pair structure. The observation of an identical rate of interception of both the intermolecular and intramolecular systems by $NaClO_4$ supports the conclusion that ion pair exchange occurs at the same intermediate; namely, the solvent-separated ion pair. For this to be valid there must be an equilibrium between the various ion pair forms of the radical anion of benzophenone and the radical cation of the amine. From the observed rates we find that $K_{eq} = k_1/k_{-1} \leq 5$.[9] Such an equilibrium is not inconsistent with our previous studies of this system.[4] In the case of NaI, the rates observed support the conclusion that the salt intercepts the intermolecular system at the contact ion pair, k_3. The decrease in rate observed for the NaI ion pair exchange with DMABB is presumably due to the necessity of NaI to undergo solvent separation prior to exchange.

In conclusion, we have used picosecond absorption spectroscopy to examine the special salt effect. By determining the rate at which sodium ion intercepts the radical anion of benzophenone from contact- and solvent-separated ion pairs, we can conclude the following about the mechanism of the special salt effect: (1) The rate of ion pair exchange is sensitive to ion pair structure. (2) The maximum rate of exchange is observed when the two ions pairs are of the same type, either solvent separated or contact. (3) The proposed mechanism involving prevention of return from the solvent-separated ion pair is valid only when the equilibrium ion pair distribution of the salt favors the solvent-separated ion pair.

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Registry No. NaI, 7681-82-5; $NaClO_4$, 7601-89-0; DEA, 91-66-7; DMABB, 73060-14-7; benzophenone, 119-61-9.

(9) In order for $NaClO_4$ to intercept the intermolecular system at the solvent-separated ion pair, an equilibrium must exist between the contact- and solvent-separated ion pairs consisting of the radical anion of benzophenone and the radical cation of the amine. From the observed rate of sodium interception and the time resolution of our experiment (the fiber optics available do not provide data between 2 and 5 ns following photolysis) we can only estimate the rate for the separation of the amine contact ion pair. In order to obtain the ion pair distributions observed at 2 and 5 ns following photolysis, the separation rate k_{-1} must be at least twice as fast as the overall exchange rate k_2. We have previously determined $k_1 = 6.0 \times 10^9$. This results in the condition that $K_{eq} = k_1/k_{-1} \leq 5$.

Evidence for Inversion of Configuration in Reactions Involving Radical Processes

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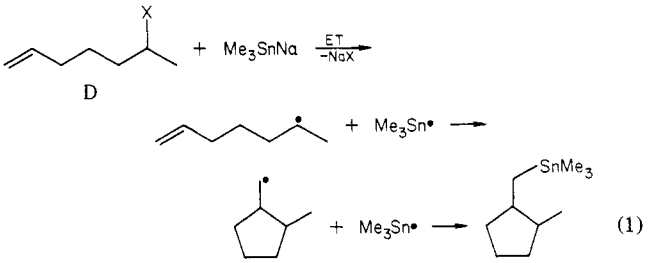
In recent years Kuivila and others have reported the occurrence of electron transfer in reactions of alkyl halides with R_3SnNa and R_3SnLi compounds to form tetraalkyltin compounds.[1-4] More recently, Kuivila has reported the use of trapping agents, such as dicyclohexylphosphine (DCPH), which convert radical intermediates to the corresponding hydrocarbons.[5] Thus, by examination of the effects of added trapping agents on the above reaction, the extent of reactions by S_N2, halogen–metal exchange (HME), or electron-transfer (ET) pathways for a variety of alkyl halides have been quantified. In general, alkyl chlorides and bromides were found to react by S_N2, ET, and HME pathways to varying extents, depending on the structure of the alkyl group. In contrast to the work of Kuivila, San Filippo recently reported that the reaction of trimethyltin sodium with (−)-2-bromooctane proceeds with inversion of configuration.[6] Kuivila, however, reported earlier that the racemate of the substrate studied by San Filippo, (±)-2-bromooctane, reacts with Me_3SnNa by a reaction pathway that involves predominant (72%) electron transfer. Thus, the lack of extensive racemization during the substitution reaction studied by San Filippo led him to state that "the additives which were employed as trapping agents must be introducing a substantial perturbation on the mechanism", and he further implied that mechanistic conclusions obtained by the use of such trapping agents cannot be applied to the same reaction when conducted without the use of traps. We believe that the earlier conclusions of Kuivila, that DCPH is an effective radical trap, are indeed correct. In an attempt to clarify this apparent dichotomy, we have carried out studies to indicate the radical nature of the reaction and also the stereochemistry of the reaction.

Previous studies involving a cyclizable alkyl halide free radical probe have employed 6-bromo-1-hexene with the result that only straight-chain tetraalkyltin products were formed[7] (Scheme I). Scheme I indicates that if k_3 is substantially greater than k_4, no cyclized product should be found even if the reaction involves radical character along the reaction pathway. On the other hand, the rate of coupling (k_3) of A and B should decrease with an increase in the steric requirement of A. Such an effect would result in a better chance of observing the cyclized product C if the reaction is indeed preceeding by an ET process. In addition, the 2-octyl halide system studied by San Filippo would be more accurately mimicked by a secondary halide probe. With this in mind, the reaction of Me_3SnNa with several 6-halo-1-heptenes, D, was examined (eq 1, Table I). When X = OTs, the only



(1)

substitution product formed has the straight-chain structure, and furthermore, DCPH has no effect on the reaction, indicating that the reaction is proceeding predominantly by an S_N2 pathway with little or no ET involved. When X = Cl (experiments 3, 4), a substantial portion of the substitution product is cyclized, indicative of radical character along the reaction pathway. Also, it is clear that DCPH is an effective radical trap and is trapping the radical more rapidly than it is cyclizing. On the other hand, DCPH has no effect on the yield of straight-chain tetraalkyltin compound, although the yield of cyclic substitution product decreased. Thus, it seems likely that the straight-chain substitution products formed from D when X = Cl or OTs are the result of direct S_N2 displacement. However, it is also clear that some reaction has taken place by an ET pathway for X = Cl, as evidenced by the formation of cyclic substitution product. When X = Br (experiments 5, 6), the major product is the cyclized substitution product (71–72%). As in the previous case where X = Cl, DCPH proved to be an effective radical trap by reducing the amount of cyclized substitution product (72–14%) while increasing substantially the

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Scheme I

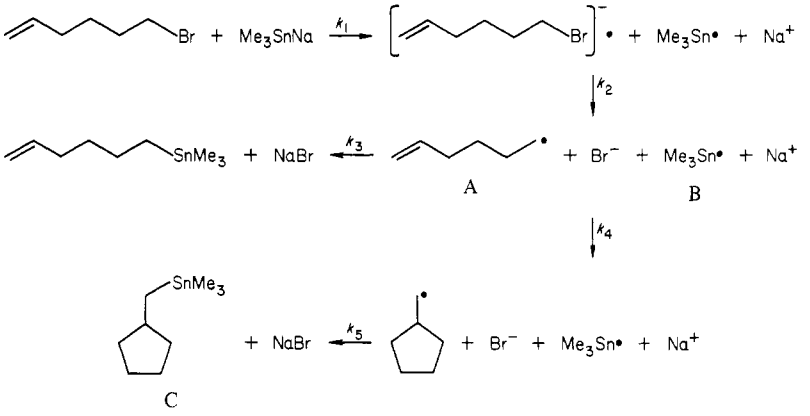
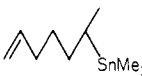
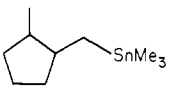


Table I. Reactions of Cyclizable Probes with Me_3SnNa[a]

expt no.	X in (probe)	order of addn[b]	additive, mol equiv	product yields, %[c]			
					 trans/cis		 trans/cis
1	OTs	inv[d]	none	96	0.0	0.0	0.0
2	OTs	inv	10 DCPH	90	0.0	tr[e]	tr
3	Cl	inv	none	53	33 (0.65)	1.0	2.1 (1.6)
4	Cl	inv	10 DCPH	54	3.4 (0.57)	10.2	3.1 (1.8)
5	Br	nor	none	4.2	71 (0.27)	2.1	3.6 (1.6)
6	Br	inv	none	11	72 (0.31)	3.0	2.0 (1.3)
7	Br	inv	10 DCPH	1.0	14 (0.27)	49	16 (1.1)

[a] Reactions were conducted at 0 °C in THF with reaction times of 3 h for chlorides and tosylates and 30 min for bromides and with equimolar amounts of reactants at 0.2 M initial concentration. Cyclizable probes[8] and Me_3SnNa were prepared as previously described. [b] "Inverse" addition indicates that a solution of Me_3SnNa was added to the substrate, while "normal" indicates the substrate solution was added to the Me_3SnNa. [c] All new compounds were isolated by preparative GLC and gave satisfactory NMR, IR, and mass spectral and C-H analytical data. Yields were determined by GLC using internal standards. In experiments 1, 3, 5, and 6, dienes were formed (8% or less), presumably by dehydrohalogenation and disproportionation. In experiments 3 and 4, unreacted starting material accounts for the remainder of the material balance. [d] Inv = inverse; nor = normal. [e] Tr = trace.

Table II. Reactions of 2-Halooctanes with Me_3SnNa[a]

expt no.	X in R*-X	$[\alpha]^{25}_D$[b,c], deg	order of addn	concn of reactants, M	$[\alpha]^{25}_D$ for R*-$SnMe_3$ products, deg		
					obsd	corr	ee, %
1	OTs	−7.55	inv[d]	0.2	+21.6	+28.4	100[e]
2	OTs	−7.26	nor	0.2	+20.1	+27.5	96.8
3	Cl	+27.6	inv	0.2	−16.2	−21.9	77.1
4	Cl	+27.6	inv	0.4	−18.7	−25.3	89.0
5	Br	+31.0	nor	0.2	−10.1	−14.1	49.6
6	Br	+31.0	inv	0.2	−11.0	−15.4	54.2
7	Br	+31.0	inv	0.2	−10.6	−14.8	52.1
8	Br	+31.0	inv	0.4	−11.4	−16.0	56.3

[a] For experimental conditions, see footnotes a-c of Table I. [b] Optical rotations were measured on a Jasco Model 5 ORD/CD instrument at λ 589 by using cyclopentane solutions. [c] The following maximum rotations ($[\alpha]^{20}_D$) for the 2-halooctanes were used: OTs, −9.93°; Cl, +37.3°; Br, +43.4°. [d] Inv = inverse; nor = normal. [e] The value of +28.4° was assumed to be the rotation of optically pure (+)-2-octyltrimethyltin.

amount of straight-chain hydrocarbon product (3–49%).

Since the results of the reaction of Me_3SnNa with the secondary bromide D indicate ET to be the major reaction pathway, the stereochemistry of the reaction of Me_3SnNa with a series of 2-halooctanes was reexamined, with the results shown in Table II. The data show that the stereoselectivity of the reaction of 2-halooctanes with Me_3SnNa decreases according to the trend OTs > Cl > Br. Although San Filippo reported that the stereochemistry of the reaction of Me_3SnNa with (−)-2-bromooctane depends on experimental parameters such as order of addition and concentration, we have found that such effects on product stereochemistry were marginal. Also the present work, utilizing cyclizable probes D, indicates complete inversion in a S_N2 fashion only for X = OTs, whereas San Filippo has indicated 98% inversion even for X = Br under some conditions.

In conclusion, the use of a cyclizable probe has provided additional evidence for the occurrence of radical character along the reaction pathway of the reaction of alkyl halides with Me_3SnNa. It is important to note that D (when X = Br) gave a 72% yield of cyclic substitution product on reaction with Me_3SnNa, indicating that at least 72% of the reaction proceeded via a process involving radical character along the reaction pathway while the reaction of Me_3SnNa with (+)-2-bromooctane proceeded with 77% inversion. We suggest that $Me_3Sn\cdot$ (denoted by Y·) attacks the backside of the radical–anion pair (R·, X^-) in the solvent cage while the front side is still protected by the leaving group (eq 2).[9] This is not unreasonable considering that the single

$$Y^- + RX \xrightarrow{\text{slow}} (Y\cdot, RX^-\cdot) \xrightarrow{\text{fast}} (Y\cdot, R\cdot, X^-) \xrightarrow{\text{fast}} RY + X^- \quad (2)$$

electron transfer between Y^- and RX should take place at the backside of the R group, and hence Y· is still in close proximity to the backside of RX^{-}· in the solvent cage when dissociation to R· and X^- takes place.[10]

Acknowledgment. We are indebted to the National Science Foundation, Grant No. CHE 78-00757, for support of this work.

Registry No. DCPH, 829-84-5; (trimethylstannyl)sodium, 16643-09-7; 6-bromo-1-heptene, 38334-98-4; 6-chloro-1-heptene, 15661-92-4; 6-(tosyloxy)-1-heptene, 59967-05-4; (-)-2-(tosyloxy)octane, 27770-99-6; (+)-2-chlorooctane, 16844-08-9; (+)-2-bromooctane, 1191-24-8; (±)-2-(trimethylstannyl)octane, 82949-86-8; (-)-2-(trimethylstannyl)octane, 79055-01-9; *cis*-2-methyl-1-(trimethylstannyl)cyclopentane, 80963-41-3; *trans*-2-methyl-1-(trimethylstannyl)cyclopentane, 80963-40-2; 1-heptane, 592-76-7; *cis*-1,2-dimethylcyclopentane, 1192-18-3; *trans*-1,2-dimethylcyclopentane, 822-50-4; 6-(trimethylstannyl)-1-heptene, 76879-52-2.

(9) After submission of this manuscript, a report appeared (Kitching, W.; Olsfowy, H. A.; Harvey, K. *J. Org. Chem.* **1982**, *47*, 1893) showing that 6-bromo-1-heptene gave substantial cyclic substitution product on reaction with Me_3SnLi, but the effect of leaving group and the relationship to the stereochemistry of the 2-octyl system were not examined.

(10) The scheme as presented in eq 2 implies that cyclization of the probe is competitive with the coupling step. Prior art would indicate that for coupling $k \sim 10^{10}$ and for cyclization $k = 10^5$. However, the data clearly show cyclization of the radical is competitive with coupling.

Inversion of Configuration in a Free-Radical Process. Mechanisms of the Reactions of Trimethylstannyl Alkalis with (+)-2-Bromooctane

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Reactions of organostannyl alkalis with organic halides, eq 1,

$$R_3SnM + R'X \rightarrow R_3SnR' + MX \qquad (1)$$

show great variations in yield of substitution product and stereochemistry depending on the nature of the halide, solvent, counterion, and other reaction parameters. The work of several groups in recent years has shown that direct S_N2 displacement, halogen–metal exchange, and electron-transfer mechanisms may be involved.[1-20] We have recently used dicyclohexylphosphine (DCPH) as a trap for intermediate free radicals of the electron-transfer mechanisms because of its efficiency as a hydrogen atom donor.[13,15] Thus the amount of reduction product formed in the presence of DCPH could be a measure of the contribution of the electron-transfer mechanism if the DCPH did not alter the mechanism(s) significantly. On the basis of such trapping studies we concluded that 2-bromooctane reacts with Me_3SnNa largely by such a mechanism in tetrahydrofuran (THF). San Filippo and Silberman have since reported that optically active 2-bromooctane reacts with complete inversion under similar conditions.[14] They concluded that DCPH perturbs the mechanism and that our results could not provide a reliable indication of the mechanisms obtaining in its absence. In order to resolve this apparent discrepancy, we chose to examine this reaction using both trapping with DCPH and stereochemistry as probes under identical reaction conditions.

Table I. Yield and Stereochemical Data for the Reaction[a]

$$Me_3SnM + 2\text{-}BrC_8H_{17} \rightarrow \underset{\mathbf{1}}{2\text{-}Me_3SnC_8H_{17}} + MBr$$

		% $Me_3SnC_8H_{17}$ when[b] M =				% ee when[c-e] M =			
		Na		K		Na		K	
entry	addend	in THF	in TG	in THF	in TG	in THF	in TG	in THF	in TG
1		60	90	83	83	58	74	63	81
2	DCPH[f]	10[g]	56	23	57	59	98	98	100
3	Diverted	50	34	60	26	57	35	49	39

[a] Trimethylstannyl alkalis prepared by the reaction hexamethyldistannane with the metal at 0 °C. Reactions were conducted at 0 °C in oven-dried vessels under argon. Initial concentrations of 2-bromooctane: 0.10–0.25 M; Me_3SnM added at once in ca. 100% excess. [b] Yields determined and isolations of 2-(trimethylstannyl)octane made by GLPC using an 0.25 in. × 16 ft column of 15% UCW 98 on Chromosorb W. Major byproducts were C_8 hydrocarbons; C_8 mass balances were 86–100%. [c] Optical rotations measured with a Pepol Model 60 electronic polarimeter with reproducibility of ±0.001° (589 nm); concentrations in pentane 0.008–0.03 g/mL. [d] Based on $[\alpha]^{20}_D$ of +43.40° for optically pure (+)-2-bromooctane.[21] No racemization occurred during reaction of bromide with a 0.5 equiv of Me_3SnNa at 0 °C in THF. For (+)-**1** $[\alpha]^{22}_D$ of +27.4° was determined by reaction of Me_3SnLi with 2-octyl tosylate in TG at 0 °C, using $[\alpha]^{20}_D$ of −9.93° for 2-octanol.[25] Previously reported values for **1** are 26.1°[14b] and 28.4°.[20] [e] Mean values from at least two experiments agreeing within ±1.1%. [f] 1.2–1.3 M. [g] With 2.9 M DCPH this yield fell to 2.9%.

Results on yields from replicate experiments agreeing within ±2% and on stereochemistry (±1.1%) are gathered in Table I. Yields are given in the first set of columns under entry 1 for control experiments. They show that in the THF Me_3SnK gives higher yields of 2-(trimethylstannyl)octane, **1**, than those obtained with Me_3SnNa, indicating a modest counterion effect. Entry 2 shows the effect of added DCPH on the yields of **1**, which are uniformly lower than those of entry 1. The figures in entry 3, the difference between the other two, represent that part of the reaction that has been diverted from formation of **1** to formation of reduction product, octane, by DCPH. A substantial solvent effect is revealed by the data for Me_3SnNa in TG as compared with THF. The yield in THF is 60% in the control experiment and drops to 10% in the presence of DCPH; in TG the yield increases to 90% and falls only to 56% in the presence of DCPH.

Data on the reproducibility of the results with Me_3SnNa in THF are available. Smith[13] obtained the same yield (60%) of **1** in a control as is reported here. This decreased to 10% in the

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