The ^1H NMR of exo hydrocarbon **9** shows two doublets of doublets at 0.93 and 0.63 ppm which have been assigned to the H_8 anti and syn protons, respectively.[16] A COSY spectrum of **12** showed an off-diagonal element between the signals at 0.93 and 1.7 ppm ($H_{2,4}$) which indicates *W* coupling between the anti bridgetop proton and protons $H_{2,4}$.

Experimental Section[17]

Diimide Reduction of *anti*-8-*tert*-Butoxy-*endo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene (4). The endo-anti **4** (496 mg, 1.5 mmol) was dissolved in 20 mL of methanol in a three-necked flask fitted with a condenser and a barium hydroxide trap under nitrogen. Freshly prepared[18] potassium azodicarboxylate (0.90 g, 4.5 mmol) was added in one portion and stirred. A methanol solution of glacial acetic acid (0.4 mL of acetic acid in 5 mL of methanol) was added dropwise using an addition funnel over a period of 30 min, and stirring was continued for 1 h. After the addition of 100 mL of water, the mixture was extracted with hexane and upon concentration white crystals of **5** were obtained (420 mg, 85%): mp 122–123 °C; ^1H NMR 7.7 (2 H, m, ArH), 7.4–6.97 (8 H, m, ArH), 3.9 (1 H, br s, H_8), 2.43 (2 H, br s, $H_{1,5}$), 1.8 (2 H, t, $H_{2,4}$), 1.16 (9 H, s, *t*-Bu), 1.1–1.6 (4 H, m, $H_{6,7}$); IR 2980, 1600, 1490, 1450, 1370 cm^{-1}; ^{13}C NMR 150.6, 141.1 (Ar ipso), 130.98, 128.21, 127.73, 127.19, 126.26, 125.63 (Ar methines), 87.89 (C_8), 72.79 (quat C in *t*-Bu), 48.66 (C_3), 42.76 ($C_{1,5}$), 28.62 ($C_{2,4}$), 28.46 ($C_{6,7}$), 22.78 (CH_3). Anal. Calcd for $C_{24}H_{28}O$: C, 86.7; H, 8.49. Found: C, 86.83; H, 8.48.

Cleavage of *anti*-8-*tert*-Butoxy-*endo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]octane (5). To 166.5 mg (0.5 mmol) of **5**, dissolved in 5 mL of 20% acetic anhydride/acetic acid (v/v) cooled in ice, was added perchloric acid (0.07 mL, 0.75 mmol), and the mixture was stirred. After 1 min, the mixture was poured over 300 g of crushed ice, neutralized with sodium carbonate, and extracted repeatedly with ether. The ether extract was washed with sodium carbonate and water, dried over anhydrous sodium sulfate, and subjected to rotational TLC to yield 145 mg (90%) of colorless crystals of rearranged 2-acetoxy-3,3-diphenyltricyclo[3.3.0.0^{4,6}]octane (**6**). Cleavage with ferric chloride[10] also afforded only **6** in 65% yield: mp 104–105 °C; ^1H NMR 7.70 (2 H, m, ArH), 7.4–7.07 (8 H, m, ArH), 5.93 (1 H, d, $J = 8$ Hz, H_2), 3.07–3.4 (1 H, m, H_4), 2.27 (1 H, q, H_6), 1.97 (3 H, s, $COCH_3$), 1.05–1.95 (6 H, env, $H_{1,5,7,8}$); IR 2960, 1750, 1600, 1500, 1450, 1260 cm^{-1}; ^{13}C NMR 169.42 (C=O), 152.33, 143.0 (Ar ipso), 130.25, 128.04, 127.27, 126.94 (Ar), 125.78 (Ar-*p*), 126.03 (Ar-*p*), 85.57 (C_2), 57.86 (C_3), 46.63 (C_1), 38.51, 33.18, 29.27, 28.62, 24.65, 20.99 (Ac CH_3). Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: C, 83.20; H, 6.96.

Reduction of 2-Acetoxy-3,3-diphenyltricyclo[3.3.0.0^{4,6}]octane (6) to Alcohol 7. Acetate **6** was reduced to alcohol **7** by LAH in ether and upon workup afforded 350 mg (65%) of crystalline solid: ^1H NMR 7.9 (2 H, m, ArH), 7.2 (8 H, m, ArH), 4.78 (1 H, t, $J = 8$ Hz, H_2), 2.83 (1 H, m, H_1), 2.15 (1 H, q, H_7), 1.93 (1 H, br, OH), 1.9–0.80 (6 H, env, $H_{4,5,6,8}$); IR 3600, 3400–3500 (bonded OH) 3120, 2895, 1600, 1500, 1450 cm^{-1}.

Oxidation of Alcohol 7 to Ketone 8. To a stirred solution of 340 mg (1.5 mmol) of PCC in 10 mL of methylene chloride was rapidly added 138 mg (0.5 mmol) of alcohol **7** in 10 mL of methylene chloride, and the orange solution quickly darkened. After the solution was stirred overnight, workup, followed by chromatography on Florisil, yielded 132 mg (100%) of colorless crystalline solid: mp 130–131 °C; ^1H NMR 7.70 (2 H, m, ArH), 7.40–7.05 (8 H, m, ArH), 2.97 (1 H, m, H_1), 2.63–0.7 (7 H, env, $H_{4,5,6,7,8}$); IR 3120, 2980, 1740, 1600, 1500, 1450, 1340 cm^{-1}; ^{13}C NMR 220.5 (C=O), 146.78, 141.06 (Ar ipso), 128.28, 128.12, 127.31 (Ar), 126.76 (Ar-*p*), 126.40 (Ar-*p*), 61.64 (C_3), 53.40 (C_1), 40.76, 35.52, 24.95, 28.87, 22.75. Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.55; H, 6.59.

Compound 9: mp 75–76 °C (lit.[1] mp 74–75 °C); ^1H NMR[13] 6.95–7.36 (10 H, m, Ar), 5.18 (2 H, t, $H_{6,7}$), 3.11 (2 H, br s, $H_{1,5}$), 2.25 (2 H, t, $H_{2,4}$), 2.01 (1 H, dt, H_{8s}), 1.71 (1 H, d, H_{8a}); 2D NMR data[19] 5.18 ($H_{6,7}$) coupled to 3.17 ($H_{1,5}$); 3.17 ($H_{1,5}$) coupled to 5.18 ($H_{6,7}$), 2.25 ($H_{2,4}$), and 2.01 (H_{8s}); 2.25 ($H_{2,4}$) coupled to 3.11 (H_{15}) and 1.71 (H_{8a}); 1.71 (H_{8a}) coupled to 2.25 ($H_{2,4}$), 3.11 ($H_{1,5}$), and 2.01 (H_{8s}); 2.01 (H_{8s}) coupled to 1.71 (H_{8a}), 5.18 ($H_{6,7}$), and 3.11 ($H_{1,5}$).

Deuterated compound 11: mp 75–77 °C; ^1H NMR 6.95–7.30 (10 H, m, Ar), 5.15 (2 H, t, $H_{6,7}$), 3.07 (2 H, br s, $H_{1,5}$), 2.25 (2 H, t, $H_{2,4}$), 1.70 (1 H, s, H_{8a}); 2D NMR data[19] 5.15 ($H_{6,7}$) coupled to 3.07 ($H_{1,5}$); 3.07 ($H_{1,5}$) coupled to 5.15 ($H_{6,7}$), 2.25 ($H_{2,4}$), and 1.7 (H_{8a}); 2.25 ($H_{2,4}$) coupled to 3.07 ($H_{1,5}$) and 1.70 (H_{8a}); 1.70 (H_{8a}) coupled to 3.07 ($H_{1,5}$) and 2.25 ($H_{2,4}$); H_{8s} not coupled to 5.15 ($H_{6,7}$).

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support, the Arthur Schmitt Foundation for Fellowships to M.P. and R.S., Abbott Laboratories for the 500-MHz COSY spectra, and M. Choubal and LUCID for assistance with the drawings.

Supplementary Material Available: ^1H and COSY NMR spectra of **9** and deuterated compound **11** (4 pages). Ordering information is given on any current masthead page.

---

[16] Wilt, J. W.; Malloy, P. T.; Mookerjee, P. K.; Sullivan, D. R. *J. Org. Chem.* 1974, *39*, 1327.

[17] Chemicals were from Aldrich, and solvents were from Fisher except where mentioned. All melting points were determined on a calibrated Fisher-Johns apparatus. Thin-layer chromatography was performed using plastic backed silica gel coated plates (EM Science and Eastman Kodak Company). Chromatographic separations were performed by rotational TLC using a Chromatotron (Harrison Research Model 7294) with 1-, 2-, and 4-mm plates coated with silica gel 60 PF_{254}, containing calcium sulfate binder (EM Science). ^1H NMR spectra were recorded at 60, 80, and 300 MHz in $CDCl_3$ solution with chemical shifts reported in δ ppm from internal TMS. ^{13}C NMR spectra were similarly recorded at 20 MHz. COSY spectra were run on a 300-MHz Varian or 500-MHz Bruker (11) in $CDCl_3$ and analyzed from contour plots. Solution IR spectra were recorded with 0.1-mm sodium chloride cells. Combustion analyses were performed by Microtech Labs, Skokie, IL.

[18] Thiele, J. *Ann.* 1892, *271*, 127.

[19] Available as supplementary material. See any current masthead page for ordering information.

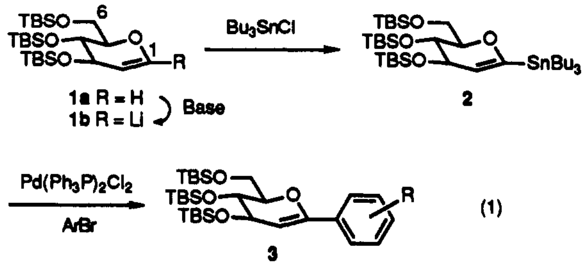
Observation of α-Silyl Carbanions in the Metalation of 3,4,6-Tri-*O*-(*tert*-butyldimethylsilyl)-D-glucal

Richard W. Friesen,* Claudio F. Sturino, Anand K. Daljeet, and Aleksandra Kolaczewska

Department of Chemistry, University of Toronto, Lash Miller Chemical Laboratories, 80 St. George St., Toronto, Ontario, Canada M5S 1A1

Received August 30, 1990

We have recently reported that 3,4,6-tri-*O*-(*tert*-butyldimethylsilyl)-1-(tributylstannyl)-D-glucal (**2**) can be efficiently utilized in palladium-catalyzed coupling reactions with aryl bromides (eq 1).[1] In connection with several



synthetic efforts directed toward the synthesis of *C*-aryl

---

[1] Friesen, R. W.; Sturino, C. F. *J. Org. Chem.* 1990, *55*, 2572.

Table I. Metalation of 3,4,6-Tri-*O*-(*tert*-butyldimethylsilyl)-D-glucal (1a) with ^{t}BuLi[a]

entry	solvent	equivalents of ^{t}BuLi	temperature (°C)	^{2}H incorporation at C1 (%)[b]	ratio of D1:SiCH$_2$*D*[c]
1	THF	0.7	0	12	2.3:1
2	THF	1.4	0	54	2.4:1
3	THF	2.1	0	73	1.5:1
4	THF	3.5	0	92	1.2:1
5	THF	4.0	0	>98	1:1.1
6	THF	2.7	-20	82	1.2:1
7	THF	2.7	-78	0	-
8	Et$_2$O	1.0	0	12	*d*
9	Et$_2$O	2.0	-45	45	2.5:1
10	Et$_2$O	2.8	0	86	1.1:1
11	Et$_2$O	3.4	0	>98	1:1.4
12	THF/pentane[e]	1.2	0	58	*d*
13	THF/pentane[e]	2.0	0	87	1.2:1
14	THF/pentane[e]	2.8	0	>98	1:1.2

[a] Metalations were carried out on approximately 1 M solutions of **1a** in the solvents indicated for 1–2 h, followed by treatment with excess D$_2$O (entries 1–5, 8, 10–14) or CD$_3$OD (entries 6, 7, 9) at the reaction temperature. [b] From integration of the H1 and H2 resonances (δ 6.32 and 4.68 ppm, respectively) in the ^{1}H NMR spectra (200 MHz, CDCl$_3$). [c] From integration of the D1 and SiCH$_2$*D* resonances (δ 6.4 and 0.06 plus 0.10 ppm, respectively) in the proton decoupled ^{2}H NMR spectra (61.4 MHz, CHCl$_3$). [d] Not measured. [e] 4–6 equiv of THF/6–9 equiv pentane as solvent.

glycoside natural products[2] by the stereocontrolled functionalization of the C1–C2 enol ether double bond in **3**,[3] we required significant quantities of the stannylglucal **2**. The C1 metalation of the highly substituted dihydropyran analogue **1a** had been reported by a number of groups[4] to require 1.5–2 equiv of ^{t}BuLi or Schlosser's[5] base. The vinyl lithio species **1b** that was presumed to be formed was subsequently reacted with a variety of electrophiles, including Bu$_3$SnCl, to provide the alkylated products corresponding to **2** in good yields. However, in our hands, and under a wide variety of reaction conditions that involved varying the amount of base (^{t}BuLi or Schlosser's), the solvent, the amount of Bu$_3$SnCl, and the temperature and time of the reaction, we were able to obtain **2** from **1a** in isolated yields of only 12–30%. All of the reaction mixtures were contaminated by varying amounts of several components that were less polar (TLC) than **2**, and which proved to be extremely difficult to separate from **2** by column chromatography.

In an attempt to clarify these results, we initiated a program to study the metalation of **1a** and the subsequent reactions of the derived anionic species with D$_2$O (or CD$_3$OD) and Bu$_3$SnCl. We report herein that the species that is obtained by the reaction of **1a** with ^{t}BuLi, and that is fully metalated at C1, is not a monoanion, but is comprised of both vinyl and α-silyl carbanions that reacts at both metalated sites with D$_2$O and Bu$_3$SnCl. We also present two efficient alternatives for obtaining 3,4,6-tri-*O*-(trialkylsilyl)-1-(tributylstannyl)-D-glucals via vinylic metalation procedures.

Results and Discussion

Utilizing metalation conditions described by Boeckman,[6] THF solutions of **1a** (ca. 1 M) were treated with ^{t}BuLi at -78 °C and allowed to react at various temperatures. Upon quenching the reaction mixtures with D$_2$O or CD$_3$OD, the degree of deprotonation at C1 was determined by inspecting the integrated ^{1}H NMR spectra of the crude reaction products. An illustrative sampling of our results, taken from a large number of experiments, are summarized in Table I, entries 1–7.

Perhaps the most surprising result is the observation that more than 2 equiv of ^{t}BuLi are necessary to achieve *complete* (>98%) vinylic deprotonation of **1a** at C1. While no metalation is observed at -78 °C (entry 7), results analogous to those obtained at 0 °C are observed at temperatures of -20 °C (entry 6). The origin of the requirement for excess ^{t}BuLi to effect quantitative C1 metalation is not completely clear. As postulated by Boeckman,[6] complexation of the metalating species by the highly oxygenated substrate is possible, as is the consumption of ^{t}BuLi through reaction with THF[7] or adventitious water. However, evidence for a third and more definitive reaction process is found upon inspection of the integrated, proton-decoupled ^{2}H NMR spectra of the deuterated materials (Table I). For those reactions that exhibit even partial C1 deprotonation and deuteration, in addition to the expected vinylic ^{2}H resonance at δ 6.4 ppm (broad), two ^{2}H resonances are observed at approximately δ 0.10 and 0.06 ppm.[8] These upfield resonances indicate that α-silyl carbanions have been formed[9–11] and trapped with D$_2$O, placing ^{2}H atoms α to silicon. Under conditions that yield quantitative metalation at C1 (Table I, entry 5), 1 full equiv of ^{2}H has been incorporated α to silicon as evidenced by the integrated ^{2}H NMR spectra. Furthermore, the mass

---

(2) (a) Daves, G. D., Jr. *Acc. Chem. Res.* **1990**, *23*, 201. (b) Hacksell, U.; Daves, G. D., Jr. *Prog. Med. Chem.* **1985**, *22*, 1.

(3) We have utilized this methodology in the synthesis of the *C*-aryl glucoside nuclei of the papulacandins (Friesen, R. W.; Sturino, C. F. *J. Org. Chem.*, in press) and chaetiacandin (Friesen, R. W.; Daljeet, A. K. *Tetrahedron Lett.*, in press).

(4) (a) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E. *J. Chem. Soc., Chem. Commun.* **1986**, 925. (b) Hanessian, S.; Martin, M.; Desai, R. C. *J. Chem. Soc., Chem. Commun.* **1986**, 926. (c) Lesimple, P.; Beau, J.-M.; Jaurand, G.; Sinay, P. *Tetrahedron Lett.* **1986**, *27*, 6201.

(5) Schlosser, M.; Strunk, S. *Tetrahedron Lett.* **1984**, *25*, 741.

(6) (a) Boeckman, R. K., Jr.; Bruza, K. J. *Tetrahedron Lett.* **1977**, *48*, 4187. (b) Boeckman, R. K., Jr.; Bruza, K. J. *Tetrahedron* **1981**, *23*, 3997.

(7) Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560.

(8) At low percentages of C1 metalation/deuteraton, the resonance at δ 0.06 ppm is the only high-field peak observed (entry 1). At higher degrees of ^{2}H incorporation at C1, the resonance at δ 0.10 ppm increases in intensity to a maximum ratio (δ 0.06 to δ 0.10) of approximately 2.6:1 (entry 5).

(9) Peterson (Peterson, D. J. *J. Organomet. Chem.* **1967**, *9*, 373) demonstrated that tetramethylsilane undergoes metalation to the extent of only 40% upon treatment with ^{n}BuLi/TMEDA complex for four days at room temperature.

(10) A wide variety of trimethylsilyl-stabilized metalated reagents of the type Me$_3$SiCH(Li)Z have been prepared and utilized in a variety of synthetic transformations. See, for example: (a) Magnus, P. *Aldrichimica Acta* **1980**, *13*, 43. (b) Magnus, P.; Roy, G. *Organometallics* **1982**, *1*, 553.

(11) Boeckman has also noted (footnote 16b in Boeckman, R. K., Jr.; Charette, A. B.; Asberom, T.; Johnston, B. H. *J. Am. Chem. Soc.* **1987**, *109*, 7553) the formation of α-silyl carbanions in the attempted deprotonation of a substituted cyclic vinyl ether.

spectrum of this deuterated material indicates the incorporation of two ^{2}H atoms.

Thus, the metalation of **1a** in THF on a TBS group(s)[12] with ^{t}BuLi occurs to an extent at least equal to that of C1 deprotonation for those species in which C1 has been fully metalated (Table I, entries 1–7). Analogous results are observed when ether or THF/pentane are used as reaction solvents (Table I, entries 8–14).

In accord with our metalation/deuteration experiments, it should not be surprising to find that quenching solutions of metalated **1a** with Bu_3SnCl should yield not only **2**, but distannylated material. In the event, treatment of **1a** with ^{t}BuLi (3.5 equiv, THF, 0 °C; see Table I, entry 4) followed by Bu_3SnCl (2.5 equiv, −78 °C) provided **2** (15%) and two separable ditin adducts (**4** (less polar) and **5** (more polar); combined yield 54%) that were identified as the nonpolar components of all our previous reaction mixtures.

The formation of the ditin products **4** and **5** from **1a** was a serious drawback to the preparation of pure **2**. From a synthetic point of view, an effective solution for avoiding overmetalation is to utilize silicon protecting groups (TIPS or TBDPS) that are less prone to α-silyl carbanion formation under the reaction conditions. Thus, treatment of a THF solution of **6** with excess ^{t}BuLi (6 equiv) at 0 °C for 1 h, followed by D_2O, cleanly provided the monodeuterated product **7**. A single ^{2}H resonance was observed at δ 6.43 ppm in the ^{2}H NMR spectrum of material that had been fully metalated and deuterated at C1 (from ^{1}H NMR). Treatment of such a metalated species with Bu_3SnCl provided the tin glucal **8** in 71% yield. Similarly, reactions of **9** provided the monodeuterio compound **10** (^{2}H NMR, δ 6.30 ppm) or the monostannylated product **11** (71% yield).[13]

4, 5 R = 2(TBS), Si(CH_2SnBu_3)Me^{t}Bu, X = $SnBu_3$
6 R = TIPS, X = H
7 R = TIPS, X = D
8 R = TIPS, X = $SnBu_3$
9 R = TBDPS, X = H
10 R = TBDPS, X = D
11 R = TBDPS, X = $SnBu_3$

Summary

We have demonstrated that reaction conditions that are required to achieve complete vinylic deprotonation of **1a** result in the production of metalated species that also contain α-silyl carbanions. The metalated species so formed react with D_2O (or CD_3OD) and Bu_3SnCl to form materials that are deuterated or stannylated α to silicon as well as at C1. The formation of α-silyl carbanions appears to be a facile process, at least in this system, and one should be aware of this possibility when conducting metalation reactions using ^{t}BuLi on highly oxygenated compounds that contain TBS protecting groups.

Experimental Section

General Procedures. Specific rotations at 25 °C were measured with a sodium D lamp in $CHCl_3$ (concentration given in g/100 mL). ^{1}H NMR spectra were recorded at the field strength indicated in $CDCl_3$ using TMS as internal standard or, for those compounds containing TBS and/or Bu_3SnCl moieties, relative to $CHCl_3$. Proton-decoupled ^{2}H NMR spectra were recorded at 61.4 MHz in $CHCl_3$ using $CDCl_3$ as internal standard. Broad band proton decoupled ^{13}C NMR spectra were recorded at 50 MHz in $CDCl_3$ using $CDCl_3$ as internal standard. DEPT ^{29}Si NMR spectra were recorded at 79.4 MHz in $CDCl_3$ using TMS as internal standard. IR spectra were recorded on neat samples. ^{t}BuLi was obtained from commercially available sources and was titrated as described by Kafron and Baclawski.[14] Solvents were anhydrous and transferred via syringes under argon atmosphere. D_2O and CD_3OD obtained from commercially available sources were 99.9 atom % D and 99.8 atom % D, respectively. Column chromatography was carried out on 230–400-mesh silica gel (40–63 μm), eluting with the solvents indicated.

General Procedure for the Metalation/Deuteration of 1a. A solution of **1a** in the appropriate solvent (see Table I; approximately 1 M) at −78 °C was treated dropwise with ^{t}BuLi (hexane solution) and allowed to react at the indicated temperature for 1–2 h. Excess D_2O or CD_3OD was then added. After stirring at room temperature for 30 min, $MgSO_4$ was added, and the solution was filtered and concentrated. The crude reaction products were inspected by ^{1}H and/or ^{2}H NMR spectroscopy. The deuterated material that was obtained from the reaction that provided a species fully metalated at C1 (Table I, entry 5) was purified by column chromatography (elution with 5% CH_2Cl_2 in hexanes, 95% recovery). This material (colorless oil), a mixture of deuterated isomers, exhibited the following properties: ^{1}H NMR (400 MHz) δ 0.05, 0.06, 0.075, and 0.078 (s each), 0.10 (s, 6 H), 0.885, 0.888, and 0.895 (s each, 9 H each), 3.76 (dd, 1 H, J = 3.4, 11.2 Hz), 3.79 (dt, 1 H, J = 1.2, 3.4 Hz), 3.89 (ddd, 1 H, J = 1.3, 3.4, 4.6 Hz), 3.93 (dd, 1 H, J = 7.4, 11.2 Hz), 3.99 (ddt, 1 H, J = 1.4, 7.4, 3.4 Hz), 4.69 (dd, 1 H, H2, J = 1.2, 4.3 Hz); ^{2}H NMR δ 0.06 and 0.10 (integrates to 1.1 times that the resonance at δ 6.40), 6.40; ^{13}C NMR δ −5.5, −5.0, −4.63, −4.56, −4.46, 17.8, 17.9, 18.3, 25.7, 25.8, 61.7, 66.7, 70.2, 80.1, 101.3; exact mass calcd for $C_{23}H_{47}D_2O_4Si_3$ $(M - CH_3)^+$ 475.3074, found 475.3086.

Stannylation of 1a. A solution of **1a** (5.30 g, 10.8 mmol) in THF (11 mL) at −78 °C was treated dropwise with ^{t}BuLi (30.1 mL of a 0.9 M solution in hexane) and stirred for 1 h at 0 °C. The solution was recooled to −78 °C, and Bu_3SnCl (7.3 mL, 27 mmol) was added. After 15 min at this temperature, water (50 mL) was added. The mixture was extracted with ether, and the combined organics were dried ($MgSO_4$) and concentrated. Flash chromatography of the residual oil on silica gel (elution with 5% CH_2Cl_2 in hexanes) provided **2** (1.23 g, 15%) and a mixture of **4** and **5** (6.20 g, 54%). 3,4,6-Tri-*O*-(*tert*-butyldimethylsilyl)-1-(tributylstannyl)-D-glucal (**2**) was obtained as a colorless oil and exhibited the following properties: $[\alpha]_D$ −25.0° (*c* 2.5); IR 2956, 2929, 2886, 1649, 1471, 1463 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.02, 0.03, and 0.06 (s each, 3 H each), 0.07 (s, 6 H), 0.08 (s, 3 H), 0.82–0.92 (m, 42 H), 1.28 (m, 6 H), 1.49 (m, 6 H), 3.72 (m, 2 H), 3.80 (m, 2 H), 3.98 (m, 1 H), 4.68 (d, 1 H, J = 3.2 Hz, J_{Sn-H} = 27.6 Hz); ^{13}C NMR δ −5.5, −5.4, −4.1, −3.9, 9.4 (J_{Sn-C} = 169 Hz), 13.5, 19.0, 25.8, 25.9, 27.1 (J_{Sn-C} = 58 Hz), 28.8 (J_{Sn-C} = 21 Hz), 62.1, 69.5, 70.6, 80.2, 113.6, 161.5; DEPT (J = 6.5 Hz) ^{29}Si NMR δ 17.5, 18.8, 19.7; exact mass calcd for $C_{32}H_{69}O_4Si_3{}^{120}Sn$ $(M - C_4H_9)^+$ 721.3525, found 721.3533.

Further purification of the mixture of ditins **4** and **5** was effected by drip column chromatography (elution with 1% CH_2Cl_2 in hexanes). The less polar material, **4**, a colorless oil, exhibited the following properties: $[\alpha]_D$ −14.4° (*c* 0.93); IR 2967, 2929, 2856, 1602, 1463, 1252, 1110, 1071, 836, 777 cm^{-1}; ^{1}H NMR (400 MHz) δ −0.39 and −0.21 (AB q, J = 13.3 Hz, J_{Sn-H} = 66 Hz), 0.01, 0.047, 0.051, 0.057, and 0.061 (s each, 3 H each), 0.86, 0.87, and 0.88 (s each, 9 H each), 3.65 (br t, 1 H, J = 4.5 Hz), 3.78 (m, 3 H), 3.88 (br t, 1 H, J = 4.0 Hz), 4.66 (d, 1 H, J = 3.7 Hz, J_{Sn-H} = 28 Hz); ^{13}C NMR δ −12.6, −4.9, −4.3, 9.3, 10.4, 13.52, 13.57, 17.8, 18.0, 19.5, 25.7, 25.9, 26.4, 27.1, 27.3, 28.8, 29.1, 63.1, 68.5, 70.9, 80.7, 113.0,

---

(12) The site(s) of α-silyl metalation is a subject of current research. Professor Tius has informed us that the metalation of a TBS protected olivose derivative (a 6-deoxy glucal) with ^{t}BuLi proceeds cleanly at C1 to provide a monometalated species. Thus, it would appear that the C6 position of **1a** is a likely candidate for the α-silyl metalation. We would like to thank Professor Tius for personal communications and a preprint of their paper that described this work. Paquette (Paquette, L. A.; Oplinger, J. A. *Tetrahedron* **1989**, *45*, 107) has also described the successful deprotonation of the same olivose derivative using Schlosser's base.

(13) It should be noted that glucals **6** and **9** are thick glassy oils and, experimentally, are somewhat difficult to work with and to obtain in rigorously anhydrous form. We presume that adventitious water is the factor responsible for the large excess of ^{t}BuLi that is required to effect complete C1 metalation with glucals **6** and **9**.

(14) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

162.8; DEPT ($J = 6.5$ Hz) ^{29}Si NMR δ 17.8, 18.5, 20.4; FAB MS 1069 $(M + H)^+$.

The more polar material, **5**, a colorless oil, exhibited the following properties: $[\alpha]_D$ −24.4° (*c* 1.24); IR 2956, 2928, 2856, 1603, 1463, 1252, 1109, 1071, 836, 778 cm^{-1}; ^{1}H NMR (400 MHz) δ −0.37 and −0.24 (AB q, 2 H, $J = 13.2$ Hz, $J_{Sn-H} = 65$ Hz), 0.01 (s, 3 H), 0.05 (s, 6 H), 0.058 and 0.064 (s each, 3 H each), 0.86, 0.87, and 0.88 (s each, 9 H each), 3.69 (m, 1 H), 3.78 (m, 3 H), 3.89 (br t, 1 H, $J = 4.0$ Hz), 4.67 (d, 1 H, $J = 3.7$ Hz, $J_{Sn-H} = 28$ Hz); ^{13}C NMR δ −12.7, −4.9, −4.34, −4.27, −4.15, 9.3, 10.4, 13.51, 13.55, 17.8, 18.0, 19.3, 25.7, 25.9, 26.4, 27.1, 27.3, 28.8, 29.0, 62.7, 68.6, 70.8, 80.6, 113.0, 162.7; DEPT ($J = 6.5$ Hz) ^{29}Si NMR δ 17.7, 18.5, 20.6; FAB MS 1069 $(M + H)^+$.

3,4,6-Tri-*O*-(triisopropylsilyl)-D-glucal (6) and 3,4,6-Tri-*O*-(*tert*-butyldiphenylsilyl)-D-glucal (9). A solution of D-glucal and imidazole (7.2 equiv) in DMF (15 mL per 500 mg of D-glucal) was treated with TIPSCl (3.6 equiv) or TBDPSCl (3.6 equiv) and the resulting mixture was heated at 70–95 °C for 24 h. If required, additional silyl chloride (1.8 equiv) was added and the solution was stirred for a further 24 h. The solution was diluted with water and extracted with ether. The organic layer was washed with water and saturated brine and dried ($MgSO_4$). Concentration and purification by column chromatography provided the products **6** (colorless oil, 76%) or **9** (colorless oil, 86%).

6: $[\alpha]_D$ −18.6° (*c* 1.99); IR 688, 892, 1061, 1251, 1469, 1651, 2868, 2945 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.03 (m, 63 H), 3.79 (dd, 1 H, $J = 3.7, 11.2$ Hz), 3.92 (dt, 1 H, $J = 5.2, 1.9$ Hz), 4.00–4.10 (m, 2 H), 4.20 (m, 1 H), 4.78 (ddd, 1 H, $J = 1.6, 5.2, 6.4$ Hz), 6.33 (d, 1 H, $J = 6.4$ Hz); ^{13}C NMR δ 11.9, 12.2, 12.3, 17.8, 17.91, 17.95, 62.0, 65.1, 70.3, 80.7, 100.4, 143.1; exact mass calcd for $C_{30}H_{63}O_4Si_3$ $(M - C_3H_7)^+$ 571.4034, found 571.4021.

9: $[\alpha]_D$ −2.2° (*c* 3.30); IR 691, 1059, 1112, 1428, 1645, 2857, 2931 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.65, 0.84, and 0.94 (s each, 9 H each), 3.64 (m, 2 H), 3.87 (m, 1 H), 4.03–4.20 (m, 2 H), 4.34 (m, 1 H), 6.20 (d, 1 H, $J = 6.4$ Hz), 7.07–7.57 (m, 30 H); ^{13}C NMR δ 18.8, 19.2, 26.7, 26.8, 27.0, 62.7, 64.9, 70.5, 80.0, 100.5, 127.7–136.2 (16 lines), 143.4; FAB MS 859 $(M - H)^+$.

3,4,6-Tri-*O*-(triisopropylsilyl)-1-(tributylstannyl)-D-glucal (8). A solution of **6** (100 mg, 0.163 mmol) in THF (2 mL) at −78 °C was treated with ^{t}BuLi (0.6 mL, 6.0 equiv), and the resulting solution was stirred at 0 °C for 1 h. Bu_3SnCl (0.48 mL, 0.57 mmol) was added at −78 °C, and the resulting solution was stirred for 15 min. The reaction mixture was diluted with water and extracted with ether. The organic layer was washed with water and saturated brine and dried ($MgSO_4$). Concentration, followed by purification by column chromatography, provided **8** as a colorless oil (105.5 mg, 71%): $[\alpha]_D$ −22.4° (*c* 2.30); IR 688, 886, 1061, 1089, 1469, 1602, 2868, 2942 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.50–1.05 (m, 78 H), 1.20–1.64 (m, 12 H), 3.84 (m, 1 H), 3.90–3.96 (m, 2 H), 4.01–4.10 (m, 2 H), 4.83 (dd, 1 H, $J = 1.6, 5.1$ Hz, $J_{Sn-H} = 29$ Hz); ^{13}C NMR δ 9.3, 11.9, 12.3, 12.4, 13.5, 17.9, 18.0, 27.1, 28.8, 62.4, 65.1, 70.3, 80.6, 111.4, 162.6; exact mass calcd for $C_{45}H_{96}O_4Si_3{}^{120}Sn$ (M^+) 904.5638, found 904.5637.

3,5,6-Tri-*O*-(*tert*-butyldiphenylsilyl)-1-(tributylstannyl)-D-glucal (11). The glucal **9** used in the following reaction was dried under high vacuum at 50 °C for 6 days prior to use. Using a procedure identical with that described above for the preparation of **8**, **9** was converted to **11** (colorless oil, 71%): $[\alpha]_D$ +27.1° (*c* 2.28); IR 622, 701, 788, 823, 1029, 1112, 1427, 1601, 2857, 2929 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.76 (s, 9 H), 0.85 (m, 15 H), 0.91 and 0.99 (s each, 9 H each), 1.15–1.70 (m, 12 H), 3.65 (m, 1 H), 3.75 (br q, 1 H, $J = 6.5$ Hz), 3.96 (m, 1 H), 4.06–4.19 (m, 2 H), 4.49 (dd, 1 H, $J = 1.6, 5.2$ Hz, $J_{Sn-H} = 29$ Hz), 7.13–7.60 (m, 30 H); ^{13}C NMR δ 8.6, 9.6, 13.8, 18.9, 19.3, 26.9, 27.0, 27.4, 29.1, 62.9, 64.8, 70.6, 79.7, 111.5, 127.7–136.3 (13 lines), 163.2; FAB MS 1149 $(M - H)^+$.

Acknowledgment. We would like to thank the Natural Sciences and Engineering Research Council of Canada and the University of Toronto for financial support of this work and the University of Toronto for an Open Fellowship (to C.F.S.).

Registry No. **1a**, 79999-47-6; **2**, 105938-00-9; **4**, 131216-77-8; **5**, 131235-96-6; **6**, 131216-78-9; **7**, 131216-79-0; **8**, 131216-80-3; **9**, 105937-90-4; **10**, 131216-81-4; **11**, 131216-82-5; D-glucal, 13265-84-4.

Supplementary Material Available: ^{1}H and ^{2}H NMR spectra of the deuterated compound resulting from complete metalation at C1 (Table I, entry 5) and copies of ^{1}H NMR spectra of **1a**, **2**, **4**, **5**, **6**, **8**, **9**, and **11** (21 pages). Ordering information is given on any current masthead page.

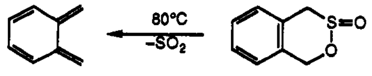
A Convenient Synthesis of 1,4-Dihydro-2,3-benzoxathiin 3-Oxide, a Useful Precursor of *o*-Quinodimethane[1]

Michael D. Hoey and Donald C. Dittmer*

Department of Chemistry, Center for Science and Technology, Syracuse University, Syracuse, New York 13244-4100

Received August 24, 1990

o-Quinodimethane[*o*-xylylene; 5,6-bis(methylene)-1,3-cyclohexadiene] (**1**) is a useful diene intermediate for Diels–Alder reactions. Its synthesis and reactions have been reviewed.[2] The sultine, 1,4-dihydro-2,3-benzoxathiin 3-oxide (**2**), is an ideal precursor because it decomposes smoothly around 80 °C and does not produce organic or inorganic byproducts except for sulfur dioxide and, in the absence of a dienophile, oligomeric and polymeric material.[3] Other methods[2] for producing **1** involve reactions of ortho-disubstituted benzene derivatives whose preparations frequently require multiple steps and/or the use of uncommon, expensive, or toxic reagents and whose decomposition to **1** either necessitates the employment of relatively high temperatures or additional reagents and workup procedures to remove byproducts. Examples of these methods include the Hofmann elimination applied to (*o*-methylbenzyl)trimethylammonium hydroxide and related compounds,[4] and the dehalogenation of α,α'-dihalo-*o*-xylenes by various reagents such as metals[5] and sodium benzenetellurolate.[6]



1 **2**

Sultine **2** has been obtained by treatment of *o*-(*tert*-butylsulfinylmethyl)benzyl alcohol with *N*-chlorosuccinimide,[7] or *o*-benzenedimethanol with 1,1′-thiobisbenzimidazole,[8] or 2-dipropynyl sulfone with acetylene cata-

---

[1] Taken from the Ph.D. Thesis of M. D. Hoey, Syracuse University, 1990.

[2] (a) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873–2889. (b) Ciganek, E. *Org. React.* **1984**, *32*, 72–374. (c) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41–61. (d) Oppolzer, W. *Synthesis* **1978**, 793–802.

[3] A review of sultines: Dittmer, D. C.; Hoey, M. D. *The Chemistry of Sulphinic Acids, Esters and Their Derivatives*; Wiley: Chichester, 1990; pp 239–273.

[4] (a) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949–954. (b) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609–7622. (c) Fujiwara, T.; Ohsaka, T.; Inoue, T.; Takeda, T. *Tetrahedron Lett.* **1988**, *48*, 6283–6286.

[5] Inaba, S.; Wehmeyer, R. M.; Forkner, M. W.; Rieke, R. *J. Org. Chem.* **1988**, *53*, 339–344 and references cited therein.

[6] Kambe, N.; Tsukamoto, T.; Miyoshi, N.; Murai, S.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3013–3018. The references in this paper provide an especially good introduction to the generation of *o*-quinodimethane.

[7] Jung, F.; Molin, M.; Van Den Elzen, R.; Durst, T. *J. Am. Chem. Soc.* **1974**, *96*, 935–936.

[8] Harpp, D. N.; Steliou, K.; Chan, T. H. *J. Am. Chem. Soc.* **1978**, *100*, 1222–1228.

0022-3263/91/1956-1947$02.50/0