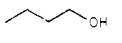
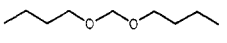
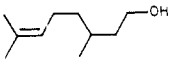
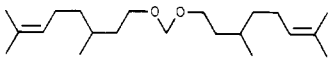
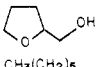
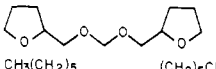
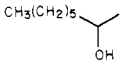
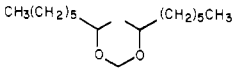
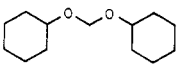
Table I. Conversion of Alcohols into Formaldehyde Acetals

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.

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(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

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

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Table I. Chlorination of Alkanes by *N*-Chloro-2,2,6,6-tetramethylpiperidine in Trifluoroacetic Acid Initiated by Fe(II)

alkane	% yield GC	relative yields 1-Cl	2-Cl	3-Cl	other
pentane[a]	*b*	6	85	9	
hexane	*b*	13	83	4	
octane	98	4	78	9	9 (4-Cl)
decane	40	5	64	8	23 (4- and 5-Cl)
decane[c]	52	6	63	7	24 (4- and 5-Cl)
dodecane	25	5	54	6	35 (4-, 5-, and 6-Cl)

[a] Identical ratios were found for photoinduced chlorination in CF_3COOH or in 10% H_2SO_4-90% CF_3COOH, and $FeSO_4$ induced chlorination in CF_3COOH. Photochlorination with the less hindered *N*-chlorodiisopropylamine gave less selectivity for 2-chloropentane (10:70:20 for 1-Cl:2-Cl:3-Cl). [b] Inconvenient to determine because of product volatility. [c] Photoinitiated.

Table II. Chlorination of Decane by Different R_2NCl

parent amine	relative yields 1-Cl	2-Cl	3-Cl	4- and 5-Cl
2,6-dimethylpiperidine	1	47	13	39
diisopropylamine	5	49	11	35
dicyclohexylamine	2	58	11	29
2,2,6,6-tetramethylpiperidine	5	64	8	23

of octane (98% yield) without further chlorination to dichloro products. Presumably similar high conversions and high yields obtain with pentane and hexane although these were not directly measured as explained in footnote *b* of Table I. As the length of the alkane increased, dichlorination increases and serves to lower the yield of monochloro product. This is presumed to be the explanation for the decreasing yields of monochloro product in the series octane to dodecane.

Under the reaction conditions, the chloroalkanes do not solvolyze to trifluoroacetates (and the trifluoroacetates do not isomerize[5]). The analytical procedure was further checked by showing that the same relative yields of isomers were observed for 20, 50, and 100% conversion of chlorodecanes to decyl acetates, using sodium acetate in refluxing acetic acid.

Experimental Section

The chlorinations were conducted by pipetting 7.5 mmol of *N*-chloroamine into a solution of 5 mmol of alkane in 20 mL of trifluoroacetic acid. The amine is slowly introduced below the surface at the periphery of the rapidly stirred solution. The $FeSO_4 \cdot 7H_2O$ (1.25 mmol) was added in one portion. The temperature was slowly increased to 45 °C over a 30-min period. This slow increase gave higher yields. After 10 min at 45 °C, 75 mL of water was added, the products were extracted with CH_2Cl_2, and the solution was dried over Na_2SO_4.

Although the chloroalkanes could be analyzed by GC (gas chromatography), better resolution was obtained with the acetates. These were prepared by refluxing the chloroalkanes for 8 h with sodium acetate in acetic acid.[5] The acetates were analyzed by GC, using 20% SE-30 on Gaschrom Q as the packing. Convenient column temperatures were 90, 109, 140, and 190 °C for the hexyl, octyl, decyl, and dodecyl acetates.

Acknowledgment. This work was supported by grants from the Fats and Proteins Research Foundation.

Registry No. *N*-Chloroamine, 10599-90-3; trifluoroacetic acid, 76-05-1; 1-hexyl acetate, 142-92-7; 2-hexyl acetate, 5953-49-1; 3-hexyl acetate, 40780-64-1; 1-octyl acetate, 112-14-1; 2-octyl acetate, 2051-50-5; 3-octyl acetate, 4864-61-3; 4-octyl acetate, 5921-87-9; 1-decyl acetate, 112-17-4; 2-decyl acetate, 1534-32-3; 3-decyl acetate, 60826-18-8; 4-decyl acetate, 60826-17-7; 5-decyl acetate, 60826-16-6; 1-dodecyl acetate, 112-66-3; 2-dodecyl acetate, 42270-47-3; 3-dodecyl acetate, 60826-26-8; 4-dodecyl acetate, 60826-25-7; 5-dodecyl acetate, 60826-24-6; 6-dodecyl acetate, 60826-23-5; pentane, 109-66-0; hexane, 110-54-3; octane, 111-65-9; decane, 124-18-5; dodecane, 112-40-3; 1-chloropentane, 543-59-9; 2-chloropentane, 625-29-6; 3-chloropentane, 616-20-6; 1-chlorohexane, 544-10-5; 2-chlorohexane, 638-28-8; 3-chlorohexane, 2346-81-8; 1-chlorooctane, 111-85-3; 2-chlorooctane, 628-61-5; 3-chlorooctane, 1117-79-9; 4-chlorooctane, 999-07-5; 1-chlorodecane, 1002-69-3; 2-chlorodecane, 1002-56-8; 3-chlorodecane, 1002-11-5; 4-chlorodecane, 999-49-5; 5-chlorodecane, 1001-31-6; 1-chlorododecane, 112-52-7; 2-chlorododecane, 2350-11-0; 3-chlorododecane, 2350-12-1; 4-chlorododecane, 2350-13-2; 5-chlorododecane, 2350-14-3; 6-chlorododecane, 26535-66-0; 1-chloro-2,6-dimethylpiperidine, 6830-30-4; *N*-chlorodiisopropylamine, 24948-81-0; *N*-chlorodicyclohexylamine, 22824-16-4; 1-chloro-2,2,6,6-tetramethylpiperidine, 32579-76-3.

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(6) W. W. Hartman and E. J. Rahrs, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 650.