Deoxygenative Functionalization of Hydroxy Groups via Xanthates with Tetraphenyldisilane

Hideo Togo,*,†,‡ Sou Matsubayashi,† Osamu Yamazaki,† and Masataka Yokoyama†,‡

Graduate School of Science and Technology, and Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba, 263-8522, Japan

Received November 2, 1999

Deoxygenation reactions of hydroxy groups in carbohydrates, nucleosides, and antibiotics are very important due to their functional conversion. Today, the most effective and practical deoxygenation method of hydroxy groups is the Barton−McCombie reaction, which is the reaction of xanthates with a tributyltin hydride/AIBN or tributyltin hydride/Et_3B system[1] or, recently, phenylsilane or diphenylsilane in the presence of peroxide or Et_3B,[2] trialkylsilane in the presence of peroxide/thiol (polarity reversal catalyst),[3] 5,10-dihydrosilanthrene/AIBN,[4] tris(trimethylsilyl)silane/AIBN,[5] dibutylphosphine oxide/AIBN or Et_3B,[6] or phosphine-borane/AIBN.[7] The Barton−McCombie reaction and the modified Barton−McCombie reaction with alternative reagents have found widespread use in organic synthesis. However, it is well-known that there are several problems in the use of tributyltin hydride, such as toxicity and disposal, workup, and complete removal of the tin species from the products. Phenylsilane, diphenylsilane, and dibutylphosphine oxide are not so reactive, though these compounds are much less toxic than the tin compound. Moreover, these systems are limited to the deoxygenation reaction. To our knowledge, only a few reports for the intermolecular addition reaction of sugar xanthate to electron deficient olefins with tributyltin hydride in moderate yields have been made.[8] Recently, we have reported the utilization of tetraaryl disilanes, which are air-stable crystals, for three types of radical reactions with alkyl bromides, such as reduction, reductive addition to olefins, and alkylation of heteroaromatic bases.[9] Here, as part of our program to develop the synthetic use of tetraaryl disilanes for organic synthesis as an environmentally benign system, we would like to report a new deoxygenative formation of alkyl radicals from alcohols via xanthates, and their reduction to the corresponding hydrocarbons, reductive addition to an activated olefin, and alkylation of heteroaromatic bases, with tetraphenyldisilane as shown in Figure 1.

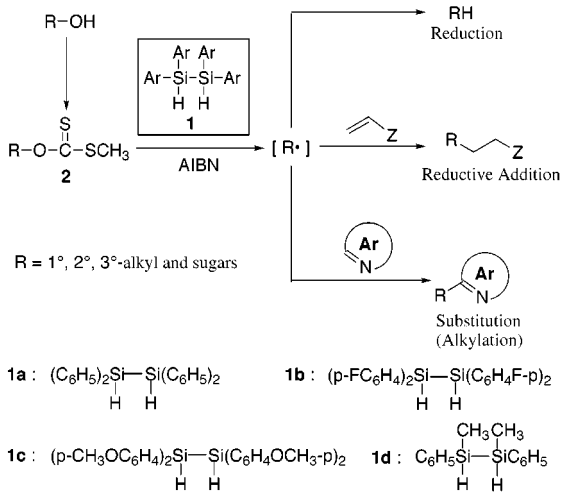


Figure 1.

At first, reactivities of disilanes **1a**−**d** in the reduction of xanthate **2** derived from diacetone-D-glucose, in the presence of AIBN in ethyl acetate were studied (entries 2−5). Disilanes **1a**, **1b**, and **1d** showed excellent reactivity, while disilane **1c** showed moderate reactivity as shown in Table 1. Thus, disilanes **1a**, **1b**, and **1d** are the most effective reagent for the deoxygenative reduction of xanthates **2**. However, the preparation of disilane **1a** is much easier and more practical than that of disilanes **1b**−**d**. Thus, disilane **1a** was used for the deoxygenative reduction of other xanthates **2**, which were derived from tertiary and secondary alcohols, and sugar compounds, to give the corresponding reduction products in good yields, though the same reaction of xanthate derived from tridecanol, a primary alcohol, gave the reduction product in moderate yield (entry 15). An imidazole thiocarbonyl group can be also used instead of a methyl dithiocarbonate group (entries 6 and 13). The present radical reaction was carried out in ethyl acetate from the environmental point of view. However, the same treatment of xanthates in benzene gave the corresponding reduction product in

* To whom correspondence should be addressed. E-mail: togo@scichem.s.chiba-u.ac.jp.

† Graduate School of Science and Technology.

‡ Department of Chemistry.

(1) (a) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574. (b) Barton, D. H. R.; Motherwell, W. B.; Stange, A. *Synthesis* **1981**, 743. (c) Rasmussen, J. R.; Slinger, C. J.; Kordish, R. J.; Newman-Evans, D. D. *J. Org. Chem.* **1981**, *46*, 4843. (d) Barton, D. H. R.; Hartwig, W.; Hay-Motherwell, R. S.; Motherwell, W. B.; Stange, A. *Tetrahedron Lett.* **1982**, *23*, 2019. (e) Robins, M. J.; Wilson, J. S.; Hansske, F. *J. Am. Chem. Soc.* **1983**, *105*, 4059. (f) Barton, D. H. R.; Crich, D.; Lobberding, A.; Zard, S. Z. *Chem. Commun.* **1985**, 646. (g) Barton, D. H. R.; Crich, D.; Lobberding, A.; Zard, S. Z. *Tetrahedron* **1986**, *42*, 2329. (h) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, 29, 6125. (i) Barton, D. H. R.; Jaszberenyi, J. C. *Tetrahedron Lett.* **1989**, *30*, 2619. (j) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *Tetrahedron Lett.* **1990**, *31*, 3991. (k) Barton, D. H. R.; Parekh, S. I.; Tse, C.-L. *Tetrahedron Lett.* **1993**, *34*, 2733.

(2) (a) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *Tetrahedron Lett.* **1990**, *31*, 4681. (b) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *Synlett* **1991**, 435.

(3) (a) Cole, S. J.; Kirwan, J. N.; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 103. (b) Allen, R. P.; Roberts, B. P.; Willis, C. R. *Chem. Commun.* **1989**, 1387.

(4) Gimisis, T.; Ballestri, M.; Ferreri, C.; Chatgilialoglu, C. *Tetrahedron Lett.* **1995**, *36*, 3897.

(5) Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188.

(6) (a) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *Tetrahedron Lett.* **1992**, *33*, 5709. (b) Jang, D. O.; Cho, D. H.; Barton, D. H. R. *Synlett* **1998**, 39.

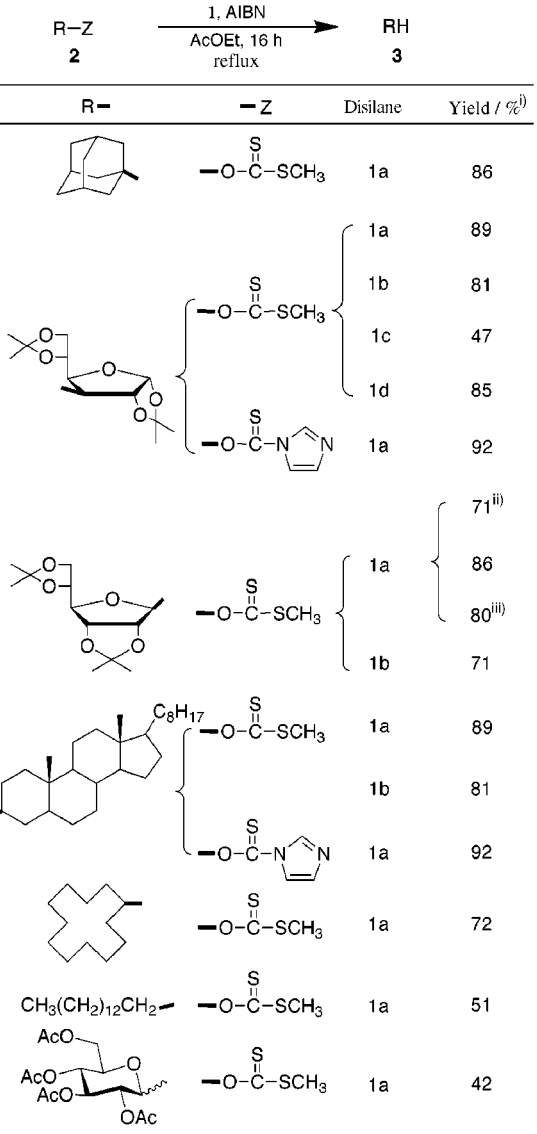
(7) Barton, D. H. R.; Jacob, M. *Tetrahedron Lett.* **1998**, *39*, 1331.

(8) (a) Giese, B.; Antonio, J.; Gomez, G.; Witzel, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 69. (b) Dupuis, J.; Giese, B.; Hartung, J.; Leising, M. *J. Am. Chem. Soc.* **1985**, *107*, 4332. (c) Araki, Y.; Endo, T.; Tanji, M.; Nagasawa, J.; Ishido, Y. *Tetrahedron Lett.* **1987**, *28*, 5853. (d) Blattner, R.; Ferrier, R. J.; Renner, R. *J. Chem. Soc., Chem. Commun.* **1987**, 1007. (e) Araki, Y. Endo, T.; Tanji, M.; Nagasawa, J.; Ishido, Y. *Tetrahedron Lett.* **1988**, *29*, 351.

(9) (a) Yamazaki, O.; Togo, H.; Matsubayashi, S.; Yokoyama, M. *Tetrahedron Lett.* **1998**, *39*, 1921. (b) Yamazaki, O.; Togo, H.; Matsubayashi, S.; Yokoyama, M. *Tetrahedron* **1999**, *55*, 3735.

10.1021/jo991715r CCC: $19.00
Published on Web 04/05/2000

Table 1. Reduction of Xanthates with Disilanes[a]



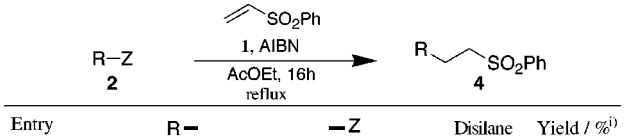
Entry	R–	–Z	Disilane	Yield / %[i)]
1		–O–C(=S)–SCH$_3$	1a	86
2			1a	89
3			1b	81
4		–O–C(=S)–SCH$_3$	1c	47
5			1d	85
6		–O–C(=S)–N(imidazole)	1a	92
7				71[ii)]
8			1a	86
9		–O–C(=S)–SCH$_3$		80[iii)]
10			1b	71
11	C_8H_{17}		1a	89
12		–O–C(=S)–SCH$_3$	1b	81
13		–O–C(=S)–N(imidazole)	1a	92
14		–O–C(=S)–SCH$_3$	1a	72
15	$CH_3(CH_2)_{12}CH_2$–	–O–C(=S)–SCH$_3$	1a	51
16	AcO, AcO, AcO, OAc	–O–C(=S)–SCH$_3$	1a	42

[a] Key: (i) xanthate/disilane/AIBN = 0.20/0.22/0.06 (mmol); (ii) reaction was carried out in benzene, instead of ethyl acetate; (iii) reaction was carried out at room temperature with triethylborane (1.2 mmol), instead of AIBN.

good yields (entry 7). Moreover, the same reduction of xanthate in the presence of disilane **1a** at room temperature using triethylborane, instead of AIBN, proceeded effectively to give the corresponding reduction product in good yield (entry 9). As a typical addition reaction, the addition reaction of xanthates **2** to phenylvinyl sulfone under the same system was carried out. The results are shown in Table 2. Disilanes **1a** and **1b** showed moderate reactivity to give the corresponding reductive addition products in moderate yields, while disilanes **1c** and **1d** were not so effective (entries 3−6). The reductive addition of other xanthates **2** to phenylvinyl sulfone using disilane **1a** in the presence of AIBN was carried out to give the corresponding reductive addition products in moderate yields, together with the reduction products **3** (20−42%). Diethylvinyl phosphonate also showed the same reactivity.

Finally, in the alkylation (substitution) of heteroaromatic bases, the alkylation of typical heteroaromatic bases with tetraphenyldisilane and xanthates in the presence of AIBN was carried out to give the corresponding alkylated compounds **5** in moderate yields, though again the same reactions with xanthates derived from primary alcohols gave poor results. Here the formation of reduction products **3** as a byproduct was observed (24−46%).

Table 2. Reductive Addition to Phenyl Vinyl Sulfone[a]



Entry	R–	–Z	Disilane	Yield / %[i)]
1		–O–C(=S)–SCH$_3$	1a	71
2			1a	69
3			1a	44
4		–O–C(=S)–SCH$_3$	1b	47
5	C_8H_{17}		1c	22
6			1d	31
7		–O–C(=S)–N(imidazole)	1a	51
8		–O–C(=S)–SCH$_3$	1a	52
9		–O–C(=S)–SCH$_3$	1a	38
10	$CH_3(CH_2)_7$–	–O–C(=S)–SCH$_3$	1a	30

[a] Key: (i) xanthate/olefin/disilane/AIBN = 0.2/0.6/0.5/0.1 (mmol).

In conclusion, the present three types of deoxygenative reactions, such as reduction, reductive addition to electron-deficient olefins, and alkylation of heteroaromatic bases with xanthates in the presence of tetraphenyldisilane and AIBN have been achieved in ethyl acetate, as an environmentally benign system.

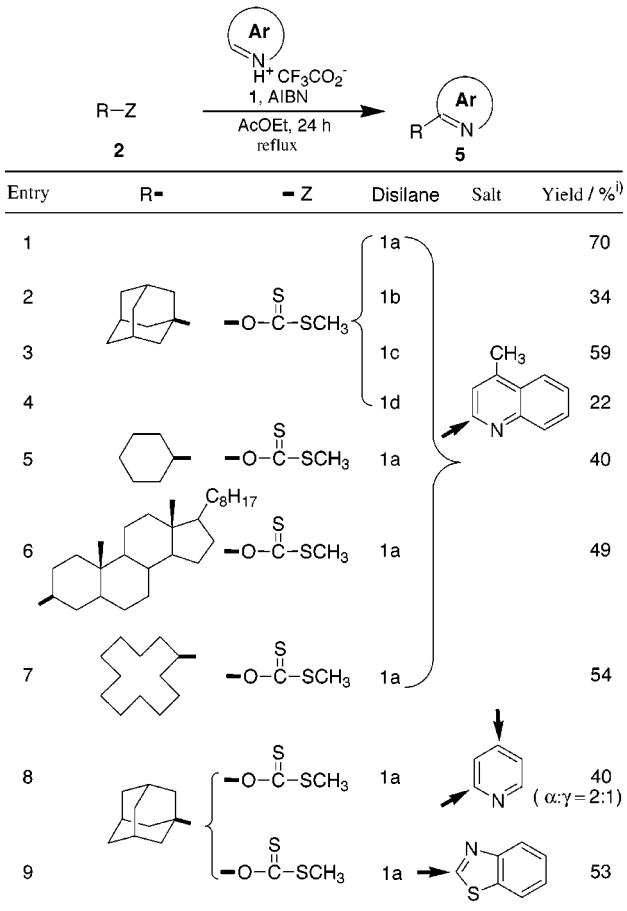
Experimental Section

General Methods. ^{1}H NMR and ^{29}Si NMR spectra were recorded on 400 and 500 MHz spectrometers, and ^{13}C NMR spectra were recorded on 100 and 125 MHz spectrometers. Chemical shifts are reported as ppm downfield from tetramethylsilane (TMS) in δ units. J values are given in Hz. The matrix of mass spectra (FAB) used 3-nitrobenzyl alcohol, and the source of the K in the FAB MS was KI. Microanalysis was performed at the Chemical Analysis Center of Chiba University. GC spectra were recorded with packed column (OV-17 and SE-30). Melting points were determined on an electrochemical apparatus in open capillary tubes and are uncorrected. Kieselgel 60 F254 was used for TLC, Wakogel C-200 was used for column chromatography, and Wakogel B-5F was used for pTLC.

Materials. Most of the alkyl halides and simple organic chemicals were commercially available. The following compounds were prepared according to the procedures described in the literature.

Tetraphenyldisilane: mp 76.5−80.5 °C (lit.[10] mp 79−80 °C); IR 2120 cm^{-1} (SiH); ($CDCl_3$, TMS) ^{1}H NMR δ = 5.19 (s, SiH), ^{29}Si NMR δ = −34.96. Tetra(*p*-methoxyphenyl)disilane: mp 122.1−124.3 °C; IR 2100 cm^{-1} (SiH); ($CDCl_3$, TMS) ^{1}H NMR δ = 5.12 (s, SiH), ^{29}Si NMR δ = −36.45. Tetra(*p*-fluorophenyl)-

Table 3. Alkylation onto Heteroaromatic Bases[a]



[a] Key: (i) xanthate/salt/**1a**/AIBN = 0.2/1.0/0.5/0.5 (mmol); →, C−C bond-forming position.

disilane: mp 105.1−106.0 (lit.[10] mp 116 °C); IR 2115 cm^{-1} (SiH) ^1H NMR δ = 5.15 (s, SiH), ^{29}Si NMR δ = −35.55. Diphenyldimethyldisilane: oil; IR 2110 cm^{-1} (SiH); ($CDCl_3$, TMS) ^1H NMR δ = 4.36−4.44 (m, SiH), ^{29}Si NMR δ = −36.37 and −36.80.

General Procedure for the Preparation of Xanthates from the Corresponding Alcohols. A mixture of alcohol (10 mmol), sodium hydride (60%; 29.2 mmol), and imidazole (0.29 mmol) in tetrahydrofuran (50 mL) was stirred for 3 h under an argon atmosphere at room temperature. Carbon disulfide (49.9 mmol) was added and the mixture stirred for 0.5 h. Then, methyl iodide (48.2 mmol) was added and the mixture stirred for 0.5 h. The reaction mixture was quenched with acetic acid (52. 4 mmol), and the resulting solution was worked up in the usual way. The organic layer was extracted with ethyl acetate and dried over Na_2SO_4. After removal of solvent, the residue was purified by pTLC or column chromatography on silica gel to give the xanthate in quantitative yield.

General Procedure for Radical Reduction with Organodisilanes. A solution of xanthate (0.2 mmol), tetraphenyldisilane (0.22 mmol), and AIBN (0.06 mmol) in ethyl acetate (1.5 mL) was refluxed for 16 h under an argon atmosphere. After the reaction, the solvent was removed, and the residue was chromatographed on silica gel.

General Procedure for Radical Addition to Phenyl Vinyl Sulfone with Organodisilanes under Thermal Conditions. A mixture of xanthate (0.2 mmol), phenyl vinyl sulfone (0.6 mmol), organodisilane (0.5 mmol), and AIBN (0.1 mmol) in ethyl acetate (1.5 mL) was stirred for 16 h at refluxing temperature under an argon atmosphere. After the reaction, solvent was removed and the residue was purified by pTLC or column chromatography on silica gel.

General Procedure for Alkylation of Heteroaromatic Bases with Organodisilane and AIBN under Thermal Conditions. AIBN (0.1 mmol) was added five times over 8 h (2 h intervals) to a solution of a heteroaromatic base (1.0 mmol), xanthate (0.2 mmol), and organodisilane (0.5 mmol) in ethyl acetate at refluxing temperature. Then, the solution was stirred for 16 h at the same temperature. The resulting solution was quenched with saturated aqueous sodium hydrogen carbonate. The organic layer was extracted with ethyl acetate and dried over Na_2SO_4. After removal of the solvent, the residue was purified by pTLC or column chromatography on silica gel.

Cholestane: mp 77.5−79.0 °C; IR (KBr) 2930, 2850, 1470, 1440, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.61−1.98 (33H, m), 0.64 (3H, s), 0.77 (3H, s), 0.85 (3H, d, J = 1.7 Hz), 0.87 (3H, d, J = 1.7 Hz), 0.90 (3H, d, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 12.09 (p), 12.24 (p), 18.68 (p), 20.82 (s), 22.21 (s), 22.58 (p), 22.83 (p), 23.85 (s), 24.20 (s), 26.87 (s), 28.02 (t), 28.27 (s), 29.08 (s), 29.12 (s), 32.20 (s), 35.54 (t), 35.82 (t), 36.19 (s), 36.25 (q), 38.71 (s), 39.53 (s), 40.14 (s), 42.60 (q), 47.05 (t), 54.78 (t), 56.31 (t), 56.65 (t). Anal. Calcd for $C_{27}H_{48}$: C, 87.02; H, 12.98. Found: C, 86.91; H, 13.13.

2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-D-glucitol: mp 66.0−67.5 °C (lit.[11] mp 71−73 °C); ^1H NMR ($CDCl_3$) δ = 2.03 (3H, s), 2.04 (6H,s), 2.10 (3H, s), 3.31 (1H, t, J = 11.0 Hz), 3.58−3.62 (1H, m), 4.04−4.23 (3H, m), 4.98−5.09 (2H, m), 5.21 (1H, t, J = 9.5 Hz); MS (FAB) found (M + H) m/z 333.

1-Deoxy-2,3,5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose: oil; IR (neat) 1460, 1370, 1210, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.34 (3H, s), 1.38 (3H, s), 1.45 (3H, s), 1.49 (3H, s), 3.48 (1H, dd, J = 7.1, 3.7 Hz), 3.50 (1H, dd, J = 10.7, 3.5 Hz), 4.01−4.14 (3H, m), 4.42 (1H, ddd, J = 6.8, 5.9, 5.0 Hz), 4.73 (1H, dd, J = 6,1, 3.7 Hz), 4.79 (1H, dd, J = 6.2, 3.6 Hz); ^{13}C NMR ($CDCl_3$) δ = 24.50 (p), 25.23 (p), 25.88 (p), 26.91 (p), 66.81 (s), 73.11 (s), 73.25 (t), 80.33 (t), 81.00 (t), 82.77 (t), 109.01 (q), 112.33(q); HRMS(FAB) found m/z 283.0921, calcd for $C_{12}H_{20}O_5K$ (M + K) 283.0948.

3-Deoxy-1,2,5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose: oil; IR (neat) 1370, 1210, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.25 (3H, s), 1.29 (3H, s), 1.36 (3H, s), 1.45 (3H, s), 1.70 (1H, ddd, J = 13.5, 10.1, 4.9 Hz), 2.12 (1H, dd, J = 13.4, 4.0 Hz), 3.72−3.79 (1H, m), 4.01−4.13 (3H, m), 4.69 (1H, t, J = 4.2 Hz), 5.72 (1H, d, J = 3.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 25.18 (p), 26.15 (p), 26.48 (p), 26.78 (p), 35.26 (s), 67.21 (s), 76.84 (t), 78.66 (t), 80.45 (t), 105.63 (t), 109.67 (q), 111.33(q); HRMS(FAB) found m/z 283.0939, calcd for $C_{12}H_{20}O_5K$ (M + K) 283.0948.

2-(1-Adamantyl)ethyl phenyl sulfone: mp 103.5−105.5 °C (lit.[12] mp 101.4−103.5 °C); ^1H NMR ($CDCl_3$) δ = 1.40 (6H, d, J = 2.4 Hz), 1.45−1.50 (2H, m), 1.57 (3H, d, J = 11.5 Hz), 1.68 (3H, d, J = 12.2 Hz), 1.93 (3H, bs), 3.04−3.08 (2H, m), 7.55−7.59 (2H, m), 7.64−7.68 (1H, m), 7.89−7.92 (2H, m); MS (FAB) found (M + H) m/z 305.

Diethyl 2-(1-adamantyl)ethylphosphonate: oil;[12] IR (neat) 1450, 1240, 1035, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.31−1.39 (2H, m), 1.33 (6H, t, J = 7.1 Hz), 1.45 (6H, d, J = 2.4 Hz), 1.59−1.72 (8H, m), 1.96 (3H, bs), 4.02−4.16 (4H, m); MS (EI) found m/z 300.

2-Cyclohexylethyl phenyl sulfone: oil;[12] IR (neat) 1445, 1310, 1150, 1085 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.81−0.90 (2H, m) 1.08−1.34 (3H, m), 1.55−1.69 (8H, m), 3.07−3.12 (2H, m), 7.55−7.59 (2H, m), 7.64−7.68 (1H, m), 7.90−7.92 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 25.98 (s), 26.25 (s), 29.61 (s), 32.76 (s), 36.62 (t), 54.37 (s), 128.03 (t), 129.25 (t), 133.59 (t), 139.28 (q); MS (FAB) found (M + H) m/z 253.

2-(3-Cholestanyl)ethyl phenyl sulfone: mp 116.0−119.5 °C; IR (KBr) 1445, 1375, 1305, 1240, 1150, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.63 (3H, s), 0.70 (3H, s), 0.85 (3H, d, J = 1.8 Hz), 0.87 (3H, d, J = 1.8 Hz), 0.89 (3H, d, J = 6.6 Hz), 0.75−2.00 (34H, m), 3.07 (2H, m), 7.55−7.59 (2H, m), 7,64−7.68 (1H,

(10) (a) Steudel, W.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 6129. (b) Winkler, H. J. S.; Gilman, H. *J. Org. Chem.* **1961**, *26*, 1265. (c) Schott, V. G.; Langecker, W. *Anorg. Allg. Chem.* **1968**, *358*, 210. (d) Linke, Karl-H.; Göhausen, H. J. *Chem. Ber.* **1973**, *106*, 3438. (e) Gerval, P.; Frainnet, E.; Lain, G.; Moulines, F. *Bull. Soc. Chim. Fr.* **1974**, *7*, 1548. (f) Boudjouk, P. Han, B. H. *Tetrahedron Lett.* **1981**, *22*, 3813.

(11) Augé, J.; David, S. *Carbohydr. Res.* **1977**, *59*, 255.

(12) (a) Togo, H.; Aoki, M.; Yokoyama, M. *Tetrahedron* **1993**, *49*, 8241. (b) Togo, H.; Aoki, M.; Yokoyama, M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2417. (c) Togo, H.; Hayashi, K.; Yokoyam, M. *Bull. Chem. Soc. Jpn.* **1994**, 67, 2522.

m), 7.89−7.92 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 12.01 (p), 12.25 (p), 18.67 (p), 20.99 (s), 22.56 (p), 22.82 (p), 23.83 (s), 24.18 (s), 28.01 (t), 28.23 (s), 28.43 (s), 28.88 (s), 29.59 (s), 32.05 (s), 35.11 (q), 35.49 (s), 35.79 (t), 35.96 (t), 36.17 (s), 37.02 (t), 38.24 (s), 39.51 (s), 40.04 (s), 42.57 (q), 46.36 (t), 54.46 (t), 54.50 (s), 56.27 (t), 56.53 (t), 128.05 (t), 129.25 (t), 133.58 (t), 139.24 (q). Anal. Calcd for $C_{35}H_{56}O_2S$: C,77.72; H, 10.44. Found: C, 77.89; H, 10.56.

***n*-Decyl phenyl sulfone:** oil;[9] IR (neat) 1445, 1305, 1150, 740, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.87 (3H, t, J = 6.9 Hz), 1.22−1.34 (14H, m), 1.67−1.74 (2H, m), 3.06−3.10 (2H, m), 7.56−7.58 (2H, m), 7.66 (1H, t, J = 7.5 Hz), 7.90−7.92 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 14.10 (p), 22.64 (s), 28.27 (s), 28.99 (s), 29.22 (s), 29.42 (s), 31.83 (s), 56.35 (s), 128.07 (t), 129.26 (t), 133.60 (t), 139.29(q); MS (FAB) found (M + H) *m*/*z* 283.

2-Cyclododecylethyl phenyl sulfone: mp 95.5−97.1 °C; IR (KBr) 1480, 1450, 1300, 1140, 1080, 750, 690, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.10−1.34 (22H, m), 1.40−1.51 (1H, m), 1.59−1.67 (2H, m), 3.06−3.12 (2H, m), 7.54−7.60 (2H, m), 7.62−7.68 (1H, m) 7.89−7.93 (2H,m); ^{13}C NMR ($CDCl_3$) δ = 21.44 (s), 23.16 (s), 23.22 (s), 24.09 (s), 24.63 (s), 27.33 (s), 28.61 (s), 33.30 (t), 54.73 (s), 128.03 (t), 129.23 (t), 133.55 (t), 139.31 (q); MS (FAB) found (M + H) *m*/*z* 337. Anal. Calcd for $C_{20}H_{32}O_2S$: C, 71.38; H, 9.58. Found: C, 71.18; H, 9.62.

2-[1-(2,3,5,6-Di-*O*-isopropylidene-α-D-*ribo*-hexofuranosyl)]-ethyl phenyl sulfone: mp 105.1−106.0 °C; IR (KBr) 1580, 1450, 1310, 1280, 1210, 1150, 1080, 750, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.31 (3H, s), 1.36 (3H, s), 1.42 (3H, s), 1.46 (3H, s), 1.81−1.87 (2H, m), 3.07−3.14 (1H, m), 3.18−3.25 (1H, m), 3.65 (1H, dd, J = 7.4, 3.7 Hz), 3.93 (1H, dd, J = 8.8, 4.6 Hz), 4.02 (1H, t, J = 7.8 Hz), 4.06 (1H, dd, J = 8.8, 6.4 Hz), 4.33−4.38 (1H, m), 4.47 (1H, dd, J = 6.1, 0.9 Hz), 4.74 (1H, dd, J = 6.1, 3.7 Hz), 7.57−7.62 (2H, m), 7.65−7.70 (1H, m), 7.9−7.93 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 23.74 (s), 24.59 (p), 25.10 (p), 26.03 (p), 26.83 (p), 52.90 (s), 66.78 (s), 73.16 (t), 80.18 (t), 80.50 (t), 82.36 (t), 84.98 (t), 109.19 (q), 112.94 (q), 127.93 (t), 129.41 (t), 133.85 (t), 138.87 (q); MS (FAB) found (M + H) *m*/*z* 413. Anal. Calcd for $C_{20}H_{28}O_7S$: C, 58.23; H, 6.84. Found: C, 57.94; H, 6.70.

2-(1-Adamantyl)-4-methylquinoline: mp 115.5−121.5 °C (lit.[9] mp 120.3−122.0 °C); ^{1}H NMR ($CDCl_3$) δ = 1.82 (6H, t, J = 3.0 Hz), 2.11 (6H, d, J = 2.9 Hz), 2.15 (3H, bs), 2.68 (3H, d, J = 1.0 Hz), 7.32 (1H, d, J = 1.0 Hz), 7.48 (1H, m), 7.64 (1H, m), 7.93 (1H, d, J = 8.3 Hz), 8.06 (1H, d, J = 8.2 Hz); MS (EI) found *m*/*z* 277.

2-Cyclohexyl-4-methylquinoline: oil;[12] IR (neat) 1600, 1450, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.25−2.04 (10H, m), 2.83−2.90 (1H, m), 7.17 (1H, s), 7.49 (1H, ddd, J = 8.3, 6.9, 1.0 Hz), 7.66 (1H, ddd, J = 8.4, 6.9, 1.2 Hz), 7.95 (1H, dd, J = 8.3, 1.2 Hz), 8.05 (1H, dd, J = 8.4, 1.0 Hz); ^{13}C NMR ($CDCl_3$) δ = 18.80 (p), 26.10 (s), 26.53 (s), 32.80 (s), 47.55 (t), 120.21 (t), 123.52 (t), 125.33 (t), 127.01 (q), 128.90 (t), 129.45 (t), 144.21 (q), 147.58 (q), 166.49(q); MS (EI) found *m*/*z* 225.

2-(3-Cholestanyl)-4-methylquinoline: mp 186.0−187.5 °C (lit.[12] mp 182.0−184.0 °C); ^{1}H NMR ($CDCl_3$) δ = 0.68 (3H, s), 0.86 (3H, d, J = 1.7 Hz), 0.88 (3H, d, J = 1.7 Hz), 0.92 (3H, d, J = 6.6 Hz), 0.94 (3H, s), 0.71−2.05 (31H, m), 2.69 (3H, s), 2.92 (1H, m), 7.19 (1H, s), 7.49 (1H, ddd, J = 8.3, 6.9, 1.0 Hz), 7.66 (1H, ddd, J = 8.4, 6.9, 1.2 Hz), 7.94 (1H, dd, J = 8.3, 1.2 Hz), 8.04 (1H, dd, J = 8.4, 1.0 Hz); MS (EI) found *m*/*z* 513.

2-(1-Adamantyl)benzothiazole: mp 103.5−104.5 °C (lit.[12] mp 102.3−104.2 °C); ^{1}H NMR ($CDCl_3$) δ = 1.82 (6H, bs), 2.16 (9H, bs), 7.33 (1H, ddd, J = 8.1, 7.2, 1.1 Hz), 7.44 (1H, ddd, J = 8.3, 7.2, 1.2 Hz), 7.86 (1H, dd, J = 8.1, 1.2 Hz), 8.0 (1H, dd, J = 8.3, 1.1 Hz); MS (EI) found *m*/*z* 269.

2-(1-Adamantyl)pyridine: mp 36.0−38.5 °C (lit.[12] mp 33.0−37.0 °C); ^{1}H NMR ($CDCl_3$) δ = 1.79 (6H, d, J = 2.7 Hz), 2.00 (6H, d, J = 3.1 Hz), 2.11 (3H, bs), 7.08 (1H, ddd, J = 7.7, 4.8, 1.0 Hz), 7.27 (1H, dt, J = 7.7, 1.0 Hz), 7.62 (1H, td, J = 7.7, 1.9 Hz), 8.58 (1H, ddd, J = 4.8, 1.9, 1.0 Hz); MS (EI) found *m*/*z* 213.

4-(1-Adamantyl)pyridine: mp 75.5−77.0 °C (lit.[12] mp 75.0−78.0 °C); ^{1}H NMR ($CDCl_3$) δ = 1.75 (3H, d, J = 12.4 Hz), 1.81 (3H, d, J = 12.4 Hz), 1.89 (6H, d, J = 2.7 Hz), 2.12 (3H, bs), 7.25 (2H, dd, J = 4.6, 1.7 Hz), 8.51 (2H, dd, J = 4.6, 1.7 Hz); MS (EI) found *m*/*z* 213.

2-Cyclododecyl-4-methylquinoline: mp 99.5−100.3 °C; IR (KBr) 1600, 1470, 1440, 760, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.20−1.80 (20H, m), 1.85−1.97 (2H, m), 2.68 (3H, s), 3.05−3.14 (1H, m) 7.13 (1H, s), 7.48 (1H, ddd, J = 8.3, 7.0, 1.2 Hz), 7.65 (1H, ddd, J = 8.5, 7.0, 1.4 Hz) 7.94 (1H, dd, J = 8.5, 1.0 Hz), 8.06 (1H, dd, J = 8.5, 0.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 18.77 (p), 22.91 (s), 23.38 (s), 23.71 (s), 23.88 (s), 23.95 (s), 30.15 (s), 43.09 (t), 121.40 (t), 123.50 (t), 125.25 (t), 126.95 (q), 128.76 (t), 129.60 (t), 143.78 (q), 147.65 (q), 166.70(q); HRMS (FAB) found *m*/*z* 310.2524, calcd for $C_{22}H_{32}N$ (M + H) 310.2535.

Acknowledgment. We are grateful for financial support from a Grant-in-Aid for Scientific Research (10640511) from the Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: Copies of ^{1}H NMR spectra for all products described in the paper. This material is available free of charge via the Internet at http://pubs.acs.org.

JO991715R