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MACRORETICULAR COPOLYMER BOUND ANALOGS OF PHENYLMERCURIC CHLORIDE, PHENYLLITHIUM, AND PHENYLDI-n-BUTYLTIN CHLORIDE

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SUMMARY

Macroreticular copolymers of styrene and 20% divinylbenzene were functionalized with resin-bound analogs of phenylmercuric chloride, phenyllithium, and phenyldi-n-butyltin chloride at levels lower than 0.05 meq per gram of resin. Resino-phenylmercuric chloride was formed by the reaction of mercuric trifluoroacetate with the resin followed by trifluoroacetate -- chloride exchange. Resino-phenyllithium was formed by the action of n-butyllithium on resino-phenylmercuric chloride and also by direct lithiation using the tetramethylethylenediamine complex of n-butyllithium. Resino-phenyllithium reacted with di-n-butyltin dichloride to form resino-phenyldi-n-butyltin chloride. In this case, relatively large quantities of resino-phenyltri-n-butyltin are also produced as a result of n-butyllithium adsorbed on the reacting polymer.

INTRODUCTION

Insoluble, cross-linked polystyrene resins have found wide application as supports for catalysts, reagents for organic synthesis, protecting groups, and as models for "infinitely dilute" solutions[1,2]. While condensation polymers containing metal-carbon bonds are relatively common[3], cross-linked polystyrenes containing metal-carbon bonds, especially when the bonds are formed on the insoluble resin, have not been extensively investigated. Functionalization of crosslinked polystyrene resins has been reviewed recently[4]. Resin-bound phenyllithium reagents have been used widely as synthetic intermediates[5,6].

Crowley and Rapoport discussed some of the problems associated with achieving intraresin site separation[2]. Grubbs, Brubaker and coworkers have shown that such separation is more readily attained on highly cross-linked, macroreticular copolymers than on the more commonly used copolymers which contain 1-2% divinylbenzene[5a]. Some synthetic studies have been done[5a,b, 7,8] on highly cross-linked macroreticular[9] copolymers, but their full potential has only recently been recognized.

To avoid intrapolymer reactions in solid-phase synthesis, we required effective site separation[8]. Calculations using a Poisson distribution of substitution points showed that very lightly substituted resins (generally less than 0.05 meq per gram of resin) were needed to assure substantial separation of active sites[8b]. Grubbs and coworkers recently described experimental evidence for catalyst site isolation and fit the observed rate data to a similar random distribution function[10]. In this paper, the chemistry of metal substitution on highly cross-linked, macroreticular resins is described with emphasis on some problems accompanying very low level substitution.

RESULTS AND DISCUSSION

Macroreticular copolymers of styrene and 20% divinylbenzene were functionalized by treatment with mercuric trifluoroacetate[11]. The resino-phenylmercuric trifluoroacetate[†] thus produced was converted to the corresponding chloride and then allowed to react with n-butyllithium to form resino-phenyllithium. Resino-

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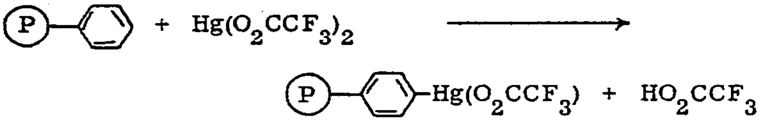
[†] "Resino-phenyl..." indicates that the substituents are attached to the aromatic ring of the polymer. Thus, they are resin-bound analogs of phenyl-substituted moieties. See footnote 13 of ref. 8.

phenyllithium was also prepared from the direct reaction of a tetramethylethylenediamine (TMEDA) complex of n-butyllithium (BuLi) with the copolymer[12, 13]. The resino-phenyllithium produced by either of the above methods reacts with di-n-butyltin dichloride to form resino-phenyldi-n-butyltin chloride.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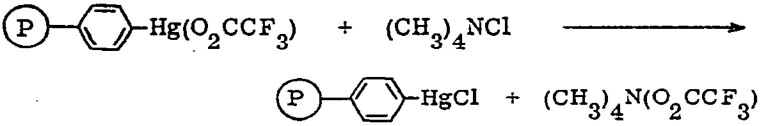
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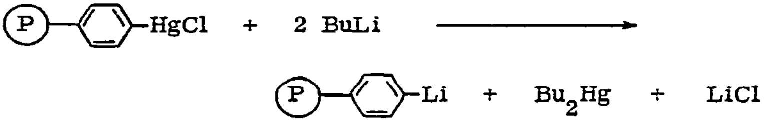
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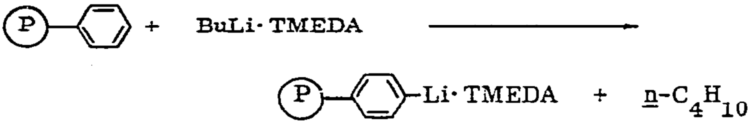
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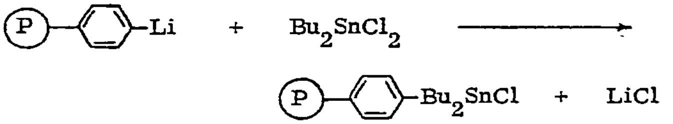
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The mercurations were performed in both dichloromethane and in methanol. The former swells the resin to approximately 142% of its dry volume, and the reaction proceeds rapidly and essentially quantitatively when 0.05 mmol of mercuric trifluoroacetate per gram of resin is allowed to react at room temperature. However, when the functionalized resin was treated with lithium napthalenide to reduce the resino-phenylmercuric chloride to elemental mercury, the grey color due to the mercury in a bisected bead, was observed to lie in an annular shell near the surface of the bead[14]. It was necessary, therefore, to use very dilute solutions of mercuric trifluoroacetate (0.0022 molar), relatively long reaction times (18 hours) and lower temperatures (0°) in order to distribute the mercury evenly. Exchange of the trifluoroacetate with chloride ion yielded the resino-phenylmercuric chloride substituted at a level of 0.04 mg-at. per gram. Even under these conditions, a weak concentration gradient was observed in some of the larger beads.

The aromatic mercuration proceeded much more slowly in methanol, a solvent which caused no swelling of the resin. In this solvent, a substantial excess of mercuric trifluoroacetate, more concentrated solutions, higher temperatures and long reaction times were required to produce a comparable level of substitution. However, when the resin was functionalized in methanol, the mercury was observed to be very evenly distributed, throughout even the largest beads. It seems likely that unswelled resins mercurated in methanol will have a greater percentage of their functional sites at, or near the surface of the internal microspheres[9] than swelled resins mercurated in dichloromethane. No difference in the reactivity or chemical properties of the two resins was observed.

Highly cross-linked polystyrene-divinylbenzene copolymers contain vinyl groups which have not undergone reaction during the process of polymerization. In Amberlite XAD-1 the concentration is ~ 0.22 meq per gram. Vinyl groups react with bromine[15], and mercury trifluoroacetate[16], and have the potential to react with many other electrophilic reagents. In order to form resino-phenyl-metal bonds exclusively, these groups were deactivated by treating the resin with n-butyllithium and tetramethylethylenediamine in toluene[17] followed by methanolysis[8,12,18]. The level of vinyl groups was decreased by a factor of at least 10 using this procedure, as determined by bromine uptake. It is likely that any groups remaining after treatment are relatively inaccessible and are less able to interfere with subsequent reactions. This method of reducing the concentration of vinyl groups in resins was described by Fyles and Leznoff who used cyclohexane as a solvent.[12] Subsequent experience in our laboratory has shown this solvent is superior to toluene for this reaction.

Resino-phenylmercuric chloride, reacted with excess n-butyllithium to form resino-phenyllithium, di-n-butylmercury, and lithium chloride (see equation 3). The extent of the reaction was determined by analyzing washings from the resin for chloride ion and for di-n-butylmercury. In one reaction, where the mercury and chlorine concentrations of the resin were 0.041 and 0.042 mg-at per gram respectively, 0.034 meq of chloride ion and 0.028 mmol of di-n-butylmercury were obtained from the washings. Thus, at least 81% of the resino-mercuric chloride groups were converted to resino-phenyllithium. Due to the inherent difficulties in washing material from the resin, it is likely that the reaction is nearly quantitative, and not all of the chloride was removed. Resino-phenyllithium has been formed by a number of other methods[4-6,12,13] including the lithium-bromine exchange reaction[19]. Our experience with this method was not very satisfactory. Untreated polymer beads were brominated using thallium acetate as catalyst. The reaction between n-butyllithium and resino-bromobenzene produced, in addition to n-bromobutane, large quantities of bromide ion. A sample of resino-bromobenzene containing 1.12 meq of bromine per gram of resin, reacted with excess n-butyllithium to yield 0.15 mmol of n-bromobutane and 0.31 meq of bromide ion. A second treatment of the resin yielded 0.015 mmol of n-bromobutane and an additional 0.31 meq of bromide ion. The bromide may arise from a coupling reaction[20] between n-butyllithium and resino-bromobenzene, between n-bromobutane and resino-phenyllithium formed by lithium-bromine exchange, or between n-butyllithium and n-bromobutane, or from a mixture of the three[†]. Since there is no simple way of knowing which reactions proceed or to what extent, it is a difficult reaction to evaluate. The total bromine found (0.80 meq per gram) was smaller

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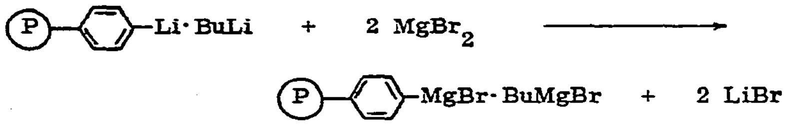
[†] Since the resino-bromobenzene for this particular study had not been treated with BuLi·TMEDA prior to bromination, some of the bromine must have been attached to positions other than the aromatic rings. The level of bromine incorporation indicated that approximately 0.26 mg-at of bromine was attached in this manner, per gram of resin. Although coupling reactions would preferentially take place at these sites, the amount of bromide produced exceeds this amount. Hence, the basic conclusions are unaffected.

than the original bromine concentration of the starting resin. Thus, it is evident that the reaction does not go to completion and considerable amounts of bromine remain attached to the resin[21].

Resino-phenyllithium can be formed directly from n-butyllithium and tetramethylethylenediamine[12,13]. In our hands, this reaction was rapid at room temperature, and produced resins which were very unevenly substituted as observed by converting a sample into resino-phenylmercuric chloride by treatment with a solution of mercuric chloride. The mercury was then visualized with lithium napthalenide. It was found necessary to treat the resin with a stoichiometric amount of n-butyllithium (0.025 meq per gram) and tetramethylethylenediamine at -78° and to slowly warm the reaction mixture while the reaction progressed. Very even distribution of mercury was seen under these circumstances. The reaction between mercuric chloride and resino-phenyllithium containing adsorbed n-butyllithium sometimes produced, in addition to resino-phenylmercuric chloride, elemental mercury; apparently this occurred more readily when resins were more highly substituted[22]. The resulting resin contained additional mercury and the uniformity of substitution was difficult to evaluate under these circumstances.

It has been noted that n-butyllithium was difficult to remove from cross-linked polystyrene resins[23]. Approximately 0.15 to 0.25 meq of n-butyllithium is adsorbed by one gram of unsubstituted, vinyl free Amberlite XAD-1. That the lithium reagent was adsorbed and not chemically bound to the resin was demonstrated by treating the resin with excess di-n-butyltin dichloride. The adsorbed n-butyllithium reacted to form tetra-n-butyltin (0.11 mmol per gram of resin) which was extracted from the resin, isolated, and quantitatively identified by ^{1}H nmr spectroscopy. The quantity of tetra-n-butyltin formed indicates that 0.22 meq of n-butyllithium had reacted. This amount therefore, was adsorbed onto the resin. The resin thereafter contained only traces of tin and chlorine indicating that essentially all of the n-butyllithium was adsorbed or it would have reacted to form resin-bound species containing tin. Attempts to remove the adsorbed *n*-butyllithium by exhaustively washing the resin with ether or toluene were unsuccessful. A sample of resino-phenyllithium, prepared from resino-phenylmercuric chloride, was treated with excess magnesium bromide in THF with the expectation that the *n*-butylmagnesium bromide which formed would be less strongly adsorbed than *n*-butyllithium. The



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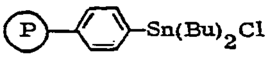
resino-phenylmagnesium bromide which formed reacted with di-*n*-butyltin dichloride to give resino-phenyldi-*n*-butyltin chloride. The chlorine-to-tin ratio of the resulting product (0.317) was higher than the chlorine-to-tin ratio of an otherwise identical resin which had not been treated with magnesium bromide (0.224). However, both resins contained the same amount of chlorine (0.00076 mg-at per gram) which is also indicative of the lower overall amount of tin incorporated. Hence, the reduction in adsorbed organometallic species was not significant.

Resino-phenyllithium reacts with di-*n*-butyltin dichloride to form resino-phenyldi-*n*-butyltin chloride (**1**, see equation 5). This reaction is accompanied by the reactions of adsorbed *n*-butyllithium. To minimize their effect, large excesses of di-*n*-butyltin dichloride were used. In these experiments the final chlorine concentration in the product was roughly 20% to 30% of that of the tin concentration. Di-*n*-butyltin dichloride may react with an adsorbed *n*-butyllithium forming



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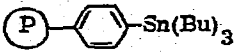
tri-*n*-butyltin chloride or tetrabutyltin. Tri-*n*-butyltin chloride may react further with resino-phenyllithium yielding resino-phenyltri-*n*-butyltin (**2**). Di-*n*-butyltin dichloride may also react with two resino-phenyllithium moieties to yield the doublyattached resino-diphenyldi-*n*-butyltin (3). In order to estimate the amount of each



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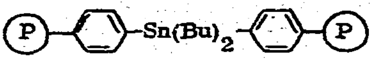

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of the species on the polymer, resino-phenyl-to-tin bonds were cleaved with hydrogen chloride[24]. The products, di-*n*-butyltin dichloride and tri-*n*-butyltin chloride, were extracted and treated with potassium hydroxide for quantitative estimation as di-*n*-butyltin oxide and bis(tri-*n*-butyltin) oxide respectively. Based on the initial tin concentration (0.0285 mg-at per gram of resin), the corresponding yields were 35% and 49%. The residual tin in the resin (16%) is assumed to be 1; the quantity there accounts for all of the tin.[†] Di-*n*-butyltin dichloride may either come from 1 or from 3. Thus, before cleavage, approximately 51% of the tin was present as 1 or as 3 and ~49% was present as 2. The high chlorine content after cleavage (0.024 mg-at per gram), together with the analysis of cleavage products, point to a substantial quantity of trapped chlorine, possibly LiCl, and suggest that the Cl:Sn ratio in the resin before cleavage was not an accurate measure of the number of Sn—Cl bonds present.

CONCLUSION

Functionalization of a macroreticular polystyrene/divinylbenzene copolymer with chlorodibutyltin groups bound only by (polymer) phenyl-to-tin bonds can be accomplished by a mercuration and lithiation route; for low level substitution, prior deactivation of unpolymerized vinyl groups is also required. The resulting resino-phenyllithium contains substantial amounts of adsorbed *n*-butyllithium which reacts with excess incoming dibutyltin dichloride giving significant amounts of tetrabutyltin and 2 in addition to 1.

[†] Cleavage of the phenyl—tin bond by HCl is expected to be much slower for 1 than for 2 or 3.[25]

EXPERIMENTAL

Purification of reagents: Toluene (Fisher) was twice distilled from sodium and benzophenone. Tetrahydrofuran (THF, Fisher) and hexane (Fisher, mixture of isomers) were twice distilled from potassium and benzophenone. Ether was twice degassed under vacuum at low temperatures and distilled from calcium hydride. Tetramethylethylenediamine (TMEDA, Aldrich 99%) was distilled from calcium hydride. Di-n-butyltin dichloride (Bu_2SnCl_2, ROC/RIC) was sublimed under vacuum. Dichloromethane (Fisher), methanol (Mallinckrodt), carbon tetrachloride (Fisher), trifluoroacetic acid (Aldrich 99% or PCR tech), n-butyllithium (BuLi, Alfa, in hexane), mercuric oxide (Mallinckrodt, red powder), tetramethylammonium chloride (Aldrich 97%), and thallium (III) acetate sesquihydrate (Aldrich) were not further purified.

The resins used in this study were obtained from the Rohm and Haas Company, Philadelphia, Pennsylvania: Amberlite XAD-1 (hereafter abbreviated XAD-1) is a macroreticular adsorbent containing 20% divinylbenzene and having a surface area of 100 m^2 per gram and an average pore diameter of 200 A. The resin was washed exhaustively with water, the "fines" being removed by flotation, and with at least four bed-volumes of methanol and dried at 100^o under vacuum (rotary evaporator) before use. All samples were treated with n-butyllithium (TMEDA complex) as described below, except as noted.

All reactions were performed under an atmosphere of purified argon except as otherwise specified. Extractions in columns or Soxhlet extractors were done in the air.

Proton nuclear magnetic resonance spectra (NMR) were taken on a Varian A60-A spectrometer and calibrated with external TMS. Gas chromatography was done by use of an Aerograph A90P3 chromatograph with a 10 ft. by 1/4 in. copper column packed with 15% Carbowax C-20m on 60/80 Chromosorb P. Neutron activation analyses were performed by R. A. Nadkarni, Materials Science Center Analytical Facility, Cornell University. Precision in these analyses is on the order of 3-5%.

Static electrical attraction was found to be a significant problem in handling dry resin beads. A Tesla coil discharged through glass walls of evacuated or argon-filled containers and completely quenched the static attraction. (Residual beads clinging to the sides were displaced by gently tapping the vessel.) The coil will not normally discharge through the wall of an air-filled container; however, the coil may be inserted through the neck of the vessel and activated.

Reactions of Amberlite XAD-1 with n-butyllithium and tetramethylethylenediamine. XAD-1 (100 g) was weighed into a large three-necked flask and suspended in toluene (130 ml). TMEDA (7.7 ml, 58 mmol) and n-butyllithium (25 ml, 2.4 N, 60 meq) were added and the resulting red-orange mixture was stirred at room temperature for 18 hours. Methanol was added to quench the reaction and then the white beads were washed free of toluene and by-products with methanol, loaded into a column, and washed with additional methanol (four bed-volumes minimum--ca. 1 liter) and dried under vacuum at 100° (rotary evaporator).

The amount of vinyl groups was evaluated by treating the resin (1-3 g) with an excess of bromine in methanol (ca. 0.5 mmol per gram of resin) in the dark. After being stirred for 15 min, the entire mixture was poured into an acidic potassium iodide solution (10 ml of 1 M HCl, 20 ml of H_2O, 15 ml of CH_3OH, 2 g of KI) and the iodine released was titrated with standard sodium thiosulfate solution using a starch indicator. The number of vinyl groups in the resin was then calculated from the bromine uptake. Vinyl groups before BuLi·TMEDA treatment: 0.218 meq per gram of resin. Vinyl groups after BuLi·TMEDA treatment: 0.022 meq per gram of resin.

Formation of resino-phenylmercuric chloride in dichloromethane. One hundred grams of XAD-1 was suspended in CH_2Cl_2 (2210 ml) in a three-necked flask, and cooled thoroughly in an ice bath. HgO (1.084 g, 5.00 mmol) dissolved in trifluoroacetic acid (25 ml) and CH_2Cl_2 (40 ml) was added to the cold resin suspension. The mixture was stirred for 18 hours at 0°; the resin was then placed in a column and washed with methanol (four bed-volumes minimum -- ~ 1 liter). The resin was stirred with a solution of $(CH_3)_4NCl$ (3 g, 27 mmol) in methanol for one hour in the air, then extracted with methanol (Soxhlet extractor) for at least 24 hours. Fresh extract was treated with a small amount (5 drops) of concentrated nitric acid and silver nitrate (5 ml of 0.05 M solution). The absence of cloudiness indicated that no chloride was present in the resin. The resin was then dried at 100° under vacuum (rotary evaporator). Anal. Found: Hg, 0.83% (0.041 mg-at per gram); Cl, 0.15% (0.042 mg-at per gram).

Formation of resino-phenylmercuric chloride in methanol. To 100 grams of XAD-1 suspended in methanol (250 ml) was added a solution of mercuric oxide (3.25 g, 15 mmol) in CF_3CO_2H (15 ml). The mixture was heated at 45° for 24 hours after which the resin was transferred to a column and washed with methanol (1 liter). The resin was stirred with a solution of $(CH_3)_4NCl$ (3 g, 27 mmol) in methanol (200 ml) in the air, for one hour. The resin was then extracted with methanol (24 hours, Soxhlet extractor). Anal. Found: Hg, 0.745% (0.037 mg-at per gram); Cl, 0.139% (0.039 mg-at per gram).

Reaction of resino-phenylmercuric chloride with lithium napthalenide. Resino-phenylmercuric chloride, from either of the above methods, (1 g) was suspended in THF (4-5 ml). Napthalene (approx 0.64 g, 5.0 mmol) and lithium wire (0.25 inch--0.025 g, 2.8 mg-at) were added, the lithium wire being added in small, freshly cut pieces under a positive argon flow. After a few seconds, the solution became dark green. Stirring was continued for 30 minutes, methanol was then added to destroy excess lithium. The grey beads were washed with methanol and air-dried. Selected beads were cleaved with a razor blade and examined under a microscope for uniformity of color. When these beads were allowed to stand in the air for 24 hours, most the the grey color was lost and the beads regained their white color due to evaporation of the mercury.

Reaction of resino-phenylmercuric chloride with n-butyllithium to form resino-phenyllithium. Resino-phenylmercuric chloride (100 g, mercurated in CH_2Cl_2, Hg, 0.041 mg-at per gram; Cl, 0.042 mg-at per gram) was placed in sufficient toluene to cover it by 2-3 mm in a 500 ml, three-necked flask. n-Butyllithium (62 ml, 2.4 N, 150 meq) was added via a gas-tight syringe and the resulting mixture was stirred for one hour at room temperature. The excess solvent was removed with a filter stick and the resin was washed with three 80 ml portions of toluene and four 100 ml portions of ether. The yellow resin product was used in subsequent reactions. Chloride and di-n-butylmercury were determined in the washings as follows: the washings were individually shaken with water and the combined aqueous layers were titrated for chloride using the modified Volhard procedure[26]. The toluene layer was treated with excess bromine and then shaken with a solution of sodium thiosulfate to remove excess bromine. The toluene solution was dried ($MgSO_4$) and analyzed for n-bromobutane by gas chromatography using ethyl acetate as an internal standard. Found: Cl^-, 0.034 mg-at per gram; Bu_2Hg, 0.028 mmol per gram.

The reaction was performed as above for resino-mercuric chloride that had been mercurated in methanol, except that 46 ml of n-butyllithium (2.4 N, 110 meq) was used.

Reaction of resino-phenyllithium with di-n-butyltin dichloride to form resino-phenyldi-n-butyltin chloride. Resino-phenylmercuric chloride (100 g, mercurated in CH_2Cl_2, Hg, 0.041 mg-at per gram; Cl, 0.042 mg-at per gram) was treated with n-butyllithium as above. A solution of Bu_2SnCl_2 (61 g, 200 mmol) in ether (75 ml) was added rapidly with stirring. The suspension of white resin and a fine precipitate was stirred at room temperature for two hours and then transferred to a Soxhlet extractor. The resin was extracted with methanol for 48 hours and dried under vacuum (100°, rotary evaporator). Anal. Found: Sn, 0.337% (0.0284 mg-at per gram); Cl, 0.038 (0.011 mg-at per gram).

Resino-phenylmercuric chloride (100 g, mercurated in methanol, Hg, 0.037 mg-at per gram; Cl, 0.039 mg-at per gram) was also treated with Bu_2SnCl_2 (12.2 g, 40 mmol) as above. Anal. Found: Sn, 0.338% (0.0285 mg-at per gram); Cl, 0.084% (0.0237 mg-at per gram).

Preparation of resino-phenyldi-n-butyltin chloride via a resino-phenyllithium intermediate prepared by direct lithiation with n-butyllithium and tetramethylethylenediamine. XAD-1 (10 g) was supended in hexane (60 ml) and TMEDA (0.328 ml, 2.5 mmol) was added via syringe. After cooling the mixture in a Dry Ice--methanol bath, n-butyllithium (1.60 ml, 1.56 N, 2.5 mmol) was added. The suspension was stirred for 5.5 hours at -78° and allowed to warm slowly to 15° over a 19.5 hour period. The pink-orange resin was then washed with three 25 ml portions of ether. A sample was removed under argon (1.28 g) and placed in a solution of mercuric chloride (1.0 mmol) in ether. This slightly grey sample was extracted with CH_3OH for 15 hours and then treated with lithium napthalenide to reveal very even mercury distribution. The remainder of the resin was treated with Bu_2SnCl_2 (6.07 g, 20 mmol) dissolved in ether (15 ml). The white resin mixture was stirred for 30 minutes, allowed to stand overnight, extracted for 24 hours with methanol (Soxhlet extractor) and dried under vacuum (100°, rotary evaporator). Anal. Found: Sn, 0.365% (0.0308 mg-at per gram); Cl, 0.023% (0.0065 mg-at per gram).

Preparation of resino-phenyldi-n-butyltin chloride via a resino-phenylmagnesium bromide intermediate and comparison with a resino-phenyllithium intermediate. Resino-phenylmercuric chloride [5 g, prepared in methanol as above except that 1 liter of CH_3OH, 1.083 g HgO (5.0 mmol) and 25 ml of CF_3CO_2H were used and the mixture was stirred for 24 hours at room temperature--Anal. Found: Hg, 0.069% (0.0034 mg-at per gram); Cl, 0.013% (0.0037 mg-at per gram)] was suspended in toluene (10 ml) and n-butyllithium (3.33 ml, 2.4 N, 8.0 mmol). After being stirred for one hour, the resin was washed with three 25 ml portions of ether, then treated with a solution of $MgBr_2$ in THF (10 ml, 0.187 N, 1.87 mmol--prepared from Mg filings and $HgBr_2$ under argon). The mixture was stirred for 45 minutes after which the resin was washed with three 25 ml portions of THF and treated with a solution of Bu_2SnCl_2 (0.607 g, 2.0 mmol) in THF (10 ml) for 45 minutes. Following extraction (CH_3OH, 24 hours) and vacuum drying (100°, rotary evaporator) the resin was analysed: Anal. Found: Sn, 0.029% (0.0024 mg-at per gram); Cl 0.0027% (0.00076 mg-at per gram).

Resino-phenylmercuric chloride (5 g from the same sample as above) was suspended in toluene (10 ml) and treated with n-butyllithium (3.33 ml, 2.4 N, 8.0 mmol) for one hour. After the yellow resin had been washed with three 25 ml portions of ether, it was treated with Bu_2SnCl_2 (0.607 g, 2.0 mmol) in ether (10 ml) for 45 minutes. Following extraction (CH_3OH, 24 hours) and vacuum drying (100°, rotary evaporator), the resin was analyzed: Anal. Found: Sn, 0.040% (0.0034 mg-at per gram); Cl, 0.0027% (0.00076 mg-at per gram).

Adsorption of n-butyllithium on unsubstituted Amberlite XAD-1 and subsequent reaction with di-n-butyltin dichloride. Unsubstituted XAD-1 (10.0 g) was covered by 2-3 mm with toluene in a small three-necked flask. The resin was then treated with n-butyllithium (4.6 ml, 2.4 N, 11 meq--1.1 meq per gram) for one hour at room temperature. After the excess solvent was removed with a syringe and the yellow resin was washed with five 15 ml portions of ether, a sample was removed (0.480 g) and quenched with methanol. The liberated base was titrated with standard acid. To the remainder of the sample were added Bu_2SnCl_2 (0.764 g, 2.51 mmol) and ether (10 ml). The mixture was stirred at room temperature for 15 minutes, then allowed to stand for 15 hours. The entire mixture was quantitatively transferred to a Soxhlet extractor and extracted with ether for 42 hours, then with methanol for 48 hours. The ether extract was shaken with two 100 ml portions of 20% aqueous KOH. The white precipitate which formed was collected on a tared frit, dried and weighed as Bu_2SnO. The ethereal solution was evaporated to dryness and the residue was dissolved in carbon tetrachloride and analyzed by NMR using an internal, toluene standard. The NMR spectrum was identical to that of an authentic sample of Bu_4Sn: NMR (CCl_4) δ 0.8-2.4 (m, $C_4\underline{H}_9$).

	ANALYSIS (mmol per 9.52 g)	ANALYSIS (mmol per gram)
Bu_2SnCl_2 added	2.51	0.263
Bu_2SnO recovered	1.47 (0.366 g)	0.154
Bu_4Sn found	1.03 (0.356 g)	0.108
Residual Sn on resin	0.044	0.0046 (0.055%)
Total Sn accounted for	2.54	0.267
Adsorbed Base (methanolysis)	2.13	0.224
BuLi required to form Bu_3Sn	2.06	0.216
Residual Cl on resin	0.00045	0.00045 (0.0016%)

Formation of resino-bromobenzene[27]. Unsubstituted XAD-1 (25 g, not treated with BuLi and TMEDA) was suspended in CCl_4 (350 ml). $Tl(OAc)_3 \cdot 1 \cdot 5H_2O$ (1.5 g) was added as a catalyst. Bromine (4.34 g, 27.2 mmol) dissolved in CCl_4 (50 ml) was added to the suspension, in the dark, over a two hour period. The color of the bromine was discharged rapidly as it was added; the mixture being stirred for five hours after addition was complete. The resin was transferred to a column and washed with 1:3:4 conc HCl--H_2O--dioxane (150 ml) and with water, methanol, dioxane, and ether (two bed-volumes each) and dried under vacuum for 24 hours. *Anal*. Expected: Br, 7.99% (1.0 mg-at per gram); Found: Br, 8.94% (1.12 mg-at per gram).

Lithium-halogen exchange of resino-bromobenzene with n-butyllithium to form resino-phenyllithium. Resino-bromobenzene (1.0 g; Br, 1.12 mg-at per gram) and toluene (2.3 ml) were mixed together in a small Schlenk tube. *n*-Butyllithium (1.7 ml, 2.4 N, 4 mmol) was added and the mixture was stirred for four hours.

The solvent was removed and the resin was washed with three 5 ml portions of toluene and three 8 ml portions of ether. The toluene washings were analyzed for n-bromobutane by gas chromatography and the ether washings were shaken with water and analyzed for chloride by the modified Volhard method[26]. The resin was again treated with butyllithium and toluene and again washed with toluene and ether. Methanol was then added to the resin and the liberated base was titrated with standard acid. Anal. Found: First BuLi treatment: BuBr, 0.15 mmol; Br^-, 0.32 meq; Second BuLi treatment: BuBr, 0.015 mmol; Br^-, 0.31 meq; Base released with methanol treatment, 0.73 meq.

Cleavage of resino-phenyldi-n-butyltin chloride with hydrogen chloride. Resino-phenyldi-n-butyltin chloride (10 g, Sn, 0.0285 mg-at per gram; Cl, 0.0237 mg-at per gram) was suspended in dichloromethane (35 ml) and cooled to -18° in an ice/salt bath. Gaseous HCl was slowly bubbled through the suspension for 15 minutes followed by a 30 minute argon purge. The mixture was transferred quantitatively to a small Soxhlet extractor, extracted with methanol over KOH for 12.5 hours, and dried under vacuum (100°, rotary evaporator). The methanol extract was evaporated to dryness, the residue was mixed with ether (50 ml) and shaken with two 25 ml portions of 20% aqueous KOH. The resulting insoluble, white precipitate was filtered and weighed as Bu_2SnO. The ether was evaporated and

	ANALYSIS (mmol per 10 g)	ANALYSIS (mmol per gram)
Initial Sn on resin	0.285	0.0285 (0.338%)
Bu_2SnO found	0.10 (0.025 g)	0.010
$(Bu_3Sn)_2O$ found	0.07 (0.042 g)	0.007
Residual Sn on resin	0.045	0.0045 (0.054%)
Tin accounted for	0.285 (100%)	0.0285
Residual Cl on resin	0.240	0.024 (0.085%)

the oily, colorless residue was redissolved in CCl_4 and analyzed by NMR using an internal, toluene standard. The NMR spectrum of the product was identical to that of an authentic sample of $(Bu_3Sn)_2O$: NMR (CCl_4) δ 1.1-2.2 (m, C_4H_9SnO).

The method of analysis was tested on known mixtures of Bu_3SnCl and Bu_2SnCl_2 with excellent results.

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