mally low barrier reported for Cp*(η^3-1,1,2-Me_3allyl)$ZrBr_2$ [$\Delta G^{\ddagger}$ = 51.5 kJ/mol], which is also distorted toward an η^1-allyl configuration due to steric crowding.[13] A much greater barrier to η^3–η^1 allyl isomerization was observed for (η^3-C_3H_5)(η^4-butadiene)CpZr [$\Delta G^{\ddagger}$ = 79.9 kJ/mol] in which the allyl ligand does not exhibit any distortion toward η^1.[5] Considered together, the X-ray and variable temperature ^1H NMR data for **3** depict a distortion toward η^1 and a degree of steric congestion unsurpassed by any other η^3-allyl zirconium compound.

Conclusions

Knowing how an allyl ligand will bind to an electron deficient (<18-electron) early transition metal and how easily it will undergo η^3 to η^1 isomerization is important in attempting to understand the reactivity of early-transition-metal allyl complexes. Under what circumstances will an allyl ligand bind η^3 versus η^1? We have previously shown that the Cp*(allyl)$ZrBr_2$ compounds (allyl = 1,1,2-trimethylallyl and 1,2,3-trimethylallyl) have η^3-bound allyls, although severe distortion toward η^1 did occur for the 1,1,2-trimethylallyl complex.[13] The Cp*$ZrBr_2$ portion of these complexes provides a relatively uncrowded environment for the allyl ligand, and so the electronic desire for η^3 outweighs the sterically favored η^1 mode. The Cp_2ZrBr moiety, on the other hand, provides a relatively crowded environment for an allyl ligand. Infrared studies have shown $Cp_2ZrCl(C_3H_5)$ and Cp_2ZrCl(2-Meallyl) to have η^1-bound allyls.[7] We have shown that Cp_2ZrBr(1,1,2-Me_3allyl), while somewhat crowded, also possesses an η^1-bound allyl. However, Cp_2ZrBr(1,2,3-Me_3allyl) was severely crowded, with its allyl ligand bound η^3. The question arises, have we increased donor ability via trimethylation to the point where electronic effects outweigh steric considerations to yield a crowded η^3 complex? We believe the answer to be no, and that the 1,2,3-trimethylallyl ligand binds η^3 not because donor ability is significantly enhanced but because η^3 is the more sterically favored mode in this case. This is supported by molecular modeling calculations, which reveal more congestion in the minimized η^1 geometry than in the minimized η^3 form of Cp_2(1,2,3-Me_3allyl)$ZrBr$.[22] Presumably, the 1,1,2-trimethylallyl ligand is η^1 bound since the bulk at the disubstituted end is too great to allow η^3 in complexes of this type no matter how good a donor the ligand is.

In conclusion, the allyl ligand appears to be an effective probe for determining the relative effect on the donor and steric properties of a ligand upon its methylation. We are continuing with work in this area, with particular interest being directed at the extent of allyl methylation necessary to achieve thermally stable electron-deficient early-transition-metal allyl halide compounds.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. 1, 109929-24-0; 2, 109929-25-1; 3, 113533-09-8; 4, 113533-10-1; 5, 113533-11-2; Cp_2ZrCl_2, 1291-32-3.

Supplementary Material Available: Tables of thermal parameters (Table III) and hydrogen atom coordinates (Table IV) (3 pages); listings of observed and calculated structure factors (Tables V and VI) (15 pages). Ordering information is given on any current masthead page.

(22) Modeling calculations were carried out by using an extended version of Allinger's MM2 force field which includes transition metals. The programs were obtained from Serena Software Inc., P.O. Box 3076, Bloomington, IN 47402.

Electrophilic Substitution with Allylic Rearrangement (S_E') Stereochemistry of Trifluoroacetolysis of Some Cyclohex-2-enylmetal Compounds

Geoffrey Wickham, David Young, and William Kitching*

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

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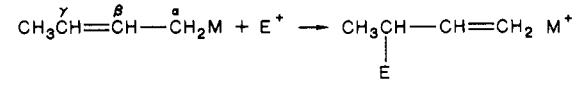
A range of (4-alkylcyclohex-2-enyl)-, (5-alkylcyclohex-2-enyl)-, and (6-alkylcyclohex-2-enyl)silanes, (4-alkylcyclohex-2-enyl)-, (5-alkylcyclohex-2-enyl)-, and (6-alkylcyclohex-2-enyl)germanes, and (4-alkylcyclohex-2-enyl)-, (5-alkylcyclohex-2-enyl)-, and (6-alkylcyclohex-2-enyl)stannanes were cleaved to the cycloalkene (and R_3MX) with trifluoroacetic acid-*d* in various solvents. Complete allylic rearrangement (γ-attack) was observed, and the preferred direction of delivery of the electrophile (formally D^+) to the γ-carbon of the allylic triad was determined by detailed ^1H, ^{13}C, and ^2H NMR analyses of the derived dibromides of the various alkyl-substituted cyclohexenes or by direct ^2H NMR analysis and comparisons with ^2H-substituted alkylcyclohexenes of established relative configurations. A highly preferred γ-anti mode of acidolysis is established for all systems, except for the *trans*-4-*tert*-butylcyclohex-2-enyl derivatives, such exception being ascribed to steric impedance of electrophile approach, promoting syn attack. Thus, overall, highly γ-regioselective and anti-stereoselective substitutions (S_E') are observed.

Introduction

Early studies of electrophilic substitutions (with simple protic acid electrophiles) of allyl groups bound to main-group metals such as silicon, tin, or mercury established their facility and high regioselectivity, resulting in essentially complete allylic rearrangement, i.e. attack at the γ-carbon of the allylic triad. Along with kinetic and other

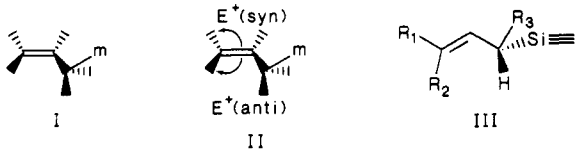
Scheme I



data, these facts indicated such demetalations to display the characteristics of S_E' (S_E2' or S_Ei') processes[1-6] (Scheme

0276-7333/88/2307-1187$01.50/0

Scheme II



I II III

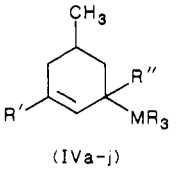
I).

In recent times, such allyl derivatives, particularly of silicon and tin, have assumed importance as allylating agents, particularly toward aldehydes, often resulting in stereocontrolled formation of homoallyl alcohols.[7,8] Of interest also, have been the bonding and conformational aspects of (σ-allyl)metal compounds,[5,9-11] and the evidence is persuasive that the conformational "well" corresponds to the c–m linkage being nearly perpendicular to the double bond plane (I) (Scheme II). Interaction of π_{cc} and σ_{c-m} operates[12-14] (with an energy raising of the former), and this $\sigma-\pi$ effect regulates the conformational profile of these allylmetal compounds and the arrangements on which γ-attack can operate most effectively.

With the increasing recognition of the synthetic value of the regiochemically reliable γ-electrophilic substitution of these derivatives,[15] a natural inquiry is whether these S_E' processes display any stereochemical preference in the sense shown (II) (Scheme II). Apart from the theoretical significance of such a preference, the synthetic appeal is the possibility of a three-carbon transfer of chirality in appropriate systems. Investigations of the stereochemical aspects of the corresponding S_N2' processes have been extensive,[16] but only relatively recently have the S_E' processes been so scrutinized.[17] In this report, we detail our studies of the stereochemical aspects of what is the most fundamental electrophilic substitution—protonic acid cleavage—with cyclohex-2-enyl derivatives.

In general, there are two approaches available for determining the stereochemical course of these reactions. The first is to use an optically active substrate, i.e. an allylmetal compound chiral at the metal-bearing carbon, of known absolute configuration and then to establish the absolute configuration of the allylicly rearranged product.

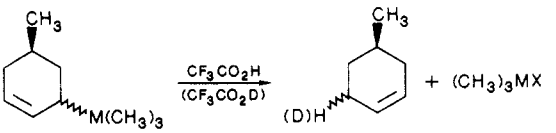
Scheme III



(IVa-j)

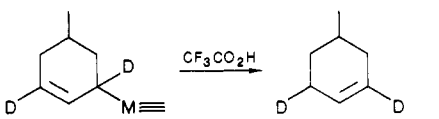
compd	M	R	R′	R″
IVa	Si	CH_3	H	H
b	Ge	CH_3	H	H
c	Ge	CH_3	D	H
d	Ge	CH_3	H	D
e	Ge	CH_3	CH_3	H
f	Sn	CH_3	H	H
g	Sn	CH_3	D	H
h	Sn	CH_3	H	D
i	Sn	CH_3	CH_3	H
j	Sn	C_6H_5	H	H

Scheme IV



M = Si, Ge, Sn

Scheme V



M = Sn	58%	42%	57%	45%
M = Ge	29%	71%	25%	75%

While intrinsically more revealing than the second approach—based on the use of a cyclic allylic system carrying a stereochemically "marking" group in addition to the allylmetal functionality—the acquisition in a reliable way of enantiomerically enriched and optically stable allylmetal compounds was not developed at the time we commenced this work. In the meantime, however, optically active allylsilanes, e.g. III (Scheme II), are now available by asymmetric cross-coupling reactions developed by Kumada and Hayashi.[18] Thus, in our approach using alkyl-substituted cyclohex-2-enyl derivatives,[19] the stereochemical course is determined by distinguishing diastereomers, not enantiomers, which generally is analytically more straightforward.

Results and Discussion

Several alkyl-substituted cyclohex-2-enylsilanes, -germanes, and stannanes have been employed in this investigation, but it is useful to commence with the 5-alkyl series because of its symmetrical and sterically unbiased allylic system.[20] The attractive features of the 5-methyl system were recognized and exploited by Goering in some pioneering mechanistic studies.[19] The range of 5-methylcyclohex-2-enyl derivaties (IV) employed in the acidolysis studies are shown in Scheme III, and the synthesis and complete characterization of these diastereomers have been reported elsewhere.[21,22]

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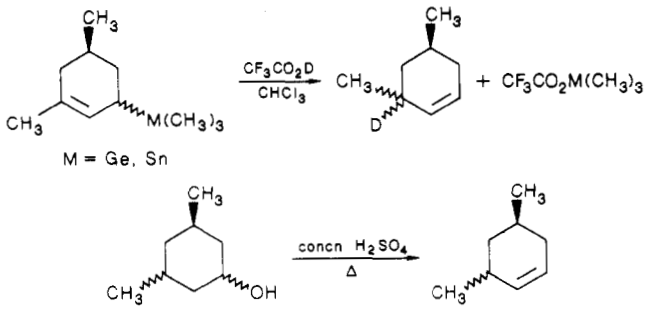
Scheme VI



The carbon–metal bonds in compounds IV were readily cleaved by trifluoroacetic acid (CF_3CO_2H or CF_3CO_2D) in either dichloromethane, chloroform, or dioxan solvent at room temperature. For compounds IVa,b,f, the reaction products were identified as 4-methylcyclohexene (or deuteriated 4-methylcyclohexene) and $(CH_3)_3MX$, by ^1H and ^{13}C NMR spectroscopy and comparisons with authentic samples (Scheme IV).

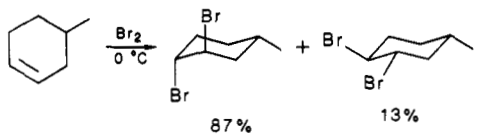
It was found that the progress of the cleavage reaction could be monitored by ^1H NMR, as the signal for $(CH_3)_3MOCOCF_3$ was well downfield (δ 0.38, 0.71, and 0.69 for M = Si, Ge, and Sn, respectively) from that for M-$(CH_3)_3$ (δ 0.0–δ 0.14) in the reactants. For compound IVj, cleavage with excess CF_3CO_2D provided significant quantities of benzene-*d*, in addition to (deuteriated) 4-methylcyclohexene. The ^{13}C NMR spectrum of the product deuterio-4-methylcyclohexene established site-specific monodeuteriation, on the basis of a clear triplet ($^1J_{^{13}C-^2H}$ = 19.5 Hz) at 24.90 ppm for C_6 (C_6 in nondeuteriated 4-methylcyclohexene resonates at 25.34 ppm, the difference being the one-bond ^2H isotope effect on the shift).

Regiochemistry. Systems IVa,b,f because of their symmetry do not provide evidence for allylic rearrangement, i.e. for the validity of the S_E' description. This evidence was obtained from reactions of mixtures of C_1 and C_3-deuteriated systems IVc,d and IVg,h. For example, the latter mixture was reacted with CF_3COOH (in chloroform) at room temperature, and the ^{13}C NMR spectrum of the chloroform solution (after removing excess acid) consisted of signals for 4-methylcyclohexene, with appropriate ^2H isotope effects and couplings. The direct ^2H NMR spectrum exhibited signals at δ 2.03 (allylic ^2H) and 5.67 (vinylic ^2H) in the ratio 57:43. These results are summarized below and also for the trimethylgermyl system (Scheme V).

The conclusion that electrophilic substitution by acid proceeded with high if not 100% regioselectivity (i.e. γ-attack) in this symmetrical system (thus justifying the S_E' description) was confirmed by studies with the systems IVa and IVi, i.e. the 3,5-dimethylcyclohex-2-enyl derivatives. Thus diastereomeric mixtures of IVa and IVi on reaction with CF_3CO_2D provided only isomeric mixtures of 3,5-dimethylcyclohexene (^2H labeled at C3) by comparison of the ^{13}C NMR with that of authentic material, acquired by dehydration of 3,5-dimethylcyclohexanol. This is summarized below in Scheme VI.

Thus, the thermodynamically less favorable dimethylcyclohexene is produced by highly regioselective γ-electrophile attachment. Further details of the stereochemical aspects of the cleavages of IVa and IVi to produce *cis*- and *trans*-3,5-dimethylcyclohexenes are discussed later.

Scheme VII



Stereochemical Analysis. 4-Methylcyclohexene System. As described above, 4-methylcyclohexene exclusively labeled at C_6 is the sole organic product from acidolysis (CF_3COOD) of diastereomeric mixtures of the *cis*- and *trans*-5-methylcyclohex-2-enyl derivatives of Si, Ge, and Sn. Direct ^2H NMR analysis of the diastereomers of 4-methyl[6-^2H]cyclohexene is not applicable as the ^2H signals are coincident (δ 2.03). An attractive approach involved the addition of a symmetrical reagent to the double bond to generate a cyclohexane, for which the well-recognized chemical shift differences between axial and equatorial positions should apply. Reduction (formal addition of H_2) to 3-deuteriomethylcyclohexanes was considered first as the ^2H shifts for the trans (axial ^2H) and cis (equatorial ^2H) isomers (δ 1.19 and 1.64) were easily established. However, several experiments indicated that hydrogenation using 5% palladium on carbon (methanol) of *cis*- and *trans*-4-methyl[6-^2H]cyclohexene did not transform into the same ratio of *cis*- and *trans*-methyl[3-^2H]cyclohexanes. Incursion of allylic C–H or C–^2H cleavage during the process was implicated, and this approach was not pursued further. Diimide reduction was attempted but also was judged to be operationally unsatisfactory for the samples involved.

Careful bromine addition to the cyclohexenes was considered next, as it had been demonstrated[23] that nonconjugated alkenes react rapidly and cleanly in chlorinated solvents and that addition to 4-methylcyclohexene provides largely the diaxial product (viz., *trans*-3,*cis*-4-dibromomethylcyclohexane (87%) with some diequatorial dibromide (13%) in chloroform (0 °C). This approach offered the practical advantage of no requirement for separation of the volatile (deuteriated) 4-methylcyclohexene from the solvents in which the cleavage was conducted (CH_2Cl_2 or $CHCl_3$) (Scheme VII).

The above finding of Marioni[23] was confirmed by us. The dibromide generated by addition of neat bromine (dropwise) to 4-methylcyclohexene ($CHCl_3$; 0 °C) was examined directly by ^1H and ^{13}C NMR. In the 100-MHz ^1H NMR spectrum, C*H*Br multiplets were observed at δ 4.01 ($W_{1/2}$ = 15 Hz) and 4.64 ($W_{1/2}$ = 6.7 Hz) in a ratio of ca. 14:86, and these signals were assigned to the (predominantly) axial and equatorial C*H*Br protons in the diequatorial and diaxial dibromides, respectively. The ^{13}C NMR spectrum consisted of two sets of signals (ca. 14:86) with the *C*HBr carbons in the diaxial dibromide at δ 53.31 and 53.63 and those in the diequatorial isomer resonating at δ 56.94 and 57.26.

The deuteriated 4-methylcyclohexene resulting from CF_3COOD cleavage of the 84:12 cis/trans mixture of (5-methylcyclohex-2-enyl)trimethylsilanes was brominated (CH_2Cl_2; 0 °C) and examined directly by ^2H and ^{13}C NMR. Appropriately the ^{13}C spectrum consisted of signals for the diaxial and diequatorial dibromides in the ratio of 86:14, while the ^2H spectrum consisted of two almost base line resolved signals at δ 1.91 and 2.44 in the ratio 26:74. This result was significantly different from that obtained by the catalytic hydrogenation procedure, which gave a 38:62 *cis*-3-deuteriomethylcyclohexane/*trans*-3-deuterio-

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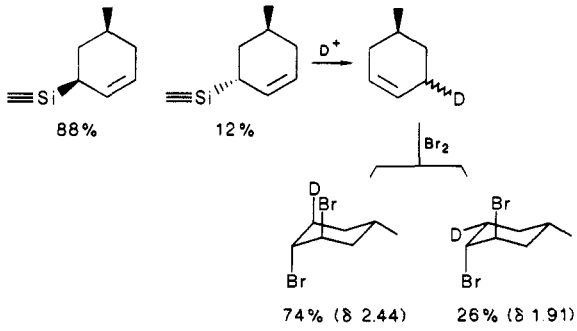
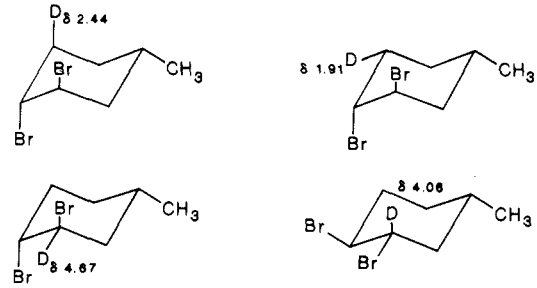
Scheme VIII



Scheme IX

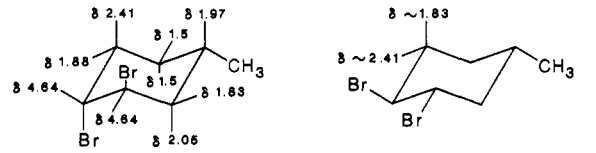


methylcyclohexane mixture. Accepting that the δ 2.44 signal (for ^2H) in the deuteriated dibromide is trans to the methyl group, the results may be summarized as below in Scheme VIII.

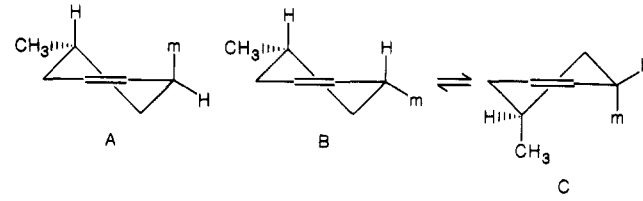
Providing that the ^2H assignments for the dibromides can be established and correction made for the presence of "diequatorial dibromide" (14%), this method has more reliability than the hydrogenation procedure. 4-Methylcyclohexanone, preferentially deuteriated at the 2-axial position, was prepared by reacting the silyl enol ether of 4-methylcyclohexanone with equal volumes of CH_3COOD/D_2O in dimethoxyethane (DME). Predominance of axial ^2H (δ 2.49; 73%) was established over equatorial ^2H (δ 2.74; 27%) (benzene solvent) by careful analysis of the 300-MHz ^1H spectrum of 4-methylcyclohexanone itself, which established that $H_{2,6}$ (axial) was at a higher field. Subsequent transformations (which were completely monitored by quantitive ^2H and ^{13}C NMR spectra) involved reduction, tosylation, and elimination (sodium methoxide) to provide (in addition to methyl ethers) 4-methylcyclohexene which was a 65:35 mixture of C_6-/C_2-deuteriated derivatives (^2H NMR). Full details of characterization and stereochemistry of these transformations are presented elsewhere.[24] Bromination ($CHCl_3$; 0 °C) was conducted, and the resulting dibromides were analyzed by ^{13}C and ^2H NMR spectra, leading to the following ^2H NMR assignments shown in Scheme IX.

These assignments were in agreement with our analysis of the 300 MHz ^2H spectrum of predominantly (86%) *trans*-3-*cis*-4-dibromomethylcyclohexane ("diaxial dibromide"). Extensive spin decoupling led to the following unambiguous chemical shifts, noting particularly H_{5a} and H_{5e} at 2.41 and 1.88 ppm, respectively, and H_{2a} (2.05 ppm) and H_{2e} (1.83 ppm) (Scheme X). Thus the axial protons at C_2 and C_5 resonate at lower field than their equatorial counterparts, a situaiton ascribable to a deshielding 1,3-diaxial interaction with bromine.[25] Furthermore, it is possible that the vicinal bromines cause shielding of

Scheme X



Scheme XI



equatorial protons, as has been reported for protons vicinal to axial OH, OAc, and SH.[25]

The observation of two signals only in the ^2H NMR spectra of the deuteriated dibromides, which were 86:14 "diaxial"/"diequatorial" dibromides, led to the necessary conclusion that the ^2H signals (i.e. axial and equatorial ^2H at C_5) in the latter dibromide were coincident with those for the "diaxial" form. This was strongly supported by careful analysis of 300-MHz ^1H spectra of various mixtures of "diaxial"/"diequatorial" dibromides generated by partial equilibration and by the ^1H spectra of the dibromides of 4-*tert*-butyl- and 4-(trimethylsilyl)cyclohexenes.[26] Utilizing the values shown above, then, for the chemical shifts of H_{5a} and H_{5e} in the "diequatorial dibromide" of 4-methylcyclohexene, it was possible to make corrections to the δ 2.41/δ 1.88 ^2H signal areas by substracting the *estimated* contributions from $^2H_{5a}$ and $^2H_{5e}$ in the "diequatorial dibromide", knowing the 86:14 ratio of "diaxial" and "diequatorial" dibromides.[24]

3,5-Dimethylcyclohexene System. Acidolysis of (3,5-dimethylcyclohex-2-enyl)metal derivatives provides 3,5-dimethylcyclohexene as the cleavage product. Catalytic hydrogenation to the *cis*- and *trans*-1,3-dimethylcyclohexanes was chosen as the analytical method, and hydrogenation of a 76:24 isomeric mixture of the *cis*- and *trans*-cyclohexenes (from dehydration of 3,5-dimethylcyclohexanol) afforded an 82:18 cis/trans mixture of 1,3-dimethylcyclohexane, on the basis of ^{13}C NMR spectra.[27] The incorporation of deuterium into the 3,5-dimethylcyclohexene product enabled complete assignment of the ^{13}C NMR shifts of both *cis*- and *trans*-3,5-dimethylcyclohexene. (Goering[28] has reported ^{13}C NMR shifts for *trans*-3,5-dimethylcyclohexene, but some of these (for the C_3 and C_5 methyls and C_4 and C_6) require reversal.) Straightforward assignment of the ^{13}C spectra of the *cis*- and *trans*-1,3-dimethylcyclohexanes confirmed that the major isomer from acidolysis was cis, and actual ratios were based on the spectra of the cyclohexenes, prior to hydrogenation. (Methyl group resonances (^{13}C) at 22.59 and 20.35 ppm were characteristic of the *cis*- and *trans*-1,3-dimethylcyclohexanes, respectively.) These chemical shifts are listed in the Experimental Section.

On the basis of the above analytical methods, the stereochemistry of trifluoroacetolysis of a range of (5-methylcyclohex-2-enyl) and (3,5-dimethylcyclohex-2-

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(28) Goering, H. L.; Schmidt, W. W.; Singleton, V. D. *J. Org. Chem.* **1979**, *44*, 2282.

Table I. Stereochemistry of Trifluoroacetolysis[a] Reactions of 5-Methyl-2-cyclohexenyl Metallics

					dibromide[c]				
					uncorr[e]		corr[f]		
entry	system[b]	cis	trans	solv	$^2H_{5a}$	$^2H_{5e}$	$^2H_{5a}$	$^2H_{5e}$	favored stereochem
1	$Si(CH_3)_3$	88	12	CH_2Cl_2	74	26	84	16	anti
2	$Ge(CH_3)_3$	90	10	$CHCl_3$	73	27	83	17	anti
3		90	10	$CHCl_3$	74	26	84	16	anti
4		90	10	dioxane	71	29[d]	81	19	anti
5		65	35	$CHCl_3$	58	42	62	38	anti
6		65	35	$CHCl_3$	59	41	63	37	anti
7		49	51	$CHCl_3$	50	50	50	50[a]	anti
8		49	51	$CHCl_3$	48	52	48	52[g]	anti
9		40	60	$CHCl_3$	45	55	43	57	anti
10		36	64	$CHCl_3$	42	58	38	62	anti
11		36	64	dioxane	45	55[d]	42	58	anti
12	$Sn(CH_3)_3$	67	33	$CHCl_3$	56	44	60	40	anti
13		59	41	$CHCl_3$	52	48	54	46	anti
14		31	69	$CHCl_3$	42	58	38	62	anti
15		31	69	$CHCl_3$	40	60	35	65	anti
16	$Sn(C_6H_5)_3$	72	28	$CHCl_3$	55	45	59	41	anti
17		31	69	$CHCl_3$	44	56	40	60	anti

[a] CF_3CO_2D. [b] Capillary gas chromatography established the cis/trans germane ratios. For the silane and stannanes, the cis/trans ratios were determined by ^{13}C NMR, comparing the intensities of signals for like carbons. The results for the stannanes were fully supported by ^{119}Sn NMR analyses. [c] Formed by the addition of bromine to the trifluoroacetolysis product (4-methylcyclohexene deuteriated at C_6) in CH_2Cl_2 or $CHCl_3$ at 0 °C. [d] The deuteriated 4-methylcyclohexene was extracted into $CHCl_3$ and brominated. [e] Area ratio of ^2H NMR signals (determined by integration) assigned to $^2H_{5a}$ (δ 2.44) and $^2H_{5e}$ (δ 1.91) in *trans*-3,*cis*-4-dibromomethylcyclohexane (diaxial dibromide). [f] Corrected for 86% diaxial dibromide and 14% diequatorial dibromide. This correction was based on the demonstration that the ^2H NMR signal for $^2H_{5e}$ in *cis*-3,*trans*-4-dibromomethylcyclohexane (diequatorial dibromide) is coincident with the signal for $^2H_{5a}$ in *trans*-3,*cis*-4-dibromomethylcyclohexane (diaxial dibromide). Similarly, the signal for $^2H_{5a}$ in the former is coincident with the signal for $^2H_{5e}$ in the latter. [g] The starting germane was actually a 51:49 (5-methyl-2-cyclohexenyl)trimethylgermane/(5-methyl-1-cyclohexenyl)trimethylgermane (i.e. allylic/vinylic germane) mixture, but trifluoroacetolysis (CF_3CO_2D) of the vinylgermane provided 4-methylcyclohexene labeled at C_2 (i.e. vinylic deuterium).

Table II. Stereochemistry of Trifluoroacetolysis Reactions[a] of 3,5-Dimethyl-2-cyclohexenyl Metallics

					3,5-Dimethylcyclohexene[c]		
entry	system[b]	cis	trans	solv	cis	trans	favored stereochem
1	$Ge(CH_3)_3$	75	25	$CHCl_3$	76	24	anti
2		72	28	$CHCl_3$	73	27	anti
3	$Sn(CH_3)_3$	72	28	$CHCl_3$	69	31	anti

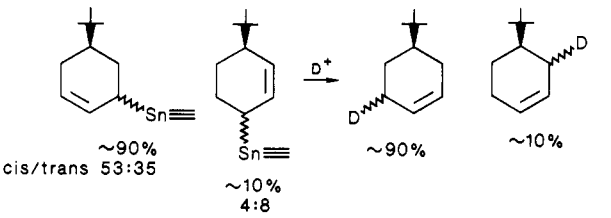
[a] CF_3CO_2D. [b] Capillary gas chromatography established the cis:trans germane ratios. The cis/trans stannane ratio was determined by ^{13}C NMR, comparing the intensities of signals for like carbons. This result was fully supported by a ^{119}Sn NMR analysis. [c] Ratios were determined by ^{13}C NMR, comparing the integrals of signals for like carbons.

enyl)metal derivatives were determined and are summarized in Tables I and II.

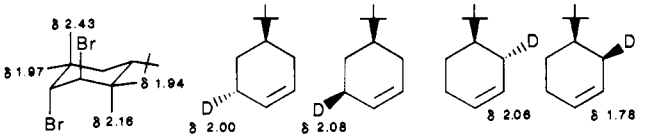
5-*tert*-Butylcyclohex-2-enyl System. The (*cis*-5-methylcyclohex-2-enyl)- and (*trans*-5-methylcyclohex-2-enyl)metal derivatives may be represented in conformational terms as shown below in Scheme XI. The trans isomer is satisfactorily depicted by arrangement A, whereas for the cis diastereomer, consideration of the B ⇌ C equilibrium is needed, as some stabilizing features, e.g. enhanced σ_{c-m}–π interaction, operate more efficiently in C and would to some degree offset the 1,3-CH_3–m interaction in C. Nevertheless, values of $J_{^{119}Sn-C5}$ in the trans (12.5 Hz) and cis isomers (46 Hz) support A and B as highly preferred for the isomers but do not exclude a significant population of C (in which π-orbital distortion at C_γ may be greater) through which the reaction may be channelled. $J_{^{119}Sn-C5}$ in the *cis*-5-*tert*-butyl compound is 47.6 Hz, suggesting little participation by C in the above equilibrium for the *cis*-5-methyl isomer. Despite this, it was desirable to employ a system in which conformational uncertainty was minimized, and the 5-*tert*-butyl derivatives were examined.[22]

Trifluoroacetolysis of mixtures of (*cis*-5-*tert*-butylcyclohex-2-enyl)- and (*trans*-5-*tert*-butylcyclohex-2-enyl)trimethylstannanes, which were contaminated with low levels of the cis (4%) and trans (8%) (4-*tert*-butylcyclohex-2-enyl)stannanes,[22] was performed in the usual way and yielded predominantly (^{13}C NMR) 6-deuterio-4-*tert*-butylcyclohexene, with a small amount (~10%) of 3-deuterio-4-*tert*-butylcyclohexene.[29] (The C_6 signal (δ 26.3) was a triplet (J = 23 Hz), indicating the major site of ^2H attachment, with a small amount (~10%) of ^2H at C_3). This system is summarized in Scheme XII.

Scheme XII



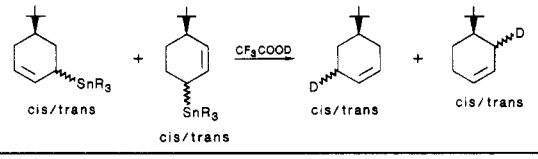
Scheme XIII



The ^2H NMR spectrum of the product consisted of three signals at δ 2.08 (44%), 2.00 (55%), and 1.78 (~1%), and for analytical purposes, the (predominantly) "diaxial dibromides" were formed, as outlined previously for 4-methylcyclohexene. The ^2H NMR spectrum of the dibromides revealed four signals at δ 2.43 (~51%), 2.15 (~5%), 1.96 (~34%), and 1.90 (~10%), and utilizing ^1H assignments established for the "diaxial dibromide" derived

(29) For a preliminary report see: Young, D.; Kitching, W.; Wickham, G. *Tetrahedron Lett.* **1983**, *24*, 5789.
(30) Young, D. Ph.D. Thesis, University of Queensland, 1986.

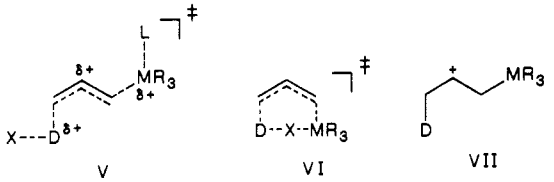
Table III. Trifluoroacetylsis of (5-*tert*-Butylcyclohex-2-enyl)stannanes



R = CH_3			
53:35	4:8	36:53	1:10
21:67	8:4	66:34[a]	>1:a
25:66	6:~3	66:~35[a]	
R = C_6H_5[b]			
44:56		53:47	
85:15		30:70	

[a] Possible overlapping of ^2H signals of 4-*tert*-butylcyclohexene. [b] Significant phenyl cleavage (yielding C_6H_5D) occurs. ^2H NMR shifts: *cis*- and *trans*-4-*tert*-butyl[6-^2H]cyclohexene at δ 2.08 and 2.00, respectively: *cis*- and *trans*-4-*tert*-butyl[3-^2H]cyclohexene at δ 1.78 and 2.06, respectively.

Scheme XIV



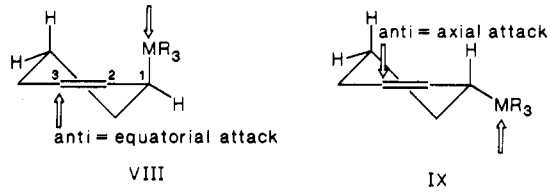
from undeuteriated 4-*tert*-butylcyclohexene, these could be identified and permit assignment of the ^2H signals of the 6- and 3-deuterio-4-*tert*-butylcyclohexenes (Scheme XIII). (In the present case, the low levels of the 4-*tert*-butylstannanes (accompanying the major 5-*tert*-butyl derivatives) provided an insight into other stereochemical aspects of acidolysis, which are discussed fully later (see Table IV), along with further information on the 3-deuterio-4-*tert*-butylcyclohexenes).

Thus, it was possible to generate the stereochemical data assembled in Table III. In the latter cases, phenyl cleavage is competitive (to yield benzene-d_1) with allylic cleavage, but use of varying amounts of acid indicated that the ratio of products did not vary; i.e., cleavage of the allylic group from the (intermediate) (5-*tert*-butylcyclohex-2-enyl)diphenylstannyl trifluoroacetate was stereochemically similar to that for the starting material.

The foregoing results demonstrate that (protonic) acid cleavage of simple cyclohex-2-enyl metallics proceeds highly regioselectively (γ-substitution) and with a highly preferred, if not 100% stereoselective anti delivery of electrophile, resulting in the incorporation of a single ^2H atom when CF_3COOD is used. This latter observation is consistent with rate-determining proton transfer to the allylmetal system, as indicated previously by Kuivila,[6] who also discussed the nature of transition states likely to be involved in S_E' protonolysis reactions. Arrangements V and VII (i.e. concerted[31] or involving a β-metallo cation) are generally considered to be most applicable (Scheme XIV).

The enhanced reactivity compared with saturated analogues and the very high γ-regioselectivity in these substitutions have been addressed in some detail previously.[9-14,32,33]

Scheme XV



On the other hand, stereochemical aspects of S_E' reactions (i.e. γ-syn or γ-anti) have been alluded to, in an oblique way, as the emphasis of the theoretical treatments of Fukui,[34] Anh,[35] and Liotta[36] was on the S_N2' process, although little extension of the approach was required to accommodate electrophilic substitution. For concerted S_E2' processes, anti stereochemistry was predicted from these qualitative approaches, and very recently Hehre[13] has presented a detailed analysis of electrophile addition to the three minima on the conformational profile of 2-silylbut-3-ene (for the two most stable arrangements, the C–Si bond is nearly perpendicular to the double bond), on the FMO assumption that proton approach will occur on the alkene face where the π-orbital (HOMO) is more concentrated.

With respect to regiochemistry, HOMO coefficients (for the three lowest energy conformers) indicated preferential γ-attack for all three,[13] and the calculations indicated minor π-orbital polarization for all three conformers, but proton addition to the two low-energy conformers of the silane was indicated to be anti. These predictions are generally in line with experiment, although Hehre[13] suggested that anti approach was associated with the tendency of the electrophile to avoid areas of high positive charge, i.e. SiH_3, rather than due to the weak polarization of the π bond because of its asymmetric environment. π-Polarization will vary with the metal group attached and would be greater for Sn than for Si.

The most striking feature of the present results in the cyclohex-2-enyl system is the high degree of anti stereoselectivity observed for both diastereomers of each system. This suggests the direction of electrophile addition may have been regulated by a balance between the directing effect of any π-orbital distortion and the normal preference for axial attack[37] on the cyclohexene π-system. Thus, two geometrical arrangements of the cyclohex-2-enyl system require consideration—the C–M bond may be either quasi-axial or quasi-equatorial. It should be kept in mind that the orbital distortion approach utilized the case of maximum σ–π interaction with the greatest orbital extension at the γ-carbon and consequently the strongest directing effect. This situation is reproduced well in the quasi-axial cyclohexenyl system, but not so efficiently when the C–M bond is quasi-equatorial. The figures below clarify this (Scheme XV).

Thus in VIII (with efficient "σ–π activation") the favored anti approach coincides with the less favored equatorial direction, but the "σ–π" anti preference dominates. The *trans*-5-methylcyclohex-2-enyl system is in this category. In IX, "σ–π" anti activation at C_γ is less pronounced, but

(31) For kinetic information on protodemetalations of allylic systems see ref 6 and: Mangravite, J. A.; Verdone, J. A.; Kuivila, H. G. *J. Organomet. Chem.* **1976**, *104*, 303. Although a fully concerted mechanism would exhibit 100% stereoselectivity, second-order kinetics does not distinguish between such a mechanism and others involving the slow or reversible formation of an intermediate. See also: Fleming, I.; Langley, J. A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1421. Fleming, I.; Marchi, D.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2578.

(32) Kreevoy, M. M.; Steinward, P. J.; Kayser, W. V. *J. Am. Chem. Soc.* **1966**, *88*, 124.

(33) Délèris, G.; Pillot, J. P.; Rayez, J. C. *Tetrahedron* **1980**, *36*, 2215.

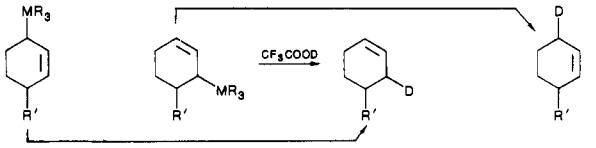
(34) Fukui, K. *Theory of Orientation and Stereoselection*; Springer-Verlag: Berlin, 1975. For a summary see ref 24.

(35) Anh, N. T. *J. Chem. Soc. D* **1968**, 1089.

(36) Liotta, C. L. *Tetrahedron Lett.* **1975**, *519*, 523.

(37) Eisenstein, O.; Klein, J.; Lefour, J. M. *Tetrahedron* **1979**, *35*, 225.

Table IV. Trifluoroacetolysis of Some 4- and 6-Alkylcyclohex-2-enyl Metallics



MR_3	R′	cis/trans	cis/trans	cis/trans[a]	cis/trans[b]	k_{syn}/k_{anti}[c,d]
$Sn(CH_3)_3$	$(CH_3)C$	33:67		17:83		2.9
		72:28		7:93		3.0
$Sn(C_6H_5)_3$[e]	$(CH_3)_3C$	11:89		14:86		5.2
		81:19		8:92		~2.0[g]
$Ge(CH_3)_3$	$(CH_3)_3C$	7:93		44:56		1.1
		83:17		10:90		~0.9[g]
$Si(CH_3)_3$	$(CH_3)_3C$	54:46		22:78		1.1
$Sn(CH_3)_3$	CH_3	41:22	14:23	20:42	38	0.1
		17:42	10:31	28:32	40	0.5
$Sn(C_6H_5)_3$[f]	CH_3	4:89	2:5	48:44	8	~0.8
		39:22	21:18	22:42	36	~.1
$Ge(CH_3)_3$	CH_3	13:87		77:23		~.13

[a] The percentage of the *cis*- and *trans*-3-deuterio-4-*tert*-butylcyclohexenes were determined from the integrated ^2H signals at δ 1.78 and 2.00. For the 4-methyl series the signals were at δ 1.60 and 2.04, respectively. [b] The ^2H signals for these isomers were coincident at δ 1.93. [c] These values refer to the proportions of syn and anti cleavages of the trans isomers of the 4-alkyl series. [d] As judged by ^{119}Sn or ^{13}C NMR spectra after partial reaction, the cis and trans isomers of the 4-*tert*-butyl derivatives had very similar reactivities. [e] Cyclohex-2-enyl cleavage occurred in preference to phenyl cleavage. [f] The importance of phenyl cleavage was not determined. [g] Approximate as based on low concentration of starting trans isomer.

now anti approach coincides with the generally preferred axial electrophile addition to the π-bond, as in the *cis*-5-methylcyclohex-2-enyl system. The anti preference is of interest in that in relatively nonpolar chlorinated solvents, molecular acid could be envisaged to deliver the proton and also to assist in the departure of the metal group (S_Ei' route) (e.g. VI), resulting necessarily in syn cleavage. However, the stereoelectronic advantage of the anti pathway clearly dominates, but studies involving a wide range of solvents and acids could be informative in this regard.

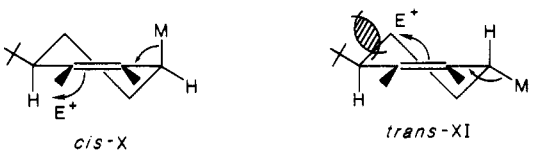
The view that "special features", e.g. conformational biassing effects, preferred axial electrophile approach, etc., peculiar to the cyclohex-2-enyl system, may prevent generalization of the finding of preferred γ-anti proton delivery is negated by other demonstrations of this preference. Perhaps the most relevant are those of Kumada and Hayashi,[38] who have employed simple optically active allylsilanes in their acidolysis studies and confirmed anti cleavage. This stereochemistry is followed for other reactions such as *tert*-butylation, acetylation, etc.[18]

These authors also demonstrated[39] that systematic reduction in the extent of $\sigma_{C-Si}-\pi$ interaction (by the progressive change $Si(CH_3)_3 \rightarrow \rightarrow \rightarrow SiF_3$) with consequent changes in the form and energy of the HOMO reduced the ease and stereoselectivity of S_E' attack.

Of the substitution reactions defined by the symbols S_N2, S_N2', and S_E2, only the first is stereochemically reliable, apparently proceeding always with inversion of configuration at carbon. The stereoelectronics are not as constraining for S_N2' and S_E2, and variable stereochemistry[16,41] has been reported. The question then arose whether the anti preference inherent in simple S_E' situations was favored to the extent that it could withstand attempted manipulation by steric or coordinative effects.

With respect to steric effects, the data in Table IV, for the cleavage of the (*cis*-4-*tert*-butylcyclohex-2-enyl)- and (*trans*-4-*tert*-butylcyclohex-2-enyl)stannanes, indicated strongly that an inviolable rule of stereochemistry would not apply to S_E' reactions. This was pursued in the following way. The preparation and characterization of a range of (*cis*-4-*tert*-butylcyclohex-2-enyl)- and (*trans*-4-*tert*-butylcyclohex-2-enyl)silanes, (*cis*-4-*tert*-butylcyclohex-2-enyl)- and (*trans*-4-*tert*-butylcyclohex-2-enyl)germanes, and (*cis*-4-*tert*-butylcyclohex-2-enyl)- and (*trans*-4-*tert*-butylcyclohex-2-enyl)stannanes have been reported elsewhere,[22,26] and these derivatives were subjected to trifluoroacetolysis (CF_3COOD) in the normal way. The sole organic product was 3-deuterio-4-*tert*-butylcyclohexene (^{13}C NMR), whose ^2H NMR spectrum consisted of signals at δ 2.00 and 1.78, assigned as below in Table IV, on the basis of dibromide formation.

Scheme XVI



The results in Table IV appear to be odd, but analysis can begin on the basis that anti cleavage of cis isomers will operate by extrapolation of the data for the 5-alkyl series. There is no significant impediment to such electrophile approach in the conformationally homogeneous cis isomers X (Scheme XVI).

This leads to the conclusion that predominate syn cleavage must operate on the trans isomers of the 4-*tert*-butylcyclohex-2-enyl systems, and this is readily understood on the basis of steric impedance of anti electrophile approach, as in XI.

If the above reasoning is correct, the *trans*-4-methylcyclohex-2-enyl derivatives should exhibit smaller k_{syn}/k_{anti} ratios, and the results in Table IV confirm this. Clearly stereoleakage occurs in acidolysis of the *trans*-4-methyl derivatives, but in all cases, a predominant anti cleavage is nevertheless observed, in contrast to the results above for the *trans*-4-*tert*-butyl compounds. Although the $\sigma-\pi$ effect in the *trans*-4-methyl series will be more pronounced in a conformation with both the methyl and the metal groups quasi-axial (and promote anti cleavage), electrophile

(38) Hayashi, T.; Ito, H.; Kumada, M. *Tetrahedron Lett.* **1982**, *23*, 4605.
(39) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Organometallics* **1987**, *6*, 884.
(40) (a) Bunton, C. A. *Nucleophilic Subsitution at a Saturated Carbon Atom*; Elsevier: New York, 1963. (b) Ingold, C. K., *Q. Rev., Chem. Soc.* **1957**, *11*, 1.
(41) Fukoto, J. M.; Jensen, F. R. *Acc. Chem. Res.* **1983**, *16*, 177.

approach is more hindered in this conformation. Thus, steric effects in the region of the δ-carbon are able to divert the S_E' stereopath from the presumed stereoelectronically favored anti mode to predominantly syn, raising the specter of a stereochemically quite fickle reaction, especially in five- and six-membered ring systems. Cyclohept-2-enyl metal derivatives undergo clear anti acidolysis,[42] and the more extensive conformational profile in these systems may better accommodate bulky substituents. This result suggests that other factors may be able to regulate the syn/anti stereo competition, and with a departing metallo group, coordinative stabilization with a donor appendage of the electrophile center may operate through a cyclic array (S_Ei') leading to syn substitution. This possibility is explored in the following paper,[43] but clearly, electrophiles sterically larger than protonic acids, e.g. aldehyde–Lewis acid adducts, may lead to either syn or anti substitution, depending on the circumstance. This is now known to be the case in cyclohex-2-enyl systems.[44]

Experimental Section

The Compounds and the Reactions. The cyclohex-2-enyl derivatives of silicon, germanium, and tin employed in this study have been fully described elsewhere.[21,22]

General Procedure for Trifluoroacetolyses. (a) Chloroform or Dichloromethane as Solvent. The cyclohexenylsilane or -germane (200 mg) and 1–2 equiv of CF_3CO_2H or CF_3CO_2D were dissolved in purified chloroform (2 mL) in a Pyrex ampule under a nitrogen atmosphere. The ampule was sealed at atmospheric pressure. Reactions were conducted at 20–45 °C, but temperature variations had no effect on the results. On completion of the reaction, the chloroform solution was washed with sodium bicarbonate solution and dried ($MgSO_4$).

A noteworthy feature of these trifluoroacetolysis reactions was than when 5-methyl-2-cyclohexenyl)- and (3,5-dimethyl-2-cyclohexenyl)trimethylgermanes were treated with 2–3 equiv of trifluoroacetic acid, intense colors were formed (deep blue and deep purple, respectively) almost immediately after mixing. This coloration decreased in intensity over a few hours. A ^1H, ^2H, and ^{13}C NMR analyses of these chloroform solutions showed that in each case the expected deuteriated cyclohexene and (trimethylgermyl)trifluoroacetate were the only products present. Importantly, the stereochemical results from these reactions were identical with those obtained from reaction of the same germane mixture with only 1–2 equiv acid (in which case no colors were observed).

(b) Dioxane as Solvent. The procedure was identical with that for chloroform as solvent except that ca. 11 equiv of CF_3CO_2D was used, and, on completion of the reaction, chloroform was added and the solution washed with water and sodium bicarbonate solution.

Acidolysis of the cyclohex-2-enylstannanes was conducted by addition of CF_3COOH (or CF_3COOD, ca. 1.2 equivs) to the stannane in chloroform (sometimes in an NMR tube). Reaction was essentially instantaneous (NMR measurements) and sometimes was accompanied by the rapid precipitation of the corresponding organotin trifluoroacetate.

A detailed description of the trifluoroacetolysis of (5-methylcyclohex-2-enyl)trimethylsilane including characterization of the products is presented below.

Trifluoroacetolysis of (5-Methyl-2-cyclohexenyl)trimethylsilane. The silane (2.0 g, 11.9 mmol) and CF_3CO_2D (1.5 g, 1.0 mL, 13.1 mmol) were dissolved in purified dichloromethane (10 mL) under a nitrogen atmosphere, and the solution was stirred at room temperature. On completion of the reaction, the dichloromethane solution was washed with water and sodium bicarbonate solution and then dried ($MgSO_4$). Distillation provided 384 mg of a fraction boiling at 101 °C, which was a mixture of hexamethyldisiloxane and C_6-deuteriated 4-methylcyclohexene. The ^1H NMR signal for hexamethyldisiloxane was at δ ($CDCl_3$) −0.04 while signals for 4-methylcyclohexene were observed at δ ($CDCl_3$) 0.91 (d, J = 6.2 Hz, CH_3), 1.18 (m, 1 H), 1.62 (m, 3 H), 2.01 (m, 2 H), and 5.60 (m, 2 H, vinylic H). In a spectrum of a commercial sample of 4-methylcyclohexene (viz. nondeuteriated), the multiplet at δ 2.01 integrated for 3 H. The ^2H NMR spectrum of the mixture of C_6-deuteriated derivatives consisted of a single peak at δ 2.03. Therefore, two of the three ^1H NMR signals at δ 2.01 were assigned to the C_6 hydrogens. The complete assignment of the ^1H NMR spectrum of 4-methylcyclohexene is presented elsewhere.[24]

Bromination Reactions. (a) In the Absence of Base. Neat bromine was added dropwise to the dried chloroform solution of deuteriated 4-methylcyclohexene (see above) at 0 °C until a slight excess was present, as indicated by a pale yellow coloration. This solution was analyzed directly by ^1H, ^2H, and ^{13}C NMR. On one occasion, a sample was purified by Kugelrohr distillation (oven 110 °C (ca. 10 mm)) and a C, H analysis obtained. Anal. Calcd for $C_7{}^1H_{11}{}^2H_1Br_2$: C, 32.70; H, 5.10. Found: C, 32.94; H, 4.81.

(b) In the Presence of Base. To the dried chloroform solution of deuteriated 4-methylcyclohexene (2 mL) was added an additional 1 mL of chloroform and 1 equiv of pyridine (based on the theoretical yield of deuteriated 4-methylcyclohexene). To the cooled solution (salt/ice) was added dropwise a volume of 1.34 M solution of bromine in chloroform equivalent to a 10% excess of bromine. The solution was stirred for 5 min and then washed with sodium metabisulfite solution, 2 M HCl, and water. The dried ($MgSO_4$) chloroform solution was examined directly by ^1H, ^2H, and ^{13}C NMR.

Thermal Equilibration of Dibromides. The 86:14 diaxial/diequatorial dibromide mixtures obtained by bromination of the C_6-deuteriated 4-methylcyclohexenes in the absence of base were sealed in Pyrex ampules (neat) under nitrogen and heated at 120 °C for 5–6 h. Chloroform was added, and the solutions were analyzed directly by ^1H, ^2H, and ^{13}C NMR. Some decomposition occurred as indicated by a darkening of the samples, but the NMR signals (^1H, ^2H, and ^{13}C) for the dibromides were the only significant ones observed.[45] The equilibrated samples were shown (by ^1H and ^{13}C NMR) to be 72:28 diaxial/diequatorial dibromide mixtures. Further heating (total of ca 45 h) at 120 °C did not alter this ratio.

3,5-Dimethylcyclohexene. A mixture of 3,5-dimethylcyclohexanol (9.0 g, 10 mL, 70.2 mmol) and concentrated sulfuric acid (0.2 mL) was heated to 160–170 °C whereupon 3,5-dimethylcyclohexene and water were collected as distillate. On completion of the reaction, the crude alkene was separated from the water and dried ($CaCl_2$). Distillation afforded 3.1 g (41%) of a 76:24 cis/trans mixture of 3,5-dimethylcyclohexenes, bp 120–122 °C (760 mm) (lit.[46] bp 126–127 °C (746 mm)). Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 87.21; H, 12.83. Mass spectrum: m/e (relative intensity) 110 ($M^{\cdot+}$, 31), 95 (100), 82 (12), 81 (21), 68 (51), 67 (39), 55 (27). ^{13}C NMR ($CDCl_3$): cis isomer, δ 21.93, 22.47, 29.24, 31.63, 34.02, 41.04, 126.01, 133.42; trans isomer, δ 21.44, 21.59, 24.37, 28.56, 33.51, 37.97, 125.40, 132.69.

Catalytic Hydrogenation of 3,5-Dimethylcyclohexene. A mixture of 3,5-dimethylcyclohexene (500 mg, 4.55 mmol), methanol (4 mL), and 10% palladium on carbon (45 mg) was stirred at room temperature under 1 atm of hydrogen. On completion of the reaction, the catalyst was removed by filtration (Supercel) and the methanol solution of 1,3-dimethylcyclohexane examined directly by ^{13}C NMR. ^{13}C NMR ($CDCl_3$): cis isomer, δ 22.59, 26.68, 33.21, 35.36, 44.86; trans isomer, δ 20.35, 20.98, 27.61, 33.99, 41.50.

NMR Spectra. Deuteriochloroform was used as solvent unless stated otherwise.

^1H NMR. Spectra were recorded either at 100 MHz in the CW mode on a JEOL JNM-PS100 spectrometer or at 100, 270, or 300 MHz in the FT mode on JEOL JNM-FX100, Bruker HX-270, and Bruker CXP-300 spectrometers, respectively. Chemical shifts were referenced to either internal tetramethylsilane (TMS, 0 ppm) or residual $CHCl_3$ (7.24 ppm).

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^{13}C NMR. Spectra were recorded at 25.05 MHz on a JEOL JNM-FX100 FT spectrometer. Generally, a 5-kHz frequency width was sampled by using either 16K data points in the single-precision mode (for deuteriated solvents) or 32K data points in the double-precision mode (for dilute solutions in deuteriated solvents or for nondeuteriated solvents). A flip angle of 30° was used, with a pulse repetition time of 2.5–3 s.

The 75.46-MHz spectra were recorded on a Bruker CXP-300 spectrometer. Spectra were accumulated by using 16K data points, a frequency width of 20 kHz, a flip angle of 30°, and a pulse repetition time of 2 s.

Chemical shifts were referenced either to chloroform (when used as solvent, 77.19 ppm) or to the center peak of the deuteriochloroform (solvent) triplet (77.00 ppm).

Polarization transfer ^{13}C NMR spectra were obtained by using the INEPT pulse sequence. The delay time prior to broad-band proton decouping and data aquisition (Δ) was set at 5.7 ms ($\sim^3/_4$ J^{-1}), thus causing methylene carbon signals to be 180° out of phase relative to methyl and methine carbon signals.

^{2}H NMR. Broad-band ^{1}H-decoupled ^{2}H NMR spectra were recorded at 15.29 MHz on a JEOL JNM-FX100 spectrometer, with the field externally locked to a ^{7}Li signal. Spectra were accumulated by using 16K data points (8K zero filled), a frequency width of 1 kHz, a 70° pulse, and a pulse repetition time of 4.19 s.

The 46.05-MHz spectra were recorded on a Bruker CXP-300 spectrometer, with the field unlocked. Spectra were accumulated by using 8K data points, a 1-kHz frequency width, a 34° pulse, and a pulse repetition time of 3 s.

Chloroform was used as solvent, with deuteriochloroform added as internal standard (7.24 ppm).

^{29}Si NMR. Broad-band ^{1}H-decoupled ^{29}Si NMR spectra were recorded at 19.79 MHz on a JEOL JNM-FX100 spectrometer, using the INEPT polarization transfer pulse sequence to obtain signal enhancement. The delay time Δ was set at 18 ms ($\sim^1/_8$ J^{-1}). A total of 16K data points were used to sample a 4 kHz frequency width. Chemical shifts were referenced to internal TMS (0 ppm).

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Registry No. *cis*-IVa, 84454-68-2; *trans*-IVa, 84454-69-3; *cis*-IVb, 83269-41-4; *trans*-IVb, 83269-42-5; *cis*-IVc, 113380-70-4; *trans*-IVc, 113380-71-5; *cis*-IVd, 113380-72-6; *trans*-IVd, 113380-73-7; *cis*-IVe, 83269-44-7; *trans*-IVe, 83269-45-8; *cis*-IVf, 74089-88-6; *trans*-IVf, 74089-89-7; *cis*-IVg, 76730-06-8; *trans*-IVg, 76730-07-9; *cis*-IVh, 76730-08-0; *trans*-IVh, 76730-09-1; *cis*-IVi, 83269-39-0; *trans*-IVi, 83269-40-3; *cis*-IVj, 83269-35-6; *trans*-IVj, 83269-36-7; CF_3CO_2H, 76-05-1; CF_3CO_2D, 599-00-8; $(CH_3)_3SiOCOCF_3$, 400-53-3; $(CH_3)_3GeOCOCF_3$, 7610-08-4; $(CH_3)_3SnOCOCF_3$, 6430-48-4; 6-deuterio-4-methylcyclohexene, 113380-74-8; 6-deuterio-1,2-dibromo-4-methylcyclohexane (isomer 1), 113380-75-9; 6-deuterio-1,2-dibromo-4-methylcyclohexane (isomer 2), 113471-72-0; 6-deuterio-1,2-dibromo-4-methylcyclohexane (isomer 3), 113471-73-1; 6-deuterio-1,2-dibromo-4-methylcyclohexane (isomer 4), 113471-74-2; (5-methyl-1-cyclohexenyl)trimethylgermane, 83269-43-6; 2-deuterio-4-methylcyclohexene, 113380-76-0; 3,5-dimethylcyclohexanol, 5441-52-1; *cis*-3,5-dimethylcyclohexene, 17516-95-9; *trans*-3,5-dimethylcyclohexene, 56021-63-7; *cis*-1,3-dimethylcyclohexane, 638-04-0; *trans*-1,3-dimethylcyclohexane, 2207-03-6; *cis*-3-deuterio-3,5-dimethylcyclohexene, 113380-77-1; *trans*-3-deuterio-3,5-dimethylcyclohexene, 113380-78-2; *cis*-(*tert*-butylcyclohex-2-en-1-yl)trimethylstannane, 84537-09-7; *trans*-(5-*tert*-butylcyclohex-2-en-1-yl)trimethylstannane, 84537-11-1; *cis*-(4-*tert*-butylcyclohex-2-en-1-yl)trimethylstannane, 89633-88-5; *trans*-(4-*tert*-butylcyclohex-2-en-1-yl)trimethylstannane, 89633-89-6; *cis*-6-deuterio-4-*tert*-butylcyclohexene, 89634-16-2; *trans*-6-deuterio-4-*tert*-butylcyclohexene, 89634-15-1; *cis*-3-deuterio-4-*tert*-butylcyclohexene, 89634-17-3; *trans*-3-deuterio-4-*tert*-butylcyclohexene, 89634-18-4; *cis*-(5-*tert*-butylcyclohex-2-en-1-yl)triphenylstannane, 89634-09-3; *trans*-(5-*tert*-butylcyclohex-2-en-1-yl)triphenylstannane, 89634-10-6; *cis*-(4-*tert*-butylcyclohex-2-en-1-yl)triphenylstannane, 89634-12-8; *trans*-(4-*tert*-butylcyclohex-2-en-1-yl)triphenylstannane, 89634-11-7; *cis*-(4-*tert*-butylcyclohex-2-en-1-yl)trimethylgermane, 89634-14-0; *trans*-(4-*tert*-butylcyclohex-2-en-1-yl)trimethylgermane, 89634-13-9; *cis*-(4-*tert*-butylcyclohex-2-en-1-yl)trimethylsilane, 84280-54-6; *trans*-(4-*tert*-butylcyclohex-2-en-1-yl)trimethylsilane, 84280-58-0; *cis*-(4-methylcyclohex-2-en-1-yl)-trimethylstannane, 89633-93-2; *trans*-(4-methylcyclohex-2-en-1-yl)trimethylstannane, 89633-92-1; *cis*-(6-methylcyclohex-2-en-1-yl)trimethylstannane, 89633-95-4; *trans*-(6-methylcyclohex-2-en-1-yl)trimethylstannane, 89633-94-3; *cis*-(4-methylcyclohex-2-en-1-yl)triphenylstannane, 94017-27-3; *trans*-(4-methylcyclohex-2-en-1-yl)triphenylstannane, 94017-28-4; *cis*-(6-methylcyclohex-2-en-1-yl)triphenylstannane, 94017-29-5; *trans*-(6-methylcyclohex-2-en-1-yl)triphenylstannane, 94017-30-8; *cis*-n4-methylcyclohex-2-en-1-yl)trimethylgermane, 84454-70-6; *trans*-(4-methylcyclohex-2-en-1-yl)trimethylgermane, 84454-71-7; *cis*-3-deuterio-4-methylcyclohexene, 113380-79-3; *trans*-3-deuterio-4-methylcyclohexene, 113380-80-6; *cis*-6-deuterio-3-methylcyclohexene, 89634-20-8.