Journal of Organometallic Chemistry, *464* (1994) C33–C34

JOM 24108PC

Preliminary Communication

Palladium catalyzed reactions of α-bromo-α,β-unsaturated carbonyl compounds with 1-(E)-alkenylboronic acids

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(Received June 3, 1993)

Abstract

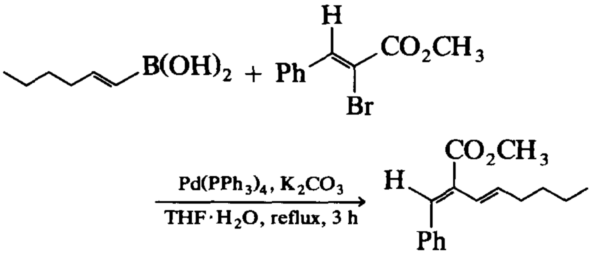
A new synthesis of functionalized 1,3-dienes is described based on the palladium catalyzed coupling reaction of 1-(E)-alkenylboronic acids with α-bromo-α,β-unsaturated carbonyl compounds.

Key words: Palladium; Alkenyl; Boronic acid; Catalysis

In a previous communication we reported the first example of the coupling reaction between 3-bromoacrylates and 1-(E)-alkenylboronic acids, catalyzed by complexes of palladium(0) [1]. The utility of this reaction was later demonstrated by its application to the synthesis of functionalized 2,4-dienes [2]. More recently, other groups have reported examples of this type of catalytic coupling using different reaction conditions [3,4]. For instance, a combination of palladium acetate and triphenylphosphine as catalyst, potassium carbonate or sodium bicarbonate as bases, and solvent systems such as ethanol–water, anhydrous ethanol or methanol, and dimethoxyethane were investigated in these reports.

In this communication we report the palladium catalyzed coupling reactions between *trans*-alkenylboronic acids and α-bromo-α,β-unsaturated carbonyl compounds. To our knowledge, this is the first example of the use of these functionalized vinylic bromides in this type of coupling reactions.

trans-1-Hexenylboronic acid (1.0 mmol, > 98% E) [5] was treated with methyl α-bromocinnamate (1.1 mmol > 95% Z) in the presence of tetrakis(triphenylphosphine)-palladium(0) (3–5% mol) and potassium carbonate (2.0 mmol), using a mixture of tetrahydrofuran-water (3 : 1, 4 ml) as solvent (eqn. (1)). The reaction mixture was refluxed until no further change was observed, as indicated by TLC analysis (3 h). After purification of the crude product by flash chromatography [6], the desired diene was obtained in 74% yield as an oily liquid which exhibited spectroscopic (IR and NMR) and analytical data (MS) in accord with the assigned structure. Retention of the double bond geometry was observed affording the stereoisomerically pure (> 90%) E,E-diene as indicated by ^{1}H NMR analysis. Application of this procedure to a series of representative α-bromo-α,β-unsaturated carbonyl compounds afforded the results shown in Table 1.



(1)

Retention of double bond geometry was observed in all cases, as estimated by ^{1}H NMR spectroscopy. The stereochemical purity of the products was better than 90%. With the exception of methyl 2-bromo-2-octadecenoate (Table 1, entry 3), the yields of products derived from *trans*-hexenylboronic acid were generally good. The lower yield obtained with the long chain ester can be attributed to an steric effect.

The reactions using *trans*-styrylboronic [5] acid gave lower yields of the expected dienes. This has been observed before by other authors in this type of coupling reactions [7]. Perhaps, the stabilizing effect of the β-phenyl ring in the alkenylboronic acid makes it less reactive towards the nucleophilic attack by the hydroxopalladium(II) complex in the transmetallation step of the proposed catalytic mechanism [7], thus lowering the yield of the corresponding product.

The reaction of *trans*-alkenyl boronic acids with α-bromo-α,β-unsaturated carbonyl compounds represents a convenient method for the preparation of stereodefined dienes in good yields. These functionalized organic compounds can be transformed into more complicated molecules. Currently we are exploring the

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0022-328X/94/$7.00
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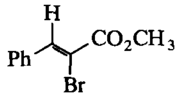
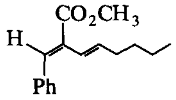
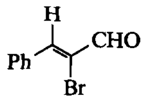
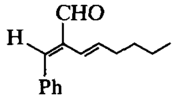
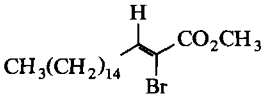
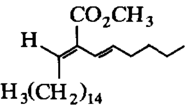
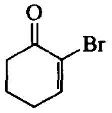
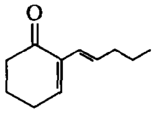
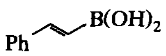
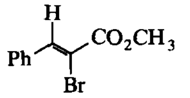
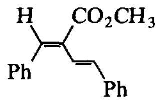
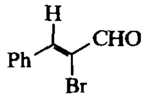
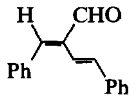
TABLE 1

Boronic acid [a]	Carbonyl compound [b]	Product [c]	Yield (%) [d]
			74
			68
			52
			60
			40
			50

[a] Isomeric purity > 98% as estimated by ^1H NMR.

[b] Isomeric purity > 95% as estimated by ^1H NMR.

[c] The stereochemical purity of products generally exceeded 90% as determined by GLC. All compounds exhibited spectral and analytical data in accord with the proposed structure.

[d] Yields of purified products.

possibility of using these dienes for the synthesis of biologically active natural products.

Acknowledgments

This research was supported by grants from the Venezuelan National Research Council (Consejo Venezolano de Investigaciones Científicas y Tecnológicas CONICIT No. S1-2091) and Simón Bolívar University (Decanato de Investigaciones No. DI-CB-33-91, Universidad Simón Bolívar).

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