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]

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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]

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

		% $Me_3SnC_8H_{17}$ 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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presence of 1.3 M DCPH, and 86% of octane was formed; our figures are 10% and 85%. San Filippo and Silberman[14b] found 14% of **1** and 85% of octane in the presence of 1.2 M DCPH. Thus excellent reproducibility is attainable.

With Me_3SnK the yields of **1** in the control experiments are the same, 83%, in both THF and TG. However, the presence of DCPH causes a decrease, to 23% in THF but only to 57% in TG; the yields diverted to octane are thus 60% and 26%, respectively. It should be noted that the yields of **1** with the two counterions are markedly different in THF in both control and trapping experiments but that these differences almost vanish in TG, in which yields are very similar.

The last four columns in the table show degrees of excess *inversion* in **1** presented as percent enantiomeric excess (ee) observed by using (+)-2-bromooctane. The stereochemistry with Me_3SnNa in THF (58% ee) is the same for the 60% of **1** formed in the control experiment as that of the 10% formed in the presence of DCPH. In TG a 74% ee is observed in the control experiment and is increased to 98% in the 56% of **1** formed in the presence of DCPH, indicative of an S_N2 mechanism. The data in column 2 show diversion of 34% of **1** diverted to octane in the presence of DCPH. Its ee would have been 35%, as can be estimated from the yield and ee data of entries 1 and 2. This is somewhat smaller than the value of 57% estimated from the data obtained in THF.

With Me_3SnK the values of percent enantiomeric excess in the control experiments are higher than those with Me_3SnNa in each solvent, and that **1** which is formed in the presence of DCPH shows complete inversion. That which was diverted to octane shows a higher percent enantiomeric excess in THF than in TG, as is the case for Me_3SnNa. However, the values for the two counterions may lie within the experimental error in TG.

Are results obtained in experiments with DCPH in the reaction mixture valid as indications of mechanisms occurring in its absence, or does it perturb the mechanisms as has been clamed?[14] Any substance added to a reaction mixture is a potential source of perturbation, and the question is one of degree. In the reactions with Me_3SnNa in THF, the presence of DCPH does not alter the stereochemistry, which should be a highly sensitive probe for distinguishing between electron-transfer (free radical) and S_N2 mechanisms. The results with DCPH show that no significant contribution from S_N2 is involved; the reaction proceeds in at least two steps; it involves a trappable intermediate, but it leads to excess inversion. The results of the other three sets of experiments are consistent with the occurrence of both mechanisms in competition with each other.

Further support for the validity of our conclusion concerning the reality of the electron-transfer process in the reactions of acyclic secondary bromides with trimethylstannyl alkalis in THF has been obtained by Kitching[18] and Ashby.[20] They showed independently that substantial cyclization occurs in the reaction of 6-bromo-1-heptene with Me_3SnLi[18] and Me_3SnNa[20] in THF to form isomeric [(2-methylcyclopentyl)methyl]trimethylstannanes as major products in addition to the normal acyclic product. Such cyclizations are generally taken to constitute diagnostic evidence for free radicals as reaction intermediates.[22]

The observation of excess inversion in the reaction of a trappable free radical is the most striking observation reported here. It clearly demonstrates that the radical is not the simple 2-octyl radical, for all available evidence indicates that it would yield racemic products due to its planarity.[23] Its structure must be such that it loses stereochemical identity with a rate constant comparable to that for the cyclization of 6-heptenyl radicals, ca. 10^5 s^{-1}.[24]

The electron-transfer mechanism appears to occur more readily via associated ion pairs because it competes more effectively with the S_N2 mechanism in the less effective cation-solvating reagent THF than in TG with both counterions. Potassium yields more S_N2 than does sodium. This pattern of solvent and counterion effects is the same as that which we observed in the reactions of trimethylstannyl alkalis with *syn*-7-bromonorbornene.[4] Preliminary results with lithium in the reaction with 2-bromooctane fall into this pattern. Continuing studies should provide more information concerning the driving forces for the competing mechanisms and the nature of the free-radical intermediates.[26]

Registry No. 1, 82918-07-8; 2-BrC_8H_{17}, 1191-24-8; Me_3SnNa, 16643-09-7; Me_3SnK, 38423-82-4.

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Photochemistry in Multichromophoric Systems: Remote Energy Transfer from Naphthyl to a C–S Bond in 2,2-Bis(naphthylmethyl)-1,3-dithianes

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1,3-Dithiane derivatives play an important role in synthetic organic chemistry.[1-5] In contrast to the vast amount of literature concerning the chemical and physical properties of cyclic mercaptans, very little has been revealed about their photochemical behavior.[6] No information concerning the photochemistry of aryl-substituted 1,3-dithio derivatives is found in the literature.

As part of our interest in the photochemistry of bichromophoric systems, we have prepared a series of cyclic dithioketals of 1,3-diaryl-2-propanones and studied their photochemical properties. These chemically stable molecules were found to be photochemically labile and to exhibit unusual, conformation-dependent radiative and nonradiative decay paths. This communication describes the photochemical reactions of 2,2-bis(naphthylmethyl)-1,3-dithianes as representative models.

We have found that irradiation of 2,2-bis(naphthylmethyl)-1,3-dithianes, **1**, in degassed hexane or benzene (ca. 0.001 M) with Pyrex-filtered ultraviolet light absorbed only by the naphthyl chromophores results in clean cleavage of a remote C–S bond. Primary products are 1,3-dinaphthyl-2-(3′-mercaptopropylthio)-1-propenes, **2**, and 1,3-dinaphthylthioacetones, **3**. Scheme I shows the general pathway observed. Thioketones **3** are not isolated but are implicated as delineated below.

All three 2,2-bis(naphthylmethyl)-1,3-dithianes were prepared by a method similar to that of Seebach and co-workers[7] and were characterized by spectroscopic and elemental analyses. Irradiation of **1a** with Pyrex-filtered light[8] for 2 h resulted in loss of starting material and the formation of three new compounds as revealed by NMR and HPLC analyses. Chromatography provided, in

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