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THE ELECTROCYCLIC INTERCONVERSION OF PERFLUORO-3-METHYLCYCLOBUTENE WITH Z- AND E-PERFLUORO-1,3-PENTADIENE

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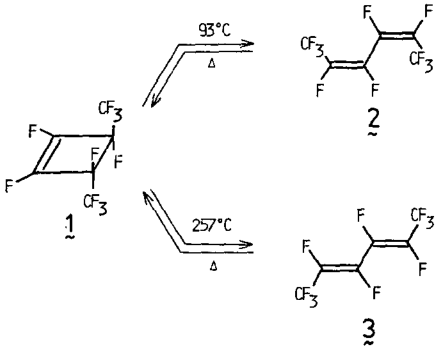
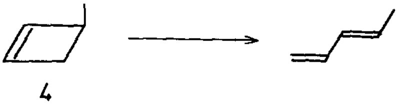
Summary: Z- and E-Perfluoro-1,3-pentadienes have been synthesized and their thermal interconversions with perfluoro-3-methylcyclobutene studied kinetically.

In 1984 we reported the kinetically preferential thermal conrotatory electrocyclic ring-opening of trans-perfluoro-3,4-dimethylcyclobutene to Z,Z- rather than E,E-perfluoro-2,4-hexadiene.[1] The result was in contrast to the ring-openings of 3-alkyl substituted and trans-3,4-dialkyl substituted cyclobutenes to form exclusively E-dienes, in what were generally considered to be sterically-controlled processes, i.e. the case of 3-methylcyclobutene:[2]



Log A = 12.1 (0.3)
E_a = 29.1 (0.5) kcal/mole
ΔH° = 5.6 (0.2) kcal/mole

Log A = 15.0 (0.4)
E_a = 50.6 (0.9) kcal/mole
ΔH° = 7.1 (0.4) kcal/mole

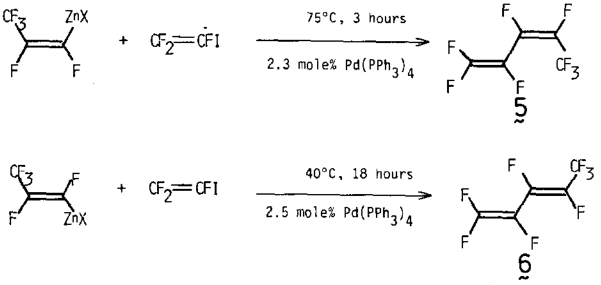


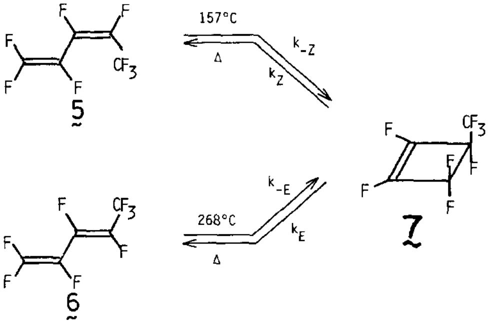
4

Log A = 13.5
E_a = 31.6 kcal/mole

The remarkable, constrasteric result obtained in the thermolysis of 1 was rationalized very nicely by Rondan and Houk, who proposed that π-donor substituents such as fluorine should have a significant kinetic propensity to rotate outwards during ring-opening.[3] Thus it was considered that the trifluoromethyl groups were of secondary importance to the fluorine substituents in determining the stereochemical outcome of the reaction.

Because of the rather unexpected and unusually dramatic kinetic results observed in the ring-opening of **1** it was considered important to test the generality and scope of the apparent effect of fluorine substituents on the cyclobutene-butadiene interconversion. A system considered of significance in understanding the overall picture was the perfluoro-3-methylcyclobutene ⇌ perfluoro Z- and E-1,3-pentadiene system. We were able to gain access to the required dienes cleanly, and specifically via the palladium-catalyzed coupling of the Z- and E-perfluoropropenyl zinc reagents with trifluorovinyl iodide.[4] Dienes **5** and **6** were formed stereospecifically in yields of 50% and 80%, respectively.[5]





Consistent with the bis-trifluoromethyl system **1**, the Z-diene **5** was found to cyclize much more readily than the E-diene **6**. Table 1 provides kinetic data for the clean, unimolecular interconversion which is indeed reversible but highly favors the cyclobutene **7** thermodynamically. Thermodynamic data are provided in Table 2.

Table 1. Activation Parameters for the Perfluoro-3-methylcyclobutene System.

	Log A	E_a[a]	ΔH‡[a]	ΔS‡[b]	Mean Temperature	
k_Z	12.6 ± 0.4	36.7 ± 0.7	35.9	-3.5	157.7°	°C
k_{-Z}	11.2 ± 0.4	28.5 ± 0.7	27.7	-10.1	157.7°	
k_E	14.7 ± 0.1	49.6 ± 0.3	48.5	5.5	268.3°	
k_{-E}	12.3 ± 0.1	39.2 ± 0.3	38.1	-5.3	268.5°	

[a] kcal/mole [b] cal/deg.

Table 2. Thermodynamic Parameters for the Perfluoro-3-methylcyclobutene System.

	7^a	5	6
ΔH°	0	10.4 ± 0.5 kcal/mole	8.2 ± 0.5
ΔS	0	10.9 ± 0.2 cal/deg.	6.6 ± 0.2

[a] The thermodynamic parameters of 5 and **6** are given relative to **7**.

The curious and yet unexplained phenomenon wherein the Z-diene 5 is thermodynamically favored over the E-diene, **6**, is again observed in this system as it was earlier in the *bis*-trifluoromethyl system **1**. Because of the greater number of ring fluorine substituents at the 4-position of **7**, the equilibrium favors the cyclobutene isomer more for **7** than was the case for **1** (i.e. 10.4 kcal for $7 \rightleftharpoons 5$, vs 5.6 kcal/mole for $1 \rightleftharpoons 2$).

The kinetic preference in ring-opening of **7** to **5** versus **6** is reflected by a ΔE_a of 12.9 kcal/mole while for the *bis*-trifluoromethyl system **1** there was a ΔE_a of 21.5 kcal/mole. According to Rondan and Houk a single fluorine substituent at the 3-position should give rise to a ΔE_a favoring outward rotation of ~13 kcal/mole.[3] When one considers that the inward rotation of a trifluoromethyl group should give rise to some steric inhibition, and thus experimentally diminish the kinetic preference of 5 over **6**, the values observed for the ring-openings of **1** and **7** are not inconsistent with the theory. It is satisfying to see that the preference for formation of 5 over **6** in the mono-trifluoromethyl system is about half that for the *bis*-trifluoromethyl system. In comparing the activation parameters of **6** with those of the *bis*-trifluoromethyl system 1, it can be seen that the $7 \rightleftharpoons 5$ equilibrium, lacking one kinetic preference for outward rotation of F, proceeds with an average E_a of 32.6 kcal/mole, 6.3 kcal *higher* than the average E_a required for $1 \rightleftharpoons 2$. Likewise the $7 \rightleftharpoons 6$ equilibrium (Avg. E_a = 44.5 kcal/mole), as would be expected, proceeds more readily than the $1 \rightleftharpoons 3$ equilibrium (Avg. E_a = 47.1 kcal/mole).

While a quantitative activation energy comparison of the hydrocarbon and fluorocarbon systems, **4** and 7, is difficult because of the large differences in these systems' thermodynamics, in view of the dramatic magnitude of the effects described in this report and in our earlier paper, there can be little doubt as to the general validity of the hypothesis that fluorine substituents in the 3- and/or 4-position of cyclobutene show a remarkable preference for outward rather than inward conrotatory rotation during electrocyclic cleavage.

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References & Footnotes

1. Dolbier, W.R. Jr.; Koroniak, H.; Burton, D.J.; Bailey, A.R.; Shaw, G.S.; Hansen, S.W. *J. Am. Chem. Soc.* **1984**, *106*, 1871.
2. Frey, H.M.; Marshall, D.C. *Trans. Faraday Soc.* **1965**, *61*, 1715.

3. (a) Rondan, N.G.; Houk, K.N. *J. Am. Chem. Soc.* **1985**, *107*, 2099; (b) Kirmse, W.; Rondan, N.G.; Houk, K.N. *J. Am. Chem. Soc.* **1984**, *106* 7989.
4. Burton, D.J.; Hansen, S.W. *J. Fluorine Chem.* **1986**, *31*, 465.
   Burton, D.J.; Heinze, P. *J. Amer. Chem. Soc.*, in press.
5. The structures of **5**, **6**, and **7** were confirmed by ^{19}F NMR and mass spectrometry: **5** - ϕ (ppm upfield from $CFCl_3$) 69.8 (m, 3F), 89.1 (dd, 1F), 105.1 (dd, 1F), 129.6 (d of complex m, 1F), 141.5 (m, 1F), 179.4 ppm (dt, 1F), $^{3}J_{cis\ \underline{F}C=C\underline{F}CF_3}$ = 7.5 Hz; **6** - ϕ 68.6 (dd, 3F), 89.5 (dd, 1F), 103.0 (dm, 1F), 153.6 and 158.3 (AB, dm, 2F), 186.9 (dtd, 1F), $^{3}J_{trans\underline{F}C=C\underline{F}CF_3}$ = 135 Hz; **7** - ϕ 75.7 (dd, 3F) , 115.6 and 117.6 (AB, dm, $^{2}J_{gemCF_2}$ = 197 Hz), 121.6 (m, 1F), 126.0 (qd, 1F), 177.9 ppm (m, 1F) (all peaks have further splitting).

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