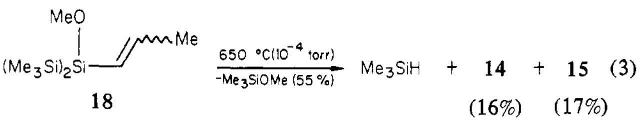
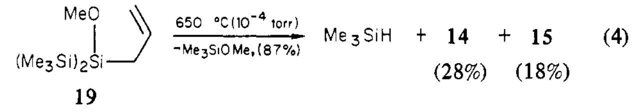
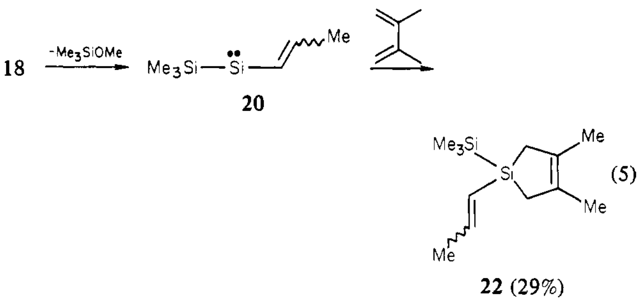
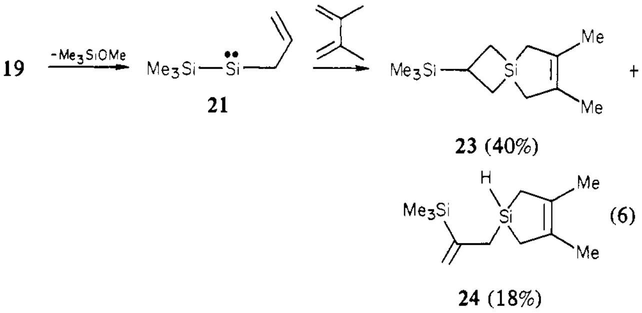




the same products (Me_3SiH, **14** and **15**) in very similar yields. Copyrolysis of **18** (eq 5) and DMBD afforded only trapping of





the initially formed silylene **20** to give silacyclopentene **22**.[9] However, copyrolysis of **19** (eq 6) and DMBD afforded in 40% yield silacyclopentene **23**,[9] clearly derived from rearrangement of silylene **21** to silylene **25** before trapping. In addition to **23**, adduct **24**[9] was formed in 18% yield. Although it is possible that **24** arises from isomerization of **23**, we favor a route involving intramolecular C–H insertion by silylene **25** to afford silabicyclo[1.1.0]butane **26** followed by ring opening to allylsilylene **27**, which is trapped by DMBD to afford adduct **24**.

The strikingly similarity of products and yields from silylenes **9**, **20**, and **21** suggests that in the absence of traps they merge on the same energy surface. At this time the only clues as to the nature of this surface are the trapping of cyclobutasilylenes **12** and **25** from **8** and **19**, respectively. One possible route for interconversion is presented in Scheme III. Currently, we are probing these reactions through chemical trapping, labeling, and direct generation of the proposed intermediates.

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged.

Registry No. 8, 83268-89-7; **10**, 83268-90-0; **13**, 83268-91-1; **18** (isomer 1), 83268-92-2; **18** (isomer 2), 83268-93-3; **19**, 83268-94-4; **22** (isomer 1), 83268-95-5; **22** (isomer 2), 83268-96-6; **23**, 83268-97-7; **24**, 83268-98-8; cyclopropyllithium, 3002-94-6; bis(trimethylsilyl)dichlorosilane, 5181-42-0; sodium methoxide, 124-41-4; 2,3-dimethyl-1,3-butadiene, 513-81-5.

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[8] **18**: Although a ca. 1:1 mixture of *cis*- and *trans*-**18** was used in these experiments, they could be separated by preparative GC. *trans*-**18**: ^1H NMR ($DCCl_3$) δ 0.20 (s, 18 H), 1.89 (d, $J = 6$ Hz, 3 H), 3.48 (s, 3 H, OMe), 5.78 (d, $J = 18$ Hz, 1 H), 6.16 (d of q, $J = 18, 6$ Hz, collapses to d, $J = 18$ Hz, with $h\nu$ at δ 1.89, 1 H). *cis*-**18**: ^1H NMR ($DCCl_3$) δ 0.16 (s, 18 H), 1.81 (d. of d, $J = 7, 1$ Hz, 3 H), 3.41 (s, 3 H, OMe), 5.46 (d of q, $J = 14, 1$ Hz, 1 H), 5.41 (center of overlapped d of q, $J = 14, 7$ Hz, 1 H). Calcd for $C_{10}H_{26}OSi_3$ (M^+, 26%) *m/e* 246.1292, measured (from cis, trans mixture) *m/e* 246.1299. **19**: ^1H NMR ($CDCl_3$) δ 0.24 (s, 18 H), 1.96 (d, 2 H, $J = 8$ Hz), 3.48 (s, 3 H, OMe), 4.73–5.14 (m, 2 H, $=CH_2$), 5.51–6.28 (m, 1 H, $=CHCH_2-$); calcd for $C_{10}H_{26}OSi_3$ (M^+, 0.2%) *m/e* 246.1292, measured *m/e* 246.1291.

[9] *trans*-**22**: (17%) ^1H NMR ($DCCl_3$) δ 0.22 (s, 9 H), 1.57 (br s, 4 H), 1.77 (br s, 6 H), 1.89 (d, $J = 6$ Hz), 5.72 (d, $J = 18$ Hz), 6.10 (d of q, $J = 18, 6$ Hz). *cis*-**22**: (12%) ^1H NMR ($DCCl_3$) δ 0.16 (s, 9 H), 1.61 (br s, 4 H), 1.74 (br s, 6 H), 1.77 (d of d, $J = 7, 1$ *hz*, 3 H), 6.43 (center of overlapped d of q, $J = 7, 14$ Hz, 1 H), 5.59 (d of q, $J = 14, 1$ Hz, 1 H). Calcd for $C_{12}H_{24}Si_2$ (M^+, 70%, from cis/trans mixture) *m/e* 224.1417, measured 224.1415). **23**: ^1H NMR ($DCCl_3$) δ 0.05 (s, 9 H), 0.77–1.47 (m, 5 H), 1.55 (br s, 4 H allylic CH_2), 1.73 (br s, 6 H allylic Me); CMR ($DCCl_3$) δ −3.71, 15.09, 17.85, 19.15, 19.26, 24.0, 27.17, 130.31, 130.80; calcd for $C_{12}H_{24}Si_2$ (M^+, 43%), *m/e* 224.1417, measured *m/e* 224.1414. **24**: ^1H NMR ($DCCl_3$) δ 0.13 (s, 9 H), 1.44 (br s, 4 H, sharpens with $h\nu$ at δ 4.14), 1.71 (br s, 6 H), 1.81 (br d, 2 H, $J = 4$ Hz, collapses to br s with $h\nu$ at δ 4.14), 4.14 (m, 1 H, SiH, collapses to s with $h\nu$ at δ 1.71–1.81), 5.22 (d, 1 H, $J = 3$ Hz), 5.47 (overlapped d of t, $J = 3, 2$ Hz, 1 H, collapses to d with $h\nu$ at 1.81; calcd for $C_{12}H_{24}Si_2$ (M^+, 11%) *m/e* 224.1417, measured 224.1420.

Direct Observation of the Special Salt Effect: Picosecond Dynamics of Ion Pair Exchange

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Received April 14, 1982

Salt effects are frequently observed in organic reactions that involve ion pair intermediates. Winstein[1] observed that the effect of added $LiClO_4$ on the rate of solvolysis of *threo*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate was an initial rate increase that could not be explained solely in terms of an ionic strength effect. The observation of this special salt effect led him to postulate two different types of ion pair intermediates, contact and solvent separated. Winstein proposed that the special salt effect resulted from the prevention of return to the contact ion pair from the solvent-separated form. This mechanism has received substantial support,[2] but its elucidation has been based on indirect observations. On the other hand, it has been reported[3] that the rate of ion pair exchange is not highly sensitive to ion pair structure. This observation indicates that the mechanism of the special salt effect should involve interception of both contact- and solvent-separated ion pair forms. To data there has been no direct experimental determination of the rates of formation of salt contact ion pairs from initially formed organic ion pairs. We have used picosecond absorption spectroscopy to determine the rate of ion pair exchange. By examining the rate of interception of organic contact and solvent-separated ion pairs by sodium contact ion pairs (NaI) and sodium solvent separated ion pairs ($NaClO_4$), we will show that the rate of interception is dependent on ion pair structure. Our results support, in part, Winstein's proposed mechanism for the special salt effect.

The picosecond absorption spectrometer has been previously described.[4] Transient absorption spectra for the photoreduction of 0.2 M benzophenone by 1.0 M *N*,*N*-diethylaniline (DEA) in the presence of 0.5 M $NaClO_4$ in acetonitrile are shown in Figure 1. We have recently reported[4] that in the absence of salt, photolysis results in a rapid electron transfer forming the solvent-separated ion pair consisting of the amine radical cation and the benzophenone radical anion (λ_{max} 720 nm). These species diffuse together within 300 ps following photolysis to form a contact ion pair (λ_{max} 690 nm). In the present study, the absorption maximum of the radical anion of benzophenone (λ_{max} 695 nm) indicates the formation of the amine contact ion pair (Figure 1A) at 200 ps following photolysis. From 500 ps to 10 ns, the absorption

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[1] (a) Winstein, S.; Robinson, G. *J. Am. Soc.* **1958**, *80*, 169. (b) Winstein, S.; Clippinger, E.; Fainberg, A.; Robinson, G. *Ibid.* **1954**, *76*, 2597.

[2] (a) Fainberg, A.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2767. (b) Fainberg, A.; Robinson, G.; Winstein, S. *Ibid.* **1956**, *78*, 2777. (c) Winstein, S.; Clippinger, E. *Ibid.* **1956**, *78*, 2784. (d) Jenny, E.; Winstein, S. *Helv. Chim. Acta* **1958**, *41*, 807.

[3] (a) Grunwald, E.; Puar, M. *J. Am. Chem. Soc.* **1967**, *89*, 6842. (b) Crampton, M.; Grunwald, E. *Ibid.* **1971**, *93*, 2987. (c) Crampton, M.; Grunwald, E. *Ibid.* **1971**, *93*, 2990.

[4] Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403. Fiber optics were used to obtain transient absorption spectra at 5, 10, 50, and 250 ns following photolysis.

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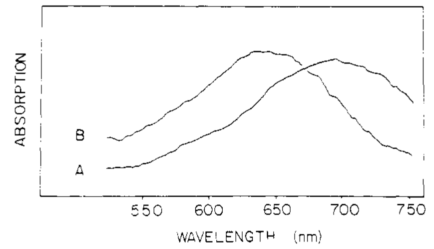


Figure 1. Transient absorption spectra for the photoreduction of 0.2 M benzophenone, 1.0 M DEA in an acetonitrile solution containing 0.5 M $NaClO_4$. The absorbance at λ_{max} is 0.3 OD: (A) 200 ps following photolysis; (B) 10 ns following photolysis.

Table I. Time Dependence of the Absorption Maximum (nm) of the Radical Anion of Benzophenone as a Function of Salt Concentrations [$NaClO_4$]

time, ns	λ_{max} (0.1 M Na^+)	λ_{max} (0.5 M Na^+)	λ_{max} (1.0 M Na^+)
0.2	695	695	659
1	690	680	660
2	680	670	655
10	660	645	645

maximum of the radical anion blue shifts from 690 to 645 nm (Figure 1B). The band at 645 nm is assigned to the sodium contact ion pair.[5] The rate of shift of the absorption maximum was observed to be dependent on the concentration of salt ([$NaClO_4$] = 0.1–1.0 M; Table I). For the following kinetic analysis, radical anion absorptions with 645 nm $\geq \lambda_{max} \leq$ 690 nm are assumed to arise from the convolution of the absorption bands of the following contact ion pairs: benzophenone radical anion–sodium cation (645 nm) and benzophenone radical anion–amine radical cation (690 nm).

The rate of formation of the salt contact ion pair from the amine contact ion pair must be limited by one of the following two processes: the rate of separation of the amine contact ion pair, k_1, or the rate of salt diffusion. In order to elucidate the rate-limiting step, it is necesary to measure the rate of salt contact ion pair formation from the amine solvent separated form. Therefore we examined the photolysis of 4-(*p*-(dimethylamino)benzyl)-benzophenone (DMABB).[6] For this molecule the photostimulated electron transfer results in the formation of a charge-transfer intermediate that is analogous to the amine solvent separated ion pair. The methylene bridge between the ketone and amine moieties prevents collapse to form the analogous amine contact ion pair. Photolysis of 0.1 M DMABB in acetonitrile results in a rapid electron transfer ($k_{ir} > 5 \times 10^{10}$ s^{-1}) to form the solvent-separated ion pair. The absorption maximum of the radical anion moiety (λ_{max} 720 nm) was found to be invariant up to 50 ns following photolysis. This is consistent with the geometric constraints of this molecule in which intermolecular contact ion pair formation between the amine and carbonyl moieties is prohibited. In the presence of 0.5 M $NaClO_4$, the radical anion absorption blue shifts from 720 to 645 nm, the endpoint being identical with that observed for the intermolecular system. In Figure 2, the absorption maximum of the radical anion is plotted vs. time following photolysis, thus showing the effect of salt on both the intermolecular and intramolecular systems. In order to study the effect of ion pair structure on the rate of ion pair exchange, we repeated the above experiments using NaI[7] in place of $NaClO_4$.

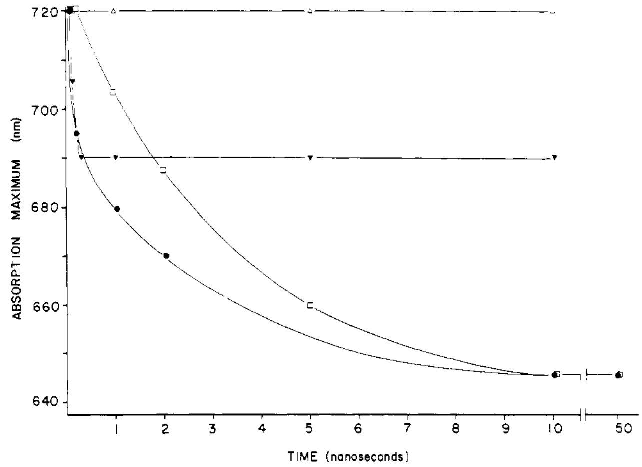
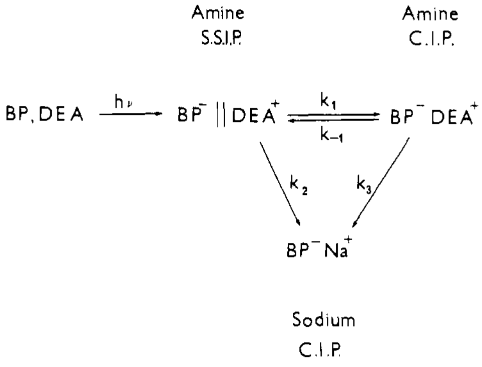


Figure 2. Absorption maximum of the radical anion of benzophenone as a function of time following photolysis: (▲) 0.1 M DMABB in acetonitrile; (□) 0.1 M DMABB, 0.5 M $NaClO_4$ in acetonitrile; (▼) 0.2 M benzophenone, 1.0 M DEA in acetonitrile; (●) 0.2 M benzophenone, 1.0 M DEA, 0.5 M $NaClO_4$ in acetonitrile.

Scheme I



The above results can be interpreted within Scheme I. For the photolysis of a 0.2 M benzophenone, 1.0 M DEA, 0.1–1.0 M $NaClO_4$ acetonitrile solution we first observe the formation of the amine contact ion pair. The rate of amine contact ion pair formation is found to be independent of salt concentration for $NaClO_4$. Deconvolution of the transient absorption spectra yielded a rate for the formation of the sodium contact ion pair from the intermolecular ketone–amine system of (7.3 ± 0.5) × 10^8 mol^{-1} s^{-1}.[8] Within experimental error, the same rate is observed by using NaI. For the photolysis of DMABB where contact ion pair formation is prohibited, we find that the rate of formation of the sodium contact ion pair is k_2 = (7.2 ± 0.5) × 10^8 mol^{-1} s^{-1} in the case of $NaClO_4$ and k_2 <1 × 10^8 mol^{-1} s^{-1} for NaI. These results demonstrate that the rate of exchange must be sensitive to ion

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(5) For photolysis in the presence of $LiClO_4$, were observe a blue shift in the radical anion absorption from 690 to 610 nm during the first 10 ns following photolysis. This blue shift is consistent with the formation of a tighter species of ion pair (Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307). From FT IR studies we do not observe any changes in the carbonyl stretching frequency of benzophenone in acetonitrile solutions containing 0.1–1.0 M $NaClO_4$, thus indicating the absence of a ground-state interaction. In addition we have performed relaxation measurements on the sodium nucleus. No appreciable change in T_1 was observed for sodium ion in the concentration range 0.001–1.0 M. This indicates that the environment of the sodium nucleus is roughly the same throughout this concentration range and supports the notion that $NaClO_4$ exists as solvent-separated ion pairs or free ions at all concentrations (Erlich, R.; Popov, A. *Ibid.* **1971**, *93*, 5629). Thus the bulk concentration of $NaClO_4$ reflects the sodium concentration available to interact with the benzophenone radical anion.

(6) Masuhara, H.; Maeda, Y.; Nakajo, H.; Mataga, N.; Tomita, K.; Tatemitsu, H.; Sakata, Y.; Misumi, W. *J. Am. Chem. Soc.* **1981**, *103*, 634.

(7) NaI exists predominantly (>97%) as a contact ion pair in acetonitrile. See: "An Investigation of Cation–Solvent Interaction by Na-23 NMR"; Richard Minasz, *Diss. Abstr. Int B* **1975**, *35(9)*, 4393. In tetramethylguanidine, conductance measurements have shown that ion pair dissociation is negligible and approximately 100% of the NaI exists as a contact ion pair for concentration greater than 10^{-2} M (Greenberg, M.; Bodner, R.; Popov, A. *J. Phys. Chem.* **1973**, *77*, 2449).

(8) Deconvolutions were performed on a Digital Minc23 lab computer. The deconvolution routine is designed to minimize the variance between the calculated and observed spectra. The rates obtained were as follows: [Na^+] = 0.1 M, $k = 7.4 \times 10^7$ s^{-1}; [Na^+] = 0.5 M, $k = 3.5 \times 10^8$ s^{-1}; [Na^+] = 1.0 M, $k = 7.4 \times 10^8$ s^{-1}. Bimolecular rate constants obtained for various salt concentrations were as follows: [Na^+] = 0.1 M, $k = 7.4 \times 10^8$ mol^{-1} s^{-1}; [Na^+] = 0.5 M, $k = 7.0 \times 10^8$ mol^{-1} s^{-1}; [Na^+] = 1.0 M, $k = 7.4 \times 10^8$ mol^{-1} s^{-1}.

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 $K_{eq} = k_1/k_{-1} \le 5$.[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.

Acknowledgment. This work is supported by a grant from the National Science Foundation, CHE-8117519.

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

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(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 $K_{eq} = k_1/k_{-1} \le 5$.

Evidence for Inversion of Configuration in Reactions Involving Radical Processes

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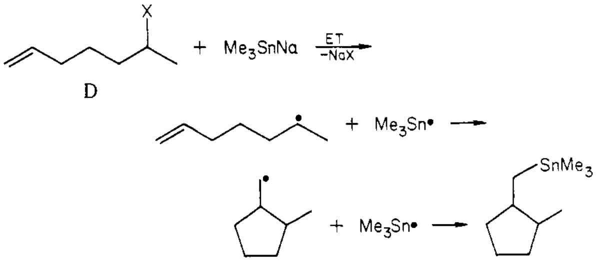
Received February 26, 1982
Revised Manuscript Received August 6, 1982

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 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



(1)

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