

temperature was kept at -30° . Again no optical rotation was observed.

C. To a solution of 48 (4.651 mg, 12.5×10^{-3} mmol) in chloroform (10 ml) was added (+)-TAPA (3.578 mg, 8×10^{-3} mmol) in chloroform (2 ml). The resulting solution was refluxed for 5 min and half of the chloroform (6 ml) was removed by distillation. After cooling and standing for 48 hr, the precipitated complex (0.988 mg) was separated from the solution by decantation and washed with 1 ml of cold chloroform. The solid was dried and then dissolved in 4 ml of chloroform and the rotation was measured. The observed values were α_{435} 0.025° , α_{546} 0.005° , and α_{578} $<0.005^\circ$. After removal of the chloroform and addition of 5 ml of ethanol the resulting circulene (0.314 mg) was filtered and washed with benzene-ethanol. This material showed no optical rotation.

Registry No.—6, 30689-70-4; 7, 35817-61-9; 8, 54844-47-2; 8 picrate, 54844-48-3; 9, 54844-49-4; 10, 54844-50-7; 11, 40516-55-0; 12, 35817-59-5; 13, 35817-60-8; 15, 30689-69-1; 16, 54844-51-8; 18, 54844-52-9; 19, 54844-53-0; 21, 54869-88-4; 22, 54844-54-1; 23, 54844-55-2; 24, 54844-56-3; 25, 54844-57-4; 26, 54844-58-5; 28, 54844-59-6; 29, 54844-60-9; 30, 54844-61-0; 31, 54844-62-1; 37, 54844-63-2; 39, 54844-64-3; 48, 54869-87-3; maleic anhydride, 108-31-6; methyl propiolate, 922-67-8; LiAlH₄, 16853-85-3.

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Polymeric Reagents. IV.¹ Synthesis and Utilization of an Insoluble Polymeric Organotin Dihydride Reagent

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The preparation of an insoluble polymeric hydride reagent has been achieved by the incorporation of *n*-butyltin dihydride functional groups onto a macroreticular polystyrene matrix. Reaction of the polymeric organotin dihydride reagent with iodoctane indicated the minimum hydride content to average 2.0 mmol/g of polymer. Utilization of the reagent for the reduction of aldehydes and ketones to alcohols and the reduction of halides to hydrocarbons is discussed. The selective reduction of only one functional group of a symmetrical difunctional aldehyde (terephthaldehyde) is also demonstrated. The regeneration and stability of the reagent are also discussed.

The chemical industry is being faced with the ever-increasing problems of pollution control and a scarcity of raw materials. Recent developments^{1,3} in the area of insoluble, regeneratable reactive polymers has resulted in the availability of many new reagents with unique properties that

are capable of providing solutions to these problems. Despite the growing list of polymers that have been used to effect oxidation, hydrogenation, alkylation, etc., there has been no report of a general reducing agent possessing a wide range of applications. We now describe our efforts di-

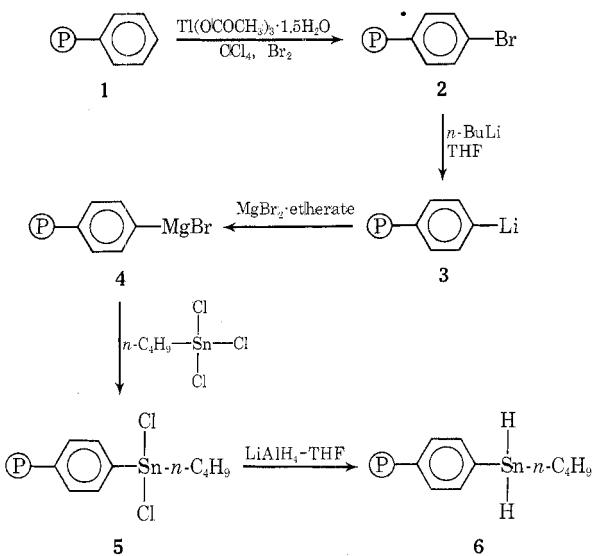
rected at the synthesis and utilization of an insoluble polymeric tin dihydride reagent.

The versatility and selectivity of organotin hydrides as reducing agents is well documented,⁴ with the dihydrides generally being more reactive but less stable than the corresponding monohydrides. Kuivila^{4c} attributed these special characteristics to the fact that the tin-hydrogen bond is weaker and less polar than both the boron-hydrogen and aluminum-hydrogen bonds. As a consequence, reduction with organotin hydrides can proceed by either free-radical chain or polar mechanisms depending on the substrate, catalysts, or reaction conditions. Thus, one might expect that an insoluble polymeric organotin dihydride reagent would include the advantages of monomeric organotin hydrides plus the advantages of a typical polymeric reagent: ease of operation and reaction work-up, avoidance of malodors and toxic vapors characteristic of tin hydrides,^{4d} and capability of regeneration. In principle a polymeric tin monohydride or trihydride can be made in the same manner as the dihydride described in this paper. The latter was chosen for study because it appeared to offer a combination of reasonable stability and sufficient chemical reactivity.

Results and Discussion

Preparation. Macroreticular polystyrene (1), Amberlite XE-305 (Rohm & Haas),⁵ was used as starting material in the preparation of polymeric organotin dihydride reagent 6 as outlined in Scheme I. A major consideration in using a

Scheme I



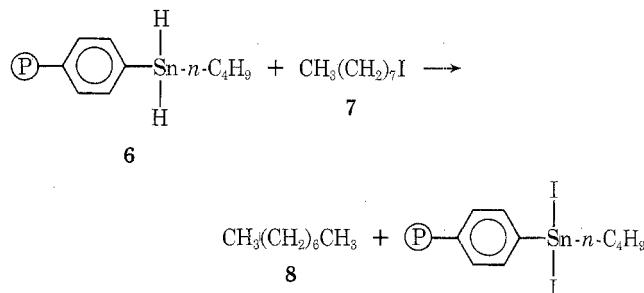
macroreticular instead of a microreticular resin is that the macroporosity and rigidity of the beads give certain advantages⁶ over the ordinary gel-type polymers such as (a) greater number of accessible reactive sites and (b) nominal shrinking and swelling properties allowing the use of a wide variety of solvents and temperatures.

Bromination of the macroreticular polystyrene 1 with bromine and ferric chloride⁷ in carbon tetrachloride proceeded to give a product containing 4.02 mmol of bromine/g of polymer.⁸ However, using thallic acetate sesquihydrate $[\text{Ti}(\text{OAc})_3 \cdot 1.5\text{H}_2\text{O}]^9$ in place of ferric chloride as catalyst gave a visually cleaner, more homogenous product containing 3.62 mmol of bromine/g. The literature¹⁰ indicates that this product should be exclusively the para-substituted bromo isomer 2. The bromo resin 2 was treated twice with *n*-butyllithium in anhydrous tetrahydrofuran under an inert atmosphere to give the lithiated resin 3. This material was not isolated, but immediately treated with freshly pre-

pared magnesium bromide-ether solution (1.5 equiv) at 0° to give the Grignard resin 4. The magnesium bromide etherate solution can be prepared according to Bachmann's¹¹ or House's method.¹² However, it was found that House's method of treating ethylene dibromide with magnesium gave a much cleaner product. Treatment of the Grignard resin 4 with excess (1.5 equiv) *n*-butyltin trichloride gave the polymeric tin dichloride 5. Elemental analysis indicated 1.2 mmol of Sn and 2.34 mmol of chlorine per gram of polymer. The final product 6 was obtained by treating the tin dichloride beads 5 with either diisobutylaluminum hydride in benzene or a solution of lithium aluminum hydride in tetrahydrofuran at room temperature. Isolation of the product was conducted under an inert atmosphere. The ir spectrum of 6 displayed a strong band at 1850 cm^{-1} which is characteristic of a Sn-H absorption. Elemental analysis (14.80% Sn, 1.25 mmol/g, ~0% Cl) indicated a maximum of 2.50 mmol of active hydride/g of polymer.

The reaction of tin dihydride resin 6 with iodoctane (7) (Scheme II) was used as a measure of the minimum hy-

Scheme II



dride content of the polymer 6. Conversion of iodoctane to octane (8) was followed by gas chromatography (4% FFAP, 7 ft × 0.25 in., on Chromosorb G, 80–100 mesh, 100°) using ethylbenzene as internal standard. The resin 6 (1.00 g) was treated with an excess of iodoctane (5 mmol) in 25 ml of anhydrous benzene to yield 1.98 mmol of octane (8), indicating a minimum of 1.98 mmol of active hydride/g of polymer.

We have found that the reaction conditions described in the Experimental Section are critical to the optimal preparation of the polymeric tin dihydride reagent. Our initial attempt resulted in the incorporation of only 0.22 mmol of tin/g of polymer based on elemental analysis. However, by paying careful attention to experimental conditions we have been able to repeatedly incorporate an average of 2.0 mmol of hydride/g of reagent.

Stability. The literature does not give a clear indication of the stability of monomeric *n*-butylphenyltin dihydride. However, it has been reported that diphenyltin dihydride decomposes slowly to diphenyltin in liquid ammonia (−33°)¹³ and to tetraphenyltin and metallic tin when heated above 100° in *vacuo*.¹⁴ Di-*n*-butyltin dihydride was observed by van der Kerk¹⁴ to be stable for up to 4 months if kept at 0° in a sealed tube. Hence, the stability of monomeric *n*-butylphenyltin dihydride should be intermediate between the conditions indicated above.

From the outset, the polymeric organotin dihydride 6 was expected to be more stable than its corresponding monomer owing to a restriction of intermolecular crosslinking and interactions created by the polymeric matrix.¹⁵ The data given in Table I give an indication of the stability of the hydride reagent 6 and surprisingly reveal that there is little difference between samples stored under an inert atmosphere at 0° and room temperature. The data also suggest that for long-term use, the reagent is best stored in

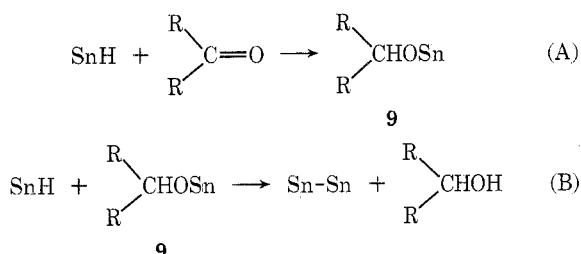
Table I
Stability Studies on the Polymeric Organotin Dihydride Reagent

Storage time, months	Storage temp, °C	Active hydride, ^a mmol/g
Fresh		2.01
1	Room	1.37
1	0	1.42
2	Room	0.80
2	0	0.76
3	Room	0.36
3	0	0.53

^a Active hydride determined by reduction of octyl iodide.

the form of its polymeric tin dichloride precursor **5** and converted to the desired hydride reagent in batches.

Reduction of Aldehydes and Ketones. The general application of monomeric organotin hydrides as reducing agents for aldehydes and ketones has received only limited attention.¹⁶ Kuivila^{4c} has reported that the reductions proceed by a two-step mechanism. Depending upon condi-



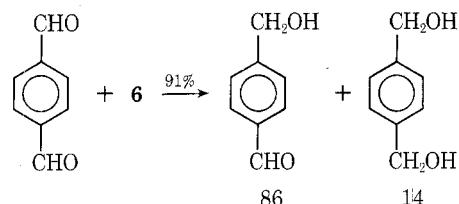
tions, only reaction A, or both A and B, may occur. The first step can be catalyzed by light, free-radical sources, Lewis acids, or heat. The second step represents an example of a general reaction between organotin hydrides and organotins containing electronegative groups bonded to tin. It should be pointed out, however, that reaction B cannot occur to any significant extent with the polymeric tin hy-

dride because of the restricted mobility of the polymer matrix.¹⁵ Hence, hydrolysis of the polymeric tin alkoxide **9** is necessary to obtain maximum yields of alcohol.¹⁷

Table II contains a summary of the results obtained from the reduction of a selected group of aldehydes and ketones with the polymeric hydride reagent **6**. In the reduction of a typical ketone, such as acetophenone, the best yields of alcohol were obtained by performing the reduction at the reflux temperature of toluene and adding the reagent **6** (3 equiv) in three separate portions.¹⁸ This suggests that some decomposition of the tin reagent occurs during the reaction.

The dramatic catalytic effect of platinum tetrachloride was illustrated by the reduction of 4-phenylcyclohexanone. In the presence of 5 mol % of catalyst this reaction was >50% complete in 4 hr at room temperature in tetrahydrofuran (compare with entry 4, Table II).

The need to hydrolyze the intermediate tin alkoxide **9** in order to isolate the reduction product can be used to advantage. Thus, reduction of an excess of the symmetrical dialdehyde terephthaldehyde (1 g, 7.5 mmol, 44% molar excess) with a limiting amount of the polymeric tin dihydride reagent **6** (4 g, 5.2 mmol of hydride) resulted in the isolation of a 91% yield of products composed of an 86:14 ratio of the monoalcohol to dialcohol, respectively. Isolation of the two products simply involved removal of the excess aldehyde by filtration, followed by hydrolysis, extraction, and purification by preparative TLC. The increase in selec-



tivity over the statistical 2:1 ratio of products is undoubtedly a result of the restricted accessibility of the remaining aldehyde group after formation of the initial tin alkoxide

Table II
Reduction of Aldehydes and Ketones via the Polymeric Tin Hydride Reagent **6**

Entry	Aldehyde or ketone	Registry no.	Reaction time, hr	Product(s)	Registry no.	Isolated product(s)		VPC analysis of distilled products
						Weight, g	Yield, %	
1	Acetophenone 0.12 g (1 mmol)	98-86-2	45	1-Phenylethanol ^a	98-85-1	0.112	92	95% alcohol 4% ketone
2	tert-Butyl methyl ketone 0.10 g (1 mmol)	75-97-8	41	3,3-Dimethylbutan-2-ol ^a	464-07-3	0.093	91	91% alcohol 8% ketone
3	Benzaldehyde 0.106 g (1 mmol)	100-52-7	40	Benzyl alcohol ^b	100-51-6	0.102	91	99+% alcohol
4	4-Phenylcyclohexanone 0.174 g (1 mmol)	4894-75-1	42	4-Phenylcyclohexanol ^{b,c}	5437-46-7	0.108	61	
5	Heptanal 0.114 g (1 mmol)	111-71-7	38	<i>n</i> -Heptanol ^a	111-70-6	0.100	86	99% alcohol 0.5% ketone
6	Benzophenone 0.182 g (1 mmol)	119-61-9	44	Benzhydrol ^{b,d}	91-01-0	0.099	54	
7	Terephthaldehyde ^e	623-27-8	24	<i>p</i> -Hydroxymethylbenzaldehyde ^{b,f} 1,4-Benzenedimethanol ^b	52010-97-6	0.556	91 ^g	
					589-29-7	0.091		

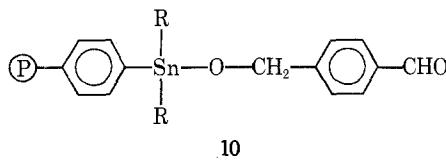
^a Product isolated by bulb-to-bulb evaporative distillation. ^b Product isolated by preparative TLC. ^c Mp 109–112°. ^d Mp 68–69°. ^e Polymeric hydride reagent added in one portion. ^f Mp 37–46°. ^g Yield based on hydride as limiting reagent (4 g, 5.2 mmol); ratio of monoalcohol to dialcohol 86:14. ^h All products were characterized by NMR and ir. All reductions were conducted in refluxing toluene with 2.5 g (1.25 mmol hydride/g, 3 equiv) of resin **6** added in three portions at 0, 18, and 30 hr unless noted otherwise.

Table III
Reduction of Alkyl and Aryl Halides via the Polymeric Tin Hydride Reagent 6^l

Halide	Registry no.	Solvent	Time, hr	Temp, °C	Product	Registry no.	Product(s) weight, g	% yield	VPC analysis of product(s)
1-Iodooctane 0.240 g (1 mmol)		THF	1.5	Room	Octane ^a		0.111	98 ^a	99+%
1-Bromoocetane ^b 0.193 g (1 mmol)	111-83-1	Benzene	30	80	Octane ^a		0.107	94 ^a	99+%
1-Bromoadamantane 0.215 g (1 mmol)	768-90-1	Benzene	18	80	Adamantane ^{c, d}	281-23-2	0.126	93	
α-Bromoaceto- phenone ^e 0.199 g (1 mmol)	70-11-1	Benzene	2	80	Acetophenone ^f	98-86-2	0.108	90	99
9-Bromoanthracene 0.257 g (1 mmol)	1564-64-3	Toluene	51	111	Anthracene ^{g, h}	120-72-7	0.143	80	
Benzyl bromide 0.171 g (1 mmol)	100-39-0	Benzene	8	80	Toluene ⁱ	108-88-3		98 ⁱ	
(2-Bromoethyl)- benzene 0.185 g (1 mmol)	103-63-9	Benzene	17	80	Ethylbenzene ^f	100-41-4	0.105	99	95 ^j
d-3-Bromocamphor 0.231 g (1 mmol)	55057-87-9	Benzene	6	80	Camphor ^{g, h}	464-49-3	0.117	84	
Prostaglandin iodide inter- mediate (11) 0.492 g (1 mmol)		THF	80	Room	Prostaglandin intermediate (12) ^g		0.315	86	

^a Solvent removed by distillation; product not purified further. ^b Four grams of resin added in two portions. ^c Product purified by sublimation (180°, 0.5 mm). ^d Mp 209–213°. ^e One gram of resin used (1.25 mequiv of hydride). ^f Product isolated by evaporative distillation. ^g Product isolated by preparative TLC. ^h Mp 216–217°. ⁱ Product not isolated; percent of product determined by VPC analysis. ^j Remainder is solvent. ^k Mp 168–173°. ^l All products were characterized by NMR and ir unless otherwise noted. Three grams of resin containing 1.25 mmol of hydride/g were used, added in one portion, unless otherwise noted.

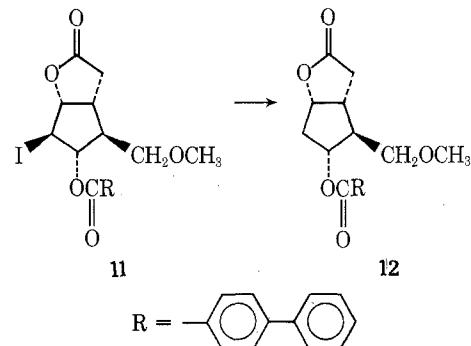
bond (see 10), as well as restricted mobility of the polymer-bound tin hydride groups.¹



Reduction of Halides. The use of organotin hydrides for the reduction^{4c} of alkyl and aryl halides in the presence of other functional groups is generally superior to lithium aluminum hydride¹⁹ or more recently introduced procedures.²⁰ As additional advantages, the polymeric tin hydride 6 offers a reagent which is free from toxic vapors and malodors and completely avoids contamination of products with residual organotin impurities.

Table III represents the scope of this method to date and illustrates the reagent's ability to reduce a halide in the presence of other functional groups. The reaction can be carried out by simply stirring the halide with the polymeric tin dihydride reagent (1.25–3.75 equiv) in an appropriate solvent at room temperature or reflux temperature (depending on halide) until the reaction is complete as determined by VPC or TLC. The solution of products is separated from the insoluble beads by filtration, combined with solvent washings of the beads, and concentrated by removal of solvent. In the majority of cases the purity of the resulting product is sufficiently high that additional purification is unnecessary. The procedure can also be applied to labile compounds such as the iodide 11 (a prostaglandin intermediate),²¹ which is reduced at room temperature in high yield to give a product, 12, free of organotin impurities.

Regeneration. One of the major advantages of an insol-



uble polymeric reagent is its potential capacity to be regenerated. The principal by-products formed during the reduction of aldehydes, ketones, and halides with the polymeric tin hydride reagent should be the polymeric tin halides, alkoxides, and hydroxides. Lithium aluminum hydride is reported^{14,22} to be an excellent reagent for reduction of the corresponding monomeric tin derivatives to tin hydrides. However, treatment of spent tin resin 6 (combined from reduction of aldehydes and ketones) with lithium aluminum hydride in THF at room temperature for 16 hr gave a material that was devoid of Sn–H absorption in the infrared spectrum and inert to iodoctane. Further exposure of this same material to LiAlH₄–THF for 3 hr at refluxing temperature (65°) resulted in beads that displayed a weak ir absorption at 1850 cm^{–1} and only 30% of the original hydride content (iodoctane standardization). Elemental analysis indicated that there had been no loss in tin content. The low content of regenerated hydride suggests that the formation of tin oxide, Sn–Sn, Sn–O–Sn, or divalent tin derivatives has occurred during the reduction–hydrolysis sequence.

Since the reduction of alkyl and aryl halides by organotin hydrides involves only free-radical hydrogen-halogen exchanges,²³ the used resin from halide reductions should be readily converted back to the polymeric organotin dihydride **6** with no loss in hydride content. Surprisingly, we have been able to regenerate only 60% of the original active hydride content in reagent **6** that has been utilized for halide reductions. Elemental analysis again indicated that there had been no loss in tin content. In addition, we have found it possible to regenerate only 10% of the active hydride that is lost in unused resin during storage. This is another strong indication that conversion of **6** to divalent tin compounds is occurring.

Experimental Section

Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer as KBr pellets. NMR spectra were recorded with a Varian T-60A instrument using tetramethylsilane as the internal standard (δ 0, CDCl_3 was the solvent). GLC analyses were carried out on a Varian Aerograph Model 920 instrument equipped with a thermal conductivity detector. The columns used were commercially available (Varian) 4% FFAP (7 ft \times 0.25 in.) on Chromosorb G (80–100 mesh). Evaporative distillation refers to bulb-to-bulb distillation under reduced pressure using a Büchi Kugelrohr oven. All solvents used were reagent grade unless specified otherwise. Anhydrous solvents were obtained by distillation from lithium aluminum hydride. Elemental analyses were performed by the Microanalytical Laboratory, Stanford University, Stanford, Calif.

Preparation of Poly(*p*-bromostyrene) (2).^{7,9} Method A. Crosslinked macroreticular resin (2% crosslinked, Amberlite XE-305) (1, 50 g) was slurried in 350 ml of carbon tetrachloride in a 2-l. three-neck round-bottom flask equipped with a dropping funnel, a condenser, and an overhead stirrer.²⁴ After stirring for 0.5 hr at room temperature, thallic acetate sesquihydrate (100 g) was added, and stirring was continued for another 0.5 hr. Then bromine (18 ml) was added dropwise and the mixture was refluxed with stirring for 2 hr, during which time the solvent color changed from deep brown to yellow. After cooling the beads were filtered and washed with concentrated HCl–dioxane (1:1, three times), water–dioxane (1:1, three times), water (six times), dilute NH_3 –dioxane (1:1, three times), dioxane (three times), THF (three times), and dry ether (three times). It was desirable to allow each of the solvents used in the washing procedure to be in contact with the beads for a 3–5-min period before filtration to allow complete penetration. The weight of the polymer after drying over calcium chloride in vacuo at 50° for 48 hr was 77 g.

Anal. Found: C, 58.11; H, 4.78; Br, 32.14.

The bromine content from elemental analysis was therefore 32.14%, which is equivalent to 4.02 mmol of bromine/g of polymer.

Method B. To a suspension of 10 g (96 mmol) of macroreticular polystyrene (Amberlite XE-305, Rohm & Haas) (1) and 0.1 g of anhydrous ferric chloride in 100 ml of carbon tetrachloride was added at room temperature a solution of 6 ml (112 mmol) of bromine (as Br_2) in 25 ml of carbon tetrachloride. The resulting mixture was stirred²⁴ at ambient temperature for 24 hr and filtered. The beads were washed with acetone until no brown filtrate was obtained, then with dioxane– H_2O (1:1), followed by dioxane. The brominated polymer was extracted overnight in a Soxhlet apparatus equipped with a Dean-Stark water separator using a 2:1 mixture of benzene and dioxane, then dried in vacuo at 50° for 24 hr. Elemental analysis of the product indicated the incorporation of 3.62 mmol of bromine/g of beads.

Anal. Calcd for $(\text{C}_8\text{H}_7\text{Br})_n$: Br, 43.70. Found: Br, 28.83.

Preparation of the Polystyrene Tin Dichloride Resin 5 from the Bromo Resin 2. The brominated crosslinked polystyrene **2** from above (67 g, 4.0 mmol/g) was suspended in 450 ml of anhydrous tetrahydrofuran in a 2-l. three-necked round-bottomed flask equipped with a mechanical stirrer,²⁴ a dropping funnel, and a condenser connected to an argon source such that the reaction flask was set up in an atmosphere of argon. After the mixture had cooled to –55° in an acetone–Dry Ice bath, commercial *n*-butyllithium in hexane (350 mmol) was added by way of a syringe with continuous stirring. After the addition was completed, the mixture was allowed to warm to room temperature and stirring was continued for an additional 30 min. The solvent was then siphoned off

after a second treatment with *n*-butyllithium in fresh THF, 500 ml of fresh tetrahydrofuran was added,²⁵ and the suspension was cooled by means of an ice–water bath. Magnesium bromide etherate (350 mmol), freshly prepared from ethylene dibromide and magnesium,¹² was next added dropwise followed immediately by the slow addition of *n*-butylltin trichloride (150 g). Stirring²⁴ was continued for 24 hr at room temperature under an argon atmosphere. The beads were collected by filtration and washed with dioxane–water (1:1, six times), water (six times), THF–water (1:1, three times), THF (three times), and dry ether (three times). After drying in vacuo at 50° for 24 hr, 78 g of the tin dichloride polymer was obtained.

Anal. Found: C, 63.47; H, 5.04; Br, 0; Cl, 8.20; Sn, 13.15.

The chloride content (8.20%) was thus 2.34 mmol/g of polymer and the tin (13.15%) 1.12 mmol/g.

Generation of the Polymeric Organotin Dihydride Reagent

6. A mechanically stirred²⁴ slurry of the polymeric tin dichloride beads prepared above (77 g), in 400 ml of anhydrous tetrahydrofuran, was cooled to –55° under an argon atmosphere and treated dropwise with an excess of lithium aluminum hydride (200 ml, 1.6 M solution) in tetrahydrofuran.²⁶ After the addition was completed the mixture was allowed to warm to room temperature and stirring was continued for another 1 hr. The resulting beads were collected by filtration under a stream of argon²⁷ and washed²⁷ rapidly with anhydrous tetrahydrofuran (ten times) followed by anhydrous ether (ten times), and finally evacuated in a desiccator at room temperature for 24 hr to give 62 g of material.

Anal. Found: C, 68.34; H, 6.02; Al, 0; Cl, 0; Sn, 14.80.

The tin content (14.80%) corresponds to 1.25 mmol/g. The maximum hydride content is therefore 2.50 mmol/g. The minimum hydride content (1.98 mmol/g) was determined as described below. The final product displayed a strong absorption at 1850 cm^{-1} (Sn–H) in the infrared spectrum (KBr pellet).

Standardization of the Polymeric Organotin Dihydride Reagent 6 with Iodoctane. One gram of accurately weighed polymeric tin dihydride reagent **6** was suspended in 25 ml of anhydrous tetrahydrofuran (dried and redistilled over lithium aluminum hydride) under an argon atmosphere and treated with a mixture of excess iodoctane (1.2 g, 5 mmol) and ethylbenzene (1 mmol) as an internal standard. The slurry was stirred at room temperature for 3 hr and the conversion of iodoctane to octane was determined by gas chromatography using a 4% FFAP column (7 ft \times 0.25 in., 100°).

As determined by VPC analysis, 1.98 mmol of iodoctane was converted to octane. Hence, reagent **6** must contain a minimum of 1.98 mmol of active hydride/g of resin.

Reduction of Acetophenone with the Polymeric Organotin Dihydride Reagent 6.

One millimole of acetophenone (0.12 g) was dissolved in 40 ml of anhydrous toluene (dried over Na). To this solution was added 1.5 g of the polymeric organotin resin containing 1.25 mmol H/g. The mixture was refluxed with stirring (overhead mechanical stirrer)²⁴ for 18 hr under an argon atmosphere. After this period of time, fresh tin resin **6** (0.5 g) was added and the reaction was continued as before. After 30 hr another batch of fresh resin **6** (0.5 g) was added and the reaction was allowed to proceed for an additional 15 hr. The resulting mixture was then cooled and beads were separated by filtration, and the filtrate was saved. The beads were then suspended in 1 N HCl–THF (1:1, 40 ml), and stirred for 1 hr at room temperature, then separated by filtration and washed with water, THF, and ether. The combined filtrates and washings were extracted with ether and the combined ether extracts were washed with water, dried with anhydrous Na_2SO_4 , and evaporated under reduced pressure to give a yellow oil. The product was purified by evaporative distillation under reduced pressure using a Buchi distillation oven to yield 0.112 g of product (92% of the theoretical). VPC analysis of this distilled product indicated the presence of 95% alcohol and 4% starting material. The product was verified by NMR, IR, and VPC retention time to be 1-phenylethanol.

The reduction of *tert*-butyl methyl ketone, benzaldehyde, 4-phenylcyclohexanone, heptanal, and benzophenone were all carried out in a similar manner. The appropriate isolation procedure is indicated in Table II.

Reduction of 4-Phenylcyclohexanone with Polymer Reagent 6 in the Presence of Platinum Tetrachloride. One millimole of 4-phenylcyclohexanone (0.174 g) and 3 g of tin resin 1 (1.25 mmol H⁺/g) in 40 ml of dry tetrahydrofuran were treated with 5 mol % of platinum tetrachloride added in one portion. The mixture was stirred at room temperature for 3 hr, after which time the used beads and catalyst were separated by filtration and washed with

dilute acid, THF, methanol, and ether. The combined filtrates were collected and extracted with three aliquots of ether. The combined ether extracts were washed with water, dried over Na_2SO_4 , and evaporated under reduced pressure to give a crude oil. Purification by preparative TLC (silica gel, 5% ether-95% CHCl_3 as eluent) afforded 0.132 g (75% of the theoretical) of 4-phenylcyclohexanol along with 19% recovered starting material.

Selective Reduction of Terephthaldehyde. A mixture of 4.0 g (5.2 mmol of active hydride) of the polymeric hydride reagent 6 and 1.0 g (7.5 mmol) of terephthaldehyde in 25 ml of dry toluene was heated overnight at reflux temperature with stirring²⁴ under an atmosphere of argon. After cooling, the beads were collected by filtration and washed first with anhydrous THF (six times), then dry ether (six times), and the washings were discarded. The insoluble beads were suspended in 1 N HCl -THF (1:1, 50 ml) and the mixture was stirred for 2 hr and then filtered. The filtrates were extracted with ether (three times), the combined extracts were dried (MgSO_4), and the solvent was removed by evaporation under reduced pressure to yield 1.02 g of crude product. Isolation by preparative TLC on silica gel (1:1 methanol-ethyl acetate) provided the desired *p*-hydroxymethylbenzaldehyde²⁸ (556 mg, mp 37-46°, 79% yield) along with 1,4-benzenedimethanol (91 mg, 13%). Both products were confirmed by NMR and ir.

Reduction of a Sensitive Alkyl Halide, Iodide 12, Utilizing the Polymeric Organotin Dihydride Reagent 6. In a reaction vessel equipped with an overhead mechanical stirrer²⁴ was placed 0.492 g (1 mmol) of the iodide 11 (prostaglandin intermediate)²¹ in 30 ml of anhydrous tetrahydrofuran. To this solution was added the polymeric organotin dihydride reagent 6 (3 g, 3.75 mmol of hydride) in one portion and the mixture was stirred at room temperature for 80 hr. The beads were separated by filtration and washed with benzene (three times), THF (three times), and dry ether (three times). The combined filtrates were collected and the solvent was removed by evaporation under reduced pressure to yield 0.376 g of a yellow oil. Purification by preparative TLC on silica gel (2:1 benzene-ethyl acetate) afforded 0.315 g (86%) of the desired product, as determined by NMR and ir comparison with an authentic sample,²¹ along with 0.022 g (4.5%) of recovered starting material.

The reductions of iodoctane, bromooctane, 1-bromoadamantan, 2-bromoacetophenone, 9-bromoanthracene, benzyl bromide, 2-bromoethylbenzene, and *d*-3-bromocamphor were also investigated. Specific reaction conditions and methods of isolation are indicated in Table III.

Attempted Regeneration of Resin 6 Recovered from Aldehyde and Ketone Reductions. The used resin 6 (25 g) was suspended in 150 ml of anhydrous tetrahydrofuran under an argon atmosphere in a 500-ml three-necked round-bottom flask equipped with a condenser, a mechanical stirrer,²⁴ and a dropping funnel. The mixture was cooled to -55° in an acetone-Dry Ice bath and treated dropwise with a solution of lithium aluminum hydride in tetrahydrofuran²⁶ (100 ml, 1 M). The mixture was stirred at room temperature for 16 hr and refluxed for an additional 3 hr. After cooling, the beads were separated by filtration under argon²⁷ and washed with anhydrous THF (three times) and dry ether (six times). Drying under vacuum (ca. 0.1 mmHg, at 20°) afforded 23 g of product. The ir of the regenerated product displayed a weaker absorption at 1850 cm^{-1} (Sn-H absorption) than the fresh resin. Standardization with iodoctane (ethylbenzene used as VPC internal standard) indicated 0.35 mmol of active hydride/g of polymer (1.25 mmol H/g for fresh resin).

Regeneration of the Used Polymeric Reagent 6 Recovered from Halide Reductions. A suspension of the spent hydride reagent 6 (7g) in 80 ml of anhydrous tetrahydrofuran under an argon atmosphere was treated at -30° with a solution of lithium aluminum hydride in THF²⁶ (40 ml, 0.90 M). The mixture was warmed

to room temperature and stirred²⁴ overnight. After heating at the reflux temperature for 3 hr the resin was isolated as described above to yield 6.5 g of beads. Standardization of the regenerated resin with excess iodoctane (followed by VPC analysis using ethylbenzene as the internal standard) indicated that the polymer contained 0.75 mmol of active hydride/g (fresh resin contained 1.25 mmol/g).

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