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Electron-Transfer, Halogen–Metal Exchange and Direct Processes in Formal Nucleophilic Substitutions on Alkyl Halides by Trimethyltinsodium

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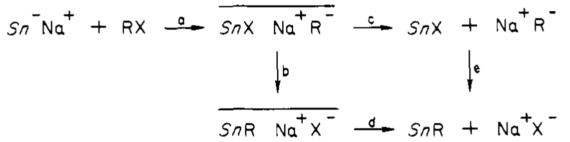
Abstract: Formal nucleophilic substitutions have been studied by simple trapping techniques designed to separate and estimate contributions of reactions proceeding by way of free radicals, by way of anions, and by way of geminate or synchronous processes. Reactions of trimethyltinsodium with organic halides in tetrahydrofuran at 0 °C were examined, using dicyclohexylphosphine for trapping free radicals and *tert*-butylamine for free anionoids. Among 22 halides included in this study nine have been shown to involve two or all three of the mechanistic pathways. Primary chlorides reacted predominantly by a direct mechanism (S_N2, geminate reaction of intermediates, or multicenter process). Branching, as in isobutyl and neopentyl, led to contributions from electron-transfer (free radical) and halogen–metal exchange (anionoid) mechanisms. Secondary bromides reacted predominantly by the ET process (major) and HME (minor) while the relative contributions from these were reversed in importance with the iodides. Triethylcarbinyl chloride reacted exclusively by elimination while the bromide reacted by ET alone or in competition with elimination. 1- and 2-bromoadamantanes reacted by ET, and 1-chloroadamantane showed no reaction after 10 days at −4 °C.

Reactions of organotin alkalis with organic halides have been used in syntheses of organotins for more than a half-century.[1] Yields of substitution products ranging from zero to quantitative have been reported. The stereochemistry has been found to be complete inversion, nonspecific, or complete retention. Thus, knowledge of the mechanisms of these reactions is of interest, would provide understanding of the behavior of organotin and other anionoids in aprotic solvents, and would be of value in selecting reaction parameters for syntheses involving specific pairs of reactants. Among the mechanisms which have been suggested are S_N2 displacement at carbon,[2-6] halogen–metal exchange by S_N2 attack on the halogen,[3] by a four-center transition state,[8] and by two successive one-electron transfers from the tin anion,[3] four-center alkyl–metal exchange,[4,7] and electron transfer (ET).[3,4,9-11] Experimental bases for these suggestions have been stereochemical,[2-11] anion trapping,[12-14] kinetics,[15] and formation of rearranged products.[9] Data combined from several sources[2,5,15] establishes the S_N2 mechanism for simple secondary chlorides in tetrahydrofuran (THF). A mechanism involving halogen–metal exchange (HME), eq 1, has been established for polyhalomethanes,[14] for 2-bromo-3-methoxybutanes,[13] and for aromatic bromides and iodides,[12] but not for simple alkyl halides. Aryl bromides form substitution product by pathways a, b, d and a, c, e of eq 1[12] (Sn = R_3Sn), whereas only a, c, e is followed by 2-bromo-3-methoxybutanes in tetraglyme (TG).[13] Evidence which suggests that the electron-transfer mechanism of eq 2, or some other radical mechanism, may occur has been reported.[4,9-11] CIDNP evidence for radical intermediates has been obtained for reactions of isopropyl and *sec*-butyl bromides and iodides, but not for cyclohexyl bromide, with trimethyltinsodium in THF and/or 1,2-dimethoxyethane (DME).[16]



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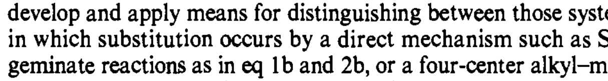

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The objective of the work described in this paper has been to develop and apply means for distinguishing between those systems in which substitution occurs by a direct mechanism such as S_N2, geminate reactions as in eq 1b and 2b, or a four-center alkyl–metal exchange from those involving carbanions as represented by eq 1a,c,e or by free radicals as represented by 2a,c,e as intermediates.[27] We chose trapping of the intermediates as the technique because it could, in principle, distinguish the three mechanistic classes and could also provide quantitative information concerning contributions of each if they occurred in competition in a given reacting system. Although ESR and CIDNP can provide valuable information concerning the involvement of free radicals in reactions neither can provide the kind of quantitative data which trapping might yield.

Results

For trapping anions we found in earlier work[12-14] that *tert*-butyl alcohol was suitable because it reacted more slowly with trimethyltinsodium than did the halides under investigation, and it reacted more rapidly with the carbanion intermediates than with tinsodium. However, the alcohol reacted faster with the tinsodium than with less reactive halides. Our observation that the reaction of bromobenzene with trimethyltinsodium in liquid ammonia yielded 95% benzene due to efficient trapping of intermediate phenyl anions suggested that an amine might be a suitable substitute for *tert*-butyl alcohol. *tert*-Butylamine (TBA) was chosen. Its pK_a, which should be greater than 35, is much less than the value of 24 for trimethyltin hydride.[17] The expectation that no

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Table I. Reaction of Trimethyltinsodium with 1-Bromoadamantane in the Presence of Trapping Reagents[a]

trap	concn, M	% RH	% $RSnMe_3$
		5	95
Et_2O	0.52	10	90
$PhCH_2NH_2$	0.50	4	95
$(PhCH_2)_2NH$	0.76	13	87
NaOMe	*b*	6	94
$NaOCH(CH_3)_2$	0.59	8	90
$PhCH(CH_3)_2$	0.55	10	90

[a] At 0 °C in THF. [b] Saturated solution.

reaction would occur between the amine and the tinsodium was tested and borne out experimentally: at least 98% of the anion was still present 24 h after a solution of the two in THF had been prepared. The efficiency of TBA as a trap was established by the observation that reaction of trimethyltinsodium with bromobenzene in THF the presence of *tert*-butyl alcohol resulted in the formation of 82% benzene while the same experiment with TBA yielded 85% benzene. The fact that the two traps differ by at least 15 pK_a units in acidity suggests that both function with unit efficiency. The amine should be selective as a trap for anions: it should be a poor hydrogen atom donor to alkyl free radicals because all of its hydrogens are primary or bonded to nitrogen (D = 93 kcal/mol), and none are α to the nitrogen. As shown below, this expectation was realized when reactions to which we ascribe a free-radical component displayed little or no discernible trapping due to added amine. Neither the amine nor its conjugate base (when trapping was observed) reacted detectably with the halide. This was expected because trimethyltinsodium is an extremely powerful nucleophile[15] and reacts much more rapidly with halides than do amine bases.

The fact that organotin anions are powerful nucleophiles, strong bases, and good reducing agents limited the choices available for potential radical traps. It seemed likely that 1-bromoadamantane would react by a free-radical mechanism so it was chosen as a substrate for testing possible traps. Results for several substances tested are shown in Table I. The low levels of trapping observed suggested that the efficiency, as measured by the rate of reaction 3a, was not high enough to compete with the radical coupling of

$$\mathrm{Ad}\cdot \xrightarrow{\mathrm{TH}} \mathrm{Ad{-}H} + \mathrm{T}\cdot \qquad (3a)$$

$$\mathrm{Ad}\cdot \xrightarrow{Sn\cdot} \mathrm{Ad{-}Sn} \qquad (3b)$$

eq 3b (TH = trap, Ad· = 1-adamantyl radical, *Sn*· = $Me_3Sn\cdot$). Dicyclohexylphosphine (DCPH) was found to possess the desired properties: its pK_a in THF is 35.7,[18] precluding its reaction as a proton donor to the trimethyltin anion, and the P–H bond dissociation energy should not differ greatly from that of phosphine (77 kcal/mol),[19] making it a good hydrogen atom donor to carbon free radicals. This is demonstrated by the fact that it is highly efficient as a chain transfer agent in vinyl polymerization.[20] 1-Bromoadamantane reacted with trimethyltinsodium in THF to produce 95% adamantyltrimethyltin and 5% adamantane. When the phosphine was present in the initial reaction mixture the yield of adamantyltrimethyltin decreased with increasing DCPH concentration, and that of adamantane increased correspondingly, as shown in Figure 1. The substitution product was not detected in the reactions at the higher DCPH concentrations. Control experiments established that the phosphine does not react with trimethyltinsodium: after 1 day in the presence of 1.2 M phosphine at least 97% of the trimethyltinsodium remained, as indicated by the amount of *n*-butyltrimethyltin formed upon addition of *n*-butyl bromide. When the bromide and DCPH were present in excess over trimethyltinsodium the yield of adamantane was less (not more) than that expected on the basis of the tinsodium initially present, indicating that the phosphine does not reduce the bromide under the reaction conditions. Furthermore, reactions conducted in the presence and absence of DCPH proceeded at the same rates within the experimental error. The pK_a of the phosphine is such that it would be expected to react with simple carbanions. This assumption was tested by using the reaction of trimethyltinsodium with bromobenzene. When *tert*-butylamine was used as a trap 85% of benzene was formed; under the same conditions with the phosphine only 30% of benzene was formed. Thus, the phosphine traps phenyl anions, but less efficiently than does the amine. This complication will be considered below.

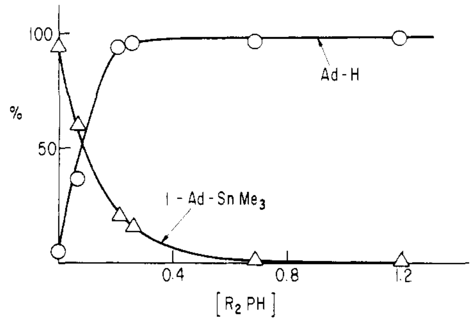

Figure 1. Effect of dicyclohexylphosphine concentration on yields of adamantane and adamantyltrimethyltin in the reaction of 1-bromoadamantane with triemthyltinsodium in tetrahydrofuran at 0 °C.

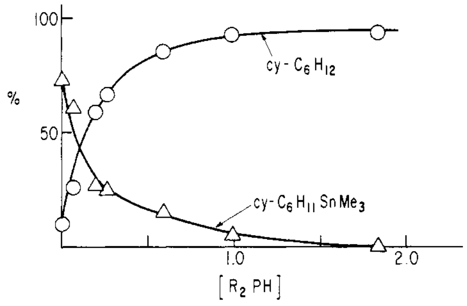

Figure 2. Effect of dicyclohexylphosphine concentration on yields of cyclohexane and cyclohexyltrimethyltin in the reaction of bromocyclohexane with trimethyltinsodium in tetrahydrofuran at 0 °C.

The bromocyclohexane system was examined to further test the utility of the phosphine as a free-radical trap. Using 4-alkylbromocyclohexanes three groups have shown that the reaction with trimethyltinsodium or -lithium is largely, or completely, nonselective.[3,9,11] Extensive free-radical involvement has been suggested.[9] We have carefully examined the products formed from the reaction of bromocyclohexane with trimethyltinsodium at 0 °C. In the absence of addends the products were 73% cyclohexyltrimethyltin, 10% cyclohexane, 9% cyclohexene, and a trace of bicyclohexyl (presumed on the basis of GLC retention time). The formation of the last three products is suggestive of disproportionation and coupling of cyclohexyl free radicals. When the reaction was conducted in the presence of increasing amounts of DCPH the yield of cyclohexane increased and that of cyclohexyltrimethyltin decreased as shown in Figure 2. The yields of cyclohexene and bicyclohexyl fell to undetectable levels. The second-order rate constant at 0 °C in THF for the reaction of bromocyclohexane with trimethyltinsodium was found to be 0.16 $M^{-1}\,s^{-1}$; in the presence of 0.30 M DCPH the value was 0.18 $M^{-1}\,s^{-1}$. Thus the trap has no significant effect on the rate. When *tert*-butylamine was present as a potential trap in the reaction of either 1-bromoadamantane or bromocyclohexane the results were the same as those of control experiments within experimental error. Hence an anion intermediate can be eliminated from consideration. These observations are consistent with the notion that DCPH is a highly efficient free-radical trap and that simple bromocyclohexanes and 1-bromoadamantane react by mechanisms involving free radicals. The absence of a significant effect of DCPH on the rates of these reactions permits the exclusion of a chain mechanism of the $S_{RN}1$ type for these substrates.

Studies with the other halides described below were conducted in THF at 0 °C except as noted. Each item of data usually

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Table II. Reactions of Trimethyltinsodium with Normal Alkyl Halides in THF[a-c]

entry	RX	$\mathrm{Me_3SnNa}$[d]	RX[d]	addend (*d*)	% RH	% $\mathrm{RSnMe_3}$	% total yield
1	1-bromobutane	0.48	0.32		<1	100	100
2		0.44	0.30	DCPH (0.81)	<1	100	100
3		0.33	0.22	TBA (1.10)	<1	99	99
4	1-chloroheptane	0.52	0.33		<1	98	98
5		0.44	0.27	DCPH (1.05)	<1	97	97
6		0.47	0.31	TBA (1.24)	<1	98	98
7	1-iodoheptane	0.32	0.17		10	89	99[e]
8		0.28	0.15	DCPH (1.25)	18	76	95
9		0.28	0.15	TBA (1.16)	24	70	94
10		0.31	0.19	TBA (2.28)	31	68	99
11		0.24	0.16	DCPH (0.88)	33	61	94
12		0.11	1.06	TBA (1.36)	4	87	101[f]

[a] $\mathrm{Me_3SnNa}$ added to halide at 0 °C. [b] $\mathrm{R_2PH}$ = dicyclohexylphosphine. [c] Yields based on halide. [d] Initial concentration, molar. [e] Trace of tetradecane. [f] Includes 10% tetradecane.

Table III. Reactions of Isobutyl and Neopentyl Halides (RX) with Trimethyltinsodium in THF[a-c]

entry	R	X	$\mathrm{Me_3SnNa}$[d]	RX[d]	addend (*d*)	% RH	% $\mathrm{RSnMe_3}$	% total yield
1	isobutyl	Cl	0.61	0.39			100	100
2		Br	0.47	0.31			98	98
3		Br	0.35	0.24	DCPH (1.20)	2	95	98
4		Br	0.41	0.28	TBA (1.15)	3	92	94
5		I	0.28	0.20		5	76	94[e]
6		I	0.22	0.17	DCPH (1.20)	39	61	100
7		I	0.25	0.18	TBA (1.22)	55	36	91
8		I	0.21	0.12	DCPH (0.62), TBA (0.68)	54	36	90
9	neopentyl	Cl	0.40	0.25			96	96
10		Cl	0.40	0.25	DCPH (2.14)	5	90	95
11		Br	0.54	0.39		1	99	100
12		Br	0.45	0.34	DCPH (1.39)	40	58	98
13		Br	0.36	0.22	TBA (1.98)	8	92	100
14		I	0.40	0.25		5	92	97
15		I	0.37	0.18	DCPH (1.60)	61	37	98
16		I	0.37	0.18	TBA (1.60)	77	22	99
17		I	0.29	0.15	DCPH (1.51), TBA (1.51)	77	22	99

[a] $\mathrm{Me_3SnNa}$ added to halide at 0 °C. [b] $\mathrm{R_2PH}$ = dicyclohexylphosphine. [c] Yields based on halide. [d] Initial concentrations, molar. [e] Includes 13% 2,5-dimethylhexane.

represents the results of replicates of at least two experiments. Reproducibility was ±3% or better. In addition to control experiments others were conducted with the traps individually present in concentrations of 1 to 2 M which were taken to represent concentrations at which maximum trapping would be effected on the basis of the data represented in Figures 1 and 2. If these results showed trapping by both DCPH and by *tert*-butylamine (TBA) additional experiments were usually conducted, using both traps to establish whether both anions and radicals were being trapped by DCPH.

Primary Halides. Results for simple primary halides are gathered in Table II. Entries 1 through 6 show that both the chloride and bromide proceeded entirely by mechanisms not involving radical or anion intermediates because no trapping by either DCPH or TBA was observed. In the case of 1-iodoheptane 10% *n*-heptane and a trace of tetradecane were observed in addition to an 89% yield of *n*-heptyltrimethyltin. The yield of heptane was increased by the presence of either trap, definitely indicating the involvement of an anion intermediate. Comparison of entries 10 and 11 shows no increase in the yield of heptane when both traps were present over that observed when only TBA was present. We conclude that only an anion mechanism (33%) in addition to direct displacement (61%) is involved. This 61% would also include any geminate reaction represented in step b of eq 1. The 18% heptane shown in entry 8 is taken to have been formed by inefficient trapping of anions by DCPH and solvent. The tetradecane is presumably formed by reaction of *n*-heptylsodium with iodoheptane because the use of a large excess of the iodide (entry 12) increases the yield of tetradecane to 10% largely at the expense of *n*-heptane.

When branching was introduced into the substrate as in the isobutyl and neopentyl chlorides no indication of trappable intermediates was observed. Isobutyl bromide showed 2–3% of trapping (entries 3 and 4, Table III), but the iodide showed 39% by DCPH (entry 6) and 55% by TBA (entry 7) while the combined traps showed 54%. Thus, we conclude that only anion is formed as an intermediate. Neopentyl bromide produced 40% neopentane (entry 12) in the presence of DCPH and 8% (entry 13) in the presence of TBA. Assuming unit efficiency of anion trapping by TBA leads to an estimate of 8% of reaction through an anion intermediate and (40 − 8) = 32% through a free-radical intermediate, while the remainder of the reaction proceeds by direct substitution or geminate reaction. The iodide, on the other hand, showed the same amounts of trapping by TBA alone and by the TBA/DCPH combination (entries 16 and 17), pointing to 77% reaction involving anion and 22% involving direct substitution or geminate reaction.

Secondary Halides. Results for 2-halooctanes are collected in Table IV. The chloride shows the formation of 4% octane in the presence of either trap. With the bromide both octene (8%) and octane (16%) were formed, along with 10% 7,8-dimethyltetradecane (entry 4) in the absence of trap. When phosphine was present no octene or tetradecane was found, but the yield of octane rose to 86% (entry 5). The presence of TBA (entry 6) caused an increase in the yield of octane to 30%, but no significant change in the yields of octene or tetradecane. The combined traps caused the octane yield to increase to 89% (entry 7). These data can be used to estimate limits of anion and radical contributions to the mechanism. The increase in the yield of octane from 16% to 30% might be taken as a measure of the anion contribution, but the 16% must also include 8% formed by disproportionation of radicals and could include a maximum of 8% formed from anions or a maximum of (30 − 8) = 22%. A better measure is probably the decrease of 16% in the yield of substitution product

Table IV. Reactions of 2-Halooctanes with Trimethyltinsodium in THF[a-c]

entry	X	Me_3SnNa[d]	RX[d]	addend (*d*)	% R(-H)	% RH	% $RSnMe_3$	% RR	% total yield
1	Cl	0.47	0.32		0	0	96	0	96
2	Cl	0.32	0.20	DCPH (1.36)	0	4	87	0	91
3	Cl	0.46	0.29	TBA (2.41)	0	4	91	0	95
4	Br	0.37	0.28		8	16	60	10	94
5	Br	0.29	0.21	DCPH (1.26)	0	86	10	0	96
6	Br	0.46	0.29	TBA (2.03)	9	30	44	10	93
7	Br	0.29	0.18	DCPH (1.12), TBA (1.48)	0	89	5	0	94
8	I	0.44	0.26		14	36	20	23	93
9	I	0.33	0.20	DCPH (1.32)	0	77	7	3	87
10	I	0.38	0.22	TBA (1.43)	13	54	14	15	96
11	I	0.28	0.17	DCPH (1.07, TBA (1.43)	0	88	4	0	92

[a] Me_3SnNa added to chloride at 25 °C, bromide and iodide at 0 °C. [b] R_2PH = dicyclohexylphosphine. [c] Yields based on halide reacted. [d] Initial concentration, molar. [e] Ratio of addend to initial halide.

Table V. Reactions of Cyclic Halides (RX) with Trimethyltinsodium in THF[a-c]

entry	R	X	Me_3SnNa[d]	RX[d]	addend (*d*)	RH	R(-H)	$RSnMe_3$	% total yield
1	cyclopentyl	Cl	0.45	0.23		2	0	97	99
2		Cl	0.35	0.18	DCPH (1.10)	5	0	92	97
3		Cl	0.37	0.19	TBA (2.58)	1	0	98	99
4		Br	0.50	0.33		30	17	47	99[e]
5		Br	0.39	0.20	DCPH (2.00)	90	0	7	97
6		Br	0.43	0.28	TBA (2.35)	45[g]		41	~92[f]
7	2-adamantyl	Br	0.46	0.27		4	0	96	100
8		Br	0.35	0.19	DCPH (1.72)	88	0	(<5)[h]	(93)
9		Br	0.36	0.24	TBA (1.20)	5	0	95	100

[a] Me_3SnNa added to bromides at 0 °C, to chlorides at 25 °C. [b] R_2PH = dicyclohexylphosphine. [c] Yields based on halide reacted. [d] Initial concentration, molar. [e] Including 5% bicyclopentyl. [f] Including 6% bicyclopentyl. [g] Estimated total yield ±10% for cyclopentane and cyclopentene due to incomplete separation from *t*-$BuNH_2$ in GC. [h] Estimated due to incomplete separation of phosphine and 2-adamantyltrimethyltin.

from 60% to 44%, as a reliable estimate of this contribution. If 5% (entry 7) of substitution product is formed by direct reactions then the radical mechanism accounts for (89 − 27) to (89 − 21) or 72 to 78% of the reaction. Figure 3 depicts the results of a more detailed trapping study by DCPH alone, using 2-bromobutane as substrate. Here, untrapped product formation amounts to 17%. If both DCPH and TBA were present this figure would undoubtedly be lower.

With 2-iodooctane the results are qualitatively similar to those for the bromide. In the absence of a trap the yield of hydrocarbons totals 73%. DCPH eliminates the octene and most of the coupling product and produces 77% octane. The amine eliminates none of the octene and part of the coupling product. Both traps together eliminate all of the octene and coupling product; an 88% yield of octane is found. If we assign unit efficiency for anion trapping and zero efficiency for radical trapping by TBA we conclude that 54% of the reaction goes via anions and (88 − 54) = 34% goes via free radicals. The remainder probably goes by S_N2 and, in part, by geminate reaction.

Results for cyclopentyl chloride and bromide are shown in the first six entries of Table V. The reaction of the chloride clearly goes predominantly by direct substitution, but entry 2 indicates a small (5%) radical contribution. The bromide reacts to the extent of at least 90% by the free-radical process. About 7% direct substitution occurs, in contrast with bromocyclohexane in which case none was detected (Figure 2).

The reaction of 2-bromoadamantane in the presence of varying concentrations of DCPH was studied, yielding a plot essentially identical with that of Figure 1 for 1-bromoadamantane (not shown). Data included in Table V are for the control experiments, for those with the highest concentration of DCPH, and those in the presence of TBA. The latter has no effect on the product distribution, and entry 8 indicates that there may be a residual untrapped contribution in the presence of DCPH.

Tertiary Halides. In earlier work[15] Reeves showed that *tert*-amyl chloride reacted with trimethyltinsodium exclusively by elimination. Triethylcarbinyl chloride evidently reacts by the same pathway: 3-ethyl-2-pentene was found as the only product derived from the triethylcarbinyl group. The bromide yielded 46% of the alkene and 54% 3-ethylpentane in the absence of addends (Table VI, entry 4). The presence of TBA has no significant effect, while the presence of DCPH increased the yield of alkane by 14% to 67% at the expense of alkene. These results could be attributed to a reaction proceeding entirely by a free-radical mechanism with incomplete trapping by DCPH in competition with disproportionation, or a competition between this mechanism and an E2 elimination.

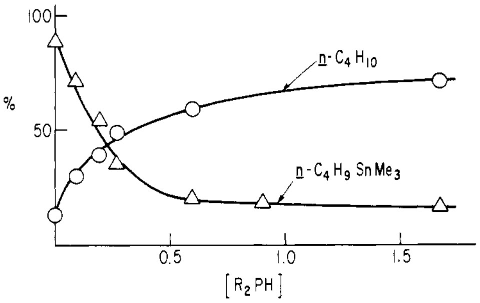

Figure 3. Effect of dicyclohexylphosphine concentration on yields of butane and *n*-butyltrimethyltin in the reaction of 1-bromobutane and trimethyltinsodium in tetrahydrofuran at 0 °C.

1-Chloroadamantane showed no reaction over a 10-day period. 1-Iodoadamantane provided a high yield of 1-adamantyltrimethyltin in the absence of addends. In the presence of DCPH the reaction was diverted completely to the formation of adamantane (entry 8 of Table VI). However, TBA also diverted reaction to adamantane formation to the extent of 21% (entry 9). Thus we assign 21% of the reaction as proceeding by an anion mechanism and the remainder by a free-radical process.

Discussion

The results presented demonstrate that DCPH can be used to trap free radicals effectively and thus provide an estimate of that fraction of a reaction which proceeds by way of these intermediates; they also reveal that TBA can be used to obtain an estimate

Table VI. Reactions of Tertiary Halides with Trimethyltinsodium in THF[a-c]

entry	*R*	*X*	Me_3SnNa[d]	*RX*[d]	addend (*d*)	% R(-H)	% RH	% $RSnMe_3$	% total yield
1	$(C_2H_5)_3C$	Cl	0.43	0.27		97	0	0	97
2		Cl	0.31	0.19	DCPH (1.03)	100	0	0	100
3		Cl	0.36	0.21	TBA (1.24)	95	0	0	95
4		Br	0.51	0.32		46	53	0	99
5		Br	0.34	0.23	DCPH (1.06)	32	67	0	99
6		Br	0.43	0.29	TBA (1.10)	46	49	0	95
7	1-adamantyl	I	0.61	0.49		0	7	88	93
8		I	0.40	0.26	DCPH (1.31)	0	99	0	99
9		I	0.41	0.17	TBA (0.97)	0	74	21	95

[a] Me_3SnNa added to halide at 0 °C. [b] DCPH = dicyclohexylphosphine; TBA = *tert*-butylamine. [c] Yields based on halide. [d] Initial concentration, molar.

Table VII. Mechanistic Components in the Reaction of Trimethyltinsodium with Alkyl Halides in THF at 0 °C

alkyl group	chloride			bromide			iodide		
	S_N2	ET	HME	S_N2	ET	HME	S_N2	ET	HME
1-alkyl	100	0	0	100	0	0	65	0	32
isobutyl	100	0	-	97	2[a]	2[a]	36	0	64
neopentyl	90	5	0	58	32	8	22	0	77
2-octyl	90	4[a]	4[a]	5	72	16	4	48	40
cyclopentyl	92	5	0	7	90	0			
cyclohexyl[c]	37	31	0[b]	0	94	4			
2-adamantyl				0	100	0			
1-adamantyl	*f*	*f*	*f*	0	100	0	0	74	25
triethylcarbinyl	0	0	0[d]	0	28[e]	0			

[a] May be HME or ET. [b] 21% dehydrochlorination. [c] At 24 °C. [d] 100% dehydrochlorination. [e] Balance may be ET, HME, or a combination of these. [f] Too slow to detect.

of the fraction proceeding by way of free carbanionoids. The fraction which is untrapped is then assumed to proceed by way of S_N2, multicenter, and geminate processes. If the assumption that trapping occurs with unit efficiency is valid then the results can be taken as quantitative, but this may not be always true even with simple radicals as indicated by the case of triethylcarbinyl bromide discussed below. It should also be emphasized that the results presented are valid only for THF as solvent under the conditions used because different mechanisms can be expected to show different sensitivities to ion aggregation and general solvent effects.[21]

Table VII contains a summary of the apportionments of mechanisms of the examples discussed above, along with a few others, classified according to their presumed primary steps: ET based on radicals trapped, HME (halogen–metal exchange) based on anions trapped, and those proceeding by way of mechanisms not involving free reactive intermediates included in the S_N2 category.

In the sequence of chlorides simple primary, secondary, and tertiary, the first two proceeded by the S_N2 process, although a small but experimentally significant extent of trapping was observed by both DCPH and TBA in case of 2-chlorooctane. Tertiary chlorides reacted only by elimination.[15] Among the bromides only S_N2 was observed in the primary case, but 58% ET, along with 22% of HME and only a minimal amount of S_N2, was detected with 2-bromooctane. This appears to contrast with the relatively high (but not accurately known) amount of inversion observed by Jensen and Davis in the reaction of 2-bromobutane with triphenyltinsodium in 1,2-dimethyoxyethane.[2] This may be due to a high nucleophilicity of triphenyltinsodium toward carbon relative to its efficiency in the ET and HME processes toward halides and to a solvent effect. The simple tertiary example, triethylcarbinyl bromide,[2] yielded 46% elimination and 49% substitution (Table VI, entry 6), suggesting a free-radical intermediate undergoing disproportionation to a large degree as might be expected from a hindered tertiary radical. However, trapping with DCPH increased the yield of reduction product by only 14% to 67%. This could be rationalized in terms of an E2 component by analogy with the chloride. It could also be due to inefficient trapping. The *β*-C–H bond in a carbon free radical has a bond dissociation energy of about 60 kcal/mol,[22] considerably lower than the value 77 kcal/mol estimated for the P–H bond. This may permit disproportionation to compete with trapping despite the large concentration of phosphine relative to free radicals present during the reaction. The HME process was observed with the *n*-alkyl iodide to the extent of 32%, and the remainder of the reaction fell into the S_N2 category. The secondary iodide revealed only 4% S_N2, along with 40% HME and 48% ET. These results are consistent with a dissociative electron transfer which would occur more readily to form a secondary than a primary radical. In contrast, the anion would be formed preferentially from the primary iodide in a rate-determining process. The smaller HME contribution from the primary iodide is attributable to effective competition from the S_N2 reaction.

These considerations are applicable also to the series *n*-aklyl, isobutyl, neopentyl. The chlorides are unexceptional in reacting by the S_N2 pathway, with neopentyl showing a small amount of the ET pathway. With this alkyl group ET becomes more apparent (32%) and HME appears to the extent of 8% with the bromide. This fact is remarkable because *n*-butyl bromide reacts about 2000 times as fast as neopentyl bromide with trimethyltinsodium.[15] It suggests that the driving force for an ET process is so low that it competes with the S_N2 process only when the latter is strongly retarded in rate. The preference for ET over HME in this case is curious because it leads to a primary radical if the process is dissociative. The trend in the series of iodides is also striking. As the alkyl group changes from normal butyl to isobutyl to neopentyl the contribution from S_N2 decreases as expected, and the HME contribution increases, but only to 77% in the case of neopentyl iodide. This strongly implies that the process is subject to significant steric hindrance which would be expected to some degree if the reaction proceeds by way of a four-center transition state as has been suggested by Eaborn for the reaction of a germyllithium with certain halides.[23]

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(21) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502.

(22) For example, in uncompleted work we have observed that in the presence of the ether 18-crown-6 the reaction can be shifted completely to the S_N2 pathway.

(23) Eaborn has obtained evidence that organogermyllithiums react by a four-center process with retention with certain halides: Eaborn, C.; Hill, R. E. E.; Simpson, P. *J. Organomet. Chem.* **1972**, *37*, 275.

These results have an intimate bearing on certain observations reported in the literature. Bock and Whitesides[6] reported that 3,3-dimethylbutyl-*1,2*-d_2 butyl bromide reacts with trimethyltinlithium with about 80% inversion. This "homoneopentyl" bromide would be expected to display behavior between that of isobutyl and neopentyl with respect to steric effects. The S_N2 rate could be decreased in this case to such a degree that some incursion of the ET mechanism would intrude and lead to loss of stereochemistry to the degree that free radicals are involved. It has also been reported that cyclopropylcarbinyl iodide reacts with trimethyltinsodium in THF to give 3-butenyltrimethyltin and cyclopropyltrimethyltin at 9 °C in a ratio 88/12.[9,10] The formation of the rearranged product was discussed in terms of a possible free-radical reaction in competition with a direct displacement. Our results with the sterically similar isobutyl iodide would suggest that an anionic intermediate is involved instead. Preliminary results in an examination of cyclopropylcarbinyl and related systems[24] reveal that this is indeed the case.

It has been observed that 1-halo-5-pentenes do not yield cyclization products in the reaction with trimethyltin alkalis[28,29] as would be expected if free radicals were intermediates. These observations would be expected on the basis of our results because simple unhindered primary halides react either by the S_N2 or HME processes. In neither case would cyclization to the cyclopentylmethyl system be expected to occur.

Cyclopentyl chloride reacted quite cleanly by the S_N2 process, displaying no more than about 5% ET. The less reactive (toward S_N2) cyclohexyl chloride displayed more complex behavior with only 37% S_N2, accompanied by 31% ET and 21% dehydrochlorination. The bromides reacted almost exclusively by ET. In our earlier study on relative reactivities of halides with trimethyltinsodium we observed that the rate ratio RBr/RCl was 200 for cyclopentyl and 2000 for cyclohexyl compared to 21 for *n*-butyl.[15] These results are easily understood now to be the result of a change in mechanism from S_N2 to ET for the cyclic bromides, but not for *n*-butyl bromide. 2-Bromoadamantane showed no trace of the S_N2 process, free radicals being trapped quantitatively. The same was true of 1-bromoadamantane, but the iodide displayed a surprisingly large (25%) HME component, along with 74% ET. The large anionic contribution is remarkable because the anion is tertiary and should be of relatively high energy. Driving force might be provided by the exchange of a C–I bond for an Sn–I bond. However, it is difficult to envision the halogen–metal exchange occurring by a four-center mechanism as suggested for the germyllithium case cited above because steric factors should be substantial in the transition state. It remains to be established whether contact ion pairs, which are required by the four-center mechanism, are actually the reactive organotinsodium species in this and other HME processes that we have observed.

When a mixture of products is formed the trapping techniques can provide information concerning their mechanistic origins if the traps have no effect on the course of the overall reaction.[30] For example, reference to Table IV, entry 4, shows the formation of 8% octene from 2-bromooctane. This is clearly of free-radical origin because the presence of DCPH prevents its formation. The 10% of the C_{16} hydrocarbon falls into the same scheme. A total of 8% of the octane must be formed by disproportionation of octyl radicals to accompany the formation of 8% octene. Thus a maximum of (16 − 8) or 8% of the rest of the octane arises from octyl anions. The presence of TBA decreases the octyltrimethyltin yield from 60% to 44%; so the difference of 16% is the amount of this product which arises from octyl anions. A total of 44% (entry 6) minus 5% (entry 7) or 39% of the substitution product comes from the free-radical process, and 5% by direct substitution or, perhaps more likely, from geminate reactions. (These figures are subject to uncertainties due to variations in mass balances which have not been normalized.) A similar analysis of data from entries 8–11 of Table IV yields the following distributions from 2-iodooctane: 14% octene and at least 14% of the octane via free radicals; the remaining 22% (36 − 14) of octane probably comes from anions. The origins of the substitution product are as follows: 4% direct substitution, (20 − 14) = 6% via anions, and (20 − 6 − 4) = 10% via radicals; coupling product results to the extent of 15% from radicals and (23 − 15) = 8% from anions.

Conclusions

Dicyclohexylphosphine and *tert*-butylamine can be used as traps for free-radical and anion intermediates, respectively, in the reactions of trimethyltinsodium with organic halides. They appear to function with unit efficiency at moderate concentrations in most cases studied and do not appear to perturb these reactions. To the degree to which these observations are valid it is possible to estimate quantitatively in any given case the contributions from reactions proceeding through free-radical intermediates, through anion intermediates, and through S_N2, geminate, and multicenter processes which do not involve trappable intermediates. Application of this approach to 22 halides has provided information concerning the effects of the alkyl group and the halide on the gross mechanism of reaction. In at least nine of these cases two or three mechanisms have been found to occur in competition.

The strategy enables one to identify reactants and conditions which can be used in planning syntheses of organotins and for more detailed mechanistic studies on electron transfer from anions to halides and of halogen–metal exchange processes. In principle it should be applicable to a variety of other nucleophiles and to substrates other than halides.

Experimental Section

General Procedures. Proton nuclear magnetic resonance spectra were obtained at 60 MHz by using a Varian A-60A instrument. Samples requiring higher resolution or greater sensitivity were obtained at 90 MHz by using a Bruker WH-90 NMR spectrometer with B-NC-12 data system. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane followed in parentheses by the multiplicity, coupling constant, number of protons, and assignment. Proton–tin-117 and -119 coupling constants are reported as ${}^xJ$(Sn–H) with the superscript denoting the number of bonds intervening between nuclei.

Analytical gas chromatographic analyses were performed on an F & M Hewlett-Packard Model 5750 instrument using a thermal-conductivity detector. Unless noted otherwise an 18 ft × 0.25 in. stainless-steel column packed with 15% SE-30 on Chromosorb W, AW-DMCS, was used. Peak areas in the chromatogram were determined by a Columbia Scientific Industries automatic digital integrator, Model CRS-208, equipped with an angular base-line corrector and a digital printer. Yields were determined by using internal-standard techniques.

All reactions with trimethyltinsodium were conducted under an inert atmosphere of high-purity nitrogen (99.996%). Tetrahydrofuran was dried by distillation from molten potassium. All other chemicals were used without further purification after being checked for purity by GLC. Tetramethyltin was a gift from M & T Chemicals, Inc.

Preparation of Trimethyltinsodium and Precursors. Preparation of Trimethylchlorotin. Under a stream of nitrogen, 116.6 g (0.448 mol) of tetrachlorotin was added to a flame-dried flask equipped with mechanical stirring bar and fitted with a reflux condenser, pressure-equalizing addition funnel, and nitrogen bubbler. Dropwise addition of 240.3 g (1.344 mol) of tetramethyltin resulted in moderate evolution of heat. Heating was continued at 60 °F with stirring overnight. An NMR spectrum of the solution in CCl_4 containing no Me_4Si gave a sharp resonance with ${}^2J$(SnCH) = 58.5 Hz [lit.[25] NMR ($CHCl_3$) ${}^2J$(SnCH) = 58.5 Hz] which was assigned to trimethylchlorotin. A weak resonance at 0.55 ppm downfield from trimethylchlorotin was assigned to dimethyldichlorotin. Additional tetramethyltin (~5 g) was added to the reaction mixture. After the reaction mixture was heated 2 h the NMR spectrum indicated only trimethylchlorotin which was then distilled pot-to-pot at 15 torr, yield 99%.

Hexamethylditin. To a flame-dried flask equipped with a dry ice cold finger, mechanical stirrer, and nitrogen bubbler was added 116.5 g (0.585 mmol) of trimethylchlorotin in 200 mL of petroleum ether. Ammonia (~0.5 L) was then condensed into flask. Under a stream of nitrogen,

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[24] Smith, G. F.; Alnajjar, M. S., studies in progress.

[25] Neumann, W. P. "The Organic Chemistry of Tin"; Wiley: New York, 1970; p 223.

[26] Gilman, H.; Rosenberg, S.; Ingham, R. K. *Chem. Rev.* **1960**, *60*, 459.

[27] A preliminary report has appeared: Kuivila, H. G.; Smith, G. F. *J. Org. Chem.* **1980**, *45*, 2918.

[28] Kitching, W., private communication.

[29] Newcomb, M.; Courtney, A. R. *J. Org. Chem.* **1980**, *45*, 1707.

[30] DCPH appears to affect the course of reaction with certain substrates not included in the present study.

13.5 g (0.586 mmol) of sodium was added over 30 min. Upon completion the resulting solution was a pale yellow. After evaporation of the ammonia, the salts were filtered under nitrogen through a glass filter and washed repeatedly with petroleum ether. The washings were combined, concentrated, and distilled to yield 91.5 g (95%) of pure hexamethylditin: bp 61 °C (12 torr) [lit.[26] bp 182 °C (756 torr)]; NMR (CCl_4) δ 0.21 (s, ^2J(SnCH) = 48 Hz, ^3J(SnSnH) = 16 Hz, $((CH_3)_3Sn)_2$) [lit.[25] NMR (C_6H_6) δ 0.22 (s, ^2J(SnCH) = 48 Hz, ^3J(SnSnCH) = 16 Hz)].

Trimethyltinsodium. In a typical reaction 0.36 g (15.6 mmol) of finely cut sodium was added to 17 mL of dry THF in a three-neck flask equipped with a Hershberg stirrer and nitrogen gas bubbler. Hexamethylditin, 2.24 g (6.8 mmol), was added and the mixture was stirred at 0 °C for 4 h. The small amount of black precipitate which had formed was allowed to settle; the supernatant was removed and centrifuged in order to remove any additional particles. The concentration of the solution was determined by reaction of a 1-mL aliquot with excess 1-bromobutane which quantitatively yields 1-butyltrimethyltin. The above solution was 0.61 M.

Reaction of Trimethyltinsodium with 1-Bromoadamantane in the Presence of *tert*-Butyl Alcohol. To 0.389 g (1.809 mmol) of 1-bromoadamantane, 0.293 g (1.74 mmol) of dodecane, and 0.485 g (6.54 mmol) of *tert*-butyl alcohol in 1 mL of THF was added 4 mL of a 0.75 M trimethyltinsodium solution at 0 °C. The vial was then cooled to −10 °C for 12 h. GLC analysis yielded 60% unreacted 1-bromoadamantane and 40% adamantane.

Reaction between Trimethyltinsodium and *tert*-Butylamine. To 1 mL of a 0.61 M solution of trimethyltinsodium in THF was added 4.53 mmol of *tert*-butylamine at 0 °C. After 24 h at −10 °C 1.32 mmol of 1-bromobutane was added and the reaction mixture analyzed by GLC indicated the formation of 98% trimethylphenyltin based on initial trimethyltinsodium.

Reaction between Trimethyltinsodium and Dicyclohexylphosphine. To 1 mL 0.47 M trimethyltinsodium solutions in THF at 0 °C were added varying amounts of dicyclohexylphosphine as shown in Table VI. The reaction mixtures were stored at −10 °C until 1-bromobutane was added at various times (ranging from 0 to 1440 min). Analysis by GLC indictaed the formation of 95 to 100% 1-butyltrimethyltin.

Reaction of Trimethyltinsodium with Bromobenzene in the Presence of *tert*-Butylamine. To a solution containing 0.085 g (0.54 mmol) of bromobenzene, 0.145 g (1.98 mmol) of *tert*-butylamine, and 0.145 g (0.40 mmol) of octane (internal standard) in 0.4 mL of THF was added 1.5 mL (0.87 mmol) of trimethyltinsodium at 0 °C. After 5 min the reaction mixture was analyzed by GLC and indicated the formation of 85% benzene and 15% trimethylphenyltin.

Reaction of Trimethyltinsodium with Bromobenzene in the Presence of *tert*-Butyl Alcohol. To a solution containing 0.081 g (0.52 mmol) of bromobenzene, 0.231 g (3.12 mmol) of *tert*-butyl alcohol, and 0.044 g (0.39 mmol) of octane in 0.2 mL of THF was added 1.5 mL (0.87 mmol) of trimethyltinsodium at 0 °C. GLC analysis of the reaction mixture yielded 82% benzene and 11% trimethylphenyltin.

Reaction of Trimethyltinsodium with Bromobenzene in the Presence of Dicyclohexylphosphine. To a solution containing 0.532 mmol of bromobenzene, 0.347 mmol of octane (internal standard), and 0.730 mmol of dicyclohexylphosphine in 0.5 mL of THF was added 1 mL of a 0.55 M trimethyltinsodium solution at 0 °C. After 5 min the solution was analyzed by GLC and indicated the formation of 30% benzene and 69% trimethylphenyltin.

Trapping Studies. The general experimental procedure for trapping studies of the reaction of trimethyltinsodium with alkyl halides with dicyclohexylphosphine and *tert*-butylamine is presented below. Any variations will be described in the appropriate sections.

Reaction of Trimethyltinsodium with 1-Bromoadamantane in the Presence of Dicyclohexylphosphine. Into nitrogen-flushed vial equipped with screw caps with Teflon bodies and valves and a silicone septum was added 0.32 mL of a THF solution at 0 °C of 0.73 M 1-bromoadamantane (0.23 mmol) and 0.57 M dodecane (0.18 mmol) and varying concentrations of DCPH (0.0, 0.107, 0.313, 0.373, 0.692, 1.14, and 2.28 mmol). Trimethyltinsodium 1 mL (0.41 mmol) was then added by syringe and the solution cooled to −10 °C for 12 h. The reaction was generally complete within 4 h. GLC analysis, temperature programmed 100–250 °C, gave the following order of elution: THF, hexamethylditin, adamantane, dodecane (internal standard), 1-bromoadamantane, 1-adamantyltrimethyltin, and DCPH. Quantitative results are presented in Figure 1.

In the Presence of TBA. In a similar experiment, 1 mL of a 0.64 M trimethyltinsodium solution was added to a solution of 0.107 g (0.50 mmol) of 1-bromoadamantane, 0.041 g (0.24 mmol) of dodecane, and 0.142 g (1.94 mmol) of *tert*-butylamine in 0.3 mL of THF at 0 °C, and cooled to −10 °C for 12 h. TBA was eluted prior to THF in the GLC analysis. 1-Adamantyltrimethyltin: NMR (CCl_4) δ 0.05 (s, ^2J(SnCH) = 48/51 Hz, 9 H, $(CH_3)_3Sn$), 1.6–2.0 (m, 15 H, $C_{10}H_{15}$). Similar experiments were conducted with other traps with the results displayed in Table I.

Kinetics. Solutions in THF at 9 °C, 0.04 to 0.07 M in trimethyltinsodium and 0.03 to 0.5 M in bromocyclohexane, were quenched at 30- to 75-s intervals by addition of *n*-butyl bromide, and the resultant solution was analyzed for *n*-butyltrimethyltin. Bimolecular rate constants were then calculated to be $0.16 \pm 0.02\ M^{-1}\ s^{-1}$. The same reactions conducted in the presence of 0.25 M dicyclohexylphosphine yielded rate constants of $0.18 \pm 0.03\ M^{-1}\ s^{-1}$.

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Electron-Transfer Reactions and Conformational Changes Associated with the Reduction of Bianthrone

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Abstract: The electrochemical reduction of the low-temperature A form of bianthrone (**1A**) at a platinum cathode in DMF proceeds in a two-electron, irreversible reaction, giving the dianion **3B** which is structurally similar to the high-temperature B form of bianthrone (**1B**), having two planar ring systems twisted about the central connecting bond. The overall reduction involves a large structural change. By contrast, **3B** is rapidly and reversibly oxidized to a structurally similar anion radical, **2B**, and then to **1B** which is not stable at room temperature and converts to **1A** as it diffuses away from the electrode. This scheme was confirmed by cyclic voltammetry and transmission-mode spectroelectrochemistry. Rate constants for both the **1A** → **1B** and **1B** → **1A** reactions were determined, and upper limits were put on the rate constants for the direct electrochemical reduction of **1A** to **2B** or **3B**.

In the past few years a number of examples have been found in which different conformations of a molecule undergo oxidation or reduction at an electrode surface at distinctly different potentials. This behavior was first noted in the oxidation of tet-

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