oxaheptanol, 99214-12-7; 3,3,3-trinitropropanol, 87695-55-4; 4,4,4-trinitrobutyric acid, 5029-46-9; potassium 3,3-dinitropropanol, 12287-13-7; potassium 3,3-dinitropropyl acetate, 94921-20-7; 3,3-dinitropropyl acetate, 29610-00-2; 3-bromopropyl acetate, 592-33-6; 3-nitropropyl acetate, 21461-49-4; 3-nitropropanol, 25182-84-7; 3-nitropropyl nitrate, 99214-14-9; 3,3,7,7-tetranitro-5-azanonane-1,9-diol 1,9-diacetate, 99214-15-0; 3,3,5,7,7-pentanitro-5-azanonane-1,9-diol 1,9-diacetate, 99232-50-5; 3-(2-acetoxyethyl)-5,5-dinitroperhydroorazepine, 99214-17-2; 2-aminoethyl acetate hydrochloride, 20739-39-3; methyl trinitrobutyrate, 5857-63-6; methyl 5-hydroxy-4,4-dinitropentanoate, 29596-18-7; 2,4,4,6-tetranitro-2,6-diaza-1,7-heptanedicarboxylic acid, 99232-49-2.

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Syntheses of 2-(2-Hydroxyethylamino) Fatty Acids

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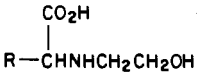
Eight 2-(2-hydroxyethylamino) fatty acids, 2-(2-hydroxyethylamino)decanoic, -undecanoic, -dodecanoic, -tetradecanoic, -hexadecanoic, -octadecanoic, -nonadecanoic, and -docosanoic acid, were synthesized by reacting 2-bromo fatty acids with more than 3 mol of 2-aminoethanol. The surface tension and the critical micelle concentration were determined for these compounds.

In an extension of my interest in the synthesis and study of the surface activity of nitrogenous surfactants derived from long chain fatty acids **1**, the 2-(2-hydroxyethylamino) fatty acids **3** were synthesized.

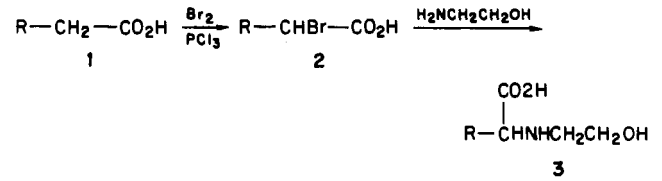


3A, R = *n*-C_8H_{17}; **3B**, R = *n*-C_9H_{19}
3C, R = *n*-$C_{10}H_{21}$; **3D**, R = *n*-$C_{12}H_{25}$
3E, R = *n*-$C_{14}H_{29}$; **3F**, R = *n*-$C_{16}H_{33}$
3G, R = *n*-$C_{17}H_{35}$; **3H**, R = *n*-$C_{20}H_{41}$

These compounds all have surface activity. The surface tensions and the critical micelle concentrations of compounds **3** were determined and are reported in Table II. The desired compounds were obtained according to the reaction pathway outlined in Scheme I. The synthesis of these compounds comprises the preparation of 2-bromo fatty acids by direct bromination of the appropriate fatty acids in the presence of phosphorous trichloride. More than 3 mol of 2-aminoethanol was allowed to react with the 2-bromo fatty acid to provide compound **3**.

The structural formulas of compounds **3** were confirmed by elemental analysis, infrared (IR) spectra, and nuclear magnetic resonance (^{1}H NMR) spectra. ^{1}H NMR spectra for **3D**, as a representative sample, exhibited the following signals (δ ppm): 0.91 (triplet, 3 H, CH_3, J = 5 Hz), 1.30 (singlet, 22 H, $C_{11}H_{22}$), 2.30 (triplet, 2 H, N–CH_2, J = 8 Hz), 3.25 (singlet, 1 H, NH), 3.60

Scheme I



(multiplet, 1 H, CH–CO_2H), 3.85 (triplet, 2 H, CH_2OH, J = 6 Hz), 4.75 (singlet, 1 H, OH). The IR spectra of **3D** showed the following bands: 3430, 3130, 1730, 720 cm^{-1}.

Experimental Section

Melting points were taken under a microscope on a Kofler hot plate and are uncorrected. ^{1}H NMR spectra were run in $CDCl_3$, on a Varian FT-80A spectrometer. The chemical shifts are in parts per million [δ values with $(CH_3)_4Si$ as internal reference]. The IR spectra, as KBr disks, were recorded on Perkin-Elmer 683 infrared spectrophotometer. The solvents were purified by standard procedures. The analytical samples of all new compounds were purified by column chromatography on silica gel (100–200 mesh) with absolute ethanol. The surface tensions were measured with a Model JZHY-180 tensiometer at room temperature with 10-min surface age (*1*). That exhibited sharp breaks in their surface tension curves which corresponded to critical micelle concentration of the compounds **3**.

***2-Bromoacids* (*2*).** These compounds were prepared by reacting dry bromine with a mixture of fatty acid and phosphorus trichloride respectively. An excess of bromine (0.2 mole), which had been previously dried with concentrated sulfuric acid, was slowly dropped into a mixture of 0.1 mole of fatty acid which was mixed with a drop of phosphorous trichloride. After most of the bromine had been added, the mixture was heated on a boiling water bath until the fumes of hydrobromic acid had practically ceased. The reddish, oily

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Table I. Melting Points of 2-Bromoacids

	compound							
	2A	2B	2C	2D	2E	2F	2G	2H
mp, °C	23.5–25	28–30	31.5–32	42–43	53–54	60–61	61–62	64.5–65.5

Table II. Characteristics of 2-(2-Hydroxyethylamino) Fatty Acids

compd	yield, %	mp, °C	surf. tension, dyn cm^{-1}	cmc,[a] 10^{-4} × mol L^{-1}
3A	84	187.5–190	48	50
3B	54	200–202	34	5
3C	78	171.5–173	37	80
3D	71	152–153.5	26	0.5
3E	82	158.5–160.5	36	0.3
3F	78	151.5–153.5	41	0.2
3G	55	164–166	49	0.1
3H	62	167–169	51	0.02

[a] Cmc = critical micelle concentration.

product was poured into warm water and washed with warm water. The products were dried and then recrystallized from acetone (*2*). Their melting points are reported in Table I.

2-(2-Hydroxyethylamino) Fatty Acids (3). The compounds **3** were synthesized by adding 2-aminoethanol to a mixture of compound **2** and potassium or sodium hydroxide in a polar solvent such as water, ethanol, and methanol to react for 7–15 h at 65–78.5 °C or reflux. After an excess of 2-aminoethanol (30–50 mmol) had been reacted with compound **2** (10 mmol), the chlorhydric acid or glacial acetic acid was added to neutralize. The resulting crystalline **3** were filtered, washed with water, and dried in a vacuum desiccator over phosphorous pentoxide. The white solid crystals of **3** were obtained. Compounds 3 were further purified by column chromatography. Their characteristics are given in Table II.

2-(2-Hydroxyethylamino)tetradecanoic acid (**3D**), as a representative sample, was prepared as follows: a mixture of 1.54 g (5 mmol) of **2D**, 1.1 mL (18 mmol) of 2-aminoethanol, and 20 mL 5% KOH ethanol solution was stirred and heated at reflux for 10 h. The solvent was removed in vacuo. The remaining residue was acidified with glacial acetic acid and then filtered, washed with water, dried in a vacuum desiccator over phosphorous pentoxide and purified by column chromatography to give a white solid 1.02 g (71%) of **3D**.

Registry No. 1A, 334-48-5; 1B, 112-37-8; 1C, 143-07-7; 1D, 544-63-8; 1E, 57-10-3; 1F, 57-11-4; 1G, 646-30-0; 1H, 112-85-6; 2A, 2623-95-2; 2B, 2623-84-9; 2C, 111-56-8; 2D, 10520-81-7; 2E, 18263-25-7; 2F, 142-94-9; 2G, 89367-98-6; 2H, 20828-43-7; 3A, 67552-88-9; 3B, 99097-95-7; 3C, 67491-92-3; 3D, 67491-93-4; 3E, 67491-94-5; 3F, 67491-95-6; 3G, 99097-96-8; 3H, 99097-97-9; $H_2NCH_2CH_2OH$, 141-43-5.

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Synthesis of Certain Cyclic Silanes

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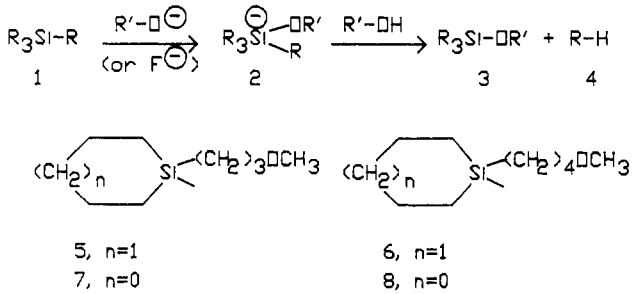
The chlorotrialkylsilanes 21–24 have been synthesized as precursors to potential steric blocking groups for alkanes and cycloalkanes. Reaction of these chlorosilanes with one of the organometallic reagents methyllithium, methylmagnesium chloride, *n*-octylmagnesium bromide, or *p*-chlorobenzylmagnesium chloride formed the silanes 25–34.

As part of our continuing interest (*1–4*) in the use of sterically bulky substituents to control reactant conformation and, in some cases, reaction stereochemistry, we initiated a study of certain trialkylsilyl substituents, R_3Si–. Such substituents, R_3Si–, have sufficient steric bulk (*5–9*) to exert control over reactant conformation in a manner similar to bulky alkyl substituents (*10*). Thus, a conformational *A* value of 2.4–2.6 kcal/mol is reported for the trimethylsilyl group (*8*, *9*). Furthermore, the susceptibility of tetraalkylsilanes **1** (Scheme I) to attack by hard nucleophiles such as F^- or $R'-O^-$ to form successively pentacoordinate intermediates **2** and cleavage products **3** and **4** (*11–16*) suggests that selective cleavage of certain steric blocking groups, R_3Si–, might be possible. In order to investigate this possibility, we

Scheme I



have studied synthetic routes to silanes incorporating the trisubstituted silyl groups **5–8**. This paper describes the synthesis and characterization of these silanes.

The syntheses began with the conversion of each dibromide **9** or **10** to the corresponding bis-Grignard reagent followed by reaction with trichlorosilane (Scheme II). Subsequent orienting experiments were performed in which 1-octene (**13**) was converted to the silane **14** via either of the hydrosilation (*17*, *18*) products **15** or **16** without rearrangement of the carbon skele-

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