after time t, and $X_\infty = 0.215$, we evaluated the rate constant, k, from the expression $\ln [X_\infty/(X_\infty - X)] = kt$.

It is not reasonable to expect a rate law of pure type for such a nondescript substance as coal, but a pseudo-first-order treatment fits the data reasonably well as shown in Figure 1. The value of X_∞ is not available from stoichiometry and must be determined by experiment. At 10 half-lives the values are 0.265 for coal sample A at 344 °C, 0.260 for coal sample B at 335 °C, and 0.268 for coal sample B with deuterated tetralin at 335 °C. Pseudounimolecular rate constants are shown in Table II.

Evaluation of Activation Volume. The activation volume, ΔV^*, is obtained from a plot of ln k vs. P according to eq 1. Figure

$$-RT(\delta \ln k/\delta P)_T = \Delta V^* \quad (1)$$

2 presents the results for the reaction of thymoquinone with tetralin at 175 °C.

Fortunately, it is possible to obtain a meaningful ΔV^* even though the rate law for the reaction is unknown. Figure 3 pertains to the procedure applied to the reaction of coal sample A with tetralin. Let the integrated form of the unknown rate law be represented as $F(X) = kt$. On the assumption that only k is a function of P, the pressure effect (k_P/k_0 = ratio of rate constants at high and low pressure) at constant X is equal to t_0/t_P. We than use the relation shown in eq 2. Some values of k_P/k_0 obtained

$$-RT(\ln k_P/k^0)\Delta P = \Delta V^* \quad (2)$$

graphically from smooth lines drawn through the measured points are 1.68 ($X = 0.09$), 1.62 ($X = 0.10$), 1.58 ($X = 0.12$), and 1.50 ($X = 0.14$). Substitution in the preceding equation gives $\Delta V^* = -26.7 \pm 2.0$ mL.

Apparent Activation Energy. Values of the pseudo-first-order rate constant for the reaction of coal sample B with tetralin at autogenic pressure in reciprocal hours are 0.058 at 310 °C, 0.212 at 335 °C, and 0.369 at 345 °C. A graph of ln k vs. $1/T$ gives $\Delta E^* = 38$ kcal (160 kJ) as shown in Figure 4.

Acknowledgment. This work was supported by U.S. Department of the Interior (Grant G-5104024).

Registry No. Tetralin, 119-64-2; thymoquinone, 490-91-5.

Further Studies of Substitution Reactions of Stannyl and Germyl Anionoids with Alkyl Bromides. Rearrangement of the 6-Hepten-2-yl Moiety[1]

William Kitching,* Henry A. Olszowy, and Karen Harvey

Department of Chemistry, University of Queensland, St. Lucia, Australia 4067

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The stereochemical outcomes of reactions of (trimethyltin)lithium, (dimethylphenyltin)lithium, (methyldiphenyltin)lithium, and (triphenyltin)lithium in tetrahydrofuran with *trans*- and *cis*-2-, 3-, and 4-methylcyclohexyl bromides have been determined on the basis of ^{1}H and ^{13}C NMR spectroscopy. The $(C_6H_5)_3SnLi$ reactions proceed stereospecifically with inversion at carbon, while the $(CH_3)_3SnLi$ reactions are nonstereospecific, as observed previously in some other systems. *cis*- and *trans*-2-methoxybromocyclohexanes and -cyclopentanes were also reacted with $(CH_3)_3SnLi$, and low yields of (2-methoxycyclohexyl)- and (2-methoxycyclopentyl)trimethylstannanes were isolated. On the basis of ^{13}C NMR spectra and deoxystannylation reactions, the former is largely (~90%) trans while the latter is exclusively trans. The pronounced stereochemical distinction between reactions of $(CH_3)_3SnLi$ and $(C_6H_5)_3SnLi$ with cyclohexyl bromides is not observed in corresponding reactions of $(CH_3)_3GeLi$ and $(C_6H_5)_3GeLi$; both are nonspecific. Certain reactions of cyclopropylcarbinyl bromide and 6-bromo-1-hexene with R_3SnLi and R_3GeLi (R = CH_3 or C_6H_5) were also studied. Rearranged product (allylcarbinyl) was observed in the reaction of cyclopropylcarbinyl bromide with $(CH_3)_3SnLi$, but cyclopentylmethyl products (from cyclization of any hex-5-enyl free radical) was not observed in any case. However, with the secondary 6-bromo-1-heptene all reagents studied (with the exception of $(C_6H_5)_3SnLi$) afforded rearranged (2-methylcyclopentyl)methyl products, consistent with the intervention of the free radical, which cyclizes rapidly. Some further estimates of the conformational A values of R_3Ge and R_3Sn are reported, and the triphenyl derivatives have significantly larger values.

The reactions of alkyl bromides with triorganotin or germylalkali reagents are useful for synthesis of the tetraorganometallics, e.g., eq 1. The stereochemical and other

$$RBr + R'_3SnM \rightarrow R'_3SnR + MBr \quad (1)$$

mechanistic aspects of this subtitution have received scrutiny,[2] and the general conclusions seem to be that for primary R groups, a predominantly direct (S_N2) displacement component (perhaps including some geminate process) is involved with $(CH_3)_3SnM$, but with secondary bromides, a configurationally unstable carbon-centered species is important. Triphenyltin alkalis, with secondary bromides,[1,3] exhibit predominantly stereochemical inversion at carbon whereas limited examination of the reactions of $(CH_3)_3GeLi$ with secondary bromides demonstrates substantial stereoleakage.[4] (Solvent and counterion effects of considerable importance can be superimposed in some systems.)[5] The reactions of certain alkylcyclohexyl bromides with $(CH_3)_3SnM$ provide product distributions consistent with the intervention of alkylcyclohexyl free radicals although other processes, e.g., carbanionic in nature, were not completely dismissed.[4,6] More recently,

(1) Some of this work has been published in preliminary form: Kitching, W.; Olszowy, H. A.; Harvey, K. *J. Org. Chem.* **1981**, *46*, 2423.
(2) Key references are contained in: Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833.
(3) Jensen, F. R.; Davis, D. D. *J. Am. Chem. Soc.* **1971**, *93*, 4047.
(4) Kitching, W.; Olszowy, H.; Waugh, J.; Doddrell, D. *J. Org. Chem.* **1978**, *43*, 898.
(5) See, for example: Kuivila, H. G.; Considine, J. L.; Kennedy, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 7206.
(6) San Fillipo, J.; Silberman, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.

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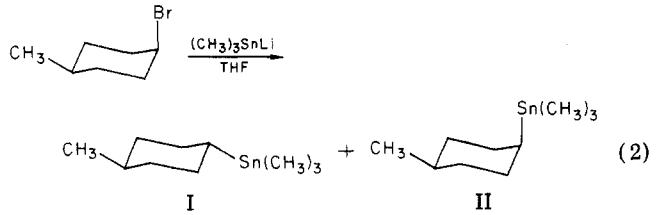
Kuivila and Smith[2] have employed dicyclohexylphosphine as a free-radical trap and *tert*-butylamine as an anion trap and demonstrated that the cyclohexyl bromide/$(CH_3)_3SnNa$ (THF) system involves very largely electron-transfer processes. For example, at the highest phosphine/Sn ratio employed (8.81) cyclohexane was the only product observed, and hence direct displacement or germinate processes are negligible. A complete mechanistic dissection of the reactions of $(CH_3)_3SnNa$ with alkyl halides has been provided by Kuivila.[2]

At the time Kuivila and Smith were utilizing their trapping techniques for radicals and anion intervention in alkyl halide–(trimethyltin)sodium reactions, we were continuing our stereochemical studies with additional alkyl and methoxycyclohexyl bromides and subjecting $(C_6H_5)_3SnLi$ (THF) to examination, as it appeared to react with alkyl bromides in a stereocontrolled fashion. After demonstrating the strict inversion of configuration at carbon that accompanies the reactions of $(C_6H_5)_3SnLi$ with the cyclohexyl bromides, we also studied the "mixed" reagents $(CH_3)_2(C_6H_5)SnLi$ and $CH_3(C_6H_5)_2SnLi$ to establish what level of methylation at tin was necessary to induce electron-transfer processes. We also endeavored to provide chemical evidence (rearrangements) for free-radical intervention from studies with 6-bromo-1-hexene [1,7] and the secondary 6-bromo-1-heptene.[1] The germyllithium reagents $(CH_3)_3GeLi$ and $(C_6H_5)_3GeLi$ have been utilized in reactions with various alkyl bromides, and product stereochemistry and rearrangements were established. Finally, ^{13}C NMR examination of some of the cyclohexyltin and germanium compounds acquired in this work provides additional insights into the conformational preferences of some metal groups.

Results

(a) $(CH_3)_3SnLi$ Reactions with Cyclohexyl Bromides. Previously we had reported that the reaction of *cis*-4-methylcyclohexyl bromide with $(CH_3)_3SnLi$ (THF solvent) produced a ca. 2:1 I/II mixture of the *trans*- and *cis*-stannanes[4] (eq 2).

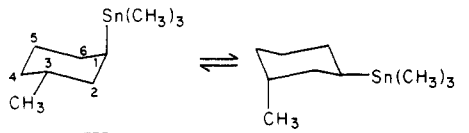


I II (2)

To make this aspect of our study complete, we have also examined the corresponding reactions with *trans*-4-methylcyclohexyl bromide, as well as with the cis, trans pairs of the 2- and 3-methylcyclohexyl bromides. *cis*-4-Methyl-, *trans*-3-methyl-, and *cis*-2-methylcyclohexyl bromides are the predominant (>90%, ^1H and ^{13}C NMR) isomers resulting from the triphenylphosphine–bromine procedure for transforming the alcohols. Capillary VPC examination of the bromide obtained from 4-methyl cyclohexanol (70:30 trans/cis) by this procedure indicated a minor proportion (~2–5%) of another isomer (suspected to be *trans*-3-methylcyclohexyl bromide). The *trans*-4-methyl-, *cis*-3-methyl-, and *trans*-2-methylcyclohexyl bromides were obtained by application of the procedure developed by Jensen.[8] This involves formation (via the Grignard reagent) of the appropriate (methylcyclohexyl)mercuric bromides, the cis and trans isomers of which can be separated by fractional crystallization. The predominant (*trans*-4-, *cis*-3-, and *trans*-2-methylcyclohexyl)mercuric bromides are least soluble, and on aerobic cleavage by bromine in pyridine (retention at carbon)[8] provide the corresponding *trans*-4-, *cis*-3-, and *trans*-2-methylcyclohexyl bromides in good yield.

Reaction of *trans*-4-methylcyclohexyl bromide with $(CH_3)_3SnLi$ in THF in the normal way provided a mixture of the isomeric *trans*- and *cis*-(4-methylcyclohexyl)trimethyl stannanes. On the basis of ^{13}C and ^1H NMR analyses, the ratio of stannane isomers was essentially identical with that found for the reaction of the *cis*-bromide, viz., 70:30 trans/cis. This predominance of the thermodynamically more stable stannane isomer applies for the 3- and 2-methylcyclohexyl bromide reactions. Thus in the 3-series, the ratio of cis/trans is ca. 80:20, and in the 2-series, trans/cis is 90:10, irrespective of the starting bromide isomer.

Previously we discussed in detail the ^1H and ^{13}C NMR characteristics of the isomeric (4-methylcyclohexyl)trimethylstannanes,[4] and similar considerations allow definite identification of the *cis*- and *trans*-(2- and 3-methylcyclohexyl)stannane isomers. A full listing of ^{13}C parameters is located in Table VI (supplmentary material), but the important features are the following. In (diequatorial) *cis*-3-methylcyclohexylstannane, ^{13}C chemical shifts of −12.04 and 23.00 ppm are appropriate for equatorial $SnCH_3$ and C-CH_3, and the presence of two large vicinal couplings between $^{117,119}Sn$ and C_3 and C_5 of 63.6 and 70.7 Hz confirms this.[9,10] In the conformationally inhomogeneous trans-3 isomer, a δ_{CH_3Sn} of −9.99 and δ_{CH_3C} of 21.73 are appropriate for comparable populations of the two conformers III and IV (eq 3). (The *A* values of CH_3 and



III IV (3)

$Sn(CH_3)_3$ are 1.74 and ca. 1.00 kcal/mol, respectively.)[9,11,12] A much reduced vicinal coupling from $^{119,117}Sn$ to C_3 and C_5 is now expected[10] (reduced average dihedral angle), and values of ~24 (C_3) and 26.3 Hz (C_5) are observed and parallel our observations in the 4-methyl series. Close agreement between observed and calculated ^{13}C shifts is observed on the basis of additivity of substituent effects in these systems. The ^1H NMR data are concordant with equatorial $Sn(CH_3)_3$ resonating at higher field. In the 2-methyl system, large vicinal couplings (from $^{117,119}Sn$) of ca. 57 and 66 Hz to C_3 and C_5 confirm the trans isomer as being predominant, and all other details of the ^{13}C and ^1H spectra are completely consistent with the 90:10 trans/cis distribution.

cis-2-Methylcyclopentyl bromide (from reeaction of the trans alcohol with phosphorous tribromide) was also reacted with $(CH_3)_3SnLi$, and a 91:9 mixture of the (2-methylcyclopentyl)trimethylstannanes was formed. In the ^{13}C NMR spectrum of the major isomer, vicinal couplings of 7.3 Hz (CCH_3) and 57.38 (C_4) (to vicinal ring carbon)

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(8) Jensen, F. R., Gale, L. H., *J. Am. Chem. Soc.* **1960**, *82*, 145, 148.
(9) Kitching, W.; Doddrell, D.; Grutzner, J. B. *J. Organomet. Chem.* **1976**, *107*, C5.
(10) Doddrell, D.; Burfitt, I.; Kitching, W., Bullpitt, M.; Lee, C.; Mynott, C. J.; Considine, J. L.; Kuivila, H. G.; Sarina, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1640.
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Table I

$$RBr + (CH_3)_{3-x}(C_6H_5)_xMLi \xrightarrow[15\ ^\circ C]{solvent} RM(CH_3)_{3-x}(C_6H_5)_x$$

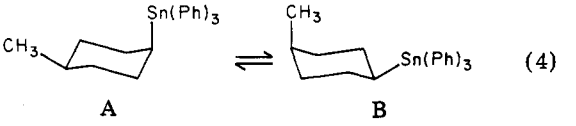
entry	R[a] in RBr	M	x	solvent	R[a] (in product) trans/cis ratio	% yield[e]	product bp, °C (mm)
1	*trans*-4-methylcyclohexyl	Sn	0	THF	68:32	46	63 (4)
2[b]	*cis*-4-methylcyclohexyl	Sn	0	THF	70:30	35	57-59 (3)
3	*trans*-3-methylcyclohexyl (90% trans)	Sn	0	THF	24:76	38	75 (5)
4	*cis*-3-methylcyclohexyl (85% cis)	Sn	0	THF	33:67	80	63 (5)
5	*trans*-2-methylcyclohexyl (87% trans)	Sn	0	THF	85:15	50	68 (4)
6	*cis*-2-methylcyclohexyl	Sn	0	THF	90:10	14	77-78 (5)
7	*trans*-4-methylcyclohexyl	Sn	3	THF	<5:>95	69	73.5[f]
8	*cis*-4-methylcyclohexyl	Sn	3	THF	>95:<5	25	71.5[f]
9	*trans*-3-methylcyclohexyl	Sn	3	THF	<5:>95	60	66[f]
10[c]	*trans*-2-methoxycyclohexyl	Sn	0	THF	92:8	15	62 (0.4)
11[c]	*cis*-2-methoxycyclohexyl	Sn	0	THF	85:15	<5	80 (1.5)
12[c]	*trans*-2-methoxycyclopentyl	Sn	0	THF	100:0	5	79 (8)
13[c]	*cis*-methoxycyclopentyl	Sn	0	THF	100:0	5	80 (8)
14[d]	*cis*-2-methylcyclopentyl	Sn	0	THF	91:9	40	50 (5)
15	*trans*-4-methylcyclohexyl	Ge	0	HMPA	27:73	~50	~90 (30)
16	*cis*-4-methylcyclohexyl	Ge	0	HMPA	30:70	~50	~90 (30)
17	*trans*-4-methylcyclohexyl	Ge	3	THF	34:66	75	[g]
18	*cis*-4-methylcyclohexyl	Ge	3	THF	45:55	75	[g]
19	*trans*-4-methylcyclohexyl	Sn	1	THF	68:32	75	[g]
20	*cis*-4-methylcyclohexyl	Sn	1	THF	81:19	68	122 (1)
21	*trans*-4-methylcyclohexyl	Sn	2	THF	66:34	56	[g]
22	*cis*-4-methylcyclohexyl	Sn	2	THF	88:12	55	[g]
23	*trans*-2-methylcyclopentyl tosylate	Sn	0	THF	0:100	41	52 (5)

[a] Based on ^1H and ^{13}CNMR examination. [b] Reaction for HMPA solvent provided a product with a trans/cis ratio of 66:34, in reduced overall yield. [c] Product ratios are based on ^1H and ^{13}C NMR examination and relative rates of deoxystannylation. [d] Stannane product different from the (pure) isomer obtained as in entry 23. [e] Yields refer to isolated (distilled or recrystallized) compound. All new products had satisfactory C and H analyses. [f] Melting point. [g] Viscous oil.

were observed, while corresponding couplings of 36.6 and 44.0 Hz were identified for the minor isomer. On the basis of reasonable conformations for these isomers and the relationship between $^3J_{^{119}Sn-^{13}C}$ and the dihedral angle,[10] the major one was concluded to be trans. This was confirmed by the identity of the minor isomer with the stannane obtained from the reaction of *trans*-2-methylcyclopentyl tosylate with $(CH_3)_3SnLi$, a reaction established[4,13] as proceeding with inversion of configuration with various alkylcycloalkyl tosylates.

(b) (Triphenyltin)lithium Reactions with Cyclohexyl Bromides. The spectroscopic characteristics of the $(CH_3)_3Sn$ group are extremely valuable from a diagnostic viewpoint, and, of course, this aspect is lacking in the triphenyltin derivatives. Nevertheless, vicinal $^{119,117}Sn-^{13}C$ coupling and chemical shifts of CCH_3 are quite adequate for assignment purposes. We first prepared and examined cyclohexyltriphenylstannane so as to provide a measure of the various coupling constants and substitutent chemical shifts of the largely *equatorial* $(C_6H_5)_3Sn$ group. [The *A* value of $Sn(C_6H_5)_3$ is ~1.4 kcal/mol (see later)]. A vicinal coupling of 65.7 Hz (to C_3, C_5) was measured, and α, β, and γ effects of ca. 0.98 4.81, and 1.95 ppm were calculated.

Reaction of *cis*-4-methylcyclohexyl bromide with $(C_6H_5)_3SnLi$ (THF solvent) provided essentially one isomer of (4-methylcyclohexyl)triphenylstannane on the basis of ^1H and ^{13}C spectra. This isomer (mp 73.5 °C) was shown to be trans by the ^{13}C shift of the CCH_3 (23.12 ppm) and the large *vicinal* coupling of 73.3 Hz. Calculated shifts, based on SCS values for equatorial CH_3 and $Sn(C_6H_5)_3$, were in close agreement with those observed. *trans*-4-Methylcyclohexyl bromide (>99%), on reaction with $(C_6H_5)_3SnLi$, provided the other isomer (mp 71.5 °C) having a CCH_3 shift of 21.22 ppm and a vicinal ($^{119}Sn-^{13}C$) coupling of 30.0 Hz. As outlined previously, the cis isomer must be treated as conformationally inhomogeneous but with an anticipated slight preference for structure A.



A B (4)

Conformation B, with an axial CCH_3 is responsible for the higher field position of this resonance (21.22 ppm) compared with that in the diequatorial trans isomer. In addition, A is responsible for the reduced "average" vicinal $^{119}Sn-^{13}C$ coupling constant.

The above specificities in the 4-methyl series apply also with *trans*-3-methylcyclohexyl bromide. Reaction in the normal way provided a (3-methylcyclohexyl)trimethylstannane (mp 66 °C) which on the basis of its CCH_3 resonance (22.90 ppm) and vicinal couplings to ^{119}Sn [68.4 (C_3) and 72 Hz (C_5)] has both substituents equatorial. The product is thus *cis*-(3-methylcyclohexyl)triphenylstannane.

(c) (Diphenylmethyltin)- and (Phenyldimethyltin)lithium Reactions with Cyclohexyl Bromide. The "mixed" tinlithium reagents were prepared in the usual way (THF solvent), and each was reacted with both *cis*- and *trans*-4-methylcyclohexyl)bromides. The configurations of the stannane isomers were established very largely on the basis of ^{13}C chemical shifts and $^{119}Sn-^{13}C$ couplings as detailed previously. The isomer ratios are listed in Table I.

As indicated in Table I, the lithio reagent prepared from analytically pure dimethylphenyltin chloride behavied straightforwardly with *cis*- and *trans*-4-methylcyclohexyl bromides. However, the use of dimethylphenyltin chloride, contaminated with biphenyl, produced a more complex product mixture. In particular, (4-methylcyclohexyl)trimethylstannanes were formed in substantial amounts, requiring some redistribution of the organic groups on tin. This was supported by the product mixture obtained when

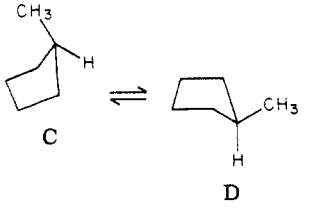
(13) Koermer, G. S.; Hall, M. L.; Traylor, T. G. *J. Am. Chem. Soc.* **1972**, *94*, 7206.

the "contaminated" tin–lithium reagent was reacted with methyl iodide. Tetramethyltin (~33%), trimethylphenyltin (50%), and diphenyldimethyltin (~17%) were observed. We consider it likely that biphenyl contamination as well as the time interval between preparation and addition of the alkyl bromide to these unsymmetrical tin–lithium reagents may be important factors as well as significant dissociation in the sence $C_6H_5(CH_3)_2SnLi \rightleftharpoons C_6H_5Li + (CH_3)_2Sn$ etc. The reactions of the unsymmetrical diphenylmethyltin chloride showed no waywardness and were known to be free of biphenyl. These aspects and the importance of distannylenes in the reactions of sterically congested R_3SnLi reagents are receiving further scrutiny.[25]

(d) Reactions of (Trimethyltin)lithium with 2-Methoxycycloalkyl Bromides. *trans*-2-Methoxycyclohexyl bromide, on reaction with ca. 2 molar equiv of $(CH_3)_3SnLi$, provided substantial amounts of cyclohexene and $(CH_3)_6Sn_2$ together with a low yield (~15% after distillation) of (2-methyoxycyclohexyl)trimethylstannane. On the basis of ^1H NMR intensities of CH_3Sn signals at 0.02 and 0.04 ppm and methoxyl signals at 3.29 and 3.48 ppm, an isomeric ratio of ca. 92:8 was indicated. The major isomer was identified as being trans on the basis of (a) its facile deoxystannylation[14,15] resulting from addition of acetic acid to a $CDCl_3$ solution and (b) its ^{13}C spectrum which exhibited two large vicinal couplings to ^{119}Sn and other appropriate shifts, in particular $\delta(SnCH_3)$ at −10.79 ppm. The minor isomer, resistant to deoxystannylation under the above conditions, showed $\delta(CH_3Sn)$ at −9.38 ppm and $\delta(OCH_3)$ at 57.17 ppm. Although this cis isomer is conformationally inhomogeneous, an estimate of shifts could be made and were in satisfactory agreement with those observed. In the ^1H spectrum, the major H–C–OCH_3 resonance at δ 3.06 clearly exhibited two large couplings (~12 Hz) as appropriate for the trans isomer, and this signal appeared at higher field than the narrower analogous signal (δ 4.06) in the cis isomer.

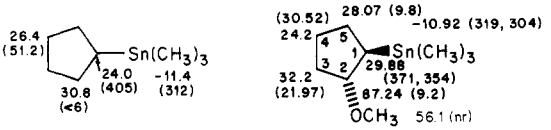
cis-2-Methoxycyclohexyl bromide appeared to be unreported, and we prepared it by reduction of 2-bromocyclohexanone with lithium aluminum hydride (which provided largely *cis*-2-bromocyclohexanol) followed by several treatments with diazomethane ($BF_3{\cdot}Et_2O$ catalysis). This bromide (94% cis) on reaction with $(CH_3)_3SnLi$ led, in low yield, to a mixture of the stannanes judged to have a trans/cis ratio of 85/15.

trans-2-Methoxycyclopentyl bromide (~100%) with $(CH_3)_3SnLi$ (2 equiv) provided a moderate yield (~30%) of (2-methoxycyclopentyl)trimethylstannane which was isomerically pure (prior to distillation) as judged from ^1H and ^{13}C NMR spectra. Understanding of the effects of substituents on the ^{13}C spectra of cyclopentanes is not extensive, and the steep potential wells associated with cyclohexyl conformations are generally lacking in cyclopentanes, but the free pseudorotation of cyclopentane itself can be arrested by a group such as methyl which largely restricts the process to those conformations in which the group is pseudoequatorial (D).[16] The energy difference



C ⇌ D (5)

between these envelope conformations is estimated to be ~0.50 kcal/mol,[17] much less than the corresponding value in methyl cyclohexane (1.74 kcal/mol). We had anticipated that comparisons of vicinal $^{119,117}Sn–^{13}C$ couplings in cyclopentyl derivatives may have been useful, and some data are shown below (δ values with couplings given in hertz in parentheses).



The relatively large coupling (51.2 Hz) for cyclopentyltrimethylstannane is consistent with an equatorial $Sn(CH_3)_3$ in the envelope conformation (see D). In the 2-methoxy relative, vicinal couplings are now significantly smaller (30.52 and 21.97 Hz), but the reduction to C_3 (adjacent to methoxy) has precedent in (methoxycyclohexyl)stannanes[4] and mercurials.[18,19] However, the reduction to C_4, perhaps partly associated with the electron-donating effect of methoxy, strongly suggests the importance of additional conformers in the 2-methoxy stannane with an overall reduction in the average dihedral angle. Further studies on metallo derivatives of cyclopentane might prove informative, as the large metal couplings are easily measured and are sensitive to conformational changes. This is particularly so as vicinal $^1H–^1H$ couplings and low temperature (limiting) spectra do not have the simple applicability in cyclopentanes as they do in cyclohexanes.[16]

The trans nature of this (2-methoxycyclopentyl)trimethylstannane was confirmed by its efficient deoxystannylation (acetic acid in $CDCl_3$).[14,15] Previously Kreevoy[20] had demonstrated that *cis*- and *trans*-2-methoxycyclopentylmercurials exhibited quite different rates of deoxymercuration and in fact have been used (below) to selectively destroy the trans isomer in admixture with the cis.

cis-2-Methoxycyclopentyl bromide was obtained by bromine cleavage of *cis*-(2-methoxycyclopentyl)mercuric chloride, in turn acquired by acid-catalyzed equilibration of the readily obtained trans mercurial and selective (HCl) destruction of the residual trans mercurial. Reaction of $(CH_3)_3SnLi$ with this (100%) cis bromide provided an isomerically pure product, identical on the basis of ^1H NMR and deoxystannylation with that described above. Hence both *cis*- and *trans*-2-methoxycyclopentyl bromides afford only *trans*-(2-methoxycyclopentyl)trimethylstannane, together with elimination product.

(e) Reaction of $(CH_3)_3GeLi$ with *trans*-4-Methylcyclohexyl Bromide. Previously we reported that *cis*-4-methylcyclohexyl bromide reacted with $(CH_3)_3GeLi$ (HMPA solvent) to yield predominantly (~70%) *cis*-(4-methylcyclohexyl)trimethylgermane,[4] in contrast to the reaction with $(CH_3)_3SnLi$ which yielded predominantly trans product. To complete the stereochemical picture, we now report that the *trans*-4-methylcyclohexyl bromide, with $(CH_3)_3GeLi$ also provides the predominantly cis (~73:27) germane, on the basis of intensities of $(CH_3)_3Ge$ and

(14) Fish, R. H.; Broline, B. M. *J. Organomet. Chem.* **1978**, *159*, 255.
(15) Davis, D. .; Jacocks, H. M. *J. Organomet. Chem.* **1981**, *206*, 33.
(16) Lipnick, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 2941 and references therein.
(17) Pitzer, K. S.; Donath, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 3213.
(18) Kitching, W.; Praeger, D.; Doddrell, D.; Anet, F. A. L.; Krane, J. *Tetrahedron Lett.* **1975**, 759.
(19) Kitching, W.; Atkins, A. A.; Wickham. G.; Alberts, V. *J. Org. Chem.* **1981**, *46*, 563.
(20) Kreevoy, M. M.; Gilje, J. W.; Ditsch, L. T.; Batorewics, W.; Turner, M. A. *J. Org. Chem.* **1962**, *27*, 726.

CCH_3 in both the ^{13}C and ^1H spectra, which were described in detail in our previous report.[4] Thus either bromide affords essentially the same cis/trans mixture of germane isomers.

(f) Reaction of $(C_6H_5)_3GeLi$ with *cis*- and *trans*-4-Methylcyclohexyl Bromide. An isomeric mixture of *cis*- and *trans*-(4-methylcyclohexyl)triphenylgermanes (together with hexaphenyldigermane) was obtained from the cis bromide, and from the ^{13}C and ^1H spectra (CH_3 doublets overlapping at δ 0.86 and 0.88 with the latter more intense) it was clear that the cis isomer predominated slightly (~55%) over the trans (~45%). Of interest are the ^{13}C shifts of the CCH_3 signals at 23.02 (trans) and 18.18 ppm in the cis isomer. This latter shift is significantly to higher field of the CCH_3 signal in *cis*-(4-methylcyclohexyl)trimethylgermane (19.62 ppm) and indicates the *A* value of $(C_6H_5)_3Ge$ to be significantly larger than that for $(CH_3)_3Ge$ (~2.02–2.1 kcal/mol). Similarly, the CCH_3 shifts of 21.22 and 22.00 ppm for the *cis*-4-(methylcyclohexyl)triphenyl- and -trimethylstannanes, respectively, confirm $Sn(C_6H_5)_3$ to have a larger *A* value than $Sn(CH_3)_3$ (see later).

Reaction with the trans bromide was similar except that the product germane was now a 34:66 trans/cis mixture. The full listing of isomer distributions found for reactions of the various metalloidal alkalis with cycloalkylbromides is assembled in Table I.

(g) Reactions of $(CH_3)_3SnLi$ with Cyclopropylcarbinyl Bromide. After commencing our program utilizing the above bromide as a mechanistic probe for free-radical involvement in these substitutions, a paper appeared describing the reactions of several metalate anions with this bromide. San Filippo and co-workers reported[6] that the allylcarbinylstannane/cyclopropylcarbinylstannane ratio was 17:83 for $(CH_3)_3SnLi$ in THF at 0 °C. This ratio was found to be a function of the temperature, gegenion, etc., and rearrangement was found to be more important for the iodide. Our less extensive studies[21] (curtailed after the appearance of San Filippo's report) confirm the presence of rearranged product (^1H NMR) but differ somewhat from the distribution reported, in that rearranged product was predominant and in one experiment was almost exclusive. The reasons for these differences have not been explored, but Kuivila has this system under study, and anion involvement in some cases is established.[2]

(h) Reactions of $(C_6H_5)_3SnLi$ with Cyclopropylcarbinyl Bromide. This procedure yielded unrearranged (cyclopropylcarbinyl)triphenylstannane, isolated as a crystalline solid (mp 46–47 °C) and characterized by its ^1H NMR spectra which exhibited a typical cyclopropylcarbinyl pattern with major resonances at δ 0.22 (2 H), 0.61 (2 H), and 1.09 (1 H) and a clean doublet ($J \approx 6.5$ Hz) at 1.65 (2 H), coupled to ^{119}Sn ($J \approx 55$ Hz). The ^{13}C spectrum showed only high-field resonances at 8.76 (41.6 Hz, $C_{3,4}$), 8.89 (C_2), and 17.25 ppm (C_1) (J = 393.0 and 376.4 Hz to $^{119,117}Sn$). That no rearranged allylcarbinyl isomer was present was confirmed by its synthesis from 4-bromo-1-butene and $(C_6H_5)_3SnLi$. This material (mp 112.7 °C) showed the expected features for a terminal vinyl group (CH_2=CH) in its ^1H [δ 4.95 (2 H) and 5.87 (1 H)] and ^{13}C (113.82 and 141.15 ppm) NMR spectra. Other spectral features were wholly concordant with the (allylcarbinyl)-triphenylstannane structure.

(i) Reactions with 6-Bromo-1-hexene. Detection of products with the rearranged cyclopentylmethyl skeleton (see discussion) would constitute prima facie evidence for the intermediacy of the free hex-5-enyl radical. To characterize the anticipated rearrangement products spectroscopically, we synthesized both (cyclopentylmethyltriphenyl- and -trimethylstannanes, the former from cyclopentylmethyl bromide and $(C_6H_5)_3SnLi$ and the latter from the tosylate with $(CH_3)_3SnLi$. In the ^1H NMR spectra, these compounds exhibit a high-field doublet ($J \approx 7$–8 Hz) for $CH_2Sn(CH_3)_3$ (δ 0.94) and $CH_2Sn(C_6H_5)_3$ (δ 1.71) and lack vinylic absorption. The expected pattern of shifts appears in the ^{13}C spectra.

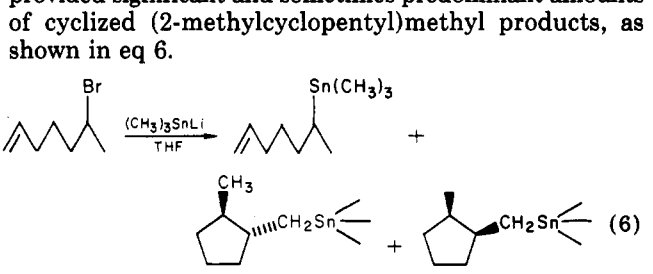
Reaction of 6-bromo-1-hexene with $(C_6H_5)_3SnLi$, utilizing THF as the solvent, provided a viscous oil, which did not crystallize but analysis of which corresponded satisfactorily to $(C_6H_5)_3SnC_6H_{11}$. ^1H NMR established the structure as unrearranged 1-hexenylstannane. Thus the pattern for a terminal vinyl group at δ 5.77 (1 H) and 4.93 (2 H) together with higher field absorption from δ 1.13 to 2.13 (8 H) are appropriate. The ^{13}C spectrum was concordant and in particular exhibited vinyl signals at 139.04 (CH_2=CH) and 114.33 ppm (CH_2=) together with four high-field signals. An unchanged outcome was observed when HMPA was substituted for THF.

Similarly, reaction of 6-bromo-1-hexene with $(CH_3)_3SnLi$, utilizing both THF and HMPA as solvents and direct NMR examination of the total (crude) product, provided only unrearranged (1-hexenyl)trimethylstannane. Distilled material showed ^1H absorptions (CCl_4) centered at δ 5.75 (1 H), 5.00 (2 H), 2.12 (2 H), 1.50 (4 H), 0.88 (2 H), and 0.08 (9 H, $Sn(CH_3)_3$). ^{13}C shifts at 114.14 (CH_2=) and 139.03 ppm (CH_2=CH) (with higher field signals) confirm this conclusion.

Reactions of 6-bromo-1-hexene with $(CH_3)_3GeLi$ and $(C_6H_5)_3GeLi$ were also conducted, and the oils obtained from these reactions were very largely (analyses and NMR spectra) the germane product, which, on the basis of the NMR data outlined above, were essentially exclusively unrearranged 1-hexenyl in nature. On one occasion, when a small amount of naphthalene was used to initiate the formation of $(C_6H_5)_3GeLi$ (from $(C_6H_5)_6Ge_2$) in THF, minor (~5%) ^{13}C signals, completely consistent with (cyclopentylmethyl)triphenylgermane, were observed. Repetition of the procedure, without addition of naphthalene, provided unrearranged 1-hexenylgermane only.

Thus, no rearrangement accompanied the reaction of 1-hexenyl bromide with $(CH_3)_3SnLi$, $(C_6H_5)_3SnLi$, $(CH_3)_3GeLi$, or $(C_6H_5)_3GeLi$.

(j) Reactions of 6-Bromo-1-heptene. To provide more meaningful comparisons with the secondary alkylcyclohexylbromide systems, various tin- and germyllithium reagents were reacted with 6-bromo-1-heptene. On the basis of careful ^1H (100 and 270 MHz) and ^{13}C NMR examinations of total product, it was clear that all reagents employed, with the exception of $(C_6H_5)_3SnLi$ (Figure 1) provided significant and sometimes predominant amounts of cyclized (2-methylcyclopentyl)methyl products, as shown in eq 6.



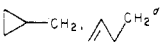
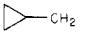
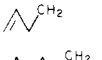
(6)

The ^{13}C spectra were particulary informative (figures 1 and 2) and could be assigned confidently on the basis of the chemical shifts of *cis*- and *trans*-1,2-dimethylcyclopentanes, the substituent effects of the various MR_3 groups

(21) Harvey, K.; M. S. Thesis, University of Queensland, 1981.

Table II

$$RBr + (CH_3)_{3-x}(C_6H_5)_xMLi \xrightarrow[\text{solvent}]{15\ ^\circ C} RM(CH_3)_{3-x}(C_6H_5)_x$$

entry[a]	R (in RBr)	M	x	solvent	R (in product)	% yield	bp, °C (mm)
1		Sn	0	THF		c	78 (50)
2		Sn	3	THF			46-47[e]
3		Sn	3	THF		~80	97-99[e]
4		Sn	0	THF		91	68 (10)
5	b	Sn	3	THF	b	70	f
6	b	Ge	0	HMPA	b	45	79 (42)
7	b	Ge	3	THF	b	78	f

[a] Product ratios were established by ^1H and ^{13}C NMR examination, and yields refer to isolated yields of distilled or crystallized materials. Isomer ratios are derived from examination of (total) crude product. [b] Same as entry 4. [c] See ref 2 and 6. [d] Variable ratios. [e] Melting point. [f] Viscous oil.

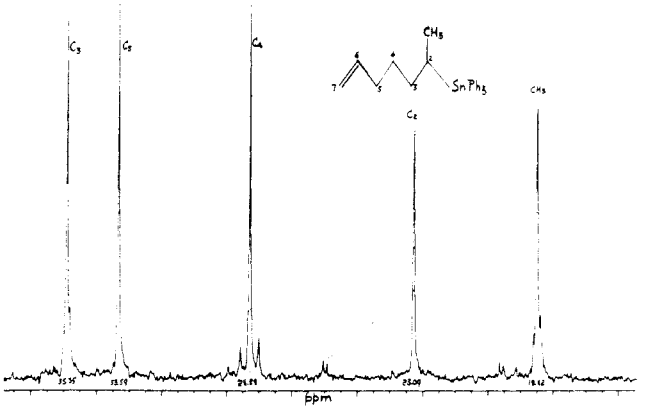
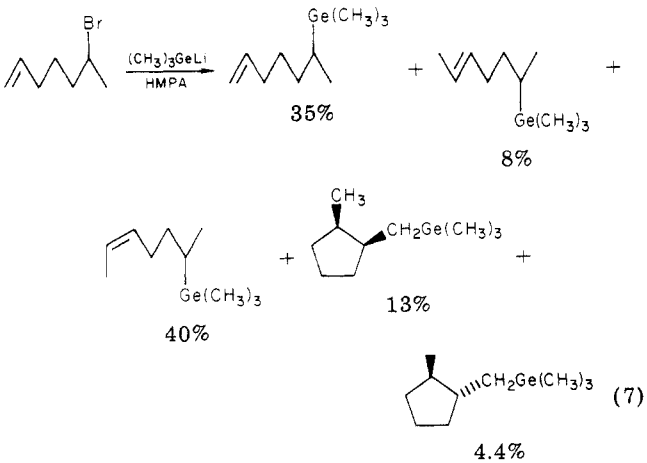


Figure 1. 67.89-MHz (proton-decoupled) carbon-13 spectrum of the triphenyltin compound produced by reacting 6-bromo-1-heptene with (triphenyltin)lithium in tetrahydrofuran. [The signals corresponding to C_6 (139.04 ppm) and C_7 (114.35 ppm) have been omitted]. Signals corresponding to cyclized [(2-methylcyclopentyl)methyl] derivatives are not discernible.

(on chemical shifts), and values of $^{119}Sn-^{13}C$ spin-coupling constants. The chemical shifts for the cis and trans isomers are very characteristic, and it is to be noted that the cis/trans ratio is ~2.7 in all cases. The noncyclized trimethylgermane fraction was a mixture of ca. 35% 6-germyl-1-heptene, 40% *cis*-6-germyl-2-heptene, and 8% *trans*-6-germyl-2-heptene (eq 7).



(7)

This olefin isomerization in the basic HMPA medium is not surprising, and the isomer ratio of ca. 5 (favoring cis) in the 2-heptene product is consistent with carbanion involvement in the double bond shift.[22] Reactions of

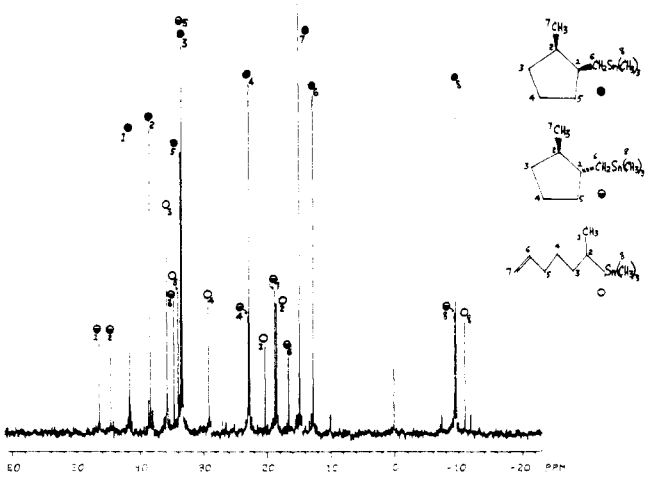


Figure 2. 67.89-MHz (proton-decoupled) carbon-13 spectrum of the trimethyltin compounds produced by reacting 6-bromo-1-heptene with (trimethyltin)lithium in tetrahydrofuran. [The signals corresponding to C_6 (139.03 ppm) and C_7 (114.35 ppm) in the open-chain isomer are not shown.] *cis*-[(2-Methylcyclopentyl)methyl]trimethylstannane is clearly predominant. A full listing of chemical shifts and $^{13}C-^{117,119}Sn$ coupling constants is shown in Table VI (supplementary material).

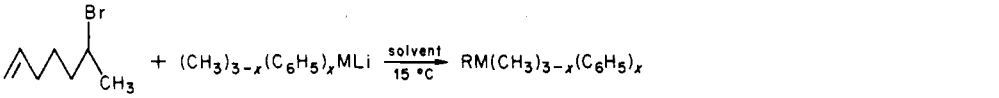
certain (allylic) cycloalkenyl chlorides with germyllithium reagents in HMPA can afford significant amounts of vinyl derivatives.[23] The full listing of results is contained in Tables II and III.

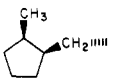
Discussion

The results demonstrate varying stereochemistry attending the formation of carbon–tin or germanium bonds by displacement of bromide by the corresponding metalloidal anions. In the case of $(C_6H_5)_3SnLi$, the outcome as far as we could determine with the various methylcyclohexyl bromides was uniformly inversion of configuration at carbon, a result best accommodated by direct displacement of bromide by a nucleophilic $(C_6H_5)_3SnLi$ species. The high specificities observed indicate a very low level involvement of any intermediate carbon centred species. The complete absence of any rearrangement in the cyclopropylcarbinyl bromide reaction, regarded as being extraordinarily sensitive[6] to free-radical involvement, is persuasive evidence that radial formation and indeed

(22) Schriesheim, A.; Rowe, C. A. *Tetrahedron Lett.* **1962**, *10*, 405.
(23) Wickham, G., research in progress.

Table III



entry[a]	M	x	solvent	rel % yield for R (in product)			total yield, %	bp, °C (mm)
								
1	Sn	0	THF	21	58	21	60	67-69 (5)
2	Sn	1	THF	15	61	24	86	117-120 (1)
3	Sn	2	THF	86	10	4	93	*c*
4	Sn	3	THF	100			83	*c*
5[b]	Ge	0	HMPA	83	13	4.4	52	80-84 (20)
6	Ge	3	THF	68	22.4	9.6	27	*c*
7	Sn	0	HMPA	82	13	5	16	64-68 (5)

[a] See footnote *a* of Table II. [b] The 83% noncyclized produce germane consisted of 35% 6-germyl-1-heptene, 40% *cis*-6-germyl-2-heptene, and 8% *trans*-6-germyl-2-heptene. [c] Viscous oil.

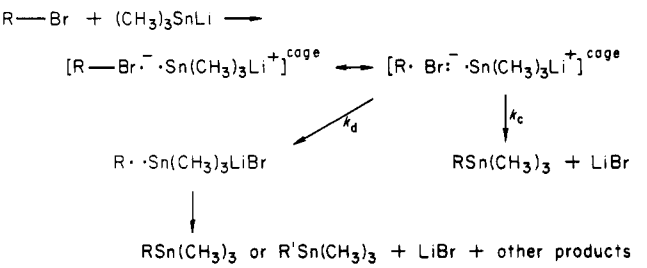
anion formation,[2] from $(C_6H_5)_3SnLi$, are not important. No rearranged products occur in the 6-bromo-1-hexene–$(C_6H_5)_3Sn$ system, in agreement with the report of Newcomb.[7] Evidence from other systems capable of providing stereochemical conclusions largely agrees with our findings for the methylcycohexyl bromides. Jensen and Davis reported[3] that $(C_6H_5)_3SnNa$ (DME solvent) in its reaction with (*S*)-(+)-*sec*-butyl bromide or chloride proceeded with configurational inversion to the extents of 88% and 90%, respectively. Some stereoleakage, however, is indicated, and the different counterion (Na^+) and solvent could reasonably promote an electron-transfer radical process. This is supported by the very recent report[24] that 1-hexenyl bromide on reaction with $(C_6H_5)_3SnK$ (DME solvent) affords ca. 30% of (cyclized) (cyclopentylmethyl)stannane. Fish[14] has established that *trans*-2-methoxycyclohexyl bromide on reaction with $(C_6H_5)_3SnNa$ yields *cis*-(2-methoxycyclohexyl)triphenylstannane. Thus it appears that the reactions of $(C_6H_5)_3SnLi$ (THF solvent) with secondary bromides proceed with a very high level of inversion at carbon, and the S_N2 mechanism, which seems to proceed always with inversion, appears to be the best description. This stereochemical course allows the synthesis of various (methylcyclohexyl)triphenylstannanes, which can be converted into various other derivatives by bromine cleavage of phenyl groups, followed by alkylation.[25] Use of more polar triphenylstannyl alkalis in better cation-solvating solvents [e.g., $(C_6H_5)_3SnK$ in DME] appears to induce significant levels of stereoleakage.[3,24]

The present results extend the information regarding the stereoleakage accompanying $(CH_3)_3SnLi$ reactions with secondary bromides. A carbon-centred intermediate incapable of sustaining the configuration is clearly involved, and careful trapping studies of Kuivila establish the importance of cyclohexyl radicals to the near exclusion of direct displacement or geminate processes.[2] In Scheme I $(CH_3)_3SnLi$ has been represented for simplicity as a monomer, although in reality it is probably a cluster arrangement (cf. alkyllithiums) the structure of which is solvent dependent. [The presumed cluster $((CH_3)_3SnLi)_n$ may also be a source of $(CH_3)_3Sn\cdot$ in the final product step.] According to this scheme, rearranged product would be associated with the k_d step, as geminate combination (k_c) would be faster.

San Filippo et al. concluded from their studies with 4-*tert*-butylcyclohexyl bromides that two competing reaction pathways were involved, viz., a free-radical route in addition to a stereospecific one (at low temperatures), although some prospect of the operation of a "carbanion mechanism" was entertained.[6] The dominance of the thermodynamically more stable products in the reactions with the 2-, 3-, and 4-alkylcyclohexyl bromides could be regarded as being consistent with extensive "product development" in the transition state for formation of the C–$Sn(CH_3)_3$ bond. The species providing the $(CH_3)_3Sn$ group is not clear but could be a sterically large aggregated assembly. Nevertheless, the predominance (up to 70%) of trans product in the abstraction step of a presumed 4-methylcyclohexyl radical is exceptional when compared with product ratios established for various reactions of this radical.[26] The distributions either favor cis product by significant amounts (~70%) or are close to statistical. It is true that these $(CH_3)_3Sn$ species offer few meaningful comparisons with donor groups previously studied, but comparisons with the $(CH_3)_3Ge$ system would seem to be in order. Support for an important contribution from a free (noncaged) radical route was based on the observation of rearranged allylcarbinyl product from the cyclopropylcarbinyl precursor. Our limited studies confirm this rearrangement, but involvement of the anion, known to undergo facile ring opening, also cannot be absolutely excluded. In fact, recent evidence[2] strongly supports its involvement. We regard the cyclopropylcarbinyl halide system as being a somewhat ambiguous probe for radical involvement in organometal anion reactions.[27]

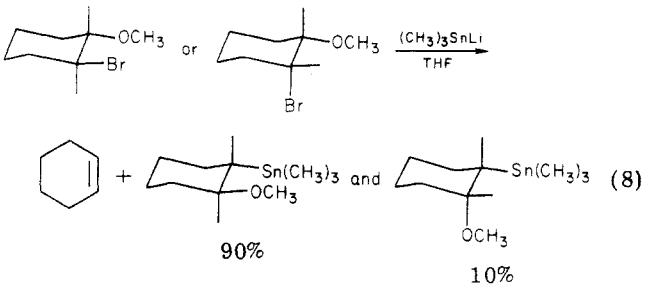
It seemed to us that examination of 2-methoxycyclohexyl bromides would be instructive from the viewpoint of possible carbanion involvement. Both *cis*- and *trans*-2-methoxycyclohexyl bromides lead predominantly to cy-

Scheme I. Electron Transfer



(24) Corriu, R. J. P., Guerin, C. *J. Organomet. Chem.* **1980**, *197*, C19.
(25) Olszowy, H., research in progress. See also ref 3.
(26) Jensen, F. R.; Gale, L. H.; Rodgers, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 5793.
(27) E.g., see: Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 635.

clohexene and low yields of a trans (90%) cis (~10%) mixture of stannanes (eq 8). The great predominance of



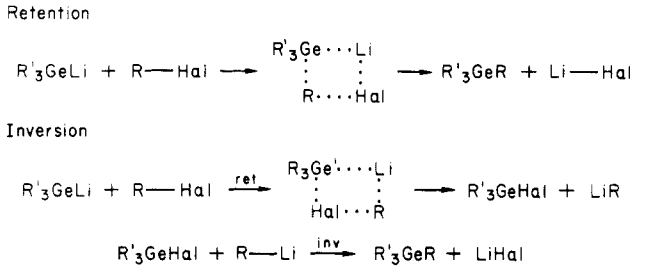
(8)

elimination (for THF) agrees with the general findings of Kuivila,[28] as does the completely nonspecific nature of the substitution. In this system, no information is available on alkene stereochemistry, but several reasonable mechanisms can be written and vary in importance for each isomer. E2 and cyclic syn mechanisms are plausible as is an E1cB variant [$(CH_3)_3Sn^-$ at bromine], producing a 2-methoxycyclohexyl anion which could rapidly lose OCH_3 or after inversion etc. yield a *cis*-/*trans*-stannane mixture. It is also possible that a free-radical component may be partially or completely responsible for the substitution product, with the 2-methoxycyclohexyl radical providing mainly trans product. Similar considerations apply to the 2-methoxycyclopentyl bromide reactions, with each isomer providing exclusively *trans*-(2-methoxycyclopentyl)trimethylstannane. Our careful studies[19] of the $NaBD_4$ reduction of *cis*- and *trans*-(2-methoxycyclohexyl- and -cyclopentyl) mercurials provide trans/cis ratios of ca. 55:45 and 90:10, respectively, but in these radical reductions, the donor is now probably RHgH, and substantial differences in the nature of the product-forming step (H abstaction) almost certainly exist. Nevertheless, trapping experiments[28] for the reaction of $(CH_3)_3SnNa$ with 2-bromo-3-methoxybutane provide strong support for an anionic intermediate, and on this basis a 2-methoxycyclohexyl or -cyclopentyl anion may be involved in the systems described here. In contrast, $(C_6H_5)_3SnNa$ reacts with strict inversion with *trans*-1-bromo-2-methoxycyclohexane,[14] a result further emphasizing the different behavior of $(C_6H_5)_3Sn$ and $(CH_3)_3Sn$ alkalis toward alkyl bromides.

The reactions of $(CH_3)_3GeLi$ with *cis*- and *trans*-4-methylcyclohexyl bromides provide an interesting comparison with the $(CH_3)_3SnLi$ reactions from the viewpoint of the trans/cis ratio in the products. As indicated earlier, either bromide provides a mixture of the germanes, with the cis isomer (~70%) predominating, a distribution characteristic of a number of reactions involving 4-methylcyclohexyl radicals, including the carefully determined result for borodeuteride reduction of (4-methylcyclohexyl)mercuric bromides.[19] Accepting that the reactions of alkylcyclohexyl bromides with $(CH_3)_3SnLi$ are free radical in nature, one can see that the free-radical reactions of $(CH_3)_3GeLi$ (see later) must differ in the product-forming step, viz., abstraction of $(CH_3)_3Ge$. In HMPA, a good cation solvator, the degree of aggregation is probably slight. The trans product predominance in the $(CH_3)_3SnLi$ reactions was ascribed to development of product character in the abstraction step, with the presumed bulky $(CH_3)_3Sn$ group (in a cluster in THF) approaching *equatorially*. This persistence of trans product obtains also in HMPA where the donor assembly is probably largely disaggregated and under the conditions under which the $(CH_3)_3GeLi$ reactions were conducted.

(28) Kuivila, H. G.; Choi, Y. M. *J. Org. Chem.* **1979**, *44*, 4774.

Scheme II



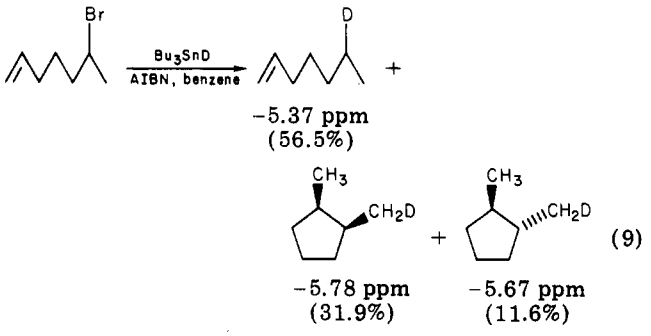
The data for the 6-bromo-1-hexene reactions, producing no rearranged product, suggests that this primary bromide reacts very largely by a direct (S_N2) pathway for all R_3MLi systems examined, in agreement with other data[2] for primary bromides. $(C_6H_5)_3GeLi$ with *cis*-4-methylcyclohexyl bromide produces a slight excess of cis (~55%) over trans (~45%) substitution product as does the reaction of trans bromide (34:66 trans/cis). Thus, in the case of the cis bromide, at least 55% of product must arise by other than S_N2 displacement and 34% in the case of the trans bromide. However, more precise estimates of the S_N2 component require assumptions concerning the cis/trans ratio involved in the likely radical pathway. If this ratio is 70:30 (as found for $(CH_3)_3Ge$), indications are that the S_N2 component is of some importance (~20%) for the cis bromide but insignificant for the trans bromide.

Previously, Eaborn, Hill, and Simpson[29] had examined some substitution reactions of optically active ethyl(1-naphthyl)phenylgermyllithium (R'_3Ge^*Li) with alkyl halides and identified systems proceeding with predominant retention of configuration at germanium (alkyl bromides and chlorides) or predominant inversion (alkyl iodides and benzyl bromide) although no levels of stereospecificity were established. The retention reactions were suggested to involve direct, four-center coupling between R'_3Ge^*Li and RX, while inversion resulted from halogen–lithium exchange (retention) followed by coupling between R'_3GeX and RLi proceeding with inversion (see Scheme II). Our results establish that a single-step four-center retentive process cannot be important for $(CH_3)_3GeLi$ reactions with cyclohexyl bromides, but the connection between our systems and those of Eaborn[29] is not direct. Some correspondence between R'_3Ge^*Li and $(C_6H_5)_3GeLi$ in behavior toward alkyl halides would be reasonable, and complete absence of electron-transfer processes with R'_3Ge^*Li would be surprising. Some knowledge of the stereochemistry at carbon in the reactions of ethyl(1-naphthyl)phenylgermylithium would be illuminating and is being undertaken.

A substantial difference in S_N2 reactivity of a secondary cyclohexyl bromide and the primary 6-bromo-1-hexane is to be expected. Indeed, primary bromides are known to react with a high level of specificity (inversion) with $(CH_3)_3SnLi$, and the S_N2 route is indicated.[2] To investigate this question, we examined the reaction of 6-bromo-1-heptene, a secondary bromide, the radical from of which is known to cyclize irreversibly to the (2-methylcyclopentyl)methyl radical.[30,31] The results are in Table III, and it is clear that, except for the reaction of $(C_6H_5)_3SnLi$ (discussed previously), the proportion of cyclized product is generally quite substantial and in some cases predom-

(29) Eaborn, C.; Hill, R. E. F.; Simpson, P. *J. Organomet. Chem.* **1972**, *37*, 275.
(30) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355.
(31) Beckwith, A. L. J.; Blair, I.; Phillipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 1613 and references therein.

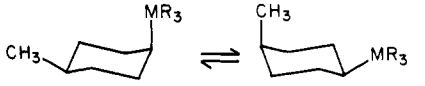
inant. As stereochemsitry (cis/trans) is determined in the cyclization step prior to abstraction, this ratio should be constant for all entries. This is borne out by the data in Table II where the cis/trans ratio ranges from 2.7 to 2.4 (with entry 5; with higher uncertainties giving a ratio of 2.9). Previously determined values of k_c/k_t were 2.8, 2.9, and 2.35.[30,31] We conducted the reduction of 6-bromo-1-heptene with tributylstannane-*d* in the presence of AIBN (refluxing benzene) and examined the product hydrocarbons by ^{2}H NMR. The results are shown in eq 9 and



provide k_{cis}/k_{trans} = 2.75 (^{2}H chemical shifts in parts per million relative to internal $CDCl_3$). ^{13}C examination of the solution and comparison of the signals for the cis and trans isomers yielded a slightly lower value (2.45).

These results establish the importance of the free-radical pathway in the reaction of the secondary 6-bromo-1-heptene and accord with Kuivila's conclusion[2] based on trapping studies that cyclohexyl bromides react very largely, if not exclusively, by a radical route. We have not studied the effects of dilution, temperature, etc., but varying degrees of cyclization could, no doubt, be achieved by these devices. An important finding is that the change from $(C_6H_5)_3SnLi$ to $CH_3(C_6H_5)_2SnLi$, i.e., monomethylation at tin, has an important effect on the oxidation potential of the R_3SnLi species so that electron transfer and radical formation become very important. Thus, for the reactions involving $(C_6H_5)_3SnLi$, $(C_6H_5)_2CH_3SnLi$, and $(C_6H_5)(CH_3)_2SnLi$, the percentage of rearranged (2-methylcyclopentyl)methyl product increases from 0% through 14% to 85%. There is a correspondence of these data with the product distributions resulting from reactions with the *cis*- and *trans*-4-methylcyclohexyl bromides. While $(C_6H_5)_3SnLi$ reacts with complete inversion with both bromides, $(C_6H_5)_2(CH_3)SnLi$ appears to favor the S_N2 (or some stereoequivalent pathway) to ca. 60% with the cis bromide but sparingly (~5%) with the trans bromide. The $C_6H_5(CH_3)_2SnLi$ data are consistent with almost no S_N2 component with the trans bromide but ca. 30% with the cis bromide. While these dissections are subject to sizable uncertainties [due, for example, to the assumption that a ca. 70:30 trans/cis product distribution will characterize the free-radical reactions of $(C_6H_5)_2CH_3SnLi$ and $C_6H_5(CH_3)_2SnLi$], the trends are reassuring. The precise reasons for the differing effects of phenyl vs. methyl at tin in these anionoids are not clear, but we have planned ^{13}C and ^{119}Sn NMR studies to determine if and to what degree Sn–aryl π interactions are a feature regulating the apparent high nucleophilicity (to carbon) of $(C_6H_5)_3SnLi$.[32]

Conformational *A* Values of Triorganotin and Germanium Groups. We have reported that the conformational *A* values of $(CH_3)_3Ge$,[4] $(CH_3)_3Sn$,[9] and $(CH_3)_3Pb$[9] are 2.1–2.2, 1.06 ± 0.14, and 0.67 ± 0.06 kcal/mol, respectively ($A = \Delta G° = RT \ln K$ for the axial ⇄ equatorial equilibrium in the cyclohexane derivatives). We subsequently demonstrated that the CCH_3 and $Sn(CH_3)_3$ chemical shifts for the mobile *cis*-(4-methylcyclohexyl)-trimethylstannane (ambient temperature), when combined with the authentic values for such axial and equatorial groups, provided *A* values in close agreement with that based on direct observation of the conformers at low temperature.[4] Subsequently, ^{1}H NMR examination[11] of 1-methoxy-4-(trimethylstannyl)cyclohexanes provided an *A* value for $(CH_3)_3Sn$ of 0.94 ± 0.03 kcal/mol, in close agreement with that (1.06 ± 0.14) initially reported.[9] (Low-temperature ^{119}Sn NMR provides a value of ca. 1.00 kcal/mol.)[33] These studies indicate that deviations from ^{13}C chemical shift additivity in 4-methylcyclohexyl derivatives of tin and germanium are small and confirm that *A* values of useful precision can be obtained by this "counterpoise" approach with the *cis*-4-methylcyclohexyl isomers.[34] We have utilized this approach to provide *A* values for $(C_6H_5)_3Sn$, $(C_6H_5)_3Ge$, $(C_6H_5)(CH_3)_2Sn$, and $(C_6H_5)_2(CH_3)Sn$. When values of 23.47 and 17.43 ppm are employed as standard values for the chemical shifts of equatorial and axial CCH_3,[12,34] it is a simple matter to calculate equilibrium constants for the various *cis*-4-methylcyclohexyl derivatives under ambient conditions.



With an *A* value of 1.74 kcal/mol for the methyl group, and on the assumption of additivity of conformational free energies,[4,11,34] the *A* values listed below in Table IV can be derived.

The triphenyl derivatives clearly are sterically more demanding than the trimethyl derivatives, and the difference is more marked between the two germanium compounds. With the triphenylmetal group axially disposed, relief of ortho–ortho repulsions between the phenyl groups by canting generates phenyl–axial 3,5-H interactions. This difference between $(CH_3)_3M$ and $(C_6H_5)_3M$ will be more severe when the cyclohexyl–M bound is shorter. The presence of at least one methyl group on tin permits a conformation with that group internal to the ring to predominate, and this probably largely accounts for the rel-

Table IV. Conformational *A* Values of Triorganometal Groups Based on *cis*-4-Methylcyclohexyl Derivatives

MR_3	^{1}H NMR, δ (C-CH_3)	*A* value, kcal/mol
$Ge(CH_3)_3$	19.62	2.07
$Ge(C_6H_5)_3$	18.16	2.90
$Sn(CH_3)_3$	*a*	1.06 ± 0.14[a]
$Sn(CH_3)_3$	*a*	0.94 ± 0.03[11]
$Sn(CH_3)_3$	22.00	1.06
$Sn(CH_3)_2(C_6H_5)$	21.93	1.08
$SnCH_3(C_6H_5)_2$	21.69	1.20
$Sn(C_6H_5)_3$	21.20	1.44[b,c]
$Sn(i\text{-}Pr)_3$	21.95	1.10
$Pb(CH_3)_3$	*a*	0.67 ± 0.06[9]

[a] Low-temperature observation on the cyclohexyl derivative. [b] Fish[14] has reported a value of ~1.5 kcal/mol. [c] A concordant value is obtained by considering the 273 K ^{13}C spectrum of pure *cis*-(4-methylcyclohexyl)triphenylstannane, in which signals for the separate conformers can be identified.[21]

(32) In this connection, for NMR studies of various phenylsilyllithium reagents see: Olah, G. A.; Hunadi, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6989.

(33) Unpublished results.

(34) Kitching, W.; Olszowy, H.; Adcock, W. *Org. Magn. Reson.* **1981**, *15*, 230 and references therein.

Table V. Characteristics of Alkyl Bromides (RBr)

R in KBr	stereochemistry[a]	typical yields,[b] %	bp, °C (mm)	lit. bp, °C (mm)	^{1}H NMR[c]
cis-4-methylcyclohexyl[d,e]	>95% cis	60	72 (20)	57-57.8 (9.5)[8]	CHBr, 4.57 (12)
trans-3-methylcyclohexyl[d,f]	90% trans	40	84-86 (40)	55-60 (10)[n,44]	CHBr, 4.70 (12)
cis-2-methylcyclohexyl[d,g]	>95% cis	51	87 (40)	68 (19)[45]	CHBr, 4.34 (10)
trans-4-methylcyclohexyl[h]	>95% trans	84	69 (20)	57 (9.5)[8]	CHBr, 3.90 (28)
cis-3-methylcyclohexyl[h]	85% cis	76	67-69 (20)	55-60 (10)[n,44]	CHBr, 4.06 (26)
trans-2-methylcyclohexyl[h]	87% trans	82	73-74 (25)	59-60 (15)[o,44]	CHBr, 3.77 (26)
cis-2-methylcyclopentyl[i]	>95% cis	67	66 (45)	45.5-49.5 (20)[p,46]	CHBr, 4.37 (9)
trans-2-methoxycyclohexyl[j]	>95% trans	90	72 (9)	75-75.5 (10)[47]	CHBr, 4.0 (24); OMe, 3.45; CHOMe, 3.30 (24)
trans-2-methoxycyclopentyl[j]	>95% trans	46	69 (12)		CHBr, 4.3, (12); OMe, 3.37; CHOMe, 4.0 (12)
cis-2-methoxycyclohexyl[k]	95% cis	72	60-61 (3)		CHBr, 4.50 (12); OMe, 337; CHOMe, 3.19 (14)
cis-2-methoxycyclopentyl[l]	>95% cis	20	65 (9)		CHBr, 4.30 (12); OMe, 3.32; CHOMe (m), CHOMe, 3.50 (18)
cyclopropylcarbinyl[m]		79	101-104 (760)	102-104 (760)[15]	CH_2Br, 3.31 (d, $J \approx 7$ Hz)

[a] From ^{1}H and ^{13}C NMR and/or GC analysis. [b] After distillation, carbon and hydrogen analyses were satisfactory for the assigned structures. [c] Approximately 10% $CDCl_3$ solutions; chemical shifts are downfield from internal Me_4Si. Data are given as follows: assignment, chemical shift (δ) (width at half-height in hertz). [d] Prepared by bromination of the alcohol with Ph_3PBr_2 in dry CH_3CN according to a slightly modified method of Wiley et al.[36] [e] From commercial 4-methylcyclohexanol (70% trans/30% cis). [f] From 90% *cis*-/10% *trans*-3-methylcyclohexanol prepared by $LiAlH_4$ reduction of 3-methylcyclohexanone. [g] From 75% *trans*-/25% *cis*-2-methylcyclohexanol prepared by $LiAlH_4$ reduction of ketone; the isolated product consisted of 60% of the desired alkyl bromide plus 40% 1-bromo-1-methylcyclohexane which was largely removed by treatment of the mixture with the stoichiometric amount of $AgNO_3$ in CH_3OH followed by distillation. [h] Prepared by Br_2/pyridine cleavage of the diequatorial-rich methylcyclohexylmercuric bromide which was obtained from the methylcyclohexyl Grignard and $HgBr_2$ as described by Jensen and Gale.[8] [i] *i*-PBr_3 treatment of pure *trans*-2-methylcyclopentanol[37] as described;[38] approximately 40% of the isolated product was identified as 1-bromo-1-methylcyclopentane. [j] Prepared by treatment of the cycloalkene with *N*-bromosuccinimide/CH_3OH in the usual way.[39] [k] From the interaction of $CH_2N_2/BF_3\cdot(CH_3CH_2)_2O$ catalyst[40] and *cis*-2-bromocyclohexanol (95% cis) which was obtained by $LiAlH_4$ reduction of freshly prepared 2-bromocyclohexanone.[41] [l] Pure *trans*-(2-methoxycyclopentyl)mercuric acetate (from cyclopentene and $Hg(OAc)_2$ in CH_3OH according to Brook et al.[42]) was readily converted to the corresponding chloride by treatment with excess 15% aqueous NaCl. Acid-induced isomerization (1.1 equiv of 70% $HClO_4$, in the dark, ~40 °C for 1 h in CH_3OH solvent) of the *trans*-(2-methoxycyclopentyl)mercuric chloride furnished a mixture of two isomers which was rich (~75%) in the cis isomer. The trans isomer in the mixed mercury chlorides was preferentially destroyed with a stoichiometric amount of concentrated HCl in acetone. The resultant >95% *cis*-2-(methoxycyclopentyl)mercuric chloride was then subjected to a Br_2/pyridine[8] cleavage to provide >95% *cis*-2-methoxycyclopentyl bromide. [m] (3-Butenyl)tributylstannane was cleaved with Br_2/CH_2Cl_2 at low temperature in the reported fashion.[43] [n] For a 60% cis/40% trans isomeric mixture. [o] Reported boiling point for the 1:12 cis/trans isomeric mixture. [p] Reported boiling point for 2-methylcyclopentyl bromide of unspecified stereochemistry.

atively large difference between $Sn(CH_3)(C_6H_5)_2$ and $Sn(C_6H_5)_3$ ($\Delta A = 0.24$) compared with that for $Sn(CH_3)_3$ and $Sn(CH_3)_2(C_6H_5)$ ($\Delta A = 0.02$). The near identity of *A* values for $Sn(CH_3)_3$ and $Sn(i\text{-}Pr)_3$ is likewise associated with the sufficiently long C–Sn bond and the availability of a conformation with the $(CH_3)_2$C–H bond directed towards the axial 3,5-hydrogens.

Some general correspondence between these *A* values and the γ effects of these (axial) metal groups may be reasonable, as the γ effect is generally considered to reflect compressional polarization of the γ-C–H bonds, with increased shielding of C(γ).[35] The values we have been able to calculate are −1.19 [$(CH_3)_3Sn$] −0.83 [$(C_6H_5)_3Sn$], −2.07 [$(CH_3)_3Ge$], and −4.88 ppm [$(C_6H_5)_3Ge$], with significant uncertainty in the latter value, as it is based on a relatively one-sided equilibrium in *cis*-(4-methylcyclohexyl)triphenylgermane. Although a trend of increasing γ effects with *A* values is observed [except for $(C_6H_5)_3Sn$] a number of factors need consideration.

Experimental Section

NMR Spectra. ^{1}H spectra were obtained for ca. 10% solutions in $CDCl_3$ (internal Me_4Si) by utilizing the JEOL JNM MH-100 or JEOL PS-100 spectrometer in this Department. Some spectra were also obtained at 270 MHz (Bruker) at the National NMR Center, Canberra, Australia.

^{13}C spectra were obtained on the JEOL FX-100 at 25.05 MHz or at 67.89 MHz (Bruker) in the Fourier transform mode (internal

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(47) Winstein, S.; Henderson, R. B. *J. Am. Chem. Soc.* **1943**, *65*, 2196.

^2H lock) for $CDCl_3$ solutions, and chemical shifts are referenced to internal Me_4Si.

Alkyl Bromides. The cycloalkyl bromides were prepared by established methods, and physical properties for some of these are listed in Table V.

6-Bromo-1-hexene was commercially available or was prepared by bromination of the alcohol with PBr_3/pyridine, according to a slightly modified method of Johnson and Owyang[48] as described below in the preparation of 6-bromo-1-heptene. The yield of 1-bromo-5-hexene was 31%; bp 58 °C (25 mm) [lit.[49] bp 47 °C (17 nm)].

6-Bromo-1-heptene. 4-Penten-1-ol, prepared by the method of Brooks and Snyder,[50] was brominated wtih PBr_3/pyridine by a modification of the method described by Johnson and Owyang.[48] Thus, 55.3 g (0.204 mol) of PBr_3 was placed into a dry 250-mL vacuum distillation flask fitted with a pressure-equalizing dropping funnel through which a gentle stream of N_2 gas was passed. A mixture of 4-penten-1-ol (52.7 g, 0.613 mol) and dry pyridine (16.1 g, 0.204 mol) was then added dropwise to the well-stirred and cooled (−5 °C) neat PBr_3 reagent during a period of about 90 min. After complete addition, stirring was maintained at −5 °C for 30 min and then at room temperature for 2 h. The reaction mixture was then vacuum distilled, and all volatile material was collected. The distillate was taken up in ether and washed with water, and the organic phase was separated, dried ($MgSO_4$), and concentrated. Vacuum distillation of the crude oil furnished pure 1-bromo-4-pentene: yield 60%; bp 60 °C (80 mm) [lit.[49] bp 56 °C (75 mm)]. Treatment of the Grignard reagent from 1-bromo-4-pentene with excess acetaldehyde in diethyl ether at 0 °C provides a 60/40 mixture of 6-hydroxy-1-heptene and 6-oxo-1-heptene. This mixture was treated with $NaBH_4$/aqueous NaOH in the usual way to provide pure 6-hydroxy-1-heptene: 73% yield; bp 61 °C (12 mm) [lit.[49] bp 61 °C (12 mm)]. ^1H and ^{13}C NMR analysis of the distilled product indicated complete absence of the ketone. PBr_3 treatment of 6-hydroxy-1-heptene in the manner described above provides ~55% yields of pure 6-bromo-1-heptene, bp 62 °C (20 mm) [lit.[51] bp 72 °C (20 mm)].

***trans*-2-Methylcyclopentyl tosylate** was prepared in 94% yield from *trans*-2-methylcyclopentyl alcohol[37] and tosyl chloride in pyridine as described by Tipson[52] except that the reaction mixture was allowed to stand at room temperature overnight. The clear viscous oil did not crystallize (hexane/pentane), but the ^1H NMR spectrum was completely consistent with the assigned structure: ^1H NMR (10% $CDCl_3$ solution) δ 0.84 (CH_3CH, J = 7 Hz), 4.34 (CHOTS, $w_{1/2}$ = 10 Hz), 2.41 ($ArCH_3$), 7.32, 7.73 (Ar, AB pattern). The reported melting point for the title compound is 33.8–34.5 °C.[37]

$Me_{3-x}Ph_xSnCl$ Compounds. Trimethyl tin chloride (Me_3SnCl) was commercially available or was prepared from Me_4Sn[53] and $SnCl_4$. Triphenyl tin chloride (Ph_3SnCl) was also commercially available but was recrystallized twice from dry ethanol before use. Diphenylmethyltin chloride ($Ph_2MeSnCl$) was prepared in 92% yields by the acid cleavage of triphenylmethyltin [readily prepared from Ph_3SnCl and MeMgI; mp 63 °C (Lit.[54] mp 60–61 °C)] with 1.0 equiv of hydrochloric acid in methanol at reflux for 2 h. methanol and ether (from the workup) were removed by low-pressure pumping at room temperature: ^1H NMR (10% $CDCl_3$ solution) δ 0.98 (Me, J (^1H–^{119}Sn) = 58 Hz) 7.3–7.4 (Ar). The boiling point for $Ph_2MeSnCl$ is 129–130 °C (0.15 mm).[55] Phenyldimethyltin chloride ($PhMe_2SnCl$) was prepared by reacting $(CH_3)_2SnCl_2$ with a large excess of phenylmagnesium bromide to provide predominantly $(C_6H_5)_2Sn(CH_3)_2$ and minor amounts of the coupled product biphenyl (~2–5%). The crude product was subjected to a hydrochloric acid cleavage as described above followed by a vacuum distillation of the crude isolated oil, with the pot temperature not exceeding 100 °C. Biphenyl was removed from the distillate by elution with pentane on a silica gel column; $PhMe_2SnCl$ was then recovered from the column by elution with a 50/50 pentane–ether mixture. The chromatographic procedure was carried out twice before the $PhMe_2SnCl$ was vacuum distilled at a pot temperature of ~100 °C: for 86 °C (2 mm); ^1H NMR (10% $CDCl_3$ solution) δ 0.82 (Me, J (^1H–^{119}Sn) = 60 Hz) 7.3–7.8 (Ar). The presence of possible disproportionation products in the distilled product could not be detected as evidenced from ^1H and ^{13}C NMR spectra. Anal. Calcd fro $C_8H_{11}ClSn$: C, 36.71; H, 4.21. Found: C, 36.67; H, 4.35.

Reaction of Alkyl Bromides with $Me_{3-x}Ph_xMLi$ Compounds (M = Sn, Ge). Solvents THF and HMPA (hexamethylphosphoric triamide) were freshly prepared as previously described.[4] $Me_{3-x}Ph_xSnLi$ compounds were freshly prepared in the same manner as previously described for Me_3SnLi[4] from the corresponding $Me_{3-x}Ph_xSnCl$ and Li metal in THF or HMPA solvent. Me_3GeLi (in HMPA solvent) and Ph_3GeLi (in THF solvent) were prepared according to published procedures[56] from commercially available Me_3GeBr and Ph_3GeBr (or Ph_6Ge_2). In general, the alkyl bromide (0.95 equiv) was dissolved in a small amount of solvent and was added dropwise to the cooled (~15 °C) $Me_{3-x}Ph_xMLi$ solution. Reaction between the lithio reagent and alkyl bromide was allowed to proceed for at least 4 h at ~20 °C before the workup with the exception of the reactions involving Ph_3SnLi which were allowed to proceed for 1 week at ~20 °C. An excess (2 equiv) of Me_3SnLi was necessary for reactions with *cis*- or *trans*-2-methoxycyclohexyl (and pentyl) bromides because of the coupling reaction to produce hexamethylditin. NMR data for the various products from reactions of the alkyl bromides and $Me_{3-x}Ph_xMLi$ are collected in Tables VI and VII (supplementary material), and experimental characteristics are outlined in Tables I and II.

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Registry No. *cis*-1-Bromo-4-methylcyclohexane, 28046-90-4; *trans*-1-bromo-4-methylcyclohexane, 28046-91-5; *cis*-1-bromo-3-methylcyclohexane, 28046-88-0; *trans*-1-bromo-3-methylcyclohexane, 28046-89-1; *cis*-1-bromo-2-methylcyclohexane, 28046-84-6; *trans*-1-bromo-2-methylcyclohexane, 28046-85-7; *cis*-1-bromo-2-methoxycyclohexane, 51332-48-0; *trans*-1-bromo-2-methoxycyclohexane, 5927-93-5; *cis*-1-bromo-2-methoxycyclopentane, 51475-11-7; *trans*-1-bromo-2-methoxycyclopentane, 51422-76-5; *cis*-1-bromo-2-methylcyclopentane, 80607-05-2; *trans*-2-methylcyclopentyltosylate, 80963-37-7; (bromomethyl)cyclopropane, 7051-34-5; 4-bromo-1-butene, 5162-44-7; 6-bromo-1-hexene, 2695-47-8; trimethyl(cyclopropylmethyl)stannane, 51675-53-7; 3-butenyltrimethylstannane, 17314-38-4; 6-bromo-1-heptene, 38334-98-4; *trans*-trimethyl(4-methylcyclohexyl)stannane, 64871-26-7; *cis*-trimethyl(4-methylcyclohexyl)stannane, 64871-27-8; *cis*-trimethyl(3-methylcyclohexyl)stannane, 80963-38-8; *trans*-trimethyl(3-methylcyclohexyl)-stannane, 80963-39-9; *trans*-trimethyl(2-methylcyclohexyl)stannane, 15095-85-9; *cis*-trimethyl(2-methylcyclohexyl)stannane, 15095-94-0; *trans*-trimethyl(4-methylcyclohexyl)germane, 64871-31-4; *cis*-trimethyl(4-methylcyclohexyl)germane, 64871-32-5; *trans*-trimethyl(2-methylcyclopentyl)stannane, 80963-40-2; *cis*-trimethyl(2-methylcyclopentyl)stannane, 80963-41-3; *trans*-dimethylphenyl(4-methylcyclohexyl)stannane, 80963-42-4; Cis-dimethylphenyl(4-methylcyclohexyl)stannane, 80963-43-5; *trans*-methyldiphenyl(4-methylcyclohexyl)stannane, 80963-44-6; *cis*-methyldiphenyl(4-methylcyclohexyl)stannane, 80963-45-7; *trans*-triphenyl(4-methylcyclohexyl)-stannane, 80963-46-8; *cis*-triphenyl(4-methylcyclohexyl)stannane, 80963-47-9; *cis*-triphenyl(3-methylcyclohexyl)stannane, 80963-48-0; *trans*-triphenyl(4-methylcyclohexyl)germane, 76879-66-8; *cis*-triphenyl(4-methylcyclohexyl)germane, 76879-65-7; *trans*-trimethyl(2-methoxycyclohexyl)stannane, 80963-49-1; *cis*-trimethyl(2-methoxycyclohexyl)stannane, 80963-50-4; *trans*-trimethyl(2-methoxycyclopentyl)stannane, 80963-51-5; triphenyl(cyclopropylmethyl)stannane,

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80963-52-6; triphenyl(3-butenyl)stannane, 29972-16-5; trimethyl(5-hexenyl)stannane, 73017-74-0; trimethyl(cyclopentylmethyl)stannane, 73017-75-1; triphenyl(cyclopentylmethyl)stannane, 76001-27-9; triphenyl(5-hexenyl)stannane, 73017-73-9; trimethyl(5-hexenyl)germane, 80963-53-7; triphenyl(5-hexenyl)germane, 76001-24-6; trimethyl(6-hepten-2-yl)stannane, 76879-52-2; *cis*-trimethyl(2-methylcyclopentylmethyl)stannane, 76879-57-7; *trans*-trimethyl(2-methylcyclopentylmethyl)stannane, 76879-58-8; dimethylphenyl(6-hepten-2-yl)stannane, 76879-53-3; *cis*-dimethylphenyl(2-methylcyclopentylmethyl)stannane, 76879-59-9; *trans*-dimethylphenyl(2-methylcyclopentylmethyl)stannnane, 76879-60-2; methyldiphenyl(6-hepten-2-yl)stannane, 76879-54-4; *cis*-methyldiphenyl(2-methylcyclopentylmethyl)stannane, 76879-61-3; *trans*-methyldiphenyl(2-methylcyclopentylmethyl)stannane, 76879-62-4; triphenyl(6-hepten-2-yl)stannane, 76879-55-5; triphenyl(6-hepten-2-yl)germane, 76879-56-6; *cis*-triphenyl(2-methylcyclopentylmethyl)germane, 76900-25-9; *trans*-triphenyl(2-methylcyclopentylmethyl)germane, 76900-26-0; trimethyl(6-hepten-2-yl)germane, 76879-49-7; trimethyl(5(*Z*)-hepten-2-yl)germane, 76879-50-0; trimethyl(5(*E*)-hepten-2-yl)germane, 76879-51-1; *cis*-trimethyl(2-methylcyclopentylmethyl)germane, 76879-63-5; *trans*-trimethyl(2-methylcyclopentylmethyl)germane, 76879-64-6; 2-deuterio-6-heptene, 80963-54-8; *cis*-1-(deuteromethyl)-2-methylcyclopentane, 80963-55-9; *trans*-1-(deuteriomethyl)-2-methylcyclopentane, 80963-56-0; ntrimethylstannyl)lithium, 17946-71-3; (dimethylphenystannyl)lithium, 76879-67-9; (methyldiphenylstannyl)lithium, 4167-85-5; (triphenylstannyl)lithium, 4167-90-2; (trimethylgermyl)lithium, 18489-76-4; (triphenylgermyl)-lithium, 3839-32-5.

Supplementary Material Available: Tables of the observed and calculated ^{13}C NMR chemical shifts (and $^{13}C-^{119}Sn$ couplings) for the products of the reactions between substituted cyclohexyl bromides with $Me_{3-x}Ph_xMLi$ (M = Sn, Ge) and also for the corresponding reactions with 6-bromo-1-exene and 6-bromo-1-heptene (Tables VI and VII) (7 pages). Ordering information is given on any current masthead page.

Oxidatively Assisted Nucleophilic Substitution/Elimination of Alkyl Iodides in Alcoholic Media. A Further Study

Robert I. Davidson and Paul J. Kropp*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

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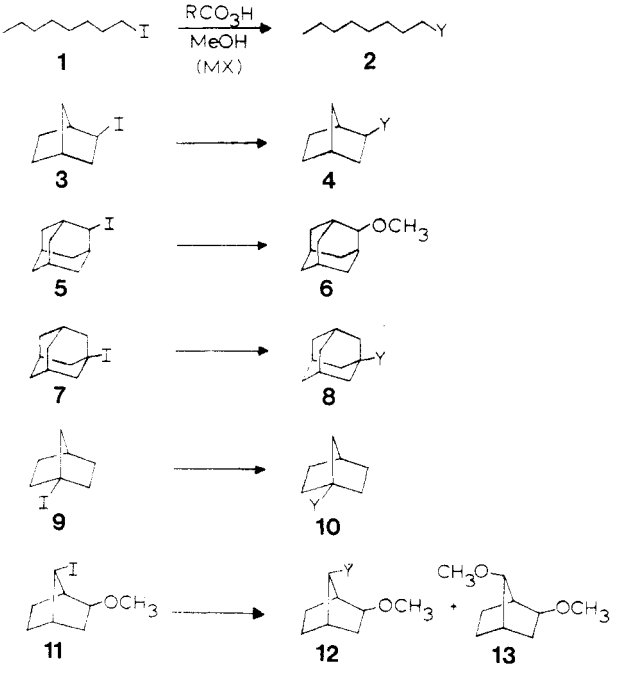
Oxidation of a series of alkyl halides with alcoholic 3-chloroperoxybenzoic acid afforded the results outlined in Charts I–III and Tables I–III. The reaction was found to be a powerful and convenient method for effecting nucleophilic substitution in a variety of systems, including the highly inert 1- and 7-bicyclo[2.2.1]heptyl systems. Qualitatively, the number of molar equivalents of oxidant required varied inversely with the expected ease of substitution for a given system. A mechanism is suggested whereby the iodide is oxidized stepwise to a species RIO_n in which n is an integer sufficiently large that the system in question will undergo nucleophilic substitution or elimination. Reaction in the presence of added chloride or bromide ion usually resulted in a facilitation of reaction rate and a decrease in the number of molar equivalents of oxidant required; the principal product under these conditions was usually the corresponding chloride or bromide.

Treatment of alkyl iodides with peroxy acids has been the subject of several recent papers.[1-5] In nonnucleophilic media simple alkyl iodides are converted principally to the corresponding alcohols, while elimination is the predominant pathway for more complex systems.[3-5] However, when simple alkyl iodides are oxidized in solvents such as methanol or acetic acid, nucleophilic substitution occurs instead.[1,2,4] Iodoso intermediates (RIO) have been proposed to account for this behavior.[2-5] We now report the results of a detailed, systematic study of the oxidation of alkyl iodides with 3-chloroperoxybenzoic acid in alcoholic media which show that this reaction affords an exceptionally mild but powerful, efficient, and selective method for effecting nucleophilic substitution of many systems. Some additional insight into the mechanism of the reaction was also obtained.

Results

The alkyl iodides selected for study, along with the products resulting from their oxidation with 3-chloroperoxybenzoic acid, are shown in Charts I–III. The results from oxidation in methanolic solution are summarized in Table I. Most of the alkyl iodides afforded methyl ether substitution products upon oxidation. (+)-(*S*)-2-Iodooctane (**17**) which was 76% optically pure[6] afforded (-)-(*R*)-ether **18** (Y = OCH_3) which was 25% optically pure[7] (33% net inversion). One system, 3,3-dimethyl-1-iodopropane (**25**) underwent accompanying rearrangement, and three systems (**14**, **19**, and **29**) apparently underwent initial

Chart I



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