Carbon–Halogen Bonding Studies. Halogen Redistribution Reactions between Alkyl or Acetyl Halides and Tri-*n*-butyltin Halides

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Abstract: The equilibrium positions have been determined for the halogen redistribution reactions of tri-*n*-butyltin halides with a variety of structurally different types of alkyl halides and with acetyl halides. These have been related through the reaction $\Delta G°$ values to carbon–halogen bond dissociation energy differences. It is suggested that the trends observed in the latter may provide evidence for the existence of a small steric bond weakening effect in the order C–I > C–Br > C–Cl bonds on going from methyl to primary, secondary, and tertiary alkyl halides. On the other hand, with the 2,3-π bond containing allyl, benzyl, and propargyl halides, α-haloacetones, and haloacetonitriles, there may be some type of electronic carbon–halogen bond strengthening effect which lies in the order C–I > C–Br > C–Cl. Finally, for the acetyl halides, the data are in agreement with increases in bond strengths resulting from π contributions being in the order C–Cl > C–Br > C–I.

Introduction

In the course of our recent studies[1,2] of the mechanisms of uncatalyzed and halide ion catalyzed halogen redistribution reactions between carbon of alkyl halides and tin of tri-*n*-butyltin halides, it was observed that the reactions all proceeded to readily measurable equilibrium positions:

$$\mathrm{Bu_3SnX + RX' \rightleftarrows Bu_3SnX' + RX}$$

For equilibria of this type, where the species on both sides of the equilibrium are closely similar, one might anticipate that the $\Delta S°$ values should be close to zero. If so, then $\Delta G°$ for these equilibria approximate $\Delta H°$ which can be related to the dissociation energies of the bonds being made and broken in achieving equilibrium as follows:

$$\Delta H° = DH°(\mathrm{Bu_3SnX}) + DH°(\mathrm{RX'}) - DH°(\mathrm{Bu_3SnX'}) - DH°(\mathrm{RX})$$

$$\Delta H° = [DH°(\mathrm{Bu_3SnX}) - DH°(\mathrm{Bu_3SnX'})] - [DH°(\mathrm{RX}) - DH°(\mathrm{RX'})]$$

Thus, the $\Delta G°$ values represent the difference between a given tin–halogen bond-dissociation energy difference and the corresponding carbon–halogen bond-dissociation energy difference. Consequently, consideration of the trends in $\Delta G°$ produced by changes in the alkyl halide structure for the reactions with tri-*n*-butyltin halides should provide important information concerning possible steric or electronic effects upon the relative strengths of carbon–halogen bonds. This is an area which has received considerable theoretical[3] and experimental[4] attention in recent years.

Results and Discussion

Before entering into the study of structural effects upon the halogen redistribution reactions between tri-*n*-butyltin halides and alkyl halides, a representative system was examined to ascertain whether the expectation of zero or near-zero $\Delta S°$ values for the reactions was tenable. This was done by studying the reactions of tri-*n*-butyltin chloride with benzyl bromide and with benzyl iodide at various temperatures. These reactions were chosen because of their convenient rates for attaining equilibrium, and also because of the ease with which they could be accurately analyzed using NMR techniques not requiring prior workup.

The equilibrium positions were determined in each case on a single reaction mixture whose temperature was raised in steps from 50 to 100 to 150 °C and then lowered back down in steps to 100 and 50 °C. As is seen from the data in Table I, the equilibrium constants for the reactions did change with temperature. However, the $\Delta G°$ values within experimental error were independent of temperature, indicating that, for all of the halogen redistribution reactions between alkyl halides and tri-*n*-butyltin halides, one can assume that $\Delta S° = 0$. Also, one can assume that $\Delta G° = \Delta H°$ and is temperature independent over the range of at least ~50 to ~150 °C.

The results of our initial studies of structural effects upon the halogen redistribution reactions between carbon and tin are summarized in Table II. The compositions of the equilibrium mixtures were determined by NMR or GLC techniques as described in the Experimental Section. Included in this study were examples of saturated and π-bond-containing alkyl halides as well as acetyl halides. The accuracy of the method is shown by the internal consistency of the results available for a number of the systems. Thus, $\Delta G°$ for a $\mathrm{Bu_3SnCl + RI}$ reaction minus $\Delta G°$ for the $\mathrm{Bu_3SnBr + RI}$ reaction should equal $\Delta G°$ for the corresponding $\mathrm{Bu_3SnCl + RBr}$ reaction within experimental error.

For most of the systems investigated, the redistribution reactions proceeded without significant sideproduct formation. However, in the cases of the isopropyl iodide with tri-*n*-butyltin chloride and the *tert*-butyl bromide with tri-*n*-butyltin chloride or tri-*n*-butyltin iodide reactions, *ca.* 15, 30, and 20% respectively, dehydrohalogenation to propylene or isobutylene had taken place by the time equilibrium was reached. Also, in the reactions of propargyl bromide or chloride with tri-*n*-butyltin iodide, ca. 15 and 50%, respectively, of allenyl iodide had formed by the time equilibrium was reached.

The concurrent propargyl iodide–allenyl iodide rearrangement[5] involved in the propargyl halide reactions presented only minor problems since the reaction mixtures in these cases could still be completely analyzed. Thus, the allenyl iodide formation could be easily corrected for in the K_{eq} calculations. However, for the isopropyl and *tert*-butyl halide cases, the situation was considerably more complicated because the eliminated hydrogen halides reacted quantitatively with the tri-*n*-butyltin halides to produce di-*n*-butyltin dihalides and *n*-butane. Thus, the reaction mixtures contained both tri-*n*-butyltin halides and di-*n*-butyltin dihalides whose relative amounts unfortunately could not be precisely determined. However, we had previously noted[6] in the reactions of benzhydryl bromide or benzyl bromide with di-*n*-butyltin dichloride in 1:1 mole ratios that, within experimental error, the same equilibrium positions were attained as for the reactions of these alkyl halides with tri-*n*-butyltin chloride in 1:2 mole

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Table I. The Reactions of Tri-*n*-butyltin Chloride with Benzyl Bromide or with Benzyl Iodide, Neat, in 1:1 Mole Ratios at Various Temperatures

$C_6H_5CH_2X$, X	temp, °C	% $C_6H_5CH_2Cl$ at equil	K_{eq}	$\Delta G°$, kcal mol^{-1}
Br	50	62 ± 1	2.7 ± 0.2	−0.6 ± 0.1
Br	100	61 ± 1	2.4 ± 0.2	−0.6 ± 0.1
Br	150	60 ± 1	2.3 ± 0.2	−0.7 ± 0.1
Br	100	61 ± 1	2.4 ± 0.2	−0.6 ± 0.1
Br	50	63 ± 1	2.9 ± 0.2	−0.7 ± 0.1
I	50	33 ± 1	0.24 ± 0.03	+0.9 ± 0.1
I	100	37 ± 1	0.34 ± 0.03	+0.8 ± 0.1
I	150	39 ± 1	0.41 ± 0.03	+0.8 ± 0.1
I	100	36 ± 1	0.32 ± 0.03	+0.8 ± 0.1
I	50	33 ± 1	0.24 ± 0.03	+0.9 ± 0.1

ratios. This suggested, for the isopropyl and *tert*-butyl halide cases where dehydrohalogenation was a problem, that the equilibrium constants might be calculated simply on the basis of the concentrations of the different types of tin-halogen bonds in the reaction mixtures. The validity of this approach was demonstrated for the *tert*-butyl bromide with tri-*n*-butyltin chloride or iodide reactions where the equilibrium constants for the halogen redistributions, when calculated using the tin-halogen bond concentration method, were found to be invariant within experimental error over the range of 30-75 and 20-60% isobutylene (i.e., di-*n*-butyltin dihalide) formation, respectively.

Returning to the data in Table II, the $\Delta G°$ values (i.e., $\Delta H°$ values) measured for each of the reaction systems represent the difference between a given tri-*n*-butyltin halide bond-dissociation energy difference and the corresponding alkyl halide bond-dissociation energy difference. Thus, a positive $\Delta G°$ value means that the carbon-halogen bond-dissociation energy difference is smaller than the corresponding tin-halogen bond-dissociation energy difference, and vice versa.

However, a more meaningful way to consider the data is as shown in Table III where the $\Delta\Delta G°$ values (i.e., $\Delta\Delta H°$ values) given represent the difference between an alkyl halide bond-dissociation energy difference of interest and the corresponding *n*-propyl halide bond-dissociation energy difference:

$$\Delta\Delta G° = \Delta\Delta H° = \Delta G°(Bu_3SnX + n\text{-}PrX') - \Delta G°(Bu_3SnX + RX')$$

$$\Delta\Delta G° = [DH°(RX) - DH°(RX')] - [DH°(n\text{-}PrX) - DH°(n\text{-}PrX')]$$

A positive $\Delta\Delta G°$ value thus means that the carbon-halogen bond-dissociation energy difference for the alkyl halide system is larger than that for the corresponding *n*-propyl halides, and vice versa. The *n*-propyl halides were chosen as the basis standards for this treatment because this would enable ready comparisons with the data for the allyl, propargyl, and benzyl systems studied which were also mostly formally primary alkyl halides.

In considering the data in Table III, it is noted that the range of values for the carbon-halogen bond-dissociation energy differences of the alkyl halides examined is small. These vary only by ca. ±3, ±2, and ±1 kcal mol^{-1}, respectively, with structure for the CCl-CI, CBr-CI, and CCl-CBr bond-dissociation energy differences. Thus, any effects of structure in the systems examined on bonding differences between carbon

Table II. Reactions of Various Alkyl Halides with Tri-*n*-butyltin Halides, Neat, in 1:1 Mole Ratios

Bu_3SnX, X	RX′	rxn temp, °C	% RX[a] at equil	K_{eq}	$\Delta G°$, kcal mol^{-1},[b] at rxn temp
Cl	CH_3I	100	34	0.27 ± 0.02	+1.0 ± 0.1
Br	CH_3I	100	20	0.063 ± 0.008	+2.0 ± 0.1
Cl	CH_3Br	100			(−1.0 ± 0.2)
Cl	$CH_3CH_2CH_2I$	100	55	1.5 ± 0.1	−0.3 ± 0.1
Br	$CH_3CH_2CH_2I$	100	34	0.27 ± 0.02	+1.0 ± 0.1
Cl	$CH_3CH_2CH_2Br$	100	71	6.0 ± 0.6	−1.3 ± 0.1
Cl	$CH_3C(CH_3)HI$	125		7.9 ± 0.8[c]	−1.6 ± 0.1
Br	$CH_3(CH_3)HI$	125	49	0.92 ± 0.08	+0.1 ± 0.1
Cl	$CH_3(CH_3)HBr$	125	75	9.0 ± 1.0	−1.7 ± 0.1
Cl	$CH_3C(CH_3)_2I$	100			(−2.5 ± 0.2)
Br	$CH_3C(CH_3)_2I$	100		2.3 ± 0.2[c,d]	−0.6 ± 0.1
Cl	$CH_3C(CH_3)_2Br$	100		12 ± 3[c]	−1.9 ± 0.1
Cl	$H_2C{=}CHCH_2I$	50			(+0.8 ± 0.2)
Br	$H_2C{=}CHCH_2I$	50	20	0.063 ± 0.008	+1.8 ± 0.1
Cl	$H_2C{=}CHCH_2Br$	50	69	5.0 ± 0.4	−1.0 ± 0.1
Cl	$O{=}C(CH_3)CH_2I$	50	26	0.12 ± 0.02[d]	+1.4 ± 0.1
Br	$O{=}C(CH_3)CH_2I$	50			(+2.4 ± 0.2)
Cl	$O{=}C(CH_3)CH_2Br$	50	67	4.1 ± 0.4[d]	−1.0 ± 0.1
Cl	$HC{\equiv}CCH_2I$	50		0.059 ± 0.005[d,e]	+1.8 ± 0.1
Br	$HC{\equiv}CCH_2I$	50		0.029 ± 0.002[d,e]	+2.3 ± 0.1
Cl	$HC{\equiv}CCH_2Br$	50		2.5 ± 0.2	−0.6 ± 0.1
Cl	$N{\equiv}CCH_2I$	50	13	0.002 ± 0.005[d]	+2.5 ± 0.1
Br	$N{\equiv}CCH_2I$	50			(+2.9 ± 0.2)
Cl	$N{\equiv}CCH_2Br$	50	58	1.9 ± 0.2[d]	−0.4 ± 0.1
Cl	$C_6H_5CH_2I$	50	34	0.27 ± 0.02	+0.8 ± 0.1
Br	$C_6H_5CH_2I$	50	26	0.12 ± 0.02	+1.4 ± 0.1
Cl	$C_6H_5CH_2Br$	50	63	2.9 ± 0.3	+0.7 ± 0.1
Cl	$(C_6H_5)_2CHI$	50	50	0.0 ± 0.1[d]	0.0 ± 0.1
Br	$(C_6H_5)_2CHI$	50	29	0.17 ± 0.01[d]	+1.1 ± 0.1
Cl	$(C_6H_5)_2CHBr$	50	71	6.0 ± 0.6	−1.2 ± 0.1
Cl	$CH_3C({=}O)I$	40	92	130 ± 40[d]	−3.0 ± 0.1
Br	$CH_3C({=}O)I$	40	65	3.4 ± 0.4[d]	−0.8 ± 0.1
Cl	$CH_3C({=}O)Br$	40	84	28 ± 4	−2.1 ± 0.1

[a] Determined after ~10 reaction half-lives. The runs in most cases were done at least in duplicate, and the values given are reproducible to ±1%. [b] The values in parentheses were not determined experimentally, but by calculation from other data. [c] Reaction was accompanied by significant olefin formation. Thus, the % RX at equilibrium is not listed. [d] Run in the reverse direction from that indicated. [e] Reaction was accompanied by some allenyl halide formation. Thus, the % RX at equilibrium is not listed.

Table III. $\Delta\Delta G°$ Values for the Reactions of Various Alkyl Halides with Tri-*n*-butyltin Halides, Neat, in 1:1 Mole Ratios[a]

alkyl halide system	$\Delta\Delta G°$ values,[b] kcal mol^{-1}: Bu_3SnCl + RI	Bu_3SnBr + RI	Bu_3SnCl + RBr
CH_3X	−1.3	−1.0	−0.3
$CH_3CH_2CH_2X$	(0)	(0)	(0)
$(CH_3)_2CHX$	+1.3	+0.8	+0.4
$(CH_3)_3CX$	+2.2	+1.6	+0.6
$H_2C{=}CHCH_2X$	−1.1	−0.8	−0.3
$O{=}C(CH_3)CH_2X$	−1.7	−1.4	−0.3
$HC{\equiv}CCH_2X$	−2.1	−1.3	−0.7
$N{\equiv}CCH_2X$	−2.8	−1.9	−0.9
$C_6H_5CH_2X$	−1.1	−0.4	−0.6
$(C_6H_5)_2CHX$	−0.3	−0.1	−0.1
$O{=}C(CH_3)X$	+2.7	+1.8	+0.8

[a] $\Delta\Delta G°$ values were calculated by subtracting $\Delta G°$ for reaction of RX from $\Delta G°$ for reaction of $CH_3CH_2CH_2X$. The $\Delta G°$ values were all assumed to be temperature independent and were taken from Table II. [b] ±0.2–0.3 kcal mol^{-1}.

and halogen must be energetically rather small. A similar conclusion can be drawn from considering the extensive list of bond-dissociation energies tabulated by Egger and Cocks[7] where the CCl–CI, CBr–CI, and CCl–CBr bond-dissociation energy differences which can be calculated all fall within the limits of ca. 28 ± 4, 15 ± 2, and 13 ± 2 kcal mol^{-1}, respectively.

Despite the rather small energy differences involved, the data in Table III reveal some very interesting trends which because of the accuracy of the present results must be meaningful. These trends could not in most cases, however, have been deduced with any reliability from looking directly at calorimetrically determined carbon–halogen bond-dissociation energy values because of their estimated[7] ±1.5 kcal mol^{-1} uncertainty.

The most obvious of the trends in Table III is that for the simple saturated alkyl halides where the $\Delta\Delta G°$ values gradually increase in the order methyl < *n*-propyl < isopropyl < *tert*-butyl. It is believed that this may reflect the presence of small steric effects which weaken the carbon–halogen bonds in the order C–I > C–Br > C–Cl with tertiary > secondary > primary > CH_3. Thus, for example, in the methyl halides neither the C–Cl, C–Br, or C–I bond strength should be affected to any great extent by steric effects, but in the *tert*-butyl halides any steric effects would be expected to cause carbon–halogen bond weakening in the order C–I > C–Br > C–Cl. However, it must be pointed out that, based solely on the present data, one cannot exclude the possibility that the trend in the carbon–halogen bond-dissociation energy differences in this series of compounds is instead due to some type of electronic effect.

In the hope of obtaining further information concerning the effects of structure on bonding with non-π-bond-containing alkyl halides, some additional primary alkyl halide data were gathered which are tabulated in Table IV. The $\Delta\Delta G°$ values shown in Table V for these reactions reveal that, except possibly for the case of the bromomethyl halides, all of the primary alkyl halides studied exhibit very similar bond-dissociation energy differences. This clearly shows the absence of any significant steric effects on carbon–halogen bond-dissociation energies produced by substituents further removed than the halogen-bearing carbon. However, these substituents do strongly affect the rates of attaining equilibrium in the reactions. For example, the reactions with the isobutyl halides had to be run at 125 instead of 100 °C, and even then were slow. This is not surprising, however, since the reaction rates presumably are a function of steric effects in a five-coordinate carbon-containing activated complex for a bimolecular displacement process.[2] By contrast, any steric effects which may be manifested in the equilibrium constants are for four-coordinate carbon.

For the halomethyl halides which were examined, there may be some type of polar electronic effects coming into play. However, unless these are being obscured by counteracting steric effects, they must be small in magnitude. The reason for what appears to be a small selective C–Br bond-weakening effect in the bromomethyl halides relative to the corresponding C–Cl and C–I bonds is unknown, but we do feel it is real and not due to experimental error.

Returning to Table III and to the π-bond-containing "primary" alkyl halides, it is observed that the carbon–halogen bond-dissociation energy differences of these are all at least slightly smaller than are those for the corresponding saturated primary alkyl halides. The order of magnitude for these decreases lies roughly in the order allyl, benzyl halides < α-haloacetones < propargyl halides < haloacetonitriles. However, adding a phenyl substituent to the benzyl system, as in the benzhydryl halides, results in a small recovery in the bond-dissociation energy differences.

Table IV. Reaction of Various Primary Alkyl Halides with Tri-*n*-butyltin Halides, Neat, in 1:1 Mole Ratios[a]

Bu_3SnX, X	RX′	rxn temp, °C	% RX[b] at equil	K_{eq}	$\Delta G°$, kcal mol^{-1}, at rxn temp
Cl	CH_3CH_2I	100	55	1.5 ± 0.1	−0.3 ± 0.1
Br	CH_3CH_2I	100	38	0.38 ± 0.03	+0.7 ± 0.1
Cl	CH_3CH_2Br	100	67	4.1 ± 0.4	−1.0 ± 0.1
Cl	$(CH_3)_2CHCH_2I$	125	55	1.5 ± 0.1	−0.3 ± 0.1
Br	$(CH_3)_2CHCH_2I$	125	33	0.24 ± 0.03	+1.1 ± 0.1
Cl	$(CH_3)_2CHCH_2Br$	125	70	5.4 ± 0.6	−1.3 ± 0.3
Cl	$CH_3(CH_2)_6CH_2I$	100	56	1.6 ± 0.2	−0.3 ± 0.1
Br	$CH_3(CH_2)_6CH_2I$	100	36	0.32 ± 0.03	+0.8 ± 0.1
Cl	$CH_3(CH_2)_6CH_2Br$	100	70	5.4 ± 0.6	−1.3 ± 0.1
Cl	$ClCH_2I$	100		0.91 ± 0.1[c]	+0.1 ± 0.1
Br	$ClCH_2I$	100			(+1.2 ± 0.2)
Cl	$ClCH_2Br$	100		4.2 ± 0.5[b]	−1.1 ± 0.1
Cl	$BrCH_2I$	100			(−0.3 ± 0.2)
Br	$BrCH_2I$	100		0.11 ± 0.02[d]	+1.6 ± 0.1
Cl	$BrCH_2Br$	100		12.8 ± 1.4	−1.9 ± 0.1
Cl	ICH_2I	100		0.91 ± 0.1	+0.1 ± 0.1
Br	ICH_2I	100		0.19 ± 0.02	+1.2 ± 0.1
Cl	ICH_2Br	100			(−1.1 ± 0.2)

[a] See footnotes *a* and *b* for Table II. [b] Actually determined during the reaction of CH_2Br_2 + *n*-Bu_3SnCl. [c] Actually determined during the reaction of CH_2I_2 + *n*-Bu_3SnCl. [d] Actually determined during the reaction of CH_2I_2 with *n*-Bu_3SnBr.

Table V. $\Delta\Delta G°$ Values for the Reaction of Various Primary Alkyl Halides with Tri-*n*-butyltin Halides, Neat, in 1:1 Mole Ratios[a]

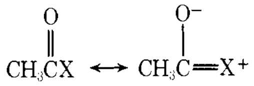
alkyl halide system	$\Delta\Delta G°$ values, kcal mol^{-1} [b]		
	Bu_3SnCl +RI	Bu_3SnBr +RI	Bu_3SnCl +RBr
CH_3CH_2X	0	+0.3	−0.3
$CH_3CH_2CH_2X$	(0)	(0)	(0)
$(CH_3)_2CHCH_2X$	0	−0.1	0
$CH_3(CH_2)_6CH_2X$	0	+0.2	0
$ClCH_2X$	−0.4	−0.2	−0.2
$BrCH_2X$	0	−0.6	+0.6
ICH_2X	−0.4	−0.2	−0.2

[a] $\Delta\Delta G°$ values were calculated by subtracting $\Delta G°$ for reaction of RX from $\Delta G°$ for reaction of $CH_3CH_2CH_2X$. The $\Delta G°$ values were all assumed to be temperature independent and were taken from Tables II and IV. [b] ±0.2–0.3 kcal mol^{-1}.

We suggest that the decreases in the carbon–halogen bond-dissociation energy differences in the above π-bond-containing systems compared with those in the corresponding saturated alkyl halides may be due to a bond-strengthening electronic effect which is most important in the order C–I > C–Br > C–Cl. The behavior then in the benzhydryl system could involve a combination of opposing steric and electronic effects. However, what the precise nature of the bond-strengthening electronic effect is has thus far eluded us.

In a brief study attempting to obtain more information concerning the nature of the carbon–halogen bonding in the benzyl system, we have measured the equilibrium positions in the reactions of several ring-substituted benzyl halides with tri-*n*-butyltin halides. The data obtained for these runs, which are given in Table VI together with the data for the unsubstituted system, indicate that ring-substituent effects on the bond-dissociation energy differences in the benzyl halide system must be small. In fact, within experimental error the ring substituents appear to have no effect upon the CCl–CBr bond-dissociation energy difference.

Finally, returning to the last entry in Table III, the $\Delta\Delta G°$ values for the acetyl halides are relatively large and positive compared with those of all of the alkyl halides studied except *tert*-butyl. These increases may be explained in terms of π contributions to the carbon–halogen bonding of the type shown. This would be expected to increase bond strengths in the order C–Cl > C–Br > C–I.



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}X \longleftrightarrow CH_3\overset{\overset{\displaystyle O^-}{|}}{C}{=}X^+$$

In conclusion, the results of the present study provide unique insight into some of the problems and phenomena involved in carbon–halogen bonding and the related area of halomethyl-substituent effects. It is hoped that they will serve to stimulate further experimental and theoretical studies leading to a better understanding of bonding interactions with the halogens.

Experimental Section

All melting points and boiling points are uncorrected. NMR spectra were run using Varian A-60A or EM360 instruments, and GLC analyses were carried out using an Aerograph A90 P3 instrument.

Tri-*n*-butyltin Halides. Tri-*n*-butyltin chloride was obtained commercially (Aldrich) and redistilled before use. Tri-*n*-butyltin iodide was synthesized by reaction of tri-*n*-butyltin chloride with potassium iodide in acetone: bp 152 °C (6 mm), n^{22}_D 1.5270 (lit.[8] bp 168 °C (8 mm), n^{20}_D 1.5345).

Alkyl and Acetyl Halides. Except as noted below, all of the alkyl and acetyl halides used in this work were obtained commercially and, if necessary, redistilled or recrystallized before use. Benzyl iodide was prepared by the reaction of benzyl chloride with potassium iodide in acetone: bp 52–53 °C (0.5 mm), n^{22}_D 1.6342 (lit.[9] bp 93 °C (10 mm), n^{25}_D 1.6334). Benzhydryl bromide, mp 43–44 °C (lit.[10] mp 42 °C) was prepared by *N*-bromosuccinimide bromination of diphenylmethane and purified by reduced pressure distillation. *p*-Methoxybenzyl chloride was prepared by reaction of *p*-methoxybenzyl alcohol with 37% aqueous HCl at room temperature for 4 h: n^{22}_D 1.5545 (lit.[11] n^{20}_D 1.5491).

General Equilibration Procedures. For those reactions which were to be followed using quantitative NMR techniques, ~1.5–2.0-mmol quantities of the alkyl halide and tri-*n*-butyltin halide together with ~0.08–0.1 mmol of pyridine were carefully weighed into an NMR tube. The pyridine was used for "in situ" generation of an *N*-alkylpyridinium halide catalyst for the reactions. The tube was then swept with nitrogen, sealed, and heated in a constant-temperature oil bath at the desired temperature until periodic examination showed no further changes in the composition of the reaction mixture. Then the mixtures were heated for a further period such that ~10 reaction half-lives total time had elapsed before final analysis. Runs which were followed using GLC techniques were done similarly but on ~10–20-mmol scale and the reaction mixtures were divided up into a number of small sealed Pyrex ampules. Most of the runs were carried out at least in duplicate, and the results shown are averages of the observed values. The errors given are estimates based on the results of multiple runs and from controls done to determine the accuracies of the analytical methods. Except for selected cases, only the relative molar amounts of the alkyl halides present in the reaction mixtures were experimentally determined. The actual amounts of tri-*n*-butyltin halides and alkyl halides present were calculated after correcting for the quaternary ammonium halide catalyst formation assuming that $RX_e + RX'_e = RX'_i$; $Bu_3SnX_e + Bu_3SnX'_e = Bu_3SnX_i$; and $Bu_3SnX'_e = RX'_i - RX'_e$, where i refers to initially weighed in quantities of

Table VI. Reactions of Various Benzyl Halides with Tri-*n*-Butyltin Halides, Neat, in 1:1 Mole Ratios at 50 °C

Bu_3SnX, X	RX′	% RX[a] at equil	K_{eq}	$\Delta G°$, kcal mol^{-1},[b] at 323 K
Cl	$C_6H_5CH_2I$	34	0.27 ± 0.02	+0.8 ± 0.1
Br	$C_6H_5CH_2I$	26	0.12 ± 0.02	+1.4 ± 0.1
Cl	$C_6H_5CH_2Br$	63	2.9 ± 0.3	−0.7 ± 0.1
Cl	*p*-$CH_3OC_6H_4CH_2I$	27	0.14 ± 0.02[c]c	+1.3 ± 0.1
Br	*p*-$CH_3OC_6H_4CH_2I$			(+1.8 ± 0.2)
Cl	*p*-$CH_3OC_6H_4CH_2Br$	60	2.3 ± 0.1[c]	−0.5 ± 0.1
Cl	*p*-$CH_3C_6H_4CH_2I$	30	0.18 ± 0.02[c]	+1.1 ± 0.1
Br	*p*-$CH_3C_6H_4CH_2I$			(+1.8 ± 0.2)
Cl	*p*-$CH_3C_6H_5CH_2Br$	63	2.9 ± 0.3[c]	−0.7 ± 0.1
Cl	*m*-$FC_6H_4CH_2I$	28	0.15 ± 0.02[c]	+1.2 ± 0.1
Br	*m*-$FC_6H_5CH_2I$			(+2.1 ± 0.2)
Cl	*m*-$FC_6H_5CH_2Br$	65	3.4 ± 0.4	−0.9 ± 0.1
Cl	*p*-$NO_2C_6H_4CH_2I$	38	0.38 ± 0.03[c,d]	+0.6 ± 0.1
Br	*p*-$NO_2C_6H_4CH_2I$			(+1.3 ± 0.2)
Cl	*p*-$NO_2C_6H_4CH_2Br$	63	2.9 ± 0.3	−0.7 ± 0.1

[a] Determined after ~10 reaction half-lives for runs in most cases done at least in duplicate. [b] Values in parentheses were not determined experimentally, but by calculation from other data. [c] Run in the reverse direction from that indicated. [d] Done in benzene solution.

Table VII. Approximate NMR Chemical Shifts[a] of Selected Alkyl Halide Protons in Neat, 1:1 Mole Ratio Reactions of the Alkyl Halides with Tri-*n*-butylin Halides

system	δ, ppm from Me_4Si			system	δ, ppm from Me_4Si		
	Cl	Br	I		Cl	Br	I
CH_3-	3.1	2.6	2.2	$\mathrm{H_2C{=}CHC}\mathit{H}_2$-	4.0	3.9	3.8
$\mathrm{CH_3C}\mathit{H}_2$-	3.6	3.5	3.2	$\mathrm{C_6H_5C}\mathit{H}_2$-	4.5	4.4	4.4
$\mathrm{CH_3CH_2C}\mathit{H}_2$-	3.5	3.4	3.2	$m\text{-}\mathrm{FC_6H_4C}\mathit{H}_2$-	4.5	4.4	4.4
$\mathrm{CH_3(CH_2)_6C}\mathit{H}_2$-	3.5	3.4	3.2	$p\text{-}\mathrm{NO_2C_6H_4C}\mathit{H}_2$-[b]	3.6	3.4	3.1
$\mathrm{(CH_3)_2CHC}\mathit{H}_2$-	3.4	3.3	3.1	$p\text{-}\mathrm{CH_3OC_6H_4C}\mathit{H}_2$-	4.5	4.4	4.4
$ClCH_2$-	5.6	5.4	5.2	$p\text{-}\mathrm{CH_3C_6H_4C}\mathit{H}_2$-	4.4	4.3	4.4
$BrCH_2$-	5.2	5.0	4.6	$\mathrm{(CH_3)_2C}\mathit{H}$-	4.1	4.2	4.3
ICH_2-	5.0	4.8	4.1	$(CH_3)_3C$-	1.6	1.8	2.0
$N{\equiv}CCH_2$-	4.3	4.0	3.7	$\mathrm{(C_6H_5)_2C}\mathit{H}$-	6.0	6.1	6.4
CH_3COCH_2-	4.2	4.0	3.9	CH_3CO-	2.6	2.7	2.9
$HC{\equiv}CCH_2$-	4.1	3.9	3.7	$\mathrm{H_2C{=}C{=}C}\mathit{H}$-		6.0	5.8

[a] These values vary slightly in different reaction mixtures and thus should only be taken as indicative of the general absorption patterns.
[b] Done in benzene solution.

reactants and e refers to the quantities of material present in the reaction mixture after establishment of equilibrium.

NMR Analysis. NMR analyses of the reaction mixtures were done by careful integration of each absorption of interest at least four times using when possible full-scale integrals for highest accuracy. The average integral values were used in the calculations. For cases where overlapping multiplets were encountered, controls were run on weighed out mixtures for calibration purposes. For the various organic halides encountered, the approximate chemical shifts in the reaction mixtures for the absorptions used in the analyses are as listed in Table VII. Note however, that these values varied slightly in the different reaction mixtures and thus should only be taken as indicative of the general absorption patterns.

GLC Analyses. These were carried out at least in duplicate using experimentally determined thermoconductivity factors in calculations. For the *n*-octyl halides, the NMR results were checked using a 10 ft × 0.25 in. stainless steel 20% diisodecyl phthalate on 60-80 mesh HMDS treated Chromosorb W column run at 135 °C using a helium flow of 100 mL/min. The retention times under these conditions follow: *n*-octyl chloride, 7; *n*-octyl bromide, 12; *n*-octyl iodide, 20 min. The allyl halides were analyzed on the same column but at 85 °C using a helium flow of 50 mL/min. The retention times under these conditions follow: allyl chloride, 4; allyl bromide, 6; allyl iodide, 11 min. The *tert*-butyl halides were analyzed on a 10 ft × 0.25 in. stainless steel 10% SE-30 on 60-80 mesh acid-base washed DMDCS treated Chromosorb P column run at 60 °C using a helium flow of 75 mL/min. The retention times under these conditions follow: isobutylene, 2; butane, 2.5; *tert*-butyl chloride, 6; *tert*-butyl bromide, 11; *tert*-butyl iodide, 23 min. The percentages of olefin elimination product were also checked by NMR.

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