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ARTICLE

Stereospecific Synthesis of Both (*E*)- and (*Z*)-1,3-Alkynes Based on Stereodefined Alkenylboronate Esters

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ABSTRACT

The stereodefined synthesis of 1,3-alkynes based on *in situ* generated stereodefined alkenylcopper reagents is presented. The hydroboration of alkynes with dibromoborane-methyl sulfide complex followed by treatment with trimethylene glycol provides stable (*E*)-1-alkenylboronate esters. These boronate esters readily undergo “ate” complexes with a hindered base such as potassium-*t*-butoxide. The transmetalation of the alkenyl group from boron to copper *via* the “ate” complexes retains the original stereochemistry defined from the starting alkenylboronate esters. The effect of representative bases on stereodefined alkenylboronate esters and subsequent reaction of these boronate esters in the transmetalation reaction with copper(I) bromide-methyl sulfide is investigated. The resulting stereodefined alkenylcopper species generated *in situ* readily couple with 1-bromo-1-alkynes to give the corresponding 1,3-alkynes with retention of stereochemistry. Since (*Z*)-1-alkenylboronate esters are easily accessible, both *cis* and *trans* isomeric 1,3-alkynes are synthesized.

KEYWORDS

Stereospecific synthesis, 1,3-Alkynes, Alkenylboronate esters.

INTRODUCTION

Many insect pheromones [1,2] contain a conjugated *cis*, *trans*-diene grouping. Because conjugated 1,3-enynes are readily converted to the corresponding conjugated *cis*, *trans*-dienes by a simple hydroboration-protonolysis sequence [3], the stereospecific synthesis of conjugated enynes is a highly desirable goal. Low yield procedures of several complexes have been described for the synthesis of conjugated enynes [4]. Some of these require the prior stereoselective synthesis of alkenyl halides [5]. Negishi and coworkers [6,7] developed a highly stereoselective synthesis of conjugated enynes and utilized the procedure for the synthesis of two insect pheromones. Suzuki and coworkers [8] synthesized the conjugated *trans*-enynes utilizing the palladium-catalyzed reaction of 1-alkenylboranes with 1-halo-1-alkynes.

Previously, the stereoselective syntheses of symmetrical conjugated dienes [9] and conjugated *trans*-enynes [10] from alkenyldialkylboranes *via* the reaction with sodium methoxide

(eqn. 4). Using the above procedure, the representative (*Z*)-1,3-alkenyne were prepared (Table-1).

TABLE-1
STEREOSPECIFIC SYNTHESIS OF BOTH (*E*)- AND (*Z*)-1,3-ALKENYNE BASED ON STEREODEFINED ALKENYLBORONATE ESTERS

No.	R and R' =	Yield (%) ^a
1	I, <i>n</i> -C ₄ H ₉	82
2	I, -C(CH ₃) ₃	78
3	I, (CH ₂) ₃ Cl	72
4	II, <i>n</i> -C ₄ H ₉	68
5	II, -C(CH ₃) ₃	72
6	II, -(CH ₂) ₃ Cl	73

^aAll of the reactions were carried out on a 10 mmol scale and the yields are isolated yields.

Conclusion

The stereodefined alkenylcopper intermediates generated *in situ* from (*E*)- and (*Z*)-1- alkenylboronate esters *via* transmetalation with copper(I) bromide-methyl sulfide complex in the presence of a hindered base such as potassium-*t*-butoxide readily undergo a coupling reaction with 1-bromo-1-alkynes to provide stereodefined 1,3-alkenyne. Using the present procedure, both (*E*)- and (*Z*)-1,3-alkenyne are prepared in high stereochemical purities. Since the both (*E*)- and (*Z*)-1-alkenyl-boronate esters are readily prepared and stored at 0 °C under nitrogen atmosphere for considerable length of time, the present procedure is useful in preparing stereodefined 1,3-alkenyne in high stereochemical purities.

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