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Synthesis of Poly(alcohol)s by Hydroboration/Oxidation of Poly(methylallene) Prepared by π-Allylnickel-Catalyzed Living Coordination Polymerization

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Summary

The π-allylnickel-catalyzed living coordination polymerization of methylallene gave
polymers with predictable molecular weight and narrow molecular weight distribution
in high yields. The polymers possessing various microstructural units (i.e., the ratio
of the 1,2- and the 2,3-polymerizations), produced by varying the nature of the
catalyst and the solvents, were subjected to the hydroboration with borane reagents
such as borane tetrahydrofuran complex ($BH_3\bullet THF$) and 9-borabicyclo[3.3.1]nonane
(9-BBN). Subsequent oxidation gave poly(alcohol)s whose hydroxy-content could be
varied by the borane reagents used. For example, the quantitative conversion of the
double bonds in poly(methylallene) into the hydroxy group was attained by
the hydroboration using an excess amount of $BH_3\bullet THF$. Thermal properties of
poly(alcohol)s were found to be dependent upon the microstructure and the hydroxy-
content of the polymers.

Introduction

Chemical transformation of reactive polymers is an important method for the
preparation of novel materials with diverse functions. Among the reactive polymers,
those with unsaturated systems are attractive for versatile transformations on the basis
of a variety of addition reactions toward the unsaturated systems. For example,
chemical transformation of poly(butadiene) into versatile functional materials has
been reported by means of addition reactions such as hydrogenation, epoxidation,
hydroboration/oxidation, and hydrosilylation reactions [1,2].
Polymers possessing hydroxy groups such as poly(vinyl alcohol), ethylene–vinyl
alcohol (EVAL) copolymer, and poly(2-hydroxyethyl methacrylate) are known to
serve as useful functional materials and precursors for various functional materials [3].
Nevertheless, their synthesis often implies rather complicated steps (e.g., the
protection, the polymerization, and the deprotection). Thus, polymer reactions are
important alternative methods to prepare polymers possessing hydroxy groups.

We reported the living coordination polymerization of allene derivatives by [(π-allyl)NiOCOCF$_3$]$_2$ (**1**) to give polymers with predictable molecular weight and narrow molecular weight distribution in high yields [4]. Two important features of this living polymerization are the possibility to incorporate versatile functional groups as substituents of the monomers and the precision control of microstructure of the polymers (i.e., the ratio of the 1,2- and the 2,3-polymerizations) by the catalysts and the solvents. For example, well-defined polymers containing hydroxy groups could be synthesized directly by the polymerization of hydroxy-containing allene derivatives [4i]. Alternatively, the chemical transformation of the unsaturated systems in the well-defined poly(allene)s might also be convenient for preparation of hydroxy-substituted polymers [5]. The hydroboration reaction is known to proceed smoothly under mild conditions, leading to the effective formation of alcohols by subsequent oxidation. Thus, the synthesis of well-defined poly(alcohol)s was carried out by the hydroboration/oxidation of poly(allene)s prepared by the π-allylnickel-catalyzed living coordination polymerization. For the present study, poly(methylallene) with varied microstructure was employed to evaluate the reactivity of two kinds of double bonds toward the hydroboration process.

Experimental

Materials and Instruments

A toluene solution of [(π-allyl)NiOCOCF$_3$]$_2$ (**1**) was prepared by the previously reported method [6]. Methylallene (**2**) was prepared as reported and purified by the trap–to–trap distillation under nitrogen (bp *ca.* 20 °C [lit. bp *ca.* 20 °C]) [7]. Toluene and THF were dried over sodium and distilled under nitrogen. Allyl trifluoroacetate and tributylphosphine were distilled under nitrogen. Tricyclohexylphosphine (PCy$_3$), BH$_3$•THF (1.03 M), and 9-BBN in THF (0.50 M) were used as received from Aldrich. Other reagents were used as received. All the polymerizations and the hydroboration reactions were carried out under nitrogen.

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECP-300 instrument using tetramethylsilane as an internal standard (300 MHz and 75 MHz for ^{1}H-NMR and ^{13}C-NMR, respectively). Fourier transform infrared (IR) spectra were recorded on a JASCO FT/IR-5300 instrument. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC-10AS equipped with Tosoh TSK-gel GMH$_{HR}$-M tandem columns using CHCl$_3$ as an eluent at 35 °C. Polystyrene standards were used for calibration. Thermogravimetric analyses (TGA) were performed on a Shimadzu TGA-50 instrument. Differential scanning calorimetry (DSC) measurements were performed on a Shimadzu DSC-60 instrument. TGA and DSC measurements were performed under nitrogen at a scan rate of 10 °C/min.

Coordination Polymerization of Methylallene (**2**) (Typical Procedure)

To an ample equipped with a three way cock and a magnetic stirrer bar, were added a toluene solution of **1** (0.013 M, 1.0 ml, 0.013 mmol) and **2** (0.054 g, 1.0 mmol, [**2**]/[**1**] = 80) at −78 °C under nitrogen. The resulting ample was sealed and kept stirring at ambient temperature for 12 h. The solution was precipitated into acetone

and dried under vacuum to isolate a polymer (**3A**) in 94 % yield (0.051 g). ^{1}H-NMR (CDCl$_3$, δ in ppm): 1.10 (>CH—CH_3, br, 3H x 0.1), 1.53 (C=CH—CH_3, br, 3H x 0.9), 2.58 (C=CH—CH_2—CH=C, br, 2H x 0.9), 2.73 (—CH<, br, 1H x 0.1), 4.75 (>C=CH_2, br, 2H x 0.1), 5.30 (>C=CH—CH$_3$, br, 1H x 0.9); x:y (in Scheme 1) = 10:90. ^{13}C-NMR (CDCl$_3$, δ in ppm): 13.5 (C=C—CH$_3$), 18.5 (>C—CH$_3$), 37.3 (C=C—CH$_2$—C=C), 45.8 (—CH<), 109.1 (>C=CH$_2$), 120.6 (>C=CH—CH$_3$), 135.2 (>C=CH—), 146.0 (>C=CH$_2$); IR (film, cm^{-1}): 3029, 2969, 2917, 2861, 1640, 1451, 1433, 1383, 1362, 1290, 1231, 1169, 1071, 1026, 895, 833, 760.

The other polymerization systems including those in the presence of other phosphine ligands and those in an alcoholic solvent obeyed this protocol. (**3B**: L = PBu$_3$, Solvent = EtOH/toluene (v/v = 1/1) and **3C**: L = PCy$_3$, Solvent = EtOH/toluene (v/v = 1/1)) and the polymers with different microstructural units (**3B**: x:y = 50:50 and **3C**: x:y = 70:30) were likewise isolated by precipitation into acetone and dried under vacuum.

Hydroboration of 3A–3C (Typical Procedure for the Synthesis of 4Ba)

To a three-necked flask containing a THF (2.00 ml) solution of **3B** (54.0 mg, 1.00 mmol unit, x:y = 50:50) was added BH$_3$•THF (1.03 M, 1.17 ml, 1.20 mmol, 3.60 equiv of the B—H group to the double bonds) at 0 °C and the mixture was kept stirring at that temperature for 30 min and then at ambient temperature for 1 h. To the resulting solution, a mixture of aqueous NaOH (3.0 M, 1.0 ml) and aqueous H$_2$O$_2$ (30 %, 1.0 ml) was added at 0 °C and the mixture was kept stirring at ambient temperature for an additional 2 h. After washing the resulting mixture with a large excess amount of MeOH/water (v/v = 1/1) using permeable membrane for 5 h, a polymer (**4Ba**) was collected in 98 % yield (70.6 mg) by precipitation into hexane. The hydroxy-content of **4Ba** was confirmed to be quantitative by its ^{1}H-NMR spectrum. ^{1}H-NMR (DMSO-d_6, δ in ppm): 0.78 (—CH_3, br, 3H), 0.90–2.65 (>CH—CH$_2$—, >CH—CH$_3$, C—CH_2—C, >CH—CH—, 2H x 0.5 (a) + 3H x 0.5 (b)), 3.00–3.95 (—CH_2—OH, >CH—OH, 2H x 0.5 (a) + 1H x 0.5 (b)), 4.12 (OH, br, 1H); a:b:c:d (in Scheme 2) = 50:50:0:0; ^{13}C-NMR (DMSO-d_6, δ in ppm): 12.5 (>CH—CH$_3$), 20.3 (—CHOH—CH$_3$), 25.5–47.0 (>CH—CH$_2$—, >CH—CH$_3$, >CH—CH—, C—CH$_2$—C), 61.6 (—CH$_2$—O), 67.1 (>CH—O); IR (film, cm^{-1}): 3333, 2967, 2936, 2886, 1460, 1381, 1314, 1107, 1034, 912.

Likewise, the hydroboration of **3A** and **3C** by BH$_3$•THF and that of **3B** by 9-BBN were performed to give polymers with various microstructures and the hydroxy-contents.

4Bb (from **3B** (x:y = 50:50), 9-BBN (1.2 equiv to the C=C units)): 89 % yield; ^{1}H-NMR (CDCl$_3$, δ in ppm): 0.50–1.40 (>C—CH_3, —CHOH—CH_3, >CH—CH_2—C, 3H x 0.21 + 3H x 0.29 + 3H x 0.08 + 2H x 0.08), 1.40–3.10 (>CH—CH$_3$, =C—CH_2—C, —OH, 1H x 0.21 + 1H x 0.29 + 2H x 0.42 + 1H x 0.29 + 1H x 0.08), 1.60 (=CH—CH_3, br, 3H x 0.42), 3.10–3.98 (>CH—OH, —CH_2—OH, 2H x 0.29 + 1H x 0.08), 4.92 (>C=CH_2, br, 2H x 0.21), 5.30 (>C=CH—CH$_3$, br, 1H x 0.42); a:b:c:d (in Scheme 2) = 29:8:21:42; ^{13}C-NMR (CDCl$_3$, δ in ppm): 13.7 (C=C—CH$_3$), 19.6 (>C—CH$_3$, —CHOH—CH$_3$), 22.0–49.0 (>CH—CH$_3$, C=C—CH$_2$—C, >CH—CH$_2$—, >CH—CH—, C—CH$_2$—C), 62.8 (—CH$_2$—OH), 67.1 (>CH—OH), 109.3 (>C=CH$_2$), 120.8 (>C=CH—CH$_3$), 134.7 (>C=CH—), 141.2 (>C=CH$_2$); IR (film, cm^{-1}): 3382, 3084, 2967, 2930, 2886, 1638, 1456, 1375, 1034, 908, 835, 733.

*Acetylation of **4Ba***

To a three-necked flask containing a pyridine (5.50 ml) solution of **4Ba** (64.9 mg, 0.90 mmol unit, a:b:c:d = 50:50:0:0) was added acetic anhydride (1.38 g, 13.5 mmol, 15.0 equiv excess to the hydroxy units in **4Ba**) and the mixture was kept stirring at 35 °C for 5 h. An acetylated polymer (**5Ba**) was collected in 98 % yield (94.0 mg) by precipitation into MeOH/water (v/v = 1/2). The acetyl-content of the polymer was confirmed to be quantitative by its ^{1}H-NMR spectrum. ^{1}H-NMR (CDCl$_3$, δ in ppm): 0.87 (—CH_3, br, 3H), 1.05–2.80 (>CH—CH_2—, >CH—CH_3, C—CH_2—C, >CH—CH—, 2H x 0.5 (a) + 3H x 0.5 (b)), 2.03 (—OCOCH_3, br, 3H), 4.06 (—CH_2—O, br, 2H x 0.5 (a)), 5.01 (>CH—O, br, 2H x 0.5 (b)); a:b:c:d (in Scheme 2) = 50:50:0:0; ^{13}C-NMR (CDCl$_3$, δ in ppm): 11.4 (>CH—CH$_3$), 14.0 (—CHOAc—CH$_3$), 20.9 (—CH$_2$—OCO—CH$_3$), 21.2 (>CH—OCO—CH$_3$), 25.0–51.0 (>CH—CH$_2$—, >CH—CH$_3$, >CH—CH—, C—CH$_2$—C), 65.3 (—CH$_2$—O), 71.5 (>CH—O), 170.4 (>CH—OCO—), 170.9 (—CH$_2$—OCO—); IR (film, cm^{-1}): 2967, 2936, 2880, 1734, 1460, 1373, 1246, 1038, 953, 756.

Results and Discussion

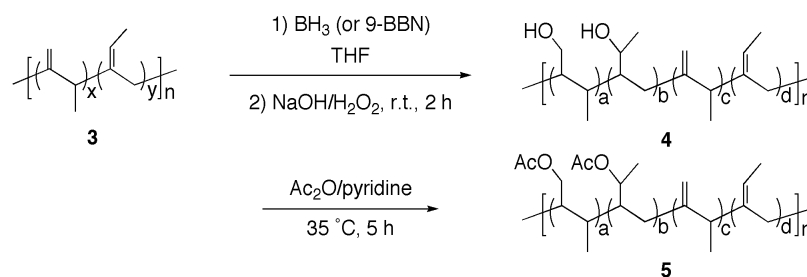*Conversion of Poly(methylallene) into Poly(alcohol)s*

As we described previously in the polymerization of *n*-alkylallenes [4e], the living coordination polymerization of **2** (80 equiv) proceeded smoothly by **1** at ambient temperature to give a narrowly dispersed polymer (**3A**, M_n = 5,900, M_w/M_n = 1.11) in a high yield whose 1,2- to 2,3-polymerization ratio (x:y) was 10:90 (Scheme 1). Likewise, polymers (**3B** and **3C**) with various contents of the 1,2- and the 2,3-polymerized units (x:y = 50:50 and 70:30, respectively) were prepared by modification of the polymerization conditions [8] and they were subjected to the conversion into poly(alcohol)s.
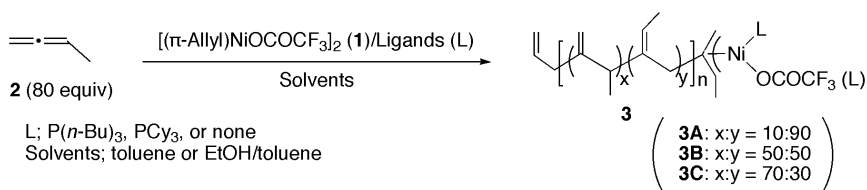
Scheme 1. Living coordination polymerization of **2** by **1**.

The hydroboration of **3A**, **3B**, and **3C** was carried out by using BH$_3$•THF at 0 °C for 30 min and then at ambient temperature for 1 h. Subsequent oxidation by H$_2$O$_2$/NaOH was carried out at 0 °C to ambient temperature for 2 h. The resulting mixture was washed with a large excess amount of MeOH/water (v/v = 1/1) using permeable membrane to remove inorganic salts [9]. Finally, white powdery polymers (**4Aa**, **4Ba**, and **4Ca**) were isolated in high yields by precipitation into acetone (Scheme 2 and Table 1). The poly(alcohol)s thus obtained are soluble in MeOH, EtOH, and DMSO, but insoluble in hexane, CHCl$_3$, and acetone. In all cases, the double bonds in both the 1,2- and the 2,3-polymerized units of **3** were converted quantitatively into the hydroxy

groups irrespective of their microstructure as convinced by their ^{1}H-NMR spectra [10]. In the case of **3B** (x:y = 50:50), for example, peaks for >C=CH_2 and >C=CH—CH$_3$ are observed at 4.75 and 5.30 ppm, respectively (Figure 1a). These peaks disappeared completely and new peaks for the methylene (>CH—CH_2—OH) and the methine (>CH—CH(OH)CH$_3$) are observed at 3.00–3.95 ppm in the spectrum of **4Ba** (Figure 1b). The high efficiency of this polymer reaction was supported further by the acetylation of **4Ba** with acetic anhydride. The quantitative conversion of the hydroxy groups of **4Ba** into the acetyloxy moieties was supported by its ^{1}H-NMR and IR spectra. The acetylated polymer (**5Ba**) is soluble in CHCl$_3$ and acetone but insoluble in hexane, MeOH, and DMSO. The GPC measurement (eluent: CHCl$_3$) of the acetylated polymer (**5Ba**) indicates that the polymer has narrow molecular weight distribution (M_n = 4,600, M_w/M_n = 1.17), supporting that neither the hydroboration/oxidation nor the acetylation involved any side reactions such as the cross-linking and the scission of the main chain of the polymers.

Scheme 2. Conversion of **3** into poly(alcohol)s (**4**) and their acetylated form (**5**).

Table 1. Conversion of poly(methylallene)s (**3A–3C**) into poly(alcohol)s.

	Poly(methylallene)s					Poly(alcohol)s		
Run	Polymer	x:y[a]	M_n[b]	M_w/M_n[b]	Borane	Conditions	Polymer	Yield(%)[c]	a:b:c:d[a]
1	**3A**	10:90	5,900	1.11	BH$_3$	r.t., 1 h	**4Aa**	98	10:90:0:0
2	**3B**	50:50	4,400	1.07	BH$_3$	r.t., 1 h	**4Ba**[d]	98	50:50:0:0
3	**3B**	50:50	4,400	1.07	9-BBN	30 °C, 12 h	**4Bb**	89	29:8:21:42
4	**3C**	70:30	4,700	1.04	BH$_3$	r.t., 1 h	**4Ca**	97	70:30:0:0

a) Determined by ^{1}H-NMR.
b) Estimated by GPC (CHCl$_3$, polystyrene Std).
c) Isolated yield after precipitation into acetone.
d) The molecular weight of the polymer obtained after acetylation (**5Ba**) was estimated by GPC (CHCl$_3$, polystyrene Std) to be M_n = 4,600, M_w/M_n = 1.17.

The use of 9-BBN (1.2 equiv to the C=C units) for the hydroboration of **3B** (x:y = 50:50) resulted in the formation of a polymer (**4Bb**) containing both the hydroxy groups and the unreacted double bonds. The poly(alcohol) thus obtained is soluble not only in the good solvents for **4Ba** (i.e., MeOH, EtOH, and DMSO) but also in CHCl$_3$

and acetone, reflecting upon the lower content of the hydroxy groups. The detailed information of the microstructural units in **4Bb** could be obtained by its ^{1}H-NMR analysis (Figure 1c). That is, a new broad peak for >CH—OH and —CH_2—OH was observed at 3.58 ppm besides the peaks at 4.92 ppm and 5.30 ppm attributable to >C=CH_2 and >C=CH—CH$_3$, respectively. The integral ratio of these peaks indicated that 58 % of the 1,2- and 16 % of the 2,3-polymerized units in **3B** were converted into the corresponding hydroxy groups. Namely, the less substituted double bond in the 1,2-polymerized units was found to be more reactive than the trisubstituted one in the 2,3-polymerized units toward the hydroboration with 9-BBN [11].
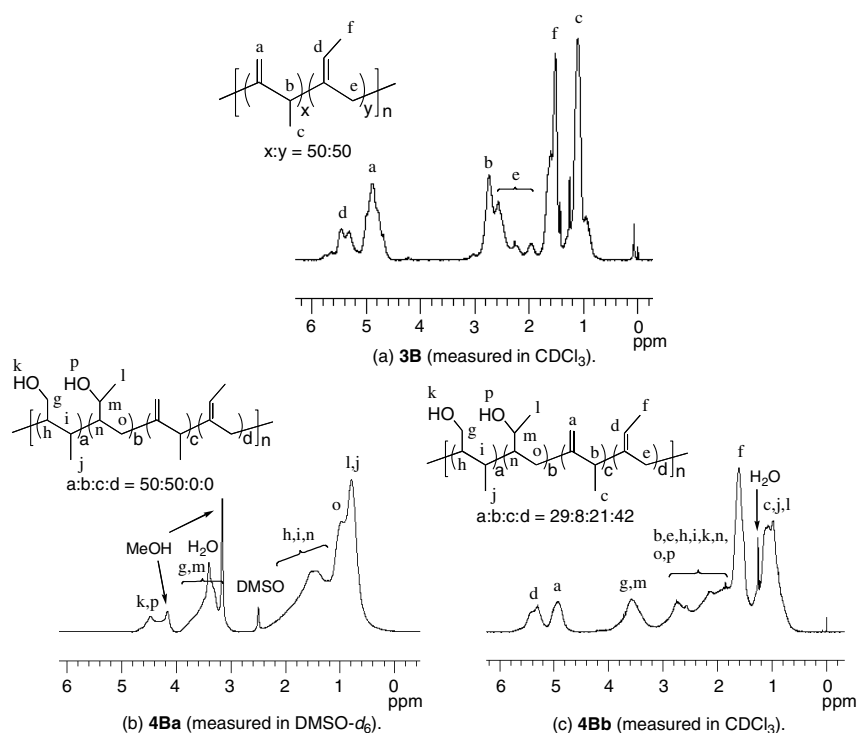

Figure 1. ^{1}H-NMR spectra of poly(methylallene) (**3B**) and hydroxy-containing polymers (**4Ba** and **4Bb**).

Thermal Properties of Poly(3) and Poly(alcohol)

Thermal properties of poly(alcohol)s were evaluated by DSC and TGA measurements (Table 2). The glass transition temperature (T_g) and the 10 % weight loss temperature (T_{d10}) of the poly(alcohol)s (**4**) were relatively high compared with those of **3**. Within the series of the polymers with varied ratio of the hydroxy-content (**3B**: 0 %, **4Bb**: 37 %, and **4Ba**: 100 %), both T_{d10} and T_g were found to increase as the ratio of the hydroxy-content increased. In the case of the polymers with quantitative hydroxy-content (**4Aa**, **4Ba**, and **4Ca**), T_g of the polymers was found to increase as the content of the 1,2-polymerized units increased. T_{d10} also increased as the content of the

primary alcohol units derived from the 1,2-polymerized units increased (i.e., T_{d10}'s of **4Aa**, **4Ba**, and **4Ca** were 265 °C, 271 °C, and 283 °C, respectively), presumably because the secondary alcohol units derived from the 2,3-polymerized units are more susceptible toward the thermal dehydration than that of the primary alcohol units [12].

Table 2. Thermal Properties of Poly(alcohol)s.

Run	x:y	Polymer	T_{d10} (°C)[a]	T_g (°C)[b]
1	10:90	**4Aa**	265	90
2	50:50	**4Ba**	271	124
3	50:50	**4Bb**	268	57
4	70:30	**4Ca**	283	129
5	50:50	**3B**	261	< r.t.

a) Estimated by TGA (10 °C/min, under N_2).
b) Estimated by DSC (10 °C/min, under N_2).

Conclusions

Poly(methylallene)s containing various microstructural units (x:y = 10:90 – 70:30), which were obtained by the allylnickel-catalyzed living coordination polymerization of methylallene, were subjected to the hydroboration with borane reagents such as $BH_3 \cdot THF$ and 9-BBN and subsequent oxidation to give poly(alcohol)s with various microstructure and hydroxy-content. That is, the double bonds in the starting polymer were converted quantitatively into alcohol moieties by the hydroboration using $BH_3 \cdot THF$ while the partial and the 1,2-unit-selective conversion was attainable by using 9-BBN. Thermal properties (the glass transition and the 10 % weight loss temperatures) of poly(alcohol)s were dependent upon the microstructure and the hydroxy-content of the polymers.

References and Notes

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5. To demonstrate the possibility of the chemical modification of the double bonds in the poly(allene)s, we described the hydrosilylation reaction of poly(allene) (poly(1,2-propadiene)) to give polymers having silane-coupling units. In this case, the 75 % of the exomethylene units ($>C=CH_2$) was silylated under the heating conditions. See, Taguchi M, Tomita I, Endo T (2000) Macromol Chem Phys 201:2322

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8. The microstructure of the polymers from substituted allenes is controllable by the anionic ligands (X), neutral ligands (L), and the polymerization solvents. We would like to report the details in the forth-coming paper.

9. If the polymer was isolated by precipitation without washing carefully by permeable membrane, the polymer became barely soluble in organic solvents probably by the cross-linking reaction between the hydroxy groups in the polymer and boric acid derivatives.

10. The hydroboration of both α,α-disubstituted and α,α,β-trisubstituted olefins (e.g., $CH_2=C(CH_3)C_2H_5$ and $CH_3CH=C(CH_3)_2$, respectively) by $BH_3 \bullet THF$ is known to give the anti-Markovnikov adducts in more than 98 % selectivity. Thus, the present polymer reactions are believed to proceed in an analogous selectivity, resulting in the preferential formation of less substituted alcohol units. See: Brown HC and Zweifel G (1960) J Am Chem Soc 82:4708.

11. The result obtained here is in good accordance with the fact that α,α-disubstituted olefins are more susceptible than trisubstituted ones to the selective hydroboration reagents such as 9-BBN. See: (a) Brown HC, Liotta R, Scouten CG (1976) J Am Chem Soc 98:5297 (b) Brown HC, Moerikofer AW (1963) J Am Chem Soc 85:2063

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