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Mechanism of the Decomposition of Silacyclobutane to Silylene and Propene

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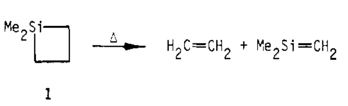
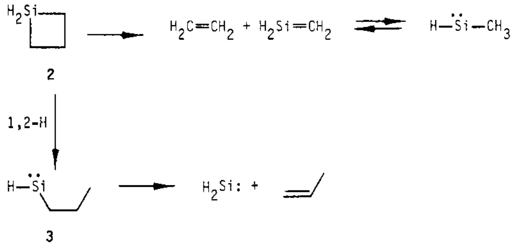
Abstract: The mechanism of the title reaction was determined by a detailed study of the pyrolysis of 1,1-dideuterio-1-silacyclobutane. It is concluded from the observations that the propene was a mixture of d_0, d_1, and d_2 species and that the deuterium was located on all of the carbons. The decomposition is initiated by a 1,2-migration of D from silicon to carbon to produce *n*-propylsilylene, which *reversibly* forms a silacyclopropane before ultimately decomposing to silylene and propene.

Silacyclobutane thermolysis has had a pivotal role in organosilicon chemistry since 1968 when it was conclusively demonstrated[1] that gas-phase pyrolysis of 1,1-dimethyl-1-silacyclobutane (**1**) produced a clean, unimolecular decomposition to ethene and dimethylsilene. The cleanliness of this pyrolysis stands in contrast to that of the parent silacyclobutane (**2**), which was shown in 1983 to decompose to ethene, propene, and three organosilicon reactive intermediates.[2] Although the anomalous path leading to silylene (SiH_2) and propene can be easily rationalized by a stepwise sequence of Si–C bond homolyses, we have questioned this path largely on the basis that, if correct, propene should also be produced from **1**. Thus, with cognizance that alkylsilyl hydrides can extrude alkanes (e.g., $Me_2SiH_2 \rightarrow CH_4 + MeHSi$:),[3] we have suggested[4] that this process proceeds by initial isomerization of **2** via a reductive elimination to form *n*-propylsilylene (**3**), which in turn decomposes to propene and SiH_2, and have demonstrated that this latter process does indeed occur when propylsilylenes are independently generated.





In order to gain evidence for the first step of our proposed mechanism, we have carried out and report here a detailed study of the thermolysis of 1,1-dideuteriosilacyclobutane (**4**).

Results and Discussion

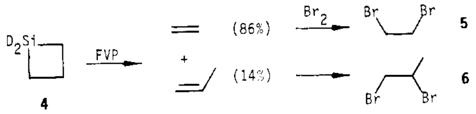
Flash vacuum pyrolysis (FVP) of **4** (<1% SiH) was conducted at ca. 700 °C[5] at 0.1–0.2 Torr in the reaction zone. The pyrolysate was collected at −196 °C, and the most volatile products were separated by trap-to-trap distillation at −78 °C. The remaining pyrolysate was almost solely (>90%) unreacted **4**, which was isolated by preparative GC and found by ^1H NMR analysis to contain 0.093 SiH, corresponding to ca. 5% D/H exchange. A series of FVP's of **4** were run from 580 to 750 °C, and the SiH incorporation into unreacted **4** was determined by ^1H NMR to range from 5 to 8%. ^2H NMR analysis revealed no scrambling of deuterium onto the carbons of **4**. Thus, if indeed **4** isomerizes to silylene **7**, the reaction is not significantly reversible.

Table I. Deuteriation of Propene and Ethene from FVP of **4**

ion	ion intens[a]	ref ion intens[b]	cor intens[c]	mol % deuteriated species
		Ethene (M = 28)		
M − 2	1.50	5.79		
M − 1	1.54	2.05		
M	100.00	100.00	100.0	90 (d_0)
M + 1	13.20	3.76	9.44	9 (d_1)
M + 2	2.49	0.26	2.23	1 (d_2)
		Propene (M = 42)		
M − 2	0.83	0.06		
M − 1	0.34	0.41		
M	37.81	100.00	37.81	22 (d_0)
M + 1	100.00	7.63[d]	97.13	56 (d_1)
M + 2	46.39	0.40	39.01	22 (d_2)
M + 3	6.27	0.01		
M + 4	1.16	0.01		

[a] Measured on a Finnigan GCMS, 12 eV, cooled capillary column. [b] Undeuteriated propene or ethene run at same time and conditions. [c] Calculted by the method of Biemann.[6] [d] Elevated M + 1 at 12 eV suggests an ion–molecule reaction.

Since Si–D/H scrambling in **4** is always <10%, any significant deuterium incorporation in propene must come in the decomposition of **4**. The gaseous pyrolysis products consisted mainly of ethene (86%) and propene (14%), and the results of GCMS analysis of these products are given in Table I. The percentages of d_0, d_1, and d_2 species were calculated by the method of Biemann[6] using the mass spectral intensities of the M, M + 1, and M + 2 peaks of C_2H_4 and C_3H_6. The olefinic products were also analyzed by bromination of the gaseous products and examination of the resulting 1,2-dibromoethane (**5**) and 1,2-dibromopropane (**6**). The results of mass spectral analysis of both **5** and **6** are given in Table II and are seen to be quite similar to those obtained from analysis of the olefins directly.



Analysis of the data in Tables I and II reveals that while the ethylene from **4** is largely undeuteriated (similar to the amount of Si–H incorporation in recovered **4**), ca. 75% of the propene contained at least one deuterium. This is consistent with the mechanism for silacyclobutane decomposition initiated by a 1,2-D shift (**4** → **7**) and totally inconsistent with direct extrusion of SiD_2

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(1) Flowers, M. C.; Gusel'nikov, L. E. *J. Chem. Soc.* B **1968**, 419.

(2) Conlin, R. T.; Gill, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 618.

(3) Ring, M. A.; O'Neal, H. E.; Rickborn, S. F.; Sawrey, B. A. *Organometallics* **1983**, *2*, 1891.

(4) Davidson, I. M. T.; Fenton, A.; s. Ijadi-Maghsoodi, S.; Scampton, R. J.; Aunder, N.; Grobe, J.; Tillman, N.; Barton, T. J. *Organometallics* **1984**, *3*, 1593.

(5) Results from runs at 690 and 710 °C did not differ significantly.

(6) Biemann, K. *Mass Spectrometry, Organic Chemical Applications*; McGraw-Hill: New York, 1982; pp 223-227.

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Table II. Yield and Percent Deuterium Incorporation for 1,2-Dibromomethane (**5**) and 1,2-Dibromopropane (**6**) Formed from Flash Vacuum Pyrolysate of **4**

run[a]	yield, %	ion	ion intens[b]	cor intens[c]	mol % deuterated species[c]
		Compound **5** (M = 186)			
1	*d*	M − 1	1.50		
		M	51.27	51.27	78 (d_0)
		M + 1	16.53	13.78	21 (d_1)
		M + 2	100.00	1.08	1 (d_2)
		M + 3	27.09		
		M + 4	53.00		
		M + 5	13.65		
		M + 6	3.04		
		Compound **6** (M = 200)			
	d	M − 1			
		M	1.18	1.18	19 (d_0)
		M + 1	3.33	3.32	53 (d_1)
		M + 2	3.89	1.55	25 (d_2)
		M + 3	6.72	0.16	3 (d_3)
		M + 4	4.15	0.00	0
		M + 5	3.39		
		M + 6	1.39		
		Compound **5** (M = 186)			
2	55	M − 1	4		
		M	169	169	81 (d_0)
		M + 1	40	29	14 (d_1)
		M + 2	333	3	1 (d_2)
		M + 3	74	7	3 (d_3)
		M + 4	167		
		M + 5	36		
		Compound **6** (M = 200)			
	10	M − 2	16		
		M − 1	3		
		M	43[e]	43	26 (d_0)
		M + 1	105	103	62 (d_1)
		M + 2	105	17	10 (d_2)
		M + 3	206	2	1 (d_3)
		M + 4	100		
		M + 5	103		
		M + 6	38		

[a] Run 1, Finnigan 4023 GCMS, 20 eV; run 2, Kratos MS-50 mass spectrometer, GC-prepped samples, 26 eV. [b] Measured ion intensity of deuteriated samples. [c] Calculated by the method of Biemann.[6] The following reference spectra were used. Run 1: undeuteriated 139, M − 1 = 1.67, M = 52.22, M + 1 = 2.80, M + 2 = 100.00, M + 3 = 1.85, M + 4 = 48.27, M + 5 = 0.97; undeuteriated 140, M − 1 = 0.05, M = 6.25, M + 1 = 0.08, M + 2 = 12.20, M + 3 = 0.38, M + 4 = 5.68, M + 5 = 0.11. Run 2: undeuteriated 139, M − 1 = 5, M = 265, M + 1 = 15, M + 2 = 515, M + 3 = 15, M + 4 = 251, M + 5 = 6; undeuteriated 140, M − 2 = 16, M − 1 = 3, M = 203, M + 1 = 10, M + 2 = 394, M + 3 = 15, M + 4 = 191, M + 5 = 7. [d] Yield not obtained. [e] Measured mass *m/e* 199.88362 ($C_3H_6{}^{79}Br_2$).

Table III. Deuterium Distribution in 1,2-Dibromopropane (**6**) from Pyrolysis of **4**

run[a]	shift, ppm (δ scale)[b]	carbon[c]	rel intens[d]
1	2.89	1	11.4
	3.18	1	10.7
	3.51	2	17.1
	1.26	3	62.1
2	2.88	1	10.9
	3.17	1	9.5
	3.52	2	16.8
	1.25	3	62.9

[a] ^2H NMR spectra determined on a Bruker WM-300 spectrometer (46 MHz) in benzene solution. [b] Chemical shifts referenced to natural-abundance deuterium in benzene solvent. [c] Signal assigned for deuterium substituted on C_1, C_2, or C_3. The two sites on C_1 are diastereotopic. [d] Normalized to 100 total.

from the four-membered ring. However, extrusion of silylene from silylene **7** either by a β-elimination or by a process of β-insertion to form silirane **8** followed by decomposition would result in only the formation of monodeuteriated propene with the deuterium located exclusively at the 3-position.

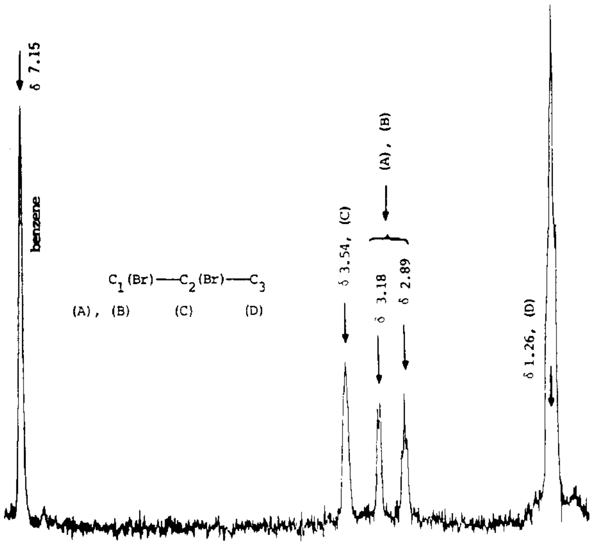
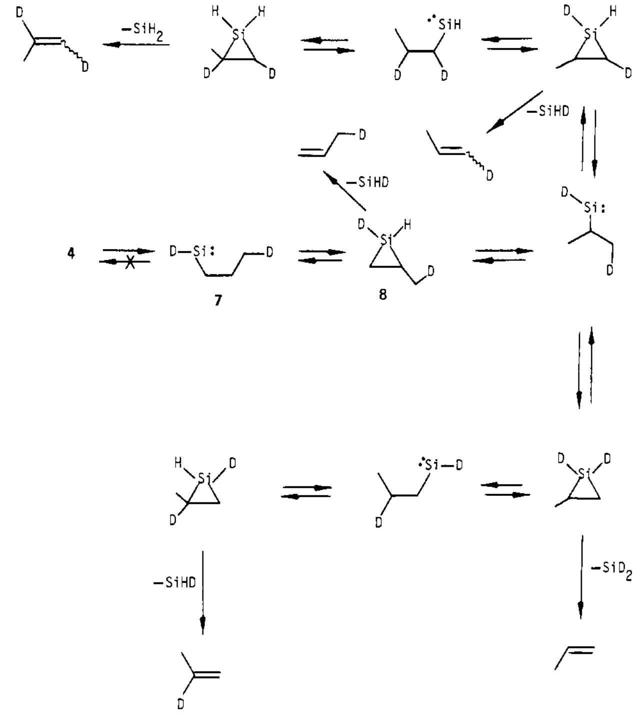
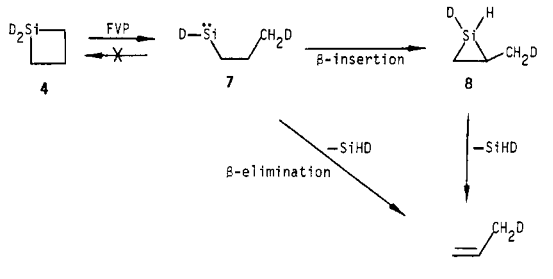


Figure 1. ^2H NMR of 1,2-dibromopropane (**6**) from bromination of the pyrolysis products from the FVP of **4** (benzene solution, 46 MHz; insert indicates assignment of the resonances; see Table III for integrations).

Scheme I

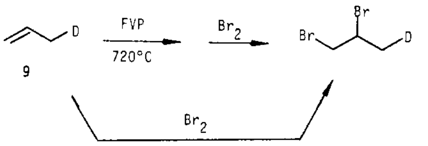




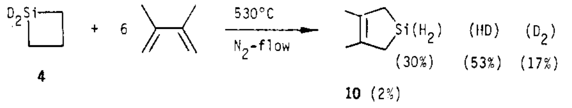
Since both methods of analysis reveal significant amounts of propene-d_0 and -d_2 and since no deuterium incorporation onto the ring carbons of recovered **4** was detected by ^2H NMR, the D/H scrambling must occur after an essentially irreversible isomerization of **4**. Scheme I accounts for this scrambling by including *reversible* silacyclopropane formation via β-CH insertion by propylsilylenes.

Scheme I, which is not intended to be all-inclusive, not only demonstrates how propylsilylene/silacyclopropane equilibria can account for the formation of propene-d_0, -d_1, and -d_2 but also shows that if this mechanistic reasoning is correct, the deuterium will be positionally scrambled. The location of deuterium on propene was determined by examination of the ^{2}H NMR spectrum of 1,2-dibromopropane (**6**). This spectrum (Figure 1) clearly shows that deuterium is indeed located at all positions, with the majority (63%) of the "allylic" position as would be expected from Scheme I if full equilibrium was not established. The integrations of the individual deuterium absorptions are given for two independent runs in Table III.

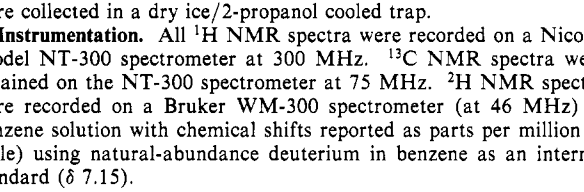
To determine the validity of bromination of propene for the determination of D labeling, 3-deuteriopropene (**9**) was synthesized and brominated. The resulting 1,2-dibromopropane was 96% monodeuteriated (mass spectrum) and contained deuterium only in the 3-position (^{2}H NMR). FVP of **9** was conducted at 720 °C, and the pyrolysate was brominated to produce 1,2-dibromopropane which was 93% monodeuteriated, exclusively at the 3-position. Thus, deuterium-labeled propene is positionally stable under our pyrolysis conditions, and analysis of the brominated products is a valid method for label location.



If deuteriated propene and silylene are formed in the same process (Scheme I), the extent of deuteriation of silylene should complement the extent of deuteriation of propene. One expects similar relative amounts of SiHD and propene-d_1 while propene-d_0 and -d_2 should respectively correspond with SiD_2 and SiH_2. This was qualitatively confirmed by conducting a copyrolysis of **4** and 2,3-dimethylbutadiene to trap silylene as the silacyclopentene adduct **10**. From mass spectral analysis of the M − 2 through M + 3 ion intensities (referenced to the spectrum of authentic **10**-h_2), **10** was found to be 30% d_0, 53% d_1, and 17% d_2, in quite good agreement with the values of 22% d_2, 56% d_1, and 22% d_0 obtained from direct analysis of the propene from **4**. The ^{2}H NMR spectrum of **10** showed only Si–D absorption (no C–D absorption), while the IR spectrum showed both Si–D and Si–H stretches, and the ^{1}H NMR possessed a significant (1.2 H) Si–H resonance. Thus, **10** is clearly formed as only three isomers—**10**-h_2, **10**-hd, and **10**-d_2. The correlation between D incorporation in **10** and in propene is remarkably good considering that the experimental conditions are quite different (N_2-flow copyrolysis at 540 °C vs FVP at 700 °C) and that the yield of **10** was extremely low. Repeated copyrolyses did not afford yields of **10** above 2%, which was bothersome in that the yield of propene from **2** or **4** was ca. 20%. However, the low yields of adduct **10** are at least partly due to the thermal instability of **10** under our experimental conditions. When an authentic sample of **10**-d_2 was copyrolyzed with a 10.7-fold molar excess of dimethylbutadiene at 535 °C, **10** was recovered in only 18% yield but was determined to be 91% **10**-d_2, with no positional scrambling of the label detectable by ^{2}H NMR.



The thermolysis of 1-methyl-1-deuterio-1-silacyclobutane (**11**) was examined by FVP at 710 °C. Ethene and propene were both formed, although the relative amount of propene was considerably less than from **2** or **4**. GCMS analysis showed <10% deuteriation of ethene, while most of the propene was deuteriated. Unfortunately, reliable numbers of deuterium incorporation in propene could not be obtained by GCMS due to overlap of "impurity" peaks with the GC peak of propene. However, bromination of the gaseous olefins proved a solution. Dibromoethane (**5**, 29%) was 6% **5**-d_1 and 94% **5**-d_0 while dibromopropane (**6**) consisted of 68% **6**-d_1 and 32% **6**-d_0, with *no* **6**-d_2 detectable. The ^{2}H NMR spectrum of **6** showed only a single peak at δ 1.26, corresponding to deuterium at C-3. However, the signal-to-noise ratio from the miniscule sample was too low to determine whether or not absorptions were present for deuteriums at C-1 and/or C-2. At any rate, *most* of the label is at C-3. These results are consistent with a mechanism of isomerization of **11** to methylpropylsilylene (**12**) followed by methylsilylene extrusion. The formation of both propene-d_1 and -d_0 from **11** again suggests scrambling by silylene/silirane equilibria.



In summary, the demonstration that 1-deuteriated silacyclobutane decomposition produces propene which is deuteriated in varying amounts and in all positions is taken as clear evidence that one path for silacyclobutane thermal decomposition involves a 1,2-hydrogen shift from silicon to carbon to produce a propylsilylene which decomposes to products via a *reversible* formation of silacyclopropanes through β-CH insertion. We will report in a separate paper our studies with alkylsilylenes further confirming this latter assertion.

Experimental Section

General Procedures for Pyrolyses. Flash vacuum pyrolyses (FVP) were performed by slowly distilling compounds through a heated, seasoned horizontal quartz pyrolysis tube (16-mm i.d., 200 mm long) packed with quartz chips and collecting the products in a trap cooled by liquid nitrogen. The tube was evacuated by a Varian oil diffusion pump to ca. 10^{-5} Torr measured by an ion gauge placed behind a liquid N_2 cooled trap. The rate of pyrolysis (typically 0.1 g/h) was modulated by sample cooling to maintain a constant pressure (measured at the ion gauge), typically 10^{-4}–10^{-3} Torr. The pyrolysis tube was heated with a Lindberg oven. Temperatures were measured at the center and were controlled by an Omega CN 300 temperature controller.

Gaseous products were distilled into a second trap and could be sampled via a gastight syringe through a septum and analyzed by GC or GCMS.

Flow copyrolyses were conducted in a vertical quartz pyrolysis tube packed with seasoned quartz chips. Samples were added to the top of the tube by syringe, and the pyrolysate was swept through the quartz tube with a gas flow, typically at a flow rate of 35 mL/min. The products were collected in a dry ice/2-propanol cooled trap.

Instrumentation. All ^{1}H NMR spectra were recorded on a Nicolet Model NT-300 spectrometer at 300 MHz. ^{13}C NMR spectra were obtained on the NT-300 spectrometer at 75 MHz. ^{2}H NMR spectra were recorded on a Bruker WM-300 spectrometer (at 46 MHz) in benzene solution with chemical shifts reported as parts per million (δ scale) using natural-abundance deuterium in benzene as an internal standard (δ 7.15).

Capillary gas chromatographic (GC) analyses were performed on a Hewlett-Packard Model 5890 or 5790 GC using either a 12- or 30-m RSL-150 column. Preparative GC was performed on a Varian Model 920 or 1700 GC. Chromatography of light gas samples was performed with a Fisher Series 4800 GC with thermal conductivity (TC) detection. Columns employed were either a $^1/_8$ in. × 30 ft 23% SP-1700 on Chromosorb P-AW column or a $^1/_8$ in. × 6 ft Unibeads 2S column. GCMS of gas samples was performed on a Finnigan Model 4023 GCMS using the Unibeads 2S column unless otherwise specified.

Exact mass measurements were obtained on a Kratos MS-50 mass spectrometer at 70 eV. Quantitative mass spectra for deuterium analyses were obtained on either the Finnigan 4023 GCMS or a Kratos MS-50 mass spectrometer (neat samples).

IR spectra were recorded on either a Beckman IR 4250 or an IBM IR 98 (FTIR). GC infrared spectra (GCIR) were obtained on the IBM IR 98 spectrometer attached to a Hewlett-Packard 5800 GC equipped with a 30-m capillary column. All GC yields were calculated with predetermined response factors and are absolute.

Boiling points are reported uncorrected. Elemental analyses were performed by MicAnal (Tucson, AZ).

Synthesis of 1-Silacyclobutane (2). The synthesis of **2** was conducted by a modification of the procedure of Laane.[7] 1,1-Dichlorosilacyclobutane (7.1 g, 0.050 mol) was added dropwise via syringe to a stirring slurry of $LiAlH_4$ (1.13 g, 0.030 mol) in dibutyl ether (50 mL) at −23 °C under N_2. After addition, the solution was gradually warmed to room temperature and stirred overnight. The product and solvent were then trap-to-trap distilled from +25 to −78 °C under vacuum (increased gradually from 50 Torr of full vacuum). Final distillation through a 5 in. × $^1/_2$ in. fractionating column packed with glass helices afforded 2.4 g (0.032 mol, 67%) of **2**, bp 43–45 °C. Final purification was achieved by preparative GC (20-ft 20% SE-30 on Chromosorb W column, 60 °C isothermal).

Synthesis of 1,1-Dideuterio-1-silacyclobutane (4). Compound **4**[7] was prepared in 61% yield according to the procedure described for **2** except that $LiAlD_4$ was used in place of $LiAlH_4$. Final purification was by preparative GC. ^1H NMR analysis indicated that essentially quantitative deuteration was obtained: ^1H NMR (C_6D_6) δ 1.02 (t, J = 8 Hz, 4.0 H), 2.12 (pentet, J = 8 Hz, 2.0 H). Only a *very* small SiH peak could be detected at δ 4.66 (m, ~0.01 H). MS *m/e* (% relative intensity) 76 (1.9), 75 (5.0), 74 (65.1), 73 (19.3), 72 (22.6), 71 (10.9), 70 (7.5), 47 (12.2), 46 (100.0), 45 (87.8), 44 (69.7), 43 (27.9), 42 (17.0). ^2H NMR (C_6H_6) showed only a SiD peak at δ 4.67.

FVP of 1-Silacyclobutane (2) and Trapping of Products in Bromine. FVP of **2** was conducted at 710 °C, and the pyrolysate, initially trapped in a liquid N_2 cooled trap, was distilled under vacuum into a gas bulb cooled to −196 °C fitted with a greaseless vacuum stopcock containing a twofold molar excess of Br_2. After standing overnight, this mixture was dissolved in 50 mL of H_2CCl_2 and washed with saturated Na_2SO_3 in 1/1 $MeOH/H_2O$ until the color was removed and then twice with 100 mL of water. After drying ($MgSO_4$), the solvent was removed by rotary evaporation, and the yellow residue was extracted into 1.5 mL of hexane. Analysis of capillary GC indicated the formation of 1,2-dibromoethane (**5**) (run 1, 47%; run 2, 41%) and 1,2-dibromopropane (**6**) (run 1, 11%; run 2, 13%).

FVP of 1,1-Dideuterio-1-silacyclobutane (4). FVP's of **4** were conducted by slowly distilling (typical scale: 0.2545 g, 3.44 mmol) at temperatures ranging from 580 to 750 °C and collecting the products at −196 °C. During the pyrolysis the vacuum rose from an initial value of 2 × 10^{-5} Torr, indicating the formation of noncondensables (e.g., H_2), and the rate of distillation was controlled by cooling the sample of **4** with a dry ice/*i*-PrOH bath to maintain a constant pressure (measured at the ion gauge) of 10^{-4}–10^{-3} Torr. Warming of the collected pyrolysate to room temperature resulted in considerable effervescence. The remaining liquid, representing from 24% to 58% mass recovery in seven runs, was analyzed by capillary GC and GCMS and found to consist of a single major component (>90%) identified as **4**. The recovered **4** was isolated by preparative GC (20-ft 20% SE-30 Chromosorb W column, 60 °C isothermal). Analysis by ^2H NMR showed *only* a SiD resonance at δ 4.67. Analysis by ^1H NMR showed some SiH formation with integration values of 0.09 H and 0.16 H for the seven runs, representing from 5% to 8% D exchange (as SiH formation), respectively.

The pyrolysis was repeated at 690 °C and the gases were collected and analyzed. GC and GCMS (18 eV) identified ethene as the major component along with propene in lesser amounts. Observed ion intensities for the ethene and propene and calculated deuterium incorporations for the ethene and propene are presented in Table I. The calculation of the % D incorporation was performed by the method of Biemann.[6] GC analysis of the gas sample using literature TC response factors[8] afforded an estimate of the relative yields as 86 mol % ethene and 14 mol % propene.

GCMS also detected another component, base peak *m/e* 46, possibly deuteriated methylsilane: MS *m/e* (% relative intensity) (18 eV) 50 (2.9), 49 (18.8), 48 (51.1), 47 (72.4), 46 (100.0), 45 (43.7), 44 (11.9), 31 (16.5).

FVP of 1,1-Dideuterio-1-silacyclobutane (4) and Trapping of Products in Bromine. The FVP of **4** (0.6008 g, 8.12 mmol) was repeated at 710 °C and the products were trapped at −196 °C. The pyrolysate was distilled into a gas-collection flask at −196 °C which contained excess Br_2 (3.3 g, 21 mmol). After warming to room temperature and sitting overnight, the contents were extracted into H_2CCl_2 (50 mL), washed with saturated Na_2SO_3 in 1/1 $MeOH/H_2O$, and washed twice with water. After drying ($MgSO_4$) and solvent removal, a yellow oil remained, which was extracted into 1.5 mL of hexane. This solution was analyzed by capillary GC and GCMS, and the products were isolated by preparative GC (15-ft 15% SE-30 on Chromosorb W column, 100 °C isothermal). Only two significant products were detected, identified as 1,2-dibromoethane (**5**) (55%) and 1,2-dibromopropane (**6**) (10%) by comparison of GC, GCMS, and ^1H NMR spectra with authentic samples. Deuterium incorporation was determined by measurement of mass spectral ion intensities and calculated.[6] Mass spectral data along with % D incorporation results and yield data are summarized in Table II. Two separate runs were examined; run 1 employed the Finnigan 4023 GCMS system for analysis of the unseparated mixture, while run 2 used a Kratos MS-50 on samples of **5** and **6** which had been isolated by preparative GC.

Spectral characteristics for 1,2-dibromopropane (**5**) were as follows: ^1H NMR (C_6D_6) δ 1.27–1.37 (m, 3 H), 2.92 (t, J = 10 Hz, 1 H), 3.22 (d of d, J = 10 Hz, J' = 4 Hz, 1 H), 3.54–3.66 (m, 1 H). This matched an authentic sample of undeuteriated **5** with the exception of the multiplet centered at δ 1.32, which was a doublet (J = 6.5 Hz) in the undeuteriated sample. ^2H NMR (C_6H_6) δ 1.26 (m, deuteriums on methyl), 2.89 (m) and 3.18 (m) (both diastereotopic methylene deuteriums), 3.54 (m, methine D) (Figure 1). Relative integration of the deuterium signals and distribution of deuterium in the dibromopropane are shown in Table III. The results of two runs are shown. Run 1 and run 2 of Tables II and III correspond.

Synthesis of 1-Deuterio-1-methyl-1-silacyclobutane (11). Compound **11** was prepared by a method similar to that described for **4**.[9] In a typical procedure 4.0 g of 1-chloro-1-methyl-1-silacyclobutane (0.033 mol) was added dropwise via syringe to a stirring slurry of $LiAlD_4$ (0.50 g, 0.012 mol) in 35 mL of dry dibutyl ether at −23 °C under N_2. After stirring for 1 h at −23 °C, the solution was warmed to room temperature and stirred overnight. Trap-to-trap distillation (+25 to −78 °C under vacuum) afforded a solution of **11** in Bu_2O free of $LiAlD_4$. Fractional distillation at 1 atm of pressure through a 6 in. × $^1/_2$ in. column packed with glass helices yielded 2.0 g (0.023 mol, 69%) of product, bp 64–65 °C. Final purification was achieved by preparative GC (10-ft 10% SE-30 on Chromosorb W column, 60 °C isothermal): ^1H NMR (C_6D_6) δ 0.15 (s, 3 H), 0.80–1.00 (m, 2 H), 1.06–1.22 (m, 2 H), 1.96–2.27 (m, 2 H) (no trace of SiH by ^1H NMR); IR (neat) 2970 (s), 2930 (s), 2860 (w), 2120 (vw) (residual SiH), 1540 (s) (SiD), 1390 (w), 1245 (m), 1115 (m), 865 (m), 780 (m) cm^{-1}; MS *m/e* (% relative intensity) 87 (25), 60 (12), 59 (100), 58 (45), 46 (16), 45 (51), 43 (71), 41 (12).

FVP of 1-Deuterio-1-methyl-1-silacyclobutane (11). Compound **11** (0.081 g, 0.931 mmol) was distilled through a horizontal quartz-packed pyrolysis tube at 710 °C at 5 × 10^{-4} Torr. The pyrolysate was collected (−196 °C) and then distilled under vacuum into a gas-collection flask. Analysis by GCMS (70 eV) indicated the presence of deuteriated ethene (<10% deuteration): MS *m/e* (% relative intensity) 30 (0.8), 29 (10.7), 28 (100.0), 27 (67.0), 26 (66.9), 25 (10.0), 24 (2.7); reference (undeuteriated) ethene run at the same time and conditions, MS *m/e* (% relative intensity) 30 (0.0), 29 (2.0), 28 (100.0), 27 (46.9), 26 (48.2), 25 (7.2), 24 (1.9). Also detected in a much smaller amount was deuteriated propene: MS *m/e* (% relative intensity) (70 eV) 44 (3.3), 43 (48.0), 42 (100.0), 41 (76.5), 40 (45.8), 39 (62.5), 38 (18.0), 37 (10.6), 36 (1.9); reference propene run at the same time and conditions, MS *m/e* (% relative intensity) 43 (2.6), 42 (69.3), 41 (100.0), 40 (25.7), 39 (72.2), 38 (18.0), 37 (10.9), 28 (3.9), 27 (40.7), 26 (10.4). The deuteriated propene peak in the GCMS was contaminated with unidentified impurities; therefore, the mass spectral ion intensities of the propene in this experiment are uncertain, and the deuteration results obtained by bromination (vide infra) provide better quantitation.

FVP of 1-Deuterio-1-methyl-1-silacyclobutane (11) and Trapping of Products in Bromine. FVP of **11** (0.7241 g, 8.33 mmol) was conducted at 710 °C at 5 × 10^{-4} Torr, and the gas products were distilled under vacuum into a gas-collection flask containing excess Br_2 (2.0 g, 12.5 mmol). After warming to 25 °C, the mixture stood for 2 h, was dissolved in 50 mL of H_2CCl_2, washed with saturated Na_2SO_3 in 1/1 $MeOH/H_2O$, washed with 3 × 75 mL water, and dried ($MgSO_4$). The solvent was removed to leave a yellow oil, which was extracted into 1 mL of hexane. Analysis of capillary GC and GCMS identified 1,2-dibromoethane (**5**) (29%) and 1,2-dibromopropane (**6**) (1%). **6** was isolated by preparative GC. The ^2H NMR of **6** showed a single peak at δ 1.26 (s). Very small resonances at ca. δ 3.0, 3.3, and 3.6 may be present (integrating to $\leq$15% of the methyl deuteride resonance at δ 1.26) and may belong to **6**; however, the sample obtained was too dilute (only milligram quantities of **6** could be isolated) to allow any definite assignment of these faint signals, even after a 10 000-scan accumulation. The mass spectra of **5** and **6** were obtained at 21–25 eV and percent deuterium results are presented in the text.

Preparation of 3-Deuteriopropene (9). A total of 19.5 g (0.161 mol) of allyl bromide in 200 mL of dry ether was added dropwise under N_2, at a rate sufficient to maintain a gentle reflux, to a stirring slurry of Mg (5.0 g, 0.21 mol) in which the reaction had been initiated with a crystal of iodine and 0.5 g (0.004 mol) of allyl bromide. After the addition was

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complete, the solution was refluxed an additional 2 h. After the mixture cooled to room temperature, the Grignard reagent was quenched by a dropwise addition of D_2O. The gas thus liberated was passed through an ethylene glycol/dry ice cooled condenser and a $CaSO_4$ drying tube and was frozen at −196 °C. The trap containing the frozen propene was isolated from the reaction setup and evacuated to less than 1 Torr, and the gas was condensed into a steel gas cylinder at −196 °C, keeping the trap cooled to −78 °C to minimize contamination by trace ether or other impurities. Obtained was 1.7 g (23%) of **9**.

Preparation of 1,2-Dibromo-3-deuteriopropane. The preparation of 3-deuteriopropene was repeated as described above, except that the propene generated was passed through liquid Br_2 (10 mL) instead of the −196 °C trap. The resulting mixture was extracted into pentane and washed with saturated Na_2SO_4 in 1/1 $MeOH/H_2O$ until the Br_2 color was removed. The organic phase was washed twice with 100 mL of water, dried ($MgSO_4$), and rotary evaporated to leave 6.1 g (0.030 mol, 35%) of nearly pure 1,2-dibromo-3-deuteriopropane. An analytical sample was isolated by preparative GC (15-ft 15% SE-30 on Chromosorb W column, 100 °C isothermal): ^1H NMR (C_6D_6) δ 1.31 (d of t where triplet is 1:1:1, $J_{H-H} = 6.5$ Hz, $J_{D-H} = 2.0$ Hz, 2 H), 2.96 (apparent t, $J = 10.0$ Hz, 1 H), 3.25 (d of d, $J = 10.0$ Hz, $J' = 4.4$ Hz, 1 H), 3.61 (m, apparent sextet, 1 H); ^{13}C NMR (C_6D_6) δ 23.70 (t, $J_{D-C} = 19.3$ Hz), 37.78, 45.93; ^2H NMR (C_6H_6) δ 1.30 (m). The following MS ion intensities were used to calculate % D incorporation (Finnigan 4023 GCMS, 18 eV): *m/e* (% relative intensity) 200 (M^+) (2.28), 201 (51.26), 202 (6.11), 203 (100.00), 204 (5.46), 205 (46.97), 206 (1.63); reference (undeuteriated) **6**, *m/e* (% relative intensity) 200 (M^+) (52.46), 201 (2.79), 202 (100.00), 203 (4.24), 204 (47.94), 205 (1.89), 206 (0.27). A calculation[6] of % D incorporation gives 96% d_1 and 4% d_0.

Pyrolysis of 3-Deuteriopropene (9). Compound **9** (50 mL at STP) was passed through a horizontal quartz-packed pyrolysis tube at 10^{-3} Torr at 720 °C, and the products were collected in a liquid N_2 cooled trap. The product was distilled into a gas-collection flask containing 0.25 mL of Br_2 at −196 °C. After warming to room temperature, the products were extracted into H_2CCl_2, washed with saturated Na_2SO_3 in 1/1 $MeOH/H_2O$, washed with water, dried, and rotary evaporated. A yellow oil remained which contained 1,2-dibromopropane as the major product. A sample isolated by preparative GC had ^1H NMR, ^{13}C NMR, and ^2H NMR spectral characteristics identical with those of **6** prepared by direct bromination of **9**. The mass spectral ion intensities were (Finnigan GCMS, 18 eV) as follows: *m/e* (% relative intensity) 200 (3.82), 201 (52.70), 202 (8.10), 203 (100.00), 204 (5.44), 205 (49.46), 206 (2.32); reference (undeuteriated) **6**, *m/e* (% relative intensity) 200 (M^+) (52.67), 201 (0.69), 202 (100.00), 203 (2.10), 204 (48.54), 205 (1.73), 206 (0.15). a calculation[6] of % D incorporation indicates the product is 93% d_1 and 7% d_0. There was a 97% retention of the deuterium label in the pyrolyzed **9**.

Synthesis of 3,4-Dimethyl-1-silacyclopent-3-ene (10). First 1,1-dichloro-3,4-dimethyl-1-silacyclopent-3-ene was prepared by dropwise addition of 16.4 g of hexachlorodisilane (0.61 mol) dissolved in 30.4 g (0.37 mol) of 2,3-dimethylbutadiene to a vertical quartz-packed pyrolysis tube at 610 °C swept with a N_2 flow of 60 mL/min. The products were collected in a −78 °C trap and distilled at 1 atm of pressure to remove unreacted butadiene. Distillation at 30 Torr through a 4 in. × $^1/_2$ in. column packed with glass helices yielded a continuous fraction with the boiling range 82–90 °C, 8.9 g, of approximately 85% pure product (by capillary GC, uncorrected FID response). An analytical sample was obtained by preparative GC (14-ft 15% SE-30 on Chromosorb W column, 100 °C initial, 8 °C/min ramp): ^1H NMR (C_6D_6) δ 1.36 (s, 6 H), 1.55 (s, 4 H); ^{13}C NMR (C_6D_6) δ 18.49, 29.08, 129.28; IR (neat) 2980, 2905 (s), 2845, 1445 (s), 1390 (s), 1370, 1165 (vs), 1105, 970, 780 (vs), 760 (vs), 745 (vs), 685 cm^{-1}; MS *m/e* (% relative intensity) 182 (10), 180 (M^+) (15), 167 (9), 165 (14), 144 (13), 140 (7), 138 (10), 129 (13), 82 (50), 81 (14), 67 (100), 65 (23), 63 (44), 54 (24), 53 (20); calcd for $C_6H_{10}Cl_2Si$ *m/e* 179.99289, measured *m/e* 179.99290.

A THF solution of the dichloride (1.0 g) was then added dropwise to a stirring slurry of $LiAlH_4$ (0.15 g, 3.95 mmol) in 5 mL of THF under N_2 at −23 °C. After addition, the solution was warmed to room temperature and stirred overnight. The solution was trap-to-trap distilled under vacuum from +25 °C to a −78 °C trap. Analysis by capillary GC showed the distillate contained 0.407 g of **10** (3.64 mmol, 53% based on hexachlorodisilane). Final purification was achieved by preparative GC (14-ft 15% SE-30 on Chromosorb W column, 70 °C initial, 8 °C/min ramp). Compound **10**: ^1H NMR (C_6H_6) δ 1.43 (broad s, 4 H), 1.59 (s, 6 H), 4.04 (pentet, $J = 3.7$ Hz, collapses to s with $h\nu$ at 1.43); ^{13}C NMR (C_6D_6) δ 19.11, 19.16, 131.00; IR (neat) 2950, 2900 (s), 2880 (s), 2850 (s), 2850, 2130 (vs) (SiH), 1435, 1165 (s), 940 (vs), 895, 805 (vs), 790 (vs) cm^{-1}; MS *m/e* (% relative intensity) 112 (M^+) (81), 111 (40), 97 (100), 95 (46), 84 (38), 83 (43), 71 (34), 70 (54), 69 (48), 67 (39), 55 (81), 53 (35); calcd for $C_6H_{12}Si$ *m/e* 112.07083, measured *m/e* 112.07116. Anal. Calcd for $C_6H_{12}Si$: C, 64.20; H, 10.79. Found: C, 63.92; H, 11.03.

Table IV. Mass Spectral Data for **10**-d_2

compd	ion (M = 112)	ion intens	cor ion intens[a]	mol % deuterated species[a]
10-d_2, unpyrolyzed	M − 2	1		
	M − 1	0		
	M	10	10	1 (d_0)
	M + 1	37	36	3 (d_1)
	M + 2	1015	1015	95 (d_2)
	M + 3	121	4	0
	M + 4	39		
	M + 5	3		
10-d_2, pyrolyzed with $Me_2C_4H_4$	M − 2	10		
	M − 1	3		
	M	36, 9[b]	45[c]	4 (d_0)
	M + 1	56	51	4 (d_1)
	M + 2	1112	1103	91 (d_2)
	M + 3	144	15	1 (d_3)
	M + 4	44		
	M + 5	4		

[a] Calculated[6] using the following reference spectrum for **10**-h_2 determined at the same time and conditions: M − 2 = 13, M − 1 = 4, M = 409, M + 1 = 47, M + 2 = 15, M + 3 = 1, M + 4 = 0, M + 5 = 0. [b] Two ions were found; the ion for **10**-h_2 was not identified. [c] The total intensity for the ions at M = 112 was used (see note *b*); hence these calculated values represent the maximum amount of **10**-*hd*.

Copyrolysis of 1,1-Dideuterio-1-silacyclobutane (4) with 2,3-Dimethyl-1,3-butadiene. Compound **4** dissolved in a 4.7- to 6.2-fold molar excess of the butadiene was added dropwise via syringe drive to a vertical quartz-packed pyrolysis tube swept with a N_2 flow of 35 mL/min, and the products were collected at −78 °C. The pyrolysis was conducted at 520, 530, and 540 °C (at 570 °C only *very* minor yields of adducts were obtained). Capillary GC and GCMS indicated the formation of the same products as described in the analogous copyrolysis of **1**,[2] although deuteriated. Products were isolated by preparative GC (15-ft 15% SE-30 on Chromosorb W column, 50 °C initial, 4 °C/min ramp) and identified on the basis of their ^1H NMR, IR, and MS characteristics as deuteriated 3,4-dimethyl-1-silacyclohex-3-ene (12–21%), deuteriated 1,3,4-trimethyl-1-silacyclopent-3-ene (7–9%), and deuteriated 3,4-dimethyl-1-silacyclopent-3-ene (**10**) (1–2%). The mass recovery was 73–81%.

Compound **10** could not be totally purified by preparative GC, and small impurity peaks in the NMR could not be avoided, although the spectrum of **10** was clearly distinguishable. Unreacted **4** was found in only small (≤3%) amounts.

The three products had the following spectral properties. For deuteriated silacyclohexene: ^1H NMR (C_6D_6) δ 0.69 (t, $J = 6.7$ Hz, collapses to s with $h\nu$ at 1.99, 2 H), 1.27 (s, 2 H), 1.59 (s, 3 H), 1.65 (s, 3 H), 1.99 (t, $J = 6.7$ Hz, collapses to s with $h\nu$ at 0.69, 2 H) (a small SiH peak was found at δ 3.87 (broad s, 0.06 H)); ^2H NMR (C_6H_6) δ 3.89 (s) (no other resonances were found); IR (GC-FTIR) 2940 (s), 2865 (m), 2140 (vw) (residual SiH), 1560 (vs) (SiD) cm^{-1}. For deuteriated trimethylsilacyclopentene: ^1H NMR (C_6D_6) δ 0.07 (m, 2.6 H), 1.29 (d, $J = 18$ Hz, 2.0 H), 1.58 (d, $J = 18$ Hz, integral undetermined due to unknown impurity), 1.67 (s, 6 H), 4.36 (m, apparent sextet, $J = 3.3$ Hz, 0.25 H); ^2H NMR (C_6H_6) δ 0.05 (apparent 1:2:1 t, $J_{H-D} = 2.0$ Hz, 0.79 D), 4.37 (s, 1.00 D); IR (GC-FTIR) 2915 (vs), 2130 (s) (SiH), 1560 (vs) (SiD), 1180 (s), 890, 800 (vs) cm^{-1}. For **10** (deuteriated): ^1H NMR (C_6D_6) δ 1.43 (s, 4.0 H), 1.59 (s, 6.0 H), 4.04 (pentet, $J = 3.8$ Hz, 1.2 H); ^2H NMR (C_6H_6) δ 4.04 (SiD) (no other resonances were found); IR (GC-FTIR) 2915 (s), 2130 (vs) (SiH), 1560 (s) (SiD) cm^{-1}.

Mass spectra of the deuteriated adducts were determined at 12 eV (Finnigan 4023 GCMS) and compared with reference spectra of authentic undeuteriated compounds determined at the same time and conditions. Corrected ion intensities and percent deuterium results were calculated,[6] but for both silacyclopentene adducts, the large M − 1 ion in the reference sample diminished the accuracy of these calculations and, therefore, the results are at best close estimates of the true deuterium incorporation.

It should be noted that while the silene Diels–Alder adduct, the silacyclohexene, is >95% dideuteriated with the D_2 exclusively on silicon, the methylsilylene adduct, 3,4-dimethyl-1-silacyclopent-3-ene, is only 48% D_2 (33% d_1, 19% d_0) although as expected[2] the deuteriums are found only on Si and SiMe.

Synthesis of 1,1-Dideuterio-3,4-dimethyl-1-silacyclopent-3-ene (10-d_2). Compound **10**-d_2 was prepared by the same method in 43% overall yield (by GC) from hexachlorodisilane. Final purification was obtained on an

8-ft 15% SE-30 on Chromosorb W column (70 °C isothermal). ^{1}H NMR (C_6D_6) δ 1.42 (s, 4 H), 1.64 (s, 6 H) (no SiH was found); IR (neat) 2985 (m), 2915 (s), 2885 (s), 2860 (s), 2140 (vw) (residual SiH), 1560 (vs) (SiD), 1445 (m), 1175 (s), 765 (s), 735 (s), 680 (vs) cm^{-1} (the very weak band at 2140 cm^{-1} indicates only a trace of SiH); MS *m/e* (% relative intensity) (10.3 eV, Kratos MS-50, neat sample) 116 (3.8), 115 (11.9), 114 (100.0), 113 (3.6), 112 (1.0). Mass spectral measurements (Kratos MS-50, neat samples) and calculation[6] indicated **10** was ≥95% d_2.

Flow Pyrolysis of 10-d_2 in Excess 2,3-Dimethyl-1,3-butadiene. A solution of 0.2075 g of **10**-d_2 (1.82 mmol) dissolved in 1.5990 g (19.5 mmol) of 2,3-dimethyl-1,3-butadiene was slowly added dropwise via syringe drive to a vertical quartz-packed pyrolysis tube at 535 °C swept with a N_2 flow of 35 mL/min. The products were collected at −78 °C with a 67% mass recovery. The major components of the pyrolysate were recovered **10**-d_2 (18% GC yield) and dimethylbutadiene. Preparative GC of the recovered **10** (8-ft 15% SE-30 on Chromosorb W column, 70 °C isothermal) afforded a sample whose spectral characteristics were little changed from those of unpyrolyzed **10**-d_2: ^{1}H NMR (C_6D_6) δ 1.42 (s, 4 H), 1.64 (s, 6 H); ^{2}H NMR (C_6H_6) δ 4.0 (s) (no other signals were found); IR (neat) 2985 (m), 2915 (s), 2885 (s), 2860 (m), 2140 (w) (SiH), 1560 (vs) (SiD), 1175 (s), 765 (s), 735 (s), 680 (vs) cm^{-1} (the band at 2140 cm^{-1} has increased somewhat in intensity relative to unpyrolyzed **10**-d_2). The mass spectra (10.3 eV, Kratos MS-50, neat samples) are given in Table IV.

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Induction of Asymmetry by a Remote Chiral Center in the Amide Acetal Claisen Rearrangement

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Abstract: The room-temperature preparation of *N,O*- and *N,S*-ketene acetals, which undergo facile sigmatropic rearrangement, from amides and thioamides has made possible the use of a remote chiral auxiliary to induce relative asymmetry in the rearrangement. *N*-Propionylprolinol and *N*-thiopropionylprolinol derivatives were converted into ketene acetals. Amide acetal Claisen rearrangements formed products with relative and internal induction of asymmetry. Products were formed in 50–70% isolated yields with average relative asymmetric induction of 4.7 to 1. The sense of asymmetric induction was opposite when the products of the amides were compared with those of the thioamides.

N-Propionylproline derivatives, **1**, have been used to prepare asymmetric *N,O*-ketene acetals, which can be employed in room-temperature amide acetal sigmatropic rearrangements.[1] This is the first report of an ambient-temperature amide acetal Claisen rearrangement where relative asymmetry[2] was induced by a remote asymmetric center not immediately adjacent to the rearranging framework.

Asymmetric syntheses employing Claisen rearrangements (Table I), widely used for the stereoselective construction of acyclic systems,[3] have often required an enantiomerically pure alcohol component for the transmission of asymmetry along the allylic array. Relative asymmetric induction by remotely placed substituents has been much less frequently employed. Chiral centers placed in rigid adjacent cyclic systems such as steroids,[4] terpenes,[5] butyrolactones,[6] and oxazolines[7] have effectively induced asymmetry. Where chelation is possible, as in ester enolate Claisen rearrangements, asymmetric β-carbons bearing a hydroxyl have induced relative asymmetry.[3e,8] Chiral substituents at either carbon 1[9] or carbon 6[10] of the network undergoing a 2,3- or 3,3-sigmatropic rearrangement have also induced relative asymmetry.

For the successful induction of internal and relative asymmetry, rearrangement at low temperature of a reactive, asymmetric allylic *N,O*-ketene acetal was required. 1-[(2*S*)-(Hydroxymethyl)-pyrrolid-1-yl]propionic acid[11] (**1a**) was protected as its *O*-benzyl ether. Treatment of 1-(methoxypropylidene)-2(*S*)-[(benzyloxy)methyl]pyrrolidinium trifluoromethanesulfonate (**2b**), formed by alkylation of **1b** with methyl trifluoromethanesulfonate, with 3 equiv of the lithium salt of (*E*)- or (*Z*)-2-buten-1-ol led directly to formation of the amides **3b** and **4b** or **5b** and **6b**, respectively, as the major products of the rearrangement.

Both internal and relative asymmetric induction were only modest.[12] The *tert*-butyldimethylsilyl ether, **1c**, was subjected

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