Table X. Atom Coordinates and U_{eq} for Cp*$_2$ScCH$_3$ (**2**)

atom	x^a	y	z	$U_{eq}{}^b$
Sc	2029 (2)	495 (1)	1131 (1)	53 (0.3)
C1	249 (8)	−913 (8)	579 (6)	72 (3)
C2	1362 (17)	−602 (10)	175 (4)	78 (3)
C3	2718 (14)	−1018 (11)	353 (6)	94 (4)
C4	2615 (17)	−1597 (9)	867 (7)	100 (4)
C5	1060 (19)	−1602 (9)	1061 (5)	90 (4)
C6	−1500 (11)	−856 (14)	576 (10)	313 (11)
C7	1113 (29)	100 (10)	−404 (5)	334 (10)
C8	4244 (19)	−919 (13)	−79 (8)	241 (7)
C9	4009 (22)	−2203 (13)	1168 (11)	315 (10)
C10	451 (38)	−2361 (14)	1537 (6)	367 (11)
C11	65 (11)	1859 (10)	1569 (5)	82 (3)
C12	1416 (13)	2489 (7)	1568 (4)	72 (3)
C13	2458 (10)	1959 (12)	1982 (5)	84 (4)
C14	1604 (17)	951 (10)	2239 (4)	93 (4)
C15	169 (15)	977 (9)	1965 (6)	92 (4)
C16	−1359 (12)	2274 (10)	1200 (6)	155 (4)
C17	1792 (14)	3624 (8)	1190 (5)	151 (4)
C18	4001 (14)	2394 (15)	2178 (6)	218 (6)
C19	2175 (26)	151 (12)	2729 (4)	284 (9)
C20	−1291 (15)	263 (11)	2165 (6)	183 (5)
C21	4259 (13)	1293 (9)	757 (5)	156 (4)

[a] x, y, and z have been multiplied by 10^4. [b] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33}) \times 10^3$; $\sigma U_{eq} = 6^{-1/2}\langle \sigma U_{ii}/U_{ii} \rangle U_{eq}$.

dinates in Table XIII, and bond lengths and angles in Table XV. (Tables XI, XIII, XV are found in the Supplementary Material.) The final value of the secondary extinction parameter is 1.55 (16) × 10^{-6}. The atoms numbered 1 and 2 are the pyridyl atoms bound to scandium. Atoms C3–C6 are the remaining atoms (carbons) of the pyridyl ring. C11–C15 and C31–C35 are the (η^5-C$_5$Me$_5$) inner ring carbons, and C21–C25 and C41–C45 are the methyl groups associated with them, respectively.

Structure Determination for (η^5-C$_5$Me$_5$)$_2$ScCH$_3$. A crystal approximately 0.3 × 0.3 × 0.2 mm, that appeared satisfactory from an oscillation photograph, was centered on a Syntex P2$_1$ diffractometer equipped with graphite-monochromated Mo Kα radiation. An orthorhombic cell was found, and cell dimensions were obtained from a least-squares fit to the setting angles of 15 reflections (various forms of six independent reflections) with 20° < 2Θ < 26°. Systematic absences observed in the data of $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l, l = 2n + 1$ are unique for the space group no. 19, $P2_12_12_1$. Five octants of data (hkl, $hk\bar{l}$, $\bar{h}k\bar{l}$, $h\bar{k}\bar{l}$, and $\bar{h}\bar{k}\bar{l}$) were collected with 4° < 2Θ < 40° and one octant, hkl, with 40° < 2Θ < 50°, a total of 6684 reflections. The data were merged (goodness of fit = 1.04) to give 2076 independent reflections, of which 1859 had $F_o > 0$ and 1143 had $(F_o{}^2) > 3\sigma(F_o{}^2)$. Three check reflections monitored every 97 reflections showed linear decay of 1.5% in F over the 230 h required to collect the data. The data were corrected for this decay and reduced to $F_o{}^2$; variances were assigned as described above. The least-squares refinement used all 2076 data and minimized the quantity $\Sigma w(F_o{}^2 - F_c{}^2)^2$, where $w = 1/\sigma^2(F_o{}^2)$. No absorption correction was made because of the small value of μr_{max}. A Patterson map gave scandium coordinates, and successive structure factor-Fourier calculations located the remaining atoms. Hydrogen atoms on the Cp* methyl groups were introduced, based on difference maps calculated in the planes where they were expected, and included in the subsequent calculations as constant contributions to the structure factors, with isotropic B of 10.0 Å^2. Six cycles of full matrix least squares, the hydrogen atoms being repositioned two times, concluded the refinement; the final $R = 0.113$ for all the data with $F_o{}^2 > 0$ and 0.072 for data with $F_o{}^2 > 3\sigma(F_o{}^2)$. The goodness of fit was $S = 2.98$, where n = number of data = 2076 and p = number of parameters. In the final refinement no parameter shifted more than one-half its standard deviation. A final difference map showed no excursion greater than ±0.44 e/Å^3. Crystal data are given in Table VIII and atom coordinates in Table X. Calculations were done by using the programs of the CRYRM crystallographic computing system[64] on a VAX 11/780 computer; the final drawing was done by using ORTEP.[65]

Acknowledgment. We thank Dr. Patricia Watson of the DuPont Company for her assistance in portions of this work as well as for helpful discussions. J.E.B. and M.E.T. thank the DuPont Company for inviting M.E.T. to DuPont to carry out some of the experiments. We thank Pamela Shapiro for contributing to the preparation of this manuscript. Discussions with Dr. Kim Shugart and Professor William A. Goddard III were very helpful. This work was supported by the National Science Foundation (Grant No. CHE-8303735) by the USDOE Office of Energy Research, Office of Basic Energy Sciences (Grant No. DE-FG03-85ER13431), and by Shell Company Foundation which are gratefully acknowledged. The use of the Southern California Regional NMR Facility, supported by National Science Foundation Grant No. CHE 7916324, is also gratefully acknowledged. J.E.B. and M.E.T. thank the Atlantic Richfield Company for a graduate fellowship to M.E.T.

Supplementary Material Available: U_{ij}'s in Table XI and XII, hydrogen atom coordinates in Tables XIII and XIV, and bond lengths and angles in the Tables XV and XVI (6 pages); structure factor tables (16 pages). Ordering information is given on any current masthead page.

Kinetic and Thermodynamic Studies of the Thermal Electrocyclic Interconversions of Perfluorinated Dienes and Cyclobutenes

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Abstract: Detailed kinetic and thermodynamic analyses were carried out for the thermal interconversions of (Z,Z)- and (E,E)-perfluoro-2,4-hexadienes with *trans*-perfluoro-3,4-dimethylcyclobutene, (E,Z)-perfluoro-2,4-hexadiene with perfluoro-*cis*-3,4-dimethylcyclobutene, (Z,Z)- and (E,E)-perfluoro-3,5-octadienes with *trans*-perfluoro-3,4-diethylcyclobutene, and (Z)- and (E)-perfluoro-1,3-pentadiene with perfluoro-3-methylcyclobutene. In each case the (Z,Z)- or (Z)-dienes exhibited substantial kinetic advantage over the (E,E)- or (E)-dienes in their cyclization processes.

The elegant stereochemical studies of Criegee in 1959 on the ring opening of *cis*- and *trans*-1,2,3,4-tetramethylcyclobutenes[1] were the first to demonstrate unambiguously the conrotatory nature of the cyclobutene–butadiene electrocyclic interconversion. It wasn't until 1965, of course, that the classic papers of Woodward

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[†] University of Florida.

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(1) Criegee, R.; Noll, K. *Liebigs Ann. Chem.* **1959**, *627*, 1; *Chem. Ber.* **1965**, *98*, 2339.

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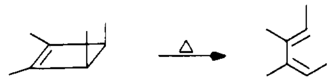
Table I. Activation Parameters for the Perfluoro-2,4-hexadiene System

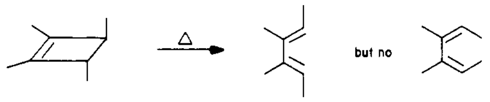
	log A	E_a^{e}	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$	$\Delta G^{\ddagger a}$	mean temp, °C
k_{EE}	15.4 ± 0.4	50.6 ± 0.9	49.5	7.0	45.8	257.8
k_{-EE}	12.5 ± 0.4	43.6 ± 0.9	42.5	−4.5	44.9	257.8
k_{ZZ}	12.1 ± 0.3	29.1 ± 0.5	28.3	−5.4	30.3	93.8
k_{-ZZ}	10.4 ± 0.3	23.5 ± 0.5	22.8	−13.2	27.6	93.8
k_{EZ}	13.9 ± 0.3	38.1 ± 0.7	37.1	2.0	36.2	207.8
k_{-EZ}	11.1 ± 0.3	32.7 ± 0.7	31.8	−10.5	36.8	207.8

[a] In kcal/mol. [b] In cal/deg.

and Hoffmann rationalized such empirical observations in terms of orbital symmetry.[2]

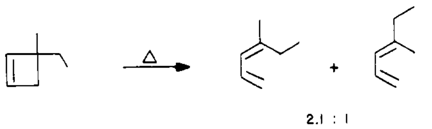


1 2



3 4 5

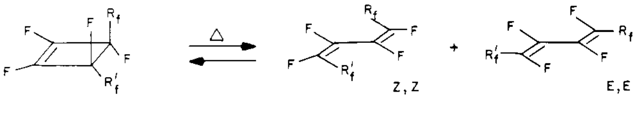
The question of why none of the isomeric (Z,Z)-diene, also able to be formed via conrotatory opening, had been observed in the thermolysis of 3 was not addressed by early workers except in terms of a probable *steric* rationale. Later, when results began to appear which were obviously inconsistent with the steric argument i.e., the ring opening of 3-ethyl-3-methylcyclobutene,[3] there arose a need for an alternative approach to the problem. Curry and Stevens proposed that since methyl is the poorest donor of the alkyls, the residual negative charge about methyl will experience more repulsion of C_4 upon inward rotation than will occur for better donor groups.[3]



The need for better and more quantitative understanding of the factors involved in determining the mode of rotation in cyclobutene ring opening was dramatized by our recent preliminary report of the kinetic behavior of the isomeric perfluoro-2,4-hexadienes in their reversible cyclobutene formation,[4] work which has been expanded and more fully interpreted in the present report.

Further related examples of the effect of chloro, methoxy, and acetoxy substituents upon cyclobutene ring opening were reported by Kirmse et al. shortly thereafter,[5] thus indicating that such effects were not unique to fluorine. These authors also presented a theoretical rationale for their and our results which was consistent with the kind of dramatic kinetic effects we have observed and report further upon in this paper.

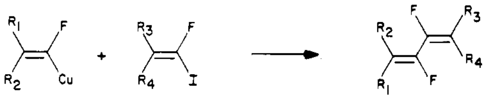
In order to better understand the effect of substituents upon the kinetics and stereochemistry of the cyclobutene–butadiene electrocyclic process, we have examined in detail the kinetic and thermodynamic parameters for the reversible ring opening of three perfluorinated cyclobutene systems, the *cis*- and *trans*-3,4-dimethylcyclobutene system, **17** and **6**, the *trans*-3,4-diethylcyclobutene system, **7**, and the 3-methylcyclobutene system, **8**.



6: $R_f = R_f' = CF_3$
7: $R_f = R_f' = C_2F_5$
8: $R_f = CF_3$, $R_f' = F$

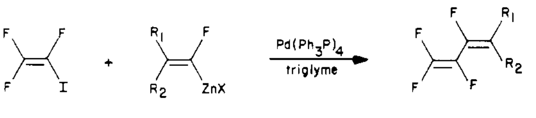
Syntheses

The perfluoro-2,4-hexadiene and -3,5-octadiene systems were approached synthetically via the preparation of the respective dienes using methodology developed within the Burton group.[6]



9: $R_1 = R_3 = CF_3$, $R_2 = R_4 = F$
10: $R_2 = R_4 = CF_3$, $R_1 = R_3 = F$
11: $R_1 = R_4 = CF_3$, $R_2 = R_3 = F$
12: $R_1 = R_3 = C_2F_5$, $R_2 = R_4 = F$
13: $R_2 = R_4 = C_2F_5$, $R_1 = R_3 = F$
14: $R_1 = R_4 = C_2F_5$, $R_2 = R_3 = F$

The perfluoro-1,3-pentadienes **15** and **16** were synthesized via a modification of a procedure of Heinze,[7] wherein the isomeric perfluoropropenylzinc reagents were coupled with trifluorovinyl iodide in the presence of tetrakis(triphenylphosphine)palladium. Triglyme was used as the solvent in order to facilitate the isolation of the dienes. No reaction occurred at room temperature, in contrast to related work of Normant.[8]



15: $R_1 = F$, $R_2 = CF_3$
16: $R_1 = CF_3$, $R_2 = F$

The isomeric dienes were fully characterized spectroscopically. Of key significance were the vicinal vinyl F–F coupling constants which allowed the distinguishing of the Z and E isomers. For the Z,Z isomers **10** and **13**, these coupling constants were found to be 5.1 and <2 Hz, respectively, while for the E,E isomers they were 145 and 123 Hz, respectively. For the (E)-diene **16**, the coupling was 135 Hz, while for the (Z)-diene **15** it was 7.5 Hz. Such distinctively disparate coupling constants as these have ample precedent for the distinguishing of Z and E isomers.[9]

Results and Discussion

Perfluoro-2,4-hexadiene System. The cyclizations of the isomeric perfluoro-2,4-hexadienes were the first studies to be undertaken. The rates for these reversible processes, and all others presented in this paper, were obtained in the gas phase at pressures

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(2) Woodward, R. b.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395.

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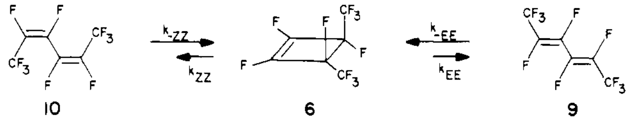
Table II. Thermodynamic Parameters for the Perfluoro-2,4-hexadiene System[a]

	6	17	10	9	11
$\Delta H°$	0	1.4 ± 0.1	5.6 ± 0.2	6.8 ± 0.3	7.1 ± 0.4
ΔS^c	0	−1.3 ± 0.1	+7.8 ± 0.1	11.2 ± 0.1	9.9 ± 0.1

[a] The thermodynamic parameters are given relative to **6**. [b] In kcal/mol. [c] In cal/deg.

between 10 and 20 torr, and good first-order behavior was observed.



10 6 9

11 17

An Arrhenius plot of the rate data provided the activation parameters given in Table I, while a van't Hoff plot of the equilibrium data gave the thermodynamic parameters in Table II.

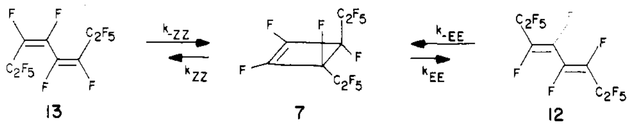
Because of the general difficulty we experienced in obtaining reliable equilibrium data in this system, and because of the unexpected finding that the (*Z*,*Z*)-diene **10** was actually more stable than the (*E*,*E*)-diene **9**, a careful and more comprehensive study of the equilibrium data for the perfluoro-2,4-hexadiene system was undertaken utilizing a much broader temperature range and many more points than had been used in the earlier study.[4] As a result the thermodynamic values presented in Table II, while within the error limits of the earlier reported values, are much more precise. Typical equilibrium constants for the perfluoro-2,4-hexadiene system are as follows (at 332.8 °C): **6**/**17** = 6.52, **10**/**17** = 3.30, **9**/**17** = 2.69, **11**/**17** = 6.42. (See Table XIV for complete data.) The use of the new equilibrium data of course gave rise to small changes in the activation parameters which are reflected in Table I. The observed log *A* value for k_{EE} (15.4) is high for cyclobutene ring opening,[10] and future work should indicate whether this value is an anomaly or has significance to the specific system.

As discussed in our earlier report on this system, the differences in rate for the (*Z*,*Z*)-diene ⇌ cyclobutene equilibrium as compared to the (*E*,*E*)-diene ⇌ cyclobutene equilibrium are both dramatic and unprecedented ($k_{ZZ}/k_{EE} = 1.9 \times 10^9$ at 111.5 °C). According to the values given in Table I, this amounts to a ΔE_a for the ring-opening processes of 21.5 kcal/mol and a ΔE_a for the cyclization reactions of 20.1 kcal/mol. As one can see, the (*Z*,*Z*)-diene **10** is in equilibrium with cyclobutene **6** at 94 °C, while temperatures of 258 °C are necessary to reach comparable rates of interconversions for the *E*,*E* isomer **9** with **6**. Not unexpectedly the (*E*,*Z*)-diene **11** interconverts with perfluoro-*cis*-3,4-dimethylcyclobutene, **17**, at intermediate rates and temperatures.

At 258 °C, during the equilibration of *E*,*E* isomer **6** and the *Z*,*Z* isomer, a slow leakage to the *E*,*Z* system (**11** + **17**) was detected. Because of the kinetic complexities of this interconversion, it was not possible to determine whether the isomerization occurred via a disrotatory ring opening of the cyclobutenes, or whether it derived from geometrical isomerization of the dienes. An approximate activation energy of 42 kcal/mol was calculated for the leakage process, and such a number is consistent with expectations for either mechanism.[11,12]

Perfluoro-3,5-octadiene System. The study of the perfluoro-3,5-octadiene system was undertaken to observe what if any effect an increase in steric bulk of the perfluoroalkyl substituents would have upon the kinetic and thermodynamic profile of the equilibria.

Kinetic data was obtained only for cyclization of the (*Z*,*Z*)- and (*E*,*E*)-dienes, i.e., **13** and **12** ⇌ **7**, while equilibrium data was obtained for all four GC-visible components. (*cis*-3,4-Diethylcyclobutene, **18**, could not be observed in equilibrium with **7**, **12**, **13**, **14**.) As Tables III and IV indicate, there was no dramatic effect of changing the trifluoromethyl groups to pentafluoroethyl groups, other than those changes due to the increase in steric bulk.



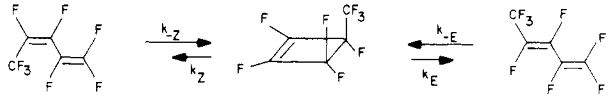
13 7 12

One can see from Table IV that, somewhat surprisingly, all three of the bis(pentafluoroethyl) dienes are more stable relative to *trans*-cyclobutene (**7**) than were their bis(trifluoromethyl) counterparts. Apparently the vicinal C_2F_5/F interactions of **7** are affected more deleteriously than are the cis interactions of C_2F_5 in the dienes **13** and **14**. Note that in the perfluoro-3,4-octadiene system, the (*E*,*E*)-diene **12** is slightly more stable than the (*Z*,*Z*)-diene **13**, while in the perfluoro-2,4-hexadiene system the opposite was true, a fact consistent with a relative lack of steric effect of CF_3 in the hexadiene system combined with the emergence of a steric effect for C_2F_5 in the octadiene system.

The kinetic picture for the 3,4-octadiene system, as seen in Table III, shows that while the ring-opening E_a's and $\Delta G^‡$'s are lowered relative to the 2,4-hexadiene system (i.e, k_{ZZ} and k_{EE}), those for cyclization (k_{-ZZ} and k_{-EE}) are not much different. This is, as noted above, probably a reflection of the increase in stability of dienes **12** and **13** relative to cyclobutene **7**. For all extents and purposes, the cyclization processes appear to be independent of whether the R_f substituent is CF_3 or C_2F_5.

While the interconversion of (*E*,*Z*)-3,5-octadiene, **14**, and *cis*-3,4-diethylcyclobutene, **18**, could not be examined because the latter was so unstable as to be unobservable in equilibrium with **14**, leakage between the *E*,*E*/*Z*,*Z* system and *E*,*Z* system could be measured. A log *A* of 13.1 ± 0.6 and an E_a of 46.2 ± 1.7 kcal/mol were attributable to this process, whose value was similar to that observed for leakage in the 2,4-hexadiene system.

Perfluoro-1,3-pentadiene System. In a test to determine the kinetic effect of a *single* $CFCF_3$ site on butadiene cyclization rates, the (*Z*)- and (*E*)-perfluoro-1,3-pentadienes, **15** and **16**, were examined as to their rates of electrocyclic cyclization to perfluoro-3-methylcyclobutene, **8**.[13] Indeed it was found that as in



15 8 16

the 2,4-hexadiene and 3,5-octadiene systems, the (*Z*)-diene underwent cyclization much more readily than the (*E*)-diene. Table V provides the activation parameters and Table VI the thermodynamic parameters for these thermal, gas-phase interconversions.

As one can see from Table VI, the equilibrium lies far toward the cyclobutene product **8** in this system, with only 0.5% of **15** and 0.3% of **16** being present at equilibrium at 200 °C. Consistent with the 2,4-hexadiene results, the (*Z*)-diene **15** proved to be 2.2 kcal/mol more stable than the (*E*)-diene **16**. While the CF_3 group is considered to be quite sizable i.e., about as sterically demanding as an isopropyl group,[14] apparently its size is not the deciding factor in the *Z*/*E* relative stability. Theoretical work on conformational effects in butadienes would seem to indicate that *planarity* of a perfluorinated diene is not an important stabilizing factor.[15]

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Table III. Activation Parameters for the Perfluoro-3,5-octadiene System

	log A	E_a[a]	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$	$\Delta G^{\ddagger a}$	mean temp, °C
k_{ZZ}	11.9 ± 0.5	27.0 ± 0.8	26.3	−6.3	28.6	92.4
k_{-ZZ}	10.1 ± 0.5	23.4 ± 0.8	22.7	−14.5	28.0	92.4
k_{EE}	13.6 ± 0.5	44.8 ± 1.4	43.6	0.6	43.4	308.5
k_{-EE}	11.9 ± 0.5	42.0 ± 1.4	40.8	−7.2	45.0	308.5

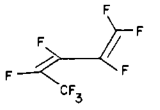
[a] In kcal/mol. [b] In cal/deg.

Table IV. Thermodynamic Parameters for the Perfluoro-3,5-octadiene System[a]

	7	14	13	12
$\Delta H^{\circ b}$	0	3.4 ± 0.2	3.6 ± 0.3	2.8 ± 0.1
ΔS^{c}	0	9.8 ± 0.1	8.2 ± 0.1	7.7 ± 0.1

[a] The thermodynamic parameters are all given relative to 7. [b] In kcal/mol. [c] In cal/deg.

Hence, conformations with the two double bonds orthogonal to each other, such as **19**, could well be involved such that the cis F/CF_3 interaction of the E isomer might be more destabilizing than the alternate $CF_2{=}CF/CF_3$ interaction of the Z isomer. At present there is no thermodynamic data available which give specific insight into Z and E CF_3/F interactions.



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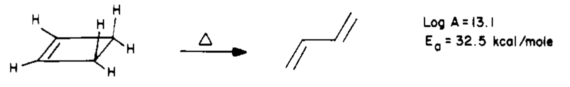
Kinetically the preference for outward rotation of F along with inward rotation of CF_3 in the ring opening of **8** was reflected by a ΔE_a of 12.9 kcal/mol. This compares with the 21.5 kcal/mol ΔE_a observed for the bis(trifluoromethyl) system **6**. According to Rondan and Houk, a single fluorine substituent at the 3-position should give rise to a ΔE_a favoring outward rotation of ~13 kcal/mol.[5b] The results are certainly in line with expectations according to theory, and it is satisfying to see that the effect for the monotrifluoromethyl system **8** is about half that of the bis(trifluoromethyl) system.

The required activation energy for ring opening of the parent cyclobutene (**20**) to butadiene is 32.5 kcal/mol,[15] this for a process *exothermic* to the extent of −16.5 kcal/mol. With ring opening



20

for the trans-perfluoro system **6** being endothermic by 5.6 kcal/mol and still having a lower E_a (29.1 kcal/mol), one can be certain that the net effects of the fluorine and CF_3 substituents of **6** are beneficial to the transition state for the electrocyclic process.

Because of the great variation in the thermodynamics for the hydrocarbon vs. the fluorocarbon systems, it is difficult to compare these systems directly and unambiguously. We believe that, for comparison purposes, taking the *average* of the forward and reverse processes provides a number which has validity as a measure of relative transition-state stabilization.

Table VII provides a summary of available pertinent data on cyclobutene–butadiene isomerizations, and one can see that most of these reactions have activation energies which lie between 37 and 40 kcal/mol. While methyl groups at positions 3 and/or 4 do seem to enhance the rate when they can rotate outward, the effect is not dramatic. In fact the apparent deleterious effect of a methyl at either of the vinyl position, i.e., 1,3- and 1,4-dimethylcyclobutene, seems at least as significant.

Note that the perfluorocyclobutene system is only slightly above the described "normal" range of activation energies, while the perfluoro-*cis*-3,4-dimethylcyclobutene system shows only a slight enhancement of rate. On the other hand, the perfluoro-*trans*-3,4-dimethyl, *trans*-3,4-diethyl-, and 3-methylcyclobutene systems each exhibit dramatic transition-state lowerings, for their respective formation of ZZ, ZZ, and Z isomers, with average E_a's of 26.3, 25.2, and 32.6 kcal/mol, respectively. Contrarily the average activation energies for formation of the respective (EE), (EE), and (E)-dienes from these same cyclobutenes show a distinct rate retardation (average E_a's of 47.1, 43.4, and 44.4 kcal/mol, respectively).

The lowerings of transition-state energies exhibited by **6**, **7**, and **8** in the formation of the (Z)-dienes in all likelihood derive from an apparent strong kinetic advantage for "outward" rotation for fluorine substituents at the 3- and 4-positions of cyclobutene, as has recently been proposed by Rondan and Houk.[5b] They contend that π-donor substituents, of which fluorine must be considered one of the best, should have a significant kinetic propensity to rotate outward during cyclobutene ring openings. Apparently the CF_3 substituent more or less goes along for the ride and is not a major factor in the activation barrier picture. Indeed we have found that a single CF_3 substituent at the 3-position of cyclobutene has a diminished relative propensity to rotate outward vs. inward than a CH_3 group.[24]

The large 11–12 kcal/mol lowering of average E_a observed for Z,Z-isomer formation from **6** and **7** and the similar 5.5 kcal/mol lowering observed for (Z)-diene formation from **8** were seen in spite of the fact that the R_f groups must be encountering some steric repulsion during their required inward rotation. Likewise the 9, 5.3, and 6.3 kcal/mol increases in E_a observed for their respective ring openings to the (E,E)- and (E)-dienes show a comparable inhibition of ring opening when the fluorine substituents *must* rotate inward.

From the results obtained thus far in these three perfluorinated systems, there has unambiguously been demonstrated a consistent and dramatic kinetic preference for outward rotation of fluorine substituents, with concomitant inward rotation of CF_3 or C_2F_5 groups, in the electrocyclic ring opening of cyclobutenes. Since these large observed substituent effects are obviously contrary to steric expectations, the rationale proposed by Rondan and Houk is attractive as providing a reasonable mechanistic explanation for the results.

Further quantitative insight into the specific kinetic effects of fluorine and R_f at various combinations of the 1-, 2-, 3-, and 4-positions of cyclobutene await studies of specific non-perfluoro systems. Such investigations are presently nearing completion.

Experimental Section

For thermal isomerization studies, pure (over 95% purity) perfluorodienes as well as perfluorocyclobutenes were used. To purify the starting materials, GLPC separations were accomplished on a Varian Aerograph 90 P with helium as a carrier gas and fitted with a 20-ft. × $^1/_4$-in. column of 20% SE-30 on Chrom P 60/80 at room temperature. All product ratios and kinetic data were obtained by GLPC using a

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Table V. Activation Parameters for the Perfluoro-1,3-pentadiene System

	log A	E_a[a]	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]	$\Delta G^{\ddagger}$[a]	mean temp, °C
k_Z	12.6 ± 0.4	36.7 ± 0.7	35.9	−3.5	37.4	157.7
k_{-Z}	11.2 ± 0.4	28.5 ± 0.7	27.7	−10.1	32.1	157.7
k_E	14.7 ± 0.1	49.6 ± 0.3	48.5	5.5	45.5	268.3
k_{-E}	12.3 ± 0.1	39.2 ± 0.3	38.1	−5.3	41.0	268.3

[a] In kcal/mol. [b] In cal/deg.

Table VI. Thermodynamic Parameters for the Perfluoro-1,3-pentadiene System[a]

	8	**15**	**16**
ΔH°[b]	0	8.2 ± 0.5	10.4 ± 0.5
ΔS^{c}	0	6.6 ± 0.2	10.9 ± 0.2

[a] The thermodynamic parameters are relative to **8**. [b] In kcal/mol. [c] In cal/deg.

Hewlett-Packard 5710A gas chromatograph fitted with a flame ionization detector and a gas injection system and coupled to a Hewlett-Packard 3380S integrator. In this case a 20-ft. × $^1/_8$-in. column of 20% $AgNO_3$–$PhCH_2CN$ on Chrom P 60/80 was used in the temperature range −5 to −15 °C.

All ^{19}F NMR spectra were obtained in $CDCl_3$ at ambient temperature by using a Nicolet NT 300 spectrometer at 282.3 MHz with $CFCl_3$ as an internal standard.

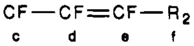
The isomeric perfluoro-2,4-hexadienes as well as the isomeric perfluoro-3,5-octadienes were prepared via the coupling of isomeric perfluoro propenyl- and -butenylcopper reagents with isomeric perfluoropropenyl and -butenyl iodides.[6,7] See Tables VIII–X for NMR data.

Preparation of (*E*)-$CF_3CF{=}CFCF{=}CF_2$ from (*Z*)-$CF_3CF{=}CFZnI$ and $CF_2{=}CFI$. (*Z*)-$CF_3CF{=}CFZnI$ was prepared from 15.4 g of

Table VII. Activation Energies for Cyclobutene–Butadiene Interconversions

substituent	ring-opening log A	ring-opening E_a, kcal/mol	cyclization E_a	av E_a	ΔH°	product stereochem	ref
	13.1	32.5	43.7	38.1	−11.2		16
3-Me	13.5	31.5	43.8	37.7	−12.3	*E*	17
3,3-Me_2	13.9	36.1	48.8	42.5	−12.7		18
trans-3,4-Me_2	14.0	30.6	43.9	37.3	−13.3	*E,E*	5a
cis-3,4-Me_2	13.7	34.0	47.3	40.7	−13.3	*E,Z*	19
F-*trans*-3,4-Me_2	12.1	29.1	23.5	26.3	+5.6	*Z,Z*	this work
F-*trans*-3,4-Me_2	15.0	50.6	43.6	47.1	+7.1	*E,E*	this work
F-*cis*-3,4-Me_2	13.9	38.1	32.7	35.4	+6.8	*E,Z*	this work
F-1,2-Me_2	13.6	46.0	36.6	41.3	+9.4		20
F	14.1	47.1	35.4	41.3	+11.7		21
1,3-Me_2	13.6	33.0	45.0	39.0	−12	*E*	18
1,2,3,4-*trans*-Me_4	13.9	33.6	46.2	39.9	−12.6	*E,E*	22
1-Me	13.8	35.1	46.2	40.7	−11.1		17
1,4-Me_2	13.5	33.4	45.4	39.4	−12.0	*E*	23
F-*trans*-3,4-Et_2	11.9	27.0	23.4	25.2	+3.6	*Z,Z*	this work
F-*trans*-3,4-Et_2	13.6	44.8	42.0	43.4	+2.8	*E,E*	this work
F-3-Me	12.6	36.7	28.5	32.6	+8.2	*Z*	this work
F-3-Me	14.7	49.6	39.2	44.4	+10.4	*E*	this work

Table VIII. ^{19}F Chemical Shifts.[a] Perfluorodienes


$$\underset{a}{R_1}-\underset{b}{CF}=\underset{c}{CF}-\underset{d}{CF}=\underset{e}{CF}-\underset{f}{R_2}$$

compd	chemical shifts (ϕ) a	b	c	d	e	f
9 (*E,E*)	69.1 (m)	153.5 (dm)	157.0 (dm)	157.0 (dm)	153.5 (dm)	69.1 (m)
10 (*Z,Z*)	69.8 (ddd)	139.0 (qm)	126.9 (m)	126.9 (m)	139.0 (qm)	69.8 (ddd)
11 (*Z,E*)	70.3 (dq)	140.2 (m)	135.0 (dm)	147.5 (dm)	153.4 (dm)	69.3 (ddd)
12 (*E,E*)	84.9 (m, CF_3) 121.5 (m, CF_2)	152.5 (dm)	154.5 (dm)	154.5 (dm)	150.5 (dm)	84.9 (m, CF_3) 121.5 (m, CF_2)
13 (*Z,Z*)	83.9 (m, CF_3) 121.2 (m, CF_2)	136.8 (m)	118.7 (m)	118.7 (m)	136.8 (m)	83.9 (m, CF_3) 121.2 (m, CF_2)
14 (*Z,E*)	84.8 (m, CF_3) 121.7 (m, CF_2)	137.6 (m)	127.6 (m)	143.2 (m)	150.5 (dm)	84.1 (m, CF_3) 122.0 (m, CF_2)
15 (*Z*) (R_2 = F)	69.8 (m)	141.5 (m)	129.6 (dm)	179.4 (dm)	105.1 (ddm)	89.1 (ddm)
16 (*E*) (R_2 = F)	68.6 (ddm)	153.6 (dm)	158.3 (dm)	186.9 (dtd)	103.0 (dm)	89.5 (ddd)

[a] In $CDCl_3$; ϕ = ppm upfield from internal standard $CFCl_3$.

Table IX. ^{19}F Coupling Constants. Perfluorodienes[a]

compd	couplings, Hz ab	ac	ad	bc	bd	be	cd	ce	de	df	ef
9 (*E,E*)				*145*					*145*		
10 (*Z,Z*)	10.1	5.1		*5.1*					*5.1*	5.1	10.1
11 (*Z,E*)	10	5.5	5.5	*5*			38.2		*142.3*	20.8	10
12 (*E,E*)				*123*					*123*		
13 (*Z,Z*)	14.1			*<2*					*<2*		14.1
14 (*Z,E*)				*<3*			41.2		*125*	24.5	11.8
15 (*Z*)(R_2 = F)	10.7			*7.5*			35.6	15	*119.0*	*35.6*	33.0
16 (*E*)(R_2 = F)	10.4	21.5		*135*	14.9	24.2	30.	16.4	*115.3*	*30*	40.3

[a] Vicinal vinyl F–F couplings are italic.

Table X. ^{19}F Chemical Shifts. Perfluorocyclobutenes[a]

	chemical shifts (ϕ)					
compd	a	b	c	d	e	f
6 (trans)	120.8 (m)	120.8 (m)	179.7 (m)	179.7 (m)	75.5 (dm, (J_{de} = 5.5 Hz)	75.5 (dm, J_{cf} = 5.5 Hz)
17 (cis)	117.7 (m)	117.7 (m)	170.2 (m)	170.2 (m)	74.1 (m)	74.1 (m)
7 (trans)	119.3 (m)	119.3 (m)	175.1 (m)	175.1 (m)	82.2 (m, CF_3) 118.2, 127.1 (AB, m, CF_2)	82.2 (m, CF_3) 118.2, 127.1 (AB, m, CF_2)
8 (R_2 = F)	121.6 (m)	126.0 (dq, J_{be} = 10 Hz)	177.9 (m)	115.6 (AB, dm, J_{df} = 197 Hz)	75.7 (dd, J_{ce} = 10, J_{be} = 10 Hz)	117.6 (AB, dm, J_{df} = 197 Hz)

[a] In $CDCl_3$; ϕ = ppm upfield from internal standard $CFCl_3$.

Table XI. Rate Data for **6** ⇌ **10** Interconversion

temp, °C	10^6k_{ZZ}	10^4k_{-ZZ}
111.5	39.2 ± 0.3	11.03 ± 0.1
104.5	20.4 ± 0.3	6.58 ± 0.1
98.0	10.4 ± 0.1	3.81 ± 0.04
90.25	4.74 ± 0.04	2.04 ± 0.02
83.0	1.99 ± 0.02	1.00 ± 0.01
76.5	0.86 ± 0.01	0.50 ± 0.007

Table XII. Rate Data for the **17** ⇌ **11** Interconversion

temp, °C	10^5k_{EZ}	10^5k_{-EZ}
217.0	78.5 ± 0.9	34.7 ± 0.5
213.25	57.2 ± 0.9	26.4 ± 0.4
209.0	41.0 ± 0.6	19.8 ± 0.3
206.25	33.1 ± 0.1	16.57 ± 0.06
203.0	25.6 ± 0.1	13.30 ± 0.06
199.25	17.5828 ± 0.1	9.56 ± 0.05

(*Z*)-$CF_3CF{=}CFI$ (60 mmol) and 5.0 g of activated zinc (77 mmol) in 35 mL of triglyme (TG) in a dry, 50-mL flask equipped with a water-cooled condenser topped with a glass tee. The apparatus was maintained under an inert atmosphere. The mixture was stirred with a magnetic stirring bar at room temperature for 3 h. The zinc reagent was filtered with a Schlenk funnel under nitrogen, and 10 mL of TG was used to rinse the funnel. The zinc reagent was placed in a 100-mL, round-bottomed flask equipped with a stirring bar, two stoppers, and a stopcock which led to a trap cooled with dry ice/isopropyl alcohol. To the zinc reagent was added 10.0 g of $CF_2{=}CFI$ (48 mmol) and 1.4 g of $Pd(PPh_3)_4$ (2.5 mol %), and the reaction mixture was stirred and heated at 40 °C for 30 h. The trap contained 4.2 g of material, and the pot contents were distilled at room temperature and 50 mmHg to give an additional 4.0 g for a total of 8.2 g of product that was >95% pure by ^{19}F NMR for an 80% yield. IR (gas cell, room temperature, 20 mmHg): 1776.2 ($CF{=}CF_2$, w), 1408.8 (w), 1346.1 (w), 1313.8 (s), 1228.5 (s), 1183.7 (s), 1141.1 (w), 1077.6 (w), 860 cm^{-1}. Mass spectrum: $C_5F_8^+$, 212, (15.7%); $C_2F_7^+$, 193, (24.9%); $C_4F_5^+$, 143, (77.3%); $C_4F_4^+$, 124, (22.4%); $C_3F_3^+$, 93, (100%); CF_3^+, 69, (21.8%). High resolution mass spectrum gave a parent ion of 211.9872. See Tables VIII–X for ^{19}F NMR data.

When this same reaction was conducted at 75 °C for 6 h, the yield was 55%.

Preparation of (*Z*)-$CF_3CF{=}CFCF{=}CF_2$ from (*E*)-$CF_3CF{=}CFZnI$ and $CF_2{=}CFI$. (*E*)-$CF_3CF{=}CFZnI$ was prepared from 11.4 g of (*E*)-$CF_3CF{=}CFI$ (44 mmol) and 4.0 g of activated zinc (61 mmol) in 20 mL of TG in a 50-mL flask equipped with a water-cooled condenser topped with a glass tee. The apparatus was maintained under an inert atmosphere, and the mixture was stirred with a magnetic stirring bar for 3 h at room temperature. The zinc reagent was Schlenk filtered under argon into a dry, 100-mL, round-bottomed flask equipped with stirring bar and a dry ice/isopropyl alcohol condenser. To the zinc reagent, 8.2 of $CF_2{=}CFI$ (39 mmol) and 1.0 g of $Pd(PPh_3)_4$ (2.3 mol %) were added, and the mixture was stirred at 75 °C for 3 h. The pot contents were distilled at 50 mmHg at room temperature to give 4.2 g of >95% pure (^{19}F NMR analysis) product for a 50% yield. IR (gas cell, 5 mmHg): 1780 (m), 1720 (m), 1370 (s), 1345 (s), 1225 (s), 1185 (s), 1060 (s), 920 (m), 750 cm^{-1} (w). Mass spectrum: $C_5F_8^+$, 212, (11.0%); $C_2F_7^+$, 193, (12.1%); $C_4F_6^+$, 162, (18.5%); $C_4F_5^+$, 143, (79.6%); $C_4F_4^+$, 124, (18.9%); $C_3F_3^+$, 93, (100.0%); $C_3F_2^+$, 74, (18.0%); CF_3^+, 69, (28.2%). See Tables VIII–X for ^{19}F NMR data.

Thermal Isomerizations and Kinetics. General Procedure. All thermal isomerizations were carried out in highly conditioned, spherical, Pyrex vessels of 150–250-mL capacity. These vessels were submerged in a stirred, thermostated, molten salt bath (eutectic mixture, 50–50 by weight of $NaNO_2$ and KNO_3, mp ~150 °C). Temperature was measured via a Chromel–Alumel thermocouple in coordination with a Tinsley Type

Table XIII. Rate Data for the **6** ⇌ **9** Interconversion

temp, °C	10^7k_{obsd}	K^a	10^6k_{-EE}	$10^7k_{EE}{}^b$
272.5	45.4 ± 1.0	0.30	11.0 ± 0.3	59.2 ± 1.0
268.0	29.0 ± 0.8	0.29	7.38 ± 0.2	37.5 ± 0.8
263.0	19.8 ± 0.5	0.28	5.29 ± 0.16	25.3 ± 0.5
256.25	10.7 ± 0.1	0.26	3.06 ± 0.03	13.4 ± 0.1
247.25	5.18 ± 0.1	0.24	1.63 ± 0.03	6.41 ± 0.1
240.75	2.54 ± 0.07	0.22	0.86 ± 0.05	3.11 ± 0.1

[a] K = **10**/**6**. [b] $k_{EE} = k_{obsd}(1 + K)$.

Table XIV. Equilibrium Ratios for Perfluoro-2,4-hexadiene System

temp, °C	**6**	**10**	**17**	**11**	**9**
405.75	5.73	4.76	1	10.34	4.45
397.25	5.80	4.58	1	9.83	4.21
389.20	5.88	4.41	1	9.37	3.99
381.75	5.96	4.26	1	8.95	3.80
370.40	6.07	4.03	1	8.32	3.52
355.75	6.24	3.74	1	7.55	3.18
349.75	6.31	3.62	1	7.25	3.04
343.50	6.38	3.50	1	6.94	2.91
337.75	6.45	3.39	1	6.66	2.79
332.75	6.52	3.30	1	6.42	2.69

Table XV. Rate Data for **7** ⇌ **13** Interconversion

temp, °C	10^5k_{ZZ}	10^5k_{-ZZ}
69.6	0.53 ± 0.05	1.75 ± 0.05
79.0	1.27 ± 0.05	3.60 ± 0.05
88.5	3.08 ± 0.1	7.63 ± 0.10
97.5	9.12 ± 0.3	20.0 ± 0.3
101.5	13.9 ± 0.5	28.9 ± 0.5
107.25	27.4 ± 0.06	52.9 ± 0.6

Table XVI. Rate Data for **7** ⇌ **12** Interconversion

temp, °C	10^4k_{EE}, s^{-1}	10^4k_{obsd}, s^{-1}	K^a	10^4k_{EE},[b] s^{-1}
327.0	4.27 ± 0.02	4.78 ± 0.02	2.98	19.0 ± 0.1
319.75	3.28 ± 0.02	3.66 ± 0.02	2.87	14.18 ± 0.1
314.25	2.22 ± 0.02	2.48 ± 0.02	2.79	9.39 ± 0.1
302.6	0.99 ± 0.01	1.10 ± 0.01	2.62	3.98 ± 0.05
296.5	0.716 ± 0.005	0.79 ± 0.005	2.53	2.81 ± 0.02
292	0.515 ± 0.003	0.570 ± 0.003	2.47	1.98 ± 0.01

[a] K = **13**/**7**. [b] $k_{EE} = k_{obsd}(1 + K)$.

Table XVII. Equilibrium Ratios for the Perfluoro-3,5-octadiene System

temp, °C	**13**	**7**	**14**	**12**
327.0	2.98	1	7.77	4.45
319.75	2.87	1	7.50	4.33
314.25	2.79	1	7.30	4.23
302.6	2.62	1	6.87	4.03
296.5	2.53	1	6.66	3.92
292.0	2.47	1	6.50	3.84

Table XVIII. Rate Data for **8** ⇌ **15** Interconversion

temp, °C	10^7k_Z	10^4k_{-Z}
131.0	0.607 ± 0.003	0.559 ± 0.003
150.5	4.74 ± 0.02	2.79 ± 0.01
157.25	9.02 ± 0.05	4.55 ± 0.03
165.25	18.9 ± 0.1	8.02 ± 0.05
168.25	29.0 ± 0.2	11.55 ± 0.07
175.0	55.9 ± 0.3	19.4 ± 0.1

Table XIX. Rate Data for (**8** + **15**) $\rightleftharpoons$ **16** Interconversion

temp, °C	10^5k_{-E}	10^7k_{obsd}	K^a	$10^7k_E{}^b$
219.0	0.883 ± 0.007	0.462 ± 0.004	0.0065	0.0465 ± 0.004
257.25	14.9 ± 0.1	16.7 ± 0.1	0.0119	16.9 ± 0.1
269.0	35.9 ± 0.2	49.8 ± 0.3	0.0141	50.5 ± 0.3
283.75	91.5 ± 0.3	163.8 ± 0.5	0.0173	166.6 ± 0.5
288.25	124.3 ± 0.5	239.9 ± 0.9	0.0183	244.3 ± 0.9
293.25	164.7 ± 0.5	345.2 ± 1.0	0.0195	352. ± 1.0

[a] K = **15**/**8**. [b] $k_E = k_{\mathrm{obsd}}(1 + K)$.

Table XX. Equilibrium Ratios for the Perfluoro-1,3-pentadiene System

temp, °C	**8**	**15**	**16**
200.1	294.2	1.38	1
209.6	235.7	1.31	1
219.5	188.9	1.25	1
228.4	156.0	1.20	1
257.25	88.0	1.05	1
269.0	71.0	1.00	1
283.75	54.9	0.95	1
288.25	51.0	0.93	1
293.25	46.9	0.91	1

3387E potentiometer. The thermocouple was immersed in a well which was placed midway between the center of the two pyrolysis vessels. The temperature of the bath was controlled by using a Hallikainen (now Totco Instrument). Thermocontrol Proportional Controller with a platinum resistance probe. For low-temperature runs (below 160 °C), a similar apparatus was used: the pyrolysis vessels were immersed in silicon oil bath, with the Omega Proportioning Thermocontroller Model 49 with platinum resistance probe. The temperature was constant to 0.1 °C. Thermocouple-derived temperatures were calibrated with thermometers (Brooklyn Thermometer Co.). The thermocouple and thermometers temperatures were found to be close enough that any possible systematic error in the precision in reading of the temperature was found to contribute a smaller error than the standard deviation in the activation parameters.

The starting materials (perfluorodienes or/and perfluorocyclobutenes) were introduced into the pyrolysis vessels by expansion from the contiguous vacuum line. Initial pressure of kinetic runs varied between 4 and 12 mmHg of a starting material. The test runs at higher pressure of a starting material (25–30 mmHg) did not show any significant differences in obtained kinetic parameters.

Each kinetic pyrolysis run was sampled at least 6–8 times by removing a small fraction of the pyrolysis mixture by expansion into a small section of the vacuum line into a vessel, diluting with argon (total pressure ~400–500 mmHg), and removing to make multiple GLPC injections via a gas sampling valve. As indicated above, a Hewlett-Packard 5710A gas chromatograph in conjunction with a Hewlett-Packard 3380S integrator was used for all these analyses. Base-line resolution of peaks was observed under all GLPC quantitative studies. Each point in a rate constant is an average of at least three GLPC runs. Each rate constant plot contains at least six points, while all reported rate constants and activation parameters were derived by a linear least-square analysis of the experimental data, with each such analysis yielding a correlation coefficient of at least 0.999. Rate constants for the 2,4-hexadiene system are given in Tables XI–XIII, the 3,5-octadiene system in Tables XV and XVI, and the 1,3-pentadiene system in Tables XVIII and XIX. To determine the thermodynamic parameters, the thermal equilibria of investigated systems have been studied. The starting material was introduced to the reaction vessel and pyrolyzed for at least 10 half-lives, and then at least 3 independent samples of reaction mixture (within next 2 half-lives) were taken and analyzed. The equilibrium data were found to be identical despite the starting materials which have been used (perfluorodienes and appropriate perfluorocyclobutene). To determine the thermodynamic parameters for the above-described systems, the data at at least six different temperatures have been taken into consideration and derived by a linear least-squares analysis, yielding a correlation coefficient of at least 0.997. Equilibrium data for the three systems are provided in Tables XIV, XVII, and XX.

The gas sampling technique utilized in all of the above-described studies introduced multiple pressure variations per run. The fact that good unimolecular behavior was nevertheless always observed for over 5 half-lives indicates clearly the lack of significant surface effect problems. The kinetic apparatus as well as a technique utilized in determining rate constants is modeled after the apparatus and technique of Dr. H. M. Frey, University of Reading, England.

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Anti, Vicinal Hydrogen–Hydrogen Interactions. A Fundamental Shift Effect in ^{13}C NMR Spectroscopy

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Abstract: The spatial disposition of two vicinal hydrogens in an anti stereochemical relationship contributes to a downfield shift for each of the carbon atoms involved. Applications of this shift effect to both configurational and conformational stereochemical analyses are discussed.

The dependence of ^{13}C NMR spectral shifts on the spatial position of γ substituents (the γ effect) represents one of the most powerful features of carbon NMR spectroscopy. Following the lead of key researchers in this area,[1-3] we have recently correlated in a highly precise fashion stereochemical and conformational properties of molecules with ^{13}C spectral data.[4,5] These results

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