

A New Reaction of Aryl Aldehydes with Aryl Acetylenes in the Presence of Boron Trihalides[†]

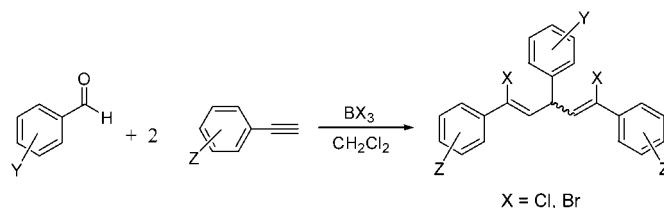
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Received February 8, 2002

ABSTRACT



The reactions of aryl aldehydes with 2 equiv of arylacetylenes in the presence of boron trichloride yield (*E,Z*)-1,3,5-triaryl-1,5-dichloro-1,4-pentadienes. Reactions carried out in the presence of boron tribromide generate the corresponding (*Z,Z*)-1,3,5-triaryl-1,5-dibromo-1,4-pentadienes.

Vinylboranes are versatile reagents in organic synthesis.¹ They are utilized in transformations such as Diels–Alder reactions,² additions to carbonyl compounds,³ and a variety of coupling reactions which generate new carbon–carbon skeletons.⁴ Vinylboranes are generally prepared via hydroboration of alkynes with boron hydrides⁵ or the haloboration of 1-alkynes.⁶ Haloboration reactions and their applications

in organic chemistry have been extensively reviewed.⁷ The reactions usually occur in a stereo-, regio-, and chemo-selective fashion via the *syn* addition of the B–X moiety to

[†] This paper is dedicated to Professor Herbert C. Brown, a pioneer in organoborane chemistry, on the occasion of his 90th birthday.

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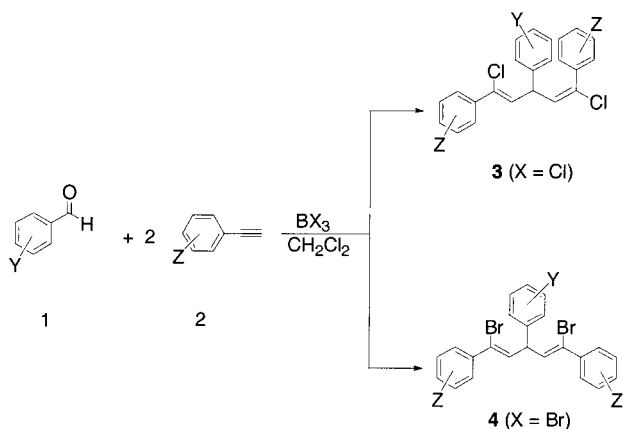
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the carbon–carbon triple bond, generating the corresponding (*Z*)-2-halo-1-alkenylborane.⁷ These halovinylborane reagents are useful synthetic intermediates and serve as precursors for alkenes, carbonyl compounds, and a variety of synthetically useful reagents.

Interestingly, although simple vinylborane derivatives have been utilized in Grignard-like reactions to produce the allylic alcohols, the reactions of halovinylborane reagents with carbonyl compounds have not been investigated.⁸ To our knowledge, only one report has appeared in which a halovinylborane reagent was utilized in a carbonyl addition reaction.⁹

Recently, we discovered a series of new organic transformations utilizing boron halide chemistry.¹⁰ We found, for example, that alkylboron chlorides will alkylate aryl aldehydes in a Grignard-like fashion.^{10b,c,e} In a continuation of these studies, we investigated the reactions of carbonyl compounds with halovinylboron halides prepared by the haloboration of alkynes via boron trihalides. We have discovered that di(halovinyl)boron halides react with aryl aldehydes to generate the dialkenylation products, 1,3,5-triaryl-1,5-dihalo-1,4-pentadienes (Scheme 1). These halo-

Scheme 1



diene derivatives are potentially useful intermediates in organic synthesis due to the multifunctionality contained in the molecules which may be utilized in subsequent substitution and coupling reactions. We wish to report the initial results of this study.

We first examined the reaction of benzaldehyde with 1 equiv of phenylacetylene in the presence of boron trichloride in CH_2Cl_2 at room temperature. To our surprise, the reaction generated a 1,4-pentadiene along with the expected allylic

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alcohol. We then examined the reaction of benzaldehyde with 2 equiv of phenylacetylene in the presence of boron trichloride and found that (*E,Z*)-1,5-dichloro-1,3,5-triphenyl-1,4-pentadiene was the major product. Only a minor quantity of the *Z,Z* isomer formed along with a small quantity of dichloromethylbenzene (due to the direct halogenation of benzaldehyde by boron trichloride as noted in our earlier studies.)^{10a–c} To minimize the formation of undesired dichloromethylbenzene, the reaction was carried out in CH_2Cl_2 at 0 °C, and 1,5-dichloro-1,3,5-triphenyl-1,4-pentadiene was isolated in good yield. Since, the bromination of aryl aldehydes by tribromoborane had been reported to be quite facile,¹¹ reactions using boron tribromide were carried out at –40 °C. Under these conditions, the corresponding (*Z,Z*)-1,3,5-triaryl-1,5-dibromo-1,4-pentadienes were produced in excellent yields along with minor quantities of the *E,Z* isomers.

A series of aldehydes were subjected to the new reaction. Essentially, all aldehydes were converted to the corresponding 1,3,5-triaryl-1,5-dihalo-1,4-pentadiene derivatives in good to excellent yields (Tables 1 and 2).¹² As can be seen from

Table 1. Synthesis of (*E,Z*)-1,3,5-Triaryl-1,5-dichloro-1,4-pentadienes

entry	Y	Z	time (h)	yield (%) ^{a,b}
1	H	H	6	65 (3a)
2	4-F	H	8	73 (3b)
3	4-Br	H	8	68 (3c)
4	4-Me	H	6	65 (3d)
5	4-CN	H	10	68 (3e) ^c
6	H	4-Me	6	67 (3f)
7	4-F	4-Me	8	63 (3g)
8	4-Me	4-Me	4	62 (3h)
9	4-F	4-F	12	76 (3i)
10	4-Me	4-F	6	62 (3j)

^a Isolated yields based on the starting aldehydes. ^b All products were characterized by elemental analyses and NMR spectroscopy. ^c Mixture of *E,Z* (40%) and *Z,Z* (60%).

the data contained in Tables 1 and 2, the reactions of arylacetylenes and aryl aldehydes bearing electron-withdrawing groups tend to proceed more slowly. The lower yields of chlorinated products, when compared to bromo products, may be due to partial polymerization of the alkynes catalyzed by boron trichloride.^{6b} Reactions involving boron tribromide are also faster than those using boron trichloride. This result is consistent with the fact that the haloboration of alkynes by boron tribromide is faster than haloborations utilizing boron trichloride.^{6,7}

Reactions involving aliphatic alkynes were also examined. However, only traces of the desired products were observed, presumably due to the rapid polymerization of the diene products. Aliphatic aldehydes are not suitable substrates for the reactions due to known enolization reactions.¹³ Interest-

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(12) Representative procedures and analytical data can be found in Supporting Information.

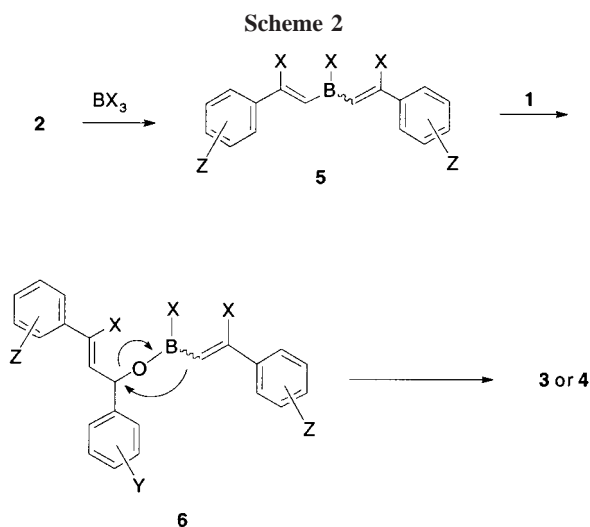
Table 2. Synthesis of (Z,Z)-1,3,5-Triaryl-1,5-dibromo-1,4-pentadienes

entry	Y	Z	time (h)	yield (%) ^{a,b}
1	4-F	H	4	91 (4a)
2	4-Cl	H	4	95 (4b)
3	4-Me	H	3	80 (4c)
4	2-Me	H	3	83 (4d)
5	4-NO ₂	H	10	80 (4e)
6	4-F	4-Me	4	80 (4f)
7	4-Br	4-Me	4	70 (4g)
8	4-F	4-Cl	10	83 (4h)
9	4-Br	4-Cl	8	74 (4i)
10	2-Me	4-Cl	6	89 (4j)

^a Isolated yields based on the starting aldehydes. ^b All products were characterized by elemental analyses and NMR spectroscopy.

ingly, reactions of nonenolizable aliphatic aldehydes such as trimethylacetaldehyde and tribromoacetaldehyde with arylacetylenes produced only allylic alcohol products.

Although a detailed mechanistic study has not yet been undertaken, the reaction most likely proceeds via the pathway outlined in Scheme 2. Haloboration of alkyne **2** would



generate **5** which would add to **1** in a Grignard-like fashion to form **6** by migration of the halovinyl group. Then, migration of the second halovinyl group would afford the final diene products. In control experiments in which BBr_3 and BCl_3 reactions were hydrolyzed prior to completion, the allylic alcohols expected from intermediate **6** were isolated from the product mixtures. In a separate experiment, 2 equiv

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of phenylacetylene were added to boron tribromide in CH_2Cl_2 to generate **5** ($X = Br, Z = H$) which was then treated with 4-chlorobenzaldehyde. The reaction generated the expected (Z,Z)-1,5-dibromo-1,4-diene (**4b**). However, the reaction is faster if boron tribromide is simply introduced to a mixture of phenylacetylene and 4-chlorobenzaldehyde in CH_2Cl_2 . At present, data is insufficient to determine whether the conversion of **6** to either **3** or **4** proceeds via concerted rearrangement or a S_N1 mechanism.¹⁴

All compounds were characterized by elemental analyses and NMR spectroscopy. The 1H and ^{13}C NMR spectra of 1,5-dichloro-1,4-diene derivatives (**3a–j**) displayed two sets of resonances for the vinyl groups, indicating that compounds (**3a–j**) are (E,Z)-dienes. In addition, a single crystal of compound 1,5-dichloro-3-(4-bromophenyl)-1,5-diphenyl-1,4-pentadiene (**3c**) was analyzed by X-ray crystallography.¹⁵ The X-ray molecular structure confirmed the NMR assignment. In contrast, the NMR spectra of each the 1,3,5-triaryl-1,5-dibromo-1,4-pentadiene derivatives (**4a–j**) showed only one set of resonance for the vinyl groups, indicating that these compounds are symmetrical (Z,Z)-dienes. The formation of (E,Z)-1,5-dichloro-1,4-pentadienes 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. Presumably, migration of the vinyl groups proceeds with retention of configuration. Similar results have been reported for haloboration of alkynes by boron trihalides.^{6b} 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.^{6b}

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

In summary, we have discovered an unusual dialkenylation of aryl aldehydes. The reaction is applicable to aryl aldehydes containing various functional groups but it is not suitable for aliphatic aldehydes. Efforts to elucidate the reaction mechanism and to utilize boron halides to synthesize enyne and diyne compounds are currently underway.

Acknowledgment. We wish to thank the U.S. Department of Energy and the Robert H. Cole Foundation for support of this research.

Supporting Information Available: Representative experimental procedures and analytical data for all compounds prepared. Details of the X-ray diffraction data and structure of compound **3c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) See Supporting Information.