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# Evidence for Electron Transfer in the Reaction of (Trimethylstannyl)sodium with Primary Alkyl Halides

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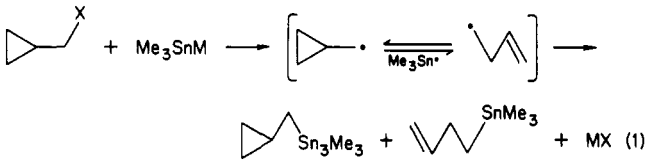
The reaction of (trimethylstannyl)sodium with primary alkyl halides has been studied in detail with emphasis on the effect of solvent and added radical and carbanion traps. Contrary to previous reports all evidence indicates that the reaction proceeds by an electron-transfer process involving radical intermediates for the systems studied.

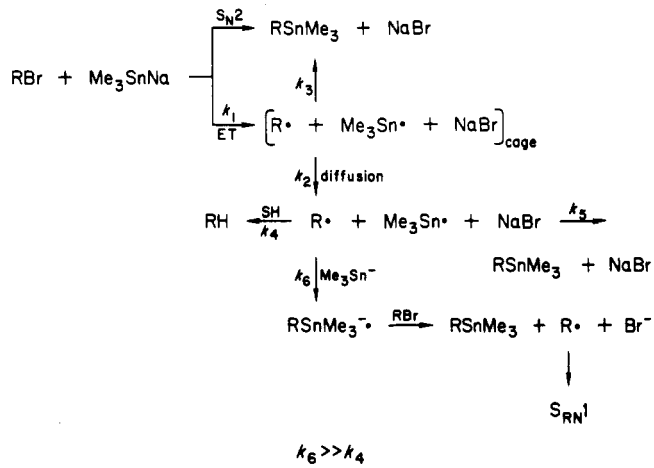
## Introduction

In recent years several mechanisms have been proposed for the formation of tetraalkyltin compounds by the reaction of organic halides with triorganostannyl alkali-metal compounds.[1] These proposals were based on a variety of stereochemical studies,[2-4] a variety of experiments in which intermediates were trapped,[5,6] and a formation of rearranged products.[7-9] The three basic mechanistic pathways which have been described are (a) a classic $S_N2$ substitution of the alkyl halide with a trialkylstannyl anion as the nucleophile, (b) substitution by an electron-transfer (ET) process, and (c) substitution by halogen–metal exchange (HME). San Filippo[7,8] has reported that trimethylstannyl anion yielded rearranged products on reaction with cyclopropylcarbinyl bromide and iodide and suggested the intermediacy of free radicals in this reaction (eq 1).

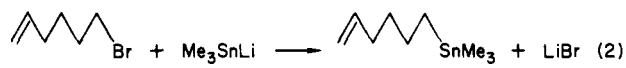



However, Newcomb[10] found no evidence for an electron-transfer pathway in the reaction of 6-bromo-1-hexene with

**Scheme I**




(trimethylstannyl)lithium in that only straight chain tetraalkyltin product was formed (eq 2), and hence these




results presented a challenge to the findings of San Filippo. Moreover, Kuivila[11] reported that reactions of (trimethylstannyl)sodium (1) with unhindered primary halides proceed exclusively by an $S_N2$ pathway. With a very sterically hindered primary bromide (neopentyl bromide), significant reaction by an ET pathway (32%) was found in reactions involving $Me_3SnNa$. Kuivila also studied the cyclopropylcarbinyl–trimethylstannyl alkali systems previously reported by San Filippo by the technique of

(1) Kuivila, H. G. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 315.
(2) Jensen, F. R.; Davis, D. D. *J. Am. Chem. Soc.* **1971**, *93*, 4047.
(3) Kuivila, H. G.; Considine, J. L.; Kennedy, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 7206.
(4) Bock, P. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2826.
(5) Kuivila, H. G; DiStefano, F. V. *J. Organomet. Chem.* **1976**, *122*, 171.
(6) Wursthorn, K. R.; Kuivila, H. G.; Smith, G. F. *J. Am. Chem. Soc.* **1978**, *100*, 2779.
(7) San Filippo, J., Jr.; Silberman, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.
(8) San Filippo, J., Jr.; Silberman, J. *J. Am. Chem. Soc.* **1982**, *104*, 2831.
(9) Alnajjar, M. S.; Kuivila, H. G. *J. Org. Chem.* **1981**, *46*, 1053.
(10) Newcomb, M.; Courtney, A. R. *J. Org. Chem.* **1980**, *45*, 1707.

(11) Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833. Professor Kuivila at a recent meeting reported to E. C. Ashby that he has recently obtained evidence of electron transfer in the reaction of $Me_3SnNa$ with a primary alkyl halide.

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**Table I. Reaction of Primary Alkyl Bromides with (Trimethylstannyl)sodium (1) in the Presence of Radical Traps[a]**

| entry | substrate | additive,[b] molar equiv | time, min | yield of product,[b] % RBr | RSnMe$_3$ | RH |
|---|---|---|---|---|---|---|
| 1 | *n*-BuBr (4) | none | 1 | 0 | 100 | ... |
| 2 | 4 | 2, 0.27 | 1.5 | 31.4 | 67.7 | ... |
| 3 | 4 | 3, 0.20 | 1.5 | 0 | 91.8 | ... |
| 4 | 4 | 2, 0.27 | 15 | 0 | 99.0 | ... |
| 5 | $(CH_3)_2CHCH_2Br$ (5) | none | 2 | 0 | 98.0 | ... |
| 6 | 5 | 2, 0.26 | 5 | 50.4 | 47.9 | ... |
| 7 | 5 | 3, 0.28 | 6 | 0 | 86.3 | ... |
| 8 | $CH_3(CH_2)_3CH(C_2H_5)CH_2Br$ (6) | none | 2 | 0 | 96.4 | 1.5 |
| 9 | 6 | 2, 0.19 | 5 | 78.7 | 18.0 | trace |
| 10 | 6 | 2, 0.39 | 6 | 98.9 | 2.1 | 0 |
| 11 | 6 | 3, 0.28 | 6 | 0 | 85.4 | <1 |

[a] Reactions were conducted by using 0.15 M concentration of bromide and 0.30 M concentration of 1 at 0 °C in THF. [b] Based on bromide.

trapping the intermediates and by the study of counerion effects. On the basis of the results of this work, Kuivila[12] reported that formation of rearranged products in reactions of cyclopropylcarbinyl halides should not be taken as prima facie evidence for kinetically free radical intermediates. Nevertheless, we have found in recent work[13] that ET is the major pathway of the reaction of $Me_3SnNa$ with secondary alkyl bromides and a radical anion scavenger [*p*-dinitrobenzene (2)] and a free radical scavenger [di-*tert*-butylnitroxyl radical (3)] does indeed trap the radical anion and free radical, respectively, and thus slows down the rate of reaction. In the above reaction the primary radical, formed after secondary radical diffusion out of the solvent cage followed by subsequent cyclization, reacts with $Me_3Sn^-$ to start the $S_{RN}1$ radical chain process. Since secondary alkyl halides can react with $Me_3SnNa$ via an ET pathway, we were anxious to determine if $Me_3SnNa$ will also react with primary alkyl halides by a similar pathway. Previous results can be explained by assuming that the substitution product is formed inside the solvent cage or outside the solvent cage assuming that the rate of straight chain radical trapped by $Me_3Sn^-$ (or $Me_3Sn\cdot$) is much faster than the rate of radical cyclization or radical trapping by solvent or DCPH. Our suggestion that explains all of the data obtained so far by ourselves and others is described in Scheme I. R· can of course cyclize after diffusion from the solvent cage to produce $R_c\cdot$ which can then do all of the same things shown for R·.

We would now like to report our studies which indicate that free radicals are formed as intermediates in the reaction of primary alkyl halides with $Me_3SnNa$.

## Results and Discussion

**Studies with Primary Alkyl Bromides.** We have examined the reaction of primary alkyl bromides with $Me_3SnNa$ in the presence of a radical anion scavenger [*p*-dinitrobenzene (2)] and a radical scavenger [di-*tert*-butylnitroxyl radical (3)] and the results are given in Table I. With *n*-butyl bromide (4), the yield of substitution product is decreased from 100% to 67.7% (entries 1 and 2) in the presence of 27 mol % of 2 in the same time period. Moreover, this reaction will proceed to completion even in the presence of 2 if it is allowed to proceed long enough (entry 4). Furthermore, we have found that increasing the steric requirement of the primary alkyl bromide results in a more effective retardation of the reaction rate on addition of 2 (compare entries 5, 6, 8, 9, and 10). These results show that these reactions are inhibited by adding 2 and that the $S_{RN}1$ chain process involving a radical anion participates in the reaction of primary alkyl bromides with $Me_3SnNa$. However, the reactions of primary alkyl bromides with $Me_3SnNa$ still proceed completely in the presence of 3 (see entries 3, 7, and 11) with the only effect that the yield of substitution product is decreased. Interestingly, a significant amount of byproduct identified (GC–MS) as the corresponding di-*tert*-butylnitroxyl alkane is formed in each reaction. Control experiments were carried out and showed that di-*tert*-butylnitroxyl radical does not react with the starting bromides. These results indciate that radical intermediates are involved in the reactions of primary alkyl bromides with $Me_3SnNa$ and that perhaps different inhibitors show different sensitivities to this radical chain process. Nevertheless, these results indicate that in proceeding to a more hindered bromide, less $S_N2$ character is observed and a higher degree of the ET pathway is involved.

Next, the reactions of 2-ethylhexyl bromide (6) with $Me_3SnNa$ were examined in different solvent systems in order to obtain further evidence concerning the radical intermediates involved in the reaction (Table II). It is known that radicals diffuse out of the solvent cage during reaction to a higher extent as the viscosity of the solvent decreases, therefore one would expect to observe more hydrocarbon product in a less viscous solvent as a result of hydrogen abstraction from the solvent as a result of increased radical diffusion from the solvent cage. Therefore, if a reaction proceeds via an ET pathway, the product distribution (substitution product vs hydrocarbon) should depend on the viscosity of the solvent. In addition to this effect, Kuivilla[12,14] has shown that a decrease in cation coordinating ability of the solvent increases the extent of the ET pathway in competition with the $S_N2$ pathway. Therefore, a more viscous, nonpolar solvent (i.e., *n*-dodecane) and a less viscous, nonpolar solvent (i.e., *n*-pentane) have been used as a cosolvent with THF separately in order to examine the viscosity effect in competition with the cation chelating effect of the solvent in the reaction of 1 with 6. Entries 1, 2, and 3 represent the reactions of $Me_3SnNa$ with 6 in THF. Dicyclohexylphosphine (DCPH) is a radical and carbanion trap; however, the yields of substitution and hydrocarbon product are unaffected by the carbanion trap *tert*-butylamine (TBA). Entries 4, 5, and 6 show that with a solvent system of lower viscosity (THF, $\eta$(0 °C) = 0.608; THF–$Et_2O$ $\eta$(0 °C) = 0.466), the reaction of $Me_3SnNa$ with 6 produces a substantially larger amount of hydrocarbon (14.6%) in the absence of additive, and the amount of hydrocarbon is increased from 14.6% to 40% by the presence of the radical trap DCPH. How-

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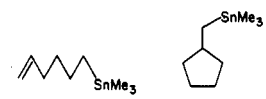
(13) Ashby, E. C.; DePriest, R. N.; Su, W.-Y. *Organometallics* **1984**, *3*, 1718.
(14) Alnajjar, M. S.; Kuvila, H. G. *J. Am. Chem. Soc.* **1985**, *107*, 416 (published after manuscript submission).

**Table II. Solvent Effects in the Reaction of 2-Ethylhexyl Bromide (6) with (Trimethylstannyl)sodium (1)[a,b]**

| entry | concn,[c] M | additive,[c] molar equiv | solv (ratio) | yield of product,[c] % $RSnMe_3$ | yield of product,[c] % RH |
|---|---|---|---|---|---|
| 1 | 0.15 | none | THF | 96.4 | 1.5 |
| 2 | 0.15 | DCPH, 2 | THF | 89.3 | 7.6 |
| 3 | 0.15 | TBA, 10 | THF | 96.1 | 1.2 |
| 4 | 0.07 | none | THF-$Et_2O$ (1:1) | 84.2 | 14.6 |
| 5 | 0.07 | DCPH, 2 | THF-$Et_2O$ (1:1) | 63.8 | 40.0 |
| 6 | 0.07 | TBA, 10 | THF-$Et_2O$ (1:1) | 81.9 | 14.8 |
| 7 | 0.07 | none | THF-$C_5H_{12}$ (1:1) | 91.0 | 8.1 |
| 8 | 0.07 | DCPH, 2 | THF-$C_5H_{12}$ (1:1) | 70.2 | 27.1 |
| 9 | 0.07 | TBA, 10 | THF-$C_5H_{12}$ (1:1) | 88.9 | 9.7 |
| 10 | 0.07 | none | THF-$C_{12}H_{26}$ (1:1) | 95.1 | 3.2 |
| 11 | 0.07 | DCPH, 2 | THF-$C_{12}H_{26}$ (1:1) | 73.9 | 24.5 |
| 12 | 0.07 | TBA, 10 | THF-$C_{12}H_{26}$ (1:1) | 95.0 | 2.7 |

[a] Reactions were conducted at 0 °C for 15 min. [b] A twofold excess of 1 was used in each reaction. [c] Based on bromide.

**Table III. Reaction of 6-Bromo-1-hexene (7) with $Me_3SnNa$ (1)[a]**

| entry | additive,[b] molar equiv | solv (ratio) | yield of product,[b] %  | | | |
|---|---|---|---|---|---|---|
| 1 | none | THF | 99 | 0 | 0 | 0 |
| 2 | none | THF-$Et_2O$ (1:1) | 89.9 | 8.2 | <1 | <1 |
| 3 | DCPH, 5 | THF-$Et_2O$ (1:1) | 81.6 | 4.2 | 7.6 | 3.1 |
| 4 | TBA, 10 | THF-$Et_2O$ (1:1) | 88.4 | 8.6 | <1 | <1 |
| 5 | none | THF-pentane (1:1) | 90.7 | 8.6 | <1 | <1 |
| 6 | DCPH, 5 | THF-pentane (1:1) | 84.1 | 6.4 | 5.0 | 2.0 |
| 7 | TBA, 10 | THF-pentane (1:1) | 90.9 | 8.7 | <1 | <1 |
| 8 | none | THF-dodecane (1:1) | 96.0 | 2.1 | ... | ... |
| 9 | DCPH, 5 | THF-dodecane (1:1) | 96.8 | >1 | 1.5 | ... |
| 10 | TBA, 10 | THF-dodecane (1:1) | 96.2 | >0 | ... | ... |
| 11 | 18-crown-6, 4 | THF-$Et_2O$ (1:1) | 99.0 | 0 | 0 | 0 |

[a] Reactions were conducted by using 0.15 M concentration of bromide and 0.30 M concentration of $Me_3SnNa$ at 0 °C for 15 min. [b] Based on the halide.

ever, in the presence of the carbanion trap TBA, the result was similar to that observed in the absence of any additive. Clearly, the hydrocarbon products have a radical precursor and are formed by the abstraction of hydrogen from the solvent and DCPH by the radical.[11] These results are consistent with both a cation chelating effect (THF–$Et_2O$ more poorly coordinates cations than pure THF) and a viscosity effect since a higher degree of radical pathway is indicated at the lower viscosity. Entries 7, 8, and 9 represent the results obtained by using the solvent system (THF–pentane, $\eta$(0 °C) = 0.404) of approximately the same viscosity as THF–$Et_2O$ ($\eta$(0 °C) = 0.466) in an attempt to separate the cation chelation and solvent viscosity effects. It is clear that the products due to radical intermediates have decreased substantially indicating that cation chelation is quite important. However, it should be pointed out that $Et_2O$ would be expected to be a better radical trap than pentane and thus part of the difference between the THF–$Et_2O$ and the THF–pentane results can be explained on this basis. If indeed cation chelation alone is important, then changing the viscosity of the solvent without changing the cation chelation ability should not result in any change in the products formed from radical precursors. The data show that as the viscosity of the solvent is increased (THF–dodecane, $\eta$(0 °C) = 1.072), the products of radical precursors (RH) decrease from 8.1, 27.1, and 9.7% (entries 7–9) to 3.2, 24.5, and 2.7% (entries 10–12), respectively. The difference is not overwhelming, but it is significant. Once again the results of the experiments using TBA (entries 6 and 9) show that carbanions are not trapped in these reactions. It is of course also possible that the effect of solvent may be due to a change in $\Delta(\Delta G^*)$ for the $S_N2$ and ET steps in Scheme I or to the competition between the $S_N2$ and $S_{RN}1$ process.

**Studies with Cyclizable Probes.** In order to obtain more mechanistic information, two cyclizable radical probes were used to study the reaction of primary alkyl halides with $Me_3SnNa$. The results of experiments involving 6-bromo-1-hexene (7) as the cyclizable primary alkyl halide probe are given in Table III. Since the tetraalkyltin compound containing the cyclized moiety derived from the primary alkyl halide probe is most reasonably attributed to the cyclization of an intermediate radical, the percentage of cyclized tetralkyltin compound and both straight chain and cyclized hydrocarbon can be assumed to indicate the minimum extent of reaction proceeding with radical involvement along the reaction pathway.

Entries 2, 3, and 4 of Table III show that in THF–$Et_2O$ (1:1) solvent, the reaction of $Me_3SnNa$ with 7 produces a substantial amount of cyclized substitution product (8.2%) in the absence of DCPH and cyclized substitution product is decreased (from 8.2% to 4.2%) by the presence of DCPH with an increase in hydrocarbon (1–10%). Similar results are obtained in the reaction using THF–pentane (1:1), a solvent system of comparable viscosity to THF–$Et_2O$ (1:1) (entries 5, 6, and 7, Table III). In THF–*n*-dodecane (1:1), a solvent of higher viscosity than THF–$Et_2O$ or THF–pentane, only a small amount of cyclized substitution product (2.4%) was found in the absence of DCPH (entry 8). However, in the presence of DCPH (entry 9), the amount of uncyclized hydrocarbon increased slightly and the amount of cyclized substitution product decreased from 2.1% to only a trace. In the presence of TBA, the result was similar to that observed in the absence of any additive. Interestingly, in THF–$Et_2O$ (1:1), in the

**Scheme II**

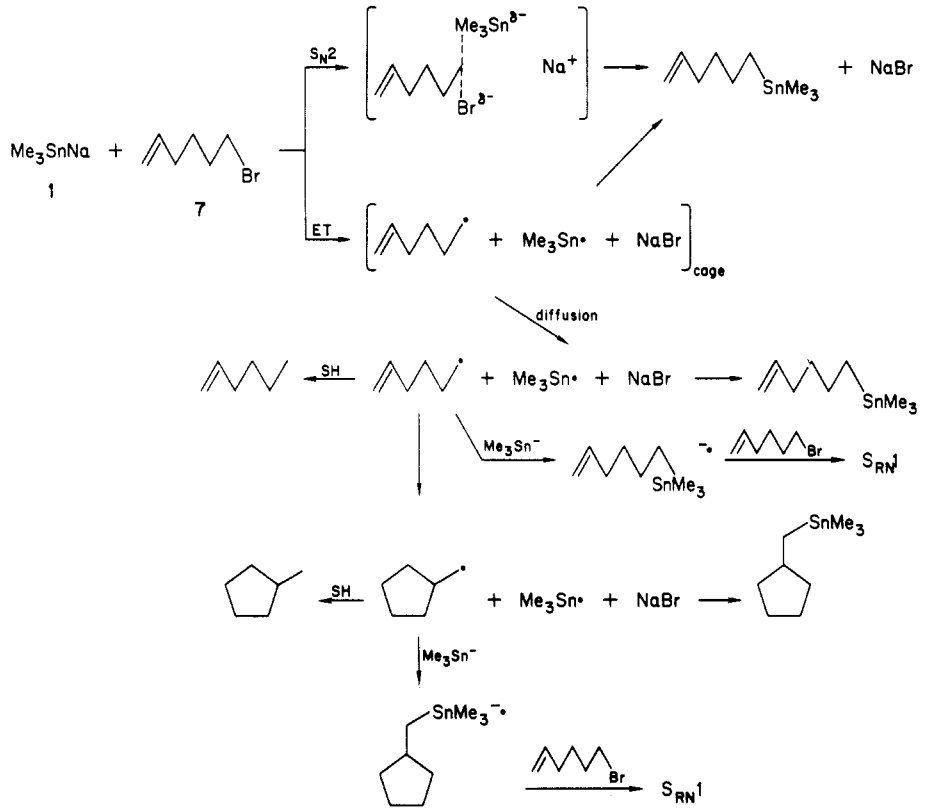
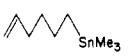



**Table IV. Reaction Profile of $Me_3SnNa$ (1) with 6-Bromo-1-hexene (7)[a]**

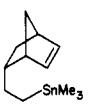
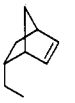
| | | yield of product,[b] % | | | |
|---|---|---|---|---|---|
| entry | solv (ratio) |  |  |  |  |
| 1 | THF-$C_{12}H_{26}$ (2:8) | 92.2 | 6.7 | ··· | ··· |
| 2 | THF-$C_{12}H_{26}$ (3:7) | 94.1 | 4.6 | ··· | ··· |
| 3 | THF-$C_{12}H_{26}$ (5:5) | 95.5 | 2.3 | ··· | ··· |
| 4 | THF-$C_{12}H_{26}$ (7:3) | 98.0 | trace | ··· | ··· |
| 5 | THF-$C_{12}H_{26}$ (9:1) | 98.8 | 0 | ··· | ··· |
| 6 | THF-$Et_2O$ (2:8) | 86.4 | 12.6 | trace | ··· |
| 7 | THF-$Et_2O$ (3:7) | 93.5 | 5.2 | ··· | ··· |
| 8 | THF-$Et_2O$ (5:5) | 98.8 | trace | ··· | ··· |
| 9 | THF-$Et_2O$ (7:3) | 98.5 | 0 | ··· | ··· |
| 10 | THF-$Et_2O$ (9:1) | 99.1 | 0 | ··· | ··· |
| 11 | THF-$C_5H_{12}$ (2:8) | 83.4 | 15.1 | trace | ··· |
| 12 | THF-$C_5H_{12}$ (3:7) | 89.9 | 9.0 | trace | ··· |
| 13 | THF-$C_5H_{12}$ (5:5) | 95.0 | 4.0 | ··· | ··· |
| 14 | THF-$C_5H_{12}$ (7:3) | 98.7 | trace | ··· | ··· |
| 15 | THF-$C_5H_{12}$ (9:1) | 98.5 | 0 | ··· | ··· |

[a] Reactions were conducted by using 0.024 M concentrations of bromide and 0.048 M concentrations of $Me_3SnNa$ at 0 °C for 15 min. [b] Yields are based on the halide.

presence of 18-crown-6, the reaction of 1 and 7 produced no cyclized substitution product (entry 11) whereas in the absence of 18-crown-6, 8.2% (entry 2) was produced. Also of interest is the comparison of cyclized substitution product reported in entries 1, 2, 5, and 8 which clearly establishes the importance of viscosity of the solvent in the observation of radical intermediates outside of the solvent cage. In summary, all of these data (Table III) indicate that cyclization of radicals take place outside of the solvent cage, more radicals form in a solvent of lower cation coordinating ability, and more radicals can diffuse out of the solvent cage in a solvent of lower viscosity (THF–$Et_2O$ or THF–pentane) than one of higher viscosity (THF–dodecane) resulting in a greater chance to form cyclized substitution product and cyclized hydrocarbon (trapped by DCPH or solvent as in Scheme II). In addition, TBA shows no effect on the product ratio indicating that carbanion intermediates are not involved in the reaction.

Furthermore, we sought to gain additional insight into the cation chelating effect and viscosity effect of the reaction of 1 with 7 by examining the reaction profile as a function of solvent ratio. The results are shown in Table IV. In all cases, no matter what solvent system was used, the results indicate that the higher extent of ET pathway is observed as the percentage of poor coordinating solvents ($Et_2O$, pentane, dodecane) is increased. More interestingly, in the case of $Et_2O$, which is a better cation complexing solvent than *n*-dodecane and also a less viscous solvent than *n*-dodecane, the amount of cyclized substitution

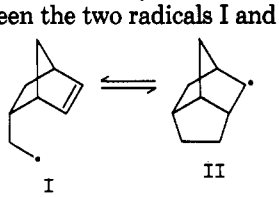
Table V. Reaction of *endo*-5-(2-Bromoethyl)-2-norbornene (8) with $Me_3SnNa$ (1)[a]

| entry | additive,[b] molar equiv | solv (ratio) | yield of product,[b] %  |  10 |  11 |
|---|---|---|---|---|---|
| 1 | none | THF | 99.0 | 0.8 | 1.0 |
| 2 | DCPH, 10 | THF | 86.0 | 9.6 | 3.2 |
| 3 | TBA, 10 | THF | 99.0 | 0 | <1 |
| 4 | none | THF-$Et_2O$ (1:1) | 98.0 | 0 | 4.0 |
| 5 | DCPH, 10 | THF-$Et_2O$ (1:1) | 63.0 | 31.2 | 10.2 |
| 6 | TBA, 10 | THF-$Et_2O$ (1:1) | 98.0 | 0 | 3.2 |
| 7 | none | THF-pentane (1:1) | 95.0 | 0 | 1.0 |
| 8 | DCPH, 10 | THF-pentane (1:1) | 61.0 | 20.0 | 19.0 |
| 9 | TBA, 10 | THF-pentane (1:1) | 96.0 | 0 | 4.7 |

[a] Reactions were conducted by using 0.05 M concentration of bromide and 0.10 M concentration of $Me_3SnNa$ at 0 °C for 15 min. [b] Based on bromide.

product is greater than it is in the case of *n*-dodecane. If only cation complexation is important, then THF–$Et_2O$ should have produced less cyclization product than THF–dodecane; however, it produced more (12.6% vs. 6.7%). On the other hand, if viscosity is also important, then THF–dodecane would be expected to produce less cyclization product since THF–dodecane is more viscous than THF–$Et_2O$. Additionally, THF–pentane gave approximately the same results as THF–$Et_2O$. Since both THF–pentane and THF–$Et_2O$ have approximately the same viscosity, this result is not surprising if viscosity is important. Once again THF–$Et_2O$ is a better cation coordinating solvent than THF–pentane so that if only cation coordination is important, THF–$Et_2O$ should have produced significantly less cyclized substitution product than THF–pentane; and it did not.

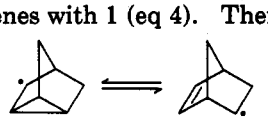
Next, we examined the reaction of $Me_3SnNa$ with a new radical probe, *endo*-5-(2-bromoethyl)-2-norbornene[15] (8) and the results are presented in Table V. We have found that this probe cyclizes approximately 100 times faster than 6-bromo-1-hexene. In general, these results are in good agreement with the previous study which indicates that primary alkyl bromides react with $Me_3SnNa$ by an ET pathway to a significant degree except that significantly higher percentages of radical products are detected using this probe (experiments 5 and 8). A unique aspect of the data reported in Table V is that in no case is there any cyclized substitution product formed. This can be explained on the basis that alkyl radicals diffuse from the solvent cage to form the more stable secondary-alkyl radical which should react with trimethyltin anion (or radical) more slowly than a primary alkyl radical because of increased steric hindrance; hence, more hydrocarbon is produced. This is more easily rationalized if there is an equilibrium between the two radicals I and II (eq 3). This



(3)

I II

is not unexpected since Kuivilla[9] has reported an equilibrium involving the intermediate radicals III and IV found in the reactions of the 5-halo-2-norbornenes and 3-halonortricyclenes with 1 (eq 4). Therefore, the yield



(4)

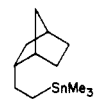
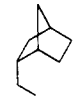
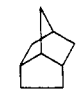
III IV

of cyclized and straight chain hydrocarbon products 10 and 11 should be increased on addition of DCPH. Furthermore, the yield of uncyclized hydrocarbon 10 is decreased from 31% to 20% and cyclized hydrocarbon 11 is increased from 10% to 19% by changing the solvent from THF–$Et_2O$ to THF–pentane (entries 5 and 8). These results suggest that the cyclization of radicals takes place outside the solvent cage and that the straight chain radicals have more chance to be trapped in THF–$Et_2O$ compared to THF–pentane because $Et_2O$ is a better hydrogen atom donor than pentane.

**Studies with a Primary Alkyl Iodide.** In earlier work[11] Kuivilla showed that primary alkyl iodides react with $Me_3SnNa$ by both $S_N2$ (65%) and HME (32%) pathways but found no evidence for ET. Now, we have examined the reaction of the new probe *endo*-5-(2-iodoethyl)-2-norbornene (9) with $Me_3SnNa$, and the results are given in Table VI. With this iodide both 10 (7.3%) and 11 (2.6%) were formed in the absence of a trap (entry 1). The yield of substitution product decreased (from 90.5% to 60.0%) in the presence of 10 molar equiv DCPH with an increase in 10 (from 7.3% to 14.1%) and 11 (from 2.6% to 25.3%) (entry 3). The presence of 10 TBA caused an increase in the yield of 10 to 22.3% (entry 5). The combined traps show that the yields of both 10 and 11 are increased to 33.0% and to 19.0%, respectively (entry 6). Since TBA is known to trap carbanions efficiently,[11] these results indicate that at least 22% of the reaction proceeds via a carbanion intermediate, and since 10 DCPH + 10 TBA produced 52% hydrocarbon, it is clear that at least half of the hydrocarbon produced had a radical precursor. When the reaction of $Me_3SnNa$ with 9 was carried out in the presence of 2 (*p*-dinitrobenzene) and 3 (di-*tert*-butylnitroxyl radical) separately, the rate of reaction was affected by these scavengers. Expectantly, these results suggest that three basic mechanistic pathways ($S_N2$, HME, and ET) are involved in the reaction of $Me_3SnNa$ with 9 (Scheme III).

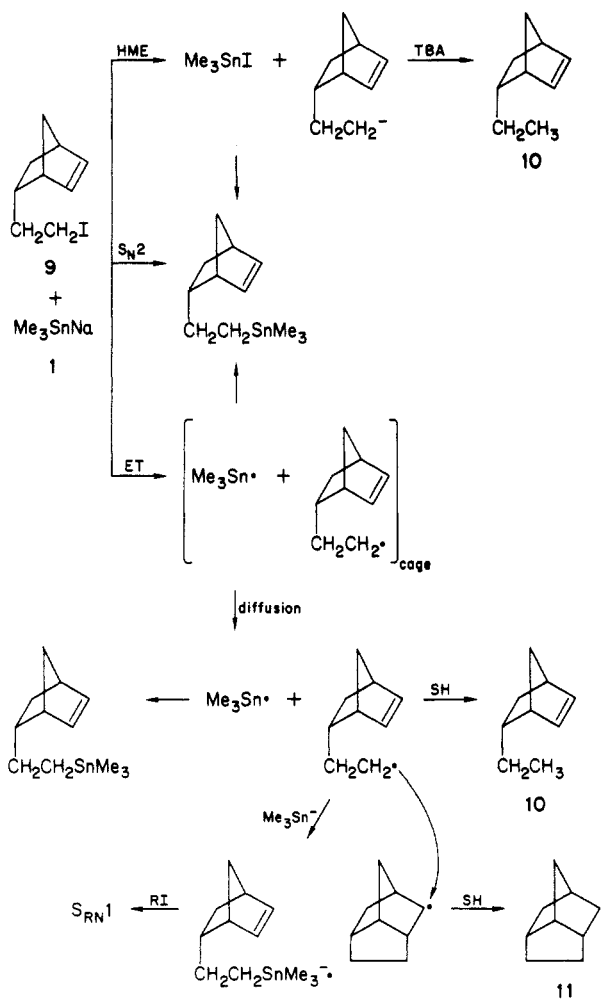
Unexpectantly, no 11 is formed in the presence of TBA (entry 5). It is possible that TBA is a better cation complexing agent than THF and the $S_N2$ process becomes more favorable. This view is based on the fact that 2.6% of 11 was found in pure THF (entry 1), some of which should have a radical precursor, yet none of 11 was found when 10 molar equiv of TBA was used. If that much TBA changed the course of the reaction to be more $S_N2$-like because of increased cation complexing by TBA, then the above result is easily understood. Furthermore, the earlier data involving the bromide show that when the reaction proceeds via an ET pathway, two hydrocarbon products

Table VI. Reaction of *endo*-5-(2-Iodoethyl)-2-norbornene (9) with $Me_3SnNa$ (1)[a]

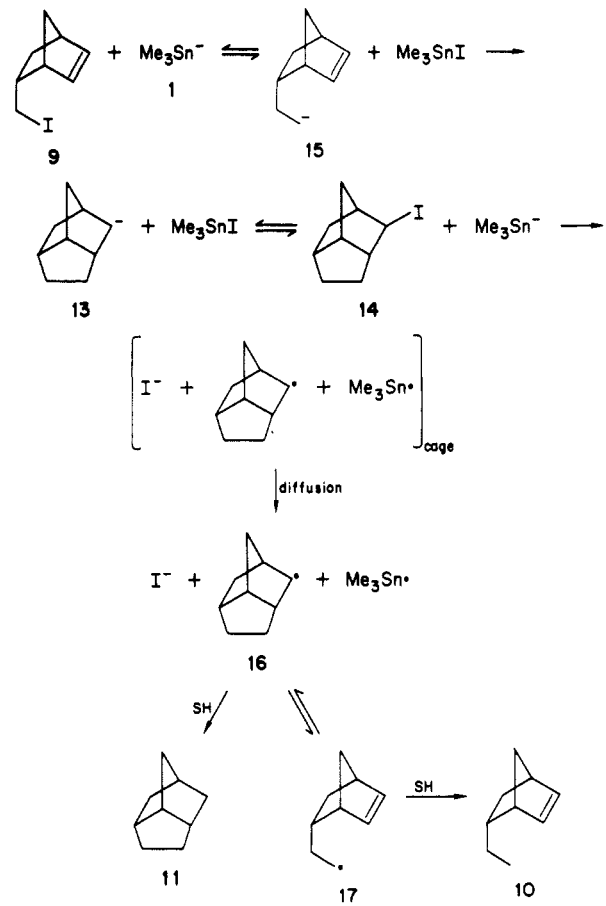
| entry | additive,[b] molar equiv | temp, °C | yield of product,[b] % | | |
|---|---|---|---|---|---|
| | | |  |  |  |
| | | | SnMe3 | 10 | 11 |
| 1 | none | 0 | 90.5 | 7.3 | 2.6 |
| 2 | DCPH, 1 | 0 | 51.5 | 20.1 | 30.0 |
| 3 | DCPH, 10 | 0 | 60.0 | 14.1 | 25.3 |
| 4 | TBA, 1 | 0 | 75.3 | 15.0 | 5.2 |
| 5 | TBA, 10 | 0 | 75.0 | 22.3 | 0 |
| 6 | DCPH, 10; TBA, 10 | 0 | 48.6 | 33.0 | 19.0 |
| 7 | none | −23 | 96.0 | 3.0 | 3.5 |
| 8 | DCPH, 10 | −23 | 80.0 | 7.4 | 14.2 |
| 9 | TBA, 10 | −23 | 95.0 | 3.0 | 0.5 |
| 10 | none | −78 | 97.0 | 0 | 0 |
| 11 | DCPH, 10 | −78 | 90.0 | 2.7 | 2.0 |
| 12 | TBA, 10 | −78 | 96.0 | trace | trace |

[a] Reactions were conducted by using 0.05 M concentration of iodide and 0.1 M concentration of $Me_3SnNa$ in THF for 15 min. [b] Based on iodide.

**Scheme III**




**Scheme IV**




are formed in a ratio of 3:1 (10:11) in THF in the presence of DCPH (entry 2, Table V). This ratio is different from the ratios observed with the iodide (entries 3 and 6, Table VI). It seems therefore that there must be another pathway in addition to the pathways shown in Scheme III that would be particularly open to reactions with iodide that would result in a higher ratio of cyclized to uncyclized hydrocarbon. It turns out that the carbanion **15** can cyclize to **13** and then a second HME process can occur followed by ET between the new secondary iodide **14** and **1** (Scheme IV). Therefore, DCPH is able to trap the intermediate radical **16** that is produced not only from radical but also from carbanion **13**, and thus the higher ratio of cyclized to uncyclized hydrocarbons for iodides vs. bromides is explained. Of course, part of the hydrocarbon products come from carbanion trapped by DCPH. In the presence of DCPH and TBA (entry 6) the amount of cyclized hydrocarbon is greater than expected since no cyclized hydrocarbon was produced in the presence of 10 TBA alone (entry 5). Possibly DCPH has made TBA a weaker proton donor through hydrogen bonding and therefore a poorer carbanion trap. The fact that TBA addition to the brom-

ide (entry 3, Table V) resulted in less than 1% hydrocarbon formation indicates that HME is not very important in the case of the bromides; however, in the case of the iodide, 22% of the uncyclized hydrocarbon was formed (entry 5) indicating that HME is much more important in the mechanistic pathway describing the iodide reaction than the bromide reaction.

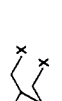
In addition, when a smaller amount of radical trap DCPH was used (entry 2) in the reaction of $Me_3SnNa$ with **9**, more hydrocarbons **10** and **11** were formed than when more DCPH was used (entry 3). Again, this result indicates that radical escape from the solvent cage in the less viscous solvent (THF + 1 molar equiv of DCPH) is easier compared to the more viscous solvent (THF + 10 molar equiv of DCPH). Moreover, when the reactions were carried out at lower temperatures (−23 and −78 °C), the yield of substitution product was increased dramatically. Lowering the reaction temperature should increase the viscosity of the solvent and hence the amount of uncyclized substitution product (entries 7–12). As suggested earlier, these results can also be due to a change in $\Delta(\Delta G^{\ddagger})$ for the three reaction pathways ($S_N2$, HME, and ET) in Scheme III. Especially, the HME pathway becomes less favorable at lower temperature as evidenced by the small amount of **10** and **11** formed by carbanion trapping (entries 9 and 12).

**Studies with Dihaloalkane.** Next, we examined the reaction of **1** with the *exo,cis*-1,2-bis(halomethyl)bicyclo-[2.2.1]heptanes (**18** and **19**), and the results are shown in Table VII. Entry 1 shows that the reaction of *1* with dibromide **18** produces a substantial amount of disubstituted product **23** (69.5%), monosubstituted hydrocarbon **22** (7.5%), and cyclized hydrocarbon **21** (19.7%) in the absence of any additive. It is clear that both **21** and **22** can be formed by both ET and HME, and thus $S_N2$ can be completely excluded as a pathway for **21** and for the hydrocarbon portion of **22**. The method of evaluation used earlier to distinguish ET from HME, i.e., DCPH trap for radicals and carbanions and TBA trap just for carbanions, was used in this study as well. When DCPH was added (entry 2), the amount of disubstituted product **23** was substantially decreased from 69.5% to 36.7% and the amount of **22** increased from 7.5% to 31%. In order to determine the involvement of a carbanion intermediate, TBA was used resulting in an increase in the amount of **22** formed (7.5–20.2%) and a decrease in the amount of **21** and **23**. Entry 4 shows that **24** is an intermediate in this reaction and the precursor to **22**. These results clearly indicate that both ET and HME are involved in this reaction to a similar extent and the reaction pathways are represented by Scheme V.

When the reaction of **1** with **19** (the corresponding iodide) was studied, substantially different results were obtained. The major product was the cyclized hydrocarbon **21** which can be formed by both ET and HME pathways (Scheme V). Entry 6 shows that DCPH is an effective trap by decreasing the amount of **21** formed from 89.8 to 76.4% and increasing the amount of **20** formed from <1 to 6.3%. Since TBA addition (entry 7) shows no trapping, one can assume that the DCPH result is due to trapping just the radical; therefore, ET represents at least part of what is happening in this reaction.

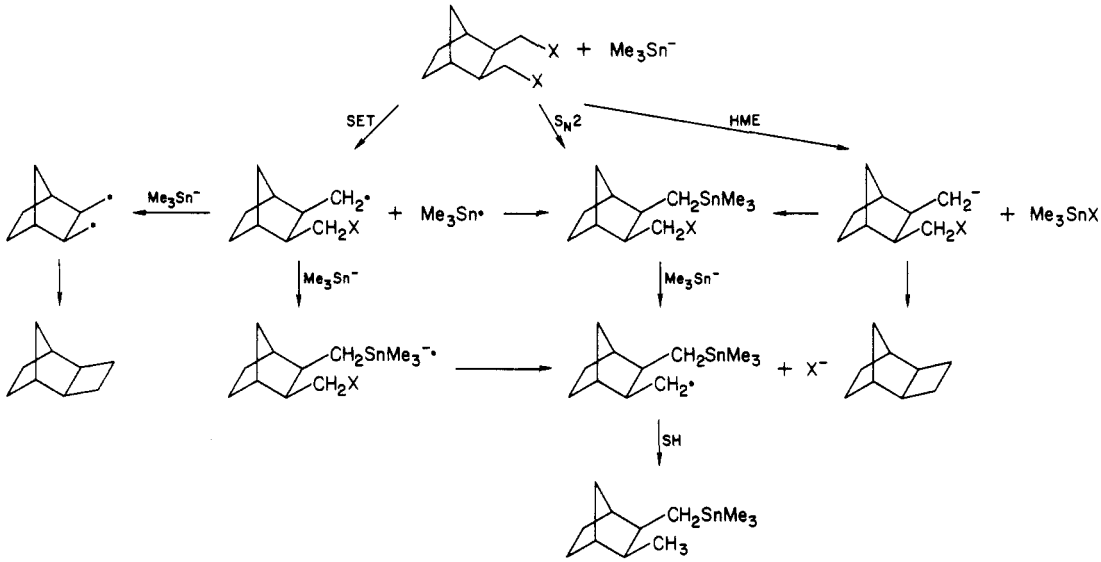
Since it is not possible to form the major product **21** by an $S_N2$ process, this leaves only HME as another possible reaction pathway. Since TBA was effective in trapping the carbanion precursor to **21** in the reaction with the bromide (entry 3), this does not mean that it would be effective in trapping the carbanion precursor to **21** pro-

**Table VII. Reaction of *exo,cis*-1,2-Bis(halomethyl)bicyclo[2.2.1]heptane (18 and 19) with $Me_3SnNa$ (1) in THF[a]**

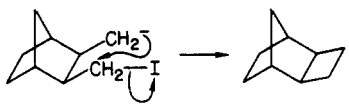
| entry | X | temp, °C | additive,[b] molar equiv |  20 |  21 |  22 |  23 |  24 |  |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Br (18) | 0 | none | <1 | 19.7 | 7.5 | 69.5 | 0 | 0 |
| 2 | Br | 0 | DCPH, 4 | 2.0 | 15.9 | 31.0 | 36.7 | 0 | 0 |
| 3 | Br | 0 | TBA, 10 | <1 | 8.9 | 20.2 | 59.2 | 0 | 0 |
| 4 | Br | −78 | none | 0 | 3.4 | 0 | 28.6 | 30 | 30 |
| 5 | I (19) | 0 | 0 | <1 | 89.8 | <1 | 1.0 | 0 | 0 |
| 6 | I | 0 | DCPH, 4 | 7.3 | 76.4 | 2.0 | <1 | 0 | 0 |
| 7 | I | 0 | TBA, 10 | 1.5 | 90.6 | <1 | <1 | 0 | 0 |
| 8 | I | −78 | none | 0 | 85.0 | <1 | 3.2 | 0 | 0 |

[a] Reactions were conducted by using 0.05 M concentrations of halide and 0.15 M concentrations of $Me_3SnNa$ for 30 min. [b] Based on halide.

**Scheme V**




duced from the iodide. This is so because iodide is a much better leaving group than bromide, and it is reasonable that the rate of intramolecular attack of the carbanion at the backside of the $CH_2$–I group is considerably faster than bimolecular abstraction of proton from TBA by the intermediate carbanion, and therefore in the former case TBA has less chance of trapping the carbanion intermediate (eq 5).




(5)

## Conclusions

The reaction of a series of primary alkyl bromides with $Me_3SnNa$ was examined. The results are inconsistent with previous reports[10,11] that radicals are not involved. By lowering the viscosity of the solvent, by lowering the cation coordinating ability of the solvent, or by running the reactions in the presence of a radical trap, it has been established that radical intermediates are involved in this type of reaction at least for the systems studied. Furthermore, the reaction of a primary alkyl iodide containing a cyclizable radical probe with $Me_3SnNa$ was also examined, and it was found that this reaction does not react exclusively via $S_N2$ and HME pathways as previously reported but also reacts via an ET pathway to a significant extent.

## Experimental Section

**General Procedures and Materials.** Solvent grade pentane was stirred over concentrated $H_2SO_4$, washed with water, dried over $MgSO_4$, and distilled from $NaAlH_4$ under nitrogen. Reagent grade diethyl ether (Fisher) and reagent grade THF were distilled under nitrogen from deep purple solutions of sodium benzophenone ketyl.

Samples of dicyclohexylphosphine (DCPH, bp 68–70 °C (0.05 mm Hg)), 1-bromobutane (bp 101–103 °C, $CaH_2$), 1-bromo-2-methylpropane (bp 90–92 °C, $CaH_2$), 2-ethylhexyl bromide (bp 75–77 °C (16 mmHg), $CaH_2$), and methyl acrylate were purchased from Aldrich and purified by distillation. Reagent grade acetone (Fisher), pyridine (Fisher), tosyl chloride (Aldrich), paraformaldehyde (Aldrich), dicyclopentadiene (Aldrich), 5-hexen-1-ol (Aldrich), lithium bromide (Aldrich), and sodium iodide (Fisher) were used as received. Resublimed magnesium chips, anhydrous metal salts, sodium dispersion, di-*tert*-butylnitroxyl radical, and hexamethylditin (bp 73–74 °C at 16 mmHg) were purchased from Alfa.

Gas chromatographic analyses were conducted on a Varian 3700 (FID) instrument coupled to a Varian CDS III electronic integrator using a DB-1 capillary column. Quantitative GLC analyses were obtained with the use of response factors, corrected peak areas, and using internal standards. Proton NMR spectra were recorded on a Varian T60 spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. Mass spectra were obtained by using a Varian MAT 1125 instrument, and carbon–hydrogen microanalyses were conducted by Atlanta Microlabs, Inc., of Atlanta, GA. Viscosities were determined by using an Ostwald viscosimeter.

**Preparation of (Trimethylstannyl)sodium (1).** Following the literature procedure,[11] 1 was prepared via the reaction of hexamethylditin with sodium dispersion at 0 °C in THF and analyzed by the reaction of an aliquot with *n*-BuBr, followed by the GLC analysis for *n*-$BuSnMe_3$.

**Preparation of 6-Bromo-1-hexene (7).** The 6-tosyl-1-hexene prepared from the corresponding alcohol (pyridine, TsCl, 0 °C) was converted to the corresponding bromide (acetone, LiBr (fivefold excess), reflux, 4 h) in 82% yield; bp 73–75 °C (73 mmHg).

**Preparation of *endo*-5-(2-Haloethyl)-2-norbornene (9 and 10).** By use of published procedure,[15] **9** and **10** were obtained. For X = Br: bp 71–73 °C (2.5 mmHg); $^1H$ NMR $\delta$ 0.5–0.6 (1 H, m), 2.6–2.8 (2 H, m), 3.4 (2 H, t, $J$ = 7 Hz), 5.8–6.2 (2 H, m). For X = I: bp 83–84 °C (2.5 mmHg); $^1H$ NMR $\delta$ 0.5–0.6 (1 H, m), 1.0–2.2 (5 H, m), 2.6–2.8 (2 H, m), 3.2 (2 H, t, $J$ = 7 Hz), 5.8–6.2 (2 H, m).

**Preparation of *exo,cis*-1,2-Bis(halomethyl)bicyclo[2.2.1]heptane (18 and 19).** By use of a published procedure,[16] **18** and **19** were obtained. For X = Br: mp 44.5–45 °C (recrystallized from MeOH); $^1H$ NMR $\delta$ 1.08–1.13 (1 H, m), 1.26–1.31 (2 H, m), 1.40–1.44 (1 H, m), 1.57–1.61 (2 H, m), 2.15–2.19 (2 H, m), 2.41–2.42 (2 H, m), 3.16–3.23 (2 H, m), 3.53–3.58 (2 H, m). For X = I: mp 80–80.5 °C (recrystallized from MeOH; lit.[16] mp 80 °C); $^1H$ NMR $\delta$ 1.05–1.10 (1 H, m), 1.23–1.31 (2 H, m), 1.38–1.44 (1 H, m), 1.55–1.63 (2 H, m), 2.11–2.21 (2 H, m), 2.47–2.49 (2 H, m), 2.93–3.02 (2 H, m), 3.37–3.44 (2 H, m).

**General Procedure for Reactions of Primary Alkyl Halides with $Me_3SnNa$ (1). Reaction of $Me_3SnNa$ with *n*-BuBr in the Presence of *p*-Dinitrobenzene (2).** To 0.5 mL of a 0.42 M solution of bromide containing 9.7 mg (0.058 mmol) of **2** in THF under $N_2$ was added 1.2 mL of a 0.35 M solution of **1** in THF at 0 °C. After a certain time period, with stirring, the reaction mixture was quenched with water and analyzed by GLC.

**Reaction of $Me_3SnNa$ (1) with 6-Bromo-1-hexene (7) in the Presence of TBA–Solvent (THF–$Et_2O$ (1:1)).** To a solution of the bromide (0.28 mmol) and TBA (2.8 mmol) in 2.6 mL of

(15) Ashby, E. C.; Pham, T. N., *Tetrahedron Lett.* **1984**, *25*, 4333.
(16) Alder, K.; Monch, J.; Wirtz, H. *Liebig Ann. Chem.* **1959**, *627*, 47.

mixed solvent (0.5 mL of dry THF and 2.1 mL of dry ether) under $N_2$ was added 1.6 mL of a 0.35 M solution of 1 in THF at 0 °C. After a certain time period, with stirring, the reaction mixture was quenched with water and analyzed by GLC. Both uncyclized and cyclized substitution products were confirmed by GC–MS and NMR spectrometry.

**Reaction of $Me_3SnNa$ (1) with *endo*-5-(2-Bromoethyl)-2-norbornene (8) in the Presence of DCPH–Solvent (THF–Pentane (1:1)).** To a solution of the bromide (0.05 mmol) and DCPH (0.05 mmol) in 0.71 mL of mixed solvent (0.21 mL of dry THF and 0.50 mL of dry pentane) under $N_2$ was added 0.29 mL of a 0.35 M solution of 1 in THF at 0 °C. After 15 min, with stirring, the reaction mixture was quenched with water and analyzed by GLC. All products were confirmed by GC–MS and NMR spectroscopies. *endo*-5-(2-(Trimethylstannyl)ethyl)-2-norbornene: $^1$H NMR $\delta$ 0.05 (9 H, s, $J$(SnCH) = 48 Hz), 0.44–1.50 (7 H, m), 1.66–2.04 (2 H, m), 2.64–2.89 (2 H, m), 5.8–6.2 (2 H, m). Anal. Calcd: C, 50.56; H, 7.79. Found: C, 50.68; H, 7.80. *endo*-5-Ethyl-2-norbornene (10): $^1$H NMR $\delta$ 0.5–0.6 (1 H, m), 0.8–0.9 (3 H, d, $J$ = 4 Hz), 1.0–1.4 (4 H, m), 1.65–1.9 (2 H, m), 2.6–2.8 (2 H, m), 5.8–6.2 (2 H, m). Tricyclo[4.2.1.0$^{3,7}$]nonane (11): $^1$H NMR $\delta$ 0.70 (1 H, m), 0.87 (1 H, m), 1.15–1.9 (12 H, m); mp 99–100 °C (lit.[17] mp 98–99 °C).

**Control Experiments: Reaction of TBA and DCPH with Halides.** In a typical experiment, 1.5 mmol of an additive under $N_2$ was added to 0.15 mmol of halide in 0.5 mL of dry THF at 0 °C. After 1 h the solution was analyzed by GLC.

**Acknowledgment.** We are indebted to the National Science Foundation Grant No. CHE 8403024 for support of this work.

**Registry No.** 1, 16643-09-7; 4, 109-65-9; 6, 18908-66-2; 7, 2695-47-8; 8, 94417-50-2; 9, 94417-49-9; 10, 32166-37-3; 11, 1521-75-1; 18, 97232-56-9; 19, 85807-80-3; 5-hexen-1-ol, 821-41-0; *endo*-5-(2-trimethylstannylethyl)-2-norbornene, 97150-43-1.

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# $^{119}$Sn NMR Spectroscopic Study on Tetraorganodistannoxanes

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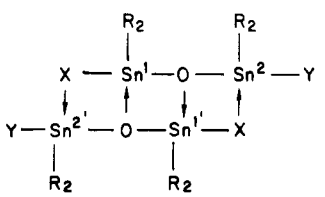
*Received February 12, 1985*

$^{119}$Sn NMR spectra of various tetraorganodistannoxanes were investigated. The two tin atoms in these compounds were successfully differentiated as expected from the dimeric formulation. The most probable assignments for these signals were provided. Tin–tin coupling was detected for the first time, and there was observed a marked difference between halogen- and oxygen-bridged distannoxanes. Observation of one kind of coupling in the former compounds can be interpreted in terms of an anionic chloride bridge, while a covalently bonded oxygen bridge is suggested on the basis of the appearance of additional coupling in the latter compounds.

## Introduction

In contrast to corresponding organosilicon analogues, a unique feature of diorganotin dihalides is the stability of partial hydrolysis products, 1,3-dihalotetraorganodistannoxanes, that can be converted, on further partial hydrolysis, to 3-halo-1-hydroxytetraorganodistannoxanes (eq 1). Due to their structural and chemical characteristics, these compounds have been studied extensively for a long time[1] and are still receiving attention.[2] It is now apparent that their facile formation and stability may be ascribed to the ladder structure

$$R_2SnCl_2 \xrightarrow{OH^-} {}^1/_2ClR_2SnOSnR_2Cl \xrightarrow{OH^-} {}^1/_2ClR_2SnOSnR_2OH \quad (1)$$




that was proposed first by Okawara et al.[3] and confirmed later by various X-ray analyses.[2,4] Contrary to these solid-state studies, solution work has been rather limited. Obviously, the structural elucidation in solution is of importance for an understanding of the chemical properties of distannoxanes such as their unusual catalytic activity for urethane formation.[5] Molecular weight measurements indicate that the dimeric formulation also is retained in solution for most distannoxanes[6] and IR spectra of isothiocyanate derivatives (X, Y = NCS) in solution show the existence of a bridging isothiocyanate group.[7] However, none of these studies can afford satisfactory information on structural properties in solution. Presumably, $^{119}$Sn NMR spectroscopy is the most promising approach to this end. Indeed, two tin resonances have been detected for

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(2) For the most recent study on this subject: Vollano, J. F.; Day, R. O.; Holmes, R. R. *Organometallics* **1984**, *3*, 745.
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(7) Wada, M.; Okawara, R. *J. Organomet. Chem.* **1967**, *8*, 261.

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