their adverse effect upon the formation and decay of the primary photoreduction product $[ReBr(CO)_3(bpy)]^-$ (eq 2). (4) While bromide ion has been reported to increase the long-term stability of the catalytic system, it appears to play no direct role in the production of CO. Likewise, reduction of bicarbonate ion (rather than CO_2) to CO can be discounted as a significant process. (5) Thermal chemistry continues to occur for several hours after the cessation of photolysis. The available evidence suggests that such behavior arises from processes unrelated to the formation of CO.

Further advances in understanding the mechanism of CO_2 reduction in this system await characterization of catalytically active Re-containing intermediates. Efforts directed along these lines are underway in this laboratory.

Reactions of Organotin Hydrides with Lithium Diisopropylamide and Organolithiums. Reactivities of the Intermediates and of the Lithium Hydride Produced

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Equimolar lithium diisopropylamide (LDA) and trimethyltin hydride (TMTH) react in tetrahydrofuran (THF) to form diisopropylamine and (trimethylstannyl)lithium, but in diethyl ether or hexanes 2 mol of TMTH is required for complete reaction and the products are diisopropylamine, hexamethylditin, and lithium hydride. When organic halides are present in this reacting system, reduction to alkane or substitution to form the trimethylalkyltin may occur depending on the nature of the halide. These and other observations suggest that (trimethylstannyl)lithium is formed as an intermediate yielding the tetraalkyltin. Studies on the products and stoichiometries of the reductions of alkyl bromides in ether and hexanes suggest that three reducing agents may be involved: TMTH, $[Me_3Sn(H)N-i-Pr_2]^-$, and $[Me_3SnSn(H)Me_3]^-$. The latter predominates in ether, and either or both of the others predominate in hexanes. Formation of methylcyclopentane from 1-bromo-5-hexene suggests involvement of a free radical mechanism. When methyllithium is used instead of LDA in the reaction with TMTH, the products are tetramethyltin and lithium hydride. This reaction can also be diverted to reduction by the presence of primary bromides. Aryl bromides react in both systems, but the yields of either substitution or reduction products are low. The lithium hydride formed in these reactions is extremely reactive as a base as shown by a brief study of its reaction with weak carbon acids and amines and as a nucleophile by its reaction with hexamethylditin to form (trimethylstannyl)lithium in THF.

Studies on the mechanisms of reactions of (triorganostannyl)alkalis with organic halides have revealed significant effects of solvent and donor addends on the competition between the S_N2 and electron-transfer mechanisms. For example, both mechanisms are observed in the reaction of (trimethylstannyl)sodium with 2-bromooctane in tetrahydrofuran (THF) and the S_N2 component increases upon addition of 18-crown-6.[1] This component disappears when the solvent is an 80:20 ether/THF mixture. Furthermore, 1-bromo-5-hexene yields no cyclized product (by way of 5-hexenyl radicals) in THF, but about 10% is formed in the ether/THF mixtures.[1,2] Observations such as these suggest that useful structure/reactivity information could be obtained if the reactions could be conducted in very poor donor solvents. Then studies could be made in a wide range of donor solvent systems by introduction of suitable donor addends. The method which has been used for the preparation of (organostannyl)alkalis in most mechanistic studies involves the reaction of the metal with hexalkylditin; however, this method is unsatisfactory in poor donor solvents such as ethyl ether. Therefore, it was decided to explore use of an alternative method that did not involve reduction by the alkali metal.

Lithium Diisopropylamide

The method of Still[3] that involves the reaction of the triorganotin hydride with lithium diisopropylamide (LDA) (eq 1) and provides essentially quantitative yields of (trialkylstannyl)lithium in THF was explored.

$$Me_3SnH + i\text{-}Pr_2NLi \rightarrow Me_3SnLi + i\text{-}Pr_2NH \quad (1)$$
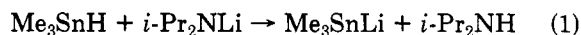
When equimolar amounts of the reactants of eq 1 were mixed in cyclohexane or diethyl ether at 0 °C and allowed to stand, a white precipitate formed and NMR showed the presence of hexamethylditin and equal amounts of LDA and diisopropylamine. The presence of the unreacted LDA suggested that the stoichiometry of the reaction which occurred was that of eq 2, and this was confirmed by its

$$2Me_3SnH + i\text{-}Pr_2NLi \xrightarrow[\text{hexanes}]{\text{ether or}} (Me_3Sn)_2 + i\text{-}Pr_2NH + LiH \quad (2)$$
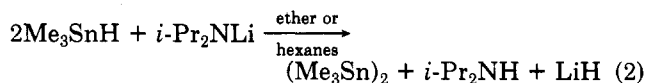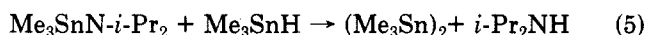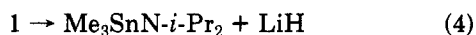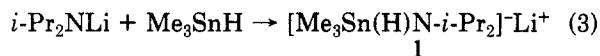
absence in the reaction product mixture when this stoi-

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(2) Ashby, E. C.; Su, W.-Y.; Pham, T. N. *Organometallics* **1985**, *4*, 1493.
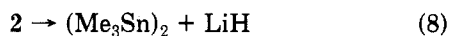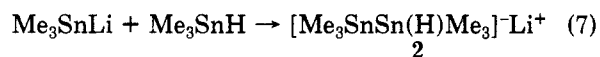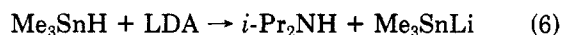(3) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.

chiometry was used. Upon hydrolysis the LiH dissolved and 1 mol of hydrogen was evolved. Similar results were obtained with tri-*n*-butyltin hydride and triethyltin hydride. However, triphenyltin hydride in ether yielded a yellow solution and no precipitate of LiH, suggesting the formation of (triphenylstannyl)lithium. This was confirmed by addition of methyl iodide that led to the formation of methyltriphenyltin in 74% isolated yield. Presumably this difference between the phenyl and alkyl analogues is due to the greater stability of (triphenylstannyl)lithium, reflected in the greater acidity of the phenyl analogue by about 7 pK_a units,[4] although the bulk of the phenyl groups may also play a role.

Perhaps the most obvious possible mechanism for the reaction with trimethyltin hydride (TMTH) is represented in eq 3-5. Although LDA normally functions as a base,

$$i\text{-}Pr_2NLi + Me_3SnH \rightarrow [Me_3Sn(H)N\text{-}i\text{-}Pr_2]^-Li^+ \quad (3)$$
$$\mathbf{1}$$

$$\mathbf{1} \rightarrow Me_3SnN\text{-}i\text{-}Pr_2 + LiH \quad (4)$$

$$Me_3SnN\text{-}i\text{-}Pr_2 + Me_3SnH \rightarrow (Me_3Sn)_2 + i\text{-}Pr_2NH \quad (5)$$

it might function as a donor ligand to form the hydrido ate complex **1**. This could react with the lithium ion to form the hydride and the tin amide (eq 4). The latter, in turn, could react with TMTH to form hexamethylditin and diisopropylamine (eq 5). To test this the reaction of eq 5 was carried out with the authentic reactants; it proceeded to the extent of only 26% in 2 h at 25 °C, whereas the reaction of eq 2 was complete in less than 30 min at 0 °C. Thus eq 3-5 do not comprise a valid mechanism.

An alternative scheme is represented in eq 6-8. In this scheme the formation of (trimethylstannyl)lithium occurs as originally expected, but it reacts with TMTH to form the ditin ate complex **2**. This then fragments to form

$$Me_3SnH + LDA \rightarrow i\text{-}Pr_2NH + Me_3SnLi \quad (6)$$

$$Me_3SnLi + Me_3SnH \rightarrow [Me_3SnSn(H)Me_3]^-Li^+ \quad (7)$$
$$\mathbf{2}$$

$$\mathbf{2} \rightarrow (Me_3Sn)_2 + LiH \quad (8)$$

lithium hydride and the ditin. Precedent for nucleophilic substitutions analogous to eq 3, 4 and 7, 8 comes from reactions of alkyllithiums with tetraorganotins, leading to displacement of carbanions.[5-9] We have also observed that mixtures of (trimethylstannyl)sodium and hexamethylditin give only one methyl proton signal in the NMR spectra with chemical shifts intermediate between those of the individual species. Broadening of the lines is also observed, indicating rapid exchange of the tins on the NMR time scale.[10] More recently Kozima et al. have reported similar observations using both ${}^1H$ and ${}^{119}Sn$ NMR spectroscopy, with ditins and (trialkylstannyl)lithiums.[11] As will be described below competition between proton abstraction

Figure 1. Rate of ditin formation as function of tin hydride, amide, and solvent at 0 °C: a, $2Me_3SnH$ + LDA in ether; b, $2Bu_3SnH$ + LDA in ether; c, $2Me_3SnH$ + LDA in hexanes; d, $2Bu_3SnH$ + LDA in hexanes; e, $2Me_3SnH$ + Ph_2NLi in ether.

and displacement of hydride can occur when TMTH is treated with methyllithium in the presence of a strong cation coordinating agent. Thus it seemed reasonable to expect that TMTH and (trimethylstannyl)lithium could undergo hydrogen–lithium exchange (eq 9) in THF in preference to the nucleophilic process of eq 7. In order

$$Me_3SnH + Me_3Sn*Li \rightleftarrows Me_3SnLi + Me_3Sn*H \quad (9)$$
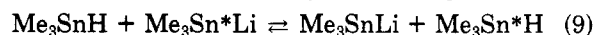
to test this, (trimethylstannyl)lithium was treated with triethyltin hydride and triphenyltin hydride in separate experiments in THF. In each case TMTH was shown to be formed, thus demonstrating the occurrence of the reactions analogous to eq 10. In neither case was the formation of lithium hydride observed.

In order to obtain direct evidence for the nucleophilic displacement analogous to eq 7 and 8 (trimethyltannyl)-lithium was prepared in ether according to Still[12] (eq 10) and treated with TMTH and triethyltin hydride (eq 11 and 12). The reactants of eq 11 yielded 83% of hexa-

$$(Me_3Sn)_2 + MeLi \rightarrow Me_3SnLi + Me_4Sn \quad (10)$$

$$Me_3SnLi + Me_3SnH \rightarrow (Me_3Sn)_2 + LiH \quad (11)$$

$$Me_3SnLi + Et_3SnH \rightarrow Et_3SnSnMe_3 + LiH \quad (12)$$

methylditin and that of eq 12 yielded 30% of the mixed ditin along with 15% of hexamethylditin and 17% of hexaethylditin. The appearance of all three ditins confirms the participation of the reversible lithium–hydride exchange (eq 9).

If the scheme of eq 6-8 is valid, and the initial step is rate-determining, the overall rate should depend on the acidity of the tin hydride and the strength of the base. Figure 1 shows the rates of ditin formation for two tin hydrides, two bases, and two solvents. TMTH reacts with LDA faster than does tri-*n*-butyltin hydride (TBTH); each reacts faster in ether than in hexanes, and LDA reacts faster than the weaker base lithium diphenylamide. These observations are consistent with this proposal, although steric effects might play a role in the TBTH case in slowing the rate of reaction 7. The greater rate in ether is attributable to the importance of solvation in the formation and stability of (trimethylstannyl)lithium.

Evidence for the existence of the hydridostannate **2** was sought by a ${}^{119}Sn$ NMR study. When 2 equiv of TMTH

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(11) Kobayashi, K.; Kawanisi, M.; Kozima, S.; Hitomi, T.; Iwamura, H.; Sugawara, T. *J. Organomet. Chem.* **1981**, *217*, 315.
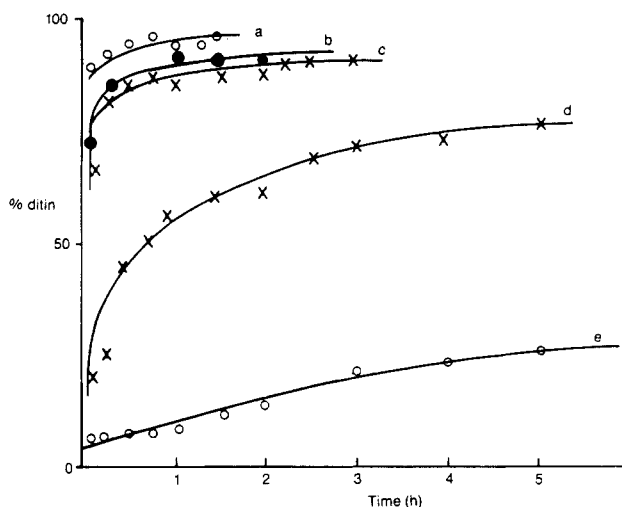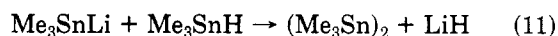
(12) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836.

Table I. Reactions of Alkyl Halides (1 equiv) with Me₃SnH (2 equiv) and LDA (1 equiv) at 0 °C

entry	R–X	solv	R–H	R–SnMe₃	Me₆Sn₂
1	1-bromooctane	Et₂O	90	8	92
2	1-bromooctane	hexanes	93	7	40
3	(chloromethyl)tri-methylsilane	Et₂O		78	19
4	(chloromethyl)tri-methylsilane	hexanes		66	29
5	1-chloroheptane	Et₂O	2	27	68
6	1-chloroheptane	hexanes	9	32	65
7	(chloromethyl)tri-methylsilane[a]	Et₂O		89	9
8	(chloromethyl)tri-methylsilane[a]	hexanes		71	26
9	1-chloroheptane[a]	Et₂O	2	56	42
10	1-chloroheptane[a]	hexanes	8	63	34

[a] 5 equiv of halide used.

Table II. Reactions of Alkyl Halides (1 equiv) with R₃SnH (1 equiv) and LDA (1 equiv) at 0 °C[a]

| entry	R–X	solv	addend	R–H	Me₆Sn₂
1	1-bromooctane	Et₂O		54	95
2	1-bromooctane	hexanes		70	50
3	1-bromooctane	hexanes	a, b	91	5
4	1-bromooctane	hexanes	b, c	83	2
5	1-bromoadamantane	Et₂O		56	88
6	1-bromoadamantane	hexanes		80	40
7	1-iodoheptane	Et₂O		78	26
8	1-iodoheptane	hexanes		94	0
9	1-bromooctane[d]	hexanes		97	0

[a] To 1 mmol of 1-bromooctane and 1 mmol of TMTH in 2 mL of Et₂O or hexanes at 0 °C was added 1 mmol of LDA in 0.6 mL of cyclohexane; the mixture was stirred 20 min, quenched, and analyzed by GLPC. [b] 10 mol % benzoquinone. [c] 5 mol % *m*-dinitrobenzene. [d] Bu₃SnH used instead of Me₃SnH.

Table III. Effect of LDA Added on Extent of Reduction of 1-Bromooctane in the Presence of 1 equiv of Me₃SnH in Hexanes[a]

added: LDA, equiv	0.25	0.50	0.75	1.00
found: octane, %	32	58	67	74
1-bromooctane, %	67	40	29	14
hexamethyldistannane, %			32	56

[a] To a solution of 1.0 mmol of 1-bromooctane and 1.0 mmol of TMTH and 1 mL of hexanes at 0 °C were added four 0.25-mmol increments of LDA (1.6 M solution in cyclohexane); the solution was analyzed by GLPC 10 min after each addition.

and 1 equiv of LDA were mixed at −85 °C in ether, only the signal at −101.0 ppm for TMTH was observed. When the temperature was raised to −40 °C, a signal for hexamethylditin at −112.0 ppm and a very weak and broad one for (trimethylstannyl)lithium and −189.2 ppm appeared, along with the TMTH signal shifted to −105.0 ppm. The same experiment in hexanes showed the TMTH signal at −104.2 ppm at −85 °C. At −40 °C this signal appeared at −104.8 ppm and was accompanied by one at −111.2 ppm due to hexamethylditin. No signal attributable to (trimethylstannyl)lithium was observed. These observations imply that, if **2** is indeed formed, it is present in such a low concentration that it could not be detected and that eq 7 is not rapid and reversible on the NMR time scale because both of the reactants show distinct signals. Furthermore, the lifetime of Me₃SnLi in hexanes is so short, or its solubility is so low, that it cannot be detected in these experiments, but its presence is established in ether.

As the NMR experiment in ether indicated the presence of Me₃SnLi, it was decided to seek to trap it by chemical reaction. When the reaction of LDA and TMTH was conducted in the presence of 1-chloroheptane, low yields of heptyltrimethyltin were obtained, along with substantial amounts of hexamethyltin, entries 5 and 6, Table I. An excess of chloroheptane provided a higher yield of substitution product, entries 9 and 10. We interpret this to be the result of the reaction of the stannyllithium with the chloroheptane in competition with the reactions of eq 7 and 8. When (chloromethyl)trimethylsilane was used, higher yields of substitution product were found, entries 3, 4, 7, and 8. Yields of hexamethylditin were much lower. When bromooctane was used, two important differences were observed, entries 1 and 2. First, the major product was octane. This was striking because 1-bromooctane and (chloromethyl)trimethylsilane react at essentially the same rates with (trimethylstannyl)lithium in THF at 20 °C to form the respective substitution products.[13] Thus the pathway leading to octane in the present case occurs much more rapidly than that leading to substitution. The other difference is the very large dependence of the yield of hexamethylditin on the solvent, despite nearly quantitative yields of octane in each case. (The balance of the trimethyltin groups are in the aqueous layer and do not show up in the GLPC analysis used to obtain the data in the table.) This suggests that one reducing agent is operating in ether and another participates in hexanes. Lithium

hydride is not involved: if the reaction of eq 2 is allowed to go to completion and bromooctane is then added, no significant reduction occurs. As ditin is the tin product in ether, compound **2** is a likely candidate as the reducing agent (eq 13). This reaction, preceded by reactions 1 and 7, results in the proper stoichiometry.

$$2 + BrC_8H_{17} \rightarrow (Me_3Sn)_2 + C_8H_{18} + LiBr \quad (13)$$
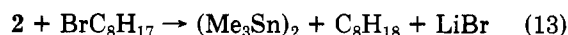
The second reductant requires a different stoichiometry. This is seen in Table II which presents results from reactions in which only 1 equiv of TMTH was used per equivalent each of LDA and halide. As seen in entry 1 the yield of octane in ether is only 54% while 95% of the tin appears as ditin. In hexane (entry 2), however, the yield of octane is 70% and that of ditin is only 50%. Similar results are seen in entries 5 and 6 for bromoadamantane. Thus this second reductant appears to require a 1:1:1 stoichiometry. Another point of significance is the effect of the inhibitors benzoquinone and *m*-dinitrobenzene. The yield of ditin drops to near zero and the yield of octane increases to 91% and 83%, entries 3 and 4. This is a clear indication that the process responsible for the reduction in ether is strongly inhibited relative to that which appears in hexanes. TMTH itself must be considered as a candidate for the second reductant.

The rate of the uncatalyzed reduction of primary bromides such as 1-bromooctane by TMTH is very slow under the conditions of these experiments. For example, no detectable reduction was observed within 1 h. However, if an electron-transfer process from an anion to the halide occurs, free radicals would be generated which could initiate the free radical chain reduction. To test this, increments of LDA were added to a 1:1 mixture of 1-bromooctane and TMTH, and the product mixture analyzed by GLPC. It can be seen from the results in Table III for the addition of 0.25 and 0.50 equiv of LDA the extent of reduction slightly exceeds the amount added, so there appears to be some reduction by TMTH; however, this is not evident when 0.75 equiv is added. On the other

(13) Prezzavento, B. A. Ph.D. dissertation, State University of New York at Albany, 1985.

Table IV. Effect of LDA Added on Extent of Reduction of 1-Iodoheptane in the Presence of 1 equiv of Me₃SnH in Hexanes[a]

added: LDA, equiv	0.2	0.4	0.6	0.8	1.0
found:[b] heptane, %	74	84	94	98	99
1-iodoheptane, %	24	13	5	0	0

[a] Procedure and scale of reaction same as for Table III. [b] No hexamethyldistannane found.

Table V. Reaction of 6-Bromo-1-hexene with n equiv of Me₃SnH and 1 equiv of LDA[a]

entry	n	solv	⌂//	⬡	⬠//	Me₃Sn₂[b]
1	2[c]	Et₂O	71[c]	20	0.28	
2	2	Et₂O	77	16	0.21	97
3	2	hexanes	76	18	0.24	27
4	1[c]	Et₂O	51	45	0.88	
5	1	Et₂O	41	18	0.44	86
6	1[c]	hexanes	51	46	0.90	
7	1	hexanes	45	32	0.71	48

[a] To 1.04 mmol of 6-bromo-1-hexene in 2 mL of ether or hexanes was added 1.04 mmol of LDA in 0.66 mL of cyclohexane at 0 °C; after 20 min the reaction mixture was quenched with water and analyzed by GLPC. [b] Actual yield in %. [c] Photoinduced reaction without addition of LDA.

hand, the results in Table IV for 1-iodoheptane show clear-cut initiation. For example the addition of 0.4 equiv of LDA leads to an 84% yield of heptane. This is understandable because the chain lengths in the reduction of iodides with TMTH must be considerably greater than those for bromides, as reflected in their high rates of reduction.[14] The likely participation of TMTH is also seen in entries 7 and 8 of Table II for this iodide in which only 26% of ditin is formed in ether and none in hexanes. What is the fate of the tin in such a case? ¹H, ¹³C, and ¹¹⁹Sn NMR examination of the product mixtures showed that it appears as trimethyltin diisopropylamide, presumably according to reactions 14 and 15. However, the same

$$Me_3SnH + BrC_8H_{17} \rightarrow Me_3SnBr + C_8H_{18} \quad (14)$$

$$Me_3SnBr + i\text{-}Pr_2NLi \rightarrow Me_3SnN\text{-}i\text{-}Pr_2 + LiBr \quad (15)$$

stoichiometry is required if the reducing agent is the hydridotin amide 1 (eq 16). In view of the nature of the data presented in Tables III and IV it appears that eq 16 may be important for the bromides and eq 14 for the iodide.

$$1 + BrC_8H_{17} \rightarrow C_8H_{18} + LiBr + Me_3SnN\text{-}i\text{-}Pr_2 \quad (16)$$
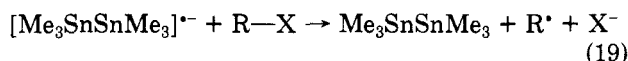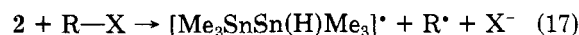
Implicit in the discussion of mechanism above is the assumption that the reductions occur by free radical chain processes. Therefore the behavior of 6-bromo-1-hexene was briefly examined, with the results shown in Table V. Entries 1, 4, and 6 are for the photoinitiated reduction by TMTH alone. Entries 1 and 4 show that in ether the proportion of product resulting from cyclization of the 5-hexenyl radical is smaller when the initial TMTH concentration is larger, as expected. The result in hexane (entry 6) is very similar to that of the corresponding experiment (entry 4) in ether. The reactions in the presence of LDA show a pattern of higher ditin yields in ether vs. hexanes seen before. The ratio of methylcyclopentane to 1-hexene is about the same for the first three entries. In view of the fact that the postulated reducing agent in ether, 2, is present in exceedingly small concentrations, this would be unexpected unless 2 is an exceptionally good hydrogen atom donor. That the similarity in these ratios is coin-

Table VI. Reactions of p-Bromotoluene (1 equiv) with Me₃SnH (2 equiv) and LDA (1 equiv)[a]

entry	solv	Ar–H[b]	Ar–SnMe₃[b]	Me₆Sn₂[b]
1	Et₂O	4	55	41
2	hexanes	7	58	32
3	Et₂O[c]	6	41	33
4	hexanes[c]	15	47	33

[a] To 1.02 mmol of p-bromotoluene and 2.04 mmol of TMTH in 2 mL of Et₂O or hexanes at 0 °C was added 1 mmol of LDA in 0.64 mL of cyclohexane; after 20 min the solution was quenched with water and analyzed by GLPC. [b] Actual yields in %. [c] Reaction in the presence of 5 equiv of i-Pr₂NH.

cidental is seen by comparing entry 4 with 5 and entry 6 with 7 in which the proportion of methylcyclohexane is considerably lower in the LDA-induced reactions decreased when the initial TMTH concentration is halved. The chain process that can be written for 2 is shown in eq 17–19.

$$2 + R\text{—}X \rightarrow [Me_3SnSn(H)Me_3]^{\cdot} + R^{\cdot} + X^- \quad (17)$$

$$R^{\cdot} + 2 \rightarrow R\text{—}H + [Me_3SnSnMe_3]^{\cdot-} \quad (18)$$

$$[Me_3SnSnMe_3]^{\cdot-} + R\text{—}X \rightarrow Me_3SnSnMe_3 + R^{\cdot} + X^- \quad (19)$$

The inhibition reflected in the data of Table II should affect reactions 18 and 19 only, because carbon radicals are involved in each of the three chain mechanisms considered, but this process differs due to participation of distannane radicals. Chain termination could occur by reaction of the benzoquinone and the m-dinitrobenzene with the radical anion formed in eq 18 or the radical formed in eq 17, or both. The ate radical should have a very weak Sn–H bond that would make it an exceptionally efficient hydrogen atom donor, thus accounting for the efficiency in trapping the hexenyl radical. The radical anion formed in eq 18 must be an exceptionally good electron donor. Thus the overall reduction can be very fast via long chains as required by the apparently low concentration of 2. This makes it particularly susceptible to inhibition.
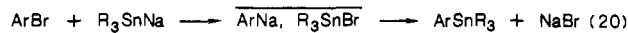
The mechanistic postulates presented above can be summarized as follows. Three reducing agents may be operating: TMTH, hydridotin amide ate complex, 1, and the hydridodistannane ate complex, 2. The latter appears to be the major one in ether with bromoheptane, and TMTH appears to dominate in hexanes in the reduction of iodoheptane. However, all three may be competing with varying degrees of importance depending on the solvent and the substrate. The data at hand do not justify a more detailed specification of the mechanistic picture. (Trimethylstannyl)lithium is actually formed as shown by the formation of tetraalkyltins upon reaction with chlorides. It can also react with TMTH to form the ate complex 2 that can decompose to form lithium hydride and hexamethylditin. If halides that are particularly susceptible to electron transfer or bromine atom abstraction are present, reduction by 1, 2, or TMTH occurs so fast that substitution by the stannyllithium does not compete effectively.

Aryl Halides

A brief study was made to ascertain how aryl bromides behave in this reducing system. p-Bromotoluene was allowed to react with 1 equiv of LDA and 2 equiv of TMTH in ether and hexanes with the results shown in entries 1 and 2 of Table VI. Small amounts of toluene along with fair yields of trimethyl-p-tolyltin and hexamethylditin were formed. When a fivefold excess of diisopropylamine was used (entries 3 and 4), the yield of toluene increased

(14) Wursthorn, K. R.; Kuivila, H. G.; Smith, G. F. *J. Am. Chem. Soc.* 1978, *100*, 279.

primarily at the expense of the tetraorganotin with little, if any, effect on the yield of ditin. These results are explicable in terms of the established mechanism for the reactions of (trialkylstannyl)alkalis with aryl bromides.[14] This is initiated by a halogen–metal exchange reaction and reaction of the resulting aryl anion with the tin halide to form substitution product either in a geminate reaction or after diffusion and reencounter (eq 20). In the presence

$$\text{ArBr} + \text{R}_3\text{SnNa} \longrightarrow \overline{\text{ArNa, R}_3\text{SnBr}} \longrightarrow \text{ArSnR}_3 + \text{NaBr} \quad (20)$$

$$\text{NaA} + \text{ArH} \xleftarrow{\text{HA}} \text{ArNa} + \text{R}_3\text{SnBr} \xrightarrow{\text{R}_3\text{SnNa}} (\text{R}_3\text{Sn})_2 \quad (21)$$

of a proton donor the free aryl anion can be trapped by acid HA, which is the amine in the present instance. This is a very weak acid, making the trapping of the aryl anions as toluene rather inefficient. The ditin is presumed to be formed by the competing overall process of eq 21. Formation of toluene via free radical reduction by a hydride species is considered unlikely because bromide abstraction from the benzene ring by organotin radicals is very slow in comparison to abstraction from alkyl groups.

Alkyllithiums

If the hypothesis that the ditin ate hydride 2 can function as a highly effective reducing agent is valid, then such complexes with nucleophiles other than the triorganotin anion should also be effective. Organolithiums offered special promise because they have been shown to function as nucleophiles for displacement of organic groups such as carbanions from tin.[7,9,15–19] Indeed, Reich has reported compelling ^{119}Sn and ^{1}H NMR evidence for the formation of Me$_5$SnLi in THF/HMPA at −80 °C; he also offered evidence for mixed phenyl/methyl pentaorganostannates.[20] With respect to the displacement of the hydride ion, Wittig[21] reported that methyllithium reacted in ether with triphenyltin hydride by proton abstraction, but Gilman[22] reported formation of lithium hydride instead (eq 22). The validity of this result is supported by the

$$\text{Ph}_3\text{SnH} + \text{MeLi} \rightarrow \text{Ph}_3\text{SnMe} + \text{LiH} \quad (22)$$
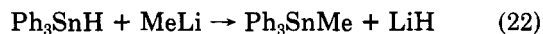
recent observation by Weichmann and Tzschach[23] of the formation of lithium hydride and butyltricyclohexyltin from the reaction of tricyclohexyltin hydride with butyllithium and that by Newcomb of the formation of tetrabutyltin from the reaction of butyllithium with TBTH.[24]

When we treated TMTH in ether or hydrocarbons with n-butyllithium in hexane, lithium hydride and n-butyltrimethyltin were formed. The rate of this reaction proved to be very sensitive to the donor power of the solvent as shown in Figure 2: the reaction is complete in a matter of minutes in ether/hexanes; it requires hours in hexanes, alone; and the rate is intermediate in benzene/hexanes. We therefore followed the approach of Reich[20] in seeking

(15) Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1959**, *24*, 1395; **1961**, *26*, 4797.

(16) Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1961**, *83*, 883; **1962**, *84*, 361.

(17) Seyferth, D.; Vaughan, L. F. *J. Org. Chem.* **1964**, *86*, 883.

(18) Suzuki, R. *J. Organomet. Chem.* **1964**, *1*, 437.

(19) Seyferth, D.; Suzuki, R.; Murphy, C. J.; Sabet, C. R. *J. Organomet. Chem.* **1964**, *2*, 431.

(20) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102.

(21) Wittig, G.; Meyer, F. J.; Lange, G. *Liebig's Ann. Chem.* **1951**, *571*, 12. These authors did observe the formation of tetraphenyltin from phenyllithium and triphenyltin hydride.

(22) Gilman, H.; Rosenberg, S. D. *J. Am. Chem. Soc.* **1953**, *75*, 3592.

(23) Weichmann, H.; Tzschach, K. A. *Z. Anorg. Allg. Chem.* **1979**, *458*, 291.

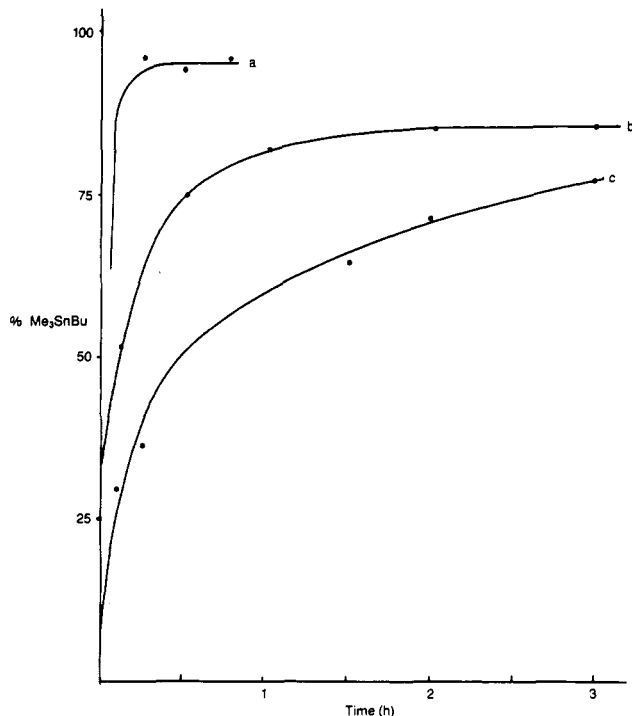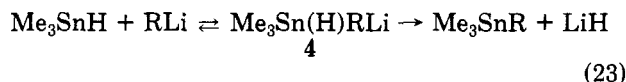(24) Newcomb, M.; Smith, M. G. *J. Organomet. Chem.* **1982**, *228*, 61.

Figure 2. Effect of solvent on rate of reaction of BuLi with Me$_3$SnH at 0 °C: a, in ether/hexanes, 1/1; b, in benzene/hexanes, 1/1; c, in hexanes. To 2.20 mmol of TMTH in 1 mL of ether, benzene, or hexanes at 0 °C was added 2.2 mmol of n-BuLi in 1 mL of hexanes; samples were removed, quenched with water, and analyzed by GLPC.

^{119}Sn NMR spectroscopic evidence for the presence of an ate complex as an intermediate in this formal hydride displacement reaction. When TMTH and n-butyllithium in hexane were mixed at liquid-nitrogen temperature and placed in the NMR probe at −90 °C, the only [119]Sn signal due to TMTH appeared at −103.1 ppm. As the temperature was raised, this signal was gradually replaced by one at −0.6 ppm due to n-butyltrimethyltin. At 25 °C this signal was 15 times the intensity of that due to TMTH, which did not shift significantly during the course of the experiment. No other signals were observed. In a similar experiment with methyllithium in ether/THF/hexane (2/2/1) at −125 °C only a signal for tetramethyltin at −1.3 ppm was observed after about a minute. Similarly, n-butyllithium and tri-n-butyltin hydride reacted rapidly under the same conditions, and only the signal at −13.3 ppm for tetrabutyltin was observed at −125 °C. When the solvent mixture was ether/THF/pentane/HMPA (2/2/1/0.8) for the methyllithium–TMTH system, signals appeared after 5 min at −0.2 (Me$_4$Sn), −172.5 (Me$_3$SnLi), and −278.3 ppm (Me$_5$SnLi) in a ratio of 1:1:0.3. A precipitate of lithium hydride was present in the reaction solution at the end of each experiment. No high field signal that might be attributed to Me$_4$Sn(H)Li was observed.

These observations lead to several conclusions. First, reaction between the tin hydride and organolithium is facilitated by donor solvents. There is no significant change in the chemical shift of the [119]Sn signal of TMTH that could be taken as clear evidence for rapid reversible formation of 4 as in eq 23. If, as we believe likely, this

$$\text{Me}_3\text{SnH} + \text{RLi} \rightleftarrows \text{Me}_3\text{Sn(H)RLi} \rightarrow \text{Me}_3\text{SnR} + \text{LiH}$$
$$\mathbf{4}$$

$$(23)$$

equilibrium is established it lies far to the left. Loss of lithium hydride from 4 is rendered irreversible by its high lattice energy. If the solvent contains a good enough donor

Table VII. Reactions of Halides R–X with Triorganotin Hydrides R′₃SnH and Butyllithium in Hexanes[a]

entry	R–X	R′	time	product yields, %		
				R–H	R–X	R′₃SnBu
1	1-chloroheptane	Me	15 min	0	94	36
2	1-chloroheptane	Me	4 h	6	75	93
3	1-bromoheptane	Me	5 min	98	0	93
4	1-bromoheptane	Bu	15 min	95	5	b
5	1-bromoheptane	Cy	15 min	97	0	b
6	2-bromoheptane	Me	5 min	96	0	93
7	3-bromo-3-ethyl-pentane	Me	15 min	96	0	97
8	1-bromoadamantane	Me	15 min	97	0	95
9	o-bromotoluene	Me	15 min	15	81	34
10	o-bromotoluene[c]	Me	5 h	28	68	75
11	2-bromomesitylene	Me	15 min	11	86	33
12	2-bromomesitylene[c]	Me	5 h	38	59	83
13	1-iodoheptane	Me	15 min	92	4	98

[a] 0.4–0.6 M solutions at 0 °C. [b] Yield of R′₃SnBu not determined. [c] At reflux temperature.

species such as HMPA, both proton abstraction to form Me₃SnLi and hydride displacement from 4 occur in competition.

As might be anticipated from the data plotted in Figure 2, the formation of hexamethylditin and lithium hydride from TMTH and methyllithium is fast in ether and THF. When these reactants are mixed in ether at 0 °C and 1-bromooctane is added 15 min later, only 9% of octane was formed and 88% of unreacted bromide remained; in THF under the same conditions only 2% of octane appeared and 93% of the unreacted bromide was found. A similar experiment in hexanes in which the TMTH and n-butyllithium were stirred for 3 h at ambient temperature before addition of 1-bromoheptane yielded 7% of heptane and 86% of unreacted bromide along with 99% of n-butyltrimethyltin.

In seeking evidence for 4 it was assumed that it would display the high reactivity of the postulated ate complex 2. In order to do this solutions of TMTH with various bromides initially present were treated with n-butyllithium and the product mixtures analyzed by GLPC for alkane, halide, and n-butyltrimethyltin. Results are gathered in Table VII. Entries 1 and 2 show that 1-chloroheptane is virtually unreactive in the system. Even after 4 h only 6% of heptane was formed with TMTH. 1-Bromoheptane, on the other hand, underwent virtually complete reduction with TMTH, tributyltin hydride, and tricyclohexyltin hydride within 15 min. Similarly 2-bromooctane and 3-bromo-3-ethylpentane were completely reduced within the same time interval, as was 1-bromoadamantane, entries 3–8. As seen in entry 13 1-iodoheptane was also readily reduced. o-Bromotoluene and mesityl bromide showed slow reduction at 0 °C, but this increased upon reflux for 5 h to a maximum of 38% in the case of the latter. In view of the low yields with these aromatic bromides no further studies were made.

The possibility that TMTH is the reducing agent for the aliphatic halides was examined. In view of its slow reaction with primary bromides the reduction would have to be initiated by free radicals formed, in this case by reaction of species formed from the reaction of TMTH and the alkyllithium. To test this a solution of 1-bromoheptane and TMTH in hexanes was treated with increments of butyllithium, and the yield of heptane formed was determined. If the butyllithium initiated the chain reduction by TMTH, the extent of reduction should exceed the amount of butyllithium added. As seen in Table VIII this was not the case. The extent of reduction of the bromide corresponded very closely with the amount of n-butyl-

Table VIII. Effect of Butyllithium Added on Extent of Reduction of 1-Bromoheptane[a]

|				
mmol added				
BuLi	0.55	1.10	1.65	2.2
mmol present				
heptane	0.54	1.18	1.70	2.3
butyltrimethyltin	0.48	0.98	1.51	2.1
bromoheptane	1.70	1.13	0.54	0.0

[a] To 2.20 mmol of TMTH and 2.20 mmol of 1-bromoheptane in 2 mL of hexanes at 0 °C was added 2.20 mmol of n-BuLi in 0.9 mL of hexane in four 0.55-mmol increments; GLPC analysis 5 min after each addition.

Table IX. Reactivity of LiH with Weak Acids[a]

LiH prepared from	% yield of H₂[b]			
	Me₂SO	piperidine	2-penta-none	diethyl-amine
MeLi (Et₂O)	101	32	94	8
BuLi (hexanes)	87	29	77	13
LDA (Et₂O)	86	45	84	14
LDA (hexanes)	92	72	93	14

[a] All reactions carried out at 0 °C. [b] Yields of H₂ attained after 30 min.

lithium added. A reasonable alternative for the reductant is the ate complex 4. The reduction (eq 24) in hexane is

$$4 + R-Br \rightarrow LiBr + R-H + Me_3SnBu \quad (24)$$
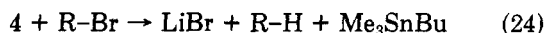
fast compared to the conversion of 4 to lithium hydride and tetraalkyltin. As suggested above the equilibrium of eq 23 must lie far to the left. Therefore, the rates for the forward and reverse reactions should both be very high in order for the reaction of 4 with the bromide to occur as fast as it does.

Despite the fact the system does not initiate the free radical chain reduction of the bromide by TMTH the reduction does involve free radical intermediates. When equimolar amounts of 3-bromo-3-ethylpentane and 1-bromoheptane were allowed to compete for 1 mol of TMTH in the presence of n-butyllithium 95% of 3-ethylpentane and 5% of heptane were formed. This reactivity pattern is consistent with formation of a free radical by bromine atom abstraction or dissociative electron transfer to the bromide. Also, reduction of 6-bromo-1-hexene led to the formation of both methyl-cyclopentane (30%) and 1-hexene (56%). A chain process analogous to eq 17–19 can be written in which 2 is replaced by 4 and the chain carrying organotin species are [Me₃Sn(H)Bu]⁻ and [Me₃SnBu]⁻, respectively, in eq 17–19.

Reactivity of the Lithium Hydride

Although the lithium hydride formed in the reactions of the organotin hydrides with either LDA or organo-lithiums showed very low reactivity toward halides, enormously greater reactivity in proton abstraction from weak acids was observed in comparison with commercial LiH dispersion. The results obtained with four preparations of LiH in reactions with weak acids at 0 °C are gathered in Table IX. Dimethyl sulfoxide (Me₂SO) reacted with each to virtual completion within a couple of minutes, as did 2-pentanone. Piperidine was somewhat less reactive and diethylamine the least reactive. The yields of hydrogen given are those observed after 10 min. Rapid initial evolution was followed by a marked decrease with the amines. The LiH formed from the alkyllithiums was granular in appearance, that formed from LDA in hexanes was gelatinous, and that formed in ether was intermediate in appearance. It appears from the data in Table IX that the gelatinous material was the most re-
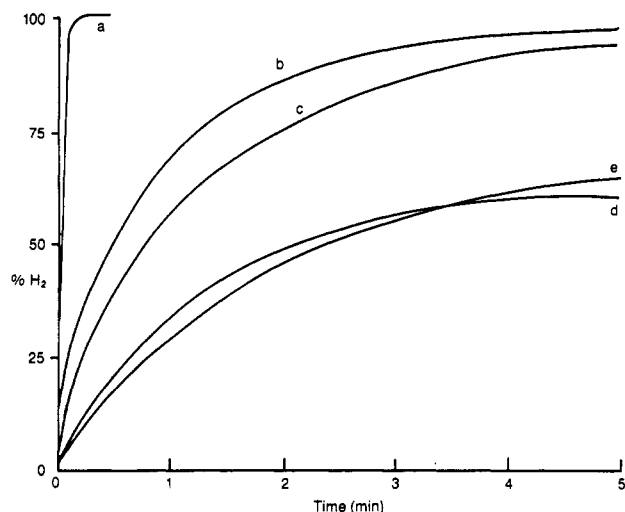
Figure 3. Effect of aging on reactivity of lithium hydride on rate of hydrogen formation upon reaction with Me_2SO: a, fresh; b, after 18 h; c, after 44 h; d, after 96 h; e, after 120 h. LiH was prepared by reaction of 1.5 mmol of MeLi and 1.5 mmol of TMTH in Et_2O at 0 °C; after appropriate time 1 mL of Me_2SO was added and evolution of hydrogen monitored.

active. This, coupled with a rapid fall off in rate of hydrogen, evolution suggests that particle size of the LiH is fairly important in determining its reactivity. To test this samples were prepared and allowed to age for varying periods before reaction with Me_2SO with the results shown in Figure 3. It can be seen that the fresh material was highly reactive but that profound decreases in reactivity occurred with aging. This is consistent with the idea that aging leads to dissolution of the smallest particles and redeposition of the material on the larger particles. Alternatively, there might be a slow transition from a metastable LiH lattice initially formed to the highly stable lattice of the material prepared by the thermal lithium–hydrogen reaction used to prepare the material commercially.

A very convenient and inexpensive method for the preparation of alkali-metal hydrides has been reported recently.[25] LiH was prepared in hexane containing tetramethylethylenediamine by the reaction of *n*-butyllithium with dihydrogen. This product appears to be comparable in reactivity to our preparation, which, however, does not require the presence of a strong donor species in its preparation.[26]

The hydride also cleaves the tin–tin bond in solvent THF. This was shown by preparing it, along with hexamethylditin, from the reaction of LDA with 2 equiv of TMTH in hexanes, according to eq 2. GLPC analysis showed 91% of hexamethylditin. Addition of an equal volume of THF resulted in dissolution of most of the lithium hydride. Further addition of 1 equiv of 1-bromooctane resulted in the formation of 50% of trimethyloctyltin and the presence of 50% of unreacted hexamethylditin. Another reaction with hydride prepared by the reaction of TMTH with butyllithium in ether resulted in the formation of 43% of trimethyloctyltin with 41% of unreacted hexamethylditin. These observations suggest that, if hexamethylditin is formed in THF by the sequence of reactions 6–8, the latter two reactions are reversible, thus resulting in (6) as the overall reaction in

(25) Klusener, P. A. A.; Brandsma, L.; Verkruijsse, H. D.; Schleyer, P. v. R.; Friedel, T.; Pi, R. *Angew. Chem.* **1986**, *98*, 458.

(26) Yet another method for preparation of LiH has been reported since this paper was submitted: Kowalski, C. J.; Lal, S. S. *J. Am. Chem. Soc.* **1986**, *108*, 5356.

this solvent. Germane to these observations are those of Corriu and Guerin, who showed that potassium and sodium hydrides react with hexaphenyl- and hexa-*n*-butylditin to form the corresponding (organostannyl)alkalis in dimethoxyethane.[27] Commercial lithium hydride dispersion does not react with hexamethylditin in THF. This points up the critical importance of the physical nature of the alkali hydride in determining its reactivity. The observations reported in our work further emphasize the role of the solvent in determining the ease of formation of (organostannyl)alkalis: solvation plays an extremely important role which is greater for the alkyl than for the aryl derivatives.

Experimental Section

General Procedures and Materials. All experiments employing organotin hydrides and anions were carried out under an atmosphere of argon. Organotin hydrides were prepared by reduction of the appropriate organotin halides with $LiAlH_4$. Organic halides (Aldrich) were reagent grade and were used without further purification. LDA in cyclohexane was purchased from Lithco; methyllithium in diethyl ether and *n*-butyllithium in hexane were purchased from Aldrich. Tetraalkyltin compounds were prepared via the Grignard route, trimethyltriethylditin was prepared from trimethyltin diisopropylamide and triethyltin hydride, and hexaalkylditins were prepared from the chlorides and Na/NH_3. Trimethyltin diisopropylamide was prepared from trimethyltin chloride and LDA. THF and hexanes were distilled from $LiAlH_4$; TMEDA, HMPA, and benzene from sodium. Dry diethyl ether was purchased from Mallinckrodt.

^1H NMR spectra were determined on a Varian EM 360A spectrometer at 60 MHz, with Me_4Si as internal standard, ^{13}C and ^{119}Sn analyses were performed on a Varian XL 300 spectrometer with either internal Me_4Si or external tetramethyltin as a standard. Low-temperature ^{119}Sn NMR studies were performed by mixing the reactants at liquid-nitrogen temperature with ca. 0.3 M initial concentration and warming the sample in the probe to the desired temperature. Analytical gas chromatographic analyses were performed on a HP 5890A instrument equipped with a thermal conductivity detector, a HP 3392A integrator, and a 30 m × 0.53 mm column with cross-linked methylsilicone gum film. Yields were determined with internal standard techniques from areas obtained by digital integration using authentic samples. Nonane was used as internal standard and distilled from molten sodium prior to use.

Reaction of Trimethyltin Hydride and LDA (2:1). General Procedure. LDA (1.88 mmol, in 1 mL of cyclohexane) was placed in a Schlenk tube at 0 °C. TMTH (0.62 g, 3.76 mmol, 0.46 mL) was added, and the reaction mixture was stirred for 30 min. Lithium hydride separated as a white solid. Hydrolysis yielded hydrogen (1.84 mmol, 98%). GC analysis showed the formation of hexamethylditin (1.75 mmol, 93%). A similar experiment in diethyl ether yielded hydrogen (1.75 mmol, 93%) and hexamethylditin (1.56 mmol, 83%).

Reaction of Trialkyltin Hydrides and LDA (2:1) in Diethyl Ether. General Procedure. Triethyltin hydride (0.49 g, 2.38 mmol) in 3 mL of diethyl ether was cooled to 0 °C. LDA (1.19 mmol, 1.6 M in cyclohexane) was added via syringe, and the reaction mixture was stirred for 60 min at room temperature. Lithium hydride separated as a white precipitate. Hydrolysis yielded hydrogen (1.08 mmol, 91%). The organic layer afforded hexaethylditin (1.09 mmol, 92%). A similar experiment with TMTH gave hydrogen (95%) and hexamethylditin (90%); a similar experiment with tributyltin hydride yielded hydrogen (90%) and hexabutylditin (94%).

Reaction of Triphenyltin Hydride with LDA in Diethyl Ether. Triphenyltin hydride (1.00 g, 2.85 mmol) in 6 mL of diethyl ether was placed in a Schlenk tube and cooled to 0 °C. LDA (2.90 mmol, 1.6 M solution in cyclohexane) was added via syringe, and the reaction mixture was stirred for 1 h at room temperature. An initially formed precipitate dissolved, and the solution turned yellow. Then the reaction mixture was cooled

(27) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *197*, C19.

to 0 °C and treated with excess methyl iodide. After 15 min of additional stirring the mixture was quenched with 2 mL of water. The crude product obtained after aqueous workup was recrystallized from ethanol giving triphenylmethyltin (0.77 g, 74%): mp 59–60 °C; ^{1}H NMR (CDCl$_3$) 0.86 (s, 3 H, [2]J_{SnH} = 55 Hz), 7.23 ppm (m, 15 H).

Reaction of TMTH with Trimethyltin Diisopropylamide in Diethyl Ether. A Schlenk tube was charged with trimethyltin diisopropylamide (0.33 g, 1.25 mmol) and TMTH (0.21 g, 1.25 mmol, 0.15 mL) in 3 mL of diethyl ether. After the mixture was stirred for 2 h at room temperature, GC analysis showed the formation of hexamethylditin (26%), besides unreacted starting material.

Reaction of (Trimethylstannyl)lithium with Triethyltin Hydride in Diethyl Ether. Hexamethylditin (0.37 g, 1.12 mmol) in 5 mL of diethyl ether was treated with methyllithium (1.20 mmol, 1.00 M in diethyl ether) at room temperature. After being stirred for 30 min, the reaction mixture was cooled to 0 °C and triethyltin hydride (0.23 g, 1.12 mmol) was added dropwise. A white precipitate formed immediately. The reaction mixture was hydrolyzed and subjected to GC analysis, showing hexamethylditin (15%), hexaethylditin (17%), and trimethyltriethylditin (30%).

Reaction of (Trimethylstannyl)lithium with Trimethyltin Hydride in Diethyl Ether. Hexamethyldistannane (0.37 g, 1.12 mmol) in 2 mL of diethyl ether was treated with methyllithium (1.12 mmol, 1 M solution in diethyl ether). After being stirred for 30 min at 0 °C, the reaction mixture was analyzed by GC, showing the presence of hexamethyldistannane (0.12 mmol, 11%). Then TMTH (0.18 g, 1.12 mmol, 0.13 mL) was added via syringe. A white precipitate (LiH) was formed immediately. After the mixture stirred for an additional 30 min at room temperature, the apparatus was connected to a gas measuring device, cooled to 0 °C, and quenched with 1 mL of water, yielding hydrogen (0.83 mmol, 74%). GC analysis of the organic layer showed the presence of hexamethyldistannane (0.93 mmol, 83%).

Reaction between (Trimethylstannyl)lithium and Triethyltin Hydride in THF. To a solution of methyllithium (1.00 mmol) in 2 mL of THF hexamethyldistannane (0.33 g, 1.02 mmol) at 0 °C. After the mixture was stirred for 15 min, triethyltin hydride (0.15 g, 1.2 mmol) was dropped into the now yellowish mixture. After 15 min of additional stirring at room temperature, the reaction mixture was cooled to 0 °C and quenched with excess 1-bromoheptane. GC analysis showed the formation of TMTH (0.24 mmol, 24%). A similar experiment with (trimethylstannyl)lithium and triphenyltin hydride afforded TMTH (17%).

Reaction of 1-Bromooctane and Lithium Hydride from TMTH/LDA Reaction. Lithium hydride was prepared by reacting TMTH (0.33 g, 2.00 mmol, 0.24 mL) with LDA (1.00 mmol, 1.6 M in cyclohexanes) in 2 mL of hexanes for 3 h at room temperature and precipitated as a white solid. Then 1-bromooctane (0.19 g, 1.00 mmol, 0.17 mL) was added and the reaction mixture stirred for additional 3 h at room temperature. GC analysis afforded octane (0.05 mmol, 5%), hexamethylditin (0.89 mmol, 89%), and 1-bromooctane (0.85 mmol, 85%).

Reaction of Alkyl Halides with TMTH and LDA (1:2:1). General Procedure. 1-Bromooctane (0.19 g, 0.96 mmol, 0.17 mL) and TMTH (0.32 g, 1.92 mmol, 0.32 mL) in 2 mL of diethyl ether were cooled to 0 °C. Then LDA (0.96 mmol, 1.6 M in cyclohexane) was dropped in, and after 20–25 min of stirring at room temperature the reaction mixture was quenched with 1 mL of water and subjected to GC analysis. Results are gathered in Table I. A reaction mixture was prepared as described above and subjected to NMR analysis, indicating the presence of trimethyltin diisopropylamide: ^{1}H NMR δ 0.22 (SnMe$_3$, [2]J_{SnH} = 52 Hz); ^{13}C NMR δ –4.71 (SnCH$_3$, [1]J_{SnC} = 382 Hz), 26.83 (CH$_3$), 49.61 (CH); ^{119}Sn NMR δ 37.5. Besides hexamethylditin: ^{1}H NMR δ 0.22 ([2]J_{SnH} = 48 Hz, [3]J_{SnH} = 16 Hz, SnMe$_3$); ^{13}C NMR δ –10.4; ^{119}Sn NMR: δ 108.8 ([1]J([119]Sn–[119]Sn) = 4442 Hz).

Reactions of LDA and Lithium Diphenylamide with Trialkyltin Hydrides (1:2) in Different Solvents. Rate Study. General Procedure. Trialkyltin hydride (2 mmol) in 2 mL of an appropriate solvent was placed in a Schlenk tube and cooled to 0 °C. Then LDA (1 mmol, 1.6 M solution in cyclohexane) was added and the course of the reaction followed by GC analysis. For that purpose samples were removed periodically, quenched with water, and analyzed by GC. Lithium diphenylamide was

prepared immediately before use by reaction of methyllithium (1 mmol in 2 mL of diethyl ether) with diphenylamine (0.19 g, 1.10 mmol) at 0 °C; then TMTH was added to this solution. Yields of hexamethylditin vs. time are plotted in Figure 1.

Reduction of Organic Halides with *n*-Butyllithium/ TMTH Reagent in Hexanes. General Procedure. 1-Bromoheptane (0.99 mmol, 0.18 g, 0.16 mL) and TMTH (0.99 mmol, 0.16 g, 0.12 mL) in 2 mL of hexanes were cooled to 0 °C. Then *n*-butyllithium (0.99 mmol, 2.40 M in hexane) was added, and after being stirred for an appropriate time, the reaction mixture was quenched with 1 mL of water and analyzed by GC. Results are gathered in Table VII.

Reaction of Methyllithium with TMTH and 1-Bromooctane in Diethyl Ether. TMTH (1.00 mmol, 0.17 g, 0.12 mL) and 1-bromooctane (0.19 g, 1.00 mmol, 0.17 mL) in 1 mL of diethyl ether were cooled to 0 °C. Then methyllithium (1.00 mmol, 1.00 M solution in diethyl ether) was added. Immediately a white solid precipitated. The slurry was stirred for 15 min at room temperature, connected to a gas measuring device, and hydrolyzed with 1 mL of water, yielding hydrogen (83%). GC analysis of the organic layer showed the presence of 1-bromooctane (0.88 mmol, 88%) and octane (0.09 mmol, 9%).

Reaction of Methyllithium with TMTH and 1-Bromooctane in THF. TMTH (1.10 mmol, 0.18 g, 0.13 mL) and 1-bromooctane (1.10 mmol, 0.21 g, 0.18 mL) in 1 mL of THF were cooled to 0 °C. Then methyllithium (1.10 mmol) in 1 mL THF was added. The resulting mixture was stirred for 15 min at room temperature, connected to a gas measuring device, and hydrolyzed with 1 mL of water, yielding hydrogen (0.97 mmol, 88%). GC analysis of the organic layer showed the presence of 1-bromooctane (1.02 mmol, 93%), octane (0.02 mmol, 2%), and octyltrimethyltin (0.02 mmol, 2%).

Attempted Reduction of 1-Bromoheptane with Lithium Hydride Formed from TMTH and *n*-Butyllithium. *n*-Butyllithium (1.50 mmol, 2.40 M solution in hexane) was added to a solution of TMTH (0.25 g, 1.50 mmol, 0.18 mL) in 2 mL of hexanes and stirred for 3 h at room temperature. Lithium hydride separated as a white precipitate. To this slurry was added 1-bromoheptane (1.50 mmol, 0.27 g, 0.24 mL). The reaction mixture was heated to reflux for 2 h and then analyzed by GC, indicating the presence of heptane (0.11 mmol, 7%, 1-bromoheptane (0.90 mmol, 86%) and butyltrimethyltin (1.49 mmol, 99%).

Competitive Reduction of 3-Ethyl-3-bromopentane and 1-Bromoheptane with TMTH/*n*-Butyllithium Reagent. *n*-Butyllithium (0.81 mmol, 0.70 M solution in hexane) was added to a mixture of 1-bromoheptane (0.15 g, 0.81 mmol, 0.13 mL) and 3-ethyl-3-bromoheptane in 2 mL of hexanes. After 15 min of stirring at 0 °C, the mixture was quenched with 1 mL of water and analyzed by GC, indicating the presence of 3-ethylpentane (0.68 mmol, 84%), heptane (0.04 mmol, 5%), and 3-ethyl-2-pentene (0.09 mmol, 11%).

Reaction of TMTH/*n*-Butyllithium Reagent with 6-Bromo-1-hexene. TMTH (0.17 g, 1.00 mmol, 0.12 mL) and 6-bromo-1-hexene (0.18 g, 1.08 mmol, 0.15 mL) in 1 mL of octane were cooled to 0 °C. Then *n*-butyllithium (1.00 mmol in 2 mL of octane) was added via syringe. After being stirred for 15 min, the reaction mixture was quenched with 2 mL of water and analyzed by GC, indicating the presence of methylcyclopentane (0.30 mmol, 30%), 1-hexene (0.56 mmol, 56%), and butyltrimethyltin (0.78 mmol, 78%).

Reaction of Lithium Hydride from TMTH/LDA Reaction with Hexamethylditin. TMTH (3.30 g, 2.00 mmol, 2.40 mL) and LDA (1.00 mmol, 1.60 M in cyclohexane) in 2 mL hexane were stirred for 1 h at room temperature. Lithium hydride precipitated and GC analysis showed 91% yield of hexamethylditin. After addition of 2 mL of THF most of the precipitate dissolved and the mixture turned yellow. After 2 h of stirring at room temperature the mixture was treated with 1-bromooctane (0.19 g, 1.00 mmol, 0.17 mL) and stirred for additional 15 min. Then the reaction mixture was quenched with 1 mL of water and the organic layer analyzed by GC, indicating the presence of octyltrimethyltin (0.50 mmol, 50%) and hexamethylditin (0.50 mmol, 50%). A similar reaction in diethyl ether yielded octyltrimethyltin (54%); 47% hexamethylditin remained unconsumed.

Reaction of Lithium Hydride from *n*-Butyllithium/ TMTH Reaction with Hexamethylditin. Lithium hydride was

prepared by stirring TMTH (0.17 g, 1.00 mmol, 0.12 mL) with methyllithium (1.00 mmol) in 2 mL of diethyl ether for 20 min at room temperature. After the addition of hexamethylditin (0.33 g, 1.00 mmol) the slurry was cooled to 0 °C and 2 mL of THF was added. Some precipitate dissolved, and the reaction mixture turned slightly yellow. After the mixture was stirred for 1 h, 1-bromooctane (0.21 g, 1.10 mmol, 0.18 mL) was added. The reaction mixture was stirred for additional 20 min before quenching with 2 mL of water. GC analysis showed the presence of octyltrimethyltin (0.43 mmol, 43%) and hexamethylditin (0.41 mmol, 41%).

Reactions of Lithium Hydride Formed from TMTH/Alkyllithium with Weak Acids. Methyllithium (1.50 mmol) in 1.5 mL of diethyl ether or *n*-butyllithium (1.50 mmol) in 1.5 mL of hexanes was treated with TMTH (0.25 g, 1.50 mmol, 0.18 mL) at 0 °C. After being stirred for 20 min (MeLi) and 5 h (BuLi), respectively, at room temperature, the reaction mixture was cooled to 0 °C and quenched with an excess (1 mL) of the appropriate reagent. Yields of hydrogen obtained after 10 min are gathered in Table IX.

Reactions of Lithium Hydride Formed from TMTH/LDA with Weak Acids. LDA (1.00 mmol, 1.6 M in cyclohexane) and TMTH (0.33 g, 2.00 mmol, 0.24 mL) in 2 mL of an appropriate solvent (hexanes or diethyl ether) were stirred for 1 h at room temperature. The resulting slurry was cooled to 0 °C, connected

to a gas measuring device, and quenched with 1 mL of the appropriate reagent. Yields of hydrogen obtained after 10 min are gathered in Table IX.

Aggregation States and Exchange Properties of Alkyllithium Compounds in Hydrocarbon Solvent from ^{13}C–^{6}Li Coupling

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Variable-temperature ^{13}C and ^{6}Li NMR data are reported for 12 ^{6}Li-enriched alkyllithium compounds in cyclopentane solution (R = ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, isopentyl, isobutyl, 2-methylbutyl, 2-ethylbutyl, isopropyl, *sec*-pentyl, *tert*-butyl, *tert*-pentyl). ^{13}C–^{6}Li coupling was observed for the branched-chain compounds at low temperature except isopentyllithium-^{6}Li. Coupling was not observed for the straight-chain compounds except *n*-propyllithium-^{6}Li. The observed coupling ranges from 2.2 to 6.2 Hz. The value of the observed coupling and the coupling patterns have been used to assign the aggregation states and exchange properties of these compounds. Branching β to the lithium atom results in hexamers that are rapidly fluxional over all temperatures, but whose interaggregate exchange can be slowed at low temperatures. Branching α to the lithium atom produces either equilibrium mixtures of hexamers and tetramers for secondary compounds or tetramers for tertiary compounds. For the process $(RLi)_6 \rightleftharpoons {}^3/_2(RLi)_4$, Δ*H* was found to be 6.4 ± 0.4 and 2.7 ± 0.7 kcal/mol for isopropyllithium and *sec*-pentyllithium, respectively. Line-shape analysis of the fluxional exchange of the tetrameric aggregates suggests a different fluxional exchange mechanism for the secondary compounds than for the tertiary compounds.

Introduction

Recent years have seen a renewed interest in the reactivity, structure, and bonding of organolithium compounds. A large amount of structural and theoretical information is now available.[1,2] There has also been an increasing number of NMR solution studies, adding to the understanding of aggregation states and exchange properties of organolithium compounds in solution.[3–7] One of

the major developments in the study of the solution behavior of these compounds has been the ability to observe ^{13}C–^{6}Li coupling. ^{13}C–^{7}Li coupling was very early used to establish the tetrahedral structure of methyllithium tetramers,[8] but the observation of such coupling was in general limited to coordinating solvents. ^{13}C–^{7}Li coupling was observed for only a few alkyllithium compounds in hydrocarbon solvent.[9] This was a disadvantage since ag-

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