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Reducing Alkyl Halides Using a Polymer-Bound Crown Ether/Tin Hydride Cocatalyst

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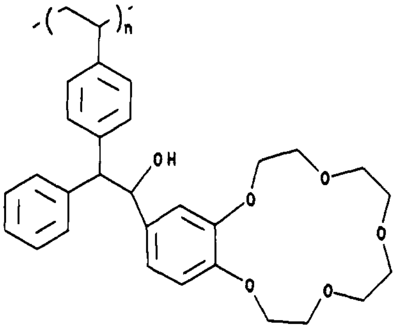
Summary: In this paper the synthesis and application of a novel macromolecular cocatalyst in which both reactive sites are on the same polymer matrix is described. Using this macromolecular cocatalyst, it was found that alkyl halide groups could be conveniently transformed into the corresponding hydrocarbon moiety in moderate yields.

While there have been numerous accounts depicting the advantages of using insoluble macromolecular reagents in catalytic studies, the use of multiple polymeric species in the same reaction vessel is a relatively recent approach.[1] Specific examples involve cases in which the insolubility of two polymeric reagents or catalysts allow reactions that are mutually destructive (when soluble reagents are used) to take place in the same step of a synthesis scheme.[2] Here we portray a somewhat different approach in which mutually compatible cocatalysts are bound to a single polymeric support. This strategy allows for simultaneous reactions to be carried out in the same vessel, while eliminating the steps required to separate the polymeric reagents. Specifically, we describe the use of 2% divinylbenzene cross-linked polystyrene containing both crown ether and organotin dichloride appendages as a cocatalytic system for reducing alkyl halides to alkanes.

Recently, it has been shown that alkyl halides could be reduced using both polymer-bound crown ethers and/or polymer-bound tin reagents under phase-transfer conditions in aprotic solvents.[3,4] In each case, the polymer-bound catalysts were added as individual species, necessitating an additional step to separate polymers at the end of the reaction. By attaching both catalysts to the same polymer support, we eliminated this extra step by taking advantage of the fact that sites on cross-linked polymers are not completely isolated from one another. This particular methodology was chosen because it has been shown that lightly cross-linked polymers are sufficiently mobile to allow site–site interactions.[5,6]

The polymer containing only the crown ether appendage was prepared by deprotonating 1.0 g (0.8 mequiv of active methylene units/g of polymer) of phenylmethylated polystyrene[7] (2% divinylbenzene cross-linked) with excess n-BuLi in dry THF at 0 °C under a nitrogen atmosphere. Quenching the dark purple polymer with 0.25 g (0.8 mmol) of 4′-formylbenzo-15-crown-5[8] yielded the crude product. The yellow polymer was subjected to Soxhlet extraction with THF for ca. 24 h to remove any unreacted crown ether. The polymer was isolated by filtration and dried, yielding 1.09 g of **1**. The identity of **1** was confirmed by infrared analysis which indicated the presence of the crown ether by the appearance of new absorption bands between 1200 and 1000 cm^{-1}. The loading of the crown ether (0.3 mequiv of crown/g of polymer) was determined by the increase in weight of the polymer and the weight of the unreacted crown ether that was recovered.



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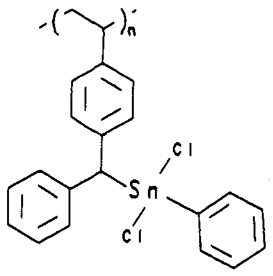

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Polystyrene-bound phenyltin dichloride, **2**, was synthesized in the same general manner as **1**, except that 0.5 mL (excess) of phenyltin trichloride was added to the anion derived from 1.0 g of phenylmethylated polystyrene. As previously described, the polymer was extractd with hot THF, filtered, and dried to yield the product. Subsequent infrared spectroscopic analysis proved to be inconclusive in verifying the presence of the organotin chloride on the polymer. Since direct verification of the identity of the tin catalyst was not available to use, we used two pieces of indirect evidence to confirm that the tin halide was present. The first piece of evidence was the elemental analysis of the polymer, which indicated the loading of organotin species on **2** was 0.59 mequiv of tin catalyst/g

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[6] We are currently investigating the kinetics forming tin hydrides from tin halides via phase-transfer catalysis.

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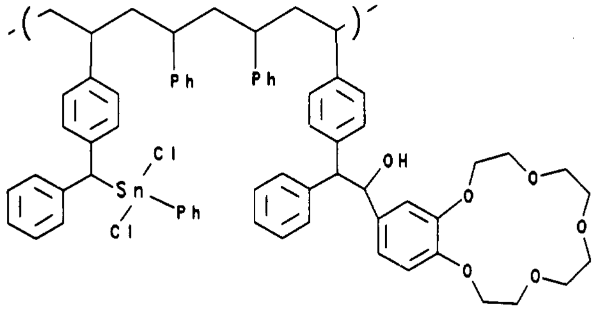
of polymer. However, since this estimate did not consider the presence of additional nonreactive organotin species, we decided to determine the loading of active catalyst. This was accomplished by comparing the pseudo-first-order rate constants of reactions when the [crown] was increased until the tin catalyst became the rate-limiting species. At the point in which the [crown] was equal to the active hydride on the polymer, the pseudo-first-order rate constants became essentially constant.[9] This technique showed the loading of active hydride on **2** to be 0.5 mequiv of catalyst/g of polymer which indicated that ca. 15% cross-linking of the tin halide occurred.

The polystyrene containing both catalytic species, **3**, was prepared by deprotonating 0.5 g of **1** with excess *n*-BuLi in dry THF under nitrogen at room temperature. To the resulting dark purple polymer was added 0.5 mL of phenyltin trichloride. The mixture was stirred for 24 h at room temperature, and the product was isolated and analyzed as described for **2**. The loadings of crown and active tin hydride on **3** were determined to be 0.3 mequiv/g of polymer and 0.4 mequiv/g of polymer, respectively. When the loading of active tin was compared to an elemental analysis of 0.72 mequiv of tin/g of polymer, it was apparent that considerable cross-linking (ca. 46%) had occurred.



3

The reduction reaction was carried out in a two-necked, 250-mL, round-bottomed flask equipped with septa, magnetic stirring bar, and a reflux condenser. The flask was then charged with the equivalent of 0.15 mmol of crown ether, 25–100% excess of the tin reagent, 0.5–0.6 mmol of hexane as an internal standard, 25–30 mL of toluene, and at least a 10-fold excess of solid $NaBH_4$. The resulting heterogeneous mixture was heated to 100 °C with an oil bath. After the temperature had stabilized, 1.2–1.5 mmol of the alkyl bromide was added to the reaction vessel. The course of the reaction was monitored by gas chromatography by periodic removal of 0.5–1.0-mL aliquots of the reaction mixture.[10] At the end of the reaction, the polymer was separated from the mixture by simple filtration, yielding a clear solution of the product mixture. The rate constants obtained from this study may be found in Table I.

Table I. Kinetic Data for Reducing Primary Alkyl Bromides[a]

substrate	crown ether	tin reagent	$K \times 10^5$ (s^{-1} $[crown]^{-1}$)
1-bromooctane	benzo-15-crown-5	Bu_3SnCl	360
1-bromooctane	benzo-15-crown-5	**2**	95
1-bromooctane	**1**	Bu_3SnCl	92
1-bromooctane	**1**	**2**	4
1-bromooctane	**3**	**3**	203
1-bromododecane	benzo-15-crown-5	Bu_3SnCl	330
1-bromododecane	benzo-15-crown-5	**2**	109
1-bromododecane	**1**	Bu_3SnCl	115
1-bromododecane	**3**	**3**	192
1-bromododecane	**1**	**2**	3

[a] The specific reaction conditions are described in the text.

From the data provided in Table I, it was found that the activities of all the polymer-bound catalysts (**1**, **2**, and **3**) were 2–4 times lower than those of the soluble catalysts used as controls. While this occurrence was not unexpected, it was interesting to note that the reactions using **3** proceeded faster than those using **1** or **2** as a catalyst. In fact, we found that having both catalytic species on the the same polymer resulted in a 40–48% increase in the activity of the catalyst. As an additional control reaction, it was shown that using two cross-linked polymers was not a viable alternative to this system because the immiscibility of the two polymers did not allow the catalysts to interact. As a result, the rate constants were effectively zero.

As a means of showing synthetic utility, we carried out the reduction on a 20.3-mmol scale using 1-bromododecane as the starting material under the same conditions described for the kinetic studies. The reaction was terminated after 24 h to yield 12.9 mmol (64%) of purified dodecane (^1H NMR ($CDCl_3$): δ 1.2 (multiplet, 20 H), 0.9 (triplet, 6 H)).[11-13]

In summary, a cross-linked polymer support containing two different reactive sites may be used in synthesis reactions. The successful demonstration using catalytic species that must interact during the course of the reaction also illustrates that 2% divinylbenzene cross-linked polystyrene is sufficiently mobile to preclude complete site–site isolation of the functional groups. In addition, when multiple functional groups are placed on the same polymer support, the overall activity of the catalytic system may be increased when they are compared to polymeric systems which contain one of the reactive sites. Currently, studies involving the loading of the catalysts are underway to determine the source of this increased activity.

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(9) It has been shown previously that this reaction is first-order in [crown], see ref 3a.

(10) In some cases, the progress of the reaction was monitored by ^1H NMR using a weighed amount of TMS as both the chemical shift reference and the quantitative internal standard.

(11) A control reaction using soluble catalysts yielded 74% of purified product under the same conditions.

(12) No radical coupling of the alkyl chains was noted in the sample of the purified product.

(13) In order to determine if borane was being generated during the process, 11-bromoundecanoic acid was reduced on a 20-mmol scale to yield 1-undecanol in 70% yield (purified).