3294 © *1992 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***65***, *3294—3299 (1992)* [Vol. 65, No. 12

The Hydroboration of 3-Chloro-1-iodo-1-propyne with Dialkylboranes, and Its Application to the Syntheses of Some Geminally Dialkylated Propene Derivatives

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(Received July 1, 1992)

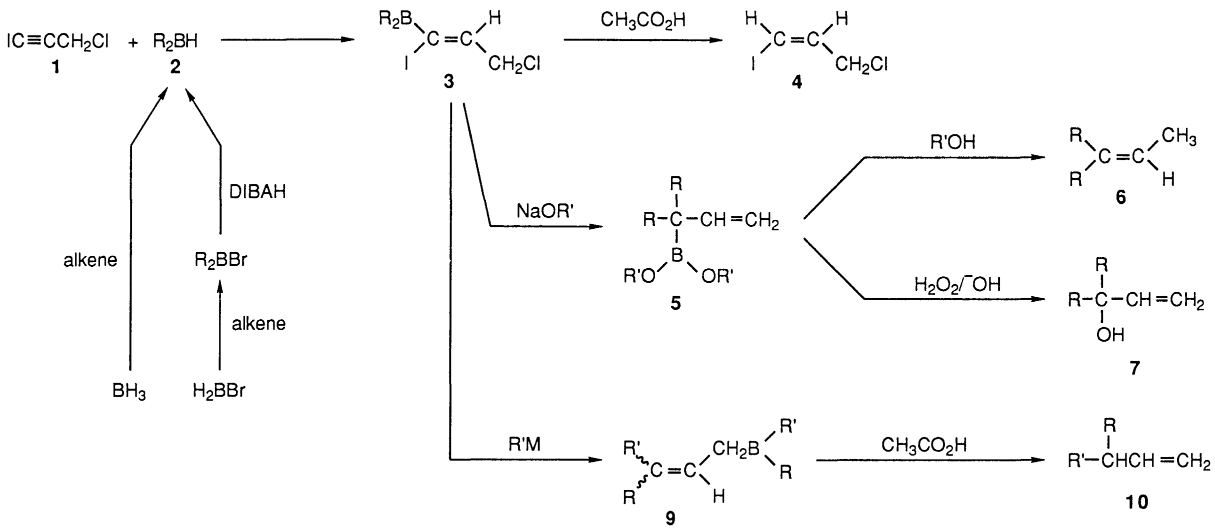
3-Chloro-1-iodo-1-propyne is smoothly hydroborated with dialkylboranes, giving (*Z*)-(3-chloro-1-iodo-1-propenyl)dialkylboranes exclusively. Subsequent treatment of the hydroboration mixture with sodium methoxide or aqueous sodium hydroxide results in migration of two alkyl groups from the boron atom to the α-alkenyl carbon atom to provide dialkylated allylboranes, which are protonolyzed with methanol or water to produce 1,1-dialkyl-1-propenes. Oxidation of the allylboranes with alkaline hydrogen peroxide prior to protonolysis gives 1,1-dialkyl-2-propen-1-ols. Treatment of (*Z*)-(3-chloro-1-iodo-1-propenyl)dicyclohexylborane with Grignard reagents, followed by protonolysis with acetic acid, provides 3-alkyl-3-cyclohexyl-1-propenes in which the alkyl group is derived from Grignard reagent.

Alkenylboranes having a halogen atom at a position very close to the alkenyl moiety can be utilized for a variety of organic transformations.[1] The reaction of such alkenyldialkylboranes with bases results in the intramolecular displacement of the halogen atom by the alkyl group on the boron atom to provide modified alkenylboranes with a new carbon–carbon bond.[2] In the course of the synthetic study on (haloalkenyl)dialkylboranes,[3] we have been interested in doubly functionalized alkenylboranes which were expected to be potential intermediates.[4]

We now report that 3-chloro-1-iodo-1-propyne (**1**) is smoothly hydroborated with dialkylboranes and the resulting (*Z*)-(3-chloro-1-iodo-1-propenyl)dialkylboranes (**3**) are interesting intermediates which may provide some different types of geminally dialkyl-substituted propenes by varing the subsequent treatment with base.

Results and Discussion

Hydroboration of **1** with an equimolar amount of dicyclohexylborane (**2a**) or bis(1,2-dimethylpropyl)borane (**2b**) in tetrahydrofuran (THF) proceeded smoothly at 0 °C, and was accomplished after 2 h, when a GLC analysis of the reaction mixture showed the



		vinylic H, δ	allylic H, δ
3a	; R= c-C_6H_{11}	5.77 (t, *J*=6.8 Hz)	4.24 (d, *J*=6.8 Hz)
3b	; R=$(CH_3)_2CHCH(CH_3)$	5.89 (t, *J*=6.8 Hz) 5.91 (t, *J*=6.8 Hz) (A mixture of diastereoisomers)	4.25 (d, *J*=6.8 Hz)

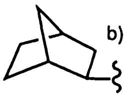
Scheme 1.

absence of unreacted **1** and also a hydrolysis of the reaction mixture, evolving no hydrogen, indicated the absence of unreacted hydride of **2a** or **2b**. The ^{1}H NMR study of the reaction product, obtained after removal of THF under reduced pressure, showed a triplet in the alkenyl proton region and a doublet in the α-monosubstituted aliphatic proton region indicating that the dialkylboryl group was introduced into the terminal carbon atom regioselectively. A treatment of each hydroboration mixture with acetic acid[5)] provided (*Z*)-3-chloro-1-iodo-1-propene (**4**) quantitatively and stereoselectively (Scheme 1). These results showed that the hydroboration provided (*Z*)-(3-chloro-1-iodo-1-propenyl)dicyclohexylborane (**3a**) or (*Z*)-(3-chloro-1-propenyl)bis(1,2-dimethylpropyl)borane (**3b**), a doubly functionalized alkenylborane, stereo- and regioselectively. The resulting **3** has two different types of halogen atoms, an alkenyl and an allyl halogen atom, both of which might participate in the base-assisted elimination. Therefore, it seemed of interest to examine the reaction of **3** with base in which the new carbon–carbon bond should be formed via the elimination of the halogen atom and the subsequent intramolecular rearrangement.

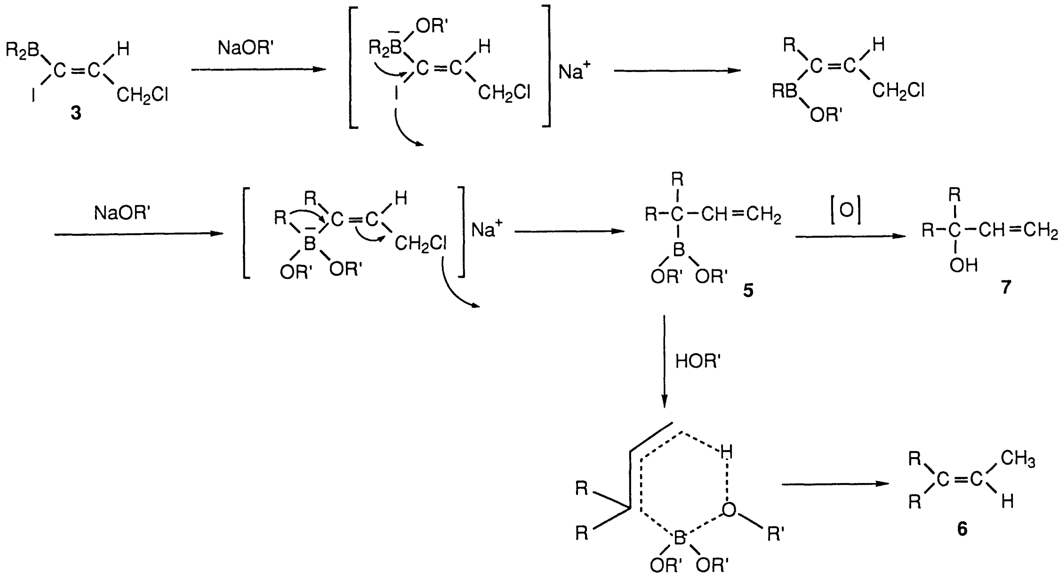
At first, sodium methoxide in methanol was added to the hydroboration mixture (**3a**) at 0 °C. After the reaction at room temperature for 1 h, the mixture was worked up and the products were isolated by column chromatography on silica gel to provide 1,1-dicyclohexyl-1-propene (**6a**) in 77% yield based on **1**. Similarly 3-(1,2-dimethylpropyl)-4,5-dimethyl-2-hexene (**6b**) was isolated in 66% yield via **3b**.

These results demonstrate that both of the alkyl groups on the dialkylboryl moiety migrated from the boron atom to the adjacent carbon atom with eliminations of the two halogen atoms. Thus it seemed that above reaction might be used as a method for the synthesis of geminally dialkylated propene. Therefore, we additionally examined similar reaction using such dialkylboranes as derived from terminal or sterically unhindered internal alkenes which could not form dialkylboranes effectively by usual hydroboration with BH_3. Thus such alkenes were hydroborated with monobromoborane–dimethyl sulfide complex [$BH_2Br \cdot S(CH_3)_2$] by the method described in the literature,[6)] and the resulting dialkylbromoboranes were treated with an equimolar amount of diisobutylaluminium hydride (DIBAH)[7)] to give the desired dialkylboranes. Then **1** was hydroborated with a stoichiometric amount of the dialkylborane (**2c**—**f**) thus prepared, in a mixture of diethyl ether and hexanes at 0 °C for 3 h and additionally at room temperature for 2 h. The hydroboration mixture was added to a mixture of aqueous sodium

Table 1. Yields of 1,1-Dialkyl-1-propene (**6**) and 1,1-Dialkyl-2-propen-1-ol (**7**)

R of R_2BH (**2**)	Product and Yield/%[a)]	
	$\mathrm{R_2C{=}C(H)CH_3}$ (**6**)	$\mathrm{R{-}CR(OH){-}CH{=}CH_2}$ (**7**)
c-C_6H_{11}	77	79
$(CH_3)_2CHCH(CH_3)$	66	72
n-C_6H_{13}[b)]	49 (5)[c)]	55
n-$C_3H_7CH(CH_3)CH_2$[b)]	76	
$C_6H_5CH(CH_3)CH_2$[b)]	65	
 b) (*exo*-)	54	

a) Isolated yields and based on **1** employed. b) Prepared by hydridation of R_2BBr with DIBAH. c) In the absence of HMPT.



Scheme 2.

hydroxide, hexamethylphosphoric triamide (HMPT), and THF at −15 °C, and then the reaction mixture was stirred for 1 h at room temperature to provide 1,1-dialkyl-1-propenes (**6c**—**f**) in acceptably good yields based on starting **1**. In the absence of HMPT, the yields of **6c**—**f** decreased markedly. These results are summarized in Table 1.

The reaction is presumed to proceed as shown in Scheme 2. Thus, the reaction of **3** with one equivalent of sodium methoxide or aqueous sodium hydroxide results in the base-induced intramolecular displacement of iodine atom by one of the two alkyl groups on the boron atom via an ate complex, followed by the migration of another alkyl group from the boron atom to the adjacent carbon atom with a shift of the double bond and an elimination of chlorine atom in a S_N2' manner via another ate complex with one more equivalent of sodium methoxide or aqueous sodium hydroxide to produce the corresponding allylborane (**5**). Then **5** is protonolyzed with methanol or water through a six-membered cyclic transition state[8] to provide **6**. Besides, on the prior elimination of the vinylic iodine atom to that of the allylic chlorine atom, an explanation is going to be performed later (in Scheme 3 and the related descriptions).

Previously, Zweifel et al. reported a synthesis of trisubstituted alkenes via protonation–iodination of lithium trialkyl-1-alkynylborates, where the two alkyl groups of trialkylboryl moiety migrated stepwise to 1-alkynyl carbon atom through the formation of 1,2-disubstituted vinylboranes.[9] Although the present reaction provided trisubstituted alkenes by the two alkyl groups migration similarly, it must have proceeded through the formation of the allylborane intermediate as described above, in contrast with the Zweifel's reaction.

Besides, when the reaction of **3** with aqueous sodium hydroxide was carried out at −15 °C, the formation of **6** was negligibly small. Therefore, with an expectation for a synthesis of allyl alcohol compounds, we examined the subsequent oxidative treatment of this base-treated reaction mixture with aqueous hydrogen peroxide at the same temperature (−15 °C). Thus, the treatement provided 1,1-dialkyl-2-propen-1-ol (**7a**—**c**), the desired products, in acceptably good yields in some cases (Table 1). These results not only support the reaction mechanism via **5** depicted in Scheme 2 but also suggest that above base treatment-oxidation sequence may become a method for the synthesis of 1,1-dialkylated allyl alcohol.

Another interesting type of the migration was observed when alkyllithium or Grignard reagent was employed as the base. For example, a treatment of **3a**, which afforded the best result in above reaction, with two equimolar amounts of methyllithium in diethyl ether in the presence of HMPT at −78 °C then room temperature, followed by protonolysis with acetic acid, provided 3-cyclohexyl-1-butene (**10a**) in 64% yield contaminated with a small amount of 3,3-dicyclohexyl-1-propene (**11**) (Scheme 1).

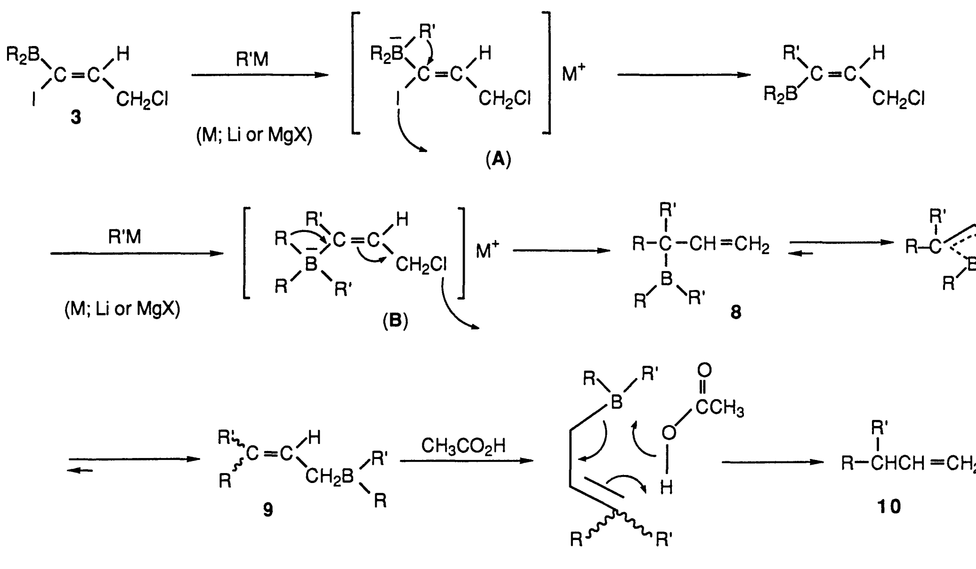
The formation of **10a** demonstrated that methyllithium acted not only as an agent for the elimination of the halogen atoms but also as an agent for supply of methyl group. Therefore, with an expectation that above reaction might be used generally for the synthesis of 3,3-dialkyl-1-propene having two different alkyl groups on the allylic carbon atom, some Grignard reagents and alkyllithiums were employed as the base. As appeared in Table 2, methyllithium and primary alkyl or allyl Grignard reagents provided relatively good results, though butyllithium and secondary alkylmagnesium bromide provided very poor results.

A reaction mechanism, including two sets of "an ate complex formation and a 1,2-migration of the alkyl group from the boron atom assisted by an elimination of the halogen atom" in a similar manner as above (in Scheme 2 and the related descriptions), is proposed for the above reaction as shown in Scheme 3. Hereon the first ate complex (**A**) is more likely to result in the prior elimination of the vinylic iodine atom to that of the allylic chlorine atom and the superior migration of R′(methyl, ethyl or allyl) to that of R (cyclohexyl), as estimated from our previous study (described in the Ref. 10). And the second ate complex (**B**) presumably results in the elimination of the allylic chlorine atom with the superior migration of R to that of R′, as estimated from Zweifel's previous work (described in the Ref. 11). Then the resulting allylborane **8** isomerizes to a more thermodynamically stable isomer **9**,[8,11] which forms **10** by subsequent protonolysis with acetic acid.[11]

Table 2. Yields of 3-Cyclohexyl-1-alkenes (**10**) and 3,3-Dicyclohexyl-1-propene (**11**)

R′M	Product and Yield/%[a]	
	$c\text{-}C_6H_{11}\overset{R'}{C}HCH{=}CH_2$ (**10**)	$(c\text{-}C_6H_{11})_2CHCH{=}CH_2$ (**11**)
CH_3Li	64	5
$n\text{-}C_4H_9Li$	0	17
CH_3MgI	52	10
C_2H_5MgBr	50	7
$(CH_3)_2CHMgBr$	0	13
$CH_2{=}CHCH_2MgBr$	75 (71)[b]	0

a) Determined by GLC and based on **1** employed. b) Isolated yield.



Scheme 3.

Above mechanism seems to be reasonable in consideration of the distribution of the products (**10** and **11**).

The present study revealed that the hydroboration of 3-chloro-1-iodo-1-propyne with dialkylboranes smoothly provided (*Z*)-(3-chloro-1-iodo-1-propenyl)dialkylboranes and the resulted doubly functionalized potential alkenylboranes were applicable to the synthesis of some geminally dialkylated propene derivatives, for example, via the subsequent reactions with basic agents.

Experimental

Instruments. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-200 (200 MHz) FT NMR spectrometer for a $CDCl_3$ solution containing TMS as the internal standard. IR spectra were recorded for liquid films inserted between NaCl plates in a Hitachi 285 spectrometer. Mass spectra were recorded with a Hitachi M-52 mass spectrometer. GLC analyses using the internal standard method were performed with a Hitachi 163 gas chromatograph equipped with a glass column (10% PEG-20M on Diasolid M, 2 m or 5% FFAP on Diasolid M, 1 m), a flame ionization detector, and a Shimadzu C-R3A Chromatopac digital integrator-recorder.

Materials. Alkenes and solvents in the reactions were used after purification by methods generally employed in similar organoborane chemistry.[12] 3-Chloro-1-iodo-1-propyne was prepared by a method described in the literature.[13] A 1.0 mol dm^{-3} solution of $BH_2Br \cdot S(CH_3)_2$ in dichloromethane, a 1.0 mol dm^{-3} solution of diisobutylaluminium hydride (DIBAH) in hexanes, and a 1.4 mol dm^{-3} solution of methyllithium in diethyl ether were obtained from Aldrich Chemicals. A solution of BH_3 in THF was prepared by a method described in the literature.[14] HMPT was distilled under vacuum from calcium hydride, and stored over Molecular Sieves-4A. Organic halides were dried over calcium chloride, purified by distillation, and stored under an argon atmosphere.

Representative Procedure. Synthesis of 1,1-Dicyclohexyl-1-propene (6a). A dry 100 cm^3 round-bottom flask, equipped with a gas inlet for argon, a septum inlet, and a magnetic stirring bar, was flushed with argon. In the flask, dicyclohexylborane (**2a**) (10 mmol) was prepared by the hydroboration of cyclohexene (1.64 g, 20 mmol) with BH_3 (10 mmol) in THF at 0 °C for 2 h. 3-Chloro-1-iodo-1-propyne (**1**) (2.00 g, 10 mmol) was added to **2a** at −15 °C, and the reaction mixture was stirred for 2 h at 0 °C to complete the hydroboration. To the reaction mixture (**3a**) was added a solution of 2 mol dm^{-3} sodium methoxide (20 cm^3) in methanol at −15 °C, and the solution was stirred for 1 h at room temperature. After the reaction, for the oxidative decomposition of a small amount of the unreacted organoborane residue, the contents was treated with 3 mol dm^{-3} aqueous sodium hydroxide (3.3 cm^3) and 30% hydrogen peroxide (3 cm^3) for 1 h at 0 °C. Then, the reaction mixture was extracted three times with diethyl ether, the combined extracts were washed with brine, and dried over anhydrous sodium sulfate. After removal of solvents on a rotary evaporator under reduced pressure, the products were isolated by column chromatography on silica gel (Wakogel Q-50), with pentane as eluent, to give **6a** as a liquid (1.59 g, 77% yield).

Synthesis of 3-Hexyl-2-nonene (6c). The experimental setup was the same as described in the synthesis of **6a**. The flask was cooled to 0 °C and charged with a solution of $BH_2Br \cdot S(CH_3)_2$ (10 cm^3, 10 mmol) in dichloromethane. To the stirred solution was added 1-hexene (1.68 g, 20 mmol), and the reaction mixture was stirred for 2 h at 25 °C to complete the hydroboration. After removal of dichloromethane and dimethyl sulfide under reduced pressure with a water aspirator, dry diethyl ether (40 cm^3) and dry dimethyl sulfide (2 cm^3) were added to the neat dihexylbromoborane at 0 °C, and the solution was stirred for 0.5 h at the same temperature. 3-Chloro-1-iodo-1-propyne (**1**) (2.00 g, 10 mmol) was added to the cooled solution (−78 °C), followed by the slow addition of a solution of DIBAH (10 cm^3, 10 mmol) in hexanes. The reaction mixture was brought to 0 °C, and stirred for 3 h at the same temperature and for an additional 2 h at room temperature to complete the hydroboration.

In another argon flushed 200 cm^3 round-bottom flask with the same equipments as described above was placed 6 mol dm^{-3} aqueous sodium hydroxide (10 cm^3), THF (20 cm^3), and HMPT (10 cm^3), and then the flask was cooled to −15 °C.

To this flask was transferred slowly the above hydroboration mixture using a "double-ended needle" [a length of stainless-steel needle tubing (ca. 50 cm) which was pointed to a standard bevel on both ends],12) and the reaction mixture was stirred for 1 h at room temperature. After the same work-up as described in the synthesis of **6a**, the products were isolated by column chromatography on silica gel (Wakogel Q-50), with pentane as eluent, to give **6c** as a liquid (1.03 g, 49% yield).

Synthesis of 1,1-Dicyclohexyl-2-propen-1-ol (7a). To the hydroboration mixture (**3a**) prepared using **1** (10 mmol) and **2a** (10 mmol) as described in the synthesis of **6a** were added 3 mol dm^{-3} aqueous sodium hydroxide (15 cm^3) and 30% hydrogen peroxide (10 cm^3) at −15 °C, and then the reaction mixture was stirred for 1 h at 0 °C. After the same work-up as described in the synthesis of **6a**, the products were isolated by column chromatography on silica gel (Wakogel Q-50), with a mixture of pentane and diethyl ether (85 : 15) as eluent, to give **7a** as a liquid (1.76 g, 79% yield).

Reaction of 3a with Methyllithium. The hydroboration of **1** (20 mmol) with **2a** (20 mmol) was carried out in a 200 cm^3 round-bottom flask as described in the synthesis of **6a**. To the hydroboration mixture (**3a**) at 0 °C was added dry HMPT (10 cm^3), and the solution was cooled to −78 °C immediately. A solution of methyllithium (28.6 cm^3, 40 mmol) in diethyl ether was added dropwise to the cooled solution, and the mixture was stirred for 0.5 h at the same temperature. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. Acetic acid (20 cm^3) was added to the solution at 0 °C, and the reaction mixture was stirred for 4 h at room temperature. The mixture was treated with water, and extracted three times with pentane. The combined extracts were washed with aqueous potassium carbonate and with brine, and dried over anhydrous sodium sulfate. After removal of solvents on a rotary evaporator under reduced pressure, products **10a** and **11** were collected from the residue by column chromatography on silica gel (Wakogel Q-50), with pentane as eluent, respectively.

Synthesis of 3-Cyclohexyl-1,5-hexadiene (10d). To the hydroboration mixture (**3a**) prepared using **1** (10 mmol) and **2a** (10 mmol) as described in the synthesis of **6a** was added dry HMPT (5 cm^3) at 0 °C, and the solution was cooled to −50 °C immediately. A solution of allylmagnesium bromide (20 mmol) in diethyl ether, prepared in another flask, was added dropwise to the cooled solution by using a "double-ended needle" (described above),12) and the mixture was stirred for 0.5 h at the same temperature. The reaction mixture was allowed to warm to room temperature and stirred overnight. Acetic acid (10 cm^3) was added to the solution at 0 °C, and the reaction mixture was stirred for 4 h at room temperature. After the same work-up as described in the reaction of **3a** with methyllithium, the products were isolated by column chromatography on silica gel (Wakogel Q-50), with pentane as eluent, to give **10d** as a liquid (1.17g, 71% yield).

The products were identified by following data.

(*Z*)-3-Chloro-1-iodo-1-propene (4): ^{1}H NMR δ=4.13 (d, *J*=6.8 Hz, 2H) and 6.3—6.6 (m, 2H); ^{13}C NMR δ=45.58 (–CH$_2$–), 86.79 (–CH=), and 136.68 (–CH=); IR (neat) 3060, 2920, 2850, 1600, 1450, 1430, 1370, 1305, 1245, 1210, 750, and 655 cm^{-1}; MS *m*/*z* 202 and 204 (M$^+$). Found: C, 17.95; H, 0.55%. Calcd for C_3H_4ClI: C, 17.80; H, 0.50%.

1,1-Dicyclohexyl-1-propene (6a): ^{1}H NMR δ=1.0—2.0 (m, 21H), 1.60 (d, *J*=6.8 Hz, 3H), 2.2—2.55 (m, 1H), and 5.16 (q, *J*=6.8 Hz, 1H); ^{13}C NMR δ=12.98 (CH$_3$–), 26.29 (–CH$_2$–), 26.39 (–CH$_2$–), 26.85 (–CH$_2$– ×2), 27.26 (–CH$_2$– ×2), 30.84 (–CH$_2$– ×2), 34.93 (–CH$_2$– ×2), 40.28 (>CH–), 40.55 (>CH–), 115.61 (–CH=), and 150.81 (>C=); IR (neat) 2920, 2840, 1420, 970, 890, and 810 cm^{-1}; MS *m*/*z* 206 (M$^+$). Found: C, 87.15; H, 12.85%. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70%.

3-(1,2-Dimethylpropyl)-4,5-dimethyl-2-hexene (6b): (A mixture of two diastereoisomers): ^{1}H NMR δ=0.8—1.1 (m, 18H), 1.5—1.85 (m, 6H), 1.95—2.3 (m, 1H), and 5.18 (q, *J*=6.8 Hz) and 5.23 (q, *J*=6.8 Hz) (1H); ^{13}C NMR δ=13.35, 13.79, 16.85, 17.29, 18.17, 18.31, 18.94, 20.96, 21.09, 21.99, 22.23, and 22.42 (7 CH$_3$–), 31.23, 31.33 (2C), 32.59, 41.32, 41.91, 43.71, and 43.80 (4 >CH–), 117.32 and 117.53 (–CH=), and 148.14 and 148.60 (>C=); IR (neat) 2960, 2870, 1450, 1370, 1150, 1100, 975, 950, 890, and 825 cm^{-1}; MS *m*/*z* 182 (M$^+$). Found: C, 85.57; H, 14.43%. Calcd for $C_{13}H_{26}$: C, 85.63; H, 14.37%.

3-Hexyl-2-nonene (6c): ^{1}H NMR δ=0.8—1.0 (m, 6H), 1.1—1.5 (m, 16H), 1.57 (d, *J*=6.8 Hz, 3H), 1.9—2.1 (m, 4H), and 5.18 (q, *J*=6.8 Hz, 1H); ^{13}C NMR δ=13.18 (CH$_3$–), 14.13 (CH$_3$– ×2), 22.69 (–CH$_2$– ×2), 28.21 (–CH$_2$– ×2), 29.21 (–CH$_2$–), 29.45 (–CH$_2$–), 29.70 (–CH$_2$–), 31.84 (–CH$_2$– ×2), 37.04 (–CH$_2$–), 117.97 (–CH=), and 140.74 (>C=); IR (neat) 2960, 2925, 2850, 1460, 1375, 1020, 820, and 720 cm^{-1}; MS *m*/*z* 210 (M$^+$). Found: C, 85.68; H, 14.32%. Calcd for $C_{15}H_{30}$: C, 85.63; H, 14.37%.

3-(2-Methylpentyl)-5-methyl-2-octene (6d): (A mixture of two diastereoisomers): ^{1}H NMR δ=0.7—0.95 (m, 12H), 1.0—2.1 (m, 14H), 1.45—1.65 (m, 3H), and 5.15—5.35 (m, 1H); ^{13}C NMR δ=13.47 (CH$_3$–), 14.37 (CH$_3$– ×2), 19.48 (CH$_3$–), 19.72 (CH$_3$–), 20.21, 20.26, and 20.33 (2–CH$_2$–), 30.50 and 30.60 (>CH–), 31.20 and 31.30 (>CH–), 36.39 and 36.75 (–CH$_2$–), 39.13 and 39.26 (–CH$_2$–), 39.55 and 39.67 (–CH$_2$–), 44.92 and 45.22 (–CH$_2$–), 120.67 (–CH=), and 138.07 (>C=); IR (neat) 2960, 2920, 2860, 1450, 1375, 1150, 945, 835, 770, and 735 cm^{-1}; MS *m*/*z* 210 (M$^+$). Found: C, 85.70; H, 14.30%. Calcd for $C_{15}H_{30}$: C, 85.63; H, 14.37%.

3-(2-Phenylpropyl)-5-phenyl-2-hexene (6e): (A mixture of two diastereoisomers): ^{1}H NMR δ=1.05—1.3 (m, 6H), 1.3—1.6 (m, 3H), 1.95—2.4 (m, 4H), 2.7—2.95 (m, 2H), 5.18 (q, *J*=6.8 Hz) and 5.29 (q, *J*=6.8 Hz) (1H), and 7.0—7.4 (m, 10H); ^{13}C MMR δ=13.35 and 13.42 (CH$_3$–), 20.87 and 21.06 (CH$_3$–), 21.52 and 21.64 (CH$_3$–), 37.84, 38.11, 38.23, 38.40 (2 >CH–), 38.28 (–CH$_2$–), 45.94 and 46.02 (–CH$_2$–), 122.32 (–CH=), 125.73 (–CH=), 125.88 (–CH=), 126.90 (–CH= ×2), 126.95 (–CH= ×2), 128.16 (–CH= ×2), 128.21 (–CH= ×2), 136.36 and 136.58 (>C=), and 147.33, 147.62, 147.67, and 147.84 (2>C=); IR (neat) 3060, 3020, 2960, 2920, 1595, 1490, 1445, 1370, 1070, 1010, 905, 830, 755, and 695 cm^{-1}; MS *m*/*z* 278 (M$^+$). Found: C, 90.70; H, 9.30%. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41%.

1,1-Bis(*exo*-bicyclo[2.2.1]hept-2-yl)-1-propene (6f): (A mixture of two diastereoisomers): ^{1}H NMR δ=1.0—1.7 (m, 19H), 1.95—2.3 (m, 5H), 2.4—2.6 (m, 1H), and 5.05—5.25 (m, 1 H); ^{13}C NMR δ=13.64 and 13.76 (CH$_3$–), 28.67 (2C), 28.84, 28.94, 30.57, 30.62, 31.57 (2C), 35.73, and 36.09 (5 –CH$_2$–), 36.17 (2C), 36.43, and 36.53 (2 >CH–), 37.50 (2C), 38.19, 38.36, 39.04, and 39.67 (3 –CH$_2$–), 41.03, 41.18, 42.22, 42.66, 42.93, 43.00, and 43.20 (2C) (4 >CH–), 115.39 and 115.71 (–CH=), and 149.43 (>C=); IR (neat) 2940, 2860, 1470, 1445, 1305, 1295, 1205, 1140, 1030, 935, 875, 835, 810, and 750 cm^{-1}; MS *m*/*z* 230 (M$^+$). Found: C, 88.54; H, 11.46%. Calcd for $C_{17}H_{26}$: C, 88.63; H, 11.37%.

1,1-Dicyclohexyl-2-propen-1-ol (7a): ^{1}H NMR δ=0.85—2.1 (m, 23H), 5.10 (dd, *J*=8.8 and 2 Hz, 1H), 5.17 (d, *J*=2 Hz, 1H), and 5.6—5.85 (m, 1H); ^{13}C NMR δ=26.07 (–CH$_2$– ×2), 26.58 (-CH$_2$- ×2), 26.63 (-CH$_2$- ×2), 26.85 (-CH$_2$- ×2), 27.29 (-CH$_2$- ×2), 42.69 (>CH- ×2), 79.25 (>C<), 113.11 (CH$_2$=), and 141.54 (-CH=); IR (neat) 3500, 2920, 2850, 1445, 1405, 1310, 1165, 995, 965, 915, 890, and 730 cm^{-1}; MS *m*/*z* 222 (M$^+$). Found: C, 80.96; H, 11.85%. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79; O, 7.19%.

3-(1,2-Dimethylpropyl)-4,5-dimethyl-1-hexen-3-ol (7b): (A mixture of four diastereoisomers): ^{1}H NMR δ=0.7—1.0 (m, 18H), 1.15—1.4 (m, 1H), 1.6—2.2 (m, 4H), 4.5—5.3 (m, 2H), and 5.65—5.9 (m, 1H); IR (neat) 3375, 2960, 2870, 1460, 1390, 1365, 1265, 1170, 1100, 1065, 1005, 955, 915, and 710 cm^{-1}; MS *m*/*z* 198 (M$^+$). Found: C, 78.60; H, 13.25%. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21; O, 8.07%.

3-Hexyl-1-nonen-3-ol (7c): ^{1}H NMR δ=0.8—0.95 (m, 6H), 1.1—1.75 (m, 21H), 5.08 (dd, *J*=10.7 and 1.5 Hz, 1H), 5.18 (dd, *J*=17.6 and 1.5 Hz, 1H), and 5.7—5.9 (m, 1H); ^{13}C NMR δ=14.08 (CH$_3$- ×2), 22.62 (-CH$_2$- ×2), 23.40 (-CH$_2$- ×2), 29.77 (-CH$_2$- ×2), 31.81 (-CH$_2$- ×2), 40.81 (>CH- ×2), 75.50 (>C<), 112.04 (CH$_2$=), and 144.24 (-CH=); IR (neat) 3450, 3080, 2925, 2855, 1460, 1410, 1375, 1140, 1060, 995, 950, 915, and 725 cm^{-1}; MS *m*/*z* 226 (M$^+$). Found: C, 79.46; H, 13.30%. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.35; O, 7.07%.

3-Cyclohexyl-1-butene (10a): ^{1}H NMR δ=0.96 (d, *J*=6.8 Hz, 3H), 1.0—2.05 (m, 12H), 4.8—5.0 (m, 2H), and 5.6—5.85 (m, 1H); ^{13}C NMR δ=17.10 (CH$_3$-), 26.66 (-CH$_2$- ×3), 30.23 (-CH$_2$-), 30.33 (-CH$_2$-), 42.83 (>CH-), 43.51 (>CH-), 112.96 (CH$_2$=), and 143.63 (-CH=); IR (neat) 3070, 2920, 2845, 1640, 1445, 1410, 1370, 1260, 990, 910, 890, and 840 cm^{-1}; MS *m*/*z* 138 (M$^+$). Found: C, 86.96; H, 13.04%. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12%.

3,3-Dicyclohexyl-1-propene (11): ^{1}H NMR δ=0.7—2.0 (m, 23H), 4.83 (dd, *J*=17.1 and 2.4 Hz, 1H), 4.99 (dd, *J*=10.2 and 2.4 Hz, 1H), and 5.4—5.65 (m, 1H); ^{13}C NMR δ=26.70 (-CH$_2$- ×2), 26.78 (-CH$_2$- ×4), 29.60 (-CH$_2$- ×2), 31.81 (-CH$_2$- ×2), 37.41 (>CH- ×2), 56.19 (>CH-), 115.73 (CH$_2$=), and 139.77 (-CH=); IR (neat) 3060, 2910, 2840, 1630, 1440, 1410, 1340, 1260, 995, 970, 910, 890, 840, and 725 cm^{-1}; MS *m*/*z* 206 (M$^+$). Found: C, 87.41; H, 12.59%. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70%.

3-Cyclohexyl-1-pentene (10b): ^{1}H NMR δ=0.82 (t, *J*=7.3 Hz, 3H), 0.9—2.05 (m, 14H), 4.90 (dd, *J*=17.1 and 2.4 Hz, 1H), 4.98 (dd, *J*=10.7 and 2.4 Hz, 1H), and 5.4—5.65 (m, 1H); ^{13}C NMR δ=12.08 (CH$_3$-), 24.39 (-CH$_2$-), 26.73 (-CH$_2$- ×3), 29.72 (-CH$_2$-), 31.20 (-CH$_2$-), 41.52 (>CH-), 52.03 (>CH-), 114.93 (CH$_2$=), and 141.47 (-CH=); IR (neat) 3070, 2920, 2845, 1635, 1445, 1415, 1375, 1260, 995, 905, and 890 cm^{-1}; MS *m*/*z* 152 (M$^+$). Found: C, 86.85; H, 13.15%. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24%.

3-Cyclohexyl-1,5-hexadiene (10d): ^{1}H NMR δ=0.8—1.4 (m, 14H), 4.8—5.1 (m, 4H), and 5.45—5.85 (m, 2H); ^{13}C NMR δ=26.61 (-CH$_2$-), 26.66 (-CH$_2$- ×2), 29.38 (-CH$_2$-), 31.11 (-CH$_2$-), 36.36 (-CH$_2$-), 41.06 (>CH-), 49.79 (>CH-), 115.05 (CH$_2$=), 115.18 (CH$_2$=), 137.75 (-CH=), and 140.86 (-CH=); IR (neat) 3070, 2980, 2920, 2850, 1815, 1640, 1445, 1415, 1345, 1260, 995, 910, 845, 730, and 700 cm^{-1}; MS *m*/*z* 164 (M$^+$). Found: C, 87.87; H, 12.13%. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27%.

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