

each member of the classes of  $D_3-32$  symmetry the number of conformational isomers is the same and their enumeration is quite analogous. The same is true for each member of the  $C_2-2$  class.

As an example of the enumeration within the  $D_3-32$  class we take the  $\Delta(\Lambda\Lambda\Lambda)$  (or  $\Lambda(\Delta\Delta\Delta)$ ) configuration whose conformational isomers are given in Figure 10. The number of isomers corresponding to the different conformations is

$\delta_6$	1 isomer	
$\delta_5\lambda$	1 isomer	
$\delta_4\lambda_2$	4 isomers	(7)
$\delta_3\lambda_3$	4 isomers	

with an obvious symmetry about  $\delta_3\lambda_3$  so that we altogether get the number of isomers from the three first classes twice and that from the fourth class only once, altogether 16 isomers.

The four possible  $\Delta(\Lambda\Lambda\Lambda)\delta_4\lambda_2$  isomers (Figure 10) correspond to the four different distances between a pair of circles containing the conformation descriptors. The three first isomers have  $C_2-2$  symmetry; the last one has no symmetry. The  $\Delta(\Lambda\Lambda\Lambda)\delta_3\lambda_3$  isomers correspond to the four possible triangles, having the centers of the descriptor circles as their corners. One of these isomers has  $C_3-3$  symmetry; the others have no symmetry.

As our second example we take  $\Delta(\Lambda\Lambda\Lambda)$  (or  $\Lambda(\Delta\Delta\Delta)$ ), belonging to the  $C_2-2$  configurational class. Here the conformational isomers may be enumerated as follows

$\delta_6$	1 isomer
$\delta_5\lambda$	3 isomers
$\delta_4\lambda_2$	9 isomers
$\delta_3\lambda_3$	10 isomers

giving in this case 36 isomers. The first 13 isomers are given in Figure 11. Only four of these isomers have the full symmetry of the configuration. The  $\delta_4\lambda_2$  isomers fall into three classes, each containing three isomers. The first class has the  $\lambda$ 's symmetrically disposed with respect to the twofold axis of the compounded configuration. The second class has the  $\lambda$ 's unsymmetrically disposed, one on each side of the twofold axis, and the third has the  $\lambda$ 's disposed on the same side of the twofold axis. The  $\delta_3\lambda_3$  isomers (Figure 12) consist of six having one pair of  $\lambda$ 's disposed symmetrically about the twofold axis, three with one pair of  $\lambda$ 's disposed unsymmetrically about the twofold axis, and finally one isomer with all the  $\lambda$ 's on the same side of this axis in the projection.

Thus each of the four  $D_3-32$  classes corresponds to 16 isomers and each of the four  $C_2-2$  classes corresponds to 36 isomers giving altogether 208 due to the interplay of configurational and conformational isomerism. Of these 208 isomers 2 catoptromers were found by X-ray analysis on a dithionate of the cation. One of these is shown in Figure 13. It corresponds to the sixth isomer of Figure 11 when this is associated with the compounded configuration



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## Studies in Organometallic Rearrangements. I. Kinetics of the Thermal Isomerization of Trimethylsilylindene. A System of Two Consecutive Reversible First-Order Reactions

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The reversible thermal isomerization of the positional isomers of trimethylsilylindene has been studied in the temperature range 146–201°. The rearrangement proceeds in a stepwise linear manner: 2-isomer  $\rightleftharpoons$  1-isomer  $\rightleftharpoons$  3-isomer. Rate constants and activation parameters for the forward and reverse reactions are reported. At equilibrium, the mixture contains 31% 2-isomer, 54% 1-isomer, and 15% 3-isomer. A general method is described for the determination of rate constants in a system of two consecutive, reversible, first-order reactions.

The migratory behavior of triorganosilyl groups bound to cyclopentadiene<sup>2–4</sup> and indene<sup>5–7</sup> has been well documented. By contrast the kinetically slower process of hydrogen migration has received much less attention. In the case of trimethylsilylcyclopentadiene, the kinetics<sup>3</sup> and thermodynamic equilibria<sup>4</sup> have been reported. For substituted indenenes, base-cata-

lyzed<sup>8</sup> and thermal<sup>9,10</sup> hydrogen migrations have been studied. Only one reference has been made to the thermal isomerization of silylindenenes,<sup>7</sup> and no kinetic data were given. We have studied the kinetics of the thermal isomerization of the positional isomers of trimethylsilylindene and determined the activation parameters for the rearrangement process. We also have devised a method for the analysis of systems involving two consecutive reversible first-order reactions.

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### Experimental Section

**General Data.**—All manipulations were carried out in an atmosphere of purified nitrogen. The compounds 1-trimethylsilylindene<sup>6</sup> and 2-trimethylsilylindene<sup>6</sup> 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. 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 Meade Microanalytical Laboratory, Amherst, Mass.

**Preparation of 2-Dimethylsilylindene.**—Magnesium metal turnings (1.2 g, 0.05 g-atom) in a 1-l., three-neck flask equipped with a mechanical stirrer, dropping funnel, and condenser were treated with ethyl bromide (3 ml) in THF (20 ml) and stirred until the reaction became vigorous. The solution was removed by syringe and the activated magnesium was washed with THF (3 × 20 ml) and covered with THF (35 ml). A small portion (~2 ml) of a solution of 2-bromoindene (9.0 g, 0.05 mol) in THF (20 ml) was added and the mixture was stirred vigorously until the reaction began. The flask was chilled in an ice-water bath and the remaining solution was added dropwise over a 40-min period. The Grignard reagent was then allowed to warm to room temperature and a solution of dimethylchlorosilane (4.8 g, 0.05 mol) in THF (5 ml) was added dropwise. The mixture was refluxed for 4 hr and allowed to stand overnight. Water (~50 ml) was added, followed by THF (25 ml) and ether (50 ml), and the ether layer was separated, dried (MgSO<sub>4</sub>), and concentrated by rotary evaporation. The remainder was vacuum distilled. After a small forerun, identified as indene by its nmr spectrum, the product was collected at 85° (4 mm) and purified by redistillation at 80° (4 mm). *Anal.* Calcd for C<sub>11</sub>H<sub>14</sub>Si: C, 75.79; H, 8.09. Found: C, 75.70; H, 8.10.

The proton nmr spectrum (~0.25 M, CCl<sub>4</sub> solution) had the following resonances:  $\tau$  2.8 (complex multiplet, 5 H), 5.74 (septet,  $J = 3.8$  Hz, 1 H), 6.67 (doublet,  $J = 1.9$  Hz, 2 H), 9.67 (doublet,  $J = 3.8$  Hz, 6 H).

The mass spectrum showed the molecular ion (C<sub>11</sub>H<sub>14</sub><sup>+</sup>Si) at  $m/e$  174. Other prominent peaks appeared at  $m/e$  159 (C<sub>10</sub>H<sub>11</sub>Si), 131 (C<sub>9</sub>H<sub>7</sub>Si), 115 (C<sub>8</sub>H<sub>7</sub>), 59 (C<sub>8</sub>H<sub>6</sub>Si), and 43 (CH<sub>3</sub>Si).

Infrared bands were observed at 3070 (m), 3053 (w), 3033 (w), 3025 (w), 2963 (m), 2904 (m), 2885 (w), 2769 (vw), 2116 (s, br), 1531 (m), 1456 (m), 1386 (m), 1291 (w), 1256 (sh), 1246 (s), 1204 (w), 1194 (w), 1120 (w), 1096 (w), 1036 (s), 915 (w), 885 (vs, br), 869 (w), 852 (w), 830 (s), 764 (sh), 758 (s), 750 (s), 721 (s), 715 (s), 700 (vw), and 653 (w) cm<sup>-1</sup>.

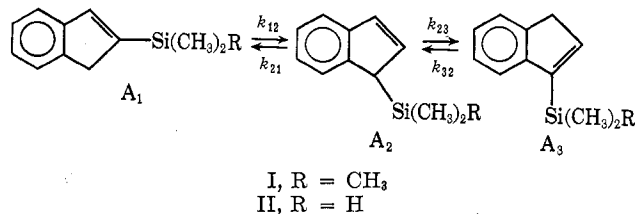
**Gas-Liquid Chromatography.**—Pure samples of the above compounds for spectral measurements, analyses, and kinetic studies were obtained by glpc on a Hewlett-Packard Model 5750 chromatograph equipped with a thermal conductivity detector. A column (0.25 in. × 26 in.) packed with 15% SE-30 on Chromosorb W was employed using helium elution. In a typical separation at 150° (50 psi He pressure) 1-trimethylsilylindene was eluted with a retention time of 1.9 min and 2-trimethylsilylindene with a retention time of 2.7 min.

**Kinetic Studies.**—Solutions in diphenyl ether or neat samples of the appropriate silylindene were sealed in an nmr tube and immersed in a constant-temperature bath (temperature control ±1°). The samples were withdrawn periodically and immediately cooled to room temperature, and the spectra were recorded and integrated. The reactions were conveniently followed by monitoring the appearance and disappearance of the methylsilyl signals due to the starting materials and products, respectively. For the trimethylsilylindenes the resonances appeared at  $\tau$  10.10 (singlet, 1-isomer), 9.79 (singlet, 2-isomer), 9.68 (singlet, 3-isomer). For the analogous dimethylsilylindenes the signals appeared at  $\tau$  10.11 (doublet, 1-isomer), 9.74 (doublet, 2-isomer), and 9.67 (doublet, 3-isomer). The final concentrations were determined from the samples after equilibration for several hours. For each data point the spectrum was carefully integrated at least four times and the average value used. Although the sample discolored during the reaction, no extraneous signals were observed in the nmr spectrum. Other workers<sup>7,10</sup> have similarly reported the absence of any significant decomposition or intermolecular exchange reactions under these conditions.

### Results

**Kinetic Studies.**—The thermal isomerization of 1-trimethylsilylindene was studied at 201, 185, 172, 146

(neat samples), and 193° (diphenyl ether solution). Samples of the 2-isomer were equilibrated at 184 and 174° and the rate of isomerization was followed at 200° (diphenyl ether solution). In addition, for comparison, the isomerization of 2-dimethylsilylindene at 200° (diphenyl ether solution) was also studied. The results are summarized in the following reaction scheme.<sup>11</sup>



Thus, in samples of the 2-isomer, the isomerization is observed to proceed with the appearance of the 1-isomer and, subsequently, the 3-isomer. Equilibration of samples of the 1-isomer occurs with the simultaneous appearance of the 2- and 3-isomers, accompanied by a decrease in the relative amount of the 1-isomer. The rate of isomerization is temperature dependent, occurring more rapidly at higher temperature. For example, at 200° the equilibrium is established within 90 min while at 146° 90 hr is required to obtain the equilibrium mixture. Typical sets of data are presented in Figures 1 and 2.

The equilibrium concentrations are remarkably insensitive to temperature in the range studied (Figure 3), and the results presented here are in good agreement with the value at 155° previously reported by Larrabee and Dowden.<sup>7</sup> By contrast the equilibrium between the positional isomers<sup>12</sup> of the analogous trimethylsilylcyclopentadienes is strongly temperature dependent.<sup>4</sup>

From plots of  $\ln K$  vs.  $1/T$  the following parameters were determined.

$$\Delta H_{12} = \Delta H_f^\circ(1\text{-isomer}) - \Delta H_f^\circ(2\text{-isomer}) = +0.51 \pm 0.05 \text{ kcal/mol}$$

$$\Delta H_{23} = \Delta H_f^\circ(3\text{-isomer}) - \Delta H_f^\circ(1\text{-isomer}) = -0.42 \pm 0.05 \text{ kcal/mol}$$

$$\Delta S_{12} = \Delta S^\circ(1\text{-isomer}) - \Delta S^\circ(2\text{-isomer}) = +2.2 \pm 0.1 \text{ eu}$$

$$\Delta S_{23} = \Delta S^\circ(3\text{-isomer}) - \Delta S^\circ(1\text{-isomer}) = -3.5 \pm 0.1 \text{ eu}$$

**Method of Analysis.**—Although the principles for solving complex reversible kinetic systems have been known for some time,<sup>13-15</sup> simple techniques for their practical application have not been generally avail-

(11) The abbreviations A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub> used in the rate expressions below correspond to the 2-, 1-, and 3-isomers, respectively.

(12) Note: the 5-, 1-, and 2-isomers of trimethylsilylcyclopentadiene correspond to the 1-, 2-, and 3-isomers, respectively, of trimethylsilylindene.

(13) N. M. Rodiguin and E. N. Rodiguina, "Consecutive Chemical Reactions," Van Nostrand, New York, N. Y., 1964.

(14) J. J. Manock and D. C. Hopper, *J. Chem. Educ.*, **48**, 530 (1971).

(15) E. McLaughlin and R. W. Rozett, *Chem. Technol.*, 120 (1971). The solutions to the general first-order, three-component system require the roots of the determinantal equation:  $\gamma^3 - \gamma(k_{12} + k_{21} + k_{23} + k_{32} + k_{31} + k_{13}) + (k_{21}k_{12} + k_{12}k_{23} + k_{13}k_{32} + k_{21}k_{32} + k_{13}k_{21} + k_{12}k_{31} + k_{13}k_{23} + k_{31}k_{23}) = 0$ .

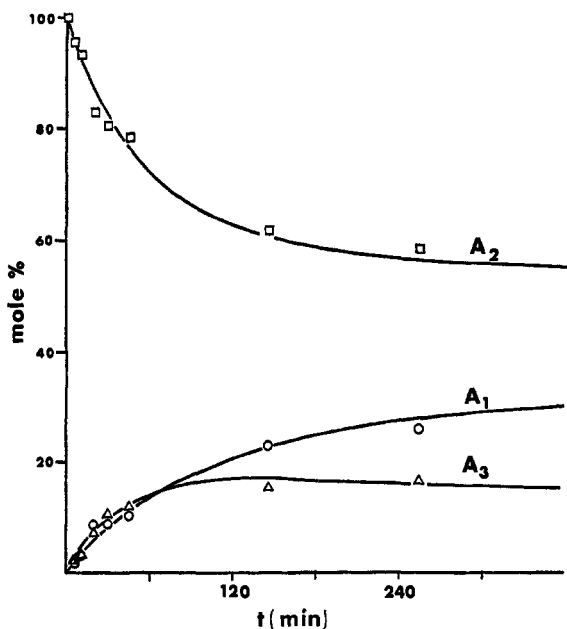


Figure 1.—Thermolysis of 1-trimethylsilylindene at 185°. Points are experimental values for  $A_1$  (O),  $A_2$  (□), and  $A_3$  (Δ). Solid curves have been calculated using the "best" rate constants derived by the  $\sigma$  method. Concentrations are expressed as percentages of the total isomeric mixture.

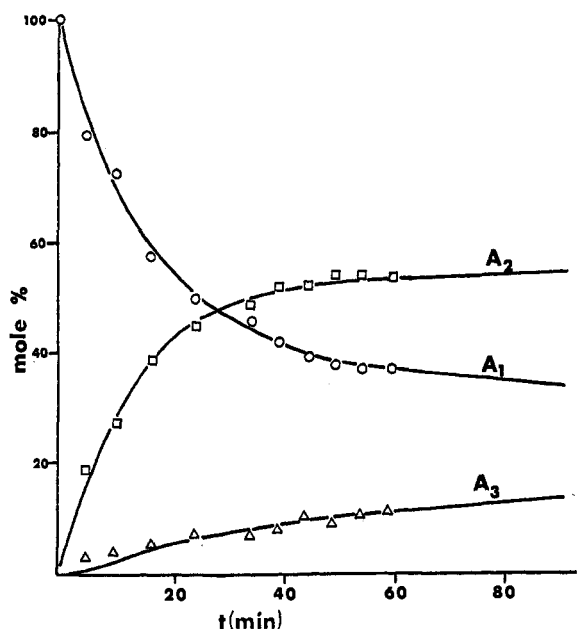


Figure 2.—Thermolysis of 2-trimethylsilylindene at 200°. Points are experimental values for  $A_1$  (O),  $A_2$  (□), and  $A_3$  (Δ). Solid curves have been calculated using the "best" rate constants derived by the  $\sigma$  method.

able.<sup>16</sup> The general equations for the concentrations of  $A_1$ ,  $A_2$ , and  $A_3$ , for the linear reversible first-order system, as obtained by the method of Laplace transform, are given below. Case 1 and case 3 have been derived elsewhere.<sup>13</sup> Case 2 is outlined briefly in the Appendix.

Case 1:  $A_{00} = A_1 = 100\%$ ,  $A_2 = A_3 = 0$  at  $t = 0$

(16) The method described here utilizes a nonlinear least-squares determination of the unknown rate constants. Other applications of this general technique have included the calculation of nmr coupling constants of molecules which exhibit conformational isomerization (see, e.g., G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Amer. Chem. Soc.*, **89**, 1135 (1967)).

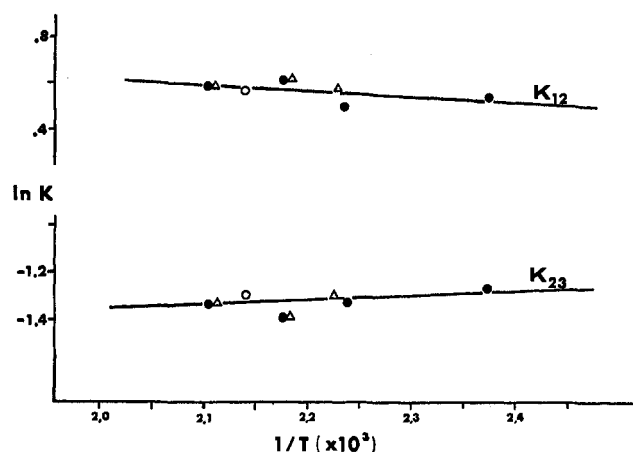


Figure 3.—Variations in the equilibrium constants,  $K_{12}$  and  $K_{23}$ , with temperature: ●, neat samples; ○, diphenyl ether solution. Equilibria were achieved starting with the 1-isomer (●, ○) and 2-isomer (Δ).

$$A_1 = A_{00} \left[ \frac{k_{21}k_{32}}{\gamma_1\gamma_2} + \sum_{i=1}^2 \frac{\gamma_i^2 - \gamma_i[k_{21} + k_{32} + k_{23}] + k_{21}k_{32}}{\gamma_i(\gamma_i - \gamma_{i\pm 1})} e^{-\gamma_i t} \right] \quad (1)$$

$$A_2 = A_{00} \left[ \frac{k_{12}k_{32}}{\gamma_1\gamma_2} + \sum_{i=1}^2 \frac{k_{12}(k_{32} - \gamma_i)}{\gamma_i(\gamma_i - \gamma_{i\pm 1})} e^{-\gamma_i t} \right] \quad (2)$$

$$A_3 = A_{00} \left[ \frac{k_{12}k_{23}}{\gamma_1\gamma_2} + \sum_{i=1}^2 \frac{k_{12}k_{23}}{\gamma_i(\gamma_i - \gamma_{i\pm 1})} e^{-\gamma_i t} \right] \quad (3)$$

Case 2:  $A_{00} = A_2 = 100\%$ ,  $A_1 = A_3 = 0$  at  $t = 0$

$$A_1 = A_{00} \left[ \frac{k_{21}k_{32}}{\gamma_1\gamma_2} + \sum_{i=1}^2 \frac{k_{21}(k_{32} - \gamma_i)}{\gamma_i(\gamma_i - \gamma_{i\pm 1})} e^{-\gamma_i t} \right] \quad (4)$$

$$A_2 = A_{00} \left[ \frac{k_{12}k_{32}}{\gamma_1\gamma_2} + \sum_{i=1}^2 \frac{\gamma_i^2 - \gamma_i(k_{12} + k_{32}) + k_{12}k_{32}}{\gamma_i(\gamma_i - \gamma_{i\pm 1})} e^{-\gamma_i t} \right] \quad (5)$$

$$A_3 = A_{00} \left[ \frac{k_{12}k_{23}}{\gamma_1\gamma_2} + \sum_{i=1}^2 \frac{k_{23}(k_{12} - \gamma_i)}{\gamma_i(\gamma_i - \gamma_{i\pm 1})} e^{-\gamma_i t} \right] \quad (6)$$

Case 3:  $A_{00} = A_3 = 100\%$ ,  $A_1 = A_2 = 0$  at  $t = 0$

This case is equivalent to case 1 where the subscripts 1 and 3 are exchanged. The solution of the determinantal equation

$$\gamma^2 - \gamma(k_{12} + k_{23} + k_{21} + k_{32}) + k_{12}k_{23} + k_{12}k_{32} + k_{21}k_{32} = 0 \quad (7)$$

gives the roots

$$\gamma_1 = 1/2(p + q) \quad (8)$$

$$\gamma_2 = 1/2(p - q) \quad (9)$$

where

$$p = k_{12} + k_{23} + k_{21} + k_{32} \quad (10)$$

$$q = [p^2 - 4(k_{12}k_{23} + k_{12}k_{32} + k_{21}k_{32})]^{1/2} \quad (11)$$

The general equations 1–6 cannot be conveniently solved for the rate constants explicitly. However, when the proper values of the rate constants are used

in the general equations, the calculated values of  $[A_1]$ ,  $[A_2]$ , and  $[A_3]$  will agree with the experimentally determined values.

We have defined a new function,  $\sigma$  (eq 12), as the sum of the square of the differences between the experimental concentrations and the calculated values using the general equations (for the appropriate case) for given values<sup>17</sup> of  $k_{12}$ ,  $k_{23}$ ,  $K_{12}$ , and  $K_{23}$  summed over the three concentrations ( $i = 1 \rightarrow 3$ ) for each data point ( $t = 1 \rightarrow N$ ).

$$\sigma = \sum_{t=1}^N \sum_{i=1}^3 ([A_i]_{t, \text{calcd}} - [A_i]_{t, \text{obsd}})^2 \quad (12)$$

In general, for arbitrary values of the parameters  $k_{12}$ ,  $k_{23}$ ,  $K_{12}$ , and  $K_{23}$ ,  $\sigma$  will be a large number. However, when the proper values of these parameters are utilized so that the calculated values of  $[A_1]$ ,  $[A_2]$ , and  $[A_3]$  are in maximum agreement with the experimental values,  $\sigma$  will be minimized. In a typical calculation, a plausible range<sup>17</sup> of values of  $k_{12}$ ,  $k_{23}$ ,  $K_{12}$ , and  $K_{23}$  is chosen to generate a  $\sigma$  matrix and expanded about that point until  $k_{12}$ ,  $k_{23}$ ,  $K_{12}$ , and  $K_{23}$  have been determined to an adequate degree of precision. The values of these parameters which give rise to the smallest  $\sigma$  (*i.e.*, the most satisfactory agreement between the calculated and experimental values of  $[A_1]$ ,  $[A_2]$ , and  $[A_3]$ ) are chosen as the "best" values of the rate and equilibrium constants. A computer program has been written which generates the  $\sigma$  matrix for a range of values of the variables using the experimental data and the appropriate set of equations (case 1, 2, or 3) and iterates through three cycles of refinement.<sup>18,19</sup>

Table I lists the experimental concentrations and

TABLE I  
EXPERIMENTAL AND CALCULATED CONCENTRATIONS  
FOR THE ISOMERIZATION OF  
1-TRIMETHYLSILYLINDENE AT 185°

$t$ , min	$A_1^a$	$A_2$	$A_3$
0	0.0 (0.0) <sup>b</sup>	100.0 (100.0)	0.0 (0.0)
5	2.0 (1.5)	95.4 (96.3)	2.6 (2.2)
10	3.3 (3.0)	93.5 (92.9)	3.3 (4.1)
30	8.8 (8.0)	80.5 (82.3)	10.7 (9.7)
45	10.3 (11.0)	78.3 (76.7)	11.4 (12.3)
1335	30.9 (31.7)	54.3 (53.8)	14.8 (14.5)
3700	32.5 (31.7)	53.1 (53.8)	14.2 (14.5)

<sup>a</sup> Concentrations expressed as percentages of the total isomeric mixture. <sup>b</sup> Calculated values in parentheses.  $\sigma = 13.5$ .

the calculated values using the rate constants obtained by the  $\sigma$  method for a typical kinetic run. Inspection of the table reveals that the maximum difference between experimental and calculated values is less than the uncertainty in the experimental values.

The rate constants for the rearrangements of the

(17) At equilibrium  $K_{12} = [A_2]/[A_1] = k_{12}/k_{21}$  and  $K_{23} = [A_3]/[A_2] = k_{23}/k_{32}$ . The equilibrium constants  $K_{12}$  and  $K_{23}$  are chosen as variables rather than the two reverse rate constants ( $k_{21}$  and  $k_{32}$ ) since plausible ranges for these variables are readily obtained from the experimental data.

(18) The program, written in Fortran IV,<sup>19</sup> was run on a Raytheon 706 (16K) computer. A typical calculation, for which the ranges of  $k_{12}$  and  $k_{23}$  were initially chosen as  $10 \rightarrow 10^{-5} \text{ min}^{-1}$ , and  $K_{12}$  and  $K_{23}$  were varied  $\pm 25\%$  of their experimental values, required 12 min of computing time. For each cycle of refinement, the rate constants ( $k$ 's) were varied in eight increments and the equilibrium constants ( $K$ 's) in four increments. After three cycles the changes in the variables, the calculated concentrations, and  $\sigma$  were less than their respective uncertainties.

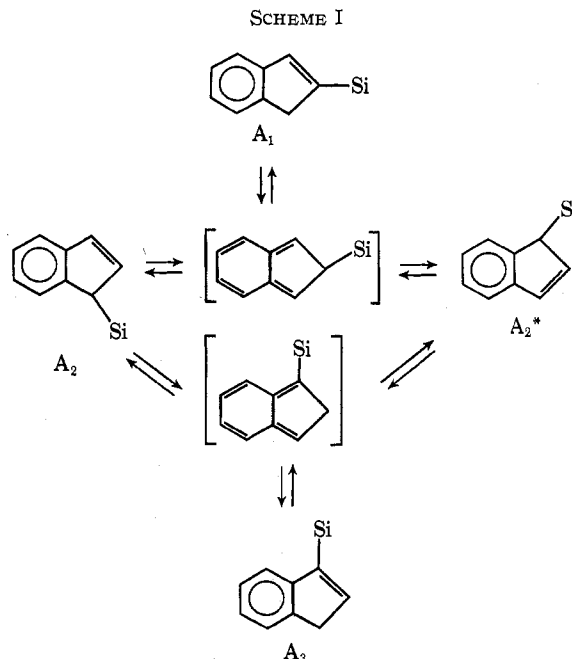
(19) A listing of the program is available from the authors.

silylindenes, as obtained by the  $\sigma$  method, are presented in Table II. Consistent results were obtained for trimethylsilylindene on both neat samples and in diphenyl ether solution, using both the 1- and 2-isomers as starting materials. For comparison, the results for dimethylsilylindene are also included.

Arrhenius plots for the four rate constants were linear, and the activation parameters are given in Table III.

## Discussion

**Analysis of Results.**—The isomerization of trimethylsilylindene proceeds *via* a series of 1,2-hydrogen and silicon shifts as depicted in Scheme I. By this mecha-



nism the formation of  $A_3$  from  $A_1$  requires the initial formation of  $A_2$ , in agreement with the experimental results. The rates reported here are comparable in magnitude to those observed for isomerizations *via* 1,2-hydrogen shifts in organic substituted indenenes. For example, the rate<sup>10</sup> of isomerization of 1-phenylindene to 3-phenylindene is  $5.7 \times 10^{-5} \text{ sec}^{-1}$  at  $150^\circ$ , and 1-deuterioindene undergoes rearrangement at  $220^\circ$  in the gas phase with a rate constant<sup>20</sup> of  $7.6 \times 10^{-5} \text{ sec}^{-1}$ . All of the results on these and other systems are consistent with an *intramolecular* pathway for the rearrangements.<sup>21</sup>

The free energies of activation at  $200^\circ$  ( $\Delta G^\ddagger$ ) for the forward and reverse paths of the reaction  $A_1 \rightleftharpoons A_2$  were determined to be  $35.0 \pm 0.1$  and  $35.4 \pm 0.2$  kcal/mol, respectively, while for the reaction  $A_2 \rightleftharpoons A_3$  the values were  $36.0 \pm 0.2$  and  $32.6 \pm 0.3$  kcal/mol. Because of the narrow temperature range ( $\sim 50^\circ$ ) in which these rearrangements could be conveniently studied, the corresponding values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are

(20) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964).

(21) No hydrogen-deuterium scrambling was observed to occur during the reversible thermal isomerization of 1-deuterio-1,3-dimethylindene in neat samples or in diphenyl ether solution. The rate constants for the formation of the 2-deuterio isomer were determined to be  $5.9 \pm 0.9 \times 10^{-5} \text{ sec}^{-1}$  (neat) and  $4.9 \pm 1.0 \times 10^{-5} \text{ sec}^{-1}$  (diphenyl ether solution) at  $200^\circ$ . At  $170^\circ$  the rate constant was  $6.4 \pm 1.1 \times 10^{-5} \text{ sec}^{-1}$  (neat). The Arrhenius activation energy for this process was estimated to be  $30 \pm 2$  kcal/mol: A. Davison and P. E. Rakita, unpublished results.

TABLE II  
 RATE CONSTANTS FOR THE THERMOLYSIS OF 1-TRIMETHYLSILYLINDENE

$T, ^\circ\text{C}$	$k_{12}^a$	$k_{23}$	$k_{32}$	$k_{21}$	$(\sigma/3N)^{1/2}$
201	$9.9 \pm 1.0 \times 10^{-4}$	$3.1 \pm 0.4 \times 10^{-4}$	$12.4 \pm 4.1 \times 10^{-4}$	$5.1 \pm 1.0 \times 10^{-4}$	0.87 <sup>e</sup>
193 <sup>b</sup>	$3.2 \pm 0.5 \times 10^{-4}$	$1.2 \pm 0.3 \times 10^{-4}$	$4.8 \pm 1.8 \times 10^{-4}$	$1.7 \pm 0.5 \times 10^{-4}$	0.80
185	$9.1 \pm 0.9 \times 10^{-5}$	$7.7 \pm 1.1 \times 10^{-5}$	$2.9 \pm 0.9 \times 10^{-4}$	$5.3 \pm 1.1 \times 10^{-5}$	0.80
172	$8.6 \pm 1.1 \times 10^{-5}$	$5.2 \pm 0.4 \times 10^{-5}$	$1.5 \pm 0.5 \times 10^{-4}$	$6.0 \pm 1.1 \times 10^{-5}$	0.59
146	$3.5 \pm 0.2 \times 10^{-6}$	$7.5 \pm 0.8 \times 10^{-6}$	$2.8 \pm 0.8 \times 10^{-5}$	$2.3 \pm 0.3 \times 10^{-6}$	0.82
200 <sup>b,c</sup>	$7.0 \pm 0.4 \times 10^{-4}$	$2.5 \pm 0.5 \times 10^{-4}$	$11.5 \pm 4.4 \times 10^{-4}$	$4.6 \pm 0.7 \times 10^{-4}$	0.81
200 <sup>b,d</sup>	$5.3 \pm 0.5 \times 10^{-4}$	$2.2 \pm 0.5 \times 10^{-4}$	$6.9 \pm 1.1 \times 10^{-4}$	$3.4 \pm 0.7 \times 10^{-4}$	0.67

<sup>a</sup> Rate constants in  $\text{sec}^{-1}$ . <sup>b</sup> Diphenyl ether solution. <sup>c</sup> Starting with 2-trimethylsilylindene. <sup>d</sup> Starting with 2-dimethylsilylindene. <sup>e</sup> Rms deviation per data point.

 TABLE III  
 ACTIVATION PARAMETERS FOR THE THERMOLYSIS  
 OF 1-TRIMETHYLSILYLINDENE

Reaction	$\Delta G^\ddagger$ , kcal/mol <sup>a</sup>	$\Delta H^\ddagger$ , kcal/mol <sup>b</sup>	$\Delta S^\ddagger$ , eu <sup>c</sup>	$E_a$ , kcal/mol	Log A
$A_1 \rightarrow A_2$	$35.0 \pm 0.1$	$37.1 \pm 4$	$+4.3 \pm 8$	38.0	14.4
$A_2 \rightarrow A_1$	$35.4 \pm 0.2$	$35.8 \pm 5$	$-0.4 \pm 10$	36.7	13.5
$A_2 \rightarrow A_3$	$36.0 \pm 0.2$	$24.3 \pm 4$	$-25.0 \pm 8$	25.2	8.0
$A_3 \rightarrow A_2$	$32.6 \pm 0.3$	$25.5 \pm 5$	$-19.6 \pm 10$	26.4	9.2

<sup>a</sup> Evaluated at 200° from the equation  $k = (kT/h) \exp(-\Delta G^\ddagger/RT)$ . <sup>b</sup>  $\Delta H^\ddagger = E_a - RT$  (at 200°). <sup>c</sup>  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ .

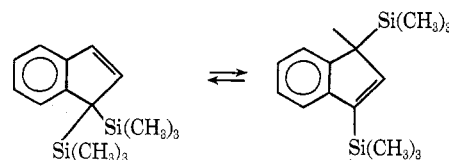
accompanied by relatively large uncertainties. Even allowing for these generous error limits, appreciable differences remain in the activation parameters for the two processes  $A_1 \rightleftharpoons A_2$  and  $A_2 \rightleftharpoons A_3$ . The former equilibrium ( $A_1 \rightleftharpoons A_2$ ) involves sequential hydrogen and silicon shifts, while the latter reaction ( $A_2 \rightleftharpoons A_3$ ) proceeds *via* two consecutive hydrogen shifts. In view of the similarity of the species involved in these two steps, the demonstrated *intramolecularity* of the rearrangement, and the similarity of these reactions to other studies of hydrogen and organosilicon shifts, it is presently unclear why such large differences should exist in the activation parameters.<sup>22</sup> We are not disposed to offer a rationalization for these results at this time.<sup>23</sup> For comparison, the fluxional trimethylsilyl rearrangement  $A_2 \rightleftharpoons A_2^*$  has an activation energy<sup>6</sup> of  $\sim 25$  kcal/mol and an entropy of activation of  $-3$  eu.

The small values of  $\Delta H$  and  $\Delta S$  for the positional isomers of trimethylsilylindenes are noteworthy in comparison with studies of related cyclopentadiene and indene systems. While the distribution of isomers of trimethylsilylcyclopentadiene<sup>4</sup> is the same as is found here (*i.e.*, 5-isomer > 1-isomer > 2-isomer), the equilibria are strongly temperature dependent. Moreover, the rates of rearrangement *via* hydrogen and silicon shifts<sup>3</sup> are several orders of magnitude higher than those observed here.

(22) Large negative entropies of activation have been reported for phenyl migrations in indenyl systems<sup>10</sup> where solvation of a polar transition state is presumed to be in part responsible. Similar anomalous activation parameters were noted for the fluxional rearrangements of some substituted (1,2,7-trihaptobenzyl)(pentahaptocyclopentadienyl) dicarbonyl compounds of molybdenum and tungsten: F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 1339 (1969).

(23) To ascertain the possible importance of the solvent in determining the activation parameters, a series of kinetic studies at 185° was carried out in various concentrations of diphenyl ether, decalin, and benzonitrile. In each case, except for the latter solvent, good agreement ( $\sigma_{\text{min}} < 3N$ ) was obtained between experimental and calculated concentrations. The small changes (<50%) in the rate constants with changes in concentration and solvent indicate that in solvents of low polarity medium effects are minimal. In all cases the equilibrium concentrations were in agreement with the values obtained on neat samples. Extensive decomposition, as evidenced by the appearance of additional signals in the trimethylsilyl region of the nmr spectrum, occurred in benzonitrile, which precluded meaningful rate studies. Studies currently in progress on related disubstituted systems should provide further information on the detailed mechanism of the rearrangement.

In the case of the methyl- and phenyl-substituted indenenes, whereas the rates of hydrogen migration are comparable to the values observed for the silylindenes, the product distributions at equilibrium overwhelmingly favor a single positional isomer (with the methyl or phenyl substituent(s) in the 2 and/or 3 position(s)).<sup>10</sup> In the only other silylindene system reported in the literature,<sup>6</sup> the temperature dependence of the equilibrium between 1,1-bis(trimethylsilyl)indene and 1,3-bis(trimethylsilyl)indene



gives  $\Delta H = 2.3 \pm 0.3$  kcal/mol and  $\Delta S = +6.6 \pm 0.1$  eu, but the rate constants for the rearrangement were not determined.

**The  $\sigma$  Method.**—The rate constants can be obtained in a straightforward manner directly from the experimental data by the  $\sigma$  method. The following points should be noted about the procedure. (1) No prior assumptions about the magnitude of the rate constants need be made (but see footnote 17). If the proper values of the variables are included in the initial ranges used in the calculation, a minimum  $\sigma$  value will appear within the matrix. If the proper values are outside the ranges, a minimum  $\sigma$  value will appear at an edge or corner.<sup>24</sup> (2) All of the data points are utilized for each calculation. The four variables ( $k_{12}$ ,  $k_{23}$ ,  $K_{12}$ , and  $K_{23}$ ) are determined using all three concentrations at each time interval. (3) The complete concentration expressions (for the appropriate case) are used without restrictive approximations.

The behavior of the  $\sigma$  surface near its minimum value determines the precision with which the four variables can be ascertained. Provided that  $\sigma$  is a sensitive and rapidly varying function of the variables, a well-defined and narrow minimum will appear in the  $\sigma$  surface (*i.e.*, a "pit" in the  $\sigma$  map). The function defined in eq 12 meets these criteria. Inspection of tabulated values from the  $\sigma$  matrix revealed that  $\sigma$  can be approximated by a parabolic function of each of the four variables in the neighborhood of  $\sigma_{\text{min}}$ . No relatively flat regions or multiple minima were encountered near  $\sigma_{\text{min}}$ , and convergence to the final values of the four parameters was independent of the initial values chosen.

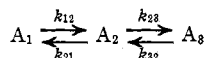
(24) The method of initial rates can be used for  $[A_1]$  to obtain an order of magnitude value of  $k_{12}$ . The relative sizes of  $k_{23}$  and  $k_{12}$  can be determined from the plot of  $[A_2]$  vs. time. If  $k_{12} > k_{23}$  then  $[A_2]$  will go through a maximum. If  $k_{12} < k_{23}$ ,  $[A_2]$  will approach a maximum value as  $t \rightarrow \infty$ . See, *e.g.*, T. M. Lowry and W. T. John, *J. Chem. Soc.*, **97**, 2634 (1910).

The error limits reported in Table II represent the ranges of the variables for which  $\sigma_{\min} < 1.5\sigma_{\min}$ . In all cases  $1.5\sigma_{\min} \leq 3N$  where  $N$  = number of data points (eq 12). Excellent agreement between the calculated and experimental concentrations could be obtained provided this criterion was met. By contrast, calculations for which  $\sigma_{\min} > 3N$  were found to be relatively insensitive to large changes in the variables, exhibiting little or no change in either  $\sigma_{\min}$  or the calculated concentrations. These situations arose when the experimental data contained large uncertainties. Thus, a useful empirical criterion for the reliability of the calculated rate constants appears to be  $\sigma_{\min} < 3N$ .

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#### Appendix

Case 2:  $A00 = A_2 = 100\%$ ,  $A_1 = A_3 = 0$  at  $t = 0$



$$d[A_1]/dt = k_{21}[A_2] - k_{12}[A_1]$$

$$d[A_2]/dt = k_{12}[A_1] - (k_{21} + k_{23})[A_2] + k_{32}[A_3]$$

$$d[A_3]/dt = k_{23}[A_2] - k_{32}[A_3]$$

Replacing  $d/dt$  by the operator  $P$  and recalling that at  $t = 0$ ,  $[A_2] = A00$

$$P[A_1] = k_{21}[A_2] - k_{12}[A_1]$$

$$P[A_2] - PA00 = k_{12}[A_1] - (k_{21} + k_{23})[A_2] + k_{32}[A_3]$$

$$P[A_3] = k_{23}[A_2] - k_{32}[A_3]$$

Solving these in succession gives

$$[A_1] = \frac{k_{21}A00(P + k_{32})}{(P + \gamma_1)(P + \gamma_2)}$$

$$[A_2] = \frac{A00(P + k_{32})(P + k_{12})}{(P + \gamma_1)(P + \gamma_2)}$$

$$[A_3] = \frac{k_{23}(A00)(P + k_{12})}{(P + \gamma_1)(P + \gamma_2)}$$

where  $\gamma_1$  and  $\gamma_2$  are the roots of the quadratic equation

$$\gamma^2 + \gamma(k_{12} + k_{23} + k_{21} + k_{32}) + k_{12}k_{23} + k_{32}k_{21} + k_{12}k_{32} = 0$$

Transforming to the originals (ref 13, eq 8, 12, and 8) gives

$$\begin{aligned} [A_1] &= \text{eq 4} \\ [A_2] &= \text{eq 5} \\ [A_3] &= \text{eq 6} \end{aligned}$$

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## Organoantimony Compounds. VI.<sup>1</sup> Oxybis(triorganoantimony) Diperchlorates and Their Complexes with Oxygen-Donor Lewis Bases

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Preparation and structural aspects of oxybis(triorganoantimony) diperchlorates  $(R_3Sb)_2O(ClO_4)_2$ , where  $R = Ph$  or  $Me$ , have been reinvestigated. Previously reported  $(Ph_3Sb)_2O(ClO_4)_2$  has been shown to be a hydrate. In contradiction to the conclusions reached in previous studies, the anhydrous diperchlorates are indicated to contain pentacoordinate antimony in the solid state. Complexes containing pentacoordinate cations  $[(R_3SbL)_2O]^{2+}$ , where  $L = DMA, DMSO, DPSO, pyO, Ph_3PO,$  and  $Ph_3AsO$ , have also been isolated and characterized by infrared spectroscopic and conductance measurements.

### Introduction

Preparation and infrared spectra of oxybis(triorganoantimony) diperchlorates<sup>2,3</sup>  $(R_3SbOSbR_3)(ClO_4)_2$ , where  $R = Me$  or  $Ph$ , were reported a few years ago. On the basis of the ir spectroscopic data,<sup>2,3</sup> in the solid state, these compounds were considered to contain the cation  $(R_3SbOSbR_3)^{2+}$ . Recent studies on the analogous oxybis(triphenylbismuth) diperchlorate<sup>4</sup> showed that this compound exists in two forms, hydrated and anhydrous. The hydrated form is orthorhombic and appears to contain the dihydrated cation  $[(Ph_3Bi)_2O(OH_2)_2]^{2+}$ . The anhydrous form is monoclinic and its

ir spectrum indicated a nonionic structure. A subsequent single-crystal X-ray diffraction study<sup>5</sup> has now confirmed that in the anhydrous compound the perchlorates are coordinated to bismuth atoms and that each bismuth atom has a slightly distorted trigonal-bipyramidal configuration. Since the perchlorate ir frequencies reported for the oxybis(triphenylantimony) diperchlorate in the previous work<sup>2</sup> were similar to those observed for the hydrated oxybis(triphenylbismuth) diperchlorate,<sup>4</sup> it led us to believe that the previously reported ir data<sup>2</sup> were obtained on the hydrated species. We, therefore, reinvestigated the preparation and structural aspects of oxybis(triphenylantimony) diperchlorate and our results show that the previously reported ir spectrum<sup>2</sup> is in fact due to the hydrated species and

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