Table I. ^{57}Fe Mössbauer Data for Ferrocenyl Phosphorus Compounds

compound	temp, K	isomer shift[a,b]	quadrupole splitting[a]
ferrocene[c]	300	0.454	2.396
Fc_2PCl	300	0.435	2.296
$[Fc_2P]^+[AlCl_4]^-$	60	0.525	2.328
$(Fc_2PCl)Fe(CO)_4$	60	0.534 (Fc)	2.323 (Fc)
		−0.103	2.474
		$[Fe(CO)_4]$	$[Fe(CO)_4]$
$[(Fc_2P)Fe(CO)_4]^+[AlCl_4]^-$	60	0.524 (Fc)	2.259 (Fc)
		−0.103	2.322
		$[Fe(CO)_4]$	$[Fe(CO)_4]$
$[(Me_2N)_2PFe(CO)_4]^+[AlCl_4]^-$	60	−0.031	1.896
		$[Fe(CO)_4]$	$[Fe(CO)_4]$

[a] In mm/s. [b] Relative to metallic Fe. [c] Data derived from ref 14.

solution consisted of a singlet at +183 ppm compared to +82 ppm for Fc_2PCl, thus indicating the development of positive charge at phosphorus. The presence of the $AlCl_4^-$ anion was indicated by a sharp singlet ($W_h \sim 6$ Hz, δ 102.2) in the ^{27}Al NMR spectrum.[8]

Elegant work by Bock and co-workers[9] has shown that Al_2Cl_6 in CH_2Cl_2 can function as an oxidizing agent toward substrates possessing valence electrons less tightly bound than ~7.9 eV. Since the first ionization potential of ferrocene is ~6.9 eV[10] and it is known to react with Al_2Cl_6 in CH_2Cl_2,[11,12] the possibility of oxidation of Fc_2PCl to a mixed-valence[13] bridged ferrocene (**2**) was considered. Since ^{57}Fe Mössbauer spectroscopy can differentiate between ferrocenyl and ferricenyl moieties,[14,15] we have employed this technique for distinguishing between the chloride ion abstraction and one-electron oxidation reaction modes. Ferrocene and ferrocenyl groups are manifested spectroscopically by a well-resolved doublet with a quadrupole splitting of 2–2.5 mm/s, while ferricenyl groups are evidenced by a small or vanishing quadrupole splitting. If the rate of electron transfer between a ferrocenyl and a ferricenyl group in a mixed-valence bridged ferrocene (such as **2**) exceeds the inherent ^{57}Fe Mössbauer time scale, an averaged doublet will be observed. The Mössbauer spectra of Fc_2PCl and the product of its reaction with Al_2Cl_6 (Table I) are both typical of ferrocenyl compounds; hence it is clear that the phosphenium ion, **1**, is produced and not the ferricenyl substituted species, **2**.

Treatment of $(Fc_2PCl)Fe(CO)_4$ (**3**)[16] with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 at 0 °C produced a red-brown solution. The ^{31}P NMR spectrum of this solution consists of a singlet at +280 ppm, which falls in the region observed for other (phosphenium)$Fe(CO)_4$ complexes,[17] and represents an appreciable downfield shift from the starting material (+161 ppm). The ^{57}Fe Mössbauer spectrum of **3** (Table I) consists of two doublets, with an intensity ratio, as revealed by quantitative analysis,[18] of 1.8:1. The more intense doublet has isomer shift (IS) and quadrupole splitting (QS) values typical of those of ferrocenyl compounds,[14,15] and the less intense signal has Mössbauer parameters similar to those which have been reported for other $Fe(CO)_4$ complexes.[19] The reaction product of **3** and Al_2Cl_6 exhibited a ^{57}Fe Mössbauer spectrum similar to that of **3**, and, as in the case of **1**, these data are consistent only with the presence of a phosphenium ion, viz., $[(Fc_2P)Fe(CO)_4]^+[AlCl_4]^-$ (**4**).

Collins and Pettit[19] have demonstrated that for the ^{57}Fe Mössbauer spectra of $LFe(CO)_4$ complexes, a graph of IS vs. QS is linear and may be employed to estimate the relative σ-donor or π-acceptor capabilities of the ligand, L. This approach may be used to compare the bonding in **4** with that in other (phosphenium)$Fe(CO)_4$ tetracarbonyl complexes, and for this purpose, we have obtained the Mössbauer spectrum of the well-established complex, $(Me_2N)_2P^+Fe(CO)_4$.[17b] We find that the IS and QS values for the amino compound fall in the π-acceptor region of the Collins–Pettit graph. The conclusion that $(Me_2N)_2P^+$ is a good π acceptor is in excellent accord both with vibrational spectroscopic data[17] and with observations made by Bennett and Parry[20] concerning the facility of exchange of free CO with $(R_2N)_2P^+Fe(CO)_4$. This is not the case with **4**, which falls on the graph in the tertiary phosphine region, thus indicating that **1** is a poor π acceptor in comparison with $(Me_2N)_2P^+$. Thus, the position of **4** on the Collins–Pettit graph would seem to imply that ferrocenyl substitution disperses the positive charge from the phosphorus more effectively than dimethylamino substitution. This view is supported by the ^{31}P chemical shifts of **1** and **4**, which are upfield from their dimethylamino counterparts (264[1c] and 311 ppm,[17] respectively).

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE79-10155) and the Robert A. Welch Foundation for generous financial support and to Mr. Tim Eakin for assistance in obtaining ^{57}Fe Mössbauer spectra.

(8) Akitt, J. W. *Annu. Rep. NMR Spectrosc.* **1972**, *5*, 465–556.
(9) (a) Bock, H.; Brähler, G.; Fritz, G.; Matern, E. *Angew Chem., Int. Ed. Engl.* **1976**, *15*, 699–700. (b) Bock, H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 4429–4438. (c) Bock, H.; Kaim, W.; Connolly, J. W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 700–701. (d) Bock, H.; Kaim, W.; Nöth, H.; Semkow, A. *J. Am. Chem. Soc.* **1980**, *102*, 4421–4428. (e) Bock, H.; Kaim, W. *Chem. Ber.* **1978**, *111*, 3552–3572.
(10) Cowley, A. H. *Prog. Inorg. Chem.* **1979**, *26*, 45–160 and references therein.
(11) Previously reported work has suggested ferricenium formation as the first step: Nesmeyanov, A. N.; Korshak, V. V.; Voevodskii, V. V.; Kochetkova, N. S.; Sosin, S. L.; Materikova, R. B.; Bolotnikova, T. N.; Chibrikin, V. M.; Bazhin, N. M. *Dokl. Akad. Nauk SSSR* **1961**, *137*, 1370–1373. Goldberg, S. I. *J. Am. Chem. Soc.* **1962**, *84*, 3022. Astruc, D.; Dabard, R.; Martin, M.; Batail, P.; Grandjean, D. *Tetrahedron Lett.* **1976**, 829–832.
(12) Under anhydrous conditions treatment of ferrocene with Al_2Cl_6 in CH_2Cl_2 gives a dark green solution, and the ^{57}Fe Mössbauer spectrum (60 K) indicated ferricenium formation (broad singlet which can be computer resolved into a doublet with IS = 0.474 and QS = 0.235 mm/s).
(13) Cowan, D. O.; LeVanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1–7. See also: Morrison, W. H., Jr.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2331–2346.
(14) Fluck, E.; Hausser, F. *Z. Anorg. Allg. Chem.* **1973**, *396*, 257–260.
(15) See, for example: Kramer, J. A.; Herbstein, F. H.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1980**, *102*, 2293–2301.
(16) This dark, orange solid compound (mp 155–160 °C dec) was made by the action of $Fe_2(CO)_9$ on Fc_2PCl in *n*-hexane solution at 50 °C. It was characterized by elemental analysis, ^{13}C NMR, IR [$\bar{\nu}_{CO}$ = 2040 (s), 1970 (s), and 1930 (vs) cm^{-1}], and mass spectrometry.
(17) (a) Light, R. W.; Paine, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 2230–2231. (b) Montemayor, R. G.; Sauer, D. T.; Fleming, Sr. S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *Ibid.* **1978**, *100*, 2231–2233.
(18) Collins, R. L.; Eakin, T.; Clewlow, J. "Quantitative Analysis Using Mössbauer Spectroscopy", paper presented at the 176th National Meeting of the American Chemical Society, Houston, Texas; March 23–28, 1980; American Chemical Society: Washington, DC, 1980.
(19) Collins, R. L.; Pettit, R. *J. Chem. Phys.* **1963**, *39*, 3433–3436.
(20) Bennett, D. W.; Parry, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 755–757.

Thermal Rearrangement of 1,1-Difluorospiropentane

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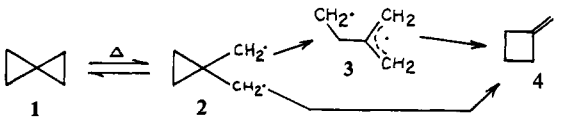
The thermal unimolecular rearrangement of spiropentane to methylenecyclobutane is an interesting and complex reaction, the mechanism of which has been investigated in detail.

Initial cleavage of the peripheral C_1–C_2 bond, rather than the C_1–C_3 bond, was demonstrated by Gajewski,[1] while reversibility of this step was detected by Gilbert.[2] Activation parameters for



$\log A = 15.9$, $E_a = 57.6$ kcal/mol

(1) Gajewski, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 3688.
(2) Gilbert, J. C. *Tetrahedron* **1969**, *25*, 1459.

0002-7863/81/1503-715$01.00/0 © 1981 American Chemical Society

Table I. Rates for 5 → 6[a]

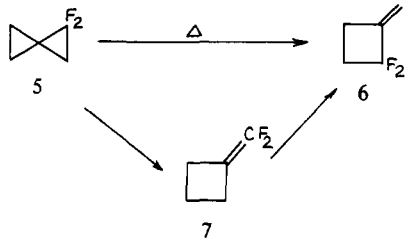
$k \times 10^5$	0.577	1.20	2.24	3.46	5.45	9.42
T, °C	321.15	329.75	337.65	343.45	349.3	356.95

[a] Activation parameters: $\log A = 16.1 \pm 0.2$, $E_a = 58.0 \pm 0.5$ kcal/mol, $\Delta G^{\ddagger} = 49.6$ kcal/mol, $\Delta S^{\ddagger} = 11.7$ eu, $(k_5/k_1)_{340} = 1.2$.

the rearrangement were determined by Flowers and Frey.[3] Whether **2** ring expands directly to **4** or whether a second intermediate (**3**) is involved is not totally clear, although **4** certainly automerizes via a species such as **3**.[4] All in all, one can feel fairly confident about the basic mechanistic pathway for the conversion of **1** to **4**.

We have demonstrated in recent work that *gem*-difluoro substitution on a cyclopropane ring gives rise to enhanced reactivity with respect to thermal isomerizations, with the bond *opposite* to the CF_2 group seeming to be weakened significantly more (9–10 kcal/mol)[5] than the adjacent bound (1–2 kcal/mol).[6] Substitution of *gem*-difluoro substituents on spiropentane could have a drastic and interesting effect on its thermal behavior.

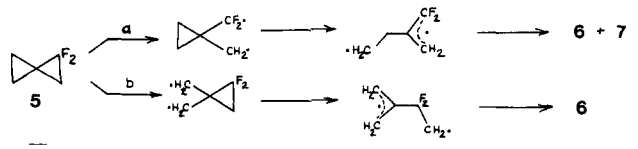
We wish to report at this time our investigation of the thermal rearrangement of 1,1-difluorospiropentane.[7] **5** rearranged in the gas phase[8] to yield a single product, 2,2-difluoromethylenecyclobutane (**6**), in >85% yield.[9] Rate constants were obtained



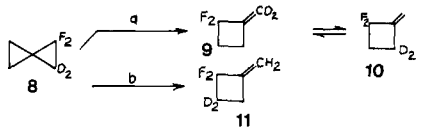
for six temperatures (see Table I), and an Arrhenius plot of these data gave a good straight line, with the frequency factor and energy of activation being calculated by the method of least squares.

In the apparently regiospecific formation of **6**, there was the possibility that 1-(difluoromethylene)cyclobutane (**7**) might have been formed competitively, with subsequent rearrangement to the more stable **6**. To test this, **7** was synthesized[10] and subjected to the reaction conditions, where it did indeed rearrange rapidly to **6**. At 340.0 °C, the rate constants for **5** → **6** and for **7** → **6** were determined to be 2.68×10^{-5} and 1.85×10^{-4}, respectively.[12] By computer simulation of the pyrolysis of **5** it was determined that **7** *should be detectable* if a significant fraction of the formation of **6** were to proceed via **7**. Indeed a peak was detected which had the same retention time as **7**, the concentration of which could be quantitatively simulated by the computer if one assumed that

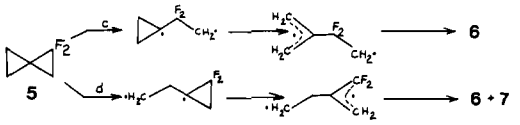
Scheme I



Scheme II



Scheme III



10.5% of the thermolysis of **5** proceeded via **7**. Its concentration reached a maximum of 4% of the total product at 0.5 half-life.

The activation parameters for **1** and **5** are very similar, with the isomerization of **5** proceeding only slightly faster. This result is inconsistent with initial radial (C_2–C_3) bond cleavage, since the incremental enhancement which is associated with *opposite* bond cleavage[5] was obviously not observed. The modest enhancement can, however, be nicely rationalized in terms of initial C_1–C_2 or C_4–C_5 cleavage.[6]

Accordingly, mechanisms a and b in Scheme I are the likely pathways for the rearrangement of **5**, and they parallel closely the accepted mechanisms for rearrangement of the unfluorinated **1**. These two mechanisms might be expected to compete with one another, in view of the small kinetic effect of the CF_2 group. The selectivity of formation of **6** can be readily expalined by either process. In (a), one would expect ring expansion to the $-CF_2\cdot$ site to be significantly favored over that to the $-CH_2\cdot$ site, since there is definitely a large thermodynamic advantage for sp^3- over sp^2-hybridized CF_2.[13] For (b), it should definitely be expected that the weaker C_2–C_3 bond (opposite to the CF_2 group) would be the bond to rearrange.[15]

Unlike the pyrolysis of **1**, pyrolysis of **5** produces no allenic and ethylenic products, although very low pressure conditions which might favor such products were not specifically examined. As in other *gem*-difluorocyclopropane systems, the only competitive process was that of CF_2: extrusion, in this case observed only in trace amounts.

An evaluation of the partitioning between mechanisms a and b is feasible by examining the rearrangement of 2,2-dideuterio-1,1-difluorospiropentane, **8** (Scheme II).[17] When **8** was allowed to rearrange at 339.6 °C, deuterated isomers **9**, **10**, and **11** were obtained in the ratio of 26:37:37 as determined from the ^1H and ^{19}F spectra of the product mixture.[19] Thus pathways a and b

(3) Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1961**, 5550.
(4) Doering, W. von E.; Gilbert, J. C. *Tetrahedron, Suppl.* **1966**, *7*, 397.
(5) Dolbier, W. R., Jr.; Enoch, H. O. *J. Am. Chem. Soc.* **1977**, 99, 4532.
(6) Dolbier, W. R., Jr.; Fielder, T. H. *J. Am. Chem. Soc.* **1978**, *100*, 5577.
(7) 1,1-Difluorospiropentane was synthesized via the addition of CF_2: (from thermolysis of HFPO) to methylenecyclopropane. Spectral properties of **5**: IR (gas) ν_{max} 1240 cm^{-1}; NMR ($CDCl_3$) δ 0.9–1.25 (complex m, 4 H), 1.62 (t, J = 5.3 Hz, 2 H); ϕ 132.89 (complex m). Mass spectroscopy gave M^+ as 104.04318 [standard deviation = 0.002 (19.3 ppm)]. Calculated M^+ was 104.04376 [deviation = 0.00058 (-5.5 ppm)].
(8) The kinetics were carried out in a well-conditioned Pyrex vessel immersed in a thermostated salt bath. The rates were determined by GLPC, and good first-order character was observed for >5 half-lives.
(9) Spectral properties of **6**: IR (gas) ν_{max} 1310 cm^{-1}; NMR ($CDCl_3$), δ 2.43–2.76 (nonvinyl, complex m, 4 H), 5.49 and 5.15 (vinyl, complex m, 2 H); ϕ 94.49 (m). Mass spectroscopy gave M^+ as 104.0445 [standard deviation = 0.000102 (9.8 ppm)]. Calcualted M^+ was 104.04376 [deviation = 0.00029 (2.8 ppm)].
(10) **7** was prepared from cyclobutanone via modification of Burton's difluoro Wittig reaction.[11] It could be characterized by its spectral characteristics: IR ($C{=}CF_2$) ν_{max} 1795 cm^{-1}; NMR ($CDCl_3$) δ 2.22 (complex m, 2 H), δ 2.83 (complex m, 4 H); ϕ 99.24 (complex pentad, J = 3.6 Hz).
(11) (a) Hayashi, S.-I.; Nakai, T.; Ishikawa, N.; Burton, D. J.; Naae, D. G.; Kesling, H. S. *Chem. Lett.* **1979**, 983. (b) Naae, D. G.; Burton, D. J. *Synth. Commun.* **1973**, *3*, 197.
(12) The kinetic details of the thermal isomerization of **7** will be reported in full at a later date.
(13) For example, the Cope rearrangement of 1,1-difluoro-1,5-hexadiene to 3,4-difluoro-1,5-hexadiene has a $\Delta G^{\circ} = -5$ kcal/mol.[14]
(14) Dolbier, W. R., Jr.; Medinger, K., unpublished results.
(15) We have direct corroboration of this expectation through the observation that the (2,2-difluorocyclopropyl)carbinyl radical rearranges *only* to the 2,2-difluorobut-3-enyl radical.[16]
(16) Dolbier, W. R., Jr.; Sellers, S. F., unpublished results.
(17) **8** was synthesized via the addition of CF_2: (from $PhHgCF_3$) to (dideuteriomethylene)cyclopropane.[18] **8**: NMR ($CDCl_3$) δ 1.15 (complex m); ϕ 135.69 (complex m). Mass spectroscopy gave M^+ as 106.05571 [standard deviation = 0.00248 (23.4 ppm)]. Calcualted M^+ was 106.05631 [deviation = 0.00042 (4.0 ppm)].
(18) Dolbier, W. R., Jr.; Alonso, J. H. *J. Am. Chem. Soc.* **1973**, 95, 4421.
(19) **9**, **10**, and **11**: ^1H NMR ($CDCl_3$) δ 5.47, 5.15 (vinylic, each a pentuplet of doublets with relative integrals 1.0:7.6:16.6:8.1:1.1), 2.41–2.76 (nonvinyl, m), with relative integrals vinyl:cyclobutyl = 1:2.21; this indicates the presence of ~37% of **9**; ^{19}F NMR: ϕ 94.49 (a multiplet with vicinal H–F coupling of 11.8 Hz and similar to that of **6**, due in this case to **9** and **10**) and ϕ 94.85 (a narrower multiplet with no vicinal H–F coupling, and due to **11**).[20] The relative ^{19}F integrals were 2.8:1, thus indicating the presence of ~26% of **11**. A more detailed discussion of the interpretation of these spectra will be presented in the full paper, which will be submitted soon.

were indeed competitive, with (a) being favored ca. 3:1. An isotope effect was observed by comparison of k_5 to k_8 with $k_5/k_8 = 1.15 \pm 0.02$. A relatively large secondary deuterium isotope effect was to be expected for pathway a,[22] while pathway b probably would not give rise to a significant effect, since the discriminatory step in (b) should be a very low E_a process.[23]

Two other possible mechanisms can be considered (Scheme III). While the first step of mechanism c should be substantially enhanced for **5** relative to **1**, we consider neither (c) nor (d) as viable alternatives to (a) and (b) because of the very high E_a associated with the *second* step of the mechanisms.[25-27]

Therefore, in conclusion, it appears that **5** rearranges via two competitive processes, (a) and (b), regioselectively to **6**. The kinetic parameters for the rearrangement, as well as its regiochemistry, are consistent with the previously demonstrated effects of geminal fluorine substitution on cyclopropane systems.

Acknowledgment. We thank the National Science Foundation for partial support of this research and Professor W. S. Brey for assistance in interpretation of the NMR data.

(20) The observed isotope effect on the ^{19}F chemical shift of **11** is consistent with earlier reports of such effects.[21]

(21) (a) Lambert, J. B.; Greifenstein, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 5120. (b) Kanazawa, Y.; Baldesweiler, J. D.; Craig, N. C. *J. Mol. Spectrosc.* **1965**, *16*, 325.

(22) In a similar, but lower, E_a rearrangement, the thermal rearrangement of dideuteriobis(cyclopropylidene) gave rise to a $k_H/k_D = 1.21$.[18]

(23) Rearrangement of **2** to **3** (or directly to **4**) should have an $E_a < 6$ kcal/mol (the E_a for cyclopropylcarbinyl → allylcarbinyl radical).[24]

(24) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024.

(25) Cyclopropyl radical cleavage to allyl radical has been estimated experimentally to have an $E_a \simeq 20$–22 kcal/mol.[26]

(26) Greig, G.; Thynne, J. C. J. *Trans. Faraday Soc.* **1966**, *62*, 3338; **1967**, *63*, 1369.

(27) Reversible cleavage of the C_2–C_3 bond of **5** may indeed be an enhanced but blind alley pathway.

Thermal Rearrangements of 1,1,2,2- and 1,1,4,4-Tetrafluorospiropentanes

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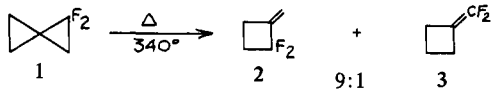
In the preceding communication, we reported that a single pair of geminal fluorine substituents on a spiropentane system, such as **1**, exerted a dominating effect on the regiochemistry of its rearrangement to methylenecyclobutanes **2** and **3** but had little kinetic effect on the reaction.[1] On the other hand, the kinetic



$\log A = 16.1$, $E_a = 58.0$ kcal/mol

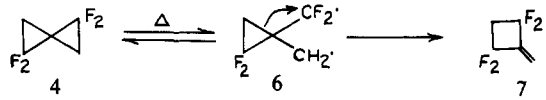
effect of a *second* pair of geminal fluorine substituents is expected to be *much* more dramatic, as demonstrated by our recently reported study of the tetrafluoromethylenecyclopropane system.[2] We wish to report at this time our investigation of the thermal isomerizations of 1,1,4,4- and 1,1,2,2-tetrafluorospiropentanes, **4** and **5**.[3-6] Both compounds rearrange *regiospecifically*, with

Table I. Rates of 4 → 7

T, °C	311.6	317.35	320.9	326.7	334.5
$k \times 10^5$	2.76	4.30	5.48	8.29	14.9

the second CF_2 group exerting significantly more kinetic effect than did the first. These effects, as well as the observation of unusual pressure effects, allow one to gain significant insight into the effect of fluorine substituents on thermal cyclopropane processes.

1,1,4,4-Tetrafluorospiropentane (**4**) underwent rearrangement cleanly, via a smooth, unimolecular process, to a single product, 2,2,4,4-tetrafluoromethylenecyclobutane (**7**) in >90% yield.[7] Rate

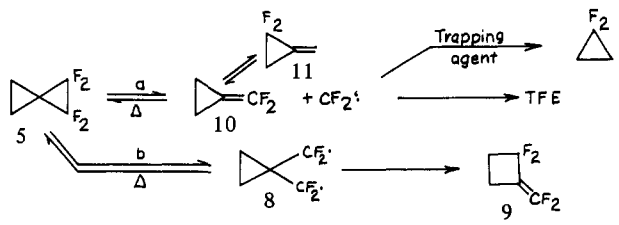


$\log A = 14.8$, $E_a = 51.7$ kcal/mol

constants were obtained for five temperatures (see Table I),[8] and an Arrhenius plot of these data gave a good straight line, with the frequency factor and energy of activation being determined by the method of least squares (see Table III).

The regiospecificity of this reaction is explicable if one considers the thermodynamic preference of the $-CF_2\cdot$ site as the terminus for ring expansion of **6** and when one considers the fact that the weaker C_3–C_5 bond should also preferentially be the one to migrate.[1] The fact that **4** rearranges ~10 times faster (at 340 °C) than **1** (a $\Delta\Delta G^{\ddagger}$ of 2.4 kcal/mol) is entirely consistent with what is known about the spiropentane–methylenecyclobutane interconversion mechanism. Since the rearrangement of diradical **6** to **7** is considered to be a kinetically significant step,[9] one would expect the *weakening* of the rearranging bond to give rise to a rate enhancement.

The thermolysis of **5** likewise proceeded smoothly to a single rearrangement product, 2,2-difluoro-1-(difluoromethylene)-cyclobutane (**9**),[10,11] in 92% yield. However, in this case, a



(1) Dolbier, W. R., Jr.; Sellers, S. F.; Al-Sader, B. H.; Elsheimer, S. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Dolbier, W. R., Jr.; Sellers, S. F.; Al-Sader, B. H.; Smart, B. E. *J. Am. Chem. Soc.* **1980**, *102*, 5398.

(3) Presented in part at the 9th International Symposium on Fluorine Chemistry in Avignon, France, Sept 1979.

(4) **4** and **5** were synthesized via the addition of CF_2: (from hexafluoropropylene oxide) to allene at 180–190 °C. Under these conditions isomerization of the initially formed methylenecyclopropanes is occurring, and hence, both **4** and **5** can be prepared simultaneously in high yield. The ratio of **4**:**5** is greatly temperature dependent, with lower temperature favoring **4**.

(5) The observation of **5** as a product in CF_2: reactions with allene has been recently reported: Birchall, J. M.; Fields, R.; Haszeldine, R. M.; McLean, R. J. *J. Fluorine Chem.* **1980**, *15*, 487. Interestingly, they were not able to detect any **4** in their product mixtures.

(6) Spectral properties of **4**: IR (gas) ν_{max} 1230, 1260 cm^{-1}; NMR (CCl_4) δ 2.00–2.54 (complex m); ϕ 133.4 (complex m). Mass spectroscopy gave M^+ as 140.02386 [standard deviation = 0.00133 (9.5 ppm)]. Calculated M^+ was 140.02491 [deviation = −0.00094 (6.7 ppm)]. Spectral properties of **5**: IR gas ν_{max} 1220, 1260 cm^{-1}; NMR ($CDCl_3$) δ 1.5 (pentad, J = 2.4 Hz); ϕ 142.82 (pentad, J = 2.4 Hz). Mass spectroscopy gave M^+ as 140.02327 [standard deviation = 0.00278 (19.8 ppm)]. Calcualted M^+ was 140.02491 [deviation = −0.00164 (11.7 ppm)].

(7) Spectral properties of **7**: IR (gas) ν_{max} 1190 cm^{-1}; NMR ($CDCl_3$) δ 3.22 (pentad, J = 9 Hz, 2 H), 5.92 (pentad, J = 2 Hz, 2 H); ϕ 97.98 (t of t, J = 2, 9 Hz). Mass spectroscopy gave M^+ as 140.02478 [standard deviation = 0.00113 (8 ppm)]. Calculated M^+ was 140.02491 [deviation = −0.00013 (0.9 ppm)].

(8) The kinetics were carried out at pressures varying from 4 to 20 mm in a *well-conditioned* Pyrex vessel immersed in a thermostated salt bath. The rates were determined by GLPC for the appearance of products. Kinetic runs using an internal standard and examining loss of **4** and **5** were consistent with the data in Tables I and II.

(9) Gilbert, J. C. *Tetrahedron* **1969**, *25*, 1459.

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