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ARTICLE

Highly Novel Diastereoselective Synthesis of (*E*)-1-Aryl-1-alkenes

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ABSTRACT

A convenient, novel synthesis of (*E*)-1-phenyl-1-alkenes based on (*Z*)-1-bromo-1-alkenylboronate esters will be developed. α -Bromo-(*Z*)-1-alkenylboronate esters readily available from literature procedures will undergo a reaction with phenyllithium in tetrahydrofuran to provide the corresponding “ate” complexes. These “ate” complexes will then undergo intramolecular nucleophilic substitution reactions to provide the corresponding (*E*)-1-alkenylboronate esters containing a phenyl moiety which upon protonolysis with acetic acid will afford the corresponding (*E*)-1-phenyl-1-alkenes. All (*E*)-1-phenyl-1-alkenes were characterized by PMR and CMR spectral data successfully.

KEYWORDS

Diastereoselective synthesis, (*E*)-1-Aryl-1-alkenes, Boronate.

INTRODUCTION

The synthesis of (*E*)-1-alkenylboronate esters containing a phenyl group in high stereochemical purities is an important synthetic goal because these could be transformed into a variety of products. Because of the utility of (*E*)-1-phenyl-1-alkenes, it is advantageous to have an efficient and simple method of synthesizing these compounds. A previous study has reported the stereoselective synthesis of (*Z*)-1-bromo-1-alkenylboronate esters by hydroboration of 1-bromo-1-alkynes followed by addition of 1,3-propane diol [1]. The reaction of these (*Z*)-1-bromo-1-alkenylboronate esters with different nucleophiles, including Grignard reagents, hydrides and organolithium reagents, is well documented in literature [2-9]. The reaction of (*Z*)-1-bromo-1-alkenylboronate esters with a nucleophilic reagent such as phenyl lithium was not explored previously. Consequently, we undertook this study and revealed the results of our investigation.

EXPERIMENTAL

Reagents and solvents were of analytical grade and used without further purification. Melting points were recorded on a Mel-Temp melting point apparatus, in open capillaries and are uncorrected. The ¹H NMR (200 MHz) spectra were recorded on a Bruker AMX 400 MHz NMR spectrometer. The chemical shifts (δ ppm) and coupling constants (*J* Hz) are reported in the standard fashion.

Synthesis: The required starting compounds, 1-bromo-1-alkynes and (*Z*)-1-bromo-1-alkenylboronate esters, were synth-

esized using procedures previously established in literature [9]. Typical experimental procedure calls for the reaction of (*Z*)-1-bromo-1-hexenylboronate ester in ether with phenyl lithium at $-78\text{ }^{\circ}\text{C}$ in an inert atmosphere. The reaction was stirred for 1 h under these conditions. The reaction mixture was allowed to stir overnight at room temperature. After aqueous workup of the mixture, the resulting boronic acid was esterified with 1,3-propane diol. The solvents were then pumped off and the resulting product was isolated by distillation to provide the corresponding (*E*)-1-hexenylboronate ester containing the phenyl moiety in 78% yield. This was then protonolyzed with acetic acid under reflux for 4 h. After purification, the corresponding (*E*)-1-phenyl-1-hexene was isolated in 80% yield. Using this procedure, representative (*E*)-1-alkenylboronate esters containing the phenyl moiety were prepared and representative (*E*)-1-phenyl-1-alkenes were synthesized (Table-1).

E-Phenyl-1-hexene: IR (neat, ν_{max}): 1645, 1594, 964, 740 and 690. NMR (CDCl_3/TMS) δ ppm: 0.80-1.03 (distorted t, 3H), 1.16-1.53 (m, 4H), 2.00-2.33 (m, 2H), 5.83-6.10 (m, 2H) and 7.03-7.26 (m, 5H).

2-Methyl-(*E*)-3-octene: IR (neat, ν_{max}): 1655 and 967 cm^{-1} (C-C). NMR (CDCl_3/TMS) δ ppm: 0.83-1.03 (m, 9H), 1.16-1.53 (m, 4H), 5.83-2.46 (m, 3H) and 5.26-5.46 (m, 2H). In each of the compounds, it exhibited PMR peaks at aromatic region 7.03-87.26 (m, 5H) and 5.83-6.10 (olefinic region, m, 2H).

RESULTS AND DISCUSSION

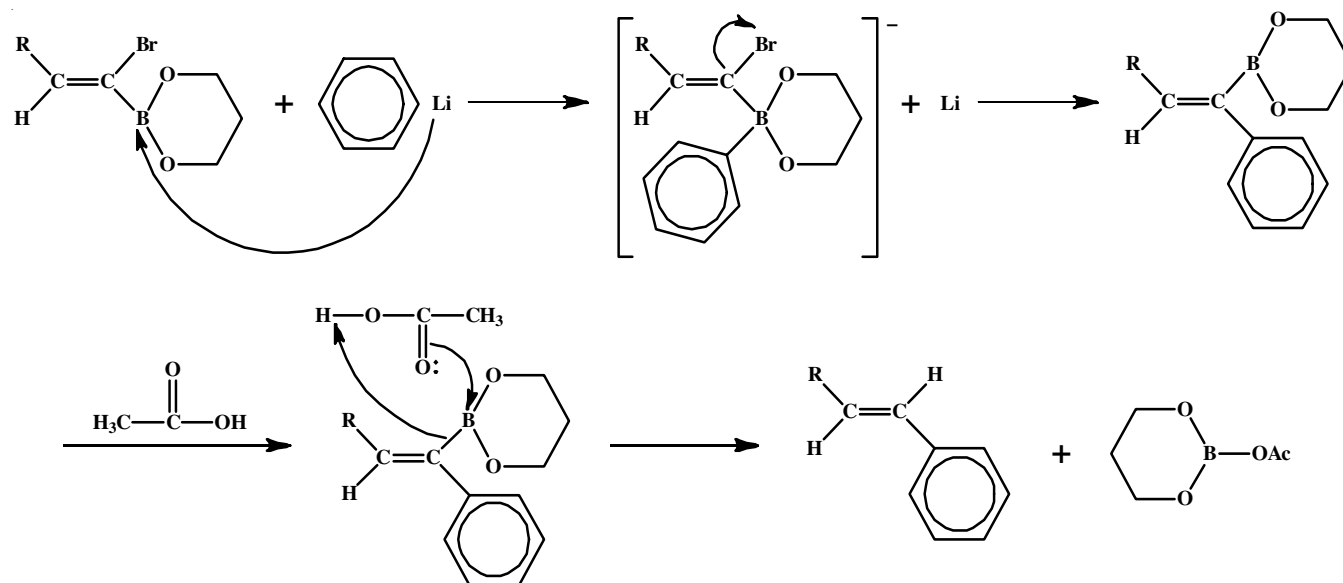
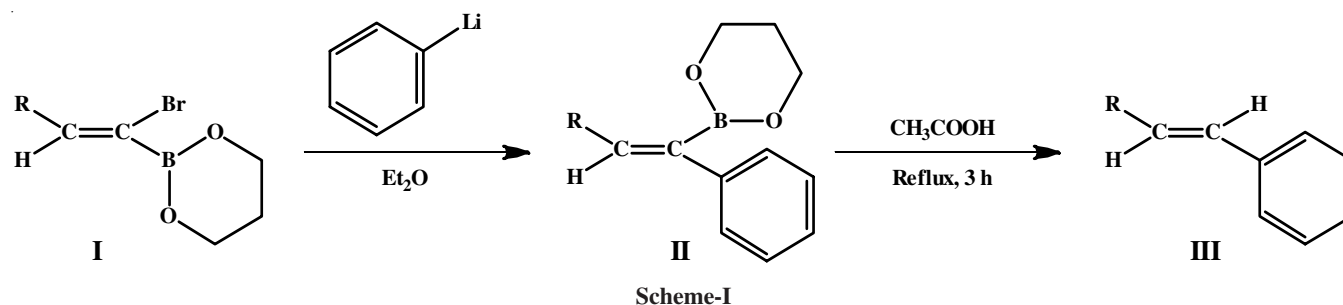
In this investigation, a new nucleophilic reagent, phenyl lithium in tetrahydrofuran is utilized to provide the corresponding tetracoordinated boron complexes. After workup followed by esterification with 1,3-propane diol, the corresponding (*E*)-1-alkenylboronate esters were isolated and then protonolyzed with acetic acid (**Scheme-I**). Thus, a general convenient synthesis of (*E*)-1-phenyl-1-alkenylboronate esters based on (*Z*)-1-bromo-1-alkenylboronate ester intermediates (Table-1) is described in the presence of acetic acid (Table-1).

TABLE-1
SYNTHESIS OF *E*-1-PHENYL-1-ALKENES (**Scheme-I**)^a

No.	R	II Yield (%) ^b	III Yield (%) ^c
1	<i>n</i> -C ₄ H ₉	84	68
2	<i>n</i> -C ₅ H ₁₁	82	72
3	<i>n</i> -C ₆ H ₁₃	87	75
4	<i>n</i> -(CH ₂) ₅ Cl	78	76
5	-C(CH ₃) ₃	76	82
6	-CH ₂ CH ₂ CH(CH ₃) ₂	83	74

^aAll the reactions were carried out on a 5 mmol scale. ^bIsolated yields based on I, ^cIsolated yields based on II.

The proposed mechanism for the oxidation of (*E*)-1-alkenylboronate ester containing the phenyl moiety is shown in **Scheme-II**.



Presumably, the starting compound, (*Z*)-1-bromo-1-alkenylboronate ester, could react with phenyl lithium and form an 'ate' complex. This complex would then undergo anionotropic rearrangement in which the phenyl moiety would migrate from boron to the adjacent alkenyl carbon, resulting in inversion of configuration. This would provide the (*E*)-trisubstituted boron intermediate containing the phenyl moiety, which would then be protonolyzed to provide the (*E*)-1-phenyl-1-alkenes. It is worth to observe that nucleophilic substitution reactions on *sp*² carbon are difficult to achieve. We are able to accomplish that with boron induced reaction. The boron intermediates (II) were isolated and characterized for the first time.

Conclusion

In summation, a novel synthetic method is developed for the synthesis of highly diastereoselective synthesis of (*E*)-1-alkenylboronate esters containing a phenyl moiety. Their structures were confirmed by protonolysis to (*E*)-1-Phenyl-1-Alkenes and by NMR spectral data.

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