Pergamon

Tetrahedron 57 (2001) 10241–10246

TETRAHEDRON

Stereoselective synthesis of sugar allenes and their hydrosilylation catalyzed by biscobaltoctacarbonyl

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Received 22 August 2001; accepted 17 October 2001

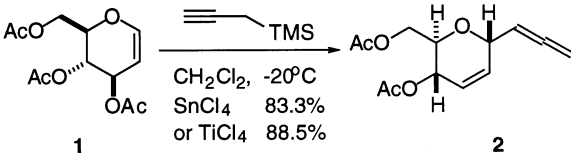
Abstract—Stereoselective introduction of allenyl group to glycals has been developed with propargyltrimethylsilane under the catalysis of a Lewis acid to produce largely the α-sugar allenes in good yields. The subsequent hydrosilylations of these sugar allenes were catalyzed by biscobaltoctacarbonyl to obtain the corresponding vinylsilanes. Stereochemical selectivity is also discussed.

1. Introduction

Allenes and acetylenes have occupied a central place among the many synthetic tools which are useful for the carbon–carbon bond formation as well as organic functional group preparation. *C*-Alkynylation has been one of the useful reactions since it allows the introduction of the carbon chains to sugar chirons. Applications of Hosomi–Sakurai[1] reaction to sugars were reported first from Danishefsky[2] and then from this laboratory[3] in the syntheses directing toward some natural products to show the current method being highly stereoselective to a sugar nucleus as chiral pool. Introduction of an alkynyl (acetylenic) groups to sugar nuclei (tetrahydro- or dihydro-pyran rings) has also been developed for synthesis of sugar-acetylenes, key compounds toward various natural products.[4–9] We have further been exploring to introduce allenyl group to sugar nucleus under the similar method as well as to examine further transformation, such as hydrosilylation, of the allenyl group by means of cobalt-complexes.[10] These should lead us to develop a new methodology in the synthesis of optically active compounds. We herein report these results.

2. Results and discussion

In recent years, propargyltrimethylsilane has been shown to be a useful starting material for the synthesis of monosubstituted allenes,[11] so we selected this reagent as carbon sources of allenyl groups. The reaction of tri-*O*-acetyl-D-glucal **1** with propargyltrimethylsilane (Eq. (1)) was firstly examined, while Vogel reported the same reaction during a disaccharide synthesis.[12] This glycal **1** was stirred with 1.5 equiv. of $HC{\equiv}CCH_2SiMe_3$ in dichloromethane solvent at −20°C to obtain exclusively the α-*C*-allenyl derivative **2** in 83.3% yield in case of $SnCl_4$ as catalyst. This reaction can also be catalyzed by $TiCl_4$ to give **2** in 88.5% yield.



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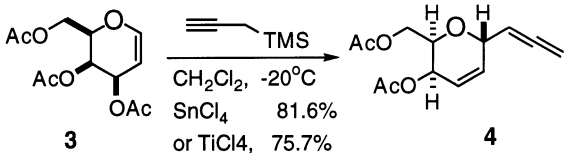

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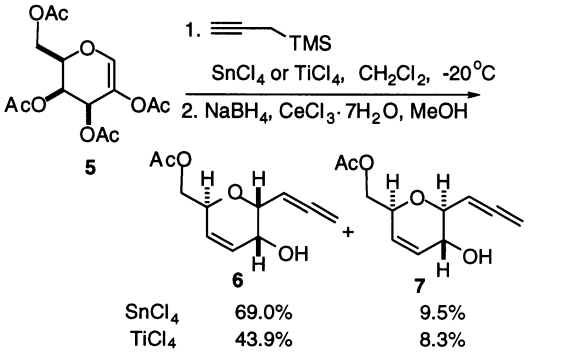

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Reaction between tri-*O*-acetyl-D-galactal **3** and propargyltrimethylsilane (Eq. (2)) under the catalysis of $SnCl_4$ or $TiCl_4$ also provided α-*C* allenyl product **4** in 81.6 or 75.7% yield, respectively. Similarly, 2,3,4,6-tetra-*O*-acetyl-D-glucal **5** reacted with propargyltrimethylsilane (Eq. (3)) under the same conditions, then reduced with $NaBH_4$/

Keywords: sugar allenes; biscobaltoctacarbonyl; hydrosilylation.

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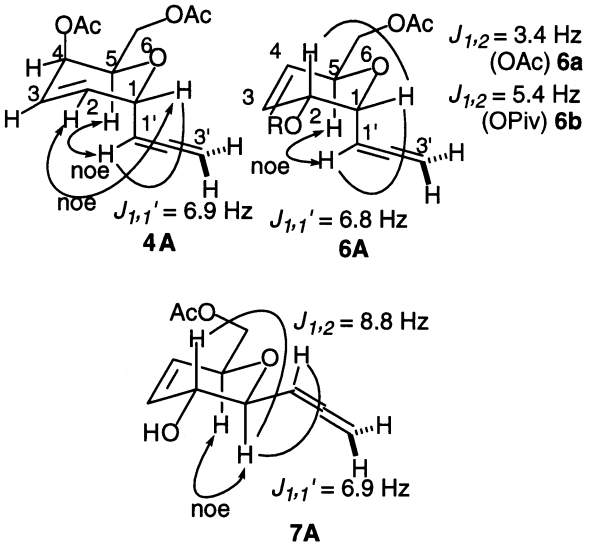
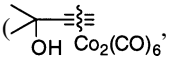


Figure 1. NMR data of compounds **4**, **6** and **7**.

$CeCl_3 \cdot 7H_2O$ to obtain largely the α-allenyl product **6** and considerably the β-allenyl product **7** in 78.5 or 52.2% combined yield, respectively. Their ratio (α/β) was 7.3:1 by the catalyst of $SnCl_4$ but was 5.2:1 as of $TiCl_4$.

The stereochemistry of these products was established through NMR including NOESY experiments (Fig. 1). In the allenyl compound **4** (**4A** in Fig. 1) the cross peak between H-1 and H-5 was not found, while the ones were observed between H-1 and H-1′, H-1′ and H-5. These indicated the *trans*-relationship of the C-1 and C-5 substituents as well as the conformation to be **4A** as shown in Fig. 1. The stereochemistry of compound **6** has been proven to be C-1,2 *cis* configuration as shown in **6A** (Fig. 1), particularly from the values $J_{1,2}$=3.4 Hz (**6a**) and 5.4 Hz (**6b**). These data suggested that the allenyl group situated at α-axial orientation in compound **6**. On the other hand, observation of the cross peak between H-1 and H-5 in the NOESY spectrum of the minor product **7** suggested the *syn*-axial relationship (**7A**) between these protons. This is so far the first example to obtain the beta orientation even as minor product.[9,13]

Hydrosilylation of these sugar allenes was anticipated under catalysis of a complex of acetylenebiscobalthexacarbonyl or biscobalt-octacarbonyl.[10] We examined the hydrosilylation of the allene **2** using the biscobalthexacarbonyl complex of 2-methyl-3-butyn-2-ol ( , **8**) as catalyst, which had shown very good catalytic activity in the general hydrosilylation of sugar acetylenes (Eq. (4)).[10] The allene **2** reacted with Et_3SiH under catalysis of **8** (3 mol%, entry 1, Table 1) by heating at 60°C for 5 h but no product was detected by TLC. Addition of stoichiometric amount of the catalyst yielded products (entry 2). By addition of $Co_2(CO)_8$ (100 mol%, entry 3), a new spot also appeared at R_f 0.52 on a silica gel TLC (hexane/Et_2O=1:1). After isolation of the product by flash chromatography, it was a mixture of two regio-isomeric vinylsilanes **9**[14] and **10** in the ratio of 2:1, which was determined from its ^1H NMR and ^{13}C NMR spectra (Eq. (4)). In order to optimize reaction conditions, we changed the amounts of catalyst and/or reaction temperature in order to improve the chemical yields and the ratio of **9** and **10**. As summarized in Table 1, no reaction conditions changed the product ratio between the two regioisomeric vinylsilanes **9** and **10**, but can improve the chemical yield (entry 5).

The allene **4** reacted with $Co_2(CO)_8$ (2.5 equiv.) at room temperature for 3 h to give a mixture of two regioisomeric vinylsilanes **11** and **12** in 78.2% yield, when allene **4** reacted with $Co_2(CO)_8$ (1.5 equiv.) at 60°C for 1 h to obtain a mixture in 68.5% yield. Their ratio (**11/12**) was 2:1 in both cases.

The allene **6** was subjected to $Co_2(CO)_8$ (2.5 equiv.) at 60°C to obtain a mixture of vinylsilanes **13** and **14** in 50.9% yield. In this case, the ratio was 3:1 (Table 2, entry 1). Different ratio of the regioisomers suggested that the protective group of the 2-hydroxyl group could effect on the ratio of the

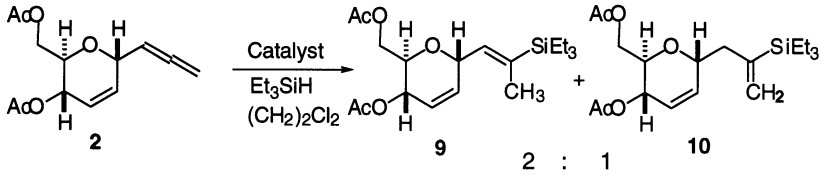


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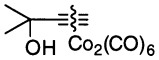
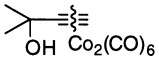
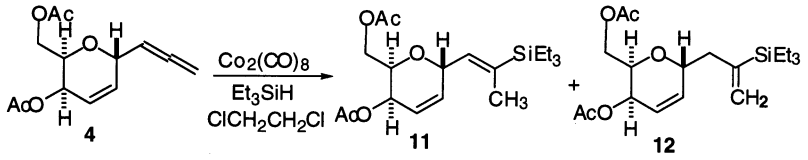
Table 1. Effects of catalysts on hydrosilylation of the allene **2**

Entry	Catalyst	Mol%	Time (min)	Temperature (°C)	Yield (%)[a]	Ratio **9/10**[b]
1		3	300	60	0	–
2		100	240	60	59.5[c]	2:1
3	$Co_2(CO)_8$	100	60	60	72.0	2:1
4	$Co_2(CO)_8$	150	60	60	69.4	2:1
5	$Co_2(CO)_8$	250	100	25	81.5	2:1

[a] Isolated yield.
[b] The ratio of vinylsilanes **9** and **10** was calculated by ^1H NMR spectra.
[c] The starting material was recovered in 23% yield.



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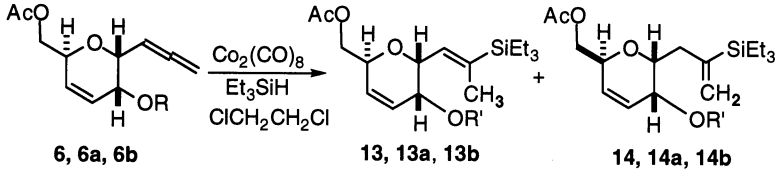

(6)

Table 2. Effects of substituents on regioselectivity and yields in hydrosilylation (Eq. (6))

Entry	Compound	R	R′	Yield (%)	Ratio **13/14**
1	**6**	H	$SiEt_3$	50.9	3:1
2	**6a**	Ac	Ac	50.0	4:1
3	**6b**	Piv	Piv	67.1	10:1

regioselectivity. When the 2-hydroxyl group of allene **6** was esterified as acetate **6a** (entry 2) or as pivalate **6b** (entry 3), the ratios of the corresponding vinylsilanes, after the treatment with $Co_2(CO)_8$ (1.5 equiv.) at 60°C, were determined to be 4:1 and 10:1, respectively. These indicated that the regioselectivity of hydrosilylation of sugar allene was affected by the steric hindrance of 2-protective group. In general, hydrosilylation of *endo*-acetylene-biscobalthexacarbonyl complexes[6,8] provides vinyl silanes having the silyl group at a position away from the neighboring carbon chain. Thus, we conclude that this hydrosilylation occurs to render the stereochemistry of the products so that the bulky silyl group with less steric repulsive interaction. The effect of such steric bulk has been recorded in the equilibrium between the alpha–beta epimers of sugar-acetylenes (the similar acetylene biscobalthexacarbonyl complex).[6,8,15]

In summary, we have developed a new method for stereoselective introduction of the allenyl group to several glycals in practically good yields; and hydrosilylation of these allenyl derivatives which are catalyzed by biscobaltoctacarbonyl or in situ-complex under substantial sterechemical control by an existing neighboring bulky substituent.

3. Experimental

3.1. General procedures

Infrared (IR) spectra of all products were measured as liquid films on a Paragon 1000 FT-IR spectrometer and are reported in wave number (cm^{-1}). ^1H and ^{13}C NMR, NOESY spectra were recorded in $CDCl_3$ solutions with $CHCl_3$ for ^1H (500 or 600 MHz), $CDCl_3$ for ^{13}C (125 or 150 MHz) as an internal standard on a JEOL instrument. Chemical shifts are expressed in ppm (δ) and coupling constants in Hertz (Hz); Optical rotation were measured on a JASCO P-1010-TG polarimeter. High-resolution or low-resolution mass spectra (FAB and EI) were obtained on a JEOL JMS-700 spectrometer. Elemental analyses were performed by the Analytical Laboratory, School of Bioagricultural Sciences, Nagoya University. Analytical TLC was conducted on 0.25 mm E. Merck silica gel 60F-254 plates. Column chromatography was performed with Merck silica gel 60 (40–50 μm). Dichloromethane was dried over CaH_2. All other commercially available reagents were used as received.

3.2. Synthesis of sugar allenes

3.2.1. Allene 2 from tri-*O*-acetyl-D-glucal. To a mixture of tri-*O*-acetyl-D-glucal **1** (54.4 mg, 0.2 mmol) and propargyltrimethylsilane (59.5 μl, 0.4 mmol) in 4 ml dry CH_2Cl_2 was added slowly a solution of $SnCl_4$ (0.2 mmol) in 1 ml dry CH_2Cl_2 at −20°C under Ar atmosphere. The mixture was stirred for 30 min. and then poured into cooled 6 ml 10% $KNa[CH(OH)COO]_2$, the organic layer was separated and the water layer was extracted with CH_2Cl_2 (10 ml×3). The combined organic layer was washed with saturated $NaHCO_3$ (10 ml), distilled water (10 ml) and brine (10 ml), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (silica gel: 12 g, hexane/Et_2O=4:1) to give a colorless oil **2** (42 mg, 83.3%). $[\alpha]_D^{29.5}=-55.4$ (*c* 0.466, $CHCl_3$). ^1H NMR δ 2.13 (s, 6H, CH_3COO–×2), 3.92 (ddd, 1H, *J*=8.3, 5.6, 2.9 Hz, H-5), 4.23 (ddd, 2H, *J*=13.7, 5.6, 2.9 Hz, H-6), 4.86 (ddd, 1H, *J*=5.4, 3.0, 2.0 Hz, H-1), 4.88 (dd, 2H, *J*=5.4, 1.5 Hz, CH_2=C=), 5.26 (ddd, 1H, *J*=8.3, 3.0, 2.0 Hz, H-4), 5.30 (q, 1H, *J*=5.4 Hz, CH=C=), 5.82 (dt, 1H, *J*=10.8, 2.0 Hz, H-3), 5.91 (ddd, 1H, *J*=10.8, 3.0, 2.0 Hz, H-2). ^{13}C NMR δ 20.8 (CH_3), 21.0 (CH_3), 63.1 (C-6), 65.1 (C-4), 68.6 (C-5), 70.6 (C-1), 77.2 (CH_2=), 89.5 (CH=), 125.1 (C-3), 130.7 (C-2), 170.3 (C=O), 170.9 (C=O), 209.1 (=C=). EI-MS *m/z* (relative intensity) 253 (M^++1, 33), 213 (M^+−CH=C=CH_2, 30), 193 (M^+−OAc, 90), 111 (213−OAc−Ac, 100). IR (neat) λ 3008, 2996, 1953, 1737, 1387, 1286, 1021, 867. Anal. calcd for $C_{13}H_{16}O_5$: C 61.90, H 6.39, found: C 61.77, H 6.72.

3.2.2. Allene 4 from tri-*O*-acetyl-D-galactal. The procedure is same as in Section 3.2.1 to get a colorless oil with 81.6% yield. $[\alpha]_D^{32}=-214.9$ (*c* 0.48, $CHCl_3$). ^1H NMR δ 2.08 (s, 3H, CH_3COO-), 2.09 (s, 3H, CH_3COO), 4.13 (m, 1H, H-5), 4.24 (ddd, 2H, *J*=11.7, 3.9, 6.4 Hz, H-6), 4.82 (dt, 1H, *J*=5.9, 2.9 Hz, CH_2=C=), 4.91 (m, 1H, H-1), 5.04 (dd, 1H, *J*=4.9, 2.0 Hz, H-4), 5.25 (dt, 1H, *J*=6.9, 5.4 Hz, CH=C=), 6.07 (dd, 1H, *J*=10.3, 3.5 Hz, H-2), 6.02 (ddd, 1H, *J*=10.3, 4.9, 2.0 Hz, H-3). ^{13}C NMR λ 20.8 (CH_3), 20.9 (CH_3), 63.0 (C-5), 63.6 (C-4), 68.2 (C-6), 70.7 (C-1), 77.2 (CH_2=), 88.8 (CH=), 122.4 (C-3), 133.5 (C-2), 170.5 (C=O), 170.7 (C=O), 209.1 (=C=). EI-MS *m/z* (relative intensity) 253 (M^++1, 18), 213 (M^+−CH=C=CH_2, 20), 193 (M^+−OAc, 45), 111 (213−OAc−Ac, 100). IR (neat) λ 2996, 1950, 1735, 1390, 1270, 1050, 870. Anal. calcd for $C_{13}H_{16}O_5$: C 61.90, H 6.39, found: C 61.55, H 6.64.

3.2.3. Allene 6 and 7 from 2,3,4,6-tetra-*O*-acetyl-D-glucal. To a mixture of 2,3,4,6-tetra-*O*-acetyl-D-glucal **5** (69.3 mg, 0.2 mmol) and propargyltrimethylsilane (59.5 μl, 0.4 mmol) in 4 ml dry CH_2Cl_2, a solution of $SnCl_4$ (0.2 mmol) in 1 ml dry CH_2Cl_2 was added slowly at −20°C under Ar atmosphere. The mixture was stirred for 60 min and then poured into cooled 6 ml 10% $KNa[CH(OH)COO]_2$, the organic layer was separated and the water layer was extracted with CH_2Cl_2 (10 ml×3). The combined organic layer was washed with saturated $NaHCO_3$ (10 ml), distilled water (10 ml) and brine (10 ml), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude product (60 mg).

To a solution of above crude product in 5 ml MeOH was added $NaBH_4$ (45 mg, 1.2 mmol) and $CeCl_3{\cdot}7H_2O$ (223.6 mg, 0.6 mmol) at 0°C. After addition, the mixture was stirred for 3 h at room temperature and poured into saturated NH_4Cl (10 ml). The organic layer was separated and the water layer was extracted with CH_2Cl_2 (10 ml×3). The combined organic layer was washed with saturated $NaHCO_3$ (10 ml), distilled water (10 ml) and brine (10 ml), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give yellow oil (60 mg). The residue was purified by silica gel column chromatography (silica gel: 30 g, hexane/Et_2O=4:1) to give two colorless oils **6** (29 mg, 69.0%) and **7** (4 mg, 9.5%).

Compound **6**: $[\alpha]_D^{32.6}=-98.9$ (*c* 0.35, $CHCl_3$). ^1H NMR δ 2.12 (s, 3H, CH_3COO-), 4.03 (m, 1H, H-2), 4.09 (dd, 1H, *J*=11.7, 3.8 Hz, H-6), 4.28 (dd, 1H, *J*=11.7, 7.4 Hz, H-6), 4.49 (m, 2H, H-5 and H-1), 4.89 (ddd, 2H, *J*=11.2, 6.8, 1.94 Hz, CH_2=C), 5.38 (q, 1H, *J*=6.8 Hz, CH=C=), 5.83 (dd, 1H, *J*=10.3, 2.5 Hz, H-4), 6.12 (ddd, 1H, *J*=10.3, 4.4, 2.0 Hz, H-3). ^{13}C NMR: δ 20.7 (CH_3), 63.9 (C-2), 64.0 (C-6), 70.8 (C-5), 72.3 (C-1), 76.6 (CH_2=), 87.3 (CH=), 127.7 (C-4), 129.4 (C-3), 170.8 (C=O), 209.2 (=C=). EI-MS *m/z* (relative intensity) 167 (M^+−Ac, 38), 149 (M^+−Ac-H_2O, 100). IR (neat): λ 3537, 3010, 2967, 1955, 1737, 1342, 1286, 1026, 842. Anal. calcd for $C_{13}H_{16}O_5$: C 62.85, H 6.71, found: C 62.61, H 7.22. Compound **7**: $[\alpha]_D^{34}=-95.4$ (*c* 0.21, $CHCl_3$). ^1H NMR δ 2.06 (s, 3H, CH_3COO-), 3.87 (ddt, 1H, *J*=8.8, 6.9, 2.0 Hz, H-1), 4.07 (ddd, 2H, *J*=11.7, 5.9, 3.0 Hz, H-6), 4.13 (dd, 1H, *J*=8.8, 2.0 Hz, H-2), 4.39 (m, 1H, H-5), 4.88 (ddd, 1H, *J*=11.3, 6.9, 2.0 Hz, H-3′), 4.94 (ddd, 1H, *J*=11.3, 6.4, 2.0 Hz, H-3′), 5.31 (q, 1H, *J*=6.9 Hz, CH=C=), 5.70 (dt, 1H, *J*=10.3, 2.0 Hz, H-3), 5.95 (ddd, 1H, *J*=10.3, 2.5, 2.0 Hz, H-4). ^{13}C NMR: δ 21.0 (CH_3), 66.1 (C-6), 67.3 (C-2), 73.4 (C-5), 77.2 (C-1), 77.3 (CH_2=), 89.9 (CH=C=), 127.2 (C-3), 130.9 (C-4), 172.7 (C=O), 208.9 (=C=). EI-MS *m/z* (relative intensity) 209 (M^+−1, 21), 177 (M^+−CH_3-H_2O, 100), 167 (M^+−OAc, 35), 149 (M^+−Ac−H_2O, 77), 133 (M^+−OAc-H_2O, 40). IR (neat): λ 3557, 3005, 2996, 2867, 1953, 1736, 1350, 1080 1020, 850.

3.3. Esterification of allene 6

3.3.1. Acetylated allene 6a. To a mixture of **6** (40 mg, 0.19 mmol), pyridine (30 mg, 0.38 mmol) and DMAP (5.0 mg, 0.038 mmol) in 4 ml dry CH_2Cl_2 was added a solution of Ac_2O (39 mg, 0.38 mmol) in 2 ml dry CH_2Cl_2 at ice-water bath under Ar atmosphere. After stirring at room temperature for 5 h, the mixture was poured into 10 ml ice-water and extracted with CH_2Cl_2 (15 ml×3). The combined organic layer was washed with distilled water and brine, dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to provide a crude oil (50 mg). The residue was purified by silica gel chromatography (silica gel: 8 g, hexane/Et_2O=6:1) to get a colorless oil **6a** (44 mg, 92%). $[\alpha]_D^{32}=-93.5$ (*c* 1.0, $CHCl_3$). ^1H NMR δ 2.04 (s, 6H, CH_3CO-×2), 4.06 (dd, 1H, *J*=11.7, 3.9 Hz, H-6), 4.28 (dd, 1H, *J*=11.7, 6.9 Hz, H-6), 4.50 (ddd, 1H, *J*=6.9, 3.9, 2.9 Hz, H-5), 4.59 (ddt, 1H, *J*=6.8, 3.4, 2.0 Hz, H-1), 4.79, 4.85 (ddd, 2H, *J*=11.2, 6.9, 2.0 Hz, CH_2=), 5.15 (ddd, 1H, *J*=4.4, 3.4, 1.0 Hz, H-2), 5.23 (q, 1H, *J*=6.9 Hz, H-1′), 5.90 (ddd, 1H, *J*=10.3, 2.9, 1.0 Hz, H-4), 6.01 (ddd, 1H, *J*=10.3, 4.4, 2.5 Hz, H-3). ^{13}C NMR δ 20.9 (CH_3), 21.0 (CH_3), 64.1 (C-6), 65.7 (C-2), 70.3 (C-1), 70.6 (C-5), 76.7 (CH_2=), 87.1 (C-1′), 125.5 (C-3), 129.7 (C-4), 170.5 (C=O), 170.9 (C=O), 209.4 (=C=). FAB-MS *m/z* (relative intensity) 253 (M^++H, 52), 193 (M^+−CH_3COO-, 63), 154 (M^+−CH_3COO−CH=C=CH_2, 100), 149 (M^+−CH_3COO−CH_3CO−H, 88), 133 (M^+−CH_3COO×2-H, 78). IR (neat) λ 3014, 1953, 1730, 1368, 1220, 1183, 1037, 846.

3.3.2. Pivalated allene 6b. The procedure was same as in Section 3.3.1 in quantitative yield. $[\alpha]_D^{31}=-72.1$ (*c* 0.96, $CHCl_3$). ^1H NMR δ 1.19 (s, 9H, $(CH_3)_3CCO$), 2.04 (s, 3H, CH_3CO-), 4.08 (dd, 1H, *J*=11.8, 3.9 Hz, H-6), 4.25 (dd, 1H, *J*=11.8, 7.3 Hz, H-6), 4.49 (ddd, 1H, *J*=7.3, 3.9, 2.5 Hz, H-5), 4.64 (ddt, 1H, *J*=6.8, 5.4, 2.0 Hz, H-1), 4.76, 4.84 (ddd, 2H, *J*=11.2, 6.8, 2.0 Hz, CH_2=), 5.16 (ddd, 1H, *J*=5.4, 3.9, 1.5 Hz, H-2), 5.23 (q, 1H, *J*=6.9 Hz, H-1′), 5.84 (ddd, 1H, *J*=10.3, 2.5, 1.5 Hz, H-4), 5.94 (ddd, 1H, *J*=10.3, 3.9, 2.5 Hz, H-3). ^{13}C NMR δ 20.7 (CH_3), 26.9 (CH_3×3), 38.7 (*C*C=O), 64.2 (C-6), 65.2 (C-2), 69.9 (C-1), 70.5 (C-5), 76.8 (CH_2=), 86.6 (C-1′), 125.6 (C-3), 129.0 (C-4), 170.6 (CH_3C=O), 177.7 ($(CH_3)_3CC$=O), 209.3 (=C=). FAB-MS *m/z* (relative intensity) 295 (M^++H, 38), 193 (M^+−$(CH_3)_3COO-$, 63), 154 (M^+−$(CH_3)_3COO$−CH=C=CH_2, 48), 133 (M^+−$(CH_3)_3COO$−CH_3COO−H, 100). IR (neat): λ 3020, 2975, 1952, 1723, 1479, 1368, 1277, 1231, 1155, 1036. HRMS (FAB) Cacld for $C_{16}H_{23}O_5$ ($M+H^+$) 295.1545, found 295.1486.

3.4. Hydrosilylation of sugar allenes

General procedures. To a mixture of sugar allene (0.1 mmol) and Et_3SiH (500 μl, 3.0 mmol) in 2 ml 1,2-dichloroethane was added a solution of $Co_2(CO)_8$ (84.4 mg, 0.25 mmol) in 2 ml 1,2-dichloroethane at room temperature under Ar atmosphere. After the reaction was completed, the mixture was evaporated under reduced pressure and the residue was purified by silica gel column chromatography to give a mixture of vinylsilanes.

3.4.1. Vinylsilanes 9 and 10 from allene 2. Compound **9**: ^{1}H NMR: δ 0.62 (q, 6H, J=7.6 Hz, $Si(CH_2CH_3)_3$), 0.93 (t, 9H, J=7.6 Hz, $Si(CH_2CH_3)_3$), 1.78 (d, 3H, J=1.5 Hz, CH_3); 2.10 (s, 3H, CH_3CO), 2.11 (s, 3H, CH_3CO), 3.98 (ddd, 1H, J=8.5, 6.4, 3.5 Hz, H-5), 4.16–4.28 (ddd, 2H, J=13.2, 6.4, 3.5 Hz, H-6), 5.12 (m, 1H, H-1); 5.18 (ddd, 1H, J=8.5, 4.25, 1.8 Hz, H-4), 5.76 (dd, 1H, J=5.4, 1.45 Hz, H-1′), 5.81 (ddd, 1H, J=10.3, 2.5, 2.0 Hz, H-2), 5.86 (dt, 1H, J=10.3, 1.5 Hz, H-3).^{13}C NMR δ 2.44, 7.37, 15.8, 21.1, 63.2, 64.9, 69.0, 70.2, 123.36, 123.43, 132.2, 135.9, 170.5, 170.9. Compound **10**: ^{1}H NMR δ 0.62 (q, 6H, J=7.6 Hz, $Si(CH_2CH_3)_3$), 0.93 (t, 9H, J=7.6 Hz, $Si(CH_2CH_3)_3$), 2.09 (s, 3H, CH_3CO), 2.10 (s, 3H, CH_3CO), 2.31 (dd, 1H, J= 15.2, 3.5 Hz, H-1′), 2.54 (dd, 1H, J=15.2, 7.5 Hz, H-1′), 3.98 (ddd, 1H, J=9.8, 6.4, 3.5 Hz, H-5), 4.13–4.29 (ddd, 2H, J=11.7, 5.8, 3.5 Hz, H-6), 4.36 (m, 1H, H-1); 5.18 (ddd, 1H, J=8.5, 4.3, 1.8 Hz, H-4), 5.47 (d, 2H, J=1.5 Hz, CH_2=), 5.76 (d, 1H, J=10.3 Hz, H-2), 5.95 (d, 1H, J= 10.3 Hz, H-3). ^{13}C NMR: δ 2.94, 7.37, 20.8, 21.1, 62.9, 65.2, 69.7, 70.7, 128.6, 133.4, 139.2, 144.5, 170.5, 170.9. EI-MS m/z (relative intensity) 369 (M^++H, 2), 115 [$(CH_3CH_2)_3Si^+$, 88], 87 [$(CH_3CH_2)_2SiH^+$, 100]; HRMS (FAB) cacld for $C_{19}H_{33}O_5Si$ (M+H^+) 369.2097, found 369.2065.

3.4.2. Vinylsilanes 11 and 12 from allene 4. Compound **11**: ^{1}H NMR: δ 0.62 [q, 6H, J=8.3 Hz, $(CH_3CH_2)_3Si$–], 0.95 [t, 9H, J=8.3 Hz, $(CH_3CH_2)_3Si$–], 1.81 (d, 3H, J=1.5 Hz, CH_3C=), 2.06 (s, 3H, CH_3CO), 2.11 (s, 3H, CH_3CO), 4.10 (ddd, 1H, J=9.8, 4.4, 2.5 Hz, H-5), 4.13 (ddd, 2H, J=10.8, 4.4, 2.5 Hz, H-6), 5.06 (dd, 1H, J=4.4, 2.0 Hz, H-4), 5.13 (dd, 1H, J=6.4, 2.0 Hz, H-1), 5.73 (dq, 1H, J= 6.4, 1.5 Hz, H-1′), 5.96 (ddd, 1H, J=10.3, 4.4, 1.5 Hz, H-2), 6.03 (dd, 1H, J=10.3, 4.4 Hz, H-3). ^{13}C NMR: δ 2.42, 7.30, 15.8, 20.8, 20.9, 63.3, 63.9, 68.9, 69.5, 121.4, 134.6, 144.3, 170.7, 170.6.

Compound **12**: ^{1}H NMR δ 0.62 (q, 6H, J=8.3 Hz, $(CH_3CH_2)_3Si$–), 0.95 [t, 9H, J=8.3 Hz, $(CH_3CH_2)_3Si$–], 2.07 (s, 3H, CH_3CO), 2.10 (s, 3H, CH_3CO), 2.26 (dd, 1H, J=13.7, 5.9 Hz, H-1′), 2.46 (dd, 1H, J=13.7, 7.8 Hz, H-1′), 4.09 (ddd, 1H, J=9.8, 4.4, 2.9 Hz, H-5), 4.12 (ddd, 2H, J=10.8, 4.4, 2.5 Hz, H-6), 4.40 (ddd, 1H, J=7.8, 5.9, 2.5 Hz, H-1), 5.06 (dd, 1H, J=4.9, 2.9 Hz, H-4), 5.40, 5.76 (d, 2H, J=3.0 Hz, CH_2=), 5.92 (dd, 1H, J=9.3, 2.0 Hz, H-2), 5.94 (dd, J=9.3,.4.9, 2.0 Hz, H-3). ^{13}C NMR δ 2.93, 7.33, 20.8, 20.9, 38.5, 62.9, 64.0, 67.8, 71.6, 128.8, 135.4, 137.6, 144.3, 170.6, 170.7. EI-MS m/z (relative intensity) 369 (M^++H, 6), 251 (M^+−CH_2CH_3×2-Ac, 11), 213 [M^+−CH_2=C($SiCH_2CH_3)_3CH_2$, 15], 115 [$(CH_3CH_2)_3Si^+$–, 88]; HRMS (FAB) cacld for C19$H_{33}O_5Si$ (M+H^+) 369.2097, found 369.2088.

3.4.3. Vinylsilanes 13 and 14 from allene 6. Compound **13**: ^{1}H NMR δ 0.55 (m, 12H, $Si(CH_2CH_3)_3$×2), 0.92 (m, 18H, $Si(CH_2CH_3)_3$×2), 1.78 (d, 3H, J=2.0 Hz, CH_3C=), 2.03 (s, 3H, CH_3CO), 4.06 (dd, 1H, J=11.6, 4.0 Hz, H-6), 4.13 (dd, 1H, J=11.6, 8.3 Hz, H-6), 4.23 (ddd, 1H, J=8.3, 4.0, 2.0 Hz, H-5), 4.32 (dt, 1H, J=4.6, 2.5 Hz, H-2), 4.72 (dd, 1H, J=6.7, 4.6 Hz, H-1), 5.63 (dt, 1H, J=10.4, 2.5 Hz, H-4), 5.86 (dt, 1H, J=10.4, 2.5 Hz, H-3), 5.92 (dq, 1H, J=6.7, 2.0 Hz, H-1′). ^{13}C NMR δ 2.56, 4.94, 6.75, 7.38, 15.7, 20.9, 65.0, 65.6, 68.7, 76.8, 126.4, 130.6, 135.3, 141.9, 171.1.

Compound **14**: ^{1}H NMR δ 0.55 (m, 12H, $Si(CH_2CH_3)_3$×2), 0.92 (m, 18H, $Si(CH_2CH_3)_3$×2), 2.03 (s, 3H, CH_3CO), 2.39 (m, 2H, H-1′), 4.05 (dd, 1H, J=11.6, 4.0 Hz, H-6), 4.12 (dd, 1H, J=11.6, 7.0 Hz, H-6), 4.24 (ddd, 1H, J=7.0, 4.0, 2.8 Hz, H-5), 4.34 (dt, 1H, J=3.4, 2.0 Hz, H-2), 5.76 (dt, 1H, J=10.4, 2.8, 1.5 Hz, H-4), 5.88 (ddd, 1H, J=10.4, 3.4, 2.3 Hz, H-3), 5.38, 5.82 (dd, 1H, J=3.1, 1.5 Hz, CH_2=). ^{13}C NMR δ 2.94, 5.10, 6.80, 7.40, 21.1, 34.0, 64.8, 65.1, 69.3, 73.4, 127.1, 127.2, 130.6, 145.8, 171.1. EI-MS m/z (relative intensity) 411 (M^+−CH_2CH_3, 1), 381 (M^+−CH_3CO, 3), 299 [M^+−CH_2=C–$Si(CH_2CH_3)_3$, 21], 256 [M^+−CH_2=C–$Si(CH_2CH_3)_3$–CH_3CO, 95], 115 [$(CH_3CH_2)_3Si^+$–, 100].

3.4.4. Vinylsilanes 13a and 14a from allene 6a. Compound **13a**: ^{1}H NMR δ 0.58 (q, 6H, J=7.8 Hz, $Si(CH_2CH_3)_3$), 0.90 (t, 9H, J=7.8 Hz, $Si(CH_2CH_3)_3$), 1.73 (d, 3H, J=2.0 Hz, CH_3C=), 2.01 (s, 3H, CH_3CO), 2.05 (s, 3H, CH_3CO), 4.07 (dd, 1H, J=11.7, 3.9 Hz, H-6), 4.32 (dd, 1H, J=11.7, 6.9 Hz, H-6), 4.45 (ddd, 1H, J=6.9, 3.9, 2.5 Hz, H-5), 4.88 (dt, 1H, J=6.9, 3.4 Hz, H-1), 5.17 (dt, 1H, J=3.4, 1.0 Hz, H-2), 5.72 (dq, 1H, J=6.8, 2.0 Hz, H-1′), 5.93 (ddd, 1H, J=10.3, 2.9, 1.0 Hz, H-4), 6.03 (ddd, 1H, J=10.3, 4.9, 2.5 Hz, H-3). ^{13}C NMR δ 2.48 (3×C), 7.31 (3×C), 15.9, 20.8 (2×C), 64.0, 65.4, 67.8, 70.3, 125.6, 130.0, 134.7, 140.0, 170.4. 170.8.

Compound **14a**: ^{1}H NMR δ 0.59 (q, 6H, J=7.8 Hz, $Si(CH_2CH_3)_3$), 0.90 (t, 9H, J=7.8 Hz, $Si(CH_2CH_3)_3$), 2.03 (s, 3H, CH_3CO), 2.09 (s, 3H, CH_3CO), 2.37 (m, 2H, H-1′), 3.83 (m, 1H, H-1), 4.02 (dd, 1H, J=11.7, 3.4 Hz, H-6), 4.28 (dd, 1H, J=11.7, 7.8 Hz, H-6), 4.47 (ddd, 1H, J=7.8, 3.4, 2.5 Hz, H-5), 4.93 (dd, 1H, J=5.4, 2.5 Hz, H-2), 5.39, 5.70 (d, 1H, J=3.0 Hz, CH_2=), 5.89 (dt, 1H, J=10.3, 2.5 Hz, H-4), 6.12 (ddd, 1H, J=10.3, 5.4, 2.5 Hz, H-3). ^{13}C NMR δ 2.90, 7.31, 20.8, 36.4, 63.7, 64.9, 69.9, 71.2, 125.4, 127.9, 130.4, 144.3, 170.4, 170.8. FAB-MS m/z (relative intensity) 391 (M^++Na, 13), 369 (M^++H, 24), 309 (M^+−CH_3COO, 48), 249 (M^+−CH_3COO×2-H, 53), 154 [CH_2=C(CH_3)–$Si(CH_2CH_3)_3$, 77]; HRMS (FAB) cacld for $C_{19}H_{33}O_5Si$ (M+H^+) 369.2097, found 369.2073.

3.4.5. Vinylsilanes 13b and 14b from allene 6b. Compound **13b**: ^{1}H NMR: δ 0.55 (q, 6H, J=7.8 Hz, $Si(CH_2CH_3)_3$), 0.92 (t, 9H, $Si(CH_2CH_3)_3$), 1.14 (s, 9H, $(CH_3)_3CCO$), 1.74 (d, 3H, J=2.0 Hz, CH_3C=), 2.05 (s, 3H, CH_3CO), 4.07 (dd, 1H, J=11.7, 3.4 Hz, H-6), 4.29 (dd, 1H, J=11.7, 6.8 Hz, H-6), 4.40 (m, 1H, H-5), 4.89 (dd, 1H, J=6.8, 3.9 Hz, H-1), 4.72 (dt, 1H, J=4.4, 1.5 Hz, H-2), 5.76 (dq, 1H, J=6.7, 1.5 Hz, H-1′), 5.88 (ddd, 1H, J=10.7, 2.9, 1.5 Hz, H-4), 6.0 (ddd, 1H, J=10.7, 4.4, 2.5 Hz, H-3). ^{13}C NMR: δ 2.50, 7.39, 15.8, 20.9, 27.1,

38.8, 64.3, 65.4, 67.6, 69.9, 126.1, 129.4, 134.3, 141.2, 170.9, 178.0.

Compound **14b**: ^{1}H NMR δ 0.50 (q, 6H, J=7.8 Hz, $Si(CH_2CH_3)_3$), 0.92 (t, 9H, $Si(CH_2CH_3)_3$), 1.13 (s, 9H, $(CH_3)_3CCO$), 2.07 (s, 3H, CH_3CO), 2.29 2.39 (ddd, 2H, J=14.7, 7.8, 5.4 Hz, H-1′), 3.98 (m, 1H, H-1), 4.01 (dd, 1H, J=11.7, 3.4Hz, H-6), 4.32 (dd, 1H, J=11.7, 7.9 Hz, H-6), 4.49 (m, 1H, H-5), 4.93 (m, 1H, H-2), 5.38, 5.73 (d, 2H, J=2.9 Hz, CH_2=), 5.90 (ddd, 1H, J=11.2, 5.3, 2.9 Hz, H-4), 6.08 (ddd, 1H, J=11.2, 4.4, 2.5 Hz, H-3). ^{13}C NMR: δ 2.06, 7.61, 20.9, 27.3, 36.2, 38.8, 63.9, 65.9, 67.9, 70.5, 125.5, 127.7, 130.1, 144.5, 170.9, 178.0. EI-MS m/z (relative intensity) 433 (M^++Na, 13), 411 (M^++H, 18), 309 (M^+-CH_3CO, 3), 309 [$M^+-(CH_3)_3COO$, 42], 249 [$M^+-CH_3COO-(CH_3)_3COO$–H, 53], 115 [$(CH_3CH_2)_3Si^+$–, 100]; HRMS (FAB) cacld for $C_{22}H_{39}O_5Si$ ($M+H^+$) 411.2567, found 411.2510.

Acknowledgements

The authors thank JSPS for the research grant and post-doctoral fellowship to G. H.

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