Synthesis of Functionalized Allylsilicone Compounds *via* Rhodium-Catalyzed Conjugate Addition of (*E*)- or (*Z*)-[3-Trimethylsilyl-1-propenyl]boronic Acids to Enones

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Received

Abstract: The rhodium-catalyzed conjugate addition of (*E*)-$Me_3SiCH_2CH=CHB(O^iPr)_2$ or (*Z*)-$Me_3SiCH_2(C_4H_9)C=CHB(O^iPr)_2$ to enones provided a novel method for the synthesis of allylsilicone compounds possessing a carbonyl group in the same molecule, which are versatile intermediates for intramolecular allylsilylation, giving cyclobutanols on treatment with Bu_4NF.

Key words: allylsilicone, alkenylboronic acid, rhodium catalyst, conjugate addition, cyclobutanol

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We recently reported that various rhodium(I) complexes catalyze addition reactions of organoboronic acids. The conjugate 1,4-addition[1] of aryl- and 1-alkenylboronic acids to α,β-unsaturated ketones, esters, or amides and 1,2-addition[2] to aldehydes or imines proceed smoothly in the presence of an Rh(acac)/phosphine complex. The protocol was recently extended to arylation of unactivated alkenes such as norbornene and vinylarenes[3] and to asymmetric conjugate additions[4] to α,β-unsaturated carbonyl compounds by using a rhodium(I)-binap complex. Among them, the reactions of arylboronic acids have been studied extensively, but little attention has been paid the reactions of 1-alkenylboronic acids or esters. Here, we report a rhodium-catalyzed conjugate addition of (3-trimethylsilyl-1-propenyl)boronates (**2** and **3**) to enones for the synthesis of functionalized allylsilanes having a carbonyl group in the same molecule, which are versatile intermediates for intramolecular allylsilylation (Scheme 1).

<<Scheme 1>>

Two 1-alkenylboronates (**2** and **3**) were synthesized by the reported procedure for the synthesis of 1-alkenylboronates *via* a haloboration-coupling sequence.[5] Addition of BBr_3 to acetylene to yield (*E*)-$CH(Br)=CHB(O^iPr)_2$ was followed by coupling with Me_3SiCH_2ZnCl (2 equivalents) in the presence of $PdCl_2(PPh_3)_2$ (3 mol%). This two-step procedure gave **2** in a yield of 60%. An analogous reaction with 1-hexyne afforded the (*Z*)-isomer **3** in 51% yield. Both reactions afforded the allylsilane derivatives of boronic esters with complete retention of the configuration of the double bond.

These two boronates were then subjected to rhodium-catalyzed 1,4-addition to enones. However, the catalyst effective for the related conjugate addition of arylboronic acids, (Rh(acac)(coe)-dppp or dppb in an aqueous dioxane,[1] resulted in low yields in the addition of **2** to 4-phenyl-3-buten-2-one. Phosphine-free complexes such as $[RhCl(cod)]_2$ were finally found to be excellent catalysts at 100 °C in aqueous methanol or in a single aqueous medium. Coupling selectively occurred at the C-B

bond, and the C-Si bond remained intact during the reaction. Representative results are summarized in Table 1.

<<Table 1>>

Addition of **2** or **3** to the representative enones proceeded smoothly at 100 °C in the presence of $[RhCl(cod)]_2$ (1.5 mol%) in aqueous methanol. High isolated yields often exceeding 90% were easily achieved for the representative α,β-unsaturated ketones (entries 1-4, 6-13). Although the corresponding aldehydes resulted in significantly low yields with several byproducts, $[RhOH(cod)]_2$[1d] was found to be a better catalyst to provide **4e** (43%) (entry 5). The stepwise addition to dibenzalacetone afforded a double-addition product (**4h** and **5e**), depending upon the stoichiometry of **2** or **3** (entries 8 and 13). (*E*)- and (*Z*)-configurations of **2** and **3** were completely retained.

Allylsilanes thus synthesized (**4**, **5**) are versatile intermediates for intramolecular allylsilylation, as was previously demonstrated in five- or six-membered cyclization.[6,7] Lewis acids such as $TiCl_4$ and BF_3, and F-bases such as tetrabutylammonium fluoride (TBAF) and CsF have been used for cyclization. Although the treatment of **4** or **5** with BF_3 or $TiCl_4$ failed to yield any cyclization products, it was very interesting that TBAF[8] selectively provided cyclobutanols (**6**) as the sole product at a temperature lower than 0 °C. On the other hand, six-membered cyclization to **7** was predominat at room temperature (r.t. for 1 h, 34% for **4d**). Thus, the reaction provided a kinetic product **6** at a temperature lower than 0°C, while the reversibility of TBAF-induced allylsilylation[9] led to cyclohexanol (**7**) at higher temperature. The stereochemistry established by NOESY demonstrated the selective formation of **6** for (*E*)-allylsilanes (**4**).

<<Scheme 2>>

Typical procedures. The synthesis of 2-ethenyl-1-methyl-3-phenylcyclobutanol (**6d**) is representative. A flask charged with $[RhCl(cod)]_2$ (0.015 mmol, 3 mol%) was flashed with argon. Methanol (3 ml), water (1 ml), 4-phenyl-3-buten-2-one (1 mmol), and **2** (2 mmol) were successively added. The resulting mixture was then stirred at 100 °C for 20 h. Chromatography over silica gel with hexane/ether (9/1) gave 7-trimethylsilyl-4-phenyl-5-hepten-2-one (**4d**) in 84% yield. To a solution of **4d** (0.5 mmol) in THF (10 ml) was added a solution of Bu_4NF in THF (Aldrich; 1.0 M, 0.75 mmol) at 0 °C. After being stirred for 1 h, the product was extracted with ether, washed with brine, and dried over $MgSO_4$. Chromatography over silica gel with hexane/ether (9/1) afforded **6a** in 79%. IR (neat) 3350 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 3H), 2.06 - 2.13 (m, 1H), 2.27 (bs, 1H), 2.39 (dd, *J* = 7.05, 11.0 Hz, 1H), 2.86 - 2.93 (m, 2H), 5.10 (d, *J* = 16.8 Hz, 1H), 5.10 (d, *J* = 11.5 Hz, 1H), 5.92 (ddd, *J* = 6.7, 11.5, 16.1 Hz,

1H), 7.18 - 7.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 135.9, 128.3, 126.6, 126.1, 116.7, 72.3, 59.7, 42.7, 45.5, 23.0; MS (EI): *m/z* 188(M^+, 13), 171(6), 147(8), 130(100), 115(8), 91(17), 73(10), 53(10), 43(28); HRMS calcd for $C_{13}H_{16}O$ 188.1201, found 188.1201.

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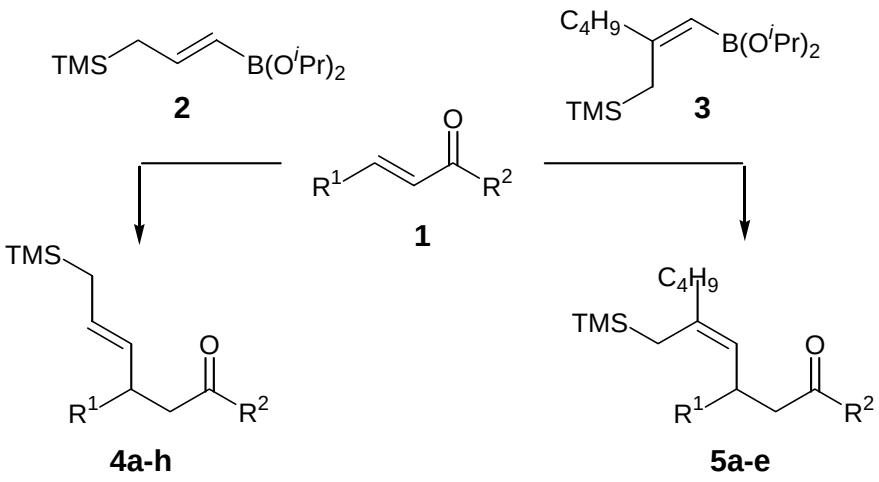
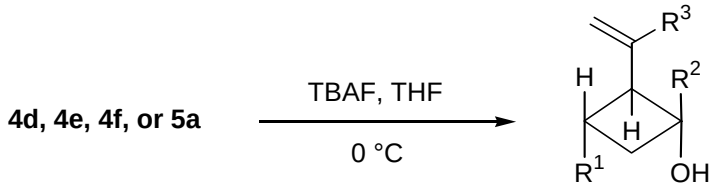
Table 1. Rhodium-Catalyzed 1,4-Addition of **2** or **3** to Enones[a]

entry	R^1=	R^2=	**2/3**	product No	yield/%
1[b]	H	Me	**2**	**4a**	81
2[b]	CH_3	Ph	**2**	**4b**	93
3	Ph	Ph	**2**	**4c**	94
4	Ph	Me	**2**	**4d**	84
5[c]	Ph	H	**2**	**4e**	43
6	*cyclo*-C_6H_{11}	Me	**2**	**4f**	62
7	2-cyclohexenone		**2**	**4g**	60
8[d]	Ph	CH=CHPh	**2**	**4h**	71
9	Ph	Me	**3**	**5a**	79
10	Ph	Ph	**3**	**5b**	84
11	CH_3	C_4H_9	**3**	**5c**	65
12	2-cyclohexenone		**3**	**5d**	53
13[d]	Ph	CH=CHPh	**3**	**5e**	98

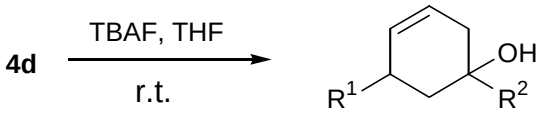
a) All reactions were carried out at 100 °C for 20 h in the presence of **2** or **3** (2 eqs), $[RhCl(cod)]_2$ (1.5 mol%) in MeOH/H_2O (3/1), unless otherwise noted. b) **2** or **3** (1.2 eqs) was used. c) $[RhOH(cod)]_2$ (1.5 mol%) was used. d) The double addition to two double bonds was conducted in the presence of **2** or **3** (4 eqs).



Scheme 1. Rhodium-Catalyzed 1,4-Addition to Enones



6a: R^1 = Ph, R^2 = Me, R^3 = H (79%)
6b: R^1 = Ph, R^2 = H, R^3 = H (65%)
6c: R^1 = *cyclo*-C_6H_{12}, R^2 = Me, R^3 = H (38%)
6d: R^1 = Ph, R^2 = Me, R^3 = C_4H_9 (83%)



7a: R^1 = Ph, R^2 = Me, R^3 = H (34%)

Scheme 2. Four- or Six-Membered Cyclization *via* Intramolecular Allylsilylation