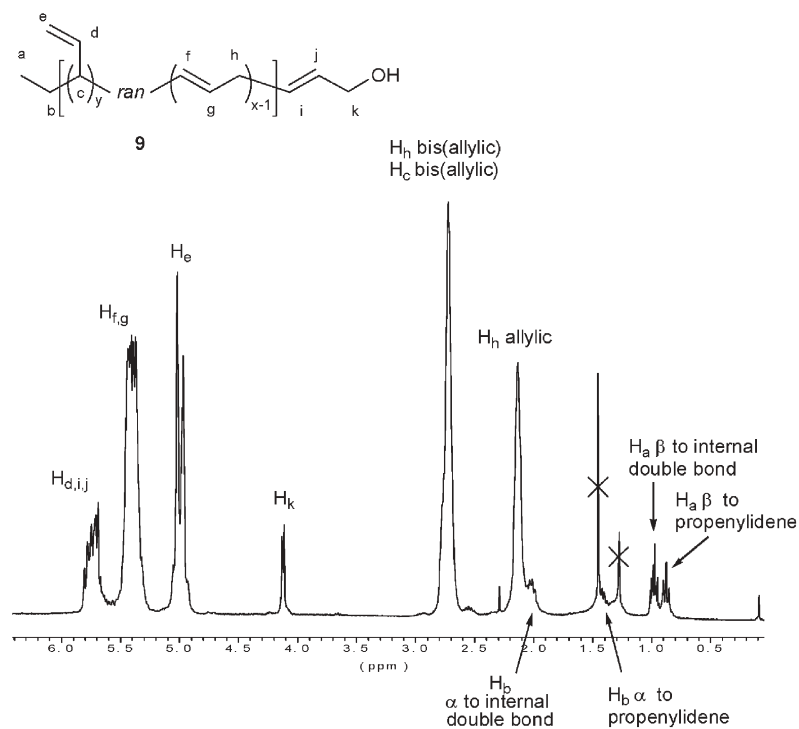
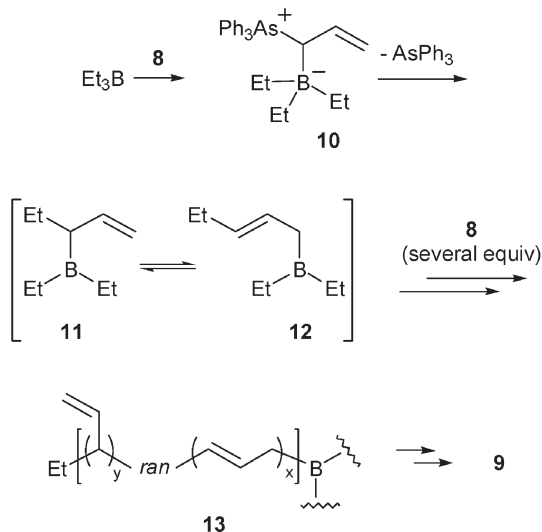


Fig. 1 ^1H NMR spectrum of polymer **9**.

Oligomer **9** is a poly(propenylene/propenylidene) copolymer, according to its ^1H NMR spectrum (Fig. 1). Characteristic signals corresponding to the bis(allylic) protons at $\delta = 2.5\text{--}2.8$ ppm and to the α -hydroxyl methylenic protons at $\delta = 4.12$ ppm were observed. The ratio of double bonds located in the main chain *versus* in the pendant groups, estimated by ^1H NMR, varied from 1.9 to 2.4.

Thus in the polymerization of ylide **8**, the successive chain elongations do not always involve a rearranged allylic organoborane (Scheme 2). In the first steps, formation of ate complex **10** is followed by 1,2-migration of an alkyl substituent from boron to carbon. The allylic organoborane **11** formed may then rearrange to isomer **12** or react with ylide **8**.



Scheme 2 Mechanism of formation of polymer **9**.

The [1,3] sigmatropic rearrangement may then happen, or not, at each cycle, leading to a random copolymer. A polymeric organoborane **13** is eventually obtained from the process, leading to alcohol copolymer **9** after oxidation. It is noteworthy that the absence of an alkyl substituent on the 2-position of the double bond in intermediates such as **11** makes it less susceptible to rearrange, indicating that the boron atom is less crowded in **11** than in **6**.

The ylide **14** derived from prenyltriphenylarsonium tetrafluoroborate⁷ was found to be less stable than **8**. At $0\text{ }^\circ\text{C}$, it decomposed rapidly. Hence, **14** was generated at $-40\text{ }^\circ\text{C}$, using either potassium hexamethyldisilazide or *tert*-butyllithium as the base, then the boron compound was added, either at $-40\text{ }^\circ\text{C}$ or at $-20\text{ }^\circ\text{C}$. In all cases, the compounds obtained were polymers corresponding to the general formula **15** (Table 2).

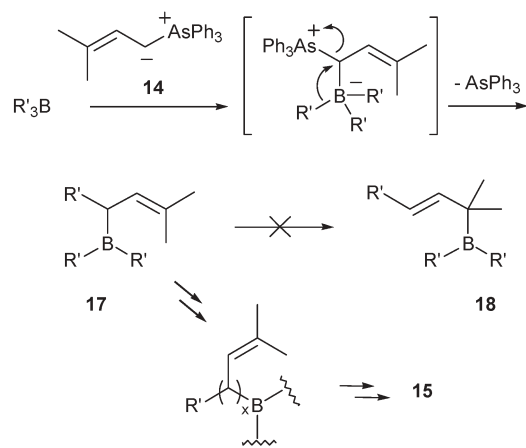
Reactions of Bu_3B with 9 equiv. of ylide led to oligomers, having a degree of polymerization (determined by NMR) higher than expected (entry 1). The oligomer obtained from the reaction of triethylborane with 9 equiv. of **14** had a degree of polymerization of 4.9, as determined by SEC (entry 2). Several attempts to obtain compounds having a higher degree of polymerization, by using higher ylide/boron compound ratio, failed, leading only to much lower yields of products. This could be due to an excessive crowding by three secondary alkyl groups around the boron atom, after several elongation cycles. An oligomer having a 9.7 degree of polymerization was isolated by reaction of methyl diethylborinate with 9 equiv. of **14** (entry 3).

A polymer having a much higher DP was obtained from the reaction of hexyl-1,3,2-dioxaborinane (**16**), although in lower yield (entry 4). This is probably due to two reasons: a) the crowding around the boron atom does not increase significantly during the polymerization, because the elongation occurs along a single

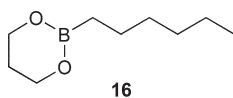
Table 2 Preparation of oligomer or polymer **15**^a

Entry	Boron compound	T/°C	DP _{calcd}	DP _{NMR}	DP _{SEC}	M _n	PDI	Yield (%)
1	Bu ₃ B	-20	3	5				78
2	Et ₃ B	-40	3	12.8	4.9	478	1.26	46
3	Et ₂ BOMe	-40	4.5	14.1	9.7	860	1.22	53
4	Boronate 16	-20 to RT	10		306	20950	1.56	21

^a See Table 1 for abbreviations meaning and supporting information for polymer analysis.

**Scheme 3** Mechanism of formation of polymer **15**.

substituent, b) the allylic boronates formed after the first insertion are much more reactive than alkylboronate **16**.



In the ¹H NMR spectra of polymer **15**, characteristic signals corresponding to the ethylenic protons ($\delta = 5.1\text{--}4.8$ ppm), to the α -hydroxyl protons ($\delta = 4.07$ ppm) and to the methyl protons ($\delta = 1.3\text{--}1.7$ ppm) were observed. The signals in the spectrum of polymer **15** having a larger DP are much broader.

The mechanism of formation of polymer **15** is summarized in the Scheme 3. At each step, a dimethylpropenylidene moiety is inserted into a carbon–boron bond and no [1,3] sigmatropic rearrangement occurs. This can be explained by considering that

adduct **17** is expected to be much more stable than the allylic organoborane **18** that would result from the rearrangement, in which the boron atom is in a very crowded position. Hence, the results obtained agree well with the observations of Mikhailov concerning the rearrangement rates of allylic boranes.³

In conclusion, the outcome of the boron-mediated polymerization of ylides derived from allylic arsonium salts depends on the possibility of [1,3] sigmatropic rearrangements occurring, which is related to the substitution of the double bond. New oligomers or polymers were obtained: polymer **15**, in which adjacent carbon atoms in the main chain are substituted by a prenyl group and copolymer **9** having double bonds located in the main chain or in pendant vinyl groups. The properties of these materials are currently under evaluation.

We thank Mrs P. Lixon (CEA, DRECAM) for performing the SEC analysis of one of the polymers.

Notes and references

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