Radical Allylations with Trimethyl[2-[(tributylstannyl)methyl]-2-propenyl]silane or Trimethyl[2-[(triphenylstannyl)-methyl]-2-propenyl]silane

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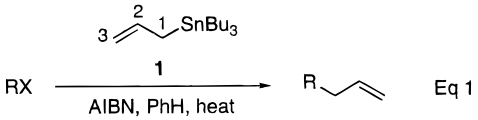
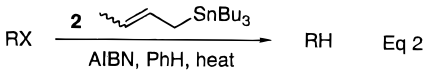
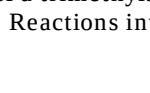
Radical allylation of the type illustrated in eq 1 (X = halogen) is a well-established and synthetically important reaction.[1−4] Various radical sources, besides alkyl halides, are suitable,[1a,b,d,e,h,k,l,5] and the reaction can be

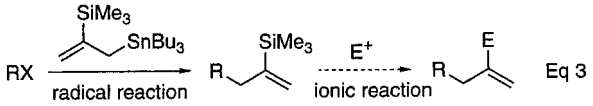


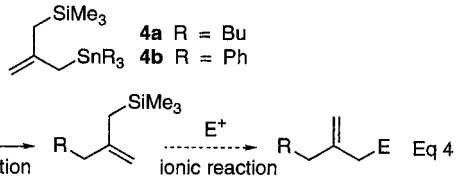
carried out both by thermal or photochemical procedures. A number of related processes have also been reported in which radical leaving groups other than $R_3Sn^{\cdot}$ are involved,[5a,b,6] and much work has been done to identify what substituents can be tolerated on the allyl unit. In the case of allylstannanes (general formula **1**), alkyl substitution at C(1) or C(3) does not appear to be synthetically useful[7]—at least as a general rule—because of facile 1,3-tin migration[8] and the fact that crotylstannanes (**2**) are good hydrogen donors, so that, instead of being allylated, the initial radical is reduced (eq 2).[1a,j,9]



Oxygen substituents at C(1) have also been examined; intramolecular processes with AcO at C(1) are successful,[10] but intermolcular reactions when the C(1) substituent is $MeOCH_2O$ do not work.[8a] It would seem that, besides the parent compound (**1**[11]), only C(2)-substituted allylstannanes are of general synthetic utility[12] for radical allylation. In these compounds, of course, the 1,3-stannane migration is degenerate. Electron-withdrawing groups at C(2),[1c,h,5c,e,6b,d,8a,13] especially CO_2R, provide useful reagents (**3**, X = CO_2R, R' = Bu), as do alkyl (**3**, X = Me, R′ = Bu)[1c,g,h,4b,d,e,6b,9c,14] or silyl groups[1h,l,5c,15] (**3**, X = $SiMe_3$, R' = Bu, Ph).[16,17] In the case of silane **3** (X = $SiMe_3$, R′ = Bu, Ph), allylation is facilitated when the attacking radical is nucleophilic[15] and this can be interpreted[15b] in terms of a polar transition state that is favored by the ability of a trimethylsilyl group to stabilize an α negative charge. Reactions involving **3** (X = $SiMe_3$) serve as a link between radical and *vinyl*silane chemistry (as expressed by eq 3, E^+ = electrophile). We report here experiments that link radical and *allyl*silane reactions[18] by means of the reagents **4a** and **4b** (see eq 4, E^+ = electrophile).







(1) (a) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079. (b) Blaszczak, L. C.; Armour, H. K.; Halligan, N. G. *Tetrahedron Lett.* **1990**, *31*, 5693. (c) Curran, D. P.; Shen, W.; Zhang, J.; Heffner, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 6738. (d) Grøtli, M; Undheim, K. *Acta Chem. Scand.* **1995**, *49*, 217. (e) Guindon, Y.; Guérin, B.; Chabot, C.; Mackintosh, N.; Ogilvie, W. W. *Synlett* **1995**, 449. (f) Kosugi, M.; Kurino, K.; Takayama, K.; Migita, T. *J. Organomet. Chem.* **1973**, *56*, C11. (g) Kraus, G. A.; Andersh, B.; Su, Q.; Shi, J. *Tetrahedron Lett* **1993**, *34*, 1741. (h) Landais, Y.; Planchenault, D. *Tetrahedron* **1995**, *51*, 12097. (i) Migita, T.; Nagai, K.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2480. (j) Grignon, J.; Servens, C.; Pereyre, M. *J. Organomet. Chem.* **1975**, *96*, 225. (k) Radinov, R.; Mero, C. L.; McPhail, A. T.; Porter, N. A. *Tetrahedron Lett.* **1995**, *36*, 8183. (l) Renaud, P.; Carrupt, P.-A.; Gerster, M.; Schenk, K. *Tetrahedron Lett.* **1994**, *35*, 1703.

(2) Intramolecular allylic displacement of $SnBu_3$: Curran, D. P.; van Elburg, P. A. *Tetrahedron Lett.* **1989**, *30*, 2501.

(3) Rate constants for allylation: Curran, D. P.; van Elburg, P. A.; Giese, B.; Gilges, S. *Tetrahedron Lett.* **1990**, *31*, 2861.

(4) Intermolecular allylation can be done directly, or after other radical reactions, such as cyclization, carbonylation, intermolecular radical addition, etc.: e.g., (a) see ref 1c. (b) Mizuno, K.; Ikeda, M.; Toda, S.; Otsuji, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1288. (c) Wu, J. H.; Radinov, R.; Porter, N. A. *J. Am. Chem. Soc.* **1995**, *117*, 11029. (d) Ryu, I.; Yamazaki, H.; Kusano, K.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 8558. (e) Ryu, I.; Yamazaki, H.; Ogawa, A.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1993**, *115*, 1187. (f) Tamao, K.; Nagata, K.; Ito, Y.; Maeda, K.; Shiro, M. *Synlett* **1994**, 257. (g) Moriya, O.; Kakihana, M.; Urata, Y.; Sugizaki, T.; Kageyama, T.; Ueno, Y.; Endo, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1401. (h) Sibi, M. P.; Ji, J. *J. Org. Chem.* **1996**, *61*, 6090. (i) Keck, G. E.; Kordik, C. P. *Tetrahedron Lett.* **1993**, *34*, 6875.

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(7) But compare ref 5d and Fliri, H.; Mak, C.-P. *J. Org. Chem.* **1985**, *50*, 3438. Yoshida, Y.; Ono, N.; Sato, F. *J. Org. Chem.* **1994**, *59*, 6153.

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(9) (a) Keck, G. E.; Yates, J. B. *J. Organomet. Chem.* **1983**, *248*, C21. But compare the following: (b) Easton, C. J.; Scharfbillig, T. M. *J. Org. Chem.* **1990**, *55*, 384. (c) Hamon, D. P. G.; Massy-Westropp, R. A.; Razzino, P. *Tetrahedron* **1995**, *51*, 4183.

(10) Danishefsky, S. J.; Panek, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 917.

(11) Usually, R = Bu. For R = Ph, see refs 1c, 4f, 5a, 5b, 6b; for R = Me, see refs 1f, 1i, 6b.

(12) For an exception, see ref 8a.

(13) Baldwin, J. E.; Adlington, R. M.; Mitchell, M. B.; Robertson, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1574. Feldman, K. S.; Bobo, J. S.; Tewalt, G. L. *J. Org. Chem.* **1992**, *57*, 4573. Giese, B.; Linker, T.; Muhn, R. *Tetrahedron* **1989**, *45*, 935. Giese, B.; Linker, T. *Synthesis* **1992**, 46.

(14) Baldwin, J. E.; Fieldhouse, R.; Russel, A. T. *Tetrahedron Lett.* **1993**, *34*, 5491. Keck, G. E.; Enholm, E. J.; Kachensky, D. F. *Tetrahedron Lett.* **1984**, *25*, 1867.

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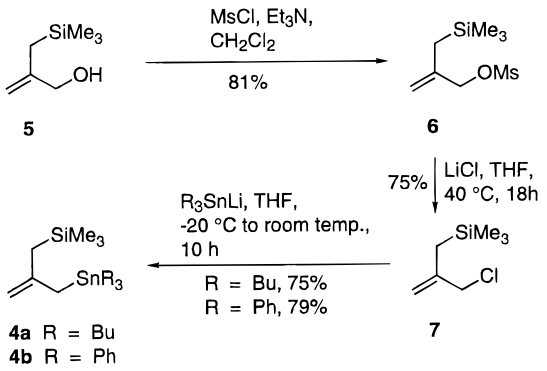
(16) For **3** (X = $SnMe_3$), see refs 1g, 6b, 6c.

S0022-3263(97)00552-5 CCC: $14.00

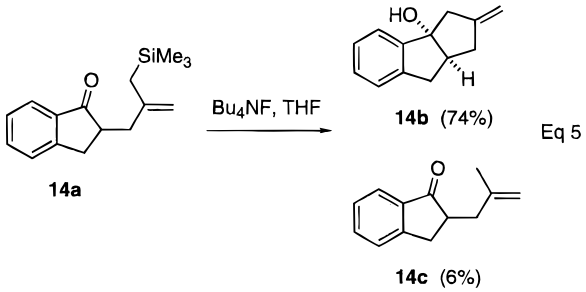
Scheme 1



Reagent **4a**[19,20] was most conveniently prepared by the route summarized in Scheme 1, which simply represents a different combination of known steps from that used previously.[19] The compound, which should be purified by distillation, since it decomposes during chromatography over silica gel, may be stored in a refrigerator for up to 8 weeks without appreciable decomposition. Older material should be redistilled before use. The triphenyl analog (**4b**) was made by an analogous route (*cf.* Scheme 1). Our impression is that the compound is a little more stable than **4a**, and its performance in radical allylations may be slightly better. Unlike the reagents **4a** and **4b**, the allylsilanes that are produced in the radical reactions are stable to flash chromatography over silica gel.

An extensive survey, using mainly **4a**, suggested that the best conditions for allylation involve photochemical initiation at a temperature below 20 °C, using a medium pressure mercury lamp with Pyrex filtration, and in the presence of AIBN. The reactions may be run in PhH or DME. Thermal conditions appear to be less efficient than the photochemical method, but only one case (Table 1, entry 9) was studied carefully by both methods. Our experiments also suggest that the facility of reaction is rather sensitive to the nature of the starting material. Allylation of methyl *p*-iodobenzoate was not very successful (Table 1, entry 2), and experiments with nucleophilic radicals did not always work well; the results shown in the table (entries 1, 3−7) represent the best of several attempts in each case. The main competing process is reduction of the starting halide, and we assume that the allyl reagent is the source of the hydrogen (cf. eq 2). However, electrophilic radicals generally behave well (Table 1, entries 8−17), and the reaction is reliable in such cases. Presumably, this pattern is related to the ability of the $SiMe_3$ substituent to stabilize a partial positive charge that develops at C(2) in the transition state. Primary and secondary electrophilic radicals are allylated, and suitable substituents on the radical carbon are C═O, SO_2Ph, or CO_2R (R = Me, Et). Surprisingly, 2-bromopropionitrile led to a complex mixture under our standard conditions.

Finally, in one case, we demonstrated the link between radical and allylsilane reactions. This was done by treating **14a** with TBAF, a process that afforded **14b** (74%) and a small amount (6%) of **14c** (eq 5).



Experimental Section

General Procedures. The same general procedures as used previously[21] were followed. The following photochemical equipment was used: (a) Rayonet photochemical reactor, 3000 Å, four 21-W lamps used, (b) Hanovia, medium pressure Hg lamp, type SH (140 W), and (c) General Electric sunlamp (275 W). The symbols s′, d′, t′, and q′ used for ^{13}C NMR signals indicate zero, one, two, or three attached hydrogens, respectively.

Trimethyl[2-[(tributylstannyl)methyl]-2-propenyl]silane (4a).[19a] A literature procedure[19a] for converting **7** (see below for preparation of **7**) into **4a** was followed with minor modifications. *n*-BuLi (2.5 M in hexanes, 2.65 mL, 6.63 mmol) was added to a stirred and cooled (0 °C) solution of *i*-Pr_2NH (1.0 mL, 7.24 mmol) in dry THF (6.5 mL). Stirring at 0 °C was continued for 10 min, and Bu_3SnH (1.62 mL, 5.84 mmol) was then added. Stirring was continued for another 30 min, and the solution was then cooled to −20 °C. Chloride **7** (1.00 g, 6.15 mmol) was added neat by syringe. The syringe was rinsed once with dry THF (0.5 mL), and the rinsing was added to the mixture. At this point, the cold bath was removed and the solution was stirred for 10 h, poured into ice-cold water (15 mL), and extracted with Et_2O. The organic extract was dried (Na_2SO_4) and evaporated. Kugelrohr distillation (oil pump) of the residue gave **4a** (1.842 g, 75%) as a clear oil: bp 100−105 °C (0.100 mmHg) [lit.[19a] bp 132−135 °C (0.4 mmHg)]; FTIR (film) 2956, 2925, 857 cm^{-1}; ^1H NMR (acetone-d_6, 400 MHz) δ 0.05 (s, 9 H), 0.80−0.95 (m, 15 H), 1.25−1.40 (m, 6 H), 1.42−1.65 [m including br s (2 H) at δ 1.50), 8 H in all], 1.80 (br s, 2 H), 4.23 (br s, 1 H), 4.40 (br s, 1 H); ^{13}C NMR (acetone-d_6, 75.5 MHz) δ −1.14 (q′), 10.04 (t′), 13.96 (q′), 22.30 (t′), 28.03 (t′), 29.60 (t′), 29.87 (t′), 103.49 (t′), 148.22 (s′); exact mass, *m*/*z* calcd for $C_{19}H_{42}Si^{120}Sn$ 418.20779, found 418.20890.

Trimethyl[2-[(triphenylstannyl)methyl]-2-propenyl]silane (4b). NaH (60% w/w dispersion in oil) (192 mg, 4.8 mmol), in a dry 50-mL round-bottomed flask, was washed with dry THF (3 × 5 mL) under Ar and then suspended (magnetic stirring) in THF (10 mL). A solution of Ph_3SnH (1.40 g, 4.0 mmol) in THF (2 mL) was added by cannula at 0 °C over 1 min. The cold bath was removed, and stirring was continued for 30 min. A solution of **7** (845.2 mg, 5.2 mmol) in THF (2 mL) was added by cannula at 0 °C over ca. 2 min, the cold bath was removed, and stirring was continued for 6 h. The mixture was diluted with water (1 mL) and extracted with Et_2O. The organic extract was dried (Na_2SO_4) and evaporated. The residue was diluted with acetone, and the insoluble material was filtered off and washed with acetone. Evaporation of the combined filtrates and Kugelrohr distillation of the residue (oil-pump) gave **4b** (1.5070 g, 79%) as a colorless oil containing slight impurities (^1H NMR, 360 MHz): bp 145−152 °C (0.3 mmHg); FTIR (CH_2Cl_2 cast) 1612 cm^{-1}; ^1H NMR (C_6D_6, 360 MHz) δ −0.02 (s, 9 H), 1.55 (s, 2 H), 2.49 (s, $^2J_{SnCH}$ = 72.6 Hz, 2 H), 4.51−4.57 (m, $^4J_{SnCCCH}$ = 20.6 Hz, 1 H), 4.78−4.85 (m, $^4J_{SnCCCH}$ = 22.0 Hz, 1 H), 7.13−7.23 (m, 9 H), 7.55−7.71 (m, 6 H); ^{13}C NMR (C_6D_6, 75.5 MHz) δ −1.27 (q′), 24.09 (t′), 29.37 (t′), 106.40 (t′), 128.85 (d′, $^3J_{SnCCC}$ = 48.0 Hz), 129.25 (d′, $^4J_{SnCCCC}$ = 10.7 Hz), 137.43 (d′, $^2J_{SnCC}$ = 34.9 Hz), 139.26 (s′), 145.55 (s′); exact mass *m*/*z* calcd for $C_{25}H_{30}Si^{120}Sn$ 478.11389, found 478.11394.

2-[(Trimethylsilyl)methyl]-2-propenyl Methanesulfonate (6).[22] MsCl (5.35 mL, 69.12 mmol) in dry CH_2Cl_2 (50 mL) was

(17) For reactions of a system with two allylic tin units, see: Chandrasekhar, S.; Latour, S.; Wuest, J. D.; Zacharie, B. *J. Org. Chem.* **1983**, *48*, 3810.

(18) Fleming, I. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, p 563.

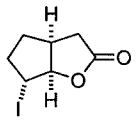
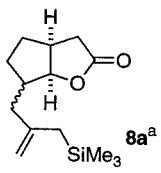
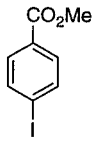
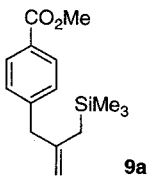
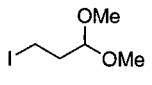
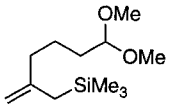
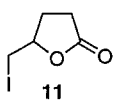
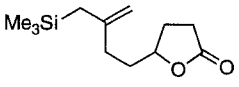
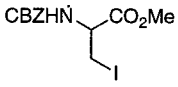
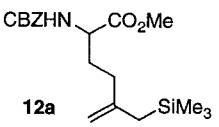
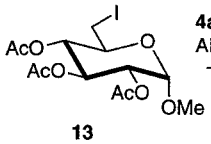
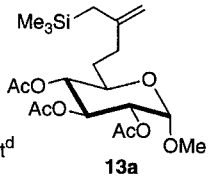
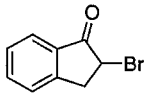
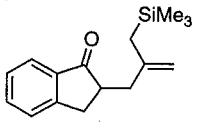
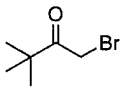
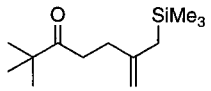
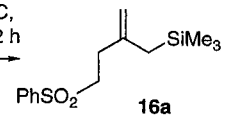
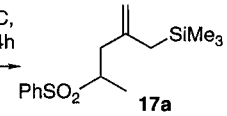
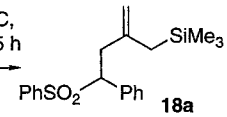
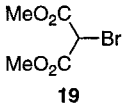
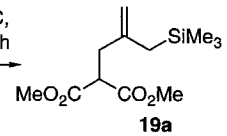
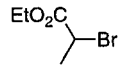
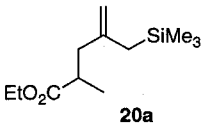
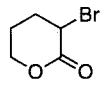
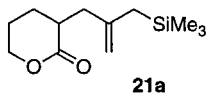
(19) (a) Kang, K.-T.; U, J. S.; Park, D. K.; Kim, J. G.; Kim, W. J. *Bull. Korean Chem. Soc.* **1995**, *16*, 464. (b) Majetich, G.; Nishidie, H.; Zhang, Y. *J. Chem. Soc., Perkin Trans. 1* **1995**, 453.

(20) Reagent **4a** is not stable to silica chromatography (cf. ref 19b).

(21) Clive, D. L. J.; Wickens, P. L.; Sgarbi, P. W. M. *J. Org. Chem.* **1996**, *61*, 7426.

(22) Trost, B. M.; Vincent, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 5680.

Table 1

	Substrate	Conditions and yield	Product
1	 **8**	**4a**, PhH, 15-20 °C, Hanovia, 15 h → 68%	 **8a**[a]
2	 **9**	**4a**, DME, room temp., ABCC,[b] 3000 A,[c] 24 h → 51% + methyl benzoate (47%) by ^{1}H NMR.	 **9a**
3	 **10**	**4a**, PhH, room temp., AIBN, Hanovia, 12 h → 72%	 **10a**
4	 **11**	**4a**, PhH, 15-20 °C, Hanovia, 17 h → 75%	 **11a**
5	 **12**	**4a**, PhH, 15-20 °C, Hanovia, 20 h → 74%	 **12a**
6	 **13**	**4a**, DME, 15-20 °C, AIBN, Hanovia, 9 h → 45% + 51% reduction product[d]	 **13a**
7	**13**	**4b**, DME, 15-20 °C, AIBN, Hanovia, 20 h → 42% + 52% reduction product[d]	**13a**
8	 **14**	**4a**, PhH, 15-20 °C, sunlamp, 3 h → 86%	 **14a**
9	**14**	**4a**, PhH, reflux, AIBN, 2 h → 68% (77% corrected for recovered **14**)	**14a**
10	 **15**	**4a**, PhH,15-20 °C, Hanovia, 15 h → 59%	 **15a**
11	$PhSO_2CH_2Cl$ **16**	**4b**, DME, 15-20 °C, AIBN, Hanovia, 12 h → 85%	 **16a**
12	**16**	**4a**, DME, 15-20 °C, AIBN, Hanovia, 12 h → 81%	**16a**
13	$PhSO_2CH(Cl)Me$ **17**	**4b**, DME, 15-20 °C, AIBN, Hanovia, 24h → 70%	 **17a**
14	$PhSO_2CH(Cl)Ph$ **18**	**4b**, DME, 15-20 °C, AIBN, Hanovia, 25 h → 43%	 **18a**
15	 **19**	**4b**, PhH, 15-20 °C, AIBN, Hanovia, 8 h → 90%	 **19a**
16	 **20**	**4b**, DME, 15-20 °C, AIBN, Hanovia, 20 h → 70%	 **20a**
17	 **21**	**4b**, DME, 15-20 °C, AIBN, Hanovia,12 h → 81%	 **21a**

[a] 9.3:1 isomer ratio. [b] ABCC = 1,1′-azobis(cyclohexanecarbonitrile). [c] Rayonet reactor. [d] Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-glucopyranoside (**13b**).

added by cannula to a stirred and cooled (0 °C) solution of **5**[23] (5.001 g, 34.7 mmol) in a mixture of dry CH_2Cl_2 (100 mL) and Et_3N (14.5 mL, 104 mmol). After the addition, which took *ca.* 8 min, the cold bath was removed and the mixture was stirred for 1.5 h. Water (100 mL) was added, and the mixture was extracted with CH_2Cl_2. The organic extract was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (5 × 23 cm), using 5:95 acetone−hexane, gave **6** (6.26 g, 81%) as a colorless oil: FTIR (CH_2Cl_2 cast) 1358, 1176, 853 cm^{-1}; ^{1}H NMR (acetone-d_6, 200 MHz) δ 0.05 (s, 9 H), 1.65 (s, 2 H), 3.10 (s, 3 H), 4.60 (s, 2 H), 4.85 (br s, 1 H), 5.04 (br s, 1 H); ^{13}C NMR (acetone-d_6, 75.5 MHz) δ −1.43 (q′), 23.33 (t′), 37.55 (q′), 74.01 (t′), 112.19 (t′), 141.73 (s′); exact mass, *m*/*z* calcd for $C_8H_{18}O_3SSi$ 222.07460, found 222.07449. Anal. Calcd for $C_8H_{18}O_3SSi$: C, 43.21; H, 8.16. Found: C, 43.26; H, 8.38.

3-Chloro-2-[(trimethylsilyl)methyl]-1-propene (7).[19a] LiCl (3.6 g, 84.9 mmol, drying is not necessary) was added to a solution of **6** (6.52 g, 29.36 mmol) in dry THF (80 mL), and the mixture was stirred at 40 °C for 18 h, by which stage a white suspension had formed. The mixture was washed with brine (50 mL), and the aqueous layer was extracted with Et_2O. The organic extract was dried ($MgSO_4$), concentrated to *ca.* 15 mL, and passed through a pad of silica gel (2 × 5 cm), using hexane (80 mL). Evaporation of the filtrate and Kugelrohr distillation of the residue (85 °C, water aspirator) [lit.[19a] 75 °C (31 mmHg)] gave **7** (3.56 g, 75%) as a clear liquid: FTIR (film) 853 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz) δ −0.10 (s, 9 H), 1.53 (d, J = 1 Hz, 2 H), 3.68 (d, J = 1 Hz, 2 H), 4.59 (br s, 1 H), 4.84 (br s, 1 H); ^{13}C NMR (C_6D_6, 75.5 MHz) δ −1.55 (q′), 23.73 (t′), 49.81 (t′), 112.31 (t′), 143.33 (s′); exact mass, *m*/*z* calcd for $C_7H_{15}{}^{35}ClSi$ 162.06316, found 162.06310. Anal. Calcd for $C_7H_{15}ClSi$: C, 51.67; H, 9.29; Cl, 21.79. Found: C, 52.07; H, 9.40; Cl, 21.29.

(23) Trost, B. M.; Chan, D. M. T.; Nanninga, T. N. *Org. Synth.* **1984**, *62*, 58.

(3aα,6α,6aα)- and (3aα,6β,6aα)-Hexahydro-6-[2-[(trimethylsilyl)methyl]-2-propenyl]-2*H*-cyclopenta[*b*]furan-2-one (8a). Iodo lactone **8**[24] (159 mg, 0.63 mmol) and **4a** (608 mg, 1.46 mmol) were weighed into a Pyrex test tube (1 × 10 cm). The tube was closed with a rubber septum, kept under oil pump vacuum for 10 min, and then filled with Ar. This procedure was repeated once more, and dry PhH (1 mL) was then added. The tube was mounted in a slanting position with its base immersed in a water bath kept at 15 to 20 °C and irradiated (Hanovia, 140 W) for 15 h (Ar atmosphere). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 25 cm), using 5:95 acetone−hexane, gave **8a** (108 mg, 68%) as an inseparable 9.3:1 mixture (^{1}H NMR) of isomers: FTIR (benzene cast) 1776 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 0.0 (s, 9 H), 0.80−1.0 (m, 2 H), 1.35−1.49 (m, 3 H) 1.50−1.70 (m, 2 H), 1.71−1.90 (m, 2 H), 1.91−2.25 (m, 3 H), 4.11 (dd, J = 6.9, 2.3 Hz, 1 H), 4.63 (s, 2 H); ^{13}C NMR (benzene-d_6, 75.5 MHz) (peaks for the minor isomer are indicated by an asterisk) δ −1.31 (q′), −0.97 (q′)*, 26.19 (t′), 27.29 (t′)*, 28.99 (t′)*, 29.85 (t′), 31.62 (t′), 32.49 (t′)*, 35.52 (t′), 36.34 (t′)*, 37.37 (d′)*, 37.65 (d′), 37.73 (t′)*, 41.04 (t′), 43.93 (d′), 44.74 (d′)*, 86.06 (d′)*, 89.48 (d′), 108.40 (t′)*, 109.41 (t′), 145.40 (s′), 146.12 (s′)*, 175.83 (s′) (several of the peaks coincide); exact mass, m/z calcd for $C_{14}H_{24}O_2Si$ 252.15456, found 252.15378.

Methyl 4-[2-[(Trimethylsilyl)methyl]-2-propenyl]benzoate (9a). A solution of **9** (100 mg, 0.38 mmol), **4a** (638.5 mg, 1.53 mmol), and 1,1′-azobis(cyclohexanecarbonitrile) (19 mg, 0.076 mmol) in dry DME (0.8 mL), contained in a Pyrex test tube (1 × 10 cm) closed by a septum, was degassed with a vigorous stream of Ar, which was passed through the solution for 6 min. The mixture was then irradiated for 24 h at room temperature (Rayonet, 3000 Å). The resulting cloudy mixture was diluted with Et_2O (2 mL), and DBU (3 drops) was added with shaking. The resulting solid was filtered off and washed with Et_2O. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.5 × 23 cm), using 1:4:200 Et_3N−EtOAc−hexane, gave a mixture of **9a** and methyl benzoate (75 mg). The material contained 51 mol % **9a** and 47 mol % methyl benzoate as judged by its ^{1}H NMR (360 MHz) spectrum.

In another experiment, a sample of **9a** was obtained as a colorless oil by flash chromatography over silica gel, using 1.5:98.5 EtOAc−hexane: FTIR (hexane cast) 1725 cm^{-1}; ^{1}H NMR (acetone-d_6, 400 MHz) δ 0.05 (s, 9 H), 1.52 (s, 2 H), 3.38 (s, 2 H), 3.86 (s, 3 H), 4.60 (br s, 1 H), 4.66 (br s, 1 H), 7.34 (br d, J = 8.34 Hz, 2 H), 7.94 (br d, J = 8.34 Hz, 2 H); ^{13}C NMR (acetone-d_6, 75.5 MHz) δ −1.21 (q′), 26.66 (t′), 45.44 (t′), 52.17 (q′), 110.33 (t′), 129.16 (s′), 130.13 (d′), 130.21 (d′), 146.39 (s′), 147.22 (s′), 167.18 (s′); exact mass, m/z calcd for $C_{15}H_{22}O_2Si$ 262.13892, found 262.13842.

1-Iodo-3,3-dimethoxypropane (10). The literature procedure for the corresponding ethylene ketal[25] was followed, with some modifications. Freshly distilled Me_3SiCl (15.3 mL, 120 mmol) was added over 1 min to a stirred and cooled (0 °C) solution of acrolein (6.7 mL, 100 mmol) and dry NaI (18 g, 120 mmol) in dry MeCN (250 mL). The resulting yellow solution was stirred for 5 min, and then dry MeOH (9.72 mL, 240 mmol) was added in one portion. Stirring was continued for 5 min, and the solution was then poured into 5% saturated aqueous $NaHCO_3$ (100 mL) overlaid with pentane (300 mL). The mixture was shaken, and the bottom layer was removed. The residual two organic phases were washed with 5% aqueous $Na_2S_2O_3$ (80 mL) and then with brine (7 × 100 mL), at which point only the top layer remained. The organic extract was dried (K_2CO_3) and evaporated. The residual oil was dissolved in pentane (20 mL) and filtered through a short column of basic, grade 3 alumina (3 × 8 cm), using pentane (100 mL). Evaporation of the filtrate gave **10** (13.9 g, 60%) as an oil: FTIR (CH_2Cl_2 cast) 2988, 2952, 2935, 2908, 2830, 1458, 1443 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 2.04−2.11 (m, 2 H), 3.12 (t, J = 7 Hz, 2 H), 3.31, (s, 6 H), 4.42 (t, J = 5.5 Hz, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ −0.14 (t′), 36.47 (t′), 53.51 (q′), 104.42 (d′); exact mass, m/z calcd for $C_5H_{11}IO_2$ 229.98038, found 229.98022. A satisfactory combustion analysis could not be obtained.

[2-(4,4-Dimethoxybutyl)-2-propenyl]trimethylsilane (10a). A solution of **10** (84.3 mg, 0.367 mmol), **4a** (311 mg, 0.75 mmol), and AIBN (9 mg, 0.055 mmol) in dry PhH (0.9 mL), contained in a Pyrex test tube (1 × 10 cm) closed by a septum, was degassed with a vigorous stream of Ar, which was passed through the solution for 6 min. The mixture was then irradiated for 12 h at room temperature (Hanovia, 140 W). The resulting cloudy solution was evaporated, and flash chromatography of the residue over silica gel (1.5 × 15 cm), using 2.5:97.5 EtOAc−hexane (containing 1% Et_3N), gave **10a** (61.0 mg, 72%) as a colorless oil: FTIR (benzene cast) 856 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 0.02 (s, 9 H), 1.49 (br s, 2 H), 1.50−1.70 (m, 4 H), 1.96 (t, J = 7.28 Hz, 2 H), 3.15 (s, 6 H), 4.33 (t, J = 5.5 Hz, 1 H), 4.64 (br s, 1 H), 4.74 (br s, 1 H); ^{13}C NMR (benzene-d_6, 75.5 MHz) δ −1.28 (q′), 23.24 (t′), 26.75 (t′), 32.52 (t′), 38.36 (t′), 52.18 (q′), 104.58 (d′), 107.71 (t′), 147.32 (s′). A satisfactory mass spectrum (EI, CI, and FAB) could not be obtained.

Dihydro-5-[3-[(trimethylsilyl)methyl]-3-butenyl]-2(3*H*)-furanone (11a). Iodo lactone **11**[26] (98.7 mg, 0.436 mmol) and **4a** (395.6 mg, 0.873 mmol) were weighed into a Pyrex test tube (1 × 10 cm). The tube was closed with a rubber septum, kept under vacuum for 10 min, and then filled with Ar. Dry PhH (1 mL) was added, and the mixture was irradiated (Hanovia, 140 W) for 17 h, exactly as described for **8**. Evaporation of the solvent and flash chromatography of the residue over silica gel (1.5 × 23 cm), using 1:9 acetone−hexane, and again over silica gel (1 × 20 cm), using, 1:9 EtOAc−hexane, gave **11a**[27] (74.3 mg, 75%) as a colorless oil: FTIR (benzene cast) 1777 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 0.0 (s, 9 H), 0.92−1.05 (m, 1 H), 1.25−1.40 (m, 2 H), 1.42 (br s, 2 H), 1.48−1.60 (m, 1 H), 1.75−2.02 (m, 4 H), 3.75−3.85 (m, 1 H), 4.59−4.64 (m, 2 H); ^{13}C NMR (benzene-d_6, 75.5 MHz) δ −1.36 (q′), 26.93 (t′), 27.73 (t′), 28.52 (t′), 33.98 (t′), 34.06 (t′), 79.26 (d′), 107.80 (t′), 146.40 (s′), 175.44 (s′); exact mass, m/z calcd for $C_{12}H_{22}O_2Si$ 226.13892, found 226.13824.

Methyl 2,3,4-Tri-*O*-acetyl-6,7,8,9-tetradeoxy-8-[(trimethylsilyl)methyl]-α-D-*gluco*-non-8-enopyranoside (13a). (a) Use of 4a. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside[28] (**13**) (100 mg, 0.23 mmol), AIBN (3.8 mg, 0.023 mmol), and **4a** (384.8 mg, 0.92 mmol) in dry DME (1 mL), contained in a Pyrex test tube (1 × 10 cm) closed by a septum, was degassed with a vigorous stream of Ar, which was passed through the solution for 6 min. The mixture was then irradiated (Hanovia, 140 W) for 9 h at 15−20 °C (cold water bath). The resulting cloudy solution, containing some white precipitate, was diluted with Et_2O (2 mL), and DBU (3 drops) was added with shaking. The solid was filtered off and washed with Et_2O. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.5 × 23 cm), using 1:4 EtOAc−hexane, gave methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-glucopyranoside[29] (**13b**) (36 mg, 51%) as a colorless oil. The fraction containing **13a** was rechromatographed over silica gel (0.5 × 14 cm), using 2:98 Et_2O−CH_2Cl_2, to give **13a** (45.4 mg, 45%) as a colorless oil.

Compound **13a**: FTIR (CH_2Cl_2 cast) 1754, 1633, 1225 cm^{-1}; ^{1}H NMR (C_6D_6, 360 MHz) δ 0.03 (s, 9 H), 1.51 (s, 2 H), 1.61−1.85 (m, 11 H), 1.98−2.08 (m, 1 H), 2.27−2.34 (m, 1 H), 2.99 (s, 3 H), 3.75−3.81 (m, 1 H), 4.65 (s, 1 H), 4.75 (dd, J = 2.8, 1.3 Hz, 1 H), 4.88 (d, J = 3.7 Hz, 1 H), 5.07 (dd, J = 10.3, 3.7 Hz, 1 H), 5.14 (dd, J = 9.9, 9.4 Hz, 1 H), 5.88 (dd, J = 10.3, 9.4 Hz, 1 H); ^{13}C NMR (C_6D_6, 75.5 MHz) δ −1.32 (q′), 20.21 (q′), 20.37 (q′), 26.94 (t′), 29.87 (t′), 33.86 (t′), 54.86 (q′), 68.35 (d′), 70.84 (d′), 71.69 (d′), 72.77 (d′), 96.99 (d′), 107.88 (t′), 146.94 (s′), 169.35 (s′), 169.68 (s′), 169.75 (s′); exact mass, m/z calcd for $C_{20}H_{34}O_8Si$ 430.20230, found 430.20232.

Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-glucopyranoside[29] (13b): FTIR (CH_2Cl_2 cast) 1751, 1248, 1225 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.19 (d, J = 6.3 Hz, 3 H), 2.00 (s, 3 H), 2.03 (s, 3 H), 2.06 (s, 3 H), 3.38 (s, 3 H), 3.82−3.95 (m, 1 H), 4.79 (dd, J = 9.6, 9.6 Hz, 1 H), 4.83−4.89 (m, 2 H), 5.39−5.46 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 17.19 (q′), 20.69 (q′), 55.24 (q′), 64.90 (d′), 70.07 (d′), 71.23 (d′), 73.80 (d′), 96.59 (d′), 169.84 (s′),

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(27) Reaction with the corresponding bromide (Cambie, R. C.; Rutledge, P. S.; Somerville, R. F.; Woodgate, P. D. *Synthesis* **1988**, 1009) gave **11a** in only 6% yield.
(28) Garegg, P. J.; Samuelsson, B. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2866.
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170.09 (s′), 170.19 (s′); exact mass, *m*/*z* calcd for $C_{12}H_{17}O_7$ 273.09744 (M − OCH_3), found 273.09718.

(b) Use of 4b. The above procedure was followed, using **13**[28] (60 mg, 0.14 mmol), AIBN (4.6 mg, 0.028 mmol), **4b** (267 mg, 0.56 mmol), and DME (0.8 mL), with an irradiation time of 20 h. The resulting cloudy solution, containing some white precipitate, was diluted with Et_2O (2 mL), and DBU (3 drops) was added with shaking. The solid was filtered off and washed with Et_2O. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 × 23 cm), using 3:7 EtOAc−hexane, gave **13b** (31 mg, 52%) as a colorless oil. The fraction containing **13a** was rechromatographed over silica gel (0.5 × 14 cm), using 2:98 Et_2O−CH_2Cl_2, to give **13a** (18 mg, 42%) as a colorless oil.

2-[2-[(Trimethylsilyl)methyl]-2-propenyl]indan-1-one (14a). (a) Photochemical Method. Except for the use of a different lamp, the procedure for **8a** was followed, using **14**[30] (38 mg, 0.18 mmol), **4a** (150 mg, 0.36 mmol), dry PhH (0.5 mL), and an irradiation period (sunlamp) of 3 h. Evaporation of the solvent and flash chromatography of the residue twice over silica gel (1.5 × 25 cm), using 5:95 acetone−hexane for the first chromatography and 2.5:97.5 EtOAc−hexane for the second, gave **14a** (40.1 mg, 86%) as a colorless oil: FTIR (benzene cast) 1713, 848 cm^{-1}; ^1H NMR (benzene-d_6, 400 MHz) δ 0.03 (s, 9 H), 1.45 (d, J = 2.1 Hz, 2 H), 1.83 (dd, J = 14.5, 10.5 Hz, 1 H), 2.45−2.60 (m, 2 H), 2.75−2.85 (m, 2 H), 4.57 (br s, 1 H), 4.62 (br s, 1 H), 6.9−7.0 (m, 2 H), 7.10−7.14 (dd, J = 7.4, 1.2 Hz, 1 H), 7.80 (d, J = 7.7 Hz, 1 H); ^{13}C NMR (benzene-d_6, 75.5 MHz) δ −1.29 (q′), 26.48 (t′), 32.87 (t′), 40.27 (t′), 45.79 (d′), 108.82 (t′), 124.03 (d′), 126.64 (d′), 127.42 (d′), 134.28 (d′), 137.40 (s′), 145.79 (s′), 153.60 (s′), 206.70 (s′); exact mass, *m*/*z* calcd for $C_{16}H_{22}OSi$ 258.14398, found 258.14427.

(b) Thermal Method. A mixture of **14** (93.1 mg, 0.44 mmol), **4a** (366.7 mg, 0.88 mmol), and AIBN (7.22 mg, 0.044 mmol) in PhH (1.2 mL) was refluxed under Ar for 2 h. Evaporation of the solvent and flash chromatography of the residue twice over silica gel (1.5 × 23 cm), using 2.5% EtOAc−hexane, gave **14a** (78 mg, 68%, 77% after correction for recovered **14**), identical with material obtained by the photochemical procedure.

(30) House, H. O.; Paragamian, V.; Ro, R. S.; Wluka, D. J. *J. Am. Chem. Soc.* **1960**, *82*, 1452.

2,3,8,8a-Tetrahydro-2-methylenecyclopent[*a*]inden-3a(1*H*)-ol (14b) and 2-(2-Methyl-2-propenyl)indan-1-one (14c). Bu_4NF (1 M in THF, 0.36 mL, 0.36 mmol) was added to a stirred solution of **14a** (90 mg, 0.349 mmol) in dry THF (16 mL), and stirring was continued for 30 min. The mixture was then poured into a separatory funnel containing saturated aqueous NH_4Cl (30 mL) and extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.5 × 25 cm), using 6:94 EtOAc−hexane, gave **14b** (48 mg, 74%) as a white solid along with the minor product **14c** (4 mg, 5.7%). Compound **14b**: mp 67−68 °C; FTIR (benzene cast) 3346 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz) δ 1.55 (s, 1 H), 1.9 (d, J = 15.6 Hz, 1 H), 2.3 (dd, J = 15.9, 4.8 Hz, 1 H), 2.36−2.53 (m, 1 H), 2.60−2.82 (m, 3 H), 2.95 (dd, J = 15.9, 7.9 Hz, 1 H), 4.75 (quintuplet, J = 1.95 Hz, 2 H), 6.90−7.13 (m, 3 H), 7.20−7.30 (m, 1 H); ^{13}C NMR (C_6D_6, 75.5 MHz) δ 37.20 (t′), 39.48 (t′), 46.90 (t′), 52.26 (d′), 91.63 (s′), 106.83 (t′), 123.84 (d′), 125.18 (d′), 127.32 (d′), 128.46 (d′), 142.56 (s′), 147.85 (s′), 150.70 (s′); exact mass, *m*/*z* calcd for $C_{13}H_{14}O$ 186.10446, found 186.10383. Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.80; H, 7.49.

Compound **14c**: ^1H NMR (benzene-d_6, 200 MHz) δ 1.52 (s, 3 H), 1.80 (dd, J = 15, 11 Hz, 1 H), 2.30−2.55 (m, 2 H), 2.58−2.85 (m, 2 H), 4.60 (s, 1 H), 4.72 (s, 1 H), 6.85−7.01 (m, 2 H), 7.10 (br d, J = 6 Hz, 1 H), 7.82 (br d, J = 8 Hz, 1 H); exact mass, *m*/*z* calcd for $C_{13}H_{14}O$ 186.10446, found 186.10474.

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Supporting Information Available: NMR spectra for new compounds that were not analyzed, experimental procedures for **12a**, **15a**, and **16a**−**21a**, and additional references related to the topics described in ref 1, 5, and 6 (25 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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