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Studies in Organometallic Rearrangements
V. Substituent Effects on the Fluxional Rearrangements and Isomerization of Indenyl Silanes and Stannanes[a]

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The fluxional (metallotropic) rearrangements and isomerization (prototropic) reactions of a series of methyl substituted indenyl derivatives of silicon and tin have been examined. Methyl substitution at C(4) and C(7) on the six-membered ring was found to lower the activation energies for both processes whereas methyl substitution at C(2) on the five membered ring raises the activation energies, compared with the unsubstituted derivatives. The variation in free energies of activation based on substituent position occurs in a manner parallel to that predicted from consideration of the π-electron densities in the indenyl group.

Introduction

The study of fluxional rearrangements of σ-bonded cyclopentadienyl and indenyl derivatives of main-group and transition series metals has revealed considerable information about the nature of degenerate intramolecular rearrangements. Recently, attention has focused on the influence of substituents on the dynamics of the rearrangements, particularly for the substituted cyclopentadienyl derivatives of germanium[1], mercury[2], silicon[3], and tin[3]. Ring substituents of the alkyl type lead to negligible[1,3] or significant[2a] reduction of the rate of metal migration. In several cases[2a,4], substituents have been reported to cause static structures to be adopted. In no case have ring substituents lead to acceleration of the migratory rate.

In a series of papers[5–8], we have presented some aspects of the multifaceted chemistry of compounds of the type $C_9H_7MR_3$ (M = Si, Sn). The silicon compounds undergo a thermal isomerization to distribute the SiR_3 group over all three positions of the five-membered ring and the kinetic and thermodynamic parameters for the reversible isomerization processes have been reported[5]. The equilibrium distribution of isomers, but not the activation parameters for isomerization, was found to be sensitive to the nature of the substituents (R) on the silicon[6]. Anions formed by metallation of the neutral compounds display ambident behavior toward electrophiles to give kinetic products which in several cases rearrange to more thermodynamically stable isomers[7,8].

For a related series of substituted cyclopentadienyl compounds, it was found[3,9] that methyl substitution on the cyclopentadienyl ring does not significantly alter the fluxional character of the metal-to-ring bond. Because the indenyl group allows for substitution both at positions adjacent to and distant from the centers of migration, we sought to extend these studies to the fluxional behavior and thermal isomerization of a group of indenyl compounds of silicon and tin with methyl substituents on the five- and six-membered rings of the indene. We report here results which demonstrate that the rate of migration can be accelerated *or* retarded, depending on the positions of the (methyl) substituents.

Experimental

General Data

All manipulations were carried out in an atmosphere of purified nitrogen. The compounds 1-trimethylsilyl-3-methylindene[10], 2-methylindene[11], and 4,7-dimethylindene[12] were prepared as described in the literature. The infrared spectra were recorded on liquid films between NaCl plates. Nmr spectra were obtained using a Jeolco C60-HL spectrometer equipped with a variable temperature probe. Cyclohexane was used as an internal reference. High temperature spectra and kinetic studies were carried out on neat samples; those at low temperature in CS_2 solution. Mass spectra were obtained at 75 eV with a Hitachi Perkin–Elmer RMU-6E spectrometer. Elemental analysis were performed by Meade Microanalytical Laboratory, Amherst, Mass., and Galbraith Laboratories, Inc., Knoxville, Tenn. Glpc separations were obtained using a Varian Aero-

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graph 90-P3 equipped with a thermal conductivity detector. Columns packed with 3% UC-W98 on 60/80 Chromosorb W (1/4 × 60″, 1/4 × 120″), 3% SE-30 on 100/120 Varsport 30 (1/4 × 48″), or 20% SE-30 on 60/80 Chromosorb W (1/4 × 120″) were employed using helium elution. Typical separations were carried out at 125–140° C with a flow rate of 30 ml/min.

Kinetic Studies

Procedures for monitoring the kinetics of the isomerization reactions and extracting the rate constants from the data have been described elsewhere[5].

The rate constants were determined by the σ-method from a kinetic analysis treatment which allows $A_i \mp B_i \mp 100\%$ at $t = 0.0$. The derivation of the rate laws is given in reference 5 and the computer program is available from one of the authors (P.E.R.).

The free energy of activation, $\Delta G^{\ddagger}$, for the fluxional process, was evaluated from variable temperature ^{1}H-nmr data at the coalescence temperature using the equation $k = (k_BT/h)\exp(-\Delta G^{\ddagger}/RT)$ where $k = (\pi/\sqrt{2})(\Delta\nu)$ at coalescence; $\Delta\nu$ = peak separation observed at the slow-exchange limit.

For compounds IIIa and IIIb, the slow-exchange peak separation, $\Delta\nu$, was taken as the difference in chemical shift for the singlet resonances of the 4-methyl and 7-methyl groups (giving error limits for $\Delta G^{\ddagger}$ of ~0.1 kcal/mol). For compounds IIa and IIb, the coalescence of the resonances assigned to H(1) and H(3) was used. Since these signals are multiplets due to coupling with $CH_3(2)$, the estimated error in $\Delta G^{\ddagger}$ is ~0.3 kcal/mol.

Preparation of 1-Trimethylsilyl-4,7-dimethylindene (IIIa)

To a suspension of 4,7-dimethylindenyl lithium [prepared from the reaction of 4,7-dimethylindene[12] (4.99 g, 0.035 mol) and *n*-butyl lithium (16 ml, 2.34*M* in hexane) in 30 ml ether] was added dropwise with stirring a solution of trimethylchlorosilane (4.08 g, 0.038 mol) in ether (90 ml), and the mixture was stirred under reflux for 1 hour. Water (90 ml) was added, and the organic layer was separated, dried ($MgSO_4$), and concentrated by rotary evaporation at room temperature. Vacuum distillation of the crude product gave a forerun of recovered 4,7-dimethylindene and the product at 64–65° C/0.005 Torr. The yield was 0.9 g (12% based on 4,7-dimethylindene). *Anal.:* Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.31. Found: C, 77.67; H, 9.33.

The mass spectrum showed the molecular ion ($C_{14}H_{20}{}^{28}Si$) at m/e 216. Other prominent peaks appeared at m/e 201 ($C_{13}H_{17}{}^{28}Si$); 143 ($C_{11}H_{11}$); 128 ($C_{10}H_8$); 73 ($C_3H_9{}^{28}Si$).

Infrared bands were observed at 3040m, 3005m, 2955vs, 2895m, 2885m, 1535m, 1490s, 1445m (br), 1410vw, 1380m, 1265(sh), 1255vs, 1225vw, 1155vw, 1125w, 1110w, 1070m, 1035m, 1010m, 970m, 935w, 910w, 875(sh), 865s, 840vs (br), 800s, 750s, 708s, 687m (br) cm^{-1}.

The proton nmr spectrum had the following resonances: δ 0.00 (s, 9H), 2.34 (s, 3H), 2.55 (s, 3H), 3.48 (t, 1H), 6.54 (d, 1H), 6.60 (d, 1H), 7.05 (s, 2H) ppm.

Preparation of 1-Trimethylstannyl-4,7-dimethylindene (IIIb)

A suspension of 4,7-dimethylindenyl lithium, prepared from 4,7-dimethylindene[12] (7.25 g, 0.0435 mol) in hexane (40 ml) and *n*-butyllithium (30 ml), 2.34*M* in hexane) and hexane (50 ml), was treated with trimethyltin chloride (8.67 g, 0.0435 mol) in hexane (50 ml) and the resulting mixture was stirred at reflux for 4 hours. The suspension was filtered under N_2 to remove the LiCl and the hexane was removed under reduced pressure at room temperature. The product, a colorless moisture-sensitive liquid was obtained by distillation at 110–112° C/0.25 Torr. The yield was 4.7 g (35% based on 4,7-dimethylindene). *Anal.:* Calcd for $C_{14}H_{20}Sn$: C, 54.78; H, 6.57. Found: C, 54.55, H, 6.72.

Infrared bands were observed at 3048w, 3025(sh), 2970m, 2920s, 2860m, 1840w, 1695w, 1610w, 1525w, 1485s, 1455m, 1380m, 1262(sh), 1257w, 1239w, 1187w, 1154w, 1103w, 1057s, 987w, 952m, 917s, 848w, 807s, 792s, 777s, 720 cm^{-1}.

The proton nmr spectrum (neat, room temperature) had the following resonances: δ –0.02 (s, 9H), $J_{117,\,119_{Sn-CH_3}}$ = 51, 54 Hz); 2.38 (s, 6H); 6.72 (t, 1H; J = 3.0 Hz); 7.0 (m, 3H) ppm.

Preparation of 1-Trimethylsilyl-2-methylindene (IIa)

The compound $(CH_3)_3SiC_9H_6(CH_3)$ was prepared by a procedure analogous to that described above for IIIa, from 2-methylindene[11]. The product, a clear liquid, was obtained in 60% yield (based on 2-methylindene) by vacuum distillation at 64–65° C/0.5 Torr. *Anal.* Calcd for $C_{13}H_{18}Si$: C, 77.15; H, 8.96. Found: C, 77.46; H, 9.30.

Infrared bands were observed at 3048m, 3010m, 3950s, 290m, 2860(sh), 1593m, 1460s, 1450(sh), 1440(sh), 1410w, 1380w, 1299m, 1268m, 1258vs, 1222m, 1192m, 1050s, 1011s, 930w, 915m, 883(sh), 838vs(br), 774m, 753vs, 735m, 700s, 680 cm^{-1}.

The mass spectrum showed the molecular ion ($C_{13}H_{18}{}^{28}Si$) at m/e 202. Other prominent peaks appeared at m/e 187 ($C_{12}H_{15}{}^{28}Si$); 129 ($C_{10}H_9$); 73 ($C_3H_9{}^{28}Si$); 59 ($C_2H_7{}^{28}Si$).

The proton nmr spectrum (CCl_4) had the following resonances: δ –0.09 (s, 9H); 2.17 (double doublet, 3H, J = 1.5 Hz, J = 0.6 Hz); 3.22 (m, 1H); 6.56 (m, 1H); 7.2 (m, 4H) ppm.

Preparation of 1-Trimethylstannyl-2-methylindene (IIb)

The compound $(CH_3)_3SnC_9H_6CH_3$ was prepared from 2-methylindene[11] by a procedure analogous to that given above for IIIb. Pure samples for analysis and nmr measurements were obtained by glpc (3% SE-30 on Varsport 30 column) at 120° C, retention time 16.3 min at 30 ml/min. *Anal.* Calcd for $C_{13}H_{18}Sn$: C, 53.29; H, 6.19. Found: C, 53.38, H, 6.31.

The mass spectrum showed the molecular ion ($C_{13}H_{18}{}^{120}Sn$) at m/e 294 (isotope peaks 292, 290 for ^{118}Sn and ^{116}Sn, respectively, intensity ratio 1:0.75: 0.44). Other prominent peaks appeared at m/e 279 (277, 275), $C_{12}H_{15}Sn$; 249 (247, 245), $C_{10}H_9Sn$; 165 (163, 161), $Sn(CH_3)_3$; 129, $C_{10}H_9$; 128, $C_{10}H_8$.

The proton nmr spectrum (CS_2) displayed the following resonances: 0.02 (S, 9H, $J_{117,119Sn-CH_3}$ = 50.1, 51.9 Hz), 2.14 (s, 3H, $J_{117,119Sn-CH_3(2)}$ = 6.6 Hz), 3.72 (s, 1H, $J_{117,119Sn-H(1)}$ = 87 Hz), 6.39 (s, 1H), $J_{117,119Sn-H(3)}$ = 15 Hz), ~7.1 (m, 4H) ppm.

Preparation of 2-Trimethylsilyl-4,7-dimethylindene (VII)

Thermolysis of a pure sample of 1-trimethylsilyl-4,7-dimethylindene (IIIa) in a sealed tube at 180° C for 2 hours resulted in an equilibrium mixture of 85% (VII) and 15% (IIIa). The isomers were separated by glpc (3% UC-W98 on 60/80 Chromosorb W column) at 150° C and 30 ml/min. *Anal. Calcd for* $C_{14}H_{20}Si$: C, 77.71; H, 9.31. Found: C, 77.89; H, 9.42.

Infrared bands were observed at 3040(m), 3005(m), 2955(s), 2920(vs), 2895(m), 2885(m), 1600(w), 1545(s), 1490(s), 1445(m,br), 1390(m), 1380(m), 1265(sh), 1255(vs), 1070(s), 1040(s), 1020(sh), 910(m), 875(vs), 850(sh), 840(vs,br), 801(s), 750(s), 730(m), 710(w), 685(w) cm^{-1}.

The proton nmr spectrum had the following resonances (δ): 0.33 (s, 9H); 2.43 (s, 3H); 2.53 (s, 3H); 3.38 (d, 2H, J = 2.0 Hz); 7.05 (2H); 7.35 (t, 1H, J = 2.0 Hz) ppm.

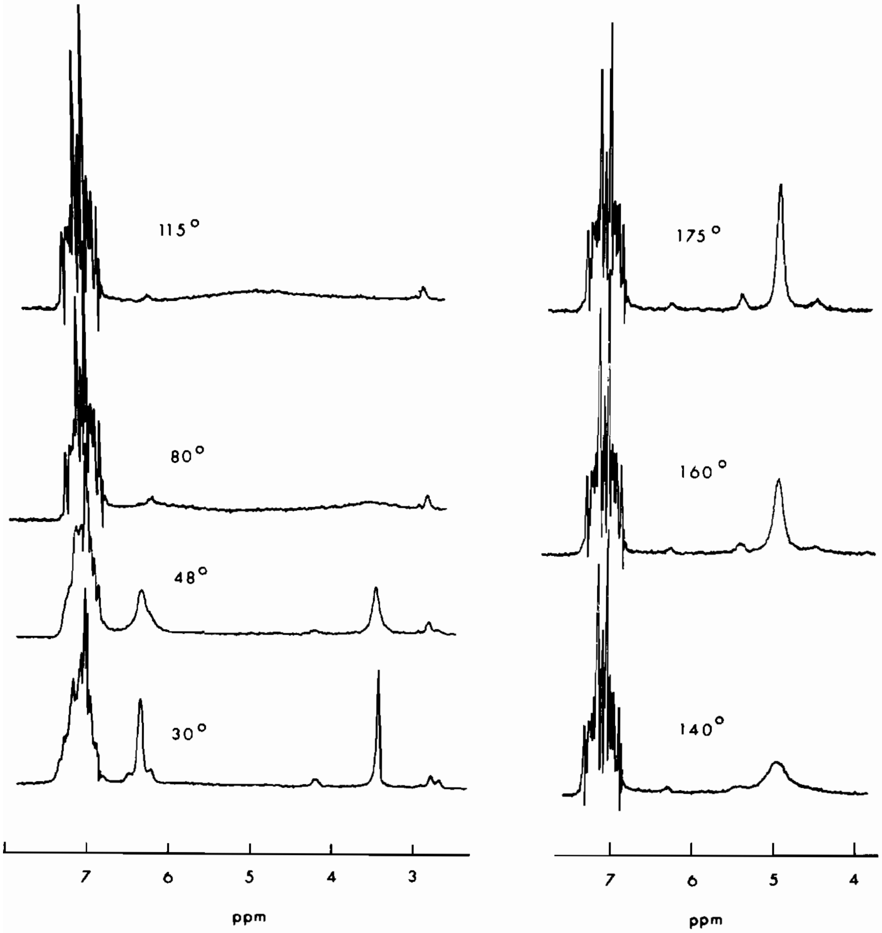


Figure 1. Variable temperature proton nmr spectrum of 1-trimethylstannyl-2-methylindene at 60 MHz, in the region δ 3–7 ppm, at temperatures 30° to 175° C.

Preparation of 3-Trimethylsilyl-2-methylindene (VI)

Thermolysis of a pure sample of 1-trimethylsilyl-2-methylindene (IIa) at 200° C for 24 hours resulted in an equilibrium mixture of 9% (VI) and 91% (IIa). This minor component of the equilibrium mixture was not isolated, but was identified by its characteristic proton nmr spectrum (δ): 0.36 (s, 9H), 2.17 (t, 3H), 3.17 (m, 2H), 7.2 (m, 4H) ppm.

Results

Variable Temperature NMR Studies

The proton nmr spectra of IIb in the region δ 3–7 over the temperature range 30°–175° C are presented in Figure 1. At room temperature the compound displays a slow-exchange spectrum with resonances at 7.1 (4H); 6.39 (1H, $J_{Sn^{117,119}-H} = 15$ Hz); 3.72 (1H, $J_{Sn^{117,119}-H} = 87$ Hz); 2.14 (3H, $J_{Sn^{117,119}-H} = 6.6$ Hz); and 0.02 ppm (9H, $J_{Sn^{117,119}-H} = 50.1, 51.9$ Hz) assigned to the aromatic, H(3), H(1), CH_3(2), and $Sn(CH_3)_3$ protons, respectively. As the temperature is increased, the resonances at 6.39 and at 3.72, together with the respective tin satellites, broaden and collapse into the baseline at about 110° C. Additional changes occur in the aromatic and methyl resonances, the latter going from an unsymmetrical three line pattern to a symmetrical triplet. Above 115° C a new resonance appears at 4.97, at the average position of H(1) and H(3) and assigned to the coalesced resonances, which sharpens with increasing temperature. Tin-117,119 satellite resonances are observed for this signal with $J_{117,119} = 56$ Hz.

The corresponding silicon compound, IIa, exhibits the onset of fluxional behavior at a temperature about 180° C higher than that observed for the tin compound. As a consequence only broadening of the resonances assigned to H(1) and H(3) occurred below 200° C. Changes in the CH_3(2) resonance (Figure 2) clearly demonstrate the onset of fluxional behavior. The patpatern changes from a pair of doublets ($J_{H(1)-CH_3} = 0.6$ Hz, $J_{H(3)-CH_3} = 1.5$ Hz) to a symmetrical triplet ($J_{ave\ H(1)+H(3)-CH_3} = 1.05$ Hz).

For compound IIIb the slow exchange spectrum is observed below about –70° C (Figure 3). The spectrum consists of resonances at 6.9 (2H), 6.78 (1H), 6.58 (1H), 4.01 (1H, $J_{Sn^{117,119}-H} = 92$ Hz), 2.31 and 2.45 (6H), and –0.02 (9H, $J_{Sn^{117,119}-H} = 51, 54$ Hz), assigned to H(5) and H(6), H(3), H(2), H(1), CH_3 (4 and 7), and $Sn(CH_3)_3$, respectively. As the temperature is increased, the methyl resonances CH_3(4) and CH_3(7) broaden and coalesce at –15° C (Figure 4). The signals assigned to H(1) and H(3) broaden and disappear (Figure 3) at +4° C while the resonance for H(2) becomes a symmetrical triplet, J = 4 Hz. Above 40° C (Figure 5) a new signal appears at 5.43 with

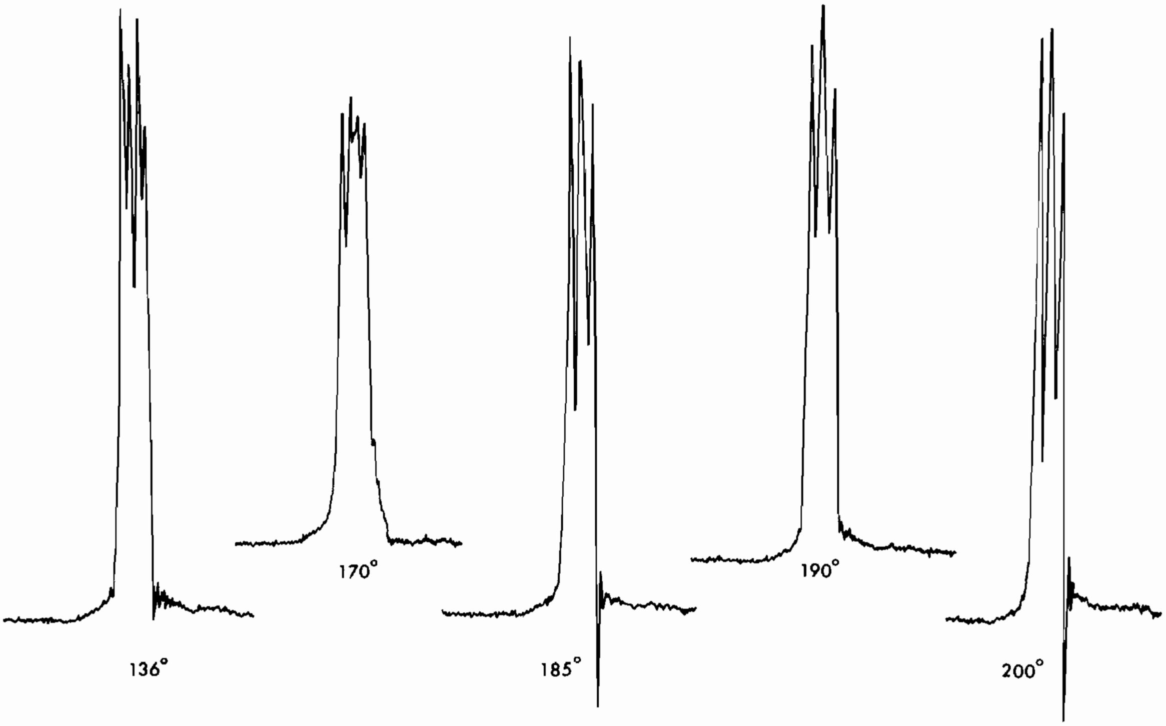


Figure 2. Variable temperature proton nmr spectrum of the 2-methyl peak, δ 2.17 ppm, of 1-trimethylsilyl-2-methylindene at temperatures 136° to 200° C.

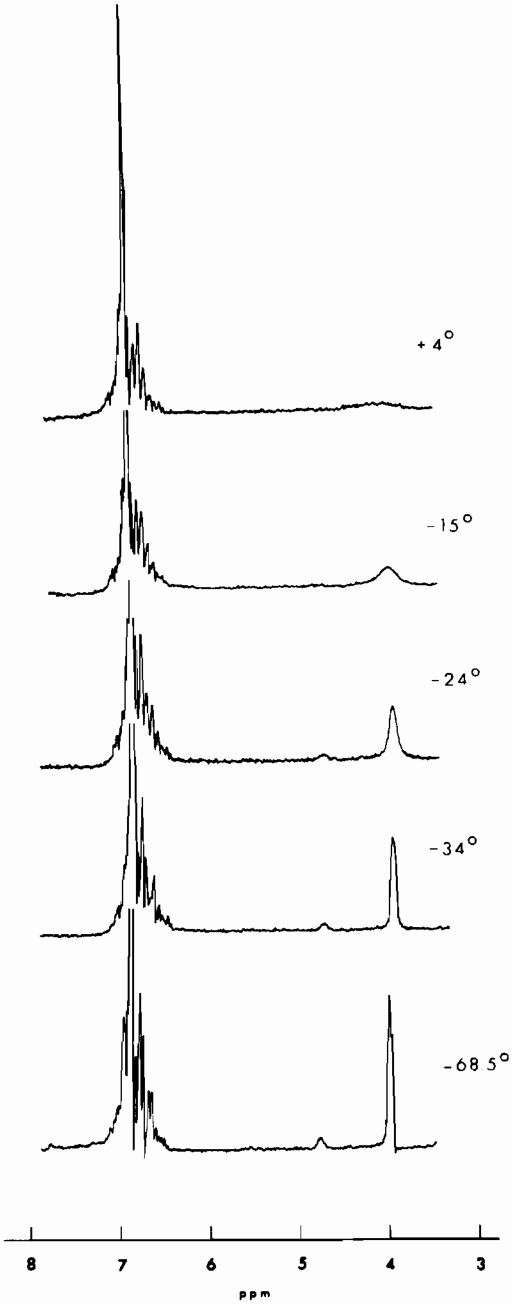


Figure 3. Variable temperature proton nmr of 1-trimethylstannyl-4,7-dimethylindene at 60 MHz in the region δ 3–8 ppm, at temperatures −68.5° to 4° C.

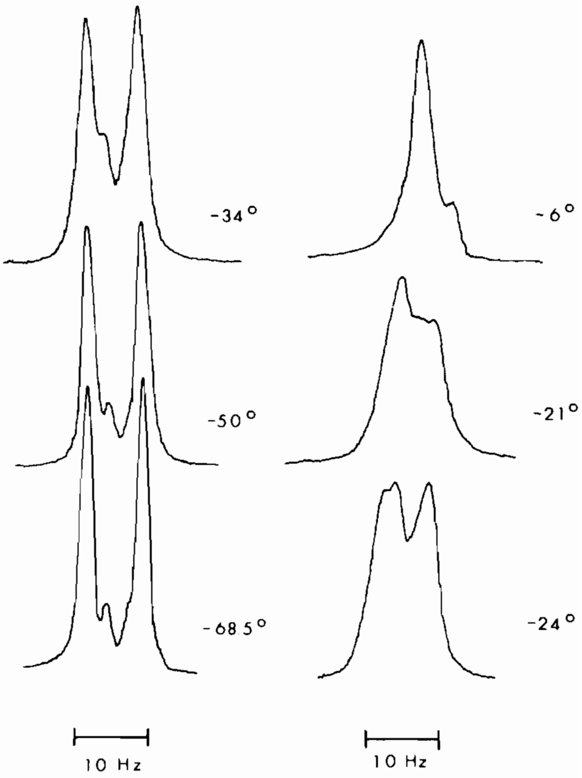


Figure 4. Variable temperature proton nmr of the 4,7-dimethyl region, δ 2.38 (expanded × 1/5) of 1-trimethylstannyl-4,7-dimethylindene at temperatures −68.5° to −6° C.

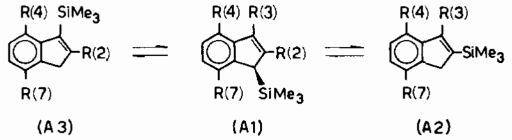
tin satellites ($J_{Sn^{117,119}-H}$ = 56 Hz) and at the fast exchange limit (about 115° C) is a doublet (J = 4 Hz) of relative area 2 assigned to the averaged resonances of H(1) and H(3).

Comparable changes occur in the spectrum of IIIa. The coalescence of the $CH_3(4)$ and $CH_3(7)$ signals occurs at 125° C and broadening of the H(1) and H(3) resonances is observed above 150° C. Above 180° C compound IIIa undergoes a rapid isomerization to 2-trimethylsilyl-4,7-dimethylindene.

Isomerization Reactions

The kinetics of the thermal isomerization reactions of compounds IIa, IIIa, and IV were studied at several temperatures in the range 140°–200° C. The results are summarized in the scheme.

SCHEME



Compound	R(2)	R(3)	R(4)	R(7)
II a	CH_3	H	H	H
IIIa	H	H	CH_3	CH_3
IV	H	CH_3	H	H

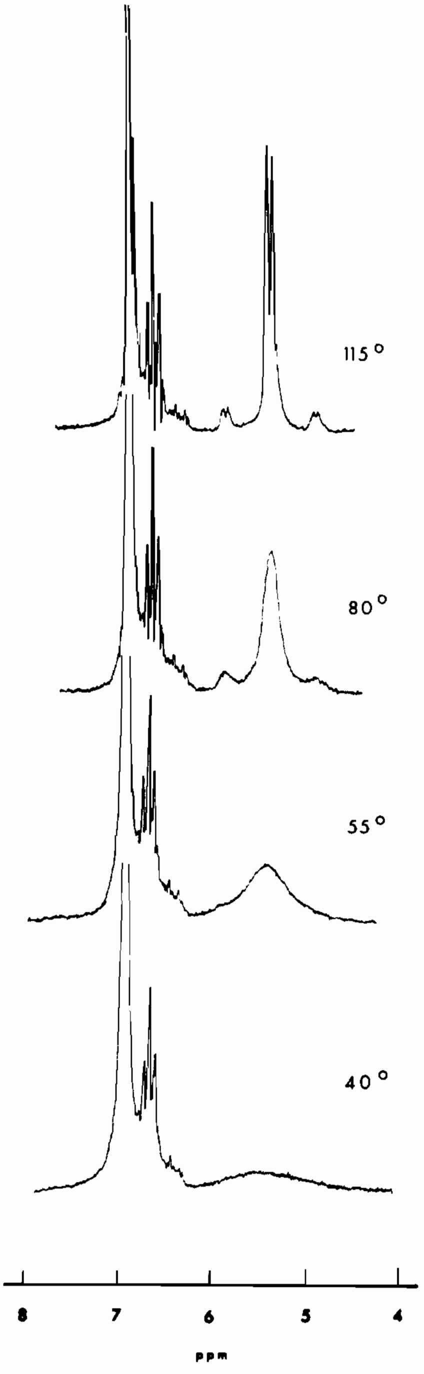


Figure 5. Variable temperature proton nmr of 1-trimethylstannyl-4,7-dimethylindene at 60 MHz in the region δ 4–8, at temperatures 40° to 115° C.

The thermal isomerization reactions of each of these compounds were observed to proceed *via* only one of the two available pathways (*viz.* A3 ⇆ A1 or A1 ⇆ A2). Thus, these reactions unlike those described previously[5,6], could be studied as reversible, first-order, two-component systems. The analogous stannyl compounds displayed no isomerization under these conditions. The rate of isomerization was found to be temperature dependent, but the equilibrium distribution of the isomers is essentially independent of temperature in the range studied, as observed for the unsubstituted silylindenes[6]. For compounds IIa, IIIa, and IV, no isomerization of the 1-isomer was observed over a period of five hours at temperature below 140° C. A typical set of data is presented in Table I and Figure 5. The temperature range in which these reactions could be conveniently studied varied with respect to the position of the substituent on the indene ring. The equilibrium between the compounds (IIa ⇆ VI) and (IV ⇆ V) could be conveniently studied in the temperature range 150°–200° C. Compound IIa, however, was rapidly isomerized above to 180° C to compound

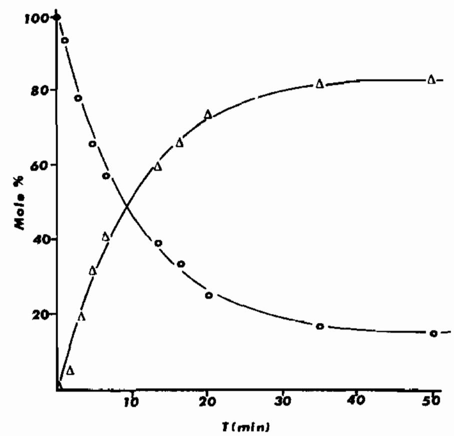


Figure 6. Thermolysis of 1-trimethylsilyl-4,7-dimethylindene at 182° C. Points are experimental values for A_1 (o), A_2 (Δ). Solid curves have been calculated using the "best" rate constants derived by the σ-method.

TABLE I. Experimental and Calculated Concentrations for the Isomerization of 1-Trimethylsilyl-4,7-dimethylindene at 184° C.

t (min)	IIIa		VII	
0.0	100.00[a]	(100.00)[b]	0.00	(0.00)
1.0	94.60	(92.41)	5.94	(7.59)
3.0	79.26	(79.15)	20.74	(20.85)
5.0	67.52	(68.09)	32.48	(31.91)
7.0	58.06	(58.86)	41.94	(41.14)
13.5	38.94	(38.18)	61.06	(61.82)
16.0	33.23	(32.95)	66.77	(67.05)
20.0	26.35	(26.70)	73.65	(73.30)
35.0	16.07	(16.07)	83.93	(83.93)

[a] Concentrations expressed as percentages of the total isomeric mixture. [b] Calculated values in parenthesis. Rms $\sigma = 0.7$.

TABLE II. Rate Constants for the Thermolysis of Group IVA Substituted Indenes.

Compound	Temp (° C)	k_{12}[a]	k_{21}	RMS σ[b]
IIa ⇌ VI	200	$1.0 \pm 0.2 \times 10^{-5}$	$1.0 \pm 0.2 \times 10^{-4}$	0.14
	175	$1.0 \pm 0.2 \times 10^{-6}$	$1.1 \pm 0.2 \times 10^{-5}$	0.70
	150	$1.0 \pm 0.2 \times 10^{-7}$	$1.1 \pm 0.2 \times 10^{-6}$	0.80
IV ⇌ V	200	$2.9 \pm 0.6 \times 10^{-5}$	$1.5 \pm 0.3 \times 10^{-4}$	0.5
	175	$2.5 \pm 0.5 \times 10^{-6}$	$1.3 \pm 0.2 \times 10^{-5}$	0.4
	150	$2.5 \pm 0.5 \times 10^{-7}$	$1.3 \pm 0.2 \times 10^{-6}$	0.9
IIIa ⇌ VII	182	$1.3 \pm 0.2 \times 10^{-3}$	$1.9 \pm 0.4 \times 10^{-4}$	0.7
	169	$4.4 \pm 0.8 \times 10^{-4}$	$9.1 \pm 1.8 \times 10^{-5}$	0.8
	156	$1.4 \pm 0.2 \times 10^{-4}$	$2.2 \pm 0.4 \times 10^{-5}$	0.4
	142	$4.1 \pm 0.8 \times 10^{-5}$	$8.2 \pm 1.6 \times 10^{-6}$	1.0

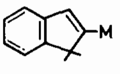
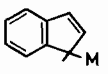
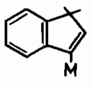
[a] Rate constants in $\sec^{-1}$. [b] RMS deviation per data point, $[(\sigma/3N)^{1/2}]$.

TABLE III. Thermodynamic Differences between the Positional Isomers of the Silyl Substituted Indenes.

Compound	ΔH[a] (kcal/mol)	ΔS (eu)
IIa ⇌ VI	$+0.4 \pm 0.04$	-2.4 ± 0.2
IV ⇌ V	$+0.5 \pm 0.05$	-2.0 ± 0.2
IIIa ⇌ VII	-0.6 ± 0.06	$+1.4 \pm 0.2$

[a] $\Delta H = \Delta H°_f$(1-isomer) $- \Delta H°_f$(2-isomer). $\Delta S = \Delta S°$(1-isomer) $- \Delta S°$(2-isomer).

TABLE IV. Equilibrium Distribution of Isomers for the Silyl Substituted Indenes.

Compound			
2-Methylindene	×[a]	91[b]	9
3-Methylindene	16	84	×
4,7-Dimethylindene	85	15	×

[a] × = none observed; est. < 2 mol%. [b] Mol%; all values are ± 2 mol %.

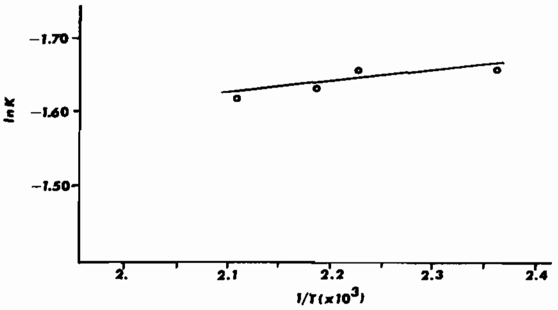


Figure 7. Variation in the equilibrium constant K with temperature for the equilibrium IV ⇆ V.

VII, and was therefore studied in the range 140°–180° C. The rate constants for these rearrangements are presented in Table II.

From plots of $\ln K_{eq}$ *vs.* 1/T (° K), the parameters ΔH and ΔS were determined (Table III and Figure 7). The variation in isomeric distribution at equilibrium as a function of the substituents on the indene skeleton is given in Table IV.

Activation Energies

From plots of ln*k* *vs.* 1/T(° K) the activation parameters for isomerization were obtained (Table V).

From Table V, we observe that substitution of a CH_3 group at the C(2) and C(3) positions of the five membered ring raises the free energy of activation, whereas substitution at C(4,7) of the six membered ring lowers the free energy of activation.

Although the stannyl compounds did not display an isomerization reaction, even though they were stable for up to 3 hours at 180° C, the fluxional process for these compounds was examined.

The free energies of activation for the metallotropic rearrangements are presented in Table VI. The same trend in activation parameters based on substituents is observed for the fluxional process (metallotropic rearrangement) as for the prototropic migration (isomerization). Furthermore, the magnitude of the variation in activation energy, based on substituent position, agrees very well between the two types of rearrangements.

Discussion

The variation in the activation energy for the fluxional (metallotropic) process for the silicon and tin derivatives of methyl substituted indenes is given in Table VI. For the silicon compounds the values range from 21.8 kcal/mol (IIIa) to 23.8 kcal/mol (Ia) to

TABLE V. Activation Parameters for the Thermolysis of Group IVA Substituted Indenes.

Compound	Reaction	E_a (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)[a]	$\Delta S^{\ddagger}$ (eu)[b]	$\Delta G^{\ddagger}$ (kcal/mol)[c]
IIa $\rightleftharpoons$ VI	$A_1 \rightarrow A_3$	36.7	35.8 ± 4	–7.0 ± 8	39.0 ± 0.2
	$A_1 \leftarrow A_3$	36.2	35.3 ± 4	–3.4 ± 8	36.8 ± 0.2
IV $\rightleftharpoons$ V	$A_1 \rightarrow A_2$	37.7	36.8 ± 4	–2.8 ± 8	38.1 ± 0.2
	$A_1 \leftarrow A_2$	37.5	36.6 ± 4	0.0 ± 8	36.6 ± 0.2
IIIa $\rightleftharpoons$ VII	$A_1 \rightarrow A_2$	32.7	31.8 ± 4	–3.0 ± 8	33.2 ± 0.2
	$A_1 \leftarrow A_2$	30.5	29.6 ± 4	–11.0 ± 8	34.4 ± 0.2

[a] $\Delta H^{\ddagger} = E_a - RT$ (at 200° C or 182° C). [b] $\Delta S^{\ddagger} = R\ln(k_ih/kT) + (E_a - RT)/T$. [c] $\Delta G^{\ddagger} = -RT\ln(k_ih/kT)$.

TABLE VI. Activation Parameters for the Fluxional Rearrangements of Substituted Indenyl Silanes and Stannanes.

Compound	IIa[b]	IIb	IIIa[c]	IIIb	Ia[b,d]	Ib
$\Delta G^{\ddagger}$[a], kcal/mol	26.5	18.6	21.8	14.0	23.8	15.0

[a] Evaluated at the coalescence temperature from the equation $k = (k_BT/h)\exp(-\Delta G^{\ddagger}/RT)$ where $k = (\pi/\sqrt{2}\,\Delta\nu)$ at the coalescence, $\Delta\nu$ = peak separation observed at slow-exchange limit. [b] $\Delta\nu$ evaluated from H(1) and H(3); error limits ~0.3 kcal/mol. [c] $\Delta\nu$ evaluated from $CH_3(4)$ and $CH_3(7)$; error limits ~0.1 kcal/mol. [d] Data for Ia and Ib from reference 16.

26.5 kcal/mol (IIa), whereas for the tin derivatives the values are 14.0, 15.0, and 18.6 kcal/mol for (IIIb), (Ib), and (IIb). It is noteworthy that variation of the position of the methyl substituent(s) alters the $\Delta G^{\ddagger}$ for both the silyl and stannyl migration by approximately 4.5 kcal/mol, and in a manner parallel to that predicted from consideration of the π-electron densities in the indenyl moiety (*vide infra*).

The isomerization of group IVa substituted indenes proceeds *via* a series of 1,2-hydrogen and silicon shifts depicted in the Scheme. By this mechanism the formation of the 2-trimethylsilyl isomer requires an initial silyl group migration followed by a hydrogen migration. The formation of the 3-trimethylsilyl isomer requires two consecutive 1,2-hydrogen shifts. The rates reported here are comparable in magnitude to those observed for the isomerization *via* 1,2-hydrogen shifts in monosubstituted organic and silyl indenes.[6, 13]

In contrast to the mono-substituted silylindenes described in reference 6 which showed very little change in the free energy of activation for the forward and reverse pathways, the ring-substituted group IVa indenes display sizable differences in the free energy of activation between the two pathways. The magnitude is dependent upon the positions of the substituent(s) on the indene skeleton. The free energies of activation for the 1-trimethylsilyl-3-methylindene (IV) $\leftrightarrows$ 2-trimethylsilyl-3-methylindene (V) are $\Delta G^{\ddagger}$ = 38.1 ± 0.2 kcal/mol and $\Delta G^{\ddagger}$ = 36.6 ± 0.2 kcal/mol, respectively. For the 1-trimethylsilyl-2-methylindene (IIa) $\leftrightarrows$ 3-trimethylsilyl-2-methylindene (VI) we observed a free energy of activation $\Delta G^{\ddagger}$ = 39.0 ± 0.2 kcal/mol and $\Delta G^{\ddagger}$ = 36.8 ± 0.2 kcal/mol, respectively. Substitution onto the six membered ring results in a lowering of the free energy of activation ($\Delta G^{\ddagger}$ = 33.3 ± 0.2 kcal/mol and $\Delta G^{\ddagger}$ = 34.4 ± 0.2 kcal/mol) for the equilibrium between the compounds IIIa $\rightleftharpoons$ VII, respectively. The large negative entropies observed in several of the silyl-substituted indenes[6] were not observed for these reactions.

From the relatively low activation energies for the migration and the demonstrated intramolecularity of the reactions, it has been proposed that the rearrangement proceeds through transition states and/or intermediates which involve little if any charge separation during the migration process.[14] The transition state for rearrangement can be pictured as consisting of an indenyl radical and a radical formed from the migrating group M. Although a detailed MO calculation of both the ground state and the transition state would be necessary to accurately evaluate the effects on the energetics of the transition state of substitution onto the various sites on the indene ring, we can estimate the direction and approximate magnitude of the changes using very crude assumptions.[15] Examination of the normalized-electron populations for the indenyl radical, obtained from Hückel MO-calculations, reveals that the smallest π-electron density occurs at C(4) and C(7), while the largest electron density occurs at C(2), C(5) and C(6). Thus, substitution of electron-donating methyl groups at C(4) and C(7) might be expected to stabilize the transition state or intermediate for rearrangement (as 1,4-dimethyl substitution on a butadiene group), whereas substitution at C(2), C(5) and C(6) would be expected to destabilize the transition state or intermediate relative to the unsubstituted compounds. This is in agreement with our results. It should be stressed that this method is insufficient to explain the exact *magnitudes* of the differences in the ΔG^{+} values obtained for the various reactions, but does correctly predict the *relative order*. In addition, steric effects must be included, although their exact importance is hard to ascertain. We have observed[6] a ratio of 30:55:15 for the isomeric distribution of trimethylsilylindene and 34:28:28 for diphenylmethylsilylindene (2-isomer, 1-isomer, 3-isomer, respectively). This suggests that the steric interaction between the silyl group at the 3-position and H(4) is not large. However, the rearrangement of 1-trimethylsilyl-1-methylindene $\leftrightarrows$ 1-trimethylsilyl-3-methylindene *via* a silyl group migration demonstrates clearly that the effect of a methyl group on the carbon to which the silyl group is attached is significant. In fact, we observe[7] a lowering of the free energy of activation for the silyl group migration in this compound of about 5 kcal/mol.

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