Organometallics **1989,** *8,* 168–175

Kinetics and Mechanism of the Thermal Decomposition of (*E*)- and (*Z*)-1,1,2,3-Tetramethylsiletane

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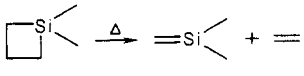
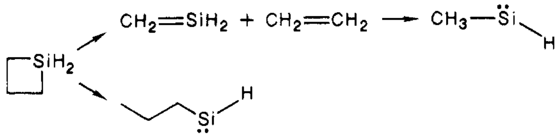
Received April 11, 1988

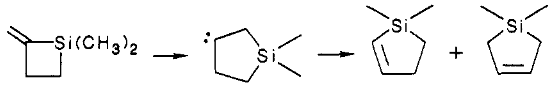
The synthesis of (*E*)- and (*Z*)-1,1,2,3-tetramethylsiletanes is described. Pyrolysis of either isomer at 398.2 °C provides the same products but in different amounts: propene, (*E*)- and (*Z*)-2-butene, allylethyldimethylsilane, dimethylpropylvinylsilane, the respective geometric isomers, 1,1,2,3,3-pentamethyl-1,3-disiletane, 1-ethyl-1,1-dimethyl-2-vinyl-2,2-dimethyldisilane, and (*E*)- and (*Z*)-1,1,2,3,3,4-hexamethyl-1,3-disiletane. Mechanisms involving di- and trimethylsilenes are described for disilane formation, and rate constants of the elementary steps for the fragmentation reactions are reported. The stereochemistry of the 2 + 2 fragmentation exhibits a fivefold preference for retention in the 2-butene fragment for both isomers. A thermochemical analysis suggests that the stabilizing influence of a silicon atom directs the initial site of ring opening exclusively to the carbon–carbon bond of 1,1-dialkylsiletanes.

The earliest suggestion that silenes are the primary reactive intermediates from the gas-phase thermal decomposition of siletanes is well-supported in the chemical trapping[1] and kinetic studies[1] of Gusel'nikov and coworkers. Variation of substituents on the silicon atom in the four-membered ring has permitted a survey of the reactivity of a large number of silenes formed in the 2 + 2 cycloreversion of the appropriately substituted siletane.[3]



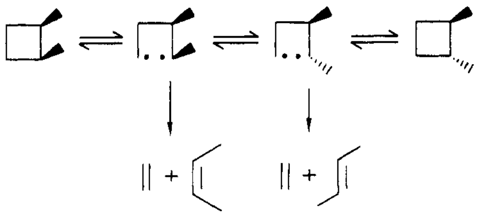
In only two cases have significant mechanistic departures from thermal reactions of analogous hydrocarbons been reported for these siletanes. In the first, Barton and Davidson[4] uncovered a minor pathway for the decomposition of hydridosiletanes, an α-hydrogen migration to the adjacent ring methylene. This competes with the major pathway,[5] fragmentation to hydridosilenes which thermally isomerize to methylsilylenes (eq 1).[6] In the other, Conlin, Huffaker, and Kwak found that 2-methylene-1,1-dimethylsiletane thermally ring expands with almost no fragmentation to allene and 1,1-dimethylsilene (eq 2).[7]


(1)


(2)

A probable first step in the two atypical ring openings involves cleavage of a silicon–carbon bond in conjunction with additional molecular reorganization. In these examples, the original carbon–carbon bonds appear to remain intact until secondary processes lead to stable products. For the more typical cycloreversion, however, the results of Barton,[8] Sommer,[9] and Weber[10] suggest that carbon–carbon breaking precedes cleavage of the silicon–carbon bond in 2-methyl- or 2-phenylsiletanes.

The prevailing notion that 1,4-biradicaloids are transients in the 2 + 2 fragmentation of most four-membered rings is based on analysis of the stereochemistry of the reactants and products. This hypothesis has had substantial support from both experiment and theory.[11] Loss of reactant stereochemistry can be rationalized by rotational processes in the diradical which compete effectively with the β-scission and recyclization steps. The stereochemistry of a 1,4-diyl, perturbed by a heavier atom such as silicon, has not been studied. However, the magnitude of stabilization of such radical centers either α[12] or β[13,14] to a silicon atom has recently been reported and provides useful insight to the interpretation of the work described here.



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† University of North Texas.

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(1) Nametkin, N. S.; Gusel'nikov, L. E.; Ushakova, R. L.; Vdovin, V. M. *Dokl. Akad. Nauk SSSR* **1971**, *201*, 1365.

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(3) (a) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (b) Michl, J.; Rabbe, G. *Chem. Rev.* **1985**, *85*, 419.

(4) Davidson, I. M. T.; Fenton, A.; Ijadi-Maghsoodi, S.; Scampton, R. J.; Auner, N.; Grobe, J.; Tillman, N.; Barton, T. J. *Organometallics* **1984**, *3*, 1593. The activation parameters for this rearrangement have recently been determined: Barton, T. J.; Timmons, N. *J. Am. Chem. Soc.* **1987**, *109*, 6711.

(5) (a) Conlin, R. T.; Wood, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 1843. (b) Conlin, R. T.; Kwak, Y.-W. *Organometallics* **1984**, *3*, 918.

(6) Conlin, R. T.; Kwak, Y.-W. *J. Am. Chem. Soc.* **1986**, *108*, 834.

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(8) Barton, T. J.; Marquardt, G.; Kilgour, J. A. *J. Organomet. Chem.* **1975**, *85*, 317.

(9) Golino, C. M.; Bush, R. D.; On, P.; Sommer, L. H. *J. Am. Chem. Soc.* **1975**, *95*, 1957.

(10) Valkovich, P. B.; Ito, T. I.; Weber, W. P. *J. Org. Chem.* **1974**, *39*, 3543.

(11) The pertinence of the role diradicals in the course of thermal rearrangements of small rings remains questionable. The problem has been discussed in many reviews. See: Dervan, P. B.; Dougherty, D. A. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 107–151.

(12) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(13) Conlin, R. T.; Kwak, Y.-W. *Organometallics* **1986**, *5*, 1205.

(14) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207.

(15) Ikan, R.; Gottlieb, R. *Synth. Commun.* **1973**, *3*, 407.

(16) Magid, R. M.; Fruchey, O. S.; Johnson, W. L.; Allen, T. G. *J. Org. Chem.* **1979**, *44*, 359.

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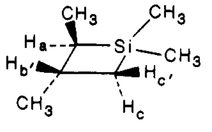
Table I. Optimized Rate Constants for the Thermal Decomposition and Isomerization of (*E*)- and (*Z*)-1 at 398.2 °C

(*Z*)-1 step[a]	*k* (s^{-1})	uncertainty	(*E*)-1 step[a]	*k* (s^{-1})	uncertainty
1	1.30×10^{-4}	±5%	5	2.40×10^{-5}	±15%
2	3.00×10^{-5}	±6%	6	1.45×10^{-5}	±6%
3	6.92×10^{-6}	±12%	7	2.50×10^{-6}	±12%
4	5.38×10^{-4}	±3%	8	1.60×10^{-4}	±3%
4a	4.63×10^{-4}	±3%	8a	1.34×10^{-4}	±5%
4b	5.58×10^{-5}	±7%	8b	2.14×10^{-5}	±10%
4c	1.86×10^{-5}	±16%	8c	4.99×10^{-6}	±30%
overall	7.05×10^{-4}	±2%	overall	2.01×10^{-4}	±2%

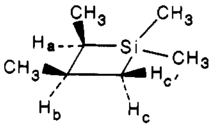
[a] $k_4 = k_{4a} + k_{4b} + k_{4c}$ and $k_8 = k_{8a} + k_{8b} + k_{8c}$.

Results

Synthesis of (*Z*)- and (*E*)-1,1,2,3-Tetramethylsiletane (1). The required compounds were prepared by the sequence of hydrosilylation and ring closure. The first attempts at the synthesis, chloroplatinic acid catalyzed addition of a silicon–hydrogen bond to 3-bromo-2-methyl-1-butene,[15] were unsuccessful due to the rapid loss of HBr from the allylic position. Hydrosilylation of the corresponding 3-chloro-2-methyl-1-butene[16] with dimethylchlorosilane, however, provided (3-chloro-2-methylbutyl)dimethylchlorosilane in high yield (>85%). Ring closure to a mixture of *E* and *Z* isomers of 1,1,2,3-tetramethylsiletane (1) was accomplished with either Na/K in xylene (45% yield) or Mg in THF (70%). The ratios of *E* to *Z* products were similar for both metal/solvent systems: 1.5 with NaK/xylene and 1.3 with Mg/THF, the latter method preferred.[17] The structures of 1 are based on spectroscopic data including NMR, IR, and mass spectra and elemental analysis as described in the Experimental Section.



(*E*)-1



(*Z*)-1

The configurations of the two four-membered rings were determined from proton and carbon NMR spectra. In the proton spectra of the diastereomers, $H_{b'}$ of the *E* isomer is significantly more shielded than H_b of the *Z* isomer (i.e. δ 1.74 and 2.51, respectively). This interaction in a four-membered ring between a hydrogen and a vicinal cis methyl group, as in (*E*)-1, has been described previously in the assignment of configurations to the isomeric 2,3-dimethyloxetanes.[18] In addition to the proton spectra, carbon NMR provides features that also characteristically distinguish between cis- and trans-substituted four-membered rings. For example, the methyl chemical shifts of (*Z*)-1 are found further upfield, 9.23 and 19.18 ppm, than the corresponding positions of the methyl shifts observed for the (*E*)-1, 13.46 and 24.06 ppm. Examples of shielding of the methyl groups in the *Z* isomer relative to the *E* isomer are known for 2,3-dimethyloxetane[18] (δ 13.0 and 16.9: δ 17.5 and 22.8, respectively) and for (*Z*)- and (*E*)-1,2-dimethylsiletane[19] (δ −7.0 and 15.6: δ −2.3 and 17.3, respectively).

Pyrolysis Product Distribution. Both (*E*)- and (*Z*)-tetramethylsiletane isomers, when pyrolyzed separately at 398.2 °C provide the same products. The quantitative distributions, although differing slightly from one isomer to the other, fall within the following ranges: propene (3) (+1,1,2-trimethylsilene), 65–75%; (*Z*)- and (*E*)-2-butenes (2 and 4, respectively) (+1,1-dimethylsilene), 4–10%; allylethyldimethylsilane (5), 7–12%; dimethylpropylvinylsilane (6), 2–4%; and geometric isomerization, which is variable according to starting isomer and reaction time (but does not exceed 19% in any case). Silene formation was confirmed by the presence of the following dimers (disilanes): 1,1,2,3,3-pentamethyl-1,3-disiletane (7), 2–3%; 1,1,1-ethyldimethyl-2,2,2-vinyldimethyldisilane (8), 1%; and (*E*)- and (*Z*)-1,1,2,3,3,4-hexamethyl-1,3-disiletanes (9 and 10, respectively) 16–18% and 9–11%, respectively. Although quantitative agreement is not exact, the yields and distributions of these dimers are in reasonable accord with expectations based on the alkene yields. In addition to these products, gas chromatograms showed the presence of several other small peaks at the less than 1% level, indicating considerable minor product complexity. When pyrolyzed with the presence of added air, the amounts of some of these minor products increased significantly, suggesting that some at least may result from reaction with traces of oxygen in the system. For those products associated with the major pathways, detailed quantitative yields are given in Tables VIII and IX in the Experimental Section. For the products monitored, these yields correspond to the following (observed) percentage distributions:

	product				
reactant	3	2 + 4	5	6	isomer
(*Z*)-1	66.7 ± 2.2	5.4 ± 0.9	8.1 ± 0.5	3.0 ± 0.6	16.9 ± 2.2
(*E*)-1	72.4 ± 3.6	9.3 ± 1.0	10.4 ± 1.5	2.6 ± 0.9	5.6 ± 5.1

These distributions cover conversions up to 70% in the case of (*Z*)-1 and 86% in the case of (*E*)-1. In the case of (*Z*)-1 the distribution appears to be nearly time invariant, but for (*E*)-1 it definitely is not. The proportion of the geometric isomer (i.e. (*Z*)-1) is initially high (ca. 12%) but falls to low values (<1%) at high conversions as a result of its greater thermal instability. This causes the other products (apparently) to increase in proportion with increasing conversion. The figures for (*E*)-1 are further distorted by difficulties in analysis for 5 and 6 at low conversion. This results in a slight overestimate of the average percentages of other products.

Measurements of the proportions of (*Z*)- and (*E*)-2-butenes (2 and 4, respectively) indicate predominant retention of stereochemistry in these decompositions. Starting from (*Z*)-1, the 2-butene is 79 ± 3% 2 up to 50% decomposition. Starting from (*E*)-1, the 2-butene is 85 ± 3% 4 up to 70% decomposition. In both cases there is a trend toward lower percentages with increasing conversion. Diastereomeric 2-butenes were stable under the conditions of these experiments.

Kinetic Analysis. The complexity of this system with its many products and simultaneous interconversion and decomposition of both starting isomers led us to adopt an approach of kinetic modeling rather than an oversimplified

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(17) Ratios of *E*/*Z* products were variable in the course of several Mg/THF ring closure reactions.

(18) Ewing, D. F.; Holbrook, K. A.; Scott, R. A. *Org. Magn. Reson.* **1975**, *7*, 554.

(19) McFinnie, B. G.; Bhacca, N. S.; Cartledge, F. K.; Fayssoux, J. *J. Am. Chem. Soc.* **1974**, *96*, 2637.

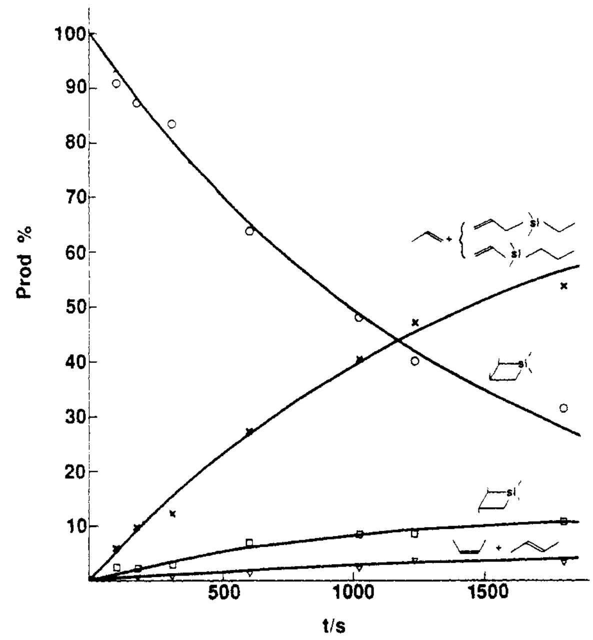
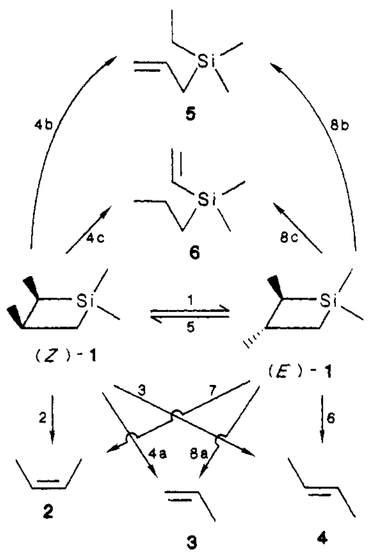


Figure 1. Product distribution in pyrolysis of (*E*)-1 at *T* = 398.2 °C.

Scheme I



fitting to logarithmic (i.e. first order) decay plots. In this approach the coupled first-order rate processes of Scheme I were integrated by using a numerical integration routine which calculates the product distribution from either isomer as a function of time using a trial set of rate constants.[20] At each time of interest, comparison can be made with the experimental product distribution. Rate constants were then adjusted and the calculations repeated until the differences between calculated and observed product distribution were minimized. The final values for the rate constants are shown in Table I.

The fitting routine does not contain sensitivity analysis, and so the uncertainties represent an eyeball assessment of the limits of the fit; i.e. they attempt to take account of scatter in the data. They do not incorporate systematic uncertainties (such as analytical calibration errors), and to that extent are probably an underestimate. The data fit is shown in Figures 1–3, which show respectively the decomposition data of (*Z*)-1, (*E*)-1 via the major pathways and the extent of loss of stereolabel in the product 2-butenes. The solid lines appearing in each of the three figures are the calculated values. Noteworthy features, apart from the general quality of the fit, are (i) the expected observation of a maximum in (*Z*)-1 during decomposition of (E)-1 (Figure 2) and (ii) predicted changes in the ratios of the 2-butenes with time resulting from secondary decomposition of the stereoisomer of the starting compound in each case (Figure 3). This latter effect is more marked in the case of the decomposition of (*E*)-1.

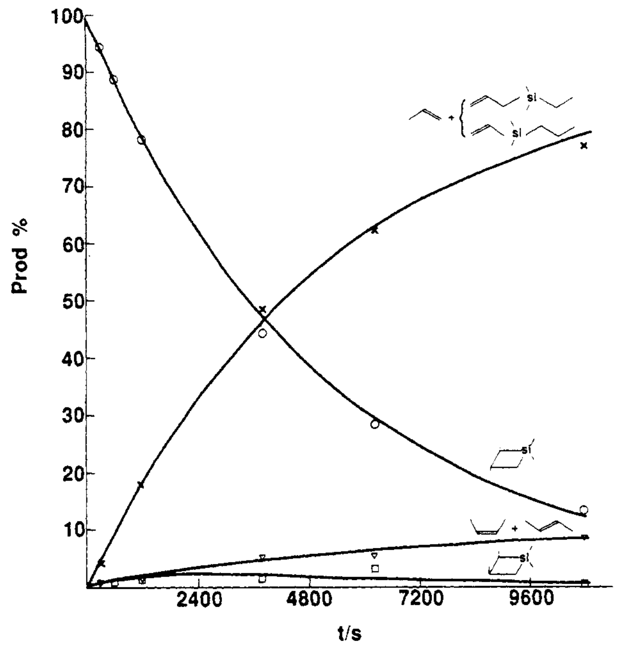


Figure 2. Product distribution in pyrolysis of (*Z*)-1 at *T* = 398.2 °C.

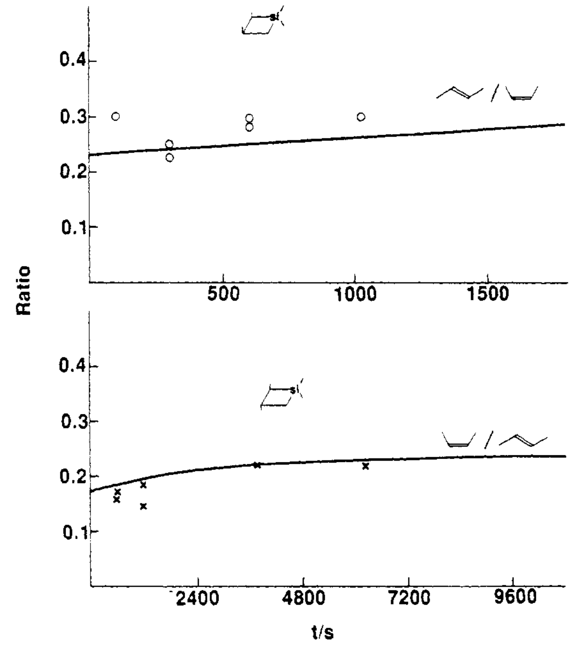


Figure 3. Butene ratios in 1,1,2,3-tetramethyl-1-siletane pyrolysis at *T* = 398.2 °C.

Discussion

General Information. The modeling accounts for the observed variations in product distribution with time, particularly in the case of (*E*)-1. The rate constants of Table I permit a more sharply defined analysis than that

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[20] Gear, C. W. In *Information Processing*; Morrell, Ed.; North Holland: Amsterdam, 1968, Vol. 1, p 187.

Table II. Analysis of Pathways in the Thermal Decomposition of (*E*)- and (*Z*)-1 at 398.2 °C

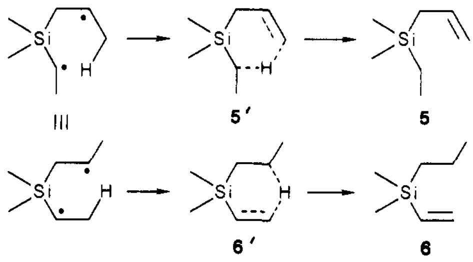
pathway	(*Z*)-1 (%)	(*E*)-1 (%)
fragmentations		
total	70.9	75.0
propene	65.7	66.5
2-butenes	5.2	8.5
isomerizations		
total	29.1	25.0
geometric	18.4	11.9
structural	10.6	13.1

based on product studies alone. Table II shows the breakdown of pathways for each compound. In spite of the fact that (*Z*)-1 decomposes 3.5 times faster than (*E*)-1, the pattern of decomposition is fairly similar in both cases. Given the uncertainties in rate constant values, a complete mechanistic interpretation is held in abeyance. The greater extent of geometric isomerization of (*Z*)-1 is understandable in terms of relief of repulsion due to cis-vicinal methyl groups in the four-membered ring. Clearly, however, this is not substantial enough to prevent formation of any (*Z*)-1 from (*E*)-1. If geometric isomerization is left out of consideration, the remaining pathway proportions from each compound become closer still.

Fragmentation. Fragmentation is dominated by propene formation. Clearly the site of methyl substitution dictates predominant fission at the most highly substituted C–C bond. Methyl group interaction in (*Z*)-1, while obviously affecting the overall rate, does not appear to lead to significant differences in the major fragmentation pathway. Analysis of the minor 2-butene formation pathway is hampered by the higher uncertainties associated with lower yields. Thus it is not clear why the relative yield of 2-butenes should be higher from (*E*)-1 than (*Z*)-1. It is possible that this might be indirectly associated with the lower stability of (*Z*)-1. Thus for both (*E*)-1 and (*Z*)-1 this pathway involving cleavage of the least substituted C–C bond should be relatively immune to the methyl group interactions relieved in the major fragmentation. In that case, if these effects enhance all the pathways for (*Z*)-1 except minor ones, 2-butene formation will be lower for (*Z*)-1 than (*E*)-1. The stereospecificity of 2-butene formation is obtained by either extrapolation of the ratio to zero conversion or consideration of the appropriate ratios of the model. For (*Z*)-1, $k_2/k_3 = 4.3$ (±0.5), and for (*E*)-1, $k_6/k_7 = 5.8$ (±0.7). Stereoretention is high in both cases indicating that second bond breaking (Si–C bond) competes effectively with bond rotation, if a diradical intermediate is assumed (see later).

Structural Isomerization. Structural isomerization is known to occur in the pyrolyses of 1,1,2-trimethylsiletane (11)[8] and 1,1,3-trimethylsiletane (12).[21] Migration of a hydrogen from an exocyclic methyl group on carbon to an α- or β-ring carbon produces the products ethyldimethylvinylsilane (10%)[8] and allyltrimethylsilane (20%),[21] respectively. Similarly, we observe allylethyldimethylsilane (5) and dimethylpropylvinylsilane (6) by analogous pathways in both (*E*)- and (*Z*)-1 pyrolyses. The major acyclic isomer is 5 as might be expected from the product yields in the trimethylsiletane pyrolyses mentioned above. Within experimental error, the ratio 5:6, 3.6, is the same for both (*E*)- and (*Z*)-1 although the modeling suggests a slightly higher value for (*E*)-1. No significance should, however, be attached to this because of the analytical difficulties already cited.

Scheme II



Scheme III

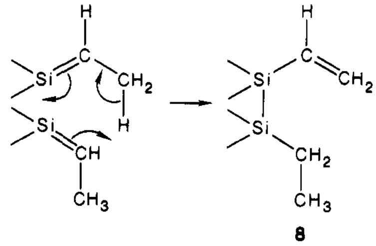


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Table III. Kineics of Pathways for Decomposition of (*E*)- and (*Z*)-1,2-Dimethylcyclobutane[27]

reactant	product	log *A* (s^{-1})	E_a (kcal mol^{-1})	10^5k (s^{-1}) (398.2 °C)	%
(*Z*)-15	$2C_3H_6$	15.48	60.4	6.60	69
	$C_4H_8 + C_2H_4$	15.57	63.0	1.16	12
	(*E*)-15	14.81	60.1	1.77	19
	butene stereochemistry: $E/Z \simeq 0.56$ (14% conversion)				
(*E*)-15	$2C_3H_6$	15.45	61.6	2.50	70
	$C_4H_8 + C_2H_4$	15.46	63.4	0.665	19
	(*Z*)-15	14.57	61.3	0.413	12
	butene stereochemistry: $Z/E \simeq 0.13$ (14% conversion)				

The total yield of structural isomers is slightly lower for (*E*)- and (*Z*)-1 than for the trimethylsiletanes. It has been claimed in the kinetic study of 1,1,3-trimethylsiletane[21] that the ratio of isomerization to fragmentation products remained constant from 380 to 420 °C. In the present case, temperature variation studies have not been carried out. Nevertheless it appears likely that previously proposed[22] six-membered ring transition states requiring cleavage of the more substituted C–C bond are involved as shown in Scheme II. One possible explanation for preference of 5 over 6 may be the extra stability (and therefore lower reactivity) of the radical center β to the silicon compared to that α to silicon (see later).

Dimerization. The formation of propene with the accompanying 1,1,2-trimethylsilene (13) and butene with 1,1-dimethylsilene (14) from 1 is indicated by the near statistical distribution of silene dimers 7–10. The absence of 1,1,3,3-tetramethyl-1,3-disiletane is likely due to the low concentration of 14. The disiletanes 9 and 10 are produced by the "normal" head to tail dimerization.[22]

The product 1-ethyl-1,1-dimethyl-2-vinyl-2,2-dimethyldisilane (8) is interesting. Recently, Brook has described a variety of stabilized 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)silenes, which dimerize to 1,2-disilacyclobutanes, in head to head fashion.[23] The resulting 1,1,2,2,3,4-hexamethyl-1,2-disiletane, by analogy to the octamethyl-1,2-disiletane,[24] would be expected to yield the acyclic disilane 8.[25] Another possible mechanism, not

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[21] Gusel'nikov, L. E.; Nametkin, N. S.; Dogopolov, N. N. *J. Organomet. Chem.* **1979**, *169*, 165.

[22] Gusel'nikov, L. E.; Konobeeveskii, V. M.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akademii Nauk SSSR* **1977**, *235*, 791.

[23] Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.

[24] Davidson, I. M. T.; Ostah, N. A.; Seyferth, D.; Duncan, D. P. *J. Organomet. Chem.* **1980**, *187*, 297.

Table IV. Ratios of Fragmentation Pathways in (*E*)- and (*Z*)-1 Compared with (*E*)- and (*Z*)-15

ratio[a]	(*Z*)-1	(*E*)-1	(*Z*)-15	(*E*)-15
propene/2-butenes	12.5	7.9	5.8	3.7

[a] In the cases of (*E*)- (*Z*)-15, propene yields are halved to take account of reaction symmetry.

Table V. Comparison of 2-Butene Stereochemistry Resulting from the Decomposition of (*Z*)-1, (*Z*)-15, (*E*)-1, and (*E*)-15

product ratio	(*Z*)-1	(*Z*)-15	product ratio	(*E*)-1	(*E*)-15
(*E*)-2-butene/ (*Z*)-2-butene	0.23 ± 0.05	0.56	(*Z*)-2-butene/ (*E*)-2-butene	0.16 ± 0.03	0.13

Table VI. Kinetic Parameters and Relative Rate Constants for Decomposition of Selected Siletanes

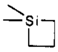
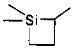
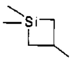
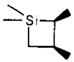
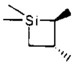
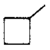
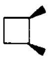
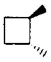
molecule	log *A* (s^{-1})	E_a (kcal mol^{-1})	10^4k (s^{-1}) (398.2 °C)	rel rate	ref
	15.64	62.5	0.20	1	2, 35
	15.45	60.6	0.53	2.7	30
	16.39	63.3	0.62	3.1	21
			7.00	35	this work
			1.97	10	this work

Table VII. Kinetic Parameters and Relative Rate Constants for the Decomposition of Selected Cyclobutanes

molecule	log *A* (s^{-1})	E_a (kcal mol^{-1})	10^4k (s^{-1}) (398.2 °C)	rel rate	ref
	15.6	62.5	0.18	1	34
	15.64	62.0	0.29	1.6	36
	15.68	61.0	0.67	3.7	37
	15.68	60.8	0.78	4.3	27
	15.67	62.0	0.31	1.7	27

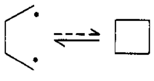
requiring the intervention of a 1,2-disiletane, is that 1,1,2-trimethylsilene (13) undergoes a bimolecular "ene" reaction with itself to produce 8 in a single step (Scheme III).[26]

Comparison with Other Four-Membered-Ring Pyrolyses. Comparison of (*E*)- and (*Z*)-1 to hydrocarbon analogues (*E*)- and (*Z*)-1,2-dimethylcyclobutanes (15) is instructive. The relative product distributions from the decomposition of (*E*)-1 and (*Z*)-1,2-dimethylcyclobutane[27,28] at 398 °C, as calculated from the Arrhenius equation using the activation parameters, are given in Table III. In general the pattern of thermal decomposition is similar to that for the (*E*)- and (*Z*)-siletanes, methyl-labeled at C(2) and C(3).

The primary differences between the two are the following: (i) Both siletanes react faster than the corresponding hydrocarbons. (ii) Isomerization products via H-shift pathways occur only from the C-methylated siletanes, although the percentages of *E*/*Z* isomerization are almost identical for 1 and 15. (iii) Ring splitting across the more substituent C–C bond (i.e. propene formation) is the major fragmentation pathway for both isomers and is more dominant in the siletanes (Table IV). This may be a consequence of the slightly different nonbonded interactions present in cyclobutane and silacyclobutane. Since the C–C–C bond angle of the siletane ring is greater than of cyclobutane, the exocyclic methyl groups on C(2) and C(3) of the silacycle are expected to be in closer proximity. Relief of this additional strain might be expressed by the higher propene/butene ratio from the siletane. (iv) While differences in the stereochemistry of 2-butene formation are observed, they do not offer obvious or definitive mechanistic interpretation.[29] In all cases stereoretention is high, but, as shown in Table V, (*Z*)-1 provides relatively more stereoretention than (*Z*)-15, while (*E*)-1 gives similar stereoretention to (*E*)-15. In both Si and C ring systems, however, the trans isomer fragments with greater stereospecificity.

Table VI provides a comparison of kinetic parameters known for various di-, tri-, and tetramethyl-substituted siletanes. In Table VII, the same type of information is given for methylated cyclobutanes. Several salient features require comment: (i) In the series of dimethylsiletanes, one C-methylation in either the 2- or 3-position increases the rate of decomposition by a factor of approximately 3 relative to 1,1-dimethylsiletane (16). This rate enhancement is about twice that observed for methylcyclobutane. (ii) Surprisingly, a second *C*-methyl group accelerates decomposition by a factor of 35 for (*Z*)-1 and 10 for (*E*)-1. In contrast, the effect of two vicinal methyl groups on cyclobutane is significantly smaller. (iii) Nevertheless, the same trend favoring faster reaction of the *Z* isomer relative to the *E* isomer is observed for both the siletane (3.5) and the hydrocarbon (2.5). These enhanced methyl substituent effects suggest greater transition-state stabilization for the siletanes.

Thermochemistry. Thermochemical kinetics with its explicit assumptions provides a valuable method of focusing thermodynamic data on problems in kinetics.[31] As a reference point, the well-known fragmentation of cyclobutane, considered here as a hypothetical biradical process, is compared to that of dimethylsiletane.



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[25] The possibility of a 1,2-disilacyclobutane or a 1,4-biradical containing a silicon–silicon bond as a precursor for the formation of 8 from dimerization of 13 has been considered recently. Yeh, M. H.; Linder, L.; Hoffman, D. K.; Barton, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7849. Unlike Barton and co-workers, we do not observe the isomerization of 13 in our experimental conditions: lower temperature and higher silene concentration.

[26] The mechanistic description was originally proposed as an alternative to the thermal hydrosilylation of a silene. Jones, M., Jr.; Coleman, B. *Rev. Chem. Intermed.* **1981**, *4*, 297.

[27] Gerberich, H. R.; Walters, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 3935, 4884.

[28] Wang, Y.-S.; Chickos, J. S. *J. Org. Chem.* **1987**, *52*, 4777.

[29] In early experiments on the pyrolysis of (*E*)- and (*Z*)-1 (the first twenty-some pyrolyses in a new quartz reaction vessel), retention of stereochemistry in the butene fragment was very high (>95%). Although rate constants for decomposition and for the extent of stereoretention from 1 were duplicated in a packed reaction vessel (increase in surface to volume of 12) and did not change with repeated seasoning of the reaction bulbs in both Denton and Reading, these unusual early results on butene stereochemistry could not be duplicated.

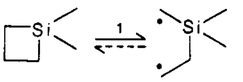
[30] Arrhenius parameters for the decomposition of 1,1,2-trimethylsilacyclobutane have been reported by L. E. Gusel'nikov at the 8th International Symposium on Organosilicon Chemistry; St. Louis, MO, June 1987.

[31] Benson, S. W. *Thermochemical Kinetics*; Wiley-Interscience: New York, 1976.

The experimental enthalpy for ring opening of cyclobutane, $\Delta H°$, may be closely estimated by subtracting from the dissociation enthalpy of the central bond of *n*-butane (a model also producing two primary radical centers), the ring strain enthalpy of cyclobutane, i.e., $\Delta H° = D(\text{C-C}) - \text{ring strain}$. Substituting current values in the above,[32,33] we obtain $\Delta H°$ (kcal mol^{-1}) = 86.5 − 26.2 = 60.3. In comparison to the known experimental activation energy E_a = 62.5 kcal mol^{-1} [34] there is but a small difference, 2.2 kcal mol^{-1}, that is probably close to the size of the experimental error in the thermodynamic terms and might be attributed to the activation barrier for recombination of 1,4-diyl centers.

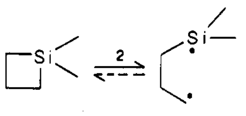
The circumstances of dimethylsiletane decomposition are complicated by two possible sites of initial ring opening, the silicon–carbon or carbon–carbon bond. From study of the thermolysis of 1,1,2-trimethylsilatane where a methyl label on the 2-carbon atom was used as a mechanistic probe, Barton et al.[8] concluded that carbon–carbon cleavage is the main reaction path producing the isolated silene reaction products. Our thermochemical analysis, therefore, seeks (i) to check whether biradical formation resulting from fragmentation of a C–C bond has a significant energetic advantage over that for an Si–C bond and (ii) to verify that the energy involved closely parallels the experimental activation energy. For this purpose the prototype, dimethylsiletane itself,[2,35] is taken as the example.

The enthalpy change for C–C bond breaking is estimated as for the cyclobutane case but with extra allowance for the stabilization effects of the silicon atom on the developing α- and β-radical sites.



Recent experimental studies suggest that these α- and β-stabilization effects of silicon are 0.5[12] and 3.0[13,14] kcal mol^{-1}, respectively. An estimate of the ring strain for 1,1-dimethylsiletane of E_s = 22 ± 3 kcal mol^{-1} comes from the recent application of group additivity to organosilicon compounds.[38] Consideration of these factors in the equation above gives $\Delta H°$ (kcal mol^{-1}) = 86.5 − 22 − 3 − 0.5 = 61. The difference between the experimental E_a and this thermochemically derived value is 62.5 − 61 = 1.5 kcal mol^{-1}, in close parallel to the cyclobutane case. We note that the error limits of E_s exceed the size of ring closure barrier.

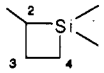
The enthalpy change for Si–C bond breaking is estimated as before.



In this case there are not thought to be any special interaction effects of silicon with the developing radical center. The appropriate model Si–C bond dissociation energy is $D(\text{Me}_3\text{Si-Et})$. This has not been measured directly, but from the group additivity estimate[38] for $\Delta H_f°(\text{Me}_3\text{SiEt})$ and known $\Delta H_f°$ values for SiMe_3[12] and C_2H_5,[33] we estimate $D(\text{Me}_3\text{Si-Et})$ = 87.2 kcal mol^{-1}. With the same strain energy, $\Delta H_2°$ (kcal mol^{-1}) = 87.2 − 22 = 65.2. Thus if this estimate is correct, it exceeds the experimental activation energy and effectively rules out initial cleavage at the Si–C bond.

Accepting, however, that some uncertainties attach to these numbers, a comparison of predicted rates can be made on the reasonable assumption that biradical formation would be rate determining. At 400 °C, a typical temperature for static pyrolyses, the ratio k_1/k_2 is approximated by $\exp(\Delta H_2 - \Delta H_1)/RT \approx 23$. At 700 °C, a temperature more typical of those used in flash vacuum pyrolyses $k_1/k_2 \approx 9$. Thus under both conditions, the thermochemistry supports the contention that fragmentation is initiated at the C-C bond in dimethylsiletane.

Although the effects of methyl groups on the ring breaking enthalpies associated with these two types of bond in siletanes are not known, the similarity of the Arrhenius parameters for 1,1,2- and 1,1,3-trimethylsiletanes suggests only small effects. Interestingly, these arguments, while supporting the conclusion of Barton et al.[8] that initial C–C cleavage represents the major reaction path for 1,1,2-trimethylsiletane, tend to point up the probability that the minor reaction path also occurs with initial C–C cleavage (at the less substituted C–C bond). Thus in the unsymmetrical 1,1,2-trimethylsiletane, $\text{C}_3\text{–C}_4$ fragmentation is still favored over Si–C_2 breaking.



With the conclusion that initial C–C bond breaking is dominant, the explanation for more marked methyl group substituent effects in siletanes as opposed to cyclobutanes becomes more elusive. Since the energetic advantage of C–C over Si–C bond breaking apparently derives in large part from the stabilization of the β-radical center by silicon, an explanation first offered by Barton et al.,[8] then the methyl groups may offer some small but subtle modifications (enhancement) to this interaction and also possibly to the α-interaction.[39]

The situation described above has additional experimental support when unsaturated carbon substituents such as phenyl and vinyl groups are placed on the 2- and 3-ring carbon atoms, respectively.[10,40] Product studies require no initial Si–C bond cleavage. In conclusion, there is little difference between the experimental activation energy and the thermochemical estimates of the energy for the fragmentation of 1,1-dimethyl-1-siletane. This situation resembles the case of cyclobutane. Although ΔH_{rxn} for fragmentation of siletanes to alkenes and silenes is much more endothermic than for cyclobutanes, curiously, the extent of stereochemical scrambling in the diyl is not significantly affected.

Experimental Section

General Data. Proton NMR spectra were recorded on a Hitachi Perkin-Elmer R24B 60-MHz spectrometer using meth-

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[32] For a discussion of the impact of upwardly revised heats of formation of alkyl radicals on cyclobutane pyrolysis, see: Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279.

[33] On the basis of original thermochemistry[31] apart from the revised of $\Delta H_f°(\text{C}_2\text{H}_5)$ = 28.2 kcal mol^{-1} from: Brouard, M.; Lightfoot, P. D.; Pilling, M. J. *J. Phys. Chem.* **1986**, *90*, 445.

[34] Genaux, C. T.; Kern, F.; Walters, W. D. *J. Am. Chem. Soc.* **1953**, *75*, 6196. Carr, R. W.; Walters, W. D. *J. Phys. Chem.* **1963**, *67*, 1370.

[35] Basu, S.; Davidson, I. M. T.; Laupert, R.; Potzinger, P. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 1282.

[36] Pataracchia, A. F.; Walters, W. D. *J. Phys. Chem.* **1964**, *68*, 3894.

[37] Rotoli, P. C. M.S. Thesis, University of Rochester, 1963, quoted in ref 21.

[38] Walsh, R. "Thermochemistry" In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988.

[39] It should be pointed out that these interaction energies are not wholly agreed. Slightly different values have been suggested by: Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Magsoodi, S.; Revis, A.; Paul, G. C. *Organometallics* **1987**, *6*, 644.

[40] Conlin, R. T.; Bobbitt, K. L. *Organometallics* **1987**, *6*, 1406.

ylene chloride as an internal standard, and carbon NMR spectra were obtained on a JEOL FX 90Q spectrometer with D_2O or $CDCl_3$ as a lock solvent. High-resolution (360-MHz) NMR spectra of (*E*)-1 and (*Z*)-1 were recorded on a Nicolet spectrometer at the regional NSF facility at Colorado State University or on a Varian 300-MHz VXR spectrometer at UNT. All chemical shifts are reported in parts per million downfield from external tetramethylsilane. Infrared spectra were recorded in gas-phase cells with approximately 10 Torr of sample or in a 5% carbon tetrachloride solution on a Perkin-Elmer 1330 spectrometer calibrated to polystyrene. Preparative gas chromatography was performed on a Varian 90A GLC (thermal conductivity detector). When the reaction products were not isolated, yields were calculated from response factors by using cyclohexane as an internal standard. Analytical gas chromatography was performed on a HP 5840A GLC (flame ionization detector) equipped with a Valco gas sampling port. Mass spectra were determined on a HP 5970A mass selective analyzer coupled to a HP 5790A gas chromatograph. Elemental analyses were performed by the Midwest Center for Microanalysis, and exact mass measurements were determined at the Midwest Center for Mass Spectrometry.

Synthesis of (3-Chloro-2-methylbutyl)dimethylchlorosilane. To a 25-mL three-neck flask containing 5.0 g (49 mmol) of 3-chloro-2-methyl-1-butene[13] and hexachloroplatinic acid (200 mg) was added dimethylchlorosilane (5.2 g, 55 mmol) dropwise over a period of 1 h. The mildly exothermic reaction was stirred for 2 h at room temperature and for 10 h at 55 °C. The reaction mixture was cooled, flash distilled in order to separate the products from the catalyst, and then slowly heated until unreacted dimethylchlorosilane was removed. Analytical gas chromatography (10% SP2100 on Supelcoport, 10 ft) indicated two diastereomers present in >85% yield. Samples of the diastereomers were purified but not separated by preparative GC (20% OV 17 on Chromosorb W, 10 ft, 60 °C) for subsequent characterization. ^{1}H NMR (neat mixture): δ 0.70 (6 H, s, $(CH_3)_2Si$), 1.22 (2 H, d, *J* = 6.7 Hz, CH_2Si), 1.35 (3 H, d, *J* = 7.1 Hz, CH_3CSi), 1.65 (3 H, d, *J* = 6 Hz, CH_3CCl), 2.21 (1 H, m, CH), 4.12 (1 H, m, CH). ^{13}C NMR (neat mixture): δ 2.73 (q), 17.36 (t), 18.86 (t), 21.47 (q), 21.98 (q), 22.37 (q), 23.80 (q), 36.48 (d), 36.74 (d), 64.96 (d), 65.09 (d). MS: *m/e* (relative intensity): 137 (67), 135 (100), 115 (41), 113 (60), 95 (99), 93 (98), 54 (78).

Synthesis of (*E*)- and (*Z*)-1,1,2,3-Tetramethyl-1-siletane (1). A mixture of 8.6 g (43 mmol) of the diastereomers was added to 3.1 g of magnesium in 100 mL of THF and mechanically stirred at 25 °C for 2 h at room temperature and 55 °C for 16 h. The reaction mixture was cooled in an ice bath, and a saturated solution of ammonium chloride was added. The copious precipitate was filtered and washed with ether. The combined filtrates were placed in a separatory funnel, washed successively with water, 5% $NaHCO_3$, brine, and water, and dried with Na_2SO_4. The products (*E*)-1 and (*Z*)-1, obtained in 70% yield, were concentrated by distillation and chromatographically purified (20% OV-17 on Chromobsorb W, 0.25 in. × 25 ft). With the oven temperature at 55 °C and a flow rate of 50 mL/min, product retention times were 10.5 min for the *E* and 16.5 min for the *Z* isomer.

(*E*)-1: ^{1}H NMR (neat) δ 0.17 (3 H, s, CH_3Si), 0.21 (3 H, s, CH_3Si), 0.42 (1 H, dd, *J* = 12.60 Hz, *J* = 10.82 Hz, CH_cSi), 0.78 (1 H, app q, CH_aSi), 0.95 (3 H, d, *J* = 7.2 Hz, CH_3CSi), 1.08 (3 H, d, *J* = 6.4 Hz, CH_3CCSi), 1.10 (1 H, m, $CH_{c'}Si$), 1.74 (1 H, m, $CCH_{b'}C$); ^{13}C NMR (neat) δ −5.66 (q), 0.52 (q), 13.46 (q), 20.74 (t), 24.06 (q), 31.28 (d), 36.22 (d); ^{29}Si NMR (neat) δ 7.68; IR (gas) 2955 (s), 2912 (s), 2877 (s), 1467 (m), 1253 (w), 1145 (w), 1067 (w), 1042 (w), 981 (m), 972 (m), 845 (s), 822 (s), 732 (m); GC/MS, *m/e* (relative intensity) 128 (10), 113 (4), 87 (12), 86 (94), 73 (16), 72 (55), 59 (44), 58 (100), 55 (11), 45 (15), 44 (22), 43 (48). Anal. Calcd: C, 65.52; H, 12.57. Found: C, 65.26; H, 12.58.

(*Z*)-1: ^{1}H NMR (neat) δ 0.19 (3 H, s, CH_3Si), 0.23 (3 H, s, CH_3Si), 0.66 (1 H, dd, *J* = 12.86 Hz, *J* = 7.71 Hz, $CH_{c'}Si$), 0.95 (3 H, d, *J* = 8.0 Hz, CH_3CSi), 1.00 (3 H, d, *J* = 7.02 Hz, CH_3CCSi), 1.10 (1 H, ddd, *J* = 12.86 Hz, 7.71 Hz, 4.10 Hz, CH_cSi), 1.38 (1 H, app q, CH_aSi), 2.51 (1 H, app q, CCH_bCSi); ^{13}C NMR (neat) δ −2.60 (q), −1.37 (q), 9.23 (q), 19.18 (q), 20.35 (t), 24.45 (d), 30.37 (d); ^{29}Si NMR (neat) δ 10.97; IR (gas) 2955 (s), 2925 (s), 2882 (s), 1464 (m), 1255 (s), 1157 (w), 1067 (w), 975 (m), 967 (m), 847 (s), 805 (s), 707 (m); GC/MS, *m/e* (relative intensity) 128 (9), 113 (5), 87 (11), 86 (100), 73 (15), 72 (56), 59 (36), 58 (91), 45 (12), 44 (20), 43 (41). Anal. Calcd: C, 65.52; H, 12.57. Found: C, 65.09; H, 12.37.

Table VIII. Mixture Composition from Pyrolysis of (*Z*)-1

	% composition					
time (s)	reactant ((*Z*)-1)	propene (3)	2-butene (2) + (4)	(*E*)-1	6	5
100	91.16	4.63	0.36	2.51	0.32	1.02
180	87.50	8.20	0.60	2.36	0.38	0.96
310	83.53	10.62	0.95	3.06	0.54	1.30
600	64.01	23.25	1.63	6.86	1.27	2.99
1020	48.32	35.07	2.46	8.63	1.36	4.15
1230	40.25	41.17	3.74	8.77	1.45	4.61
1800	31.72	46.59	3.56	10.63	1.61	5.88

Table IX. Mixture Composition from Pyrolysis of (*E*)-1

	% composition					
time (s)	reactant (*E*)-1	propene (3)	butene (2) + (4)	(*Z*)-1	6	5
300	94.45	4.27	0.61	0.67	tr[a]	tr
600	88.80	9.03	1.17	1.00	tr	tr
1200	78.16	16.01	2.08	1.66	tr	2.09
3780	44.51	41.95	5.16	1.68	0.95	5.75
6240	28.60	52.32	5.77	(3.21)	1.96	8.14
10800	13.53	63.04	8.73	0.45	2.96	11.29

[a] tr = trace.

Pyrolysis Kinetics. These were carried out in static reactors in the vapor phase at both Reading and Denton using equipment previously described.[13,41] The products of (*E*)-1 and (*Z*)-1, viz., alkenes 2–4 and silanes 5–10, are known compounds. For identification purposes, gas chromatographic retention times were characterized with samples obtained commercially or synthesized independently. A number of different columns were used for analysis. In Denton, alkene separations were achieved on a 3% picric acid/graphite column (3 ft × 0.125 in., 50 °C) and silanes on an SP2100 column, described earlier or an SP 2250 (15% w/w #100 Supelcoport, 10 ft × 0.125 in., 100 °C). At Reading, a Silicon Fluid column (15% on 60/80 Chromosorb P, 12 ft × 0.125 in.) separated the alkenes at 0 °C and the silanes at 80 °C. In both laboratories, detection was by FID and relative product yields on each column were based on calibrated gas mixtures for alkene products. It was, however, assumed that silane isomers had identical response factors. With the complex product mixtures produced in these pyrolyses, it was found more convenient and reliable to compare hydrocarbon and silane yields relative to cyclohexane as an inert internal standard (as mixtures with (*E*)-1 and (*Z*)-1 prior to a series of runs).

Tables VIII and IX show the time evolution of the distribution of major products (and reactants) in pyrolysis mixtures at 398.2 ± 0.3 °C. A number of other runs, carried out at different pressures of reactant (1–6 Torr) or at higher pressures with added inert gas N_2 up to 25 Torr, indicated no pressure dependence on the rate constants.

Ratios of (*Z*)- and (*E*)-2-butenes, 2 and 4, respectively, were also determined during the present experiments and were found to be very sensitive to the presence of adventitious air, which tended (i) to increase yields of 2 and 4 and (ii) to equilibrate the ratio of 2/4. After the reactants were carefully degassed, reproducible ratios were found which were independent of reactant starting pressure. These are shown in the Results.

Synthesis of Allylethyldimethylsilane (5).[42] To a solution of allyl Grignard (from allyl bromide (4.0 g, 33 mmol) and Mg (3.0 g, 125 mmol) in 30 mL of diethyl ether) in a 100-mL, three-neck round-bottom flask, equipped with a reflux condenser, dropping funnel, and magnetic stirring bar, was added 1.73 g (14 mmol) of chloroethyldimethylsilane. The reaction mixture was stirred for 2 h at room temperature and for 1 h at 45 °C until the chlorosilane had disappeared. The reaction mixture was then poured onto a 50-mL solution of cold saturated ammonium

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[41] Chickos, J. S.; Frey, H. M. *J. Chem. Soc., Perkin Trans. 2* **1987**, 365.

[42] Mironov, V. F.; Pogononkina, N. A. *Izv. Akad. Nauk SSSR* **1959**, *1*, 85.

chloride. The organic layer was separated, washed with H_2O, and dried over anhydrous sodium sulfate (GC yield, 60% on OV-17 as described above). The authentic sample was used to identify **5** from the kinetic pyrolyses. ^{13}C NMR (neat): δ –5.07 (q), 6.05 (t), 6.50 (q), 22.24 (t), 112.11 (t), 133.96 (d).

Synthesis of Dimethylpropylvinylsilane (6).[43] To a solution of propyl Grignard (from bromopropane (4.1 g, 33 mmol) and Mg (3.0 g, 125 mmol) in 30 mL of diethyl ether) in a 100-mL three-neck round-bottom flask equipped with a reflux condenser, dropping funnel, and magnetic stirring bar was added 1.70 g (14 mmol) of chlorodimethylvinylsilane. The reaction mixture was allowed to stir at room temperature for 2 h and at 45 °C for 1 h until the chlorosilane had disappeared. The typical Grignard workup afforded **6**, 70% GC yield (20% SF-96 on Chromosorb W, $^1/_4$ in. × 20 ft). ^{13}C NMR (neat): δ –4.10 (q), 16.84 (t), 17.60 (q), 17.63 (t), 130.51 (t), 138.32 (d).

Synthesis of 1-Ethyl-1,1-dimethyl-2-vinyl-2,2-dimethyl-1,2-disilane (8).[44] To a 100-mL flask containing 0.5 g (71 mmol) of Li wire $^1/_4$ in. × $^1/_8$ in. pieces) and 50 mL of tetrahydrofuran (THF), under Ar, was added a solution of 2.0 g (16 mmol) of chloroethyldimethylsilane and 2.0 g (16.3 mmol) of chlorodimethylvinylsilane. The flask was immersed in a water-filled ultrasound laboratory cleaner,[45] and after 3 h, the liquid in the flask was flash distilled under vacuum. Product **8** was isolated by fractional distillation, 40% yield (1.12 g, bp 77 °C (30 Torr). ^{13}C NMR (neat): δ –5.07 (q), –4.55 (q), 6.50 (t), 7.61 (q), 130.19 (t), 138.50 (d).

Acknowledgment. Support of this research from the following is gratefully acknowledged: R. A. Welch Foundation, Dow-Corning Corp. (R.T.C.), SERC (R.W.), and University of Missouri—St. Louis (J.S.C.) is gratefully acknowledged. We also thank the NMR facility at Colorado State University, sponsored by NSF, for high-resoltuion spectra.

Registry No. (*E*)-1, 117309-73-6; (*Z*)-1, 117309-74-7; **2**, 590-18-1; **3**, 115-07-1; **4**, 624-64-6; **5**, 18292-34-7; **6**, 28857-41-2; **8**, 57080-70-3; $(CH_3)_2Si(H)Cl$, 1066-35-9; $(CH_3)_2Si(Et)Cl$, 6917-76-6; $(CH_3)_2Si(CH{=}CH_2)Cl$, 1719-58-0; $(CH_3)_2Si{=}CHCH_3$, 55395-25-0; $(CH_3)_2Si{=}CH_2$, 4112-23-6; (*R**,*R**)-(3-chloro-2-methylbutyl)dimethylchlorosilane, 117309-71-4; (*R**,*S**)-(3-chloro-2-methylbutyl)dimethylchlorosilane, 117309-72-5; 3-chloro-2-methyl-1-butene, 5166-35-8.

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Photolysis of Acetyltetracarbonylcobalt(I) in Low-Temperature Matrices: Unusual Behavior for a Coordinatively Unsaturated Intermediate

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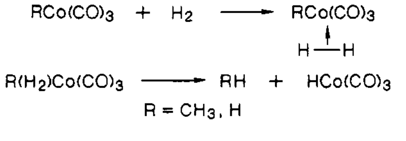
Received April 13, 1988

The ultraviolet photolysis of acetyltetracarbonylcobalt(I) in argon matrices produces $CH_3COCo(CO)_3$ which rearranges to form $CH_3Co(CO)_4$ upon subsequent irradiation. Although nominally coordinatively unsaturated, $CH_3COCo(CO)_3$ fails to react with CO or H_2 in the matrix, suggesting that the vacant coordination site is protected. The spectrum of the intermediate was fully characterized over the region from 2200 to 700 cm^{-1} by using both dispersive and Fourier transform infrared instruments. A band at 1685.9 cm^{-1} is assigned to the C–O stretch of the acetyl group. The anomolously low intensity exhibited by this band and the unusual lack of reactivity of a fragment which is nominally coordinatively unsaturated suggest that the carbonyl group is bonded in an unusual fashion, perhaps in an η^2 mode. The stabilization afforded $CH_3COCo(CO)_3$ by interactions with the acetyl group must become established as the CO is in the process of leaving because there is very little ^{13}CO incorporation during the formation of $CH_3COCo(CO)_3$ in a ^{13}CO matrix.

In the course of matrix-isolation studies of reactions of molecular hydrogen with coordinatively unsaturated transition-metal complexes, we have found that $RCo(CO)_3$ (R = H, CH_3) combines with dihydrogen to form complexes in which the hydrogen is coordinated, presumably as an η^2 ligand.[1] When irradiated with ultraviolet light, these complexes undergo cleavage reactions leading to RH and species derived from $HCo(CO)_3$.



$$RCo(CO)_3 + H_2 \longrightarrow \underset{H-H}{\overset{}{RCo(CO)_3}}$$

$$R(H_2)Co(CO)_3 \longrightarrow RH + HCo(CO)_3$$

$$R = CH_3, H$$

Thinking that $CH_3COCo(CO)_4$ might behave in a similar fashion, we undertook studies of $CH_3COCo(CO)_4$ in hydrogen containing matrices. In this instance what was reasonably a coordinatively unsaturated complex was characterized, but it was surprising when it did not give any evidence of reaction with dihydrogen. Further investigation showed the species was unreactive toward CO as well. This prompted a detailed study of the nature of the intermediate.

Experimental Section

$CH_3Co(CO)_4$ was prepared by adding dimethyl sulfate to $NaCo(CO)_4$ while pumping on the mixture. $CH_3Co(CO)_4$, being the most volatile component, was pumped out. On occasion, it was redistilled at 0.1 mmHg pressure at 0 °C to remove dimethyl sulfate which had been carried over in the crude product. Typ-

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