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Rhodium-catalyzed Dehydroborylation of Styrenes with Naphthalene-1,8-diaminatoborane [(dan)BH]: New Synthesis of Masked *β*-Borylstyrenes as New Phenylene–Vinylene Cross-coupling Modules

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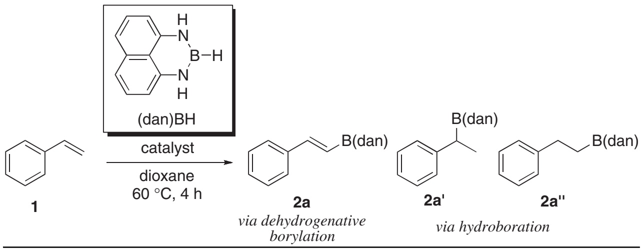
Styrene derivatives underwent dehydroborylation with naphthalene-1,8-diaminatoborane [(dan)BH] in the presence of a cationic rhodium complex, giving *β*-borylstyrene derivatives in good yields. Thus prepared *β*-borylstyrenes bearing a chlorine or B(pin) group on their aromatic rings were utilized for the synthesis of highly conjugated molecules through stepwise cross-coupling, taking advantage of the dan group as an effective protective group for a boronyl group.

Organoboronic acids play important roles in synthetic organic chemistry as versatile synthetic intermediates exhibiting balanced stability and reactivity.[1] Recent interest has focused on the control of their reactivity by easily attachable and/or removable groups on the boron atoms. For instance, reactivity improvement has been accomplished by introduction of trimethylolethane (2-hydroxymethyl-2-methyl-1,3-propanediol) through formation of its borate salts.[2] Introduction of an *ortho*-directing group derived from 2-(pyrazolyl)aniline onto the boron atom has enabled Ru-catalyzed *ortho*-silylation of arylboronic acids.[3] Increasing attention has also been paid to a protective group for a boronyl group [$B(OH)_2$], which provides reliable ways to highly functionalized organoboronic acids.[4,5] Through temporary protection of a boronyl group, iterative Suzuki–Miyaura coupling has been accomplished for the sequence-selective synthesis of oligoarene derivatives.[4–6]

We have been involved in the chemistry of naphthalene-1,8-diaminatoborane [(dan)BH], of which the dan group serves as a highly efficient protective group for a boronyl group.[4,6] The dan-protected organoboronic acids have been prepared conveniently by condensation of the corresponding organoboronic acids with 1,8-diaminonaphthalene. On the other hand, we have recently established a method for direct introduction of a B(dan) group into organic molecules by using B(dan)-based boron reagents.[7] The direct synthesis of dan-protected organoboronic acids seems highly beneficial in that one can escape handling organoboronic acids, which are sometimes unstable and difficult to purify. In this report, selective synthesis of masked (*E*)-*β*-styrylboronic acids via transition-metal-catalyzed dehydroborylation[8–10] with (dan)BH is described. Although we have recently reported the synthesis of masked (*E*)-*β*-styrylboronic acids as coupling modules for the synthesis of oligo(phenylene–vinylene)s via hydroboration of 1-arylalkynes,[7] the present reaction provides a more selective way to the modules from styrenes, which are much less expensive and more easily available than arylalkynes.

Dehydroborylation of styrene with (dan)BH was examined in the presence of transition-metal catalysts (Table 1). Iridium catalysts, which we found effective for hydroboration of alkynes with (dan)BH, afforded a mixture of hydroboration and dehydroborylation products (Entries 1 and 2). Although a ruthenium chloride complex resulted in low conversion of **1**, the desirable alkenylborane was obtained as a major product in the presence of a ruthenium carbonyl complex albeit in low yield (Entries 3 and 4). A neutral rhodium catalyst known as an effective catalyst for dehydroborylation with pinacolborane completely failed to catalyze the reaction with (dan)BH (Entry 5). Cationic rhodium catalyst was found to be the best catalyst for dehydroborylation with (dan)BH, resulting in high yield (99%), product selectivity (99%), and stereoselectivity (>99% *E*) (Entry 6). Use of PPh_3 as a ligand significantly lowered the catalyst activity (Entry 7). In these reactions, styrene also served as a receptor of eliminated hydrogen atoms, forming ethylbenzene as a by-product. The dehydroborylation product was easily separated from the hydroboration products as well as from ethylbenzene by silica gel column chromatography.

Table 1. Optimization of dehydroborylation of styrene with (dan)BH[a]

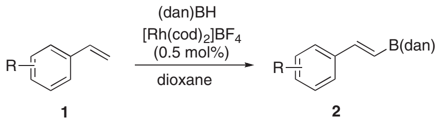


Entry	Catalyst	Ligand	Yield **2a**[b]/%	**2a**:**2a′**:**2a″**
1	$[IrCl(cod)]_2$	—	27	30:51:19
2	$[Ir(cod)_2]BF_4$	—	26	28:48:24
3	$[RuCl_2(p\text{-cymene})]_2$	—	6	6:8:86
4	$Ru_3(CO)_{12}$	—	44	82:0:18
5	$[RhCl(cod)]_2$	—	0	—
6	$[Rh(cod)_2]BF_4$	—	99 (91)	99[c]:0.6:0.7
7	$[Rh(cod)_2]BF_4$	PPh_3	5	5:86:9

[a]A mixture of **1a** (0.3 mmol), styrene (0.75 mmol), transition-metal complex (1.5 µmol, Ir, Ru, or Rh), and ligand (3.3 µmol) in dioxane was stirred at 60 °C for 4 h under a nitrogen atmosphere. [b]GC yield. Isolated yield is shown in the parentheses. [c]>99% *E*.

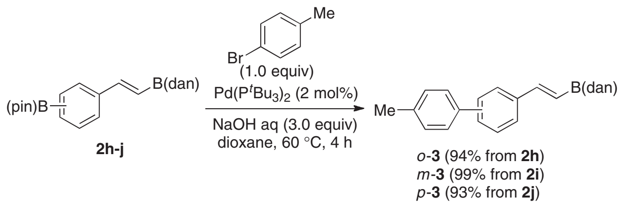
Under the optimized reaction conditions, dehydroborylation of several styrene derivatives were carried out (Table 2). Styrenes bearing *p*-substituents such as methyl, methoxy,

Table 2. Rhodium–catalyzed dehydrogenative borylation of styrene derivatives with (dan)BH[a]



Entry	R	Temp/°C	Time/h	Yield[b]/%
1	*p*-Me (**2b**)	60	4	93
2	*p*-MeO (**2c**)	60	4	94
3	*p*-F (**2d**)	60	4	93
4	*p*-Cl (**2e**)	60	4	83
5	*p*-CO$_2$Et (**2f**)	60	4	85
6	*o*-Me (**2g**)	60	4	82
7	*o*-B(pin) (**2h**)	80	24	59
8	*m*-B(pin) (**2i**)	60	4	67
9	*p*-B(pin) (**2j**)	60	24	84

[a] A mixture of **1** (0.3 mmol), styrene (0.75 mmol), [Rh(cod)$_2$]BF$_4$ (1.5 µmol) in dioxane was stirred under a nitrogen atmosphere. [b] Isolated yield for isomerically pure material.

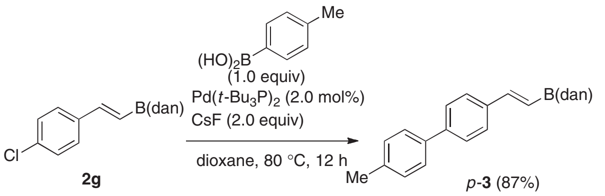


Scheme 1.

fluorine, chlorine, and ethoxycarbonyl groups afforded the corresponding β-styrylboranes selectively in high yields (Entries 1–5). It should be remarked that bromo-substituted styrenes failed to give desired borylation products. *ortho*-Substituted styrene also afforded the corresponding product in good yield (Entry 6). We were particularly interested in synthesizing phenylene–vinylene coupling modules that carry two differentiable coupling sites in the molecule for use in the synthesis of highly conjugated molecules. Dehydroborylation of styrenes bearing a B(pin) group at their *o*-, *m*-, and *p*-positions successfully afforded the corresponding bisborylstyrenes **2h**–**2j** (Entries 7–9).

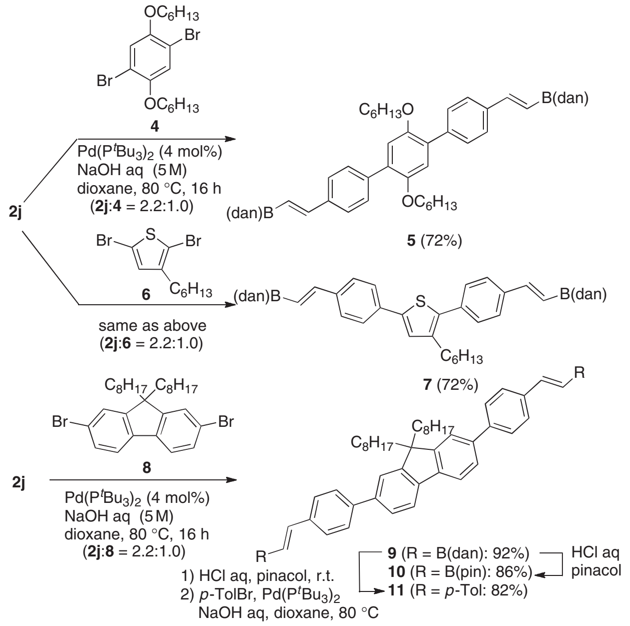
Modules **2h**–**2j** were cross-coupled with *p*-tolyl bromide (Scheme 1). In the presence of Pd(t-Bu$_3$P)$_2$ with aqueous NaOH as a base,[11] C–C bond formation took place exclusively at the B(pin) group on the aromatic ring, leaving the B(dan) group at the alkenyl carbon atom intact.

Coupling module **2g** bearing a chlorine group on the aromatic ring successfully gave the alkenylborane product *p*-**3** in a reaction with tolylboronic acid (eq 1).



(1)

Phenylene–vinylene coupling module **2j** was applicable to the synthesis of diborylated building blocks for the synthesis of highly conjugated molecules **5**, **7**, and **9** bearing benzene, thiophene, and fluorene rings as the cores of the structures (Scheme 2). In the case of product **9**, the dan protection was replaced with a pin group by treatment with aqueous acid in the presence of pinacol. It should be remarked that the standard unmasking procedure using aqueous acids resulted in minor, but significant formation of protodeboration by-products. Interestingly, the B(pin) derivative **10** was fluorescent ($\lambda_{ex} = 347$ nm; $\lambda_{em} = 424$ nm, $\Phi = 0.67$), whereas the corresponding B(dan) derivative **9** showed much weaker fluorescence ($\lambda_{ex} = 357$ nm; $\lambda_{em} = 392$, 410 nm, $\Phi = 0.29$). Cross-coupling of **10** with tolyl bromide proceeded in good yield to give **11**.[12]



Scheme 2.

In summary, dehydroborylation of styrene derivatives with (dan)BH has been efficiently catalyzed by a cationic rhodium(I) complex, giving β-borylstyrene derivatives in good yields. The β-borylstyrene derivatives have served as useful building blocks for the synthesis of highly conjugated molecules through stepwise Suzuki–Miyaura coupling.

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