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NEW CONVENIENT APPROACH TO THE PREPARATION OF (Z)-ALLYLIC BORONATES VIA CATALYTIC 1,4-HYDROBORATION OF 1,3-DIENES WITH CATECHOLBORANE

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Summary: Hydroboration of 1,3-butadiene, isoprene, myrcene, 2,3-dimethyl-1,3-butadiene, and 1,3-cyclohexadiene with catecholborane (1,3,2-benzodioxaborole) in the presence of $Pd(PPh_3)_4$ or $Rh_4(CO)_{12}$ catalysts proceeds smoothly to provide 2-[(Z)-2-alkyl-2-butenyl]-1,3,2-benzodioxaboroles in very high regio- and stereoselectivity.

Much attention is being denoted to the reactions of allylic boron reagents with carbonyl compounds for the synthesis of homoallylic alchols in high diastereoselectivity[1] or enantioselectivity.[1,2] (E)- and (Z)-Crotylboronates[1,2] were prepared by the method originally reported by Schlosser[3] from (E)- and (Z)-crotylpotassiums and haloboron compounds, The procedure, in spite of the multi-step process, has an advantage that the both (E)- and (Z)-crotylborates are obtained over 95% of isomeric purity. An alternative route[4] to further subsitituted allylic boronates from halomethylborates and (E)- or (Z)-alkenyllithiums was also reported. On the other hand, it is known that selective monohydroboration of some dienes, such as 1,3-cyclohexadiene[5] and 3-methyl-1,2-butadiene[6], affords allylic boranes. Although the hydroboration approach is simple and convenient, the method is not applicable to usual 1,3-dienes because the hydroboration mainly occurs at the terminal double bond to give homoallylic boranes. In this paper, we wish to report a catalytic 1,4-hydroboration of 1,3-dienes with catecholborane in the presence of $Pd(PPh_3)_4$ or $Rh_4(CO)_{12}$ to afford (Z)-allylic boronates with high isomeric purity, as shown in Eqs. 1 and 2.

The optimum conditions for carrying out the reaction of Eq. 1 were studied by using isoprene in the presence of various catalysts. The results are summarized in Table 1. Noth[7] have previously reported that alkenes or alkynes can be hydroborated with catecholborane in the presence of a catalytic amount of $ClRh(PPh_3)_3$ under extreamly mild conditions. Although we have extended the reaction for the hydroboration of 1,3-dienes, unsatisfactory results have been obtained. For example, the reaction of isoprene with catecholborane in benzene in the presence of 1 mole % of $ClRh(PPh_3)_3$ for 16 h at room

Table 1. Effects of Reaction Conditions for Catalytic Hydroboration of Isoprene (Eq. 1)[a].

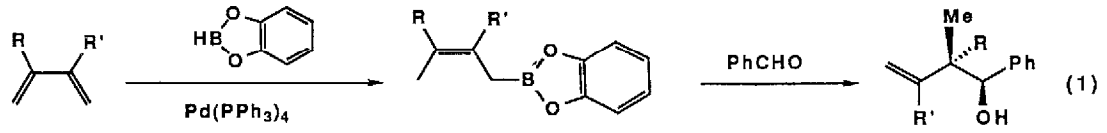
entry	catalyst	solvent	Yield (%) of **2b**[b]
1	$Pd(PPh_3)_4$	benzene	89
2	$Pd(PPh_3)_4$	THF	77
3	$PdCl_2(PPh_3)_2$	benzene	81
4	$Pd(OAc)_2$	benzene	24
5	$RhCl(PPh_3)_3$	benzene	2
6	$RhCl(CO)(PPh_3)_2$	benzene	19

[a]To a solution of isoprene (1.1 mmol) and catalyst (1.5 mole %) in 2 ml of a solvent was added neat catecholborane (1 mmol), and the mixture was stirred for 16 h at room temperature. Then, benzaldehyde (1.1 mmol) was added at 0 °C and the stirring was continued for 3 h at room temperature.
[b]GLC yields based on catecholborane.

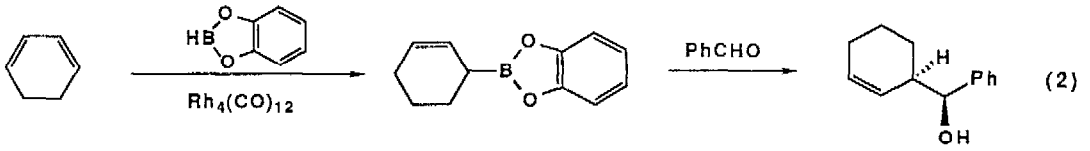
temperature, followed by quenching the allylic boronate (**1b**) with benzaldehyde gives homoallylic alchol (**2b**) in only a 2 % yield. It is known[8]that certain olefins such as ethylene and 1,3-butadiene are especially good ligands which, therefore appear to be inactive for hydrogenation by the Wilkinson catalyst. The best yield of **2b**[9] is obtained by using 1.5 mole % of $Pd(PPh_3)_4$ in benzene (entry 1). The conditions also give good results for 1,3-butadiene, myrcene, and 2,3-dimethyl-1,3-butadiene (Eq. 1). After quenching with benzaldehyde, the corresponding erythro alchols are obtained in high yields (**2a**,[10] 81 %; **2c**,[11] 77 %; **2d**, 81 %) and high diastereoselectivity over 99 %.

2-[(Z)-2-Methyl-2-butenyl]-1,3,2-benzodioxaborole (**1b**)[12] is readily isolated from the reaction mixture by distillation in a yield of 90 %. The ^{13}C NMR spectrum indicates that the reaction proceeds extreamly regio- and stereoselectively to afford (Z)-allylic boronates as a sole product. 1,3-Butadiene give 2-[(Z)-crotyl]-1,3,2-benzodioxaborole (**1a**) in a yield of 87 %, with almost 100 % pure (Z)-cofiguration, established by comparison of the ^{13}C NMR spectra of **1a**[13] and (E)-isomer.[14] Additionally, the erythro selectivity in the addition to benzaldehyde (>99 % by ^1H NMR) supports the (Z)-cnfiguration of **1.**

Although the palladium-catalyzed hydroboration proceeds nicely only with 1,3-butadiene derivatives



1a : R=H, R'=H — **2a** 81%
1b : R=H, R'=Me — **2b** 89%
1c : R=H, R'=$CH_2CH_2CH{=}C(CH_3)_2$ — **2c** 77%
1d : R=Me, R'=Me — **2d** 81%

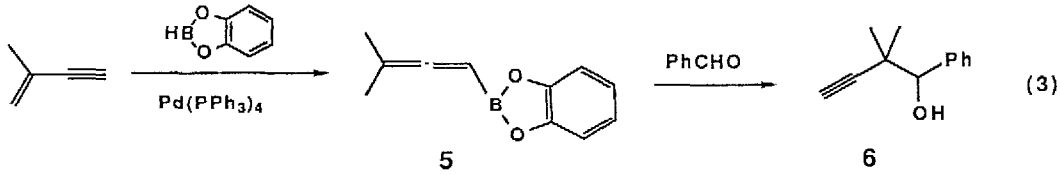


(2)

3 4 92%

subsitituted at 2- and 3-carbon, the hydroboration of 1,3-pentadiene and cyclic dienes is sluggish, affording less than 10% of homoallylic alchols under such conditions. In contrast, we have found that the hydroboration of cyclic 1,3-dienes takes place readily in the presence of Rh-catalysts. Among the catalysts it has been found that $Rh_4(CO)_{12}$ is most active for the hydroboration of 1,3-cyclohexadiene to give **4** in a yield of 92% after the treatment with benzaldehyde (Eq. 2).

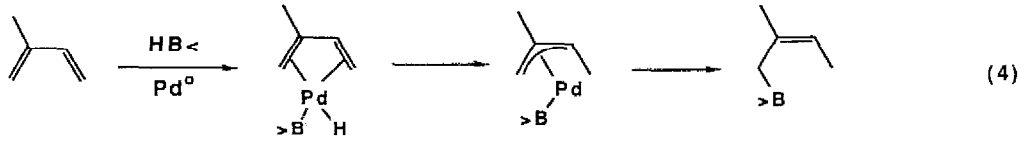
The related hydroboration of conjugated enyne illustrated in Eq. 3 gives an allenic boronate (**5**), followed by quenching with benzaldehyde at 60 °C for 2 h to afford **6** in a yield of 57%.



(3)

5 6

It should be noted that the feature of the reaction quite resembles that of platinum or palladium catalyzed hydrosilylation[15] of dienes. The formation of (Z)-allylic boronates can be explained by the similar mechanism[15c] reported by Ojima. The present results imply that the reaction involves an extremely regioselective hydride transfer from an oxidative adduct[7] obtained from Pd(0) and catecholborane to the coordinated 1,3-diene to produce the π-allylic boronylpalladium complex. Reductive elimination then give (Z)-allylic boronate as shown in Eq. 4.



(4)

The experimental procedure for the synthesis of 2-[(Z)-crotyl]-1,3,2-benzodioxaborole is representative. In a dry 100 mL-flask equipped with a magnetic stirring bar and three-way stopcock was placed $Pd(PPh_3)_4$ (0.145g, 0.125 mmol), and flushed with nitrogen. Anhydrous benzene (40 mL) was added. Then, 700 mL (ca. 30 mmol) of gaseous butadiene was bubbled slowly into the vigorously stirred solution through the septum inlet by means of a hypodermic syringe. 1,3,2-Benzodioxaborole (catecholborane) (3.25 mL, 26 mmol) freshly distilled was added slowly over 15 min at room temperature (exothermic!). The stopcock was closed, and the resulting mixture was stirred for 16 h at room temperature. Distillation in vacuo gave 3.93 g (87 %) of 2-[(Z)-crotyl]-1,3,2-benzodioxaborole[13] as a clear oil, bp 62-64 °C / 0.22 mmHg.

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9) **2b**; ^{1}H NMR($CDCl_3$) δ= 1.00 (d, 3H, J=7.0Hz), 1.73 (m, 3H), 1.89 (broad s, 1H), 2.49 (dq, 1H, J=5.7 and 6.6 Hz), 2.65-4.90 (m, 3H), 7.3 (s, 5H). The methyl protons for the corresponding threo isomer[16] at 0.78 (d, 3H, J=7.0Hz) and 1.78 (m, 3H).

10) **2a**; The assignment of configuration and isomeric purity were determined by the ^{1}H NMR[1a] data.

11) **2c**; ^{1}H NMR($CDCl_3$) δ= 0.97 (d, 3H, J=6.8Hz), 1.59 (s, 1H), 1.60 (s, 3H), 1.90 (d, 1H, J=2.2Hz), 1.95-2.20 (m, 4H), 2.49 (dq, 1H, J=4.8 and 4.2Hz), 4.7 (dd, 1H, 2.2 and 4.7Hz), 4.91 (s, 2H), 5.06 (broad s, 1H), 7.1-7.4 (m, 5H). The corresponding threo isomer[16] showed a doublet of methyl protons at 0.81 (d, 3H, J=7.0Hz).

12) **1b**; Bp 58°C/0.3 mmHg; ^{13}C NMR 13.71, 25.64, 112.37, 119.13, 122.57, 131.17, 148.29.

13) **1a**; Bp 62-64 °C/0.22mmHg; ^{13}C NMR(CDCl3) 12.68, 112.31, 122.56, 123.34, 125.16, 148.18.

14) 2-[(E)-Crotyl]-1,3,2-benzodioxaborole (E/Z=7:3) was prepared by the following procedure. To a solution of tricrotylborane (E/Z=9/1) (25 mmol) in THF (15 ml) was added a solution of catechol (25 mmol) in THF (10 ml) at room temperature. After refluxing for 2 h, (E)-crotylborate was obtained by distillation in a yield of 65 %, bp 63 °C/0.1mmHg; ^{13}C NMR 18.09, 112.32, 122.57, 124.23, 126.89, 148.16.

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