Nonionic Superbase-Catalyzed Silylation of Alcohols

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Received January 27, 1997[⊗]

Herein we report a very effective and mild procedure for the silyl protection of a wide variety of substrate alcohols, including primary, secondary, allylic, propargylic, benzylic, hindered secondary, tertiary, acid-sensitive, and base-sensitive alcohols and also hindered phenols. The silylation reagent used is *tert*-butyldimethylsilyl chloride (TBDMSCl) and the catalyst is $P(MeNCH_2CH_2)_3N$, **1b**, both of which are commercially available. The reactions are carried out in acetonitrile from 24 to 40 °C and on rare occasions in DMF from 24 to 80 °C. The effect of solvent, catalyst concentration, and temperature and reaction time on the silylation of alcohols and the excellent compatibility of our method with a variety of functional groups is discussed. An efficient method for recycling the catalyst is also presented. Although representative primary alcohols, secondary alcohols, and phenols were silylated using the more sterically hindered reagent *tert*-butyldiphenylsilyl chloride (TBDPSCl) in the presence of **1b** as a catalyst, tertiary alcohols were recovered unchanged.

Introduction

The importance of protecting the hydroxyl group in synthetic organic chemistry is reflected by the currently rather continuous appearance in the literature of syntheses of biologically active molecules possessing hydroxyl groups. Among the many trialkylsilyl reagents used to protect such groups, *tert*-butyldimethylsilyl chloride (TBDMSCl) and *tert*-butyldiphenylsilyl chloride (TBDPSCl) have been the most popular, ever since the introduction of TBDMSCl in 1972 by Corey[1] and of TBDPSCl in 1975 by Hanessian.[2] Sterically hindered reagents of this type confer augmented stability on the derivatized substrate over the trimethylsilylated analogues. Thus the larger *tert*-butyl substituent hinders attack at the silicon atom of the silyl ether, thereby rendering the protected substrate more stable toward hydrolysis in weakly acidic or basic media and toward oxidative and reductive conditions frequently encountered in subsequent synthetic steps.[3] The stability and the facile specific removal of these protecting groups under very mild conditions have been major factors in their widespread use in the synthesis of a variety of compounds including ribonucleosides,[4] carbohydrates,[5] analogues of thromboxane A_2,[6] leukotrienes,[7] steroids,[8] and antibiotics.[9]

A variety of methods have been reported for the derivatization of alcohols with the TBDMS[10] and TBDPS[11] moieties. Currently, preparations of the corresponding silyl ethers are most satisfactorily and popularly achieved by reacting the alcohol with a molar excess of imidazole using dimethyl formamide as a solvent.[1,2] Other solvents were found to be unsuitable for this transformation. A problem with TBDMSCl and TBDPSCl has been the difficulty of silylating hindered secondary alcohols, tertiary alcohols, and hindered phenols. An advantage of the TBDPS group is that its phenyl group is a chromophore that facilitates the detection of products on chromatograms by spectrophotometric methods; a feature not shared by the TBDMS group. Moreover, the TBDPS moiety is more robust than the TBDMS group, and hence efficient introduction of the former moiety is of particular interest in organic synthesis. Recently, Hardinger et al. reported the silylation of primary and secondary alcohols in 69−99% yield using TBDPSCl in DMF with $AgNO_3$, NH_4NO_3, or NH_4ClO_4.[11d]

Herein we report a very effective and mild procedure for the silyl protection of a wide variety of OH-containing substrates, including primary, secondary, allylic, propargylic, benzylic, hindered secondary, tertiary, acid-sensitive, and base-sensitive alcohols and also hindered phenols. For this purpose the commercially available and relatively inexpensive silylating reagent TBDMSCl is used in the presence of the commercially available catalyst **1b** which was first reported from our laboratories.[12] The reactions are carried out in acetonitrile as a solvent from 24 to 40 °C, and on rare occasions in DMF from 24 to 80 °C. The effect of solvent, catalyst concentration, reaction time, and temperature on the silylation of alcohols is discussed, and an efficient method for

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

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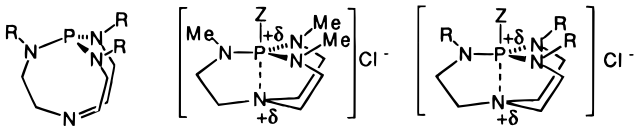
S0022-3263(97)00149-7 CCC: $14.00



1a, R = H
1b, R = Me
1c, R = *i*-Pr

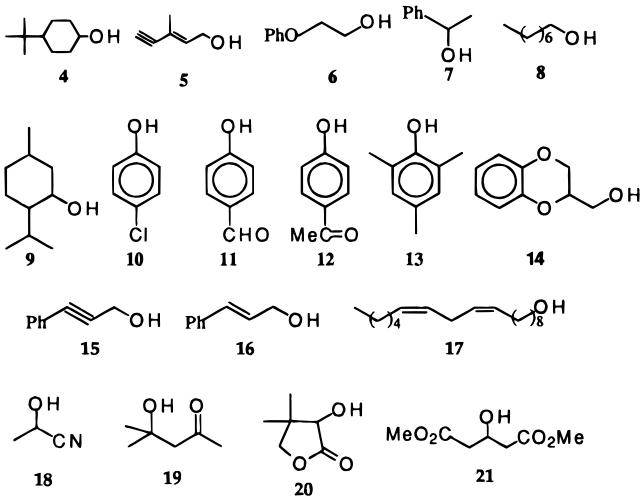
2a, Z = *t*-BuSiPh$_2$
2b, Z = *t*-BuSiMe$_2$

3a, R = H, Z = *t*-BuSiPh$_2$
3b, R = Me, Z = H

recycling the catalyst is presented. Representative primary alcohols, secondary alcohols, and phenols were silylated using *tert*-butyldiphenylsilyl chloride (TBDPSCl) in the presence of **1b** as a catalyst, but tertiary alcohols were recovered unchanged in this reaction. A preliminary communication of our silylation results with TBDMSCl in the presence of **1b** has appeared.[13]

Results

Tables 1 and 2 summarize the efficiency, the functional group compatibility, and scope of our procedure using alcohols **4**−**21** as candidate substrates in reaction 1. The



ROH + TBDPSCl/TBDMSCl $\xrightarrow[1.1\ \text{eq. Et}_3\text{N}]{\text{cat. 1b}}$ ROTBDPS/ROTBDMS (1)

TBDPS silylation of benzyl alcohol was carried out using 0.1 mmol of **1b** as a catalyst, 1.0 mmol of benzyl alcohol, and 1.1 mmol each of Et_3N and TBDPSCl in 3.0 mL of solvent at 50 °C over a period of 24 h under a nitrogen atmosphere. The influence of solvents on the yield of TBDPS benzyl ether in reaction 1 can be seen in the following data: benzene, 20%; acetonitrile, 22%; THF, 24%; DMF, 99%. This result prompted us to compare the yields of TBDPS cyclohexyl ether obtained with different silylation catalysts under the same conditions. Thus silylation of 2.0 mmol of cyclohexanol with 2.1 mmol each of TBDPSCl and triethylamine in the presence of 0.4 mmol of the silylation catalyst in 3.0 mL of DMF at 50 °C for 24 h under N_2 revealed the following yields after workup as described in method B in the Experimental Section: DMAP, 36%; DBU, 73%; TMG, 36%; **1b**, 98%.

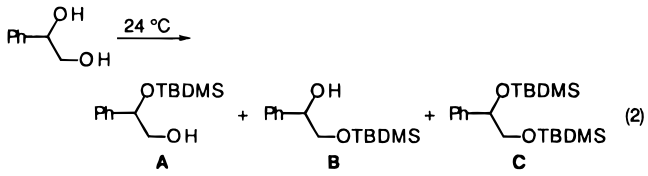
Using the convenient solvent MeCN, reaction 1 for the silylation of (±)-menthol [(±)-**9**] with TBDMSCl at 24 °C in the presence of **1b** is effected in 99% yield in 3 h (Table 2). Literature reports of this reaction at the same temperature consistently utilize the less convenient solvent DMF for alternate catalysts (DBU, 20 min, 91%;[10b] TMG, 1 h, 88%;[10a] DMAP, 12 h, 99%;[10f] 2 equiv of imidazole, no Et_3N, 3 h, 71%[14]). Using TBDMSOTf to silylate (±)-**9** in the presence of 1.1 equiv Et_3N at 24 °C gave a 99% yield of silylated product in 3 h.

Table 1. Conditions for the Preparation of TBDPS Ethers Using 1b as a Catalyst[a]

alcohol[b]	equiv of **1b**	eluent ratio[c]	time (h)	temp (°C)	solvent	% yield
8	0.1	85:15	12	24	DMF	98
10	0.2	80:20	24	24	DMF	90
15	0.3	85:15	24	50	DMF	98
16	0.1	85:15	15	24	DMF	98
cyclohexanol	0.2	80:20	24	24	DMF	67
cyclohexanol	0.2	80:20	24	50	DMF	98
linalool	0.5	80:20	24	80	neat	0
1-methylcyclohexanol	0.5	80:20	24	80	neat	0

[a] No attempt was made to maximize yields by optimizing the reaction time, the temperature, and the concentration of **1b**. [b] The alcohols are commercially available and were used as received. [c] Hexanes/ethyl acetate on a silica gel column.

The ratio of the yields of the chromatographically separated[10f] silylation products from the combination of 1.0 equiv of TBDMSCl with the diol in reaction 2 was



97:3 **A**:**C** using 0.1 equiv of **1b** and 1.0 equiv of Et_3N in MeCN after 12 h. This compares with literature ratios of 59:11:30 **A**:**B**:**C** (2.2 equiv of imidazole, no Et_3N, DMF, 12 h)[10f] and 95:5 **A**:**C** (0.04 equiv of DMAP, 1.1 equiv of Et_3N, CH_2Cl_2, 12 h).[10f]

Reaction 3 is not chemoselective and proceeded in poor yield despite the use of a silanized (2% TMSCl in hexanes) silica gel column (eluent: 50/50 pentane:ether

$$HOCH_2CMe_2NH_2 + TBDMSCl \xrightarrow[1.1\ \text{eq Et}_3\text{N, 3 h}]{\text{MeCN, 24 °C}} TBDMSOCH_2CMe_2NH_2 + HOCH_2CMe_2NHTBDMS \quad (3)$$

D **E**

followed by 10% addition of ether by volume after each 50 mL of eluent passage, until 50 mL of ether was consumed). Thus a 14% yield of **D** was realized as a white solid in the initial fraction and 12% of **E** as a yellow solid was obtained in the second.

The combination of *o*-hydroxybenzoic acid with 1.0 equiv of TBDMSCl, 1.0 equiv Et_3N, and 0.2 equiv **1b** in MeCN gave, after 3 h at 24 °C, only starting materials on chromatographic workup on a silanized column (eluent: 80:20 hexanes:EtOAc followed after 50 mL of eluent passage by 50 mL of 70:30 eluent and then 50 mL of 60:40 eluent).

Discussion

The generally favorable effect of polar solvents on the silylation of alcohols under the conditions employed here may be rationalized on the basis of ions **2a** and **2b** being formed as an active intermediate in the reaction involving **1b** and the corresponding silyl chloride. Although we were unable to detect **2a** and **2b** by ^1H and ^{31}P NMR spectroscopies, its analogue **3a** was observed and char-

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Table 2. Conditions for the Preparation of TBDMS Ethers Using 1b as a Catalyst[a]

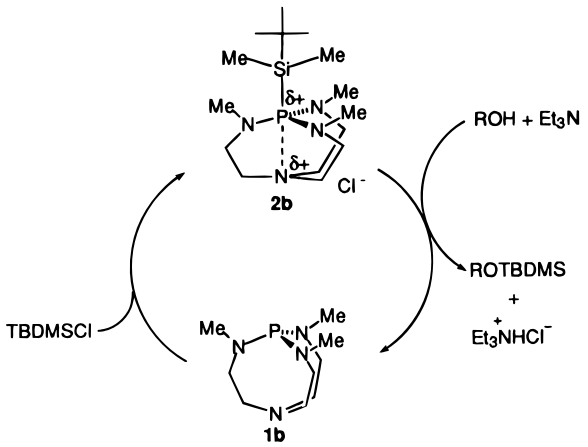
alcohol[b]	equiv of **1b**	eluent ratio[c]	time (h)	temp (°C)	solvent	% yield
4	0.2	95:5	3	24	CH_3CN	99
	0.2	95:5	3	24	CH_2Cl_2	73
	d	95:5	3	24	CH_2Cl_2	72
		95:5	3	24	CH_2Cl_2	30
5	0.2	95:5	2	24	CH_3CN	99
6	0.2	95:5	0.3	24	CH_3CN	99
(±)-**7**	0.2	95:5	3	24	CH_3CN	99
8	0.2	97:3	0.2	24	CH_3CN	99
(±)-**9**	0.2	100:0	3	24	CH_3CN	99
11	0.1	95:5	12	24	CH_3CN	90
12	0.1	80:20	2	24	CH_3CN	99
13	0.2	100:0	4	24	CH_3CN	50
	0.36	100:0	12	24	CH_3CN	85
(±)-**14**	0.2	92:8[e]	0.2	24	CH_3CN	80
	0.2	92:8[e]	0.2	24	DMF	96
15	0.2	90:10	0.2	24	CH_3CN	96
16	0.2	95:5	0.2	24	CH_3CN	99
17	0.2	100:0	2	24	CH_3CN	88
(±)-**18**	0.2	90:10	0.2	24	CH_3CN	90
	0.2	90:10	0.2	24	neat	90
19	0.2	90:10	24	80	DMF	60
	0.4	90:10	24	80	DMF	80
	0.2	90:10	24	80	neat	60
(±)-**20**	0.2	80:20	3	24	CH_3CN	42
	0.2	80:20	12	40	DMF	86
(±)-**21**	0.2	85:15	3	40	CH_3CN	86
		85:15	3	40	CH_3CN	35
	f	85:15	3	40	CH_3CN	37

[a] No attempt was made to maximize yields by optimizing reaction times, the temperature, and the concentration of **1b**. [b] All the alcohols, except for **21**, are commercially available and were used as received. Alcohol **21** was prepared by the reduction of the corresponding ketone by a method analogous to that used for other ketones.[21] [c] Hexanes/ethyl acetate on a silica gel column unless otherwise specified. [d] 0.2 equiv of **1c** was used. [e] A silica gel column neutralized with 1% Et_3N in hexanes was used. [f] 0.2 equiv of **3b** was used.

acterized by ^1H and ^{31}P NMR spectroscopies as we reported in a preliminary account.[13] An analogous silylating intermediate derived from the catalysts DMAP,[10f] DBU,[10b] and TMG[10a] has been postulated but none of these intermediates was observed directly. It should be noted that Et_3N does not catalyze alcohol silylation.[10f] It was found in the present work that the TBDMS silylation of **21** using **1b** as a catalyst provided an 86% yield of the silylated product (Table 2) whereas the same reaction run without **1b** gave only a 35% yield. Cation **3b** does not function as the catalyst under our reaction conditions, since the yield of the TBDMS ether of **21** was almost the same (37%) when **3b** was employed. These studies indicate that the P-silylating intermediates **2a** and **2b** may be present in very small concentrations (probably due to steric hindrance of the methyl groups on **1b**), thus precluding detection by ^1H and ^{31}P NMR spectroscopies.

Partial formation of the transannular PN_{ax} bond in the intermediate **2a** and **2b** may reflect both the increased strain and decreased entropy associated with the establishment of three five-membered rings in these cations, which counterbalance the electron-withdrawing power of the apical substituent. Another factor possibly favoring transannular interaction when **1b** is electrophilically attacked by the silyl reagent is the nearly planar configuration of N_{ax} in **1c**[15] (and very probably in **1b**). The transannulation process that accompanies the formation of intermediates **2a** and **2b** can be viewed as an S_N2

Scheme 1



formation of a five-coordinate intermediate, with the unusual feature that the nucleophilic atom (N_{ax}) completes its inversion from its already nearly planar stereochemistry[15] in the bridgehead position of the bicyclic structure **1b**. Apparently the augmented nucleophilicity and basicity of phosphorus in molecules of type **1** stemming from the transannular bonding that accompanies the reaction play an important role in the rate of formation and stability, respectively, of cations of type **2** and **3.** It is worth noting in this respect that **1a** is more basic than **1b** for reasons that are not obvious.[16]

Under the conditions employed for the silylation of alcohols in this work, we believe that the silyl group of **2a** and **2b** is activated by loose binding of the ion pair, thus facilitating attack of a nucleophile on the silicon, and subsequently affording the silyl ether as shown for **2b** in Scheme 1. This mechanism is analogous to that proposed for silylations involving DBU.[10b]

In Table 1 it is seen that a fatty alcohol such as *n*-octyl alcohol (**8**) was silylated at room temperature and secondary alcohols such as **9** and cyclohexanol were silylated in high yields at 55 °C in DMF using TBDPSCl. The yield of the TBDPS ether of cyclohexanol obtained by our method (Table 1) was comparable with that obtained in Hardinger's procedure which involves the use of TBDPSCl in DMF with $AgNO_3$, NH_4NO_3, or NH_4ClO_4.[11d] Moreover, phenols and tertiary alcohols (unspecified) in Hardinger's work[11d] were recovered unreacted according to that report, whereas phenol **10** was silylated in high yield using our approach. As in Hardinger's work, tertiary alcohols such as linalool and 1-methylcyclohexanol were also recovered unreacted under our conditions (Table 1). Recently, an efficient selective desilylation of TBDMS phenolic ethers in the presence of TBDPS phenolic ethers using 5 mol % of $PdCl_2(CH_3CN)_2$ was reported.[17] This information should promote the use of the TBDMS and TBDPS moieties as a protecting groups for phenols.

It has been reported that the silylation of **4** using 0.2 equiv of TMG in the presence of TBDMSCl and Et_3N resulted in an 87% yield of the silylated product at room temperature in acetonitrile,[10a] whereas this silylation using 0.33 equiv of DMAP in the presence of TBDMSCl and Et_3N gave an 85% yield of silylated product at 25 °C in DMF.[10f] Compound **4** was silylated in 99% and 73% yield in acetonitrile and methylene chloride, respectively,

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by our procedure using **1b**. When the more hindered nonionic base **1c** was used as the catalyst for silylating **4** (Table 2) in methylene chloride, again a 73% yield of the silylated product was obtained under the same conditions, whereas a control reaction without catalyst gave only a 30% yield of the silylated product (Table 2). The reason for the lower yield of the silylated product of **4** using either **1a** or **1c** in methylene chloride compared with acetonitrile is not clear.

We note in the present work that the acid-sensitive alcohol **14**, the base-sensitive alcohol **20**, and a long-chain alcohol as in the case of linoleoyl alcohol **17** were silylated with TBDMSCl in high yields (Table 2). This table also indicates that *n*-octyl alcohol **8** is cleanly silylated at room temperature in acetonitrile, whereas under the same conditions using TMG as a catalyst, this alcohol is silylated in 93% yield.[10a] Secondary alcohols were silylated to the corresponding TBDMS ethers in excellent yields in less than 4 h in acetonitrile (Table 2). The TBDMS silylation of alcohols **18** and **19** whether carried out in the absence or presence of a solvent under the same conditions gave similar yields of the silylated products (Table 2).

From Tables 1 and 2 it is clear that our method is compatibile with a variety of functional groups including aldehydes, esters, nitriles, ketones, lactones, ethers, and methylene-interrupted double bonds. It is observed from these tables that, in general, a longer reaction time, a higher catalyst concentration, a more polar solvent, and a higher temperature lead to augmented yields of silylated products. Recently Nelson and Crouch[18] published a review of selective deprotection schemes for a variety of silyl ethers which should increase the use of TBDMS and TBDPS protecting groups in organic synthesis. It should be noted that TMSCl is dehydrohalogenated by **1b** giving $(Me_2SiCH_2)_2$,[19] hence precluding the use of TMSCl for alcohol silylation using our procedure.

Catalyst **1b** has good solubility both in polar solvents such as THF, diethyl ether, acetonitrile, pyridine, and DMF and in nonpolar solvents such as pentane, benzene, and hexane. Another advantage of **1b** over conventional silylation catalysts is that it is converted to crystalline **3b** which is easily separated from the triethylammonium hydrochloride and the silylated product formed in the reaction. Because **3b** is quite insoluble in nonpolar and relatively weakly polar solvents such as diethyl ether, ethyl acetate, pentane, and toluene, it can be easily separated by filtration and recycled to **1b** in a single step using KO-*t*-Bu. To the best of our knowledge, no recovery process for other silylation catalysts has been recorded. This may be attributed to the considerable solubility of the protonated forms of such catalysts in a variety of solvents, thus inhibiting recycling efforts. For example, protonated DBU salts are quite soluble in both polar as well as nonpolar solvents.

Conclusions

The nonionic superbase **1b** is a superior catalyst for alcohol and phenol protective silylations under mild conditions using TBDMSCl and TBDPSCl. The advantages of using **1b** as a silylation catalyst are (1) the yields of the silylated alcohols and phenols are high, (2) acetonitrile or tetrahydrofuran can be used for the preparation of TBDMS ethers in cases where the use of DMF as a solvent is not desirable or practical, (3) the catalyst can be recycled in high yields, (4) the catalyst is compatible with a variety of functional groups, (5) catalyst **1b** is commercially available (Strem Chemical Co.), and (6) acid- and base-sensitive alcohols can be efficiently silylated by our approach (see methods A and C in the Experimental Section) because only 0.05 mL of water is required for quenching **1b**. Similar yields of silylated alcohols can be obtained with or without a solvent. Minor disadvantages of **1b** are that it cannot be used for TMSCl reactions or for the silylation of tertiary alcohols with TBDPSCl.

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Experimental Section

Benzene and tetrahydrofuran were distilled from Na–benzophenone, acetonitrile was distilled from calcium hydride, triethylamine was distilled from potassium hydroxide, and methylene chloride was distilled from P_4O_{10}. Anhydrous DMF, TBDMSCl, TBDPSCl, dimethyl 3-oxoglutarate, 1-phenyl-1,2-ethanediol, salicylic acid, and 2-amino-2-methyl-1-propanol were purchased from Aldrich Chemical Co. and were used as received. The bases **1b**[12] and **1c**[15] were prepared according to our previously published method and were stored under nitrogen. All reactions and distillations were carried out under a nitrogen or argon atmosphere. The products were found to be >97% pure by ^{1}H NMR analysis.

General Preparative Procedure for 1b-Catalyzed Silylations of Alcohols. Method A. In a 100 mL flask was dissolved a catalytic amount of **1b** (Table 2) in 5.0 mL of dry acetonitrile. To this was added 0.82 g (5.5 mmol) of TBDMSCl followed by the addition of 0.76 mL (5.5 mmol) of Et_3N. After the mixture was stirred for 5 min, 5.0 mmol of the alcohol was added with continued stirring at the temperature stated in Table 2. After the stated reaction time in this table, 0.05 mL of water was added with stirring. After evaporation of ~95% of the solvent under vacuum, 20 mL of ether was added and stirring was continued for 5 min more to precipitate **3b** as a white solid. The mixture was filtered, and the residue was washed with 2 × 5 mL of ether. The residue was collected for subsequent recycling to **1b**. The organic layer was dried with anhydrous sodium sulfate followed by concentration under vacuum to afford the crude silyl ether which was purified by chromatography on silica gel using gradient elution. Thus after the column was loaded with the crude silyl ether, the polarity of the eluent was increased in steps of 5% using 50 mL of eluent in each step, starting from 50 mL of 100% hexanes and ending with the ratio of the eluent indicated in Table 2.

Method B. In a 100 mL flask was dissolved a catalytic amount of **1b** (Tables 1 and 2) in 3 mL of dry DMF under nitrogen. After addition of 2.1 mmol of the silyl chloride, followed by 0.29 mL (2.1 mmol) of Et_3N, the mixture was stirred for 5 min. Then 2.0 mmol of the alcohol was added with continued stirring at the temperatures stated in Tables 1 and 2. After the stated reaction times in these tables, 5 mL of water was added with stirring. This was followed by the addition of 20 mL of ethyl acetate and stirring for 5 min more. The organic layer was washed with 5 mL of aqueous saturated sodium bicarbonate and then with 5 mL of water. After the organic layer was dried over anhydrous sodium sulfate, the mixture was filtered. The filtrate was concentrated under vacuum at ~40 °C affording the crude silyl ether which was purified by chromatography on silica gel using gradient elution as described in method A.

Method C. To a 100 mL flask containing a catalytic amount of **1b** (Table 2) was added 0.82 g (5.5 mmol) of TBDMSCl followed by the addition of 0.76 mL (5.5 mmol) of Et_3N. After the mixture was stirred for 5 min, 5.0 mmol of the alcohol was added with continued stirring at the temperature stated in Table 2. After the reaction time stated in that table, the mixture was diluted with 5 mL of acetonitrile. To this was added 0.05 mL of water with stirring. The mixture

was then filtered and the residue was washed with 2 × 5 mL of ether. After evaporation of ~95% of the solvent, 20 mL of ether was added and stirring was continued for 5 min more to precipitate **3b** as a white solid. The mixture was then filtered and the residue washed with 2 × 5 mL of ether. The residue was dried under vacuum and saved for recycling to **1b**. The organic layer was dried with anhydrous sodium sulfate and filtered, and then the filtrate was concentrated under vacuum, affording the crude silyl ether which was purified by chromatography on silica gel using gradient elution as described in method A.

Method D. In a 100 mL flask was dissolved 0.2 mmol of the catalyst (Table 2) in 5 mL of dry methylene chloride. To this was added 0.17 g (1.1 mmol) of TBDMSCl followed by the addition of 0.15 mL (1.1 mmol) of Et_3N. The mixture was stirred for 5 min, after which 1.0 mmol of alcohol **4** was added with continued stirring at 24 °C. After 3 h, 0.01 mL of water was added with stirring. The mixture was filtered, the residue was washed with 2 × 5 mL of ether, and then ~95% of the solvent was evaporated under vacuum. Ether (20 mL) was added, and stirring was continued for 5 min more to precipitate **3b** as a white solid. The mixture was filtered, and the residue was washed with 2 × 5 mL of ether. The organic layer was dried with anhydrous sodium sulfate and filtered, and then the filtrate was concentrated under vacuum. The crude silyl ether which remained was purified by chromatography on silica gel using gradient elution as described in method A to give 0.200 g (73%) of the silylated product.

Preparation of 21 from Dimethyl 3-Oxoglutarate. To a 100 mL flask containing 2.0 mL (14 mmol) of dimethyl 3-oxoglutarate in 15 mL of methanol was added 0.24 g (6.8 mmol) of sodium borohydride in small portions over 5 min. The reaction mixture was stirred for 1 h, and then 5 mL of water was added. The aqueous layer was extracted with 2 × 20 mL of ethyl acetate. The organic layer was dried with anhydrous sodium sulfate and then it was filtered. The filtrate was concentrated under vacuum, affording the crude dimethyl 3-hydroxyglutarate which was purified by chromatography on silica gel using 65:35 hexanes:ethyl acetate as the eluent to give 1.7 g of **21** in 72% yield after evaporation of the solvents. The ^{1}H NMR of the product compared favorably with that reported in the literature.[20]

Recycling of 1b. The residues (~4 g) obtained from methods A and C were deprotonated using 1.4 equiv of KO-*t*-Bu in 10 mL of acetonitrile in a Schlenk flask. The resulting suspension was stirred overnight under nitrogen at 24 °C after which the solvent was evaporated under vacuum at ~40 °C. Pentane (50 mL) was added, and the suspension was stirred overnight under nitrogen. The clear pentane layer was transferred to another Schlenk flask via a cannula or a syringe, and then the solvent was evaporated under vacuum at 24 °C to give a white solid which on sublimation (50 °C/100 mTorr) gave pure **1b** in ~80% yield.

Acknowledgment. The authors thank the Center for Advanced Technology Development of Iowa State University and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for grant support of this research.

Supporting Information Available: Compound characterizational data, NMR peak assignments, and ^{1}H NMR spectra (28 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.

JO9701492

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