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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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Abstract: The rhodium-catalyzed conjugate addition of (*E*)-Me₃SiCH₂CH=CHB(O^{*i*}Pr)₂ or (*Z*)-Me₃SiCH₂(C₄H₉)C=CHB(O^{*i*}Pr)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 Bu₄NF.

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

We recently reported that various rhodium(I) complexes catalyze addition reactions of organoboronic acids. The conjugate 1,4-addition¹ of aryl- and 1-alkenylboronic acids to α,β -unsaturated ketones, esters, or amides and 1,2-addition² 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 vinylarenes³ and to asymmetric conjugate additions⁴ 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 BBr₃ to acetylene to yield (*E*)-CH(Br)=CHB(O^{*i*}Pr)₂ was followed by coupling with Me₃SiCH₂ZnCl (2 equivalents) in the presence of PdCl₂(PPh₃)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 TiCl₄ and BF₃, and F-bases such as tetrabutylammonium fluoride (TBAF) and CsF have been used for cyclization. Although the treatment of **4** or **5** with BF₃ or TiCl₄ failed to yield any cyclization products, it was very interesting that TBAF⁸ 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 predominant 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 allylsilylation⁹ 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 Bu₄NF 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 MgSO₄. Chromatography over silica gel with hexane/ether (9/1) afforded **6a** in 79%. IR (neat) 3350 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): 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 C₁₃H₁₆O 188.1201, found 1 8 8 . 1 2 0 1 .

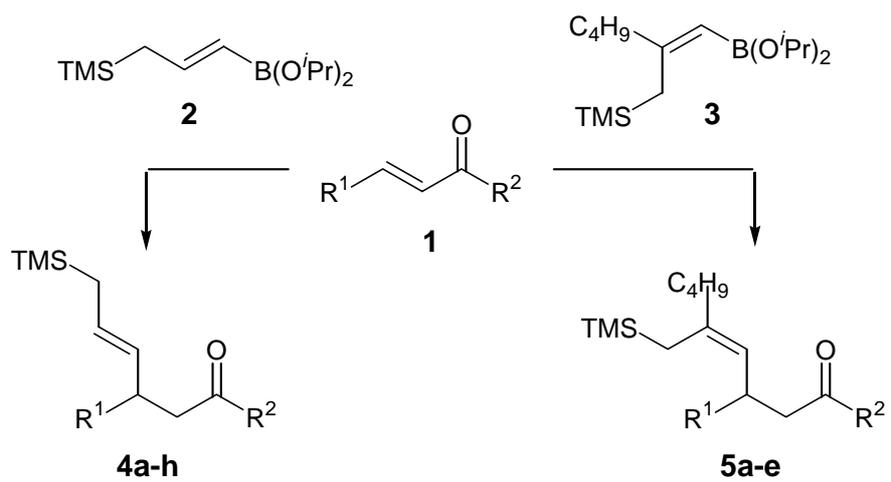
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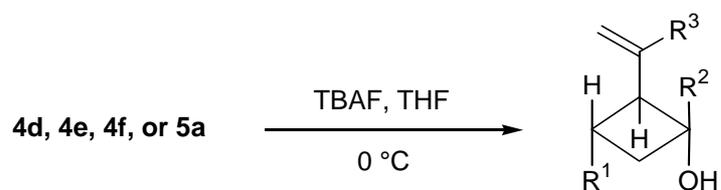
Table 1. Rhodium-Catalyzed 1,4-Addition of **2** or **3** to Enones^a

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	<i>cyclo</i> -C ₆ H 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 ₄ H 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/H₂O (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

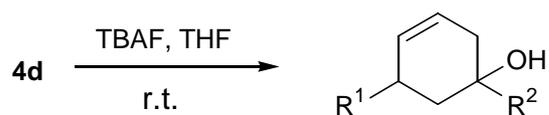


6a: $R^1 = \text{Ph}, R^2 = \text{Me}, R^3 = \text{H}$ (79%)

6b: $R^1 = \text{Ph}, R^2 = \text{H}, R^3 = \text{H}$ (65%)

6c: $R^1 = \text{cyclo-C}_6\text{H}_{12}, R^2 = \text{Me}, R^3 = \text{H}$ (38%)

6d: $R^1 = \text{Ph}, R^2 = \text{Me}, R^3 = \text{C}_4\text{H}_9$ (83%)



7a: $R^1 = \text{Ph}, R^2 = \text{Me}, R^3 = \text{H}$ (34%)

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