Reductive Cleavage of Carbon–Halogen Bonds by Tri-n-butyltin Hydride, Lithium 4,4'-Dimethylbenzophenone Ketyl, and Metallic Magnesium[1]
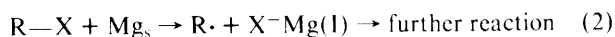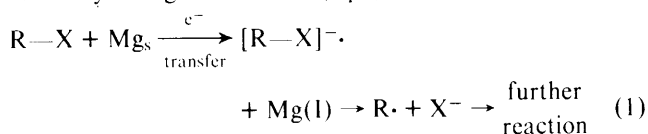
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Abstract: Rate–structure profiles are compared for four reactions: reduction of alkyl chlorides and bromides with tri-n-butyltin hydride (Et_2O, 35 °C and 0 °C, respectively), reduction of alkyl bromides with lithium 4,4'-dimethylbenzophenone ketyl (THF, 24 °C), and reaction of alkyl chlorides with metallic magnesium (Et_2O, 0 °C). All four rate–structure profiles are linearly correlated (correlation coefficient $r > 0.80$). The similarity of these profiles suggests that the carbon–halogen bond is significantly broken in the transition state for each type of reaction. Electrochemical reduction potentials of a limited number of alkyl halides also correlate linearly with these rates. The similarity of the rate–structure profile for reaction of alkyl halides at a magnesium surface to those of homogeneous reactions supports the inference that reaction at the magnesium surface is not complicated by adsorption or other heterogeneous phenomena.

Introduction

The formation of alkyl Grignard reagents from alkyl halides and metallic magnesium occurs by a mechanism which involves, at least in part, reductive cleavage of the carbon–halogen bond and formation of free alkyl radicals.[2–9] Structure–reactivity profiles obtained from nonmass transport limited reactions of alkyl chlorides and alkyl bromides are compatible with two limiting mechanisms for the carbon–halogen bond-breaking step. The first is transfer of an electron from magnesium metal to the alkyl halide, and generation of an alkyl halide radical anion and a (formally) magnesium(I) species (eq 1: in this equation, Mg_s denotes a surface magnesium atom; Mg(I) might be either a surface or a soluble species). The second is halogen atom abstraction from the alkyl halide by a magnesium atom (eq 2).

$$R{-}X + Mg_s \xrightarrow[\text{transfer}]{e^-} [R{-}X]^{-\cdot}$$

$$+\ Mg(I) \rightarrow R\cdot + X^- \rightarrow \begin{array}{c}\text{further}\\ \text{reaction}\end{array} \quad (1)$$

$$R{-}X + Mg_s \rightarrow R\cdot + X^-Mg(I) \rightarrow \text{further reaction} \quad (2)$$

The first reaction is an outer sphere electron transfer reaction; the second is an inner sphere electron transfer. Although both pathways ultimately generate an alkyl radical and a halide ion, they differ, at least formally, in three respects. First, an outer sphere electron transfer mechanism involves electron donation to the C–X antibonding orbital. Although population of this σ^* orbital will increase the C–X bond length to some unknown extent, it may not change the hybridization at the carbon bonded to halogen significantly. By contrast, inner sphere electron transfer breaks the carbon–halogen bond in the transition state, and should be accompanied by changes in hybridization at carbon. Second, outer sphere electron transfer does not require interaction between magnesium and the halogen atom in the transition state, while inner sphere transfer involves the formation of a halogen–magnesium bond. Third, inner sphere electron transfer necessarily requires that the alkyl radicals be generated initially very close to the magnesium surface; outer sphere electron transfer resulting in formation of an intermediate alkyl halide radical anion with finite lifetime would allow initial generation of alkyl radicals to occur at some separation from the magnesium surface.

The question relevant to the mechanism of formation of Grignard reagents posed by these limiting alternatives concerns the intermediacy of alkyl halide radical anions: Are these species discrete intermediates along the reaction coordinate leading from alkyl halide reactant to organomagnesium product? The intermediacy of these species in the formation of Grignard reagents is part of a broader and unresolved question concerning their existence in *any* organic reaction. Pulse radiolysis of alkyl halides in cyclohexane has been interpreted as identifying a methyl chloride radical anion ($\tau_{1/2} \simeq 3 \times 10^{-8}$ s),[10] and aryl halide radical anions have been reported.[11] Reactions of 5-hexenyl halides with disodium tetraphenylethylene dianion in methyltetrahydrofuran[12] and of alkyl halides with aromatic radical anions in THF[13] have been considered to suggest alkyl halide radical anions. The chemical studies are amenable to different interpretations,[13,14] and the existence of alkyl halide radical anions as reaction intermediates is not established.

This paper compares rate–structure profiles for three reactions in ethereal solvents: reactions of alkyl chlorides with metallic magnesium, reduction of alkyl chlorides with tri-n-butyltin hydride under free radical conditions (an inner sphere reaction),[15] and reduction of alkyl bromides with lithium 4,4'-dimethylbenzophenone ketyl (a single-electron transfer reaction).[16,17] The choice of reduction of alkyl chlorides with tri-n-butyltin hydride and of alkyl bromides with lithium 4,4'-dimethylbenzophenone ketyl to model plausible processes involved in reaction of alkyl chlorides with magnesium was based on several considerations. Tri-n-butyltin radical, rather than chromous ion[18] or phenyl radical,[19] was used as a reagent to effect halogen abstraction for two reasons: first the abstracting center is an electrically neutral, sterically hindered metal atom and may resemble a magnesium surface atom. Second, the large difference in electronegativity between tin and magnesium notwithstanding, a previous examination established similar Hammet ρ values for the reactions of substituted *aryl* halides with tri-n-butyltin hydride and magnesium and suggested similar charge distributions in the rate-limiting transition states.[8] The choice of lithium 4,4'-dimethylbenzophenone ketyl reduction of alkyl bromides as a model for electron transfer was based on the experimental demonstration by Garst et al. that the analogous reaction of lithium benzophenone ketyl with alkyl *iodides* is as free of S_N2 components as any homogeneous electron transfer system so far examined.[16] The rate of reaction of this ketyl with alkyl

Table I. Relative Rates ($k_{rel} = k_{RX}/k_{c-C_5H_9X}$) for Reduction of Alkyl Halides and Related Electrochemical Reduction Potentials[a]

	$k_{RX}/k_{c-C_5H_6X}$					$E_{1/2}$	
R	Bu₃SnH RCl Et₂O, 35 °C	(CH₃C₆H₄)₂CO⁻·Li⁺ RBr THF, 24 °C	Bu₃SnH[b] RBr Et₂O, 0 °C	Mg[b] RCl Et₂O, 0 °C	Hg[c] RBr DMF, 25 °C	C[c,d] RCl DMF, 25 °C
1. c-C₅H₉	1	1	1	1	−2.19	
2. c-C₆H₁₁	0.31	0.085	0.60	0.55	−2.29	
3. c-C₇H₁₃	1.3	0.61	1.5	2.4	−2.27	
4. c-C₈H₁₅	2.0	1.2	1.7	3.5		
5. n-C₅H₁₁	0.23	0.082	0.69	0.17	−2.26	−2.79
6. (CH₃)₃CCH₂	0.12	0.0056	0.49	0.053	−2.37	−2.83
7. R'CH₂CHCH₃[e]	0.67	0.19	0.91	0.91	−2.26	−2.66
8. R'CH₂C(CH₃)₂[f]	4.3	1.7	2.9	1.9	−2.19	−2.60

[a] Experimental uncertainty is estimated to be ca ±10% for all relative rate data. [b] Reference 6. [c] Reference 20. [d] Reference 21. [e] R' = CH₃CH₂ for reaction of RCl and Bu₃SnH and for reduction of RCl at a glassy carbon electrode; R' = CH₃ for reaction of RCl with Mg and RBr with aryl ketyl and Bu₃SnH, and for reduction of RBr at a Hg cathode. [f] R' = CH₃CH₂ for reaction of RBr with aryl ketyl; R' = CH₃ for reactions of RCl with Mg and Bu₃SnH; R' = H for reaction of RBr and Bu₃SnH and for reduction of RCl at glassy carbon and RBr at Hg cathodes.
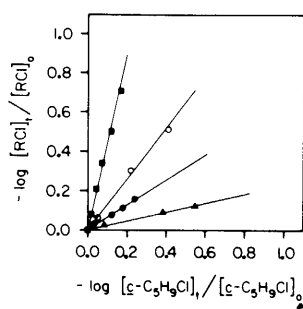

Figure 1. Competitive kinetics experiments used to estimate relative rates of reduction of alkyl chlorides by reaction with tri-n-butyltin hydride in diethyl ether at 35 °C (hv, azobisisobutyronitrile).

Figure 2. Competitive kinetics data used to estimate relative rates of reduction of alkyl bromides by lithium 4,4'-dimethylbenzophenone ketyl (THF, 24 ± 1 °C).

bromides at 25 °C was, however, inconveniently slow. By substituting methyl groups in the aromatic rings of the ketyl, its reactivity was increased by approximately a factor of ten, and rates of reduction of alkyl bromides (but not of the less reactive alkyl chlorides) could be followed conveniently. Ideally we might have preferred a reagent which would reduce alkyl chlorides, since our most extensive (nonmass transport limited) rate series for reaction with magnesium involves alkyl chlorides; nonetheless, the available evidence indicates that the rates of reaction of alkyl chlorides and bromides with magnesium are linearly correlated when the latter are not mass-transport limited, and the effort required to develop a convenient single-electron reducing agent for alkyl chlorides did not seem justified.

Results

Rate-structure profiles for both the reduction of alkyl chlorides by tri-n-butyltin hydride in diethyl ether, and for the reduction of alkyl bromides with lithium 4,4'-dimethylbenzophenone ketyl in THF, were obtained by using competitive kinetics.[5] The disappearance of two alkyl halides reacting with an excess of reducing agent was followed by GLC: plots of log [(R₁X)ₜ/(R₁X)₀] against log [(R₂X)ₜ/(R₂X)₀] were linear to greater than 70% consumption of the more reactive halide, and evaluation of the slope, employing linear regression analysis, yielded $k_{rel} = k_1/k_2$ directly (eq 3).

$$\log [(R_1X)_t/(R_1X)_0] = k_1/k_2 \log [(R_2X)_t/(R_2X)_0] \quad (3)$$

Representative data (relative to cyclopentyl chloride) are shown in Figure 1 for tri-n-butyltin hydride reductions; data (relative to cyclopentyl bromide) are shown for reductions with lithium 4,4'-dimethylbenzophenone ketyl in Figure 2. Results are summarized in Table I, together with comparable rates of
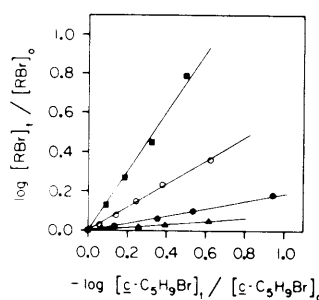
reduction of alkyl bromides with tri-n-butyltin hydride (Et₂O, 0 °C, hv, AIBN) and rates of reaction of alkyl chlorides with magnesium (Et₂O, 0 °C), both taken from previous work.[6] In addition, this table includes half-wave potentials taken from the literature for reduction of alkyl halides at mercury and glassy carbon cathodes.[20,21]

For comparison with previous work, absolute rate constants were also determined for the reactions of cyclopentyl bromide with ketyls in THF. With an excess of ketyl, the reactions followed pseudo-first-order kinetics.

$$-d[RX]/dt = k[RX][Ar_2COLi] \quad (4)$$

Rate constants (defined for eq 4) were: for (p-CH₃C₆H₄)₂CO⁻·Li⁺, $k = 1.5 \times 10^{-3}$ L mol⁻¹ s⁻¹ (24 °C, THF); for (C₆H₅)₂CO⁻·Li⁺, $k = 9.5 \times 10^{-5}$ L mol⁻¹ s⁻¹ (20 °C, THF). The datum for lithium benzophenone ketyl is comparable to reported literature data.[22] The order of reactivity of alkyl bromides with 4,4'-dimethylbenzophenone ketyl (tertiary > secondary > primary) and the absence of O-alkylated product in the reduction of n-pentyl bromide suggest that nucleophilic displacements by the ketyl oxygen are unimportant, in analogy with Garst's work.[16]

The major objectives of this work are to determine whether the homogeneous reductions of alkyl halides by tri-n-butyltin radicals and by lithium 4,4'-dimethylbenzophenone ketyl radical anions are distinguishable on the basis of rate-structure correlations, and to use information derived from this analysis to classify the transition state for the heterogenous reaction of alkyl chlorides with magnesium. An immediate conclusion from the data summarized in Table I which is pertinent to these objectives is that *the rate-structure profiles for all three reactions are linearly related.* Figure 3 gives plots of particular relevance to this conclusion. Table II summarizes the correlation coefficients and least-squares slopes for these plots, and

Table II. Correlation Coefficients (and Least-Squares Slopes) Characterizing Linear Free Energy Correlations between Reactions Which Reduce Alkyl Halides[a]

	RCl + Mg (Et₂O, 0 °C)	RCl + Bu₃SnH	RBr + Bu₃SnH	RBr + (CH₃C₆H₄)₂COLi	RCl ($E_{1/2}$)
RCl + Bu₃SnH (Et₂O, 35 °C)	0.90 (1.5)[b]				
RBr + Bu₃SnH (Et₂O, 0 °C)	0.82 (3.2)[b]	0.97 (2.0)[b]			
RBR + (CH₃C₆H₄)₂COLi (THF, 24 °C)	0.93 (0.78)[b]	0.94 (0.62)[b]	0.87 (0.31)[b]		
RCl ($E_{1/2}$, C, DMF, 25 °C)	0.99 (6.5)[c]	0.96 (6.3)[c]	0.91 (3.1)[c]	0.93 (9.5)[c]	
RBr ($E_{1/2}$, Hg, DMF, 25 °C)	0.74 (9.5)[d]	0.73 (4.3)[d]	0.81 (8.4)[d]	0.93 (13)[d]	0.85 (0.69)[c]

[a] These parameters are derived from plots of log k vs. log k', or from log k vs. $E_{1/2}$. [b] The relative rates of reaction of eight alkyl halides are included in this correlation: cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, *n*-pentyl, 1-halo-1-alkylethane, and 2-halo-2-alkylpropane (cf. footnotes *e* and *f* of Table I). [c] Only the four acyclic alkyl halides listed in footnote *b* are compared. [d] Seven alkyl halides (all of those listed in footnote *b* except cyclooctyl) are correlated.

for plots from each of the remaining pairwise sets of data summarized in Table I.

Two features of these data are relevant to their accuracy and deserve brief comment. First, the rates of reaction of alkyl chlorides and alkyl bromides with tri-*n*-butyltin hydride were obtained in independent sets of experiments by different individuals. The excellent correlation between these sets of relative rates establishes their internal consistency. The rates of reaction of tri-*n*-butyltin radical with alkyl chlorides are approximately 10^2 more sensitive to changes in alkyl group structure than those with alkyl bromides. This observation is consistent with greater bond reorganization in the transition state for cleavage of the carbon–chlorine bond than for cleavage of the weaker carbon–bromine bond. In principle, a similar check on the accuracy of the rate data for reduction of alkyl bromides by lithium 4,4'-dimethylbenzophenone ketyl might have been obtained by comparison with relative rates of reaction of alkyl iodides with lithium benzophenone ketyl, but this comparison has not been made. Second, in correlations of the rates of reaction of alkyl chlorides with magnesium with rates of reaction of alkyl chlorides and alkyl bromides with tri-*n*-butyltin radical, the point 8 for tertiary alkyl halides falls significantly off the best least-squares line. It is not possible to establish the internal consistency and reliability of the relative reaction of alkyl halides with magnesium by the same technique used with tri-*n*-butyltin hydride—that is, by establishing a good linear correlation between data obtained independently for alkyl bromides and alkyl chlorides—because only a limited number of alkyl bromides react with magnesium at less than mass-transport-limited rates. The tertiary alkyl point has, however, been rechecked carefully and is reproducible. The apparently anomalously slow rate of reaction of tertiary alkyl chloride with magnesium is thus not an experimental artifact and may reflect steric requirements for approach of a hindered carbon center to the magnesium surface. The data for tertiary alkyl halides have been included in calculating the correlation coefficients in Table II. Significantly improved correlations are obtained for comparison of the reaction of alkyl chlorides with magnesium and the reduction of alkyl chlorides and bromides by tri-*n*-butyltin radical if the data for reaction of tertiary alkyl halides are deleted ($r = 0.97$ and 0.92, respectively). In any case, these considerations do not substantially alter the mechanistic picture.

Discussion

The rates of reaction of the alkyl halides used in these structure–reactivity studies would be expected to reflect, among other structural features, changes in the hybridization of the carbon atom attached to halogen in going from the ground state to the rate-limiting transition state.[23,24] The observation of a linear correlation between reaction of these alkyl halides with tri-*n*-butyltin radical, with diaryl ketyl, and with magnesium indicates that the carbon–halogen bond is broken
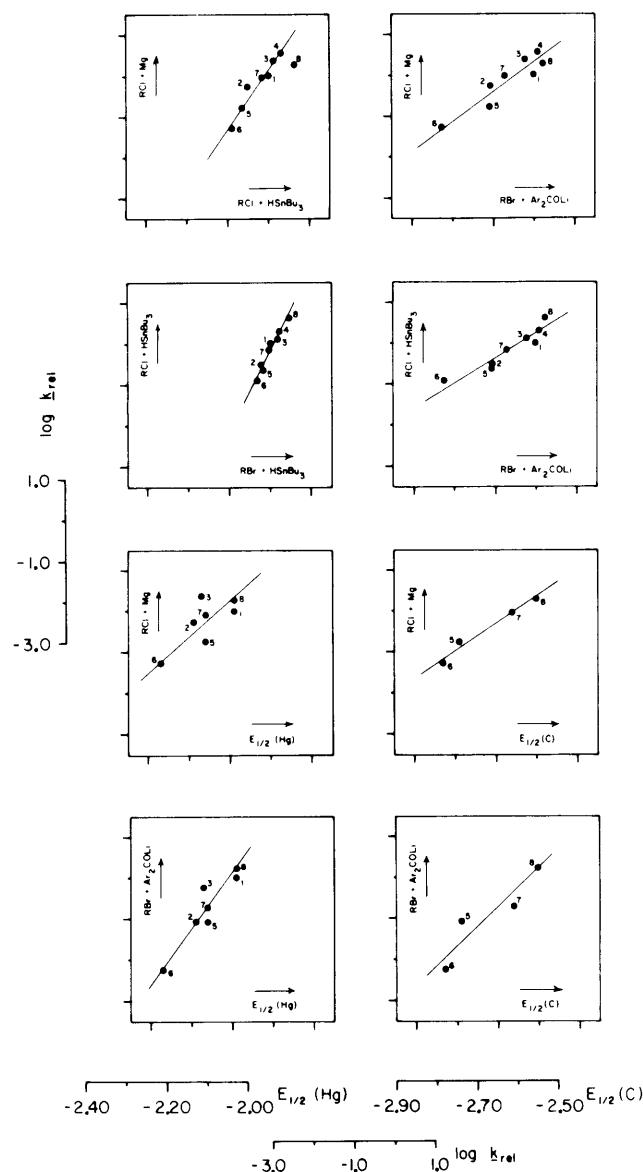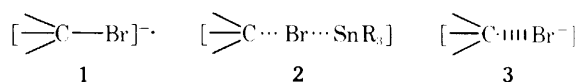

Figure 3. Correlations of data summarized in Table I. Correlation coefficients are listed in Table II. Ordinates are in all cases log k_{rel}. Abscissas are $E_{1/2}$ (V) for electrochemical reductions and are log k_{rel} for other reactions.

to an appreciable and similar extent in all three processes. The inference of appreciable carbon–halogen bond breaking in the transition state for tri-*n*-butyltin radical is expected.[25,26] The observation of rehybridization at carbon in the transition state for reduction by lithium diaryl ketyl is compatible with a reaction in which carbon–halogen bond breaking is concerted

with electron transfer. It may, however, also be compatible with formation of an intermediate alkyl halide radical anion, provided that lengthening and weakening of the carbon-halogen bond occurs concurrently with electron transfer. In either event, these three types of reactions are essentially indistinguishable, when examined by using a comparison of rate-structure profiles derived from this set of aliphatic halides. Previous work with aryl halides indicated a similar sensitivity in rates of reaction with both magnesium and tri-*n*-butyltin radical to substituents on the aryl ring.[8]

The potential-structure profile for electrochemical reduction of alkyl bromides at a mercury cathode shows only a general correlation with the rate-structure profiles characterizing reactions of alkyl halides with magnesium and tri-*n*-butyltin radicals, while electrochemical reduction of alkyl chlorides at a glassy carbon cathode is characterized by an apparently higher correlation (Table II).[27] The data for reduction at glassy carbon include only four acyclic alkyl halides, however. If the reduction of only the corresponding acyclic alkyl bromides at mercury is considered, correlations comparable to those for reduction at carbon are obtained. Thus, although the limited data available for electrochemical reductions make quantitative mechanistic comparison of the reduction of alkyl halides by homogeneous reagents and electrochemical methods difficult, it appears qualitatively that relative reactivities of organic halides are closely similar in reactions with tri-*n*-butyltin radicals, diaryl ketyls, magnesium metal, and carbon and mercury cathodes.[28]

The bearing of this work on the long-standing question of the existence of alkyl halide radical anions deserves brief comment. The linear correlation between rate-structure profiles for the three reductions of alkyl halides with ketyl, tin hydride, and magnesium is compatible with paths in which there are no intermediates between starting materials and products for each, but cannot rigorously exclude either a path involving an intermediate *after* the rate-determining transition state, or one in which superficially different reactions (e.g., halogen abstraction by Bu₃Sn· and formation of a short-lived RX⁻· by electron transfer) coincidentally show similar changes in hybridization at the carbon originally bonded to halogen in their respective transition states. The roughly comparable influence of changes in structure on the rate of each reaction suggests, however, that carbon-halogen bond breaking is significant and similar for each, and argues against a reaction coordinate involving any intermediate very similar in geometry to the starting material. Thus, if an alkyl halide radical anion is formed as an intermediate in reaction of an alkyl halide with 4,4'-dimethylbenzophenone ketyl or magnesium, and if the structure of this radical anion resembles the transition state for its formation or decomposition, its structure must be similar in the hybridization and charge on carbon bonded to halogen to that for the transition state for abstraction of a halogen atom by tri-*n*-butyltin radical. A close similarity between these two structures (1 and 2) cannot be excluded but would be surprising; an intermediate of structure 3[14] might be expected to resemble transition state 2 in hybridization and charge on carbon.

$$[\underset{}{\diagup}\!\!\diagdown C\!-\!Br]^{-}\!\cdot \qquad [\underset{}{\diagup}\!\!\diagdown C\cdots Br\cdots SnR_3] \qquad [\underset{}{\diagup}\!\!\diagdown C\cdots Br^{-}]$$
    1   2   3

The original question of whether the reaction of alkyl halides with magnesium proceeds by an inner sphere or outer sphere pathway thus has not been resolved by this work. Moreover, it probably cannot be resolved by an experimental approach based on qualitative comparisons of rate-structure profiles with those for reactions which might be expected to exemplify these mechanistic limits, since all of these profiles appear to be linearly correlated with one another. It is possible that an

incomplete set of model reactions was examined in this work, and that none provides an example of, e.g., an outer sphere electron transfer reaction generating an intermediate alkyl halide radical anion. In this event, examination of some other reaction might yield a distinguishable rate-structure profile characteristic of this type of reaction. Even if such a reaction exists, however, the work of Endicott et al.[26] emphasizes that well-defined inner and outer sphere electron transfer processes may exhibit linearly correlated rate-structure profiles. Thus it is not evident that rate-structure profiles for reductions of alkyl halides will be sensitive to this distinction.

Experimental Section

General Methods. Most alkyl halides were obtained from Aldrich, Eastman, or Chemical Samples Co.; 2-bromo-2-methylpentane was synthesized by standard literature procedures.[29] Alkyl halides were checked for purity by GLC before use, and impure samples were passed through a column of Woelm Activity-I alumina and distilled. Tri-*n*-butyltin hydride was prepared by literature methods,[30] distilled, and stored in a Schlenk flask under argon in the dark. Azobisisobutyronitrile (AIBN) was recrystallized from 95% ethanol to mp 103-104 °C (lit.[31] mp 102-103 °C) and stored at 1 °C in the dark. Benzopinacol was used as received from Aldrich, and 4,4',4'',4'''-tetramethylbenzopinacol was synthesized from commercial 4,4'-dimethylbenzophenone[32] and had mp 173-174 °C (lit.[32] mp 175-177 °C). 4,4'-Dimethylbenzhydryl pentyl ether and 1,1-di-*p*-tolylhexanol were synthesized by standard literature procedures.[33] Methyllithium was used as received from Alfa-Ventron Corp. and was titrated before use by the Gilman double titration method, using 1,2-dibromoethane.[34] Diethyl ether and THF were distilled from disodium benzophenone dianion under argon. Except where noted, unexceptional inert atmosphere syringe and cannula techniques were employed.[35] An Ultraviolet Products, Inc., Model UVSL-25 long wavelength UV lamp was used to irradiate tri-*n*-butyltin hydride reductions. GLC analyses were carried out by using flame ionization instruments equipped with electronic integrators.

Reductions of Alkyl Chlorides with Tri-*n*-butyltin Hydride. All reductions were performed in a similar manner. Reaction aliquots were quenched either with CCl₄, or by cooling to 0 °C (control experiments confirmed that the reduction of alkyl chlorides with tri-*n*-butyltin hydride is negligible at 0 °C in diethyl ether). Typically, to a 25-mL round-bottomed flask equipped with a magnetic stirring bar and reflux condenser and flushed with argon were added ether (8.0 mL) and tri-*n*-butyltin hydride (1.8 mL, 6.8 mmol). The solution was brought to reflux, and a solution of AIBN (0.017 g, 0.11 mmol), a hydrocarbon GLC standard (40 µL), and two different alkyl chlorides (40 µL each, approximately 0.40 mmol) in ether (1 mL) was added. An aliquot (0.5 mL) was removed, and the flask was illuminated with a long wavelength UV lamp. Additional aliquots were removed periodically. Relative rates were obtained by evaluating the slope of log ([R₁Cl]ₜ/[R₁Cl]₀) vs. log ([R₂Cl]ₜ/[R₂Cl]₀).

Determination of the Rate of Reduction of Cyclopentyl Bromide with Lithium Benzophenone Ketyl. The rate constant was determined under pseudo-first-order conditions employing excess lithium benzophenone ketyl. Argon was scrubbed by bubbling through a purple solution of disodium benzophenone dianion in THF. To a 15-mL centrifuge tube which had been stoppered with a No-Air septum and flame dried under an argon stream was added THF (7 mL) and benzopinacol (0.75 g, 2.1 mmol). After dissolution of the benzopinacol, it was transferred to a 35-mL, flame-dried, high-pressure vial equipped with a magnetic stirring bar and sealed with a butyl rubber septum and crown cap. The temperature was maintained at 20 °C with a water bath. To this vigorously stirred solution were added methyllithium (1.7 M in ether, 2.0 mL, 3.4 mmol) and 50 µL each of *n*-octane (internal GLC standard) and cyclopentyl bromide (0.47 mmol). Aliquots (0.5-0.8 mL) were removed after 0.5, 18, 39, 60, 90, 120, 180, and 253 min and quenched with water. A pseudo-first-order plot of log ([*c*-pentylBr]ₜ/[*c*-pentylBr]₀) vs. time was linear over the first 2 h (30% reaction). Evaluation of this plot gave $k = 9.5 \times 10^{-5}$ L mol⁻¹ s⁻¹.

Reduction of *n*-Pentyl Bromide with Lithium 4,4'-Dimethylbenzophenone. To a vigorously stirred solution of 4,4',4'',4'''-tetramethylbenzopinacol (0.6 g, 1.4 mmol) in THF (17 mL) was added MeLi (1.3 M in diethyl ether, 2.0 mL, 2.6 mmol), *n*-nonane (40 µL, GLC stan-

dard), and *n*-pentyl bromide (120 μL, 0.97 mmol). Aliquots (1 mL) were removed every 8 h, quenched with methanol, and analyzed by GLC. As the reaction progressed, a compound was formed possessing a retention time equal to that of 1,1,-di-*p*-tolyhexanol and different from that of 4,4′-dimethylbenzhydryl pentyl ether.

Reductions of Alkyl Bromides with Lithium 4,4′-Dimethylbenzophenone Ketyl. All reductions were performed in a similar manner. Argon was scrubbed by bubbling through a purple solution of disodium benzophenone dianion in THF. Reactions were performed in 35-mL high-pressure glass vials equipped with magnetic stirring bars, sealed with butyl rubber septa and crown caps, and flame dried under an argon stream. Typically, a solution of 4,4′,4″,4′″-tetramethylbenzopinacol (0.50 g, 1.2 mmol) in THF (20 mL) was purged for 0.5 h with argon and transferred to a sealed high-pressure vial. The temperature was maintained at 24 ± 1 °C with a water bath. To this vigorously stirred solution was added MeLi (1.6 M in ether, 1.3 mL, 2.1 mmol) and 25 μL each of *n*-alkane (internal GLC standard) and two alkyl bromides (approximately 0.2 mmol of each). Aliquots (0.5 mL) were periodically removed, quenched with methanol or water, and analyzed by GLC. The absolute rate constant for the reduction of cyclopentyl bromide by lithium 4,4′-dimethylbenzophenone ketyl was obtained from plots of log ([*c*-pentylBr]ₜ/[*c*-pentylBr]₀) vs. time under pseudo-first-order conditions.

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(26) We note explicitly that the common assumptions that reaction of tri-*n*-butyltin radical with an alkyl halide proceeds by inner sphere electron transfer with halogen bridging and that ketyl reductions occur by outer sphere electron transfer are not rigorously proved. For example, a pathway for reduction of RX with Bu₃Sn· involving initial electron transfer and formation of an *ion pair* with structure RX⁻·Bu₃Sn⁺ or R·X⁻Bu₃Sn⁺ followed by rapid Sn–X bond formation is difficult to exclude. Conversely, reaction of RX with Ar₂CO⁻·M⁺ might involve inner sphere transfer through bridging halogen and metal ion (Ar₂CO⁻····M⁺···XR). Present work suggests that rate–structure profiles may not be very useful in making distinctions of this type. Work in better defined inorganic electron-transfer reactions has also established that rate–structure profiles for inner and outer sphere electron transfer reactions may be linearly correlated and reinforces this conclusion (Durham, B.; Endicott, J. F.; Wong, C.-L.; Rillema, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 847–857).
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$$\log k = 8.5E° + a \qquad \qquad \text{(i)}$$

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