injected into a Gow-Mac Series 550 gas chromatograph fitted in series with an 8 ft molecular sieves column followed by a 6 ft Poropak N column. This particular configuration is designed for the separation and identification of atmospheric gases. The chromatogram showed no indication of the presence of any O_2 in the gas sample.

Products of the Decomposition of 1b. Thioseleninate **1b** (2.0 mmol) prepared from unrecrystallized benzeneseleninic acid was dissolved in 10 mL of acetone and allowed to stand at room temperature until decomposition was complete. The acetone was then removed under reduced pressure, and the residue was dissolved in chloroform and extracted several times with aqueous sodium carbonate. The chloroform solution was dried (Na_2SO_4), the solvent removed, and the residue chromatographed on silica gel with hexane as eluent. The chromatography yielded *tert*-butyl disulfide (0.92 mmol), diphenyl diselenide (0.54 mmol), and a small amount of *tert*-butyl benzeneselenenyl sulfide (0.05 mmol), each identical with known samples[2] of these compounds.

The aqueous extracts were concentrated in volume and then carefully acidified with 6 N sulfuric acid. The benzeneseleninic acid (0.70 mmol, mp 122–123 °C) that crystallized out after acidification was filtered off and its identity further confirmed by comparison of its infrared spectrum (KBr) with that of the known sample of this acid mentioned in the paragraph dealing with preparation and purification of materials.

Registry No. **1b**, 67680-11-9; *t*-BuSSBu-*t*, 110-06-5; PhSeSePh, 1666-13-3; PhSeSBu-*t*, 67680-10-8; $PhSeO_2H$, 6996-92-5.

Two New Amphiphilic Catalysts for Ester Hydrolysis

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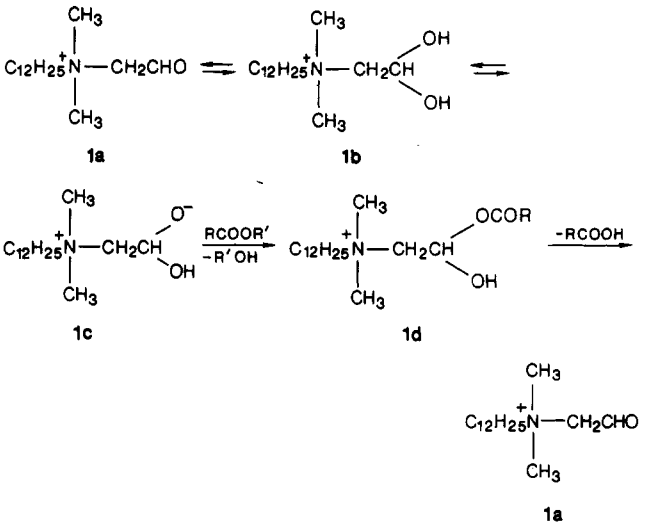
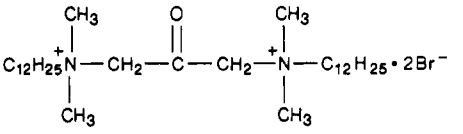
In 1985 we reported a functionalized surfactant (**1a**) capable of catalyzing the hydrolysis of carboxylic and phosphate esters.[1] Although many examples of functionalized surfactants have been published,[2-12] few exhibit true turnover behavior[1,11] as does **1a**. Thus, under mildly basic conditions **1a** hydrates to **1b**, acylates to **1d**, and then ejects the carboxyl to reform the original catalyst **1a**. Rate accelerations with *p*-nitrophenyl diphenyl phosphate were found to be a substantial (but hardly enzyme-like) 1800-fold. In this paper, we examine the esterolytic activity of two new systems, **2** and **3**, which could, it was initially



hoped, manifest even greater catalytic accelerations. Since **2** and **3** are dicationic, the pK_a of their hydrates should



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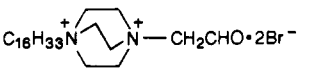

3

be less than the 10.9 observed for **1b**. Consequently, formation of the nucleophilic oxyanion would be favored under the physiological conditions where we wished to operate.

Surface tension measurements on **2** revealed a critical micelle concentration of 4.3×10^{-4} M (half that of **1**). Hydration behavior, on the other hand, differs markedly between **1** and **2**. Whereas **1** is totally hydrated in water at all pH values, **2** requires pH 10 (borate buffer) for the ^{13}C NMR peak of the carbonyl (194 ppm) to disappear. A mixture of ketone, hydrate, and enolate was observed for **2** at pH 9, and at neutrality only traces of hydrate (with its characteristic hydrate carbon signal at 80 ppm) are present. Apparently, banking the carbonyl of **2** with two electronegative quaternary ammonium groups is not sufficient to overcome the general preference for hydration that aldehydes have over ketones.[13]

The catalytic ability of **2** toward *p*-nitrophenyl hexanoate was disappointing. Thus, 2.0 mM **2** at pH 8.0 and 25.0 °C gave a $k_{obsd} = 6.5 \times 10^{-5}$ s^{-1} which is only 8-fold larger than in the absence of **2**. Elevating the pH to 10.0, in order to increase the concentration of hydrate, led to a $k_{obsd} = 1.4 \times 10^{-3}$ s^{-1}, which is only 2-fold greater than background. It seems clear that both hydration equilibria and acyl-transfer rates are adversely affected by steric affects, and hence we investigated **3** where (a) the aldehyde functionality is maintained and (b) the ammonium group proximate to the reactive center is tied back in the bicyclic ring system, thereby minimizing steric problems.

Compound **3** has a critical micelle concentration, determined tensiometrically, of 2.0×10^{-3} M. This high value for a hexadecyl surfactant no doubt reflects electrostic repulsions involved when two cationic charges *per chain* are forced to reside at the micelle surface. As expected,

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3 exists totally as the hydrate even in the solid state. Thus, the elemental analysis of 3 corresponds to the hydrate solvated by $^1/_2H_2O$. The ^{13}C NMR spectrum in $CDCl_3$ shows a hydrate carbon at 84 ppm, while ^1H NMR spectra have a methine proton at 4.5 ppm in $CDCl_3$ and 5.7 ppm in D_2O but no aldehyde proton in either solvent.

Catalysis of *p*-nitrophenyl diphenyl phosphate hydrolysis by 3.0 mM 3 in a pH 9.0 M borate buffer at 25.0 °C leads to a $k_{obsd} = 8.2 \times 10^{-3}$ s^{-1} (750 times faster than hydrolysis in the same buffer without 3). Although this micellar rate is large relative to many published in the literature,[2] it does not match that associated with 1. Packing problems, manifest in the high critical concentration of 3, may also be affecting the catalytic efficiency. Thus, the struggle to achieve enzyme-like efficiencies within the confines of a turnover mechanism must continue. Compounds 2 and 3 are, however, unusual dicationic surfactants, and hence we are now reporting their synthesis and properties.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton magnetic resonance spectra were recorded on a Nicolet FT-360 high-resolution spectrometer at 360 MHz. The carbon-13 nuclear magnetic resonance spectra were obtained from a Bruker AP-200-SY NMR spectrometer at 50 MHz or a Varian CFT-20 NMR spectrometer at 20 MHz. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Ultraviolet absorption spectra were measured on a Hewlett-Packard 8451A diode Array spectrophotometer with a H-P 7470A plotter. Elemental analyses were performed by Atlantic Microlabs Inc., Atlanta, GA.

Chemicals. 1-Bromohexadecane, 1,4-diazabicyclo[2.2.2]octane, 1,4-dibromobutene, 1,3-dichloroacetone, and lithium bromide were purchased from Aldrich Chemical Co. *N,N*-Dimethyl-*N*-dodecylamine was purchased from Kodak.

1,3-Dibromo-2-propanone.[14] 1,3-Dichloro-2-propanone was washed with cold diethyl ether until no brown color remained and then was dried under reduced pressure, mp 39–41.5 °C. To a stirred solution of dichloro-2-propanone (3.20 g, 25.2 mmol) in 100 mL of acetone at 0 °C was added LiBr (22.0 g, 253 mmol). The solution was allowed to warm to room temperature where it was stirred 48 h. An additional 10.0 g of LiBr and 50 mL of acetone were added to the reaction mixture, and stirring was continued 24 h more. Removing the solvent gave an off-white solid, which was dissolved in water and extracted twice with dichloromethane. The combined dichloromethane solutions were washed with cold water, cooled to 0 °C, filtered, dried over anhydrous $MgSO_4$, and stripped of solvent to afford 4.5 g (83%) of a yellow oil: IR (neat) 2940, 1730, 1390, 1275–1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.15 (s).

Compound 2. *N,N*-Dimethyl-*N*-dodecylamine (6.78 g, 31.8 mmol) was slowly added with magnetic stirring to a solution of 1,3-dibromo-2-propanone (3.43 g, 15.8 mmol) in 50 mL of anhydrous ether at room temperature under a N_2 atmosphere. The solution turned from clear to dull yellow and then to dark brown as the amine was added. After 2 h the viscosity of the mixture prevented stirring. A yellow liquid was decanted, leaving a solid, which was washed with diethyl ether to remove excess starting amine. The ether was evaporated to yield 9.8 g of crude product (97%). Several recrystallizations from hot acetone afforded pure product: 4.2 g (41%); mp 80 °C dec; IR (KBr) 2920, 2850, 1749, 1465, 1375, 890, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.67 (s, 4 H), 3.55 (m, 4 H), 3.45 (s, 12 H), 1.84 (br s, 4 H), 1.35 (4 H), 1.25 (32 H), 0.87 (t, J = 6.9 Hz, 6 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 193.90, 67.99, 67.27, 57.51, 51.65, 31.82, 29.50, 29.31, 28.98, 26.18, 22.61, 16.01, 14.00. Anal. Calcd for $C_{31}H_{66}Br_2N_2O$: C, 57.92; H, 10.35; N, 4.28. Found: C, 57.68; H, 10.36; N, 4.20.

1-Hexadecyl-1,4-diazabicyclo[2.2.2]octane, Bromide Salt. In a 50-mL, round-bottom flask, 1,4-diazabicyclo[2.2.2]octane (2.24 g, 20.0 mmol) was stirred with 15 mL of anhydrous ethyl ether and cooled to −78 °C. 1-Bromohexadecane (6.10 g, 6.10 mL, 20.0 mmol) was added dropwise to this solution while stirring. The reaction mixture was allowed to warm to room temperature and stirred an additional 8 h. The resulting white precipitate was filtered, rinsed with ethyl ether, and recrystallized with hot CCl_4–toluene with filtration. After two recrystallizations 3.7 g (44%) of pure product was recovered: mp 108–109 °C; IR (KBr) 2920, 2851, 1469, 1377, 1101, 1058, 851, 796, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.65 (t, 2 H, J = 7.2 Hz), 3.49 (m, 2 H), 3.24 (t, 2 H, J = 7.2 Hz), 2.00 (br s, 2 H), 1.73 (2 H), 1.32 (2 H), 1.22 (22 H), 0.85 (t, 3 H, J = 6.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 64.3, 52.2, 45.1, 31.5, 29.3, 29.1, 29.0, 28.9, 26.1, 21.8, 14.0.

Compound 3. In a dry, 50-mL, round-bottom flask fitted with a reflux condenser and flushed with N_2, a solution of 1-hexadecyl-1,4-diazabicyclo[2.2.2]octane, bromide salt (3.00 g, 7.18 mmol), in 20 mL of CH_3CN (previously dried over CaH_2 and distilled from P_2O_5) was stirred and warmed slightly to ensure complete solubility. To this solution was added bromoacetaldehyde (3.00 g, 24.4 mmol in CH_2Cl_2) via syringe while stirring. A white precipitate immediately fell out of solution. The mixture was heated to reflux and stirred overnight. The off-white solid was filtered under reduced pressure and washed first with CH_3CN and then several times with anhydrous ethyl ether. The off-white powder quickly hydrated when exposed to the air leaving 3.90 g of a tan, gummy solid. The solid was dissolved in H_2O, heated, and filtered twice. A white, fluffy solid remained after freeze-drying the filtrate: 3.4 g (85%); mp 167–168 °C; IR (D_2O, ZnBr cells) 3541–2845, 1202 cm^{-1}; ^1H NMR (D_2O) δ 5.70 (t, 1 H), 4.32 (m, 6 H), 4.24 (m, 6 H), 3.76 (m, 2 H), 3.35 (s, 2 H), 1.93 (2 H), 1.42 (2 H), 1.30 (24 H), 0.88 (t, 3 H, J = 6.5 Hz); ^{13}C NMR (50 MHz, D_2O) δ 84.45, 65.40, 52.49, 51.31, 32.01, 30.00, 29.88, 29.73, 29.67, 26.10, 22.68, 22.16, 13.93. Anal. Calcd for $C_{24}H_{50}N_2O_2 \cdot {}^1/_2H_2O$: C, 50.78; H, 9.06; N, 4.96. Found: C, 50.64; H, 9.07; N, 5.00.

Kinetic Studies. All kinetic measurements were performed at 25 °C on a Hewlett-Packard 8451A diode array spectrophotometer. Stock solutions of esters were prepared in acetonitrile (0.005 M). Reactions were initiated by injecting 25 μL of the ester solution into 3 mL of micellar solution preequilibrated at 25 °C and were monitored at 400 nm for the absorbance of 4-nitrophenol. All buffers were prepared from doubly distilled water. Borate buffer was used for solutions of 2 at pH 10 and adjusted with 0.4 N NaOH. Solutions of 2 at pH 8 were prepared in phosphate buffer and adjusted with 0.1 N NaOH. Ethyl morpholine buffer was used for all solutions of 3 to avoid problems of precipitation encountered with borate solutions. Rate constants were obtained from computer-generated values of the log of the absorbance with time. Correlation coefficients were >0.999.

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Registry No. 2, 108868-22-0; 3, 108868-23-1; $CH_3(CH_2)_4C(O)O$-*p*-$C_6H_4NO_2$, 956-75-2; *p*-$NO_2C_6H_4PPh_2$, 10359-36-1; $ClCH_2C(O)CH_2Cl$, 534-07-6; $BrCH_2C(O)CH_2Br$, 816-39-7; $CH_3(CH_2)_{11}NMe_2$, 112-18-5; $CH_3(CH_2)_{15}Br$, 112-82-3; 1,4-diazabicyclo[2.2.2]octane, 280-57-9; 1-hexadecyl-1,4-diazabicyclo[2.2.2]octane bromide salt, 62634-16-6.

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Acid Chloride to Ester Formation: Mechanism of SO_2–Amine Interference

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Introduction

Acid chlorides have been reported to be effectively converted to their esters in a reaction which uses a base to both neutralize the liberated hydrogen chloride and also to catalyze the reaction (Schotten–Baumann procedure).[1]

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