

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 ¹⁹F 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 dideuteriois(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 \rightarrow 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 $E_a \approx 20-22$ kcal/mol.²⁶

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

(27) Reversible cleavage of the C₂-C₃ bond of **5** may indeed be an enhanced but blind alley pathway.

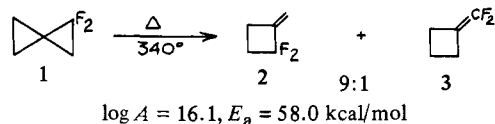
Thermal Rearrangements of 1,1,2,2- and 1,1,4,4-Tetrafluorospirpentanes

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In the preceding communication, we reported that a single pair of geminal fluorine substituents on a spirpentane 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



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-tetrafluorospirpentanes, **4** and **5**.³⁻⁶ Both compounds rearrange regioselectively, with

(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.

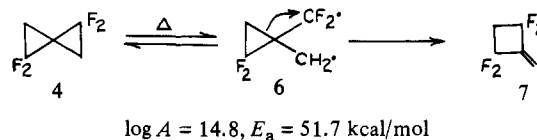
(3) Presented in part at the 9th International Symposium on Fluorine Chemistry in Avignon, France, Sept 1979.

Table I. Rates of 4 \rightarrow 7

$T, ^\circ\text{C}$	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 CF₂ 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.

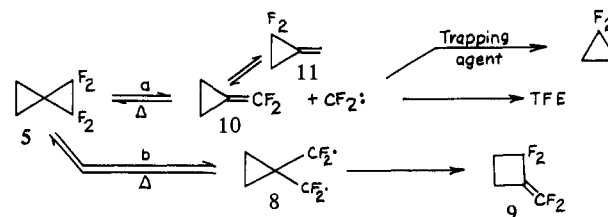
1,1,4,4-Tetrafluorospirpentane (**4**) underwent rearrangement cleanly, via a smooth, unimolecular process, to a single product, 2,2,4,4-tetrafluoromethylenecyclobutane (**7**) in >90% yield.⁷ Rate



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 regioselectivity of this reaction is explicable if one considers the thermodynamic preference of the -CF₂ site as the terminus for ring expansion of **6** and when one considers the fact that the weaker C₃-C₅ bond should also preferentially be the one to migrate.¹ The fact that **4** rearranges ~ 10 times faster (at 340 $^\circ\text{C}$) than **1** (a $\Delta\Delta G^\ddagger$ of 2.4 kcal/mol) is entirely consistent with what is known about the spirpentane-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



(4) **4** and **5** were synthesized via the addition of CF₂ (from hexafluoropropylene oxide) to allene at 180-190 $^\circ\text{C}$. 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 CF₂ 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 (CCl₄) 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 (CDCl₃) 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)]. Calculated M^+ was 140.02491 [deviation = -0.00164 (11.7 ppm)].

(7) Spectral properties of **7**: IR (gas) ν_{max} 1190 cm^{-1} ; NMR (CDCl₃) 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.

Table II. Rates of 5 → 9 + 10

T, °C	271.5	274.25	281.25	285.0	286.4	292.5	297.5	303.0
k × 10 ⁴	0.904	1.13	1.85	2.59	2.85	4.45	6.62	9.89
(10 + 11)/9	1.50	1.52	1.545	1.575	1.59	1.63	1.70	1.77

Table III. Activation Parameters

	log A	E _a ^a	ΔH [‡] a,b	ΔS [‡] b	ΔG [‡] a,b
1 → 2 + 3	16.1 ± 0.1	58.0 ± 0.4	56.8	11.7	49.6
4 → 7	14.75 ± 0.2	51.7 ± 0.6	50.5	5.6	47.2
5 → 9 + 10	14.95 ± 0.2	47.4 ± 0.5	46.3	6.7	42.5
5 → 9	13.75 ± 0.1	45.35 ± 0.3	44.2	1.2	43.6
5 → 10	15.2 ± 0.2	48.55 ± 0.4	47.4	7.8	43.1

^a kcal/mol. ^b Calculated for mean temperatures: 339.7 °C for 1, 322.0 °C for 4, and 286.3 °C for 5.

significant fraction of the reaction proceeded via an extrusion of CF₂.¹² The overall rates of rearrangement of 5 for eight temperatures⁸ are given in Table II, along with the observed ratios of (a):(b) as measured by the ratios of (10 + 11)/9.

The rearrangement of 5 to 9 proceeds 140 times faster than that of difluorospirpentane (1) at 340 °C. This enhancement amounts to a ΔΔG[‡] of 6.0 kcal/mol, a value which is comparable to that of the tetrafluoromethylenecyclopropane system wherein the second CF₂ group gives rise to a ΔΔG[‡] of 7.4 kcal/mol for homolysis of the bond *between* the CF₂ groups.² Thus, it appears that while a single CF₂ group in a cyclopropane ring does not lead to a significant weakening of bonds adjacent to it, *two* such groups do indeed cause a substantial weakening of that adjacent bond between them.

The extrusion of CF₂ from 5 is probably a concerted process, although involvement of intermediate 8 cannot be rigorously excluded. Why should extrusion compete effectively with rearrangement in the case of 5 when it did not for either 1 or 4? The answer comes from the fact that while adding the second CF₂ group enhances rearrangement by 6 kcal/mol, it is expected to enhance CF₂ extrusion by ~8 kcal/mol. This expectation derives from the known relative propensities of 1,1-difluorocyclopropane (log A = 14.1, E_a = 56.4 kcal/mol) and 1,1,2,2-tetrafluorocyclopropane (log A = 15.3, E_a = 48.5 kcal/mol) to extrude CF₂.^{13b} In fact, at 340 °C, 5 loses CF₂: at about the same rate (a factor of 0.80) as does 1,1,2,2-tetrafluorocyclopropane.

An unexpected and mechanistically significant pressure dependence on the ratio of (a):(b) was detected in this reaction. As has been reported earlier, the extrusion of CF₂ from difluorocyclopropanes is a *reversible* process, and in order to determine accurate rates for processes a and b it was necessary to add a CF₂ trapping agent. Isobutylene (I) was chosen because of its known ability to irreversibly add CF₂ at these temperatures. The addition of I did indeed eliminate return of CF₂: and allowed good first-order kinetics to be observed for the thermal processes of 5. However, very noticeable was a *sharp increase* in the ratio of (a):(b) (as measured by the ratio of (10 + 11)/9 not only when I was added but also, although less dramatic, when an inert gas was added (see Table IV)). While an increase in ratio was to be expected for the addition of I, due to the inhibition of return of 10 to 5, the effect of added argon was unexpected. A number

(10) Spectral properties of 9: NMR (CDCl₃) δ 2.3-3.1 (complex m); φ 91.11 (complex m), 85.0 (midpoint) (AB with further splitting, J_{AB} = 36 Hz, Δν_{AB} = 780.8 cm⁻¹). Mass spectroscopy gave M⁺ as 140.02404 [standard deviation = 0.00191 (13.6 ppm)]. Calculated M⁺ was 140.02491 [deviation = 0.00087 (6.2 ppm)].

(11) Products 7 and 9 were found *not* to be thermally interconvertible under the reaction conditions.

(12) The extrusion of CF₂ from fluorine-substituted cyclopropanes is a well-known process.¹³

(13) (a) Mitsch, R. A.; Neuvar, E. W. *J. Phys. Chem.* **1966**, *70*, 546. (b) Herbert, F. P.; Kerr, J. A.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1965**, 5710. (c) Atkinson, B.; McKeagan, D. *J. Chem. Soc., Chem. Commun.* **1966**, 189. (d) Quero, E. D.; Ferrero, J. C.; Staricco, E. H. *Int. J. Chem. Kinet.* **1977**, *9*, 339.

(14) The errors given are standard deviations and demonstrate the good precision of the data. The accuracy of the activation parameters is, however, somewhat less certain; we would estimate log A ± 1 unit, and E_a ± 1 kcal/mol.

Table IV. Ratios (10 + 11)/9 (at 270 °C)

reaction time, min	gas added		
	none (4 mm neat)	argon (200 mm)	I (60 mm) + argon (140 mm)
20	0.80	0.96	1.49
60	0.54	0.81	1.48
160	0.42	0.60	1.50

of control experiments served to elucidate the cause of these effects.

First, the rate of decomposition of 5 was found to be *independent* of trapping agent concentration. Second, 2,3-dimethyl-2-butene (T) had a relative trapping efficiency of 2.03 relative to I. These experiments rule out direct interaction of trapping agent with either 5 or intermediate 6¹⁵ and indicated that the alkene was merely trapping CF₂.

If, in the absence of trapping agent, CF₂ returned to 5 via addition to 10, why then is there no concomitant addition to 11 able to be observed? (10 and 11 rapidly equilibrate under the reaction conditions.¹⁸) It was able to be demonstrated in a control study that CF₂ adds to 10 40 times faster than to 11. With the ratio of 10:11 = 4.3, the rate of addition to 11 should be only 1/170 that of addition to 10; hence, it is undetectable.¹⁹

The effect of added inert gas is most easily explained if one assumes that when CF₂ is extruded from 5, it is formed *in a vibrationally excited state*. Under low-pressure conditions the "hot" CF₂ is consumed, relatively indiscriminately, either by addition to 10 (return to 5) or by dimerization (formation of TFE). However, when "cooled" by collision with any diluent gas, the CF₂ becomes more discriminating in its reactions and shows a greater preference for the dimerization process which has almost no E_a associated with it.²⁰ This hypothesis is strongly supported by our observation that under *neat* conditions (4 mm of 5) the ratio of 9/TFE = 10.9, after ~160 min at 270 °C, and the (10 + 11)/9 ratio is 0.42, while in the presence of 200-mm argon under the same conditions, 9/TFE = 6.8 and (10 + 11)/9 = 0.60.

Hexafluorospirpentane and perfluorospirpentane have been synthesized and are currently under kinetic investigation. Upon completion of this work a full report and discussion on the incremental effects of CF₂ groups on spirpentane thermolyses will be forthcoming.

Acknowledgment. We thank the National Science Foundation for partial support of this research.

(15) Diradical 6 should be intercepted more rapidly by I than by T,¹⁶ while CF₂ has been shown to be trapped more efficiently by T.¹⁷

(16) Pearson, J. M.; Szwarc, M. *Trans. Faraday Soc.* **1964**, *60*, 553.

(17) Mitsch, R. A.; Rodgers, A. S. *Int. J. Chem. Kinet.* **1966**, *1*, 439.

(18) Dolbier, W. R., Jr.; Fielder, T. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 5577.

(19) This control was run at 180 °C (the temperature at which HFPO decomposes). Hence the ratio of reactivity at ~270 °C where most of our control reactions with 5 were run should be somewhat smaller.

(20) Dalby, F. W. *J. Chem. Phys.* **1964**, *41*, 2297.

The Cation-Radical Catalyzed Diels-Alder Reaction

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The especially high reactivity of electron-deficient dienophiles in the Diels-Alder reaction is a familiar characteristic of this strategic synthetic reaction.¹ Although Lewis acids can enhance