Attempts to improve the yield on this reaction by using different batches of VOF_3 or TFA (freshly opened, old or of different lot numbers), different reaction times, lower temperatures, and FSO_3H catalysis were unsuccessful. Many times only TLC evidence for product formation in small yield could be observed.

2,3,8,9-Tetramethoxy-4-(trifluoroacetoxy)benzo[*c*]phenanthridine (6). A solution of 1 (257 mg) in 35 mL of 5% trifluoroacetic anhydride in CH_2Cl_2 was added dropwise to a stirred suspension of VOF_3 (880 mg) in 35 mL of the same solvent at 25 °C for 40 min. This was followed by the workup above which yielded 331 mg of crude material. This was chromatographed on silica gel (EtOAc) to yield 230 mg (50%) of **6**: mp 257–260 °C; ^1H NMR ($CDCl_3$) δ 4.07 (s, 3 H), 4.11 (s, 6 H), 4.20 (s, 3 H), 7.41 (s, 1 H), 7.46 (s, 1 H), 7.87 (s, 1 H), 7.88 (d, J = 9 Hz, 1 H), 8.38 (d, J = 9 Hz, 1 H), 9.12 (s, 1 H); IR (KBr) 1721 and 1619 cm^{-1}; UV λ_{max}^{EtOH} (log ϵ) 370 (3.40), 352 (3.54), 328 (sh, 4.03), 313 (4.29), 282 (4.82), 227 nm (4.43); MS *m/e* (rel intensity) 445.113 (7, calcd for $C_{23}H_{18}NF_3O_5$: 445.114), 376 (100, $M^+ - CF_3$), 360 (12), 332 (7), 188 (11).

4,4′-Bis[*N*-(3,4-dimethoxyphenylmethyl)]-1-(6,7-dimethoxy)naphthylamine (7). Oxidation of **3** was performed in a two-compartment H cell partitioned by a glass frit. The substrate (827 mg) was dissolved in 100 mL of CH_3CN containing 0.1 M $LiClO_4$ electrolyate. A cylindrical platinum electrode was used as the anode and a "Scoopla" as the cathode. The oxidation was performed at 25 °C and at a constant potential of 1.0 V until 2 F/mol were passed. Evaporation of excess CH_3CN (with 5 mL of solvent left at the finish to avoid an explosion from reacting perchloric acid), addition of water (75 mL), extraction with CH_2Cl_2 (3 × 75 mL), and evaporation of the solvent (after drying) gave the crude product (774 mg), which was observed to be a complex mixture by TLC analysis. Chromatography on silica gel ($CHCl_3$) yielded five fractions: fraction 2 (40 mg) was identified as 3,4-dimethoxybenzaldehyde by NMR, fraction 3 (328 mg, 42%) contained the major product **7**, and fraction 4 (282 mg) was observed to be a mixture of **7** and other products.

Fraction 3 was recrystallized from CH_2Cl_2/cyclohexane to give pure **7**: mp 148.5–152 °C; ^1H NMR ($CDCl_3$) δ 3.54 (s, 6 H), 3.93 (s, 12 H), 4.01 (s, 6 H), 4.51 (s, 4 H), 6.70–7.36 (m, 14 H); IR (KBr) δ 3200, 1630, 1595, 1515, 1495 cm^{-1}; MS *m/e* (rel intensity) 704 (36), 554 (42), 404 (73), 403 (35), 207 (34), 152 (50), 151 (100); UV λ_{max}^{EtOH} (log ϵ) 333 (4.19), 263 (4.61), 221 (4.85), 202 nm (4.92). Anal. Calcd for $C_{42}H_{44}N_2O_8$: C, 71.57; H, 6.29; N, 3.97. Found: C, 70.92; H, 6.56; N, 3.96.

4,4′-Bis[*N*-(2-bromo-4,5-dimethoxyphenylmethyl)]-1-(6,7-dimethoxy)naphthylamine (8). This product was obtained by anodic oxidation at 1.2 V of **4** (799 mg) in 100 mL of CH_3CN containing 0.1 M $LiClO_4$ ($Ag|Ag^+$ reference electrode) until 2 F/mol of current was passed. The crude product (836 mg) was isolated as above. Chromatography on silica gel (EtOAc) gave **8** (48%): mp 134–136 °C (CH_2Cl_2/cyclohexane); ^1H NMR ($CDCl_3$) δ 3.60 (s, 6 H), 3.81 (s, 6 H), 3.92 (s, 6 H), 4.04 (s, 6 H), 4.61 (br s, 6 H), 6.72 (d, J = 8 Hz, 2 H), 6.92 (s, 2 H), 7.15 (s, 3 H), 7.25 (s, 3 H), 7.29 (d, J = 8 Hz, 2 H); IR (KBr) 3200, 1625, 1600, 1500, 1465, 1440, 1390 cm^{-1}; UV λ_{max}^{EtOH} (log ϵ) 331 (4.27), 263 (4.68), 239 sh (4.84), 220 (4.94), 205 nm (5.00). Anal. Calcd for $C_{42}H_{42}N_2O_8Br_2$: C, 58.48; H, 4.91; N, 3.26. Found: C, 58.36; H, 4.90; N, 3.21.

Structures for the dimers could be reasonably assigned based upon the following data. Both dimers could be oxidized (see below) to imine dimers which were then independently hydrolyzed to yield the same dimeric naphthylamine. This meant that dimerization (in both cases) was at a site on the naphthylamine moiety rather than on the dimethoxybenzyl or bromodimethoxybenzyl moieties. A key to the site of dimerization was evident in the ^1H-NMR spectra for the dimers, the imine dimers (see below), and the naphthylamine dimer hydrolysis product. Each had a six-proton singlet for two methoxy groups in the 3.5–3.6-ppm region. This is considerably upfield from any of the other aromatic methoxyls and is a result of one methoxy on each naphthalene by the π-electron cloud of the other naphthalene. The ^1H NMR of the hydrolysis product from both imine dimers was extremely simple and symmetrical (see below). It consisted of two identical pairs of methoxy absorptions, one at 3.60 and the other at 4.07, and an aromatic AB pattern superimposed by two singlets. These data could best be accounted for by assigning structure **9** to the naphthylamine and hence structures **7** and **8** to the electrochemically produced dimers.

Oxidation and Degradation of 7 and 8. **7** (125 mg) was dissolved in 3 mL of $CHCl_3$ containing "active" MnO_2[10] (149 mg) and refluxed for 3.5 h. An additional 10 mL of $CHCl_3$ was added, and the solution was filtered through Celite and evaporated to give the crude product (75%). Recrystallization from CH_3NO_2 gave **4,4′-bis[*N*-3,4-dimethoxyphenylmethylene]-1-(6,7-dimethoxy)naphthylamine**: mp 281–281.5 °C; ^1H NMR ($CDCl_3$) δ 3.60 (s, 6 H), 4.02 (s, 6 H), 4.07 (s, 12 H), 6.87–7.60 (m, 10 H), 7.84 (s, 4 H), 8.67 (s, 2 H); IR (KBr) 1620 cm^{-1}; MS *m/e* (rel intensity) 700 (34), 280 (16), 209 (15), 208 (22), 207 (100), 166 (14), 151 (24), 111 (16), 109 (12), 97 (33), 95 (31), 85 (23), 83 (32), 81 (19), 71 (47), 69 (42); UV λ_{max}^{EtOH} (log ϵ) 315 (sh), 275, 230, 204 nm. Anal. Calcd for $C_{42}H_{40}N_2O_8$: C, 71.99; H, 5.75; N, 4.00. Found: C, 71.77; H, 6.02; N, 3.86.

In a similar manner, **8** (130 mg) in 10 mL of $CHCl_3$ containing 226 mg of "active" MnO_2 was refluxed for 3 h. Workup as above gave the crude product (75%), which was recrystallized from CH_3NO_2 to give **4,4′-bis[*N*-(2-bromo-4,5-dimethoxyphenylmethylene)]-1-(6,7-dimethoxy)naphthylamine**: mp 285–288.5 °C; ^1H NMR ($CDCl_3$) δ 3.64 (s, 6 H), 4.03 (s, 6 H), 4.08 (s, 12 H), 6.92 (s, 2 H), 7.18–7.55 (m, 6 H), 7.87 (s, 2 H), 8.08 (s, 2 H), 9.05 (s, 2 H); IR (KBr) 1620 cm^{-1}; UV λ_{max}^{EtOH} 332, 289 (sh), 241, 220, 203 nm. Anal. Calcd for $C_{42}H_{38}N_2O_8Br_2$: C, 58.75; H, 4.46; N, 3.26. Found: C, 58.64; H, 4.54; N, 3.05.

Each imine dimer (64 mg) was hydrolyzed for 1 h on a steam bath in 15 mL of EtOH containing 2 drops of concentrated HCl. The solvent was evaporated, 15 mL of $CHCl_3$ was added, and this solution was extracted with 1 M H_2SO_4 (2 × 15 mL). The aqueous layer was separated, made basic with $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$ was dried and evaporated to leave 30 mg of a dark oil which was crystallized from ether to yield **9**: mp 111 °C dec; ^1H NMR ($CDCl_3$) δ 3.60 (s, 6 H), 4.07 (s, 6 H), 6.85 (d, J = 7 Hz, 2 H), 6.89 (s, 2 H), 7.20 (s, 2 H), 7.24 (d, J = 7 Hz, 2 H). Instability of the product precluded the obtaining of additional analytical data.

Registry No.—**1**, 68152-23-8; **2**, 56517-04-5; **3**, 68152-24-9; **4**, 68152-25-0; **5**, 15462-10-9; **6**, 68152-26-1; **7**, 68152-27-2; **8**, 68152-28-3; **9**, 68152-29-4; 6,7-dimethoxynaphthylamine, 52401-42-0; 3,4-dimethoxybenzaldehyde, 120-14-9; 2-bromo-4,5-dimethoxybenzaldehyde, 5392-10-9; 4,4′-bis[*N*-3,4-dimethoxyphenylmethylene]-1-(6,7-dimethoxy)naphthylamine, 68152-30-7; 4,4′-bis[*N*-(2-bromo-4,5-dimethoxyphenylmethylene)]-1-(6,7-dimethoxy)naphthylamine, 68152-31-8.

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Synthesis of 1,2-Glycols via Coupling of the Trimethylsilyl Ethers of Primary Alcohols

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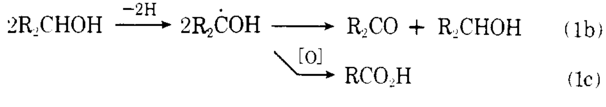
The synthesis of 1,2-glycols is generally approached by two quite different paths: (1) oxidation of olefins by a variety of procedures; or (2) bimolecular reduction of aldehydes and ketones.[1] A third method, oxidative or dehydrogenative dimerization of alcohols (eq 1a), is not useful because of disproportionation of intermediate radicals (eq 1b) or overoxidation (eq 1c).



$$2R_2CHOH \xrightarrow{-2H} 2R_2\dot{C}OH \longrightarrow HOCR_2CR_2OH \qquad (1a)$$

$$2R_2\dot{C}OH \longrightarrow R_2CO + R_2CHOH \qquad (1b)$$

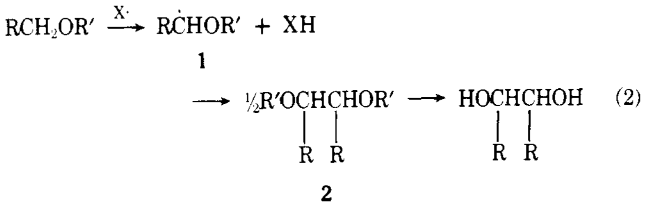
$$2R_2\dot{C}OH \xrightarrow{[O]} RCO_2H \qquad (1c)$$

For example, Ladygin and Saraeva[2] have shown that the ratio of coupling to disproportionation is approximately 3/2 for the hydroxymethyl radical generated by the pulse radiolysis of liquid methanol in the absence of oxygen. In the presence of oxygen, the major product of the reaction is formic acid and not ethylene glycol.[3]

This paper describes a method for the formation of 1,2-glycols by the free-radical dimerization of primary alcohols without the production of undesirable side products.

Because the initial hydrogen abstraction in the primary alcohol must take place from carbon and not from the hydroxyl group, a protecting group for the hydroxyl is necessary. Two different properties are needed for the protecting group: (1) it must be easy to remove; and (2) it must not rearrange or leave the alkoxy group during the coupling step. The following discussion amplifies these considerations.

The radical **1** produced from a protected alcohol has two possible fates: dimerization to a protected glycol **2** (eq 2) and β scission (eq 3)



$$\mathrm{RCH_2OR'} \xrightarrow{X\cdot} \underset{\mathbf{1}}{\mathrm{R\dot{C}HOR'}} + \mathrm{XH}$$

$$\longrightarrow \tfrac{1}{2}\underset{\mathbf{2}}{\mathrm{R'O\underset{R}{C}H\underset{R}{C}HOR'}} \longrightarrow \mathrm{HO\underset{R}{C}H\underset{R}{C}HOH} \qquad (2)$$

$$\underset{\mathbf{1}}{\mathrm{R\dot{C}HOR'}} \rightarrow \mathrm{RCH{=}O} + \mathrm{R'\cdot} \qquad (3)$$

Removal of the protecting group R′ from **2** would generate the glycol. The β-scission reaction of radicals of the type **1** where R′ is bound to oxygen by a carbon atom is well documented.[4-7] For example, thermochemical calculations on the reaction of a methyl radical with methyl *tert*-butyl ether show that β scission is a mildly exothermic process for this case.[8-12]

$$\begin{array}{lllll} & \mathrm{CH_3\cdot} + & \mathrm{CH_3OC(CH_3)_3} & & \\ \Delta H^\circ_f & +34.1 & +70.0 & & \\ & & \rightarrow \mathrm{CH_4} + & \mathrm{CH_2{=}O} + & \mathrm{(CH_3)_3C\cdot} \\ & & -17.9 & -27.7 & +8.3 \end{array} \qquad (4)$$

$$\Delta H_{\mathrm{reaction}} = -1.4\ \mathrm{kcal/mol}$$

Experience with the chemistry of trimethylsilyl ethers in our studies on the acyloin condensation[13,14] led us to consider the use of the trimethylsilyl protecting group in an alcohol dimerization reaction. The trimethylsilyl group is easily alcoholized.[15]

$$\mathrm{ROSi(CH_3)_3} + \mathrm{R'OH} \rightleftharpoons \mathrm{ROH} + \mathrm{R'OSi(CH_3)_3} \qquad (5)$$

Furthermore, free-radical attack occurs exclusively on methoxyl carbon in methoxytrimethylsilane.[16]

Thermochemical calculations show that because of the strong silicon–oxygen bond in methoxytrimethylsilane, the β-scission reaction is quite endothermic[17,18]

$$\begin{array}{lllll} & \mathrm{CH_3\cdot} + & \mathrm{CH_3OSi(CH_3)_3} \rightarrow & \mathrm{CH_4} & \\ \Delta H^\circ_f & +34.1 & -143.0 & -17.9 & \\ & & & + \mathrm{CH_2{=}O} + & \mathrm{(CH_3)_3Si\cdot} \\ & & & -27.7 & -25.6 \end{array} \qquad (6)$$

$$\Delta H_{\mathrm{reaction}} = +37.7\ \mathrm{kcal/mol}$$

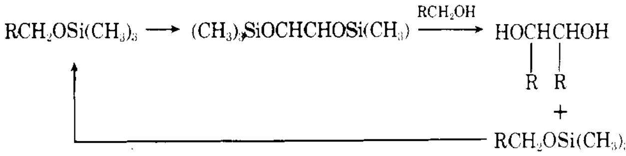
On both practical and theoretical grounds, trimethylsilyl is an ideal protecting group for the development of a synthesis of 1,2-glycols via the free-radical coupling of primary alcohols. Furthermore, the ready alcoholysis of trimethylsilyl ethers allows the development of a process for the synthesis of 1,2-glycols in which the trimethylsilyl group is recycled back to the coupling step (Scheme I).[19]

Table I. Free-Radical Coupling of Alcohols and Alkoxytrimethylsilanes with Di-*tert*-butyl Peroxide (DTBP)

alcohol or silane[a]	products for R = H (% yield)[b]	products for R = Si(CH$_3$)$_3$ (% yield)[c]
CH$_3$OR [**3a,b**]	(–CH$_2$OH)$_2$ (26)[d]	(–CH$_2$OR)$_2$ [**4**] (46) + (CH$_2$OR)$_2$CHOR [**5**] (10)
CH$_3$CH$_2$OR [**6a,b**]	(CH$_3$C(H)(OH)–)$_2$[e] (41)	(CH$_3$C(H)(OR)–)$_2$[e] [**7**] (43)
C$_6$H$_5$CH$_2$OR [**9a,b**]	(C$_6$H$_5$C(H)(OH)–)$_2$[e] [**8**] (69)	(C$_6$H$_5$C(H)(OR)–)$_2$[e] [**10**] (89)
CH$_3$)$_2$CHOR [**11a,b**]	[(CH$_3$)$_2$C(OH)–]$_2$ [**12**] (89)	mixture

[a] R = H (**3a, 6a, 9a, 11a**) or R = Si(CH$_3$)$_3$ (**3b, 6b, 9b, 11b**). [b] Based on 4.8 mol % DTBP, ref 20 and 21. [c] Based on 10 mol % DTBP, present work. [d] The yield can be raised to 49% if 0.5 mol % DTBP is used, ref 21. [e] Ca. 1:1 meso/*dl* mixtures.

Scheme I



$$\mathrm{RCH_2OSi(CH_3)_3} \longrightarrow \mathrm{(CH_3)_3SiOCHCHOSi(CH_3)_3} \xrightarrow{\mathrm{RCH_2OH}} \mathrm{HO\underset{R}{C}H\underset{R}{C}HOH} + \mathrm{RCH_2OSi(CH_3)_3}$$

Results

This paper details the results of our studies on the free-radical coupling of alkoxytrimethylsilanes. As examples of protected primary alcohols, the dimerization of methoxytrimethylsilane, ethoxytrimethylsilane, and benzyloxytrimethylsilane are compared to the previously published free-radical dimerizations of methanol, ethanol, and benzyl alcohol.[20,21] As an example of a protected secondary alcohol, the attempted free-radical dimerization of 2-propyloxytrimethylsilane is compared with that of 2-propanol.[20,21]

In this study, the free-radical dimerization reactions were carried out using di-*tert*-butyl peroxide (DTBP) at 10 mol % concentration, whereas those of the alcohols were carried out at 4.8 mol % of DTBP.[20,21] Both azobis(isobutyronitrile) and benzoyl peroxide failed as coupling reagents for methoxytrimethylsilane.[22]

Table I compares the results of our study with those of previous work. In all cases, except for 2-propyloxytrimethylsilane, the yields of dimers were higher from the silanes at higher silane conversion than from the alcohols. For example, the coupling of methoxytrimethylsilane yielded ethylene glycol bis(trimethylsilyl) ether (46%) and glycerol tris(trimethylsilyl) ether (10%) at 10 mol % DTBP concentration. Methanolysis gave a 98% recovery of mixture of ethylene glycol and glycerol. Ethylene glycol (26%) was obtained from methanol at 4.8 mol % DTBP concentration.[20,21] When the DTBP concentration was lowered to 0.5 mol % in methanol, a 49% yield of ethylene glycol was obtained.[21]

The dimerization reactions of ethoxytrimethylsilane and benzyloxytrimethylsilane produced (after removal of the trimethylsilyl group) an ca. 1:1 mixture of *dl*- and *meso*-2,3-butanediol and dihydrobenzoin, respectively. When the dimerization of 2-propyloxytrimethylsilane was attempted, mixtures of at least six components were obtained. After methanolysis, GLC examination of the residue showed that pinacol was only a minor component of the mixture.

Experimental Section

Methoxytrimethylsilane (3b). To 55.2 g (2.4 g-atom) of sodium under nitrogen in a 2-L, three-necked, round-bottomed flask fitted with addition funnel, Hershberg stirrer, reflux condenser, and nitrogen pad was added 1 L of xylene. A coarse sodium dispersion was prepared by first heating the mixture until the sodium melted and then rapidly stirring to break up the molten sodium. The flask was cooled to room temperature and 90 mL (ca. 2.2 mol) of anhydrous methanol was added. When all signs of gas evolution stopped, 217.2 g (2.0 mol) of chlorotrimethylsilane was added over 3 h. The mixture was stirred overnight at room temperature. After the reflux condenser was replaced by a Claisen head and condenser, the product was distilled (bp 45–58 °C (760 mm)) under nitrogen. Redistillation through a 1 m Vigreaux column under nitrogen gave 129 g (1.24 mol, 62%) of methoxytrimethylsilane, bp 57–58 °C (760 mm).

Ethoxytrimethylsilane (6b) was prepared using the same procedure.

Benzyloxytrimethylsilane (9b), 2-propyloxytrimethylsilane (11b), ethylene glycol bis(trimethylsilyl) ether (4) glyceroltris(trimethylsilyl) ether (5), and 2,3-butanediol bis(trimethylsilyl) ether (7) were prepared using established literature procedures.[23] **Dihydrobenzoin (8)** was prepared by the PtO_2-catalyzed hydrogenation of benzoin.[24]

Coupling of Methoxytrimethylsilane (3b). To a 300-mL Parr autoclave was added 26.0 g (250 mmol) of methoxytrimethylsilane and 3.65 g (25 mmol) of di-*tert*-butyl peroxide. The autoclave was pressured to 200 psig with nitrogen and heated and stirred at 145 °C for 16 h and cooled and the products were analyzed by GLC. GLC analyses were carried out on a Varian Model 2800 gas chromatograph using a 3.1 m × 1.5 mm 3% SE-30 on Chromosorb W column programmed from 75 °C (isothermal for 1 min) to 260 °C at 10 °C/min using dodecane as an internal standard. At a flow rate of 12 mL/min, retention times were: ethylene glycol bis(trimethylsilyl) ether (4), 3.8 min; dodecane, 7.5 min; and glycerol tris(trimethylsilyl) ether (5), 8.5 min. A third, unidentified, component ($\sim$2%) had a retention time of 14 min. The yield of ethylene glycol bis(trimethylsilyl) ether was 11.6 mmol (46%), while that of the glycerol derivative was 1.7 mmol (10%).

A second identical reaction was worked up to isolate ethylene glycol. Methoxytrimethylsilane was distilled from the reaction mixture and methanol was added to the residue. The mixture was brought to reflux and the methoxytrimethylsilane was slowly distilled off. The syrupy residue (0.83 g, 98% recovery) was treated with benzoyl chloride/pyridine.[25] The isolated solid was recrystallized from methanol–water to yield ethylene glycol dibenzoate, mp 71.6–72 °C. The mixture melting point with an authentic sample showed no depression. The NMR spectra of the two samples were superimposable.

Coupling of Ethoxytrimethylsilane (6b). Ethoxytrimethylsilane (82 g, 750 mmol) and di-*tert*-butyl peroxide (11 g, 75 mmol) were combined in a 300-mL Parr autoclave and stirred and heated at 145 °C for 16 h. The autoclave was cooled and the reaction mixture distilled to recover unreacted starting material. The residue was distilled through a 15-cm Vigreaux column to yield 7.4 g (32 mmol, 43%) of a 1:1 mixture of *meso*- and *dl*-2,3-butane diolbis(trimethylsilyl) ether (7), bp 36 °C (10 mm), and 2.4 g of a higher boiling mixture of several components (bp 95–105 °C (10 mm)).[26]

By comparison with an authentic sample, the dimer **7** was shown to consist of a 1:1 meso/*dl* mixture by GLC (2 m × 3 mm 3% SE-30 on Chromosorb W, 100 °C). After ethanolysis of **7**, the NMR spectrum of the dioxolanes prepared from the diols and formaldehyde confirmed the 1:1 meso/*dl* mixture.[27]

Coupling of Benzyloxytrimethylsilane (9). To 18.1 g (100 mmol) of benzyloxytrimethylsilane in a 100-mL round-bottomed flask equipped with magnetic stirrer and air condenser was added, under nitrogen, 1.46 g (10 mmol) of di-*tert*-butyl peroxide. The mixture was heated at 145 °C under nitrogen for 16 h. The reaction mixure was fractionally distilled through a 15-cm Vigreaux column to recover unreacted starting material. The distillate (bp 90–92 °C (15 mm)) contained a trace of benzaldehyde by NMR.

The NMR spectrum of the residue (3.2 g, 8.9 mmol, 89%) was consistent with a 1:1 meso/*dl* mixture of dihydrobenzoin bis(trimethylsilyl) ethers (**10**). The product was treated with ethanolic sodium hydroxide to cleave it to dihydrobenzoin (**8**). GLC analysis on the isolated dihydrobenzoin (2 m × 3 mm 3% SE-30 on Chromosorb W, 140–200 °C at 20 °C/min) showed that it consisted of a 1:1 mixture of meso and *dl* diastereomers by comparison with authentic samples.

Attempted Coupling of 2-Propyloxytrimethylsilane (11). 2-Propyloxytrimethylsilane (92g, 697 mmol) and di-*tert*-butyl peroxide (10.4g, 70 mmol) were heated at 145 °C in the 300-mL autoclave for 16 h. After the mixture was cooled, unreacted starting material was distilled off. The distillation residue (2.2 g) showed at least six components by GLC. Treatment of this residue with methanol and reexamination of the product mixture by GLC showed that pinacol (**12**) was a minor component of the mixture by spiking with an authentic sample.

Registry No.—**3b,** 1825-61-2; **6b,** 1825-62-3; **9b,** 14642-79-6; **11b,** 1825-64-5; **4,** 7381-30-8; **5,** 6787-10-6; *meso*-**7,** 53229-15-5; *dl*-**7,** 53274-85-4; *meso*-**10,** 6186-14-7; *dl*-**10,** 6186-15-8; chlorotrimethylsilane, 75-77-4; methanol, 67-56-1; ethanol, 64-17-5; DTBP, 110-05-4.

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Neutral Hydrolysis of Ketene Bis(2-methoxyethyl) Acetal in Water in the Presence of *tert*-Butyl Alcohol, Tetra-*n*-butylammonium Bromide, and Potassium Bromide. Effects of Hydrophobic Hydration

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The study of solvation of organic molecules in water is hampered by the lack of a general and quantitative theory for the aqueous liquid state.[1] However, both experiment and theory have provided unequivocal evidence for the occurrence of hydrophobic hydration which is associated with the peculiar water ordering process around apolar groups in the molecule.[2]

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