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$P(MeNCH_2CH_2)_3N$: An Efficient Catalyst for the Desilylation of *tert*-Butyldimethylsilyl Ethers

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tert-Butyldimethylsilyl (TBDMS) ethers of primary, secondary, and tertiary alcohols and phenolic TBDMS ethers are desilylated to their corresponding alcohols and phenols, respectively, in DMSO, at 80 °C, in 68−94% yield in the presence of 0.2−0.4 equiv of $P(MeNCH_2CH_2)_3N$. Using $P(i\text{-}PrNCH_2CH_2)_3N$ as the catalyst, 85−97% yields of desilylated alcohols were obtained from TBDMS ethers of 1-octanol, 2-phenoxyethanol, and racemic α-phenyl ethanol. These are the first examples of desilylations of silyl ethers catalyzed by nonionic bases. Both catalysts were much less effective for the desilylation of *tert*-butyldiphenylsilyl (TBDPS) ethers (22−45% yield) under the same conditions as used for TBDMS ethers. Possible pathways involving nucleophilic attack of the anion of the solvent molecule (generated by the catalyst) at the Si−O bond of silyl ether or a prior activation of the silyl ether by the catalyst via a P−Si interaction followed by nucleophilic attack of the solvent anion are proposed on the basis of ^1H and ^{31}P NMR experimental data.

Introduction

Ever since its discovery,[1] the *tert*-butyldimethylsilyl (TBDMS) group has become one of the most popular protective groups for OH groups in organic synthesis because of the ease with which it can be introduced and removed.[2] Methods generally used to cleave Si−O bond in TBDMSOR ethers for parent alcohol regeneration include (1) acid-catalyzed Si−O cleavage with HF,[3] AcOH,[1,4] CF_3COOH,[5] TsOH,[6] HCl,[3c,4c,7] H_2SO_4;[8] Lewis acids such as BF_3[9a] and Me_2BBr,[9b] and (2) Lewis base-catalyzed Si−O cleavage employing fluoride ion.[1,3b,e,f,9a,10] Other reagents such as a carboxylic acid resin,[11] salts of BF_4^-,[12] $(Me_2N)_3S[F_2SiMe_3]$,[13] KO_2,[14] organotin reagents,[15] NBS,[16] $t\text{-}BuOOH/MoO_2(acac)_2$,[17] $LiAlH_4$,[18] ceric ammonium nitrate,[19] LiOH,[20] I_2,[21] and LiCl[22] have also been reported to desilylate TBDMS ethers of alcohols. Although CCl_4/MeOH is efficient only for desilylating TBDMS ethers of primary alcohols,[23] CBr_4/MeOH is effective for deprotecting TBDMS, *tert*-butyldiphenylsilyl (TBDPS) and triisopropylsilyl (TIPS) ethers of primary and secondary alcohols and phenols.[24] Transition metal-catalyzed desilylation of TBDMS ethers is effected with $PdCl_2(CH_3CN)_2$,[25] or $Sc(OTf)_3$,[26] and $CeCl_3 \cdot 7H_2O$/NaI was

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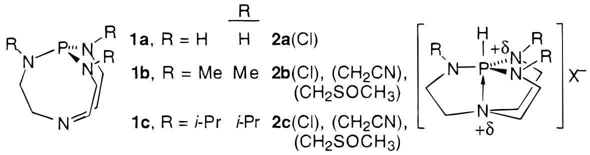
reported to hydrolyze TBDMS, TBDPS, and TIPS ethers to alcohols in acetonitrile.[27] Selective deprotection of a Et_3Si group in the presence of a TBDMS group with a mesoporous silica MCM-41/MeOH system has also been reported recently.[28] The stability order TBDPS > TBDMS > TMS for these protective groups in silyl ethers with respect to hydrolysis has been ascribed to their decreasing steric bulk. Thus TMS ethers can be deprotected under relatively mild conditions,[29] TBDPS ethers are generally desilylated to their corresponding alcohols under the same conditions as those used for TBDMS ethers,[2] (e.g., using HF,[30] fluoride ion,[31] LiOH,[32] BF_3,[33] or LiCl[22]) although harsher conditions and longer times are necessary in some cases.



1a, R = H H **2a**(Cl)

1b, R = Me Me **2b**(Cl), (CH_2CN), (CH_2SOCH_3)

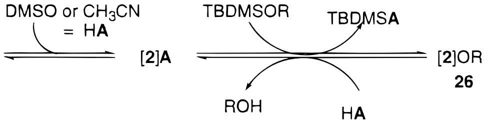
1c, R = *i*-Pr *i*-Pr **2c**(Cl), (CH_2CN), (CH_2SOCH_3)

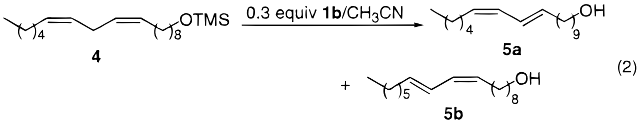
In the course of our ongoing studies[34] on new synthetic applications of exceedingly strong nonionic bases and catalysts of type **1** first reported from our laboratories, we discovered that **1b** is an efficient and mild catalyst for transforming a variety of alcohols to their corresponding TBDMS or TBDPS ethers using TBDMSCl or TBDPSCl in the presence of excess Et_3N in CH_3CN or DMF (eq 1).[35] In a recent investigation of the conjugation of

$$\text{ROH + TBDMSCl/TBDPSCl} \xrightarrow[\text{1.1 equiv Et}_3\text{N}]{\text{cat. }\mathbf{1b}} \text{TBDMSOR/TBDPSOR} \quad (1)$$

the TMS ether (**4**) of linoleyl alcohol catalyzed by **1b** in CH_3CN at 40 °C, we discovered that a catalytic amount of **1b** causes quantitative desilylation of **4** to give the conjugated alcohols (*trans,cis*-**5a** and *cis,trans*-**5b**) in a 1 to 1 ratio (eq 2).[36] Thus we speculated that our nonionic superbases **1b** and **1c** might be useful for desilylating silyl ethers.

Scheme 1

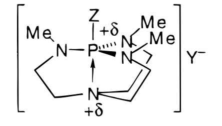




Herein we report for the first time an efficient catalytic procedure for removing the protective TBDMS group from a variety of TBDMSOR ethers using a nonionic base, namely, **1b** as the catalyst. Some desilylations of TBDPSOR ethers using a nonionic base, namely **1b**, are also described and several desilylation reactions employing **1c** as the catalyst are also presented. Possible pathways are proposed for these desilylations.

Results and Discussion

Proazaphosphatranes **1** are powerful nonionic bases forming the remarkably stable azaphosphatrane cations **2a**−**c** as their chloride salts. The order of basicity is **1b** < **1c**, and **1b** has been shown to be capable of deprotonating acetonitrile to its corresponding anion $^-CH_2CN$,[37] which initiates a variety of reactions.[34] The ^1H and ^{31}P NMR spectra of **1b** (or **1c**) in DMSO also indicate in the present work that **1b** and **1c** deprotonate this solvent.



3a, Z = *t*-BuMe₂Si, Y = Cl

3b, Z = C(O)Ph, Y = $PhCO_2$

3c, Z = C(O)OEt, Y = Cl

The nucleophilicity and basicity of **1a**−**c** stems from transannular bond formation between the phosphorus atom and the bridgehead nitrogen atom as shown in cation **2**. Partial transannulation in species of type **3** plays an important role in the formation and stability of these cationic intermediates in catalytic reactions.[34o,p,35,38b] Thus it is plausible that anion **A** [**A** = $^-CH_2CN$ or $^-CH_2S(O)CH_3$] generated by **1b** or **1c** via solvent deprotonation nucleophilically attacks the Si−O bond of a silyl ether to form TBDMS**A** (or TBDPS**A**) while liberating RO^- which extracts a solvent proton to form the deprotected alcohol (Scheme 1). ^{31}P NMR experiments in $CD_3S(O)CD_3$ revealed that some **1b** (or **1c**) and **2b** (or **2c**) were present during the entire course of the reaction [for deuterated base, δ ca. −10.6 ppm (t, $^1J_{PD} \cong 140$ Hz) triplet; for free base, (δ ca. 110−120 ppm (s)]. Interestingly, during the reaction of TBDMS ether **7** [i.e.,

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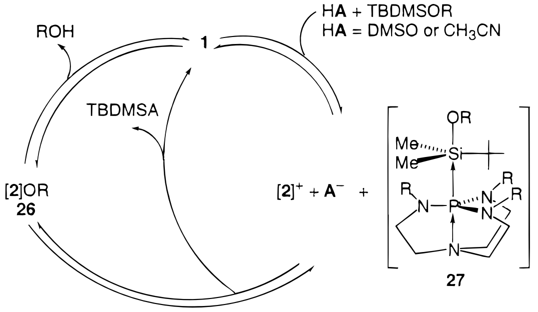
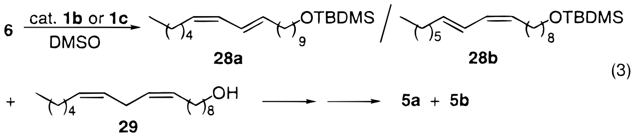
Scheme 2



CH$_3$(CH$_2$)$_6$CH$_2$OTBDMS] with **1b** (40 mol %) in CD$_3$S(O)CD$_3$ at room temperature, three sets of triplets were observed at low field in the ^{1}H NMR spectra of the reaction mixture. These triplets are assigned to three different types of −OCH$_2$− groups. Thus the triplet at 3.55 ppm is assigned to the starting silyl ether and the triplet at 3.35 ppm is associated with the deprotected alcohol. These assignments were arrived at by comparing these spectra with those of the starting silyl ether and the deprotected alcohol, respectively. The third triplet at 3.43 ppm is assigned to a new species formed during the reaction that may be an intermediate such as **26** in Scheme 1 or **27** in Scheme 2. As the reaction proceeded and after more than half the amount of the starting silyl ether (88.3% conversion of **7** at 71 h) became deprotected, this new triplet became undetectable due to the low concentration of the intermediate. For the same reaction in DMSO-d_6 at 80 °C, this triplet was also observed, and again it disappeared as the reaction reached completion. Similar results were obtained in the reactions of **8** and **14** with **1b** at room temperature or at a higher temperature (e.g., 50 °C) although the signals (a third triplet peak for **8** and a third quartet peak for **14**) were not so strong as those in the former reaction. Although ^{31}P NMR spectra of these reactions showed no convincing evidence for the formation of **27**, our previous investigations revealed the possible formation of analogues of **27**, i.e., cationic intermediates of type **3**.[34o,p,35,38a] Using the relatively sterically hindered silyl ether (±)-**15** as a substrate, no similar phenomenon was observed in the ^{1}H NMR spectra of the reaction mixture in DMSO-d_6 whether the reaction temperature was ambient or 80 °C, demonstrating that steric factors probably play an important role in the formation of an intermediate such as **27**. It should be noted that the steric hindrance order of **1b** and **1c** is **1c** > **1b**. TBDMS**A** or TBDPS**A** were presumably formed although efforts to isolate these species were not successful. Thus repeated attempts to separate the mixture by preparative TLC resulted in a poorly developed brown strip near the starting line that upon collection and washing with CHCl$_3$ and filtration was shown by NMR spectroscopy to contain a largely uninterpretable mixture.

Reactions carried out in deuterated solvents under the same reaction conditions showed the order DMSO-d_6 > CD$_3$CN > CD$_3$COCD$_3$ ≥ CD$_3$OD ≫ C$_6$D$_6$ for the relative rates of desilylation of TBDMS ethers catalyzed by **1b**. It is known that some primary TBDMS ethers (such as allylic, homoallylic, benzylic, and aryl derivatives) can be hydrolyzed in DMSO/H$_2$O at 90 °C although all other primary and secondary TBDMS ethers remain unaffected under these conditions.[39] In addition, it was noted that desilylation of (±)-**13** catalyzed by **1b** was more efficient in DMSO than in CH$_3$CN (Table 1). It is perhaps not unreasonable to expect that the strong polarity of DMSO molecules may favor the formation of alcohols from less-polar silyl ethers. Thus DMSO was deemed to be the reaction solvent of choice. That desilylations under the conditions described here are not proceeding by ordinary base-promoted silyl cleavage is supported by the failure of TBDMS ethers such as (±)-**13** to desilylate in the presence of 40 mol % **1b** in C$_6$D$_6$ at 50 °C over 62 h. Evaporation of the filtrate followed by ^{1}H NMR analysis revealed the presence of DMSO, protonated catalyst (presumably as the **A** salt) and a TBDMS-containing compound (presumably TBDMS**A**). The strong polarity of the components of this mixture may be responsible for the poor separation.

Complete desilylation of linoleyl TBDMS ether **6** was accompanied by the formation of a 1:1 ratio of conjugated alcohols **5a** and **5b** in 90% yield (reaction 3 and Table 1). The TMS analogue of **6**, namely **4**, is also easily desilylated and isomerized to produce the same alcohols under relatively milder conditions using CH$_3$CN as the solvent at 40 °C in the presence of **1b** or **1c**.[36] On the basis of that study it is suggested that possible intermediates in the reaction of **6** and **1b** or **1c** in DMSO are those shown in reaction 3. Competitive cleavage of the Si−O bond and isomerization of CH$_2$-separated carbon−carbon double bond lead to the conjugated TBDMS ethers **28a** and **28b**, and linoleyl alcohol (**29**). The desilylation of **28a** and **28b** and isomerization of **29** then give rise to the final products **5a** and **5b**. Another possible intermediate is the alkoxyl anion of **29** since superbases **1b** and **1c** are known to deprotonate alcohols.[36,38] For TBDMS ethers **7**−**13** derived from primary alcohols, 80−94% desilylation yields were achieved. Silyl ethers **14**−**18** derived from secondary alcohols, silyl ethers **19**−**21** derived from tertiary alcohols, and phenolic ethers **22** and **23** were desilylated to their corresponding products in moderate to good yields (Table 1). Catalyst **1c** was also efficient for desilylating TBDMS ethers **7**, **8,** and (±)-**15** to their corresponding products in 85−97% yield (Table 2). Although **1b** and **1c** are efficient catalysts for deprotecting TBDMS ethers, both of them failed to desilylate TBDPS ethers efficiently. TBDMS ether (e.g., **22** in Table 1) was much more efficiently desilylated than its TBDPS ether, i.e., **25**, under the same conditions (Table 2). The desilylation of **24** and **25** provided products in only 22 to 45% yields, respectively (Table 2). The greater steric hindrance of the TBDPS group compared with that of the TBDMS group coupled with the bulkiness of **1b** and **1c** may account for the low yields in these cases.



Experimental Section

Acetonitrile was distilled over P$_4$O$_{10}$ under nitrogen. The nonionic superbases **1b**[34q] and **1c**[38b] were prepared according to our previously published methods although **1b** is commercially available.[40] TBDMS and TBDPS ethers were pre-

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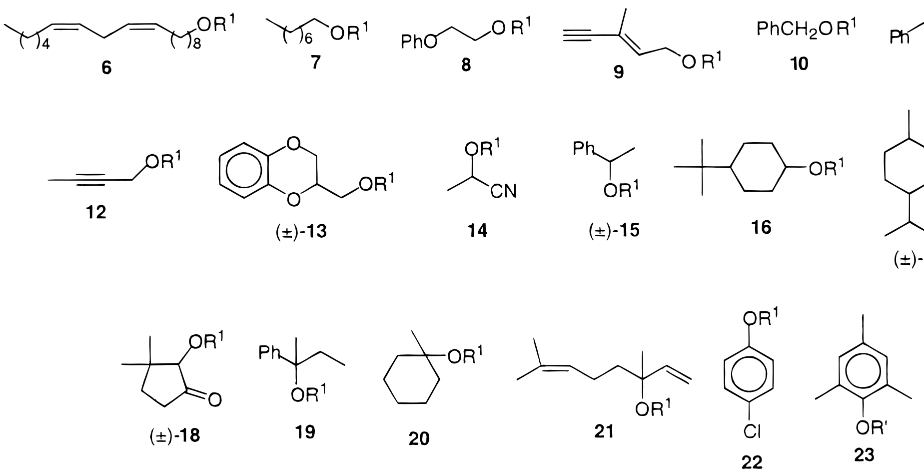
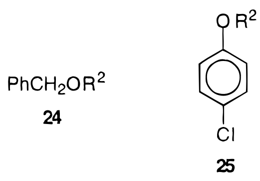
Table 1. Desilylation of TBDMS Ethers to Corresponding Alcohols Using 1b as a Catalyst[a]



TBDMS ethers[b]	equiv of **1b**	temp/time (°C/h)	eluent ratios (v/v)[c]	alcohol yield (%)[d]	TBDMS ethers[b]	equiv of **1b**	temp/time (°C/h)	eluent ratios (v/v)[c]	alcohol yield (%)[d]
6	0.3	80/36	10:1	90[e]	(±)-**15**	0.2	80/24	5:2	89
7	0.2	80/34	5:1	94	**16**	0.3	80/36	10:1	68
8	0.3	80/36	5:1	90	(±)-**17**	0.3	80/36	5:2	85
9	0.3	80/36	5:1	84	(±)-**18**	0.3	80/36	5:1	89
10	0.3	80/30	5:1	80	**19**	0.4	80/27	5:2	68
11	0.3	80/36	5:1	89	**20**	0.3	80/36	5:1	87
12	0.25	80/36	5:1	83	**21**	0.3	80/36	5:1	81
(±)-**13**	0.2	80/24	5:1	90	**22**	0.3	80/24	5:1	94
	0.4	80/36	5:1	81[f]	**23**	0.2	80/24	5:1	85
14	0.2	80/19	5:2	80					

[a] No attempt was made to maximize yields by optimizing reaction times, temperatures, and the concentrations of **1b**. The solvent is DMSO except where indicated. [b] The preparation of all the ethers was reported in our previous papers.[35] [c] *n*-Hexane/THF. [d] Isolated yield was obtained by preparative TLC on silica gel. [e] The ratio of **5a**/**5b** was ca. 1/1 as determined by ^{1}H NMR spectroscopy and GC and by comparison with such spectra reported in the literature.[36] [f] The solvent was CH_3CN.

Table 2. Desilylation of TBDPS Ethers Using 1b or 1c as a Catalyst and Desilylation of TBDMS ethers using 1c as a Catalyst[a]



R^1 = TBDMS, R^2 = TBDPS

silyl ether[b]	equiv of **1b** or **1c**	temp/time (°C/h)	eluent ratio[c]	alcohol yield (%)[d]
24	**1b** (0.4)	80/36	5:1	22
24	**1c** (0.4)	80/36	5:1	25
25	**1b** (0.3)	80/24	10:1	30
25	**1b** (0.3)	80/36	10:1	39
25	**1c** (0.3)	80/36	10:1	45
7	**1c** (0.2)	80/24	5:1	85
8	**1c** (0.2)	80/36	5:1	95
(±)-**15**	**1c** (0.2)	80/36	5:1	97

[a] No attempt was made to maximize yields by optimizing reaction times, temperatures, and the concentrations of **1b** and **1c**. The solvent was DMSO. [b] The preparations of the ethers were reported in our previous papers.[35] [c] *n*-Hexane/THF. [d] The isolated yield was obtained by TLC on silica gel.

pared as reported earlier from our laboratories.[35] The desilylated products were characterized by mass and NMR spectroscopies and were found to be >95% pure by ^{1}H NMR analysis. Moreover, ^{1}H and ^{13}C NMR spectra of all the isolated products except **5a**/**5b**[35] were compared with those of the authentic samples or those in the literature.[41]

General Procedure for Desilylation. DMSO (or CH_3CN as indicated in Table 1) (4 mL) was added under nitrogen to a 25 mL round-bottom flask charged with catalyst (as indicated in Tables 1 and 2). Then the silyl ether substrate (1.0 mmol) was introduced through the rubber septum via a syringe. The reaction mixture was stirred at 80 °C for the time indicated in Tables 1 and 2, and after cooling the mixture to room temperature, it was poured into 150 mL of water followed by extraction with $CHCl_3$ (5×40 mL). The organic layer was dried overnight with $MgSO_4$ and then filtered. The organic phase was concentrated to ca. 1.5 mL by rotary evaporation and subjected to TLC separation on silica gel with the appropriate eluent as indicated in Tables 1 and 2. The NMR reactions were performed in a 5 mm NMR tube sealed with a rubber septum in a manner similar to that described above.

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Supporting Information Available: Compound characterizational data, NMR peak assignments, and copies of ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) Strem Chemical Co.

(41) The Aldrich Library of ^{13}C and ^{1}H NMR Spectra, 1993, Vol. 1.