THE JOURNAL OF Organic Chemistry

VOLUME 47, NUMBER 1 | JANUARY 1, 1982

Thermal Isomerizations of *cis*- and *trans*-2,2-Difluoro-3-methyl-1-vinylcyclopropane

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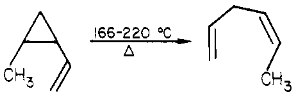
Received July 13, 1981

The thermal isomerizations of *cis*- and *trans*-2,2-difluoro-3-methyl-1-vinylcyclopropane (**4** and **5**) proceed in a manner reminiscent of the respective hydrocarbon systems. 3,3-Difluoro-1,4-hexadiene (**8**) is the sole product from **4** while 3,3-difluoro-4-methylcyclopentene (**9**) is the major product from **5**. Both **4**, in undergoing its concerted H-shift process, and **5**, in rearranging via a diradical process, exhibit the 8–10 kcal/mol incremental activation energy lowering which is expected for reactions involving cleavage of that cyclopropane carbon–carbon bond which is opposite the *gem*-difluoro substituent.

Thermal homo[1,5] hydrogen shifts have been observed for a number of *cis*-2-alkyl-1-vinylcyclopropyl systems in recent years, with the initial studies having been those of the parent system in 1964 by Ellis and Frey[1] and in 1965 by Roth and Konig.[2]



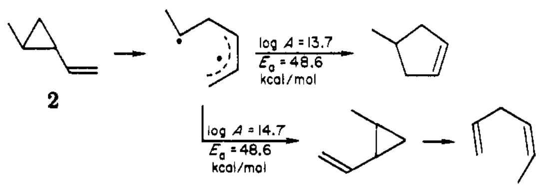
(1)

1

log A = 11.03; E_a = 31.2 kcal/mol

The low A factor, corresponding to a significant loss of entropy ($\Delta S^{\ddagger} \simeq -11.6$ eu) in the transition state, along with the low activation energy led the authors to propose a concerted mechanism for hydrogen transfer and cyclopropane ring cleavage. Such facile hydrogen transfers have also been observed in other monocyclic and bicyclic vinylcyclopropane systems where similar six-membered transition states were structurally accessible.[3]

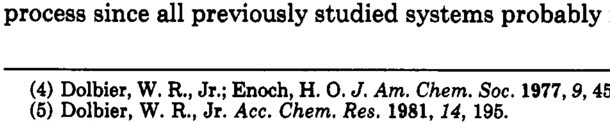
Consistent with the proposed concerted mechanism was the fact that *trans*-2-methyl-1-vinylcyclopropane (**2**, eq 2) isomerized with activation parameters which were substantially greater than those for the cis isomer and which were totally consistent with a mechanism involving rate-determining homolytic cleavage of the cyclopropane ring to give a stabilized diradical which could partition between cyclization to a cyclopentane product and C–C bond rotation, cyclization, and rapid H transfer. H transfer was found to proceed at a rate 11.7 times as fast as the cyclization process.



(2a)

(2b)

gem-Difluoro substituents on a cyclopropane ring have been shown to give rise to a specific kinetic weakening of the C–C bond opposite the CF_2 group. Such weakening has been observed in geometrical isomerizations,[4,5] vinylcyclopropane rearrangements,[5-7] and in the cyclopropylcarbinyl–allylcarbinyl radical rearrangement.[5,6] For example, it has been shown that 2,2-difluorovinylcyclopropane (**3**) rearranges via highly regioselective cleavage of its C_1–C_3 bond to form 3,3-difluorocyclopentene (eq 3) with a lowering of activation energy of 9.4 kcal/mol.[5,7]



(3)

3

96%

4%

As a further probe of the effect of *gem*-difluoro substituents on sigmatropic processes of cyclopropanes, it seemed appropriate to examine a probable *concerted* process since all previously studied systems probably in-

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[1] Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 5578.

[2] Roth, W. R.; Konig, J. *Justus Liebigs Ann. Chem.* **1965**, *688*, 28.

[3] (a) Glass, D. S.; Boikess, R. J.; Winstein, S. *Tetrahedron Lett.* **1966**, 999. (b) Grimme, W. *Chem. Ber.* **1965**, *98*, 756. (c) Ohloff, G. *Tetrahedron Lett.* **1965**, 3795. (d) Schroeder, G.; Oth, J. F. M. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 414. (e) Frey, H. M. *Chem. Rev.* **1969**, *69*, 114.

[4] Dolbier, W. R., Jr.; Enoch, H. O. *J. Am. Chem. Soc.* **1977**, *9*, 4532.

[5] Dolbier, W. R., Jr. *Acc. Chem. Res.* **1981**, *14*, 195.

[6] Dolbier, W. R., Jr.; Al-Sader, B. H.; Sellers, S. F.; Koroniak, H. *J. Am. Chem. Soc.* **1981**, *103*, 2138.

[7] Dolbier, W. R., Jr.; Sellers, S. F., submitted for publication in *J. Am. Chem. Soc.*

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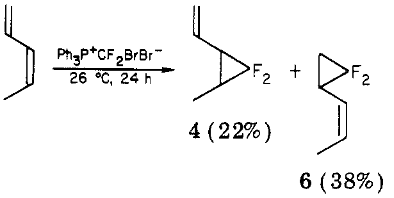
Table I. Rates for Conversion of 4 to 8

temp, °C	52.65	58.15	66.65	74.4	80.4	86.9
rate × 10^5	0.544 ± 0.007	0.886 ± 0.008	1.98 ± 0.014	4.40 ± 0.04	8.74 ± 0.10	15.0 ± 0.18

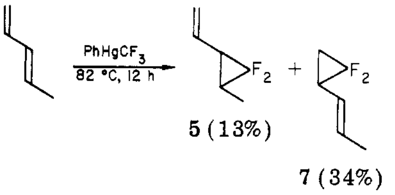
volved homolytic cleavage to diradical intermediates. Thus, the thermal homo[1,5] hydrogen shift of *cis*-2,2-difluoro-3-methyl-1-vinylcyclopropane was investigated along with the higher energy thermal isomerization of its trans isomer.

Results

The *cis*- and *trans*-2,2-difluoro-3-methyl-1-vinylcyclopropanes (**4** and **5**) were prepared by addition of difluorocarbene to *cis*- and *trans*-piperylene, respectively (eq 4 and 5). Burton's method of CF_2: addition,[8] which could be carried out at room temperature, was utilized for preparation of the more labile **4**, while Seyferth's method of CF_2: addition[9] was successfully used for preparation of **5**. Products **4**–**7** were characterized by their IR, their ^1H and ^{19}F NMR, and their high-resolution mass spectra (see the Experimental Section). It should be noted that in each case the less highly substituted double bond of the diene was found to react more rapidly with difluorocarbene. Such selectivity of carbene addition to dienes is perhaps not widely recognized but is, it seems, a general phenomenon, and Moss has rationalized it reasonably.[10]

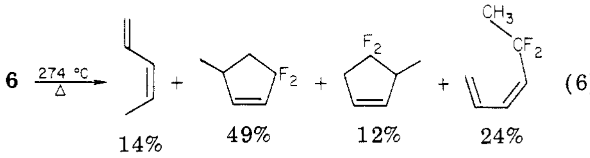


(4)

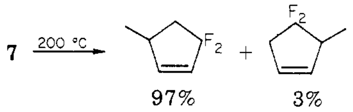


(5)

The isomers **4**–**7** were each pyrolyzed in the gas phase and/or in solution, and each underwent a clean, unimolecular rearrangement. The thermolyses of **6** and **7** (eq 6 and 7) have been reported in detail earlier.[7] These isomers



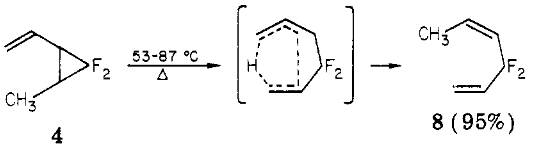
(6)



(7)

undergo for the most part the expected C_1–C_3 homolyses to diradicals, leading to mostly [1,3] sigmatropic rearrangement products, and these results will not be discussed further here.

Isomer **4**, on the other hand, rearranged in a manner similar to that for the hydrocarbon (eq 8) exclusively via

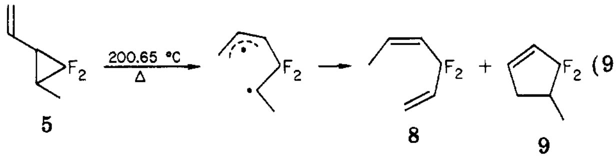


(8)

log A = 10.3; E_a = 23.4 kcal/mol

the homo[1,5] hydrogen shift process. The process was initially investigated at 150 °C in the gas phase, and kinetics determinations were carried out in *n*-decane solution at six temperatures with *n*-heptane as an internal standard (see Table I). *cis*-3,3-Difluoro-1,4-hexadiene (**8**) was formed as the sole product in >95% yield. **8** was characterized by its IR, ^1H and ^{19}F NMR, and its mass spectra. The activation parameters for the rearrangement of **4** to **8** were determined by a least-squares analysis of the Arrhenius plot of the rate data.

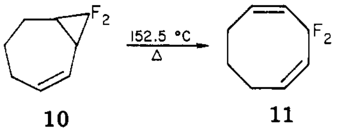
Isomer **5** was found to rearrange smoothly at 200 °C to two products (eq 9), one corresponding to the H-shift product **8** while the other, major product **9**, was that which would result from the [1,3] sigmatropic rearrangement. The ratio of **9** to **8** was 1.9:1.



(9)

$k = 1.32 \times 10^{-4}$

In a related study, it was found that 8,8-difluorobicyclo[5.1.0]oct-2-ene (**10**) prepared in 22% yield by the addition of CF_2: to 1,3-cycloheptadiene, was converted in a process similar to that observed for the hydrocarbon[13] to a single product, 3,3-difluoro-1,4-cyclooctadiene (**11**, eq 10).



(10)

$k_{152.5} = 4.47 \times 10^{-4}$

Discussion

The homo[1,5] hydrogen shift rearrangement of **4** to **8** exhibits a significant rate enhancement relative to that of the hydrocarbon system **1**. At 100 °C, **4** rearranged at a rate of 6890 times that of **1**. This corresponds to a $\Delta\Delta G^{\ddagger}$ of −9.0 kcal/mol. This value corresponds well with the incremental decreases in $\Delta G^{\ddagger}$ for the geometrical isomerization and vinylcyclopropane rearrangements of *gem*-difluorocyclopropanes (−8.2 and −9.6 kcal/mol, respectively) and is an indication that the weakening of the bond opposite the CF_2 group seen in these homolytic processes

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[8] Burton, D. J.; Naae, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 8467.

[9] Seyferth, D.; Hopper, S. P. *J. Org. Chem.* **1972**, *37*, 4070.

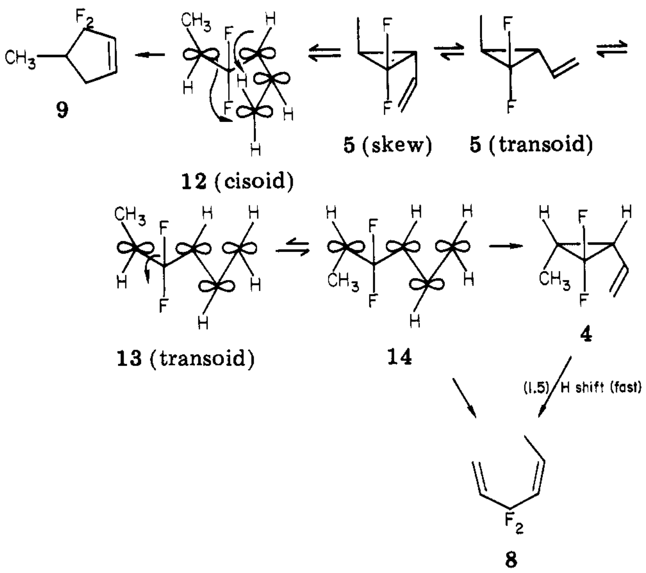
[10] Moss, R. A. "Carbenes"; Jones, M., Jr., Mors, R. A., Eds., Wiley: New York, 1973; Vol. 1, p 153.

[11] (a) Dolbier, W. R., Jr.; Fielder, T. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 5577. (b) Dolbier, W. R., Jr.; Sellers, S. F.; Al-Sader, B. H.; Smart, B. E. *Ibid.* **1980**, *102*, 5398.

[12] (a) Dolbier, W. R., Jr.; Sellers, S. F.; Al-Sader, B. H.; Elsheimer, S. *J. Am. Chem. Soc.* **1981**, *103*, 715. (b) Dolbier, W. R., Jr.; Sellers, S. F.; Al-Sader, B. H.; Fielder, T. J., Jr. *Ibid.* **1981**, *103*, 717. (c) Dolbier, W. R., Jr.; Sellers, S. F.; Smart, B. E. *Tetrahedron Lett.* **1981**, *22*, 2953.

[13] Dolbier, W. R., Jr.; Sellers, S. F.; Al-Sader, B. H.; Fielder, T. H., Jr.; Elsheimer, S.; Smart, B. E. *Isr. J. Chem.*, in press.

Scheme I



is also observed in the concerted conversion of 4 to 8. As in the hydrocarbon system 1, the concerted mechanism is marked by a *low A* factor which corresponds to a significantly *negative* entropy of activation ($\Delta S^\ddagger = -13.5$ eu for 4 as compared to −11.6 eu for 1). In contrast, *all* of the homolytic processes which we have examined, be they geometric isomerizations[4] or vinylcyclopropane,[7] methylenecyclopropane[11] or spiropentane rearrangements,[12] exhibit small to moderate positive entropies of activation, as might be expected for diradical-forming processes.

In a similar process, the bicyclo[5.1.0] system 10 also exhibited the expected substantial rate enhancement relative to the hydrocarbon system in undergoing its clean homo[1,5] sigmatropic hydrogen shift. At 152.5 °C 10 rearranged 1500 times faster than the hydrocarbon system. This reflects a $\Delta\Delta G^\ddagger$ of −6.1 kcal/mol. Neither 7,7-difluorobicyclo[4.1.0]hept-2-ene nor 6,6-difluorobicyclo-[3.1.0]hex-2-ene underwent analogous hydrogen shift processes. Their interesting thermal rearrangements will be reported in a subsequent paper.

The thermolysis of *trans*-2,2-difluoro-3-methyl-1-vinylcyclopropane (5), which because of molecular constraints cannot undergo a concerted hydrogen shift process, proceeded at a rate considerably slower than that of its cis isomer 4 ($k_4/k_5 = 2805$ at 200.6 °C). The rate was consistent with expectations for a process involving initial homolytic cleavage of the C_1–C_3 bond, followed by conformational processes which would lead to a partitioning between cyclization to cyclopentene product 9, and undergoing a hydrogen shift to product 8. Consistent with the diradical mechanism is the fact that 5 rearranged at a rate ~10 000 times that of its hydrocarbon analogue 2. This corresponds to a $\Delta\Delta G^\ddagger$ of −10.5 kcal/mol.

It is interesting to note the significant difference in product ratios for thermolysis of 5 vs. its hydrocarbon analogue 2. Hydrocarbon 2 rearranged to give *92%* of the hydrogen shift product, with only 8% of the cyclopentene product being formed. In contrast, 5 rearranged preferentially via the vinylcyclopropane rearrangement to 9 (64%), with the hydrogen shift process constituting only a minor (36%) pathway.

Mechanistic Scheme I gives some insight into those factors which may give rise to this difference.

It should be noted that cleavage of the more stable and thus more populous transoid 5 can lead only to hydrogen shift product 8 via C_2–C_3 bond rotation, converting diradical 13 to 14 which can either convert directly to 8 or do so via 4. Vinylcyclopropane-type rearrangement product 9 can only be formed via cleavage of skewed 5 to cisoid diradical 12 which then via a suprafacial 1,3-migration of C_3 may cyclize to 9.

The difference in product ratios for pyrolysis of 2 and 5 most likely arises from one of a number of possible sources within the scheme. The equilibrium between skewed and transoid 5 could be displaced to the left, the conversion of diradical 13 to 14 via rotation of either C_1–C_2 or C_2–C_3 could be diminished by the presence of the geminal fluorine substituent at C_2, or the suprafacial migration of C_3, converting diradical 12 to product 9, could be *enhanced* by these substituents. There is no evidence as to which of these modifications in diradical behavior actually is responsible for the differences observed.

Conclusion

The thermal isomerizations of both *cis*- and *trans*-2,2-difluoro-3-methyl-1-vinylcyclopropanes are reminiscent of the thermal rearrangements of the respective hydrocarbon systems. Both the cis isomer, in undergoing its *concerted* H-shift process, and the trans isomer, in rearranging via homolytic cleavage to a diradical, exhibit the 8–9-kcal/mol incremental activation energy lowering which is expected for reactions involving cleavage of that cyclopropane carbon–carbon bond which is opposite the *gem*-difluoro substituents.

Experimental Section

All GLC separations were accomplished on a Varian Aerograph 90-P with helium as the carrier gas and fitted with one of the following columns: column A, 18 ft × $^1/_4$ in., 20% SE-30 on Chrom P 60/80; column B, 10 ft × $^1/_4$ in., 10% DNP on Chrom P 60/80; column C, 20 ft × $^1/_4$ in., 20% ODPN on Chrom P 60/80. All product ratios and kinetic data were obtained by GLC on a Hewlett-Packard 5710A fitted with a flame-ionization detector and a gas-injection system and coupled to a Hewlett-Packard 3380 integrator. Thermolyses were carried out in well-conditioned Pyrex vessels suspended in a thermostated molten salt bath, as described previously.[13] All IR spectra, unless otherwise stated, were obtained from liquid films between KBr disks on a Perkin-Elmer 283B. NMR spectra were obtained in $CDCl_3$ at ambient temperature on a Varian XL-100 at 100.1 MHz for ^{1}H and 94.06 MHz for ^{19}F spectra or on an FX 90 at 25.2 MHz for ^{13}C proton decoupled spectra. The internal standard for ^{1}H and ^{13}C was Me_4Si and for ^{19}F was $CFCl_3$. Mass spectra were obtained on an AEI MS-30. Compounds in this report were not available in the quantities required for combustion analysis; moreover, the majority were unstable in the neat state at room temperature. Exact masses were obtained for all new compounds, and the purity of the samples was verified in each case by ^{19}F and ^{1}H NMR as well as by GLC.

Addition of Difluorocarbene to *trans*-Piperylene. In a 50-mL Carius tube were placed 5.0 g of [(trifluoromethyl)-phenyl]mercury[9] (0.0142 mol), 6.4 g of sodium iodide (3 × 0.0142 mol), 25 mg of tetra-*n*-butylammonium iodide, and 25 mg of 18-crown-6-ether in a dry box; all materials scrupulously dried. The Carius tube was then attached to a vacuum line and evacuated, and 2.0 g of piperylene (Aldrich, mostly trans, 0.029 mol) was transferred from calcium hydride into the tube. The tube was then sealed in vacuo and heated at 82 °C for 12 h in an oil bath. The tube was then cooled and opened, and all volatile materials were vacuum transferred and separated by VPC column C (50 °C, flow rate 50 mL min^{-1}) to give unreacted starting material plus 0.22 g (12.9%) of 5: IR 733, 842, 910, 964, 1000, 1038, 1149, 1203 (s), 1257 (s), 1420, 1480 (s), 1648, 2988 cm^{-1}; ^{1}H NMR δ 5.0–5.73 (vinyl, complex m, 3 H), 1.2–1.9 (CH, overlapping complex m, 2 H), 1.23 (CH_3, complex m, 3 H); ^{19}F NMR ϕ 138.95 (midpoint, AB, $J_{AB} = 155.5$ Hz, $\Delta\nu_{AB} = 305.05$ Hz; downfield F, complex d, $J = 14.0$ Hz; upfield F, complex d, $J = 13.03$ Hz); mass spectrum, m/e 118.0593 ± 0.00048 (M^+; 4.0 ppm), calcd for $C_6H_8F_2$

m/e 118.0594 (deviation −0.0001; 1.2 ppm), other major fragments *m/e* 103 (base), 97, 90, 83, 78, 77, 67, 64, 53, 51, 41, 39; bp 78.5–79.5 °C.

For **7**: 0.57 g (34.2%); IR (gas) 965, 1015, 1029, 1110, 1205 (s), 1272, 1320, 1477 (s), 2935 cm^{-1}; ^1H NMR δ 5.03–5.78 (vinyl, complex m, 2 H), 1.75–2.27 (allylic, complex m, 1 H), 1.70 (CH_3, d, $J = 6.3$ Hz, 3 H), 1.04–1.7 (cyclopropyl, complex m, 2 H); ^{19}F NMR ϕ 135.39 (midpoint, AB, $J_{AB} = 155.2$ Hz, $\Delta\nu_{AB} = 1259.9$ Hz; downfield F, complex t, $J_{F,cis\text{-}H} = 12.5$ Hz; upfield F, complex dd, $J_{F,cis\text{-}H} = 13$ Hz, $J_{F,trans\text{-}H} = 4.9$ Hz); mass spectrum, *m/e* 118.0597 ± 0.0004 (M^+; 3.2 ppm), calcd for $C_6H_8F_2$ *m/e* 118.0594 (deviation 0.0003; 2.4 ppm), other major fragments *m/e* 103 (base), 97, 90, 83, 77, 67, 53, 51, 41, 39; bp 79.5–81 °C.

Addition of Difluorocarbene to *cis*-Piperylene. Difluorocarbene was added to *cis*-piperylene (Tridon-Fluka) in the manner of Burton et al.[8] as described above to give the following products separated by VPC column C (ambient temperature, flow rate 150 mL min^{-1}).

4: 21.9% yield, IR, 937, 1100, 1130, 1205, 1280 (s), 1477 (s), 1642, 3000 cm^{-1}; ^1H NMR (0 °C) δ 5.14–5.59 (vinyl, complex m, 3 H), 2.0–2.4 and 1.59–2.0 (CH, 2 complex, 1 H each), 1.12 (CH_3, complex m, 3 H); ^{19}F NMR ϕ 138.46 (midpoint, AB, $J_{AB} = 154.55$ Hz, $\Delta\nu_{AB} = 2463{,}71$ Hz; downfield F, complex t, $J_{F,cis\text{-}H} = 14$ Hz; upfield F, br s); mass spectrum, *m/e* 118.0595 ± 0.000 58 (M^+; 4.9 ppm), calcd for $C_6H_8F_2$ *m/e* 118.0594 (deviation 0.000 08; 0.7 ppm), other major fragments *m/e* 103 (base), 97, 90, 83, 77, 67, 64, 53, 51, 41, 39.

6: 37.7% yield; IR, 740, 937, 1013, 1098, 1225 (s), 1300, 1370, 1470 (s), 1670 (w), 3050 cm^{-1}; ^1H NMR δ 5.5–6.1 and 4.65–5.5 (vinyl, 2 complex m, 1 H each), 2.0–2.8 (allylic, complex m, 1 H), 1.7 (CH_3, d, $J = 6$ Hz, 3 H), 1.6–2.2 and 0.75–1.6 (cyclopropyl CH_2, 2 complex m, 1 H each); ^{19}F NMR ϕ 135.06 (midpoint, AB, $J_{AB} = 155$ Hz, $\Delta\nu_{AB} = 1237.3$ Hz; downfield F, complex t, $J = 13.5$ Hz to each *cis*-H; upfield F, ddd, $J_{F,cis\text{-}H} = 13.5$ Hz, other $J = 2$, 5 Hz); mass spectrum, *m/e* 118.060 27 ± 0.0022 (M^+; 18.7 ppm), calcd for $C_6H_8F_2$ *m/e* 118.0594 (deviation −0.000 86; 7.3 ppm), other major fragments *m/e* 103 (base), 97, 83, 78, 77, 67, 53, 51, 41, 39; bp 71.5–73 °C.

Pyrolysis of 5. Pyrolysis of **5** in the gas phase at 275 °C for 5 min gave two products which were separated by GLC, column C (50 °C, 50 mL min^{-1}).

8: 34% yield; IR (gas) 990, 1119 (s), 1412, 1655, 2940, 3055 cm^{-1}; ^1H NMR (0 °C) δ 5.38–6.17 (vinylic, complex m, 5 H), 1.82 (CH_3, complex m, 3 H); ^{19}F NMR ϕ 88.76 (complex m); mass spectrum, *m/e* 118.0589 ± 0.0009 (M^+; 7.6 ppm), calcd for $C_6H_8F_2$ *m/e* 118.0594 (deviation −0.000 51; 4.3 ppm), other major fragments *m/e* 103 (base), 98, 97, 91, 77, 71, 67, 51, 39.

9: 66% yield; IR (gas) ν_{max} 738, 982, 1150 (s), 1186 (s), 1363, 1450, 1620 (w), 2945, 2982 cm^{-1}; ^1H NMR (0 °C) δ 5.87–6.31 (vinyl, complex m, 2 H), 2.61 (CH_2, complex m, 2 H), 2.16 (CH, complex m, 1 H), 1.17 (CH_3, dd, $J = 2.3$, 6.9 Hz); ^{19}F NMR ϕ 94.54 (midpoint, AB, $J_{AB} = 250.8$ Hz, $\Delta\nu_{AB} = 818.5$ Hz), both F's complex additional splitting; ^{13}C NMR δ 141.1 (C_1, t, $^3J_{C,F} = 11$ Hz), 127.3 (C_2, dd, $^2J_{C,F} = 26.2$, 29.3 Hz), 39.1 (C_4, t, $^2J_{C,F} = 24$ Hz), 38.0 (C_5, d, $^3J_{C,F} = 5.5$ Hz), 13.0 (C_6, d, $^3J_{C,F} = 9.8$ Hz); mass spectrum, *m/e* 118.0591 ± 0.000 42 (M^+; 3.6 ppm), calcd for $C_6H_8F_2$ *m/e* 118.0594 (deviation −0.000 30; 2.5 ppm), other major fragments *m/e* 103 (base), 98, 97, 90, 77, 67, 51, 39. Condensation of a product mixture directly into an NMR tube for ^{19}F analysis gave product ratios and mass balances consistent with the quantitative GLC results.

Pyrolysis of 4. Pyrolysis of **4** at 150 °C for 20 min gave the product **8**, identified by comparison of its spectra with those reported above for the pyrolysis of **5**.

Kinetics for Conversion of 4 to 8. A solution of 0.05% **4** and 0.03% *n*-heptane in *n*-decane was prepared. For each of six temperatures, seven 80-μL samples were sealed in Pyrex tubes (0.3 cm i.d. × 8 cm) and immersed in a thermostated, insulated, and stirred oil bath. The tubes were removed at appropriate intervals and immediately cooled in ice. Each sample was then opened and analyzed twice by GLC using a $^1/_8$ in. × 20 ft ODPN column at ambient temperature. Comparison of internal standard-product integrals indicated that the yield of **8** was >95% at 35 half-lives, a result which was consistent with direct, quantitative ^{19}F NMR analysis of the product mixture. Temperatures in the oil bath were measured by using a Chromel-Alumel thermocouple in conjugation with a Rubicon Instruments potentiometer. The rates obtained, from a least-squares analysis, are given in Table I. The Arrhenius activation parameters were obtained by a least-squares treatment of the rate data in Table I: $\log A = 10.34 \pm 0.30$, $E_a = 23.35 \pm 0.5$ kcal/mol, $\Delta S^\ddagger = -13.5$ eu, $\Delta G^\ddagger = 27.3$ kcal/mol at 69.7 °C.

Rate Determination for Conversion of 5 to 8 and 9. The rate of conversion of **5** to **8** and **9** was determined in the gas phase at 200.65 °C as previously described:[13] $k_{overall} = 3.90 \times 10^{-4}$ with $k_9/k_8 = 1.94$.

Synthesis of 8,8-Difluorobicyclo[5.1.0]oct-2-ene (10). Difluorocarbene was added to 1,3-cycloheptadiene in the manner described above by utilizing 1.5 g (0.016 mol) of 1,3-cycloheptadiene, 2.5 g (0.0071 mol) of $PhHgCF_3$, 3.20 g of NaI, 10 mg of $n\text{-}Bu_4N^+I^-$, and 10 mg of 18-crown-6. The sealed tube was heated for 20 h at 80–85 °C. Product **10** (0.23 g, 22.5% yield) was obtained, slightly contaminated with pyrolysis product **11**: IR 926, 1145 (s), 1205, 1294, 1456 (s), 1640 (vw), 1670 (vw), 2940 cm^{-1}; ^1H NMR δ 1.3–2.6 (aliphatic, complex m, 8 H), 5.3–5.9 (vinyl, complex m, 2 H); ^{19}F NMR ϕ 138.5 (midpoint, $J_{AB} = 149.9$ Hz, $\Delta\nu_{AB} = 2382.7$ Hz); mass spectrum, *m/e* 144.0756 ± 0.000 99 (M^+, 10% of base; 6.9 ppm), calcd for $C_8H_{10}F_2$ *m/e* 144.0751 (deviation 0.000 58; 4.0 ppm), other major fragments *m/e* 129, 116, 115, 109, 103, 97, 93 (base), 91, 79, 77, 67, 66, 51, 41, 39.

Thermolysis of 10. Thermolysis of **10** was carried out at 152.5 °C in the gas phase. The rate of conversion of **10** → **11** was found to be 4.47×10^{-4}. A single product was formed, and it was determined to be 3,3-difluoro-1,4-cyclooctadiene (**11**): IR 999 (s), 1080 (s), 1227, 1402, 1410, 1465, 1669, 2958 cm^{-1}; ^1H NMR δ 1.5–3.0 (aliphatic, complex, 6 H), 5.6–6.3 (vinyl, complex, 4 H); ^{19}F NMR ϕ 68.03 ("singlet" with unresolved splitting); mass spectrum, *m/e* 144.0751 ± 0.00145 (M^+, 12% of base; 10.1 ppm), calcd for $C_8H_{10}F_2$ *m/e* 144.0751 (deviation 0.0001; 0.8 ppm), other major fragments *m/e* 129, 116, 115, 109, 103 (base), 97, 96, 80, 79, 77, 67, 51, 41, 39.

Acknowledgment. We acknowledge with thanks the support of this research in part by the National Science Foundation.

Registry No. **4**, 79517-49-0; **5**, 79517-50-3; **6**, 79517-51-4; **7**, 79517-52-5; **8**, 79517-53-6; **9**, 79517-54-7; **10**, 79517-55-8; **11**, 79517-56-9; *trans*-piperylene, 2004-70-8; *cis*-piperylene, 1574-41-0; difluorocarbene, 2154-59-8; 1,3-cycloheptadiene, 4054-38-0.