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# Syntheses with organoboranes. IX. Vinyl- and 1-alkenyldichloroboranes as ethylene and 1-alkene equivalents for the Diels–Alder reaction

Marek Zaidlewicz *, Jacek R. Binkul, Wojciech Sokół

*Faculty of Chemistry, Nicolaus Copernicus University, PL-7-100 Toruń, Poland*

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**Abstract**

Vinyl- and 1-alkenyldichloroboranes were used as dienophiles for the Diels–Alder reaction with representative aliphatic and cyclic 1,3-dienes. The organoborane adducts were transformed into the corresponding olefins either by protonolysis or by oxidation–mesylation–reduction. Direct protonolysis of the adducts gave in most cases mixtures of olefins whereas the reduction of mesylates with lithium triethylborohydride produced pure olefins in good yields. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Diels–Alder reaction; Vinylic organoborane dienophiles

## 1. Introduction

The Diels–Alder reaction is one of the most important methods for the construction of six-membered rings. Among a variety of useful dienophiles the simplest one ethylene and 1-alkenes react sluggishly [1]. Consequently, their equivalents are highly desirable and a few such compounds have been introduced [2]. Vinylic organoboranes are good candidates for that purpose, provided they would be sufficiently reactive and the carbon-boron bond of the adduct could be transformed into the carbon–hydrogen bond without isomerization of the double bond. Recently, it has been shown that in contrast to vinylic boronates, vinylic dialkyl- and dihalogenoboranes are considerably more reactive dienophiles [3–8]. They are synthetically attractive since the organoborane adducts can be functionalized by further transformations of the carbon–boron bond.

Protonolysis of trialkylboranes can be achieved by heating with carboxylic acids, but little is known on the reaction course of alkenylboranes with isolated double bonds under these conditions [9]. Racemization due to the double-bond shift has been observed in protonolysis of the monohydroboration product of (+)-limonene [10]. Other methods for the transformation of carbon–boron bond into carbon–hydrogen bond are also known [11,12]. However, the scope of these reactions is not well delineated. Consequently, we undertook a study on the vinylic dialkyl- and dihalogenoboranes as ethylene and 1-alkene equivalents for the Diels–Alder reaction.

## 2. Results and discussion

The following vinylboranes were used as dienophiles: dibromovinylborane (**1**), dichlorovinylborane (**2**), di-*n*-butylvinylborane (**3**) and B-vinyl-3,6-dimethylborepane (**4**) (B-vinyl-DMB). They are readily prepared from boron tribromide, boron trichloride, di-*n*-butylbromo-

* Corresponding author. Fax: +48-56-6542-477.
*E-mail address:* zaidlevi@chem.uni.torun.pl (M. Zaidlewicz)


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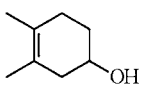
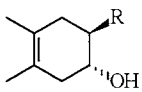
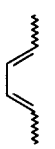
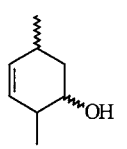
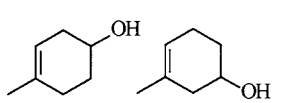
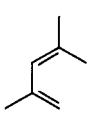
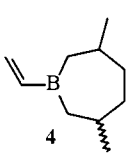
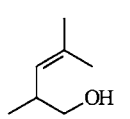
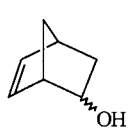
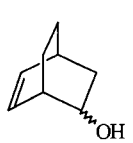
borane and B-chloro-3,6-dimethylborepane, respectively, by the reaction with tetravinyltin or tri-*n*-butylvinyltin [4,13–15]. In the preparation of dibromovinylborane, the unreacted boron tribromide is conveniently removed by complexation with dimethyl sulfide.

The reactivity of **1-4** was tested for the reaction with 2,3-dimethyl-1,3-butadiene (**8**) monitored by $^{11}$B-NMR analysis. The results shown in Table 1 indicate high reactivity of dibromovinylborane. The reaction was exothermic and the temperature had to be carefully controlled. Dichlorovinylborane was less reactive but

Table 1
The reaction of vinylic organoboranes **1-7** with dienes **8-13** and oxidation[a]

| Diene | Vinylic organoborane | Temp. °C | Time h | Adduct $^{11}$B NMR δ, ppm | Adduct Yield[b] % | Product alcohol Composition % | | Product alcohol Yield[c] % |
|---|---|---|---|---|---|---|---|---|
| | $H_2C$=CHBBr$_2$ **1** | −10 | 0.25 | 65.0 | >95 | | | 81 |
| | $H_2C$=CHBCl$_2$ **2** | 25 | 1 | 61.3 | >95 |  | | 70 |
|  | $H_2C$=CHBBu$^n_2$ **3** | 80 | 6 | 84.2 | 85 | | | 65 |
| **8** | E-$C_4H_9$CH=CHBCl$_2$ **5** | 105 | 12 | 63.9 | >95 |  | R = *n*-$C_4H_9$ | 61 |
| | E-$C_6H_{13}$CH=CHBCl$_2$ **6** | 105 | 12 | 62.8 | >95 | | R = *n*-$C_6H_{13}$ | 80 |
| | E-PhCH=CHBCl$_2$ **7** | 105 | 12 | 62.4 | >95 | | R = Ph | 80 |
|  **9** | $H_2C$=CHBCl$_2$ **2** | 50 | 2 | 63.4 | >95 |  | | 65 |
|  **10** | $H_2C$=CHBCl$_2$ **2** | 0 | 1 | 63.2 | >95 |  60 | 40 | 72 |
|  **11** |  **4** | 140 | 24 | — | — |  | | 50 |
|  **12** | $H_2C$=CHBCl$_2$ **2** | 0 | 0.5 | 63.5 | >95 |  | *endo: exo* 84 : 16 | 57 |
|  **13** | $H_2C$=CHBCl$_2$ **2** | 50 | 2 | 63.9 | >95 |  | *endo* | 70 |
| | $H_2C$=CHBBu$^n_2$ **3** | 60 | 24 | 84.9 | 74 | | *endo:exo* 70 : 30 | 50 |

[a] The cycloaddition reactions were carried out with neat reagents.
[b] Based on $^{11}$B - NMR.
[c] Isolated yield.

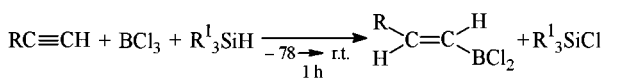
the addition proceeded at room temperature. Dialkylvinylboranes **3** and **4** were of similar reactivity, considerably lower as compared to **1** and **2**.

Other dienes used for the study were 2,4-hexadiene (**9**), isoprene (**10**), 2,4-dimethyl-1,3-pentadiene (**11**), 1,3-cyclopentadiene (**12**) and 1,3-cyclohexadiene (**13**). The addition reactions were carried out with neat reagents. To avoid thermal isomerization of organoborane adducts the most reactive vinylboranes **1** and **2** were preferred and the temperature of the addition reactions was kept as low as possible. However, the reactions with dibromovinylborane were difficult to control, oligomerization of dienes was observed and the yields of adducts varied. The reactions with dichlorovinylborane (**2**) were free from these inconveniences. Thus, the dienes **8**–**10**, **12** and **13** reacted with **2** at temperatures not exceeding 60°C to give the corresponding adducts. Oxidation of the adducts with alkaline hydrogen peroxide under standard conditions produced unsaturated alcohols shown in Table 1. Isoprene and **2** gave adducts oxidized to a mixture of 4-methylcyclohex-3-enol and 3-methylcyclohex-3-enol (3: 2). A mixture of *endo*- and *exo*-5-norbonen-2-ol (84:16) was obtained from **2** and 1,3-cyclopentadiene. The addition of **2** to 1,3-cyclohexadiene was highly stereoselective leading after oxidation to *endo*-bicyclo[2.2.2]oct-5-en-2-ol. The reaction is a convenient one pot synthesis of this alcohol which can be readily converted to the corresponding ketone. Synthesis of both these compounds by other procedures is tedious, requires several steps including chromatographic separations and fractional crystallization [16]. The addition of di-*n*-butylvinylborane to 1,3-cyclohexadiene was less stereoselective producing a mixture of *endo*- and *exo*-adducts (7: 3). It was interesting to examine the addition of the most reactive vinylboranes **1** and **2** to 2,4-dimethyl-1,3-pentadiene (**11**) which could afford an adduct with a quaternary carbon atom. The reactions of **11** with **1** and **2** were exothermic and no unreacted diene was left after 1 h as indicated by GC analysis. However, the $^{11}$B-NMR spectra of both reaction mixtures showed only signals corresponding to unreacted **1** or **2**. Apparently, the Lewis acidity of **1** and **2** was sufficient to induce oligomerization of **11** which is sensitive to acids. It dimerized and trimerized when formed by dehydration of 2,4-dimethylpent-3-en-2-ol which could not be isolated from the reaction of mesitil oxide with methylmagnesium iodide. Dehydration of the alcohol prepared using methylmagnesium chloride had to be carefully controlled. Less acidic vinylborane **3** did not induce oligomerization of **11** but no other signals than the starting material was observed in the $^{11}$B-NMR spectrum after heating the mixture of **3** and **11** for 12 h at 100°C.

Heating **11** with B-vinyl-DMB (**4**) at 140°C for 24 h gave a product showing a signal at $\delta$ 86.0 in the $^{11}$B-NMR spectrum, characteristic for trialkylboranes. However, its oxidation produced 2,4-dimethylpent-3-en-1-ol and no cyclic alcohol corresponding to the Diels–Alder adduct was obtained. Most probably the prolonged heating at high temperature caused dehydroboration of **4** and monohydroboration of **11**. It is relevant that similarly substituted 4-methyl-1,3-pentadiene adds sluggishly and in low yields even to highly reactive dienophiles, e.g. maleic anhydride and tetracyanoethylene [17].

The reactivity order of vinylboranes **1**–**4** pointed to 1-alkenyldibromoboranes as the first choice homologous dienophiles. Complexes of these organoboranes with dimethyl sulfide are readily available by the monohydroboration of 1-alkynes with dibromoborane-dimethyl sulfide [18]. However, in contrast to highly exothermic reaction of dibromovinylborane with 2,3-dimethyl-1,3-butadiene, no reaction was observed when dibromo(E-1-hexen-1-yl)borane-dimethyl sulfide (**14**) was mixed with the diene at room temperature. Heating the mixture at 100°C for 12 h followed by oxidation produced *trans*-6-butyl-3,4-dimethylcyclohex-3-enol in low yield. Much lower reactivity of **14** as compared to uncomplexed **1** can be explained by strong complexation with dimethyl sulfide, however, it has been reported that such complexes react with 1,3-dienes when refluxed in benzene solution to give the corresponding adducts [8]. Carrying out the reaction of **14** with **8** under these conditions a dark reaction mixture was obtained and oxidation of the adduct produced *trans*-6-butyl-3,4-dimethylcyclohex-3-enol only in a moderate yield.

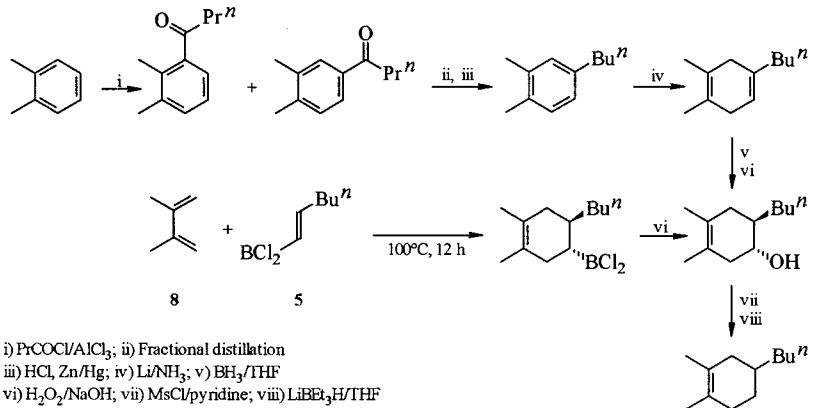
To avoid these inconveniences, we turned to 1-alkenyldichloroboranes which can be prepared by the monohydroboration of 1-alkynes with dichloroborane diethyl etherate [19]. Although the procedure works well, the reagent has only limited stability and its reactivity is too low for the direct reaction. Liberation of free dichloroborane from the etherate adds an additional step to the synthesis. Recently, hydroboration of alkenes with dichloroborane generated in situ by the reduction of boron trichloride with trialkylsilanes was reported [20]. The procedure is very simple and does not require a separate preparation of the reagent. Consequently, we used it for the synthesis of 1-alkenyldichloroboranes **5-7** from 1-hexyne, 1-octyne and phenylacetylene, respectively (Eq. (1)).




(1)

**5** R = *n*-$C_4H_9$; $R^1 = CH_3$
**6** R = *n*-$C_6H_{13}$; $R^1 = C_2H_5$
**7** R = Ph; $R^1 = C_2H_5$

The compounds **5**–**7** isolated by simple distillation were colorless liquids stable over long periods when




Scheme 1.

stored at 0°C. No exothermic reaction was observed upon mixing **5** with 2,3-dimethyl-1,3-butadiene at room temperature. After heating the mixture at 100°C for 12 h a signal at $\delta$ 53.00 in the $^{11}$B-NMR spectrum corresponding to **5** disappeared and a signal of the adduct at $\delta$ 63.92 appeared. Oxidation of the adduct gave *trans*-6-butyl-3,4-dimethyl-cyclohex-3-enol identified by comparison ($^1$H-NMR, $^{13}$C-NMR) with a sample prepared as shown in Scheme 1. No isomeric alcohols were detected in the oxidation product indicating no thermal isomerization of the adduct.

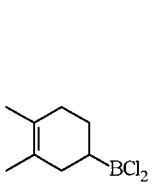
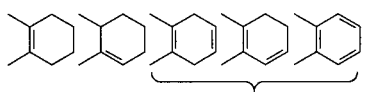
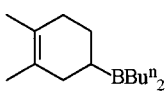
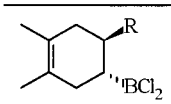
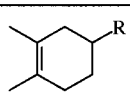
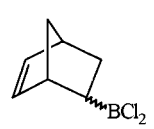
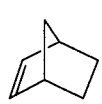
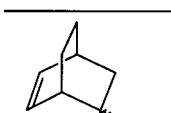
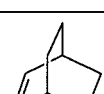
Initially, protonolysis of the organoborane adducts was carried out with propionic acid. Adducts prepared from dichlorovinylborane were treated with two equivalents of sodium methoxide to avoid the formation of hydrogen chloride and then refluxed with propionic acid for 2 h. Under these conditions the adducts of **2** with **8, 12** and **13** gave 1,2-dimethylcyclohexene, norbornene and bicyclo[2.2.2]oct-2-ene, respectively (Table 2). However, the yields were low to moderate and 1,2-dimethylcyclohexene partially isomerized in the acidic reaction medium. At longer reaction times the yield was slightly higher but 1,2-dimethylcyclohexene isomerized more extensively and dehydrogenation products were also formed (Table 2). Heating the adduct with propionic acid in ethylene glycol gave similar results. Clearly, the yields of olefins obtained by direct protonolysis of the adducts with propionic acid are not high and the reaction scope is limited to cases when the product olefin is relatively stable in acidic medium. To circumvent these inconveniences the organoborane adducts were oxidized to the corresponding alcohols, which in turn were transformed into mesylates or tosylates reduced with lithium aluminum hydride. This indirect route worked better giving olefins in 40–60% overall yield. However, 1,2-dimethylcyclohexene obtained in this way was constantly contaminated with 1,2-dimethyl-1,4-cyclohexadiene regardless of the reaction temperature (room temperature, reflux) or the solvent used (diethyl ether, tetrahydrofuran). Fortunately, the undesired side reaction leading to the elimination product could be avoided by using lithium triethylborohydride instead of lithium aluminum hydride. The reaction sequence oxidation–mesylation–reduction with lithium triethylborohydride worked well with all the adducts shown in Table 2 affording the corresponding olefins in $\geq$80% yield and excellent purity.

Other methods of transformation of the organoborane adducts into olefins were also tried. Thus, heating the adduct prepared from **3** and **8** with sodium hydroxide in ethylene glycol at 140–200°C gave a mixture of 1,2- and 1,6-dimethylcyclohexene (Table 2). It is interesting to note that though tri-*n*-hexylborane and dicyclohexylborane, similarly to tri-*n*-butylborane [12], were cleanly transformed into *n*-hexane and cyclohexane, respectively, primary trialkylboranes branched in β-position gave preferentially elimination products under these conditions. Thus, (+)-limonene was monohydroborated with dicyclohexylborane and the product was heated with sodium hydroxide in ethylene glycol at 180–200°C. The distillate was identified as (+)-limonene showing the same rotation as the starting material. Under the same conditions trimyrtanylborane derived from β-pinene gave a mixture of *trans*-pinane and β-pinene. A facile protonolysis of tributylborane with anhydrous hydrogen fluoride has also been reported [11]. However, heating the adduct prepared from **3** and **8** with a mixture of boron trifluoride etherate and water (1: 3) or with tetramethylammonium fluoride tetrahydrate gave a mixture of 1,2-, 1,6-dimethylcyclohexene and dehydrogenation products (Table 2).

## 3. Conclusion

Vinyl-and 1-alkenyldichloroboranes are highly reactive toward 1,3-dienes and the corresponding adducts can be prepared at temperatures below 100°C. Only 2,4-dimethyl-1,3-pentadiene disubstituted at the termi-

Table 2
Transformation of organoborane adducts into olefins by protonolysis or oxidation–mesylation–reduction

| Adduct | Reagent | Conditions | Product hydrocarbon | | | | |
|---|---|---|---|---|---|---|---|
| | | | Composition % | | | | Yield[a] % |
|  | 1. $NaOH/H_2O_2$<br>2. MsCl/pyridine<br>3. $LiBEt_3H$ | THF, 4 h, 60°C |  | | | | 81[b] |
| | 1. $NaOH/H_2O_2$<br>2. MsCl/pyridine<br>3. $LiAlH_4$ | $Et_2O$, 25°C, 15h<br>reflux, 5 h |  |  | | | 60[b] |
| | | | 75 | 25 | | | |
| | 1. MeONa<br>2. $C_2H_5COOH$ | reflux, 2h |  |  | | | |
| | | | 82 | 18 | | | 20 |
| | | |  | | | | |
|  | EtCOOH | reflux, 4h | 22 | 66 | | 12 | 36 |
| | $Me_4NF{\cdot}4H_2O$[d] | 150°C, 3h (autoclave) | 58 | | | 42 | 6 |
| | $BF_3{\cdot}Et_2O$, $H_2O$[e] | 100°C, 3h (autoclave) | 10 | 70 | | 20 | 8 |
| | NaOH $HOCH_2CH_2OH$ | 140→200°C, 0.5 h | 39 | 27 | | 34 | 19 |
|  | 1. $NaOH/H_2O_2$<br>2. MsCl/pyridine<br>3. $LiBEt_3H$ | THF, 4 h, 60°C |  | | | R = $n$-$C_4H_9$<br>R = $n$-$C_6H_{13}$<br>R = Ph | 80<br>82[b]<br>83[b] |
| | 1. $NaOH/H_2O_2$<br>2. MsCl/pyridine<br>3. $LiBEt_3H$ | THF, 4 h, 60°C | | | | | 85[b] |
|  | 1. MeONa<br>2. $C_2H_5COOH$ | reflux, 3h |  | | | | 9 |
| | 1. $NaOH/H_2O_2$<br>2. MsCl/pyridine<br>3. $LiAlH_4$ | $Et_2O$, r.t., 12h<br>reflux, 5h | | | | | 41[b] |
|  | 1. $NaOH/H_2O_2$<br>2. MsCl/pyridine<br>3. $LiBEt_3H$ | THF, 4 h, 60°C |  | | | | 83[b] |
| | 1. MeONa<br>2. $C_2H_5COOH$ | reflux, 4h | | | | | 50 |

[a] Isolated yield.
[b] Crude intermediate alcohol and mesylate were used.
[c] Products identified by GC–MS comparison with authentic samples.
[d] The molar ratio organoborane:$Me_4NF \cdot 4H_2O = 1:4$.
[e] The molar ratio organoborane:$BF_3OEt_2$:$H_2O = 1:2:6$.

nal position was unreactive. The addition of dichlorovinylborane to 1,3-cyclohexadiene was highly *endo*-selective. The adducts were stable for prolonged periods. They were cleanly transformed into the corresponding olefins by the sequence oxidation–mesylation–reduction with lithium triethylborohydride. Direct protonolysis with propionic acid is limited to adducts giving olefins stable in acidic medium. Alkylcyclohexenes substituted at the homoallylic position, bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.2]oct-2-enes can be conveniently prepared by this method.

## 4. Experimental

All glassware used for work with organoboranes was kept in an oven at 150°C overnight, assembled hot and cooled in a steam of dry nitrogen. $^{1}$H, $^{13}$C and $^{11}$B-NMR spectra were recorded on a Varian Gemini 200 spectrometer. GC–MS analyses were obtained with Finnigan MAT ITD. 800 instrument (EI, 70 eV). GC analyses were performed on a Hewlett Packard HP-5890 gas chromatograph equipped with a 30 m × 0.32 mm Supelcowax 10 capillary column. IR spectra were recorded on a Specord 75, Carl Zeiss, Jena, instrument.

### 4.1. Materials

Tetravinyltin [21], dichlorovinylborane [14], di-*n*-butylvinylborane [15] and B-vinyl-DMB [4] were prepared according to the literature. Tetrahydrofuran was distilled from benzophenone ketyl prior to use. Isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-cyclopentadiene, 1,3-cyclohexadiene, 2,4-hexadiene (mixture of isomers) were commercial products. 2,4-Dimethyl-1,3-pentadiene was prepared by dehydration of 2,4-dimethylpent-3-en-2-ol with potassium hydrogen sulfate. The alcohol was prepared by the reaction of mesitil oxide with methylmagnesium chloride.

### 4.2. Dibromovinylborane (**1**)

Tetravinyltin (14.80 g, 65 mmol) was added to a mixture of tribromoborane (65.50 g, 0.26 mol) and mercury (5.00 g) at 0°C. The mixture was stirred for 1 h at room temperature, and the liquid was decanted from the solid. Distillation gave 40.00 g, b.p. 28–30°C 50 mm$^{-1}$ Hg, $^{11}$B-NMR (neat), $\delta$, 53.85 and 37.70 (3:1), the signals corresponding to dibromovinylborane and tribromoborane, respectively. Dimethyl sulfide (2.54 g, 41 mmol) was added to the distillate at 0°C, the mixture was stirred for 1 h at room temperature and the product was isolated by distillation, 25.50 g, 50% yield, b.p. 28°C 60 mm$^{-1}$ Hg; $^{11}$B-NMR (pentane), $\delta$, 53.85.Lit. [13], b.p. 93–94°C.

### 4.3. Synthesis of 1-alkenyldichloroboranes

#### 4.3.1. Dichloro(E-1-hexen-1-yl)borane (**5**)

A mixture of 1-hexyne (6.00 g, 73 mmol) and trimethylsilane (5.30 g, 71 mmol) was slowly added with stirring to trichloroborane (7.68 g, 65 mmol) at −78 to −70°C. The mixture was allowed to warm to room temperature and the product was isolated by distillation, 9.02 g, 84%, b.p. 60–62°C 20 mm$^{-1}$ Hg; $^{11}$B-NMR (neat), $\delta$, 53.12; $^{1}$H-NMR ($CDCl_3$), $\delta$, 0.92 (t, $J = 7$ Hz, 3H, $CH_3$), 1.43 (m, 4H, $CH_2$), 2.30 (qd, $J = 7$ Hz, $J = 1.4$ Hz, 2H, $CH_2$), 6.07 (dt, $J = 17$ Hz, $J = 1.4$ Hz, 1H, CH), 7.20 (dt, $J = 17$ Hz, $J = 6.6$ Hz, 1H, CH).

#### 4.3.2. Dichloro(E-1-octen-1-yl)borane (**6**)

Prepared as described above from 1-octyne using triethylsilane instead of trimethylsilane, 70% yield, b.p. 52–54°C 1 mm$^{-1}$ Hg; $^{11}$B-NMR (neat), $\delta$, 52.93; $^{1}$H-NMR ($CDCl_3$), $\delta$ 0.88 (t, $J = 6$ Hz, 3H, $CH_3$), 1.33 (m, 6H, $CH_2$), 1.48 (quintet, $J = 6$ Hz, 2H, $CH_2$), 2.29 (qd, $J = 7$ Hz, $J = 2$ Hz, 2H, $CH_2$), 6.07 (dt, $J = 7$ Hz, $J = 2$ Hz, 1H, CH), 7.20 (dt, $J = 17$ Hz, $J = 6$ Hz, 1H, CH).

#### 4.3.3. Dichloro(E-2-phenylethen-1-yl)borane (**7**)

Prepared as described above from phenylacetylene, using triethylsilane instead of trimethylsilane, 57% yield, b.p. 70–72°C 1 mm$^{-1}$ Hg; $^{11}$B-NMR (neat), $\delta$ 52.79; $^{1}$H-NMR ($CDCl_3$), $\delta$ 6.74 (d, $J = 18$ Hz, 1H, CH), 7.45 (m, 3H, CH), 7.63 (m, 2H, CH), 7.83 (d, $J = 18$ Hz, 1H, CH).

### 4.4. trans-6-Butyl-3,4-dimethylcyclohex-3-enol

A mixture of dichloro(E-1-hexen-1-yl)borane (2.16 g, 13 mmol) and 2,3-dimethyl-1,3-butadiene (2.18 g, 26.5 mmol) was sealed in an ampule and kept at 100°C for 12 h. $^{11}$B-NMR (neat), $\delta$ 63.92. The crude reaction product was dissolved in tetrahydrofuran (13 ml), the solution was cooled to 0°C and 3 M sodium hydroxide (15 ml, 45 mmol) followed with 30% hydrogen peroxide (1.5 ml, 15 mmol) was added keeping the temperature below 20°C. The mixture was stirred for 1 h at room temperature and then for 1 h at 50°C. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 15 ml). Extracts were combined with the organic layer, washed with saturated brine (10 ml) and dried over magnesium sulfate. The product was isolated by distillation, 1.46 g, 61%, b.p. 90–93°C 1 mm$^{-1}$ Hg, identified by comparison ($^{1}$H and $^{13}$C-NMR) with an authentic sample prepared by the monohydroboration-oxidation of 4-butyl-1,2-dimethyl-1,4-cyclohexadiene.

$^{1}$H-NMR ($CDCl_3$), $\delta$ 0.88 (t, $J = 7$ Hz, 3H, $CH_3$), 1.20–1.40 (m, 6H, $CH_2$), 1.57 (s, 6H, $CH_3$), 1.47–1.77 (m, 2H, $CH_2$), 1.83 (s, 1H, OH), 1.89–2.05 (m, 1H, CH), 2.05–2.60 (m, 2H, $CH_2$), 3.54 (m, 1H, CH); $^{13}$C-NMR ($CDCl_3$), $\delta$ 13.91 ($CH_3$), 18.43 ($CH_3$), 18.63 ($CH_3$), 22.88 ($CH_2$), 28.86 ($CH_2$), 31.36 ($CH_2$), 36.06 ($CH_2$), 40.08 ($CH_2$), 40.57 (CH), 71.46 (CH), 122.88 (C), 124.68 (C). Lit. [8], b.p. 65–70°C 0.05 mm$^{-1}$ Hg.

### 4.5. trans-6-Hexyl-3,4-dimethylcyclohex-3-enol

Prepared as described above from dichloro(E-1-octen-1-yl)borane and 2,3-dimethyl-1,3-butadiene, 80% yield, bp 110–112°C 1 mm$^{-1}$ Hg; $^{1}$H-NMR ($CDCl_3$), $\delta$ 0.85 (t, $J = 7$ Hz, 3H, $CH_3$), 1.20–1.40 (m, 10H, $CH_2$), 1.60 (s, 6H, $CH_3$), 1.70 (s, 1H, OH), 1.50–1.80 (m, 2H, $CH_2$), 1.85–2.05 (m, 1H, CH), 2.05–2.35 (m, 2H, $CH_2$), 3.55

(m, 1H, CH); $^{13}$C-NMR ($CDCl_3$), $\delta$ 13.98 ($CH_3$), 18.53 ($CH_3$), 18.74 ($CH_3$), 22.59 ($CH_2$), 26.67 ($CH_2$), 29.61 ($CH_2$), 31.75 ($CH_2$), 31.82 ($CH_2$), 36.08 ($CH_2$), 40.16 ($CH_2$), 40.67 (CH), 71.58 (CH), 122.67 (C), 124.80 (C); Anal. Calc. for $C_{14}H_{26}O$ C 79.92, H 12.48. Found: C 80.02, H 12.41.

### 4.6. trans-3,4-Dimethyl-6-phenylcyclohex-3-enol

Prepared as described above from dichloro(E-2-phenylethen-1-yl)borane and 2,3-dimethyl-1,3-butadiene, 80% yield, b.p. 110–115°C 1 mm$^{-1}$ Hg; $^1$H-NMR ($CDCl_3$), $\delta$ 1.58 (s, 1H, OH), 1.60 (s, 3H, $CH_3$), 1.65 (s, 3H, $CH_3$), 2.00–2.45 (m, 4H, $CH_2$), 2.75 (q, $J = 7$ Hz, 1H, CH), 4.05 (m, 1H, CH), 7.25 (m, 5H, CH); $^{13}$C-NMR ($CDCl_3$), $\delta$ 18.26 ($CH_3$), 18.79 ($CH_3$), 39.93 ($CH_2$), 40.06 ($CH_2$), 49.37 (CH), 71.26 (CH), 123.69 (C), 125.14 (C), 126.94 (CH), 128.04 (2CH), 128.88 (2CH), 142.55 (C); Anal. Calc. for $C_{14}H_{18}O$ C 83.11, H 8.98. Found: C 83.02, H 8.90.

### 4.7. 3,4-Dimethylbutyrophenone

Butyryl chloride (53.27 g, 0.50 mol) was added with stirring to a mixture of *o*-xylene (159.25 g, 1.5 mol) and anhydrous aluminum chloride (80.00 g, 0.6 mol) at 50–60°C and stirring was continued at this temperature for 1 h. The mixture was poured into 15% hydrochloric acid (150 ml) and ice (150 g). The organic layer was separated, washed with water (50 ml), 10% sodium hydroxide solution (50 ml), water (50 ml) and dried with magnesium sulfate. Distillation gave a mixture of 2,3-dimethyl- and 3,4-dimethylbutyrophenone, 55.29 g, 63%, b.p. 90–110°C 1 mm$^{-1}$ Hg. 3,4-Dimethylbutyrophenone was isolated by fractional distillation on a 'Spaltrohr' concentric tube column, 21.90 g, 25%, b.p. 95–97°C 1 mm$^{-1}$ Hg; $^1$H-NMR ($CDCl_3$), $\delta$ 1.00 (t, $J = 7$ Hz, 3H, $CH_3$), 1.75 (sextet, $J = 7$ Hz, 2H, $CH_2$), 2.30 (s, 6H, $CH_3$), 2.90 (t, $J = 7$ Hz, 2H, $CH_2$), 7.20 (d, $J = 8$ Hz, 1H, CH), 7.70 (m, 2H, CH); $^{13}$C-NMR ($CDCl_3$), $\delta$ 13.81 ($CH_3$), 17.85 ($CH_2$), 19.67 ($CH_3$), 19.87 ($CH_3$), 40.33 ($CH_2$), 125.75 (CH), 129.14 (CH), 129.68 (CH), 135.02 (C), 136.78 (C), 142.25 (C), 200.39 (C=O).

### 4.8. 4-Butyl-1,2-dimethylbenzene

A mixture of zinc granules (65.37 g, 1 mol), water (100 ml), mercury(II) chloride (5.00 g) and concentrated hydrochloric acid (10 ml) was shaken for 5 min and the liquid was decanted. Water (50 ml) and concentrated hydrochloric acid (75 ml) was added followed with 3,4-dimethylbutyrophenone (17.63 g, 0.1 mol). The mixture was stirred at reflux for 6 h. The organic layer was separated and the aqueous layer was extracted with petroleum ether (50 ml). The organic solutions were combined, washed with water (20 ml), 5% sodium hydroxide solution (20 ml), water (20 ml) and dried over magnesium sulfate. The product was isolated by distillation, 9.51 g, 59%, b.p. 64–65°C 1 mm$^{-1}$ Hg; $^1$H-NMR ($CDCl_3$), $\delta$ 1.00 (t, $J = 7$ Hz, 3H, $CH_3$), 1.43 (sextet, $J = 7$ Hz, 2H, $CH_2$), 1.66 (quintet, $J = 7$ Hz, 2H, $CH_2$), 2.30 (s, 3H, $CH_3$), 2.32 (s, 3H, $CH_3$), 2.62 (t, $J = 7$ Hz, 2H, $CH_2$), 7.05 (m, 3H, CH); $^{13}$C-NMR ($CDCl_3$), $\delta$ 13.87 ($CH_3$), 19.18 ($CH_3$), 19.64 ($CH_3$), 22.37 ($CH_2$), 33.81 ($CH_2$), 35.15 ($CH_2$), 125.77 (CH), 129.52 (CH), 129.83 (CH), 133.58 (C), 136.25 (C), 140.40 (C); Anal. Calc. for $C_{12}H_{18}$ C 88.82, H 11.18. Found: C 88.63, H 11.12.

### 4.9. 4-Butyl-1,2-dimethyl-1,4-cyclohexadiene

Lithium (1.74 g, 0.25 mol) was added in pieces to a stirred mixture of liquid ammonia (150 ml), diethyl ether (25 ml), anhydrous ethanol (18 ml, 0.3 mol) and 4-butyl-1,2-dimethylbenzene (8.15 g, 50 mmol). The mixture was stirred for 3 h and left overnight at room temperature. Water (50 ml) was added, the organic layer was separated and the aqueous layer was extracted with petroleum ether ($3 \times 30$ ml). Extracts were combined with the organic layer and dried with magnesium sulfate. The product was isolated by distillation, 3.04 g, 37%, b.p. 55–56°C 1 mm$^{-1}$ Hg; $^1$H-NMR ($CDCl_3$), $\delta$ 0.92 (t, $J = 7$ Hz, 3H, $CH_3$), 1.20–1.35 (m, 4H, $CH_2$), 1.65 (s, 3H, $CH_3$), 1.66 (s, 3H, $CH_3$), 1.95 (t, $J = 7$ Hz, 2H, $CH_2$), 2.40–2.55 (m, 4H, $CH_2$), 5.40 (m, 1H, CH); $^{13}$C-NMR ($CDCl_3$), $\delta$ 13.84 ($CH_3$), 18.06 ($CH_3$), 18.33 ($CH_3$), 22.34 ($CH_2$), 29.56 ($CH_2$), 33.72 ($CH_2$), 35.93 ($CH_2$), 36.56 ($CH_2$), 118.26 (CH), 123.05 (C), 123.12 (C), 135.57 (C); Anal. Calc. for $C_{12}H_{20}$ (164.29), C 87.73, H 12.27. Found: C 87.56, H 12.20.

### 4.10. exo- and endo-5-Norbornen-2-ol

Dichlorovinylborane (5.44 g, 50 mmol) was cooled to $-20$°C and 1,3-cyclopentadiene (3.30 g, 50 mmol) was slowly added under nitrogen keeping the temperature of the reaction mixture at $-20$–0°C. The mixture was left at 0°C for 1 h and then it was allowed to warm to room temperature. $^{11}$B-NMR (neat), $\delta$ 63.50. The crude adduct thus obtained was dissolved in tetrahydrofuran (50 ml). The solution was cooled to 0°C and 6 M aqueous sodium hydroxide (30 ml, 180 mmol) was added with stirring followed with 30% aqueous hydrogen peroxide (6.5 ml, 65 mmol) added dropwise at 0–20°C. After the addition was completed, the mixture was stirred for 1 h at 50°C and saturated with sodium chloride. The organic layer was separated and the aqueous layer was extracted with diethyl ether ($2 \times 20$ ml). The organic solutions were combined, washed with saturated brine ($2 \times 20$ ml) and dried over magnesium sulfate. Solvents were removed and the product was isolated by sublimation, 3.15 g, 57%. GC analysis showed *exo*- and *endo*-5-norbornen-2-ol (16:84) identified by comparison with an authentic sam-

ple, (90% *exo*- and 10% *endo*) prepared by the monohydroboration–oxidation of norbornadiene.

### 4.11. 2-Norbornene

Methanesulfonyl chloride (4.01 g, 35 mmol) was slowly added with stirring at −5–0°C to a solution of *exo*- and *endo*-5-norbornen-2-ol (16:84, 3.30 g, 30 mmol) and triethylamine (6.07 g, 60 mmol) in methylene chloride (100 ml). The mixture was left at 0–5°C for 24 h, washed with cold water (3 × 20 ml), 10% hydrochloric acid (2 × 20 ml), saturated sodium bicarbonate solution (2 × 20 ml) and dried with magnesium sulfate. The solvent was removed under vacuum at room temperature and crude methanesulfonate was obtained, 5.01 g, 89%, IR (film) 2950 $cm^{-1}$ and no absorpion characteristic for the hydroxyl group. The methanesulfonate was disolved in dry diethyl ether (20 ml) and the solution was added to a mixture of lithium aluminum hydride (1.14 g, 30 mmol) and diethyl ether (60 ml). The mixture was stirred overnight at room temperature and then refluxed for 5 h. A 5 M aqueous sodium hydroxide (8 ml, 40 mmol) was added and the mixture was stirred for 0.5 h. The solution was decanted and the solid was washed with diethyl ether (3 × 30 ml). The combined etheral solution was washed with saturated brine (2 × 25 ml) and dried with magnesium sulfate. The product was isolated by distillation under vacuum, 1.16 g, 41% yield, m.p. 44–46°C and identified by comparison (GC) with a commercial sample.

### 4.12. 3,4-Dimethylcyclohex-3-enol

2,3-Dimethyl-1,3-butadiene (5.00 g, 60 mmol) was added to dichlorovinylborane (6.40 g, 59 mmol) with stirring at −10°C. The cooling bath was removed and the mixture was carefully stirred at room temperature for 0.5 h cooling in a water bath and then tetrahydrofuran (30 ml) was added. The solution was cooled to 0°C and 3 M aqueous sodium hydroxide (60 ml, 180 mmol) was added followed with 30% aqueous hydrogen peroxide (6.5 ml, 65 mmol) added dropwise at 0–20°C. After the addition was completed, the mixture was stirred for 1 h at 50°C and saturated with sodium chloride. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 x 20 ml). The organic solutions were combined, washed with saturated brine (2 × 20 ml) and dried over magnesium sulfate. Solvents were removed and the product was isolated by distillation, 5.20 g, 70%, b.p. 65°C 0.1 $mm^{-1}$ Hg; $^1$H-NMR ($CDCl_3$), $\delta$ 1.58 (s, 6H, $CH_3$), 1.7–2.3 (m, 7H, CH), 3.90 (m, 1H, CH); $^{13}$C-NMR ($CDCl_3$), $\delta$ 18.18 ($CH_3$), 18.72 ($CH_3$), 29.71 ($CH_2$), 31.18 ($CH_2$), 40.19 ($CH_2$), 66.97 (CH), 122.61 (C), 124.81 (C). Lit. [22], b.p. 109–112°C 32 $mm^{-1}$ Hg.

### 4.13. 1,2-Dimethylcyclohexene

#### 4.13.1. Reduction of 3,4-dimethylcyclohex-3-enol mesylate with lithium aluminum hydride

3,4-Dimethylcyclohex-3-enol (3.79 g, 30 mmol) was mesylated as described above to give 2.62 g, 93% of crude mesylate, IR (film) 2900 $cm^{-1}$ and no absorption characteristic for the hydroxyl group. The mesylate was reduced with lithium aluminum hydride (1.90 g, 50 mmol) in diethyl ether (80 ml) as described above to gave 1.98 g of the product identified by comparison (GC and GCMS) with authentic samples as a mixture of 1,2-dimethylcyclohexene and 1,2-dimethyl-1,4-cyclohexadiene (3: 1). The mixture was dissolved in diethyl ether (5 ml) and borane–dimethyl sulfide (0.3 ml, 3 mmol) was added at 0°C. The solution was left overnight at room temperature. Distillation under 1 mm Hg and redistillation at normal pressure gave 1.42 g, 43% of 1,2-dimethylcyclohexene, b.p. 135–136°C; $^1$H-NMR ($CDCl_3$), $\delta$ 1.45–1.70 (m, 4H, $CH_2$), 1.59 (s, 6H, $CH_3$), 1.80–2.00 (m, 4H, $CH_2$); $^{13}$C-NMR ($CDCl_3$), $\delta$ 19.14 ($CH_3$), 23.50 ($CH_2$), 31.74 ($CH_2$), 125.63 (C=C); GCMS (EI, 70 eV) $z/e = 110$ ($M^+$,24), 95 (46), 81 (50), 67 (100). Lit. [23], b.p. 135–136°C.

#### 4.13.2. Reduction of 3,4-dimethylcyclohex-3-enol mesylate with lithium triethylborohydride

A 1 M solution of lithium triethylborohydride in tetrahydrofuran (44 ml, 44 mmol) was added in one portion to a solution of 3,4-dimethylcyclohex-3-enol mesylate (4.26 g, 21 mmol) in tetrahydrofuran at room temperature. The mixture was stirred at 60°C for 4 h and left at room temperature for 48 h. A 3 M aqueous sodium hydroxide (15 ml, 45 mmol) was added followed slowly with hydrogen peroxide (30%, 20 ml), the mixture was stirred for 3 h at room temperature and saturated with potassium carbonate. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 20 ml). The organic solutions were combined, washed with brine and dried with magnesium sulfate. Solvents were removed and 1,2-dimethylcyclohexene was isolated by distillation, 1.88 g, 81%, b.p. 135–136°C, GC analysis > 98%.

### 4.14. endo-Bicyclo[2.2.2]oct-5-en-2-ol

1,3-Cyclohexadiene (4.00 g, 50 mmol) was slowly added to dichlorovinylborane (4.34 g, 40 mmol) at 0°C under nitrogen, and the mixture was kept at room temperature for 1 h. $^{11}$B-NMR (neat), $\delta$, 63.90 and no signals of dichlorovinylborane at 52.66. Tetrahydrofuran (30 ml) was added followed with 3 M aqueous sodium hydroxide (50 ml, 150 mmol) and 30% aqueous hydrogen peroxide solution (5 ml, 50 mmol) added dropwise with stirring at a rate to keep the temperature of the reaction mixture below 30°C. After the addition

was completed the mixture was stirred at 50°C for 1 h to ensure complete oxidation and saturated with sodium chloride. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 20 ml). The combined organic solution was washed with brine (2 × 15 ml) and dried with magnesium sulfate. The product was isolated by sublimation, 3.48 g, 70% yield, m.p. 166–167°C, 97% GC pure; $^1$H-NMR ($CDCl_3$), $\delta$ 1.00-1.50 (m, 5H, $CH_2$), 1.48 (s, 1H, OH), 1.96 (ddd, $J = 12$ Hz, 8 Hz, 2 Hz, 1H, $CH_2$), 2.55 (m,1H, CH), 2.70 (m, 1H, CH), 3.90 (dm, $J = 8$ Hz, 1H, CH), 6.10 (t, $J = 7$ Hz, 1H, CH), 6.45 (t, $J = 7$ Hz, 1H, CH); $^{13}$C-NMR ($CDCl_3$), $\delta$ 21.60 ($CH_2$), 23.62 ($CH_2$), 29.72 (CH), 37.29 (CH), 38.60 ($CH_2$), 69.89 (CH), 129, 59 (CH), 135.88 (CH). Lit. [24], m.p. 166–168.5°C.

### 4.15. Bicyclo[2.2.2]oct-2-ene

To the adduct prepared as described above from dichlorovinylborane (1.09 g, 10 mmol) and 1,3-cyclohexadiene (0.80 g, 10 mmol), a 1.0 M solution of sodium methoxide in methanol (21 ml, 21 mmol) was added at −10°C and the mixture was stirred for 0.5 h. Methanol was removed under vacuum at room temperature, propionic acid (1.56 g, 21 mmol) was added and the mixture was refluxed for 2 h, cooled to room temperature and a 2 M sodium hydroxide solution (20 ml) was added. The mixture was extracted with diethyl ether (3 × 20 ml), the combined extracts were washed with brine (2 × 20 ml) and dried over magnesium sulfate. Solvent was removed and the product was isolated by distillation, 0.55 g, 50%, m.p. 111–112°C; GCMS (EI, 70 eV) $z/e = 108$ ($M^+$, 15), 80 (30), 79 (100), 66 (80). Lit. [25], m.p. 111–112°C.

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