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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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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Table I. Reductions with $LiBH_3CRR'CN \cdot xC_4H_8O_2$ in Tetrahydrofuran

carbonyl compd	product	percentage conversn[a] R = R′ = H	R = R′ = CH_3	R = H, R′ = Ph
3-pentanone	3-pentanol	100	96	78
2,2,4,4-tetramethyl-3-pentanone	2,2,4,4-tetramethyl-3-pentanol	65	8	4
benzaldehyde	benzyl alcohol	100	99	97
cinnamaldehyde	cinnamyl alcohol	100	99	99
acetophenone	α-methylbenzyl alcohol	100	99	99
benzophenone	benzhydrol	100	99	88
phthalic anhydride	phthalide	100	99	99
succinic anhydride	γ-butyrolactone	100	99	99
4-*tert*-butylcyclohexanone	4-*tert*-butylcyclohexanol[b]	95 (trans 97, cis 3)	89 (trans 93, cis 7)	75 (trans 88, cis 12)
norcamphor	norborneol[b]	99 (endo 81, exo 19)	99 (endo 66, exo 33)	99 (endo 44, exo 55)
benzaldehyde and	benzyl alcohol	100	99	98
acetophenone	α-methylbenzyl alcohol	20	18	18
benzoyl chloride	benzyl alcohol	100	99	99
n-hexanoyl chloride	*n*-hexanol	100	99	99
benzoic acid	salt formation	–	–	–
hexanoic acid	salt formation	–	–	–
ethyl benzoate	no reaction	–	–	–
ethyl hexanoate	no reaction	–	–	–

[a] One hundred percent conversion means that no starting material could be detected on GC. [b] Percentage of isomers was determined from the integration of the α-proton of the isomeric alcohols.

Inspection of Table I shows that all three reagents reduce aldehydes, ketones, acid chlorides, and anhydrides. The extent of the reduction is dependent on the type of carbonyl compound as well as on the reagent, although large differences are not observed. The (α-cyanomethyl)trihydroborate (1) is comparatively strong among the three reagents. As would be expected, the sterically hindered tetramethyl-3-pentanone is reduced to a lesser extent with all three reagents, but least with (α-cyano-α-phenylmethyl)trihydroborate (3). This could be due to less hydridic character of the reagent resulting from the electron-withdrawing phenyl group and/or due to the steric effect of the phenyl ring. Similar reactivity is observed with 3-pentanone, benzophenone, and 4-*tert*-butylcyclohexanone. In the reduction of cinnamaldehyde, there is no indication of 1,4-reduction taking place. Comparison with authentic samples of 3-phenyl-1-propanal and 3-phenyl-1-propanol showed no corresponding products in the GC of the reaction mixture but only cinnamyl alcohol. Lithium triethylborohydride, a powerful reducing agent, is known to reduce cinnamaldehyde to cinnamyl alcohol rapidly followed by a slow uptake of a second hydride to reduce the double bond.[4] However, use of excess (α-cyanoalkyl)trihydroborate did not reduce the double bond under the reaction conditions. It is not unexpected since these reagents are relatively milder than lithium triethylborohydride.

Reduction of acid chlorides with 2.4 equiv of hydride produced the corresponding alcohols. In order to test the possibility of partial reduction of acid chloride to aldehyde, we used stoichiometric amounts (1 equiv of hydride) of reagents at low temperature. Analysis of the reaction mixture showed the presence of aldehyde in less than 0.5%; other products were the corresponding acids and alcohols.

The formation of isomeric alcohols from 4-*tert*-butylcyclohexanone was consistent with more cis alcohol formed as the size of the reagent molecule increases. However, the results from the reduction of norcamphor were opposite those expected (more exo than endo alcohol formed as the size of the reagent molecule increased). There are some literature precedents for such unusual behavior of bulky reagents in the reduction of cyclic ketones[5] which may be applicable.

All three reagents selectively reduce the aldehyde in the presence of ketone at low temperature as is evident from the reduction of mixed benzaldehyde–acetophenone. In the reduction of benzaldehyde (6 mmol) in the presence of acetophenone (6 mmol), 2.4 mmol of reagent (0.6 equiv of hydride) was used. The reagent first reduced the aldehyde followed by ketone with the excess hydride. The percentage of alcohol from ketone corresponds to the excess of reagent. This indicates that the aldehyde is reduced preferentially in the presence of ketone at low temperature. Esters and acids are not reduced with all three reagents under these reaction conditions. With acids, evolution of hydrogen ensues after addition of the reagent and no further reaction takes place even after long refluxing. Carboxylic acids are regenerated from their lithium salts by hydrolysis as is evident from GC analysis.

When the reactivity of these three reagents with organic functional groups is compared with that of $LiBH_4$[6] and $LiBH_3CN$,[7] the reactivity of the lithium (α-cyanoalkyl)trihydroborates appears to be intermediate in reducing power between tetrahydroborate and cyanotrihydroborate. For example, $LiBH_4$ reduces esters, whereas these reagents did not; and $LiBH_3CN$ did not reduce benzophenone, but these reagents could.

The reaction of Me_3NHCl with reagent 1 is complete in 75 min whereas reagents 2 and 3 take 4 h to complete 90 and 86% reaction, respectively. This reactivity is similar qualitatively to the hydridic character observed in the reduction of functional groups.

Experimental Section

Materials. All glassware was dried in an oven at 120 °C and assembled in a stream of dry nitrogen gas. All the reactions were carried out under a dry nitrogen atmosphere. Hypodermic syringes were used to transfer solutions. THF was refluxed over sodium and distilled when dry (benzophenone indicator). The reducing reagents $LiBH_3CRR'CN \cdot xC_4H_8O_2$ ($x = 1 \pm 0.05$) were

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prepared according to reported procedures.[3] A 0.6 M solution of the reagents in dry THF was prepared immediately prior to the reduction experiments. The organic compounds for reduction studies were obtained from Aldrich as were authentic samples of expected final products.

All reaction products were analyzed on a Hewlett-Packard 5830A GC instrument equipped with a HP18850A integrator/plotter and 5% Carbowax OV-101 (25 ft × 0.32 mm) column. The IR spectra were recorded on a Perkin-Elmer 1750 FT spectrometer. The ^{11}B NMR spectra were obtained on a JEOL FX-90Q FT NMR spectrometer operating at 28.69 MHz; shifts were measured with respect to external $BF_3 \cdot OEt_2$; ^1H NMR spectra were obtained on a Varian XL-300 spectrometer using TMS as an internal standard.

Procedure for the Reduction. The reduction of benzaldehyde in THF is representative. A 50-mL flask was fitted with a rubber syringe cap on its inlet port, a reflux condensor connected to a paraffin oil bubbler, and a magnetic stirring bar. A sample of 6 mmol (0.64 g) of benzaldehyde dissolved in 8 mL of dry THF was placed in the flask, and 2.4 mmol of reagent (4 mL, 0.6 M THF solution) was introduced via a syringe. The mixture was stirred for 30 min at room temperature and 1 h at reflux. After cooling, 0.5 mL of water was added, and the reaction mixture was stirred for 10 min, followed by addition of 0.75 mL of 30% hydrogen peroxide and refluxing for 1 h. The solution was cooled, dried over anhydrous K_2CO_3, and subjected to GC analysis.

In the reduction of 4-*tert*-butylcyclohexanone, norcamphor, and mixed benzaldehyde–acetophenone, the reagent solution was added at −10 °C, and the reaction mixture was stirred for 30 min at that temperature and then slowly brought to room temperature. The rest of the procedure corresponds to the one described above.

In the reduction of succinic anhydride and phthalic anhydride, 4.8 mmol of the reagent and 6 mmol of the anhydride were used, following the typical procedure described for benzaldehyde. After hydrolysis with hydrogen peroxide, the reaction mixture was treated with 2 mL of 6 N hydrochloric acid, gently refluxed for 1 h, cooled, dried over K_2CO_3, and analyzed on GC. In the reduction of acid chlorides to alcohols, 4.8 mmol of the reagent and 6 mmol of the acid chloride were used, following the typical procedure. In the partial reduction of acid chlorides to aldehydes, 4 mmol of the reagent was added to 12 mmol of acid chloride at −60 °C, and the temperature was maintained there for 1 h and at room temperature for 1 h, followed by hydrolysis with 2 N HCl (H_2O_2 addition was avoided to prevent oxidation of aldehyde if formed).

Reaction of $LiBH_3CRR'CN \cdot xC_4H_8O_2$ with Me_3NHCl. Trimethylamine hydrochloride (15 mmol) and $LiBH_3CRR'CN \cdot xC_4H_8O_2$ (10 mmol) were placed in a dry flask, dry THF (25 mL) was added, and the mixture was stirred under a nitrogen atmosphere at room temperature. The ^{11}B NMR spectra were taken of aliquots to monitor the progress of the reaction as time progressed (15, 30, 75, 120, and 240 min). The percentage of product formation was calculated from the chemical shift integration ratio of product to starting material. After 4 h, the reaction mixture was refluxed for 30 min, cooled, and filtered to remove LiCl and excess Me_3NHCl. The THF was removed from the filtrate on a rotary evaporator. The residue obtained was dissolved in 50 mL of CH_2Cl_2, washed with cold water (2 × 15 mL), and dried over Na_2SO_4. Upon solvent removal, the pure $Me_3N-BH_2CRR'CN$ was obtained. $Me_3N-BH_2CH_2CN$: colorless thick oil; isolated yield 91%; IR (neat) 3000 and 950 (CH), 2400 and 2372 (BH), 2221 cm^{-1} (C≡N); ^{11}B NMR ($CDCl_3$) δ 4.5 ppm (t, J_{B-H} = 99 Hz); ^1H NMR ($CDCl_3$) δ 1.4 (S, br, 2 H), 2.65 (s, 9 H).

The yields and spectral data of $Me_3N-BH_2C(Me)_2CN$ and $Me_3N-BH_2CH(Ph)CN$ correspond to the reported values.[8]

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The Reduction of (Chloromethyl)pyridines and (Chloromethyl)quinolines by Triphenyltin Hydride. The Nature of the Chlorine Atom Transfer Step[1]

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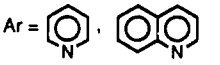
Introduction

In previous papers, we reported our findings on hydrogen atom abstraction from a series of homoaryl and heteroarylmethanes by *tert*-butoxyl[2] and undecyl[3] radicals. As part of this on going investigation on atom transfer from derivatives of methylated pyridines and quinolines, we report our results on chlorine atom transfer to triphenyltin radical. Reduction of organic halides with Group IVB hydrides is a reaction which has received intense investigation. This special attention is spurred by its growing synthetic utility[4] and suitability for mechanistic studies.[5] Gleicher and Soppe-Mbang investigated chlorine atom transfer from polycyclic homoarylmethyl chlorides[6] and related oxygen-containing heteroarylmethyl chlorides[7] to the nucleophilic[5a,8] triphenyltin radical at 70 °C. These workers utilized SCF–PPP–MO calculations to evaluate charge development in the transition state.[9] It was concluded that the rate-determining step is a direct atom abstraction and that the transition state involves an appreciable negative charge development at the benzylic carbon.[7]

It is of interest to extend this application of MO theory to the investigation of chlorine atom transfer from nitrogen containing heteroarylmethyl chlorides to triphenyltin radical (eq 1).

$$ArCH_2Cl + Ph_3Sn^{\bullet} \xrightarrow{70\ ^\circ C} ArC\dot{H}_2 + Ph_3SnCl \qquad (1)$$

Ar = 

Results and Discussion

The majority of the substrates utilized in this study were prepared by literature procedures. The relative reactivities of the heteroarylmethyl chlorides to 1-(chloromethyl)-naphthalene were determined by a direct competitive kinetic approach.[10] Using an internal standard, the relative areas of the CH_2Cl NMR signals in final reaction mixtures were compared to those found in the starting materials.

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