NMR spectrum suggests the presence of only one *dl* pair.

2-Methyl-3-(trimethylsilyl)-5-propyl-2,5-dihydrofuran (2b): colorless liquid; IR (neat) 1600 (C=C), 1250, 1125, 835, 750, 690 cm^{-1}; ^1H NMR δ 6.0 (br, 1 H), 5.2–4.6 (m, 2 H), 1.5 (br, 4 H), 1.33 (d, 3 H, J = 6 Hz), 0.95 (t, 3 H), 0.13 (s, 9 H); ^{13}C NMR δ 144.6, 139.6, 86.4, 86.0, 39.2, 23.7, 18.8, 14.2, -1.1; MS, m/e 198 (M^+).

2-Methyl-3-(trimethylsilyl)-5-propylfuran (0.248 g, 51% yield) was obtained when the cyclization reaction of **1b** (0.495 g, 2.5 mmol) was carried out under air. The product (colorless liquid) had the following: IR (neat) 1555, 1250, 1200, 835, 750, 690 cm^{-1}; ^1H NMR δ 5.9 (s, 1 H), 2.52 (t, 2 H, J = 7 Hz), 2.26 (s, 3 H), 1.9–1.3 (m, 2 H), 0.93 (t, 3 H), 0.17 (s, 9 H).

2-Isopropyl-3-(trimethylsilyl)-5-propyl-2,5-dihydrofuran (2c): colorless liquid; IR (neat) 1600 (C=C), 1250, 1030, 885, 830, 750, 690 cm^{-1}; ^1H NMR δ 6.0 (br, 1 H), 4.9–4.5 (m, 2 H), 2.0–1.2 (m, 5 H), 1.1–0.8 (br, 3 H), 1.06 (d, 3 H, J = 7 Hz), 0.75 (d, 3 H, J = 7 Hz), 0.13 (s, 9 H); ^{13}C NMR δ 142.2, 140.7, 94.9, 86.4, 38.3, 31.7, 20.8, 19.3, 15.5, 14.3, -1.1; MS, m/e 226 (M^+).

3-(Trimethylsilyl)-2-pentyl-5-propyl-2,5-dihydrofuran (2d): colorless liquid; IR (neat) 1600 (C=C), 1250, 835, 750, 690 cm^{-1}; ^1H NMR δ 5.97 (br, 1 H), 5.1–4.5 (br, 2 H), 1.80–1.13 (br, 12 H), 0.92 (br, 6 H), 0.13 (s, 9 H); ^{13}C NMR δ 143.3, 140.0, 90.0, 86.4, 39.1, 37.0, 32.0, 25.3, 22.7, 19.0, 14.2, 14.1, -1.0. The column on further elution gave 3-(trimethylsilyl)-2-pentyl-5-propylfuran (0.101 g, 8% yield). This air oxidized adduct was not observed by GLC before column chromatography. The product had the following: colorless liquid: IR (neat) 1550, 1245, 835, 755, 690 cm^{-1}; ^1H NMR δ 5.86 (s, 1 H), 2.53 (t, 6 H, J = 7 Hz), 1.89–1.18 (br, 8 H), 1.1–0.8 (m, 6 H), 0.2 (s, 9 H).

2,2-Pentamethylene-3-(trimethylsilyl)-5-propyl-2,5-dihydrofuran (2e): colorless liquid; IR (neat) 1595, 1250, 830, 755, 690 cm^{-1}; ^1H NMR (C_6D_6) δ 5.95 (d, 1 H, J = 1 Hz), 4.97–4.63 (br, 1 H), 2.00–1.30 (br, 14 H), 0.93 (br, 3 H), 0.13 (s, 9 H); ^{13}C NMR (C_6D_6) δ 148.2, 140.8, 93.2, 84.6, 39.5, 39.3, 37.3, 26.1, 23.2, 22.9, 19.4, 14.5, -0.04; MS, m/e 252 (M^+). Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. Found: C, 71.36; H, 11.22.

2,2-Diethyl-3-(trimethylsilyl)-5-propyl-2,5-dihydrofuran (2f): colorless liquid; IR (neat) 1595, 1455, 1250, 1145, 1080, 995, 950, 835, 750, 690 cm^{-1}; ^1H NMR δ 6.1 (d, 1 H, J = 2 Hz), 4.7 (br, 1 H), 1.8–1.3 (br, 8 H), 0.85 (t, 9 H), 0.13 (s, 9 H). The column on further elution with petroleum ether/ether (98:2) gave 3-ethyl-4-(trimethylsilyl)-3-nonen-5-one (0.058 g, 10% yield of a 2.5-mmol reaction) as a colorless liquid: IR (neat) 1685 (s, C=O), 1600 (C=C), 1250, 1145, 1070, 1015, 835, 755, 690 cm^{-1}; ^1H NMR δ 2.50–1.24 (m, 10 H), 0.94 (t, 9 H), 0.07 (s, 9 H).

2-Methyl-3-(trimethylsilyl)-2-octen-4-one (4g). The product was isolated by using a mixture of petroleum ether and ether (98:2) as eluent. The product had the following: colorless liquid; IR (neat) 1685 (C=O), 1615 (C=C), 1250, 1150, 835, 755, 690 cm^{-1}; ^1H NMR (C_6D_6) δ 2.3 (t, 2 H), 1.75 (s, 3 H), 1.62 (s, 3 H), 1.6–1.1 (br, 4 H), 0.85 (t, 3 H), 0.12 (s, 9 H); ^{13}C NMR δ 212.8, 144.5, 142.8, 44.5, 25.4, 24.0, 23.6, 22.5, 14.0, 0.0. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.73; H, 11.28.

2-Methyl-3-(trimethylsilyl)-2-penten-4-one (4h): colorless liquid: IR (neat) 1680 (C=O), 1610 (C=C), 1250, 1190, 900, 835, 750, 685 cm^{-1}; ^1H NMR δ 2.15 (s, 3 H), 1.83 (s, 3 H), 1.72 (s, 3 H), 0.18 (s, 9 H); ^{13}C NMR δ 210.9, 144.2, 143.1, 32.1, 24.0, 23.5, -0.07; MS, m/e 170 (M^+). Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.70; H, 10.46.

1,1-Pentamethylene-2-(trimethylsilyl)-1-buten-3-one (4i): colorless liquid; IR (neat) 1680 (C=O), 1610 (C=C), 1350, 1250, 1185, 835, 755, 690cm^{-1}; ^1H NMR δ 2.16 (s, 3 H), 2.1 (br, 4 H), 1.55 (br, 6 H), 0.16 (s, 9 H); ^{13}C NMR δ 210.9, 152.1, 139.3, 34.6, 34.3, 32.7, 28.4, 26.1, 0.1.

1,4-Bis[1-(trimethylsilyl)-1,2-propadienyl]-1,4-cyclohexanediol (5) was prepared from 1,4-cyclohexanedione by using the procedure described previously.[5] A white solid (1.443 g, 86% yield of a 10-mmol reaction) was obtained after column chromatography (silica gel, 98:2 petroleum ether/ether). The product had the following: mp 35 °C; IR (melt) 3530 (OH), 1930 (C=C=C), 1445, 1360, 1315, 1240, 980, 860, 835, 815, 755, 685 cm^{-1}; ^1H NMR δ 4.45 (s, 4 H), 2.2–1.3 (m, 10 H), 0.18 (s, 18 H); ^{13}C NMR δ 207.2, 106.3, 72.4, 71.8, 34.4, 0.6.

1,4-Bis[1-(trimethylsilyl)-1,2-propadienyl]-7-oxabicyclo[2.2.1]heptane (6) (0.374 g, 45% yield of a 2.5-mmol reaction) was isolated by column chromatography (silica gel, 98:2 petroleum ether/ether) as a white solid: mp 40–42 °C; IR (melt) 1930 (C=C=C), 1250, 1185, 1060, 990, 970, 880, 840, 755, 690 cm^{-1}; ^1H NMR δ 4.35 (s, 4 H), 1.65 (s, 8 H), 0.15 (s, 18 H); ^{13}C NMR δ 208.7, 98.6, 85.9, 69.9, 37.5, -0.01; MS, m/e 318 (M^+). Anal. Calcd for $C_{18}H_{30}OSi_2$: C, 67.86; H, 9.49. Found: C, 67.83; H, 9.68.

5,5-Pentamethylene-4-(trimethylsilyl)-2(5*H*)-furanone (10) (0.281 g, 50% yield) was obtained from **1e** (0.625 g, 2.5 mmol) by carrying out the cyclization reaction under air. The product had the following: white crystalline solid (mp 108–110 °C); IR (KBr) 1735 (s, C=O), 1440, 1270, 1245, 1210, 1130, 985, 955, 935, 900, 880, 870, 830, 755, 735, 690 cm^{-1}; ^1H NMR δ 6.32 (s, 1 H), 2.1–1.5 (br, 10 H), 0.3 (s, 9 H); ^{13}C NMR δ 178.7, 172.4 128.7, 93.1, 35.2, 24.8, 22.3, -0.9; MS, m/e 224 (M^+). Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.98. Found: C, 64.62; H, 8.98. The spirolactone **10** was also obtained by placing dihydrofuran **2e** (0.356 g) in a 10-mL flask with periodic opening of the stopper to alow air oxidation. Within 72 h, 0.258 g (82% yield) of **10** was isolated as a crystalline solid after recrystallization from 60–80 °C petroleum ether. The liquid in the flask before recrystallization was found to contain 1-propanol by a GC/MS spectrometer.

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Registry No. **1a**, 87655-84-3; **1b**, 99947-98-5; **1c**, 87655-82-1; **1d**, 87655-80-9; **1e**, 87655-90-1; **1f**, 87655-88-7; **1g**, 87655-86-5; **1h**, 79015-65-9; **1i**, 79015-67-1; **2a**, 99947-99-6; **2b**, 99948-00-2; **2c**, 99948-01-3; **2d**, 99948-02-4; **2e**, 99948-03-5; **2f**, 99948-04-6; **4g**, 99948-06-8; **4h**, 99948-07-9; **4i**, 99948-08-0; **5**, 99948-09-1; **6**, 99948-10-4; **10**, 99948-11-5; $AgNO_3$, 7783-99-5; 3-ethyl-4-(trimethylsilyl)-3-nonen-5-one, 99948-05-7; 2-methyl-3-(trimethylsilyl)-5-propylfuran, 86918-01-6; 3-(trimethylsilyl)-2-pentyl-5-propylfuran, 99965-47-6.

Kinetics of Some Methylenecyclopropane Rearrangements

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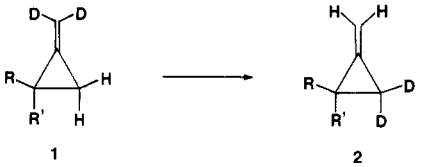
In pursuing our work on the thermolysis of 4-methylene-1-pyrazolines[1] we required information relating to the degenerate rearrangement of methylenecyclopropane and methyl-substituted methylenecyclopropanes. Gilbert[2a] had earlier observed a facile degenerate rearrangement at 52 °C of **1a** ⇄ **2a**, and our products, **1b** and **2b**, were observed to be slowly interconverting under the conditions required to thermolyze the pyrazoline reactants.



1 2

a R=R'=C_6H_5
b R=R'=CH_3
c R=R'=H
d R=H; R'=CD_2=CD

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(2) (a) Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 2168–2169. (b) Gilbert, J. C.; Higley, D. P. *Tetrahedron Lett.* **1973**, 2075–2078.

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Table I. First-Order Rate Constants and Kinetic Parameters for the Rearrangement 1c ⇄ 2c (760 torr)

temp, °C (±0.05 °C)	$10^5 k_{obsd}$,[a] s^{-1}	activation parameters
190.00	0.943 ± 0.017	E_a = 41.2 ± 0.8 kcal mol^{-1}
200.00	2.43 ± 0.06	log A = 14.4 ± 0.4
210.00	6.03 ± 0.04	

[a] Where $k_{obsd} = 2k_{1c,2c} + k_{2c,1c}$, the rate of approach to equilibrium.

Table II. First-Order Rate Constants and Kinetic Parameters for the Degenerate Rearrangement of 1b ⇄ 2b (760 torr)

temp, °C (±0.05 °C)	$10^5 k_{obsd}$,[a] s^{-1}	activation parameters
170.00	3.24 ± 0.03	E_a = 38.5 ± 0.4 kcal mol^{-1}
180.00	8.91 ± 0.08	log A = 14.5 ± 0.2
190.10	21.6 ± 0.04	

[a] Where $k_{obsd} = k_{1b,2b} + k_{2b,1b}$, the rate of approach to equilibrium.

Table III. Kinetic Data for the Rearrangement of 2,2-Dimethylmethylenecyclopropane to Isopropylidenecyclopropane (3 ⇄ 4)

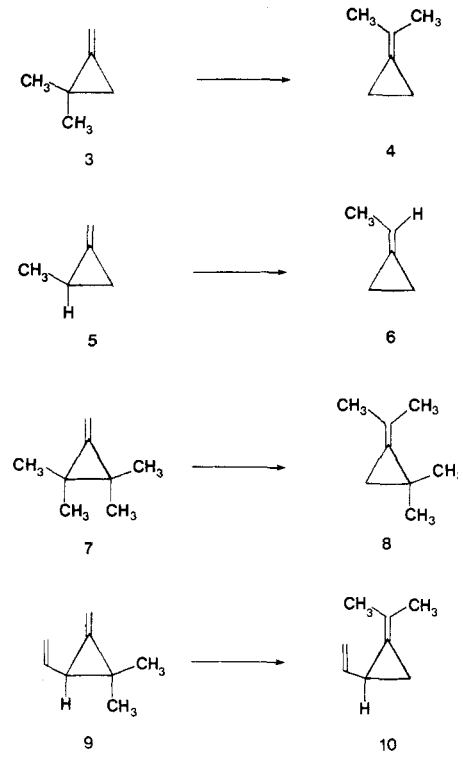
temp, °C (±0.05 °C)	$10^5 k_{obsd}$,[a] s^{-1}	activation parameters
180.00	4.19 ± 0.03	E_a = 42.0 ± 0.3 kcal mol^{-1}
190.10	10.5 ± 0.3	log A = 14.89 ± 0.15
200.00	30.1 ± 0.2	

[a] Where $k_{obsd} = k_{3,4} + 2k_{4,3}$, the rate of approach to equilibrium.

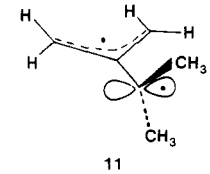
In order to obtain accurate initial product ratios we have studied the interconversion of **1b** and **2b**. As a reference we have also examined the isomerization[3] of dideuteriomethylenecyclopropane (**1c**) and methylenecyclopropane-*2,2-d*$_2$ (**2c**) and wish to report these and analogous rearrangements. Table I reports kinetic parameters for the equilibration of **1c** ⇄ **2c**, the rates were measured by ^{1}H NMR, from samples heated for the appropriate time at a pressure of approximately 760 torr at 190–210 °C. The degenerate rearrangement of **1b** ⇄ **2b** was studied, in the gas phase, over a similar temperature range and is reported in Table II. The less facile rearrangement of 2,2-dimethylmethylenecyclopropane (**3**) to isopropylidenecyclopropane (**4**) was studied, using GC methods, and its kinetic data are listed in Table III.

Discussion

Table IV lists activation parameters ($\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$) for specific processes and compares the rates with those of analogous processes observed by others. Chesick[5] studied the equilibration of 2-methylmethylenecyclopropane (**5**) and ethylidenecyclopropane (**6**). For those cases in Table IV wherein the product and reactant are in equilibrium ($0.1 \leq K \leq 10$) the activation parameters have been calculated for the process shown, and a statistical correction of 0.5 has been applied to both the first and seventh entries since the exocyclic methylene in these cases can migrate



to two equivalent ring sites. It is interesting to note that in those cases wherein the pivoting carbon is stabilized by resonance, e.g., a vinyl or phenyl group, a negative entropy of activation is observed. This is to be expected since a loss of rotational freedom is required for the resonance interaction. The data in Table IV are entirely consistent with Doering and Roth's[8] observation that "the atom which bears the substituent(s) more highly stabilizing a free radical assumes the role of pivot in the rearrangement". By heating to a higher temperature one can, if thermodynamically favorable, observe the less stabilizing group acting as a pivot (compare entries 3 and 5 in Table IV). The rearrangements listed as entries 1, 5, and 6 in Table IV have very similar rate and activation enthalpies.[9] Entry 3 implies that the two methyl substituents of **1b** contribute a 2.9 kcal mol^{-1} decrease in activation energy when on the pivoting carbon. This is somewhat smaller than the 5.4 kcal mol^{-1} stabilization[10] expected for the dimethyl Chesick intermediate **11** and may well be an indication that the



intermediate does indeed exist as an energy minimum and that the transition state to the formation of the intermediate manifests only a portion of the calculated stabilization.[11] On this basis we may also expect the transfor-

(3) Slafer et al. (Slafer, W. D.; English, A. D.; Harris, D. O.; Shellhamer, D. F.; Meshishnek, M. J.; Aue, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 6638–6646) have reported a rate constant at 209 °C for the interconversion of methylenecyclopropane-*2,2,3,3-d*$_4$ to methylenecyclopropane-*2,2-d*$_2$ from which an activation energy has been estimated.[4]

(4) Kirmse, W.; Murawski, H.-R. *J. Chem. Soc., Chem. Commun.* **1977**, 122–123.

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(9) Gajewski and Chou (Gajewski, J. J.; Chou, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 5696–5707) have observed a secondary deuterium kinetic isotope effect k_H/k_D = 1.31 for the isomerization of *trans*-2,3-dimethyl-1-dideuteriomethylenecyclopropane to 2-methylethylidenecyclopropane-*3,3-d*$_2$ thus a direct comparison of entries 1–4 with 5–8 in Table I should taken into consideration this otherwise unobservable component.

(10) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1977**, *99*, 2053–2060. Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 967–972.

(11) Buchwalter (Buchwalter, S. L. *Tetrahedron* **1984**, *40*, 5097–5112) has recently discussed the role of the Chesick intermediate in such rearrangements.

Table IV. Comparison of Activation Parameters and Specific Rate Constants for Some Methylenecyclopropane Rearrangements

entry	rearrangement	$\log_{10} A$, s^{-1}	$\Delta S^{\ddagger}_{180}$	$\Delta H^{\ddagger}_{180}$, kcal mol^{-1}	k_{180}, s^{-1}	relative rates	ref
1	**1c** → **2c**	13.73 ± 0.38	1.5 ± 2	40.5 ± 0.8	5.4×10^{-7} [a]	1	this work
2	**1a** → **2a**	10.47	−13.4	21.9	3.0×10^{-1}	5.5×10^{5}	2a
3	**1b** → **2b**	14.20 ± 0.22	3.6 ± 1.0	37.6 ± 0.5	4.46×10^{-5}	82	this work
4	**1d** → **2d**	11.5	−8.7	24.0	3.1×10^{-1}	5.7×10^{5}	2b
5	**3** → **4**	14.69 ± 0.21	5.9 ± 0.9	40.9 ± 0.3	3.36×10^{-6}	6.2	this work
6	**5** → **6**	13.88	2.2	39.2 ± 0.6	3.47×10^{-6}	6.4	5
7	**7** → **8**	14.0 ± 0.2	2.7 ± 0.5	35.5 ± 0.4	2.57×10^{-4} [a]	476	6
8	**9** → **10**	12.1	−6.0	23.8	1.57	2.9×10^{6}	7

[a] Corrected statistically for the number of equivalent cyclopropane positions.

mations **7** → **8** and **1b** → **2b** to be very similar, and indeed they differ in rate by only a factor of 5.8. The decrease in activation enthalpy on going to the tetramethyl compound **7** may well be due to an increased ground state energy for **7** due to the opposed methyl groups on the cyclopropane ring. This is supported by the observations[6] that $K_{180\,°C} = 653 \pm 33$ for the equilibrium **7** ⇄ **8** and $\Delta H = -5.2 \pm 0.2$ kcal mol^{-1} whereas $K_{180\,°C} = 4.12$ and $\Delta H = -1.17$ kcal mol^{-1} for **3** ⇄ **4**.

Experimental Section

Cyclopropylmethanol-α,α-d_2. Pulverized lithium aluminum deuteride (5.0 g, 0.12 mol) was refluxed in 300 mL of ether for 1 h under nitrogen. After the mixture was cooled to 0 °C methyl cyclopropane carboxylate (20 g, 0.2 mol) in 60 mL of ether was added dropwise and then refluxed for 10 h. Upon cooling the reaction mixture was treated with 5 mL of water, 5 mL of 15% sodium hydroxide, and 15 mL of water successively. Filtration, drying of the ether layer with magnesium sulfate, and distillation gave the product bp 120 °C (710 torr) [lit. value[12] bp 123 °C (1 atm)], 13 g: 90% yield; ^{1}H NMR ($CDCl_3$) δ 0.2 (m, 2 H), 0.5 (m, 2 H), 1.1 (m, 1 H), 1.9 (s, 1 H); ^{2}H NMR indicated >99% deuterium on the carbinyl carbon.

Cyclopropylmethyl Bromide-α,α-d_2. Cyclopropylmethanol-α,α-d_2 (6.4 g, 87 mmol) in 70 mL of dry DMF was mixed with freshly distilled tributylphosphine (22 mL, 89 mmol) under a nitrogen atmosphere.[13] Bromine (14.2 g, 88 mmol) was added slowly while the temperature was maintained below 50 °C. The volatile components were removed by distillation, up to 40 °C (14 torr), and trapped in a receiver cooled to −80 °C. Cold water was added to the distillate and the organic product extracted with pentane (4 × 25 mL) dried, concentrated, and distilled to give 8 g (69% yield): bp 100 °C (710 torr);[14] ^{1}H NMR ($CDCl_3$) δ 0.37 (m, 2 H), 0.75 (m, 2 H), 1.30 (m, 1 H) [indicated >98% isotopic purity]; ^{2}H NMR indicated deuterium at only one position.

Dideuteriomethylenecyclopropane (1c). The dehydrohalogenation was essentially that outlined by Dolbier.[15] Potassium *tert*-butoxide (8 g, 71 mmol) was added to 80 mL of dry Me_2SO under nitrogen. Cyclopropylmethyl bromide-α,α-d_2 (8 g, 59 mmol) was added over 0.5 h and the temperature was maintained at 35 °C. All volatile components were trapped in a receiver cooled to −80 °C. The product was purified by trap-to-trap distillation to give 2 g (61% yield): bp 10 °C (1 atm); ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 4 H), 5.38 (s, 0.012 H) [and indicated 99 ± 1% deuterium at the exomethylene position].

2,2-Dimethylmethylenecyclopropane-3,3-d_2. The synthesis of the nondeuterated material by two successive reductions of 2,2-dibromo-3,3-dimethylmethylenecyclopropane using tri-*n*-butyltin hydride has been described earlier.[16] With freshly prepared tri-*n*-butyltin deuteride,[17] 2,2-dimethylmethylcyclopropane-3,3-d_2 was prepared in 24% yield: ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 6 H), 5.26 (s, 1 H), 5.36 (s, 1 H); ^{2}H NMR indicated >99% of deuterium on the cyclopropyl ring.

Kinetic Measurements. Pyrex break-seals (18-mm diameter, 70 mm long) were evacuated and flamed before filling with 20 μL of sample transferred by trap-to-trap distillation. The tubes were immersed in a well stirred silicon oil bath for the appropriate length of time and then quenched in ice–water. The temperature was controlled by a Melabs Model CTC-1A proportional temperature controller and measured by an HP Model 2801A quartz thermometer calibrated by the National Bureau of Standards. The temperature stability of the oil bath was monitored by recording the analogue output of an HP Model 2802A platinum resistance thermometer with an HP Model 3420B digital voltmeter coupled to a strip chart recorder. The variation of temperature during any run was always less than 0.04 °C. The break-seals were reattached to the vacuum line and the contents transferred to an NMR tube containing $CDCl_3$. The tubes were then sealed and submitted to analysis using a 400-MHz ^{1}H NMR. The infinity tubes for the isomerization **1c** ⇄ **2c** gave $K = [\mathbf{2c}]/[\mathbf{1c}] = 0.50 \pm 0.02$ at 210 °C, and for **1b** ⇄ **2b**, $K = [\mathbf{2b}]/[\mathbf{1b}] = 1.00 \pm 0.04$. Each rate constant was calculated from 10 points by using duplicate tubes at each time. The least-squares analysis for all runs gave a correlation coefficient of 0.999 or better.

The samples for the isomerization **3** ⇄ **4** were analyzed by gas chromatography using toluene as a diluent and a 20-ft OV 101 on Chromosorb W column at 50 °C. Quintuple analysis on each of two samples were used to calculate each kinetic point. The equilibrium data for **3** ⇄ **4** were reported earlier.[6] The rates were calculated by using seven or more points, and each rate constant had a correlation coefficient of 0.999 or better.

Acknowledgment. We thank the NMR Spectral Services Laboratory at the University of Alberta for analysis, NSERC for funding, and Dr. H. Tokunaga for some preliminary work.

Registry No. **1b**, 99810-72-7; **1c**, 65264-10-0; **2b**, 99838-31-0; **3**, 4372-94-5; methyl cyclopropanecarboxylate, 2868-37-3; cyclopropylmethanol-α,α-d_2, 90568-07-3; cyclopropylmethyl bromide-α,α-d_2, 99838-30-9; 2,2-dibromo-3,3-dimethylmethylenecyclopropane, 5239-69-0.

(12) Smith, L. I.; McKenzie, S., Jr. *J. Org. Chem.* **1950**, *15*, 74–80.
(13) This is essentially the procedure of Wiley et al. (Wiley, G. A.; Hershkowitz, R. L.; Rein, R. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964–965) and gave no evidence of rearranged bromide.
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A Mercury-Mediated Acyl Migration in a Pinacol-Type Rearrangement. Model Studies toward the Synthesis of Fredericamycin A

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Fredericamycin A (**1**) contains a 1,4-diketospiro[4.4]-nonane structure and it exhibits both antibiotic and antitumor activity.[1] The novel spiro ring system possesses

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