Stereoselective Synthesis of *E*-Olefins by the Reaction of Alkenylboranes with Palladium Acetate

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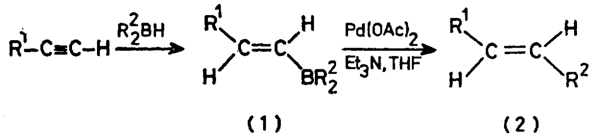
Summary Alkenyldialkylboranes (**1**) react smoothly at room temperature with $Pd(OAc)_2$–Et_3N to produce *E*-olefins (**2**) stereoselectively in moderate to high yields.

We recently reported that alkenylboranes can stereoselectively give reactive alkenylcopper compounds by transmetallation from B to Cu using methylcopper.[1] We have examined if the alkenyl group of the borane could be stereoselectively transferred to another transition metal.[2] We chose palladium as the transition metal, and investigated the reaction of alkenylboranes with various palladium salts.[3] Palladium acetate in tetrahydrofuran (THF) reacted with (**1**) to produce *E*-olefins (**2**) (Scheme 1). The results are summarized in the Table.



Scheme 1

Table. Reaction of (**1**) with $Pd(OAc)_2$–Et_3N to give the *E*-olefins (**2**) (Scheme 1).[a]

	R^1	R^2	% Yield of (**2**)[b]
a;	Ph	$CHMeCHMe_2$[c]	98(86)
b;	Ph	Cyclohexyl[c]	58
c;	Ph	2-Methylcyclohexyl[c]	(86)
d;	Bu^t	$CHMeCHMe_2$[d]	74(58)
e;	$Cl[CH_2]_3$	$CHMeCHMe_2$[d]	(61)

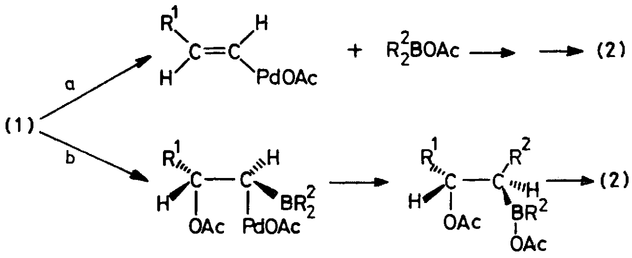
[a] All reactions were performed on a 1 mmol scale. Isolation was carried out on a 5 mmol scale. [b] Identified by i.r. and ^1H n.m.r. spectroscopy, elemental analysis, and/or comparison with the authentic materials. Yields by g.l.c., based on the acetylenes (isolated yields are in parentheses). [c] Catalytic amounts (7 mole %) of Et_3N were used. [d] Stoicheiometric amounts of Et_3N were used.

The stereochemistry of the product in each case was $> 96\%$ *E*, shown by g.l.c. and ^1H n.m.r. and i.r. spectroscopy. The reaction of alkenylboranes with other palladium salts, such as $PdCl_2$, $Pd(acac)_2$, Pd_2(dibenzylideneacetone)$_3$, and $Pd(PPh_3)_4$, did not give satisfactory results. All attempts to carry out the reaction catalytically with $Pd(OAc)_2$ were unsuccessful. The effect of triethylamine deserves comment. With the styryl compounds (**1a**—**c**), use of a catalytic amount of Et_3N gave highest yields, whereas for the alkyl compounds (**1d** and **e**) a stoicheiometric amount was required for satisfactory yields (*ca.* 30% yield in the presence of 0·05 mmol of Et_3N).

Zweifel has reported the stereoselective synthesis of *E*-olefins from alkenylboranes using BrCN.[4] Attempts to use this method with the styryl boranes (**1a**—**c**) failed; the reaction of (**1a**) with BrCN gave styrene instead of (**2a**). Consequently, the present reaction offers a noteworthy addition to the existing methodology and seems to involve an interesting problem in boron and palladium chemistry.

Two mechanisms may be considered (Scheme 2): (a) an intermolecular coupling process *via* the alkenyl palladium by analogy with transmetallation of B to Hg[2] and Pd,[3] and (b) an intramolecular process.

A mixture of (**1a**) and dicyclohexylacyloxyborane was treated with $Pd(OAc)_2$–Et_3N, but the cross coupling product (*β*-cyclohexylstyrene) was not obtained, thus eliminating mechanism (a). Therefore, the intramolecular mechanism is postulated; *cis* acetoxypalladation,[5] followed by migration with inversion,[6] and then *cis* *β*-elimination.[6]



SCHEME 2

The following procedure for the synthesis of (**2a**) from (**1a**) is representative. A solution of (**1a**) (5 mmol) in THF was added to a stirred mixture of $Pd(OAc)_2$ (5 mmol), Et_3N (0·35 mmol), and dry THF (50 ml) under N_2. The mixture was stirred overnight, and then filtered through an alumina column to remove precipitated Pd metal. Distillation gave (**2a**), 86%, b.p 71—72 °C at 1 mmHg.

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[2] For transmetallation from B to Hg, see R. C. Larock, S. K. Gupta, and H. C. Brown, *J. Amer. Chem. Soc.*, 1972, **94**, 4371.

[3] For transmetallation from B to Pd, see H. A. Dieck and R. F. Heck, *J. Org. Chem.*, 1975, **40**, 1083.

[4] G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *J. Amer. Chem. Soc.*, 1972, **94**, 6560.

[5] P. M. Henry, *Adv. Organometallic Chem.*, 1975, **13**, 363. Normally, acetoxypalladation in acetic acid proceeds in a *trans* fashion.

[6] E. Negishi, G. Lew, and T. Yoshida, *J. Org. Chem.*, 1974, **39**, 2321; G. L. Larson and A. Hernandex, *J. Organometallic Chem.*, 1975, **102**, 123.