amine hydrochlorides with ethyl *m*-[(*N*,*N*-di-*n*-hexadecylamino)methyl]thiobenzimidate dihydrochloride, **2**, leading to amidines, **3**.

It is likely that the mechanism of this reaction involves tetrahedral intermediates possibly similar to the well-known $A_{AC}2$ acid catalyzed ester hydrolysis mechanism described by Ingold.[9] The thioimidate analogy to the $A_{AC}2$ ester hydrolysis mechanism is shown in Scheme II.

The rate of formation of **9** should be a function of the concentrations of protonated thioimidate[10] **5** (or **4** which would be in rapid tautomerism) and free amine, R_1R_2NH, which is in equilibrium with its conjugate acid. At low acid concentration, neutral thioimidate **6** fragments to nitrile and thiol, decreasing the concentration of **5** (or **4**). A strongly acidic medium decreases the concentration of free nucleophile RNH_2. The adduct **7** is analogous to the $A_{AC}2$ hydrolysis intermediate.[9] Intermediate **8** probably does not contribute significantly to the generation of amidine **9**, since it corresponds to the $B_{AC}2$ intermediate generated during base-catalyzed ester hydrolysis, as described by Ingold.[9] Controlling the acid concentration with a buffer in this otherwise aprotic organic solvent thus provides for significant concentration of free amine, while preventing rapid base-catalyzed reversion of thioimidate to nitrile. A similar principle has been employed in the preparation of guanidines, using pyridinium hydrochloride/pyridine buffers.[11]

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra of $CDCl_3$ solutions (Me_4Si, δ 0) were recorded on a Varian A60 spectrometer. IR spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer, using the stipulated solvents, and are reported in reciprocal centimeters. Microanalyses were performed by Pfizer Central Research microanalysis laboratory, Groton, Conn.

Starting amines were commercially available and used without further purification. Amidines were prepared by the procedure given below, except for variations as defined in the footnotes to Table I. NMR and IR spectra of all compounds prepared were consistent with the proposed structures.

Preparation of *N*-Cyclopentyl-*n*-[(di-*n*-hexadecylamino)methyl]benzamidine Dihydrochloride. Ethyl *m*-[(di-*n*-hexadecylamino)methyl]thiobenzimidate dihydrochloride (**2**) (1.074 g; 1.5 mmol) was added to a solution of cyclopentylamine (2.55 mg; 3.0 mmol) and glacial acetic acid (0.3 mL; 5.3 mmol) in 10 mL of $CHCl_3$. The mixture was held at room temperature for 72 h, diluted to 300 mL with $CHCl_3$, washed with 3 × 50 mL of saturated $NaHCO_3$ and 3 × 50 mL of brine, dried (Na_2SO_4), and filtered. The filtrate was acidified with a 10% solution of anhydrous HCl in 5 mL of dioxane and then evaporated in vacuo to an oil. The oil was crystallized from warm 1,2-dimethoxyethane: 850 mg (77%); R_f 0.30 (4:1 benzene–ethanol on silicic acid); mp 78 °C (gel formation); IR (KBr) 1681, 1626, 1471 cm^{-1}; NMR δ 0.8–2.5 (m, 70), 2.6–3.5 (m, 4), 4.3–4.8 (m, 3), 7.3–8.6 (m, 4), 9.1–12.0 (m, 4). Anal. Calcd for $C_{45}H_{83}N_3 \cdot 2HCl \cdot 0.5H_2O$: C, 72.24; H, 11.39; N, 5.62. Found: C, 72.16; H, 11.63; N, 5.75.

Preparation of Ethyl *m*-[(Di-*n*-hexadecylamino)methyl]thiobenzimidate Dihydrochloride (2). A mixture of *m*-[(di-*n*-hexadecylamino)methyl]benzonitrile[12] (23.2 g; 0.04 mol), ethanthiol (6.0 mL; 0.08 mol) and chloroform (100 mL) was saturated with dry hydrogen chloride for 30 min at 20–25 °C. It was then stoppered and held for 6 days at 5 °C. The mixture was evaporated in vacuo to a foam which was crystallized by trituration with 1,2-dimethoxyethane. The crude product was recrystallized from hot 1,2-dimethoxyethane–chloroform: 24.6 g (88%); R_f 0.72 (4:1 benzene–ethanol on silicic acid); mp 109–111 °C; IR (CH_2Cl_2) 1620 cm^{-1}; NMR δ 0.6–2.2 (m, 65 [0.89 broad s]), 2.8–3.4 (m, 4), 3.74 (q, J = 8 Hz, 2), 4.2–4.7 (m, 2), 7.4–8.8 (m, 4). Anal. Calcd for $C_{42}H_{78}N_2S \cdot 2HCl$: C, 70.45; H, 11.26; N, 3.91. Found: C, 70.34; H, 10.94; N, 3.89.

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Registry No. **2**, 63290-29-9; **3** (R = CH_3), 71359-33-6; **3** (R = CH_2CH_3), 71393-18-5; **3** (R = $CH(CH_3)_2$), 71359-34-7; **3** (R = $CH_2CH{=}CH_2$), 71359-35-8; **3** (R = c-C_5H_9), 71359-36-9; **3** (R = $CH_2C_6H_5$), 71359-37-0; **3** (R = CH_2CF_3), 71359-38-1; **3** (R = CH_2-c-C_3H_5), 71359-39-2; **3** (R = 3-CH_3-4-OHC_6H_3), 71359-40-5; **3** (R = C_6H_5), 71359-41-6; CH_3NH_2, 74-89-5; $CH_3CH_2NH_2$, 75-04-7; $CH_2{=}CHCH_2NH_2$, 107-11-9; c-$C_5H_9NH_2$, 1003-03-8; $C_6H_5CH_2NH_2$, 100-46-9; $CF_3CH_2NH_2$, 753-90-2; C_3H_5-c-CH_2NH_2, 2516-47-4; 3-CH_3-4-$OHC_6H_3NH_2$, 2835-96-3; $C_6H_5NH_2$, 62-53-3; $(CH_3)_2CHNH_2$, 75-31-0; *m*-[(di-*n*-hexadecylamino)methyl]benzonitrile, 59050-99-6; ethanethiol, 75-08-1.

(9) Tetrahedral intermediates have been described in the bimolecular acid-catalyzed acyl–oxygen cleavage, $A_{AC}2$, mechanism for ester formation

or hydrolysis, as well as the corresponding base-catalyzed, $B_{AC}2$, mechanism for ester hydrolysis. Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, N. Y., 1969; pp 1129–1157.

(10) Thioimidate formation likely proceeds via addition of thiol to the protonated nitrile. For other examples of nitrilium ions see: Borch, R. F. *Chem Commun.* **1968**, 442–3. Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627–9.

(11) Unpublished results.

(12) This nitrile was prepared from *m*-(bromomethyl)benzonitrile, di-*n*-hexadecylamine, and K_2CO_3 in dimethylacetamide at 80 °C (mp 26–7 °C, *i*-PrOH) as described in U.S. Patent 3 872 171 (March 1975).

Convenient Conversion of Alcohols into Formaldehyde Acetals or Ethers

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In our development of new methods for the conversion of alcohols into trimethylsilyl (Me_3Si) ethers,[1] we wished to explore the potential use of various neutral catalysts. In particular, we reasoned that chlorotrimethylsilane (Me_3SiCl) and dimethyl sulfoxide (Me_2SO) would react to give an adduct which might silate alcohols (eq 1).

$$Me_2SO + Me_3SiCl \rightarrow [CH_3S^+(OMe_3Si)CH_3Cl^-] \xrightarrow{ROH} ROMe_3Si + Me_2SO \quad (1)$$

This would be of great significance because of the anticipated mild conditions of the conversion.

Indeed, Me_3SiCl and Me_2SO do give a solid when mixed in either ether or benzene, but when this is allowed to react with an alcohol in refluxing benzene overnight, the product is not the Me_3Si ether but rather the formaldehyde acetal (eq 2).

$$Me_2SO + Me_3SiCl \rightarrow \xrightarrow{ROH} ROCH_2OR \quad (2)$$

This reaction is a general one and gives respectable yields of pure products (see Table I). The acetals can be obtained at room temperature in ether, but 4 days are needed

(1) For example, see Pinnick, H. W.; Bal, B. S.; Lajis, N. H. *Tetrahedron Lett.* **1978**, 4261.

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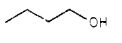
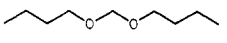
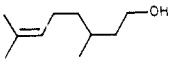
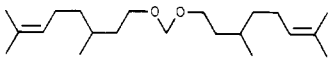
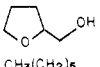
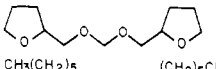
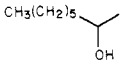
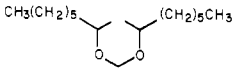
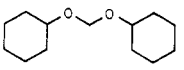
Table I. Conversion of Alcohols into Formaldehyde Acetals

alcohol	acetal[a]	% yield (yield in g)[b]
		81 (3.22)
$CH_3(CH_2)_7OH$	$CH_3(CH_2)_7OCH_2O(CH_2)_7CH_3$	96 (3.27)
		79 (3.24)
		78 (2.12)
		81 (2.76)
		84 (2.23)

[a] All products have satisfactory ^1H NMR, ^{13}C NMR, and IR spectra. In addition, new compounds have correct combustion data. [b] All yields refer to isolated products and are pure by TLC.

for complete reaction. This preparation of formaldehyde acetals offers a convenient alternative to the use of formaldehyde and acid,[2] which seems to be more generally useful for diols than simple alcohols,[2,3] and methylene chloride–base, which is limited to diols.[4]

Benzylic alcohols give the corresponding ethers when treated with Me_3SiCl and Me_2SO. Thus, benzyl alcohol gives a 93% yield (4.95 g) of dibenzyl ether and α-phenylethanol produces the corresponding ether in 87% yield (2.62 g).

The mechanism of these transformations is not known; however, the acetal methylene clearly is derived from the methyl group of Me_2SO since Me_2SO-d_6 leads to the labeled acetal (eq 3)[5] and becomes the best way to prepare these compounds.

$$CH_3(CH_2)_7OH \xrightarrow[Me_3SiCl]{Me_2SO\text{-}d_6} CH_3(CH_2)_7OCD_2O(CH_2)_7CH_3 \quad (3)$$

A typical experimental procedure follows.

Preparation of the 1-Octanol Acetal of Formaldehyde. A solution of Me_2SO (1.95 g, 25.0 mmol) in 20 mL of benzene is cooled to 0 °C,[6] and 2.70 g (25.0 mmol) of Me_3SiCl is added. This mixture is stirred for 10 min, and 3.25 g (25.0 mmol) of 1-octanol is added. This causes the formation of additional white solid which dissolves after the reaction mixture is heated. After being refluxed overnight, the mixture is cooled, 0.2 g of lithium aluminum hydride[7] is added, and heat is applied again for 4 h. The reaction mixture is cooled to room temperature and quenched with water. The benzene is washed with water, the water is extracted with ether, and the combined organic layers are dried over anhydrous $MgSO_4$, filtered, and concentrated. Distillation gives 3.27 g (96%) of the formaldehyde acetal: ^1H NMR (CCl_4) δ 0.9 (m, 6 H), 1.1–1.6 (br s, 24 H), 3.45 (t, J = 6 Hz, 4 H), 4.5 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.143, 22.823, 26.481, 29.505, 29.602, 29.993, 32.041, 67.886, 95.393; IR (neat) 2950, 2880, 1500, 1410, 1140, 1100, 1060 cm^{-1}. Anal. Calcd: C, 74.94; H, 13.31. Found: C, 74.77; H, 13.31.

Registry No. 1-Butanol, 71-36-3; 1-octanol, 111-87-5; 3,7-dimethyl-6-octen-1-ol, 106-22-9; tetrahydro-2-furanmethanol, 97-99-4; 2-octanol, 123-96-6; cyclohexanol, 108-93-0; 1-butanol formaldehyde acetal, 2568-90-3; 1-octanol formaldehyde acetal, 16849-79-9; 3,7-dimethyl-6-octen-1-ol formaldehyde acetal, 71316-96-6; tetrahydro-2-furanmethanol formaldehyde acetal, 7445-44-5; 2-octanol formaldehyde acetal, 71316-97-7; cyclohexanol formaldehyde acetal, 1453-21-0; formaldehyde, 50-00-0.

(2) (a) Adams, E. W.; Adkins, H. *J. Am. Chem. Soc.* **1925**, *47*, 1358. (b) Zaganiaris, J. N. *Chem. Ber.* **1938**, *71*, 2002. (c) Vogel, A. I. *J. Chem. Soc.* **1948**, 616. (d) Pattison, D. B. *J. Org. Chem.* **1957**, *22*, 662.

(3) (a) Barker, S. A.; Bourne, E. J. *Adv. Carbohydr. Chem.* **1952**, *7*, 137. (b) de Belder, A. N. *Ibid.* **1965**, *20*, 219.

(4) (a) Brimacombe, J. S.; Foster, A. B.; Jones, B. D.; Willard, J. J. *J. Chem. Soc. C* **1967**, 2404. (b) Kim, K. S.; Szarek, W. A. *Synthesis* **1978**, 48.

(5) This product was identified by ^1H NMR, ^{13}C NMR, and IR spectra, as well as by comparison with the nondeuterated material.

(6) This reaction can be run at room temperature but is exothermic. A white solid is formed.

(7) This hydride treatment is necessary in order to destroy a sulfur compound odor in the crude product; however, the product is pure by NMR without reduction.

Selective Formation of 2-Chloroalkanes from Linear Alkanes

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Chlorinations by R_2NCl involve $R_2NH^+\cdot$ intermediates.[1] Large steric effects can be introduced by varying the size and shape of R.[2-4] This effect has now been studied on hexane, octane, decane, and dodecane by using the highly hindered *N*-chloro-2,2,6,6-tetramethylpiperidine (Table I). A study has also been made on decane, using four R_2NCl species (Table II). Selectivity for 2-chloroalkanes is realized. Although this is not as synthetically important as the production of the 1-chloroalkane, it is still a significant step in reaching the goal of terminal functionalization.

The selectivity for 2-chloroalkanes seems to be largely due to steric effects in the aminium radical and not to conformational effects in the alkane chain. This is indicated by the reduction in selectivity when a less hindered radical is used (footnote *a* of Table I) and the fact that selectivity decreases with increasing length of alkane in a manner anticipated from statistical effects.

It has been shown that a chloro substituent inhibits chlorination at nearby carbon atoms and that this inhibition persists out to carbons which are separated from the chloro group by six CH_2 units.[1] As a result, the 50% excess of *N*-chloroamine led to complete monochlorination

(1) N. Deno, *Methods Free-Radical Chem.*, **3**, 135 (1972).

(2) N. Deno, R. Fishbein, and J. C. Wyckoff, *J. Am. Chem. Soc.*, **93**, 2065 (1971).

(3) N. Deno, D. G. Pohl, and H. J. Spinelli, *Bioorg. Chem.*, **3**, 66 (1974).

(4) N. Deno and E. J. Jedziniak, *Tetrahedron Lett.*, 1259 (1976).

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