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STUDIES IN ORGANOMETALLIC REARRANGEMENTS

II. KINETICS OF THE THERMAL ISOMERIZATION OF SUBSTITUTED SILYL INDENES

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SUMMARY

The reversible thermal isomerization of the positional isomers of several substituted silyl indenes [$C_9H_7SiR_3$; $R_3 = (CH_3)_2C_6H_5$, $(CH_3)_2(OCH_3)$, $(CH_3)_2(CH_2Cl)$, $CH_3(C_6H_5)_2$, $(C_6H_5)_3$] has been studied. Rate constants, equilibrium constants, and activation parameters for the forward and reverse reactions are reported. The equilibrium distribution of isomers, but not the activation parameters, is found to be sensitive to the nature of the substituents on the silicon. The thermal behavior of 1-(trimethylstannyl)indene is also reported.

INTRODUCTION

In a previous paper[1] we reported the kinetic and thermodynamic parameters for the thermal isomerization of (trimethylsilyl)indene. It was shown that at equilibrium the trimethylsilyl group is distributed over all three positions of the five membered ring and that the equilibrium concentrations are remarkably insensitive to temperature, by contrast with analogous (trimethylsilyl)cyclopentadienes[2]. Unusually large negative entropies of activation were obtained for the rearrangement of 1-(trimethylsilyl)indene to the 3-isomer. We have therefore studied the thermal isomerization of a series of substituted 1-silylindenes to ascertain the factors which govern the shape of the reaction profile and the energetics of the rearrangement process. We report here the results for the derivatives substituted at the silicon atom. For comparison, we have also studied the thermal reactions of 1-(trimethylstannyl)indene at 140°, 150°, and 175°.

EXPERIMENTAL

General data

All manipulations were carried out in an atmosphere of purified nitrogen.

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The compounds 1-(dimethylphenylsilyl)indene[3], 1-(trimethylstannyl)indene[4] and 1-(triphenylsilyl)indene[5] were prepared as described in the literature. Infrared spectra were recorded on liquid films or KBr pellets using a Perkin–Elmer 257 spectrophotometer. NMR spectra were obtained using a Jeolco C60-HL spectrometer. Cyclohexane was used as an internal reference. Mass spectra were obtained at 75 eV with a Hitachi–Perkin–Elmer RMU-6E spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Gas chromatographic separations and purifications were carried out using a Varian Aerograph Model 90-P3 chromatograph equipped with a thermal conductivity detector. Columns (1/4" × 60" and 1/4" × 120") packed with 15% SE-30 on Chromosorb W were employed using helium elution. Typical separations were carried out at 125° and a flow rate of 30 ml/min.

1-(*Diphenylmethylsilyl*)*indene*

The compound $(C_6H_5)_2CH_3SiC_9H_7$ was prepared by the general procedure described earlier[3] from indenyllithium and chlorodiphenylmethylsilane. The product was obtained as an off-white powder, which was recrystallized from n-hexane to give colorless crystals. m.p. 96–98°. (Found: C, 84.35; H, 6.48. $C_{22}H_{20}Si$ calcd.: C, 84.56,; H, 6.45%.)

Infrared bands (cm^{-1}) were observed at 3030 s, 3025 (sh), 3101 m, 1655 w, 1610 vw, 1581 m, 1560 w, 1540 (sh), 1500 vw, 1485 m, 1450 vw, 1423 s, 1380 w, 1330 w, 1305 w, 1260 w, 1185 w, 1155 (sh), 1120 vs, 1070 m, 1025 m, 1000 s, 918 w, 850 vs(br), 832 vs, 791 (sh), 765 (sh), 732 s, 675 vs(br).

The mass spectrum showed the molecular ion ($C_{22}H_{20}{}^{28}Si$) at *m/e* 312. Other prominent peaks appeared at *m/e* 297 ($C_{21}H_{17}{}^{28}Si$), 197 ($C_{13}H_{13}{}^{28}Si$), 182 ($C_{12}H_{10}$-${}^{28}Si$), 115 (C_9H_7), 105 ($C_6H_5{}^{28}Si$), 43 ($CH_3{}^{28}Si$).

The PMR spectrum (CS_2 solution) had the following resonances: τ 2.65 (multiplet); 3.10 (complex multiplet); 3.44 (double doublet, B portion of ABX pattern, 1H, J_{AB} 5.4, J_{BX} 1.8 Hz); 6.02 (triplet, X portion of ABX pattern, 1H, $J_{AX} \approx J_{BX}$ 1.5 Hz); 9.88 ppm (singlet, 3H).

1-(*Dimethylchloromethylsilyl*)*indene*

The compound $(CH_3)_2(CH_2Cl)SiC_9H_7$ was prepared in the same manner as above using chlorodimethyl(chloromethyl)silane. The crude product was stripped of solvent leaving an oily residue, which was purified by vacuum distillation. The product was collected at 85–87°/0.05 mmHg as a clear colorless liquid. (Found: C, 64.63; H, 6.87. $C_{12}H_{15}ClSi$ calcd.: C, 64.69; H, 6.79%.)

Infrared bands (cm^{-1}) were observed at 3035 (sh), 3030 m, 3005 w, 2962 s, 2925 m, 2900 w, 1455 m, 1450 s, 1392 m, 1360 w, 1308 vw, 1252 vs, 1220 m, 1190 m, 1178 w, 1155 vw, 1141 w, 1110 m, 1100 w, 1070 (sh), 1028 vs, 975 s, 930 w, 915 vw, 878 s, 860 s, 835 vs(br), 825 vs(br), 809 vs, 780 vs, 760 vs, 750 (sh), 730 m, 712 s, 650 m.

The mass spectrum showed the molecular ion ($C_{12}H_{15}{}^{35}Cl^{28}Si$) at *m/e* 222. Other prominent peaks appeared at *m/e* 207 ($C_{11}H_{12}{}^{35}Cl^{28}Si$), 115 ($C_9H_7$) and 107 ($C_3H_8{}^{35}Cl^{28}Si$).

The proton NMR spectrum (CS_2 solution) had the following resonances: τ 2.70 (multiplet, 4H); 3.10 (double doublet, A portion of ABX pattern, J_{AB} 5.4, J_{AX} 1.5, $J_{\text{A-aromatic H}}$ 0.6 Hz); 3.44 (double doublet, B portion of ABX pattern, 1H, J_{AB}

5.4 J_{BX} 1.8 Hz); 6.38 (triplet, X portion of ABX pattern, 1H, $J_{AX} \approx J_{BX}$ 1.5 Hz); 7.38 (singlet, 2H); 10.08 ppm (singlet, 6 H).

1-(*Dimethylmethoxysilyl*)*indene*

A modification to the published procedure[6] was used to obtain 1-(dimethylmethoxysilyl)indene in 90% yield. The product was obtained by distillation at 68°/ 0.05 mm as a clear colorless liquid. (Found: C, 70.77; H, 7.93. $C_{12}H_{16}OSi$ calcd.: C, 70.53; H, 7.89%.)

Infrared bands (cm^{-1}) were observed at 3050 m, 3005 w, 2960 s, 2939 m, 2900 m, 2825 s, 1460 m, 1450 s, 1392 m, 1360 w, 1308 vw, 1252 vs, 1220 m, 1190 m, 1178 w, 1155 vw, 1141 w, 1110 m, 1100 w, 1070 (sh), 1028 vs, 975 s, 930 w, 915 vw, 878 s, 860 s, 835 vs(br), 825 vs, 809 vs, 780 vs, 760 vs, 750 w, 730 m, 712 s, 650 m.

The mass spectrum showed the molecular ion ($C_{12}H_{16}O^{28}Si$) at *m/e* 204. Other prominent peaks appeared at *m/e* 189 ($C_{11}H_{13}OSi$), 115 (C_9H_7), 89 (C_3H_9O-^{28}Si), 59 ($CH_3O^{28}Si$).

The PMR spectrum (CS_2 solution) had the following resonances: τ 2.75 (multiplet, 4H); 3.13 (double doublet, A portion of ABX pattern, 1H, J_{AB} 5.4, J_{AX} 1.65, $J_{A-\text{aromatic H}}$ 0.75 Hz); 3.43 (double doublet, B portion of ABX pattern, 1H, J_{AB} 5.4, J_{BX} 1.8 Hz); 6.49 (triplet, X portion of ABX pattern, 1H, $J_{AX} \approx J_{BX}$ 1.5 Hz); 6.68 (singlet, 3H); 10.14 ppm (singlet, 6H).

Reaction of 1-(*trimethylstannyl*)*indene with maleic anhydride*

To a solution of 1.98 g (0.02 mol) of maleic anhydride in 100 ml of freshly distilled benzene under nitrogen was added 5 ml (0.02 mol) of freshly prepared 1-(trimethylstannyl)indene. The mixture immediately became bright yellow. The solution was stirred for two days at room temperature during which it turned light orange. The mixture was refluxed for 3 h, cooled, and the benzene was removed at ca. 10 mmHg, leaving a tangerine colored solid. The solid was recrystallized from n-hexane to give a yellow crystalline product. NMR spectra of the yellow compound ($CDCl_3$ and CS_2 solution) revealed a small amount of impurities as well as the desired adduct. Repeated attempts to purify the complex by recrystallization failed to give an analytically pure sample of the air and/or moisture sensitive compound.

The PMR spectrum ($CDCl_3$ solution) displayed resonances attributable[7] to the adduct: τ 2.58 (multiplet, 4 H); 5.85 (multiplet, 2 H); 6.12 (multiplet, 2 H); 7.3 (triplet, J 1.5 Hz, 1 H); 10.10 ppm (singlet, 9 H, J $^{117,119}Sn-CH_3$ 52.5 Hz).

The mass spectrum had an extremely weak peak for the molecular ion $C_{16}H_{18}$-$O_3{}^{120}Sn$ at *m/e* 378. Prominent peaks were observed at 363 ($M-CH_3$), 263 ($M-C_9$-H_7), 235 ($C_9H_7{}^{120}Sn$), 165 ($C_3H_9{}^{120}Sn$).

Kinetic studies

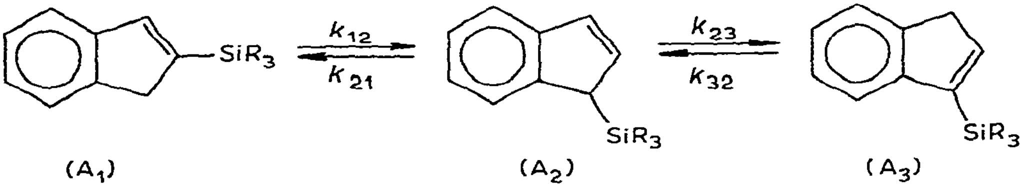
The isomerization reactions were carried out as described previously[1]. The reactions were conveniently monitored by following the appearance and disappearance of the methylsilyl resonances of the products and starting materials, respectively [except in the case of the (triphenylsilyl)indene isomers where the allylic hydrogen resonances were used]. In addition, for the dimethyl(chloromethyl) compound, additional sets of data were obtained by monitoring the chloromethyl proton signals of reactants and products. As a further check on the data, *p*-di(tert-butyl)benzene was used as an internal standard and the concentrations of reactants and products *vs.* the internal standard were also obtained[8].

RESULTS

Kinetic studies

The thermal isomerizations were studied at several temperatures in the range 150–200° on neat samples and in diphenyl ether solution. The results are summarized in Scheme 1.

SCHEME 1



(1)

	$R(1)$	$R(2)$	$R(3)$
(I)	CH_3	CH_3	CH_3
(II)	CH_3	CH_3	H
(III)	CH_3	CH_3	OCH_3
(IV)	CH_3	CH_3	C_6H_5
(V)	CH_3	CH_3	CH_2Cl
(VI)	CH_3	C_6H_5	C_6H_5
(VII)	C_6H_5	C_6H_5	C_6H_5

TABLE 1

EXPERIMENTAL AND CALCULATED CONCENTRATIONS FOR THE ISOMERIZATION OF 1-(DIMETHYLMETHOXYSILYL)INDENE AT 199°

t(min)	$A_1{}^a$		A_2		A_3	
0	0.0	(0.0)^b	100.00	(100.00)	0.0	(0.0)
8	11.22	(10.78)	80.86	(80.33)	7.92	(8.89)
13	16.76	(15.33)	71.30	(72.28)	11.94	(12.40)
16	17.10	(17.48)	69.22	(68.54)	13.68	(13.98)
20	19.86	(19.82)	64.38	(64.56)	15.76	(15.62)
25	21.43	(22.08)	61.45	(60.81)	17.12	(17.10)
30	23.88	(23.79)	58.24	(58.09)	17.88	(18.13)
35	24.74	(25.08)	55.70	(56.10)	19.56	(18.82)
40	26.35	(26.06)	53.85	(54.65)	19.80	(19.29)
45	26.51	(26.81)	52.21	(53.60)	21.27	(19.59)
60	26.77	(28.19)	54.12	(51.84)	19.10	(19.97)
80	29.69	(28.99)	51.66	(51.02)	18.65	(19.99)
150	29.17	(29.56)	50.03	(50.65)	20.80	(19.79)
745	30.59	(29.61)	50.07	(50.64)	19.34	(19.75)

[a] Concentrations expressed as percentages of the total isomeric mixture. [b] Calculated values in parenthesis. R.m.s. σ 0.78.

A typical set of data is presented in Table 1 and in Fig. 1. As in the case of (trimethylsilyl)indene (I), the rate of isomerization is temperature dependent but the equilibrium distribution of isomers is essentially independent of temperature in the range studied. For compounds (I)–(VII), no isomerization of the 1-isomer was observed over a period

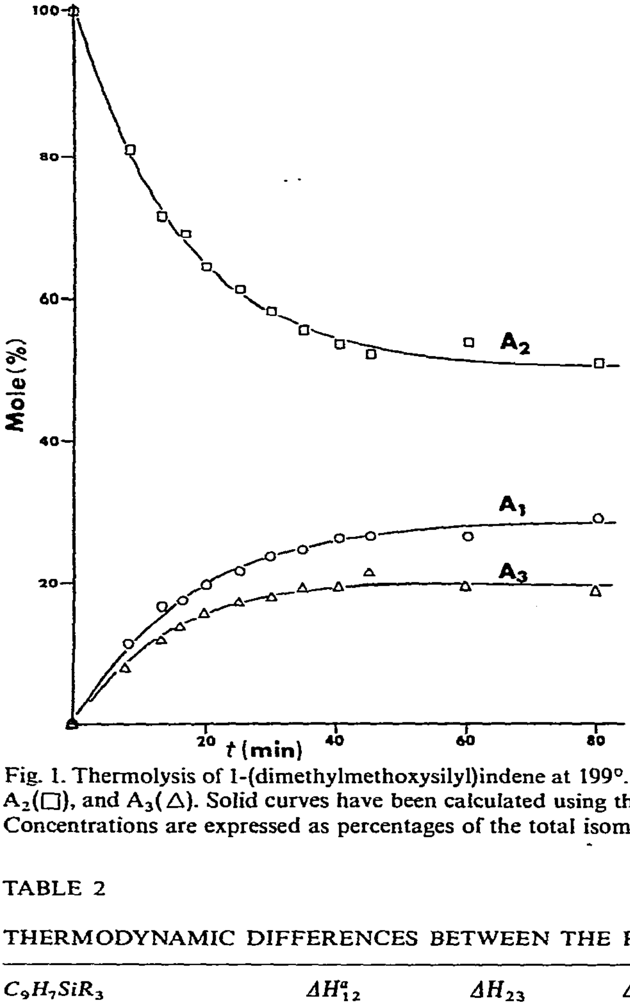


Fig. 1. Thermolysis of 1-(dimethylmethoxysilyl)indene at 199°. Points are experimental values for A_1 (○), A_2 (□), and A_3 (△). Solid curves have been calculated using the rate constants derived by the σ-method. Concentrations are expressed as percentages of the total isomeric mixture.

TABLE 2

THERMODYNAMIC DIFFERENCES BETWEEN THE POSITIONAL ISOMERS OF $C_9H_7SiR_3$

$C_9H_7SiR_3$	ΔH^a_{12} (kcal/mol)	ΔH_{23} (kcal/mol)	ΔS_{12} (cal/(mol·degree))	ΔS_{23} (cal/(mol·degree))
$SiR_3 = SiMe_3$	$+0.51 \pm 0.05$	-0.42 ± 0.05	$+2.2 \pm 0.1$	-3.5 ± 0.1
$SiMe_2Ph$	$+0.58 \pm 0.06$	-0.57 ± 0.06	$+1.7 \pm 0.1$	-3.3 ± 0.1
$SiMe_2(OMe)$	-0.23 ± 0.04	-0.62 ± 0.06	$+0.5 \pm 0.1$	-3.2 ± 0.1
$SiMe_2(CH_2Cl)$	$+0.01 \pm 0.04$	-0.24 ± 0.05	$+0.2 \pm 0.2$	-2.3 ± 0.2
$SiMePh_2$	-0.63 ± 0.06	$+0.79 \pm 0.08$	-1.7 ± 0.2	$+1.4 \pm 0.2$

[a] $\Delta H_{12} = \Delta H_f^0$(1-isomer) $- \Delta H_f^0$(2-isomer)
$\Delta H_{23} = \Delta H_f^0$(2-isomer) $- \Delta H_f^0$(3-isomer)
$\Delta S_{12} = \Delta S^0$(1-isomer) $- \Delta S^0$(2-isomer)
$\Delta S_{23} = \Delta S^0$(2-isomer) $- \Delta S^0$(3-isomer)

TABLE 3

EQUILIBRIUM DISTRIBUTION OF ISOMERS FOR THE SUBSTITUTED SILYLINDENES $C_9H_7SiR_3$

Compound	A_1	A_2	A_3
(I)	31[a]	54	15
(II)	30	54	16
(III)	30	50	20
(IV)	36	47	17
(V)	39	43	18
(VI)	38	34	28
(VII)	[b]	21	[b]

[a] Mole %. [b] Isomers not separated.

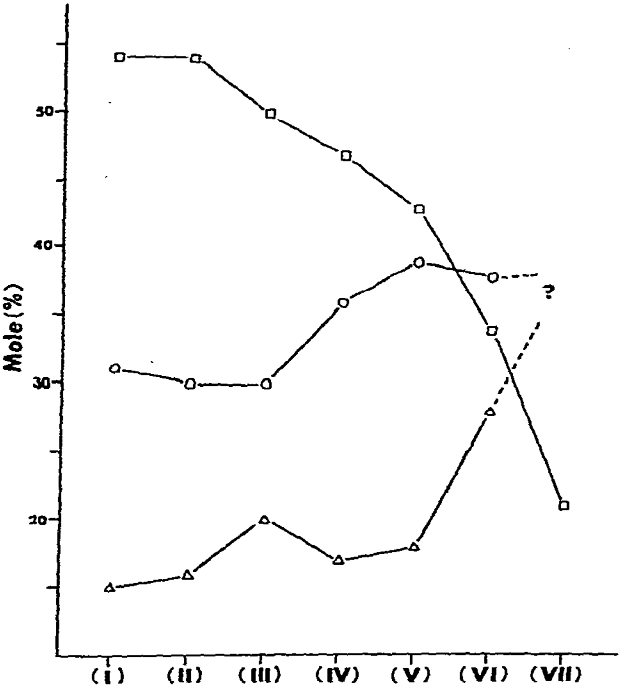


Fig. 2. Variation in the isomer distribution at equilibrium of the substituted silylindenes: A_1(○); A_2(□); A_3(△). See Table 3.

of 5 h at temperatures below 140°*. From plots of ln K_{eq} *vs.* $1/T$ the parameters in Table 2 were determined.

The variation in isomer distribution at equilibrium with substituents at the silicon atom is given in Table 3 and Fig. 2. Large variations from the values observed

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* For compounds (I)–(VII) the reactions could be conveniently followed to equilibrium in the temperature range 150° (several days) to 200° (< 90 min), whereas for ring-substituted indenylsilanes the reaction times and temperature ranges for which the isomerization could be studied were strongly dependent on the nature and position of the substituents on the indenyl ring. P. E. Rakita and G. A. Taylor, to be published.

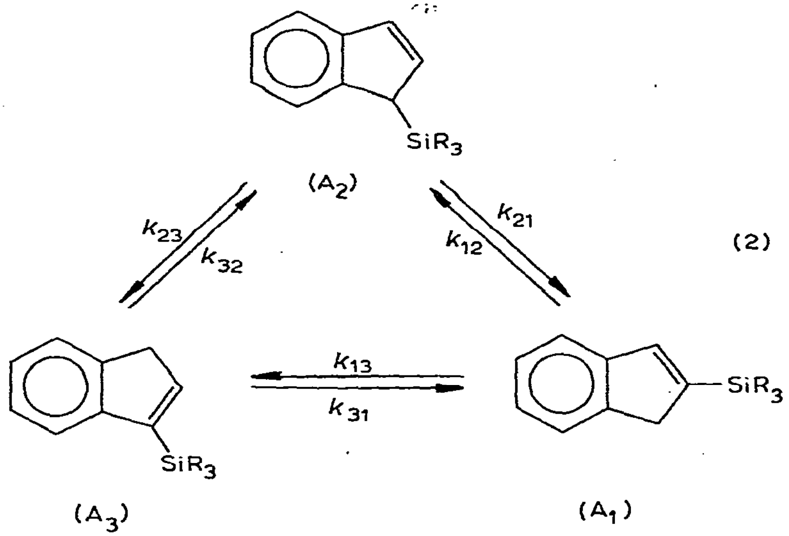
for (trimethylsilyl)indene (I) were obtained for the diphenylmethylsilyl (VI) and triphenylsilyl (VII) derivatives, the most notable change being a decrease in the relative amount of the 1-isomer with a concommitant increase in the percentage of 3-isomer. At equilibrium (VII) contains only 21 % 1-isomer with the remaining 79 % due to the 2- and/or 3-isomer. Unfortunately, the separate resonances (in the allylic region) due to the 2- and 3-isomers could not be resolved. Attempts to separate isomers by VPC and recrystallization proved unsuccessful.

Method of analysis

In Part I, the rate constants were determined by the σ-method[1] from a kinetic analysis treatment which required that $A_i = 100\%$ at $t=0$ and A_j, A_k $(\neq A_i) = 0\%$ at $t=0$. We have modified the procedure to include the completely general linear three-component case wherein at $t=0$ any non-equilibrium distribution of isomers ($A_i \neq 100\%$, $A_j, A_k \neq 0\%$) can be used* . Other applications of this analysis technique have recently been reported[9,10].

Although the data are readily accommodated by a linear three-component isomerization scheme, it seemed desirable to ascertain the possibility of an additional reaction pathway $A_1 \rightleftarrows A_3$, leading to a cyclic three-component system, (Scheme 2).

SCHEME 2



Accordingly, the data for (diphenylmethylsilyl)indene (VI) were also analyzed using the σ-method with the general equations incorporating the additional reaction pathway $A_1 \rightleftarrows A_3$ and the rate constants k_{13} and k_{31}. Small values of $(\sigma/3N)^{\frac{1}{2}}$ (see ref. 1) were obtained only when values of k_{13} and k_{31} were 10^{-2} less than the other four rate constants, and r.m.s. σ-values approached within acceptable limits the values obtained from the linear case only when k_{13} and k_{31} were at least 10^{-6} smaller than k_{12}, k_{21},

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* A copy of the program in Fortran IV is available from the authors.

TABLE 4

RATE CONSTANTS FOR THE THERMOLYSIS OF SUBSTITUTED SILYLINDENES

Compound	*temp.* (°C)	k_{12}[a]	k_{21}	k_{23}	k_{32}	*r.m.s.* σ[b]
(III)	199	$4.9 \pm 0.5 \times 10^{-4}$	$2.8 \pm 0.4 \times 10^{-4}$	$2.4 \pm 0.5 \times 10^{-4}$	$6.2 \pm 1.8 \times 10^{-4}$	0.78
	186	$1.6 \pm 0.2 \times 10^{-4}$	$8.8 \pm 1.3 \times 10^{-5}$	$8.2 \pm 1.6 \times 10^{-5}$	$2.2 \pm 0.7 \times 10^{-4}$	0.80
	173	$5.1 \pm 0.5 \times 10^{-5}$	$2.8 \pm 0.4 \times 10^{-5}$	$2.9 \pm 0.6 \times 10^{-5}$	$7.4 \pm 2.2 \times 10^{-5}$	0.90
	150	$5.5 \pm 0.6 \times 10^{-6}$	$3.1 \pm 0.5 \times 10^{-6}$	$3.4 \pm 0.7 \times 10^{-6}$	$8.7 \pm 2.6 \times 10^{-6}$	0.76
(IV)	200	$7.3 \pm 0.7 \times 10^{-4}$	$5.2 \pm 0.8 \times 10^{-4}$	$1.8 \pm 0.4 \times 10^{-4}$	$4.2 \pm 1.2 \times 10^{-4}$	0.80
	194	$3.8 \pm 0.4 \times 10^{-4}$	$2.9 \pm 0.7 \times 10^{-4}$	$1.2 \pm 0.3 \times 10^{-4}$	$3.0 \pm 0.9 \times 10^{-4}$	1.13
	182	$1.4 \pm 0.2 \times 10^{-4}$	$9.7 \pm 1.2 \times 10^{-5}$	$4.5 \pm 0.9 \times 10^{-5}$	$1.2 \pm 0.4 \times 10^{-4}$	0.60
	174	$6.7 \pm 0.9 \times 10^{-5}$	$4.5 \pm 1.0 \times 10^{-5}$	$2.4 \pm 0.5 \times 10^{-5}$	$7.0 \pm 2.0 \times 10^{-5}$	1.21
	155	$1.3 \pm 0.2 \times 10^{-5}$	$8.5 \pm 1.1 \times 10^{-6}$	$6.4 \pm 1.2 \times 10^{-6}$	$2.1 \pm 0.6 \times 10^{-5}$	0.54
(V)	199	$3.4 \pm 0.3 \times 10^{-4}$	$2.9 \pm 0.5 \times 10^{-4}$	$4.3 \pm 0.8 \times 10^{-4}$	$1.3 \pm 0.4 \times 10^{-3}$	0.97
	185	$1.3 \pm 0.2 \times 10^{-4}$	$1.0 \pm 0.2 \times 10^{-4}$	$1.8 \pm 0.4 \times 10^{-4}$	$5.6 \pm 1.8 \times 10^{-4}$	1.00
	173	$3.7 \pm 0.4 \times 10^{-5}$	$3.1 \pm 0.5 \times 10^{-5}$	$8.1 \pm 1.6 \times 10^{-5}$	$2.7 \pm 0.9 \times 10^{-4}$	0.98
	150	$4.7 \pm 0.5 \times 10^{-6}$	$3.8 \pm 0.6 \times 10^{-6}$	$1.6 \pm 0.3 \times 10^{-5}$	$5.9 \pm 1.9 \times 10^{-5}$	1.15
(VI)	199	$4.4 \pm 0.4 \times 10^{-4}$	$6.2 \pm 0.9 \times 10^{-4}$	$3.3 \pm 0.6 \times 10^{-4}$	$3.6 \pm 1.0 \times 10^{-4}$	1.03
	186	$1.8 \pm 0.2 \times 10^{-4}$	$2.4 \pm 0.4 \times 10^{-4}$	$1.4 \pm 0.3 \times 10^{-4}$	$1.7 \pm 0.5 \times 10^{-4}$	1.02
	173	$4.7 \pm 0.5 \times 10^{-5}$	$5.6 \pm 0.8 \times 10^{-5}$	$4.2 \pm 0.8 \times 10^{-5}$	$5.1 \pm 1.5 \times 10^{-5}$	0.81
	156	$1.1 \pm 0.1 \times 10^{-5}$	$1.4 \pm 0.2 \times 10^{-5}$	$9.6 \pm 1.9 \times 10^{-6}$	$1.0 \pm 0.3 \times 10^{-5}$	0.51

[a] Rate constants in $\sec^{-1}$. [b] R.m.s. deviation per data point.

TABLE 5

ACTIVATION PARAMETERS FOR THE THERMOLYSIS OF SUBSTITUTED SILYLINDENES

Compound	*Reaction*	E_a (*kcal/mol*)	$\Delta H^{\ne}$ (*kcal/mol*)[a]	$\Delta S^{\ne}$ (*cal/(mol · degree)*)[b]	$\Delta G^{\ne}$ (*kcal/mol*)[c]	*Ref.*
(I)	$A_1 \rightarrow A_2$	38.0	37.1 ± 4	$+\ 4.3 \pm 8$	35.0 ± 0.1	1
	$A_2 \rightarrow A_1$	36.7	35.8 ± 5	$-\ 0.4 \pm 10$	35.4 ± 0.2	
	$A_2 \rightarrow A_3$	25.2	24.3 ± 4	-25.0 ± 8	36.0 ± 0.2	
	$A_3 \rightarrow A_2$	26.4	25.5 ± 5	-19.6 ± 10	32.6 ± 0.3	
(III)	$A_1 \rightarrow A_2$	36.2	35.3 ± 4	0.0 ± 8	35.4 ± 0.1	This work
	$A_2 \rightarrow A_1$	36.5	35.6 ± 4	$-\ 0.7 \pm 8$	35.9 ± 0.2	
	$A_2 \rightarrow A_3$	34.6	33.7 ± 4	$-\ 5.0 \pm 8$	35.9 ± 0.1	
	$A_3 \rightarrow A_2$	34.5	33.6 ± 4	$-\ 3.2 \pm 10$	35.0 ± 0.2	
(IV)	$A_1 \rightarrow A_2$	35.4	34.5 ± 4	$-\ 1.2 \pm 8$	35.1 ± 0.1	This work
	$A_2 \rightarrow A_1$	37.0	36.1 ± 5	$+\ 0.7 \pm 10$	35.4 ± 0.2	
	$A_2 \rightarrow A_3$	29.9	29.0 ± 4	-15.5 ± 8	36.3 ± 0.2	
	$A_3 \rightarrow A_2$	27.0	26.1 ± 5	-20.0 ± 10	35.3 ± 0.3	
(V)	$A_1 \rightarrow A_2$	35.3	34.4 ± 4	$-\ 2.6 \pm 10$	35.6 ± 0.2	This work
	$A_2 \rightarrow A_1$	35.4	34.5 ± 5	$-\ 2.7 \pm 10$	35.8 ± 0.3	
	$A_2 \rightarrow A_3$	26.6	25.7 ± 4	-20.6 ± 10	35.4 ± 0.2	
	$A_3 \rightarrow A_2$	25.0	24.1 ± 5	-21.9 ± 10	34.4 ± 0.3	
(VI)	$A_1 \rightarrow A_2$	35.6	34.7 ± 4	$-\ 1.4 \pm 8$	35.4 ± 0.1	This work
	$A_2 \rightarrow A_1$	36.4	35.5 ± 5	$+\ 1.0 \pm 10$	35.9 ± 0.2	
	$A_2 \rightarrow A_3$	33.8	32.9 ± 4	$-\ 6.0 \pm 8$	35.9 ± 0.2	
	$A_3 \rightarrow A_2$	33.8	32.9 ± 5	$-\ 5.5 \pm 10$	35.0 ± 0.3	

[a] $\Delta H^{\ne} = E_a - R \cdot T$ (at 200°). [b] $\Delta S^{\ne} = R\ln(k_i \cdot h/k \cdot T) + (E_a - R \cdot T)/T$. [c] $\Delta G^{\ne} = -R \cdot T\ln(k_i \cdot h/k \cdot T)$.

k_{23}, and k_{32}. These results are in accord with our earlier data[1] and lend strong support to Scheme 1.

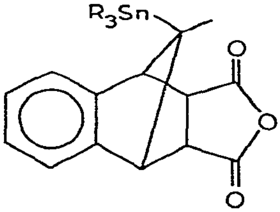
The rate constants for the rearrangements of the silylindenes (III)–(VI) are presented in Table 4. Arrhenius plots were linear, and the activation parameters are given in Table 5.

Other reactions

Treatment of 1-methyl- or substituted 1-methyl-indenes with alkylamines results in a rapid and quantitative isomerization at room temperature to the 3-methyl isomer[11-13]. By contrast, treatment of 1-(trimethylsilyl)indene with triethylamine and pyridine produced no reaction. When 1-(trimethylsilyl)indene was treated with an equimolar amount of n-butyllithium in ether/hexane and the reaction mixture quenched with acidified water, the recovered (trimethylsilyl)indene consisted of 83% 1-isomer and 17% 3-isomer. No evidence for 2-isomer or free indene was observed. Reaction of 1-(trimethylsilyl)indene with potassium metal in ether followed by aqueous workup led to rapid decomposition as evidenced by the appearance of several signals in the trimethylsilyl region of the NMR spectrum. No attempt was made to identify or separate the products.

Samples of 1-(trimethylstannyl)indene heated in sealed tubes under nitrogen at 140° and 150° were unchanged after 16 h. At temperatures above 175° rapid decomposition occurred as evidenced by considerable darkening of the samples, the appearance of several new resonances in the CH_3–Sn region of the NMR spectrum, and ultimately by the deposition of a gray solid.

Maleic anhydride reacts with 1-(trimethylstannyl)indene to form an addition product analogous to that reported[7] for the 1-triphenylstannyl compound. The pattern of resonances in the NMR spectrum is consistent with the Diels–Alder addition product. The similarity in the mass spectra of the adducts is evidenced by the prominence of peaks assigned to the fragments M–R(R = CH_3 or C_6H_5) and M–C_9H_7 for the two compounds.



DISCUSSION

The kinetic data for the isomerization of the substituted silylindenes can be accommodated by Scheme 1. The reaction profile is depicted schematically in Fig. 3. The pathway $A_1 \rightleftarrows A_2 \rightleftarrows A_3$ represents the thermal isomerization via hydrogen and silicon migrations, whereas the pathway $A_2^* \rightleftarrows A_2$ represents the fluxional silicon migration reported elsewhere[4]. The existence of intermediate [I1] in the reaction scheme has been demonstrated by trapping experiments[14]. We have been unsuccessful in demonstrating the existence of intermediate [I2] by comparable trapping experi-

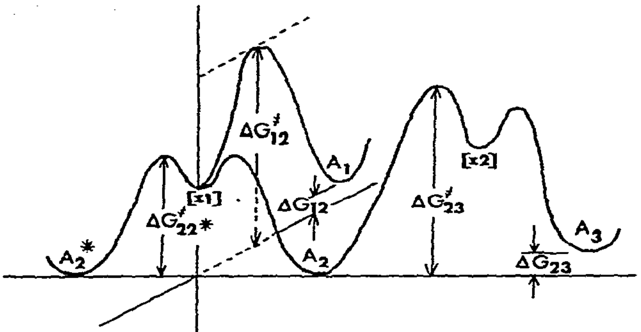
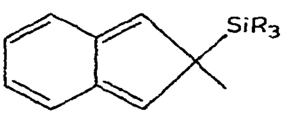
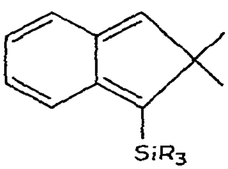


Fig. 3. Schematic reaction profile for the thermal isomerization of the silylindenes. See text.

ments using various dienophiles and the 3-isomer as starting material.



[I1]



[I2]

From the kinetic analysis of the isomerization of 1-(diphenylmethylsilyl)-indene using both the linear (Scheme 1) and cyclic (Scheme 2) three component systems, we have determined that the direct route $A_1 \rightleftharpoons A_3$ is, at best, an extremely minor pathway for rearrangement.

From the activation parameters given in Table 5 it is clear that varying the substituents on the silicon atom has a very minor effect on the free energy of activation for rearrangement. The values of $\Delta G^{\ne}$ range from 32.6 to 36.3 kcal/mole, consistent with the rate-limiting step being an intramolecular hydrogen migration.

The large negative entropies of activation noted previously[1] for the reaction $A_2 \rightleftharpoons A_3$ of (trimethylsilyl)indene also appear for the same pathway with the dimethylphenylsilyl and dimethyl(chloromethyl)silyl compounds. The dimethylmethoxy and diphenylmethyl derivatives display the expected small values of $\Delta S^{\ne}$.

The most notable consequence of varying the silicon substituents is observed in the equilibrium distribution of isomers (Table 3 and Fig. 2). No obvious trends based on electronic or steric effects are apparent from the data. Moreover, it seems that steric effects play a minor role, if any, in determining the equilibrium distribution of isomers*. Thus substitution of a trimethylsilyl group with a sterically more demanding diphenylmethylsilyl group might be expected to lead to a decrease in the relative amount of the 3-isomer (and possibly also the 1-isomer) and an increase in the 2-isomer. In

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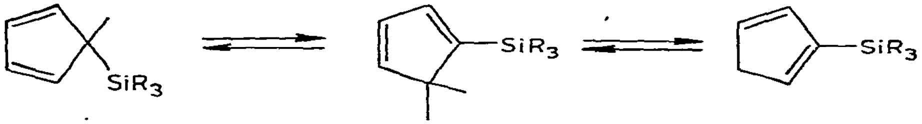
* Ring substitution of (trimethylsilyl)indene profoundly affects both the rate of isomerization (*via* hydrogen migration) and the product distribution at thermal equilibrium. 1-(Trimethylsilyl)-2-methylindene is converted upon thermolysis at 200° for 24 h to 9% 3-(trimethylsilyl)-2-methylindene. By contrast 1-(trimethylsilyl)-4,7-dimethylindene isomerizes in 35 min at 182° to 85% 2-(trimethylsilyl)-4,7-dimethylindene[16].

fact, the 2-isomer increases from 31 to 38% and the 1-isomer decreases from 54 to 34%, but the 3-isomer also increases from 15 to 28%. It is worth noting that an analogous isomerization occurs for the silicon compounds $C_5H_5Si(CH_3)_nCl_{3-n}$ (Scheme 3), for which the equilibria are both temperature and substituent dependent. In the latter case, an increase in the number of halogen atoms leads to an increase in the relative amount of vinylsilyl isomers[15].

SCHEME 3



In contrast to the organic substituted indenes, trimethylsilylindene does not isomerize in the presence of weak bases like pyridine and triethylamine. Stronger bases lead to the formation of the (trimethylsilyl)indenyl anion (with n-butyllithium)[3] or decomposition (with potassium metal).

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