1205, 1170, 1065 cm^{-1}; ^{1}H NMR δ 1.37, 1.58 (3 H × 2, each s, C(CH$_3$)$_2$), 2.07–2.57 (6 H, m, H-H-2,2′,4,4′,5,5′), 2.80 (1 H, s, OH), 4.00 (1 H, t, J = 3 Hz, H-6), 4.14 (1 H, d, J = 4.5 Hz, H-9), 5.86 (1 H, d, J = 4.5 Hz, H-8). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.69; H, 7.06.

(6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo-[4.3.0]non-1-en-3-one (11). To a stirred solution of compound **10** (3.69 g, 16.2 mmol) in pyridine (37 mL) were added methanesulfonyl chloride (2.51 mL, 32.4 mmol) and 4-(dimethylamino)pyridine (396 mg, 3.24 mmol). The mixture was stirred for 4 h and then heated at 50 °C for 26 h. The mixture was coevaporated with toluene to remove pyridine completely. The residue was partitioned between CH_2Cl_2 (60 mL) and water (60 mL). The aqueous layer was extracted with CH_2Cl_2 (60 mL × 2). The combined organic layers were dried over Na_2SO_4 and then concentrated. The residue was chromatographed on silica gel (100 g, ethyl acetate/hexane = 1:7), and the fraction corresponding to R_f 0.44 (ethanol/toluene = 1:8) was concentrated to give crystals of compound **11** (3.20 g, 94%), mp 107–108 °C: $[\alpha]^{20}_D$ +148.6° (*c* 1.14); IR ν^{KBr}_{max} 2990, 2940, 2860, 1685, 1385, 1375, 1330, 1250, 1235, 1215, 1160, 1085, 1050, 1015 cm^{-1}; ^{1}H NMR δ 1.40, 1.57 (3 H × 2, each s, C(CH$_3$)$_2$), 1.67–2.67 (4 H, m, H-4,4′,5,5′), 4.89 (1 H, t, J = 6 Hz, H-6), 5.02 (1 H, d, J = 4.5 Hz, H-9), 5.96 (1 H, d, J = 4.5 Hz, H-8), 6.08 (1 H, s, H-2). Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.75. Found: C, 62.97; H, 6.68.

(3*R*,6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo-[4.3.0]non-1-en-3-ol (12). To a stirred solution of compound **11** (3.20 g, 15.2 mmol) in ethanol (110 mL) at 0 °C was added sodium borohydride (403 mg, 10.6 mmol). After being stirred at the same temperature for 30 min, the reaction mixture was then neutralized with 1 M aqueous HCl solution. The mixture was concentrated and the residue partitioned between CH_2Cl_2 (70 mL) and water (70 mL). The aqueous layer was extracted with CH_2Cl_2 (70 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (140 g, ethyl acetate/hexane = 1:3), and the fraction corresponding to R_f 0.37 (ethanol/toluene = 1:8) was concentrated to give crystals of compound **12** (2.79 g, 86%), mp 108–109 °C: $[\alpha]^{21}_D$ +122.7° (*c* 1.18); IR ν^{KBr}_{max} 3260, 3000, 2940, 2880, 1370, 1250, 1200, 1165, 1150, 1050 cm^{-1}; ^{1}H NMR δ 1.32, 1.50 (3 H × 2, each s, C(CH$_3$)$_2$), 1.22–1.55 (2 H, m, H-4,4′ or H-5,5′), 1.95–2.35 (2 H, m, H-5,5′ or H-4,4′), 2.90–3.30 (1 H, br s, OH), 4.15–4.40 (1 H, m, H-3 or H-6), 4.40–4.70 (1 H, m, H-6 or H-3), 4.79 (1 H, d, J = 4.5 Hz, H-8), 5.74 (1 H, d, J = 4.5 Hz, H-9), 5.86 (1 H, br s, H-2). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.39; H, 7.50.

(1*S*,3*R*,6*R*,8*R*,9*R*)- and (1*R*,3*R*,6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo[4.3.0]nonan-3-ol (13 and 14). A solution of compound **12** (2.79 g, 13.1 mmol) in ethanol (40 mL) was hydrogenated in the presence of Raney nickel T-4 under atmospheric hydrogen pressure for 18 h. The catalyst was removed with a Celite pad and then the catalyst was washed with ethanol. The combined filtrate and washings were concentrated. The residue was chromatographed on silica gel (110 g, ethyl acetate/hexane = 1:4). The fraction corresponding to R_f 0.27 (ethanol/hexane = 1:8) was concentrated to give crystals of compound **13** (2.34 g, 83%), mp 122–123 °C. The fraction corresponding to R_f 0.23 was concentrated to give crystals of compound **14** (0.341 g, 12%), mp 74–76 °C. **13**: $[\alpha]^{22}_D$ −3.7° (*c* 1.28); IR ν^{KBr}_{max} 3470, 2960, 2940, 1385, 1375, 1260, 1205, 1170, 1060 cm^{-1}; ^{1}H NMR δ 1.30, 1.49 (3 H × 2, each s, C(CH$_3$)$_2$), 1.50–2.50 (7 H, m, H-1,2,2′,4,4′,5,5′), 2.59 (1 H, br s, OH), 4.05 (1 H, t, J = 2.5 Hz, H-6), 4.20 (2 H, br d, J = 4 Hz, H-3,9), 5.78 (1 H, d, J = 4 Hz, H-8). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.89; H, 8.33. **14**: $[\alpha]^{23}_D$ +15.2° (*c* 0.80); IR ν^{KBr}_{max} 3420, 3000, 2950, 2880, 1460, 1380, 1270, 1250, 1210, 1170, 1130, 1110, 1090 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.33, 1.53 (3 H × 2, each s, C(CH$_3$)$_2$), 1.30–1.51, 2.05–2.17 (5 H, 3 H, each m, H-1,2,2′,4,4′,5,5′, OH), 3.66 (1H, dt, $J_{1,6}$ = $J_{5ax,6}$ = 10.7 Hz, $J_{5eq,6}$ = 4.4 Hz, H-6), 3.71–3.79 (centered at δ 3.75, 1 H, m, H-3), 4.55 (1 H, t, $J_{1,9}$ = $J_{8,9}$ = 3.9 Hz, H-9), 5.84 (1 H, d, $J_{8,9}$ = 3.9 Hz, H-8). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.91; H, 8.35.

(1*S*,6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo-[4.3.0]nonan-3-one (3). To a stirred solution of the alcohol **13** (40.6 mg, 0.19 mmol) in CH_2Cl_2 (2 mL) were added pyridinium chlorochromate (61 mg, 0.28 mmol) and molecular sieves (60 mg). After 1 h, the mixture was concentrated. The residue was chromatographed on silica gel (1 g) and the column was eluted with ether. The ethereal fraction corresponding to R_f 0.42 (ethanol/toluene = 1:8) was concentrated to give crystals of the ketone **3** (37.0 mg, 92%), mp 82–84 °C: $[\alpha]^{23}_D$ +7.3° (*c* 0.83); IR ν^{KBr}_{max} 2990, 2980, 2920, 1715, 1380, 1370, 1250, 1200, 1170, 1145, 1080 cm^{-1}; ^{1}H NMR δ 1.31, 1.52 (3 H × 2, each s, C(CH$_3$)$_2$), 1.85–2.77 (7 H, m, H-1,2,2′,4,4′,5,5′), 4.33–4.51 (2 H, m, H-6,9), 5.92 (1 H, d, J = 4.5 Hz, H-8). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.48; H, 7.66.

(1*R*,6*R*,8*R*,9*R*)-8,9-(Isopropylidenedioxy)-7-oxabicyclo-[4.3.0]nonan-3-one (15). Compound **14** (23.0 mg, 0.10 mmol) was oxidized with pyridinium chlorochromate (46 mg) in the presence of molecular sieves (50 mg) in CH_2Cl_2 (1 mL) for 10 h. After chromatographic purification on silica gel (1 g), crystals of the ketone **15** (22.7 mg, quantitative) were obtained from the ethereal fraction of R_f 0.67 (ethanol/toluene = 1:8), mp 96.5–98 °C (lit.[1c,f] mp 98–98.5 °C): $[\alpha]^{17}_D$ −28.8° (*c* 1.05), [lit.[1c,f] $[\alpha]^{21.5}_D$ −33.7° (*c* 1.66)]. The IR and ^{1}H NMR spectra of compound **15** were identical with those of an authentic sample.[1c,f]

(1*R*,3*R*,6*R*,8*R*,9*R*)-3-(Benzoyloxy)-8,9-(isopropylidenedioxy)-7-oxabicyclo[4.3.0]nonane (16). To a stirred solution of compound **14** (14.5 mg, 0.07 mmol) in pyridine (0.5 mL) at 0 °C was added benzoyl chloride (0.012 mL, 0.1 mmol). After being stirred for 1.5 h at the same temperature, the mixture was concentrated. The residue was partitioned between CH_2Cl_2 (10 mL) and water (10 mL), and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layers were dried over Na_2SO_4 and then concentrated. The residue was chromatographed on silica gel (1.5 g, ethyl acetate/hexane = 1:15), and the fraction corresponding to R_f 0.32 (ethanol/toluene = 1:15) was concentrated to give crystals of compound **16** (16.5 mg, 77%), mp 95–96 °C: $[\alpha]^{24}_D$ +29.1° (*c* 0.83); IR ν^{KBr}_{max} 2990, 2980, 2960, 2900, 2870, 1720, 1450, 1385, 1370, 1335, 1320, 1270, 1260, 1245, 1220, 1180, 1165 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.32, 1.53 (3 H × 2, each s, C(CH$_3$)$_2$), 1.47–1.76, 2.21–2.34 (4 H, 3 H, each m, H-1,2,2′,4,4′,5,5′), 3.73 (1 H, dt, $J_{1,6}$ = $J_{5ax,6}$ = 10.4 Hz, $J_{5eq,6}$ = 3.4 Hz, H-6), 4.59 (1 H, t, $J_{1,9}$ = $J_{8,9}$ = 3.4 Hz, H-9), 5.05 (1 H, tt, $J_{2ax,3}$ = $J_{3,4ax}$ = 10.7 Hz, $J_{2eq,3}$ = $J_{3,4eq}$ = 4.3 Hz, H-3), 5.88 (1 H, d, $J_{8,9}$ = 3.4 Hz, H-8), 7.42–7.61, 8.01–8.12 (3 H, 2 H, OCOC$_6$H$_5$). Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.66; H, 6.94.

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Registry No. **4**, 2595-05-3; **5**, 4495-04-9; **6**, 63846-98-0; **7**, 113301-73-8; **8** (diast 1), 113273-90-8; **9**, 113273-92-0; **10**, 113273-93-1; **11**, 113273-94-2; **12**, 113273-95-3; **13**, 113349-53-4; **14**, 112531-62-1; **15**, 102562-00-5; **16**, 113273-96-4; **3**, 113349-52-3; **8** (diast 2), 113273-91-9.

Preparation and Characterization of Cleavable Surfactants Based on a Silicon–Oxygen Bond

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Cleavable (destructible) surfactants are stable under certain conditions but are labile under other, generally mild conditions with respect to cleavage to nonsurfactant products.[1] Thus, they are appropriate for applications in which the presence of a surfactant, after its beneficial action, can lead to any one of several problems, including

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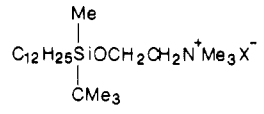
Table I. Stability/Lability Characteristics of 1b at 25 °C[a]

entry	medium	additive	pH[b]	time	% cleavage[c]
1	D_2O	none	7.0	14 days	0
2[d]	D_2O	none	7.0	6 h	0
3	D_2O	0.2 M $NaHCO_3$	8.3	38 h[e]	0
4	D_2O	0.2 M Na_2CO_3	11.8	38 h[e]	0
5	D_2O	0.2 M CD_3CO_2D	2.7	4 days	0
6	D_2O	3.3 M DCl	−0.5	10 min	70
				2 h	100
7	D_2O	0.2 M NaOD	13.3	1.5 h	47
				4.7 h	65
8	D_2O	5.0 M KF	9.1	24 h	100
9[d]	D_2O	5.0 M KF	9.1	6 h	100
10	9:1 (v/v) $CDCl_3$–THF	0.1 M n-Bu_4NF		20 min	100

[a] [1b] = 0.02 M in entries 1–9 and 0.04 M in entry 10. [b] Calculated for the perprotio systems. [c] As determined by ^1H NMR analysis; the appearance of 3 was monitored. [d] Temperature = 50 °C. [e] The solution was then diluted with D_2O to 0.1 M $NaHCO_3$ (Na_2CO_3). After an additional 5 days, there was 17% cleavage in entry 3 and 24% in entry 4.

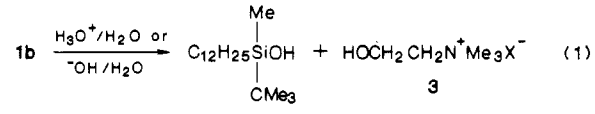
the formation of persistent emulsions. Herein, we report a study of cleavable surfactants 1.[2] They are based on a silicon–oyxgen bond and have stability/lability characteristics different than those of cleavable surfactants reported previously.[1]



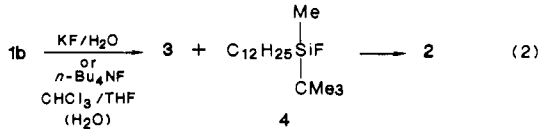
1a, X = Cl
b, X = NO_3
c, X = BPh_4

The syntheses of 1 have been described.[2] The critical micelle concentration (cmc) of **1b** in 0.01 M $NaHCO_3$ at 25 °C is 2.8×10^{-5} M. In addition to water, it is also soluble in a number of organic solvents, including $CHCl_3$ and C_6H_6. The ^1H NMR chemical shifts of several groups within **1b** were monitored as a function of concentration in C_6D_6 at 25 °C, and the results are given in Figure 1 for Me_3N and CH_2N; similar behavior (not shown) was observed for CH_2O, Me_3C, and MeSi. The curves suggest the formation of reversed micelles[3] with an apparent cmc of ca. 0.06 M. Downfield shifts on going from micellar to monomeric surfactant in benzene have also been noted for other systems.[3]

The stability/lability characteristics of **1b** were monitored by ^1H NMR and are summarized in Table I. In entries 1–7, lability is with respect to hydrolysis to **2** and **3** (eq 1). Lability is with respect to cleavage to **3** and **4** by KF in water in entries 8 and 9, and by n-Bu_4NF in $CHCl_3$–THF in entry 10 (eq 2). However, with both fluoride



(1)



(2)

reagents, **2** rather than **4** was isolated, indicating that the latter had hydrolyzed.[4] Thus, **1b** is stable in water from pH 3–12 for extended periods, but it hydrolyzes outside of this range and is cleaved by F^- in both aqueous and nonaqueous media.

Both the acid- and base-catalyzed hydrolyses of **1b** most likely proceed by attack at silicon.[5] Nucleophilic substitution at carbon is unlikely,[6] as is E2 elimination, since no $CH_2{=}CHN^+Me_3\ X^-$ was detected by ^1H NMR.[7,8] The cleavage of silyl ethers by F^- under nonaqueous conditions is an established procedure.[9] The lesser reactivity of hydrated F^- results in a slower reaction of **1b** in entries 8 and 9 than in entry 10.[10]

The catalytic abilities of **1b** were assessed in the $KMnO_4$ oxidation of piperonal (**5**) to piperonylic acid (**6**). Under micellar/emulsion conditions at 50–60 °C, **1b** was only slightly less effective as a catalyst than hexadecyltrimethylammonium bromide (HTABr).[2] Under phase-transfer conditions in H_2O–C_6H_6 mixtures at 50–55 °C, yields of **6** in duplicate runs were 61% and 65% with **1b**, 54% and 56% with HTABr, and 12% and 13% without a catalyst. Persistent emulsions complicated the extractive workup of reaction mixtures containing HTABr, but not of those containing **1b**.

In summary, **1b** has the aggregation and catalytic properties of a typical quaternary ammonium surfactant, but is differentiated by its cleavable nature, which facilitates its use as a micellar/emulsion or phase-transfer catalyst. The stability/lability characteristics of **1b** are different than, and complement, those of other cleavable surfactants.[1]

Experimental Section

General Procedures and Materials. ^1H NMR spectra (270 MHz) were recorded in $CDCl_3$ with $CHCl_3$ (δ 7.20) as internal standard unless noted otherwise. Mass spectra were obtained on a Du Pont 21-110B spectrometer at 70 eV with direct insertion. The cmc of **1b** in 0.01 M $NaHCO_3$ was measured as before.[11] All melting points are uncorrected. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA. D_2O (99.88% D, Cal Biochem), DCl–D_2O (20 wt %, 99+% D, Aldrich), and CD_3CO_2D (99.5% D, Bio Rad) were used as received.

Dodecylmethyl-*tert*-butylchlorosilane. To a stirred solution of 10 mL of hexane (distilled from $LiAlH_4$) and 14.0 mL (29.4 mmol) of 2.1 M Me_3CLi in pentane (Aldrich) under N_2 was added 8.06 g (28.4 mmol) of dodecylmethyldichlorosilane (Petrarch) during 15 min. The mixture was refluxed for 3.5 h, filtered

(2) Preliminary communication of some of these results: Jaeger, D. A.; Ward, M. D. *J. Org. Chem.* **1982**, *47*, 2221.
(3) For a discussion and examples, see: Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley-Interscience: New York, 1982; Chapter 3.
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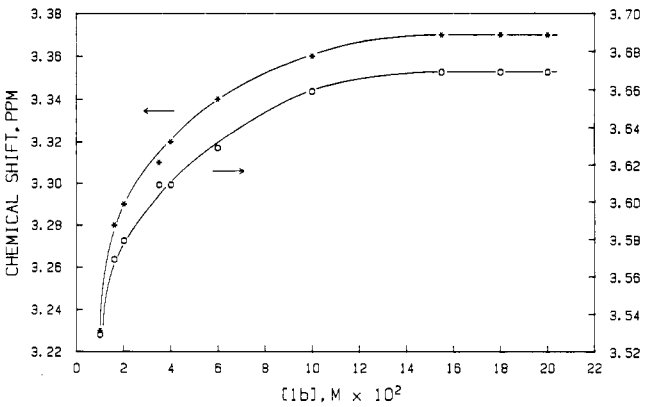

Figure 1. Dependence of ^1H NMR chemical shifts for Me_3N (*) and CH_2N (O) on [**1b**] in C_6D_6 with CH_2Cl_2 external standard.

through a glass frit, and distilled to give 7.64 g (88%) of the title compound: bp 88–90 °C (0.03 mmHg); ^1H NMR δ 1.21 (s, 20 H, $(CH_2)_{10}$), 0.92 (s, 9 H, $(CH_3)_3C$), 0.65–0.88 (m, 5 H, CH_3CH_2, CH_2Si), 0.27 (s, 3 H, CH_3Si); IR (neat) 2940 (s), 2865 (s), 1470 (s), 1368 (s), 1255 (s), 820 (s), 778 cm^{-1} (s); EI HRMS calcd for $C_{17}H_{37}{}^{28}Si^{35}Cl$ (M) 304.2352, found 304.2352.

[2-(Dodecylmethyl-*tert*-butylsiloxy)ethyl]trimethylammonium Chloride (1a). A mixture of 5.04 g (16.6 mmol) of dodecylmethyl-*tert*-butylchlorosilane, 3.50 g (25.1 mmol) of $HOCH_2CH_2N^+Me_3$ Cl^- (dried at 80 °C (0.03 mmHg)), 1.65 g (24.2 mmol) of imidazole (dried at 80 °C (0.03 mmHg)), and 40 mL of $HCONMe_2$ (dried over 4-Å molecular sieves) was held under N_2 at 50 °C for 24 h. Most of the $HCONMe_2$ was removed by distillation at ca. 20 mmHg, and the residue was dried (2 h at 80 °C (0.03 mmHg)), slurried in $CHCl_3$, and filtered. The filtrate was rotary evaporated, and the residue was dried and slurry-extracted with hexane to give 7.5 g of a viscous oil, which contained **1a**, $HOCH_2CH_2N^+Me_3$ Cl^-, and imidazole by ^1H NMR. A sample of 0.96 g was chromatographed on a 73 cm × 4.5 cm (i.d.) column of alumina (pH 7.4) packed in $CHCl_3$. Elution started with $CHCl_3$, and the EtOH content was increased by 10% (v/v) every 500 mL. All eluants contained 1% (v/v) concentrated aqueous NH_3, and 50–75-mL fractions were collected every 12 min and analyzed by TLC on 0.25-mm alumina plates eluted with 1:1 (v/v) EtOH–$CHCl_3$ and developed with I_2. Imidazole eluted with 10–20%, **1a** with 40%, and $HOCH_2CH_2N^+Me_3$ Cl^- with 50% EtOH–$CHCl_3$. The surfactant was dried over Na_2SO_4 in $CHCl_3$ and then at 90 °C (0.03 mmHg) for 4 h to give 0.63 g (73%) of **1a** as a viscous oil: ^1H NMR δ 4.02 (m, 2 H, CH_2O), 3.80 (m, 2 H, CH_2N),[12] 3.45 (s, 9 H, $(CH_3)_3N$), 1.18 (s, 20 H, $(CH_2)_{10}$), 0.82 (m, 12 H, $(CH_3)_3C$, CH_3CH_2), 0.55 (m, 2 H, CH_2Si), 0.02 (s, 3 H, CH_3Si); IR (neat) 3350 (m), 2920 (s), 2845 (s), 1630 (w), 1460 (s), 1248 (m), 1100 (s), 1055 (m), 960 (s), 860 (m), 815 (m), 770 (m), 740 (w), 650 cm^{-1} (w). The absorptions at 3350 and 1630 cm^{-1} correspond to absorbed water.

[2-(Dodecylmethyl-*tert*-butylsiloxy)ethyl]trimethylammonium Nitrate (1b). To a solution of 4.67 g (11.5 mmol) of **1a** in 30 mL of EtOH was added a solution of 2.00 g (11.8 mmol) of $AgNO_3$ in 20 mL of 1:1 (v/v) H_2O–EtOH. The AgCl was removed by filtration, and after the addition of a solution of 0.25 g of $AgNO_3$ in 5 mL of H_2O, which gave no additional precipitate, the filtrate was rotary evaporated. The residue was slurried in $CHCl_3$ and filtered, and the filtrate was rotary evaporated and dried for 4 h at 90 °C (0.03 mmHg) to give 3.01 g of crude **1b**. This material was chromatographed on a 65 cm × 4.5 cm (i.d.) column of alumina (pH 7.4) packed in $CHCl_3$. Elution started with $CHCl_3$, and the EtOH content was increased by 25% (v/v) every 500 mL. All eluants contained 1% (v/v) concentrated aqueous NH_3, and 50–60-mL fractions were collected every 10 min and analyzed as for **1a**. Elution with 1:1 (v/v) EtOH–$CHCl_3$ gave 2.59 g of surfactant, which was recrystallized twice from hexane (−10 °C) to yield, after drying at 80 °C (0.03 mmHg) for 6 h, 1.49 g (30%) of **1b**: mp 65–66 °C; ^1H NMR δ 4.04 (m, 2 H, CH_2O), 3.64 (m, 2 H, CH_2N),[12] 3.30 (s, 9 H, $(CH_3)_3N$), 1.20 (s, 20 H, $(CH_2)_{10}$), 0.83 (m, 12 H, $(CH_3)_3C$, CH_3CH_2), 0.58 (m, 2 H, CH_2Si), 0.03 (s, 3 H, CH_3Si); IR (Nujol) 1250 (m), 1210 (w), 1135 (m), 1095 (s), 960 (s), 860 (m), 825 (s), 770 (m), 732 cm^{-1} (m); cmc = 2.8×10^{-5} M in 0.01 M $NaHCO_3$ (25 °C), and the surface tension above the cmc was ca. 32 dyn/cm. Anal. Calcd for $C_{22}H_{50}SiO_4N_2$: C, 60.78; H, 11.59. Found: C, 60.82; H, 11.67.

[2-(Dodecylmethyl-*tert*-butylsiloxy)ethyl]trimethylammonium Tetraphenylborate (1c). To a solution of 0.40 g (1.0 mmol) of **1a** in 10 mL of H_2O was added a solution of 0.91 g (2.7 mmol) of $NaBPh_4$ (Alfa) in 10 mL of H_2O. The resultant precipitate, which formed immediately, was dried (2 h at 25 °C (0.03 mmHg)) and recrystallized three times from MeOH at −10 °C to give 0.13 g (19%) of **1c**: mp 175–176 °C; ^1H NMR (CD_3COCD_3 with CH_2Cl_2 (δ 5.63) internal standard) δ 7.34 (br s, 8 H, Ar H_{ortho}), 6.93 (t, J = 7 Hz, 8 H, Ar H_{meta}), 6.78 (t, J = 7 Hz, 4 H, Ar H_{para}), 4.30 (m, 2 H, CH_2O), 3.73 (m, 2 H, CH_2N), 3.40 (s, 9 H, $(CH_3)_3N$), 1.29 (s, 20 H, $(CH_2)_{10}$), 0.94 (s, 9 H, $(CH_3)_3C$), 0.88 (t, 3 H, CH_3), 0.73 (m, 2 H, CH_2Si), 0.17 (s, 3 H, CH_3Si). Anal. Calcd for $C_{46}H_{70}BNOSi$: C, 79.84; H, 10.20. Found: C, 79.71; H, 10.40.

Dodecylmethyl-*tert*-butylsilanol (2). A solution of 73.9 mg (0.170 mmol) of **1b** in 50 mL of 1.1 M hydrochloric acid was stirred for 20.5 h at 25 °C and then extracted with three 25-mL portions of hexane. The combined extracts were dried (Na_2SO_4) and yielded 46.6 mg (96%) of **2** as an oil: ^1H NMR δ 1.20 (s, 20 H, $(CH_2)_{10}$), 0.85 (m, 12 H, $(CH_3)_3C$, CH_3CH_2), 0.56 (m, 2 H, CH_2Si), 0.01 (s, 3 H, CH_3Si); IR (neat) 3330 (s), 2940 (s), 2860 (s), 1465 (s), 1360 (m), 1250 (s), 1000 (m), 930 (w), 820 (s), 775 (m), 710 cm^{-1} (w); EI HRMS calcd for $C_{17}H_{38}OSi$ 286.2692, found 286.2705. The same reaction in 1.4 M hydrochloric acid gave a 77% yield of **2** after 3 h at 25 °C.

Under N_2, a solution of 71.7 mg (0.165 mmol) of **1b** in 50 mL of aqueous 1.1 M NaOH was stirred for 18 h at 25 °C, followed by cooling to 0 °C and the addition of 4.0 mL of concentrated hydrochloric acid with resultant pH 8. Thereafter, workup as above gave 36.1 mg (75%) of **2**.

A mixture of 28 mg of KOH, 0.04 mL of MeOH, 0.17 mL of H_2O, and 0.12 g (0.39 mmol) of dodecylmethyl-*tert*-butylchlorosilane was stirred at 0 °C for 6 h and then extracted with three 10-mL portions of Et_2O. The combined extracts were dried (Na_2SO_4) and rotary evaporated to give 46 mg (41%) of **2**.

^1H NMR Spectra of 1b in C_6D_6. All glassware was oven- and then flame-dried; C_6D_6 (99.5% D, Aldrich) was dried by distillation from CaH_2 under N_2. A 5-mm NMR tube containing the **1b**–C_6D_6 solution was fitted with a coaxial insert (Wilmad WGS-5BL) filled with 1% (v/v) CH_2Cl_2–$CDCl_3$. Spectra were run at 25 °C, and CH_2Cl_2 was used as external standard (δ 5.29).

Stability/Lability Characteristics of 1b. The following procedure was used for entries 1–9 of Table I. To an oven-dried 5-mm NMR tube was added 5.5 mg (0.013 mmol) of **1b**, followed by 0.67 mL of the appropriate solvent. The resultant 0.02 M solution was held at 25 °C, and ^1H NMR spectra were recorded at various times at ambient probe temperature (23 °C) to monitor the decomposition of **1b** by comparison of the peak height for the Me_3N^+ singlet of **1b** with that of **3**.

Four of the above reaction mixtures used for entries 8 and 9 were combined after 100% cleavage and extracted with four 10-mL portions of Et_2O. The combined extracts were dried (Na_2SO_4) and rotary evaporated to give 11 mg of an oil, which contained **2** and traces of several unidentified components by ^1H NMR.

For entry 10, 0.28 mL of 1.0 M *n*-Bu_4NF (0.28 mmol) in THF containing <5 wt % H_2O (Aldrich) was added to a solution of 0.050 g (0.12 mmol) of **1b** in 2.5 mL of $CDCl_3$. ^1H NMR spectra taken 20 and 40 min later were identical and indicated the complete cleavage of the silicon–oxygen bond, since no signals for the $OCH_2CH_2N^+Me_3$ group of **1b** were observed.

A solution containing 0.075 g (0.17 mmol) of **1b** and 0.36 mL of the above *n*-Bu_4NF solution (0.36 mmol) in 5.0 mL of $CHCl_3$ was stirred at 25 °C for 20 min and then rotary evaporated (25 °C). The residue was extracted with four 25-mL portions of hexane (HPLC grade), and the combined extracts were dried (Na_2SO_4) and rotary evaporated (25 °C) to leave 0.058 g of an oil, which contained **2** and traces of several unidentified components by ^1H NMR and IR.

(12) The assignments for CH_2O and CH_2N are analogous to those for $HOCH_2CH_2N^+Me_3$ Br^- in D_2O (Birdsall, N. J. M.; Feeney, J.; Lee, A. G.; Levine, Y. K.; Metcalfe, J. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1441) and are opposite to those made previously.[2]

Oxidations of 5 in H_2O. The purification of **5** and the glassware for two parallel reactions in the same oil bath above a single magnetic stirring motor have been described.[1c] To one flask were added 0.499 g (3.33 mmol) of **5** and 66.0 mg (0.152 mmol) of **1b**, and to the other, 0.499 g of **5**, followed by the addition of 12.5 mL of H_2O to each. To each stirred system at 50–60 °C was added, during 15 min, a solution of 0.75 g (4.7 mmol) of $KMnO_4$ in 17.5 mL of H_2O. The reaction mixtures then were stirred for 150 min at 50–60 °C and worked up with the published procedure[1c] on one-half scale. For the system with **1b**, foaming was observed before the addition of $KMnO_4$ and during the wash of MnO_2. Thereafter, there was no evidence of foaming or emulsion formation beyond that in the other reaction. From the reaction with **1b**, 0.247 g (45%) of **6**, mp 229–230 °C (lit.[13] mp 230–232 °C), was obtained, and from the other, 0.164 g (30%) of **6**, mp 227–230 °C. A second reaction with **1b** identical with that above gave a 44% yield of **6**: mp 229–230 °C. In this reaction, the pH of the reaction mixture was 7 before and during the addition of the $KMnO_4$ solution and throughout the 150-min period.

Oxidations of 5 in H_2O–C_6H_6. Individual reactions were performed in glassware previously described,[1c] in an oil bath held at 50–55 °C. To the flask were added 1.00 g (6.67 mmol) of **5**, 0.131 g (0.302 mmol) of **1b**, 25 mL of H_2O, and 50 mL of C_6H_6. After a solution of 1.5 g (9.5 mmol) of $KMnO_4$ in 35 mL of H_2O was added during 30 min, the reaction mixture was stirred for an additional 150 min and filtered. The aqueous portion of the filtrate was pH 8, and the MnO_2 was washed with 50 mL of H_2O (60 °C) and 20 mL of C_6H_6. The combined filtrates were shaken vigorously to give an emulsion that persisted for 5 min. Then 0.76 mL of 1.0 M *n*-Bu_4NF (0.76 mmol) in THF was added, and the mixture was shaken vigorously for 20 min. The aqueous layer was acidified with 10% hydrochloric acid, and the resultant precipitate was collected, washed with H_2O, and dried to give 0.718 g (65%) of **6**: mp 229–230 °C. The C_6H_6 layer was dried ($MgSO_4$) and rotary evaporated to give 0.25 g of an oil, which by ^1H NMR contained predominantly **2** and **5**. An identical reaction gave 0.681 g (61%) of **6** with the same melting point.

The above procedure with the substitution of 0.110 g (0.302 mmol) of HTABr for **1b** was used for two reactions, which gave 0.623 g (56%) and 0.597 g (54%) of **6**: mp 229–230 °C. In these reactions, vigorous shaking of the combined filtrates gave an emulsion that persisted for 2–3 h. For two reactions without surfactant, the above procedure gave 0.146 g (13%) and 0.129 g (12%) of **6**: mp 229–230 °C.

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Registry No. **1a**, 81372-17-0; **1b**, 81372-19-2; **1c**, 81372-20-5; **2**, 81372-22-7; **3** (X = Cl), 67-48-1; **5**, 120-57-0; **6**, 94-53-1; Me_3CLi, 594-19-4; $AgNO_3$, 7761-88-8; $NaBPh_4$, 143-66-8; $C_{12}H_{25}(CMe_3)SiCl_2$, 18407-07-3; $C_{12}H_{25}(Me)Si(CMe_3)Cl$, 81372-21-6.

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A Convenient and Highly Chemoselective Method for the Reductive Acetylation of Azides

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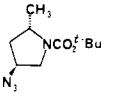
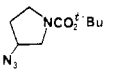
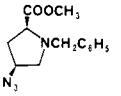
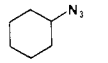
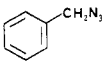
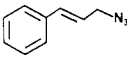
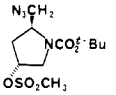
Results and Discussion

The reduction of azides to amines is an important and widely used reaction in organic synthesis.[1] It is especially useful because of the ease of synthesis and high stereoselectivity associated with the preparation of the precursor azides. Thus, the reduction represents a pivotal step in a stereoselective sequence for the preparation of amines. Several methods and reagents are available for this transformation that is often carried out by catalytic hydrogenation[2,7] or by treatment with lithium aluminum hydride.[3] Other known procedures include H_2S/pyridine/H_2O,[4] transfer hydrogenation,[5] Ph_3P,[6] H_2/Lindlar catalyst,[7] $Cr(II)/H^+$,[8] and $Na_2S/Et_3N/MeOH$.[9] Most recently, there have been reports utilizing stannous chloride/MeOH[10] and $NaBH_4$/THF/MeOH.[11] The large number of reagents that have been employed to achieve this transformation is related to a lack of chemoselectivity or relatively vigorous conditions often associated with some of these methods.

In this paper, we report a convenient and highly chemoselective reduction of azides that occurs with concomitant acetylation to give the corresponding acetamide (eq

Table I. Reductive Acylation of Azides with Thioacetic Acid

	azide (1)[13]	% yield of acetamide (2)	mp (lit. mp), °C
(a)		84	108–110
(b)		77	oil
(c)		92	62–64
(d)	$CH_3(CH_2)_6N_3$	77	oil
(e)		65	104 (104)[14]
(f)		91	58–60 (60)[14]
(g)		73	88–90
(h)		70	oil

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