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Review

The use of organoboron chlorides and bromides in organic synthesis

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Abstract

Organoboron chlorides and bromides are valuable reagents for halogenation and alkylation of aromatic aldehydes, addition of aldehydes to alkenes, and dialkenylation of aldehydes. An overview of these newly discovered reactions is presented.

Keywords: Organoboron; Halides; Alkylation; Aldehyde; Alkyne; Alkene

1. Introduction

In recent years, boron halide chemistry has attracted much attention [1]. The regioselective enolization of carbonyl compounds is one of the most important applications of organoboron halides since the resulting alkenoxyboranes have been found to be quite effective in stereodefined reactions [2]. For example, the aldol reaction of boron enolates is especially useful for attaining stereocontrol in the synthesis of α-hydroxy-carbonyl compounds and in the preparation of a wide variety of natural products [2–4].

Enantioselective reductions of prochiral carbonyl compounds to optically active alcohols also play an important role in organic synthesis, and organoboron halides are very effective stereoselective reducing agents [5]. As an example, β-chlorodiisopinocampheylborane (DIP-Chloride) is now one of the most widely used reagents for the asymmetric reduction of ketones and aldehydes [6]. The selective cleavage of ethers under mild conditions is another important transformation in which boron halides have been utilized [7]. A notable feature of the boron halide cleavage reaction is its regioselectivity [8]. The haloboration of carbon–carbon multiple bonds has also been a fruitful area of research and a wide variety of haloboranes have been found to react with terminal alkynes to produce (*Z*)-2-halo-1-alkenylboranes. The reaction occurs in a stereo-, regio-, and chemoselective fashion and has been used to synthesize numerous vinyl halides, alkadienes, alkenynes and a variety of olefinic products [9].

Boron halide derivatives have also been used to promote a number of organic reactions including condensation, alkylations as well as halogenations of alcohols, aldehydes and benzylic alcohols to the corresponding bromides [10]. Halogen exchange reactions between alkyl halides and boron trihalides have also been reported [11].

Boron halides are strong Lewis acids and readily form complexes with carbonyl compounds [12]. Boron trichloride also promotes *ene* reactions of aldehydes with alkenes as well as the Baylis-Hillman reaction of aldehydes with α,β-unsaturated ketones [13,14]. Boron trifluoride is known to catalyze the Friedel–Crafts alkylation of aromatic compounds; numerous examples have been reported in which alkenes, alcohols, and alkyl halides have been used to alkylate aromatic compounds [15]. For example, we discovered an unusual aldol-grob reaction sequence [16] as well as an *ene*/Friedel–Crafts sequence for creating large ring systems [17] utilizing BF_3 as catalyst. Recently, we focused our attention on

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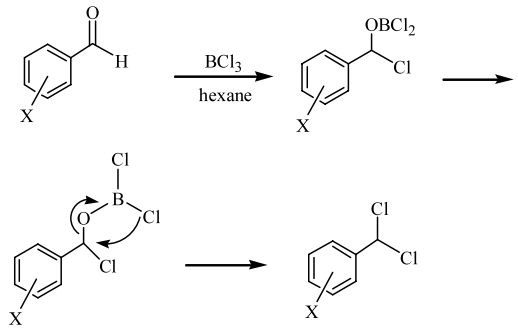


Yield : 76 - 99%

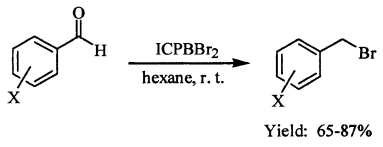
Scheme 1.

new transformations utilizing organoboron halides. Here, we present the results of our research.

2. Halogenation of aromatic aldehydes

2.1. Chlorination of aromatic aldehydes using boron trichloride

The chlorination of aldehydes to the corresponding *gem*-dichlorides is a very useful transformation in organic synthesis since the product aryldichloromethanes are of value in the pharmaceutical and agricultural industries. Generally, PCl_5 is used to generate geminal dichlorides [18]. Other methods utilize $PhCCl_3/FeCl_3$ [19], $SeO_2/MeSiCl_3$ [20], $SOCl_2$/DMF [21], $SOCl_2/(Me_2N)_3PO$ [22], and d-block metal chlorides [23]. However, these methods require either high temperature or toxic reagents.



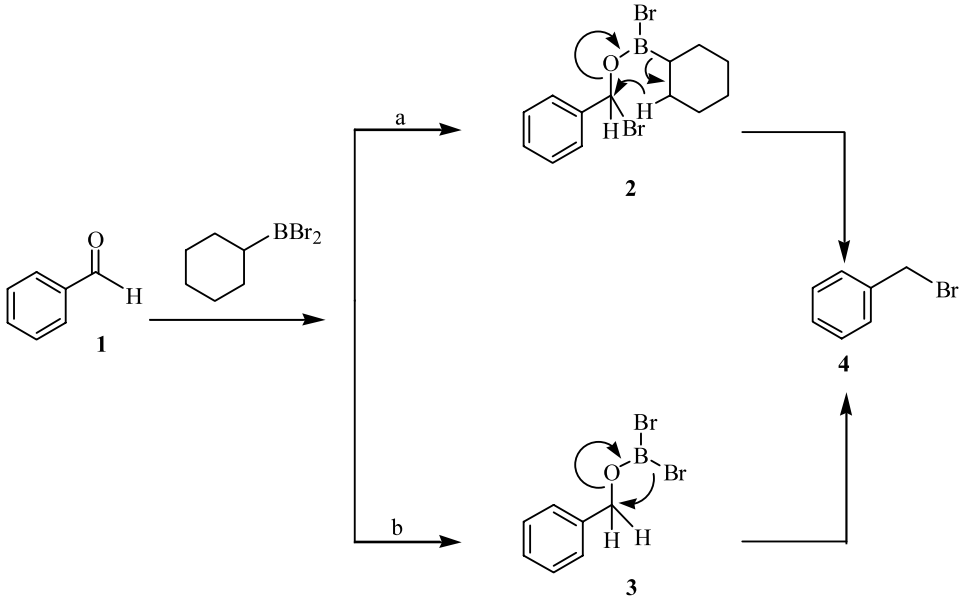
X = H, 4-Cl, 4-Br, 4-F, 2-F, 4-Me, 2-Me, 4-NO_2, 4-CN, 4-CHO, 2-Allyloxy

Scheme 2.

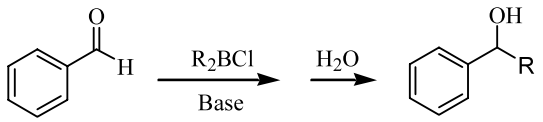
Boron trichloride had not been utilized to convert aldehydes to the corresponding dichlorides. We discovered that BCl_3 reacts with aromatic aldehydes to generate the corresponding geminal dichlorides in excellent yields (Scheme 1). A variety of aromatic aldehydes were successfully converted to the corresponding geminal dichlorides with exception of *p*-anisaldehyde because of the cleavage of the methoxy moiety by BCl_3 [24].

Solvents such as hexane, CH_2Cl_2, Et_2O and THF were evaluated. If the reaction was carried out in hexane or toluene, reflux conditions were required for complete conversion. However, aldehydes were rapidly converted to *gem*-dichlorides in CH_2Cl_2 at room temperature. Et_2O and THF are not suitable solvents due to their cleavage by BCl_3 [7].

To gain insight regarding the reaction mechanism, the reaction of benzaldehyde with BCl_3 was monitored by NMR spectroscopy. The reaction intermediate was isolated from the reaction of benzaldehyde and BCl_3 in hexane at 0 °C. The NMR spectra of the intermediate (in benzene-d_6) clearly revealed the characteristic ^1H and ^{13}C resonances at 7.02 and 92.5 ppm, respectively, for benzyloxyboron dichloride. This intermediate presumably then undergoes migration of the second chlorine to



Scheme 3.



Yield: 40 - 90%

Scheme 4.

give the final *gem*-dichloride (Scheme 1). Hydrolysis of the intermediate leads to the regeneration of the starting benzaldehyde.

2.2. Reductive bromination of aromatic aldehydes using alkylboron dibromides

Benzyl bromide derivatives are important intermediates in organic synthesis. However, the direct conversion of aromatic aldehydes to the corresponding benzyl bromides had been achieved in only two prior instances; these involved the use of a mixture of trimethylaminoborohydride and bromine [25] or the use of a mixture of lithium bromide, chlorotrimethylsilane, and tetramethyldisiloxane [26].

Dialkylboron halides had been reported to be effective reducing agents for carbonyl compounds [5,6]. In addition, boron tribromide had been used to convert benzyl alcohols to the corresponding benzyl bromides [10c]. We discovered that alkylboron dibromides such as cyclohexylboron dibromide and isopinocampheylboron dibromide (ICPBBr$_2$) readily convert aromatic aldehydes to the corresponding benzyl bromides in excellent yields (Scheme 2) [27].

Cyclohexylboron dibromide reacts slowly with aldehydes at room temperature. However, isopinocampheylboron dibromide rapidly converted aldehydes to the corresponding bromides because the isopinocampheyl group is one of the most effective groups for reducing carbonyl compounds via a β-hydrogen transfer reaction [6].

Using NMR, we found that reactions of cyclohexylboron dibromide favor pathway 'a' whereas pathway 'b' predominates when isopinocampheylboron dibromide is utilized (Scheme 3).

The reaction conditions are tolerant of a variety of functional groups. The new synthesis provides a general, high yield route to benzyl bromides from aromatic aldehydes. It is also useful for converting α,β-unsaturated aldehydes to the corresponding bromides.

3. Alkylation of aromatic aldehydes using alkylboron chloride derivatives

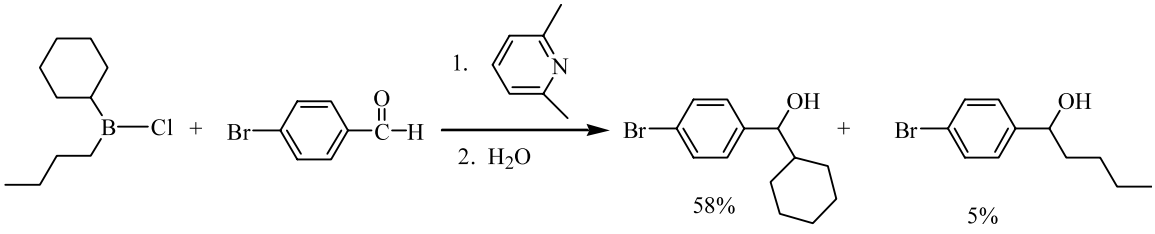
3.1. Alkylation of aryl aldehydes with dialkylboron chlorides

The alkylation of aldehydes and ketones by organometallic reagents is one of the most important reactions in synthetic organic chemistry. Generally, only reactive alkylmetals can be utilized to achieve this transformation. Organoborane reagents do not normally react with carbonyl compounds in a Grignard-like fashion with the exception of allylborane [28] and vinylborane reagents [29]. The few known alkylborane alkylation reactions require unusually reactive organoboranes [30], free radical conditions [31,32], or activation of the carbonyl groups [33,34]. Nevertheless, a Grignard-like reaction involving organoborane reagents would possess a number of synthetic advantages including stereochemical control and the fact that a large number of functional substituents are unaffected by the mild reaction conditions required in most organoborane transformations [35].

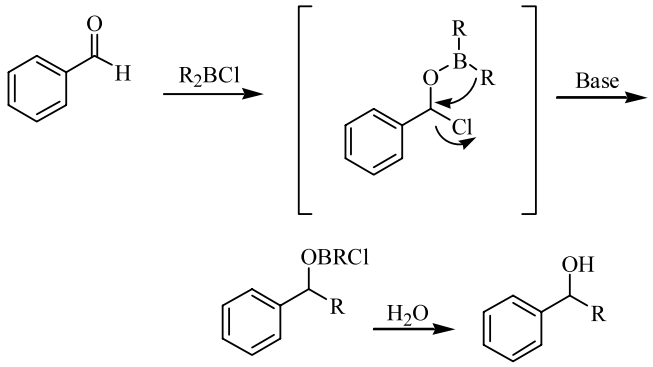
Our previously discovered conversion of aryl aldehydes to aryldichloromethane [24] led us to conclude that using an alkylboron derivative in place of boron trichloride might produce an alkylation reaction which would provide a Grignard-like addition. Alkylboron halide reagents had not been previously used to alkylate carbonyl compounds.

We first examined the reactions of alkylboron dichloride with aryl aldehydes and found that no reaction occurred at room temperature. Then, we discovered that alkylation could be achieved by simply adding a base to the reaction mixture (Scheme 4) [36].

Bases such as triethylamine, quinuclidine, pyridine, DBU, *n*-butyllithium, *t*-butoxyllithium and 2,6-lutidine were evaluated. Both bulky and strong bases produced the highest yields. Moderate yields of alkylation products, arylalkylmethanols, were obtained in all cases. Product yields are not dependent on the electronic nature of substituents of the aldehyde, but boranes



Scheme 5.

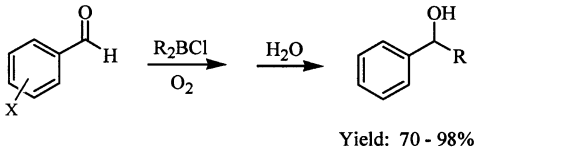


Scheme 6.

containing secondary alkyl groups produce relatively high yields of alkylation products compared to boranes containing primary alkyl groups. The alkylations also proceed faster for boranes containing secondary alkyl groups. In one reaction, 4-bromobenzaldehyde was allowed to react with *n*-butyl(cyclohexyl)boron chloride. As anticipated, the major product was cyclohexyl(4-bromophenyl)methanol isolated in 58% yield (Scheme 5).

In order to investigate the reaction mechanism, the reaction of 4-bromobenzaldehyde with dicyclohexylboron chloride was monitored by NMR spectroscopy. The NMR data suggest that the reaction proceeds via formation of a borinate ester followed by migration of the alkyl group (Scheme 6).

This new alkylation reaction provides a potentially useful alternative to traditional Grignard and organolithium reactions. The reaction occurs under mild reaction conditions and tolerates a variety of functional groups. It is limited to aromatic aldehydes that do not possess α-hydrogens due to the well-known enolization reactions that occur with dialkylboron halides. Benzyl alcohols are formed in small quantities along with the desired product (reduction predominates if the more hindered organoboranes, such as diisopinocampheylboron chloride, dinorbornylboron chloride, and di-(3-methyl-2-butyl)boron chloride are utilized).



X = H, 4-F, 4-Cl, 2-Cl, 4-Br, 4-Me, 2-Me, 4-OMe, 4-CHO, 4-CN

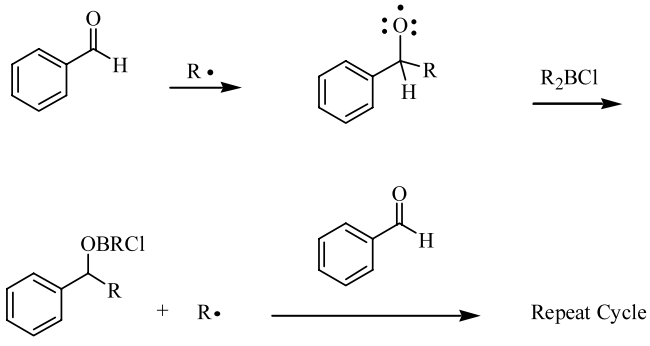
Scheme 7.

3.2. Alkylation of aryl aldehydes using dialkylboron chlorides in the presence of oxygen

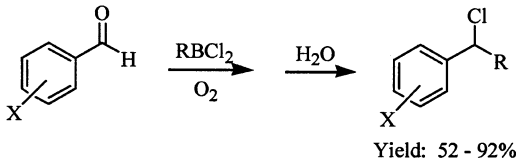
Organoboranes are known to undergo facile autoxidation in the presence of oxygen, and the reaction has been used to prepare alcohols and alkyl hydroperoxides as well as to initiate free radical reactions [37,38]. Trialkylboranes can be used to alkylate α,β-unsaturated carbonyl compounds through a free radical 1,4-addition reaction in the presence of air [39], but they do not normally react with saturated carbonyl compounds except for the reaction of formaldehyde with trialkylboranes in the presence of air [32]. We have discovered that oxygen induces the reaction of dialkylboron chlorides with aryl aldehydes to produce alkylation products in excellent yields (Scheme 7) [40]. This oxygen-induced reaction proceeds more readily than the corresponding alkylation carried out in the presence of base [36].

The reaction of dialkylboron chlorides with aryl aldehydes is a general one. A wide variety of structural and electronic modification are tolerated. This reaction proceeds most efficiently at 0 °C, partial reduction occurs at room temperature due to *β*-hydrogen transfer. In contrast to alkylation reactions carried out in the presence of base, organoboranes containing primary, secondary and hindered alkyl groups all produce excellent yields of alkylation products.

The alkylation reaction is rapid but no alkylation occurs in the presence of radical scavenger such as galvinoxyl. In addition, when both primary and secondary alkyl groups are present, as is generally the case when alkyl boron halides are formed via hydroboration, the secondary group reacts preferentially. These observations support the postulation that the reaction is occurring via a radical pathway such as the one outlined in Scheme 8.



Scheme 8.



X = H, 4-F, 4-Cl, 2-Cl, 3-Cl, 4-Br, 4-Me, 4-CHO, 3-Br, 2-Me

Scheme 9.

3.3. Chloroalkylation of aryl aldehydes using alkylboron dichlorides in the presence of oxygen

The reaction of dialkylboron chloride with aryl aldehydes in the presence of oxygen affords excellent yields of alkylarylmethanols. But only one of the alkyl groups is transferred to the carbonyl group. The reaction would be more efficient if monoalkylboron dichlorides could be utilized. Thus, we examined the reaction of alkylboron dichlorides with aryl aldehydes in the presence of oxygen. Interestingly, instead of alkylarylmethanols, the reaction produces the chloroalkylation products exclusively at room temperature (Scheme 9). We also noted that a small quantity of benzyl chloride formed along with the desired alkylation products. α,α-Dichlorotoluenes are formed in small quantities if reactions are carried out at the higher temperature.

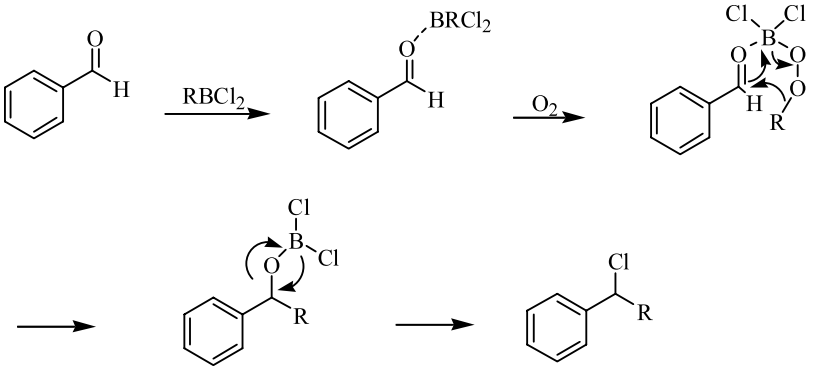
In contrast to the reaction of di(*n*-hexyl)boron chloride with aromatic aldehydes [40], isomeric products arising from migration of a secondary alkyl group are not observed in the reaction of *n*-butylboron dichloride with aryl aldehydes. This suggests that the reaction of monoalkylboron dichlorides proceeds via a different pathway. Notably, addition of the radical scavenger, galvinoxyl, did not inhibit the alkylation reaction. In addition, *n*-butyl peroxide was isolated upon hydrolysis of the reaction mixture of *n*-butylboron dichloride and benzaldehyde. Thus, the reaction most likely proceeds via oxidation of the organoborane to form a peroxide intermediate which then undergoes alkyl transfer through an intramolecular six-membered ring transition state to generate the borinate ester. The product would then form after migration of the chlorine (Scheme 10).

4. Boron halides promoted addition of aromatic aldehydes with alkenes

4.1. Synthesis of 1,3-dihalo-1,3-diarylpropanes

As noted earlier, Lewis acid-catalyzed addition of carbonyl compounds to alkenes is a very important method for forming new carbon–carbon bonds [41]. For instance, Lewis acid promoted *ene* and Baylis-Hillman reactions have been well documented [13]. However, boron trihalides have been reported to be ineffective for these reactions [42]. During our investigation of the haloboration of alkenes via boron trihalides, we discovered that BCl_3 and BBr_3 are very effective in promoting the addition of aryl aldehydes to styrenes. The reactions regioselectively produce diastereomeric mixtures of 1,3-dihalo-1,3-diaryl-propanes (Scheme 11), which are useful intermediates in organic synthesis [43].

When reactions are carried out at room temperature, halogenation of aryl aldehydes to *gem*-dihalides occurs [24]. However, BCl_3 reactions produce good yields of the desired alkylation products when carried out at 0 °C. Reactions promoted by BBr_3 must be carried out at −40 °C due to the rapid dibromo-de-oxo-bisubstitution of aryl aldehydes by BBr_3 [10e]. We noted that the freshly distilled styrenes produce only polymerization products, whereas commercially available styrenes containing 4-*tert*-butylcatechol as a stabilizer produce the corresponding 1,3-dihalo-1,3-diarylpropane in excellent



Scheme 10.

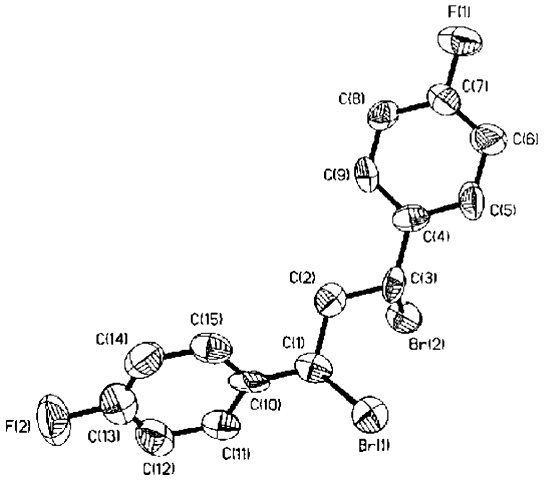
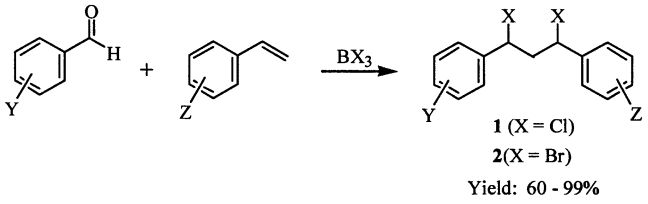


Fig. 1. Crystal structure of *anti*-isomer of 1,3-dibromo-1,3-di(4-fluorophenyl)propane.



Y=H, 4-F, 4-Cl, 4-Me, 4-CN, 4-NO_2, 2-Br, 2-F,
Z = H, 4-F, 4-Me

Scheme 11.

yields. Solvents such as hexane, toluene and CH_2Cl_2 were evaluated, and CH_2Cl_2 produces the best yields.

A series of aryl aldehydes were subjected to the reaction. Essentially all aldehydes generate 1,3-dihalo-1,3-diarylpropanes in excellent yields. Aldehydes containing electron-withdrawing functional groups such as Cl, F, CN and NO_2 react at a slower rate. In addition, we observed that the products containing electron-donating substituents tend to decompose during chromatography on silica gel. 1,3-Dibromo-1,3-diarylpropanes are especially susceptible to decomposition on silica gel.

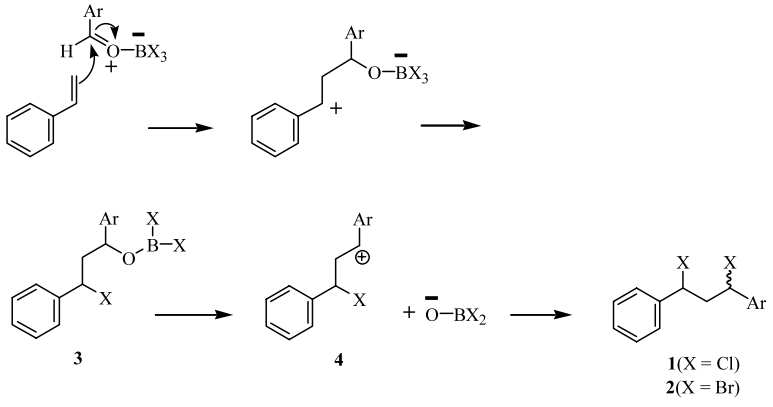
NMR analyses of the reaction mixtures revealed a nearly statistical distribution of the diastereoisomers (*syn*/*anti* ≈ 50/50). The *anti*-isomer of 1,3-dibromo-1,3-di(4-fluorophenyl)propane has been isolated and characterized by NMR and X-ray crystallography (Fig. 1).

The reaction of aryl aldehydes with styrenes presumably proceeds through coordination of the carbonyl group to the boron trihalide followed by addition of the carbonyl carbon to the alkene to form a carbocation which then adds halide to form **3**. Loss of an oxyboron moiety from **3** would then generate cation **4** as a precursor to either **1** or **2** (Scheme 12).

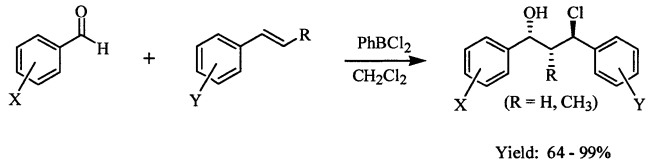
4.2. Synthesis of 1,3-diaryl-3-chloro-1-propanols

While investigating the reaction of aryl aldehydes with styrenes in the presence of boron trichloride, we detected the formation of β-chloroalcohols in low yields. We then investigated the reaction of aldehydes with alkenes in the presence of phenylboron dichloride and discovered that the reaction regioselectively produced *anti*-β-chloroalcohols in good to excellent yields (Scheme 13) [44]. These chloroalcohols are potentially useful intermediates in organic synthesis.

The reactions were carried out by introducing phenylboron dichloride to a mixture of styrenes and aryl aldehydes in CH_2Cl_2. Again, only commercially available styrenes containing 4-*tert*-butylcatechol as a stabilizer produced good yields of the desired products. A variety of aryl aldehydes were subjected to the reaction. They all produced good to excellent yields of the products. Aldehydes containing electron-donating groups such as methyl and methoxy groups require a lower reaction temperature (−20 °C) due to the facile chlorination of the product alcohols to form 1,3-

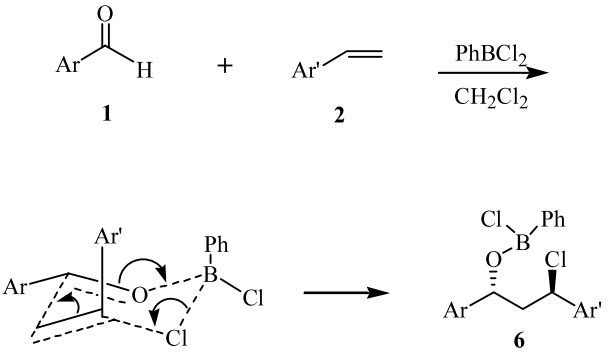


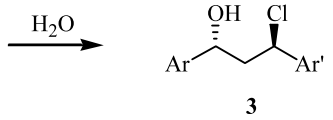
Scheme 12.



X = H, 4-F, 2-F, 4-Cl, 2-CH_3, 4-OCH_3, 4-CN, 4-NO_2,
Y = H, 4-Cl, 4-CH_3

Scheme 13.





Scheme 14.

dichloro compounds [43]. Heteroaromatic aldehydes such as 3-pyridinecarboxaldehyde react with styrenes to generate 3-chloro-1-(3-pyridyl)-3-phenylpropanols in excellent yields. However, the reactions are slow compared to the reaction of aryl aldehydes. Aliphatic aldehydes and alkenes do not undergo the desired reaction.

Interestingly, NMR data reveal that the reactions generate only one regioisomer with the aryl groups at the 1,3-positions. In addition, the reactions predominantly produced the *anti*-diastereoisomers. For styrenes, the *R*,*R*/*S*,*S*-isomers are the major products whereas (*E*)-β-methyl styrenes produce mainly *R*,*R*,*R*/*S*,*S*,*S*-isomers. A single crystal of 4-(3-chloro-1-hydroxy-2-methyl-3-phenylpropyl)-benzenenitrile was analyzed by X-ray crystallography (Fig. 2). The X-ray structure confirmed the NMR assignment.

Although a detailed mechanistic study has not been undertaken, the reaction presumably occurs via electrophilic addition of the complexed aldehyde to styrene in a concerted fashion (Scheme 14).

5. Dialkenylation of aldehydes with alkynes in the presence of boron halides

5.1. Reaction of aryl aldehydes with aryl alkynes in the presence of boron trihalides

Vinylboranes are very useful reagents in organic synthesis [45]. They are generally prepared via hydroboration of alkynes with boron hydrides [46] or the haloboration of 1-alkynes [47]. Haloboration reactions, and their applications in organic chemistry, have been extensively reviewed. Interestingly, although simple vinylborane derivatives have been utilized in Grignard-like reactions to produce allylic alcohols, the reaction of

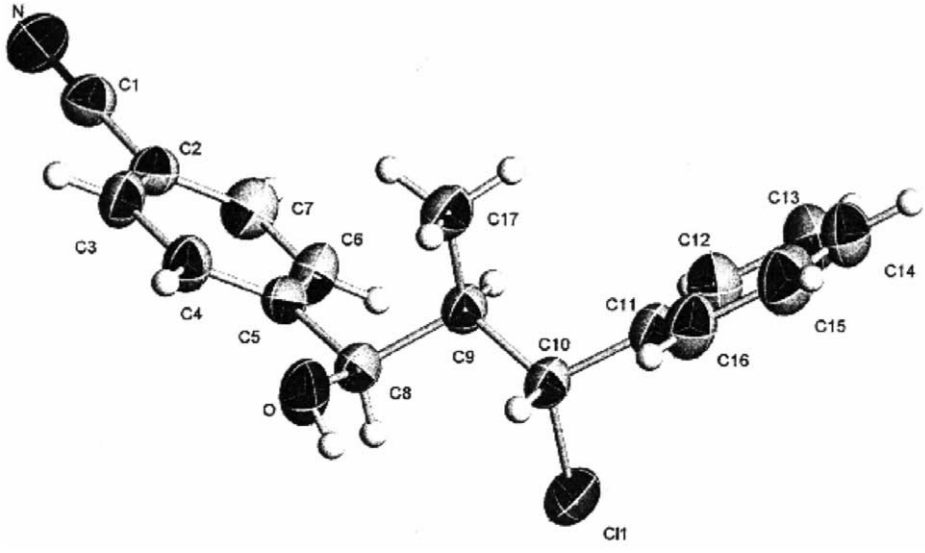
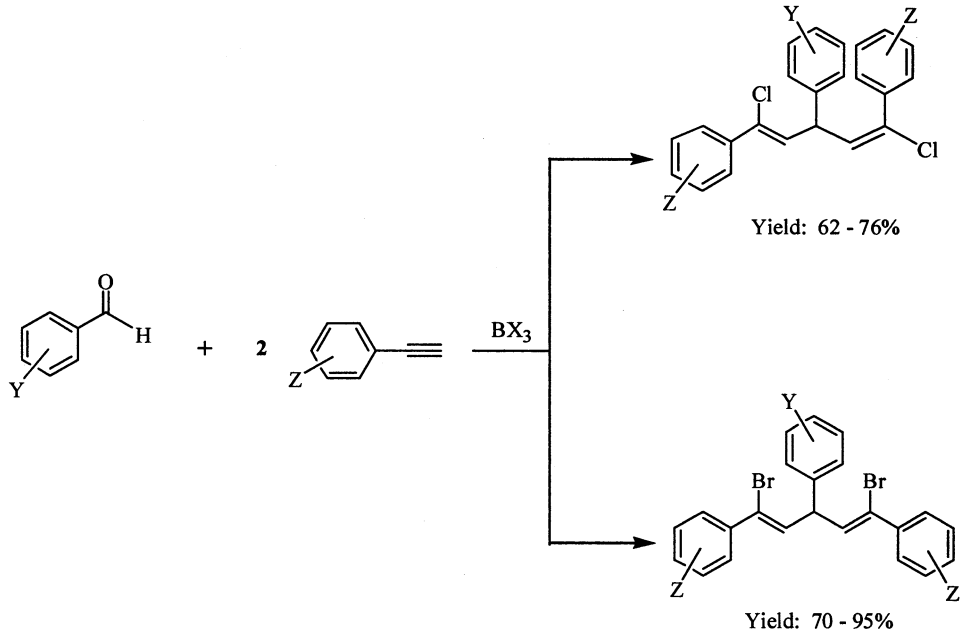


Fig. 2. Crystal structure of 4-(3-chloro-1-hydroxy-2-methyl-3-phenyl-propyl)-benzenenitrile.

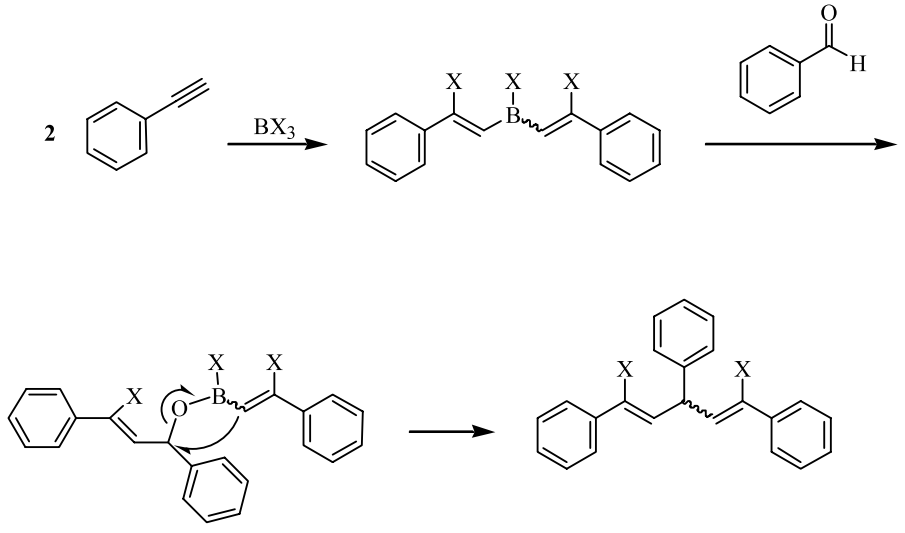


Y = H, 4-F, 4-Br, 4-Me, 4-CN, 4-NO_2, 2-Me
Z = H, 4-Me, 4-F, 4-Cl

Scheme 15.

halovinylborane reagents with carbonyl compounds has not been investigated. We discovered that di(halovinyl)boron halides, prepared via haloboration of aryl alkynes with boron trihalides, react with aryl aldehydes to generate the dialkenylation products, 1,3,5-triaryl-1,5-dihalo-1,4-pentadienes (Scheme 15) [48]. These halodiene derivatives are potentially useful intermediates in organic synthesis due to the multifunctionality contained in the molecules.

Initially, the reactions were carried out by introducing one equivalent of boron trihalides to the mixture of benzaldehyde and phenylacetylene (1:1 ratio) in CH_2Cl_2 at room temperature. The expected allylic alcohols were generated along with 1,5-dihalo-1,4-pentadienes. However, 1,4-pentadienes were the major product when benzaldehyde was allowed to react with two equivalents of phenylacetylene in the presence of the boron trihalide. Boron trichloride produced (*E*,*Z*)-1,5-dicholo-1,4-pen-



Scheme 16.

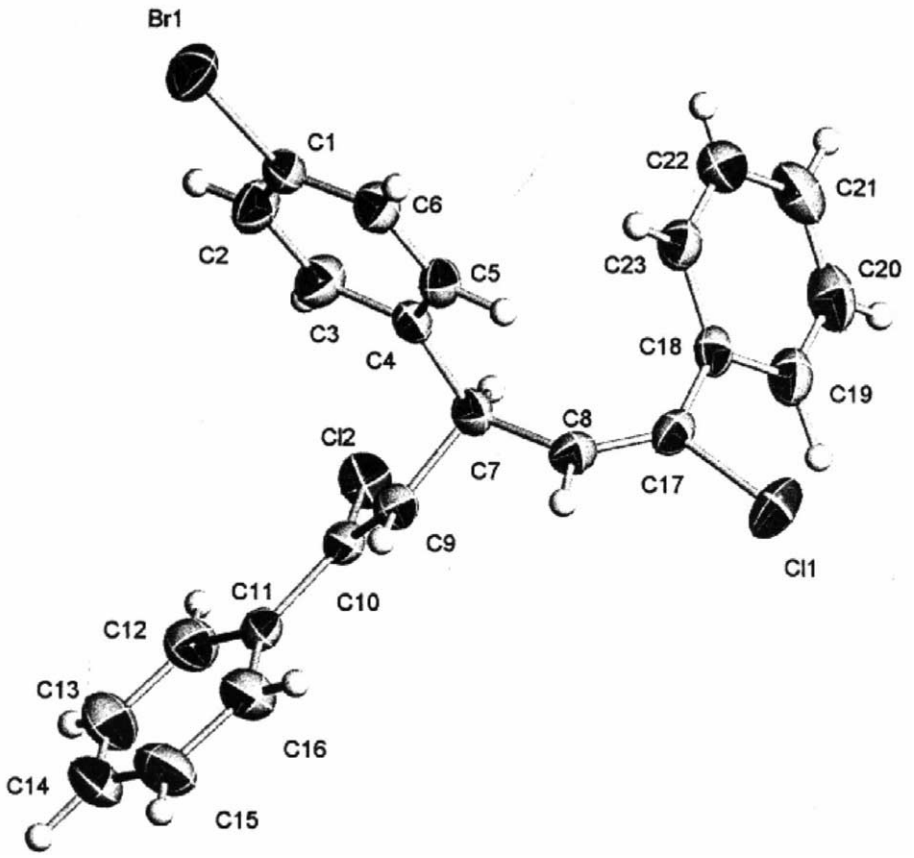


Fig. 3. Crystal structure of 1,5-dichloro-3-(4-bromophenyl)-1,5-diphenyl-1,4-pentadiene.

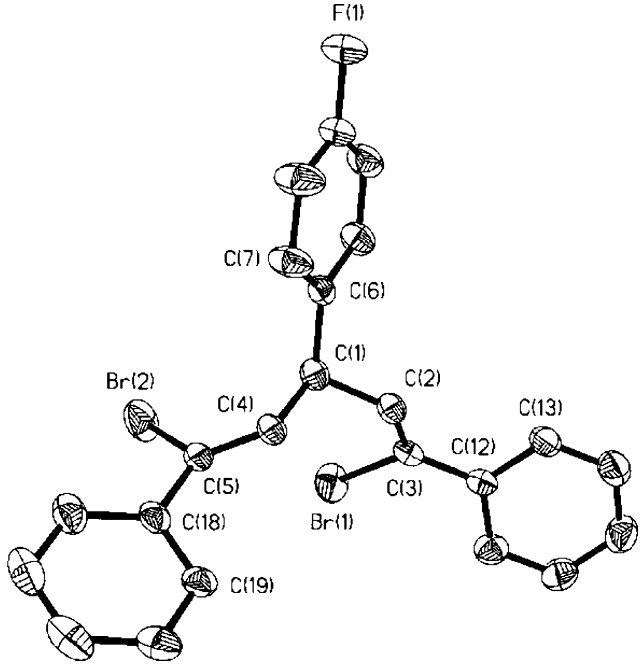


Fig. 4. Crystal structure of 1,5-dibromo-3-(4-fluorophenyl)-1,5-diphenyl-1,4-pentadiene.

tadienes at 0 °C as the major products whereas boron tribromide generated (*Z*,*Z*)-1,5-dibromo-1,4-pentadienes at −40 °C.

A series of aldehydes were subjected to the new reaction. Essentially all aldehydes are converted to the corresponding 1,5-dihalo-1,4-pentadienes in good to excellent yields. The reaction of aryl aldehydes and aryl acetylenes bearing electron-withdrawing functional groups tend to proceed more slowly. Compared to boron tribromide, boron trichloride produces lower yields of products which may be due to partial polymerization of alkynes catalyzed by boron trichloride.

Reactions involving aliphatic alkynes were also examined. However, only traces of the desired products were observed. Aliphatic aldehydes are not suitable substrates for the reactions due to known enolization reactions. Interestingly, reactions involving non-enolizable aliphatic aldehydes such as trimethylacetaldehyde and tribromoacetaldehyde with arylacetylenes produce only allylic alcohol products.

The reaction most likely proceeds via the pathway outlined in Scheme 16. Haloboration of the alkyne would generate a di(halovinyl)boron halide which would add to aldehyde in a Grignard-like fashion to form an

allyloxy intermediate by migration of the halovinyl group. Then, migration of the second halovinyl group would afford the final diene product. In control experiments in which BBr_3 and BCl_3 reactions were hydrolyzed prior to completion, allylic alcohols were isolated from the product mixtures. The formation of (*E*,*Z*)-1,5-dichloro-1,4-pentadiene products is probably due to the slow chloroboration of the second molecule of aryl acetylene, which leads to the more thermodynamically stable (*E*)-chlorovinyl addition product [49]. Presumably, migration of the vinyl groups proceeds with retention of configuration. The bromoboration of alkynes by boron tribromide is reported to be very facile and the reactions tend to form the kinetically controlled (*Z*,*Z*)-di(halovinyl)boron bromides which would then react with aryl aldehydes to generate (*Z*,*Z*)-1,5-dibromo-1,4-pentadienes [49]. Single crystals of 1,5-dichloro-3-(4-bromophenyl)-1,5-diphenyl-1,4-pentadiene (Fig. 3) and 1,5-dibromo-3-(4-fluorophenyl)-1,5-diphenyl-1,4-pentadiene (Fig. 4) were analyzed by X-ray crystallography.

Other organoboron halides, including *n*-butylboron dichloride, cyclopentylboron dichloride, and phenylboron dichloride, were also examined, but none of the desired dienes formed. These results indicate that the presence of a third halogen atom on boron is essential for the reaction.

6. Conclusion

The results summarized in this report demonstrate that organoboron halides are very effective Lewis acids, and can promote a variety of halogenation and new carbon–carbon forming reactions.

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