

20 M, 20% on Chromasorb W-HP, 180 °C) for characterization.

Cis ester (+)-2-*c* had $[\alpha]_D +36.1^\circ$ (*c* 1.85, CHCl₃); according to NMR analysis with the aid of the chiral shift reagent Eu(hfc)₃, this ester was 86% optically pure and the downfield -OCH₃ singlet was predominant. The ¹H NMR spectrum showed signals at δ 7.27 (s, 5 H), 3.45 (s, 3 H), 2.58 (d of d, *J* = 7, 9 Hz, 1 H), 1.70 (d of d, *J* = 5, 8 Hz, 1 H), 1.32 (d of d, *J* = 5, 9 Hz, 1 H); signal intensity due to residual proton at C(1) was conspicuously absent.

Trans ester (+)-2-*t*, $[\alpha]_D +281^\circ$ (*c* 2.69, CHCl₃) was 89% optically pure according to Eu(hfc)₃ analysis, with the downfield -OCH₃ signal strongest; NMR δ 7.02-7.20 (c, 5 H), 3.72 (s, 3 H), 2.53 (d of d, *J* = 6, 9 Hz, 1 H), 1.59 (d of d, *J* = 5, 9 Hz, 1 H), 1.30 (d of d, *J* = 5, 6 Hz, 1 H), and no residual proton at C(1) was seen.

(1*S*,2*R*)-*cis*-2-Phenylcyclopropanemethanol-1-²H. The cis ester (+)-2-*c* (1.20 g, 6.8 mmol) was reduced with LiAlH₄ (0.28 g, 7.3 mmol) in ether (40 mL) at reflux. A standard workup followed by drying (MgSO₄), filtration, and rotary evaporation gave 0.94 g of colorless oil (94%). The alcohol was used without further purification to avoid any possibility of optical fractionation. The crude product had NMR δ 7.27 (s, 5 H), 3.37 (d of d, *J* = 11, 20 Hz, 2 H), 2.28 (m, 1 H), 1.29 (br s, 1 H), 0.78-1.20 (c, 2 H).

(1*R*,2*R*)-(+)-*trans*-2-Deuterio-1-phenylcyclopropane ((+)-3-*t*). The alcohol prepared immediately above (0.94 g, 6.3 mmol) was oxidized with pyridinium chlorochromate (PCC, 2.24 g, 10.4 mmol) in CH₂Cl₂ (25 mL) to give 0.87 g of an aldehyde with the anticipated characteristic NMR singlet at δ 8.68. No signal at δ 9.32 for trans aldehyde was evident. This cis aldehyde (0.87 g, 5.3 mmol) was decarbonylated with Wilkinson's catalyst (5.01 g, 5.41 mmol) in benzene (50 mL) at reflux. Final purification by VPC was accomplished with a 2.5 × 0.62 cm Apiezon L column (14% on 60/80 mesh Chromasorb G-HP) at 160 °C to give 316.2 mg (42% from the alcohol) of deuteriohydrocarbon (+)-3-*t*. Capillary VPC (130 °C, column pressure 5 psi) showed that this material was 99.8% pure with three impurities present: α -methylstyrene-²H (0.05%) plus two unidentified impurities (0.05% and 0.1%). The hydrocarbon had $[\alpha]_{365} +2.16 \pm 0.02^\circ$ (*c* 28.4, isooctane) [lit.⁸ $[\alpha]_{365} +1.053^\circ$ (neat)]; NMR δ 6.98-7.36 (c, 5 H), 1.72-1.98 (m, 1.0 H), 0.92-1.02 (m, 1.0 H), 0.60-0.92 (m, 2.0 H).

(1*S*,2*S*)-*trans*-2-Phenylcyclopropanemethanol-1-²H. Ester (+)-2-*t* (1.53 g, 8.63 mmol) was reduced with LiAlH₄ (0.48 g, 12.6 mmol) in

ether (50 mL) to give 1.28 g (99%) of trans alcohol; NMR δ 6.98-7.20 (c, 5 H), 3.58 (br s, 2 H), 1.86 (br s, 1 H), 1.71-1.90 (m, 1 H), 1.89-1.02 (m, 2 H).

(1*S*,2*R*)-(-)-*cis*-2-Deuterio-1-phenylcyclopropane ((-)-3-*c*). The alcohol prepared immediately above (1.28 g, 8.58 mmol) was oxidized to the corresponding aldehyde with PCC (3.15 g, 14.6 mmol) in CH₂Cl₂ (30 mL). The product (1.20 g, 95%) had the expected NMR singlet at δ 9.32 and no detectable signal at δ 8.68. The aldehyde (1.12 g, 7.61 mmol) was then decarbonylated with Wilkinson's catalyst (7.34 g, 7.94 mmol) in benzene (40 mL) at reflux. Capillary VPC analysis showed that only two compounds were present in the VPC-purified product (483.3 mg, 53%) from the alcohol; $[\alpha]_{365} -5.15 \pm 0.01^\circ$ (*c* 43.5, isooctane): hydrocarbon (-)-3-*c* (99.9%) and α -methylstyrene (0.1%). The cyclopropane was reisolated and repurified by VPC and found to have $[\alpha]_{365} -5.16 \pm 0.02^\circ$ (*c* 15.9, isooctane), demonstrating that concentration has a negligible effect on the measured rotation and confirming that no significant racemization occurs during VPC purification. The product had NMR δ 6.98-7.38 (c, 5 H), 1.72-2.00 (m, 1.0 H), 0.92-1.00 (m, 2.0 H), 0.60-0.92 (m, 1.0 H).

Gas-Phase Pyrolyses of (-)-3-*c*. A 180- μ L sample of (-)-3-*c* and 70 μ L of dry pentane were heated at 309.3 °C for 300 min.^{7,11,17} The pyrolysate was recovered by vacuum transfer, and the phenylcyclopropane was reisolated by VPC. Similarly, 190 μ L of (-)-3-*c* and 60 μ L of dry pentane were heated for 800 min at the same temperature followed by VPC reisolation. The sample heated for 300 min had $[\alpha]_{365} -3.82 \pm 0.01^\circ$ (*c* 14.9, isooctane), while the latter, heated for 800 min, had $[\alpha]_{365} -2.35 \pm 0.02^\circ$.

Acknowledgment. We thank the Research Corporation and the National Science Foundation for partial support of this work.

Registry No. 1, 91760-01-9; (1*S*,2*S*)-(+)-2-*t*, 91760-02-0; (1*S*,2*R*)-(+)-2-*c*, 91839-88-2; (1*S*,2*R*)-(-)-3-*c*, 91839-89-3; (1*R*,2*R*)-(+)-3-*t*, 54516-61-9; (1*S*,1*R*)-*cis*-2-phenylcyclopropanemethanol-1-²H, 91760-03-1; (1*S*,2*S*)-*trans*-2-phenylcyclopropanemethanol-1-²H, 91839-90-6; methyl α -deuteriodiazoacetate, 80594-25-8; styrene, 100-42-5.

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Kinetics and Mechanism of the Pyrolysis of Allyltrimethylsilane

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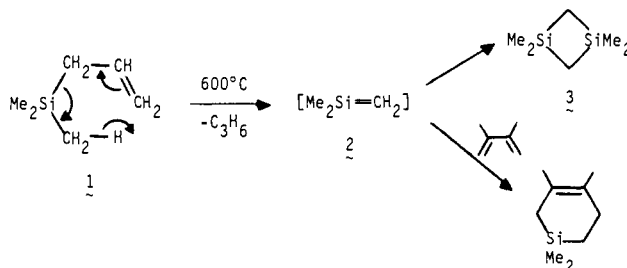
Contribution from the Departments of Chemistry, Iowa State University, Ames, Iowa 50011, and The University, Leicester LE1 7RH, Great Britain. Received January 3, 1984.

Revised Manuscript Received June 13, 1984

Abstract: The gas-phase thermal decomposition of allyltrimethylsilane has been reinvestigated by using deuterium labeling and kinetic studies of variable pressure. Trimethylvinylsilane, the major product at high pressures, is found not to be a primary product of unimolecular decomposition. Silyl radical trapping allowed kinetic separation of the two competitive primary processes of decomposition: a concerted retroene elimination of propene to directly produce a silene and Si-C bond homolysis.

The gas-phase thermal decomposition of allyltrimethylsilane (1) has received periodic attention from several research groups since 1969 when Bailey and Kaufmann¹ reported that at temperatures above 600 °C this molecule underwent a retroene elimination of propene to produce transient 2-methyl-2-silapropene (2). The formation of 2 was inferred from the formation of the usual² heat-to-tail silene dimer, 3, and by "4 + 2" trapping with 2,3-dimethyl-1,3-butadiene.

A full account of this work was never published. Indeed, the retroene conversion of 1 to 2 appeared to be discredited when in



1970 Sakurai, Hosomi, and Kumada³ reported that thermolysis of 1 at 500 °C in a nitrogen stream produced no dimer 3, and

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Scheme I

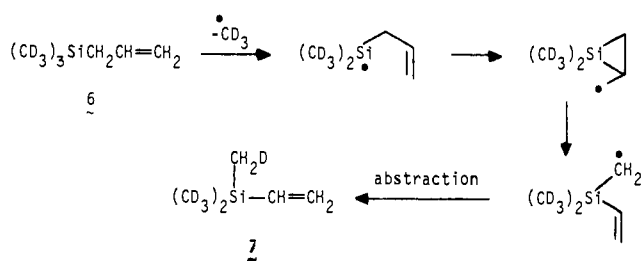
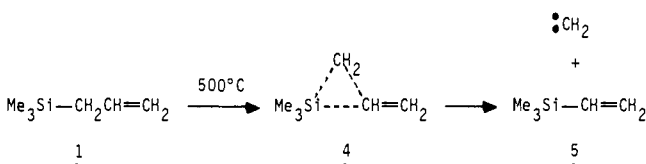


Table I. Percent D Incorporation in 6 before Pyrolysis

	mass (M = 114, mass of 1)	actual intensity	corrected intensity	mol % of deuterated 6
run 1 ^a	M + 7	208	208	1.6
	M + 8	0	0	
	M + 9	12992	12984.9	98.4
	M + 10	1362	0	
	M + 11	435		
run 2 ^b	M + 6	77	77	0.8
	M + 7	0	0	
	M + 8	302	299.1	3.0
	M + 9	9504	9469.8	96.2
	M + 10	1058	0	
	M + 11	366		

^a 25-eV scan. For 6-*d*₀: M = 1.00, M + 1 = 0.1086, M + 2 = 0.03395. ^b 16-eV scan. For 6-*d*₀: M = 1.00, M + 1 = 0.1143, M + 2 = 0.03790.

that the major products were Me₃SiH, Me₄Si, and trimethylvinylsilane (5). The formation of 5 was postulated to arise from a concerted loss of methylene through a transition state depicted as 4.



This mechanism for the formation of trimethylvinylsilane (5) was challenged by Jones and co-workers⁴ in 1979 who reported that pyrolysis of allyltris(trimethyldeuterio)silane (6) at 600 °C afforded a trimethylvinylsilane (7) containing two protons in the methyl groups. Thus, a mechanism (Scheme I) involving initial loss of a CD₃ radical followed by homoallylic rearrangement was proposed.

The results of this labeling study are certainly surprising, since if it is assumed that ΔE_{act} for CH₃ loss vs. allyl radical loss is simply $\Delta\Delta H$, then CH₃ loss would have an E_{act} ca. 14 kcal mol⁻¹ greater than the E_{act} for C₃H₅ loss.⁵ Thus, even at the reported 600 °C, allyl radicals should be produced more than 3000 times faster than methyl radicals. Therefore, we undertook a study of the kinetics of the thermal decomposition of 1. A series of pyrolyses of various pressures of 1 was carried out in sealed tubes at 550 °C. With pressures of 1 above 30 torr, 5 was a major product of decomposition. However, the yield of 5 decreased with decreasing pressure until below 0.05 torr 5 could not be detected as a product.⁶ Thus, trimethylvinylsilane (5) is not formed by

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(2) Flowers, M. C.; Gusel'nikov, L. E. *J. Chem. Soc. B* 1968, 428, 1396. Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* 1979, 79, 529.

(3) Sakurai, H.; Hosomi, A.; Kumada, M. *J. Chem. Soc., Chem. Commun.* 1970, 767.

(4) Neider, S. M.; Chambers, G. R.; Jones, M., Jr. *Tetrahedron Lett.* 1979, 40, 3793.

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Table II. Percent D Incorporation in 6 after Pyrolysis

	mass (M = 114, mass of 1)	actual intensity	corrected intensity	mol % of deuterated 6
run 1 ^a	M + 6	248	248	1.4
	M + 7	342	313.7	1.7
	M + 8	1240	1194.8	6.6
	M + 9	16224	16075.6	89.5
	M + 10	2020	137.8	0.8
	M + 11	685	0	
	M + 12	65	0	
run 2 ^a	M + 5	22	22	0.2
	M + 6	125	122.5	1.4
	M + 7	282	267.2	3.0
	M + 8	918	882.8	9.7
	M + 9	7488	7337.0	81.5
	M + 10	1120	243.6	2.7
	M + 11	398	90.6	1.0
	M + 12	69	49.4	0.5

^a 16-eV scan. For 1: M = 1.00, M + 1 = 0.1143, M + 2 = 0.0379.

methylene extrusion or by a process starting with CH₃ loss but by a bimolecular route. Since this finding appeared incompatible with the D-labeling results reported for 6, it was felt that that study begged reexamination.⁷

Nonadeuteriotrimethylchlorosilane (99% isotopic purity, Merck) was coupled with excess allylmagnesium bromide in ether to furnish 6 in 58% yield. The percent deuterium incorporation was calculated by the method of Biemann.⁸ The actual and corrected ion intensities along with the mole percent of 6 are shown in Table I. The corrected intensity is the observed intensity minus the contributions from lower mass ions. Under the conditions employed, no ions were produced from H or D loss from the molecular ions of 1 or 6.

Pyrolysis of 6 through a quartz tube packed with quartz chips heated at 630 °C (N₂ flow 30 mL min⁻¹) produced a clear, colorless liquid in 66% (run 1) and 89% (run 2) mass recoveries. Analysis of the undecomposed 6 by low electron volt mass spectroscopy revealed that in both runs protons had been incorporated into the methyl groups. After correcting for the isotopic purity of the original 6, it was found that there was a 90.9% and 84.7% retention of the D₉ label in runs 1 and 2, respectively (Table II).

The results of gas chromatographic/mass spectral (GCMS) analysis of the trimethylvinylsilane formed in the two pyrolysis runs are given in Table III.

By far the major product in both runs is 5-*d*₉ which, after correction for proton incorporation in 6, represents 50.6–56.5% (run 1) and 44.2–54.2% (run 2) of the trimethylvinylsilane. The formation of 7 with two protons incorporated in the methyl groups (M + 7 ion) is observed at a maximum of only 6%. Private communication with Professor Jones revealed that the original labeling experiments⁴ had been analyzed by ¹H NMR integration of the deuterated trimethylvinylsilane product isolated by preparative GC. The material thus isolated produced an NMR spectrum with a ratio of vinyl protons to silicon methyl protons of 1.1 to 1.0. Indeed, when we isolated deuterated trimethylvinylsilane (from run 1) by preparative GC using a new, 20% SE-30 column, the ¹H NMR spectrum possessed a vinyl/SiMe ratio of 1:2. Even when isolation (from run 2) was accomplished by preparative GC on a 20% SE-30 column aged for 3 weeks at temperatures above 150 °C with continuous helium flow, the vinyl/SiMe ratio in the ¹H NMR was ca. 4.3:1. Thus, it appears that proton exchange occurs during preparative GC. It should be noted that our labeling results (Tables I–III) were obtained by capillary GCMS under conditions where we have been unable to see any evidence for proton exchange.

Since the formation of 5 is clearly arising from a bimolecular process, we suggest that this is initiated by silicon–allyl homolysis

(6) Davidson, I. M. T.; Wood, I. T. *J. Organomet. Chem.* 1980, 202, C65.

(7) Burns, S. A. Ph.D. Thesis, Iowa State University, 1983.

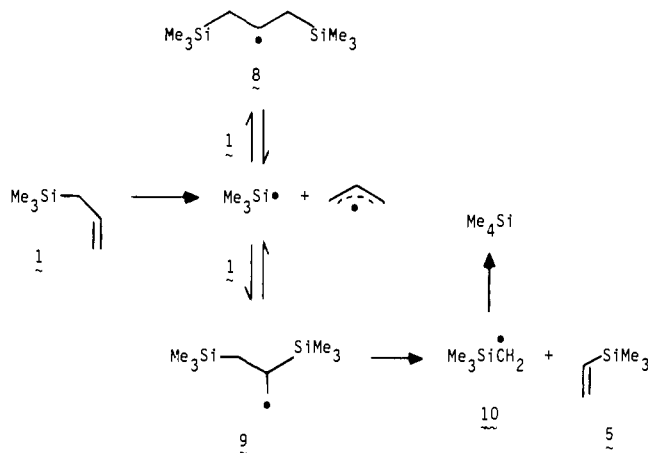
(8) Biemann, K. "Mass Spectrometry, Organic Chemical Applications"; McGraw-Hill Book Co.: New York, 1962; pp 223–225.

Table III. Percent D Incorporation in Trimethylvinylsilane

	mass (M = 100, mass of 5)	actual intensity		corrected intensity		mol % of deuterated 5		av
		14 eV ^a	16 eV ^b	14 eV	16 eV	14 eV	16 eV	
run 1	M + 4	8	2	8	2.0	0.1	0.5	0.3
	M + 5	23	10	22.2	8.9	0.4	1.3	0.9
	M + 6	67	45	64.5	44.0	1.8	3.7	2.7
	M + 7	138	115	130.7	110.3	4.5	7.5	6.0
	M + 8	270	314	254.5	301.5	12.2	14.6	13.4
	M + 9	899	1330	868.7	1266.6	51.3	49.8	50.6
	M + 10	414	692	318.4	556.0	22.5	18.2	20.3
	M + 11	135	283	67.9	178.7	7.2	3.9	5.6
M + 12	29	112	9.1	0	0	0.5	0.2	
run 2	M + 3		13		13	0	0.5	0.3
	M + 4	10	39	10	37.7	1.2	1.6	1.4
	M + 5	24	83	23.0	78.8	2.7	3.2	3.0
	M + 6	47	174	44.2	164.8	5.1	6.8	5.9
	M + 7	80	234	74.7	214.8	8.6	8.8	8.7
	M + 8	127	356	117.8	328.5	13.7	13.5	13.6
	M + 9	409	1072	394.4	1031.4	45.9	42.5	44.2
	M + 10	192	534	148.5	420.1	17.3	17.3	17.3
	M + 11	75	206	44.1	124.3	5.1	5.1	5.1
	M + 12	13	44	2.6	15.3	0.3	0.6	0.5

^aFor 5-d₀: M = 1.00, M + 1 = 0.09785, M + 2 = 0.04158. ^bFor 5-d₀: M = 1.00, M + 1 = 0.09790, M + 2 = 0.03934.

Scheme II



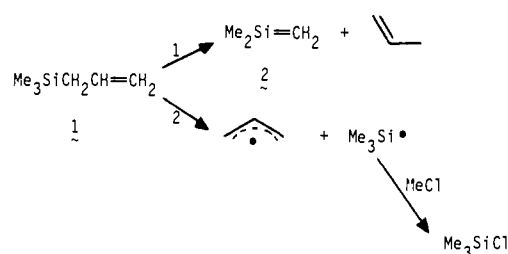
to form Me₃Si which can add to 1 by the favored terminal addition to produce the symmetrical carbon radical 8, or by internal addition to form primary radical 9 (Scheme II).

Formation of 8 will be nonproductive as β-scission regenerates 1. Radical 9 can undergo a similar reversal to 1, or C-C bond homolysis to produce 5 and radical 10. This latter radical would be expected to abstract H (or D) to afford (not exclusively) Me₄Si, which is indeed a major product of the pyrolysis of 1 at higher pressures.^{3,4} These suggestions are more reasonable and straightforward than those made previously,⁶ when it was assumed from the original labeling experiments⁴ that formation of 5 demanded loss of a methyl group from silicon.

The bimolecular nature of the pyrolysis of 1 under these conditions is consistent with the surprising formation of significant amounts (20.3% and 17.3% for runs 1 and 2) of trimethylvinylsilane containing ten deuterium atoms and ca. 5% containing eleven deuteriums! This mass spectral observation was confirmed by ²H NMR which showed the presence of vinyl deuteriums. There are at least several mechanistic schemes involving radical additions, exchanges, abstractions, and disproportionations which can be written to explain the higher deuterated products. However, our confirmation that the retroene pathway is also operative for the decomposition of 1 (vide infra) makes speculation unwarranted at this time.

The labeling experiments described above and our preliminary kinetic work⁶ gave good evidence for the bimolecular route to trimethylvinylsilane. The latter study also showed that the retroene reaction occurred as well as homolysis, as indicated by the formation of the silene dimer 3 in experiments at low pressure.

Scheme III



However, it did not yield reliable kinetic data on either of the primary pathways, which are difficult to distinguish because propene is formed in each, and because radicals from the homolysis react rapidly with silenes.⁹

We have, therefore, done further trapping and kinetic experiments, mainly by low-pressure pyrolysis (LPP). Under these conditions, the bimolecular reactions in Scheme II leading to trimethylvinylsilane and Me₄Si are unimportant. Our first approach was to try to trap silene 2 to obtain kinetic data for the retroene reaction from the formation of the trapped product. Methanol trapped 2 efficiently to give methoxytrimethylsilane, but erratic kinetics were observed, probably because surface reactions are difficult to avoid with methanol. Use of methoxytrimethylsilane itself as a trap gave the expected product,¹⁰ but the reaction was too slow to trap 2 completely. Molecular oxygen also gave the expected products,¹¹ but the resulting chemistry was too complicated for kinetic analysis. Accordingly, attempts to distinguish between homolysis and retroene processes by trapping 2 were abandoned, and we attempted to trap the Me₃Si radicals instead. This was easily achieved with chloromethane, which reacts rapidly with Me₃Si radicals to form trimethylchlorosilane, but does not react with 2 under LPP conditions (this was verified by pyrolyzing the familiar source² of 2, 1,1-dimethyl-1-silacyclobutane, with added chloromethane). The relevant reactions are in Scheme III.

In our LPP technique, overall rate constants may be measured from decay of reactant or from formation of any product. Because of a tendency of allylsilanes to adsorb on the surfaces of the

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(10) John, P.; Gowenlock, B. G.; Groome, P. *J. Chem. Soc., Chem. Commun.* **1981**, 806. Davidson, I. M. T.; Wood, I. T. *J. Chem. Soc., Chem. Commun.* **1982**, 550.

(11) Davidson, I. M. T.; Dean, C. E.; Lawrence, F. T. *J. Chem. Soc., Chem. Commun.* **1981**, 52.

Table IV. Kinetic Data for Pyrolysis of Allyltrimethylsilane with Added Chloromethane (590–670 °C)

		$\log [A]$	E , kcal	$k_{900\text{ K}}$, s^{-1}
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2 \xrightarrow{1} \text{Me}_2\text{Si}=\text{CH} + \text{CH}_2=\text{CH}_2$	$(k_1 + k_2)$	12.9 ± 0.1	59.5 ± 0.5	
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2 \xrightarrow{2} \text{Me}_3\text{Si} + \text{CH}_2=\text{CH}_2$	k_1	11.6 ± 0.5	55 ± 2	1.8 ± 10^{-2}
	k_2	15.6 ± 0.5	73 ± 2	7.5×10^{-3}

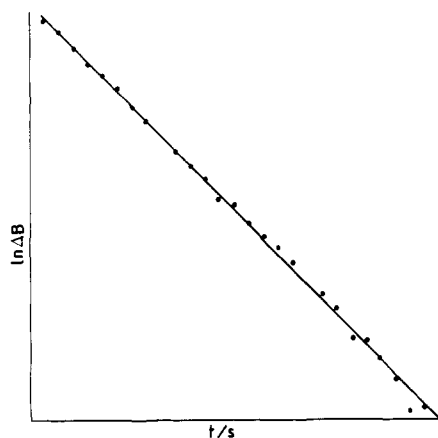


Figure 1. Plot of $\ln [B]$ vs. time (seconds) where B is the product propene, measured by the corrected m/e 41 ion intensity. From the slope, $k = 0.0517 \pm 0.0005 \text{ s}^{-1}$.

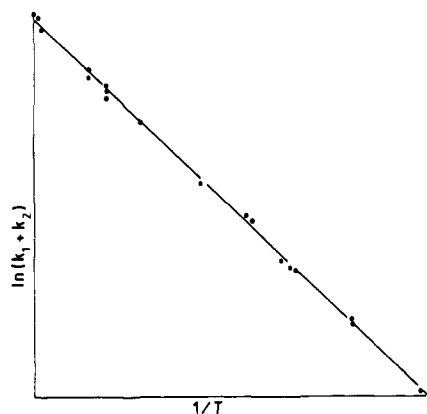
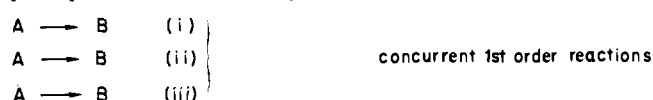


Figure 2. Arrhenius plot for $(k_1 + k_2)$, the total rate constant for decomposition of allyltrimethylsilane (1).

apparatus, the latter method was more reliable in this case. The principle of the method may be illustrated thus:



(overall rate constant for decomposition of A, $k = k_1 + k_{11} + k_{111}$)
 $d[B]/dt = k_1[A] = k_1[A_0]e^{-kt}$, where $[A_0]$ is the initial concentration of A;
 for short time intervals Δt , $d[B]/dt \approx \Delta B/\Delta t$; $\Delta[B] \approx k_1[A_0]\Delta t e^{-kt}$
 $\therefore \ln \Delta[B] = \text{constant} - kt$

Hence, the overall rate constant k may be determined from the slope of the linear plot of $\ln \Delta[B]$ vs. t . The method requires no calibration data, the relative sensitivity of the mass spectrometer to A and B being part of the constant term, and involves no assumptions as to stoichiometry of mechanism. B may, therefore, be any product, but the method is obviously more accurate if it is a major one. The overall rate constant for decomposition of 1, i.e., $(k_1 + k_2)$, was obtained in this way from the formation of the major product, propene. A typical plot is in Figure 1. Rate constant k_2 was obtained from the kinetics of formation of trimethylchlorosilane, measured by conventional means, not by the above method. Calculation of k_1 was by difference. Arrhenius plots are in Figures 2–4, with the resulting Arrhenius parameters in Table IV.

The main primary process is thus seen to be the retroene reaction 1, as originally claimed by Bailey,¹ but obscured in later work by the complexities discussed above.

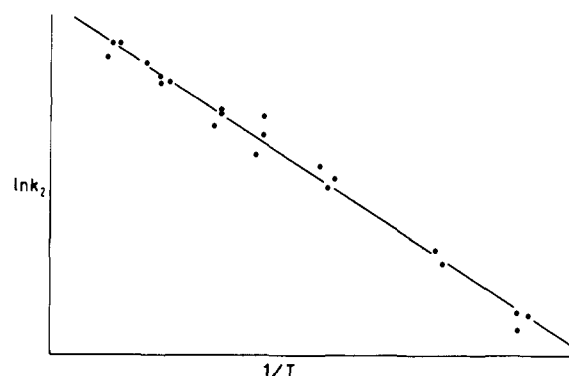


Figure 3. Arrhenius plot for k_2 (homolytic process) as measured by the formation of trimethylchlorosilane.

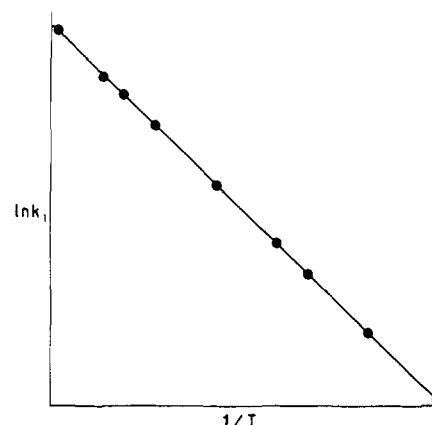
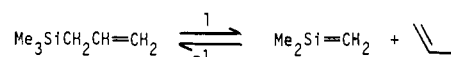


Figure 4. Derived Arrhenius plot for k_1 (retroene process).

Scheme IV



From Additivity Calculations,²¹ $\Delta S = 32 \text{ cal mol}^{-1} \text{ K}^{-1}$

$$A_1 = 10^{11.6} \text{ s}^{-1}, \therefore A_{-1} = 10^{6.4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$A_{-1} \text{ 452}^\circ\text{C},^{18} k_{-1} \sim 4.8 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$\therefore E_{-1} \sim 12 \text{ kcal mol}^{-1}$$

$$E_1 - E_{-1} = \Delta H_1 = D(\text{Me}_3\text{Si}-\text{C}_3\text{H}_5) + D(\text{Me}_2\text{SiCH}_2-\text{H}) - D_\pi - D(\text{C}_3\text{H}_5-\text{H})$$

$$55 - 12 = 43 = \quad 73 \quad + \quad 99 \quad - D_\pi - 89$$

$$\therefore D_\pi(\text{Me}_2\text{Si}=\text{CH}_2) = 40 \pm 5 \text{ kcal mol}^{-1}$$

The Arrhenius parameters for reaction 2 are entirely reasonable for rupture of a silicon–allyl bond. The A factor for such a process is expected to be $<10^{16} \text{ s}^{-1}$ because of stiffening in the transition state and a reduced increase in the moment of inertia.¹² As the allyl stabilization energy is $13.5 \text{ kcal mol}^{-1}$, a silicon–allyl bond-dissociation energy of 73 kcal mol^{-1} is equivalent to a silicon–methyl bond-dissociation energy of $87 \pm 2 \text{ kcal mol}^{-1}$, consistent with recent estimates of 89 ± 3 ¹³ and $87.5 \pm 2 \text{ kcal}$.¹⁴

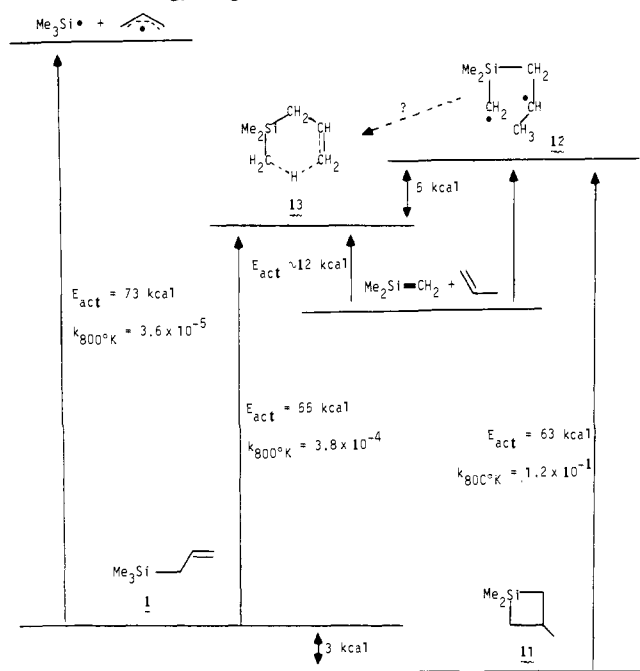
The retroene reaction 1 has similar Arrhenius parameters to those obtained for the corresponding reaction of hept-1-ene to

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Scheme V. Energy Diagram

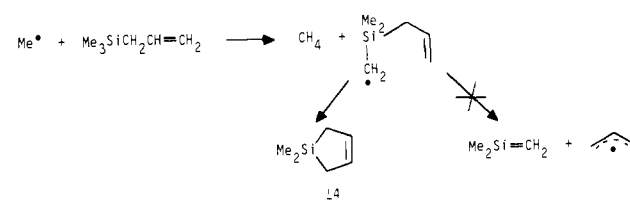


propene and but-1-ene.¹⁵ As shown in Scheme IV, the Arrhenius parameters for reaction 1 are consistent with a π -bond energy in **2** of 40 ± 5 kcal, in good agreement with recent literature values of 39 ± 5 kcal¹³ and 45 ± 5 kcal.¹⁶

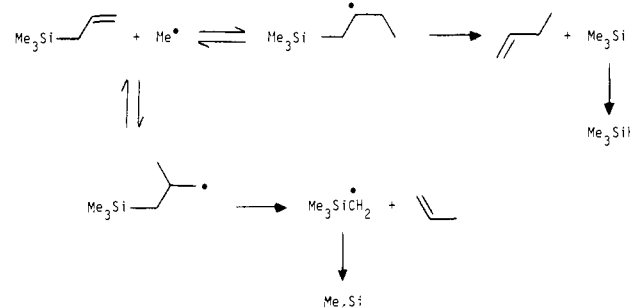
Thermal reaction of the silene **2** with propene gives allyltrimethylsilane as the main product presumably by the concerted ene reaction (the reverse of reaction 1 in Scheme III), but 1,1,3-trimethyl-1-silacyclobutane (**11**) is also formed.^{17,18} In some unpublished quantitative studies,¹⁸ approximate rate constants were measured, and the ratio of **1** to **11** was found to be ca. 7:1. Formation of **11** has been rationalized as resulting from a radical process.¹⁷ Likewise, pyrolysis¹⁹ of **11** proceeds both by decomposition (to the silene **2** and propene) and by isomerization to **1**. These two processes have approximately equal activation energies, consistent with the initial formation of a biradical,² but different A factors, leading to a ratio of rate constants for decomposition relative to isomerization of ca. 5:1. It has been noted¹⁹ that analogous pathways are observed in the pyrolysis of substituted cyclobutanes,²⁰ but isomerization is much less important than in the pyrolysis of **11**. These results are illustrated in the energy diagram, Scheme V. Rate constants for the primary pyrolysis reactions of **1** and **11** at 800 K (527 °C) are included in Scheme V to make the point that **11** is much less stable thermally than **1**. It has been suggested¹⁷ that the biradical intermediate **12** can convert to the six-center species **13** as well as dissociate, which appears to be the simplest way to link the foregoing observations. The estimated difference in the enthalpy of formation of **1** and **11** comes from the additivity scheme of O'Neal and Ring.²¹

Some further pyrolysis experiments were undertaken to confirm the mechanism suggested in Scheme II. Partial pressures of 0.2 torr of **1** were pyrolyzed in a N_2 stream in our stirred flow (SFR) apparatus²² at 592 °C under conditions which gave ca. 5% de-

Scheme VI



Scheme VII



composition. Only small amounts of trimethylvinylsilane (**5**) and Me_4Si were formed. Under the same conditions pyrolysis of a 1:1 mixture of **1** and benzyltrimethylsilane (to enhance the rate of formation of Me_3Si radicals) gave substantially greater quantities of **5** and Me_4Si , as would be expected from Scheme II.

A more elegant experiment is to generate Me_3Si radicals below the pyrolysis temperature of **1**. A suitable thermal method is the pyrolysis of dimethylmercury in the presence of Me_3SiH , but before this could be used, it was necessary to investigate the effect of the methyl radicals produced from dimethylmercury on **1**. Mixtures of **1** and dimethylmercury were pyrolyzed at 527 °C by using both the LPP and SFR techniques to aid product identification. The main silicon products were Me_3SiH , Me_4Si , and **5**, in the ratio of 4:2:1, and 1,1-dimethyl-1-silacyclopentene (**14**). Compound **14** may be envisaged as being formed as in Scheme VI.

Me_3SiH and Me_4Si would result from reactions analogous to those in Scheme II, shown in Scheme VII. These addition/homolyses would also produce but-1-ene and propene, and these olefins were observed in the product mixture. Once Me_3Si radicals have been produced, the reactions in Scheme II would occur to give **5**.

When these experiments were repeated in the presence of a fourfold excess of Me_3SiH , more **5** and less **14** was produced, exactly as expected from Schemes II and VII.

Experimental Section

Routine proton NMR spectra were recorded on a Varian EM-360 spectrometer. A Bruker WM 300 was used for high-resolution ¹HMR and ²HMR spectra. Gas chromatographic/mass spectra (GCMS) were obtained on a Finnegan Model 4023 mass spectrometer. The LPP apparatus with mass spectral detection utilized in this work has been previously described.²³

Synthesis of Tris(trideuteriomethyl)allylsilane (6). Tris(trideuterio-methyl)chlorosilane was purchased from Merck and Co., Inc., in 99% isotopic purity. A two-necked round-bottom flask was equipped with a condenser, drying tube, and septum inlet. The apparatus was flame dried and flushed with nitrogen. The flask was charged with 0.83 g (0.034 mol) of magnesium and 40 mL of dry ether. A solution of 1.0 g (0.0085 mol) of tris(trideuteriomethyl)chlorosilane in 5 mL of dry ether was added. To this stirring solution was added 2.06 g (0.0170 mol) of allyl bromide in 10 mL of ether. The reaction mixture was stirred at room temperature for 7 h followed by cooling to -23 °C (CCl_4 /dry ice) and quenching the excess Grignard reagent with 10% ammonium chloride. The two layers were separated, and the organic solution was washed with water and dried with sodium sulfate. The ether was distilled at 40 °C

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and the tris(trideuteriomethyl)allylsilane distilled through a short vigreux column at 80 °C (bp 85–6 °C) to give 0.603 g (57.6%). For run 2, the above quantities were doubled and all else remained the same, furnishing 1.2158 g (58.0%) of tris(trideuteriomethyl)allylsilane: NMR (CCl₄) δ 4.56–6.11 (vinyl m, matches that of trimethylallylsilane). The deuterium incorporation was determined by the method of Biemann⁸ and values of 6-*d*₇ (1.6%), 6-*d*₉ (98.4%) and 6-*d*₆ (0.8%), 6-*d*₈ (3.0%) and 6-*d*₉ (96.2%) were obtained in run 1 and run 2, respectively. See Table I for the ion intensities used for these calculations.

Pyrolysis of Tris(trideuteriomethyl)allylsilane (6). Run 1. Compound 6 was slowly dripped into a vertical quartz tube packed with quartz chips and heated at 630 °C with use of nitrogen as a carrier gas with a flow rate of 30 mL/min. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 60% mass recovery. Analysis of recovered 6 and the trimethylvinylsilane was done by GCMS. See Table II and Table III for the percent deuterium incorporation and the actual mass spectral intensities. Isolation of deuterated 5 was attempted by

preparative gas chromatography on a freshly packed 16 ft 20% SE 30 column: 300-MHz NMR (C₆D₆) δ 0.04–0.01 (m, 1 H), 0.40 (s, 1.25 H), 5.60–6.51 (m, 3.13 H, vinyl ABC pattern). The multiplet at δ 0.04–0.01 represents partial proton incorporation, while the singlet at δ 0.40 is an impurity, presumably from column bleed. The methyl protons in trimethylallylsilane absorb at δ 0.07.

Run 2. The flow pyrolysis in run 2 was conducted as in run 1. The pyrolyzate represented an 84.7% mass recovery. The GCMS analyses of both recovered 6 and 5 are presented in Table II and Table III, respectively. Isolation of 5 was accomplished on an aged 20 ft 20% SE 30 column: 300-MHz ¹H NMR (CCl₄) δ 0.04–0.10 (m, 1 H), 5.60–6.51 (m, 4.3 H, vinyl ABC pattern); 300-MHz ²H NMR (CCl₄) δ 0.0 (s, 1.5 D) 5.53–5.84 (m, 1 D).

Acknowledgment is made to the National Science Foundation for generous support of this work at Iowa State University. The Leicester Group acknowledges S.E.R.C. for their support.

Solvolysis of Ethenoanthracenyl Triflates. Novel Stabilized Cyclic Vinyl Cations

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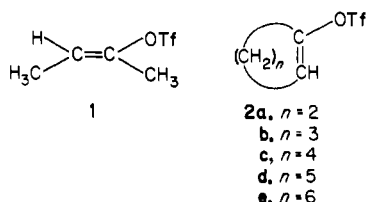
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Abstract: The solvolytic behavior of ethenoanthracenyl (3a) and etheno-9,10-dimethylantraceny (3b) triflates was examined. Despite the strain inherent in these systems, 3a reacts 10⁵ times faster than cyclohexenyl triflate and 11 times faster than the unstrained *cis*-2-butenyl triflate. These results are explained by an unusual aryl stabilization of the incipient vinyl cations.

The solvolytic behavior of cyclic vinyl systems is of interest because of the question of the effect that ring strain has on the rate of reaction.¹ Vinyl cations in cyclic systems are rigidly held in bent geometries. If such bent structures are less favorable, then the rate of solvolysis of cycloalkenyl derivatives should be slower than that of similar acyclic precursors.²

The first attempt to generate cyclic vinyl cations by solvolysis of 1-cyclohexenyl tosylates and brosylates failed, resulting in addition–elimination in formic acid, and in 50% aqueous methanol at 130 °C after 18 days only starting material was observed.³

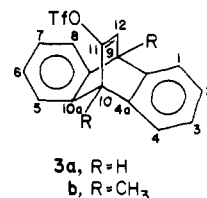
The solvolytic behavior of the cycloalkenyl triflates 2 has been extensively examined^{2,4} and compared with that⁵ of the acyclic model compound 1. In the reactions of all cycloalkenyl triflates



2 except 2b, first-order kinetics were observed. Cyclopentenyl triflate (2b) does not react via a vinyl cation intermediate⁶ and it was recovered practically unchanged in a nonnucleophilic solvent such as CF₃CH₂OH (TFE) buffered with Et₃N after 10 days at 100 °C. For the reaction of the higher homologues, 2c–2e, the kinetic data and relative reactivities^{2,4} are in accord with a vinyl cation mechanism of solvolysis. Cyclohexenyl triflate (2c) reacts

via a bent cation which has a high energy, resulting in 10⁴ times slower solvolysis² than the acyclic triflate 1. The vinyl cations resulting from triflates 2d and 2e have seven- and eight-membered rings which can reasonably accommodate the linear geometry of an sp-hybridized carbon coupled to a trigonal carbon, and hence the reactivities^{2,4} of triflates 2d and 2e are comparable to that of the geometrically unrestricted acyclic analogue.

In this paper we report further aspects of the solvolytic behavior of cyclic vinyl triflates. In particular we investigated the solvolysis of triflates 3 with the bicyclo[2.2.2]octatrien-1-yl moiety which



resembles the cyclohexenyl system in its strain and therefore would be expected to generate a vinyl cation with high energy due to ring strain. In fact, it is well-known that the strain in the bicy-

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