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Preliminary communication

THE PALLADIUM-CATALYZED "HEAD-TO-TAIL" CROSS-COUPLING REACTION OF 1-ALKENYLBORANES WITH PHENYL OR 1-ALKENYL IODIDES. A NOVEL SYNTHESIS OF 2-PHENYL-1-ALKENES OR 2-ALKYL-1,3-ALKADIENES VIA ORGANOBORANES

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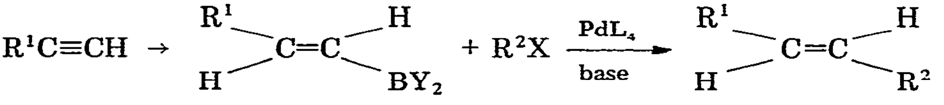
Summary

The reaction of phenyl or 1-alkenyl iodides with 1-alkenyl-1,3,2-benzodioxaboroles readily obtainable via the hydroboration of 1-alkynes, gives the corresponding "head-to-tail" cross-coupling products, 2-phenyl-1-alkenes or 2-alkyl-1,3-alkadienes, in good yields. The reaction is effectively catalyzed by catalytic amounts of palladium compounds in the presence of triethylamine.

Recently, we have reported palladium-catalyzed cross-coupling reactions of 1-alkenylboranes with organic halides such as 1-alkenyl [1], 1-alkynyl [1], aryl [2], allylic [3], and benzylic [3] halides as shown in eq. 1. These reactions are effectively catalyzed by tetrakis(triphenylphosphine)palladium in the presence of strong bases such as sodium hydroxide and alkoxides. In this communication we wish to report that a different type of reaction, 'head-to-tail' cross-coupling reaction, occurs between 1-alkenyl-1,3,2-benzodioxaboroles and phenyl or 1-alkenyl iodides in the presence of palladium compounds and triethylamine (eq. 2).



(1)

(I) (II)

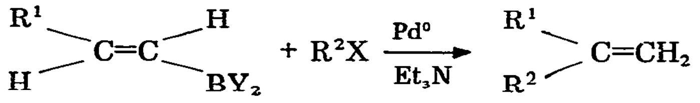
R^2 = 1-alkenyl, 1-alkynyl, aryl, allylic and benzylic
X = Br and I
Y_2 = disiamyl and 1,3,2-benzodioxaboryl

TABLE 1

PALLADIUM-CATALYZED CROSS-COUPLING REACTION OF 1-ALKENYL-1,3,2-BENZODIOXABOROLES WITH PHENYL OR 1-ALKENYL HALIDES [a]

Entry	1-Alkenylborane (I) R^1 =	R^2X	Catalyst	Base	Time (h)	Yield of products [b] II & III (%)	Distribution of II:III
1	n-Butyl	PhI	Pd black [c]	NaOEt	6	78	61:39
2	n-Butyl	PhI	Pd black [c]	NaOH	6	86	56:44
3	n-Butyl	PhI	Pd black [c]	NaOAc	6	19	21:79
4	n-Butyl	PhI	Pd black [c]	Et_3N	6	42	3:97
5	n-Butyl	PhI	Pd black [c]	Et_3N	20	94	4:96
6	n-Butyl	PhI	$Pd(PPh_3)_2$ [d]	Et_3N	20	66	8:92
7	n-Butyl	PhI	$Pd(PPh_3)_4$	Et_3N	20	54	10:90
8	n-Hexyl	PhI	Pd black [c]	Et_3N	24	94	4:96
9	Phenyl	PhI	Pd black [c]	Et_3N	24	58	36:64
10	n-Butyl	(*E*)-PhCH=CHI	Pd black [c]	Et_3N	24	61	6:94
11	n-Butyl	(*E*)-PhCH=CHBr	Pd black [c]	Et_3N	20	18	6:94
12	n-Butyl	(*E*)-HexCH=CHI	Pd black [c]	Et_3N	24	92	5:95

[a] The reaction was carried out in DMF at 80°C by using 3 mol% of the catalyst. The ratio of $Et_3N/R^2X = 5$ and NaOAc, NaOH, or $NaOEt/R^2X = 2$. [b] Based on R^2X employed and determined by GLC. [c] Prepared by reduction of $Pd(OAc)_2$ with diborane before use. [d] $Cl_2Pd(PPh_3)_2 + NaBH_4$ [6].



(2)

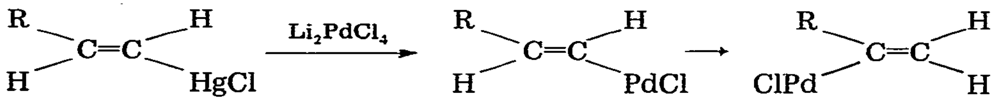
(I) (III)

R^2 = phenyl and 1-alkenyl, Y_2 = 1,3,2-benzodioxaboryl

To the palladium black prepared from $Pd(OAc)_2$ (0.0404 g, 0.18 mmol) and diborane was added a mixture of 20 ml of dimethylformamide, triethylamine (4.2 ml, 30 mmol), phenyl iodide (1.224 g, 6 mmol), and (*E*)-1-hexenyl-1,3,2-benzodioxaborole (1.33 g, 6.6 mmol) [4] under nitrogen atmosphere. After stirring the mixture at 80°C for 20 h, the residual alkenylborane was oxidized with 3 *M* NaOH and 30% H_2O_2 under the usual conditions. GLC analysis indicated the formation of 2-phenyl-1-hexene in a 91% yield, together with a small amount of 1-phenyl-1-hexene (<4%).

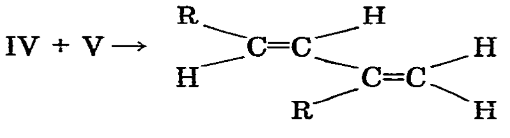
Although the use of palladium black and triethylamine was satisfactory for the present reaction, we additionally examined the use of other catalysts and bases, the results of which are summarized in Table 1. Other palladium compounds such as $Pd(PPh_3)_4$ [5] and $Pd(PPh_3)_2$ [6] were found to be also effective to the cross-coupling reaction (entries 6 and 7). However, the yields of III were slightly lower than those of the reaction employing palladium black. The product distribution of 'head-to-head' to 'head-to-tail' coupling (II : III) was markedly depended on the bases used (entries 1—4). The 'head-to-head' product (II) was preferentially produced under strongly basic conditions, as we reported previously [1—3].

The similar type of reaction to the present coupling was reported in the palladium-catalyzed 'head-to-tail' dimerization of vinylic mercurials, the mechanism of which was proposed to involve palladium hydride rearrangement of the vinylic palladium compound, as depicted in eqs. 3 and 4 [7].



(3)

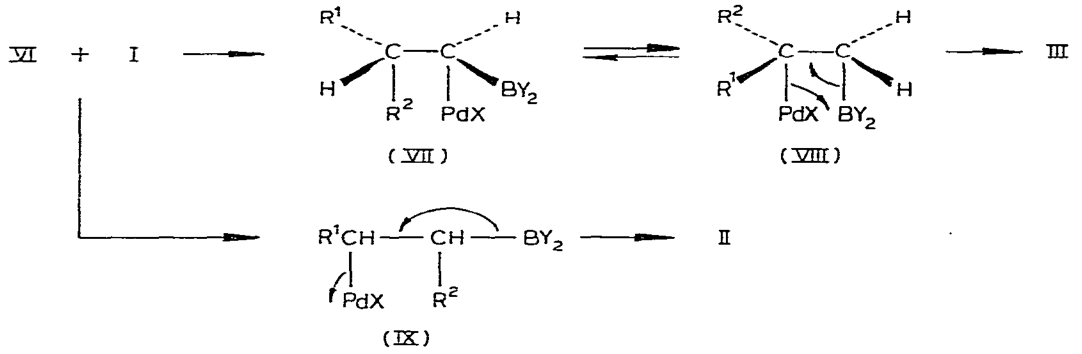
(IV) (V)



(4)

The present reaction is, however, inexplicable by such a mechanism. As an alternative, the following reaction pathways involving the addition and elimination sequence (eqs. 5—7) may be considered. Phenyl or 1-alkenyl groups in organopalladium compounds (VI) add mainly to the electron-deficient carbon of unsymmetric olefins [8] to form VII, which are readily isomerized to VIII [8]. Finally, the elimination of $XPdBY_2$ from VIII gives the corresponding 'head-to-tail' cross-coupling products (III). The minor 'head-to-head' products (II) are formed via eq. 7. On the other hand, palladium-catalyzed cross-coupling reactions of 1-alkenylboranes in the presence of strong bases such as

$$R^2X + Pd^0 \longrightarrow \underset{(VI)}{R^2PdX} \qquad (5)$$

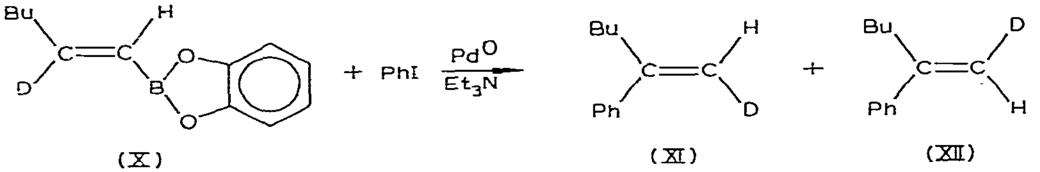


(6)

(7)

sodium hydroxide and ethoxide [1—3] have been confirmed most recently to proceed through a different reaction mechanism, which will be reported in another paper.

In order to infer the present coupling reaction mechanism, we carried out the following experiment by using D-labeled hexenylborane (X) which was prepared from 1,3,2-benzodioxaborole-d_1 and 1-hexyne (eq. 8). Under essentially the same reaction conditions, the expected products, XI and XII were obtained and the D-content was more than 96%, determined by ^{1}H NMR and mass spectral analyses. The ^{1}H NMR spectrum of the mixture showed two singlets at δ 5.03 and 5.22 ppm and their relative intensity was 75:25, indicating the ratio of XI:XII.



(8)

Although the scope and mechanistic details of the reaction remain to be further investigated, two types of regio-controlled cross-couplings, 'head-to-head' and 'head-to-tail', of 1-alkenylboranes with organic halides became available.

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