crystallization from ethanol gave the analytical sample: mp 138-144 °C; ^{1}H NMR ($CDCl_3$) δ 8.94 (s, 1 H, H-2), 8.69 (s, 4 H, pyr), 8.12 (s, 1 H, H-8), 7.20 (s, 5 H, Bz), 5.40 (s, 2 H, CH_2); IR (KBr) 1640 (m), 1580, 1325 cm^{-1}; UV (CH_3OH) 216 nm (ϵ 4.30), 290 (4.13); MS, m/e (relative intensity) 287 (61, M^+), 259 (6, M - CH_2N), 210 (8, M - C_6H_5), 91 (100, $C_7H_7^+$).

9-Benzyl-6-chloropurine was made by a modification of the procedure of Montgomery.[13] A mixture of 23.3 g (0.15 mol) of 6-chloropurine and 16.25 g of sodium carbonate in 200 mL of dimethylacetamide was stirred at room temperature as 17.5 mL of benzyl chloride was added. After 1 day a second portion of 17.5 mL of benzyl chloride was added, and the stirring was continued for an additional 2 days. The reaction mixture was poured into 2 L of water and the aqueous phase decanted from the gummy solid which formed. This solid was dissolved in 400 mL of methylene chloride, and this solution was chromatographed on a Waters Prep-LC 500 and eluted with 3:2 ethyl acetate/hexane to give 18.67 g (50.9% yield) of a tan solid (k = 2.2) identified as 9-benzyl-6-chloropurine, mp 93-95 °C (lit.[14] mp 84-8.5 °C). A second fraction (k = 6.0) of 6.69 g (18.2 % yield) of white solid (mp 148-149 °C), identified as 7-benzyl-6-chloropurine (lit.[13] mp 152-153 °C), was also obtained.

9-Benzyl-6-iodopurine was made by standard methods.[15] Five grams (20.4 mmol) of 9-benzyl-6-chloropurine was added in portions over 20 min to 25 mL of mechanically stirred, ice cold, 55% aqueous HI. The bright yellow slurry was stirred for an additional 90 min, and the temperature was kept below -5 °C. The slurry was filtered, washed with a little cold water, and then washed with acetone. The air-dried solid residue was suspended in 50 mL of water and cooled to 10 °C, and the pH was adjusted to 8.1. Filtration and drying gave 6.19 g (90.3% yield) of a yellow powder. Recrystallization from toluene/acetone gave the analytical sample: mp 152-154 °C; ^{1}H NMR ($CDCl_3$) δ 8.56 (s, 1 H, H-2), 8.06 (s, 1 H, H-8), 7.30 (s, 5 H, Bz), 5.37 (s, 2 H, CH_2); UV (CH_3OH) 275 nm (ϵ 4.06), 295 (2.97); MS, m/e (relative intensity) 336 (15, M^+), 209 (16, M - I), 91 (100, $C_7H_7^+$).

Photolysis of 9-Benzyl-6-iodopurine. A mixture of 0.5 g (1.49 mmol) of the iodopurine, 0.15 g of sodium bicarbonate, a trace of sodium thiosulfate, and 50 mL of anisole in 300 mL of acetone was placed in a quartz photochemical reactor. The mixture was irradiated for 1 h with a 450-W medium-pressure mercury lamp fitted with a Vycor sleeve. Filtration and evaporation gave 0.69 g of brown gum which was chromatographed to give 0.03 g (6.4% yield) of 9-benzyl-6-(3-methoxyphenyl)purine (mp 110-113 °C) and 0.8 g (17.0% yield) of 9-benzyl-6-(4-methoxyphenyl)purine, mp 150-153 °C. Also obtained were 0.08 g of unreacted starting material and an additional 0.08 g of an uncharacterized non-anisole-containing purine.

Registry No. **1a**, 700-00-5; **1b**, 4261-14-7; **2a**, 71-43-2; **2b**, 98-08-8; **2c**, 100-66-3; **2d**, 110-86-1; **4** (Ar = C_6H_5; R = $CH_2C_6H_5$), 83135-02-8; **4** (Ar = C_6H_5; R = CH_3), 83135-03-9; **4** (Ar = m-$CH_3OC_6H_4$; R = $CH_2C_6H_5$), 83135-04-0; **4** (Ar = p-$CH_3OC_6H_4$; R = $CH_2C_6H_5$), 83135-05-1; **4** (Ar = p-$CF_3OC_6H_4$; R = $CH_2C_6H_5$), 83135-06-2; **4** (Ar = m-$CF_3C_6H_4$; R = $CH_2C_6H_5$), 83135-07-3; **4** (Ar = 5-nitro-2-pyridyl; R = $CH_2C_6H_5$), 83135-08-4; **4** (Ar = 3-pyridyl; R = $CH_2C_6H_5$), 83135-09-5; **4** (Ar = 2-pyridyl; R = $CH_2C_6H_5$), 83135-10-8; **4** (Ar = 4-pyridyl; R = $CH_2C_6H_5$), 83135-11-9; **5**, 83135-12-0; **6**, 87-42-3; **8**, 1928-76-3; **9**, 1928-77-4; **10**, 83135-13-1; 9-benzylhypoxanthine, 14013-11-7.

(13) Montgomery, J. A.; Temple, C. *J. Am. Chem. Soc.* **1961**, *83*, 630.
(14) Greenberg, S. M.; Ross, L. O.; Robins, R. K. *J. Org. Chem.* **1959**, *24*, 1314.
(15) Elion, G. B.; Hitchings, G. H. *J. Am. Chem. Soc.* **1956**, *78*, 3508.

Reactions of (Organostannyl)- and (Organogermyl)lithium Reagents with Some (Allylic) Cyclohex-2-enyl Chlorides

Geoffrey Wickham, David Young, and William Kitching*

Chemistry Department, University of Queensland, Brisbane 4067, Australia

Received April 1, 1982

The stereo- and regiochemistries of the reactions between (trimethylgermyl)lithium, (triphenylstannyl)lithium, and (trimethylstannyl)lithium and *cis*- and *trans*-5-methyl-2-cyclohexenyl chlorides, 3,5-dimethyl-2-cyclohexenyl chlorides, and some deuterated derivatives have been investigated utilizing ^{1}H, ^{2}H, ^{13}C, and ^{119}Sn nuclear magnetic resonance spectroscopy. The major substitution pathway (forming the allylic organometallic) involves configurational inversion at carbon and is accompanied by an insignificant level of ^{2}H relocation between the allylic positions. The S_N2 mechanism is strongly implicated. Serious side reactions accompany the reactions of (trimethylgermyl)lithium generated in hexamethylphosphoric triamide (HMPA), and significant amounts of digermanes and cyclohexenyldimethylamines form. The latter almost certainly result from chloride displacement by dimethylamide ($(CH_3)_2N^-$, formed by alkali metal cleavage of HMPA), such displacement proceeding regio- and stereospecifically in accord with the S_N2 pathway. Pentamethyl(cyclohex-2-enyl)digermanes which are formed stereospecifically, are considered to result from chloride displacement by (pentamethyldigermyl)lithium, formed by dimethylgermylene insertion into (trimethylgermyl)lithium itself. Certain redistribution reactions of the pentamethyl(cyclohex-2-enyl)digermanes have been observed.

Substantial progress has been made in understanding the diverse reaction pathways of organometal anions with organic substrates, and much of this attention has been directed to the reactions of organotin alkalis with alkyl halides. Organogermyl alkalis have also been examined, and much of the available information is available in key papers.[1-5]

Some of our studies necessitated the synthesis of certain allylic germanium and tin compounds, desirably with a high level of stereo- and regiocontrol in the carbon-metal bond formation step. Information available indicated that toward secondary (cycloalkyl) bromides, $(C_6H_5)_3SnLi$ displayed "S_N2" behavior, whereas $(CH_3)_3SnLi$ and $(CH_3)_3GeLi$ reacted by free-radical routes, with associated loss of stereocontrol.[1-5] Cycloalkyl chlorides were less susceptible to electron transfer from the organotin alkalis, with an increased tendency toward stereocontrol (inver-

(1) Key references are contained in: Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833.
(2) San Filippo, J.; Silbermann, J. *J. Am. Chem. Soc.* **1981**, *103*, 5589.
(3) Kitching, W.; Olszowy, H. A.; Harvey, K. *J. Org. Chem.* **1981**, *46*, 2423.
(4) Kitching, W.; Olszowy, H. A.; Harvey, K. *J. Org. Chem.*, in press.
(5) Kitching, W.; Olszowy, H. A.; Waugh, J.; Doddrell, D. *J. Org. Chem.* **1978**, *43*, 898.

0022-3263/82/1947-4884$01.25/0

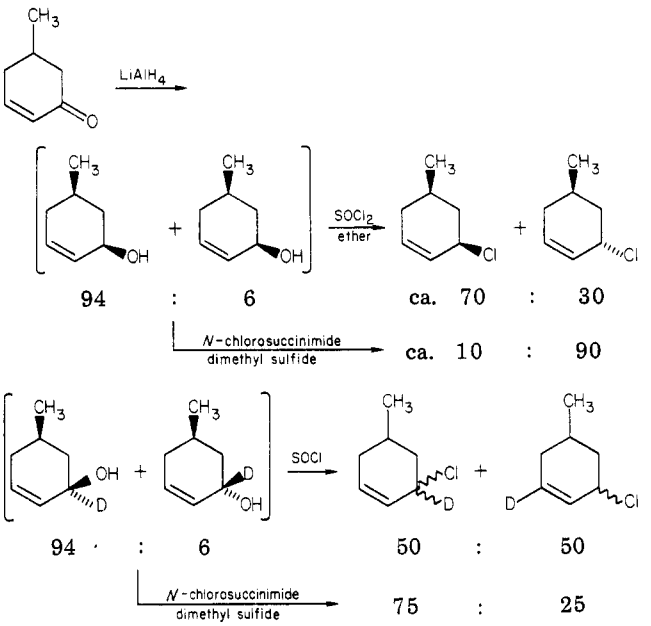
sion) at carbon.[6] These facts suggested that allylic chlorides might react with high stereospecificity toward $(C_6H_5)_3SnLi$ and perhaps also with $(CH_3)_3SnLi$ and $(CH_3)_3GeLi$. The present work was undertaken to test these proposals and the related possibility of allylic transposition (S_N2'-type process) accompanying the substitution.

Matarosso-Tchiroukhine and Cadiot[7] have investigated the reactions of R_3MLi reagents with *cis*- and *trans*-crotyl chlorides to yield the 2-butenyl metallics of retained double bond configuration, whereas the same reagents with α-methallyl chloride (3-chloro-1-butene) provided a mixture of the (*E,Z*) primary and secondary isomers. S_N-type mechanisms were suggested although the level of any "S_N2'" contribution was unclear. More recently, while some of our work was in progress, Pereyre reported[8] some observations on the same subject and concluded that $(n\text{-}C_4H_9)_3SnLi$ and $(CH_3)_3SnLi$ reacted with (mixtures of) *cis*- and *trans*-5-methyl-2-cyclohexenyl chlorides with inversion of configuration at carbon to yield the corresponding trialkylstannanes. This result was consistent with S_N2 displacement, but the importance of the S_N2' process was not established. Subsequently, Pereyre[9] investigated the reactions of $(CH_3)_3SnLi$ with the above tosylates, and the substitution was neither regio- or stereospecific. $(n\text{-}C_4H_9)_3SnLi$ was reported to react with high stereo- and regiospecificity with the same tosylates, a more appealing result.

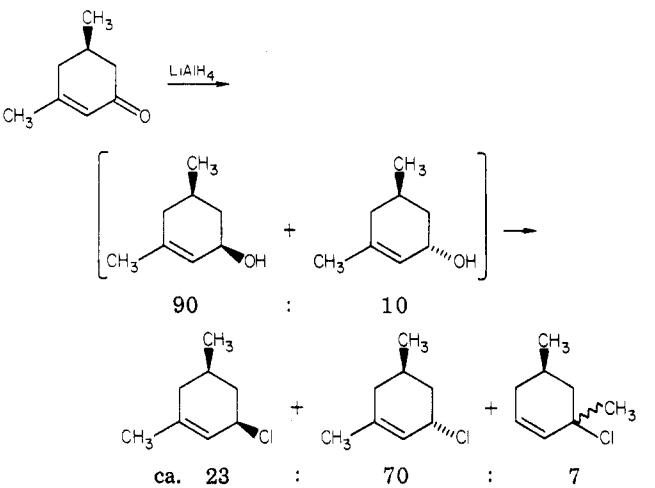
Results and Discussion

In common with Pereyre, we initially employed the 5-methyl-2-cyclohexenyl system which has been utilized extensively for mechanistic studies. The cyclohexenone can be reduced to provide a ca. 94:6 cis/trans mixture (^{13}C, VPC, hydrogenation to *cis*-3-methylcyclohexanol) of the 5-methyl-2-cyclohexenols, which have been chlorinated under several conditions. Goering[10] has reported that chlorination of isomerically pure alcohol with thionyl chloride (diethyl ether) can provide chloride with complete retention of configuration and allylic rearrangement as judged by careful infrared studies, a result apparently confirmed by Yamamoto.[11] We have never been able to repeat, to a satisfactory level of agreement, Goering's results on the chlorination, an experience shared by Pereyre[8,12] and his colleagues.[13] Therefore, we worked with isomeric mixtures, and fortunately it was possible to obtain two chloride mixtures, one rich in cis isomer (by $SOCl_2$) and the other rich in trans isomer (using the *N*-chlorosuccinimide–dimethyl sulfide chlorination).[14] By use of the 94:6 cis–trans mixture of 5-methyl-2-cyclohexenol, the usual result of $SOCl_2$ chlorination was an ca. 70:30 cis–trans

Scheme I



Scheme II



chloride mixture, based on ^{13}C NMR studies, and IR comparisons using frequencies reported[10] as being characteristic of the individual chloride isomers. On one occasion a ca. 85:15 cis–trans chloride mixture was obtained from the 94:6 cis–trans alcohol mixture, but the reasons for this result were not obvious. ^{13}C NMR examination of the product before and after distillation indicated no distillation-induced isomerization or fractionation.

Treatment of the same 94:6 cis–trans alcohol mixture with the *N*-chlorosuccinimide–dimethyl sulfide reagent of Corey,[14] provided good yields of a chloride mixture which was, however, ca. 85:15 trans/cis, implying a high level of specificity. To investigate the question of the incursion of the S_N2' mechanism (or some equivalent) in our reactions, we required a specifically (or less satisfactory, preferentially) deuterated derivative. Goering had reported[15] procedures for introducing ^2H specifically into this system. Using the 94:6 cis–trans mixture, with ^2H located exclusively at the 1-position (carrying the OH), the $SOCl_2$ chlorination provided the chloride mixture with the ^2H label distributed equally between the allylic positions. This was indicated by the ^1H NMR spectrum but completely

(6) San Filippo, J.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.
(7) Matarosso-Tchiroukhine, E.; Cadiot, P. *J. Organomet. Chem.* **1976**, *121*, 155.
(8) Dumartin, G.; Quintard, J. P.; Pereyre, M. *J. Organomet. Chem.* **1980**, *185*, C34.
(9) Quintard, J. P.; Dugueil-Castaing, M.; Dumartin, G.; Rahm, A.; Pereyre, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1004.
(10) Goering, H. L.; Nevitt, T. D.; Silversmith, E. F. *J. Am. Chem. Soc.* **1955**, *77*, 4042.
(11) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 2318.
(12) Professor M. Pereyre (Bordeaux) also observed that several chlorinations with thionyl chloride in ether of the 93:7 *cis-/trans*-5-methylcyclohex-2-enol resulted in a 70:30 cis/trans chloride mixture (private communication, Aug 1980, and ref 8).
(13) In this connection, the observations of Noyes are particularly pertinent: Lesnini, D. G.; Buckley, P. D.; Noyes, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 668.
(14) Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, 4339.
(15) Goering, H. L.; Singleton, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 7854.

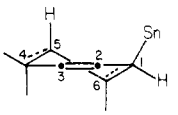
confirmed by the ^2H spectrum. (It was possible to determine the ^2H distribution between the two sites in *each* of the chloride isomers by a combination of ^2H and ^{13}C NMR; see later.) Curiously this result was also obtained by Yamomoto,[11] who nevertheless reported a cis/trans chloride ratio of 94:6. Fortunately, treatment of the ^2H-labeled alcohol with *N*-chlorosuccinimide–dimethyl sulfide provided chloride with a 75:25 distribution of the label (^2H and ^1H NMR) so that an assessment of "S_N2'" incursion could be made. These results are summarized in Scheme I.

Reduction of 3,5-dimethylcyclohexenone in the usual way provided a ca. 90:10 mixture (^{13}C NMR, VPC) of cis and trans alcohols (Scheme II), which on treatment with $SOCl_2$ yielded a chloride mixture rich in the trans isomer. ^{13}C NMR examination indicated also the presence of another isomer in ca. 10% yield, suspected to the dimethyl tertiary chloride.

Thus chlorination ($SOCl_2$) of this 3,5-dimethylcyclohexenol proceeds with predominant inversion of configuration. Chlorination using *N*-chlorosuccinimide/dimethyl sulfide was conducted also, and a very similar result, i.e., predominantly trans chloride with some tertiary chloride, was obtained.

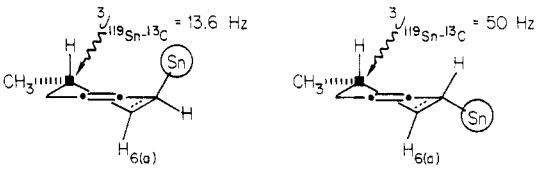
(Triphenylstannyl)lithium reactions. Initially we prepared (2-cyclohexenyl)triphenylstannane in the reported way,[16] as well as by reaction of 2-cyclohexenyl chloride with (triphenylstannyl)lithium (in tetrahydrofuran) and obtained the ^{13}C, ^{119}Sn, and ^1H NMR spectra to facilitate interpretation of the spectra of the corresponding (5-methyl-2-cyclohexenyl)tin derivatives. The ^{13}C assignments were arrived at by consideration of ^{13}C–^{119}Sn coupling constants,[17] the substituent chemical shifts of $Sn(C_6H_5)_3$ in cyclohexane derivatives,[4] and regularities in the spectra of 2-cyclohexenyl metallics generally (Table I).

The quite small *vic* ^{119}Sn–^{13}C coupling of 25.6 Hz (to C_5) requires a predominantly quasi-axial orientation of the $Sn(C_6H_5)_3$ group despite the operation of the 5-axial H interaction. This conformational preference is a consequence of a stabilizing σ–π interaction with a quasi-axial C–Sn σ-bond.[18] (2-Cyclohexenyl)triphenylstannane has a $\delta_{^{119}Sn}$ value of −130.3 ppm [relative to $(CH_3)_4Sn$; $CDCl_3$ solvent]. The most notable feature of the (300 MHz) ^1H spectrum was the broad singlet at δ 2.88 ($^2J_{^{119}Sn-H}$ = 90 Hz) associated with >C**H**Sn.



Reaction of a 70:30 cis/trans mixture of 5-methyl-2-cyclohexenyl chloride with $(C_6H_5)_3SnLi$ provided a viscous oil that did not crystallize but which analyzed appropriately for the triphenylstannane. The ^1H (300 MHz) spectrum of the mixture showed (in part) two methyl doublets at δ 0.83 ($J \approx 6$ Hz) and 0.91 ($J \approx 5$ Hz) with the former more intense (ca. 70:30), and signals for C**H**–Sn at δ 2.96 (major, $W_{1/2}$ = 13 Hz) and at δ 2.85 (minor, $W_{1/2}$ = 20 Hz), both with $^2J_{^{119}Sn-^1H}$ = 90 Hz. The ^{119}Sn spectra exhibited signals at −124.8 and −131.0 ppm [relative to internal $(CH_3)_4Sn$], and careful intensity measurements indicated a ratio of 31:69, with the higher field (−131.0 ppm) signal more intense. The reaction thus appears to be stereospecific, and the agreement between the ^{119}Sn shifts of the parent (−130.3 ppm) and the signal at −131.0 ppm suggests that the major isomer has $Sn(C_6H_5)_3$ pseudoaxial, as in the trans isomer (with C–CH_3 equatorial), indicating *inversion* of configuration at carbon. Our previous demonstrations[4,17] of an angular dependence of vicinal ^{119}Sn–^{13}C coupling in a wide range of trimethyl- and triphenylstannanes suggested this approach would be definitive. The 75.44-MHz ^{13}C spectrum of the above stannane mixture showed (in the alkyl region) two sets of five signals with the intensity ratio being ca. 2:1.

It was possible (use of 25 HHz spectra as well) to locate ^{119}Sn couplings to all alkyl carbons (except C–CH_3), and in conjunction with the assignments of the parent cyclohexenyltriphenylstannane and substituent effects of the 5-methyl group, the spectra could be assigned confidently (see later for ^2H effects on the ^{13}C spectra; Table I). C_5 in the major isomer had $J_{vic} \approx 13.6$ Hz, while in the minor isomer J_{vic} was close to 50 Hz. Thus it is the minor isomer with a large dihedral angle between ^{119}Sn and C_5 and which therefore must be cis. Other features of the spectra are in accord with this conclusion, and thus the displacement in this case is highly specific, proceeding with inversion of configuration at carbon. The reaction was repeated on another preparation of predominantly *cis*-chloride (85:15), and concordant results were obtained. We mentioned that the >C**H**Sn signal was quite broad in the minor isomer ($W_{1/2} \approx 20$ Hz) but much narrower in the major isomer ($W_{1/2} \approx 13$ Hz). Again this confirms the minor isomer to be cis, because the >C**H**Sn proton has one large vicinal coupling to $H_{6(axial)}$ (with other smaller couplings) whereas in the *trans* isomer, no large vicinal coupling is operative in the conformations favored by these stannanes. In fact, the shapes of the 1-H) methine proton signals, where they can be identified and resolved (normally at 300 MHz), define the cis or trans arrangements in isomers in this general series.



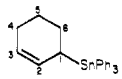
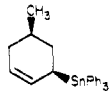
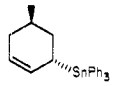
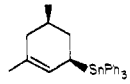
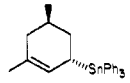
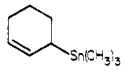
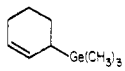
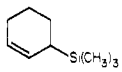
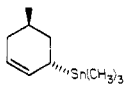
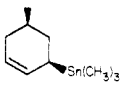
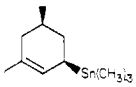
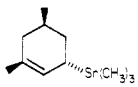
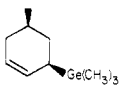
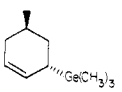
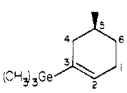
trans ($\theta \simeq 75°$) cis ($\theta \simeq 170°$)

As indicated above, a chloride mixture rich in trans isomer could be obtained utilizing dimethyl sulfide–*N*-chlorosuccinimide chlorination.[14] Reaction of $(C_6H_5)_3SnLi$ with this 85:15 trans/cis chloride gave predominantly *cis*-stannane according to all the criteria discussed in detail above. The specificity, however, appeared somewhat lower, being ca. 72:28 cis/trans, but in a duplicate run, 83:17 trans/cis chloride provided a 87:13 *cis*-/*trans*-stannane mixture.

The question of the incursion of substitution proceeding with allylic rearrangement was next considered. (From the above results, any significant S_N2' pathway would involve anti approach by the tin nucleophile.) Reduction of the enol ether with lithium aluminum deuteride[15] provided 5-methyl-3-deuteriocyclohex-2-enone, which was reduced ($LiAlH_4$) and chlorinated (*N*-chlorosuccinimide–dimethyl sulfide) to provide an 80:20 trans/cis chloride mixture (^{13}C NMR). The ^2H NMR spectrum consisted of signals at δ 5.90 and 4.63 (vinyl ^2H and methine ^2H, respectively) in the ratio of 79:21. The distribution of the ^2H label between the vinylic and allylic positions in *each* of the *two* chloro isomers could not be determined from the ^2H spectrum,

(16) Fish, R. H.; Broline, B. M. *J. Organomet. Chem.* **1978**, *159*, 255.
(17) 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.
(18) Brown, R. S.; Eaton, D. F.; Hosomi, A.; Traylor, T. G.; Wright, J. M. *J. Organomet. Chem.* **1974**, *66*, 249.

Table I. Carbon-13 NMR Data[a] for Cyclohex-2-enyl Metallics

compd[c]	chemical shift, carbon no. 1	2	3	4	5	6	others
	28.88 (389)	129.8 (45.2)	124.24 (48.7)	24.84 (16.1)	23.06 (25.6)	26.69 (19.8)	[b]
	27.84 (402)	129.21 (40.7)	125.35 (52)	33.92 (13.6)	30.30 (51)	35.99 (15.8)	22.18[b]
	29.91 (380)	129.6 (47.5)	123.10 (56.5)	33.56 (15.8)	28.59 (13.6)	34.64 (20.4)	21.91[b]
	27.61 (nl)	122.79 (42.6)	132.54 (54.9)	38.96 (14.6)	30.65 (54)	35.57 (nl)	23.80, 22.05[b]
	29.12	123.57	130.10	38.57	30.09	34.33	23.56, 21.93[b]
	26.42 (352)	130.85 (41)	121.81 (49.8)	24.96 (14.5)	22.83 (22)	26.42 (17.8)	−10.49 (307)
	27.41	128.93	124.71	25.07	22.44	24.78	−3.66
	26.12	127.88	125.33	25.05	22.61	23.73	−3.22
	27.39 (347)	130.59 (39.6)	120.64 (51.3)	33.77* (15.4)	28.35 (12.5)	34.76* (17.6)	22.42, −10.20 (305)
	25.14 (~338)	130.09 (39.6)	123.54 (45.4)	33.97 (16.2)	29.93 (46.2)	35.64 (13.9)	22.27, −11.37 (312)
	24.90 (381)	123.71 (38.1)	130.82 (49.1)	39.06 (13.2)	30.46 (52)	35.38 (16)	23.88, 22.18, −11.37 (308)
	27.13 (360)	124.39 (41.8)	127.87 (nl)	38.83 (15)	28.76 (~13)	34.59 (~17)	23.62, 22.33, −10.14 (300)
	27.56	128.22	125.03	33.82	29.31	33.48	22.17, −4.59
	27.46	128.44	122.86	32.45*	26.48	33.16*	21.56, −3.25
	26.83	132.54	139.38	36.11	28.75	30.53	21.85, −3.15

[a] Chemical shifts (in parts per million) relative to the center peak of the $CDCl_3$ triplet at 77.00 ppm. Values in parentheses are $^{119}Sn-^{13}C$ coupling constants in hertz. [b] Typical shifts for $(C_6H_5)_3Sn$ are 138.98 (Ipso), 137.26 (33.7 Hz, ortho), 128.42 (46.4 Hz, meta), and 128.80 ppm (para). [c] Numbering for ease of comparison.

as the (expected) four signals were not resolved. However, careful examination of the ^{13}C spectrum of the mixture and consideration of ^2H effects ($^{13}C-^2H$ coupling and ^2H isotope effects on ^{13}C shifts) required the conclusions that in the major trans isomer, ^2H was located ca. 75% on the vinyl carbon (25% at allylic position) and that in the cis isomer ^2H was distributed almost equally between the vinylic and allylic sites. [This implied that the formation of the cis isomer in this procedure probably involves a symmetrical (cationic) intermediate.]

The triphenyltin derivative was obtained in the usual way, and the ^{119}Sn spectrum indicated a cis (−124.8 ppm)/trans (−131.3 ppm) ratio of ca. 74:26, again in agreement with configurational inversion at carbon. The ^2H NMR spectrum of the stannane product showed signals at δ 5.72 (vinylic ^2H) and 2.93 (allylic ^2H) in the ratio of ca. 75:25, requiring very little (if any) incursion of the S_N2' pathway. Thus in the cyclohexenyl chloride systems, displacement by $(C_6H_5)_3SnLi$ proceeds predominantly, if not exclusively, by direct displacement with inversion at

carbon, a stereochemistry consistent with the S_N2 route.

The ^{119}Sn signal of the (minor) trans isomer consists of superimposed triplets with a $^2J_{Sn-^2H}$ of 14.2 Hz (calcd $^2J_{Sn-^1H}$ = 92.4 Hz) and a $^4J_{Sn-^2H}$ of ~2.9 Hz (calcd $^4J_{Sn-^1H}$ = 18.9 Hz). These triplets then correspond to the trans species with geminal and vinylic ^2H relative to $Sn(C_6H_5)_3$, and it is clear from the intensities of these triplets that (in this *trans*-stannane) ^2H is about equally distributed between the two sites, a situation that applied to the precursor *cis*-chloride. However, the ^{119}Sn signal of the (major) cis isomer consists of a (broadened) unresolved singlet flanked by two components of a triplet ($^2J_{Nn-^2H}$ = 13.7 Hz), and it is possible to estimate that ca. 70% of the ^2H label is vinylic (i.e., at C_3), in satisfactory agreement with the distribution in the precursor *trans*-chloride. It is also clear that $^4J_{Sn-^2H}$ (allylic coupling) is angularly dependent, as this coupling (~2.9 Hz) is clearly resolvable in the trans isomer [predominant pseudoaxial $Sn(C_6H_5)_3$] but not resolvable in the cis with $Sn(C_6H_5)_3$ pseudoequatorial. This observation, along with another, suggests an angular dependence for allylic Sn–^1H coupling of the type established for ^1H–^1H coupling.[19]

The chloride mixture obtained from 3,5-dimethylcyclohex-2-enol (ca. 94:6 cis/trans) with *N*-chlorosuccinimide/dimethyl sulfide was predominantly trans (~70%) together with cis (~23%) and one isomer of the tertiary allylic chloride (7%).

Comparison of the ^{13}C shifts of the major allylic chloride above with those established for the 5-methylcyclohex-2-enyl chlorides leaves no doubt as to the assignments. The 300-MHz ^1H spectrum, particularly in the >CHCl region, confirms the major isomer to be trans, as the more intense signal is narrower ($W_{1/2} \approx 11$ Hz) than the broad ($W_{1/2} \approx 23$ Hz) minor signal. Treatment of the above chloride mixture with $(C_6H_5)_3SnLi$ in the normal way provided a mixture of stannanes roughly in a 2:1 ratio on the basis of the ^{13}C spectrum (Table I). (Elimination is the result of reaction of tertiary halides with metalloidal anion reagents.[1])

The large vicinal ^{119}Sn–^{13}C coupling (54 Hz, to C_5) in the major isomer establishes it to be the *cis* isomer, a conclusion in agreement with the ^{119}Sn shifts of −125.1 (major) and −130.4 ppm (minor), when the comparisons are made with (5-methyl-cyclohex-2-enyl)triphenylstannanes (cis, −124.82 ppm; trans, −131.26 ppm). The intensity ratio of the ^{119}Sn signals (68:32) confirms inversion of configuration at carbon.

(Trimethylstannyl)lithium Reactions. Some years ago (1974) in these laboratories (Bullpitt prepared[20] (cyclohex-2-enyl)trimethylstannane and (cis- and trans-4-*tert*-butylcyclohex-2-enyl)trimethylstannane and examined aspects of their chemistry. The preparative procedures were based on lithium cleavage of the corresponding phenoxycyclohexenes and quenching with trimethylstannyl chloride, although the (trimethylstannyl)lithium route on cyclohex-2-enyl chloride was also employed. This latter approach has been studied in more detail with respect to stereochemistry, and the results are reported here. Some work along similar lines has been reported briefly by Pereyre,[8] and where comparisons are possible, there is good general agreement.

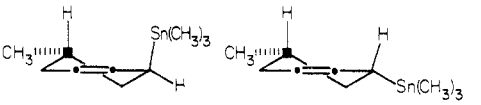
As in the triphenyltin case, we initially reprepared the (parent) (cyclohex-2-enyl)trimethylstannane and assigned its ^{13}C spectrum, the details of which are shown in Table I along with those for the analogous germanium and silicon derivatives.

The assignments were made on the basis of chemical shifts (comparisons with other cyclohexenes), ^{119}Sn–^{13}C couplings, and the α and β effects of the various metallo groups.[21]

The trimethyltin group is interesting in that its *A* value (ca. 1.0 kcal/mol)[22] is smaller than that of $Sn(C_6H_5)_3$ (ca. 1.5 kcal/mol)[4,16] and that, in addition, it has a greater capacity for σ–π interaction.[23] These facts would suggest that $Sn(CH_3)_3$ [more so than $Sn(C_6H_5)_3$] is largely quasi-axial in (cyclohex-2-enyl)trimethylstannane, and the small vicinal ^{119}Sn–^{13}C coupling (22 Hz) confirms this. Thus the σ–π interaction in these cyclohexenyl metallics is an important regulator of conformational preference.

Displacement of chloride from various cis/trans mixtures of 5-methylcyclohex-2-enyl chlorides with $(CH_3)_3SnLi$ (prepared in tetrahydrofuran in the usual way) was next examined. A ca. 70:30 cis/trans chloride mixture ($SOCl_2$ chlorination of the 94:6 cis/trans alcohols) on reaction with $(CH_3)_3SnLi$ provided the (5-methylcyclohex-2-enyl)trimethylstannanes in a 71:29 ratio as judged by the ^{119}Sn signals at −2.34 (major) and 0.37 ppm. [(Cyclohex-2-enyl)trimethylstannane has $\delta_{^{119}Sn}$ = −2.50 ppm.] The ^{13}C spectrum consisted of easily identifiable major and minor sets of signals in the ratio of 74:26 (based on comparisons of intensities of like signals), in acceptable harmony with the ^{119}Sn measurements. The question was how to relate the major and minor sets to the *cis*- and *trans*-stannanes. As outlined in the $Sn(C_6H_5)_3$ systems, the established[17] Karplus-like dependence of vicinal ^{119}Sn–^{13}C coupling on the dihedral angle, in conjunction with an insight into conformational preferences in these cyclohexenyl systems, could provide a basis for distinction.

The signals of the two sets were assigned to the carbons of the major and minor isomers on the basis of chemical shift and ^{13}C–^{119}Sn couplings (Table I), and given the preference of CCH_3 and $Sn(CH_3)_3$ for the equatorial and quasi-axial positions, respectively, the trans isomer would adopt to an overwhelming extent conformation A, whereas



A B

B would be appropriate for the cis isomer. Thus vicinal ^{119}Sn–^{13}C coupling to C_5 should be considerably greater in the cis isomer than in the trans. Thus the major isomer ($^3J_{^{119}Sn-C_5} \approx 12.5$ Hz) is trans and, in the absence of any significant S_N2' pathway, the substitution appears to be quite specific with inversion of configuration at carbon. A duplicate experiment led to the same conclusion.

We next examined the reaction of predominantly *trans*-chloride (75:25 trans/cis) preferentially labeled with ^2H at the vinylic site (~77%) as discussed previously for the $Sn(C_6H_5)_3$ reactions. The ^{119}Sn signals (complicated by ^2H coupling) were in the ratio of ca. 70:30, but with the lower field signal (ascribed above to the cis isomer) being more intense, a result consistent with inversion at carbon in each chloro isomer. (Although the ^{13}C spectrum is

(19) Professor Pereyre and co-workers[9] have utilized ^{119}Sn–^2H couplings for structural analysis for organostannanes.

(20) Bullpitt, M. Ph.D. Dissertation, University of Queensland, 1974. Kitching, W.; Adcock, W.; Marriott, M.; Doddrell, D. *J. Org. Chem.* **1976**, *41*, 1671.

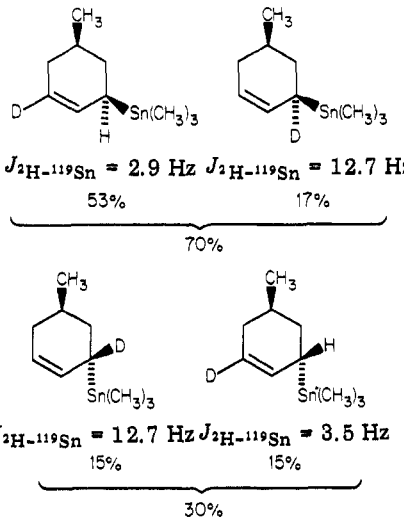
(21) Kitching, W.; Doddrell, D.; Grutzner, J. B. *J. Organomet. Chem.* **1976**, *107*, C5.

(22) Moder, T. I.; Hsu, C. C. K.; Jensen, F. R. *J. Org. Chem.* **1980**, *45*, 1008.

(23) For example, see: Hanstein, W.; Berwin, H. J.; Traylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 829 and references therein. Davis, D. D. *J. Organomet. Chem.* **1981**, *206*, 21.

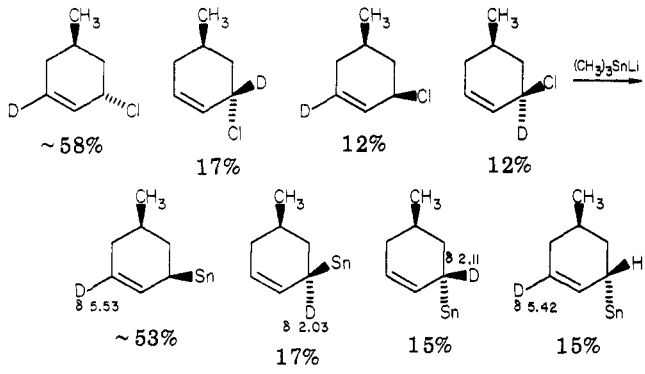
complicated by the ^2H effects, comparisons yield a cis/trans ratio of 73:27, based on the C_5 intensities.)

The fine structure in the ^{119}Sn signals, due to ^2H coupling, is particularly revealing.[9,19] For the cis isomer, the ^{119}Sn signal consists of overlapping triplets with $J_{^2H-^{119}Sn}$ values of ca. 2.9 and 12.7 Hz, for allylic and geminal ^2H–



^{119}Sn coupling, respectively. For the minor trans isomer, a slightly larger value for the allylic coupling is observed and attributed to the more favorable angular situation in this isomer. It is possible, from the intensities of the triplets, to calculate the *approximate* distribution of the four isomers, and these are shown above.

A 15.25-MHz ^2H spectrum of the (total) stannane product showed absorption regions at ca. δ 5.5 and 2.05, corresponding to vinylic and allylic ^2H. The intensity ratio was ca. 62:38, with the δ 5.5 signal being more intense. Even on allowance for errors etc., this appears to be significantly different from the ratio measured for the starting chloride [δ 5.89 (77%) and 4.63 (23%)] and could indicate a minor degree of the S_N2' route or some other ^2H-equilibrating pathway. It is clear, however, that S_N2' cannot be the major substitution mechanism. The two absorption regions consist of four signals at δ 5.53, 5.42, 2.11 ($J_{^2H-^{119}Sn}$ = 12.6 Hz) and 2.03 ($J_{^2H-^{119}Sn}$ = 12.5 Hz) for the deuterated cis and trans isomers (assignments below). The full re-



action outcome with *approximate* percentages, based on ^{13}C, ^2H, and ^{119}Sn examinations, is shown. These results demonstrate that the stereochemistry of chloride displacement by $(CH_3)_3SnLi$ is predominantly configurational inversion, a result indicative of a direct displacement mechanism (S_N2), although no kinetic data in support is available for these systems. The ^{13}C assignments shown (Table I) for the *cis*-stannane are completely confirmed from careful examination of the spectra of the deuterated compounds. However, in the case of the trans isomer, which has a ca. 50:50 distribution of ^2H between the allylic and vinylic positions, distinction between C_4 and C_6 on the basis of ^2H isotope effects is not possible.

The chloride mixture resulting from treatment of 3,5-dimethylcyclohexenol with *N*-chlorosuccinimide/dimethyl sulfide (measured to be 70% trans, 23% cis, and 7% tertiary) was reacted with $(CH_3)_3SnLi$. The isolated stannane exhibited two ^{119}Sn signals at −0.28 and −1.42 ppm with an intensity ratio of 72:28, in excellent agreement with the cis/trans chloride ratio of 23:70 or 25:75 (normalized). (Tertiary chloride would produce no substitution product.) The ^{13}C NMR spectrum consisted of two sets of signals (ca. 70:30) which could be assigned readily (Table I).

On the basis of the detailed argument presented earlier, the larger vicinal ^{119}Sn–^{13}C coupling (52 Hz) to C_5 in the major isomer identifies it as being cis, confirming inversion of configuration in the 3,5-dimethylcyclohexenyl system.

Our conclusions regarding the stereochemical aspects of the substitution by $(CH_3)_3SnLi$ with 5-methylcyclohex-2-enyl chlorides agree with those of Pereyre,[8] although the French workers did not establish the essential absence of the S_N2' (or some stereochemical equivalent) route.

(Trimethylgermyl)lithium Reactions. $(CH_3)_3GeLi$ was prepared in the reported way[5,24] (see the Experimental Section) from $(CH_3)_3GeBr$ and lithium by using hexamethylphosphoric triamide[25] $[(CH_3)_2N)_3P{=}O]$ as the solvent. Our approach was to examine the reaction between this reagent and the parent cyclohex-2-enyl chloride before undertaking any stereochemical studies with the various methyl-substituted cyclohex-2-enyl chlorides. The reaction product, after workup (Experimental Section), was passed down a short column of neutral alumina and eluted with pentane which removed the germane fraction which was subjected to distillation (seven fractions), and (cyclohex-2-enyl)trimethylgermane was the major component of the more volatile fractions [bp 78–80 °C (27 mm); 45% yield). Higher boiling components [~100 °C (1 mm)] are also formed in this reaction, and we comment on their likely nature later.

We next scrutinized the reactions of the 5-methyl- and 3,5-dimethylcyclohex-2-enyl chlorides with $(CH_3)_3GeLi$ to demonstrate the stereochemistry of the C–Ge bond-formation step. In an initial experiment a 78:22 cis/trans mixture of 5-methylcyclohex-2-enyl chlorides was added (neat) to the germyllithium solution (mobilized with dry tetrahydrofuran) at ca. 0–10 °C. A transitory deep red color formed and the solution was eventually quenched at ca. 20 °C. Standard workup and distillation afforded a germane fraction containing not only the cis and trans allylic isomers but also the vinylic isomer as well. VPC and ^1H and ^{13}C NMR examination (Table I) led to a product distribution of ca. 50% vinyl germane with about equal (~25%) amounts of the (*cis*- and *trans*-5-methylcyclohex-2-enyl)trimethylgermanes.

The ^{13}C assignments (Table I) were tentatively arrived at but later confirmed by the spectra of the ^2H-labeled compounds. The germanes lack the advantageous spectral features of the stannanes, but on the basis of chemical shifts, substituent effects, off-resonance spectra, etc., the above are unambiguous. When compared with the shifts of the corresponding stannanes, harmonious trends are noted. A feature of the spectra of these metallo derivatives is that C_3 is consistently more shielded in the trans derivatives than in the cis, and this is presumably because σ–π interactions can operate more effectively in the trans

(24) Bulten, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1971**, *29*, 397.
(25) Normant, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1046.

isomer, leading to increased shielding of C_3. The vinylic isomer [with the expected ^1H pattern (single vinyl proton) as well as ^{13}C shifts predictable from (4-methyl-1-cyclohexenyl)trimethylgermane] most reasonably arises from the allylic germane(s) (see later) and renders the observed product ratio meaningless as regards stereochemistry of the substitution process.

In an attempt to suppress the formation of vinylic isomer different experimental conditions were employed. The $(CH_3)_3GeLi$ solution (HMPA) was cooled to −78 °C, tetrahydrofuran was added for mobilization and the solution filtered. The 78:22 cis/trans chloride, dissolved in THF was added slowly to the cooled (−78 °C) germyllithium solution. The solution was quenched at low temperature. A combination of (capillary) VPC and ^{13}C and ^1H NMR established the product germane to be predominantly trans (60:40 trans/cis) with no vinylic isomers. While the overall result is net inversion of configuration at carbon, there is a significant departure from specificity, which may imply some waywardness on the part of the *cis*-chloride. A second preparation of predominantly *cis*-chloride (84:16) provided 64:36 trans/cis allylic germane, confirming a significant stereoleakage in the *cis*- and possibly the *trans*-chloride as well.

A predominantly *trans*-chloride mixture (14:86 cis/trans) was prepared (by the *N*-chlorosuccinimide/dimethyl sulfide route) and reacted with $(CH_3)_3GeLi$. No vinylic isomer was detected, and careful VPC and ^{13}C NMR examination established the cis/trans ratio in the allylgermane to be 90:10, a result in excellent agreement with inversion with each chloride isomer, but perhaps indicating slight enrichment in cis product. Taken together, the results for the chloride mixtures suggest the cis chloride is exhibiting stereoleakage in that it leads to a *trans*-/*cis*-germane ratio of ~3:1 or is preferentially undergoing another reaction (see below).

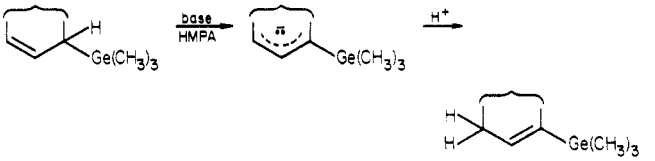
The acquisition of a germane product rich in one isomer (90% cis on the basis of ^{13}C shift arguments and analogies with the tin compounds for which ^{13}C–^{119}Sn coupling data is definitive) allowed informative 300-MHz ^1H spectra to be obtained. A full discussion is presented elsewhere,[26] but decoupling experiments established quite clearly that the major isomer was indeed cis, as deduced above. In particular the axial proton at C-6 (H_{6a}, δ 1.06) has three large couplings (11 Hz; to H_{6e}, H_{5a}, and H_{1a}) a situation that would not apply for either reasonable conformation of the trans isomer. Other details of the ^1H spectra are fully in accord with this conclusion.[26]

We considered it desirable to investigate the extent of S_N2' displacement in the germylation reactions, and a ^2H-labeled chloride was prepared as described above. ^{13}C and ^2H NMR established a cis/trans ratio of ca. 22:78 and that the ^2H label was 35% vinylic and 65% allylic. The germane fraction was shown by capillary VPC to be 64% cis (allyl) 17% trans (allyl), and 19% vinylgermane. (These ratios were in satisfactory agreement with ^{13}C NMR analysis.) Thus the allylgermane fraction had a 79:21 cis/trans ratio, although it is not clear whether one of these initially formed germanes is preferentially converted to vinylgermane. Nevertheless, net inversion is indicated with a high level of specificity.

^2H NMR analysis of the product showed allylic ^2H (at δ 1.78 and 2.08) and vinylic ^2H (at δ 5.56 and 5.64) in the ratio of 76:24. However, it is considered likely that the δ 2.08 signal is associated with (3-deuterio-5-methylcyclohex-1-enyl)trimethylgermane (vinylgermane with allylic ^2H), so that the allyl/vinyl ^2H ratio is in fact 71:29 and may be compared with the 65/35 ratio in the starting chloride. Although there are undefined aspects relating to the formation of the vinylgermane, it is clear that the S_N2' route is of minor importance in the C–Ge (allyl) bond forming reaction.

Chlorination of 3,5-dimethylcyclohex-2-enol (ca. 94:6 cis/trans) with thionyl chloride (in ether) provided predominantly *trans*-chloride as described above. Considering that tertiary halides led to no substitution product, the ratio of trans/cis (secondary chlorides) of 71:29 is the important one. Reaction with $(CH_3)_3GeLi$ led to an allylgermane fraction, the components of which could be resolved by capillary VPC and shown to be 75:25 consistent with ^{13}C and ^1H NMR. The major isomer was clearly cis on the basis of its ^{13}C spectrum. The reaction was repeated by using a different preparation of chloride (but still 71:29 trans/cis), and concordant results were obtained. Thus a highly specific displacement with inversion of configuration at carbon has occurred.

The formation of significant levels of vinylgermanes in some of these preparations is associated with the stabilizing effect of the $(CH_3)_3Ge$ group on an α carbanion,[28] formed by proton abstraction in the strongly basic HMPA medium.



We associate the transitory red color observed in some of these reactions with the germanium-stabilized allyl anion. There are interesting stereoelectronic aspects of this anion formation which are relevant to the observed *cis*-/*trans*-allylgermane ratio observed in reactions accompanied by vinylgermane formation, and detailed investigations are planned.

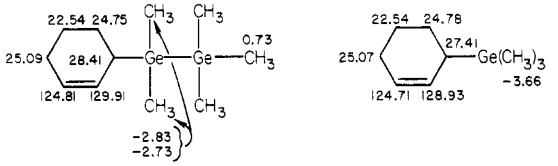
We have established that (cyclohex-2-enyl)dimethylamines can be significant byproducts in these germylation reactions and result from allyl chloride displacement by $Li^+{}^-N(CH_3)_2$, the latter being formed by lithium cleavage of HMPA.[25] Detailed examination of the ^1H, ^2H, and ^{13}C NMR spectra of the dimethylamines formed from *cis*- and *trans*-5-methylcyclohex-2-enyl chlorides requires that chloride displacement by $(CH_3)_2N^-Li^+$ proceeds with inversion at carbon and insignificant incursion of the S_N2' pathway or some equivalent.[27] Full details may be found elsewhere.[26]

Digermanes from Germylation Reactions. Higher boiling components [bp ~100 °C (1 mm)] were produced in significant amounts (8–10%) in these germylation reactions and were investigated in some detail for the cyclohex-2-enyl, 5-methyl-cyclohex-2-enyl, and 3,5-dimethylcyclohex-2-enyl systems. Previously we had noted the formation of high boiling residues from the reaction of $(CH_3)_3GeLi$ and cyclohexyl bromides, but these were not studied and were thought to be bicyclohexyls.[5,29] However, we have prepared bicyclohexenyls for the present work, and these are very minor products from the germylation of cyclohex-2-enyl chlorides.

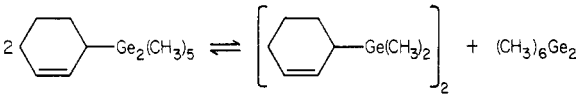
From the germylation of cyclohex-2-enyl chloride was obtained a higher boiling fraction, the ^{13}C spectrum of which contained $GeCH_3$ signals at 0.73 ppm and equiin-

(26) Wickham, G. Ph.D. Dissertation, University of Queensland, 1982.
(27) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901.
(28) Lau, P. W. K.; Chan, T. H. *Tetrahedron Lett.* **1978**, 2383. Chass, A. C.; Ehlinger, E.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1977**, 72.
(29) Waugh, J. A. Honours Thesis, University of Queensland, 1978.

tense signals at −2.83 and −2.73 ppm, the former being ca. 1.4 times as intense as the closely spaced duo. An additional $GeCH_3$ signal occurred at −0.44 ppm. Cyclohexenyl resonances were present, and these data, along with other information, lead to the suggested structure of (cyclohex-2-enyl)pentamethyldigermane for the major species. It is instructive to compare the assignments with those of authentic (cyclohex-2-enyl)trimethylgermane, and as expected the differences are marginal. (Note the chirality of C-1).



The ^1H spectrum showed $Ge(CH_3)_2$ and $Ge(CH_3)_3$ singlets as well as vinylic and other ring proton absorptions. The species corresponding to ^{13}C signal at −0.44 ppm was considered to be the symmetrical 1,2-bis(cyclohex-2-enyl)-1,1,2,2-tetramethyldigermane, formed by base-catalyzed redistribution of the unsymmetrical digermane.



This process has been well documented,[30] and equilibria were rapidly established for HMPA as the solvent with catalytic amounts of either Et_3GeLi or EtOK, as shown below.

$$(CH_3CH_2)_3Ge\text{–}Ge(CH_3)_3 \underset{\text{base}}{\overset{K = 0.12}{\rightleftharpoons}} (CH_3CH_2)_6Ge_2 + (CH_3)_6Ge_2$$

We noted the formation of significant amounts of $(CH_3)_6Ge_2$, as required by the redistribution, and of considerable interest was the ratio of symmetric to unsymmetrical digermane. This was ca. 0.30, providing $K \approx 0.10$ for our system, and such agreement indicates that the nature of the alkyl (or alkenyl) groups on germanium has little effect on the equilibrium.

We consider that the likely sequence of events leading to digermane formation is initiated by dimethylgermylene formation, which inserts into the Ge–Li bond to form (pentamethyldigermyl)lithium. This latter reagent is

$$(CH_3)_3GeLi \rightleftharpoons (CH_3)_2Ge: + CH_3Li$$

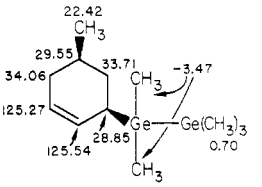
$$(CH_3)_2Ge: + (CH_3)_3GeLi \rightleftharpoons (CH_3)_5Ge_2Li\ [\rightleftharpoons (CH_3)_3Ge\text{-}\ddot{G}e\text{-}CH_3 + CH_3Li, \text{ etc.}]$$

$$(CH_3)_5Ge_2Li + RCl \rightarrow RGe_2(CH_3)_5$$

$$2RGe_2(CH_3)_5 \underset{}{\overset{\text{base}}{\rightleftharpoons}} (CH_3)_6Ge_2 + R_2(CH_3)_4Ge_2$$

responsible, by chloride displacement, for digermane formation. (Higher catenated germanes could result from $(CH_3)_7Ge_3Li$, $(CH_3)_9Ge_4Li$, etc.) An alternative but less attractive scheme involves insertion of $(CH_3)_2Ge$: into the allylic C–Cl bond, followed by rapid coupling with $(CH_3)_3GeLi$. We disfavor this explanation, on the basis of the known chemistry of germylenes and on stereochemical grounds (below).

^{13}C NMR examination of the suspected digermane fraction formed by germylation of (84%) *trans*-5-methylcyclohex-2-enyl chloride indicated one major unsymmetrical digermane, the assignments for which are shown below. The resonances at 0.70 and −3.47 ppm were

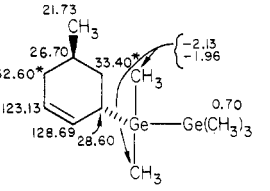


ca. 3:2 in intensity. A signal at −1.08 ppm is assigned to the symmetrical bis(*cis*-5-methylcyclohex-2-enyl)tetramethyldigermane.

The indicated cis nature of this product is required by the following observations: (i) the sp^2 carbon resonances are very similar in position to those of (*cis*-5-methylcyclohex-2-enyl)trimethylgermane (Table I: $\Delta\delta = 3.27$; cf. 3.17) but different from those of the trans isomer, with a pseudoaxial germanium group, favoring a strong σ–π interaction and causing $\Delta\delta$ to be 5.5 ppm; (ii) the C_5 chemical shift (29.55 ppm) agrees with that for *cis*-monogermane (29.6 ppm) but is different from that of the trans compound (26.78 ppm) in which γ compressional shielding [from $Ge(CH_3)_3$] will operate. Thus loss of chloride is highly specific with inversion of configuration at carbon, a result nicely compatible with displacement by (pentamethyldigermyl)lithium, in view of the demonstrated (above) behavior of $(CH_3)_3GeLi$ toward the same chloride.

Some *trans*-digermane (~10%) would be expected, and appropriate minor signals were observed. [Their assignment to the *trans*-digermane is rendered straightforward by examining the digermane fraction from germylation of a 70:30 *cis*-/*trans*-chloride mixture, with *trans*-digermane now predominating (vide infra).] Corrected $GeCH_3$ peak intensities for the unsymmetrical and symmetrical digermanes provided an equilibrium constant of 0.19.

To confirm the above conclusion of stereospecific chloride displacement by $(CH_3)_5Ge_2Li$, we also examined the digermane fractions obtained from 70:30 cis/trans chloride mixture. (*cis*- and *trans*-5-methylcyclohex-2-enyl)pentamethyldigermanes in the ratio of 44:56 cis/trans were formed, confirming stereoselectivity in the displacement process. The ^{13}C signals for the major *trans*-digermane were clearly identifiable and agreed with the minor signals observed in the ca. 90:10 *cis*-/*trans*-digermane fraction mentioned above. These are shown below.



Redistribution of the pentamethyldigermane should give rise to identifiable signals for three tetramethyldigermanes (A–C) as shown below.

$$R'\text{-}Ge_2(CH_3)_5 + R''\text{-}Ge_2(CH_3)_5 \rightleftharpoons \underset{A}{R_2'Ge_2(CH_3)_4} + \underset{B}{R_2''Ge_2(CH_3)_4} + \underset{C}{R'R''Ge_2(CH_3)_4} + (CH_3)_6Ge_2$$

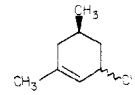
R′ = *cis*-5-methylcyclohex-2-enyl

R″ = *trans*-5-methylcyclohex-2-enyl

Species A and the cis moiety of C are associated with the $GeCH_3$ signal at −1.03, whereas B and the trans moiety of C give rise to the $GeCH_3$ signal at 0.24 ppm. Detailed

(30) van der Kerk, G. J. M. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 244. Bulten, E. J. "Chemistry of Alkylpolygermanes", Ph.D. Thesis, University of Utrecht, 1969.

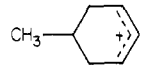
Table II. Stereochemistry and Isomer Distribution in Digermane Formation

chloride	$RGe_2(CH_3)_5$ cis/trans ratio	cis/trans ratio in $R_2Ge_2(CH_3)_4$ calcd[a]	cis/trans ratio in $R_2Ge_2(CH_3)_4$ obsd	$R_2Ge_2(CH_3)_4/RGe_2(CH_3)_5$ ratio	K
				0.3	0.09
 68:32 cis/trans	44/56	44/56	41/59	0.36	0.13
 16:84 cis/trans	87/13	87/13	87/13	0.44	0.19
 30:70 cis/trans	66/34	66/34	69/31	0.33	0.11

[a] Calculated on a statistical basis, assuming no stereochemical change for the redistribution process $2RGe_2(CH_3)_5 \overset{K}{\rightleftharpoons} R_2Ge_2(CH_3)_4 + (CH_3)_6Ge_2$ (see text).

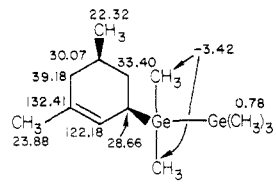
discussion of these assignments can be found elsewhere.[26]

A molecular ion was not observed in the mass spectra of the digermanes but the observed isotope pattern for $M^+ \cdot - 1$ (5%) was in satisfactory agreement with that calculated. The base peak was $(CH_3)_3GeGe(CH_3)_2$–CH_2^+, assigned on the basis of the excellent agreement between the observed and calculated isotope patterns. Other significant ions were $(CH_3)_5Ge_2^+$ (12%), $(CH_3)_3Ge^+$ (28%), and I (9%).

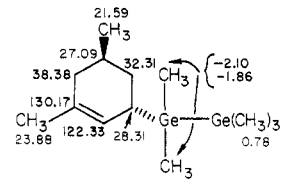


Hexamethyldigermane shows major "ion clusters" for $(CH_3)_6Ge_2^+ \cdot$, $(CH_3)_5Ge_2^+$, and $(CH_3)_3Ge^+$ (base peak), with no important "cluster" corresponding to the proposed $(CH_3)_3GeGe(CH_3)_2$–CH_2^+. This latter ion is prominent in the mass spectra of the digermanes from each of the cyclohex-2-enyl chloride reactions. Ions of low intensity corresponding to more than two germanium atoms were observed.

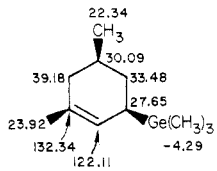
In view of the foregoing discussion, the evidence now presented is very convincing for the stereospecific formation of digermanes from the reaction of a 70:30 trans/cis mixture of 3,5-dimethylcyclohex-2-enyl chlorides with $(CH_3)_5Ge_2Li$. The higher boiling fraction contained two pentamethyldigermyl components (^{13}C), and the major and minor sets of signals could be assigned as below and are compared with the data for the corresponding monogermanes.

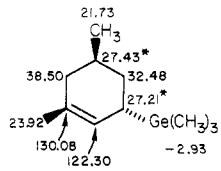


"major"



"minor"





These comparisons leave no doubt that the major digermane is cis (66%) and that the cis/trans ratio (66:34) is the inverse of that (ca. 30:70) for the starting chloride mixture. This confirms the conclusion above that digermane formation is stereospecific (with inversion). As expected, the ring carbon shifts for the cyclohex-2-enyl *mono-* and *di*germanes are very similar, but the C_1 resonance appears to suffer a ca. 1-ppm downfield shift in the digermane.

Signals assignable to $GeCH_3$ for the various tetramethyldigermanes were identified as −0.98 ppm for $R'''_2Ge_2(CH_3)_4$ and the cis moiety of $R'''R''''Ge_2(CH_3)_4$, whereas $R''''Ge_2(CH_3)_4$ and the trans moiety of $R'''R''''Ge_2(CH_3)_4$ are associated with a $GeCH_3$ signal at +0.34 ppm (R''' = *cis*-3,5-dimethylcyclohex-2-enyl and R'''' = *trans*-3,5-dimethylcyclohex-2-enyl). The reasonable mechanism proposed[30] for the base-catalyzed redistribution would not alter carbon stereochemistry and hence it is possible to calculate the proportions of the various tetramethyldigermanes and compare these with the observed values. This is done in Table II.

The data above demonstrate high stereoselectivity (inversion) in the formation of the pentamethyldigermane consistent with an S_N2-type process for the presumed (pentamethyldigermyl)lithium. The constancy in K values for the various redistribution processes would hardly seem credible unless a common phenomenon was under observation.

The present work delineates the chief features of the stannylation and germylation reactions of cyclohex-2-enyl chlorides, and permits the synthesis of cyclic allylic metallics for mechanistic studies of their various reactions. The results of such studies will be reported in the near future.

Experimental Section

Reagents. Cyclohex-2-enol was a commercial sample. 5-Methylcyclohex-2-enol and 3,5-dimethylcyclohex-2-enol were obtained by lithium aluminum hydride reduction of the ketones in the standard way.[31] Both alcohols were ca. 93:7 cis/trans mixtures as judged by VPC and ^{13}C NMR spectra and catalytic hydrogenation of the 5-methylcyclohex-2-enol to predominantly

(31) Goering, H. L.; Blanchard, J. P. *J. Am. Chem. Soc.* **1954**, *76*, 5405.

cis-3-methylcyclohexanol. In the case of 5-methylcyclohex-2-enol, deuterium was introduced at either the 3-position ($LiAlD_4$ reduction of the enol ether) or the 1-position (reduction of the ketone) as described by Goering.[15] As discussed in the text, levels and positions of ^2H incorporation in various transformations were determined by direct ^2H NMR analysis.

Cyclohex-2-enyl chloride was obtained as a clear oil (room-temperature low-pressure distillation) from chlorination of the alcohol with purified thionyl chloride in ether: ^1H NMR ($CDCl_3$) δ 5.90 (br s, 2 H, vinylic), 4.55 (br s, 1 H, $W_{1/2} \approx 10$ Hz, CHCl), 1.10–2.50 (m, 6 H, CH_2).

5-Methylcyclohex-2-enyl Chloride. (a) Using Thionyl Chloride. As detailed in the text, we were not able to repeat satisfactorily the finding of Goering[10] that chlorination of the alcohol with $SOCl_2$ (in ether) could provide chloride with complete retention of configuration and allylic rearrangement. Following the reported procedure as faithfully as possible, we obtained mixtures which were ca. 70:30 cis/trans, a distribution unaltered by the distillation process (^{13}C NMR of crude and distilled material). The use of 1 equiv of $SOCl_2$ which had been twice distilled from sulfur (under nitrogen) did not provide the reported specificity, and we were resigned to working with a predominantly cis/trans mixture. Fortunately we were able to prepare a predominantly trans/cis mixture for our stereochemical studies. The following describes our procedure.

Crude $SOCl_2$ was twice distilled from sulfur (under N_2) and subsequently stored under N_2 in a desiccator. To a magnetically stirred solution of $SOCl_2$ (1.22 mL, 17.8 mmol) in anhydrous ether (20 mL) at 0 °C (N_2) was added 5-methylcyclohex-2-enol (2.0 g, 17.8 mmol) in a small volume of ether. After about 2 min, the solution was distilled to yield a colorless oil [1.62 g, 70%; bp 57 °C (19 mm)] [lit.[10] bp 60–62 °C (25 mm)]. This distillation was performed by using a short well-insulated Vigreux column, so that the temperature of the distilling flask did not exceed 65 °C. On other occasions, after evaporation of the ether solvent at room temperature or below, the chloride (at ca. 25 °C) was flash distilled (ca. 1 mm) and trapped at −78 °C. Either of the above procedures resulted in significant loss of specificity, with the cis/trans ratio being generally 70–75:30–25, although on one occasion a mixture ca. 83% cis was obtained. All chlorides prepared were stored at −10 °C: ^1H NMR ($CDCl_3$, 300 MHz) δ 5.75 (m, 2 H, vinylic), 4.63 (m, $W_{1/2} \approx 25$ Hz, 1 H, CHCl), 2.33 (m, 5 H, ring H), 1.00 (d, $J \approx 6.3$ Hz, 3 H, CH_3 of (minor) trans), 0.99 (d, $J \approx 6.3$ Hz, 3 H, CH_3 of (major) cis isomer). As detailed in the text, a $W_{1/2}$ of ca. 25 Hz for of the CHCl signal corresponds to a pseudoaxial proton, as present in the cis isomer: mass spectrum, m/e 130, 132 (3:1), $M^{+\cdot}$.

$$M^{+\cdot} \xrightarrow{-Cl\cdot} m/z \text{ 95 (base peak)}$$

(b) Using Dimethyl Sulfide/*N*-Chlorosuccinimide.[14] Dimethyl sulfide (3.6 mL, 20% excess) was added dropwise to a cooled (0 °C) stirred solution of *N*-chlorosuccinimide (6.0 g, 10% excess) in anhydrous dichloromethane (200 mL) under N_2. The reagent mixture was further cooled (−20 °C), and 5-methylcyclohex-2-enol (5 g, 40 mmol) in dichloromethane (20 mL) was added slowly. The mixture was warmed to 0 °C, stirred for 1 h, and poured into a cold (0 °C) sodium chloride solution (200 mL). The combined ether extracts (3 × 150 mL) were washed with cold sodium chloride solution (2 × 150 mL) and dried ($MgSO_4$), and the ether was evaporated at 25 °C or below. The crude chloride was flash distilled (as outlined above) and stored at −10 °C (3.65 g, 63%).

The 300-MHz ^1H spectrum differed from that described above for the $SOCl_2$-produced chloride in that the signal at δ 4.64 (1 H, CHCl) had $W_{1/2} = 9$ Hz, characteristic of a pseudoequatorial proton, as is present in the *trans*-chloride. Also, the lower field methyl doublet was more intense, confirming the reversed isomer distribution. The ^{13}C spectrum yielded a trans/cis ratio of 89:11, indicating configurational inversion in the alcohol → chloride transformation. Preparations sometimes deviated slightly from this isomer distribution, but the trans compound was always very predominant from this chlorination of the 93% cis alcohol.

(c) Chlorinations of both 1- and 3-deuterio-5-methylcyclohex-2-enols were conducted in the described manner, and the $SOCl_2$ procedure provided a chloride mixture in which ^2H was distributed equally between the 1- and 3-positions (^1H and ^2H NMR). Chlorination using *N*-chlorosuccinimide/dimethyl sulfide on each of the 1- and 3-deuterio-5-methylcyclohex-2-enols provided deuterated chloride with net retention of deuterium at its original position. This distribution was generally 75:25 (^2H NMR).

3,5-Dimethylcyclohex-2-enone was commercially available and reduced ($LiAlH_4$) in the normal way to provide a 93:7 cis/trans mixture of 3,5-dimethylcyclohex-2-enols [bp 92–98 °C (13 mm)] which were characterized by ^{13}C and ^1H NMR spectra. In the latter, the major CHOH signal (δ 4.22) had $W_{1/2} \approx 25$ Hz, as required for a pseudoaxial proton as is present in the cis isomer, whereas the minor trans isomer exhibited CHOH as a narrower ($W_{1/2} \approx 10$ Hz) signal at δ 4.16. The vinyl region displayed a major (broadened) singlet at δ 5.31 (cis) and a minor one at δ 5.82 (trans).

3,5-Dimethylcyclohex-2-enyl chloride was prepared by chlorination of the above alcohol. Either chlorinating procedure produced a ca. 70:23:7 trans/cis/tertiary chloride mixture. The major CHCl signal (δ 4.72) had $W_{1/2} = 11$ Hz (pseudoequatorial proton as is present in trans isomer) while the minor had $W_{1/2} = 23$ Hz (δ 4.63), appropriate for the cis isomer.

Full details of the ^{13}C NMR spectra of the various cyclohex-2-enols and chlorides may be found elsewhere.[26] Yields of trimethylstannanes from the reaction of (trimethylstannyl)lithium reagents with cyclohex-2-enyl chlorides were normally in the range 60–75% after Kugelrohr distillation. Higher yields of triphenylstannanes were obtained.

(Cyclohex-2-enyl)triphenylstannane was obtained from the reaction of (triphenylstannyl)lithium and cyclohex-2-enyl chloride in tetrahydrofuran (THF). A standard workup provided a solid which was recrystallized from ethanol: 65%; mp 79–80.5 °C (lit. mp 81.5–83 °C);[16] ^1H NMR (300 MHz, $CDCl_3$) δ 5.98 and 5.57 (AB pattern, 2 H, vinylic), 2.88 (br s, $W_{1/2} \approx 13.5$ Hz, 1 H, $J_{^1H-^{119}Sn} = 90$ Hz, CHSn), 1.86 (m, 4 H, CH_2), 1.43 (m, 2 H, CH_2), as well as $(C_6H_5)_3Sn$ resonances. The ^{13}C and ^{119}Sn spectra have been presented in the text. Anal. Calcd for $C_{24}H_{24}Sn$: C, 66.86; H, 5.6. Found: C, 65.93; H, 5.50.

(*cis*- and *trans*-5-Methylcyclohex-2-enyl)triphenylstannanes were obtained (as mixtures) from analogous reactions of (triphenylstannyl)lithium with the 5-methylcyclohex-2-enyl chlorides. The crude product was a viscous oil which contained some hexaphenylditin. The oil was taken up in pentane and chromatographed on Florosil with pentane elution. Anal. Calcd for $C_{25}H_{26}Sn$: C, 67.45; H, 5.89. Found: C, 67.88; H, 6.11. Isomer ratios were based largely on the ^{119}Sn NMR before and after purification, and chromatography induced no fractionation: ^1H NMR (300 MHz, $CDCl_3$) δ 5.63 (H_3, cis), 5.51 (H_3, trans), 5.93 (H_2, cis, trans), 2.98 ($W_{1/2} \approx 13$ Hz, CHSn, trans), 2.85 ($W_{1/2} \approx 20$ Hz, CHSn, cis), 0.83 (d, CH_3, trans), 0.91 (d, CH_3, cis), 2.10 (m, 2 H) and 1.64 (m, 3 H) (ring protons). ^{13}C, ^{119}Sn, and ^2H NMR spectra have been discussed in the text.

(3,5-Dimethylcyclohex-2-enyl)triphenylstannane was obtained as an isomeric mixture from the reaction of (triphenylstannyl)lithium with a ca. 70:30 *trans*-/*cis*-chloride mixture. The product after chromatography (Florosil/pentane) was a viscous oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.78 (br s, 1 H, H_2 in each isomer), 3.09 (br s, $W_{1/2} \approx 15$ Hz, 1 H, trans), 2.96 (s, $W_{1/2} = 23$ Hz, 1 H, cis), 2.89–1.89 (m, 5 H, ring protons), 1.74 (s, allylic CH_3), 1.00 (d, $J \approx 5.7$ Hz, *cis*-CH_3), 0.95 (d, $J \approx 5.9$, *trans*-CH_3). Anal. Calcd for $C_{26}H_{28}Sn$: C, 68.01; H, 6.15. Found: C, 67.59; H, 6.15.

(Cyclohex-2-enyl)trimethylstannane was obtained from the reaction of cyclohex-2-enyl chloride and (trimethylstannyl)lithium prepared in THF in the normal way. This material was identical with a sample prepared by Bullpitt,[20] who employed a reaction sequence consisting of lithium cleavage of phenoxycyclohex-2-ene followed by addition of trimethyltin chloride: ^1H NMR (300 MHz) δ 5.60 (AB-type system, 2 H, vinylic), 1.40–2.60 (m, 7 H, ring protons), 0.10 (s, 98 H, $J_{^{119}Sn-^1H} = 50$ Hz, $(CH_3)_3Sn$).

The ^{13}C and ^{119}Sn shifts of the various trimethylstannanes are discussed in the text.

(5-Methylcyclohex-2-enyl)trimethylstannane was obtained as a clear oil from the reaction of (trimethylstannyl)lithium on mixtures of the corresponding chloride isomers. Some hexamethylditin [$(CH_3)_6Sn_2$] was also formed and was not removed by flash distillation. However, most of this impurity was "frozen out" at −10 °C, and the liquid stannane was removed and distilled [Kugelrohr oven temperature 50 °C (0.3 mm)]: ^1H NMR ($CDCl_3$,

Table III. Conditions and Outcomes of Trimethylgermylation Reactions of Cyclohex-2-enyl Chlorides

chloride[a] (cis/trans ratio)	mode of addition[b]	yield,[c] %	cis/trans/vinyl[e] ratio	bp, °C (mmHg)
A	I	30[d]	100:0[f]	78-80 (27)
B (76:24)	N	32	25:26:49[g]	80-82 (17)
B (76:24)	N	22	40:60:0	92 (27)
B (22:78)	I	40	64:17:18	82 (24)
B (16:84)	N	50	15:12:73	78 (17)
B (16:84)	I	44[d]	90:10:0	82 (21)
B (84:16)	I	54	36:64:0	87 (25)
B (70:30)	N	38[d]	43:57:0	73 (10)
C (30:70)[i]	N	24	75:25:0[h]	60-62 (4)
C (30:70)[i]	N	48	72:28:0	74-76 (9-10)

[a] A = cyclohex-2-enyl chloride; B = 5-methylcyclohex-2-enyl chloride; C = 3,5-dimethylcyclohex-2-enyl chloride. [b] N = normal addition of chloride (in THF) to $(CH_3)_3GeLi$ solution; I = inverse addition. A 25% excess of $(CH_3)_3GeLi$ (based on weight of $(CH_3)_3GeBr$) was normally employed, and the THF/HMPA ratio in the final $(CH_3)_3GeLi$ solution was 5/1. The reagents were mixed at ca. −78 °C. [c] For quenching, the reaction mixture below room temperature was added to iced water, and pentane extraction was employed. [d] Cooled H_2O added to reaction mixture at −78 °C. Yield refers to the total of isolated allyl and vinylgermanes. [e] Determined by capillary VPC and in agreement with ^{13}C and ^1H NMR spectra. [f] Anal. Calcd for $C_9H_{18}Ge$: C, 54.34; H, 9.13. Found: C, 53.06; H, 8.99. [g] Anal. Calcd for $C_{10}H_{20}Ge$: C, 56.43; H, 9.47. Found: C, 56.52; H, 9.71. [h] Anal. Calcd for $C_{11}H_{22}Ge$: C, 58.33; H, 9.77. Found: C, 58.66; H, 9.81. [i] Corrected for ca. 12% tertiary chloride which provides no germane.

300 MHz) δ 5.74 (vinylic H_2, trans), 5.70 (vinylic H_2, cis), 5.55 (vinylic H_3, cis), 5.42 (vinylic H_3, trans), 2.47–1.15 (6 H, m, ring protons including CHSn), 0.98 (d, $J \approx 6$ Hz, 3 H, CH_3, trans), 0.97 (d, $J \approx 6.5$ Hz, 3 H, CH_3, cis), 0.14 (s, 9 H, $(CH_3)_3Sn$, trans), 0.12 (s, 9 H, $(CH_3)_3Sn$, cis); mass spectrum, m/z (relative intensity) 260 (6.6, using ^{120}Sn, $M^{+\cdot}$). Anal. Calcd for $C_{10}H_{20}Sn$: C, 46.38; H, 7.78. Found: C, 46.40; H, 7.86.

(3,5-Dimethylcyclohex-2-enyl)trimethylstannane was prepared similarly and obtained as a clear oil after low-temperature flash distillation and separation of $(CH_3)_6Sn_2$ by "freezing out". [Hexamethylditin (C, 22%; H, 6%) was an impurity (^1H NMR δ 0.22)]: ^1H NMR ($CDCl_3$, 300 MHz) δ 5.39 (m, vinylic H_2, trans), 5.39 (m, vinylic H_2, cis), 1.33–2.2 (m, 6 H, ring protons), 1.66 (s, 3 H, allylic CH_3), 0.96 (d, $J \approx 6$ Hz, 3 H, CH_3, trans), 0.95 (d, $J \approx 6.0$ Hz, CH_3, cis), 0.05 (s, 9 H, $(CH_3)_3Sn$, cis and trans). Anal. Calcd for $C_{11}H_{22}Sn$: C, 48.44; H, 8.12. Found: C, 47.3; H, 6.7.

Trimethylgermylation Procedures. (Trimethylgermyl)lithium[24] was prepared from trimethylbromogermane and lithium pieces in hexamethylphosphoric triamide (HMPA), which was distilled directly from sodium (blue color) into the reaction vessel under N_2. Reaction was continued until the golden brown color just changed to blue, at which point the solution was mobilized with THF and filtered from any unreacted lithium. Variations in the mode of addition of chloride (normal or inverse), reaction temperatures, and conditions of protic quenching were made in the hope of understanding the formation of vinylic germane. In all reactions of 5-methylcyclohex-2-enyl chloride (and cyclohex-2-enyl chloride) a red-burgundy color developed, and we associate this with the trimethylgermyl-stabilized (allylic) cyclohexenyl anion, formed by deprotonation in the basic medium (see text). Low-temperature quenching appears to minimize the formation of vinylgermane, and we suggest that the cis allylic germane is more prone to loss of the α-proton than is the trans isomer. A summary of the experimental conditions and stereochemical outcomes of the germylation reactions are presented in Table II. A model procedure is described below.

Glassware was oven dried overnight, assembled hot, and allowed to cool under a N_2 stream. Alternatively, the assembled apparatus was "flamed out" under a strong N_2 stream. All manipulations were carried out under a N_2 atmosphere. Tetrahydrofuran was distilled (under N_2) from $LiAlH_4$.

Lithium metal (0.53 g, 77.2 mmol, 4 equiv) in the form of thin slivers was added to HMPA (27 mL) freshly distilled from sodium. To the cooled (ice) dark blue solution was added neat trimethylbromogermane (3.81 g, 19.3 mmol) via a syringe, whereupon the blue color was replaced by golden brown. The cooling bath was removed and the solution stirred at ambient temperature (25 °C). Intensification of the golden color was accompanied by increasing viscosity, and eventual regeneration of the blue color (ca. 1–2 h). Excess lithium was removed by filtration (glass frit separating a two-chamber apparatus), and the solution of $(CH_3)_3GeLi$ was mobilized with THF (105 mL) and then cooled to −78 °C. To this magnetically stirred solution was added the chloride (2.0 g, 15.4 mmol) in THF (30 mL; giving an overall THF/HMPA ratio of 5:1) dropwise by syringe. After about one-third of the chloride solution had been added, a red coloration developed which intensified upon further addition to "blood red". Stirring was continued (10 min), the cooling bath was removed, and water was added immediately, causing discharge of the red color. The solution (colorless) was poured into iced water and extracted with pentane which was washed thoroughly with water to remove HMPA. Drying ($MgSO_4$) and solvent removal provided 2.2 g of crude material.

No dimethylamide substitution product was detected in the preparation with predominantly *cis*-chloride. However, for the other chlorides, this product was removed by column chromatography on neutral alumina, eluting at first with pentane (germanium products) and then with chloroform (dimethylamine).

The mixture of organogermanes was subjected to vacuum distillation. (5-Methylcyclohex-2-enyl)trimethylgermane was obtained pure [1.24 g; 73 °C (10 mm)] while higher boiling material could not be fractionated [(67 °C (0.08 mm); see Table III and footnotes].

The higher boiling mixture contained three components, the relative amounts of which were determined by a combination of capillary VPC and ^{13}C NMR. Anal. Calcd for $C_{12}H_{26}Ge_2$ (61%): C, 45.66; H, 8.31. Calcd for $C_{18}H_{34}Ge_2$ (24%): C, 54.62; H, 8.67. Calcd for $C_{14}H_{22}$ [bicyclohexenyl, i.e., bis(5-methylcyclohex-2-enyl)] (15%): C, 88.34; H, 11.66. Calcd for above mixture: C, 54.21; H, 8.90. Found: C, 53.06; 8.97.

NMR Spectra. ^{13}C NMR spectra were obtained at 25.05 MHz (JEOL FX-100) for $CDCl_3$ solutions, and chemical shifts are referenced to either the center peak of the $CDCl_3$ triplet (77.00 ppm) or internal $(CH_3)_4Si$ at zero. ^{119}Sn spectra were recorded at 37.08 MHz (JEOL FX-100) for $CDCl_3$ solutions and are referenced to internal $(CH_3)_4Sn$, and all positive shifts are to lower field. Broad-band ^1H-decoupled ^2H spectra were also recorded on the JEOL FX-100 spectrometer fitted with a 10-mm multinuclear probe, which was tuned to observe ^2H at 15.29 MHz. ^2H spectra, which were accumulated by using 16K data points and a frequency width of 1 kHz (70° pulse, repetition time 4.19 s), refer to $CHCl_3$ solutions, and chemical shifts are referenced to internal $CDCl_3$ (δ 7.24). ^1H NMR spectra were recorded for $CDCl_3$ solutions at 100 (JEOL PS-100) or 300 MHz (Bruker CXP-300) with $CHCl_3$ (7.24 ppm) as an internal reference (secondary).

Acknowledgment. This research was supported in part by the Australian Research Grants Committee to whom we are grateful. High-field NMR spectra were obtained at the Brisbane NMR Center (Director, Dr. D. Doddrell; Operator-Consultant, Dr. P. Barron). Mass spectra were recorded (by Mr. G. Macfarlane) on an ARGC-funded AEI-MS902 mass spectrometer.

Registry No. Cyclohex-2-enyl chloride, 2441-97-6; *cis*-5-methylcyclohex-2-enyl chloride, 18992-30-8; *trans*-5-methylcyclohex-2-enyl chloride, 18913-27-4; *cis*-3,5-dimethylcyclohex-2-enyl chloride, 83269-46-9; *trans*-3,5-dimethylcyclohex-2-enyl chloride, 83269-47-0; (cyclohex-2-enyl)triphenylstannane, 14540-08-0; (*cis*-5-methylcyclohex-2-enyl)triphenylstannane, 83269-35-6; (*trans*-5-methylcyclohex-2-enyl)triphenylstannane, 83269-36-7; (*cis*-3,5-dimethylcyclohex-2-enyl)triphenylstannane, 83269-37-8; (*trans*-3,5-dimethylcyclohex-2-enyl)triphenylstannane, 83269-38-9; (cyclohex-2-enyl)trimethylstannane, 17314-43-1; (cyclohex-2-enyl)trimethylgermane, 7610-03-9;

(cyclohex-2-enyl)trimethylsilane, 40934-71-2; (*trans*-5-methylcyclohex-2-enyl)trimethylstannane, 74089-89-7; (*cis*-5-methylcyclohex-2-enyl)trimethylstannane, 74089-88-6; (*cis*-3,5-dimethylcyclohex-2-enyl)trimethylstannane, 83269-39-0; (*trans*-3,5-dimethylcyclohex-2-enyl)trimethylstannane, 83269-40-3; (*cis*-5-methylcyclohex-2-enyl)-trimethylgermane, 83269-41-4; (*trans*-5-methylcyclohex-2-enyl)trimethylgermane, 83269-42-5; (5-methylcyclohex-1-enyl)trimethylgermane, 83269-43-6; (*cis*-3,5-dimethylcyclohex-2-enyl)trimethylgermane, 83269-44-7; (*trans*-3,5-dimethylcyclohex-2-enyl)trimethylgermane, 83269-45-8; 5-methylcyclohex-2-enol, 3718-55-6; 3,5-dimethylcyclohex-2-enone, 1123-09-7; *cis*-3,5-dimethylcyclohex-2-enol, 32149-48-7; *trans*-3,5-dimethylcyclohex-2-enol, 83269-48-1.

New Aspects in the Chlorination of Indoles with 1-Chlorobenzotriazole and 1-Chloroisatin

C. Berti,† L. Greci,*† R. Andruzzi,‡ and A. Trazza‡

Istituto Chimico della Facoltà di Ingegneria della Università, Viale Risorgimento, 2-40136 Bologna, Italy, and Istituto Chimico della Facoltà di Ingegneria della Università, Via del Castro Laurenziano, 7-00161 Roma, Italy

Received February 11, 1982

2-Phenyl-, 1-methyl-2-phenyl-, and 2-phenyl-3-methylindole react with 1-chlorobenzotriazole and 1-chloroisatin to form essentially 3-chloroindoles. The composition of the products, which depends on the solvent used, suggests an electron-transfer process for the reactions with 1-chlorobenzotriazole. This is supported by chemical experiments and electrochemical measurements. The reactions with 1-chloroisatin, which do not involve byproduct formation, is interpreted by classical electrophilic substitution. The different reactivities of 1-chlorobenzotriazole and of 1-chloroisatin comes from the different mobility of their chlorine atom.

The chlorination of indoles, which normally occurs at C-3 of the indole nucleus, has been extensively studied,[1] and many reagents have been used for this reaction.[2] In 1972 an *N*-chloroindole was suggested as an intermediate in the chlorination of 2,3-dimethylindole with aqueous sodium hypochlorite.[3] More recently the formation and the stability of the *N*-chloroindole intermediate was detected and described by De Rosa.[4]

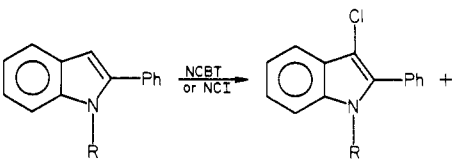
In the present paper we describe the reactions of 2-phenyl-, 1-methyl-2-phenyl-, and 2-phenyl-3-methylindole with 1-chlorobenzotriazole (NCBT), which has been successfully used in the chlorination of indole alkaloids,[5] and 1-chloroisatin (NCI), which has been recently synthesized by us.[6] Although much has been published in the way of mechanistic speculation, we now propose another possibility, which involves an electron-transfer process and which derives, above all, from the consistency of product composition.

Results

Each indole was reacted with NCBT and with NCI. All reactions were carried out in benzene, methanol, or aqueous acetonitrile at room temperature with 20% excess reagent.

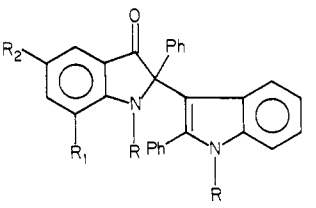
2-Phenylindole (**1a**) and 1-methyl-2-phenylindole (**1b**) with NCI gave the corresponding 3-chloro derivatives **2a** and **2b** in very good yields, independent of the solvent used (Scheme I, Table I). 2-Phenylindole with NCBT gave the 3-chloro derivative **2a** in benzene and **2a** together with 2-phenyl-2-(2-phenylindol-3-yl)-1,2-dihydro-3*H*-indol-3-one (indoxyl; **3a**) when it was reacted in methanol or aqueous acetonitrile (Scheme I, Table I). 1-Methyl-2-phenylindole (**1b**) with NCBT gave the corresponding 3-chloro derivative **2b** and indoxyls **3b–3d** when the reactions were carried out in methanol and products **2b** and **3b** when benzene was the reaction solvent, whereas when aqueous acetonitrile was the solvent the 3-chloro derivative was not isolated; only indoxyls **3b–3d** were formed (Scheme I, Table I). 2-Phenyl-3-methylindole reacted with NCI, forming

Scheme I



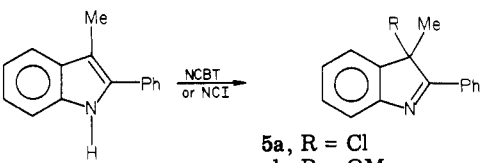
1a, R = H
b, R = Me

2



3a, R = R_1 = R_2 = H
b, R = Me; R_1 = R_2 = H
c, R = Me; R_1 = H; R_2 = Cl
d, R = Me; R_1 = R_2 = Cl

Scheme II



4

5a, R = Cl
b, R = OMe
c, R = OH
d, R = benzotriazol-1-yl

† Bologna.
‡ Roma.

(1) (a) Powers, J. C. In "Indoles"; Houlihan, W. J., Ed., Wiley-interscience: New York, 1972; Part II, pp 137–39, 155–159. (b) Sundberg, R. J. "The Chemistry of Indoles"; Academic Press: New York, 1970; pp 14–17.

(2) De Rosa, M.; Triana Alonso, J. L. *J. Org. Chem.* **1978**, 43, 3639 and references reported therein.

0022-3263/82/1947-4895$01.25/0