Synthetic utility of 1,1,2,2-tetraaryldisilanes: radical reduction of alkyl phenyl chalcogenides

Osamu Yamazaki,[a] Hideo Togo *[ab] and Masataka Yokoyama [ab]

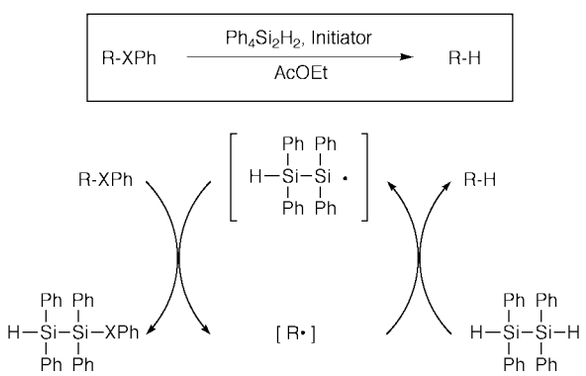
[a] *Graduate School of Science and Technology,* [b] *Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho 1-33, Inageku, Chiba 263-8522, Japan*

Received (in Cambridge, UK) 22nd July 1999, Accepted 26th August 1999

Reactivity of tetraaryldisilanes as radical reducing agents of alkyl phenyl chalcogenides initiated by Et_3B or AIBN was studied. Here, the reactivity of alkyl sulfide was poor; however, various alkyl phenyl selenides and tellurides were reduced to the corresponding hydrocarbons in good yields with 1,1,2,2-tetraphenyldisilane.

Introduction

The major approach to organic synthesis with free radical reactions usually deals with tributyltin hydride.[1] However, it is well known that there are several problems incurred in the tributyltin hydride method such as toxicity and disposal, work-up and complete removal of the tin species from the products. Therefore, other radical reagents have been required in place of tin compounds. Recently, organosilanes such as $(Me_3Si)_3SiH$ and Ph_2SiH_2 have been utilized in a wide variety of radical reactions.[2,3,4] We also reported radical reactions mediated by water-soluble organosilanes in aqueous media.[5] Generally, it is recognized that organosilanes are shown to be highly efficient and superior radical reagents compared with organotin compounds from the ecological and practical viewpoints. Recently, we have reported the utilization of tetraaryldisilanes, which are air-stable crystals, for three types of radical reactions with alkyl bromides such as reduction, reductive addition to olefins, and alkylation onto heteroaromatic bases.[6] Here, the utilization of tetraaryldisilanes **1** as a radical reducing agent with alkyl phenyl chalcogenides is demonstrated. Usually, sugar chalcogenides are much more stable than sugar halides for storage and chemical treatment. Therefore, it would be very convenient if the radical reaction of chalcogenides with tetraaryldisilanes would work effectively.

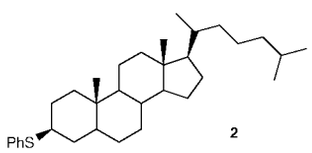
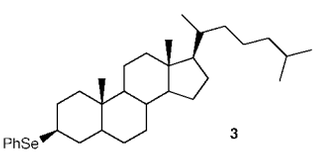
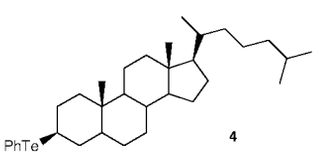


Scheme 1 Reaction mechanism.

Results and discussion

At first, the relative reactivity of alkyl phenyl chalcogenides was studied. Thus, 3-cholestanyl phenyl chalcogenides (sulfide, selenide, and telluride) were prepared from the corresponding bromides. Under aerobic conditions, triethylborane (Et_3B, 0.15 mmol) was added to a solution of 3-cholestanyl phenyl selenide **3** (Chol-SePh, 0.3 mmol) and 1,1,2,2-tetraphenyldisilane ($Ph_4Si_2H_2$, 0.45 mmol) in ethyl acetate (3 ml) at room temperature. After being stirred for 1 h, cholestane was obtained in 99% yield. In another method, Chol-SePh (0.3 mmol), $Ph_4Si_2H_2$ (0.33 mmol), and AIBN (0.15 mmol) in ethyl acetate (3 ml) were stirred under reflux conditions, and 0.15 mmol of AIBN was added after 4 h, 20 h, 27 h and 49 h (total 0.75 mmol). After 65 h, the reaction mixture was evaporated and purified to give cholestane in 52% yield and the recovered Chol-SePh in 36% yield, respectively. This result indicates that the additional AIBN is less effective. However, when the solution of Chol-SePh (0.3 mmol), $Ph_4Si_2H_2$ (0.75 mmol), and AIBN (0.75 mmol) in ethyl acetate (3 ml) was refluxed for 12 h, cholestane was obtained in 87% yield and Chol-SePh was recovered in only 5% yield. Thus, it is important to initiate the radical reduction by excess AIBN, and the reduction of 3-cholestanyl phenyl sulfide **2** and telluride **4** was carried out under the same conditions. The results are shown in Table 1.

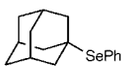
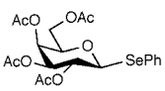
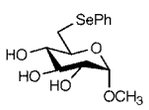
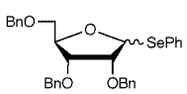
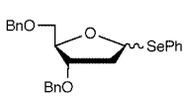
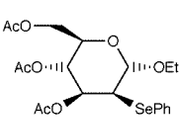
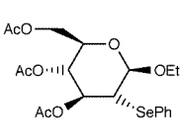
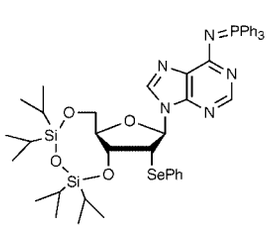
Table 1 Radical reduction of 3-cholestanyl phenyl chalcogenides to cholestane with $Ph_4Si_2H_2$

Entry	3-Chol-XPh	Initiator	Yield[a] (%)
1		Et_3B	20 (79)
2		AIBN	32 (65)
3		Et_3B	99 (0)
4		AIBN	87 (5)
5		Et_3B[b]	9 (91)
6		Et_3B[c]	trace (83)
7		AIBN[c]	trace (89)
8		Et_3B	85 (3)
9		AIBN	82 (5)

[a] Yield of recovered 3-cholestanyl phenyl chalcogenide is shown in parentheses. [b] Ph_2SiH_2 was used instead of $Ph_4Si_2H_2$. [c] Reaction was carried out without $Ph_4Si_2H_2$.

The reduction of 3-cholestanyl phenyl sulfide to cholestane initiated by Et_3B or AIBN did not proceed effectively and the starting sulfide was recovered mainly. However, 3-cholestanyl phenyl selenide and 3-cholestanyl phenyl telluride were reduced in good yields. Use of diphenylsilane instead of $Ph_4Si_2H_2$ for

Table 2 Radical reduction of RSePh to RH

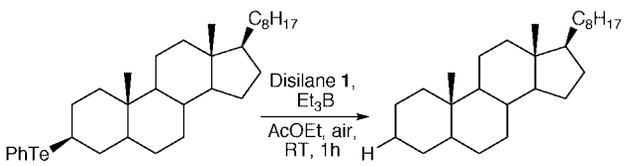
R-SePh		Initiator	Yield (%)
	**5**	Et_3B AIBN	91 100
	**6**	Et_3B AIBN	88 94
	**7**	Et_3B AIBN	91[a] 91[a]
	**8**	Et_3B AIBN	96 23
	**9**	Et_3B AIBN	26 85
	**10**	Et_3B	65
	**11**	Et_3B AIBN	79 98
	**12**	Et_3B AIBN	83 98
	**13**	Et_3B AIBN	63[b] 57[b]

[a] A mixture of direct reduction product and 1,2-rearranged reduction product. [b] A mixture of direct reduction product and *N*-deprotected reduction product ($-NH_2$).

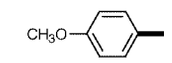
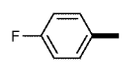
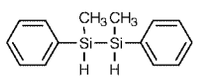
the present radical reduction of Chol-SePh under Et_3B conditions resulted in a poor yield of cholestane. Furthermore, the same radical reduction of Chol-SePh without $Ph_4Si_2H_2$ was carried out under both Et_3B and AIBN conditions. However, the starting Chol-SePh was recovered in high yields. Based on these results, radical reduction of other alkyl phenyl selenides with $Ph_4Si_2H_2$ initiated by Et_3B or AIBN was carried out, and the results are shown in Table 2.

1-Adamantyl phenyl selenide **5**, a tertiary alkyl group, and phenyl 1-tridecyl selenide **6**, a primary alkyl group, were also reduced in high yields, respectively. Then, the radical reduction of various sugar selenides with $Ph_4Si_2H_2$ was carried out. Phenyl 2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-galactopyranoside **7** was reduced in high yields under Et_3B and AIBN conditions, respectively. Here, the reduction product contained a by-product[7] which was generated by the migration of the AcO group from the 2-carbon to the 1-carbon *via* the anomer radical, followed by hydrogen abstraction to give 1,3,4,6-tetra-*O*-acetyl-D-galactose.[8] Methyl 6-deoxy-6-phenylseleno-D-glucopyranoside **8** was reduced in good yield by $Ph_4Si_2H_2$ initiated by Et_3B at room temperature; however, this sugar selenide **8** was reduced in low yield with AIBN under refluxing conditions. Here, side reactions seem to occur at refluxing temperature in ethyl acetate. In contrast to sugar selenide **8**, phenyl 2,3,5-tri-*O*-benzyl-1-seleno-D-ribofuranoside **9** was reduced in good yield by $Ph_4Si_2H_2$ with AIBN at refluxing temperature in ethyl acetate; however, in spite of the complete consumption of the starting selenide, the reduction product was obtained in low yield by $Ph_4Si_2H_2$ with Et_3B at room temperature. Probably, this low reactivity is caused by the steric hindrance of the 2-*O*-benzyl group, since phenyl 3,5-di-*O*-benzyl-2-deoxy-1-seleno-D-ribofuranoside **10** was reduced in moderate yield (65%) under Et_3B conditions. 2-Phenylselenosugars **11** and **12** were also reduced to 2-deoxyglucosides in good yields under both Et_3B and AIBN conditions. Next, the radical reduction of the 2-phenylselenoadenosine derivative was carried out. The reduction products, which were a mixture of a *N*-triphenylphosphinated compound (major) and a dephosphinated compound (minor), were obtained in moderate yields under both conditions.[9] Thus, the radical reduction of alkyl phenyl chalcogenides, especially alkyl phenyl selenides, mediated by $Ph_4Si_2H_2$ proceeded successfully to give the corresponding reduction products in good yields.

Table 3 Reactivities of organodisilanes **1a**–**1d**



Disilane **1**: $Ar_4Si_2H_2$

1a : Ar- = 
1c : Ar- = 
1b : Ar- = 
1d : 

		Yields (%)	
Entry	Disilane **1**	Chol-TePh	Chol-H
1	**1a**	3	85
2	**1b**	2	95
3	**1c**	4	88
4	**1d**	59	24

The radical reactivity of other organodisilanes towards 3-cholestanyl phenyl telluride was next investigated (Table 3). The present tetraaryldisilanes were prepared by the dehydrogenative coupling reaction of the corresponding diarylsilane in the presence of a Ti-complex.[10] The radical reduction of 3-cholestanyl phenyl telluride by organodisilane with Et_3B showed good reactivity for tetraaryldisilanes **1a**–**c**; however, reactivity for 1,2-dimethyl-1,2-diphenyldisilane **1d** was low.

Among the tetraaryldisilanes **1a**–**c**, 1,1,2,2-tetra(4-fluorophenyl)disilane **1b** was the most effective for the radical reduction. However, the use of organodisilane **1a** is practically recommended, since it is readily prepared in the best yield among organodisilanes **1a**–**d**.

Finally, in order to see the electronic effect of the aromatic ring in the radical reduction of alkyl aryl selenides initiated by Et_3B or AIBN, the reactivities of 4-chlorophenyl tridecyl selenide **14**, phenyl tridecyl selenide **6**, and 4-methoxyphenyl tridecyl selenide **15** were compared, as shown in Table 4. However, no remarkable difference in reactivity was observed among the phenyl, 4-methoxyphenyl, and 4-chlorophenyl selenides.

The present radical reductions were carried out in ethyl acetate from the environmental point of view. However, the same treatment of alkyl phenyl selenides in benzene gave the corresponding reduction products in good yields. Thus, radical reduction of Chol-SePh in benzene initiated by AIBN gave

Table 4 Radical reduction of tridecyl aryl selenides with $Ph_4Si_2H_2$

RSe-Ar		Initiator	Yield (%)
$C_{13}H_{27}Se$–C$_6$H$_4$–Cl	**14**	Et_3B	74
		AIBN	94
$C_{13}H_{27}Se$–C$_6$H$_5$	**6**	Et_3B	88
		AIBN	94
$C_{13}H_{27}Se$–C$_6$H$_4$–OCH_3	**15**	Et_3B	80
		AIBN	99

cholestane in 88% yield. An ethanol solvent was not effective under the same treatment. Consequently, it is recommended from the environmental point of view to carry out the radical reaction with organodisilanes in ethyl acetate, instead of benzene.

In conclusion, 1,1,2,2-tetraphenyldisilane is a useful reagent for radical reduction of alkyl aryl selenides and tellurides, since this organodisilane is a less toxic, air-stable, easily handled, mild reagent compared to the known reducing reagents for alkyl aryl selenides such as tin hydride,[11] tris(trimethylsilyl)-silane,[3] Raney Ni, Li-$EtNH_2$ and $NiCl_2{\cdot}6H_2O$–$NaBH_4$.[12] Furthermore, the reaction solvent, ethyl acetate, is environmentally more benign than benzene and toluene.

Experimental

General

^{1}H NMR and ^{13}C NMR spectra were obtained with JEOL-JNM-GSX400, JEOL-JNM-LA-400 and JEOL-JNM-LA-500 spectrometers. Chemical shifts are expressed in ppm downfield from TMS in δ units. Mass spectra were recorded in JEOL-HX-110 and a JEOL-JMS-ATII15 spectrometers, and the source of the K in the FAB MS is KI. IR spectra were measured with a JASCO FT/IR-200 spectrometer. Microanalysis was performed with a Perkin-Elmer 240 elemental analyser at the Chemical Analysis Center of Chiba University. GC spectra were recorded on a Shimadzu GC-8A gas chromatograph with a packed column (OV-17 and SE-30). Melting points were determined on a Yamato melting point apparatus Model MP-21. Wakogel C-200 was used for column chromatography, and Wakogel B-5F was used for PTLC. Column JAIGEL-1HF ($CHCl_3$) and JAIGEL-345-15 (CH_3OH) were used for recycling preparative HPLC (Japan Analytical Industry Co., HPLC-908). Solvents were purified and dried by standard techniques. Disilanes **1a**–**1d** were prepared by the previously reported method.[6,10]

Preparation of alkyl aryl chalcogenides

3β-Cholestanyl phenyl sulfide[13] **(2).** A mixture of 3α-cholestanyl bromide (4.5 mmol), PhSH (10 mmol) and KOH (10 mmol) in hexane–EtOH (4 : 6 ml) was stirred for 2 days at 60 °C. Then, the organic layer was extracted with $CHCl_3$ and dried over Na_2SO_4. The solution was evaporated and the residue was purified by column chromatography to give 3β-cholestanyl phenyl sulfide in 60% yield. Mp 75.5–76.5 °C (lit.,[13] mp 77–79 °C); IR (KBr) 2930, 2845, 1580, 1480, 1460, 1445, 1435, 1380, 1090, 1020, 735, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.59–1.97 (46H, m, cholestanyl), 3.06 (1H, tt, J = 12.2, 4.2 Hz, 3-CH), 7.19–7.30 (3H, m, ArH), 7.38–7.40 (2H, m, ArH); MS (EI) Found: *m*/*z* 480.

3β-Cholestanyl phenyl selenide[14] **(3).** (Typical procedure) A solution of PhSeSePh (1.5 mmol) in EtOH–THF (5 : 5 ml) was treated with $NaBH_4$, until the color of dichalcogenide disappeared. Then, 3α-cholestanyl bromide (3.3 mmol) was added to the solution and stirred overnight at 60 °C. The organic layer was extracted with $CHCl_3$ and dried over Na_2SO_4. The solution was evaporated and the residue was purified by column chromatography to give the selenide in 56% yield. Other selenides and tellurides were prepared by the same procedure. Mp 55.0–56.0 °C; IR (KBr) 2930, 2850, 1580, 1480, 1460, 1445, 1435, 1380, 1070, 1020, 730, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.58–2.01 (46H, m, cholestanyl), 3.19 (1H, tt, J = 12.4, 4.4 Hz, 3-CH), 7.24–7.28 (3H, m, ArH), 7.51–7.55 (2H, m, ArH); MS (EI) Found: *m*/*z* 528.

3β-Cholestanyl phenyl telluride[15] **(4).** 56% yield; oil; IR (Neat) 2930, 2850, 1580, 1470, 1445, 1435, 1380, 1020, 735, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.58–2.05 (46H, m, cholestanyl), 3.38 (1H, tt, J = 12.5, 4.6 Hz, 3-CH), 7.17–7.33 (3H, m, ArH), 7.75–7.81 (2H, m, ArH); MS (EI) Found: *m*/*z* 578.

Phenyl 1-tridecyl selenide (6). 97% yield; oil; IR (KBr) 2920, 2850, 1580, 1480, 1460, 1440, 1075, 1020, 730, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_3-), 1.25 (18H, br s, -CH_2-), 1.39 (2H, br t, J = 7.3 Hz, -CH_2-), 1.70 (2H, quintet, J = 7.5 Hz, -CH_2-), 2.91 (2H, t, J = 7.5 Hz, -CH_2-), 7.21–7.28 (3H, m, ArH), 7.46–7.49 (2H, m, ArH); ^{13}C NMR ($CDCl_3$) δ = 14.2(q), 22.8(t), 28.0(t), 29.2(t), 29.4(t), 29.6(t), 29.7(t), 29.7(t), 29.8(t), 29.9(t), 30.2(t), 32.0(t), 126.7(d), 129.0(d), 130.8(s), 132.4(d); MS (FAB+) Found: *m*/*z* 340; Anal. Calcd for $C_{19}H_{32}Se$: C, 67.23; H, 9.50%. Found: C, 67.23; H, 9.81%.

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-galactopyranoside[16] **(7).** 93% yield; syrup; IR (Neat) 2980, 1750, 1580, 1370, 1230, 1050, 915, 745, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.97 (3H, s, -OAc), 2.04 (3H, s, -OAc), 2.08 (3H, s, -OAc), 2.10 (3H, s, -OAc), 3.89–3.93 (1H, m, 5-CH), 4.10 (1H, dd, J = 11.4, 6.3 Hz, 6-CH), 4.17 (1H, dd, J = 11.4, 7.0 Hz, 6-CH′), 4.91 (1H, d, J = 9.9 Hz, 1-CH), 5.02 (1H, dd, J = 9.9, 3.4 Hz, 3-CH), 5.27 (1H, t, J = 9.9 Hz, 2-CH), 5.42 (1H, dd, J = 3.4, 1.0 Hz, 4-CH), 7.28–7.37 (3H, m, ArH), 7.62–7.64 (2H, m, ArH); MS (FAB+) Found: *m*/*z* (M + K) 527.

Methyl 6-deoxy-6-phenylseleno-α-D-glucopyranoside (8). 92% yield; mp 68.5–70.5 °C; IR (KBr) 3370, 3200, 2930, 2900, 1580, 1435, 1190, 1150, 1115, 1040, 740, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.05 (1H, dd, J = 12.6, 8.7 Hz, 6-CH), 3.31–3.40 (5H, m, -OCH_3, 4-CH and 6-CH), 3.51 (1H, br s, 2-CH), 3.68 (1H, t, J = 9.4 Hz, 3-CH), 3.76 (1H, td, J = 9.0, 2.5 Hz, 5-CH), 4.31 (1H, br s, -OH), 4.63 (1H, br s, -OH), 4.67 (1H, d, J = 3.6 Hz, 1-CH), 5.25 (1H, br s, -OH), 7.16–7.24 (3H, m, ArH), 7.48–7.51 (2H, m, ArH); ^{13}C NMR ($CDCl_3$) δ = 31.7(t), 57.3(q), 73.0(d), 74.2(d), 75.9(d), 76.3(d), 101.2(d), 128.7(d), 131.0(d), 132.8(s), 134.1(d); HRMS (FAB+) Found: *m*/*z* 334.0296, Calcd for $C_{13}H_{18}O_5Se$: M^+ = 334.0320.

4-Chlorophenyl 1-tridecyl selenide (14). 95% yield; mp 44.0–45.0 °C; IR (KBr) 2920, 2850, 1480, 1460, 1390, 1100, 1010, 810, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.9 Hz, CH_3-), 1.25 (18H, br s, -CH_2-), 1.38 (2H, br t, J = 7.2 Hz, -CH_2-), 1.68 (2H, quintet, J = 7.5 Hz, -CH_2-), 2.88 (2H, t, J = 7.5 Hz, -CH_2-), 7.22 (2H, dt, J = 9.0, 2.3 Hz, ArH), 7.40 (2H, dt, J = 9.0, 2.3 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ = 14.2(q), 22.8(t), 28.4(t), 29.1(t), 29.4(t), 29.6(t), 29.6(t), 29.7(t), 29.7(t), 29.8(t), 30.1(t), 32.0(t), 128.9(s), 129.2(d), 132.9(s), 133.9(d); MS (EI) Found: *m*/*z* 374; Anal. Calcd for $C_{19}H_{31}ClSe$: C, 61.04; H, 8.36%. Found: C, 60.82; H, 8.51%.

4-Methoxyphenyl 1-tridecyl selenide (15). 76% yield; mp 47.0–48.0 °C; IR (KBr) 2920, 2850, 1600, 1495, 1290, 1250, 1180, 1035, 810, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.9 Hz, CH_3-), 1.24 (18H, br s, -CH_2-), 1.36 (2H, br t, J = 7.2 Hz, -CH_2-), 1.64 (2H, quintet, J = 7.5 Hz, -CH_2-), 2.81 (2H, t, J = 7.5 Hz, -CH_2-), 3.80 (3H, s, CH_3O-), 6.81 (2H, dt, J = 9.7, 2.5 Hz, ArH), 7.46 (2H, dt, J = 9.7, 2.5 Hz, ArH); ^{13}C NMR

($CDCl_3$) δ = 14.1(q), 22.7(t), 29.1(t), 29.1(t), 29.3(t), 29.5(t), 29.6(t), 29.6(t), 29.7(t), 29.7(t), 30.2(t), 31.9(t), 55.7(q), 114.7(d), 120.3(s), 135.4(d), 159.1(s); MS (EI) Found: *m*/*z* 370; Anal. Calcd for $C_{20}H_{34}OSe$: C, 65.02; H, 9.28%. Found: C, 64.94; H, 9.50%.

1-Adamantyl phenyl selenide[4] (5). This compound was prepared in 49% yield by the literature method.[17] Mp 40.5–43.0 °C (lit.,[4] mp 42–45 °C); IR (KBr) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.61–1.69 (6H, m, adamantyl), 1.97–1.99 (9H, br s, adamantyl), 7.27–7.32 (2H, m, ArH), 7.34–7.38 (1H, m, ArH), 7.60–7.63 (2H, m, ArH); MS (EI) Found: *m*/*z* 292.

Phenyl 2,3,5-tri-*O*-benzyl-1-seleno-D-ribofuranoside (9). Compound **9** was prepared in 18% yield by the literature method.[18] Oil; IR (Neat) 3060, 3030, 2920, 2860, 1580, 1500, 1480, 1455, 1140, 1030, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.56 (1H, dd, *J* = 11.0, 3.6 Hz, 5-CH), 3.63 (1H, dd, *J* = 11.0, 3.3 Hz, 5-CH′), 3.98 (1H, t, *J* = 5.3 Hz, 3-CH), 4.18 (1H, t, *J* = 5.6 Hz, 2-CH), 4.41–4.52 (3H, m, 4-CH and -OC*H*$_2$Ph), 4.55 (1H, d, *J* = 12.2 Hz, -OC*H*$_2$Ph), 4.66 (1H, d, *J* = 11.6 Hz, -OC*H*$_2$Ph), 4.75 (1H, d, *J* = 12.2 Hz, -OC*H*$_2$Ph), 4.80 (1H, d, *J* = 11.6 Hz, -OC*H*$_2$Ph), 6.08 (1H, d, *J* = 5.6 Hz, 1-CH), 7.23–7.35 (16H, m, ArH), 7.40–7.42 (2H, m, ArH), 7.63–7.66 (2H, m, ArH); ^{13}C NMR ($CDCl_3$) δ = 69.0(t), 72.6(t), 73.2(t), 73.4(t), 77.0(d), 78.9(d), 81.1(d), 89.2(d), 126.9(d), 127.6(d), 127.6(d), 127.8(d), 127.8(d), 127.9(d), 128.3(d), 128.3(d), 128.8(d), 131.5(s), 133.5(d), 137.6(s), 138.0(s), 138.1(s); HRMS (FAB+) Found: *m*/*z* (M + K) 599.1050, Calcd for $C_{32}H_{32}O_4SeK$: $(M + K)^+$ = 599.1105.

Phenyl 3,5-di-*O*-benzyl-2-deoxy-1-seleno-D-ribofuranoside (10). Compound **10** was prepared in 5% yield by the literature method.[18] Oil; IR (Neat) 3060, 3030, 2920, 2860, 1580, 1500, 1480, 1455, 1090, 940, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.24 (1H, ddd, *J* = 13.7, 7.7, 6.0 Hz, 2-CH), 2.49 (1H, *J* = 13.7, 6.2, 2.9 Hz, 2-CH′), 3.43 (1H, dd, *J* = 10.0, 6.2 Hz, 5-CH), 3.59 (1H, dd, *J* = 10.0, 5.2 Hz, 5-CH′), 4.09 (1H, ddd, *J* = 6.0, 2.9, 2.6 Hz, 3-CH), 4.29 (1H, ddd, *J* = 6.2, 5.2, 2.6 Hz, 4-CH), 4.48 (1H, d, *J* = 11.9 Hz, -OC*H*$_2$Ph), 4.52 (1H, d, *J* = 11.9 Hz, -OC*H*$_2$Ph), 4.54 (2H, s, -OC*H*$_2$Ph), 5.84 (1H, dd, *J* = 7.7, 6.2 Hz, 1-CH), 7.23–7.36 (13H, m, ArH), 7.59–7.62 (2H, m, ArH); ^{13}C NMR ($CDCl_3$) δ = 41.6(t), 72.7(t), 73.3(t), 75.4(t), 82.3(d), 83.9(d), 86.6(d), 129.5(d), 129.6(d), 129.7(d), 129.7(d), 129.7(d), 130.4(d), 130.4(d), 130.9(d), 131.5(s), 136.2(d), 139.8(s), 140.1(s); HRMS (FAB+) Found: *m*/*z* (M + K) 493.0703. Calcd for $C_{25}H_{26}O_3SeK$: $(M + K)^+$ = 493.0686.

Ethyl 2-deoxy-2-phenylseleno-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (11) and ethyl 2-deoxy-2-phenylseleno-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (12). PhSeBr (3 mmol) was added to the solution of 3,4,6-tri-*O*-acetyl-D-glucal (3.1 mmol) in EtOH (10 ml) at 0–5 °C, then, a small amount of K_2CO_3 was added. The solution was stirred for 3 h at room temperature. After the reaction, the residue was worked up in the usual way to give a mixture of 2-phenylselenosugars (**11**:**12** = 2.4:1) in 23% yield. The stereochemistry of **11** and **12** was determined from ^1H NMR spectra of the reduction products.

11. Mp 91.0–94.0 °C; IR (KBr) 2975, 2910, 2880, 1740, 1580, 1365, 1240, 1125, 1060, 1015, 965, 745, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.23 (3H, t, *J* 7.1 Hz, -OCH$_2$C*H*$_3$), 1.68 (3H, s, -OAc), 2.04 (3H, s, -OAc), 2.13 (3H, s, -OAc), 3.51 (1H, dq, *J* = 9.8, 7.1 Hz, -OC*H*$_2$CH$_3$), 3.71 (1H, dq, *J* = 9.8, 7.1 Hz, -OC*H*$_2$CH$_3$), 3.91 (1H, dd, *J* = 3.9, 1.3 Hz, 3-CH), 3.99 (1H, ddd, *J* = 9.7, 5.0, 2.6 Hz, 5-CH), 4.15 (1H, dd, *J* = 12.1, 2.6 Hz, 6-CH), 4.20 (1H, dd, *J* = 12.1, 5.0 Hz, 6-CH′), 5.19 (1H, d, *J* = 1.3 Hz, 2-CH), 5.41–5.48 (2H, m, 1-CH and 4-CH), 7.24–7.28 (3H, m, ArH), 7.56–7.59 (2H, m, ArH); ^{13}C NMR ($CDCl_3$) δ = 14.9(q), 20.3(q), 20.7(q), 20.7(q), 48.1(d), 62.6(t), 63.7(t), 67.3(d), 68.7(d), 71.0(d), 100.2(d), 127.7(d), 129.1(d), 129.2(s), 134.2(d), 169.6(s), 170.2(s), 170.7(s); HRMS (FAB+) Found: *m*/*z* 474.0799, Calcd for $C_{20}H_{26}O_8Se$: M^+ = 474.0794.

12. Mp 78.5–80.0 °C; IR (KBr) 2980, 2930, 2880, 1745, 1735, 1580, 1380, 1245, 1225, 1155, 1100, 1040, 1020, 920, 745, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.23 (3H, t, *J* = 7.0 Hz, -OCH$_2$C*H*$_3$), 2.00 (3H, s, -OAc), 2.04 (3H, s, -OAc), 2.06 (3H, s, -OAc), 3.13 (1H, dd, *J* = 11.5, 9.1 Hz, 2-CH), 3.49–3.58 (2H, m, 5-CH and -OC*H*$_2$CH$_3$), 3.91 (1H, dq, *J* = 9.2, 7.1 Hz, -OC*H*$_2$CH$_3$), 4.07 (1H, dd, *J* = 12.1, 2.4 Hz, 6-CH), 4.26 (1H, dd, *J* = 12.1, 5.0 Hz, 6-CH′), 4.27 (1H, d, *J* = 9.1 Hz, 1-CH), 4.98 (1H, dd, *J* = 9.9, 9.2 Hz, 4-CH), 5.14 (1H, dd, *J* = 11.5, 9.2 Hz, 3-CH), 7.25–7.35 (3H, m, ArH), 7.64–7.66 (2H, m, ArH); ^{13}C NMR ($CDCl_3$) δ = 15.0(q), 20.7(q), 20.7(q), 20.8(q), 47.8(d), 62.3(t), 65.9(t), 69.9(d), 71.5(d), 72.8(d), 102.6(d), 126.7(s), 128.4(d), 129.1(d), 136.0(d), 169.7(s), 170.3(s), 170.8(s); HRMS (FAB+) Found: *m*/*z* 474.0784, Calcd for $C_{20}H_{26}O_8Se$: M^+ = 474.0794.

2′-Deoxy-2′-phenylseleno-3′,5′-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-*N*-(triphenylphosphoranylidene)adenosine (13). This compound was prepared in 31% yield from the 2′-iodoadenosine derivative by the typical procedure at room temperature. 2′-Iodoadenosine derivative was prepared from 3′,5′-*O*-protected adenosine by the literature method.[19] Viscous oil; IR (KBr) 3060, 2945, 2865, 1580, 1450, 1440, 1360, 1290, 1115, 1035, 885, 720, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.99–1.19 (28H, m, isopropyl), 4.00–4.21 (3H, m, 4′-CH and 5′-CH), 4.74 (1H, dd, *J* = 7.5, 5.0 Hz, 2′-CH), 5.29 (1H, dd, *J* = 7.5, 5.8 Hz, 3′-CH), 6.07 (1H, d, *J* = 5.0 Hz, 1′-CH), 6.94–6.96 (3H, m, ArH), 7.30–7.33 (2H, m, ArH), 7.36 (1H, s, ArH), 7.42–7.56 (9H, m, ArH), 7.86–7.92 (7H, m, ArH); ^{13}C NMR ($CDCl_3$) δ = 14.7(d), 14.9(d), 15.3(d), 15.5(d), 19.0(q), 19.1(q), 19.1(q), 19.3(q), 19.4(q), 19.4(q), 19.5(q), 51.6(d), 65.2(t), 75.3(d), 86.8(d), 92.7(d), 128.9(s), 129.3(s), 129.5(s), 129.8(d), 130.3(d), 130.4(d), 130.6(s), 130.9(d), 131.4(s), 133.9(d), 133.9(d), 135.3(d), 135.4(d), 136.9(d), 140.4(d), 151.2(s), 153.7(d), 162.9(s); HRMS (FAB+) Found: *m*/*z* (M + H) 910.2874, Calcd for $C_{46}H_{57}N_5O_4PSeSi_2$: $(M + H)^+$ = 910.2858.

Radical reduction initiated by Et_3B

Triethylborane in tetrahydropyran (0.15 ml, 1 M) was added to a mixture of alkyl phenyl chalcogenide (0.30 mmol) and organodisilane (0.45 mmol) in ethyl acetate (3.0 ml) under aerobic conditions at room temperature, and the reaction mixture was stirred for 1 h. The reaction of selenides **8**, **9** and **13** was initiated by 1.2 mmol of Et_3B. In the reactions of selenides **10** and **11**, the starting selenides remained after 1 h, so Et_3B was added again to consume the compounds **10** and **11**. After the reaction, the solvent was evaporated and the residue was purified by PTLC, and column chromatography, and recycling preparative HPLC.

Radical reduction initiated by AIBN

A solution of alkyl phenyl chalcogenide (0.30 mmol), organodisilane (0.75 mmol) and AIBN (0.75 mmol) in ethyl acetate (3.0 ml) was refluxed for 14 h under an argon atmosphere. After the reaction, the solvent was evaporated and the residue was purified by PTLC, and column chromatography, and recycling preparative HPLC.

Cholestane, adamantane, *n*-tridecane and methyl 6-deoxy-α-D-glucopyranoside

These compounds were identified with the authentic samples.[6]

1,5-Anhydro-2,3,4,6-tetra-*O*-acetyl-D-galactitol[20]

Syrup; IR (Neat) 2980, 2870, 1750, 1435, 1370, 1240, 1050, 955,

905 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.01 (3H, s, -OAc), 2.05 (3H, s, -OAc), 2.06 (3H, s, -OAc), 2.15 (3H, s, -OAc), 3.29 (1H, dd, J = 11.2, 10.3 Hz, 1-CH), 3.82 (1H, td, J = 6.5, 1.2 Hz, 5-CH), 4.09 (2H, d, J = 6.5 Hz, 6-CH), 4.19 (1H, dd, J = 11.2, 5.5 Hz, 1-CH′), 5.04 (1H, dd, J = 10.3, 3.4 Hz, 3-CH), 5.23 (1H, td, J = 10.3, 5.5 Hz, 2-CH), 5.45 (1H, dd, J = 3.4, 1.2 Hz, 4-CH); MS (FAB+) Found: *m*/*z* (M + H) 333.

1,4-Anhydro-2,3,5-tri-*O*-benzyl-D-ribitol[21]

Oil; IR (Neat) 3060, 3030, 2870, 1495, 1455, 1360, 1210, 1125, 1030, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.51 (1H, dd, J = 10.6, 4.3 Hz, 5-CH), 3.62 (1H, dd, J = 10.6, 3.3 Hz, 5-CH′), 3.91–4.09 (4H, m, 1-CH, 2-CH and 3-CH), 4.14–4.17 (1H, m, 4-CH), 4.49–4.64 (6H, m, -OCH_2Ph), 7.24–7.36 (15H, m, ArH); MS (FAB+) Found: *m*/*z* (M + K) 443.

1,4-Anhydro-2-deoxy-3,5-di-*O*-benzyl-D-erythropentitol[22]

Syrup; IR (Neat) 3060, 3030, 2860, 1495, 1455, 1365, 1205, 1100, 1030, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.00–2.04 (2H, m, 2-CH), 3.48 (1H, dd, J = 10.1, 5.1 Hz, 5-CH), 3.53 (1H, dd, J = 10.1, 5.1 Hz, 5-CH′), 3.90–4.10 (4H, m, 1-CH, 3-CH and 4-CH), 4.49 (1H, d, J = 12.1 Hz, -OCH_2Ph), 4.53 (1H, d, J = 12.1 Hz, -OCH_2Ph), 4.55 (2H, s, -OCH_2Ph), 7.26–7.38 (10H, m, ArH); ^{13}C NMR ($CDCl_3$) δ = 32.7(t), 67.7(t), 71.0(t), 71.4(t), 73.6(t), 80.9(d), 83.2(d), 127.8(d), 127.8(d), 127.8(d), 128.5(d), 128.6(d), 138.3(s); MS (FAB+) Found: *m*/*z* (M + K) 337.

Ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-α-D-arabinohexopyranoside[23]

Oil; IR (Neat) 2980, 1745, 1440, 1370, 1240, 1130, 1050, 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.22 (3H, t, J = 7.1 Hz, -OCH$_2$CH_3), 1.82 (1H, ddd, J = 12.8, 11.5, 3.7 Hz, 2-CH), 2.01 (3H, s, -OAc), 2.04 (3H, s, -OAc), 2.10 (3H, s, -OAc), 2.23 (1H, ddd, J = 12.8, 5.4, 1.2 Hz, 2-CH′), 3.46 (1H, dq, J = 9.7, 7.1 Hz, -OCH_2CH$_3$), 3.69 (1H, dq, J = 9.7, 7.1 Hz, -OCH_2CH$_3$), 3.98 (1H, ddd, J = 10.1, 4.6, 2.3 Hz, 5-CH), 4.05 (1H, dd, J = 12.1, 2.3 Hz, 6-CH), 4.31 (1H, dd, J = 12.1, 4.6 Hz, 6-CH′), 4.96–5.02 (2H, m, 1-CH and 4-CH), 5.34 (1H, ddd, J = 11.5, 9.5, 5.4 Hz, 3-CH); MS (FAB+) Found: *m*/*z* (M − OEt) 273.

Ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-β-D-arabinohexopyranoside[24]

Mp 83.5–84.5 °C (lit.,[24] mp 80–81 °C); IR (KBr) 3000, 2975, 2895, 1740, 1440, 1380, 1230, 1140, 1095, 1050, 960, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.23 (3H, t, J = 7.1 Hz, -OCH$_2$CH_3), 1.75 (1H, ddd, J = 12.6, 11.5, 9.8 Hz, 2-CH), 2.03 (3H, s, -OAc), 2.04 (3H, s, -OAc), 2.09 (3H, s, -OAc), 2.31 (1H, ddd, J = 12.6, 4.8, 2.2 Hz, 2-CH′), 3.52–3.63 (2H, m, 5-CH and -OCH_2CH$_3$), 3.94 (1H, dq, J = 9.5, 7.1 Hz, -OCH_2CH$_3$), 4.11 (1H, dd, J = 12.2, 2.5 Hz, 6-CH), 4.30 (1H, dd, J = 12.2, 4.8 Hz, 6-CH′), 4.58 (1H, dd, J = 9.8, 2.2 Hz, 1-CH), 4.96–5.06 (2H, m, 3-CH and 4-CH); MS (FAB+) Found: *m*/*z* (M − OEt) 273.

2′-Deoxy-3′,5′-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-*N*-(triphenylphosphoranylidene)adenosine

Viscous oil; IR (KBr) 3060, 2945, 2865, 1580, 1450, 1440, 1355, 1285, 1110, 1080, 1035, 885, 720, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.01–1.11 (28H, m, isopropyl), 2.59 (1H, ddd, J = 13.2, 8.5, 7.6 Hz, 2′-CH), 2.67 (1H, ddd, J = 13.2, 7.5, 2.9 Hz, 2′-CH′), 3.87 (1H, d br t, J = 7.2, 4.4 Hz, 4′-CH), 4.02 (1H, d, J = 4.8 Hz, 5′-CH), 4.02 (1H, d, J = 3.9 Hz, 5′-CH′), 4.94 (1H, m, 3′-CH), 6.27 (1H, dd, J = 7.6, 2.9 Hz, 1′-CH), 7.42–7.55 (9H, m, ArH), 7.87–7.93 (6H, m, ArH), 7.96 (1H, s, ArH), 8.05 (1H, s, ArH); ^{13}C NMR ($CDCl_3$) δ = 12.6(d), 13.0(d), 13.2(d), 13.4(d), 17.0(q), 17.0(q), 17.1(q), 17.2(q), 17.4(q), 17.4(q), 17.5(q), 17.6(q), 40.3(t), 62.5(t), 70.8(d), 82.8(d), 85.1(d), 127.1(s), 127.3(s), 128.4(d), 128.5(d), 128.6(s), 129.4(s), 131.9(d), 131.9(d), 133.4(d), 133.4(d), 137.6(d), 149.3(s), 152.0(d), 161.1(s); HRMS (FAB+) Found: *m*/*z* (M + H) 754.3322, Calcd for $C_{40}H_{53}N_5O_4PSi_2$: (M + H)$^+$ = 754.3374.

2′-Deoxy-3′,5′-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-adenosine[25]

Viscous oil; IR (KBr) 3330, 3170, 2945, 2865, 1650, 1600, 1465, 1250, 1140, 1120, 1090, 1075, 1040, 885, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.02–1.13 (28H, m, isopropyl), 2.64 (1H, ddd, J = 13.3, 9.1, 7.4 Hz, 2′-CH), 2.71 (1H, ddd, J = 13.3, 7.5, 2.7 Hz, 2′-CH′), 3.90 (1H, ddd, J = 7.5, 4.4, 3.5 Hz, 4′-CH), 4.03 (1H, dd, J = 12.4, 3.5 Hz, 5′-CH), 4.07 (1H, dd, J = 12.4, 4.4 Hz, 5′-CH′), 4.95 (1H, dt, J = 9.1, 7.5 Hz, 3′-CH), 5.67 (2H, br s, -NH_2), 6.29 (1H, dd, J = 7.4, 2.7 Hz, 1′-CH), 8.04 (1H, s, ArH), 8.32 (1H, s, ArH); HRMS (FAB+) Found: *m*/*z* (M + H) 494.2607, Calcd for $C_{22}H_{40}N_5O_4Si_2$: (M + H)$^+$ = 494.2619.

Acknowledgements

We are grateful for financial support from a Grant-in-Aid for Scientific Research (10640511) from the Ministry of Education, Science, and Culture of Japan. We thank Mr Atushi Ryokawa for the partial preparation of organodisilanes.

Notes and references

1 B. Giese, *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*, ed. J. E. Baldwin, Pergamon Press, Oxford, 1986; J. Fossey, D. Lefort and J. Sorba, *Free Radicals in Organic Chemistry*, Wiley, Chichester, 1995.
2 C. Chatgilialoglu, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1982, **104**, 5123; J. Lusztyk, B. Maillard and K. U. Ingold, *J. Org. Chem.*, 1986, **51**, 2457; B. Giese, B. Kopping and C. Chatgilialoglu, *Tetrahedron Lett.*, 1989, **30**, 681; B. Giese and K. J. Kulicke, *Synlett*, 1990, 91; D. H. R. Barton, D. O. Jang and J. Cs. Jaszberenyi, *Tetrahedron Lett.*, 1990, **31**, 4681; A. Alberti and C. Chatgilialoglu, *Tetrahedron*, 1990, **46**, 3963; S. J. Cole, J. N. Kirwan, B. P. Roberts and C. R. Willis, *J. Chem. Soc., Perkin Trans. 1*, 1991, 103; D. H. R. Barton, D. O. Jang and J. Cs. Jaszberenyi, *Synlett*, 1991, 435; D. H. R. Barton, D. O. Jang and J. Cs. Jaszberenyi, *Tetrahedron Lett.*, 1991, **32**, 2569; D. H. R. Barton, D. O. Jang and J. Cs. Jaszberenyi, *Tetrahedron Let.*, 1991, **32**, 7187; C. Chatgilialoglu, *Acc. Chem. Res.*, 1992, **25**, 188; C. Chatgilialoglu, *Chem. Rev.*, 1995, **95**, 1229; M. B. Haque and B. P. Roberts, *Tetrahedron Lett.*, 1996, **37**, 9123.
3 M. Ballestri, C. Chatgilialoglu, K. B. Clark, D. Griller, B. Giese and B. Kopping, *J. Org. Chem.*, 1991, **56**, 678.
4 D. H. R. Barton, D. O. Jang and J. Cs. Jaszberenyi, *Tetrahedron*, 1993, **49**, 7193.
5 O. Yamazaki, H. Togo, G. Nogami and M. Yokoyama, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 2519.
6 O. Yamazaki, H. Togo, S. Matsubayashi and M. Yokoyama, *Tetrahedron Lett.*, 1998, **39**, 1921; O. Yamazaki, H. Togo, S. Matsubayashi and M. Yokoyama, *Tetrahedron*, 1999, **55**, 3735.
7 A mixture of 1-deoxy derivative (**A**) and 2-deoxy derivative (**B**) was obtained as reduction products. The ratios of **A** and **B** were determined to be 92:8 (Et_3B) and 72:28 (AIBN) from ^{1}H NMR spectra, respectively.
8 H.-G. Korth, R. Sustmann, K. S. Gröninger, M. Leisung and B. Giese, *J. Org. Chem.*, 1988, **53**, 4364.
9 Direct reduction product (**C**) and *N*-deprotected reduction product (**D**) was obtained. The ratios of **C** and **D** were 95:5 (Et_3B) and 82:18 (AIBN), respectively.
10 T. Nakano, H. Nakamura and Y. Nagai, *Chem. Lett.*, 1989, 83.
11 D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Munchen, C. G. Russell, A. Singh, C. K. Wong and N. J. Curtis, *J. Am. Chem. Soc.*, 1980, **102**, 4438.
12 T. G. Back, V. I. Birss, M. Edwards and M. V. Krishna, *J. Org. Chem.*, 1988, **53**, 3815.
13 T. G. Back, D. L. Baron and K. Yang, *J. Org. Chem.*, 1993, **58**, 2407.
14 M. Sakakibara, K. Katsumata, Y. Watanabe, T. Toru and Y. Ueno, *Synthesis*, 1992, 377.
15 M. A. Lucas and C. H. Schiesser, *J. Org. Chem.*, 1996, **61**, 5754.
16 A. Mallet, J.-M. Mallet and P. Sinaÿ, *Tetrahedron: Asymmetry*, 1994, **5**, 2593.
17 H. Togo, T. Muraki and M. Yokoyama, *Synthesis*, 1995, 155.
18 W. He, H. Togo, Y. Waki and M. Yokoyama, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2425.

19 P. J. Garegg and B. Samuelsson, *J. Chem. Soc.*, *Perkin Trans. 1*, 1980, 2866.
20 J. A. Bennek and G. R. Gray, *J. Org. Chem.*, 1987, **52**, 892.
21 P. Heath, J. Mann, B. Walsh and A. H. Wadsworth, *J. Chem. Soc.*, *Perkin Trans. 1*, 1983, 2675.
22 M. Sato, *Nippon Kagaku Kaishi*, 1997, 508.
23 K. Tatsuta, K. Fujimoto, M. Kinoshita and S. Umezawa, *Carbohydr. Res.*, 1997, **54**, 85.
24 M. Michalska and J. Borowiecka, *J. Carbohydr. Chem.*, 1983, **2**, 99.
25 M. Oba and K. Nishiyama, *Tetrahedron*, 1994, **50**, 10193.

Paper 9/05937G