Protonolysis of Alkenylboranes under Neutral Condition by Treatment with Catalytic Amounts of Palladium Diacetate

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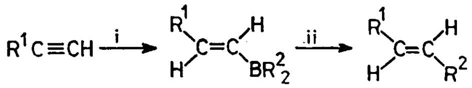
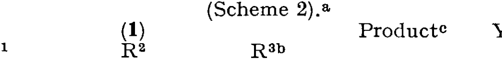
Summary Alkenyldialkylboranes (**1**) from internal alkynes undergo easy protonolysis by catalytic amounts of Pd$(OAc)_2$ to give the corresponding (*Z*)-olefins (**2**) in good yields.

PROTONOLYSIS of alkenylboranes is an important synthetic reaction in organoborane chemistry and is frequently employed in natural product synthesis.[1] Under acidic[2] or basic[3] conditions this reaction has several disadvantages, *e.g.* incompatibility with various acid- or base-sensitive functional groups and frequent need for high temperatures. We report a new, mild, neutral procedure using catalytic amounts of $Pd(OAc)_2$ at room temperature.



SCHEME 1. i, R^2_2BH; ii, $Pd(OAc)_2$, Et_3N, tetrahydrofuran.

We recently reported that treatment of alkenylboranes, prepared *via* hydroboration of terminal alkynes, with an equimolar amount of $Pd(OAc)_2$ in the presence of Et_3N produces (*E*)-olefins in good yields (Scheme 1).[4] In an attempt to broaden the scope of this procedure we examined the reaction of alkenylboranes derived from internal alkynes. To our surprise, the reaction took an entirely different course; stereoselective protonolysis occurred (Scheme 2). Detailed investigation revealed that the reaction proceeded successfully in the presence of catalytic amounts of $Pd(OAc)_2$ (5—10 mol %) and in the absence of Et_3N; the solvent itself acts a proton source. The results are summarized in the Table.



(1) (2)

SCHEME 2. i, R^3_2BH; ii, $Pd(OAc)_2$ (catalytic quantity).

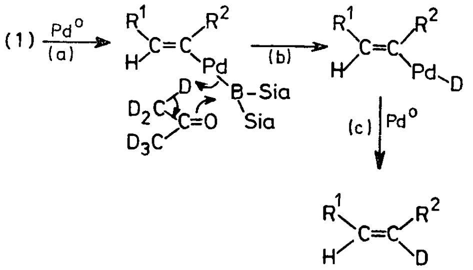
As apparent from the Table, the applicability of the new method appears general for the internal alkenes (**1**). Similar treatment of alkenylboranes derived from terminal alkynes gave unsatisfactory results, however. The reaction proceeded in each case with >99%, stereoselectivity, as shown by g.l.c. and ^1H n.m.r. and i.r. spectroscopy. Other alkenylboranes, such as dec-5-enyldicyclohexylborane and bis(dec-5-enyl)chloroborane, reacted similarly, the latter giving 1 mol. of alkene. The reaction also proceeded smoothly in acetone.

TABLE. Protonolysis of (**1**) with catalytic amounts of Pd $(OAc)_2$ (Scheme 2).[a]

	(**1**)		Product[c]	Yield[d]/%
R^1	R^2	R^{3b}		(Isoln.)
Bu^n	Bu^n	Sia	(Z)-Dec-5-ene	95
Bu^n	Bu^n	C_6H_{11}	,,	94
Hex^n	Et	Sia	(*Z*)-Dec-3-ene	(70)
Ph	Ph	Sia	*cis*-Stilbene	69[e]
Oct^n	$[CH_2]_7CO_2Me$	Sia	Methyl oleate	91
Bu^n	H	Sia	Hex-1-ene	30[f]

[a] See text for details of conditions. [b] Sia (siamyl) = $CHMeCHMe_2$; C_6H_{11} = cyclohexyl. [c] All products were identified by ^1H n.m.r. and i.r. spectroscopy and/or comparison with authentic materials. [d] By g.l.c. analysis; yields are based on the alkynes. [e] Starting material was recovered in 24% yield, owing to incomplete hydrobation. [f] The starting borane was recovered in 70% yield.

The preparation of (*Z*)-dec-3-ene is representative. Dec-3-yne (5 mmol) was hydroborated with bis-(1,2-dimethylpropyl)borane (5 mmol) in tetrahydrofuran (10 ml) at 0 °C. To this solution was added $Pd(OAc)_2$ (0·25 mmol), with rapid flushing with nitrogen, and the resulting mixture was stirred overnight at room temperature. Evaporation, followed by filtration through a column of alumina using light petroleum afforded (*Z*)-dec-3-ene (70%).



SCHEME 3. Sia = $CHMeCHMe_2$.

A mechanistic rationale which readily accounts for the observed catalytic process and deuterium labelling studies in $(CD_3)_2CO$ is shown in Scheme 3; (a) oxidative insertion of Pd^0† into the C–B bond takes place followed by (b) H-abstraction from the solvent, and (c) reductive elimination. In $(CD_3)_2CO$ 5-deuterio-(*Z*)-dec-5-ene was produced (isotopic enrichment 88%). In contrast to the alkenylboranes formed from terminal alkynes,[4] the migration of the alkyl group of (**1**) from boron to the α-carbon must presumably proceed quite sluggishly.

We thank the Ministry of Education and J.S.P.S. for support.

(*Received*, 16*th May* 1978; *Com.* 525.)

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† Active Pd^0 may be formed by the reaction of $Pd(OAc)_2$ with boranes in analogy with alanes, or by the addition of $Pd(OAc)_2$ to the double bond followed by Pd–H elimination.[4]

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