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(E)-(2-Bromoethenyl)dibromoborane. A New Precursor for (E)-1,2-Disubstituted Ethenes[1]

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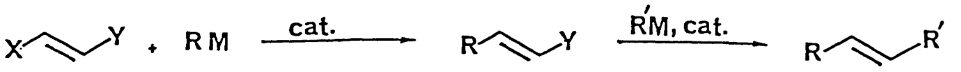
(E)-(2-Bromoethenyl)dibromoborane, prepared readily by the bromoboration of acetylene with tribromoborane, can be used as an effective precursor for the stereoselective synthesis of (E)-1,2-disubstituted ethenes.

Though 1,2-dihaloethenes[2,3] (**1a,b**) have been conveniently used as the precursors of 1,2-disubstituted ethenes by the sequential cross-coupling reactions with organometallic reagents catalyzed by transition metal complexes, the drawback is that for the application to the unsymmetrically substituted ethene synthesis, a large excess of reagent (**1**) is required in the first cross-coupling step and the isolation of mono-substituted intermediate (**3**) is crucial. 2-Bromo-1-phenylthioethene[4] (**2**), having different leaving groups, overcame this problem, but the use of organometallic reagents in both steps gave a limitation that only similar substituents could be introduced to both sides of the double bond (Eq. 1).



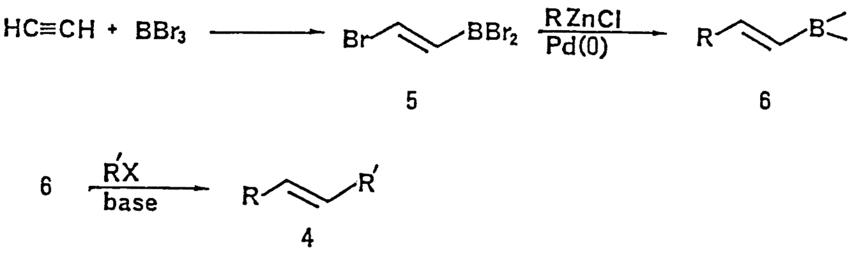
(1)

1a: X=Y=Cl
1b: X=Y=Br
2 : X=Br,Y=SPh

3

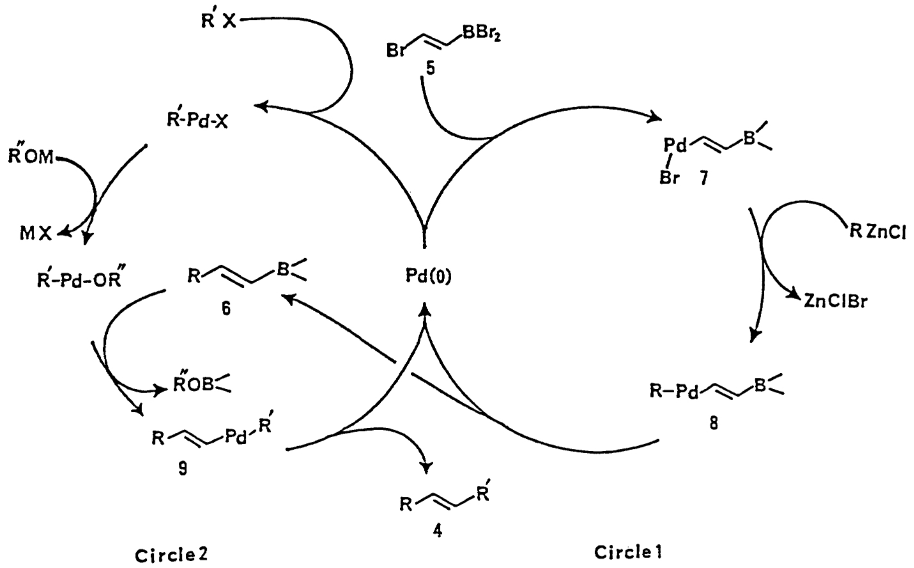
4

Recently we reported that (Z)-2-bromo-1-alkenylboranes, prepared by the bromoboration reaction of 1-alkynes, can be used for the stereoselective synthesis of trisubstituted alkenes by stepwise palladium catalyzed cross-coupling reactions.[5] In the course of that work, we have found that bromoboration of acetylene itself with tribromoborane proceeds through trans addition to give (E)-(2-bromoethenyl)dibromoborane (**5**)[6] stereoselectively, and that **5** is employed for the stereoselective synthesis of (E)-1,2-disubstituted ethenes (**4**) by the stepwise cross-coupling reactions. Substitution of the bromo moiety of **5** was carried out by the cross-coupling with an organozinc chloride catalyzed by a Pd complex, and the second substitution at the boron position was achieved by the addition of base and an organic halide (Eq. 2). Isolation of the intermediate (**6**) is not necessary and the use of a different kind of reagent in each step, an organozinc chloride and an organic halide, extends the applicability of this method for the disubstituted ethene synthesis. The versatility of this method is shown in Table 1.



(2)

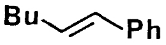
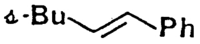
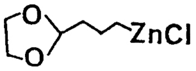
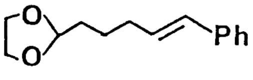
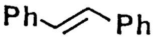
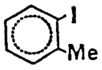
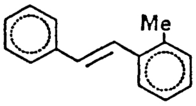
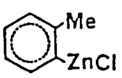
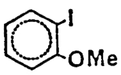
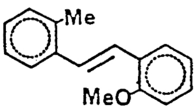
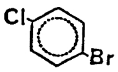
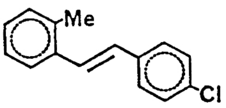
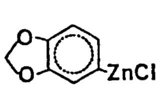
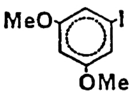
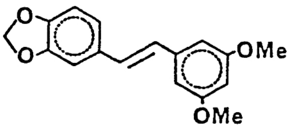
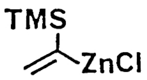
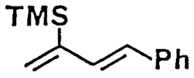
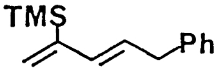
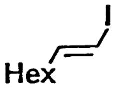
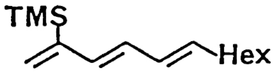
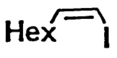
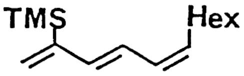
The following procedure for the preparation of (E)-1-phenyl-1-hexene is representative. To a stirred solution of (E)-(2-bromoethenyl)dibromoborane (0.277 g, 1.0 mmol)[7] in 3 mL of pentane was added $PdCl_2(PPh_3)_2$ (0.035 g, 0.05 mmol) at 0 °C under an argon atmosphere, followed by the introduction of a THF solution of butylzinc chloride (1.5 mmol).[8] After stirring at room temperature for 3 h, 10 mL of a 2 M aqueous solution of LiOH (20 mmol) and iodobenzene (0.204 g, 1.0 mmol) were added successively. The reaction mixture was heated under reflux for 15 h and then quenched with aqueous NH_4Cl. The purification with column chromatography (silica gel/hexane) after the extraction with hexane, gave the product in 70% yield.



Scheme 1.

The present stepwise cross-coupling reaction seems to proceed through the two catalytic cycles as shown in Scheme 1. In the absence of base (in Circle 1), the palladium complex oxidatively adds to the Br-C bond of **5** to form the intermediate (**7**). Transmetallation between **7** and an organozinc chloride gives

Table 1. Synthesis of (E)-1,2-Dialkylethenes[a)]

Entry	RZnCl	R'X	Product	Yield/%[b)]	I.P.[c)]
1	BuZnCl	PhI		(88)	98
2	s-BuZnCl	PhI		75[d)]	98
3		PhI		61	99
4	PhZnCl	PhI		82 (89)	98
5				63	98
6				74	99
7				67	98
8				63	98
9		PhI		(87)	99
10		$PhCH_2Cl$		75	99
11				63	95
12				68	93
13	HexC≡CZnCl	PhI		63	97

a) Unless otherwise noted, 5 mol% of $PdCl_2(PPh_3)_2$ was used as catalyst. b) Isolated yields based on (E)-(2-bromoethenyl)dibromoborane. In parentheses, GLPC yields. c) Isomeric purity determined by GLPC. d) $PdCl_2$(dppf) was used as catalyst.

the diorganopalladium (**8**), which undergoes reductive elimination to give (E)-1-alkenylborane (**6**), with the regeneration of palladium(0) complex. Under these conditions, the transmetallation from boron to palladium does not occur and **6** remains unchanged.[9] By the addition of an organic halide (R'X) and base (R"OM) in the second step of reaction (Circle 2), the organoorganoxopalladium obtained by the displacement of R'PdX with an alkoxide ion, reacts with **6** to give a diorganopalladium (**9**). The reductive elimination of **9** provides the expected disubstituted ethene (**4**), and regenerates palladium(0) complex. Further application of this reaction is now under investigation.

References

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7) (E)-(2-Bromoethenyl)dibromoborane (**5**) is prepared as follows: A 50-mL reaction flask, equipped with a magnetic stirring bar and septum inlet, was attached to a 3-L Teflon balloon. The balloon was filled with acetylene gas, and the flask was cooled to 0 °C. Tribromoborane (25 g, 0.1 mol) was introduced through septum inlet and the reaction mixture was stirred at room temperature until the acetylene gas in balloon was consumed (6-12 h). The crude product was distilled twice to give **5** as a clear colorless liquid in 70% yield. (bp 54-57 °C/13 mmHg). ^{1}H NMR ($CDCl_3$,TMS); $\delta = 7.07$ (d,J=15 Hz, 1H) and 7.96 (d, J=15 Hz, 1H) ppm.

8) BuZnCl was prepared by the addition of BuLi to a THF solution of $ZnCl_2$.

9) Previously we reported that an appropriate base such as NaOMe, NaOAc, or NaOH accelerates the transition metal catalyzed cross-coupling reaction of alkenylboranes with organic halides.[10]

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