Reactions of Alkynyldihaloboranes with 1,3-Dienes. 1,4-Alkynylborations and Stepwise Diels−Alder Reactions

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Alkynyldihaloboranes **1**−**6** are readily generated in situ from the boron−tin exchange reaction of BCl_3 or BBr_3 with the corresponding alkynylstannanes. The Diels−Alder reactions of **1**−**4** with isoprene in hexanes proceed rapidly at 25 °C, affording 1,4-cyclohexadiene products in high yield with high regioselectivity. Reactions carried out in CH_2Cl_2 exhibited an alternative product that results from the formal 1,4-alkynylboration of the diene. The alkynylboration intermediates can undergo further conversion to the Diels−Alder adducts under the reaction conditions. The mechanism of these reactions is discussed.

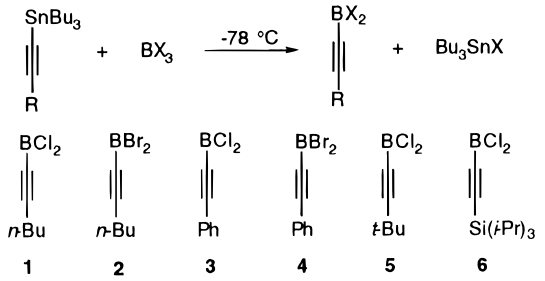
Introduction

Vinyl- and ethynylboranes have proven to be exceptional but very unusual Diels−Alder dienophiles. The abnormal reactivity trends[1] and flip-flopping regiochemical results[2,3] with these dienophiles have been rationalized by [4 atom + 3 atom] transition structures predicted by *ab initio* calculations.[3,4] In these structures, the trivalent boron atom is not an "innocent bystander," indirectly exerting an activating effect electronically by conjugation with the dienophile, as normally thought of electron-withdrawing groups. Rather, the electrophilic boron atom is intimately involved in the pericyclic transition state.

Although [(trimethylsilyl)ethynyl]-9-BBN had been a reactive and effective dienophile,[3] the utility of other alkynyldialkylboranes in Diels−Alder reactions appeared limited by low reactivity. For example, the reaction of *n*-hexynyl-9-BBN with simple dienes proceeded to less than 20% completion after prolonged heating at 130 °C. Due to the strongly electrophilic nature of a dihaloboryl group, alkynyl*dihalo*boranes were expected to be much more reactive than alkynyldialkylboranes, and the role of electrophilic attack by the boron atom in the "Diels−Alder" transition state was expected to be great. We report here that alkynyldihaloboranes are indeed extremely reactive dienophiles. However, the boron atom's involvement in some cases results in a novel reaction, the 1,4-alkynylboration of 1,3-dienes. Surprisingly, the overall Diels−Alder reaction can still occur as the sum of two unique steps.

Results and Discussion

The alkynyldihaloboranes **1**−**6** were generated in situ from the boron−tin exchange reaction of BCl_3 or BBr_3 with the corresponding alkynylstannanes at −78 °C.[3,5] On the basis of observations with subsequent Diels−Alder reactions, the alkynyldichloroboranes appeared to be stable for days at 25 °C as dilute solutions in CH_2Cl_2 or hexanes, while the alkynyldibromoboranes, generated only in hexanes, decomposed in solution over the course of hours at 25 °C. No attempt was made to isolate **1**−**6**. The complete conversion of the tributylstannyl group to Bu_3SnCl or Bu_3SnBr could be observed by ^{13}C NMR of the reaction mixtures in spectra taken immediately at ambient temperature.



Diels−Alder Reactions in Hexanes. The dienophilic reactivity and regioselectivity of alkynyldihaloboranes was surveyed in the reactions of **1**−**4** with isoprene in hexanes at 25 °C. In contrast to the low reactivity of alkynyldialkylboranes, the Diels−Alder reactions of **1** and **3** with isoprene proceeded to completion in 1 day, while the reactions of **2** and **4** were complete in a few minutes. For comparison, a reaction of isoprene with dimethyl acetylenedicarboxylate under similar conditions was <50% complete in 1 week. Outside of Lewis acid-catalyzed reactions, we are unaware of acetylenic dienophiles of comparable reactivity.

Due to complications from isomerization of intermediate β,γ-enones and competing protodeboronation, oxidative workups of these reactions were not useful for characterizing the cycloadditions. Instead, we opted for protodeboronation.[6] We initially used a complicated workup involving conversion of the presumed intermediate cyclohexenyldihaloboranes (e.g., **7**) to the corresponding dihexylboranes (e.g., **8**) with Et_3SiH/1-hexene by the Matteson procedure,[7] followed by protodeboronation with

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(1) Singleton, D. A.; Martinez, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 7423. Singleton, D. A.; Martinez, J. P.; Watson, J. V. *Tetrahedron Lett.* **1992**, *33*, 1017.

(2) Singleton, D. A.; Martinez, J. P.; Watson, J. V.; Ndip, G. M *Tetrahedron* **1992**, *48*, 5831. Singleton, D. A.; Kim, K.; Martinez, J. P. *Tetrahedron Lett.* **1993**, *34*, 3071.

(3) Singleton, D. A.; Leung, S.-W. *J. Org. Chem.* **1992**, *57*, 4796.

(4) Singleton, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 6563.

(5) Singleton, D. A.; Martinez, J. P.; Ndip, G. M. *J. Org. Chem.* **1992**, *57*, 5768.

(6) A complication caused by the use of protodeboronation was that in some cases (**10**−**13**, **20**, **26**, **27**) the nonpolar products could not be completely separated from nonpolar impurities. NMR spectra of these materials, as isolated, are given in the Supporting Information.

(7) Soundararajan, M.; Matteson, D. S. *J. Org. Chem.* **1990**, *55*, 2274.

(8) If just acetic acid is used, HCl is generated and the yields are low. The combination of triethylamine with acetic acid appears particularly effective in the protodeboronation of alkenyldichloroboranes.

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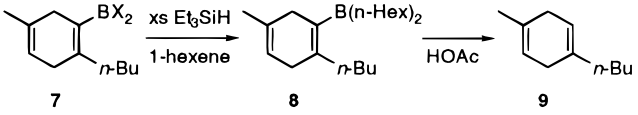
Table 1. Diels–Alder Reactions of Alkynyldihaloboranes with Isoprene in Hexanes

Alkynylborane	Reaction Conditions[a]	Product(s) and Ratio	Isolated Yield
BCl_2, *n*-Bu, **1**	25 °C, 24 h	*n*-Bu, **9**	84%
BBr_2, *n*-Bu, **2**	25 °C, 15 min	*n*-Bu, **9**	86%
BCl_2, Ph, **3**	25 °C, 22 h	Ph, Ph; 79:21; **10**, **11**	80%
BBr_2, Ph, **4**	25 °C, 15 min	Ph, Ph; 84:16; **10**, **11**	80%

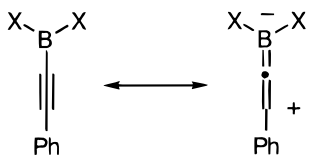
[a] Workup by treatment with excess 1-hexene/Et_3SiH then HOAc.

HOAc. Later, it was found that a direct protodeborona-



tion using a combination of acetic acid and triethylamine[8] gave comparable results. Our results are summarized in Table 1. The substituted cyclohexadiene products **9**–**11** were dehydrogenated to the corresponding aromatics by treatment with DDQ. The regiochemistries of **9**–**11** were assigned by comparison of the aromatized materials with authentic samples.

The high yields and high regioselectivity with **1** and **2** promise excellent synthetic utility for the Diels–Alder reactions of alkynyldihaloboranes in general. The presumed intermediate **7** in the formation of **9** has a "meta" orientation of the boryl group and the original alkyl substituent from the diene. This unusual preference for the meta regioisomer is in line with theoretical predictions and previous observations with [(trimethylsilyl)-ethynyl]-9-BBN,[3] although the regioselectivity is higher in the current examples. The regiochemistry of the reactions with **3** and **4**, in contrast, is enigmatic. One possible explanation is that the reversal in regioselectivity results from a decrease in electrophilicity of the boron atoms in **3** and **4** compared to **1** and **2**, due to an expected greater contribution from mesomeric resonance structures in **3** and **4**.



Reactions in CH_2Cl_2. Alkynylborations and Stepwise Diels–Alder Reactions. Reactions carried out in CH_2Cl_2 instead of hexanes generally afforded lower yields of the Diels–Alder adducts and significantly more byproducts. However, examination of these reactions provided some intriguing mechanistic insights and led to the observation of the novel 1,4-alkynylboration of dienes.

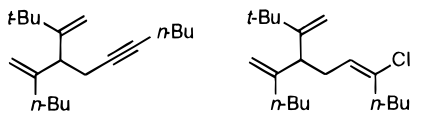
Table 2. Reaction of Alkynyldichloroboranes with Dienes in CH_2Cl_2

Alkynylborane	Diene	Reaction Conditions[a]	Total Isolated Yield[b]	Product(s) and Ratio
BCl_2, Ph, **3**		25 °C, 15 min	73%	Ph, Ph; 79:21; **10**, **11**
BCl_2, *n*-Bu, **1**		25 °C, 3 h	49%	*n*-Bu, **9**
BCl_2, *n*-Bu, **1**	*t*-Bu	25 °C, 1.25 h[c]	61%	*t*-Bu, *n*-Bu; *t*-Bu, *n*-Bu; 38:62; **12**, **13**
		32 h	39%	59:41
BCl_2, *t*-Bu, **5**	*t*-Bu	25 °C, 1 h[c]	80%	*t*-Bu, *t*-Bu; *t*-Bu, *t*-Bu; 32:68; **16**, **17**
		22 h	75%	97:3
BCl_2, *t*-Bu, **5**	Ph	25 °C, 45 min[c]	60%	Ph, *t*-Bu; Ph, *t*-Bu; 28:72; **20**, **21**
		24 h	57%	88:12
BCl_2, $Si(iPr)_3$, **6**	*t*-Bu	25 °C, 35 min[c]	90%	TIPS; TIPS; TIPS; 9:51:40; **26**, **27**, **28**
		66 h	85%	11:60:29

[a] Workup by treatment with acetic acid/triethylamine. [b] Sum of the individual isolated yields of the listed products, based on limiting diene. [c] Quenched when the diene could no longer be detected by ^1H NMR.

Our results are summarized in Table 2. The rate of Diels–Alder reactions is normally fairly insensitive to solvent polarity, but the reactions of **1** and **3** occurred much faster in the more polar CH_2Cl_2 than in hexanes. In contrast to the 22 h required for the reaction of **3** with isoprene in hexanes, the reaction in CH_2Cl_2 was complete in 15 min, affording a 73% yield of **10** and **11** in the same ratio as observed in hexanes.

The complex byproducts of the CH_2Cl_2 reactions could be separated and identified when the diene used was changed to 2-*tert*-butylbutadiene. The reaction of **1** with 2-*tert*-butylbutadiene afforded only a 23% yield of the cyclohexadiene **12** derived from protodeboronation of the Diels–Alder adduct. However, several intriguing side products were isolated, including 38% of the isomeric enyne **13** and, depending on reaction conditions, small amounts of materials tentatively identified as **14** and **15**. For reference below, the amount of **12** obtained does not change significantly at longer reaction times.



(9) (a) Mikhailov, B. M.; Bubnov, Y. N.; Bogdanov, V. S. *Zh. Obshch. Khim.* **1975**, *45*, 324, 333. (b) Mikhailov, B. M.; Bubnov, Y. N.; Tsyban, A. V. *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1978, 1594.

(10) Bühl, M.; Schleyer, P. v. R.; Ibrahim, M.; Clark, T. *J. Am. Chem. Soc.* **1991,** *113*, 2466 and references therein.

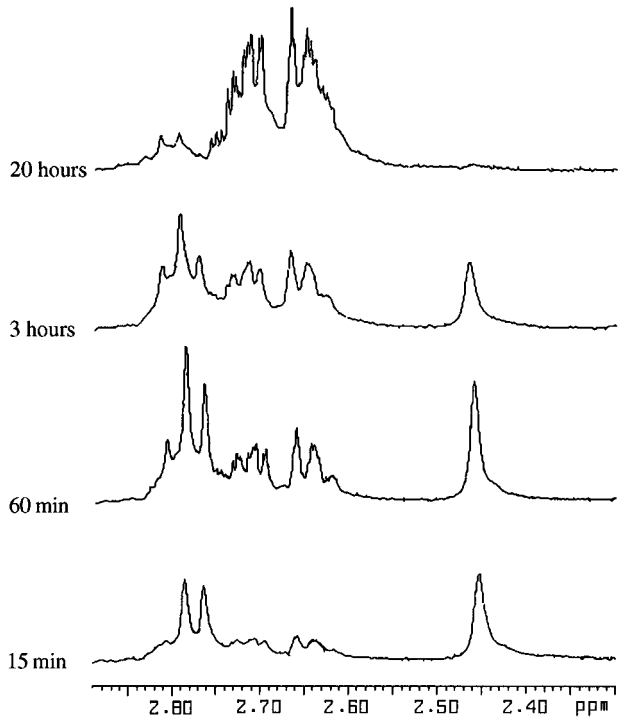
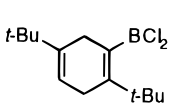


Figure 1. Time dependence of the allylic region of ^{1}H NMR in the reaction of **5** with 2-*tert*-butylbutadiene.

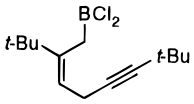
The formation of **13**−**15** suggested (vide infra) that a novel *alkynylboration* of the diene was taking place. In order to inhibit the Diels−Alder reaction and therefore possibly enhance the alkynylboration, reactions of the hindered alkynylboranes **5** and **6** were studied.

Considering the results with **1**, it was surprising to find that the Diels−Alder reaction of the hindered **5** with *tert*-butylbutadiene proceeded well in CH_2Cl_2. The reaction afforded cyclohexadiene **16** in 73% yield after 22 h at 25 °C. The 1,4-orientation of *tert*-butyl groups in **16** was apparent from the symmetry exhibited by the ^{1}H and ^{13}C spectra and was confirmed by oxidation of **16** to *p*-di-*tert*-butylbenzene with DDQ.

However, this "Diels−Alder" reaction was much more complicated than it initially appeared. On following the reaction, the diene had completely reacted within 1 h at 25 °C. In contrast to the results after a longer reaction time, workup at this stage of the reaction produced only a low yield of **16**, along with large amounts of the enyne **17**. By direct ^{1}H NMR of the reaction mixture, it could be observed that an initial intermediate exhibiting a doublet (J = 6.6 Hz, verified as a doublet using two field strengths) and singlet pattern between δ 2.4 and 3.0 slowly disappeared as the Diels−Alder adduct pattern of **18** increased (Figure 1). Considering the structure of **17** and the propensity of allylic boranes to undergo protodeboronation with allylic rearrangement,[9] the intermediate that formed **17** on workup and exhibited the 6.6 Hz doublet/singlet pattern was assigned as **19**.

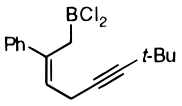


18



19

The results in the reaction of **5** with 2-phenylbutadiene were similar (Table 2). The ^{1}H NMR signal for 2-phenylbutadiene disappeared after 45 min, at which time the acyclic enyne **21** was the major product. After 24 h the cyclohexadiene product **20** was major. As with *tert*-butylbutadiene, an intermediate was observed exhibiting a 7 Hz doublet/singlet pattern in the allylic region of the ^{1}H NMR, consistent with structure **22**.



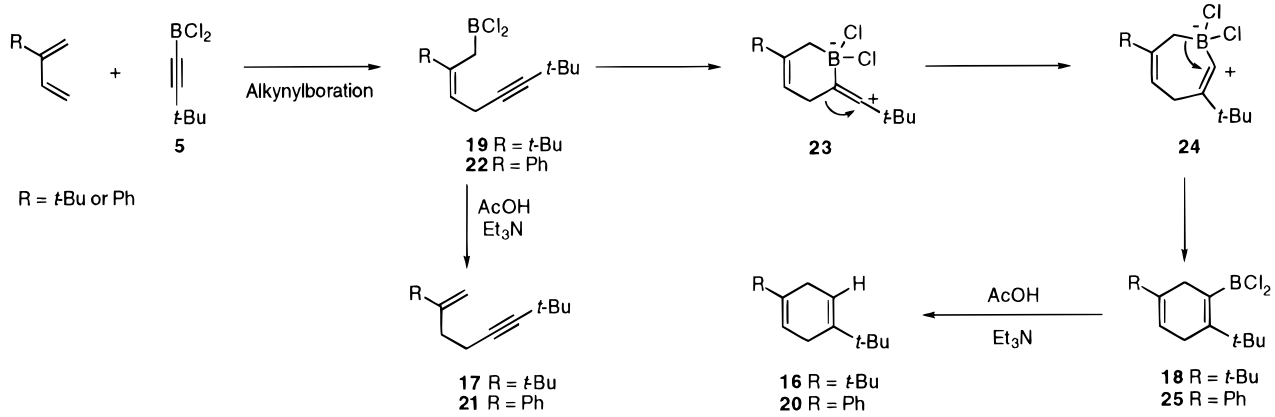
22

*On the basis of good mass-balances of **16** and **17** obtained at both short and long reaction times, **19** must be an intermediate in the formation of **16**.* Similarly, **22** appears to be an intermediate in the formation of **20**.

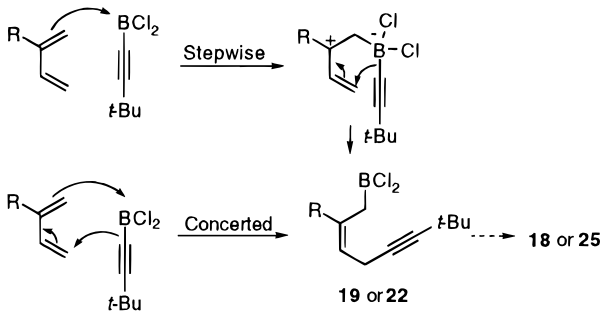
A mechanistic rationale for these results is displayed in Scheme 1. It is proposed that initially a novel 1,4-*alkynylboration* of the diene occurs to afford **19** or **22**. Because a 1,3-migration of a boryl group is often fast,[10] the formation of **19** or **22** could have been the result of either a 1,4-alkynylboration or a 1,2-alkynylboration of the least hindered double bond of the diene followed by 1,3-migration of the boryl group. However, the failure of numerous attempts to observe a 1,2-alkynylboration, using **5** with styrene, phenylacetylene, diphenylacetylene, allyltrimethylsilane, ethyl vinyl ether, and dihydropyran, suggests that a 1,4-alkynylboration is required. A possible origin for this requirement is discussed below. Protodeboronation of **19** or **22** with the usual allylic rearrangement[9] would then afford **17** or **21**.

At longer reaction times, the allyldichloroborane intermediate is proposed to undergo intramolecular addi-

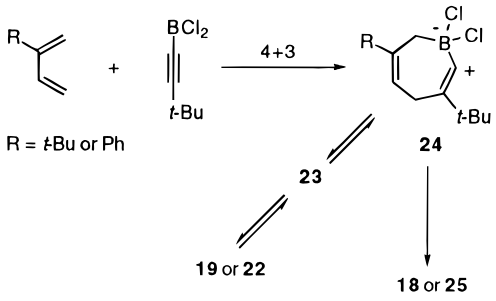
Scheme 1



Scheme 2



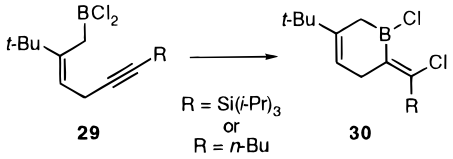
Scheme 3



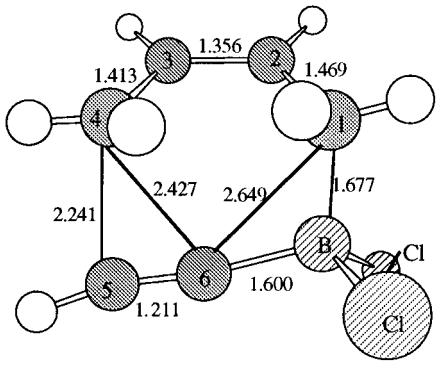
tion to the triple bond, producing a zwitterion six-membered-ring intermediate **23**. This could then rearrange to a seven-membered-ring intermediate **24** by a 1,2-alkyl group shift, and a boron-to-carbon migration of another alkyl group could then afford the Diels–Alder adducts **18** or **25**.

The reaction of **6** with *tert*-butylbutadiene went to completion in less than 30 min at 25 °C, and the reaction afforded high total yields of the cyclohexadienes **26** and **27** and the enyne **28**. The mixture of regioisomers among the Diels–Alder adducts was notably similar to that observed with **3**, with the preferred regioisomer **27** arising from a "para" orientation of dichloroboryl and *tert*-butyl groups. In this case, as had been observed with **1**, there was no significant change in the amount of the Diels–Alder adducts after prolonged stirring at room temperature.

We were puzzled by the contrasting results with **5**, where the cyclohexadiene products continue to form long into the reaction, versus **1** and **6**, where no further cyclohexadiene is formed after the initial reaction. A possible solution to this puzzle was suggested by the NMR spectra of the reaction mixtures. The 7 Hz doublet/singlet pattern observed in the reactions of **5** did not appear to be present with **1** and **6**, though new peaks overlapping with the cyclohexadiene products could be observed. This suggested that the intermediate **29** may undergo an intramolecular chloroboration of the alkyne to form **30**, which could return the observed enynes on workup. The difference in reaction of **5** could then result from a steric inhibition of the chloroboration by the *tert*-butyl groups in **19** and **22** (Scheme 2).



A Unified Mechanism. The results above show that the solution Diels–Alder reactions of alkynyldihaloboranes are at least in some cases a *stepwise* process. However, interesting insights into the origin of the alkynylboration reaction and the general regiochemical preferences in these reactions were provided by an ab initio prediction of the *concerted* cycloaddition. RHF calculations with a 6-31G* basis set predict the transition structure **31**[11] for the reaction of butadiene with ethynyldichloroborane. The [4 atom + 3 atom] character of **31** is in line with previous predictions for Diels–Alder reactions with vinyl- and ethynylboranes, although the B–C_1 bonding in **31** is much more advanced. This results in a significant partial positive charge on C_2 of the diene − 0.21 e more positive than C_3 in a Mulliken population analysis. The stabilization of this charge by electron-donating substituents on C_2 would account for the regioselectivity observed with **1**, **2**, and **5**.



31

Despite its unusual geometry, **31** is predicted to be the transition structure for a *Diels–Alder* reaction—minimization of **31** leads smoothly to the [4 atom + 2 atom] cyclohexadienylborane product without any apparent intermediate. However, the structure is suggestive regarding two other pericyclic processes. The close proximity of C_6 and C_4 in **31** suggests that a concerted alkynylboration of dienes could take place from a similar geometry. Although a stepwise ionic process for the alkynylboration cannot be ruled out (and would be consistent with the solvent effect on the rate of the reactions), the concerted process would explain why dienes undergo alkynylboration but alkenes do not.

Alternatively, the structure of **31** suggests the feasibility of a direct [4 atom + 3 atom] cycloaddition of dienes with alkynylboranes to afford the previously postulated intermediate **24** (Scheme 3). This would be isoelectronic with the well-known allowed [4 atom + 3 atom] cycloaddition of dienes with allylic cations to form seven-membered rings.[12] The formation of the zwitterionic **24** would simultaneously account for the observed solvent effect, the alkynylboration reaction, and the conversion of the alkynylboration intermediates into the Diels–Alder products.

In order to distinguish the mechanism of Schemes 1 and 2 from that of Scheme 3, the product mixture from the reaction of **5** with *tert*-butylbutadiene was analyzed at very short reaction times. Schemes 1 and 2 require the intermediacy of the alkynylboration intermediates in

(11) E = −1174.867 487. Structure **31** is fully optimized and exhibited one imaginary frequency. The predicted activation energy is 31.55 kcal/mol.

(12) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 819.

the formation of the Diels−Alder product, so that at short reaction times the amount of cyclohexadiene compared to enyne should be very low. If **24** is formed directly as in Scheme 3, the partitioning of **24** might form significant amounts of cyclohexadiene compared to enyne immediately. In the actual experiment, the ratio of **16**:**17** observed by GC after 60 s was 24:76, which is not very different from the ratio observed after 1 h (32:68). This supports the unified mechanism of Scheme 3 for these reactions, although the more complicated possibility of competing concerted and stepwise reactions cannot be rule out.

Does the same mechanism operate in the cleaner hexanes reactions? The absence of alkynylboration products in the hexanes reactions could be the result of a change in mechanism to the direct Diels−Alder or a change in the partitioning of **24** between cyclohexadiene and alkynylboration products. In this regard, the observation of an identical mixture of regioisomers from the reactions of **3** in hexanes and CH_2Cl_2 provides support for the latter interpretation by suggesting that no significant change in the mechanism of formation of the Diels−Alder adducts has occurred.

Experimental Section

All reactions were carried out in dried glassware under a positive pressure of nitrogen using standard syringe and septa techniques. The NMR spectra of aliquots of reaction mixtures containing boranes were taken as neat liquids in glass capillaries centered in NMR tubes and were referenced approximately based on the internal tributylstannyl chloride or tributylstannyl bromide. Solutions of BCl_3 and BBr_3 in hexanes or methylene chloride were used as purchased from Aldrich. (Phenylethynyl)tributylstannane,[13] (1-hexynyl)tributylstannane,[14] (3,3-dimethyl-1-butynyl)tributylstannane,[15] and [(triisopropylsilyl)ethynyl]tributylstannane[13,16] were prepared by literature procedures.

General Procedure for Formation and Reaction of Alkynyldihaloboranes (1−4) with Isoprene in Hexanes. Either (1-hexynyl)tributylstannane or (phenylethynyl)tributylstannane was added dropwise to 1.0 equiv of a 1.0 M solution of BCl_3 or BBr_3 in hexanes under N_2 at −78 °C, on a 2−2.5 mmol scale. The resulting mixture was warmed to 25 °C for 5 min and then cooled to −78 °C, and 0.6 equiv of isoprene was added dropwise. The mixture was then warmed to 25 °C for the times shown in Table 1 and then recooled to −78 °C. There was then added successively in a dropwise fashion 3 equiv of 1-hexene and 3 equiv of triethylsilane. After the mixture was stirred at −78 °C for 30 min, it was warmed to room temperature and stirred for another 2 h. All volatiles were then removed under vacuum. The residue was dissolved in 5 mL of THF, 3 mL (53 mmol) of glacial acetic acid was added, and the mixture was stirred at room temperature for 2 h. The reaction mixture was then neutralized with saturated $NaHCO_3$ solution, and the resulting mixture was then extracted with three 30-mL portions of petroleum ether. The combined extracts were rinsed with a saturated aqueous KF solution and dried over Na_2SO_4, and the solvent was removed on a rotary evaporator. The residue was chromatographed on a short column of silica gel, eluting with petroleum ether, and the solvent was removed on a rotary evaporator to afford the cyclohexadienes **9**−**11** in the yields shown in Table 1.

9: a known colorless oil;[17] ^{1}H NMR δ 5.40 (br s, 2 H), 2.55 (br s, 4 H), 1.95 (t, J = 8 Hz, 2 H), 1.65 (br s, 3 H), 1.3 (m, 4 H), 0.85 (t, J = 8 Hz, 3 H); ^{13}C NMR δ 135.27, 131.28, 118.87, 118.13, 36.84, 31.81, 30.18, 29.87, 22.88, 22.48, 13.89. Aromatization of the samples of **9** by treatment with 2 equiv of DDQ in 20 mL of THF for 2 h afforded 4-*n*-butyltoluene, which was identical by NMR and GC to authentic material.[18]

10 and **11**: isolated as colorless oily mixtures of isomers; ^{1}H NMR δ 7.52−7.20 (m, 5 H), 6.18 (m, 1 H, major), 5.80 (m, 1 H, minor), 5.60 and 5.54 (m, 1 H combined), 2.95 (m, 4 H), 1.82 and 1.78 (s, 6 H combined).[6] Aromatization of the mixtures of **10** and **11** by treatment with 2 equiv of DDQ in 20 mL of THF for 2 h afforded mixtures of 3-phenyltoluene and 4-phenyltoluene, identical by ^{1}H and ^{13}C NMR to the commercially available materials.

General Procedure for Reaction of Alkynyldichloroboranes (1, 3, 5, and 6) with Dienes in CH_2Cl_2. Either (1-hexynyl)tributylstannane, (phenylethynyl)tributylstannane, (3,3-dimethyl-1-butynyl)tributylstannane, or [(triisopropylsilyl)ethynyl]tributylstannane was added dropwise to 0.9−0.95 equiv of a 1.0 M solution of BCl_3 in CH_2Cl_2 under N_2 at −78 °C, on an ∼2 mmol scale. The resulting mixture was warmed to 25 °C for 5 min and then cooled to −78 °C, and 0.5−0.6 equiv of the diene was added dropwise. The mixture was then warmed to 25 °C for the times shown in Table 2. The reaction was then cooled to 0 °C, and ∼4 equiv of triethylamine and 3 mL (53 mmol) of glacial acetic acid were added successively. The resulting mixture was heated to 55 °C for 16−18 h. After being cooled to room temperature, the reaction mixture was neutralized with saturated $NaHCO_3$ solution and then extracted with three 15−30 mL portions of petroleum ether. The combined extracts were rinsed with a saturated aqueous KF solution and dried over anhydrous $MgSO_4$, and the solvent was removed on a rotary evaporator. The residue was flash chromatographed on a 3/4 in. × 8 in. silica gel column using petroleum ether as eluent to afford the products and yields shown in Table 2. Except for mixtures of **10**/**11** and **26**/**27**, the products were isolated individually, all as colorless liquids.[6]

12: ^{1}H NMR δ 5.50 (m, 1 H), 5.42 (m, 1 H), 2.65 (m, 4 H), 1.96 (t, 2 H), 1.30 (m, 4 H), 1.02 (s, 9 H), 0.88 (m, 3 H); ^{13}C NMR δ 142.65, 134.76, 118.48, 115.42, 36.65, 34.87, 30.27, 29.47, 29.03, 25.86, 22.51, 14.02. Aromatization of **12** by treatment with 2 equiv of DDQ in 20 mL of THF for 2 h afforded the known 1-*n*-butyl-4-*tert*-butybenzene.[19]

13: ^{1}H NMR δ 4.86 (s, 1 H), 4.65 (s, 1 H), 2.24 (br s, 4 H), 2.12 (m, 2 H), 1.40 (m, 4 H), 1.02 (s, 9 H), 0.88 (m, 3 H); ^{13}C NMR δ 156.58, 106.30, 80.22, 80.08, 36.08, 31.22, 31.00, 29.16, 21.92, 18.75, 18.44, 13.61; HRMS (EI) m/e calcd for $C_{13}H_{21}$(M^+ − 15) 177.1643, found 177.1644.

16: the ^{1}H NMR spectrum of the known **16** was identical to that previously observed;[20] ^{13}C NMR δ 142.31, 115.95, 34.75, 29.07, 26.39. Aromatization of **16** by treatment with 2 equiv of DDQ in 20 mL of THF for 2 h afforded the commercially available 1,4-di-*tert*-butylbenzene.

17: ^{1}H NMR δ 4.86 (br s, 1 H), 4.66 (br s, 1 H), 2.22 (m, 4 H), 1.18 (s, 9 H), 1.02 (s, 9 H); ^{13}C NMR δ 156.60, 106.41, 88.95, 78.48, 36.09, 31.40, 31.16, 29.21, 27.31, 18.80; HRMS (EI) m/e calcd for $C_{13}H_{21}$ (M^+ − 5) 177.1643, found 177.1649.

Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.09; H, 12.74.

20: ^{1}H NMR δ 7.50−7.22 (m, 5 H), 6.22 (m, 1 H), 5.70 (m, 1 H), 3.15 (m, 2 H), 2.96 (m, 2 H), 1.15 (s, 9); ^{13}C NMR δ 142.03, 141.28, 133.28, 128.20, 126.73, 124.89, 122.24, 115.39, 34.86, 29.11, 28.98, 26.49. Aromatization of **20** by treatment with 2 equiv of DDQ in 20 mL of THF for 2 h afforded the known 4-*tert*-butylbiphenyl.[21]

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21: ^{1}H NMR δ 7.45−7.22 (m, 5 H), 5.32 (br s, 1 H), 5.12 (br s, 1 H), 2.70 (t, J = 9 Hz, 2 H), 2.30 (t, J = 9 Hz, 2 H), 1.18 (s, 9 H); ^{13}C NMR δ 147.22, 140.92, 128.25, 127.36, 126.15, 112.98, 89.70, 77.72, 35.23, 31.36, 27.30, 18.23.

Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.26; H, 9.61.

26 and **27**: isolated as colorless oily mixtures of isomers; ^{1}H NMR δ 6.02 (m, 1 H), 5.50 (m, 1 H), 2.80−2.58 (m, 4 H), 1.24−0.95 (m, 30 H). Aromatization of the mixtures of **26** and **27** by treatment with 2 equiv of DDQ in 20 mL of THF for 2 h afforded a mixture of the known 1-*tert*-butyl-3-(triisopropylsilyl)benzene and 1-*tert*-butyl-4-(triisopropylsilyl)benzene.[22]

28: ^{1}H NMR δ 4.88 (br s, 1 H), 4.70 (br s, 1 H), 2.38 (m, 2 H), 2.28 (m, 2 H), 1.06 (s, 21 H), 1.02 (s, 9 H); ^{13}C NMR δ 156.00, 112.40, 109.19 (C). 106.87, 36.10, 30.98, 29.34, 19.82, 18.66, 11.51.

Anal. Calcd for $C_{19}H_{36}Si$: C, 78.00; H, 12.40. Found: C, 78.01; H, 12.39.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **10**/**11**, **12**, **13**, **20**, and **26**/**27** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm edition of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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