of 1 was recovered. Cessation of the reaction at the pinacol stage in DME suggests that deoxygenation of the pinacols involving cleavage of C–O bonds does not take place in this solvent. This can be explained by the formation of a thermodynamically more stable 5-membered titanium complex with DME as compared to THF, resulting in the decrease in the oxophilicity of titanium thereby preventing the cleavage of C–O bonds of titanium pinacolates to form 2.

Thus, under ultrasonic irradiation, reduction of $TiCl_3$ to low-valent Ti, deoxygenation or hydrodimerization of aromatic carbonyl compounds can be carried out at an enhanced rates at ambient temperature. Further, the E/Z ratios can be altered by using appropriate solvents. Use of DME restricted the reactions to the hydrodimerization stage (step 1) only while in THF, deoxygenation to alkenes occurred. Though influence of solvents on the reactivities of low-valent titanium has been observed earlier,[10] this, to best of our knowledge, is the first report on the effects of solvents on the stereochemistry of the products.

Experimental Section

THF was distilled freshly from benzophenone–sodium ketyl. DME was distilled over CaH_2 prior to use. *n*-Hexane and benzene were dried over sodium. All manipulations were carried out under an atmosphere of argon. Ultrasonic irradiations were carried out using Ralsonic-R-200 ultrasonic cleaning bath.

Typical Example of an Intermolecular Coupling Using $TiCl_3$/Li under Ultrasound: 2,3-Diphenyl-2-butene (2). In a typical experiment, a dry argon-filled three-necked round-bottom flask was charged with 20 mL of dry THF, 2.3 g of titanium(III) chloride (15 mmol), and 365 mg of lithium (52 mmol). The flask was then immersed to the solvent (water) level in a sonicator (200 W, 40 KHz) and sonicated at 30 °C[11] for 1 h when the color of the reaction mixture changed from violet to black (few small pieces of Li remain unreacted). Acetophenone (600 mg, 5 mmol) in dry THF (5 mL) was then added to the reaction mixture and sonicated for additional 45 min. After the completion (45 min, monitored by TLC), the reaction mixture was diluted with petroleum ether and the slurry was passed through a small pad of Florisil on a sintered-glass filter to remove inorganic salts. Removal of solvent and subsequent column chromatography (SiO_2) yielded 2,3-diphenyl-2-butene (2) (oil, 452 mg, 87%) as 1:3 mixture of E and Z isomers. The E/Z ratio was determined by GLC (3% OV-17) an by comparison of peak heights of the methyl group resonances of the two isomers (Z δ 1.87, E δ 2.14) in PMR spectrum.[1]

In cases where pinacols (3) are the reaction products (entries 4, 5, and 6), hydrolysis of the reaction mixtures was carried out with 10% cold aqueous K_2CO_3 solution followed by extraction with ether.

(10) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513–1524.
(11) The temperature of the cleaning bath was maintained at 30 °C throughout the reaction.

Stereochemical Investigations: Reduction of *syn*-8-Chloro- and Cleavage of *anti*-8-*tert*-Butoxy-*endo*-3,3-diphenyltricyclo-[3.2.1.$0^{2,4}$]oct-6-enes

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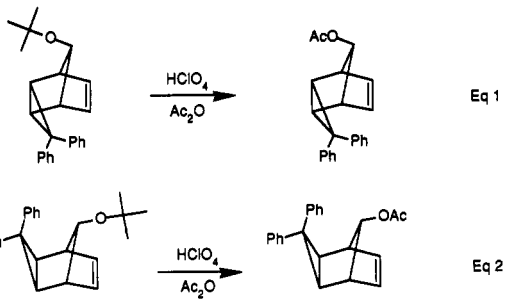
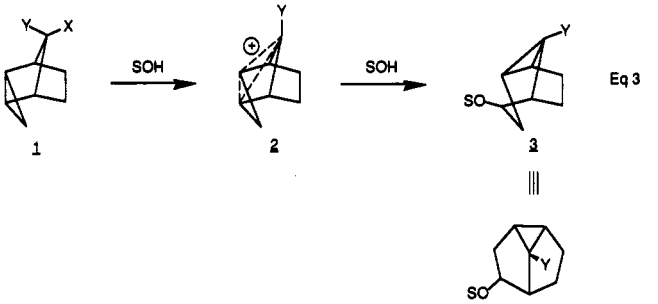
The perchloric acid/acetic anhydride cleavage of the endo-syn and exo-anti isomers of 8-*tert*-butoxy-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene lead to the corresponding acetates (eqs 1 and 2), while the exo-syn and endo-anti isomers produced complex product mixtures which were not completely characterized.[1a] *endo*-Tricyclo-[3.2.1.$0^{2,4}$]octan-*anti*-8-yl derivatives (1) are known[2] to readily[3a] undergo carbocation rearrangements to tricyclo-[3.3.0.$0^{4,6}$]octan-3-yls[3b] (3) (eq 3). *p*-Toluenesulfonic acid





catalyzed rearrangement of the *endo*-tricyclo[3.2.1.$0^{2,4}$]-octan-*anti*-8-ol (1, X = OH) in acetic acid gave 3-acetoxytricyclo[3.3.0.$0^{4,6}$]octane[2a] (3, SO = AcO) and the corresponding *anti*-8-*p*-nitrobenzoate (1, X = OPNB) gave tricyclo[3.3.0.$0^{4,6}$]octan-2-ol (3, SO = HO) in dioxane–water.[2a-c] Rearrangement of an 8-aryl-substituted *anti*-8-*p*-nitrobenzoate 1 (X = OPNB, Y = *p*-$C_6H_4OCH_3$) to 3 (SO = HO, Y = *p*-$C_6H_4OCH_3$) has also been reported.[2d] Other endo-anti derivatives have given similar products under solvolytic conditions.[4]

Since the norbornene bridgetop proton syn to the double bond is between the shielding and deshielding regions of the double bond, small structural changes in derivatives of this rigid system result in considerable ^{1}H NMR chemical shift changes.[5] Such changes make chemical shift comparisons unreliable for stereochemical assignments.

Results and Discussion

While exploring synthetic approaches that ultimately led to 8-keto and 8-methylene[6] tricyclic systems, the endo-anti ether 4[1a] was reduced with diimide[7] to 5 which

(1) (a) Wilt, J. W.; Sullivan, D. R. *J. Org. Chem.* **1975**, *40*, 1036. (b) Assignments reported at 60 MHz were confirmed in the present work at 300 MHz.
(2) (a) Haywood-Farmer, J. S.; Pincock, R. E. *J. Am. Chem. Soc.* **1969**, *91*, 3020. (b) Tanida, H.; Tsuji, T.; Irie, T. *Ibid.* **1967**, *89*, 1953. (c) Battiste, M. A.; Deyrup, C. L.; Pincock, R. E.; Haywood-Farmer, J. *Ibid.* **1967**, *89*, 1954. (d) Gassmann, P. G.; Fentiman, A. F. *Ibid.* **1970**, *92*, 2551.
(3) (a) The parent 1 (X = OPNB) is reported[2a-c] to solvolyze 10^{14} faster than bicyclo[2.2.1]heptan-7-yl-*p*-nitrobenzoate. (b) The current IUPAC name. See footnote 22b of ref 2a for other names such as tricyclo-[5.1.0.$0^{4,8}$]- or -[3.2.1.0.$0^{4,8}$]octyl that have also been used.
(4) Sargent, G. D.; Harkenham, M. A. *J. Am. Chem. Soc.* **1972**, *94*, 2892.
(5) (a) Marchand, A. P.; Rose, E. J. *J. Am. Chem. Soc.* **1968**, *90*, 3724. (b) Franzus, B.; Baird, W. C., Jr.; Chamberlain, N. F.; Hines, T.; Snyder, E. I. *Ibid.* **1968**, *90*, 3721. (c) *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*, Marchand, A. P., Ed.; Verlag Chemie: Deerfield Beach, FL, 1982.
(6) Peeran, M.; Wilt, J. W.; Tufano, M. D.; Subramanian, R.; Crumrine, D. S. *J. Org. Chem.* **1990**, *55*, 4225.
(7) LAH did not reduce 9 at room temperature or at THF reflux, though LAH reduction of a norbornene with a bridgetop *tert*-butoxy[8] group over the double bond is reported.

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‡ Died May 13, 1987.

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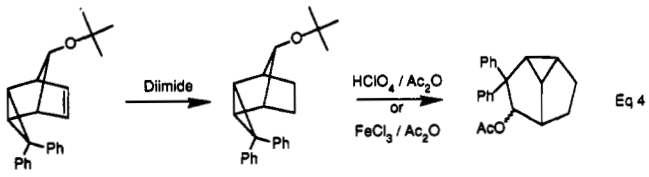
gave rapid exclusive formation of rearranged acetate **6** in 90% isolated yield which was identified as 2-acetoxy-3,3-diphenyltricyclo[3.3.0.0^{4,6}]octane. Cleavage of **5** with ferric chloride[9] also gave **6** in 65% isolated yield (eq 4).



4 **5** **6**

The lack of symmetry in the ^{1}H and ^{13}C NMR spectra of acetate **6** clearly demonstrated that it was not a diphenyltricyclo[3.2.1.0^{2,4}]octane.[10] As part of the structure determination, acetate **6** was reduced with LAH to the corresponding alcohol **7** which was subsequently oxidized with PCC to ketone **8**. Compounds **6**, **7**, and **8** showed proton and carbon NMR spectra characteristic of a quaternary ring carbon with geminal diphenyls next to an oxygenated carbon. The ^{1}H NMR doublet for the proton on the carbon bearing the acetate in ester **6** occurred at 5.93 ppm. The corresponding signal in alcohol **7** occurred at 4.78 ppm, and this ca. 1 ppm upfield shift on going from ester to alcohol is characteristic for secondary alcohols and the corresponding esters.[11] The cyclopropyl proton signals at 3.4–3.07 and 2.27 ppm, and the ^{13}C NMR data (169.42, C=O; 85.57, C_2; and 20.99, acetate CH_3) also supported the structure of acetate **6**. The structure for alcohol **7** was supported by 3600 (free OH) and 3400–3500 cm^{-1} (bonded OH) bands in the IR. The ^{1}H NMR showed a triplet at 4.78 ppm, J = 8 Hz, for the proton on the carbon bearing the OH, and the OH appeared as a broadened signal at 1.93 ppm. The structure of ketone **8** was similarly supported by a 1740 cm^{-1} IR C=O band. The ^{13}C NMR showed a carbonyl carbon at 220.5 ppm and the quaternary C_3 at 61.64 ppm. ^{1}H NMR showed a cyclopropyl proton at 2.97 ppm as a broadened triplet. The other protons were not resolved at 60 MHz.

These structures are mechanistically reasonable if the initial oxonium ion cleaved to produce *tert*-butyl alcohol and a C_8 carbocation **2** which would be stabilized by partial delocalization on the back side to the $C_{2,4}$ cyclopropyl bond.[12] Subsequent attack by acetic acid at one of these former cyclopropyl carbons would result in formation of an acetate on one side of the geminal diphenyl carbon and a new cyclopropyl bond to C_8 from the other side. The details of cyclopropyl participation and stabilization of remote carbocations have already been discussed.[2,3,12] The fast reaction and high product yield suggests that the delocalized ion is considerably more stable than the *tert*-butyl cation that would have been produced by the alternate cleavage of the initial oxonium ion intermediate. The lower energy of the stabilized cation **2** helps decrease the activation energy barrier for the observed cleavage.

Reduction of *syn*-8-Chloro-*endo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene. Hydrocarbon **9** was required for a study of phenyl participation on addition to the double bond[13] and was synthesized through a sequence of steps starting from 7-*tert*-butoxynorbornadiene,[1a] the last step being the reduction of chloride **10** using LAH. If

9 **10**

LAD were to be used instead, both the stereochemistry of reduction and ^{1}H NMR assignments of the syn and anti bridge top protons could be ascertained in a single elegant reaction. Thus compound **10** was reduced by LAD to the corresponding deuterated hydrocarbon **11**. The reduction was found to occur with retention of configuration. Although an S_N2 mechanism would have produced inversion at C_8, the necessary linear transition state would be very difficult to achieve. Ionization of the C–Cl bond via π-participation[14] could provide a delocalized bishomocyclopropyl cation which would be reduced by LAD on the side from which the chloride left, thus resulting in retention. The stereochemistry of reduction product **11** has been confirmed using 2D NMR on both **9** and **11**. The syn and anti bridgetop protons have been unequivocally assigned from the following information.

The ^{1}H NMR of **9** shows a doublet at δ 1.71 ppm (J = 9.8 Hz) and a doublet of triplets at δ 2.01 ppm (J = 9.8 Hz, J = 1.4 Hz), integrating to one proton each. These have been assigned to the H_8 anti and H_8 syn protons respectively[1b] (with respect to the cyclopropyl group). The ^{1}H NMR spectrum of deuterated compound **11** is almost identical with that of **9** except that the signal at 2.01 ppm was absent. In addition, the COSY done on **9** revealed the presence of coupling between the signals at 2.01 ppm and the vinylic protons at 5.18 ppm which was absent in the COSY done on deuterated compound **11**. The absence of W coupling to the vinyl protons in **11** proves that deuterium is syn to the cyclopropyl group which, in turn, proves that the stereochemistry was retained during reduction probably through anchimeric assistance from the double bond.[14]

11 **12**

The reduction of *exo*- and *endo*-2-bromonorbornanes by a LAH–Cu complex[15] was found to occur with 100% retention while similar reduction of *exo*- and *endo*-2-mesylnorbornanes showed 100% inversion. They suggested that copper coordination with the bromine enhances ionization, and the hydride was delivered from the same side. With a better leaving group, such as the mesylate, the hydride is delivered before the copper can coordinate. The reduction of **10** can be aided by π-participation from the anti double bond. The LAH could coordinate with the chlorine resulting in formation of a C_8 carbocation which would be stabilized by participation from the double bond and lead to retention.

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(11) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: Elmsford, NY, 1969; pp 164 and 179.
(12) Haywood-Farmer, J. *Chem. Rev.* **1974**, *74*, 328–330 and references therein.
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(15) Masamune, S.; Bates, G. S.; Georghiou, P. E. *J. Am. Chem. Soc.* **1974**, *96*, 3686.

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 ($H_{1,5}$) 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.

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(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

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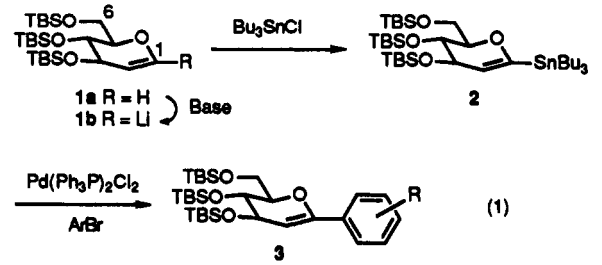
We have recently reported that 3,4,6-tri-*O*-(*tert*-butyldimethylsilyl)-1-(tributylstannyl)-D-glucal (**2**) can be efficiently utilized in palladium-catalyzed coupling reactions with aryl bromides (eq 1).[1] In connection with several



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

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