cis- and *trans*-(4-Alkylcyclohexyl)stannanes. Isomers for Stereochemical Studies of Substitution at Saturated Carbon–Tin Bonds

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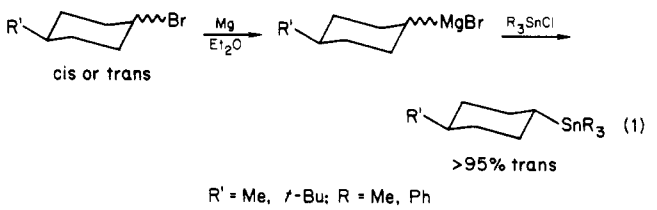
The synthesis and characterization of pure *cis*- and *trans*-(4-methylcyclohexyl)- and *cis*- and *trans*-(4-*tert*-butylcyclohexyl)triphenylstannanes are described. Their conversion, by hydrochloric acid induced dephenylation–isopropylation, to the corresponding triisopropylstannanes proceeds smoothly to provide stereoisomers capable of providing significant information with respect to brominolysis and trifluoroacetolysis of the carbon–tin bond.

Introduction

Organomercurials[1] and -stannanes[2] have proved to be revealing substrates with respect to mechanisms of bimolecular electrophilic substitution at saturated carbon, and studies with the isomeric (4-alkylcyclohexyl)-mercurials[3] have been particularly informative. Although studies of electrophilic cleavage of carbon–tin bonds have added a new dimension to our understanding in this area, the stannanes employed usually have been optical isomers, e.g., 2-butyl derivatives.[2] As a result of studies of reactions of (alkylstannyl)- and (arylstannyl)alkali reagents, e.g., $(CH_3)_3SnLi$ and $(C_6H_5)_3SnLi$, with alkyl bromides, methods became available for the stereospecific synthesis of various substituted cyclohexyltriphenylstannanes, capable of transformation to the corresponding trialkylstannanes, amenable to study of stereochemical aspects of electrophilic substitution at carbon–tin bonds.[2] Such data, while of interest in its own right, would provide valuable comparisons with data obtained with the cyclohexylmercurials. In this report, we present full details of the synthesis and characterization of *cis*- and *trans*-(4-methylcyclohexyl)- and *cis*- and *trans*-(4-*tert*-butylcyclohexyl)triphenylstannanes and -triisopropylstannanes. In the following paper, the results of polar and free radical brominolysis and trifluoroacetolysis are described.

Results and Discussion

General Information. One obvious way to obtain (4-alkylcyclohexyl)stannanes is to quench the 4-alkylcyclohexyl Grignard reagent with the appropriate triorganotin halide (R_3SnCl), and this procedure has been employed to obtain essentially pure *trans*-(4-methylcyclohexyl)trimethylstannane[4,5] (eq 1), and we have utilized the approach more recently to obtain *trans*-(4-*tert*-butylcyclohexyl)triphenylstannane. Because the same Grignard reagent is formed from either cis or trans bromide,[5] only the trans stannane is acquired by this procedure. While this is useful, direct stereospecific formation of the carbon–tin bond from stereoisomeric precursors is more attractive for its generality.



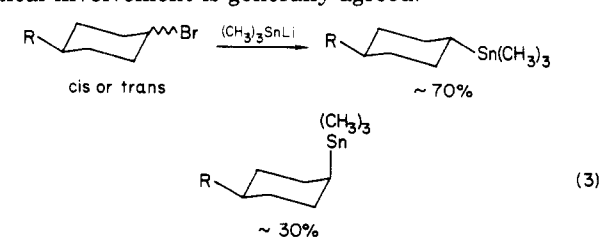
Such an approach involves displacement (from carbon) of halide and tosylate groups by organostannylalkali reagents, a reaction type that has been subjected to intensive recent scrutiny (eq 2). Although these systems

$$R'\text{–}X \xrightarrow[M = Li, Na, K]{R_3SnM} R'\text{–}SnR_3 \qquad (2)$$

$$X = Cl, Br, I, OTs$$

are now known to exhibit a rich mechanistic diversity,[6] Jensen and Davis (1971)[7] concluded that $(C_6H_5)_3SnNa$, prepared from $(C_6H_5)_3SnCl$ and sodium in 1,2-dimethoxyethane (DME), reacted with (*S*)-(+)-*sec*-butyl chloride with a high level (90%) of inversion of configuration. With (*S*)-(+)-*sec*-butyl bromide and (*R*)-(−)-*sec*-butyl iodide, the results were 88% and 71%, respectively. (This reduction in stereospecificity is now known to be associated with nonconcerted mechanisms that are important with bromides and iodides.)

However, this finding of (stereospecific) inversion is not applicable to trialkyl tin alkali reagents in reactions with secondary bromides.[6] In the context of the present work, we[4] and others[6] have demonstrated that *cis*- and *trans*-4-alkyl- and *cis*- and *trans*-3-alkylcyclohexyl bromides with trimethyltin alkali reagents provide mixtures of the corresponding trimethylstannanes, with the diequatorial product predominating, e.g., eq 3. Electron transfer/free radical involvement is generally agreed.[6]



However, with respect to $(C_6H_5)_3SnLi$/THF, we made the very pleasing observation[4] that displacement of bromide from *cis*- or *trans*-4-alkylcyclohexyl bromides occurred stereospecifically with inversion to provide the isomerically

(1) See, for example: Sayre, L. M.; Jensen, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 6001 and references therein, especially ref 3.
(2) For a recent review, see; Fukuto, J. M.; Jensen, F. R. *Acc. Chem. Res.* **1983**, *16*, 177.
(3) For this aspect, see: Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968. Jensen, F. R.; Gale, L. H. *J. Am. Chem. Soc.* **1959**, *81*, 1261.
(4) (a) Kitching, W.; Olszowy, H.; Waugh, J. A.; Doddrell, D. *J. Org. Chem.* **1978**, *43*, 898. (b) Kitching, W.; Olszowy, H.; Harvey, K. *Ibid.* **1981**, *46*, 2423. (c) Kitching, W.; Harvey, K.; Olszowy, H. *Ibid.* **1982**, *47*, 1893.
(5) For other derivatisation of this Grignard reagent see: Jensen, F. R.; Nakamaye, K. L. *J. Am. Chem. Soc.* **1968**, *90*, 3248.
(6) Key papers are cited in: Kuivila, H. G.; Alnajjar, *J. Am. Chem. Soc.* **1982**, *104*, 6146.
(7) Jensen, F. R.; Davis, D. D. *J. Am. Chem. Soc.* **1971**, *93*, 4047.

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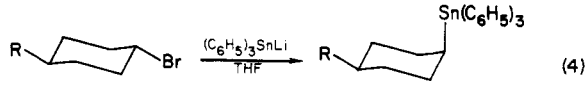
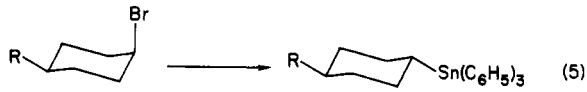
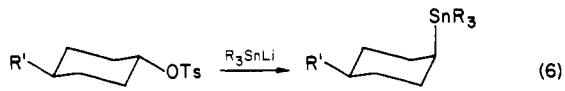
pure (4-alkylcyclohexyl)triphenylstannanes (eq 4 and 5), in agreement with the general finding of Jensen and Davis on $(C_6H_5)_3SnNa$/DME–*sec*-butyl halide system.[7]


(4)


(5)

R = Me, *t*-Bu

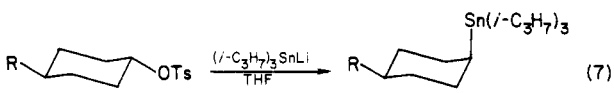
Tosylate displacement in cyclohexyl systems by R_3SnLi occurs stereospecifically with inversion for both R = phenyl and R = alkyl systems, although alkene formation can be significant (eq 6).[4a,8-10] This is the most direct procedure for acquiring pure *cis*-(4-alkylcyclohexyl)trialkylstannanes.


(6)

R' = Me, *t*-Bu; R = Ph, Me, *i*-Pr

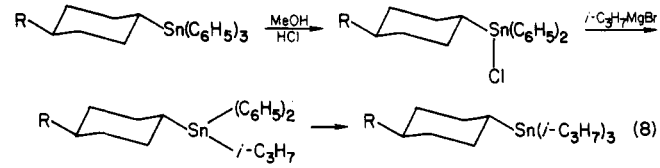
For our immediate goal of securing *cis*- and *trans*-(4-alkylcyclohexyl)stannanes appropriate for stereochemical study of substitution reactions at the carbon–tin bond, both triphenyl- and trimethylstannanes are unsuitable, as electrophilic dephenylation and demethylation are greatly favored over decyclohexylation on several grounds.[7] To induce preferred or significant cleavage of the cyclohexyl–tin bond, it is necessary to attach to tin other groups that are sluggish toward electrophilic substitution. Jensen[2] has found that highly preferential cleavage of *sec*-butyl from tin occurs in *s*-$BuSnR_3$, where R = neopentyl or isopropyl, and for our initial studies we utilized the latter, which in some respects resembles the carbon framework about C1 in the cyclohexyl group.

Thus, the acquisition of the triisopropylcyclohexylstannanes was achieved in two ways. Direct stereospecific introduction of $Sn(i\text{-}Pr)_3$ resulted when *trans*-4-alkylcyclohexyl tosylates were treated with $(i\text{-}Pr)_3SnLi$[11] (from $(i\text{-}Pr)_3SnBr$ and lithium in THF), but the yields of the resulting pure *cis*-(4-alkylcyclohexyl)triisopropylstannanes are moderate (eq 7).

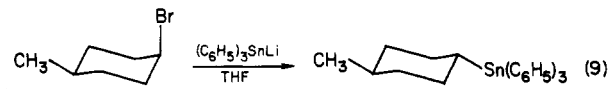

(7)

R = Me, *t*-Bu

A more generalized procedure involves manipulation of the pure *cis*- and *trans*-(4-alkylcyclohexyl)triphenylstannanes, available from stereospecific bromide displacement by $(C_6H_5)_3SnLi$ (cis and trans) or by the Grignard route from 4-alkylcyclohexyl bromides/$(C_6H_5)_3SnCl$ (trans only) (eq 8). The procedure involves sequential HCl-induced dephenylation–isopropylation (isopropyl Grignard), each step proceeding in high yield with exclusive phenyl removal.[12] These approaches have permitted the acquisition of *cis*- and *trans*-(4-methylcyclohexyl)- and *cis* and *trans*-(4-*tert*-butylcyclohexyl)triisopropylstananes.

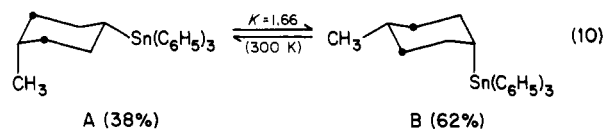

(8)

Triphenylstannanes. *trans*-(4-Methylcyclohexyl)triphenylstannane. The crystalline product obtained from the reaction of $(C_6H_5)_3SnLi$ and *cis*-4-methylcyclohexyl bromide melted sharply (73.5 °C) and appeared to be isomerically pure on the basis of a single CH_3–CH< doublet (δ 0.75 ($J \approx 8$ Hz)) (eq 9). Isomeric


(9)

homogeneity was confirmed by the appearance of five high-field (alkyl) signals in the ^{13}C NMR spectrum, and the trans configuration was established on the basis of (i) the ^{13}C shift of CH_3–CH< at δ 23.15 that is appropriate for an equatorial methyl group[13] and (ii) the vic ^{119}Sn–^{13}C coupling (to (3,5) of 73.3 Hz, requiring a dihedral angle of ca. 180°,[14] as present in the trans (diequatorial) isomer. In addition the ^{13}C NMR shifts of the stannane obtained (in very low yield) from *cis*-4-methylcyclohexyl tosylate and $(C_6H_5)_3SnLi$, agreed with those above. (Tosylate displacement by stannyl anions in all secondary systems examined proceeds with strict configurational inversion at carbon.[4a,8-10])

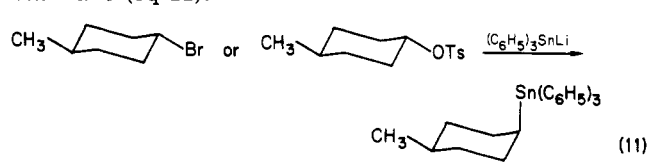
***cis*-(4-Methylcyclohexyl)triphenylstannane.** Triphenylstannylation of *trans*-4-methylcyclohexyl bromide provided an isomerically pure crystalline product (mp 71.5 °C) as evidenced by the single CH_3–CH< doublet (δ 0.76 ($J \approx 6$ Hz)) in the ^1H NMR spectrum and the ^{13}C NMR spectrum. In the latter, a smaller vic ^{119}Sn–^{13}C coupling (30.0 Hz) and the higher field CH_3–CH< signal (δ 21.22) were appropriate[4a,c] for the *cis* isomer.[13,14] As previously outlined in the trimethylstannyl series,[4a] the *cis*-triphenylstannane must be treated as a mixture of conformational isomers (A $\rightleftharpoons$ B), so that B is responsible for the reduced (averaged) vic ^{119}Sn–^{13}C coupling and A for the (averaged) higher field >CH–CH_3 signal (eq. 10). (The


(10)

A (38%) B (62%)

equilibrium constant (K = 1.66) is based on A values of 1.44 and 1.74 kcal/mol for $Sn(C_6H_5)_3$ and CH_3, respectively.[4c])

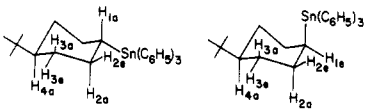
Finally, triphenylstannylation of *trans*-4-methylcyclohexyl tosylate produced (in good yield) the identical stannane (eq 11).


(11)

***trans*-(4-*tert*-Butylcyclohexyl)triphenylstannane.** This compound was obtained most conveniently by treating (4-*tert*-butylcyclohexyl)magnesium bromide with

(8) Koermer, G. S.; Hall, M. L.; Traylor, T. G. *J. Am. Chem. Soc.* **1972**, *94*, 7205.
(9) San Filippo, J.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.
(10) In ref 2, mesylate displacement (by $(C_6H_5)_3Sn$ anion) is described also.
(11) Kitching, W.; Olszowy, H. A.; Drew, G. *Organometallics* **1982**, *1*, 1244.
(12) An alternative procedure that has been successfully employed in another system[7] involves bromodephenylation–neopentylation.
(13) Booth, H.; Everett, J. R. *J. Chem. Soc., Chem. Commun.* **1976**, 278. Anet, F. A. L.; Bradley, C. N.; Buchanan, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 258.
(14) Doddrell, D.; Burfitt, I.; Kitching, W.; Bullpitt, M.; Lee, C. H.; Mynott, R. J.; Considine, J. L.; Kuivila, H. G.; Sarma, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1640.

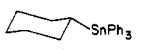
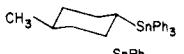
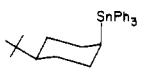
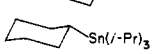
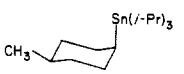
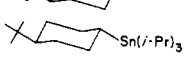
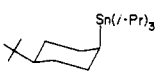
Table I. ^{1}H NMR Data for *cis*- and *trans*-(4-*tert*-Butylcyclohexyl)triphenylstannanes[a]



δ	proton	J, Hz	δ	proton	J, Hz
1.95 (t of t)[b]	H_{1a}	12.5, 3.3[a]	2.81 (br s)[d]	H_{1e}	($W_{1/2} \approx 10$ Hz)
2.20 (br d)[c]	H_{2e}	12.8	2.42 (br, d)[e]	H_{2e}	14
1.69 (br q)	H_{2a}	12.4	2.03 (br, t)[g]	H_{2a}	12.5
1.83 (br d of q)[f]	H_{3e}	12.5, 3.6	1.81 (br d)	H_{3e}	12.5
1.05 (m)[h]	H_{3a}		1.2 (q of d)	H_{3a}	12.6, 2.7
1.05 (m)[h]	H_{4a}		1.10 (t of t)	H_{4a}	12.0, 2.7
0.82 (s)	$(CH_3)_3C$		0.78 (s)	$(CH_3)_3C$	

[a] Aromatic protons at δ 7.4–7.9 in both isomers. [b] $J_{^{119}Sn} = 51$ Hz. [c] $J_{^{119}Sn} = 22$ Hz. [d] $J_{^{119}Sn} = 66$ Hz. [e] $J_{^{119}Sn} = 34$ Hz. [f] Collapses to "narrow singlet" on irradiation at δ 1.05. [g] $J_{^{119}Sn} = 170$ Hz. [h] Appear as a very broad "singlet".

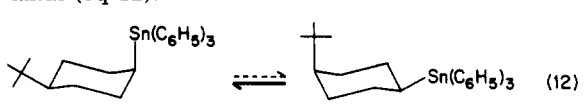
Table II. ^{13}C NMR Chemical Shifts[a] of Cyclohexylstannanes

compound	C1	C2,6	C3,5	C4	others
	28.08 (437)	31.91 (17.6)	29.05 (67.4)	26.98	
	27.85 (436)	31.60 (18.3)	37.62 (73.3)	32.87	23.15
	29.70 (430)	29.14 (14.7)	34.56 (30.0)	31.22	21.22
	28.44 (414)	32.25 (17.60)	29.90 (71.8)	48.22	27.39, 32.51
	30.17 (428)	31.19 (13.9)	26.98 (13.2)	48.57	27.27, 32.48
	26.51	32.57 (16.1)	29.44 (49.8)	27.33	13.82 (308), 22.45 (15.4)
	25.49	32.30 (16.9)	38.04 (55.0)	33.24	23.32, 13.79 (309), 22.46 (16.1)
	26.75 (303)	28.88 (13.9)	35.17 (29.3)	30.58	20.51, 14.31 (306), 22.39 (15.4)
	26.19	32.95 (16.1)	30.23 (55)	48.66	27.45, 32.54, 13.79 (309), 22.47 (16.1)
	27.15	27.91	31.86 (12.5)	48.77	27.65, 32.68, 14.72 (302), 22.27 (16.1)

[a] ^{13}C shifts in ppm are referenced to the central peak of the $CDCl_3$ triplet as 77.00 ppm. Aromatic carbon shifts deleted. Values in parentheses are ^{119}Sn–^{13}C coupling constants.

$(C_6H_5)_3SnCl$, although coupled product ("dimerization" of 4-*tert*-butylcyclohexyl) was also formed. Separation of the two (solid) products was effected by several crystallizations from pentane (in which the stannane is poorly soluble) and then from ethanol. Pure trans stannane (mp 105.5 °C) displayed a vic ^{119}Sn–^{13}C coupling of 71.8 Hz, requiring an ca. 180° dihedral angle between the interacting nuclei.[14]

***cis*-(4-*tert*-Butylcyclohexyl)triphenylstannane** was acquired by tosylate displacement ($(C_6H_5)_3SnLi$; 25 °C; 12 days) from pure *trans*-4-*tert*-butylcyclohexyl tosylate. The crude product was separated from hexaphenyldistannane by extraction with pentane followed by column chromatography. This liquid stannane (25 °C) had vic ^{119}Sn–^{13}C coupling of 13.2 Hz, as expected for an extremely "lopsided" conformational equilibrium, with the $Sn(C_6H_5)_3$ group axial (eq 12).[14]



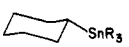
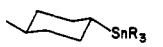
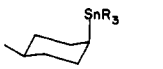
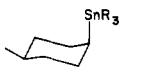
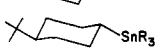
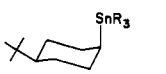
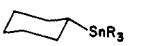
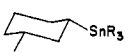
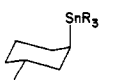
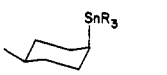
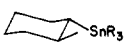
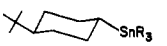
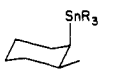
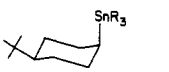
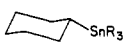
(12)

Although bromide displacement by $(C_6H_5)_3SnLi$ would provide the above (4-*tert*-butylcyclohexyl)stannanes, this route was not employed because transformation of 4-*tert*-butylcyclohexanol to the bromide (with $(C_6H_5)_3PBr_2$) was complicated by significant formation of positional (rearranged) bromoisomers.[15] We did prepare essentially pure *cis*-4-methylcyclohexyl bromide by this bromination procedure, but rearranged bromo isomers were not as significant as in the 4-*tert*-butyl case. We therefore resorted to the Hunsdiecker route to provide a mixture of *cis*- and *trans*-4-*tert*-butylcyclohexyl bromides (free of positional isomers) which could be converted to the Grignard reagent and thence to pure *trans*-(4-*tert*-butylcyclohexyl)triphenylstannane.[16] Pure *trans*-4-*tert*-butylcyclohexyl bromide was obtained from the above cis,-trans mixture by highly preferred base (elimination) destruction of the cis isomer. With considerable difficulty, we did obtain a sample of pure *cis*-4-*tert*-butylcyclohexyl bromide by direct bromination ($(C_6H_5)_3PBr_2$ of 4-*tert*-butylcyclohexanol), distillation, etc.

The *cis*- and *trans*-(4-methylcyclohexyl)- and *cis*- and *trans*-(4-*tert*-butylcyclohexyl)triphenylstannanes were characterized by their ^{1}H, ^{13}C, and ^{119}Sn NMR spectra (Tables I–III). In the cases of *cis*- and *trans*-(4-*tert*-butylcyclohexyl)triphenylstannanes, the 300-HZ ^{1}H NMR spectra were well resolved, and with minor decoupling

(15) See: Eliel, E. L.; Haber, R. G. *J. Org. Chem.* **1959**, *24*, 143.
(16) In this connection see: Jensen, F. R.; Gale, L. H. *J. Am. Chem. Soc.* **1960**, *82*, 145, 148.

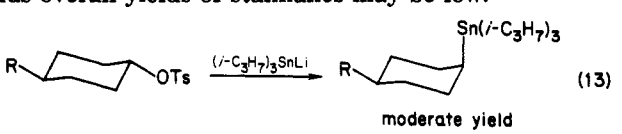
Table III. ^{119}Sn NMR Shifts[a] (Ppm) of Various Cyclohexylstannanes

entry	compound	R	shift	entry	compound	R	shift
1		CH_3	−4.47	11		i-C_3H_7	−53.81
2		CH_3	−2.79	12		i-C_3H_7	−48.78
3		CH_3	−3.27	13		i-C_3H_7	−54.39
4		CH_3	−3.65	14		i-C_3H_7	−44.17
5		CH_3	−2.99	15		C_6H_5	−118.46
6[b]		CH_3	−4.44	16		C_6H_5	−116.69
7[b]		CH_3	−1.23	17		C_6H_5	−114.36
8[b]		CH_3	−4.12	18		C_6H_5	−117.30
9[b]		CH_3	−9.09	19		C_6H_5	−114.87
10		i-C_3H_7	−55.63				

[a] Relative to internal $(CH_3)_4Sn$ as zero. $CDCl_3$ solutions. [b] See: Kitching, W.; Harvey, K.; Olszowy, H. A. *J. Org. Chem.* **1982**, *47*, 1893.

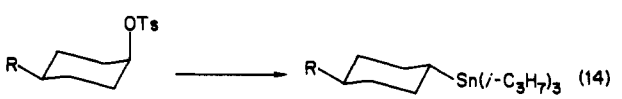
experiments, complete assignments could be made and confirm the cis or trans configurations. In particular, the isomer of mp 105.5 °C exhibited >C*H*Sn(C_6H_5)$_3$ as a clear triplet of triplets (δ 1.95 ($J \approx$ 12.5 Hz, 3.3 Hz)) with $^2J_{^{119}Sn-^1H}$ = 51 Hz. The corresponding signal in the other isomer (oil) was a broad "singlet" (δ 2.81 ($W_{1/2} \approx$ 10 Hz, $^2J_{^{119}Sn-^1H}$ = 66 Hz)), confirming the trans and cis configurations, respectively. Of some interest, was that the signal for H2a (Table I) in the cis isomer (δ 2.03 (br t) was flanked by ^{119}Sn satellites, with $^3J_{^{119}Sn-H2a} \approx$ 170 Hz, a vicinal coupling requiring an 180° dihedral angle as was present in the cis isomer.[17] In the trans isomer (θ = 60°) ^{119}Sn coupling about H2a was not identified and could not exceed ca. 30–40 Hz. The full assignments are shown in Table I.

Triisopropylstannanes. (a) Direct Triisopropylstannylation. As discussed above triphenylstannylation of cyclohexyl bromides is stereospecific. This is not the case with $(CH_3)_3SnLi$[6] and, of immediate relevance, not with $(i\text{-}C_3H_7)_3SnLi$ either.[11,18] Thus direct introduction of $(i\text{-}C_3H_7)_3Sn$ is limited to displacement of the "hard" tosylate group, a reaction which requires considerable reaction time with which elimination can compete very favorably, particularly with cis tosylates (eq 13 and 14). Thus overall yields of stannanes may be low.



(13)

moderate yield



(14)

low yield

Thus, *trans*-4-*tert*-butylcyclohexyl tosylate, on reaction with $(i\text{-}C_3H_7)_3SnLi$, led to the desired cis stannane, albeit in low yield (~20%). (Longer reaction times would undoubtedly improve this, as some unreacted tosylate remained.) In a similar fashion, *trans*-4-methylcyclohexyl tosylate was converted to cis stannane. Tosylate displacement from *cis*-4-alkylcyclohexyl systems was also conducted, and although the yields are very low (ca. 5%) due to competing elimination, pure trans stannanes could be isolated.

Direct introduction of the $(i\text{-}C_3H_7)_3Sn$ group, by quenching 4-methyl- and 4-*tert*-butylcyclohexyl Grignard reagents with $(i\text{-}C_3H_7)_3SnBr$, was examined, but in these cases, an ca. 90:10 trans/cis mixture was obtained (long reaction times needed) in contrast to trimethyl- and triphenylstannylation of these Grignards. In addition, the coproduction of 15–20% yields of coupled products (R–R), existing in several stereoisomeric forms,[18] made this route even less appealing. Although we did separate such "coupled" product from the corresponding (solid) triphenylstannanes, such separation from the (liquid) triisopropylstannanes, which have similar solubility characteristics, was more difficult. This route for acquisition of analytically pure stannanes, for the stereochemical studies, was not pursued further.

(b) Indirect Triisopropylstannylation. Protodephenylation–isopropylation of the *cis*- and *trans*-(4-alkylcyclohexyl)triphenylstannanes was best conducted stepwise, employing the stoichiometric amount of hydrochloric acid in methanol, i.e., monodephenylationisopropylation rather than di- or tridephenylation–isopropylation. (^{1}H NMR analysis of the intermediate tin chloride confirmed loss of one phenyl.) Our experience was that intermediate tin dichlorides or tin trichlorides (by solvolysis etc.) led to much lower overall yields of triisopropylstannane. Indeed the three-step conversion of a triphenylstannane to the triisopropylstannane could be conducted with 90% overall yield. As the cyclohexyl–tin bond is not severed by these procedures, no configurational change is possible in these transformations. The NMR spectral data confirm this. In this way, then, cyclohexyl-,

(17) Quintard, J. P.; Degveil-Gstaing, M.; Barbe, B.; Petrand, M. *J. Organomet. Chem.* **1982**, *234*, 41. $^3J_{^{119}Sn-^2H}$ values of ca. 20 Hz are reported for 180° dihedral angle in trimethyl- and tributyltin derivatives. These would correspond to $^3J_{^{119}Sn-^1H}$ of ca. 140 Hz, and triphenyltin derivatives would exhibit somewhat larger values.

(18) Olszowy, H. A.; Kitching, W., manuscript in preparation. Olszowy, H. A. Ph.D. Thesis, University of Queensland, 1984.

cis- and *trans*-(4-methylcyclohexyl)-, and *cis*- and *trans*-(4-*tert*-butylcyclohexyl)triisopropylstannanes were obtained.

The ^{13}C NMR spectra of the cyclohexylstannanes are assembled in Table II and contain no unexpected features. In previous reports, the substituent chemical shifts and ^{119}Sn–^{13}C coupling constants in related stannanes have been discussed[4] in detail as has the great utility of vic ^{119}Sn-^{13}C coupling in conformational deductions.[4]

^{119}Sn NMR. Our acquisition of series of *cis*- and *trans*-alkylcyclohexylstannanes raised the possibility that within such isomeric pairs, the ^{119}Sn shifts would be regular and hence informative with respect to isomer identities. Some of the ^{119}Sn shifts we have measured for various cyclohexylstannanes are assembled in Table III. Other than for the isomeric (2-methylcyclohexyl)- and (4-methylcyclohexyl)trimethylstannanes (entries 2, 3 and 8, 9), the ^{119}Sn shift of the isomer in which the tin group is predominantly axial is to lower field. A similar result has been reported for various cyclohexylmercurials.[19] While a neighbor effect (γ-methyl) accounts for the situation in entries 8, 9 there is no obvious explanation for the unique behavior of entries 2, 3. A further puzzling aspect is that within the three series of compounds, viz., trimethyl-, triisopropyl-, and triphenylstannanes, the *parent* of each series exhibits a ^{119}Sn shift to higher field than either of the 4-alkyl-substituted members within that set (again excluding entries 8, 9 for obvious reasons). Our expectation was, that if the axial or equatorial "nature" of the stannyl group was the primary determinant of the ^{119}Sn shift, the parent stannane should exhibit a shift between the extremes defined by the *cis*- and *trans*-4- (or 3-) alkyl derivatives but closer to that of the trans-4- (or *cis*-3-) alkyl derivative, as stannyl groups have an equatorial preference.[20] Thus the mere introduction of a 3- or 4-alkyl substituent causes a surprisingly significant effect on the ^{119}Sn shift.[21]

In the following paper, the stereochemical aspects of brominolysis and trifluoroacetolysis of these stannanes are discussed.

Experimental Section

Compounds. Cyclohexyl Bromides. *cis*- and *trans*-4-Methylcyclohexyl bromides were obtained by procedures described previously.[4,16] Some samples of the trans isomer were acquired by selective destruction (sodium ethoxide/ethanol) of the cis bromide in a 57:43 trans/cis bromide mixture, acquired by Hunsdiecker bromination[22] of a cis/trans (80:20) mixture of 4-methylcyclohexanecarboxylic acid.[23]

***cis*- and *trans*-4-*tert*-Butylcyclohexyl Bromide.** The modified Hunsdiecker reaction[22] was carried out with 4-*tert*-butylcyclohexanecarboxylic acid[24] to provide a bromide mixture (54%) that was 60%40 trans/cis; bp 73–78 °C (2 mm). (lit.[24] 64–65 °C (1 mm) for 50:50 mixture). *trans*-4-*tert*-Butylcyclohexyl bromide was obtained isomerically pure by base elimination of the cis isomer, as described for the corresponding 4-methyl compound: bp 66 °C (2 mm) (lit.[24] 64–65 °C (1 mm); ^1H NMR δ 3.95 (>C*H*Br, $W_{1/2} \approx 32$ Hz). *cis*-4-*tert*-Butylcyclohexyl bromide (95% cis) was synthesized in about 60% yield from commercial 4-*tert*-butylcyclohexanol (80% trans) by the triphenylphosphine–bromine method described previously: bp 71 °C (2 mm); mp 23 °C (lit.[15] bp 70 °C (2 mm); mp 23–25 °C); ^1H NMR δ 4.70 (>C*H*Br, $W_{1/2} \approx 8$ Hz).

Cyclohexylstannanes. Cyclohexyltriphenylstannane. Triphenyltin chloride (1.93 g, 50 mmol), dissolved in tetrahydrofuran, was added slowly to a cooled ethereal solution of cyclohexylmagnesium bromide (100 mmol). The reaction mixture was stirred overnight at room temperature and then quenched with water, followed by extraction with ether. The combined ether extracts were washed with water and dried ($MgSO_4$). Removal of ether provided the crude product that was crystallized twice from ethanol to afford 19.6 g (91%) of pure compound: mp 130 °C (lit.[25] 131–132 °C); ^1H NMR δ 1.0–2.3 (11 H), 7.0–7.9 (15 H). Anal. Calcd for $C_{24}H_{28}Sn$: C, 66.51; H, 6.00. Found: C, 66.75; H, 6.17.

***trans*-(4-Methylcyclohexyl)triphenylstannane.** To a cooled (~0 °C) solution of (triphenylstannyl)lithium (12 mmol), freshly prepared from triphenyltin chloride and lithium chips in tetrahydrofuran in the standard way,[4,26] was added *cis*-4-methylcyclohexyl bromide (1.77 g, 10 mmol). The solution was stirred overnight at room temperature (N_2) before a conventional workup. The crude product, an oily solid, was extracted with boiling pentane to remove most of the (insoluble) hexaphenyldistannane. The filtrate, consisting of some unreacted bromide, desired stannane, and some hexaphenyldistannane, was passed down a silica gel column (pentane, Kieselgel 40) to remove the distannane. The eluant was concentrated and the crude solid crystallized from hot ethanol to provide the target compound: 1.1 g, 25%; mp 71.5 °C; ^1H NMR δ 0.74 (d, J = 8 Hz, CH_3CH), 7.1–8.0 (15 H). Anal. Calcd for $C_{25}H_{28}Sn$: C, 67.1; H, 6.26. Found: C, 67.33; H, 6.43.

***cis*-(4-Methylcyclohexyl)triphenylstannane.** The reaction of *trans*-4-methylcyclohexyl bromide with (triphenylstannyl)-lithium in the manner described above provided *cis*-(4-methylcyclohexyl)triphenylstannane (60%): mp 73.5 °C; ^1H NMR δ 0.76 (d, J = 6 Hz CH_3–CH<), 7.1–7.8 (15 H). Anal. Calcd for $C_{25}H_{28}Sn$: C, 67.11; H, 6.26. Found: C, 67.48; H, 6.26.

trans-(4-*tert*-Butylcyclohexyl)triphenylstannane. Treatment of (4-*tert*-butylcyclohexyl)magnesium bromide (40 mmol) with triphenyltin chloride (10.4 g, 27 mmol) was followed by refluxing (1 h) and stirring for 3 days (room temperature). Workup in the manner described above provided a mixture of the desired stannane and Grignard coupled product ($C_{20}H_{38}$). Separation of these solids was effected by several crystallizations from pentane in which the hydrocarbon is more soluble. The progress of the separation was monitored by ^1H NMR (alkyl to phenyl proton ratio). Several crystallizations of the stannane from ethanol provided pure *trans*-(4-*tert*-butylcyclohexyl)triphenylstannane: 8.0 g, 60%; mp 105.5 °C. The 300-MHz ^1H NMR spectrum is presented in the text and Table I. Anal. Calcd for $C_{28}H_{34}Sn$: C, 68.71; H, 6.95. Found: C, 68.68; H, 6.93.

***cis*-(4-*tert*-Butylcyclohexyl)triphenylstannane.** *trans*-4-*tert*-Butylcyclohexyl tosylate (4.65 g, 15 mmol) was added to a freshly prepared solution of (triphenylstannyl)lithium (20 mmol), at room temperature, and the mixture was stirred for 12 days. Standard workup followed by column chroamtography (above) provided a clear viscious oil that could not be obtained crystalline; 6.3 g, 63%. Anal. Calcd for $C_{28}H_{34}Sn$: C, 68.71; H, 6.95. Found: C, 68.71; H, 6.97.

***trans*-(4-Methylcyclohexyl)triisopropylstannane.** The corresponding triphenylstannane (11.2 g, 25 mmol) was placed in a two-necked round-bottomed flask containing ethanol (40 mL) and methanol (60 mL). To this warmed (60 °C) solution was added (dropwise) concentrated hydrochloric acid (2.89 g, 25 mmol) dissolved in methanol (5 mL), and the whole was refluxed (1 h). Removal of the alcohol solvents (rotary evaporator) left an oily residue that was dissolved in anhydrous ether to which $MgSO_4$ was added. Removal of ether etc. provided *trans*-(4-methylcyclohexyl)diphenyltin chloride (10.09 g, 99%). This chloride,

(19) Barron, P. R.; Doddrell, D.; Kitching, W. *J. Organomet. Chem.* **1977**, *139*, 361.
(20) Kitching, W.; Doddrell, D.; Grutzner, J. B. *J. Organomet. Chem.* **1976**, *107*, C5. Moder, T. I.; Hsu, C. K.; Jensen, F. R. *J. Org. Chem.* **1980**, *45*, 1008.
(21) In this connection see: Adcock, W.; Kok, G. B.; Abeywickrema, A. N.; Kitching, W.; Drew, G. M., Olszowy, H. A.; Schott, I. *J. Am. Chem. Soc.* **1983**, *105*, 290.
(22) Cristol, S. J.; Firth, W. C. *J. Org. Chem.* **1961**, *26*, 280.
(23) Van Bekkum, H.; Kleis, A. A. B.; Massier, A. A.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 588.
(24) Jensen, F. R.; Gale, L. H.; Rodgers, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 5793.
(25) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459.
(26) Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963**, *28*, 237.

dissolved in ether (10 mL), was added to isopropylmagnesium bromide (50 mmol). After the mixture was stirred at room temperature (1 h), excess Grignard was carefully destroyed and a standard workup afforded *trans*-(4-methylcyclohexyl)diphenylisopropylstannane (10.0 g, 97%), which was then subjected to two successive acidolysis isopropylation sequences. *trans*-(4-Methylcyclohexyl)triisopropylstannane (7.8 g) was obtained in 90% yield based on starting triphenylstannane. (Cleavage of two phenyl groups from the triphenylstannane by acid results in poor yields of tin dichlorides probably due to oxidation, hydrolytic condensation, or polymerization): bp 89 °C (0.5 mm); ^{1}H NMR δ 1.28 (d, J = 4 Hz, 6 H, $(CH_3)_2CH$), 0.80 (d, J = 4 Hz, 3 H), CH_3–CH<), 1.3–2.1 (13 H). Anal. Calcd for $C_{16}H_{34}Sn$: C, 55.65; H, 9.86. Found: C, 55.95; H, 9.91.

Cyclohexyltriisopropylstannane was obtained from the triphenylstannane utilizing this acidolysis–isopropylation route, in 89% yield: bp 97 °C (2 mm); ^{1}H NMR δ 1.30 (d, J = 6 Hz, 6 H, $(CH_3)_2CH$), 1.4–2.0 (14 H). Anal. Calcd for $C_{15}H_{32}Sn$: C, 54.38; H, 9.67. Found: C, 54.56; H, 9.67.

***cis*-(4-*tert*-Butylcyclohexyltriisopropylstannane.** *trans*-4-*tert*-Butylcyclohexyl tosylate (6.2 g, 20 mmol) dissolved in tetrahydrofuran (15 mL) was added dropwise to a cooled (0 °C) solution (THF) of (triisopropylstannyl)lithium (25 mmol) from triisopropyltin bromide (8.2 g, 25 mmol) and lithium (0.9 g, 125 mmol). The reaction mixture was allowed to stirr for 10 days (25 °C) and subjected to a standard workup procedure. The crude oil, freed of unreacted tosylates (silica gel column; pentane; Kiesel gel 40, 70–230 mesh, Merck), consisted of the desired stannane, hexaisopropyldistannane, and tetraisopropylstannane. (See ref 11 for a pertinent discussion.) Titration of this mixture with iodine/chloroform converted distannane to the tin halide which, after removal of chloroform, was treated with excess isopropylmagnesium bromide. Standard workup yielded a colorless oil that was vacuum distilled to afford two fractions: (1) 85–90 °C (4 mm) (predominantly tetraisopropylstannane) and (2) 120 °C (0.1 mm) (1.03 g, 13%) being pure *cis*-(4-*tert*-butylcyclohexyl)triisopropylstannane; ^{1}H NMR δ 1.35 (d, J = 4 Hz, 6 H, $(CH_3)_2CH$), 0.85 (s, 9 H), 1.4–2.4 (13 H).

***cis*-(4-Methylcyclohexyl)triisopropylstannane** was obtained in 90% yield by the dephenylation–isopropylation route or less satisfactorly (18%) by tosylate displacement with (triisopropylstannyl)lithium: bp 92 °C (5 mm); ^{1}H NMR δ 1.33 (d, J = 4 Hz, 6 H, $(CH_3)_2CH$), δ 0.87 (d, J = 6 Hz, 3 H, CH_3CH), 1.4–2.2 (13 H). Anal. Calcd for $C_{16}H_{34}Sn$: C, 55.65; H, 9.86. Found: C, 55.56; H, 9.3.

***trans*-(4-*tert*-Butylcyclohexyl)triisopropylstannane** was obtained in high yield (92%) from the *trans*-triphenylstannane but in low yield (4%) from the cis tosylate: mp 118 °C (0.1 mm); ^{1}H NMR δ 1.32 (d, J = 4 Hz, 6 H, $(CH_3)_2CH$), 0.82 (s, 9 H, $(CH_3)_3C$), 1.35–2.2 (13 H). Anal. Calcd for $C_{19}H_{40}Sn$: C, 58.91; H, 10.34. Found: C, 59.72; H, 10.55.

The ^{13}C and ^{119}Sn NMR characteristics of the above stannanes are summarized in Tables II and III.

NMR Spectra. ^{1}H NMR spectra were obtained for deuteriochloroform solutions and referenced to internal tetramethylsilane, on a JEOL MH100 spectrometer. Some ^{1}H spectra (300 MHz) were obtained on the Bruker CXP-300 spectrometer at the Brisbane NMR Centre. ^{13}C NMR spectra were recorded at 25 MHz (JEOL FX-100) or 75.46 MHz (Bruker CXP-300) in the pulsed Fourier transform mode with complete proton noise decoupling. In general, 10–20% solutions ($CDCl_3$) in 10-mm tubes were employed with internal tetramethylsilane as standard. The field was (internally) locked on the ^{2}H resonance of the solvent ($CDCl_3$) or externally locked on a ^{7}Li signal. Spectra were recorded by using a 90° pulse, 5 or 10 KHz spectral widths, 8K or 16K data points, with a pulse delay of 2 s in the double precision mode. ^{119}Sn NMR spectra were obtained at 37.08 (JEOL FX-100) or 111.9 MHz (Bruker CXP-300) for 10% solutions in $CDCl_3$ solvent, using internal $(CH_3)_4Sn$ as reference.

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Registry No. $(C_6H_5)_3SnCl$, 639-58-7; $(Ph)_3SnLi$, 4167-90-2; $(i\text{-}Pr)_3SnLi$, 82544-67-0; $(i\text{-}Pr)_3SnBr$, 19464-54-1; *trans*-(4-methylcyclohexyl)triphenylstannane, 80963-46-8; *cis*-(4-methylcyclohexyl)triphenylstannane, 80963-47-9; *trans*-(4-*tert*-butylcyclohexyl)triphenylstannane, 91280-87-4; *cis*-(4-*tert*-butylcyclohexyl)triphenylstannane, 91280-88-5; *trans*-(4-methycyclohexyl)triisopropylstannane, 82544-63-6; *cis*-(4-methylcyclohexyl)triisopropylstannane, 82544-62-5; *trans*-(4-*tert*-butylcyclohexyl)triisopropylstannane, 83802-06-6; *cis*-(4-*tert*-butylcyclohexyl)triisopropylstannane, 83802-07-7; *trans*-(4-methylcyclohexyl)trimethylstannane, 64871-26-7; *cis*-(4-methylcyclohexyl)trimethylstannane, 64871-27-8; *trans*-(4-*tert*-butylcyclohexyl)trimethylstannane, 64871-28-9; *cis*-(4-*tert*-butylcyclohexyl)trimethylstannane, 38630-14-7; *trans*-(4-methylcyclohexyl)diphenyltin chloride, 91280-89-6; *trans*-(4-methylcyclohexyl)diphenylisopropylstannane, 91280-90-9; cyclohexyltriphenylstannane, 20204-06-2; cyclohexyltriisopropylstannane, 82544-60-3; cyclohexyltrimethylstannane, 3531-48-4; tetraisopropylstannane, 2949-42-0; *cis*-4-methylcyclohexyl bromide, 28046-90-4; *trans*-4-methylcyclohexyl bromide, 28046-91-5; *cis*-4-*tert*-butylcyclohexyl bromide, 5009-36-9; *trans*-4-*tert*-butylcyclohexyl bromide, 5009-37-0; 4-*tert*-butylcyclohexyl bromide, 7080-86-6; *trans*-4-*tert*-butylcyclohexyl tosylate, 7453-05-6; cyclohexyl bromide, 108-85-0; isopropyl bromide, 75-26-3; hexaisopropyldistannane, 17106-21-7.