In order to confirm the structure and absolute stereochemistry of glycosyl amine **17**, which contains all the stereochemistry required for conversion to **2** and ultimately **1**, we converted **17** to (-)-methyl ydiginate, a derivative of a primary degradation product of natural streptolydigin. Thus, treatment of **17** with methyl chlorooxalate cleanly afforded the 4'-*O*-SEM-protected (-)-methyl ydiginate **18** in 81% yield. Cleavage of the SEM ether was effected by treatment with Me_3SiI at -78 °C to afford (-)-methyl ydiginate (**4**) (74%) which was identical with that derived from natural streptolidigin by comparison of IR and ^1H NMR spectra.[28] Further confirmation of stereochemistry and absolute configuration was obtained upon acetylation of **4** (quantitative yield) to (-)-methyl 4'-*O*-acetylydiginate **19** (mp 157-159 °C, $[\alpha]^{23}_D$ -23.9° (*c* 0.590 CH_3OH)), which was identical in all respects (^1H NMR, IR, and optical rotation) with **19** (mp 157-159 °C, $[\alpha]^{32}_D$ -25° (*c* 1.13, CH_3OH)) derived from natural streptolydigin.[28,29]

Preparation of the required tetramic acid synthon **2** was then completed along the lines of our earlier studies.[5] Acylation of **17** to the highly polar and somewhat sensitive β-keto amide **20** proceeded smoothly in 53% yield upon treatment of **17** with dioxenone **21**[30] at 135 °C in xylenes, presumably via the intermediacy of the acyl ketene.[31] Final closure to the tetramic acid was effected by treatment of β-keto amide **20** with *t*-BuOK in THF at 25 °C for 18 h followed by acidification (HCl) affording **2** as a highly polar oil after chromatography on Biosil A. Nonnucleophilic bases and aprotic media proved to be best for the former transformation. The highly polar enolic nature of tetramic acid **2** complicated characterization by spectral methods, however, **2** exhibited UV absorption (λ_{max} 285 nm) characteristic of tetramic acids, and possessed IR, ^1H NMR, and field desorption mass spectra consistent with structure **2** and similar to related substances prepared previously in our laboratories.[5,7]

We are currently examining the Horner-Emmons reactions of **2**, and the application of **2**, using the aforementioned strategy, to the construction of streptolydigin (**1**) itself.

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Catalytic Reductions of Alkyl Halides Using Soluble Polyethers and Tri-*n*-butyltin Chloride as Cocatalysts

Summary: Alkyl and aryl halides can be reduced by suspensions of sodium borohydride in toluene to yield hydrocarbons in high yield by using as cocatalysts tri-*n*-butyltin chloride and polyether phase-transfer catalysts.

Sir: Phase-transfer catalysis has developed into a useful procedure in organic synthesis.[1] Recently, we have begun to study phase-transfer-catalyzed reactions under solid-liquid conditions using both conventional crown ether and polymeric catalysts including poly(ethylene glycol) derivatives and polyethylene-bound crown ether catalysts. In this communication, we describe a new procedure using either of these sorts of catalysts by which carbon-halogen bonds are reduced to carbon-hydrogen bonds using tri-*n*-butyltin chloride as a cocatalyst and a suspension of sodium borohydride as the source of the hydride.

A variety of methods exist for replacement of carbon-bonded halogen by hydride. As an outgrowth of our recent work in solid-liquid phase-transfer-catalyzed reactions,[2] we chose to examine possible procedures by which toluene suspensions of sodium borohydride could be used to effect such a process. While complex hydrides which are soluble in organic solvents are known to nucleophilically substitute hydride for halide,[3] sodium borohydride in the presence of benzo-15-crown-5 (**1**) was only a modestly effective reagent for this reaction under the conditions we used. However, suspensions of sodium borohydride in the presence of a crown ether like **1** along with tri-*n*-butyltin chloride were more reactive alkyl halide reducing agents. Apparently **1** acts as a phase-transfer catalyst to form tri-*n*-butyltin hydride from tri-*n*-butyltin chloride in toluene. The tri-*n*-butyltin hydride so formed reduces the alkyl halide. Since the product of the tin hydride reduction of an alkyl or aryl halide is a tin halide, the overall reaction shown in eq 1 used the crown ether and tri-*n*-butyltin

$$\underset{X=Cl,\ Br}{R-X} \xrightarrow[\text{excess } NaBH_4,\ C_6H_5CH_3,\ 110\ ^\circ C]{5\%\ \mathbf{1},\ \mathbf{2},\ \text{or}\ \mathbf{3},\ 5\text{-}10\%\ (n\text{-}Bu)_3SnCl} R-H \qquad (1)$$

chloride as cocatalysts. A polyethylene-bound crown ether (**2**) and poly(ethylene glycol) dimethyl ether (**3**) were also used as phase-transfer catalysts for reaction 1 although both were less active than **1**. Table I lists some representative results from these studies.

In situ formation of tin hydrides has been reported previously using alcoholic solutions of triorganotin halides and hydride reducing agents.[6-8] Ethereal solutions of the more reactive hydride source $LiAlH_4$ have also been used with catalytic amounts of dialkyltin dihalides.[9] While the

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Table I. Reductions of Alkyl Halides by Sodium Borohydride Catalyzed by Polyether Phase-Transfer Catalysts and Tri-*n*-Butyltin Chloride[a]

substrate	catalyst	$10^5 k_{obsd}$ (s^{-1})	$10^5 k_{obsd}$ (s^{-1} $M_{cat.}^{-1}$)
1-bromooctane	1	0.0[b]	0[b]
	1	0.1	25[c]
	1	1.2	300
	2	0.0[b]	0[b]
	2	0.15	54
1-bromodecane	1	0.75	200
	2	0.12	48
1-bromododecane	1	1.1[d]	275[d]
	1	2.1[d]	263[d]
	1	3.2[d]	267[d]
	2	0.13[e]	48[e]
	2	0.30[e]	53[e]
	3	0.8	60
1-bromonaphthalene	2	3.2	45
bromocyclohexane	2	0.2	72
chlorocyclohexane	3	0.12	35
1-chlorooctane	3	0.10	30
benzyl chloride	2	0.9	225
1-bromooctadecane	1	4.0	60

[a] Reactions were typically run at 110 °C using toluene suspensions containing a 12-fold excess of sodium borohydride that were 4 mM in crown catalyst (5% catalyst), 8 mM in tri-*n*-butyltin chloride. An excess of tri-*n*-butyltin chloride was used in all reactions in this table unless otherwise noted. Reactions were analyzed by GC. In all examples in this table, the starting organic halide was completely consumed. GC yields of hydrocarbons were consistently 95% or better. Reaction rates were measured by using the procedures described in ref 2. [b] No phase-transfer catalyst was used. [c] No tri-*n*-butyltin chloride was added to the reaction. [d] The amount of crown ether used in these reactions was varied from 0.004 to 0.012 M. [e] The concentration of the oligomeric crown ether was varied from 0.0024 to 0.0057 M.

first procedure uses a less reactive hydride source, it requires the use of an alcoholic solvent to prepare a solution of the hydride reagent.[8] The procedure described in this communication extends this procedure by avoiding the need to dissolve the penultimate hydride source.

Kinetic studies using varying concentrations of tri-*n*-butyltin chloride and crown ether 1 showed that mequiv ratios of $1/R_3SnCl$ of less than 1 led to lower overall reaction rates. However, if at least 1 mequiv of tin chloride were used per mequiv of crown catalyst, further changes in the amount of the tin halide did not affect the reaction rate. So long as a slight excess of tin halide was present, the reaction rate was linearly dependent on the concentration of 1 as expected.

Crown ethers 1 and 2 and the poly(ethylene glycol) derivative were all effective as cocatalysts in reaction 1. However, reactions using equivalent concentrations of 2 or 3 were slower than reactions using 1 as catalyst. We previously noted similar, lower rates for phase-transfer-catalyzed reactions using such polyethylene-bound crown ethers. Nonetheless, 2 or 3 could be used if higher amounts of the polyether catalyst were added to compensate for the lower rate.[10] The need to use larger amounts of 2 or 3 over 1 is compensated for by the fact that 2 can be recovered and reused in subsequent reactions and by the fact that 3 is less expensive than 1.

The preparation of octadecane from 1-bromooctadecane is a representative procedure for this reaction. To a dry, 250-mL round-bottomed flask equipped with a magnetic stirring bar and reflux condenser were added 5 g (125 mmol) of $NaBH_4$, 6.4 g (20 mmol) of 1-bromooctadecane, 5 g of 2 (1.8 mequiv), and 125 mL of dry toluene. Heating this heterogeneous mixture to 110 °C dissolved the oligomeric crown ether. Addition of 0.7 g (2.1 mmol) of tri-*n*-butyltin chloride at this point initiated the reaction. After 36 h, GC analysis showed that the reaction was complete and the reaction mixture was cooled to 25 °C. After filtration to remove the oligomeric crown ether and excess $NaBH_4$, the solvent was removed. The product isolated in this manner was purified by distillation to yield 4.0 g (80% yield) of octadecane. The oligomeric crown ether was recovered and reused following previously described procedures.[2] Identical procedures were effective in reactions using 3. Reactions using 1 could be carried out on a similar time scale using less catalyst or in shorter times using 10% catalyst as in this procedure.

(10) The amount of catalyst was increased from 5% to 10% in preparative runs using the oligomeric catalyst to shorten reaction times. Reactions with increased amounts of polyether catalyst did not require a concomitant increase in the amount of tin reagent.

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Total Synthesis of *dl*-Morphine[1]

Summary: The synthesis of racemic morphine from 2-allylcyclohexane-1,3-dione and isovanillin is described.

Sir: As the cornerstone strategy in our approach to the morphine ring system we desired to effect the intramolecular conjugate addition of the aryloxy anion 1 to the β-substituted vinyl sulfone terminus, thereby providing incipient α-sulfonyl anion 2 which would suffer further intramolecular alkylation providing tetracyclic sulfone 3 in a single operation (Scheme I).

Treatment of isovanillin (4) as outlined in Scheme II afforded dibromophenol 5 in 40% overall yield on large scale. Reaction of 2-allylcyclohexane-1,3-dione (6)[3] with oxalyl chloride[4] (to give 7) followed by addition–elimination with sodium benzenesulfinate provided β-sulfonyl enone 8 (74% overall). Conversion of 8 to its silyl enol ether[5] followed by MCPBA oxidation[6] afforded the α-silyloxy ketone 9. Reduction[7] of 9 provided cis alcohol 10 (62% overall from 8). Mitsunobu coupling[8] of phenol 5 with alcohol 10 produced *trans*-silyloxy aryl ether 11 which was desilylated[9] to give alcohol *t*-12 (80% for the two steps). Jones oxidation[10] of *t*-12 followed by DIBAL-H reduction[11] afforded epimeric alcohol *c*-12 (90% yield).

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