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THE THERMODYNAMIC EFFECT OF FLUORINE AS A SUBSTITUENT

VINYLIC CF_2 AND CFH AND ALLYLIC CF_2C

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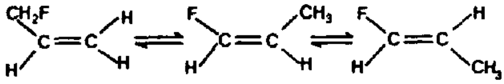
Abstract—I_2-catalyzed isomerizations of 3-fluoropropene and 3,3 - difluoropropene, and a Cope rearrangement of 1,1 - difluoro - 1,5 - hexadiene provide thermodynamic data which allow the determination of a number of important group values for contributions to ΔH_f° which when combined with those determined in the preceding paper allow the calculations of ΔH_f°'s of most simple F-substituted hydrocarbons: $[C_d\text{–}(F)(H)] = -38.4$, $[C_d\text{–}(F)_2] = -88.0$, $[C\text{–}(F)_2(C)(C_d)] = -103.9$, $[C\text{–}(F)_2(C)_2] = -104.9$ kcal/mole. A kinetic study of the conversion of 1,1 - difluoro- to 3,3 - difluoro - 1,5 - hexadiene provided activation parameters for the process: $\text{Log}\,A = 10.8$, $E_a = 33.0$ kcal/mole and $\Delta S^{\neq} = -12.2$ e.u. Incremental geminal stabilizations of F and other substituents are discussed and contrasted.

It is generally recognized that increased F-substitution on aliphatic carbon leads to increased *stabilization* of the molecule while a similar increase in F-substitution on olefinic carbon leads to *destabilization* of the molecule. While the former phenomenon is well substantiated from the available thermochemical data of fluorinated methanes and ethanes,[1] there is little thermochemical data upon which to base the latter conclusion. The assumption of destabilization by increased vinylic F-substitution derived from the fact that as one increases the degree of F-substitution on ethylene one observes an increase in reactivity (and exothermicity) for those reactions which lead to their saturation. Witness, for example, the increase in heats of hydrogenation compared to ethylene for 1,1 - difluoro-, 1,1,2 - trifluoro-, and tetrafluoroethylenes (4, 8 and 16 kcal/mole, respectively).[2]

From data such as the π-dissociation energy of tetrafluoroethylene,[3] it does appear that trifluoro and tetrafluoroethylene are indeed destabilized. However, the data is not so clear for vinylfluoride and vinylidene difluoride.[4] In this paper, thermodynamic data will be presented which we believe will demonstrate net *stabilization* of monofluoro and gem-difluoroethylenic systems. When combined with the data on allylic fluorine substitution presented in the preceding paper it is possible to come up with a set of values for group contributions to ΔH_f°'s which will allow reliable estimates to be made of heats of formation of relatively simple, partially fluorinated hydrocarbons.

Very little experimental data is available relating to the thermodynamic effect of a *single* vinyl F-substituent. Qualitative results in the fluorobullvalene system indicated a preference for nonvinylic F-substitution,[5] while a single quantitative study, that of Abell and Adolf on the HBr catalyzed equilibration of fluoropropenes, indicated that 1-fluoropropene (2 and 3) was thermodynamically *preferred* over 3-fluoropropene (1) by 4.15 kcal/mole.[6] While a theoretical study[7] qualitatively agrees with this result the quantitative reliability of the experimental data has been questioned.[8]

(1)



1 2 3

for 1→2, $\Delta H = -3.34$ kcal/mole, $\Delta S = -1.4$ e.u.
for 1→3, $\Delta H = -2.68$ kcal/mole, $\Delta S = -1.7$ e.u.
for 2→3, $\Delta H = +0.64$ kcal/mole, $\Delta S = -0.3$ e.u.

RESULTS

In our investigation we reexamined the fluoropropene equilibration (eqn 1) using an I_2 catalytic method which has been utilized effectively by Benson to examine the chloropropene system.[8] We also examined two equilibria designed to probe the effect of gem-difluorovinylic substituents, the equilibration of 1,1- and 3,3-difluoropropenes (eqn 2) and the Cope rearrangement interconversion of 1,1- and 3,3 - difluoro - 1,5 - hexadiene (eqn 3).

(2)

$$\underset{\mathbf{4}}{CH_2{=}CH\text{–}CHF_2} \overset{I_2}{\rightleftharpoons} \underset{\mathbf{5}}{CH_3\text{–}CH{=}CF_2}$$

for 4→5, $\Delta H = +2.5$ kcal/mole, $\Delta S = +0.4$ e.u.

The thermodynamic data for equilibria (1), and (2) and (3) are presented in Tables 2–4. Least squares analyses of the van't Hoff plots of the data in Tables 2 and 3 led to the thermodynamic data shown above for each reaction.

(3)

6 7

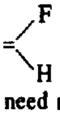
With so little 1,1 - difluoro - 1,5 - hexadiene present at equilibrium and with little temp dependence on K, a van't Hoff plot led to an unreliable fit of the data. Thus the ΔG's for the equilibrium data in Table 4 were calculated at each T and averaged to give $\Delta G = -5.1 \pm 0.3$ kcal/mole. With the reasonable assumption that $\Delta S \simeq 0 \pm 0.3$, one can estimate the ΔH for this equilibrium to be $\Delta H \simeq -5.1$ kcal/mole with a reliability probably no less than ± 0.6 kcal/mole.

The kinetic data was better, with the rates being given in Table 4. A least squares analysis of the rate data led to the following Arrhenius parameters: $\text{Log}\,A = 10.8 \pm 0.3$ kcal/mole, $E_a = 33.0 \pm 0.7$ kcal/mole with $\Delta S^{\neq} = -12.2$ e.u.

As discussed by Benson,[8] a slow build up of defluorinated species occurs in the I_2 catalyzed equilibrations. For example in the equilibration of 1, propene is seen as a product. At low temperatures the formation of propene gives rise to unreliable equilibrium data, but at the temperatures reported in Tables 2 and 3, such product formation was *not* kinetically significant. This was indicated by the *consistency* of the equilibrium data over large I_2 pressure changes and substrate pressure changes, with the resultant variation in propene buildup.

DISCUSSION

It can be seen that we obtain qualitative agreement with Abell and Adolf, results which indeed indicate that vinylic F-substitution is thermodynamically favored over allylic F-substitution. If one utilizes the group value for the allylic CH_2F group (i.e. $[C-(F)(H)_2(C_d)]$) which was estimated in the previous paper to be -52.5 kcal/mole, one can derive from this data the group value for the


$=C\begin{smallmatrix}F\\H\end{smallmatrix}$

group (i.e. $[C_d-(F)(H)]$). With $\Delta H_{1\rightarrow3} = -2.68$, one need make no further assumptions to arrive at the value of -38.4 kcal/mole for $[C_d-(F)(H)]$. From the data for the equilibrium between *cis* and *trans* 1-fluoropropene, 2 and 3, one can see that the *cis*-isomer is *more stable* by 0.64 kcal/mole. Therefore the *cis-correction* for F-alkyl interactions can be assigned the value of -0.64 kcal/mole.

Using the data for the equilibration of 3,3- and 1,1-

Table 1. Values of Incremental Geminal Stabilization (IGSTAB)[a]

	IGSTAB's						
X	CH_2X_2	CHX_3	CX_4	CH_3CHX_2	CH_3CX_3	$CH_3CX_2CH_3$	$CH_2{=}CX_2$
F	-6.15	-10.7	-12.4	-6.55	-9.8	-5.1[b]	-2.5[b]
Cl	-0.75	- 0.95	- 0.1	+1.55	+1.9	+1.5	-2.4
CH_3	-1.3	- 2.5	- 3.3	-1.15	-1.8	-0.3	-0.6
OCH_3	-6.55	-11.3	-13.4	-4.9	-8.5	-3.3	—
OCH_2CH_3				-4.1		—	—
$N(CH_3)_2$	-5.35	—	—	—	—	—	—

[a] Based upon data contained in reference 1 or as cited in this paper.

[b] Based upon estimated heats of formation.

Table 2. Equilibrium constants for I_2-catalyzed equilibration of 3-fluoropropene, 1 and *cis*- and *trans* - 1 -fluoropropene, 2 and 3

Temp.	343.9[a,b]	343.9[a,c]	356.0[a]	380.5[a]	398.0[a]	415.0[a]	430.3[a]	430.3[d]
$K_{2/3}$	1.95	.1.94	1.96	1.90	1.90	1.85	1.84	1.83
$K_{2/1}$	7.43	7.56	7.21	6.51	6.10	5.66	5.44	5.45
$K_{3/1}$	3.82	3.89	3.68	3.43	3.21	3.07	2.98	2.96

[a] Starting material 1.
[b] 90 mm of 3.
[c] 130 mm of 3.
[d] Starting material 2 + 3.

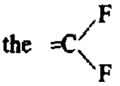
Table 3. Equilibrium constants for I_2-catalyzed equilibration of 3,3-difluoropropene, **4**, and 1,1-difluoropropene, **5**.

Temp.	378.3[a]	384.8[a]	391.5[a]	399.0[a]	405.5[a]	412.5[b]	412.8[a,c]	412.8[a,d]
$K_{4/5}$	5.96	5.79	5.68	5.60	5.48	5.34	5.42	5.35

[a] Starting material is **4**.
[b] Starting material is **5**.
[c] 60 mm **4**.
[d] 40 mm **4**.

Table 4. Rate constants and equilibrium constants for the thermal rearrangement of 1,1 - difluoro - 1,5 - hexadiene to 3,3 - difluoro - 1,5 - hexadiene.

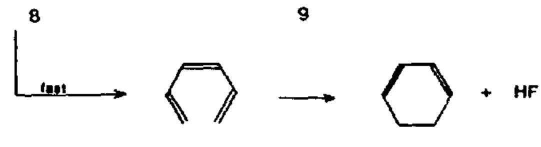
Temp.	194.3°	198.4°	202.4°	206.8°	210.7°	214.6°
k(x10^5)	2.27	3.26	4.43	5.81	7.75	10.15
K	132.5	230.4	166.9	174.8	206.2	243.9

difluoro-propene, **4** and **5**, and including one such *cis*-correction for **5**, one can similarly estimate the group value for the  $=\mathrm{C}{<}^{\mathrm{F}}_{\mathrm{F}}$ group (i.e. $[C_d\text{–}(F)_2]$) to be −88.0 kcal/mole.

In analyzing the difluorohexa - 1,5 - diene system we have the opportunity to estimate the difference between the group values $C\text{–}(F)_2(H)(C_d)$ and $C\text{–}(F)_2(C)(C_d)$. In order to do this one must estimate the F-alkyl gauche effect in **7**. Since we've already seen that a fluorine-alkyl *cis*-interaction is *stabilizing* relative to *trans*, it follows that a fluorine-alkyl gauche interaction ought to be stabilizing also. Since 3 - methyl - 1,5 - hexadiene has a gauche interaction worth +0.33 kcal/mole and the *cis*-effect of F-methyl (0.64) is a factor of −1.25 that of the *cis* - methyl - alkyl interaction (0.51, from the equilibrium of *cis* and *trans* - 1,5 - heptadiene),[9] one can approximate the probable effect of a F-substituent gauche to an alkyl group to be −0.41 kcal/mole. This estimate is supported by Hirota's microwave data for 1-fluoropropane, where it was found that the gauche conformer was *ca.* 0.5 kcal/mole more stable than the anti.[9] Since the most stable conformation of **7** should have *two* such gauche interactions, one estimates the gauche correction for **7** to be −0.82 kcal/mole.

The equilibria for **6**→**7** give an approximate $\Delta H° \simeq -5.1$ kcal/mole. Coupling that with the just-determined group value of −88.1 for $[C_d\text{–}(F)_2]$ the *cis*-F, alkyl correction for **6** of −0.64 and the estimate of the gauche interactions in **7** of −0.82, one comes up with a value of −103.9 kcal/mole for the $[C\text{–}(F)_2(C)(C_d)]$ group.

An attempt to obtain the comparable monofluoro group value, [C–(F)(H)(C)(Cd)] failed when the attempted Cope rearrangement, **8**→**9** did not compete effectively with the HF elimination process.



What this means then is that all other things being equal a molecule with a $C\text{–}CF_2\text{–}C$ linkage is *more stable* than one with a $C\text{–}CF_2H$ linkage. For example, estimation of the ΔH_f°'s for the isomers **10** and **11**, using the newly ascertained group values, leads to **10** being more stable by 1.9 kcal/mole.

$$\underset{\mathbf{10}}{CH_3CH{=}CHCF_2CH_3} \rightleftharpoons \underset{\mathbf{11}}{CHF_2CH{=}CHCH_2CH_3}$$

$$\Delta H = +1.9\ \text{kcal/mole}$$

It should be mentioned that the kinetic data for **6**→**7** is consistent with the thermodynamic results. That is, the exothermic conversion of **6**→**7** proceeded with a Log A (10.8) very similar to that of the hydrocarbon (11.1) but with a lowering of the activation energy (33.0) of 2.5 kcal/mole relative to that of the hydrocarbon system (35.5).[10]

One last reasonable manipulation will provide us with a final useful group value, that of $C\text{–}(F)_2(C)_2$. If one makes the reasonable assumption that there will be the same difference between $C\text{–}(F)_2(C)_2$ and $C\text{–}(F)_2(H)(C)$ as there is between $C\text{–}(F)_2(C)(C_d)$ and $C\text{–}(F)_2(H)(C_d)$ then one can designate the value for $C\text{–}(F)_2(C)_2$ to be −104.9 kcal/mole.

Thus in conclusion, the following group values for carbon groups containing one, two or three F-substituents should when combined with Benson's group values for the non-F-containing groups, provide *good* estimates of ΔH_f°'s for molecules which have no neighboring F group interactions:

$C\text{–}(F)_3(C) = -167.8$
$C\text{–}(F)_2(H)(C) = -108.6$
$C\text{–}(F)_2(C)_2 = -104.9$
$C\text{–}(F)(H)_2(C) = -52.7$
$C\text{–}(F)_3(C) = -166.0$

$C\text{–}(F)_2(H)(Cd) = -107.6$
$C\text{–}(F)_2(C)(Cd) = -103.9$
$C\text{–}(F)(H)_2(Cd) = -52.2$
$C_d\text{–}(F)(H) = -38.4$
$C_d\text{–}(F)_2 = -88.0$

There are *very few* heats of formation available with which one can test the reliability of these group values. Indeed, many of these published ΔH_f°'s must be considered of dubious reliability. For example, *all* of our values for difluoromethyl-type groups are dependent upon the reliability of the ΔH_f° of CH_3CHF_2 which has a published unreliability of ±2 kcal/mole.

Estimating the ΔH_f°'s for $CH_2{=}CHF$ and $CH_2{=}CF_2$ to be −32.1 and −81.7 kcal/mole, we see reasonable agreement with the experimentally determined values, −33.2 ± 0.4 and −80.1 ± 1 kcal/mole. Likewise, as mentioned before, the calculated value for $CH_3CH_2CH_2F$ (−68.2) is very close to the experimental value (−68.3). However estimation of ΔH_f° for $CF_3CH{=}CH_2$ (−151.1) is significantly at variance with the experimental value (−146.8 ± 1.6). Because one would not anticipate any marked "special" effects in any of the systems involved in determining the CF_3 group values, one must conclude it likely that either the CF_3CH_3 or the $CF_3CH{=}CH_2$ *experimental* values are unreliable, most probably the latter.

Again, it should be emphasized that these group values should only be considered valid in molecules where there are *no* other neighboring F-substituents. Attempting to estimate the ΔH_f° of $CHF{=}CF_2$, for example, (−127.5 estimated, −117.3 experimental) clearly shows a *marked destabilization interaction* by the third, vicinal F-substituent.

It may be that, as more thermodynamic data becomes available, the absolute magnitudes of the group values presented here may change. We have for example ignored any difference in the group values $[C_d\text{–}(F)(H)]$ in the molecules $CH_2{=}CHF$ and *trans* $CH_3CH{=}CHF$, making only a *cis*-correction for *cis*-$CH_3CH{=}CHF$. There may indeed be some *trans* vicinal CH_3-F interaction (likely slightly destabilizing) which we have ignored, and when appropriate data becomes available, such correction values will need to be incorporated within the scheme.

The problem has been however, the *lack* of reliable data, and we believe that the values presented in this work should allow reliable estimation of ΔH_f°'s. Certainly one should *very* reliably be able to estimate equilibria involving compounds containing the F-substituted groups described here.

Out of this work have come some very interesting correlative insights. First examining the saturated systems, we can see from the isodesmic equations below that increased geminal substitution by F gives rise to a marked and increasing incremental geminal stabilization (IGSTAB) of the system.[11] (Since IGSTAB's are most certainly model-dependent, we will define IGSTAB for our purposes

$$2CH_3CH_2F \xrightarrow[\text{IGSTAB}=-6.6]{\Delta H=-13.1\text{ kcal/mole}} CH_3CHF_2 + CH_3CH_3$$

2(−62.9)[12]   (−118.8)   (−20.1)

$$3CH_3CH_2F \xrightarrow[\text{IGSTAB}=-9.8]{\Delta H=-29.5} CH_3CF_3 + 2CH_3CH_3$$

3(−62.9)[12]   (−178.0)   2(−20.1)

as the increase in thermodynamic stabilization of a geminal-substituted system, per substituent, relative to the respective monosubstituted system, using isodesmic equations such as those above.)

Similarly one can examine allylic and vinylic systems:

$$2CH_2{=}CHCH_2F \xrightarrow[\text{IGSTAB}=-6.6]{\Delta H=-13.25} CH_2{=}CHCHF_2 + CH_2{=}CH\text{–}CH_3$$

2(−37.35)   (−92.75)   (+4.8)

$$3CH_2{=}CH\text{–}CH_2F \xrightarrow[\text{IGSTAB}=-9.8]{\Delta H=-29.45} CH_2{=}CHCF_3 + 2CH_2{=}CHCH_3$$

3(−37.35)[13]   (−151.1)[13]   2(+4.8)

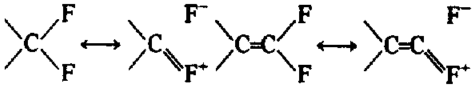
$$2CH_2{=}CHF \xrightarrow[\text{IGSTAB}=-2.5]{\Delta H=-5.0} CH_2{=}CF_2 + CH_2{=}CH_2$$

2(−32.1)[13]   (−81.7)[13]   (+12.5)

Since the incremental 0.5 kcal/mole destabilization of allylic F-substituents cancels in each of the allylic systems, the IGSTAB's for allylic and alkylic geminal F-substitution are virtually identical. On the other hand, it can be seen that the IGSTAB for vinylic F (−2.5 kcal/mole) while significant, is considerably smaller. The difference between alkylic and vinylic IGSTAB's for F provides a reasonable explanation for the observed strong driving force for vinylic CF_2 to become converted to alkylic CF_2. This thermodynamic driving force derives not from a destabilization of the vinylic CF_2 system, but merely from the *much greater* stabilization of the saturated system.

Using a 4-31G basis set[14] and calculating the total energies for the appropriate molecules, one can calculate the IGSTAB's for CH_2F_2[15] and $CH_2{=}CF_2$[16] to be −5.8 and −3.15 kcal/mol respectively, numbers not inconsistent with our values of −6.5 and −2.5 kcal/mol.

These differences in vinylic and alkylic geminal stabilization by F-substituents can be rationalized well by the "double-bond, no-bond resonance" model.[18] That is to say, a resonance contributor such as **12b**, which has no counterpart in the monofluorosystem, should afford more stabilization to **12** than **13b** should to the vinylic system **13**, since **13b** should reflect the instability of a vinyl cation.



12a **12b** **13a** **13b**

Values of IGSTAB for various substituents are listed in Table 1. A similar table has been published in a calculational study.[19] It should be noted that the IGSTAB's of ether and amino substituents are similar in magnitude of those F. However unlike the F effects, the IGSTAB's of alkoxy and dimethylamino are seen to diminish significantly as the degree of branching on the substituted carbon increases. For example, the IGSTAB's for OMe are −6.55, −4.9 and −3.3 kcal/mol for the Me, Et and 2-pr systems, respectively. Likewise the IGSTAB for Cl, which was very small, (−0.75) for the Me system actually becomes destabilizing for the Et (+1.55) and 2-Pr (+1.5) systems. These diminishments for alkoxy- and Cl-substituents likely derive from destabilizing, *steric* interactions, while F IGSTAB's seem relatively free of such variation.

EXPERIMENTAL

^{19}F NMR spectra were determined on a XL-100 instrument at 94.1 MHz. Chemical shifts are reported as ϕ in ppm from internal $CFCl_3$ with $CDCl_3$ as the solvent. All ^1H NMR spectra were determined at 60 MHz. Chemical shifts are reported as δ in ppm downfield from internal TMS with $CDCl_3$ as the solvent. IR spectra were determined on a Perkin–Elmer 283B spectrophotometer. The spectra were determined from the neat liquid between KCl plates, unless otherwise stated. Mass spectra and exact masses were determined on an AEI-MS spectrometer at

70 eV. Preparative glpc separations were accomplished on a Varian Aerograph 90-P using helium as the carrier gas and fitted with either column 1 (10′ × $\frac{1}{4}$″ 10% ODPN on Chromosorb P 60/80) or column 2 (10′ × $\frac{1}{4}$″ 10% DNP on Chromosorb P 60/80). Product ratios and kinetic data were determined on a Hewlett–Packard 5710A fitted with a flame ionization detector, gas injection system and a Hewlett–Packard 3380s integrator. Either column 3 (7′ × $\frac{1}{8}$″ 10% ODPN on Chromosorb P 60/80) or column 4 (19′ × $\frac{1}{8}$″ 19% DNP on Chromosorb P 60/80) was used.

Thermolyses were carried out in a well conditioned 100 ml pyrex vessel suspended in a thermostated molten salt bath, a system which has been described elsewhere.[20]

3-*Fluoropropene*, 1. The procedure outlined by Hoffman[21] was used to synthesize 1. A 3-necked 500 ml flask was equipped with an overhead stirrer, pressure equalized addition funnel, and distillation take-off leading to a dry ice cooled trap. 66 g KF in 200 ml dry ethylene glycol was heated to 130–150°. 70 g 3-bromopropene was added and 16.5 g of 1 was isolated, 47.5% yield, 99.9% glpc pure on column 2. The ^{19}F NMR, ^{1}H NMR and IR spectra were identical to those reported in the lit.[22]

Mass spectrum gave M$^+$ 60.0390 ± 0.0025 (41 ppm), calculated for C_3H_5F: 60.0375, deviation = 0.0015 (25 ppm); *m/e* (relative intensity): 60 (56), 59 (100), 58 (3), 57 (12), 41 (10).

1-*Fluoropropene*, 2 *and* 3. 1 was equilibrated with a catalytic amount of I_2 (see below). The equilibrium mixture of 1, 2 and 3 was transferred through a 2″ column containing 5% tetraethanepentamine on Chromosorb 60/80 and condensed into a storage vessel. Several runs were combined and 2 and 3 were isolated together by preparative glpc on column 1 at −20°. The ^{1}H NMR and ^{19}F NMR spectra were identical to those reported in the lit.[23] IR (gas), 3100, 2970, 1700 (s), 1680 (s), 1250, 1150 (s), 1130 (s), 1110, 1010 (s), 910, 745 (s) cm^{-1}; Mass spectrum gave M$^+$ 60.0383 ± 0.00097 (16 ppm), calculated for C_3H_5F 60.0375, deviation = 0.00079 (13 ppm); *m/e* (relative intensity): 60 (61), 59 (100), 58 (5), 57 (17), 39 (17).

Thermolyses of 1, 2 *and* 3. A glass storage bulb containing a few crystals of I_2 (Mallinckrodt) was connected to the vacuum line (maintained at 110°) which was attached to the pyrolysis vessel. After degassing the I_2, the storage vessel was heated and some I_2 was expanded into the pyrolysis vessel, which was then closed off from the vacuum line. The I_2 remaining in the vacuum line was recondensed into the storage bulb. The appropriate amount of 1 or the mixture of 2 and 3 was then expanded into the pyrolysis vessel. Since the vacuum line contained two well-conditioned pyrolysis vessels, two runs could be run simultaneously. It was found that the rate of propene formation varied from run to run. Equilibrium mixtures were evaluated on column 3 and the resulting data is listed in Table 2. The correlation coefficient for the van't Hoff plots were 0.963, 0.9991 and 0.9988 for 2 → 3, 1 → 2 and 1 → 3 respectively.

3,3-*Difluoropropene*, 4. A 3-necked 50 ml flask was equipped with a magnetic stirrer, rubber septum, thermometer and outlet pipe connected to a dry-ice-cooled trap. 4.2 g DAST was added to the flask and cooled to 0°. 1.5 g propenal was slowly added and stirred for 3 hr. 0.7 g 4 was collected, 98.8% glpc pure by column 3, 34% yield. The ^{1}H and ^{19}F NMR matched data published in the lit:[22a] IR (gas), 3110, 2975, 1900, 1680, 1450, 1350, 1155, 1050–1130 (s), 950, 740 cm^{-1}; Mass spectrum gave M$^+$ 78.0269 ± 0.0018 (23 ppm), calculated for $C_3H_4F_2$: 78.0281, deviation = 0.0012 (15 ppm); *m/e* (relative intensity): 78 (51), 77 (100), 76 (2), 75 (5), 64 (12), 59 (14), 57 (6), 51 (14).

1,1 *Difluoropropene*, 5. 5 was made by the method of Moss and Jennings.[24] A trap containing 0.84 g of trifluoropropane was connected to a stainless steel tube containing silica chips and heated to 700°. The other end of the tube was connected to a KOH trap, liquid N_2 cooled trap, and a vacuum source. The gas collected in the trap was separated by preparative glpc on column 1. 0.05 g 5 was collected, 7.5% yield, and 99.5% glpc pure on column 3. The ^{1}H and ^{19}F NMR and IR spectra matched those published in the lit;[25] Mass spectrum gave M$^+$ 78.02969 ± 0.00217 (28 ppm); calculated for $C_3H_4F_2$: 78.0281, deviation = 0.00058 (7 ppm); *m/e* (relative intensity); 79 (67), 78 (100), 77 (12), 76 (17), 59 (27), 58 (4), 52 (52).

Thermolysis of 4 *and* 5. 4 and 5 were pyrolyzed with a catalytic amount of I_2 between 378.3° and 412.8°. The equilibria were analysed on column 3 and the results are listed in Table 3. The mass balance was 97%, measured by pressure. The correlation coefficient for the van't Hoff plot of the data was 0.9948.

1,1-*Difluoro*-1,5-*hexadiene*, 6. 6 was prepared by the method of Burton and Naae.[26] A 100 ml 3-necked flask was equipped with a distillation take-off, constant pressure addition funnel, and a thermometer. Previously, the reagents and apparatus were dried. 4.2 g of pentenal 10.5 g dibromodifluoromethane (PCR), and 30 ml triglyme were placed in the flask. 16.3 g HMPT (Aldrich) in 20 ml triglyme was placed in the addition funnel. The reaction was cooled with ice and the HMPT was added, keeping the temp below 15°. After addition was complete, the reaction was allowed to warm to room temp and stirred for 4 hr. The product was removed by flash vacuum distillation and purified by preparative glpc on column 1. 0.56 g 6 was collected for a 9.5% yield: NMR, ϕ82.8 (1F, d $J_{F(t)F(c)} = 40$ Hz), 86.2 (1F, dd, $J_{F(c)F(t)} = 40$ Hz, $J_{F(c)H(2)} = 21$ Hz; δ 5.3–6.2 (1H, m), 4.8–5.3 (2H, m), 4.1 (1H, dtd, $J_{H(2)F(c)} = 21$ Hz, $J_{H(2)H(3)} = 8$ Hz, $J_{H(2)F(t)} = 4$ Hz), 2.15 (4H, broad s); IR (gas), 3000, 2940, 2870, 1750 (s), 1645, 1450, 1350 (s), 1240 (s), 1190 (s), 920 (s), 800 cm^{-1}; Mass spectrum gave M$^+$ 118.0593 ± 0.00057 (4.8 ppm), calculated for $C_6H_8F_2$: 118.0594, deviation = 0.000077 (0.65 ppm); *m/e* (relative intensity): 118 (1.3), 103 (3), 98 (5), 77 (100), 67 (5), 54 (16), 51 (20), 41 (24), 39 (21).

3,3 - *Difluoro* - 1,5 - *hexadiene*, 7. 20 mm of 6 was expanded into a well-conditioned pyrolysis bulb at 245°. After 30 min the products were condensed into a storage bulb. Several runs were combined and separated by preparative glpc on column 1: NMR, 97.9 (td, $J_{FH(4)} = 16.2$ Hz, $J_{FH(2)} = 9.4$ Hz; δ 5.0–6.5 (6H, m), 2.7 (2H, td, $J_{H(4)F} = 16.2$ Hz, $J_{H(4)H(5)} = 6$ Hz); IR (gas), 3100 3000, 2940, 1650, 1425 (s), 1300, 1160 (s), 1100 (s), 1040, 990 (s), 950, 925, 890 cm^{-1}; Mass spectrum gave M$^+$ 118.0577 ± 0.001 (8.7 ppm), calculated for $C_6H_8F_2$: 118.0594, deviation = 0.0017 (14.6 ppm); *m/e* (relative intensity): 118 (1.5), 103 (3), 98 (8), 90 (4), 77 (100), 67 (3), 54 (16), 51 (17), 41 (22), 39 (15).

Thermal rearrangement of 1,1 - *difluoro* - 1,5 - *hexadiene*, 6, *to* 3,3 - *difluoro* - 1,5 - *hexadiene*, 7. 5 mm of 6 was pyrolyzed at six temps between 194.3° and 214.6°. The reaction was followed by glpc using column 3. The rate constants and equilibrium constants are listed in Table 4. The $\Delta G°$ value obtained from the equilibrium constant at 194.3° was omitted and the remaining five ΔG's were averaged to yield a $\Delta G°_{avg}$ of 5.1 ± 0.3 kcal/mole at an average temp of 206.6°. The mass balance for the reaction was 99.7%, using pentane as an internal standard. The same equilibrium constant, within experimental error, was obtained starting from either 6 or 7

3 - *Fluoro* - 1,5 - *hexadiene*, 8. A 3-necked flask was equipped with a rubber septum, drying tube, alcohol thermometer, and 2 g DAST in 5 ml dry CH_2Cl_2. The soln was cooled to −78°, then 1.2 g of 1,5 - hexadien - 3 - ol(Aldrich) was slowly added. After the addition was complete, the reaction was allowed to warm to room temp. It was washed with Na_2CO_3/H_2O and dried with $MgSO_4$. 8 was isolated by preparative glpc on column 1. 0.32 g of 8, 96% glpc pure, was collected for a 25% yield: NMR, ϕ177.6 (dtd, $J_{FH(3)} = 48$ Hz, $J_{FH(4)} = 21$ Hz, $J_{FH(2)} = 14.5$ Hz); δ 4.9–6.4 (6H, m), 4.95 (1H, dq, $J_{H(3)F} = 48$ Hz, $J_{H(3)H(4)} = 6$ Hz, $J_{H(3)H(2)} = 6$ Hz), 2.45 (2H, dt, $J_{H(4)F} = 21$ Hz, $J_{H(4)H(3)} = 6$ Hz, $J_{H(4)H(5)} = 6$ Hz); IR (gas), 3100, 3005, 2940, 1650, 1430, 1340, 995 (s), 930 (s), 735 cm^{-1}. Mass spectrum gave M$^+$ 100.0688 ± 0.00094 (9.4 ppm), calculated for C_6H_9F: 100.0688, deviation = 0.00089 (8.9 ppm); *m/e* (relative intensity): 100 (1.0), 99 (2), 85 (22), 80 (21), 79 (32), 77 (14), 72 (20), 67 (13), 59 (100), 41 (44).

Attempted thermal isomerization of 3 - *fluoro* - 1,5 - *hexadiene*. 5 mm of 8 was expanded into the thermolysis bulb which was maintained at 160°. The progress of the reaction was followed by glpc on column 3. All of 8 was consumed and two major products were produced, along with many minor products. The two major products were isolated and identified by their ^{1}H NMR as 1,3,5-hexatriene and 1,3-cyclohexadiene.

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