Polar Radicals. 14.[1] On the Mechanism of Trialkylstannane Reductions. Positive ρ Values for the Tri-*n*-butylstannane Reduction of Benzyl Halides. A Correlation with σ^-

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Abstract: The relative reactivities toward reduction by tri-*n*-butylstannane of a series of substituted benzyl halides have been determined. The order of reactivity was shown to be I > Br > Cl, the same as that reported for alkyl halide reductions. Under the reaction conditions (90 °C, benzene as solvent, benzoyl peroxide initiation), both aralkyl and alkyl fluorides were shown to be completely unreactive. Activation energies were estimated for the direct abstraction of halogen by tri-*n*-butyltin radicals, and on the basis of these estimates all of the halogens would be predicted to readily undergo abstraction. To explain the nonreactivity of the fluorides several other mechanisms were considered: reversible tin radical addition to the halogen to form an intermediate with an expanded octet, and a free radical chain mechanism involving an electron-transfer reaction between the trialkyltin radical and the benzyl halide. The benzyl halide reductions showed excellent Hammett correlations with positive ρ values; all of these correlations were obtained using σ^- substituent constants. The demonstration (the first ever reported) that σ^- substituent constants correlate with the relative reactivities for reduction infers that bond breaking takes place in the transition state for the reaction. The magnitudes of the ρ values were not found, as were expected, to be in the inverse order of the relative reactivities: ρ for the iodides (+0.81), for the bromides (+0.17), and for the chlorides (+0.34). To explain the anomalously high value of ρ found for the iodide reduction, it was suggested that the benzyl iodides underwent reduction by a different mechanism than the chlorides and bromides. The relative rates of reduction of the benzyl iodides in a more polar solvent than benzene, acetonitrile, showed decreased sensitivity to substituents, whereas the reduction of the bromides and chlorides was relatively insensitive to solvent effects.

Introduction

Walling and Mayo were the first to apply the Hammett equation to radical reactions 30 years ago.[2] Since then polar effects in radical reactions and in particular such effects in hydrogen atom transfer reactions of substituted toluenes have been the object of considerable study.[3,4] Walling and Miller proposed that the polar effect observed in the photochlorination of substituted toluenes could be interpreted in terms of polar resonance structures and recognized the need for two different σ values for substituents capable of resonance interaction in the transition state.[5] Russell subsequently demonstrated that a number of pieces of data taken from the literature gave excellent correlations with σ^+ substituent constants.[6] The polar effect was rationalized in terms of perturbation by the substituent of the polar contributions inherent in the transition state. Thus, for a radical X with a greater electron affinity than carbon, the magnitude of ρ should reflect the importance of canonical form I. This argument also predicts that the Hammett relationship should change from a σ to a σ^+ correlation with radical–substrate pairs having widely differing electronegativities; these predictions have been generally substantiated.[4] However, until this study no example of a reaction having a σ^- correlation, indicative of the dominant contribution of canonical form III, has been reported.

$$\underset{\mathrm{I}}{[\mathrm{Ar}\overset{+}{\mathrm{C}}\mathrm{H}_2\cdot\cdot\mathrm{H}\cdot\cdot\cdot\overset{-}{\mathrm{X}}]^{\cdot\ddagger}} \leftrightarrow \underset{\mathrm{II}}{[\mathrm{ArCH}_2\cdot\cdot\mathrm{H}\cdot\cdot\cdot\mathrm{X}]^{\cdot\ddagger}} \leftrightarrow \underset{\mathrm{III}}{[\mathrm{Ar}\overset{-}{\mathrm{C}}\mathrm{H}_2\cdot\cdot\mathrm{H}\cdot\cdot\overset{+}{\mathrm{X}}]^{\cdot\ddagger}} \quad (1)$$

Recently Zavitsas and Pinto[7] have proposed that the observed ρ values do not reflect polar effects but are due to the differences in the bond dissociation energies (BDE) of the benzylic C–H bonds of the substituted toluenes. Subsequent to this proposal evidence which contradicted this suggestion was presented.[8,9]

The Zavitsas argument predicts a negative ρ value for all radical abstractions from substituted toluenes if the BDEs are the sole factors controlling reactivity. In contrast to this prediction, positive ρ values have been reported for abstractions by *tert*-butyl,[10,11] isopropyl,[11] 1-ethylpentyl,[12] and undecyl[13,14] radicals. The positive ρ values reported have, subsequent to their first publication, been shown to be artifacts of competitive reactions, and as such are unreliable and clearly do not constitute a test of the Zavitsas hypothesis.[1,15,16] Atom-transfer reactions to electropositive centers appear to be experimentally quite difficult to observe. The effects would be predicted to be negligibly small for reactions involving carbon–hydrogen to carbon transfers,[1] while reactions involving carbon–hydrogen to metal atom transfers would invariably be energetically unfavorable, and would proceed in the reverse.

A suitable model for the systematic study of the charge type leading to a positive ρ value appeared to be the well-known carbon–halogen to metal atom transfer sequence involved in the radical chain metal hydride reduction reactions of organic halides. Recently Sakurai and Mochida[17] have obtained a Hammett correlation for the reaction of substituted α-chlorotoluenes with triethylgermane (ρ = 0.312). However, the authors indicated that a two-step mechanism (eq 2) rather than a one-step mechanism (eq 3) could not be excluded for the abstraction of the chlorine atom.

$$\mathrm{Et_3Ge\cdot + Cl\text{-}R \rightleftharpoons [Et_3Ge\text{-}\dot{C}l\text{-}R] \rightarrow Et_3GeCl + R\cdot} \quad (2)$$

$$\mathrm{Et_3Ge\cdot + Cl\text{-}R \rightarrow Et_3GeCl + R\cdot} \quad (3)$$

This possibility is of interest as eq 2 and 3 represent two modes of reduction of organic halides which are difficult to experimentally differentiate.

Kuivila[18] has extensively studied the mechanism of the reduction of alkyl halides by triaryl- and alkylstannanes and proposed that the halogen atom is abstracted in a direct manner by the radical:

$$\mathrm{RX + \cdot SnR_3 \longrightarrow [R\cdot\cdot X\cdot\cdot\cdot SnR_3]^{\ddagger} \longrightarrow R_3Sn\text{-}X + R\cdot} \quad (4)$$

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Table I. Relative Reactivities of Substituted α-Chlorotoluenes toward Tri-*n*-butylstannane at 90 °C[a]

substituent	k/k_0[a]	σ[b]	σ^-
p-cyano	2.57[d]	0.63	1.00[e]
p-cyano	2.78 (±0.16)[f]		
m-cyano	1.87 (±0.03)	0.68	
p-carboethoxy	1.87 (±0.03)	0.52	0.68[e]
m-trifluoromethyl	1.64 (±0.04)[g]	0.42	
m-chloro	1.57 (±0.01)[c]	0.37	
m-fluoro	1.29 (±0.01)[h]	0.34	
p-chloro	1.45 (±0.04)[d]	0.23	
p-fluoro	1.17 (±0.01)	0.06	
p-phenyl	1.33 (±0.04)	0.01	0.11[i]
H	1.00	0	0
m-methyl	1.08 (±0.01)	−0.07	
p-methyl	1.04 (±0.01)	−0.17	
p-(*tert*-butyl)	0.97 (±0.01)	−0.20	

[a] Average value of three individual experiments. The error values in parentheses are standard deviations from the mean. [b] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). [c] k/k_0 for α,3-dichlorotoluene was 1.65 (±0.04) in acetonitrile. [d] k/k_0 was determined by disappearance of reactants. [e] J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, 1968. [f] Average of nine ampules. [g] L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964). [h] Average of six ampules. [i] O. Exner, "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Eds., Plenum Press, New York, 1972.

Table II. Relative Reactivities of Substituted α-Bromotoluenes toward Tri-*n*-butylstannane at 90 °C[a]

substituent	k/k_0	σ[b]	σ^-
p-cyano	1.48 (±0.06)[c]	0.63	1.00[d]
p-carboethoxy	1.31 (±0.04)	0.52	0.68[d]
m-bromo	1.15 (±0.01)[e]	0.39	
m-fluoro	1.13 (±0.01)	0.34	
p-bromo	1.20 (±0.01)	0.23	
H	1.00	0	
m-methyl	0.97 (±0.01)	−0.07	
p-methyl	0.94 (±0.03)	−0.17	

[a] Average value of three individual experiments. The error values in parentheses are standard deviations from the mean. [b] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). [c] k/k_0 for α-bromo-*p*-tolunitrile was 1.65 (±0.03) in acetonitrile. [d] Table I, footnote *e*. [e] Menapace and Kuivila reported values of 1.21 and 1.18 for this compound: L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

He suggested[18b] that these systems "promise to be useful for studies on polar effects involving the relatively electropositive tin radicals as a complement to work which has already been done on the electronegative radicals such as *tert*-butoxy and chlorine atoms". Although the abstraction mechanism (eq 4) is currently accepted, a mechanism analogous to that suggested by Sakurai for the reductions with triethylgermane[17] must also be considered (eq 5). However, the report[18c] that the relative

$$\mathrm{ArCH_2X} + \cdot\mathrm{SnR_3}$$

$$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{i}}{\left[\mathrm{ArCH_2}\overset{\delta-}{\mathrm{X}}\cdot\cdot\cdot\overset{\delta+}{\mathrm{Sn}}\mathrm{R_3}\right]^{\cdot\ddagger}} \rightleftharpoons \underset{\text{intermediate}}{\mathrm{ArCH_2}-\dot{\mathrm{X}}-\mathrm{SnR_3}}$$

$$\xrightarrow{k_2} \underset{\text{ii}}{\left[\mathrm{Ar}\overset{\delta-}{\mathrm{C}}\mathrm{H_2}\cdot\cdot\cdot\overset{\delta+}{\mathrm{X}}\mathrm{SnR_3}\right]^{\cdot\ddagger}} \longrightarrow \mathrm{ArCH_2}\cdot + \mathrm{XSnR_3} \qquad (5)$$

reactivities of the alkyl halides is RI > RBr > RCl > RF, and the fact that there is one reported case of reduction in solution of an aralkyl fluoride, $C_6H_5CF_3$,[18a,c] and also a report that both a primary alkyl fluoride and a secondary alkyl fluoride had been reduced in the vapor phase,[18d] suggests that this alternative mechanism is not correct, since the reduction of an alkyl halide by this mechanism necessitates that the halide be capable of expanding its octet. Fluorine, a first-row element, is energetically incapable of undergoing this process and would not undergo reduction by this mechanism.

Both of the alternative mechanisms, if subject to polar substituent effects, would be predicted to show Hammett equation correlations which follow σ^- substituent constants, by analogy to the reactions involving a reverse polarity which are found to follow σ^+.

A third, and hitherto ignored, mechanism, which deserves consideration, can be proposed for the reduction. This mechanism, a radical-chain process which involves in its propagation sequence an electron-transfer reaction (eq 6), is given below.

$$\mathrm{R_3Sn}\cdot + \mathrm{ArCH_2X} \rightarrow \mathrm{R_3Sn^+} + \mathrm{ArCH_2X^-}\cdot \qquad (6)$$

$$\mathrm{ArCH_2X^-}\cdot \rightarrow \mathrm{ArCH_2}\cdot + \mathrm{X^-} \qquad (7)$$

$$\mathrm{ArCH_2}\cdot + \mathrm{R_3SnH} \rightarrow \mathrm{ArCH_3} + \mathrm{R_3Sn}\cdot \qquad (8)$$

An examination of the literature leads one to the prediction that an electron-transfer process such as that depicted by eq 6 should show a positive Hammett correlation and would conceivably also show a preferred correlation with σ^- substituent constants, since the polaragraphic half-wave potentials determined for the reduction of a series of substituted benzyl bromides showed this behavior.[19]

The relative reactivities of α-halotoluenes with tri-*n*-butylstannane have, therefore, been determined in an attempt to correlate reactivity with the enthalpy of reaction, elucidate the mechanism of the reduction, and clarify the nature of substituent effects in atom-transfer reactions. The results of this study are the subject of this communication.

Results

Competitive Reactions of α-Halotoluenes with Tri-*n*-butylstannane. A number of substituted α-chlorotoluenes, α-bromotoluenes, and α-iodotoluenes were obtained commercially or were synthesized and their reactivities, relative to the parent α-halotoluene, with tri-*n*-butylstannane in solvent benzene (90 °C) were determined by measurement of the rate of appearance of the product toluenes. Several of these relative rates obtained in this manner were verified by the determination of the rates of disappearance of the reactants. In the latter cases excellent material balances were obtained for both products and reactants. The relative reactivities of the α-halotoluenes are listed in Tables I-III.

Hammett plots of log k_a/k_a^0 vs. the substituent constant, σ^-, gave quite good correlations while only fair correlations were obtained with σ substituent constants (see Table IV).

Nagai had previously examined the reduction of six α-chlorotoluenes with tri-*n*-butylstannane and reported his results in a brief abstract.[20] Using this data ρ can be calculated and shown to be in excellent agreement with our value (ρ (σ) = 0.42, r = 0.97, S_ρ = 0.05 and ρ (σ^-) = 0.33, r = 0.96, S_ρ = 0.04).

The relative reactivities of α-chlorotoluene and α-bromotoluene and of α-bromotoluene and α-iodotoluene were determined indirectly. Mixtures of α-iodotoluene and α-bromo-3-fluorotoluene and of α-bromo-3-fluorotoluene and α,3-dichlorotoluene were reacted (90 °C) with tri-*n*-butylstannane in the presence of benzoyl peroxide. α-Bromotoluene was calculated to be 496 ± 128 times more reactive than α-chlorotoluene. α-Iodotoluene was found to be 12.74 ± 0.71 times more reactive than α-bromotoluene. Kuivila has reported that α-bromotoluene was 670 times more reactive than

Table III. Relative Reactivities of Substituted α-Iodotoluenes toward Tri-*n*-butylstannane at 90 °C[a]

substituent	k/k_0 benzene	k/k_0 acetonitrile	σ^b	σ^-
p-cyano	7.29 (±0.32)[d]	2.17 (±0.21)[e]	0.63	1.00[c]
p-carboethoxy	4.36 (±0.09)		0.52	0.68[c]
m-chloro	2.12 (±0.09)	1.51 (±0.06)	0.37	
m-fluoro	1.81 (±0.03)	1.30 (±0.04)	0.34	
p-chloro	1.81 (±0.01)	1.44 (±0.03)	0.23	
p-phenyl	1.37 (±0.12)		0.01	0.11[f]
H	1.00	1.00	0	
p-methyl	0.92 (±0.02)	1.27 (±0.02)	−0.17	

[a] Average value of two individual experiments. The error values in parentheses are the standard deviations from the mean. [b] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). [c] Table I, footnote *e*. [d] This value was determined indirectly. The relative reactivity of α-iodo-*p*-tolunitrile and *p*-chloro-α-iodotoluene was found to be 4.00 (±0.17) and is the average of nine experiments. [e] Average of five experiments. [f] Table I, footnote *i*.

α-chlorotoluene, under his reaction conditions, using a more accurate multistep method for the determination of this relative rate.[18a]

In an attempt to accentuate the magnitude of the substituent effects, the reductions of a number of benzyl halides were carried out in solvent acetonitrile. As expected for a free-radical reaction the relative rates of reduction of the α-chlorotoluenes and α-bromotoluenes were only slightly enhanced (indicating a more positive ρ) (see Tables I and II, footnotes *c*). Contrary to the above results the relative rates of reduction of the α-iodotoluenes in acetonitrile were dramatically affected, and, although the Hammett correlation of these values become very poor ($r = 0.88$, $S_\rho = 0.07$), the ρ (σ^-) value obtained ($\rho = 0.24$) in this solvent was much less positive than the one obtained in solvent benzene; see Table III.

An effort was made to obtain the relative reactivity of α-bromotoluene and 3-chloro-α-iodotoluene in acetonitrile; however, consistent results were not obtained. The inconsistent results could be explained by an examination of the 200-MHz spectrum of the reaction mixture after reduction. Aside from the absorptions of the unreacted starting materials and the products formed, two new absorptions were detectable (δ 4.52 and 4.50 ppm) and were assigned to the α hydrogens of α-iodotoluene and α-bromo-3-chlorotoluene. The quantities of the four unreduced benzyl halides were approximately equal. This exchange reaction was found to occur upon heating the initial benzyl halides in acetonitrile in the absence of an initiator or of tri-*n*-butylstannane. An investigation of the exchange reaction in solvent benzene, however, showed that scrambling had occurred to less than 6% between the above benzyl bromide and iodide. Exchange (10–16%) was observed during the reduction of α-bromotoluene and α,3-dichlorotoluene in solvent acetonitrile. In this case, since the exchange reaction is small, α-bromotoluene was calculated to be approximately >100 times more reactive than α-chlorotoluene toward stannane reduction in that solvent.

Attempted Reduction of α-Fluorotoluene, α,α,α-Trifluorotoluene, Cyclohexyl Fluoride, and 1-Chloro-4-fluorobutane. Kuivila has intimated that α,α,α-trifluorotoluene may be reduced, albeit very slowly, by tri-*n*-butylstannane.[18a,c] However, as a mechanism involving an intermediate halo compound with an expanded octet is contrary to this observation, the reaction was reinvestigated. After careful purification of the substrates neither α-fluorotoluene nor α,α,α-trifluorotoluene was observed to give detectable reduction products when their reaction was carried out under the conditions reported in this paper, in solvent benzene. Furthermore, exchange reactions could not be observed (200-MHz NMR) when a mixture of α-fluorotoluene and 3-fluoro-α-iodotoluene was submitted to the normal reduction conditions in acetonitrile.

Table IV. ρ Values for the Reactions of α-Halotoluenes with Tri-*n*-butylstannane

α-halotoluene	Hammett substituent constant σ^- ρ	σ^- r	σ^- S_ρ	σ ρ	σ r	σ S_ρ
α-chloro-	0.34	0.97	0.02	0.40	0.92	0.05
α-bromo-	0.17	0.98	0.02	0.22	0.95	0.03
α-iodo-	0.81	0.99	0.05	1.05	0.94	0.16

Although cyclohexyl fluoride and 1-chloro-4-fluorobutane had been reported to react in the vapor phase by a chain reaction (30–184 °C, 0.2 h),[18d] under the conditions used for the reduction of the benzyl chlorides, the carefully purified materials failed to show any detectable reduction (<0.01%).

Discussion

The relative rates of reduction, $ArCH_2I > ArCH_2Br > ArCH_2Cl \gg ArCH_2F$, as determined by the competitive reactions agreed well with the order reported for the relative rates of reduction of the alkyl halides,[18] with the exception that α-fluorotoluene was completely unreactive under the conditions employed in this study. A search of the literature revealed that the order of the reduction always includes the fluoride,[18,21,22] although only one reduction in solution by tri-*n*-butylstannane of an alkyl or aryl fluoride, α,α,α-trifluorotoluene, has been reported.[18a,c] One example[18d] of the reduction a primary fluoride, 1-chloro-4-fluorobutane, and one example of a secondary fluoride, cyclohexyl fluoride, have been reported for their photoinitiated vapor phase reduction by trimethylstannane. Under our reaction conditions, however, no detectable reduction of the carbon–fluorine bond of these alkyl fluorides, <0.01%, could be observed. The trifluoride was reported previously to be very unreactive;[18a,c] however, in the vapor-phase reduction alkyl fluorides[18d] were reported to be quite reactive. This contradictory behavior between the liquid- and vapor-phase reactions of the two different stannanes is presently being investigated. In the case of the reaction run in solution, the α,α,α-trifluorotoluene was reported to be "largely unaffected" [18c] or "reacts very slowly" [18a] under the reaction conditions (80 °C, several hours, neat), whereas α,α,α-trichlorotoluene underwent a spontaneous exothermic reduction at room temperature. In our hands, under the conditions of this study, α,α,α-trifluorotoluene was found to be completely unreactive.

The lack of reactivity of the fluorides could be rationalized in terms of the direct atom transfer mechanism having a high activation energy for the abstraction step, eq 4. The nonreactivity could also be explained by the inability of fluorine, a first-row element, to extend its octet or by the high activation energy necessary for electron transfer to the electronegative fluorine.[23] An estimate of the energies of activation for all the halide reductions proceeding via eq 4 could be obtained by the application of either the empirical Hirschfelder rules[24] or the empirical method suggested by Semenov,[25] using the enthalpies of these reactions. Unfortunately, the bond dissociation energies of the product tin halides and α-fluorotoluene have not been reported. However, the bond dissociation energies of trimethylstannyl chloride, bromide, and iodide have been reported (or may be calculated from their heats of formation), and the corresponding BDEs of the α-chloro-, bromo-, and iodotoluenes are known. The BDE of α-fluorotoluene may be extrapolated from a comparison of the known values for the homologous series of methyl halides,[26] while the known BDE values of the trimethylstannyl halides, with the extrapolated value for trimethylstannyl fluoride, can be used as models for

Table V. Bond Dissociation Energies of Methyl, Benzyl, and Trimethylstannyl Halides (kcal/mol)

R	F	Cl	Br	I
CH_3-[a]	109	84	70	56
$C_6H_5CH_2$-[a]	(95)[b]	69	55	45
$(CH_3)_3Sn$-	(132)[b]	106 ± 4[c]	94 ± 4[d]	80 ± 4[d]

[a] Reference 46, p F-240. [b] Estimated value; see ref 23. [c] Calculated using the method described in ref *d*, using the heat of formation of trimethylstannyl chloride reported by G. A. Nash, H. A. Skinner, and W. F. Stack, *Trans. Faraday Soc.*, **61**, 640 (1965). [d] A. L. Yergey and F. W. Lampe, *J. Am. Chem. Soc.*, **87**, 4204 (1965).

Table VI. Enthalpies and Estimated Activation Energies (kcal/mol) for the Reaction $R_3Sn\cdot + C_6H_5CH_2X \rightarrow R_3SnX + C_6H_5CH_2\cdot$ (eq 4)

X	ΔH	E_a[a]
F	−37	5.2 (2.2)
Cl	−37	3.8 (2.2)
Br	−39	3.0 (1.7)
I	−35	2.5 (2.7)

[a] Values quoted were obtained using the Hirschfelder rules,[24] while the values in parentheses were calculated using the method of Semenov.[25]

the tri-*n*-butylstannyl halides (see Table V). The enthalpies of reduction of the benzyl halides by trialkylstannane could be estimated from these values and are listed in Table VI.

As can be seen all of the enthalpies are negative. The application of the Hirschfelder or Semenov rules, using this data, indicates that all of the benzylic halides are capable of undergoing a favorable abstraction process (eq 4). The error introduced in these calculations by the use of trimethylstannane as a model for the reduction reactions of tri-*n*-butylstannane should be qualitative since all of the halide reductions are predicted to be strongly exothermic and the differences expected between the methyl- and *n*-butyltrialkylstannyl halides should be small in comparison (about the same, ~3 kcal/mol, as the differences in the average BDEs reported for trimethylstannyl bromide and tri-*n*-butylstannyl bromide).[27]

It would appear from the energetics of the reaction and from the lack of reactivity of the fluoride that several mechanistic possibilities must be considered. Thus either a mechanism incorporating an intermediate with an expanded octet or a mechanism involving electron transfer is operative. However, it is possible that with different halides different modes of reduction take place. Some insight into an answer using this type of reasoning can be obtained by an examination of the relative magnitudes of the ρ values obtained for the reduction of the different halides. The relative magnitude of the ρ values should be the inverse of the relative rates since reactions which occur more rapidly should be less susceptible to substituent effects. However, as can be seen from Table IV, this is not the case since, although the bromide has a lower ρ value than the chloride, as would be predicted from their relative rates, the ρ value for the iodide is abnormally high. This result indicates that the reductions must proceed via some pathway which is highly susceptible to polar interactions in the case of the iodides but less so for the other halogens. The most obvious explanation is that there is more than one mechanism operative in these reductions. However, a consideration of the multistep mechanism, eq 5, leads to the conclusion that the ρ value would not be just a simple expression proportional to one set of relative rate constants, but would be instead due to the ratio of the observed rate constants, which are equivalent to the expression

$$\left(\frac{k}{k_0}\right)_{\text{obsd}} = \left(\frac{k_1}{k_1'}\right)\left(\frac{k_2}{k_2'}\right)\left(\frac{k_{-1}'}{k_{-1}}\right)\left(\frac{1 + k_2'/k_{-1}'}{1 + k_2/k_{-1}}\right) \tag{9}$$

The observed ρ value would then be a composite of the ρ values for the three reactions involved in this mechanism and would be a function of the four terms in the above equation. A variation in any of the rate-constant ratios could affect the magnitude of the ρ value obtained. However, the fact that the observed ρ value correlates quite well with σ^- would militate that there be some carbon–halogen bond breaking in the reaction which dominated the magnitude of the ρ value (i.e., reaction k_2) since a correlation having this substituent effect suggests that there is bond breaking in the transition state for the rate-determining step. If only one mechanism were involved, then this mechanism (eq 5) does not afford a satisfactory explanation for the relative ordering of the ρ values since, as k_2 is dominant, the iodide forming the intermediate having the weakest carbon–halogen bond would still be expected to have the smallest ρ value. The observed correlation with σ^- and the relative ordering of the magnitude of the ρ values appear to be inconsistent with the operation of a single mechanism for the halide reductions.

An attractive mechanism for the reduction of the iodides or of the bromides and chlorides involves electron transfer (eq 6) in the rate-determining step. However, there must be some bond breaking concomitant with this transfer in order to explain the correlation with σ^-. The correlation of the half-wave potentials determined for the polarographic reduction of substituted benzyl chlorides and bromides supports this proposal.[19,28] Both studies gave a positive ρ value for the reductions and the bromide was shown to correlate well with σ^- substituent constants. The results of the reductions of the benzyl chlorides[28] inferred that a possible correlation with σ^- also existed (i.e., if more substituents were studied).[29] Unfortunately, the polarographic reduction of the benzyl iodides could not be achieved;[30,31] however, it is expected that the reductions of these iodides would give similar results (i.e., a positive ρ value and correlation with σ^- substituent constants) if they could be effected. Although the electrochemical correlation with σ^- was originally not explained in this manner,[19] the mechanism for polarographic reduction of other alkyl and aryl halides has been rationalized as a dissociative electron attachment process.[32]

The choice of mechanism for the iodide reductions, as opposed to that for the bromides and chlorides, is not clear since both the ease of reduction and the ability of the halide to expand its octet favor the iodides.[33] The high ρ value observed for the iodide reductions does suggest the rather greater charge separation which would be involved in the electron-transfer process. Consistent with this argument was the large solvent effect observed when the reductions of the iodides were carried out in acetonitrile. The ρ value became more negative. The solvent effect on a transition state in which two neutral species react to form two charged species would be significant. Since an ionic halogen exchange reaction is observed (NMR studies) in acetonitrile, the observed solvent effect could also be adequately explained by the incursion of an ionic component to the reduction (i.e., one having a negative ρ value). However, the exchange reaction may be independent of the reduction. The solvent-affected component of the mechanism does not appear to be important during the reduction of the chlorides and bromides as their ρ values were slightly increased in solvent acetonitrile, a result consistent with the small effect of solvent predicted for a radical mechanism.

Conclusion

If the thermodynamic estimates are correct and all of the benzyl halides should undergo abstraction with equal facility, the lack of reactivity of the fluorides suggests an electron-transfer mechanism (eq 6) or a mechanism involving an intermediate with an expanded octet (eq 5) for the reduction of the benzyl halides with tri-*n*-butylstannane. Because of the relative magnitudes of the ρ values observed for the different halides it is suggested that the iodides are reduced by a different mechanism than the bromides and chlorides.

The observation that the positive ρ values observed correlate with σ^- substituent constants (the first ever reported case for a free radical chain reaction) not only implies bond breaking in the transition state for tin hydride reductions, but also is consistent with the general theory of polar interactions in the transition states of atom-transfer reactions.

The suggestion that tin hydride reductions under selected conditions (reactive iodides in polar media) may proceed by a polar pathway is now being investigated further, as is the proposed electron-transfer process suggested as a mode of reaction for tin hydride reductions.

Experimental Section

Materials. α-Fluorotoluene was prepared by the method of Delpuech and Beguin[34] and the product was repeatedly distilled to remove all trace of toluene and α-bromotoluene. Substrates, α-chlorotoluene (Fisher Scientific Co.), α-bromotoluene (Matheson Coleman and Bell), α,α,α-trifluorotoluene (Eastman Kodak Co.), and α-iodotoluene (Eastman Kodak Co.) were fractionally distilled through a packed column and shown to be single compounds (>99.9%) by GLC (10 ft × ⅛ in. 3% OV-101 on 100-120 mesh Chromosorb W AW).

α-Chloro-*p*-tolunitrile[35] (mp 79.5-80 °C) and α-chloro-*m*-tolunitrile[36] (mp 68-69 °C) were prepared by photochlorination of the corresponding toluenes. The purity of these compounds was checked by elemental analysis and GLC (OV-101 column). The purity of commercial samples (Aldrich Chemical Co. Ltd.) of α-chloro-*p*-xylene, α-chloro-*m*-fluorotoluene, α,3-dichlorotoluene, α-chloro-*m*-xylene, α,4-dichlorotoluene, 4-(*tert*-butyl)benzyl chloride, α-chloro-*p*-fluorotoluene, α-chloro-*p*-phenyltoluene, α-bromo-*p*-xylene, α-bromo-*p*-tolunitrile, α,4-dibromotoluene, α-bromo-*m*-fluorotoluene, α-bromo-*m*-xylene (Eastman Kodak Co.), and α,3-dibromotoluene was checked by GLC (OV-101 column). Compounds which contained toluenes or were less than 99% pure were purified by low-temperature fractional recrystallization or by fractional distillation in the case of liquids or by recrystallization from ethanol in the case of solids.

Ethyl 4-chloromethylbenzoate was prepared by passing chlorine into ethyl *p*-toluate (16.4 g, 0.1 mol) at 125 °C, irradiated by two 200-W incandescent lamps, until the weight of the ester increased by 4 g. The liquid was cooled, ether (100 mL) added, the solution washed with water (3 × 20 mL), the organic layer dried over anhydrous magnesium sulfate, and the product isolated by fractional distillation through a packed column followed by refractionation through a 12-in. spinning band column. The fraction bp 142 °C (8 mm) (lit.[37] 91-93 °C (0.6 mm)) was collected. GLC analysis showed the absence of any ethyl *p*-toluate and that the chloro ester was 93% pure. NMR analysis indicated that the impurity was the α,α-dichloro ester. Further attempts to purify the ester failed and the sample was used in the competitive experiments, without further purification.

α-Iodo-*p*-xylene,[38] *p*-chloro-α-iodotoluene,[38] *m*-chloro-α-iodotoluene,[39] *m*-fluoro-α-iodotoluene,[40] α-iodo-*p*-tolunitrile,[41] *p*-phenylbenzyl iodide,[42] fluorocyclohexane,[43] and 1-chloro-4-fluorobutane[44] were prepared by known methods. The purities of the products were checked by elemental analysis and comparison of physical properties with those reported in the literature.

Ethyl 4-iodomethylbenzoate was prepared by reaction of ethyl 4-bromomethylbenzoate[45] (20 g) with sodium iodide (95 g) in refluxing dry acetone (500 mL) for 48 h. Ether was added to precipitate the dissolved salts, the solution was filtered, and the solvents were removed. The solid organic residue was recrystallized from hexane three times to give colorless needles (mp 61.5-63.0 °C). Anal. Calcd for $C_{10}H_{11}IO_2$: C, 41.40; H, 3.82; I, 43.74; O, 11.03. Found: C, 41.24; H, 3.86; I, 44.63; O, 11.21.

The purification of toluene, *p*-xylene, *m*-xylene, *p*- and *m*-chlorotoluenes, and *p*-cyanotoluene has been reported.[15] *m*-Cyanotoluene (Eastman Kodak Co.), *m*-fluorotoluene (Eastman Kodak Co.), *p*-fluorotoluene (Aldrich Chemical Co.), 4-*tert*-butyltoluene (Aldrich Chemical Co.), *p*-phenyltoluene (Aldrich Chemical Co.), and *m*- and *p*-bromotoluenes (Eastman Kodak Co.) were distilled or recrystallized before use if their GLC analyses (OV-101 column) showed the presence of more than one compound

The tri-*n*-butylstannane (Alfa Ventron) was used without purification.

Attempted Reaction of α-Fluorotoluene with Tri-*n*-butylstannane. An aliquot (1 mL) of a solution of α-fluorotoluene (4.4 mmol), tri-*n*-butylstannane (3.0 mmol), and benzoyl peroxide (0.09 mmol) in benzene (2 mL) was degassed, sealed in a Pyrex ampule, and thermostated (20 h) at 90 °C. Analytical techniques, which had been shown capable of detecting less than 0.01% of toluene in a typical reaction mixture, indicated that α-fluorotoluene, under conditions which permitted 87% of available tri-*n*-butylstannane to reduce a mixture of α-chlorotoluenes, was, itself, not reduced.

Attempted Reaction of α,α,α-Trifluorotoluene, Fluorocyclohexane, and 1-Chloro-4-fluorobutane with Tri-*n*-butylstannane. An aliquot (1 mL) of a solution of the fluoride (10.1 mmol), tri-*n*-butylstannane (8.7 mmol), and benzoyl peroxide (0.3 mmol) in benzene (5 mL) was degassed, sealed in a Pyrex ampule, and thermostated (20 h) at 90 °C and analyzed by GLC (OV-101).

Although a sample of α,α-difluorotoluene was not available, its boiling point (139.9 °C, 760 mm)[46a] is approximately that of α-fluorotoluene (139.80 °C, 753 mm).[46b] Since no products (less than 0.001%) were detected (GLC) with a retention time between that of α,α,α-trifluorotoluene (bp 102 °C, 760 mm)[46c] and α-fluorotoluene nor were any products detected with a retention time corresponding to α-fluorotoluene or any other compound within a ±30 °C boiling point range of benzyl fluoride, it was concluded that no reduction of the trifluorotoluene had taken place.

Neither cyclohexane nor 1-chlorobutane could be detected (less than 0.01%) in the solutions of the corresponding fluorides after 20 h at 90 °C.

Competitive Reactions of Substituted α-Chlorotoluenes or α-Bromotoluenes with Tri-*n*-butylstannane. The substituted α-halotoluene (10 mmol), α-halotoluene (10 mmol), tri-*n*-butylstannane (1.0 mmol), and benzoyl peroxide (3.0 × 10^{-2} mmol) were accurately weighed into a volumetric flask and diluted to 5 mL with benzene. Aliquots (1 mL) of the solution were degassed by the freeze-thaw method and sealed in Pyrex ampules. The ampules were thermostated (90 °C) for 12 h, then opened and the toluenes formed analyzed by GLC (OV-101 column). The reactions of the α-halotolunitriles were performed using one-third of the aforementioned quantities, in benzene (5 mL), owing to their low solubility.

The competitive reactions involving α-chloro-*p*-tolunitrile were also carried out by measuring the rate of disappearance of reactants in the presence of an internal standard (*p*-xylene). Control experiments showed that known mixtures could be subjected to the reaction conditions and analytical procedures to give quantitative results. This method was also used to determine the relative reactivity of α,4-dichlorotoluene.

Competitive Reactions of Substituted α-Iodotoluenes with Tri-*n*-butylstannane. The substituted α-iodotoluene (4.0 mmol) and α-iodotoluene (4.0 mmol) were accurately weighed into a volumetric flask and diluted to 2 mL with benzene. Tri-*n*-butylstannane (4.0 × 10^{-1} mmol) and benzoyl peroxide (1.2 × 10^{-2} mmol) were weighed into a flask and the solution was diluted to 2 mL with benzene. Each solution (0.5 mL) was pipetted into the arms of an inverted U tube to keep each solution separate. The reaction vessel was degassed and thermostated at 90 °C. After equilibration, the solutions were rapidly mixed and thermostated at 90 °C for 12 h. GLC analysis was effected using a 20 ft × ⅛ in. 20% diisodecyl phthalate on Chromosorb W AW 60/80 column. The competitive reaction of α-iodo-*p*-tolunitrile was performed using *p*-chloro-α-iodotoluene in the place of α-iodotoluene.

Competitive Reactions of α-Iodotoluene and α-Bromo-3-fluorotoluene and Tri-*n*-butylstannane. The reaction was carried out in an identical manner with the competitive reactions of substituted α-iodotoluenes. The relative reactivity, $k_{\alpha\text{-iodotoluene}}/k_{\alpha\text{-bromo-3-fluorotoluene}}$, of these halotoluenes was 11.3 ± 0.6.

Competitive Reactions of α-Bromo-3-fluorotoluene and α,3-Dichlorotoluene with Tri-*n*-butylstannane. α-Bromo-3-fluorotoluene (11.9 mmol), α,3-dichlorotoluene (8.55 mmol), and *p*-xylene (1.167 × 10^{-1} mmol) were accurately weighed into a volumetric flask and diluted to 5 mL with benzene. Tri-*n*-butylstannane (1.01 mmol) and benzoyl peroxide (3.63 × 10^{-2} mmol) were accurately weighed into a second volumetric flask and diluted to 5 mL with benzene. Aliquots (1 mL) of each solution were degassed and sealed in a Pyrex ampule. The ampules were thermostated at 90 °C for 20 h and the formed toluenes analyzed by GLC (20-ft OV-101). The relative reactivity of these α-halotoluenes, $k_{\alpha\text{-bromo-3-fluorotoluene}}/k_{\alpha,3\text{-dichlorotoluene}}$, was 357 ± 92.

Competitive Reactions of Substituted α-Halotoluenes with Tri-*n*-butylstannane in Acetonitrile. The substituted α-halotoluene (4.0 mmol) and benzoyl peroxide (1.2×10^{-2} mmol) were accurately weighed into a volumetric flask and diluted to 2 mL with acetonitrile. The solution (0.75 mL) was pipetted into one arm of the reaction tube and tri-*n*-butylstannane (45 μL) was placed in the other arm. After degassing, the tube was thermostated at 90 °C and, after equilibration, the solution and the tri-*n*-butylstannane were rapidly mixed and thermostated at 90 °C for 12 h. GLC analysis was effected using the 2 ft × $^1/_8$ in 20% diisodecyl phthalate column.

Competitive Reaction of α-Bromotoluene and 3-Chloro-α-iodotoluene with Tri-*n*-butylstannane in Acetonitrile. The reaction was performed in analogous fashion to the reduction of the α-halotoluenes in acetonitrile. The 200-MHz NMR spectrum of the reaction mixture after thermostating for 15 h showed peaks of approximately equal intensity at 4.44, 4.50, 4.52, and 4.57 ppm corresponding to the absorptions due to the benzylic hydrogens of 3-chloro-α-iodotoluene, α-bromo-3-chlorotoluene, α-iodotoluene, and α-bromotoluene. A similar result was obtained when α-bromotoluene and 3-chloro-α-iodotoluene were heated (90 °C) for 15 h in acetonitrile. When the reduction was repeated in solvent benzene, less than 6% of the exchange products, α-iodotoluene and α-bromo-3-chlorotoluene, was detected by NMR.

Competitive Reaction of α,3-Dichlorotoluene and α-Bromotoluene with Tri-*n*-butylstannane in Acetonitrile. The reaction was performed in an analogous fashion to the reductions of the α-halotoluenes in acetonitrile. The 200-MHz NMR spectrum of the reaction mixture after thermostating for 15 h showed peaks at 4.49, 4.55, 4.59, and 4.63 ppm corresponding to the absorptions of the benzylic hydrogens of α-bromo-3-chlorotoluene, α-bromotoluene, α,3-dichlorotoluene, and α-chlorotoluene. The areas of the peaks at 4.63 and 4.49 ppm were 10–16% the areas of the other peaks. The relative reactivity of these α-halotoluenes, $k_{\alpha\text{-bromotoluene}}/k_{\alpha,3\text{-dichlorotoluene}}$, was greater than 70.

GLC Analysis. All quantitative values were determined using standard calibration curves determined using known mixtures of the authentic materials. The areas were determined using a HP5840A GC terminal interfaced to a HP 5840A gas chromatograph fitted with thermal conductivity detectors.

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References and Notes

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$$C_6H_5CH_2I + Hg \rightarrow C_6H_5CH_2HgI$$

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