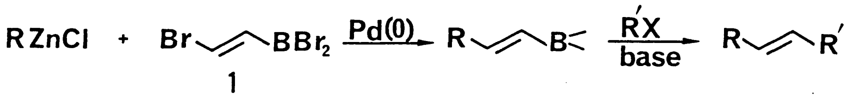
CHEMISTRY LETTERS, pp. 809-812, 1988.

(E)-(2-Bromoethenyl)diisopropoxyborane. A New Building Block for (E)-Olefins[1)]

Satoshi HYUGA, Naoko YAMASHINA, Shoji HARA, and Akira SUZUKI*
Department of Applied Chemistry, Faculty of Engineering,
Hokkaido University, Sapporo 060

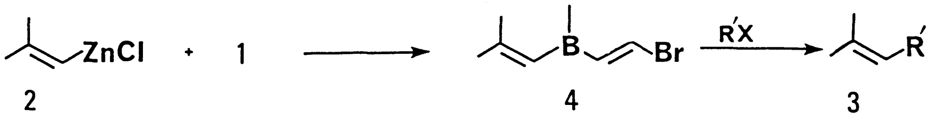
(E)-(2-Bromoethenyl)diisopropoxyborane is a useful precursor for the synthesis of (E)-olefins by the stepwise cross-coupling reaction with organozinc chlorides and then with organic halides in the presence of a base, both catalyzed by Pd complex.

Most recently we reported[2)] that the stepwise cross-coupling reaction of (E)-(2-bromoethenyl)dibromoborane (**1**) with an organozinc chloride and then with an organic halide is effectively catalyzed by a palladium complex to provide the corresponding (E)-olefin stereoselectively as shown in Eq. 1.



(1)

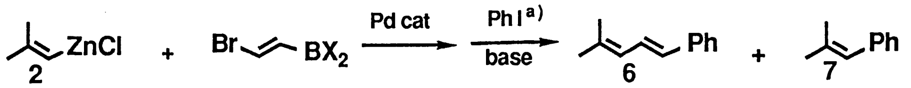
However, when alkenylzinc compounds such as **2** having no substituent at the α-carbon to zinc were employed, the desired products were obtained only in low yields, and the formation of monoene (**3**) was observed. Although **3** is a coupling product between **2** and an organic halide, R'X, such coupling cannot be expected under the present protic conditions, because **2** should be decomposed. Consequently, the possible mechanism of the formation of **3** is considered as follows. In the first step, **2** attacked non-catalytically boron part of **1** to form the alkenylborane (**4**), which then reacted with R'X to give **3** (Eq. 2).

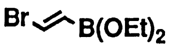
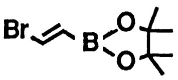
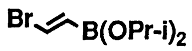


(2)

From this hypothesis, we attempted to employ (E)-(2-bromoethenyl)dialkoxyboranes (**5**),[3)] in place of **1**, to prevent the formation of the undesired by-product. Such results in the reaction with **2** are shown in Table 1. When dibromide **1** was used, the desired diene product (**6**) was obtained only in 7% yield together with the formation of monoene **7** in 84% yield. Among the dialkoxyboranes, the (E)-(2-bromoethenyl)diisopropoxyborane (**5c**) provided an excellent result, namely the expected diene (**6**) in 92% yield with a small amount (8%) of **7**. In the reaction with other organozinc compounds, the yield of the products could be also improved by the use of **5c** instead of **1**.

Table 1.



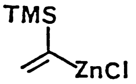
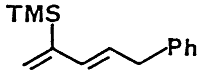
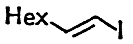
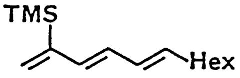
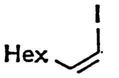
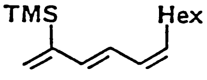
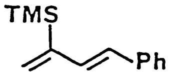
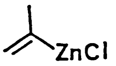
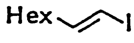
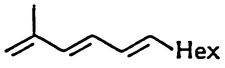
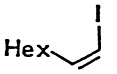
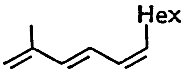
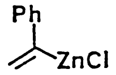
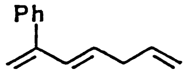
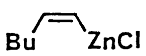
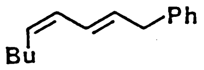
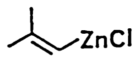
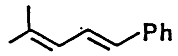
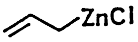
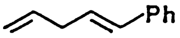
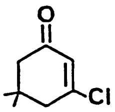
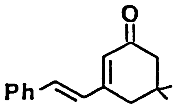
Borane	Mole. equiv. of **2** to borane	Yield of **6** / %b)	Yield of **7** / %b)
 (1)	2.0	7	84
 (5a)	1.5	54	14
 (5b)	1.5	78	13
 (5c)	1.5	77	7
	2.0	92	8

a) One equivalent of PhI to borane was used. b) GLPC yield based on borane.

The representative results for the preparation of (E)-olefins using (E)-(2-bromoethenyl)diisopropoxyborane (**5c**),[4) are summarized in Table 2. This reagent (**5c**) has advantages for the synthesis of (E)-olefins, compared with conventional precursors such as 1,2-dihaloethenes[5,6) and 1-bromo-2-phenylthioethene.[7) i) The unsymmetrically substituted olefins can be prepared readily without isolation of monoalkylated compound.[8) ii) The same palladium catalyst is employed in the both alkylation steps. iii) Relatively unstable conjugated trienes can be also prepared stereoselectively. (Entries 2,3,5, and 6 in Table 2).[9) iv) As the different type of reactants, an organozinc chloride and an organic halide, are used in each alkylation step, a variety of substituents can be introduced into the both side of (E)-double bond. v) Substituents with functional groups such as ketone, which are difficult to introduce as metallic reagents, can be readily introduced without any difficulty (Entry 16).

The following procedure for the preparation of (E)-5-phenyl-2-trimethylsilyl-1,3-pentadiene is representative. To a mixture of **5c** (235 mg, 1.0 mmol) and $(PPh_3)_2PdCl_2$ (35 mg, 0.05 mmol) in dry THF (3 mL) was added at 0 °C under an argon atmosphere, a THF solution of 1-(trimethylsilyl)vinylzinc chloride (1.5 mmol) prepared by treatment of the corresponding Grignard reagent (3.0 mL of 0.5 M solution, 1.5 mmol) with zinc chloride (1.6 mL of 1 M THF solution, 1.6 mmol). The reaction mixture was stirred at room temperature for 3 h. Aqueous lithium hydroxide (10 mL of 2 M solution, 20 mmol) and benzyl chloride (127 mg, 1.0

Table 2. Synthesis of (E)-Olefins[a)]

Entry	RZnCl	R'X[b)]	Product	Yield/%[c)]	I.P.%[d)]
1		$PhCH_2Cl$		89	99
2	″			79	96
3	″			79	96
4	″	PhI		81	97
5				65	97
6	″			74	97
7				62	99
8		$PhCH_2Cl$		76	96
9		PhI		(92)[e)]	99
10		PhI		65	97
11	HexC≡CZnCl	PhI		83[f)]	98
12	PhZnCl			(82)	99
13	″	PhI		(89)	97
14	BuZnCl	PhI		79	96
15	sec-BuZnCl	PhI		77	97
16	PhZnCl			85	99

---

a) Unless otherwise noted, 1.5 equiv. of RZnCl to 5c was used.
b) Equimolar amount of R'X with 5c was used. c) Isolated yield based on 5c and in parenthesis, GLPC yield. d) Isomeric purity determined by GLPC. e) Two equiv. of RZnCl was used. f) Three equiv. of RZnCl was used.

mmol) were added successively and the mixture was stirred under reflux for 15 h. After cooling to room temperature, the reaction mixture was quenched with aqueous solution of ammonium chloride. After extraction with hexane, the titled compound was isolated by column chromatography (silica gel/ hexane) in 89% yield (193 mg).

References

1) Organic synthesis using haloboration reactions. 14.

2) S. Hyuga, Y. Chiba, N. Yamashina, S. Hara, and A. Suzuki, Chem. Lett., 1987, 1757.

3) H. C. Brown, N. G. Bhat, and V. Somayaji, Organometallics 2, 1311 (1983).

4) (E)-(2-Bromoethenyl)diisopropoxyborane was prepared as follows. To 2-propanol (9.0 g, 150 mmol) in pentane (50 mL) was added at 0 °C (E)-(2-bromoethenyl)dibromoborane2) (13.8 g, 50 mmol) and the mixture was stirred at room temperature for 2 h. The upper layer of the reaction mixture was transferred into the distillation flask through a cannula. To the remained lower layer, pentane (10 mL) was added and the mixture was stirred vigorously. The upper layer was again transferred into the distillation flask and these operations were repeated twice. The combined pentane solution was concentrated under reduced pressure and then distilled to give 10.1 g of **5c** (86% yield). All operations were carried out under argon atmosphere. Diisopropoxyborane (**5c**) thus obtained can be stored in refrigerator under argon for a few months without any change: bp 73 °C/12 mmHg; ^{1}H NMR($CDCl_3$, TMS) δ=1.17 (d, J=6 Hz, 12H), 4.42 (m, J=6 Hz, 2H), 6.37 (d, J=15 Hz, 1H), 7.06 (d, J=15 Hz, 1H) ppm.

5) A. Carpita and R. Rossi, Tetrahedron Lett., 27, 4351 (1986).

6) S. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kondo, J. Org. Chem., 44, 2408 (1979); V. Ratovelomanana and G. Linstrumelle, Tetrahedron Lett., 22, 315 (1981); V. Ratovelomanana and G. Linstrumelle, ibid., 25, 6001 (1984); D. Guillerm and G. Linstrumelle, ibid., 27, 5857 (1986).

7) a) V. Fiandanese, G. Marchese, F. Naso, and L. Ronzini, J. Chem. Soc., Chem. Commun., 1982, 647; b) V. Fiandanese, G. Marchese, F. Naso, and L. Ronzini, J. Chem. Soc., Perkin Trans. 1, 1985, 1115; c) T. Ishiyama, N. Miyaura, and A. Suzuki, Chem. Lett., 1987, 25.

8) When unsymmetrically substituted olefins were prepared from dichloroethene, the use of dichloroethene in large excess to the Grignard reagent and isolation of the monoalkylated intermediates are crucial to prevent the product from contamination with symmetrical products.6)

9) Nickel catalysts are necessary for the substitution of a phenylthio group in 1-bromo-2-phenylthioethene with an alkyl group. In the synthesis of conjugated trienes by using 1-bromo-2-phenylthioethene, we found that such a nickel catalyst causes the isomerization of the products.7c)

(Received February 15, 1988)