of 4.7 and 2.6%, 1096 total reflections, 1072 without standards, 888 with $I_o \geq 3\sigma(I_o)$, R_{sym} for equivalent reflections = 0.019. The diffractometer was controlled by a MicroVax II computer with the NRCCAD system of programs.[7] The crystallographic calculations done with the TEXRAY[8] package on MicroVax II and VaxStation II computers, structure solved with the direct methods link MITHRIL,[9] refinement by full matrix least squares, $\sum_w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0.0025F_o^2]$, carbon, nitrogen, and oxygen parameters refined with anisotropic parameters, hydrogen atoms with isotropic terms, secondary isotropic extinction parameter = 0.00002 (4), final R, R_w and error-of-fit values of 0.047, 0.069, 1.96, minimum and maximum in final difference map of −0.13 and 0.21 e Å^{-3}.

Acknowledgment. Special thanks to Drs. Gerald Doyle and A. Bashir-Hashemi for helpful discussions and to ARDEC for financial assistance under contract DAAA21-88-C-0013. Assistance provided by Prof. Theodore Axenrod in spectral acquisition and interpretation is gratefully acknowledged. Mr. C. Campbell, ARDEC, is thanked for obtaining the DSC of 1. Drs. H. L. Ammon and C. S. Choi thank the National Science Foundation for grant number CHE-85-02155, which provided a portion of the funds for purchase of the diffractometer/MicroVax system, and the National Institutes of Health for Shared Instrumentation Award No. RR-03354 for purchase of a graphics workstation at the University of Maryland.

Supplementary Material Available: Fractional coordinates, U values, bond lengths, and bond angles for 1 (4 pages); tables of observed and calculated structure factors for 1 (6 pages). Ordering information is given on any current masthead page.

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Preparation of New Acetal Type Cleavable Surfactants from Epichlorohydrin

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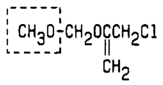
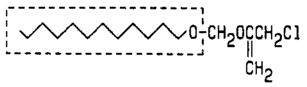
Recently, cleavable surfactants have become a focus of great interest in the field of surfactant chemistry.[1] Such compounds are designed so as to decompose into non surface active species on exposure to acid, alkali, light, or heat after fulfilling their original functions, which might include emulsification, solubilization, micellar catalytic activity, and so on. Among the various types of known cleavable surfactants, compounds in which the decomposition property can be controlled through adjustment of the solution pH seem to be the most common. In particular, there are many reports concerning acetal[2] and 1,3-dioxolane[3] types of amphiphilic compounds.

Scheme I



$$CH_3O\text{-}CH_2O\underset{\underset{CH_2}{\|}}{C}CH_2Cl$$

CDOH



2

We previously found that a series of 2-substituted 1-(chloromethyl)ethyl ethers can be synthesized regioselectively in high yields through the reaction of epoxides with organic chlorides in the presence of dodecyltrimethylammonium chloride.[4] We have also reported 2-(chloromethyl)-3,5-dioxahex-1-ene (CDOH; Scheme I) which is prepared from epichlorohydrin according to this method. This compound is stable under ambient conditions and can be applied as an effective acetonylating reagent to active proton-containing compounds under the appropriate conditions.[5] We now report that we have synthesized the allyl chloride derivative **2** (Scheme I) with a long-chain alkyloxy group in place of the methoxy group in CDOH from epichlorohydrin. We have also easily obtained the new acetal type cleavable surfactants **3**, **4**, and **5** with any one of the desired hydrophilic groups (anionic, cationic, and nonionic) through substitution reactions with **2**. In this paper, we present the preparation methods for a series of surfactants, their basic surface active properties, and their decomposition profiles in an aqueous medium through addition of acid, as determined by ^{1}H NMR measurements.

Results and Discussion

The synthetic route to acetal type surfactants **3**, **4**, and **5** is shown in Scheme II. First, chloromethylation of dodecanol was carried out in methylene chloride according to the usual procedure.[6] A solution of crude chloromethyl dodecyl ether in methylene chloride was added dropwise into a mixture of epichlorohydrin and dodecyltrimethylammonium chloride at 0 °C. The reaction mixture was stirred at 30 °C. Dichloride (**1**) was isolated by Kugelrohr distillation. The key intermediate, 2-(chloromethyl)-3,5-dioxaheptadec-1-ene (**2**), was prepared by the dehydrochlorination of **1** under phase-transfer (PT) catalytic conditions, and **2** was also isolated by Kugelrohr distillation.

The sulfonate salt type anionic surfactant **3** was prepared through a modification of the Strecker reaction.[7] In this case, both a stoichiometric amount of sodium iodide and a catalytic amount of tetrabutylammonium bisulfate

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(1) For example: (a) Cuomo, J.; Merrifield, J. H.; Keana, J. F. *J. Org. Chem.* **1980**, *45*, 4216. (b) Epstein, W. W.; Jones, D. S.; Bruenger, E.; Rilling, H. C. *Anal. Biochem.* **1982**, *119*, 304. (c) Jaeger, D. A.; Word, M. D. *J. Org. Chem.* **1982**, *47*, 2221. (d) Jaeger, D. A.; Chou, P. K.; Bolikal, D; Ok, D.; Kim, K. Y.; Huff, J. B.; Yi, E.; Porter, N. A. *J. Am. Chem. Soc.* **1988**, *110*, 5123.

(2) For example: (a) Kuwamura, T.; Takahashi, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 617. (b) Burczyk, B.; Sokołowski, A. *Tenside, Surfactants, Deterg.* **1978**, *15*, 68.

(3) For example: (a) Burczyk, B.; Węcłaś, L. *Tenside, Surfactants, Deterg.* **1980**, *17*, 21. (b) Węcłaś, L.; Burczyk, B. *Ibid.* **1981**, *18*, 19. (c) Jaeger, D. A.; Frey, M. R. *J. Org. Chem.* **1982**, *47*, 311. (d) Jaeger, D. A.; Martin, C. A.; Golich, T. G. *Ibid.* **1984**, *49*, 4545. (e) Piasecki, A. *Tenside, Surfactants, Deterg.* **1985**, *22*, 239. (f) Jaeger, D. A.; Golich, T. G. *JAOCS, J. Am. Oil Chem. Soc.* **1987**, *64*, 1550. (g) Burczyk, B.; Banaszczyk, M.; Sokołowski, A.; Piasecki, A. *Ibid.* **1988**, *65*, 1204. (h) Jaeger, D. A.; Jamrozik, J.; Golich, T. G.; Clennan, M. W.; Mohebalian, J. *J. Am. Chem. Soc.* **1989**, *111*, 3001. (i) Yamamura, S.; Nakamura, M.; Takeda, T. *JAOCS, J. Am. Oil Chem. Soc.* **1989**, *66*, 1165.

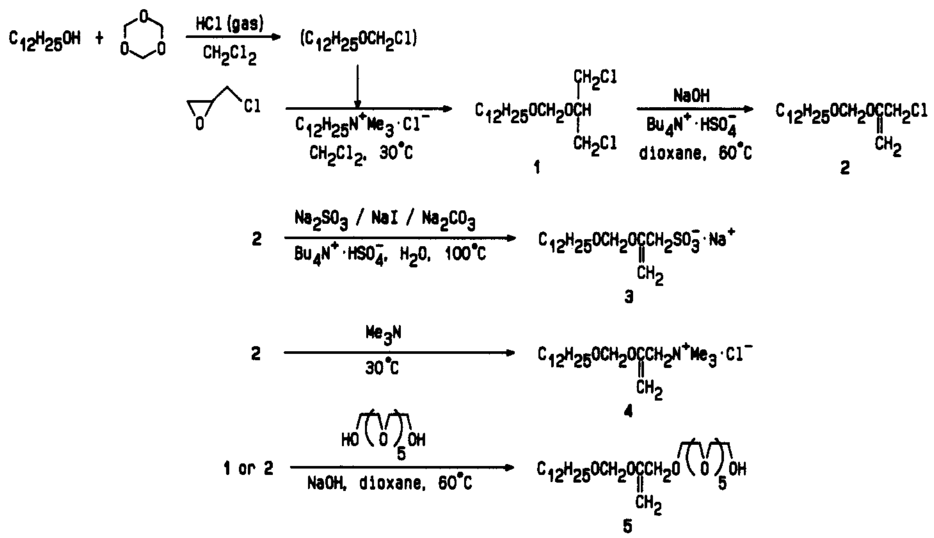
(4) Gu, X.-P.; Ikeda, I.; Okahara, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 397.

(5) (a) Gu, X.-P.; Ikeda, I.; Komada, S.; Masuyama, A.; Okahara, M. *J. Org. Chem.* **1986**, *51*, 5425. (b) Gu, X.-P.; Nishida, N.; Ikeda, I.; Okahara, M. *Ibid.* **1987**, *52*, 3192.

(6) For example: (a) Farren, J. W.; Fife, H. R.; Clark, F. E.; Garland, C. E. *J. Am. Chem. Soc.* **1925**, *47*, 2419. (b) Connor, D. S.; Klein, G. W.; Taylor, G. N. *Org. Synth.* **1972**, *52*, 16.

(7) March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure, 3rd Ed.*; John Wiley & Sons: New York, 1985; p 363.

Scheme II



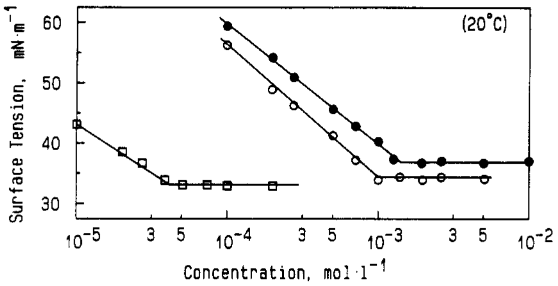


Figure 1. The surface tension vs concentration plots of neutral aqueous solutions of cleavable surfactants at 20 °C. (○), **3**; (●), **4**; (□), **5**.

were required because **2** was recovered almost quantitatively when either of these reagents was lacking in the reaction mixture. Reaction temperatures above 80 °C were required. It may be that 2-(iodomethyl)-3,5-dioxaheptadec-1-ene, which is much more reactive than **2**, is formed in situ by the halide exchange reaction under PT catalytic conditions. We previously reported that 2-(iodomethyl)-3,5-dioxahex-1-ene was obtained in 74% yield by treating CDOH with saturated aqueous potassium iodide at 80 °C for 3 h in the presence of sodium carbonate and a catalytic amount of quaternary ammonium bisulfate.[5b]

The alkyltrimethylammonium salt type cationic surfactant **4** was easily synthesized by the reaction of **2** with aqueous trimethylamine. The oligo(oxyethylene) type nonionic surfactant **5** was obtained in moderate yields by a general Williamson reaction of **2** with an excess of oligo(ethylene glycol). Furthermore, **5** could be directly synthesized from the dichloride **1**, the precursor of **2**. In the latter case, the dehydrochlorination of **1** and the nucleophilic substitution by oligo(ethylene glycol) occurred simultaneously in a mixture of sodium hydroxide and dioxane, without a PT catalyst.

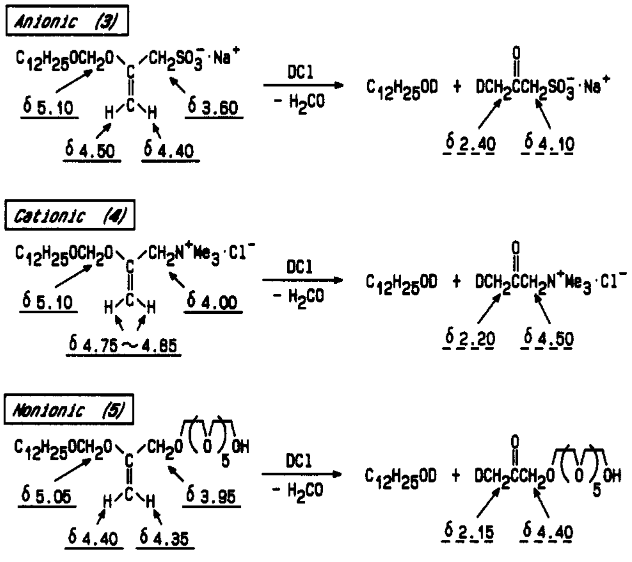
Because compounds **3**, **4**, and **5** were soluble in water at ambient temperatures, the surface tension of a series of neutral aqueous solutions of these surfactants was measured at 20 °C with a Wilhelmy tensiometer. The plots of surface tension vs concentration for these surfactants are shown in Figure 1. The Krafft point (T_{Kp}) or the cloud point (T_{cp}), the critical micellar concentration (cmc, determined from the break point of each curve in Figure 1), and the ability of these surfactants to lower surface tension above the cmc (γ_{cmc}) are summarized in Table I with data of typical surfactants bearing a dodecyl group.[8]

Table I. Krafft Point (T_{Kp}),[a] Cloud Point (T_{cp}),[a] cmc,[b] and γ_{cmc}[b] of Cleavable Surfactants 3, 4, and 5 and Reference Compounds[c]

compound	T_{Kp}, °C	T_{cp}, °C	cmc, mM	γ_{cmc}, mN m^{-1}
3	5.0	–	1.0	34.5
4	<0.0	–	1.4	37.0
5	–	43.5	0.039	32.8
$C_{12}H_{25}SO_3^-Na^+$	38.0	–	12	39.0
$C_{12}H_{25}N^+Me_3Cl^-$	3.0	–	20	39.0
$C_{12}H_{25}(OCH_2CH_2)_6OH$	–	52.0	0.087	31.0

[a] 1 wt % neutral aqueous solution. [b] At 20 °C in neutral aqueous solution. [c] Reference 8.

Scheme III



The cmc values of these cleavable surfactants are fairly small compared to those of the corresponding typical surfactants. Ionic cleavable surfactants are superior to the typical ionic surfactants in their ability to lower surface tension, but the γ_{cmc} value for a nonionic cleavable surfactant is almost the same as that for a typical surfactant. A detailed investigation into the effects of the cleavable connecting moiety [$OCH_2OC(=CH_2)CH_2$] and the length

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(8) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; John Wiley & Sons: New York, 1989; Chapters 3, 4, and 5.

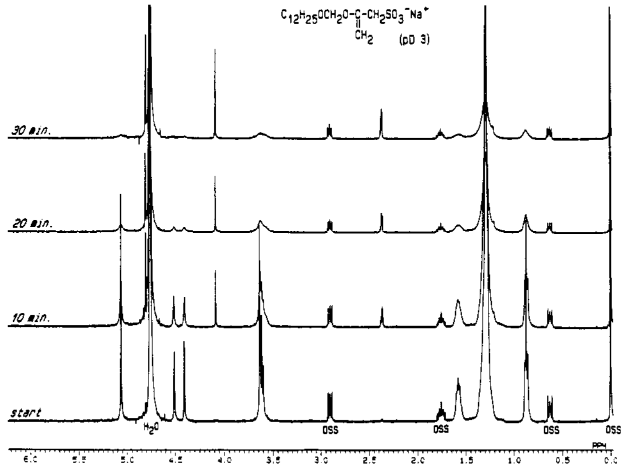

Figure 2. ^1H NMR spectral changes of a 20 mM D_2O solution of anionic cleavable surfactant **3** at 27 °C.

of the alkyl chain on surface active properties will be published elsewhere.

The decomposition properties of surfactants **3**, **4**, and **5** in D_2O by the addition of DCl were measured using ^1H NMR spectroscopy (400 MHz). Scheme III details the observed chemical shifts of protons of the cleavable connecting group and the hydrophilic fragment as a result of decomposition. Figure 2 shows selected spectral changes of an anionic cleavable surfactant (**3**) at pD 3 as an example. It is clearly observed that peaks at δ 3.60, 4.40, 4.50, and 5.10 gradually disappear, while new peaks at δ 2.40 and 4.10 appear and grow in intensity with time. The peaks at δ 4.40, 4.50, and 5.10 completely disappear after 30 min. It is also found that dodecanol, as a result of decomposition, is only sparingly soluble in the medium because the aqueous medium becomes turbid as a function of time. However, the relatively small peaks at δ 0.8, 1.2–1.6, and 3.6 assigned to dodecanol are detected after 30 min. The presence of formaldehyde was confirmed by a positive result of the silver mirror test of the decomposed solution using Tollen's reagent (a mixture of $AgNO_3$, aqueous NH_3, and aqueous NaOH). These spectral changes are also observed in the case of cationic (**4**) and nonionic (**5**) surfactants.[9]

The decomposition percentage was calculated from the integrated intensity ratio of the methylene protons of the hydrophilic fragment to the methylene protons of DSS. Figure 3 illustrates the relationship between the percentage of decomposition of anionic surfactant **3** and the time elapsed following addition of DCl at pD 3. The decomposition rate of **3** is the most rapid among cleavable surfactants investigated in this work. It decomposed completely within 30 min at pD 3 (Figure 3) and immediately at pD 1. In the case of nonionic surfactant **5** at pD 3, about 50% of **5** had decomposed after 48 h and it was completely decomposed after 90 h. However, **5** decomposed completely after 15 min at pD 1. Cationic surfactant **4** is very slow in its decomposition. It required about 1 week at pD 1 and about 48 h even at 2% DCl to decompose completely. Jaeger et al. have clarified that the stability/lability characteristics of base-sensitive cleavable ionic surfactants differ considerably depending on the terminal hydrophilic group.[10] They have ascribed the differences in reactivities for anionic and cationic surfactants to a combination of electrostatic and micellar effects. They have also reported that vesicles derived from cleavable double-chain anionic amphiphiles decompose rapidly compared to those derived from similar types of cationic amphiphiles under acidic conditions.[3h] Because all acetal type surfactants in this work form micelles at the investigated concentration (20 mM), it is surmised that the difference in the decomposition rates for **3**, **4**, and **5** may be attributed mainly to the difference in the pH values between the Stern layers of micelles and the bulk phase, as Jaeger has mentioned.[10] The local concentrations of protons near the surface of the anionic, nonionic, and cationic micelles may be higher than, similar to, or lower than the concentration of protons in the bulk phase, respectively. The surfactants studied in this work bear an acetal moiety near the hydrophilic group, so the local concentration of protons near the surface of the micelles may have a considerable effect on the decomposition characteristics of these surfactants.

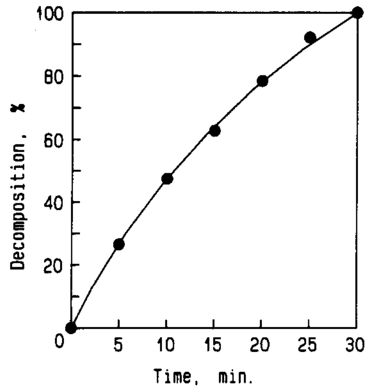

Figure 3. Relationship between the percentage of decomposition of anionic surfactant **3** and the elapsed time following addition of DCl at pD 3, 27 °C.

These new acetal type cleavable surfactants can be prepared by relatively simple methods from easily accessible commercial reagents and exhibit excellent basic surface active properties. Finally, it was confirmed that all these cleavable surfactants are stable in a nitrogen atmosphere at room temperature for at least 2 months.

Experimental Section

MS data were obtained on a JEOL JMS-DX303 mass spectrometer by a chemical ionization method. IR spectra were recorded on a Hitachi 260 spectrometer. ^1H NMR spectra were recorded at 27 °C on a JEOL-GSX400 spectrometer (400 MHz), using TMS (in the case of $CDCl_3$ solutions) or sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS; in the case of D_2O solutions) as an internal standard. GC analyses were performed on a Shimadzu gas chromatograph GC-8APF using a 1 m × 3 mm glass column packed with 3% silicone SE-30 on Celite 545.

The Krafft (T_{Kp}) or cloud point (T_{cp}) was determined by the naked eye using a 1 wt % aqueous solution of surfactant. The surface tension of a surfactant solution was measured at 20 °C with a Wilhelmy tensiometer (Shimadzu ST-1) using a series of aqueous solutions at various concentrations. All surface active properties were measured in deionized water under neutral conditions.

Starting materials, quaternary ammonium salts, and inorganic salts were commercial products and were used without further purification. Hexa(ethylene glycol) was prepared according to a previously reported method.[11] Its structure and purity were

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(9) One of the reviewers inquired regarding the possibility that the hexa(ethylene glycol) substituted acetone product from the cleavage of **5** might be displaced by chloride ion. We isolated this fragment by extraction and confirmed its structure as shown in Scheme III by a negative result of Beilstein's test and a comparison of its spectral data with those of the authentic samples (ref 5).

(10) Jaeger, D. A.; Finley, C. T.; Walter, M. R.; Martin, C. A. *J. Org. Chem.* **1986**, *51*, 3956.

confirmed by the comparison of its spectral data with those of the authentic sample.

^{1}H NMR Measurement. To a D_2O solution containing DSS and 20 mM of surfactant prepared in a NMR sample tube was added diluted deuterium chloride solution in D_2O to a defined concentration with a microsyringe. After a certain period, free induction decay (FID) signals were measured at 27 °C. For the NMR measurement, 99.8 atom % D of D_2O and 37 wt % deuterium chloride solution in D_2O (99 atom % D) were used.

1-Chloro-2-(chloromethyl)-3,5-dioxaheptadecane (1). Dry hydrogen chloride gas was passed through a glass nozzle into a 150 mL of methylene choride solution containing 55.8 g of dodecanol (0.3 mol) and 27 g of 1,3,5-trioxane (0.3 mol) at room temperature for 1 h. Calcium carbonate (40.0 g) was then added to the reaction mixture. After 4 h of stirring at 30 °C, a GC spectrum of the mixture indicated that all of the dodecanol had reacted. Dry nitrogen gas was passed into the reaction mixture for 2 h. Following filtration, the filtrate was used in the next reaction as a crude chloromethyl dodecyl ether solution without further purification. The filtrate was dropped into a mixture of epichlorohydrin (41.6 g, 0.45 mol) and dodecyltrimethylammonium chloride (2.4 g, 0.009 mol) at 0 °C. After stirring the mixture at 30 °C for 15 h, methylene chloride and unreacted epichlorohydrin were evaporated off. Compound 1 (54.9 g) was isolated by Kugelrohr distillation (100 °C/0.07 Torr) as a colorless liquid (56% yield).

2-(Chloromethyl)-3,5-dioxaheptadec-1-ene (2). A mixture of 1 (5.8 g, 0.02 mol), powdered sodium hydroxide (1.6 g, 0.04 mol), tetrabutylammonium bisulfate (0.34 g, 0.001 mol), and dioxane (10 mL) was stirred at 60 °C for 3 h. After filtration and subsequent evaporation of the filtrate, 4.5 g of 2 was obtained by Kugelrohr distillation (80 °C/0.05 Torr) as a colorless liquid. (77% yield): MS *m/e* (relative intensity) 291 ($M^+ + 1$, 30), 199 (100); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.10–1.40 (m, 18 H), 1.50–1.70 (m, 2 H), 3.58 (t, 2 H), 3.92 (s, 2 H), 4.30 (s, 1 H), 4.40 (s, 1 H), 5.08 (s, 2 H); IR (neat) ν 2900, 1650, 1100 cm^{-1}. Anal. Calcd for $C_{16}H_{31}ClO_2$: C, 66.07; H, 10.74; Cl, 12.19. Found: C, 66.25; H, 10.82; Cl, 12.07.

2-(Sulfomethyl)-3,5-dioxaheptadec-1-ene Sodium Salt (3). A mixture of 2 (1.70 g, 6 mmol), sodium sulfonate (1.52 g, 12 mmol), sodium iodide (0.90 g, 6 mmol), sodium carbonate (0.11 g, 1 mmol), tetrabutylammonium bisulfate (0.02 g), and water (3 mL) was vigorously stirred at 100 °C for 15 h. After the water was evaporated off, 50 mL of hot ethanol was added to the residue. After the insoluble solids were filtered off, 1.6 g of sulfonate 3 was obtained by recrystallization from ethanol as a white solid (74% yield): mp 132–133 °C dec; ^{1}H NMR (D_2O) δ 0.88 (t, 3 H), 1.10–1.40 (m, 18 H), 1.50–1.70 (m, 2 H), 3.60 (m, 4 H), 4.40 (s, 1 H), 4.50 (s, 1 H), 5.10 (s, 2 H); IR (KBr) ν 2900, 1640, 1220, 1100 cm^{-1}. Anal. Calcd for $C_{16}H_{31}O_5SNa$: C, 53.61; H, 8.72; S, 8.94. Found: C, 53.22; H, 8.65, S, 8.90.

2-((Trimethylammonio)methyl)-3,5-dioxaheptadec-1-ene Chloride (4). A mixture of 2 (2.90 g, 10 mmol) and a 30% aqueous solution of trimethylamine (4 mL, 20 mmol) was stirred at 30 °C for 15 h. After the water was evaporated off, 2 mL of methanol was added to the residue. The methanol solution was washed with hexane (10 × 10 mL). Evaporation of the methanol gave 3.2 g of ammonium salt 4 as a white waxy product (91% yield): MS *m/e* (relative intensity) 299 ($M^+ - 50$, 5), 130 (60), 57 (100); ^{1}H NMR (D_2O) δ 0.88 (t, 3 H), 1.10–1.40 (m, 18 H), 1.50–1.70 (m, 2 H), 3.15 (s, 9 H), 3.60 (t, 2 H), 4.00 (s, 2 H), 4.6–4.9 (two singlet peaks at δ 4.75 and 4.85, but H_2O partially overlapped), 5.10 (s, 2 H); IR (neat) ν 2900, 1640, 1460, 1120 cm^{-1}. Anal. Calcd for $C_{19}H_{40}ClNO_2$: C, 65.20; H, 11.52; Cl, 10.13; N, 4.00. Found: C, 65.19; H, 11.12; Cl, 10.04; N, 3.93.

2-(19-Hydroxy-2,5,8,11,14,17-hexaoxanonadecyl)-3,5-dioxaheptadec-1-ene (5) from Compound 2. A mixture of 2 (5.80 g, 20 mmol), hexa(ethylene glycol) (16.9 g, 60 mmol), sodium hydroxide (95% pellet; 3.37 g, 80 mmol), and dioxane (20 mL) was stirred at 60 °C for 3 h. After filtration and subsequent evaporatin of the filtrate, 7.0 g of compound 5 was isolated as a colorless liquid by silica gel column chromatography with a hexane–acetone (1:1, v/v) eluent (65% yield): MS *m/e* (relative intensity) 536 (M^+, 0.1), 101 (100), 89 (68); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.10–1.40 (m, 18 H), 1.50–1.70 (m, 2 H), 3.52–3.75 (m, 27 H), 3.95 (s, 2 H), 4.35 (s, 1 H), 4.40 (s, 1 H), 5.05 (s, 2 H); IR (neat) ν 3400, 2900, 1640, 1100 cm^{-1}. Anal. Calcd for $C_{28}H_{56}O_9$: C, 62.66; H, 10.52. Found: C, 62.38; H, 10.54.

Compound 5 from Compound 1. A mixture of 1 (5.40 g, 20 mmol), hexa(ethylene glycol) (16.9 g, 60 mmol), sodium hydroxide (95% pellet; 3.37 g, 80 mmol), and dioxane (20 mL) was stirred at 60 °C for 3 h. After using a similar procedure to that already described, 6.5 g of 5 was obtained (60% yield).

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(11) Nakatsuji, Y.; Kameda, N.; Okahara, M. *Synthesis* **1987**, 280.

Reductions of Some Functional Groups with Lithium (α-Cyanoalkyl)trihydroborate–Dioxane Complexes

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Introduction

Modification of reducing potency by changing of substituents on the central boron has resulted in a variety of hydroborate reducing reagents.[1] One of the members of this group is cyanotrihydroborate (BH_3CN^-), which has been found to be an extremely useful reagent for the selective reduction of organic functional groups.[2] Recently we reported a new class of hydroborates,[3] the (α-cyanoalkyl)trihydroborates ($BH_3CRR'CN^-$). In this paper we report reduction studies with organic functional groups as well as reactivity with $(CH_3)_3NHCl$ of this new class of hydroborates.

Results and Discussion

On the basis of the studies with known hydroborates, it was expected that the various members of the family of (α-cyanoalkyl)trihydroborates should behave as reducing agents toward saturated organic functional groups, such as aldehydes, ketones, acid chlorides, anhydrides, etc. The insertion of a CRR′ moiety between BH_3 and CN to give $BH_3CRR'CN$ provides a means of modifying the hydridic nature of the BH_3. That such substitutions had an effect was first observed in the reaction of the (α-cyanoalkyl)trihydroborates with amine hydrochloride with the dihydro reagent (1) reacting fastest followed by dimethyl (2) and phenylhydro (3). In order to examine the nature of reduction behavior of this new class of compounds and compare the effect of the various substitutents, we examined reductions of $LiBH_3CRR'CN{\cdot}xC_4H_8O_2$ ($R = R' = H$ (1); $R = R' = CH_3$(2); $R = H$, $R' = Ph$ (3)) in THF with a variety of organic functional groups (Table I). In each reaction, 6 mmol of the carbonyl compound was allowed to react with 2.4 mmol of the reagent (1.2 equiv of hydride). In the cases of the acids, acid chlorides, esters, and anhydrides, 4.8 mmol of the reagent (2.4 equiv of hydride) was used for 6 mmol of the compound.

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(1) Examples include the following: (a) Walker, E. R. H. *Chem. Soc. Rev.* **1976**, *5*, 23. (b) Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979**, *35*, 567 and references therein.

(2) Hutchins, R. O.; Natale, N. R. *Org. Prep. Proced. Int.* **1979**, *11*(5), 201.

(3) Peters, J. L.; Mittakanti, M.; Lofthouse, T. J.; Morse, K. W. *Inorg. Chem.* **1989**, *28*, 492.

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