Electron Transfer in the Reactions of Alkyl Halides with Sodium Trimethyltin

E. C. Ashby,* R. N. DePriest, and Wei-Yang Su

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received April 11, 1984

The reaction of sodium trimethyltin with alkyl halides has been studied in detail by using radical probes, stereochemical probes, and radical traps. 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 alkali-metal triorganotin compounds.[1] These proposals were based on a variety of stereochemical studies[2-4] and on a variety of experiments in which intermediates were trapped.[5,6] The three basic mechanistic pathways that have been described are as follows (Scheme I): (a) a classic S_N2 substitution of an alkyl halide with a trialkylstannyl anion as the nucleophile; (b) substitution by an electron-transfer (ET) process; (c) substitution by halogen–metal exchange (HME). Experimental support for the S_N2 process has been obtained from stereochemical studies, in which inversion of configuration at carbon occurred in the reaction of Ph_3SnNa with optically active 2-butyl bromide and chloride.[2] Other stereochemically defined alkyl halides, such as 4-*tert*-butylcyclohexyl bromide, were found to undergo substitution by Me_3SnNa in a nonstereospecific manner, which supports the existence of a radical intermediate in the electron-transfer (ET) pathway.[5-7] Additional evidence for radical intermediates has been obtained from CIDNP studies.[8] The halogen–metal exchange process was demonstrated in the reaction of Me_3SnNa with aryl halides by the isolation of ArD when 2-propanol-*d* was present in the reaction mixture.[6]

Recently, Kuivila has delineated the extent of reaction by ET, HME, and S_N2 pathways for a variety of organic halides in reactions with alkali-metal triorganotin compounds.[9,10] The involvement of the ET pathway was demonstrated by the occurrence of a hydrocarbon (RH) derived from RX when the reaction was conducted in the presence of the radical trap dicyclohexylphosphine (DCPH). DCPH has a low P–H bond dissociation energy and, hence, can trap alkyl radicals via hydrogen atom transfer (eq 1). The extent of the S_N2 pathway was evaluated by

$$R_3Sn^- + R'X \longrightarrow R_3Sn\cdot + R'X^{-}\cdot \longrightarrow R_3Sn\cdot + R'\cdot + X^- \xrightarrow{DCPH} \begin{cases} R'H \\ R_3SnR' \end{cases} \quad (1)$$

the inability of DCPH to induce the formation of RH

Scheme I

(a) S_N2 Pathway

$$R_3Sn^- + R'X \longrightarrow \left[R_3Sn^{\delta-}\cdots R'\cdots X^{\delta-}\right] \longrightarrow R_3SnR' + X^-$$

(b) ET Pathway

$$R_3Sn^- + R'X \longrightarrow R_3Sn\cdot + R'\cdot + X^- \longrightarrow R_3SnR' + X^-$$

(c) HME Pathway

$$R_3Sn^- + ArX \longrightarrow Ar^- + R_3SnX \longrightarrow ArSnR_3 + X^-$$

products in a particular system. The occurrence of a HME pathway was determined by the use of *t*-BuOH or *t*-$BuNH_2$(TBA) as a trap that protonates anionic intermediates (eq 2).[6-9] Thus, in general, Kuivila found that

$$R_3SnNa + R'X \longrightarrow R'Na + R_3SnX \xrightarrow{t\text{-BuOH or TBA}} \begin{cases} R'H \\ RSnR_3 \end{cases} \quad (2)$$

reactions of alkali-metal triorganotin compounds with unhindered primary halides proceed exclusively by an S_N2 pathway. With very sterically hindered primary bromides (neopentyl bromide) significant reaction by an ET pathway (32%) was found in reactions involving Me_3SnNa. Secondary alkyl halides were found to react with R_3SnM compounds with varying amounts of S_N2 and ET contributions depending on the structure of the alkyl group and the particular alkali-metal triorganotin compound. Aryl halides were found to react with R_3SnM by a predominant HME pathway, and all three pathways HME, ET, and S_N2 were found to be operative for secondary alkyl iodides to varying extents.

It is interesting to note that Kuivila found that 2-bromooctane reacted with Me_3SnNa by an ET pathway to the extent of 72%.[9] However, San Filippo recently reported that the reaction of Me_3SnNa with (−)-2-bromooctane proceeded (depending on exact conditions) with predominant (90%) inversion of configuration.[11] Thus, the lack of extensive racemization during the substitution reaction studied by San Filippo led him to state that "the additives that were employed as trapping agents must be introducing a substantial perturbation on the mechanism"[11] 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. In an attempt to clarify this apparent anomaly, it was decided to investigate the reactions of Me_3SnNa (1) with alkyl halides containing a cyclizable radical probe of the 5-hexenyl type. Thus, in principle the occurrence of ET in these reactions can be confirmed by the isolation of a tetraalkyltin product containing a cyclized alkyl group.

(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.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.
(8) Lyding, J. M. Ph.D. Dissertation, University of California, Berkeley, 1977.
(9) Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833.
(10) Kuivila, H. G.; Smith, G. F. *J. Org. Chem.* **1980**, *45*, 2918.
(11) San Filippo, J., Jr.; Silbermann, J. *J. Am. Chem. Soc.* **1981**, *103*, 5588.

0276-7333/84/2303-1718$01.50/0

Table I. Reaction of 6-Halo-1-heptenes with Sodium Trimethyltin (1) in THF[a]

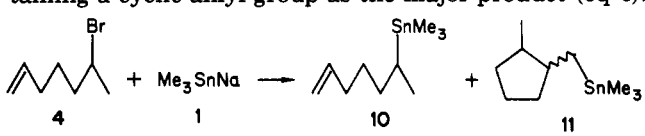
				product yield,[b] %			
entry	X in (probe)	order of additn	additive, molar equiv	10	11 (cis/trans)	12	13 (cis/trans)
1	OTs (2)	inverse	none	96.0	0.0	0.0	0.0
2	OTs	inverse	10 DCPH	89.0	0.0	0.0	0.0
3	Cl (3)	inverse	none	78.2	12.2 (4.35)	0.5	trace
4	Cl	inverse	10 DCPH	78.7	2.2 (4.40)	10.0	1.6
5	Cl	inverse	10 TBA	79.9	8.7 (4.27)	0.4	trace
6	Br (4)	inverse	none	6.1	80.7 (3.93)	2.4	2.3
7	Br	inverse	10 DCPH	2.6	14.2 (4.16)	50.2	15.8 (4.76)
8	Br	inverse	10 TBA	3.6	74.5 (4.00)	3.0	3
9	Br	inverse	10 	18.3	64.6 (4.18)	1.9	1.9
10	Br	normal	none	13.0	69.0 (4.37)	2.0	1.0
11	I (5)	inverse	none	9.5	69.2 (4.00)	8.2	8.6 (4.16)
12	I	inverse	10 DCPH	3.8	16.0 (4.12)	44.9	21.3 (4.70)
13	I	inverse	10 TBA	7.2	62.0 (4.10)	6.7	10 (4.78)
14	I	inverse	10 	18.0	52.2 (4.15)	6.2	6.4 (4.26)

[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 iodides. Equimolar amounts of reactants at 0.2 M concentration were used. [b] Absolute yields.

Previous studies involving a cyclizable alkyl halide radical probe employed 6-bromo-1-hexene with the result that only straight-chain tetraalkyltin product was formed (eq 3). This result can be attributed to the occurrence

(3)

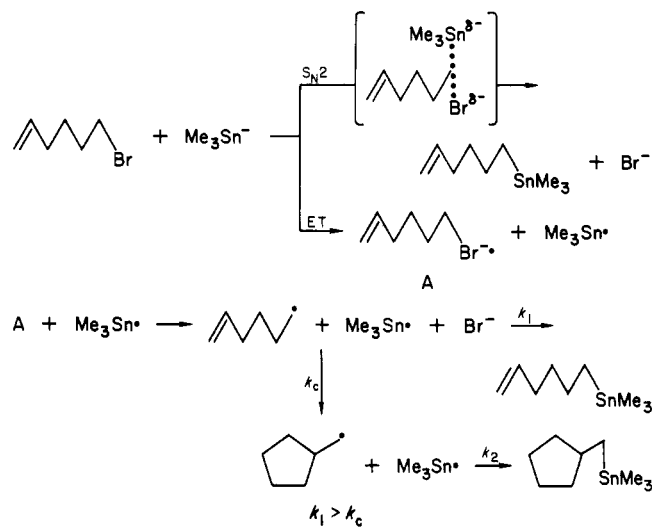
of an S_N2 process or else if ET is involved, the radical intermediate collapses to product at a rate faster than that of cyclization of the 5-hexenyl radical probe ($k_c = 10^5$),[13] as in Scheme II. However, the use of the secondary alkyl halide probes, the 6-halo-1-heptenes [X = OTs, (2), Cl (3), Br (4), I (5)] is more interesting, since these probes should have very similar steric requirements compared to the (−)-2-bromooctane studied by San Filippo and the (±)-2-bromooctane studied by Kuivila. Thus, it has been reported previously in communications from Kitching[14] and our own group[15] that the reaction of alkali-metal trimethyltin with 4 yields a tetraalkyltin compound containing a cyclic alkyl group as the major product (eq 4).



(4)

Initially, the observation of such cyclic substitution products was attributed to the occurrence of an ET process. However, it is remarkable that the extent of cyclization as depicted in eq 4 was found to be much greater than the extent of racemization in the substitution reaction of (+)-2-bromooctane with 1, under identical experimental conditions.[15] Thus, we proposed that secondary alkyl bromides, such as 4 and (+)-2-bromooctane, can react with 1 by an ET process with some type of geminate radicals as intermediates. We noted at that time that according to information in the literature, cyclization of the 6-heptenyl radical ($k_c = 10^5$) should not be competitive with coupling of radicals in a geminate process ($k \simeq 10^{10}$), a

Scheme II



point which San Filippo has elaborated upon.[16] Nevertheless, the facts are that cyclization does occur with the heptenyl probe under conditions where the 2-octyl probe indicates predominant inversion of configuration.

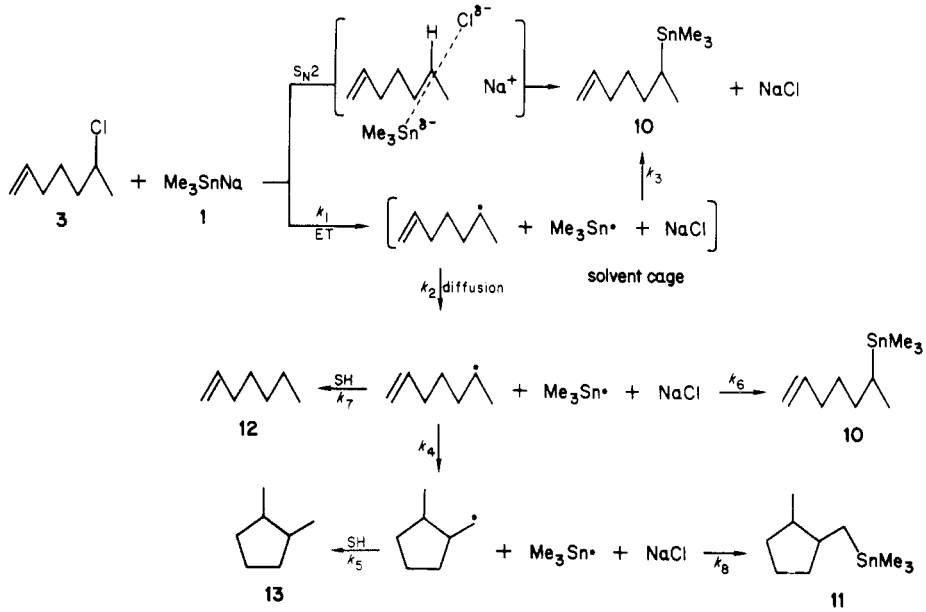
We now present full details of our studies of the reaction of alkyl halides with Me_3SnNa. Detailed studies of the reactions of the optically active 2-halooctane [X = OTs, (6), Cl (7), Br (8), I (9)] with Me_3SnNa are also presented at this time. Finally, a series of studies are presented to further elucidate the role of DCPH as a trapping agent in the reaction of alkyl halides with 1.

Results and Discussion

Studies with Cyclizable Probes. The results of experiments involving the reactions of the 6-halo-1-heptene probes with 1 are given in Table I.[17] Note that a full range of typical leaving groups (OTs, Cl, Br, I) for this reaction was examined. Since the tetraalkyltin compounds containing the cyclized moiety derived from the alkyl halide probes are most reasonably attributed to the cyclization

(12) Newcomb, M.; Courtney, A. R. *J. Org. Chem.* **1980**, *45*, 1707.
(13) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.
(14) Kitching, W.; Olszowy, H.; Harvey, K. *J. Org. Chem.* **1982**, *47*, 1893.
(15) Ashby, E. C.; DePriest, R. *J. Am. Chem. Soc.* **1982**, *104*, 6144.
(16) San Filippo, J., Jr.; Lee, K. *Organometallics* **1983**, *2*, 906.
(17) Reported previously in communication[16] have been corrected.

Scheme III



of intermediate radicals, the percentage of cyclized tetraalkyltin compound **11** can be assumed to indicate the minimum extent of reaction proceeding with radical character along the reaction pathway to product. This is particularly true when carbanion traps, such as *tert*-butylamine, show the absence of carbanion intermediates. In addition, both straight-chain **12** and cyclized hydrocarbon **13** are considered to have radical precursors and are formed by hydrogen atom abstraction from the THF solvent by the radical. Also, the ability of DCPH to divert the intermediate radical to hydrocarbon product at the expense of the tetraalkyltin product was examined.

Entries 1 and 2 of Table I demonstrate that the reaction of **1** with **2** gives the straight-chain product 1-hepten-6-yltrimethyltin (**10**) in essentially quantitative yield even in the presence of 10 equiv of DCPH. The fact that no cyclized substitution product is formed and the fact that DCPH does not cause the formation of hydrocarbon, together with the stereochemical studies discussed below, suggest that the secondary tosylate reacts with Me_3SnNa by a simple S_N2 process, devoid of any radical intermediates, and that DCPH is not inducing ET in this reaction.

Entries 3, 4, and 5 of Table I show that the reaction of **1** with **3** produces a substantial amount of cyclized substitution product **11** (12.2%) in the absence of DCPH and cyclized substitution product is decreased (from 12.2% to 2.2%) by the presence of DCPH with a proportionate increase in cyclized hydrocarbon. However, in the presence of *tert*-butylamine (TBA) as a carbanion trap, the result was similar to that in the absence of the trap. Clearly, these results indicate that the cyclized substitution product is derived from an intermediate radical which cyclized and then couples with the trimethyltin radical and that a carbanion intermediate can be eliminated from consideration. Interestingly, DCPH is apparently capable of trapping the intermediate radical before cyclization, since the hydrocarbon product (entry 4, Table I) is mostly 1-heptene (**12**), which confirms Kuivila's contention that DCPH is an efficient reagent for converting alkyl radicals to hydrocarbons by H atom transfer.[9] However, the yield of straingt-chain substitution product **10** is unaffected by added DCPH and TBA (entries 4 and 5, Table I), which indicates that both S_N2 and ET pathways are operative in the reaction of **1** with a secondary alkyl chloride (Scheme III). Of course it is possible that some of **10** is due to geminate coupling of radicals in the solvent cage which does not allow for cyclization of the probe to form **11**.

The results of experiments involving **1** and **4** (entries 6–10, Table I) indicate that the major reaction pathway involves electron transfer. Thus, when the leaving group is Br, 80.7% of the tetraalkyltin product is cyclized and only 6.1% is straight chain. It would appear from these data that the secondary bromide probe reacts by an ET pathway to a much greater extent than the corresponding chloride probe. It is interesting that unlike the previous case when X = Cl, DCPH suppresses the formation of both straight-chain and cyclic tetraalkyltin product and leads to formation of **12** as the major product (compare entries 6 and 7, Table I). This results indicates that DCPH is very effective in trapping the straight-chain radical before if forms **10** or cyclizes to **13**. This result indicates that DCPH is also trapping a significant amount of the cyclic radical before it couples with the trimethyltin radical to form **11**. Entries 11–14 (Table I) show that the reaction of **1** with **5** is comparable to that of the reaction of the bromide probe, in that the major pathway is ET leading to predominantly cyclized substitution product **11** (69%). In addition, DCPH traps both the straight-chain and cyclized radicals to form 66% of the products as hydrocarbon whereas the presence of TBA has no significant effect on product distribution. In addition, these results are in good agreement with those reported by Kuivila[9] which indicate that the reaction of **1** with a secondary bromide, 2-bromooctane, proceeds by an ET pathway to the extent of ~72%.

In addition, it has been reported previously[18] that in the reaction of **3** with Bu_3SnH at 65 °C, free hepten-2-yl radical

cyclizes to product **13** with a cis/trans ratio of 2.3, a value independent of solvent, concentration, additives, and leaving group. As expected, the cis/trans ratio of the cyclized products **11** and **13** formed in the above reactions was constant within experimental error. The high cis/

(18) Beckwith, A. L. J.; Blair, L.; Phillipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 1613.

Table II. Reaction of 6-Bromo-1-heptene (4) with Sodium Trimethyltin (1)[a]

entry	solvent	temp, °C	additive, molar equiv	concn, M	product yield,[b] % 10	11 (cis/trans)	12	13 (cis/trans)
1	THF	0	none	1.0	17.9	76.9 (3.93)	5.2	<1
2	THF	0	none	0.2	6.7	88.2 (3.93)	2.6	2.5
3	THF	0	none	0.043	4.7	89.2 (4.16)	2.3	3.8
4	HMPA	0	none	0.2	90.4	8.2 (4.78)	1.4	0.0
5	THF	0	10 DCPH	0.2	3.1	17.1 (4.16)	60.6	19.1 (4.76)
6	THF	0	5 DCPH	0.2	5.7	31.4 (4.08)	50.5	12.4 (4.10)
7	THF	0	5 DCPH	0.007	5.6	38.4 (4.26)	2.5	53.5 (4.13)
8	THF	−23	none	0.2	16.0	76.3 (4.99)	5.4	2.3
9	THF	−50	none	0.2	66.1	33.9 (6.80)		
10	THF	−78	none	0.2	94.8	5.2		
11	THF	0	10 DCPD	0.2	4.3	46.9 (4.12)	25.4 (78% d_1)	23.3 (4.51) (84% d_1)

[a] Reactions were carried out by inverse addition. Reaction time was 30 min for all reactions. [b] Yields were normalized.

Table III. Reaction of 6-Bromo-1-heptene (4) with Me_3SnNa (1)[a]

entry	additive, molar equiv	product yield, % 10	11	12	13
1	none	6.1	80.7	2.4	2.3
2	0.15 **15**	5.7	34.6	1.4	<1
3	cat. **16**	5.1	53.9	<1	<1
4	0.48 **16**	2.5	14.6	<1	<1

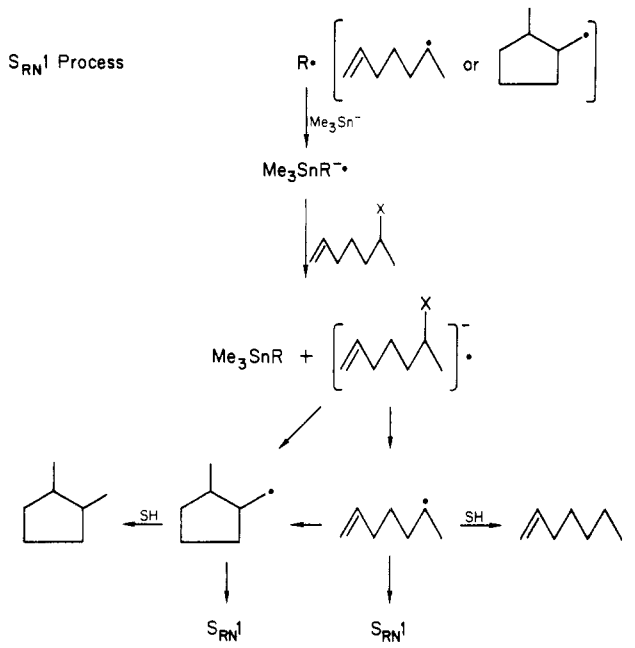
[a] Same experimental conditions as given in Table I.

trans ratio (~4–5) observed in this work is due to the fact that the experiments were carried out a 0 °C whereas the value of 2.3 was determined at 65 °C. It is known that the cis/trans ratio increases as the temperature decreases. It is also possible that the leaving group is not separated from the incipient radical before cyclization begins to take place. In any case, the observation of predominantly cis cyclic products is highly suggestive of [18,19] the occurrence of an ET pathway in the reaction of 1 with secondary halides.

An interesting aspect of the data in Table I is that the amount of cyclized substitution product is decreased and the amount of straight-chain substitution product is increased by the presence of 1,4-cyclohexdiene (14) (entries 9 and 14, Table I). Kuivila has reported that 14 has no effect in the reaction of 3-bromonortricyclene with 1 in THF.[20] Thus, we suggest[21] that the variation in the product distribution is due to the change in viscosity of the solvent system in which the cyclization of radicals takes place outside the solvent cage (Scheme III). If this is the case, the product distribution (**10**:**11**:**12**:**13**) should depend on the solvent, temperature, and even concentration. The results of experiments involving the reaction of 1 with 4 conducted under different conditions (i.e., concentration, temperature, and solvent) are given in Table II. It is known that radicals diffuse out of the solvent cage to a lesser extent in a solvent of higher viscosity (e.g., HMPA) and the yield of product formed inside the solvent cage would be expected to increase. Thus, reaction of 1 with 4 (entry 4, Table II) that was carried out in a highly viscous solvent (HMPA) leads mostly to straight-chain substitution product (90.4%) and a relatively small amount of cyclized substitution product (8.2%) compared to those results in THF (entries 1–3) when mostly cyclized substitution product is formed. We also found that the relative yield of **10** is increased dramatically by lowering the temperature which also increases the viscosity of the solvent (entries 8–10, Table II). It is, of course, also possible that the effect of cyclohexadiene (and HMPA) may also be due to a change in $\Delta(\Delta G^{\ddagger})$ for the S_N2 and ET steps in Scheme III or to the competition between the S_N2 and $S_{RN}1$ process. Entries 1–3 of Table II also show that the cyclized substitution product **11** is increased from 77% to 89% when the reactant concentration is decreased from 1.0 to 0.043 M. The cyclization rate is independent of the concentration (unimolecular reaction) whereas the rate of the bimolecular reaction decreases by lowering the concentration. Therefore, the relative yield of **11** should increase when the reaction concentration is descreased according to Scheme III. Especially, in the presence of DCPH as trapping agent, the yield of cyclized hydrocarbon **13** is dramatically increased from 12.4% to 53.5% when the concentration is decreased from 0.2 to 0.007 M (entries 6 and 7, Table II). Furthermore, in the presence of DCPD, which should be a less effective trapping agent than DCPH, the yield of **11** is increased from 17.1% to 46.9% but the yield of **10** only from 3.1% to 4.3%. Proportionately **12** is decreased from 60.6% to 25.4% but **13** is increased from 19.1% to 23.3% compared to results in DCPH (entries 5 and 11, Table II). Once again, these results show that the cyclization of radicals takes place outside the solvent cage and radicals have more chance to

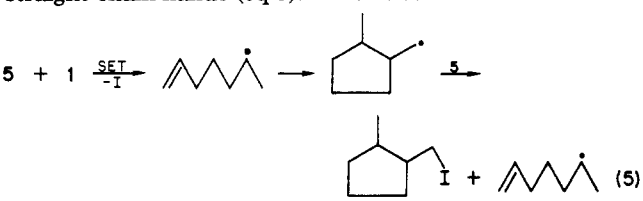
(19) Brace, N. O. *J. Org. Chem.* **1967**, *32*, 2711.
(20) Alnajjan, M. S.; Kuivila, H. G. *J. Org. Chem.* **1981**, *46*, 1053.
(21) A reviewer suggests that the effect of 1,4-cyclohexadiene could be interpreted as a mild retardation in the rate of the $S_{RN}1$ process with a larger fraction of the product arising from the S_N2 and K_3 processes of Scheme III. We believe that this suggestion is reasonable and could be another possible interpretation of these results.

Scheme IV



cyclize and then couple with trimethyltin radicals in the presence of DCPD as compared to DCPH.

Next, we examined whether or not the reaction can proceed by a free radical $S_{RN}1$ chain process. If the proposed noncage part of the reaction is correct then a free radical $S_{RN}1$ chain process can be involved in this part of the overall reaction (Scheme III). Experiments were carried out by using a radical anion scavenger [*p*-dinitrobenzene (**15**)] and a free radical scavenger [di-*tert*-butylnitroxy] radical (**16**)] to investigate the possibility of a $S_{RN}1$ process,[22,23] and the results are given in Table III. In the case of **4**, the yield of **11** is decreased from 80.7% to 34.6% in the presence of 15 mol % of **15** (entry 2, Table III) and to 14.6% in the presence of 48 mol % of **16** (entry 4, Table III) in the same period of time. In fact, the reaction is over within 1 min in the absence of the additive but is still less than 20% complete after 30 min in the presence of 48 mol % **16**. Therefore, these results show that the reactions are inhibited by adding **15** or **16** and the free radical $S_{RN}1$ chain process does participate in the reaction studied (Scheme IV). It is possible that a $S_{RN}1$ process can take place by the reaction of the cyclized radical with the straight-chain halide (eq 5). In this connection we allowed



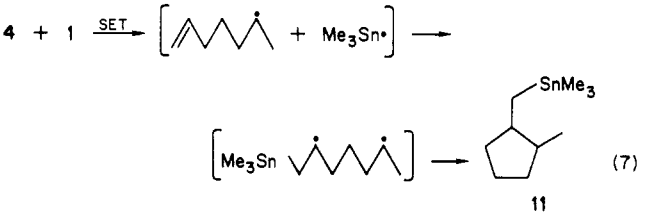
(5)

6-iodo-1-heptene (**5**) to react with only 20 mol % of **1** in THF at room temperature for 120 h in which 81% of the starting iodide was recovered and no cyclized iodide was detected (eq 6). This result indicates that a $S_{RN}1$ process to produce cyclized iodide does not occur, and therefore Scheme IV appears to represent the mechanistic pathway involved.

$$5 + 0.2\,1 \xrightarrow[\text{THF}]{120\text{ h}} \underset{2.2\%}{10} + \underset{13.8\%}{11} + \underset{1.6\%}{12} + \underset{1.5\%}{13} \qquad (6)$$

(22) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1449.
(23) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.

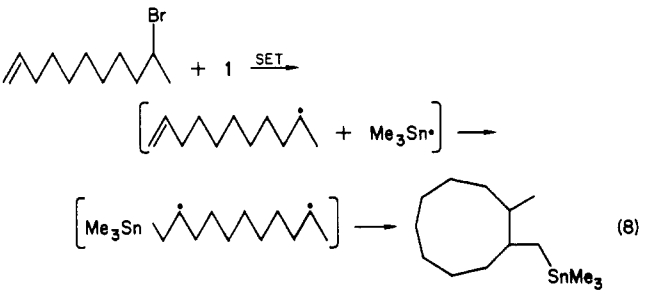
It is conceivable that the cyclic product in the reaction of Me_3SnNa with 6-bromo-1-heptene (**4**) could be produced by a process involving ET followed by attack of Me_3Sn· on the doubld bond, followed by collapse of the diradical (eq 7). Although radicals of the type $CH_2{=}CH(CH_2)_nCH_2$·



(7)

11

do not readily cyclize where $n > 5$, presumably a diradical cyclization of the type $CH_3\dot{C}H(CH_2)_7\dot{C}HCH_3$ should be possible. Thus, in order to test the possibility that Me_3Sn· may add to the double bond as in eq 7, the reaction of Me_3SnNa with 10-bromo-1-undecene was examined. Presumably, any cyclization would implicate addition of the tin radical to the olefin, as in eq 8. However, when



(8)

the reaction of Me_3SnNa with 10-bromo-1-undecene was conducted, no cyclization occurred. The only tin-substituted product was the straight-chain product that was obtained in 85% yield. Thus, this result is consistent with but does not prove that in reactions of Me_3SnNa with secondary bromides bearing a terminal olefin substituent, addition of the Me_3Sn· to the olefin does not occur.

Furthermore, we sought to gain additional insight into the mechanism of reaction of **1** with **4** by examining the reaction profile as a function of time. Since this reaction is very rapid at 0 °C, the profile studies were conducted at −23 °C. The results are shown in Table IV. In both cases, with and without DCPH, the ratio of **10** to **11** appears to be constant within experimental error throughout the course of the reaction, indicating that all products come from the same intermediate. However, the presence of DCPH caused no increase in the yield of **13** after the reactions was half over. This could be rationalized in terms of Me_3Sn· being trapped by DCPH to form Me_3SnH, which is a much better trapping agent than DCPH. Reaction of $(n\text{-Bu})_3SnH$ with **4** was found to give a 1:9 ratio of **13** to **12** at room temperature. This result indicates that at the later stage of the reaction, Me_3SnH can indeed trap straight-chain radical efficiently to produce almost only **12**.

Stereochemical Studies. Since studies with the 6-halo-1-heptenes described above indicated substantial ET for X = Cl, Br, and I, the stereochemistry of the reaction of Me_3SnNa with the series of optically active 2-halooctanes was reexamined, under experimental conditions identical with those used for the 6-halo-1-heptene studies. The results of these stereochemical studies are given in Table V. The data clearly show that the stereoselectivity decreases according to the trend OTs > Cl > Br, as judged from the optical purities of these products. The value of 28.4° was assumed to be the rotation of optically pure 2-octyltrimethyltin because the 6-tosyl-1-heptene gave only

Table IV. Reaction Profile of Sodium Trimethyltin (1) with 6-Bromo-1-heptene (4) in THF at −23 °C[a]

entry	reactn time, min	additive, molar equiv	product yield, % 10	11 (cis/trans)	11/10	12	13 (cis/trans)
1	0.5	none	3.0	6.3 (4.91)	2.1	1.8	<1
2	5	none	3.6	14.9 (4.71)	4.1	1.7	<1
3	15	none	5.1	24.5 (4.68)	4.8	2.4	<1
4	30	none	4.7	29.4 (4.51)	6.3	3.0	<1
5	45	none	6.6	32.1 (4.88)	4.9	3.4	<1
6	60	none	7.4	34.5 (4.98)	4.7	3.5	<1
7	90	none	9.3	39.4 (4.79)	4.2	3.0	<1
8	120	none	12.1	48.1 (4.69)	4.0	4.1	<1
9	160	none	13.6	51.6 (4.81)	3.8	4.8	1.3
10	300	none	14.2	67.7 (4.99)	4.8	4.8	2.0
11	0.5	10 DCPH	2.7	7.7 (4.95)	2.9	19.1	6.4 (5.21)
12	15	10 DCPH	3.3	10.8 (4.51)	3.3	33.4	11.8 (5.69)
13	30	10 DCPH	3.6	14.7 (4.82)	4.1	46.8	12.4 (5.48)
14	60	10 DCPH	6.2	19.7 (4.43)	3.2	52.4	10.9 (6.27)
15	120	10 DCPH	6.4	21.3 (4.73)	3.3	54.6	11.4 (6.04)

[a] Experiments were conducted such that each reactant in the reaction mixture was 0.2 M. All reactions were run and quenched individually.

Table V. Reactions of 2-Halooctanes with Sodium Trimethyltin (1)[a]

entry	X in R*X: $[\alpha]^{25}_D$, deg	opt purity of R*X, %	order of additn	concn of reactants, M	R*-$SnMe_3$ product[b] obsd $[\alpha]^{25}_D$, deg	corr $[\alpha]^{25}_D$, deg	% opt purity[c]	% inver[d]
1	OTs: −7.55	76.0	inverse	0.20	+21.6	+28.4	100	100
2	OTs: −7.26	73.1	inverse	0.20	+20.1	+27.5	96.8	98
3	Cl: +27.6	74.0	inverse	0.20	−16.2	−21.9	77.1	89
4	Cl: +27.6	74.0	inverse	0.40	−18.7	−25.3	89.0	94
5	Br: +31.0	71.4	normal	0.20	−10.1	−14.1	49.6	75
6	Br: +31.0	71.4	inverse	0.20	−11.0	−15.4	54.2	77
7	Br: +31.0	71.4	inverse	0.20	−10.6	−14.8	52.1	76
8	Br: +31.0	71.4	inverse	0.40	−11.4	−16.0	56.3	78
9	I: +11.6	18.3	inverse	0.20	−3.50	−19.1	67.2	83

[a] Same experimental conditions as given in Table I. See Experimental Section for details. [b] Rotations measured in cyclopentane solution. [c] Based on a rotation of 28.4° for optically pure 2-octyltrimethyltin. [d] Calculated as % inversion = 100 − [0.5(100 − % optical purity)].

S_N2-type product, which indicates that the reaction with a secondary tosylate should involve complete inversion.[24] The most striking aspect of these data is the fact that the extent of inversion is 89–94% for X = Cl, 75–78% for X = Br, and 83% for = I. 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 9). This is not unreasonable

$$Y^- + RX \xrightarrow{\text{slow}} Y\cdot,RX^{-}\cdot \xrightarrow{\text{fast}} Y\cdot,R\cdot,X^- \xrightarrow{\text{fast}} RY + X^- \quad (9)$$

considering that the single electron transfer between Y^- and RX should take place at the backside of the R group (σ^* orbital), and hence Y· is still in close proximity to the backside of R·X^- in the solvent cage before dissociation to R· and X^- takes place.

It is surprising that **4** gives a 81% yield of cyclized substitution product **11** (entry 6, Table I) upon reaction with **1** but that 2-bromooctane (**8**) of comparable structure to **4** reacts under identical conditions with 77% inversion of configuration (entry 6, Table V). Since cyclization of the 2-heptenyl radical

takes place outside of the solvent cage and thus involves a kinetically free radical, it is difficult to understand how predominant inversion of configuration could be observed for the 2-octyl system.

Table VI. Reaction of 2-Bromoheptane (17) with Me_3SnNa (1)[a]

entry	additive, molar equiv	product yield,[b] %	
1	none	81.5	12.3
2	0.15 **15**	69.5	15.1
3	cat. **16**	75.8	12.7

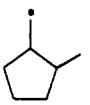
[a] Same experimental conditions as given in Table I. [b] Alkenes were formed (4% or less), presumably by dehydrohalogenation and disproportionation.

If the 2-heptenyl radical escapes the solvent cage more readily than the 2-octyl radical, one could rationalize a high degree of cyclization in the 2-heptenyl system whereas the predominant inversion of configuration of the 2-octyl system is explained by substitution of y· at the backside of R·X^- in the solvent cage.

For this reason, we examined the reactions of **1** with 2-bromoheptane (**17**) in the presence and absence of radical anion scavenger **15** or free radical scavenger **16**, and the

(24) San Filippo and Silbermann reported a maximum rotation of 26.1° for 2-octyltrimethyltin,[11] which is essentially within experimental error for the value of 28.4 used herein.

results are shown in Table VI. We found that with **17**, the yield of substitution product decreased from 81.5% to 69.5% in the presence of **15** (entries 1 and 2, Table VI) and to 75.8% in the presence of **16** (entries 1 and 3, Table VI) and with **4** from 80.7% to 34.6% and to 53.9%, respectively (entries 2 and 3, Table III). These data strongly suggest that reaction of **1** with **17** results in fewer radicals diffusing out of the solvent cage; hence the reaction products are less affected by a trapping agent. Nevertheless, it is also possible that with **4**, Δ^6-2-heptenyl radicals diffuse out of the solvent cage cyclizing to less hindered primary radicals



and then react with Me_3Sn^- in a $S_{RN}1$ chain process as a major pathway to yield **11**. In the case of 2-octyl (or heptyl) bromide, the more hindered secondary alkyl radicals do not participate in the $S_{RN}1$ chain process as readily as a primary radical because of steric hinderance, reversibility, or side reactions (eq 10). Therefore, the k_3 process of Scheme III becomes the major route to the tetraalkyltin in the reaction.[25]

$$\text{secondary R}\cdot + Me_3Sn^- \rightleftharpoons Me_3SnR^-\cdot \qquad (10)$$

Kuivila[9] has also reported that the reaction of **1** with 2-iodooctane (**9**) proceeds by an ET pathway to the extent of 48% and by a HME pathway to the extent of 40%. However, in this work we have found that the major pathway of reaction of **1** with **5** is an ET pathway. This result can be explained that with **5**, the heptenyl radicals diffuse out of the solvent cage rapidly and then the $S_{RN}1$ process is involved and the reaction is accelerated, and thus the HME pathway has less change to proceed.

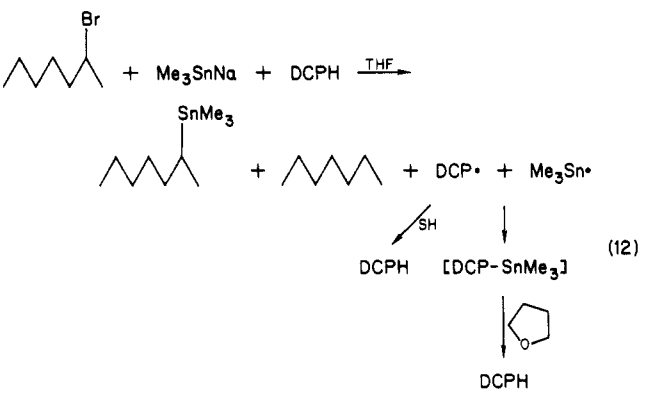
The Role of DCPH as a Agent. In connection with the stereochemistry of the reaction of **1** with the 2-haloctanes, Kuivila recently conducted some interesting experiments.[26] In particular, it was demonstrated that the stereochemistry of the substitution reaction was unaffected by the added trap, DCPH. Thus, although the yield of 2-octyltrimethyltin was reduced (to 10%) by added DCPH, the tetraalkyltin product exhibited the same optical purity as in reactions without DCPH. This is an indication that DCPH serves only to trap an intermediate radical but does not substantially alter the mechanism of the reaction of **1** with alkyl halides.

In order to investigate the action of DCPH as a radical trap in the reactions of **1** with alkyl halides more thoroughly, an experiment with deuterated DCPH was conducted. Thus, if DCPH does indeed trap a radical species by donation of a hydrogen (or deuterium) atom, then the hydrocarbon byprouct should exhibit deuterium incorporation when DCPD is employed (eq 11). For this reason,

$$Me_3SnNa + RX \xrightarrow{DCPD} R\text{-}D \qquad (11)$$

DCPD was employed as a trapping agent in the reaction of **1** with **4** (entry 11, Table II). Thus, consideration of the extent of deuteration of the trap DCPD (99% d_1) and the fact that 10 equiv of DCPD were utilized confirm that the hydrocarbon byproducts are formed predominantly by a process that transfers the deuterium of the phosphine to the carbon skeleton derived from **4**. The fact that hydrogen abstraction from DCPH does occur in the reaction of **1** with **4** is consistent with the intervention of a radical species derived from the starting bromide.

In an effort to determine the fate of the DCPH in the reaction of Me_3SnNa with alkyl halides, several investigations were conducted. In THF solvent, **17** was added to 1.0 molar equiv of DCPH (at 0.25 M concentration) at 0 °C, followed by addition of 1.0 molar equiv of **1**. After 30 min had elapsed, an aliquot was removed and hydrolyzed after which time GLC analyses indicated a 15.3% yield of 2-heptyltrimethyltin and a 75% yield of *n*-heptane. The remainder of the reaction mixture was allowed to stand in the freezer, and after the NaBr had settled out, the solution was subjected to a series of analysis. Infrared spectroscopy showed the presence of a P–H stretching band (2260 cm^{-1}, moderate), and ^{31}P NMR showed only the presence of one phosphorous species[25] (δ −27.15). Thus, the only phosphorous species formed in the reaction of 2-bromoheptane with Me_3SnNa and DCPH is in fact DCPH. Two possible explanations of this result can be offered. First, the DCP· formed by the H atom transfer can attack solvent, or second, the DCP· may couple with Me_3Sn·, as in eq 12. Presumably, the trimethyltin dicychlohexylphosphide is a powerful base[27] and can cleave THF readily to produce the observed DCPH that is obtained in the product mixture.



(12)

Another similar experiment was also carried out in which **4** was allowed to react with **1** in the presence of DCPD. A quantitative study shoowed that DCPH was formed to the same extent that DCPD was consumed (determined by IR and NMR spectroscopy). We than allowed the solution of 1 molar equiv of **4** and 10 molar equiv of DCPH to react with 0.3 molar equiv of **1** for 90 h at room temperature (eq 13). We found that the reaction does not

$$4 + 0.31 + 10\text{DCPH} \xrightarrow[\text{THF}]{90\text{ h}} \underset{1.2\%}{\mathbf{10}} + \underset{8.6\%}{\mathbf{11}} + \underset{13.3\%}{\mathbf{12}} + \underset{5.0\%}{\mathbf{13}} + \underset{69.0\%}{\mathbf{4}} \qquad (13)$$

proceed any further after a 30-min reaction time. This

(25) A reviewer suggests that there could be another chain substitution that predominates when only a secondary alkyl radical is present. Me_3Sn· was used as a chain-carrying species that leads to **10** and inverted R_4Sn·.

$$Me_3Sn\cdot + Me_3Sn^- \rightleftharpoons Me_3Sn\cdot\text{-}^-SnMe_3$$

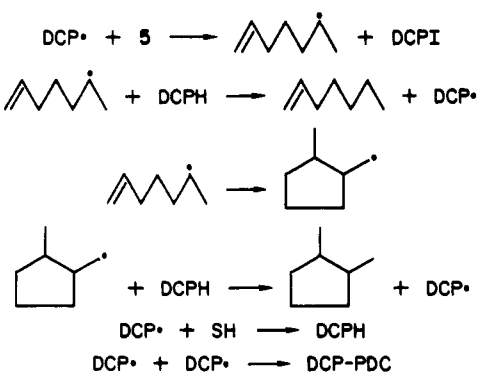
$$Me_3Sn\cdot\text{-}^-SnMe_3 + \text{secondary RX} \rightarrow [Me_3Sn\text{–}SnMe_3 + R\cdot + X^-]\ \text{cage} \rightarrow Me_3SnR\ \text{(inverted)} + Me_3Sn\cdot$$

The Δ^6-2-heptenyl system shows stronger inhibition than the 2-octyl (or 2-heptyl) systems. Perhaps different chains are involved with different sensitivieis to these inhibitors. However, Me_3Sn· is formed in both systems. If the suggested mechanism is involved in the reaction of **1** with **17** to yield tetralkyltin in the presence free radical chain inhibitors, it should also be involved in the reaction of **1** with **4** to yield a large amount of **10** in the presence of inhibitors (comparing Table III with Table VI). Therefore, it seems to us that the suggested mechanism could not play a major role in these reactions.

(26) Kuivila, H. F.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6146.

(27) Mair, L. "Organophosphorus Compounds", Kosolapoff, G., Maier, L.; Eds.; Wiley-Interscience: New York, 1972; Vol. I, pp 98, 293.

Scheme V



result indicates that DCP· does not react via a radical chain process. The reaction of **4** with 0.3 molar equiv of DCPH in the presence of AIBN at 70 °C showed that no bromide reacted. Thus all of the available data demonstrate that in the reaction of **1** with secondary bromide, DCPH serves simply as an efficient hydrogen atom donor toward an intermediate radical. However, we found that reaction of the corresponding iodide **5** with 0.2 molar equiv of **1** in the presence of 10 molar equiv of DCPH produced mostly hydrocarbon product and the reaction was completely over after 20 h, whereas only 15% iodide reacted under the same conditions in the absence of **1**. Since alkyl iodides are good electron acceptors, it is not surprising that DCP· can react with iodide by a radical chain process (Scheme V). It is clear that DCPH can provide the opportunity for a radical chain process to compete with the main process which is ET plus a free radical $S_{RN}1$ chain process, but not in the case of the bromide.

Conclusion

The reaction of a series of secondary alkyl halides containing a cyclizable radical probe with Me_3SnNa was examined, and it appears that tosylates react entirely by an S_N2 pathway. In the case of the secondary alkyl chloride, it appears that the S_N2 pathway is not the only one involved and that electron transfer is also involved. With secondary alkyl bromides and iodides, it appears that the ET pathway becomes the major pathway and that a $S_{RN}1$ process can also be involved after radicals diffuse from the solvent cage. The reaction of a series of optically active alkyl halides with Me_3SnNa was also examined, and predominant inversion of configuration was observed in all cases. These results suggest that inversion of configuration results from an ET process followed by a stereospecific reaction all inside the solvent cage. Comparing results of cycliable probes and optically active probes, it appears that a "cage effect" plays an important role. Thus, if the cyclizable probes were available in optically active forms, perhaps the stereochemistry of the cyclization process could be examined. However, such studies are not feasible at present since the rotations and configurations for neither the products nor the reactants are known. Nevertheless, considering the available data, it seems likely that the "cage effect" does make a difference between these two different series of probes. Furthermore, results also suggest that DCPH can be used as a trap for free radicals without perturbing the reactions mechanism in the cases studied.

Experimental Section

General Procedures and Materials. Solvent grade pentane, hexane, and benzene were 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 tetrahydrofuran (THF) were distilled under nitrogen from deep purple solutions of sodium benzophenone ketyl. Samples of the hydrocarbons 1-heptene, 1,2-dimethylcyclopentane, and cyclopentane were obtained from either Aldrich or Chemical samples and used as received.

Samples of dicyclohexylphosphine (DCPH, bp 68–70 °C (0.05 mmHg)), 4-bromo-1-butene (bp 98–100 °C, CaH_2), 5-bromo-1-pentene (bp 123–124 °C, CaH_2), and acetaldehyde (20–25 °C, P_2O_5) were purchased from Aldrich. Reagent grade acetone (Fisher) was distilled from P_2O_5. Reagent grade pyridine (Fisher), tosyl chloride (Aldrich), and (–)-2-octanol (Aldrich) were used as received. Resublimed magnesium chips, anhydrous metal salts, sodium dispersion, and hexamethylditin (bp 73–74 °C (16 mmHg)) were purchased from Alfa.

Preparations. Sodium trimethyltin (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*-$BuSnMe_3$.[9]

1-Hepten-6-ol. The title compound was prepared in 96% yield by the method of Ingold and Maeda[28] and exhibited the following: ^1H NMR 1.18 (3 H, d, J = 6.0 Hz), 1.20–2.55 (6 H, m) 3.30–3.97 (2 H, m, contains OH), 4.80–6.17 ppm (3 H, m); bp 74–76 °C (23 mmHg); [lit.[28] bp = 61 °C (12 mmHg)].

Tosylate of 1-Hepten-6-ol (2). To 50 mL of pyridine at 0 °C were added 19 g of tosyl chloride and 10 g of 1-hepten-6-ol. The mixture was allowed to stand at 8 °C for 98 h. After filtration, the mixture was diluted with 400 mL of pentane, washed with dilute HCl, washed with water, dried over $MgSO_4$, and desolvated in vacuo to yield 23 g of a crude yellow oil. Purification by chromatography on silica with ether–pentane (2:98) as eluent yielded analytically pure tosylate, which exhibited the following: ^1H NMR 1.08–2.20 (9 H, m, contains 3 H, d, 1.80 J = 6.0 Hz), 2.38 (3 H, s), 4.37–6.05 (3 H, m), 7.20–7.78 ppm (4 H, m); IR 3070 (unsaturated C–H), 2980 (CH), 1640 (aromatic CC), 1600 (C=C), 1490, 1360 (CH_3), 1180 cm^{-1} (S=O); mass spectrum (CI), m/e (relative intensity) 269 (100), 213 (5.89), 193 (17.05), 187 (1.00), 173 (18.43), 157 (2.55), 135 (14.76). Anal. Calcd: C, 62.65; H, 7.53. Found: C, 62.56; H, 7.55.

6-Chloro-1-heptene (3). To 150 mL of acetone were added 10 g of LiCl and 8.0 g of the crude 6-tosyl-1-heptene. After being refluxed for 48 h, the mixture was cooled, diluted with pentane, and subjected to standard workup. Distillation yielded 2.6 g (69%) of a clear oil which exhibited the following: bp 70–72 °C (81 mmHg); n^{25}_D 1.4350; ^1H NMR 1.40–2.32 (9 H, m, contains 6 H, d, 1.55 ppm, J = 6.0 Hz), 4.02 (1 H, m), 4.78–6.05 ppm (3 H, m); IR 3080 (unsaturated CH), 2940 (CH), 1640 (C=C), 1445, 1380 cm^{-1} (CH_3); GLC purity 99% on 5 ft, 10% OV101 at 90 °C, 40 mL/min; mass spectrum, m/e (relative intensity) 132 (0.50), 97 (7.70), 96 (26.05), 81 (70.69), 69 (13.59), 68 (10.58), 67 (24.00), 56 (20.16), 55 (77.24), 54 (100). Anal. Calcd: C, 63.38; H, 9.90. Found: C, 63.42; H, 9.94.

6-Bromo-1-heptene (4). By a procedure analogous to that used for **3**, **4** was prepared in 76% yield and exhibited the following: bp 64–68 °C (24 mmHg); [lit.[28] bp 72 °C (20 mmHg)]; n^{25}_D 1.4622; ^1H NMR 1.40–2.33 (9 H, m, contains d, 3 H, 1.77 ppm, J = 6.0 Hz), 3.73–4.23 (1 H, m), 4.75–6.10 ppm (3 H, m); IR 3080 (unsaturated CH), 2960 (CH), 1640 (C=C), 1440 , 1375 cm^{-1} (CH_3); mass spectrum, m/e (relative intensity) 178 (0.57), 176 (0.54), 97 (23.03), 81 (30.36), 55 (100); GLC purity 98% on 5 ft, 15% TCEP, at 120 °C, 100 mL/min. Anal. Calcd: C, 47.47; H, 7.41. Found: C, 47.55; H, 7.43.

6-Iodo-1-heptene (5). By a procedure analogous to that used for **3**, **5** was prepared in 78% yield and exhibited the following: bp 77–79 °C (25 mmHg); n^{25}_D 1.5042; ^1H NMR 1.37–2.35 (9 H, m, contains 3 H, d, 1.97 ppm, J = 6.0 Hz), 4.08 (1 H, m), 4.80–6.10 ppm (3 H, m); mass spectrum, m/e (relative intensity) 224 (0.52), 97 (14.92), 57 (9.35), 56 (4.68), 55 (100), 41 (20.33); GLC purity 99% on 6 ft, 10% Apiezon L, at 130 °C, 60 mL/min. Anal. Calcd: C, 37.51; H, 5.86. Found: C, 37.58; H, 5.89.

Optically Active 2-Halooctane (6–9). The series of optically active 2-halooctanes (OTs, Cl, Br, I) was prepared according to the method of San Filippo and Romano.[29] For X = OTs (**6**): ^1H NMR 0.85–1.62 (16 H, m), 2.43 (3 H, m), 4.53 (1 H, m), 7.20–7.80 ppm (4 H, m); IR 2930 (CH), 1605 (aromatic CC), 1455, 1370

(28) Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1979**, *101*, 4975.
(29) San Filippo, J., Jr.; Romano, L. J. *J. Org. Chem.* **1975**, *40*, 1514.

(CH_3), 1180 cm^{-1} (S=O); mass spectrum, m/e (relative intensity) 284 (0.21), 173 (18.41), 155 (70.02), 112 (86.01), 91 (100); $[\alpha]^{25}_D$ −7.55° (c 0.287 g/mL, cyclopentane), 76.0% optical purity (based on $[\alpha]$ 9.93° for 100% optical purity[29]). For X = Cl (7): n^{25}_D 1.4240; bp 68–69 °C (23 mmHg) [lit.[29] bp 74–76 °C (25 mmHg)]; $[\alpha]^{25}_D$ +27.6° (neat sample), 87.4% optical purity (based on $[\alpha]$ 31.6° for 100% optical purity[29]). For X = Br (8): n^{25}_D 1.4465; bp 80–82 °C (24 mmHg) [lit.[29] bp 74–76 °C (14 mmHg)]; $[\alpha]^{25}_D$ +31.9° (neat sample), 73.1% optical purity (based on $[\alpha]$ 43.6° for 100% optical purity[29]). For X = I (9): n^{25}_D 1.4840; bp 64–66 °C (2.0 mmHg) [lit.[29] bp 54–55 °C (1.5 mmHg)]; $[\alpha^{25}_D]$ +11.6° (neat sample), 18.3% optical purity (based on $[\alpha]$ 63.2° for 100% optical purity[29]).

Preparation of Deuteriodicyclohexylphosphine (DCPD). By use of published procedure[30,31] $(C_6H_{11})_2POOH$ was obtained [69%, mp 145.5–146 °C (lit.[30] mp 143 °C)] and then converted to the corresponding chloride [$SOCl_2$; 80%, mp 105–107 °C (lit.[30] mp 108–109 °C)]. To this chloride (12 g, 48.3 mmol) dissolved in 150 mL of dry ether was added 3 g of LAD in 50 mL of dry ether slowly. The solution was refluxed for 2 h and then 8.0 mL of D_2O added. The mixture was stirred for an hour, filtered, and concentrated by reducing the pressure. The residue was fractionally distilled to yield 6.2 g (63.8%) of DCPD, bp 81–84 °C/(0.1 mmHg). The DCPD was determined to be 99% monodeuterated, as evaluated by NMR. An infrared spectrum also confirmed the presence of DCPD (neat): 2930, 2850 (strong, CH), 2260 (trace, PH), 1645 cm^{-1} (strong, P^2H).

Preparation of 10-Bromo-1-undecene. A 250-mL flask equipped with a stir bar, addition funnel, and condenser was charged with 2.5 g of magnesium chips and flame dried in vacuo. Approximately 5 mL of THF (from a Na/Ph_2CO still) was introduced along with 1.0 mL of ethylene dibromide. After the vigorous reaction subsided, 11.3 g of 5-chloro-2-pentanone ethylene ketal [Aldrich, bp 79–81 °C/(8 mmHg)] was placed in the funnel, and a small portion was added to the magnesium. Reaction initiated in 20 min, and the remainder of the chloride was added with more THF over a 30-min period. After 4 h, unreacted magnesium was allowed to settle out and the solution was cannulated into a flask containing 0.50 g of CuBr at −78 °C. A solution of 6.8 g of 6-iodo-1-hexene in THF was added immediately, and the mixture was allowed to warm to room temperature over a 3-h period. The mixture was quenched with NH_4Cl, extracted with Et_2O, and desolvated on a rotary evaporator. The residue was dissolved in 50 mL of THF, 50 mL of 15% HCl wad added, and the solution was heated on the steam bath for 15 min and then stirred for 1 h. Standard etheral workup yield 6 g of 1-undecen-10-one: ^1H NMR (CCl_4) δ 1.27–2.25 (18 H, m), 4.80–6.05 (3 H, m); GLC $^1/_4$ in. × 12 ft Carbowax 20M, 170 °C, purity of 95%. The 1-undec-10-one was dissolved in 15 mL of MeOH and the solution added to 2.0 g of $NaBH_4$ in 25 mL of MeOH. Standard workup yielded 5.8 g of 10-hydroxy-1-undecene that was dissolved in 20 mL of dry THF, and the solution was added to 23 mL of 1.5 M $MeLi/Et_2O$ at 0 °C. After 30 min, 6.8 g of TsCl in 20 mL of THF was added and the solution was stirred at room temperature for 4 h. Standard ethereal workup yielded 10 g of an oil solid (no OH by IR), which was a mixture of the desired tosylate plus TsCl. The residue was dissolved in 150 mL of acetone in addition to 15 g of LiBr and the solution refluxed gently for 18 h. Standard ethereal workup was followed by distillation, which yielded 5 g of a pale yellow oil [82–100 °C (0.1 mmHg)]. NMR analysis of this oil revealed the presence of the desired bromo compound, contaminated by an unknwon impurity. Thus, preparative GLC (6 ft × $^1/_4$ in. 10% apiezon L, 180 °C, injector–detector 110 °C) yielded a sample of the desired bromo compound, contaminated by approximately 15% of elimination product, based on the NMR analysis: ^1H NMR (CCl_4) δ 1.05–2.20 (16.7 H, m), 3.70–4.20 (0.77 H, m), 4.75–6.10 (3.5 H, m).

The following compounds were isolated by preparative GLC from reaction mixtures.

1-Hepten-6-yltrimethyltin (10): ^1H NMR 0.057 (9 H, s, satellites, J_{SnCH} = 51 Hz), 0.81–2.41 (10 H, m), 4.81–6.02 ppm (3 H, m); IR 3060 (unsaturated CH), 2950 (CH), 1640 (C=C), 1450, 1375 cm^{-1} (CH_3): mass spectrum, m/e (relative intensity) 261 (5.68), 260 (3.45), 249 (0.26), 165 (6.70), 121 (31.3), 119 (98.12), 117 (100). Anal. Calcd: C, 46.01; H, 8.51. Found: C, 46.18; H, 8.59.

[(2-Methylcyclopentyl)methyl]trimethyltin (11): ^1H NMR 0.057 (9 H, s, satellites, J_{SnCH} = 51 Hz), 0.65–2.37 ppm (13 H, m); mass spectrum, m/e (relative intensity) 261 (7.58), 260 (4.45), 247 (98.70), 169 (17.56), 165 (100); IR 2950 (CH), 1450, 1375 cm^{-1} (CH_3); the cis/trans isomers were distinguished by GLC, as described below (see also ref 14). Anal. Calcd: C, 46.01; H, 8.51. Found: C, 46.13; H, 8.52.

2-Octyltrimethyltin: ^1H NMR 0.050 (9 H, s, J_{SnCH} = 51 Hz), 0.90–2.38 ppm (17 H, m); mass spectrum, m/e (relative intensity) 276 (6.97), 263 (98.46), 261 (76.91), 208 (19.69), 207 (100). Anal. Calcd: C, 47.68; H, 9.48. Found: C, 47.73; H, 9.52.

General Procedures for Reactions of Alkyl Halides with Me_3SnNa. Reactions were conducted in THF at 0 °C for 30 min with bromides and iodides and for 3 h with chlorides and tosylates. Reactions were generally conducted with 0.2 M concentrations of each reactant. Solutions of alkyl halides and reaction vessels were protected from light, and transfers were made via syringes. "Normal" addition indicates that a solution of the alkyl halide was added slowly to the Me_3SnNa, with rapid stirring under N_2, while "inverse" addition means that a solution of Me_3SnNa was added to the alkyl halide. Reaction mixtures were quenched with aqueous ammonium chloride, internal standards added, and GLC analyses performed. Optically active products were isolated by preparative GLC before measurements of the rotations in cyclopentane solvent.

General Procedure for Kinetics Experiments. Reaction of Sodium Trimethyltin with 6-Bromo-1-heptene. To 0.5 mL of a 0.58 M solution of bromide in THF under N_2 was added 0.95 mL of a 0.32 M solution of Me_3SnNa in THF at dry ice–CCl_4 bath temperatures. After a certain time period, with stirring, the reaction mixture was quenched with aqueous ammonium chloride and analyzed by GLC.

Reaction of Sodium Trimethyltin with 6-Bromo-1-heptene in the Presence of DCPH. To a solution of the bromide (0.29 mmol) and DCPH (2.9 mmol) in 0.5 mL of dry THF under N_2 was added 0.95 mL of a 0.32 M solution of Me_3SnNa in THF at dry ice–CCl_4 bath temperatures. After a certain time period with stirring, the reaction mixture was quenched with aqueous ammonium chloride and analyzed by GLC.

Analytical Methods. Gas chromatographic analyses were conducted on a Hewlett-Packard Model 700 instrument equipped with an FID using packed columns and preparative separations were performed on an F and M Model 720. Quantitative GLC analysis were obtained with the use of response factor corrected peak areas using internal standards. Proton NMR were recorded on a Varian T60 instrument with chemical shifts reported relative to tetramethylsilane, and ^{31}P NMR spectra were obtained on a Brucker FT 300-MHz instrument. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. Mass spectra were obtained on a Varian MAT 1125 instrument, and carbon–hydrogen microanalyses were conducted by Atlantic Microlabs, Inc., of Atlanta, Ga. Optical rotations were measured on a Josco Model 5 ORD using cyclopentane solutions of products purified by GLC.

For gas chromatographic analyses, the following columns and conditions were employed: (1) 4 ft, 8% Apiezon L, 85 °C, 40 mL/min with $C_{10}H_8$ as internal standard (relative retention times, $C_{10}H_8$, 2.54; 1-hepten-6-yltrimethyltin, 1.00; *cis*-[(2-methylcyclopentyl)methyl]trimethyltin, 1.82; *trans*-[(2-methylcyclopentyl)-methyl]trimethyltin, 1.37); (2) 20 ft, 8% Apiezon, 65 °C, 35 mL/min (relative retention times, 1-heptene, 1.14; benzene, 1.00; *trans*-1,2-dimethylcyclopentane, 1.26; *cis*-1,2-dimethylcyclopentane, 1.67).

Acknowledgment. We are indebted to the National Science Foundation Grant No. CHE 8403024 for support of this work and to Dr. Harold Banks of Atlanta University for helpful discussions.

Registry No. 1, 16643-09-7; 2, 59967-05-4; 3, 15661-92-4; 4, 38334-98-4; 5, 13389-36-1; 6, 27770-99-6; 7, 16844-08-9; 8, 1191-24-8; 9, 1809-04-7; 10, 76879-52-2; *cis*-11, 76879-57-7; *trans*-11, 76879-

(30) Issleib, K.; Brack, A. *Z. Anorg. Allg. Chem.* **1954**, *277*, 258.
(31) Issleib, K.; Tzschach, A. *Chem. Ber.* **1959**, *92*, 704.

58-8; DCPD, 91523-73-8; Me_6Sn_2, 661-69-8; Na, 7440-23-5; $CH_3CH(OH)(CH_2)_3CH{=}CH_2$, 24395-10-6; $(C_6H_{11})_2P(O)OH$, 832-39-3; $(C_6H_{11})_2PCl$, 16523-54-9; $CH_3CHBr(CH_2)_7CH{=}CH_2$, 91523-74-9; $CH_3C(O)(CH_2)_7CH{=}CH_2$, 36219-73-5; $I(CH_2)_4CH{=}CH_2$, 18922-04-8; $CH_3CH(OH)(CH_2)_7CH{=}CH_2$, 91523-75-0; (*R*)-$CH_3(CH_2)_5CH(CH_3)SnMe_3$, 79055-01-9; (*S*)-$CH_3(CH_2)_5CH(CH_3)SnMe_3$, 79054-99-2; 5-chloro-2-pentanone ethylene ketal, 5978-08-5.

Haptotropic Rearrangements and C–H Bond Activation in Indan, Indenyl, and Naphthalene Complexes of Iridium

Robert H. Crabtree* and Charles P. Parnell

Department of Chemistry, Yale University, New Haven, Connecticut 06511

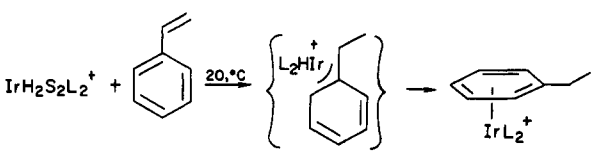
Received April 3, 1984

2-Vinylnaphthalene reacts with $[IrH_2(Me_2CO)_2L_2]A$ (1, L = PPh_3, A = SbF_6) to give $[Ir(NpEt)L_2]A$ (3, NpEt = 2-ethylnaphthalene). Below 10 °C the kinetic product has the metal bound to the ring bearing the ethyl group. Above 10 °C a 50:50 mixture of haptomers is formed in each of which the metal is bound to a different ring. Indene reacts with 1 at 25 °C to give $[Ir(\eta^6\text{-indan})L_2]A$ (4), but at 80 °C, 4 dehydrogenates to give $[Ir(\eta^5\text{-indenyl})HL_{32}]A$ (5). Indan reacts with 1 and *tert*-butylethylene (tbe) at 90 °C to give first 4 and then 5, an example of arene precoordination facilitating CH activation on the side chain. 3, 4, and 5 as well as the related $[Ir(\eta^5\text{-}C_6H_7)HL_2]A$ all react with tbe and cyclopentane at 100 °C to give $[IrCpHL_2]A$, all examples of alkane C–H activation. The conformation of the idenyl ring in 5, deduced from NMR measurements, puts H trans to the fused benzene ring, contradicting the expectation based on steric effects. A rationalization is proposed that also embraces other literature examples. 5 has largely 18-electron character with an η^5-indenyl and is chemically rather inert, but 3 has largely 16-electron character with an η^4-NpEt ligand and is chemically very reactive. ^{13}C NMR was used to determine the hapticity of the carbocyclic ligands.

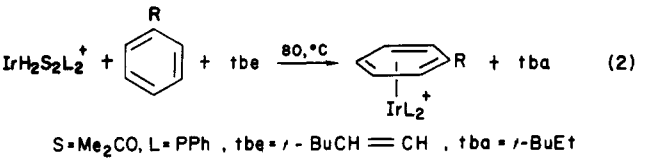
In looking for ways to generate multiple active sites on metal complexes, we have made extensive use of $[IrH_2(Me_2CO)_2(PPh_3)_2]A$ (1, A = noncoordinating anion). Both the hydrogen and the acetone can be lost to give a highly reactive system that can even dehydrogenate alkanes.[1] Unfortunately, the range of phosphorus ligands for which these acetone complexes are stable is limited, as is the range of metal systems forming acetone complexes. We therefore sought to free ourselves of this limitation by moving to removable ligands other than acetone and H. We were attracted to the idea of using η^6-arene complexes, which generate three two-electron sites if the arene were lost. The corresponding η^5-cyclohexadienyl and η^4-diene complexes were also studied for completeness. We wished to test these ideas in a known system, one we knew would be active for alkane dehydrogenation if the arene were liberated. We therefore began our studies on some bis(triphenylphosphine)iridium complexes related to 1.

Results and Discussion

Arene Complexes. We showed recently that styrene reacts with the acetone complex 1 to give $[(\eta^6\text{-PhEt})IrL_2]A$ (eq 1, L = PPh_3)[2] and that a variety of arenes (e.g., C_6H_6, PhMe) react with 1 and tbe (tbe = *tert*-butylethylene) to give $[(\eta^6\text{-ArH})IrL_2]A$ (2, ArH = arene) in a more general synthesis of the same type of complex (eq 2).[3]



(1)



(2)

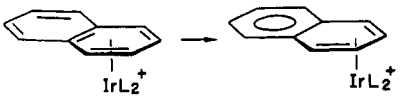
When these were heated with cyclopentane and tbe in a sealed tube at 110 °C for 18 h, we observed mostly free arene but only 5% of the alkane dehydrogenation product $[IrHCpL_2]A$ (eq 3 and 4). This suggested that the same

$$IrH_2S_2L_2^+ + 3tbe + C_5H_{10} \rightarrow IrCpHL_2^+ + 3tba + 2S \quad (3)$$

$$Ir(ArH)L_2^+ + C_5H_{10} + 2tbe \rightarrow IrCpHL_2^+ + 2tba + ArH \quad (4)$$

reactive system that can be formed directly from 1 is also formed from 2, but less effectively. This shows that the general principle seems to hold but that simple η^6-arene complexes might not be the best choice of labile ligands.

Naphthalene Complexes. We wondered whether naphthalene might be a more suitable leaving group, because the first act of arene departure may be an η^6 to η^4 rearrangement of the arene. In the case of naphthalene, this could be aided by the recovery of benzenoid character in the uncomplexed ring (eq 5).



(5)

For the synthesis of a suitable complex, we first tried the action of 2-vinylnaphthalene with 1. As expected from our experience with styrene (see eq 1), we did indeed obtain the desired $[Ir(NpEt)L_2]A$ (3, NpEt = 2-ethylnaphthalene) but as a mixture of isomers, the iridium being

(1) Crabtree, R. H.; Demou P. C.; Eden, D.; Mihelcic J. M.; Parnell, C.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994.
(2) Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2913.
(3) Crabtree, R. H.; Parnell, C. P. *Organometallics*, in press.

0276-7333/84/2303-1727$01.50/0