Alkylhalovinylboranes: a new class of Diels–Alder dienophiles†

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The Diels–Alder reactions of alkylhalovinylboranes have been investigated theoretically and experimentally. Alkylhalovinylboranes presented higher reactivity than the corresponding dialklyvinylboranes. Although endo/exo selectivities were high for the reactions with cyclopentadiene, facial selectivities for the chiral analogues were low. Our results demonstrate that the replacement of an alkyl group on the boron atom by a halogen increases the dienophilicity considerably.

Introduction

In the past decades, Singleton and others have extensively explored the synthetic utility of alkenyl-, alkenyl- and dienylboranes in Diels–Alder reactions.1–18 Given that many variations of the Diels–Alder reaction of vinylboranes have been developed, it is surprising that there is only one precedent in the use of chiral vinylboranes in asymmetric [4 + 2] cycloaddition reactions. This Diels–Alder reaction was based on the use of dialklyvinylborane 1, derived from (+)-camphene, with 2-phenyl-1,3-butadiene (Scheme 1).8 However, although the yield of the oxidized products and the para regioselectivity were high, the enantiomeric excess of the major regiosomer was lower than 10%.

One of the main goals of our group is to develop new chiral unsaturated boron compounds that exhibit high reactivity and selectivity as dienophiles in Diels–Alder reactions. Such compounds have a tremendous potential as precursors of chiral building blocks in asymmetric synthesis.

Scheme 1 Synthesis and Diels–Alder reaction of chiral dialklyvinylborane 1.**

Initially, we thought that dialklyvinylboranes 2–6 shown in Scheme 2 would be good candidates because the stereocenters are directly bonded to the boron atom, and therefore closer to the prochiral olefin than in the derivative of (+)-camphene (1).19 Furthermore, compounds 2–4 could be readily synthesized from commercial optically pure terpenes (+)-α-pinene, (+)-2-carene and (+)-3-carene.20,21 For that purpose, we tested the reaction sequence shown in Scheme 3 for (+)-α-pinene, analogous to that developed previously by Singleton for (+)-camphene (Scheme 1),8 consisting of hydroboration, transmetallation, Diels–Alder reaction and oxidation. In situ preparation of intermediates 7, 2 and 8 under inert atmosphere would avoid the manipulation of the labile boranes. Unfortunately, although numerous reactions were tested for the three chiral terpenes with different reagents and reaction conditions, we failed to detect the presence of the desired products.22 By monitoring the reaction by 1H NMR under inert atmosphere we observed that, although the hydroboration step occurred efficiently, transmetallation of the dialklyhaloboranes did not go to completion. We managed to avoid this difficulty by generating the monohaloborane free of dimethylsulfide in situ with tributylaluminum.23 Nevertheless, when using this method we could not detect the formation of product 9 either, possibly due to the competitive dimerization of the vinylboranes8 and the protodeboronation of the cycloadducts.

Alternative use of cyclohexene as an achiral model of starting alkene, to generate dicyclohexyvinylborane (10), also gave negative results. These initial results demonstrated that dialklyvinylboranes with secondary carbons attached to the boron atom, such as 2–4 and 10, are highly congested, which complicates their synthesis and the course of their Diels–Alder reactions.19

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To circumvent these problems, it occurred to us that alkylhalovinylboranes would represent an interesting alternative to dialkylvinylboranes because the boron atom would be less sterically hindered and more electron deficient, which should ultimately increase the reactivity in Diels–Alder reactions (Fig. 1).

In this paper, we present the results of a theoretical study of the Diels–Alder reactions of a number of alkylhalovinylboranes with cyclopentadiene, together with the experimental development of a one-pot procedure that includes the synthesis of the dienophiles, the Diels–Alder reaction and the oxidation of the products.

**Results and discussion**

**Model studies with cyclohexene vinylborane derivatives**

To validate our hypothesis, we first performed a comparative study of the reactivity of dicyclohexylvinylborane (10), chlorocyclohexylvinylborane (11a) and bromocyclohexylvinylborane (11b), derived from cyclohexene as achiral models of the dienophiles. Initially, we investigated the Diels–Alder reactions of vinylboranes 10, 11a and 11b with cyclopentadiene, a highly reactive and easily accessible diene, with theoretical methods. Due to the absence of chiral centres in the alkyl moiety, only endo and exo attacks should be considered, which, in turn, would give rise to diastereomeric products as racemic mixtures. After oxidation, racemic endo and exo alcohols 9 might arise.

All calculations were performed with the Gaussian 09 package.\textsuperscript{25} We carried out thorough conformational analyses to locate the lowest energy geometry for all the structures under study. Final geometry optimizations were carried out using the B3LYP hybrid functional together with the 6-31G* basis set. The selection of this level of theory was based on existing records in the literature for the modelling of Diels–Alder reactions.\textsuperscript{19,26–32} Additionally, solvent effects in dichloromethane ($\varepsilon = 8.93$) and heptane ($\varepsilon = 1.91$) were calculated for the most stable geometries of reagents, transition structures (TSs), and products using the Polarized Continuum Model of Self-Consistent Reaction Field method (PCM method).\textsuperscript{33,34} Furthermore, the molecular orbitals (MOs) of reagents were calculated to analyse the Frontier molecular orbital interactions and Natural Bond Orbitals (NBOs) analysis of TSs were performed using Wiberg bond indices for interpreting most relevant electronic interactions.\textsuperscript{35–38} Finally, we performed Intrinsic Reaction Coordinate calculations (IRC) to verify if the TSs were directly connected to the reactants and the products.

Fig. 2 shows the correlation diagrams for the Diels–Alder reactions of vinylboranes 10, 11a, and 11b with cyclopentadiene. Analysis of MOs of the reagents shows that all Diels–Alder reactions under study are of normal electron-demand dominated by the HOMO\textsubscript{diene}–LUMO\textsubscript{dienophile} interaction. As expected, the LUMOs of the vinylboranes have large

![Scheme 2](image)

**Scheme 2** Chiral dialkylvinylboranes with secondary carbons attached to boron.

![Scheme 3](image)

**Scheme 3** One-pot synthesis of chiral dialkylvinylborane 2, followed by Diels–Alder reaction and oxidation. The same procedure was tested for (+)-2-carene and (+)-3-carene and cyclohexene.

![Fig. 1](image)

**Fig. 1** Dialkylvinylboranes and alkylhalovinylboranes.

![Fig. 2](image)

**Fig. 2** Correlation diagrams for the Diels–Alder reaction of vinylboranes 10, 11a, and 11b with cyclopentadiene. Energy gaps are shown in red and blue.
coefficients on the two carbon atoms of the carbon–carbon double bond of the vinyl group, and also on the boron atoms. This feature promotes the non-classical [4 + 3] secondary orbital interaction (SOI) between the boron atom of vinylboranes and C1 of the diene, resulting in an increase in the observed endo-selectivity. Both FMOs of haloalkylvinylboranes 11a and 11b also show important coefficients in the halogen atoms too. The presence of the halogen attached to the boron atom lowers the energy gap for the HOMO–LUMO interaction of 11a and 11b is lower than the value obtained for 10, which suggests greater reactivity for alkylhalovinylboranes with respect to the corresponding dialkylvinylborane.  

Fig. 3 shows the optimized geometries of the most stable conformers for the TSs for the Diels–Alder reaction of vinylboranes 10, 11a, and 11b with cyclopentadiene, with the carbon–carbon and C6–B bond distances (in Å) and Wiberg bond indices in parentheses. C6–B distances are approximately 3.1 Å and NBOs of 0.08 and 0.06 indicating that the SOI [4 + 3] are weak. In the IRC studies no intermediate structures between reagents and TSs and between TSs and products were found, confirming that the Diels–Alder reactions under study are concerted. Although in these reactions all bonds are formed and broken in a single stage, all TSs are asynchronous with carbon–carbon distances approximately of 2.0 Å for C2–C3 and 2.6 Å for C1–C6. As shown in Fig. 3, the dienophile portion of the structures corresponding to 11a and 11b adopts the same conformation in all TSs, the halogen attached to the boron atom is anti relative to the adjacent axial hydrogen atom of the cyclohexyl group and the double bond is eclipsed with the boron–halogen bond. Table 1 shows the activation free energies (ΔG‡) calculated in the gas phase and heptane of the three systems derived from cyclohexene. As expected, the relative energies of the TSs in the gas phase are considerably higher than in solution. However, in both cases the reactions of 11a and 11b have lower activation free energies than those for 10, which in principle indicates higher reactivity for the alkylhalo-vinylborane compounds relative to the dialkylvinylborane counterpart. Also, endo TSs were computed to be more stable than the exo isomers for all systems. Selectivity calculations were performed at 298 K using the Boltzmann equation with the activation free energies calculated for the TSs. The selectivity values obtained for 10, 11a and 11b are shown in Table 1. For alkylhalovinylboranes 11a and 11b, the endo/exo selectivity is significantly higher in solution than the gas phase. The computed energies of the products also suggested that the reactions under study are exergonic (see the ESI†).

Encouraged by these promising results, we then studied and optimised the reaction sequence shown in Scheme 4. Many experiments were performed using different reaction times and temperatures, as well as number of equivalents and modes of addition of reagents. Fortunately, our hypothesis, which was supported by the calculations, proved to be correct and we managed to obtain the expected products. Initial reaction of trichloroborane with one equivalent of triethylsilane in the presence of 1.1 equivalents of cyclohexene readily gave dichloroborane, which subsequently hydroborated the starting

| Table 1 | Calculated activation free energies and endo/exo selectivities for the Diels–Alder reaction of vinylboranes 10, 11a, and 11b with cyclopentadiene. Relative activation free energies are shown in parenthesis |
|----------------|----------------|----------------|
| Vinylborane | endo | exo | (ΔG‡) kcal mol⁻¹ |
| **Gas phase** | | | |
| 10 | 32.28 (0.00) | 32.39 (0.12) | 55 : 45 |
| 11a | 30.10 (0.00) | 30.22 (0.12) | 55 : 45 |
| 11b | 27.22 (0.00) | 27.34 (0.12) | 55 : 45 |
| **Heptane** | | | |
| 10 | 16.52 (0.00) | 16.73 (0.21) | 59 : 41 |
| 11a | 12.77 (0.00) | 13.25 (0.54) | 71 : 29 |
| 11b | 10.62 (0.00) | 11.01 (0.38) | 65 : 35 |

Fig. 3  Optimized geometries of the TSs for the Diels–Alder reaction of vinylboranes 10, 11a, and 11b with cyclopentadiene, with carbon–carbon and C6–B bond distances (in Å) and Wiberg bond indices in parentheses.

Scheme 4  One-pot synthesis of chlorocyclohexylvinylborane (11a), followed by Diels–Alder reaction and oxidation.
alkene, giving rise to dichlorocyclohexylborane (12). Simultaneous addition of one equivalent of tributylvinyltin and three equivalents of cyclopentadiene successively generated the desired dienophile 11a and cycloadduct (11a+cp). Final oxidation of the reaction mixture conducted to 5-norbornen-2-ol (9) in 48% global yield with 80:20 endo/exo selectivity. The consecutive steps of the synthetic sequence were monitored by $^{11}$B NMR under inert atmosphere (Fig. 4), which allowed the optimization of the reaction conditions.

**Studies with chiral terpene vinylborane derivatives**

Having accomplished the proof of concept with the achiral models, we then turned our attention to the Diels–Alder reactions of chiral alkylhalovinylboranes derived from (−)-α-pinene, (+)-2-carene, (+)-3-carene as starting alkenes. To increase the structural diversity of the ligands, we also included (−)-myrtenol, which has the same carbon skeleton as (−)-α-pinene and allows the preparation synthetic derivatives 13–15 due to the presence of the hydroxymethyl group (for synthetic procedures see the ESI†). We figured that the presence of a heteroatom or an aromatic ring in the side chain of the dienophile would introduce further steric and electronic features, which in turn might contribute to reduce the conformational flexibility and, therefore, increase the stereoselectivity of the cycloaddition.

The Diels–Alder reactions of the resulting alkylhalovinylboranes 16–22 with cyclopentadiene were first studied theoretically (Scheme 5). In these cases, four diastereomeric Diels–Alder cycloadducts might arise from the endo and exo attacks of the diene to both faces of the double bond of the chiral alkylhalovinylborane ($Re$ and $Si$). Upon oxidation such compounds would be converted into two diastereomeric pairs of enantiomers.

As an example, the optimized geometries of the most stable conformers for the TSs for the Diels–Alder reaction of vinylborane 16a with cyclopentadiene are depicted in Fig. 5. Tables 2 and 3 present the activation free energies ($\Delta G^\ddagger$) and the stereoselectivities calculated in the gas phase and heptane for the Diels–Alder reactions of chiral alkylhalovinylboranes. In general terms, all [4 + 2] cycloadditions of chiral alkylhalovinylboranes present the same features as the reactions of cyclohexylhaloboranes 11a and 11b:

- Normal electron demand Diels–Alder reactions ($HOMO_{diene}–LUMO_{dienophile} \sim 4$ eV).
- LUMOs of the dienophiles show high coefficients on the C–C double bond, the boron and the halogen atoms.
- Concerted reactions with asynchronous TSs with classical [4 + 2] character and weak C–B [4 + 3] SOI (C$_2$–C$_3$, C$_1$–C$_6$, and C$_6$–B distances 2.0, 2.6, and 3.0 Å respectively).
- $\Delta G^\ddagger$ in heptane 13–15 kcal mol$^{-1}$ for chloroalkylboranes and 11 kcal mol$^{-1}$ for bromoalkylboranes.

![Fig. 4](image-url) $^{11}$B NMR of the consecutive steps of the synthetic sequence.

![Scheme 5](image-url) Diels–Alder reactions of chiral alkylhalovinylboranes 16–22 with cyclopentadiene.

![Fig. 5](image-url) Optimized geometries of the TSs for the Diels–Alder reaction of vinylboranes 16a with cyclopentadiene with the carbon–carbon and C6–B bond distances (in Å) and Wiberg bond indices in parentheses.
Table 2  Calculated activation free energies for the Diels–Alder reaction of alkylhalovinylboranes 16–22 with cyclopentadiene. Relative activation free energies are shown in parenthesis

| Vinylborane | Re endo | Re exo | Si endo | Si exo |
|-------------|---------|--------|---------|--------|
| Gas phase   |         |        |         |        |
| 16a         | 29.89(0.78) | 29.79(0.68) | 29.23(0.12) | 29.11(0.00) |
| 16b         | 27.32(0.42) | 27.43(0.52) | 26.90(0.00) | 26.91(0.01) |
| 17a         | 30.09(0.51) | 30.37(0.78) | 29.58(0.00) | 29.68(0.10) |
| 17b         | 28.40(1.04) | 27.72(0.53) | 27.50(0.13) | 27.37(0.00) |
| 18a         | 29.18(0.00) | 29.44(0.26) | 30.36(1.18) | 30.05(0.87) |
| 18b         | 27.31(0.30) | 27.02(0.00) | 27.71(0.69) | 27.54(0.53) |
| 19a         | 30.80(2.03) | 28.76(0.00) | 30.25(1.49) | 29.78(1.02) |
| 20a         | 29.97(0.00) | 30.64(0.67) | 30.58(0.61) | 30.78(0.80) |
| 21a         | 31.64(0.69) | 31.56(0.66) | 31.17(0.22) | 30.95(0.00) |
| 22a         | 29.30(0.74) | 29.27(0.81) | 28.56(0.00) | 28.87(0.31) |
| Heptane     |         |        |         |        |
| 16a         | 13.43(0.46) | 14.07(1.11) | 12.96(0.00) | 13.48(0.52) |
| 16b         | 11.46(0.50) | 11.67(0.71) | 10.96(0.00) | 11.20(0.24) |
| 17a         | 13.56(0.23) | 13.97(0.63) | 13.34(0.00) | 13.72(0.38) |
| 17b         | 11.65(0.27) | 11.53(0.15) | 11.40(0.02) | 11.38(0.00) |
| 18a         | 12.99(0.00) | 13.50(0.51) | 13.16(0.16) | 13.57(0.58) |
| 18b         | 10.86(0.00) | 11.14(0.28) | 11.26(0.40) | 11.06(0.21) |
| 19a         | 13.71(0.83) | 12.88(0.00) | 13.79(0.91) | 13.82(0.93) |
| 20a         | 15.40(1.38) | 14.02(0.00) | 14.02(0.00) | 14.48(0.46) |
| 21a         | 16.00(0.92) | 16.54(1.47) | 15.08(0.00) | 15.69(0.61) |
| 22a         | 14.67(1.10) | 15.15(1.59) | 13.56(0.00) | 14.07(0.51) |

Table 3  Calculated stereoselectivities for the Diels–Alder reaction of alkylhalovinylboranes 16–22 with cyclopentadiene

| Vinylborane | endo/exo | endo Re/Si | exo Re/Si | Re/Si |
|-------------|----------|------------|----------|-------|
| Gas phase   |          |            |          |       |
| 16a         | 45 : 55  | 25 : 75    | 24 : 76  | 25 : 75 |
| 16b         | 51 : 49  | 33 : 67    | 29 : 71  | 31 : 69 |
| 17a         | 56 : 44  | 30 : 70    | 24 : 76  | 27 : 73 |
| 17b         | 38 : 62  | 18 : 82    | 36 : 64  | 29 : 71 |
| 18a         | 57 : 43  | 88 : 12    | 73 : 27  | 82 : 18 |
| 18b         | 39 : 61  | 66 : 34    | 71 : 29  | 69 : 31 |
| 19a         | 9 : 91   | 29 : 71    | 85 : 15  | 80 : 20 |
| 20a         | 70 : 30  | 74 : 26    | 56 : 44  | 68 : 32 |
| 21a         | 42 : 58  | 31 : 69    | 27 : 73  | 29 : 71 |
| 22a         | 60 : 40  | 23 : 77    | 30 : 70  | 26 : 74 |
| Heptane     |          |            |          |       |
| 16a         | 72 : 28  | 31 : 69    | 27 : 73  | 30 : 70 |
| 16b         | 59 : 41  | 30 : 70    | 31 : 69  | 31 : 69 |
| 17a         | 66 : 34  | 41 : 59    | 40 : 60  | 40 : 60 |
| 17b         | 47 : 53  | 40 : 60    | 44 : 56  | 42 : 58 |
| 18a         | 68 : 32  | 57 : 43    | 53 : 47  | 56 : 44 |
| 18b         | 53 : 47  | 66 : 34    | 47 : 53  | 57 : 43 |
| 19a         | 28 : 72  | 53 : 47    | 83 : 17  | 74 : 26 |
| 20a         | 43 : 57  | 9 : 91     | 68 : 32  | 43 : 57 |
| 21a         | 73 : 27  | 18 : 82    | 19 : 81  | 18 : 82 |
| 22a         | 70 : 30  | 14 : 86    | 14 : 86  | 14 : 86 |

Computed endo/exo stereoselectivities are higher for the chloro analogues than for the bromo counterparts and vary considerably (from 28 : 72 to 27 : 28 in heptane). Likewise, Re/Si facial selectivities are variable, ranging from 74 : 26 for 19a to 14 : 86 for 22a. Since the free energies of the four TSs are within 1 kcal mol⁻¹ for most systems, none of the approximations would be clearly favoured and all cycloadducts would be formed, albeit in different amounts. Both electronic, steric and stereoelectronic effects seem to contribute to give the computed reactivities and selectivities. As found before, in all TSs the vinylborane portion adopts the same conformation in which the halogen attached to the boron atom and the hydrogen of the vicinal carbon adopt an antiperiplanar relationship and the double bond is eclipsed with the boron–halogen bond.

As a consequence the substituents of the carbon backbone (for instance, methyls for 16–18) block preferentially one face of the dienophile and the attack of the diene occurs from the other face.

As an example, in the TSs of the vinylborane derived from (−)-z-pinine (16a), the methyl shields the Re face, making the Si endo approximation more favourable (Fig. 5). The same situation is observed for the derivatives of (+)-2-carene (17), while for the (+)-3-carene counterparts (18) the facial selectivity is reversed because the methyl group is on the other side of the molecule and, therefore, steric clashes would make the attack of the Si face more difficult. The synthetic analogues derived from (−)-myrtenol 21a and 22a were predicted to give the highest endo/exo and Re/Si facial stereoselectivities.

Since the reactions conditions had already been optimised using cyclohexene as the starting alkene (Scheme 4), we next investigated the use of the chiral terpenes and synthetic derivatives as staring materials. The reaction sequences were first investigated using (+)-3-carene and different reagents as the boron source: BCl₃ (1 M in hexanes), BB₃ and HBB₂-SMe₂ (1 M in CH₂Cl₂). The reoptimised reaction conditions for the consecutive steps of the synthetic sequences were then used with the chiral terpenes and derivatives (Table 4).

(+)-Longifolene and (−)-camphene with exocyclic double bonds, which generate primary alkylhalovinylboranes 23 and 24 respectively, were also included in the experimental study (Scheme 6).
Based on the literature, and the results of our theoretical calculations, we assumed that different reactivities would be observed for boron trichloride and tribromide (Methods A and B). However, only differences in reactivity were observed in the initial steps, which had to be initiated at −40 °C for boron tribromide to avoid that temperatures increased and secondary reactions took place. $^{11}$B NMR indicated that transmetallation and Diels–Alder reactions occurred at similar rates. On the other hand, when HBB$_2$SMe$_2$ was used (Method C), much lower reactivity was observed, probably due to the lower electron deficiency on boron of the dimethyl sulfide complexes of the reacting species in the studied sequence. As a consequence, reaction times and temperatures had to be increased and yields dropped considerably perhaps as a result of secondary reactions.

In general, global yields for chiral terpenes and synthetic derivatives were comparable to those previously obtained with achiral cyclohexene, although much lower numbers were obtained for HBB$_2$SMe$_2$ and consequently only (+)-(2)- and (+)-(3)-carene were tested with Method C.

Facial selectivities (Re/Si) and resulting enantiomeric ratios and absolute configurations (R/S) of the products of oxidation (endo- and exo-5-norbornen-2-ol, 9) were determined by $^1$H NMR using a methodology developed in our group that involves the use of (S)-(+) O-acetylmandelic acid as chiral derivatising agent. Endo-selectivities were good to excellent. In particular, bromovinylboranes obtained with BBr$_3$ (Method B) gave endo/exo ratios higher than 86:14, with vinylborane 22b derived from synthetic analogue 15 displaying the best endo-selectivity (endo/exo 96:4). When BCl$_3$ was used, (+)-α-pinene-derived vinylborane 16a showed the highest endo-selectivity (endo/exo 80:20). Disappointingly, facial selectivities were low. The chlorovinylborane derived from (+)-2-carene 17a exhibited the highest chiral induction (Re/Si 30/70 for the major endo diastereoisomer). Although we hoped to get better enantiomeric ratios, such value is considerably higher than those obtained for other Diels–Alder reactions of boron-substituted dienophiles.

![Scheme 6](Image 59x79 to 275x127)

**Scheme 6** (+)-Longifolene and (−)-camphene and derived alkyhalovinylboranes 23 and 24.

**Table 4** Experimental results for the tandem hydroboration, transmetallation, Diels–Alder reaction with cyclopentadiene and oxidation for chiral terpenes and synthetic derivatives

| Terpene/vinylborane | Method$^a$ | Global yield (%) | endo/exo | endo Re/Si (R/S) | exo Re/Si (R/S) | Re/Si |
|---------------------|-----------|------------------|---------|-----------------|----------------|-------|
| (+)-α-Pinene/16a$^b$| A         | 51               | 80 : 20 | 53 : 47         | 50 : 50         | 51 : 49 |
| (+)-(2)-Carene/17a | A         | 34               | 76 : 24 | 30 : 70         | 48 : 52         | 39 : 61 |
| (+)-(3)-Carene/18a | A         | 54               | 79 : 21 | 62 : 38         | 48 : 52         | 55 : 45 |
| (−)-Myrtenol/19a   | A         | 21               | 76 : 24 | 48 : 52         | 50 : 50         | 49 : 51 |
| 13/20a             | A         | 27               | 78 : 22 | 47 : 53         | 44 : 56         | 46 : 54 |
| 14/21a             | A         | 24               | 79 : 21 | 45 : 55         | 45 : 55         | 45 : 55 |
| 15/22a             | A         | 26               | 78 : 22 | 47 : 53         | 50 : 50         | 49 : 51 |
| (+)-Longifolene/23a| A         | 42               | 79 : 21 | 44 : 56         | 50 : 50         | 47 : 53 |
| (−)-Camphene/24a   | A         | 41               | 78 : 22 | 48 : 52         | 52:48           | 50:50  |
| (+)-(2)-Pinene/16b | B         | 36               | 90 : 10 | 50 : 50         | 50 : 50         | 50 : 50 |
| (+)-(2)-Carene/17b | B         | 35               | 91 : 9  | 49 : 51         | 50 : 50         | 50 : 50 |
| (+)-(3)-Carene/18b | B         | 32               | 93 : 7  | 48 : 52         | 50 : 50         | 49 : 51 |
| 13/20b             | B         | 27               | 86 : 14 | 48 : 52         | 50 : 50         | 49 : 51 |
| 15/22b             | B         | 30               | 96 : 4  | 45 : 55         | 50 : 50         | 48 : 52 |
| (+)-Longifolene/23b| B         | 32               | 91 : 9  | 47 : 53         | 50 : 50         | 49 : 51 |
| (−)-Camphene/24b   | B         | 28               | 93 : 7  | 50 : 50         | 50 : 50         | 50 : 50 |
| (+)-(2)-Carene/17b | C         | 10               | 60 : 40 | 43 : 55         | 50 : 50         | 48 : 52 |
| (+)-(3)-Carene/18b | C         | 23               | 74 : 26 | 50 : 50         | 49 : 51         | 50 : 50 |

$^a$ Method A: (1) BCl$_3$ (1 M in hexanes, 1 mL), Et$_3$SiH (1 equiv.), alkene (1.1 equiv.), −10 °C to RT, 1 h; (2) tributylvinylstannane (1 equiv.), cyclcopentadiene (5 equiv.), 0 °C to RT, 3 h; (3) THF (3 mL), Et$_3$N (1 mL), NaOH 3 N (3 mL), H$_2$O$_2$ 30% (3 mL), 0 °C to RT, 15 h. Method B: (1) CH$_2$Cl$_2$ (1 mL), BBr$_3$ (1 mmol), Et$_3$SiH (1 equiv.), alkene (1.1 equiv.), −40 °C to RT, 2 h; (2) same as Method A, 5 h; (3) same as Method A. Method C: (1) HBB$_2$SMe$_2$ (1 M in CH$_2$Cl$_2$, 1 mL), alkene (1.1 equiv.), −10 °C to reflux, 2 h; (2) tributylvinylstannane (1 equiv.), cyclcopentadiene (5 equiv.), 0 °C to reflux, 5 h, then RT, 15 h; (3) same as Method A, 4 h. $^b$ Compounds 16a and 16b are the enantiomers of 16a and 16b, respectively.
free energies for bromovinylboranes would be 2 kcal mol\(^{-1}\), in accordance to the ones computed in the theoretical calculations. In general, experimental facial selectivities were lower than those obtained with chlorovinylboranes and than the values obtained with (+)-2-carene-derived chlorovinylborane (17a) was much higher than those described in the literature for Diels–Alder reactions of other boron-substituted dienophiles. This work contributes to a little-explored area of study, as is the use of chiral vinylboranes in asymmetric cycloaddition reactions. Finally, this novel example of the use of alkylhalovinylboranes in synthesis highlights the practical potential of such organoboron species, which may be applied to other transformations.

Conflicts of interest

There are no conflicts to declare.

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