Table III. Activation Parameters for TlI_3 Complexation at 25°

	Complexation	Dissociation
k_3	$1.75 \times 10^4\ M^{-1}\ sec^{-1}$	
k_{-3}		$24\ sec^{-1}$
$\Delta G^\ddagger$	11.65 kcal mol^{-1}	15.5 kcal mol^{-1}
$\Delta H^\ddagger$	7.24 kcal mol^{-1}	4.5 kcal mol^{-1}
$\Delta S^\ddagger$	-14.8 cal $deg^{-1}\ mol^{-1}$	-30.4 cal $deg^{-1}\ mol^{-1}$

Discussion

For K^+, an ion of approximately the same size as Tl^+, the specific rate constant for the formation of the nitrilotriacetic acid complex[11] is $2 \times 10^8\ M^{-1}\ sec^{-1}$. In comparison the rate of complex formation of thallium(I) triiodide is very slow. Two possible explanations which could account for this difference are (1) substitution rates are ligand dependent, a premise which could be tested by examining a variety of ligands and (2) from thermodynamic studies Tl(I) ion is believed to bond covalently with a variety of ligands.[9,12] This latter specific interaction could conceivably be accompanied by drastic reorganization of the first coordination sphere, perhaps even a coordination number change.

The observed rate of complex formation is rapid compared to the rate of electron transfer from Tl^+ to Tl^{3+}, *e.g.*, $7.0 \times 10^{-5}\ M^{-1}\ sec^{-1}$ in 3 M $HClO_4$.[8] If electron transfer proceeds by an inner-sphere mechanism, some other step, besides substitution into the first coordination sphere of either ion, is rate determining. The solvent exchange rate[13] on Tl^{3+} is $3 \times 10^9\ sec^{-1}$.

As evidence in support of the result from the present work we would cite the somewhat tenuous comparison with the rate of oxidation of Tl^+ by bromine[14] according to the equation

$$Tl^+ + Br_2 \rightleftharpoons TlBr_2^+ \qquad (6)$$

Although nominally the addition of a bromine molecule to Tl^+, the reaction is indeed a two-electron redox reaction. If electron transfer is rapid compared to substitution, and the substitution is mechanistically similar to I_3^- substitution, the rate of reaction would be slightly less for bromine, an uncharged molecule, than it is for the univalent triiodide ion. The value reported for reaction 6 is $0.72 \times 10^4\ M^{-1}\ sec^{-1}$.

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Pulsed ^{13}C Fourier Transform Nuclear Magnetic Resonance Spectra of Monohalo-Substituted Cyclohexanes at Low Temperatures[1]

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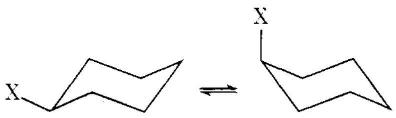
Abstract: The low-temperature pulsed ^{13}C FT nmr spectra of a series of monohalocyclohexanes have been measured. The chemical shift substituent parameters for both the isomers (*i.e.*, equatorial and axial) have been derived. The integral peak intensity data are used for the conformational energy ΔG_T determination. The energies proved to be close to those previously reported in the literature. Carbon chemical shifts at ambient temperatures are applied to determine the conformational contents by employing the substituent parameters. Various ^{13}C–^{19}F splittings have been found in the case of fluorocyclohexane, and the vicinal ^{13}C–^{19}F coupling constants have been found to be sensitive to dihedral angles. The substituents Cl, Br, I produce a strong γ effect (*ca.* 6 ppm). For fluorine, the γ effect is substantially lower (*ca.* 3.6 ppm).

Monosubstituted cyclohexanes are classical and well documented examples of conformationally flexible systems. The main interest of most studies[2] is concerned with the conformational energy at temperature T, $\Delta G°_T$ equal to $G_T(ax) - G_T(eq)$, where $G_T(ax)$ and $G_T(eq)$ are the free energies of the axial and equatorial conformers, respectively.



Previous investigations of conformational equilibria in substituted cyclohexanes used various techniques, proton magnetic resonance spectroscopy included. In particular, Jensen, *et al.*,[2c,e] found some of the conformational energies by using very careful measurements of integral intensities in the pmr spectra at low temperatures (*ca.* −90°). Two meth-

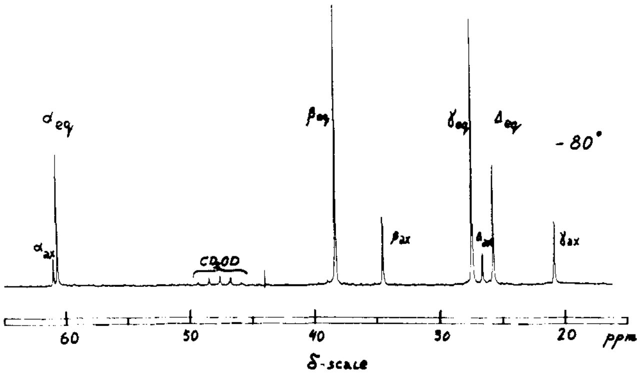


Figure 1. Pulsed ^{13}C FT nmr spectrum of chlorocyclohexane at −80°. Chemical shifts are given in parts per million in δ scale.

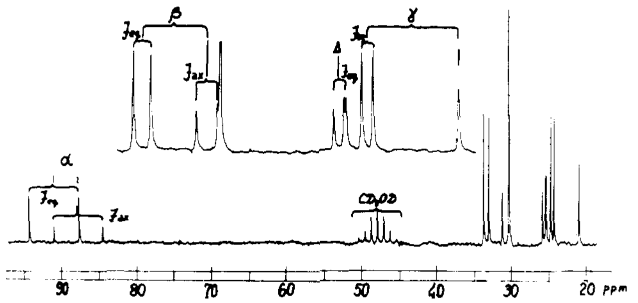


Figure 2. Pulsed ^{13}C FT nmr spectrum of fluorocyclohexane at −90° (in a mixture of methanol and acetone). Upper trace represents the high-field portion (20–35 ppm) in more detail.

ine resonances associated with both the conformers appeared in the spectra, while they were substantially spaced from other proton signals and did not overlap with one another for the substituents reported.[2c] Obviously in those cases where the methine signals noticeably overlap and/or coincide with the remaining resonances, pmr spectroscopy is inapplicable to conformational analysis. The most striking example is, perhaps, methylcyclohexane ($X = CH_3$). Its pmr spectrum is practically nonanalyzable even under the inversion averaged conditions.

Carbon-13 nuclear magnetic resonance spectroscopy is considered to be effective in this situation. ^{13}C nmr spectra recorded under complete proton decoupling conditions provide simple singlet spectra even for rather complex molecules.[3] In fact, very simple, readily interpretable spectra have been reported for some substituted cyclohexanes under both averaged[4] and stereochemically rigid conditions.[5] It is worthwhile to emphasize that usually the analysis deals[4,5] with the chemical shifts and, in particular, a so-called "γ-effect," *viz.*, an anomalous high-field displacement of the γ-carbon resonance in the axial conformer. Cheney and Grant[4b] were the first who proposed that the γ effect was due to 1,4 interactions between the axial substituent X and protons at the γ carbon. Methylated cyclohexanes are the only systems studied in this respect quite extensively;[4b,5a,b,6] however, for the simplest molecule, methylcyclohexane ($CH_3C_6H_{11}$), the carbon chemical shifts have been found only on the basis of the additivity approach. The only experimental attempt to detect the carbon resonances of the axial conformer has been made by Anet, *et al.*[5a]

The conformational energy determination for substituted cyclohexanes from the low-temperature ^{13}C nmr data has not drawn much attention. The only quantitative estimate has been performed by Schneider[5c] for trimethylsilyl cyclohexyl ether [$X = OSi(CH)_3$] (see also 5e); it seems to be very promising. One should be very careful when using the integral intensities in the ^{13}C nmr spectra, owing to the difficulties inherent in using integral peak intensities for quantitative estimates in the proton decoupled ^{13}C nmr spectra (especially if pulsed Fourier transform technique is employed).[3] However, the results of the papers[5a,c] are rather encouraging, although the accuracy reported by Schneider[5c] is, perhaps, too optimistic.[7]

In the present paper, we describe the results of a low-temperature study of ^{13}C FT nmr spectra of a series of monohalo-substituted cyclohexanes (X = F, Cl, Br, I). First, we have tried to obtain the substituent chemical shift parameters pertaining to a more general description of the γ effect, and, second, it was interesting to compare ^{13}C nmr conformational estimates with those made by proton magnetic resonance.

Experimental Section

Carbon-13 nmr spectra were measured on a Varian XL-100-15 spectrometer in pulsed FT mode using a 620/f VDM computer with 16K memory. The resonance frequency for carbon-13 nuclei was 25.16 MHz; 12-mm o.d. tubes were employed. The D heteronuclear lock and proton noise decoupling through the Gyrocode system at 100 MHz were used in the experiment. The temperature was controlled by using cooled nitrogen and measured within the accuracy of ±2°. The recalculation into a different chemical shift scale employed the following values: δ (CS_2) 192.7 and δ (C_6H_{12}) 27.5 ppm in a TMS scale.[3]

In order to obtain more reliable integral intensities,[3] we used pulse delay equal to 8–10 sec. The pulse widths of about 70 μsec were employed, corresponding to the tipping angles of about 50°. Total time of accumulation was 5–6 hr, and usually the number of transients was limited to 3–4 thousands. The limitations mentioned above made us employ concentrations of 30% (v/v) or higher. This in turn hindered low-temperature measurements as the solutes in some cases precipitated from the sample solutions.

CS_2 and methanol have proved to be the most reliable solvents for low-temperature studies. In particular, temperature as low as −80° can be obtained with CS_2 as solvent, and this was satisfactory for the measurements of iodo-, bromo-, and chlorocyclohexanes. Small additives of acetone to methanol solutions allowed us in the case of fluorocyclohexane to lower the freezing point down to −90°. It should be noted that while using even dry and degassed methanol (CD_3OH) to provide the locking signal on D nuclei, the D stabilization failed to work at as low temperatures as −80°, owing to the formation of gel-like solutions. This can be prevented to some extent through the addition of a small amount of acetone. So far, however, we could not find conditions for the normal D stabilization at a temperature as low as −100°.

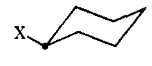
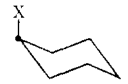
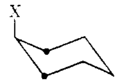
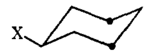
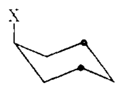
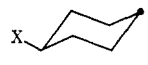
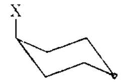
All compounds and solvents were commercial products used without purification.

Results and Discussion

A. Spectra at Low Temperatures. The ^{13}C FT nmr spectrum of chlorocyclohexane measured at −80° is presented in Figure 1. Two groups of signals are readily recognized in the spectrum, while the less intense lines belong to the carbons of the axial conformer. The assignment is based on that by Pehk and Lippmaa,[4d] given previously for the inversion-averaged spectra. Besides, use of the off-resonance technique helps to identify the methine γ carbon, and exchange broadening effects allow one to detect pairs of similar nuclei.[8] In the case of fluorocyclohexane, additional splittings due to the spin–spin coupling constants ^{13}C–^{19}F are observed (Figure 2). These splittings may be used for signal assignment as well. The chemical shift data and spin coupling constants are given in Tables I and II, respectively.

B. Exchange Effects. When the temperature is raised from −80° up, changes typical of dynamic exchange processes[8,9,5a] are observed, *viz.*, broadening, coalescence, and sharpening of the signals. Qualitative estimates of the rate constants for the ring inversion in the slow-exchange (−70°) and the fast-exchange (−10°) limits performed on

Table I. Carbon-13 Chemical Shifts in Axial and Equatorial Conformers of Monohalocyclohexanes[a]

Carbon in equatorial conformer	Substituent F	Cl	Br	I	CH_3[b]	Carbon in axial conformer
	64.38 61.12	32.80 33.12	25.13 28.35	3.64 11.30	5.90 1.40	
	5.53 2.93	10.62 6.89	11.75 7.90	13.40 9.04	9.03 5.41	
	−3.46 −7.11	−0.14 −6.61	1.35 −5.48	2.28 −4.19	0.05 −6.37	
	−2.57 −2.11	−1.81 −0.97	−1.41 −0.55	−1.67 −0.89	0.22 −0.06	

[a] Relative to cyclohexane, $\delta(C_6H_{12})$ is 27.50 ppm within the accuracy of ±0.05 ppm; for other experimental details see Table III. [b] From the calculations by Grant and Dalling.[6]

Table II. Coupling Constants J ($^{13}C-^{19}F$) in Fluorocyclohexane[a]

Carbon atom α	β	γ	δ	T, °C	Conformational state
167.0	21.5	1.0	<1	−100	Axial
172.2	17.7	11.5	2.0	−100	Equatorial
170.6[b]	19.0[b]	7.6[b]	1.5[b]	30	Inversion-averaged

[a] In hertz within the accuracy of ±0.3 Hz. [b] See also data by Pehk and Lippmaa.[4d]

the basis of the Bloch equations as modified by McConnell (two-site exchange with nonequal populations) lead to the activation energy E_{ae} of 9.5 ± 1 kcal/mol, which corresponds to transformation of the less stable axial conformer to the equatorial one.[10] This value is in accord with the value of 10.5 kcal/mol reported recently by Stokr, *et al.*,[11] in their ir study of chlorocyclohexane. It should be noted that in principle ^{13}C proton decoupled nmr spectra have some advantages over proton magnetic resonance since they allow one to avoid difficulties due to spin multiplicity effects and use more simple Bloch equations as modified by McConnell.[8,9]

C. Conformational Ratios at Low Temperatures. The integration in the FT mode permits the conformational fractions p_{eq} and p_{ax} to be established. It is well known that the integral peak intensities do not necessarily correlate with the number of carbon atoms. The deviations are due to the different spin-lattice relaxation time constants, T_1, and the different nuclear Overhauser effects. These deviations can be minimized by applying longer intervals between pulses. The pulse delay (PD) constant equal to 8-10 sec has been used by us; it is considered that PD > $T_1{}^i$ for all carbons except, probably, the α carbon. The nuclear Overhauser effects are assumed to be close to 2.99, like with pure dipole-dipole relaxation,[3] with a possible exception for the α carbon. Computer errors can be diminished by using small spectrum widths. The conformational ratios are determined as an average of all four values of $a_i = I^i{}_{eq}/I^i{}_{ax}$ where I^i is integral intensity of the ith carbon signal. For methylene carbons ($i = \beta, \gamma, \delta$) *the calculated values of* p_{eq} (Table III) do not differ much (the standard deviation is ±2%). The deviations increase (up to 5%), if α-carbon signal intensities are included. Integral intensity anomalies for the α-carbon atom have been already mentioned by Schneider.[5c] The data on the conformational contents and energies are summarized in Table III. For example, for chlorocyclohexane the fraction of the equatorial conformer turned to be equal to 0.80, which corresponds to a conformational energy $\Delta G_{193°}$ equal to 0.53 kcal/mol in excellent agreement with the data by Jensen, *et al.*[2c] For other substituents (F, Br, I), the conformational energies proved to be noticeably higher (the increment was 0.11-0.13 kcal/mol) than the "best" ΔG values reported by Jensen, *et al.*;[2c,e] a solvent effect may be the reason for this discrepancy. As far as the accuracy of ΔG_T determination is concerned, it should be mentioned that in spite of rather good reproducibility of integral peak intensities, a systematic error (up to 10% or 50 cal/mol) may interfere owing to relaxation and double resonance effects. A quantitative account for these effects needs the spin-lattice relaxation times, T_1, and nuclear Overhauser enhancements to be known. As the corresponding data are not available at present, we consider the net agreement (within ±20%) between the present and the literature data as quite satisfactory.

D. Conformational Equilibria at Ambient Temperatures through the Averaged Parameters. Conformational contents at ambient temperatures (*i.e.*, for fast ring inversion) can be found on the basis of the data on the averaged spectral parameters. If δ_{ax} and δ_{eq} are the chemical shifts for the carbon nucleus, the substituent X being in its axial and equatorial positions, respectively, then the fraction of the equatorial conformer will be determined through the relationship:

$$p_{eq} = \frac{\langle\delta\rangle - \delta_{ax}}{\delta_{eq} - \delta_{ax}}$$

where $\langle\delta\rangle$ is the averaged chemical shift. The accuracy of the conformational analysis in this case depends upon the magnitude of differences ($\delta_{ax} - \delta_{eq}$), so the estimates based on δ-carbon chemical shifts are mostly inaccurate. On the other hand, in general the approach based on chemical shift averaging requires that the temperature dependence of the chemical shift in the absence of exchange be known. Existence of such a strong temperature dependence of chemical shift, mainly due to the dependence of the averaged parameters on other equilibria which may exist in the concentrated solution (*e.g.*, association and self-association), is supported by the fact that in some cases the averaged chemical shift proved to lie beyond the limiting values δ_{ax} and δ_{eq} (*e.g.*, for α carbon in chloro- and bromocyclohexanes) (Table IV). The estimates based on the chemical shifts for β and γ carbons seem to be somewhat more realistic, but still they differ noticeably. Thus, neglect of the temperature dependence of chemical shift may lead to inaccurate (or in some cases erroneous or even meaningless) results.[12] Highly

Table III. Equilibrium Constants, K, Probabilities of the Equatorial Conformer, p_{eq}, and Conformational Energies, ΔG_T, for a Series of Monohalocyclohexanes, as Found from the Low-Temperature Pulsed ^{13}C FT Nmr Spectra

Subst	Carbon	$p_{eq}{}^a$	$K^{b,c}$	p_{eq}	ΔG_T, kcal/mol: Present study	ΔG_T, kcal/mol: Lit. data^d	Solution (present study)
F	α	75.5	2.85	0.74	0.38	0.27	$CS_2 + (CH_3)_2CO +$
	β	75.3			(183°)	(187°)	$CD_3OD + C_6H_{11}F$
	γ	73.6					(1:1:3:5)
	δ	71.2					
Cl	α	81.3	4.00	0.80	0.53	0.53	$CS_2 + C_6H_{11}Cl$
	β	80.2			(193°)	(192°)	(4:1)
	γ	80.3					CD_3OD, ext
	δ	78.4					
Br	α	80.4	4.72	0.825	0.61	0.48	$CS_2 + C_6H_{11}Br$
	β	83.1			(198°)	(192°)	(4:1)
	γ	82.7					CD_3OD, ext
	δ	83.5					
1	α	87.0	4.60	0.82	0.59	0.47	$CS_2 + C_6H_{11}I$
	β	77.8			(195°)	(193°)	(3:1)
	γ	82.1					CD_3OD, ext
	δ	79.6					

[a] $p_{eq} = a_i/(1 + a_i)$; $a_i = I_{eq}{}^i/I_{ax}{}^i$, where I^i is integral intensity of the ith carbon signal. [b] $K = p_{eq}/p_{ax}$. Experimental values of K are determined as follows: $K = {}^1/_4 \sum_{i=\alpha} a_i$. [c] For the accuracy of the determination of ΔG_T see text. [d] The "best" ΔG values are used.[2c,e]

inaccurate estimates of ΔG values at ambient temperatures prevent any reliable separation of enthalpy and entropy contributions to the conformational energy.

E. ^{13}C-^{19}F Coupling Constants. From the data on the carbon-fluorine coupling constants, one can see that the most drastic difference is observed for γ nuclei (11.5 and *ca.* 1 Hz, for equatorial and axial conformers, respectively). This difference may be attributed to the dependence of the vicinal ^3J (^{13}C-^{19}F) coupling constants upon the dihedral angle[13] formed by the planes $FC_\alpha C_\beta$ and $C_\alpha C_\beta C_\gamma$. The corresponding angles are equal to 60 and 180° for axial and equatorial conformers, respectively. Thus, if one supposes the Karplus-like equation to operate for the constant ^3J (^{13}C-^{19}F), then in fact the value of J ($\phi = 180°$) will turn to be substantially higher than the value of J ($\phi = 60°$).

F. Carbon-13 Chemical Shifts. General γ Effect. The analysis of the data (Table I) shows that there is an approximate correlation of the carbon chemical shift with the Pauling electronegativity of the halogen. It is interesting to note that while the electronegativity increases, the δ values for the α atom increase as well, and for β and γ atoms they decrease. The best correlation is observed for β carbons.

γ-Carbon chemical shifts have drawn vivid attention in the previous investigations,[4b,5a,b,6,14] especially in methylcyclohexanes. Data for methyl as substituent are also included in Table I for comparison. Note that the methyl substituent parameters have been obtained by Grant and Dalling[6] from the best-fit mean-square deviation analysis of a series of methyl-substituted cyclohexanes; however, the direct experimental evidence is still desirable. More adequate determination of the γ effect as the difference $\delta_{eq} - \delta_{ax}$ (instead of the difference $\delta_0 - \delta_{ax}$, where δ_0 is carbon chemical shift of cyclohexane) allows one to compare the effect of various substituents. From the data (Table I), one can see that γ effect is close to 6.0 ppm for all substituents, methyl group included. The only exception is fluorine for which γ effect is equal to 3.6 ppm. Thus in each case the γ carbon of the axial conformer is more shielded than that of the equatorial one. The least magnitude of the γ effect for just fluorine is not surprising as this atom has the least valence radius, thus it produces the least steric perturbations at the γ carbon. On the other hand, no clear correlations have been established with parameters specific for the group size. It is likely that starting from a minimal size, the γ effect does not increase due to some "saturation" of deformations produced by 1,4 interactions.

Table IV. Carbon-13 Chemical Shifts, $\langle\delta\rangle(^{13}C)$,[a] and Probabilities of the Equatorial Conformer Under the Inversion-Averaged Conditions (T 300°K)

Subst	Parameter	Carbon atom: α	β	γ	δ
F	$\langle\delta\rangle$	63.29	4.82	−4.76	−2.25
	p_{eq}	0.67	0.73	0.64	0.3
		±0.03	±0.03	±0.02	±0.2
Cl	$\langle\delta\rangle$	32.24	9.68	−2.09	−1.60
	p_{eq}	*b*	0.75	0.70	0.75
			±0.02	±0.01	±0.1
Br	$\langle\delta\rangle$	25.06	10.51	−1.02	−1.42
	p_{eq}	*b*	0.68	0.65	*b*
			±0.02	±0.01	
I	$\langle\delta\rangle$	4.38	12.52	0.40	−1.40
	p_{oq}	0.91	0.80	0.71	0.65
		±0.03	±0.03	±0.03	±0.1

[a] In parts per million, within the accuracy of ±0.04 ppm. [b] The condition $\delta_{eq} < \langle\delta\rangle < \delta_{ax}$ is not satisfied.

High-field displacement observed for the γ carbon can be used in order to estimate the fraction of gauche forms for acyclic compounds. For example, for 1-chloro-substituted normal alkanes, γ effect on the average is equal to 4.8 ppm (from the additivity analysis by Engelhardt, *et al.*[15]), thus indicating that the probability of the gauche form is close to $2/3$ because $\langle\delta\rangle$ is equal to 4.4 (or $2/3 \times 6.6$), as can be expected for equally populated rotational isomers.

Substituent parameters (Table I) can be also used for predicting chemical shift on the basis of the additive scheme.[16] Previously, the additivity approach has been successfully applied to methyl-substituted compounds by Grant and coworkers (see, for example ref 6) and by Schneider, *et al.*[5d] It seems to be very promising in this respect.

Conclusion

The results laid down above seem, at first, somewhat disappointing. The accuracy achieved in estimating conformational equilibrium constants through pulsed ^{13}C FT nmr techniques has turned to be worse than that of the pmr method. It should be stressed, however, that this is the case just for systems such as conformationally simple monohalocyclohexanes. As for practically important systems (*e.g.*, systems involving several equilibria), the pmr spectroscopy encounters spectra that defy any analysis and is therefore hardly applicable. On the other hand, the ^{13}C nmr technique employed under complete proton decoupling conditions produces singlets lying in a wider range of chemical shifts and may be a general-purpose approach to most conformational problems of organic chemistry. Its real accuracy (probably, not worse than 20%) is, in these cases, satisfactory for qualitative estimates.

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Silver(I)-Catalyzed Valence Isomerization of Substituted 1,8-Bishomocubanes. Stereochemical Aspects[1]

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Abstract: The preparation of the 4-methyl- and 4-acetoxymethyl-substituted *cis*-9,10-dicarbomethoxypentacyclo[$4.4.0.0^{2,5}.0^{3,8}.0^{4,7}$]decanes **10a** and **10b** was effected by acetone-sensitized photocyclization of diene anhydrides **18**, methanolysis, and esterification with diazomethane. The diene anhydrides are the sole adducts obtained upon reaction of the monosubstituted cyclooctatetraenes with maleic anhydride. These unsymmetrical bishomocubanes offer the possibility for concomitant operation of four different Ag^+-catalyzed rearrangements leading to two isomeric snoutane diesters. The distal isomer **16** is shown to be formed preferentially (82% when R = CH_3; 65% when R = CH_2OAc) in both instances. X-Ray analysis of dibrosylate **21** was utilized to establish unequivocally the structural assignment. Chemical correlation of the two major products was realized through the trimethylsnoutane **23.** Ultimate mechanistic deduction of this complicated bond reorganization must account for the stereochemical bias evidenced in this study.

Highly strained cyclobutane compounds of the 1,8-bishomocubane (**1**),[3] homocubane (**2**),[3a,c,4] cubane (**3**),[5] secocubane (**4**),[3a,6] and *syn*-tricyclooctane (**5**)[7] types are so constructed that they are capable of rapid quantitative rearrangement in the presence of transition metal catalysts.[8] The bond reorganizations are of two extreme types: (a) that promoted by Ag(I) ($4d^{10}$) and related metal ions having appreciable σ electron acceptor ability which results in thermodynamically favorable dicyclobutane–dicyclopropane bond switching; (b) that induced by transition metals such as Rh(I) ($4d^8$) with decided capacity for oxidative addition which effects cleavage of one of the four-membered rings to a diolefin. Attached ligands are known to contribute also to the course of reaction.[9] Diester **6** is a rather typical example.

1

2

3

4

5

7 **6** **8** **9**

As a consequence of the high levels of p character in the