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.

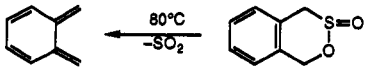
A Convenient Synthesis of 1,4-Dihydro-2,3-benzoxathiin 3-Oxide, a Useful Precursor of *o*-Quinodimethane[1]

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

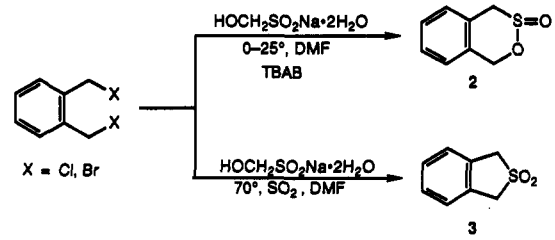
Table I. Yields of Sultine 2 from α,α′-Dihalo-o-xylenes and Rongalite

halide	temp, °C	catalyst	time, h	yield, %
Cl	60	-	48	0
Cl	25	NaI	26	70
Cl	25	TBAB	12	73
Br	0	-	48	64
Br	20	-	48	52
Br	40	-	48	46
Br	80	-	48	0
Br	0	TBAB	3	83

lyzed by Wilkinson's catalyst,[9] and by electrolysis of sulfur dioxide in the presence of α,α′-dibromo-o-xylene,[10] or by the photolysis of o-tolualdehyde in the presence of sulfur dioxide followed by borohydride reduction and cyclization by treatment with acid.[11] The sultine prepared by one of these methods has been used to generate 1 where gentle conditions and the avoidance of extraneous undesirable reagents (e.g. trimethylamine, reducing metals) are required.[12]

Earlier, we reported the trapping by norbornene of o-quinodimethane generated by treatment of α,α′-dibromo-o-xylene with sodium hydroxymethanesulfinate dihydrate (rongalite, sodium formaldehydesulfoxylate).[13] The sultine 2 was obtained in moderate yield (43–48%). Since the sultine is the likely precursor of the o-quinodimethane that was trapped, we reasoned that under milder conditions the sultine could be obtained in higher yield. Since the rongalite/α,α′-dibromo-o-xylene reaction involves only one step and less expensive reagents than the competitive photochemical o-tolualdehyde–SO_2–$NaBH_4$ route[11] to sultine 2, our new method might be preferred.[14] Related to our method is the reaction of α,α′-dibromo-o-xylene with reduced species of SO_2 obtained by electrolysis to give 2 in 67% yield.[10]

We wish to report an improved synthesis of 2 from rongalite and α,α′-dibromo- or α,α′-dichloro-o-xylene in which our previously reported yields[13] have been nearly doubled. The reaction of the dihalide with rongalite is done in N,N-dimethylformamide (DMF) in the absence of water but with addition of a catalytic amount of tetrabutylammonium bromide (TBAB) or sodium iodide. The dichloride is unreactive at 25 °C in the absence of the ammonium salt but in its presence gives 2 in 73% yield after 12 h. With a sodium iodide catalyst, a 70% yield of 2 is obtained after 26 h. The more reactive dibromide yields 83% of 2 after 3 h at 0 °C in the presence of the ammonium salt. The use of a relatively low temperature to prepare 2 is definitely advantageous since the higher temperatures needed in the absence of catalyst cause considerable polymerization of the o-quinodimethane. If benzothiophene sulfone (3) is required, the reaction of α,α′-dibromo-o-xylene with rongalite is conducted in the presence of SO_2 at 70 °C. To optimize the yield of 3, one should add the rongalite in four portions during 90 min. This periodic addition minimizes the exposure of rongalite to a temperature near its decomposition point, significant decomposition occurring at 80 °C. Sulfone 3 probably is formed by addition of sulfur dioxide to o-quinodimethane (generated in situ) as proposed by Durst et al.[7]



Experimental Section

General Procedure. A suspension of sodium hydroxymethanesulfinate (rongalite) (3.0 g, 20 mmol) was stirred with a solution of α,α′-dichloro- or α,α′-dibromo-o-xylene (10 mmol) and either sodium iodide or TBAB (2 mmol) in DMF (20 mL). The reaction mixture was worked up by addition of water (150 mL), removal of solids by filtration, extraction with ether, drying the ether solution with anhydrous magnesium sulfate, and removal of solvent. 1,4-Dihydro-2,3-benzoxathiin 3-oxide (2) was obtained as an oil whose spectroscopic properties were identical with those reported previously.[7,10,11,15] The yields and reaction conditions are given in Table I.

1,3-Dihydrobenzo[c]thiophene 2,2-Dioxide (3). The general procedure was applied to the reaction of rongalite (20 mmol) with α,α′-dibromo-o-xylene (10 mmol) except that SO_2 was passed through the reaction mixture for 20 min. The suspension was stirred at 70 °C for 4.5 h, and additional rongalite was added in four 10-mmol portions at intervals of 30 min. The reaction mixture was stirred for another 4.5 h. The workup, as described above, gave the sulfone 3 (1.26 g, 7.5 mmol, 75%): mp 146–148 °C (lit.[16] mp 150–151 °C). The ^1H NMR spectrum of 3 was identical with that previously reported.[17]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(9) Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans 1* **1988**, 1357–1364.
(10) Knittel, D.; Kastening, B. J. *J. Appl. Electrochem.* **1973**, *3*, 291–296.
(11) Durst, T.; Charlton, J. L.; Mount, D. B. *Can. J. Chem.* **1986**, *64*, 246–249.
(12) (a) Askari, S.; Lee, S.; Perkins, R. R.; Scheffer, J. R. *Can. J. Chem.* **1985**, *63*, 3526–3529. (b) Martin, N.; Behnisch, R.; Hanack, M. *J. Org. Chem.* **1989**, *54*, 2563–2568.
(13) Jarvis, W. F.; Hoey, M. D.; Finocchio, A. L.; Dittmer, D. C. *J. Org. Chem.* **1988**, *53*, 5750–5756.
(14) Of all the methods developed prior to ours, we believe the method of Durst et al.[11] to be most convenient in terms of accessibility of reagents although it requires three steps. The electrochemical method[10] is worthy of consideration, but it does require an apparatus not normally available in laboratories devoted to organic synthesis.
(15) Pirkle, W. H.; Hoekstra, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 1832–1839.
(16) Cava, M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266–4268.
(17) Durst, T.; Tetreault-Ryan, L. *Tetrahedron Lett.* **1978**, 2353–2354.

Palladium(II) Acetate–*tert*-Alkyl Isocyanide as a Highly Efficient Catalyst for the Inter- and Intramolecular Bis-silylation of Carbon–Carbon Triple Bonds

Yoshihiko Ito,* Michinori Suginome, and Masahiro Murakami

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

Received June 25, 1990

Much interest has been focused on the development of methodology for the introduction of silicon into organic molecules because such new methodology would be valuable for both the synthetic elaboration of organic molecules via organosilicon compounds and the synthesis of new silicon-containing materials.[1] Recently, new bis-silylation reactions of isocyanides[2] and alkenes[3] have been discov-

(1) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester, 1989.

0022-3263/91/1956-1948$02.50/0