Tetrahedron Vol. 38, No. 15, pp. 2411 to 2413, 1982
Printed in Great Britain.

0040-4020/82/152411-03$03.00/0
Pergamon Press Ltd.

THE THERMODYNAMIC EFFECT OF FLUORINE AS A SUBSTITUENT

ALLYLIC CF_3 AND CF_2H

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(*Received in USA* 20 *October* 1981)

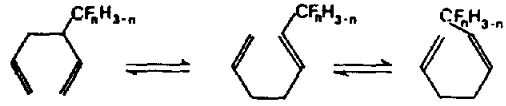
Abstract—Cope rearrangements of 7,7,7-trifluoro-1,5-heptadiene and 7,7-difluoro-1,5-heptadiene were examined to gain quantitative understanding of the thermodynamic effect of allylic fluorine substitution. Group value contributions to ΔH_f's were thus able to be determined for allylic fluorine-substituted carbon groups: $C\text{-}(F)_3(C_d) = -166.0$, $C\text{-}(F)_2(H)(C_d) = -107.6$ and $C\text{-}(F)(H)_2(C_d) = -52.2$ kcal/mole.

There are only limited published thermochemical data on fluorinated hydrocarbons and many of these have a high level of uncertainty.[1] It is therefore difficult to make reasonable estimates of the heats of formation of even relatively simple fluorinated hydrocarbons. This is in distinct contrast to one's ability to estimate very accurately heats of formation for a multitude of hydrocarbon species.[2]

Perhaps the most commonly utilized empirical method for estimating ΔH_f°'s is that of Benson wherein a molecule's ΔH_f° is assumed to be the sum of the contributions of each of its composite groups, plus any corrections for ring strain, *cis*-effects, gauche effects, etc.[2] Because of the paucity of data available, the use of Benson's published fluorine-containing group values to estimate heats of formation for any but the simplest of molecules fails miserably. Because of our interest in the kinetic and thermodynamic behavior of partially fluorinated cyclic and unsaturated hydrocarbons, we sought to obtain data which might fill some of the gaps in this area and thus allow better empirical estimates of heats of formation for molecules in which we were interested.

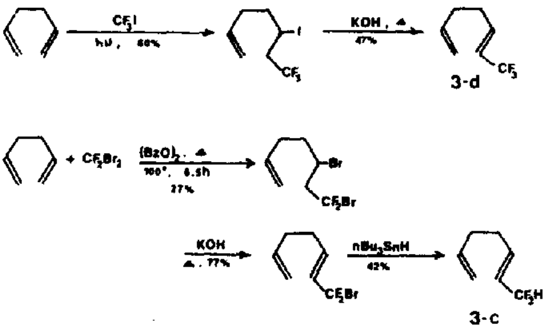
Our approach was to obtain *relative* thermodynamic data from appropriate equilibria which were chosen for their ability to provide insight into specific effects which are inestimable using currently available data.

Our initial efforts were designed to probe the thermodynamic differences between CF_3, CF_2H and CFH_2 in the allylic vs the alkylic situation. It was proposed to examine these differences *via* the Cope rearrangements represented below.



For a-d, n = 0, 1, 2 & 3

The 3-methyl-1,5-hexadiene system ($1a \rightleftharpoons 2a \rightleftharpoons 3a$) has been examined thoroughly by Solly and Frey[3] with the results that for process $1a \rightarrow 2a$, $\Delta H = -0.76$ kcal/mole, for process $1a \rightarrow 3a$, $\Delta H = -1.28$ kcal/mole, and for process $2a \rightarrow 3a$, $\Delta H = -0.51$ kcal/mole. This report will deal with the 3-(trifluoromethyl)-1,5-hexadiene system, ($1d \rightleftharpoons 2d \rightleftharpoons 3d$), and the 3-(difluoromethyl)-1,5-hexadiene system, ($1c \rightleftharpoons 2c \rightleftharpoons 3c$). Entry into these systems was gained through the syntheses of 3c and 3d by the procedures shown below.



The equilibria for each system were examined in the gas phase at eight temperatures, starting from either 1 or 3 and with high mass balance (> 95%) being observed at equilibrium in each case. The data are presented in Tables 1 and 2.

The van't Hoff plots of the equilibrium data were treated by the method of least squares to give the thermodynamic data below.

For the CF_3-system

$\Delta H^\circ_{1\rightarrow 2} = +1.47$ kcal/mole $\qquad \Delta S_{1\rightarrow 2} = +0.51$ e.u.
$\Delta H^\circ_{1\rightarrow 3} = -0.23$ $\qquad \Delta S_{1\rightarrow 3} = +1.52$
$\Delta H^\circ_{2\rightarrow 3} = -1.63$ $\qquad \Delta S_{2\rightarrow 3} = +1.12.$

For the CF_2H-system

$\Delta H^\circ_{1\rightarrow 2} = +0.56$ kcal/mole $\qquad \Delta S_{1\rightarrow 2} = -0.73$ e.u.
$\Delta H^\circ_{1\rightarrow 3} = -0.80$ $\qquad \Delta S_{1\rightarrow 3} = +0.36$
$\Delta H^\circ_{2\rightarrow 3} = -1.37$ $\qquad \Delta S_{2\rightarrow 3} = +1.1.$

Assuming that the experimentally determined values for the heats of formation of CF_3CH_3 (-178.0)[1], CF_2HCH_3 (-118.8)[1] and CFH_2CH_3 (-62.9 kcal/mole)[4] are correct as described, and *assuming* that all non-fluorine-containing groups have the values ascribed to them by Benson, one can calculate the group values for $[C\text{-}(F)_3(C)]$, $[C\text{-}(F)_2(H)(C)]$ and $[C\text{-}(F)(H)_2(C)]$ to be -167.8, -108.6 and -52.7 kcal/mole, respectively.

Table 1. Equilibrium data for 3-(trifluoromethyl)-1,5-hexadiene system

Temp	408.0°	394.4°	380.9°	368.7°	356.3°	344.6°	322.5°	321.3°
$K_{2/1}$	0.439	0.427	0.413	0.405	0.402	0.392	0.383	0.370
$K_{3/1}$	2.55	2.54	2.57	2.58	2.61	2.58	2.60	2.60
$K_{3/2}$	5.81	5.95	6.21	6.37	6.49	6.58	6.80	6.94

Table 2. Equilibrium data for 3-(difluoromethyl)-1,5-hexadiene system

Temp	409°	394.8°	381.5°	370.0°	356.4°	345.0°	332.2°	321.2°	309.9°
$K_{2/1}$	0.457	0.452	0.448	0.444	0.441	0.437	0.433	0.429	0.426
$K_{3/1}$	2.16	2.20	2.32	2.24	2.29	2.31	2.34	2.36	2.39
$K_{3/2}$	4.74	4.85	4.98	5.05	5.21	5.29	5.41	5.49	5.62

Secondly, one defines the gauche interaction of the Me group in **1a** to be +0.33 (that value required to correlate the calculated ΔH_f°'s for **1a** and **3a** with the experimental enthalpy for their equilibrium[3]). Thirdly, one defines the *cis* methyl correction for **2a** to be +0.51 kcal/mole (the experimental value for the difference in their enthalpies as ascertained from Frey's equilibration study).

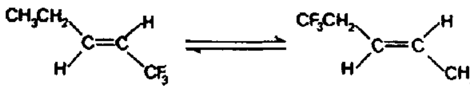
The *cis*-correction for CF_3-alkyl is equal to $\Delta H^\circ_{3d\rightarrow 2d}$ and is +1.63 kcal/mole, while that for CF_2H- alkyl is equal to its respective $\Delta H^\circ_{3c\rightarrow 2c}$ and is 1.37 kcal/mole. Obviously, the CF_3 and CF_2H groups give rise to substantially greater steric repulsions than Me.

Assuming that the magnitude of the *cis*-corrections are correlatable with the magnitudes of the respective gauche corrections found in **1** and since the CF_3 and CF_2H group *cis* corrections were 3.20 and 2.69 times greater than that of Me, the gauche corrections for CF_3 and CF_2H were designated to be 1.06 (3.2 × 0.33) and 0.89 (2.69 × 0.33) kcal/mole respectively.

Using then Benson's group values[2] for all non-F-containing groups and $\Delta H^\circ_{1\rightarrow 3}$ data above, one can calculate the group value for allylic CF_3 to be: $[C\text{–}(F)_3(Cd)] = -166.0$ kcal/mole and that for allylic CF_2H to be: $[C\text{–}(F)_2(H)(Cd) = -107.6$ kcal/mole.

When compared to the group values for the *alkylic* CF_3 and CF_2H, one finds the allylic groups to be incrementally ***more positive*** by 1.8 and 1.0 kcal/mole, respectively. The consistency of the incremental change for allylic CF_3 (0.6 per F) and CF_2H (0.5 per F) allows one to predict that the $[C\text{–}(F)(H)_2(Cd)]$ group value should be more positive than the alkylic value by 0.5 kcal/mole, and that its value should thus be −52.2 kcal/mole.

What these values indicate in a practical sense is that alkylic CF_3, CF_2H and CFH_2 groups are more stable (i.e. make a greater negative contribution to the heat of formation) than the analogous allylic groups. This is reflected by the hypothetical equilibrium below.



$\Delta H = -1.8$ kcal/mole

The values thus obtained begin to fill the gaps in the group values which are required to make accurate routine calculations of heats of formation of F-containing hydrocarbons. For example, the availability of these particular group values will allow one to evaluate, in a straightforward manner, the thermodynamic data in the following paper, where allylic and *vinylic* F-containing groups are in equilibrium.

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.

Infrared 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′ × ¼″ 10% ODPN (β,β′-oxydipropionitrile) on Chromosorb P 60/80) or column 2(10′ × ¼″ 10% DNP (Dinonylphthallate) 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′ × 1/8″ 10% ODPN on Chromosorb P 60/80) or column 4 (19′ × 1/8″ 10% 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.[5]

5-Iodo-7,7,7-trifluoro-1-heptene, **4**. 14.8 g of F_3CI and 6.5 g of 1,5-hexadiene were sealed in a 200 ml pyrex tube and irradiated in a Rayonet Photochemical Reactor. After 24 hr, the tube was cooled in liquid N_2 and opened. 11.3 g of F_3CI was recovered and the remaining mixture was vacuum distilled to yield **4**, b.p.$_4$ 48° (yield 60%): NMR, ϕ64.4 (t, $J_{FH(6)} = 10.4$ Hz); δ5.5–6.2 (1H, m), 4.9–5.4 (2H, m), 4.2 (1H, p, $J_{H(5)H(4)} = 7$ Hz, $J_{H(5)H(6)} = 7$ Hz), 2.5–3.3 (2H, m), 1.6–2.5 (4H, m); IR, 3090, 2990, 2940, 2960, 1650, 1435, 1360, 1260(s), 1150 (s), 995, 920, 580 cm^{-1}; Mass spectrum gave M^+ 277.9788 ± 0.00152 (5.5 ppm), Calc. for $C_7H_{10}F_3I$: 277.9779, deviation = 0.0007 (2.5 ppm); *m/e* (relative intensity): 278 (3.8), 237 (1), 151 (59), 131 (29), 123 (11), 41 (100).

7,7,7-Trifluoro-1,5-heptadiene, **3d**. In a 100 ml flask, equipped with a 6″ vigreux distillation apparatus, were placed 2.95 g **4** and 1.5 g KOH (pellets). These were heated at 120° for 20 min. The products were flash vacuum distilled from the solids. Preparative glpc on column 2 yielded 0.58 g **3d**, b.p. 96–97°, and 0.6 g **4**. The **3d** contained 14% of **2d**. Total yield was 47%. **2d** was not isolated separate from **3d** but it was unambiguously identified by quantitative correlation of glpc and ^{19}F NMR. It's ^{19}F absorption was clearly resolved from that of **3d**: ^{19}FNMR (**2d**) ϕ58.9 (d of t, $J_{FH(6)} = 8.3$ Hz; $J_{FH(4)} = 2.2$ Hz); (**3d**), ϕ64.6 (two mult's, $J_{FH(6)} = 6.2$ Hz); other spectra of the mixture (84% **3d**, 16% **2d**): ^{1}HNMR, δ5.3–6.8 (m, 3H), 4.8–5.3 (m, 2H), 2.1–2.5 (broad s, 4H); IR (gas); 3100 (w), 2950 (m), 2860 (w), 1690 (m), 1650 (w), 1450 (w), 1425 (w), 1330 (m), 1275 (s), 1200 (w), 1125 (s), 980 (m), 920 (s) cm^{-1}; Mass spectrum gave M$^+$ 150.0647 ± 0.00168 (11.2 ppm), Calc. for $C_7H_9F_3$: 150.0650, deviation = 0.00086 (5.8 ppm); *m/e* (relative intensity); 150 (0.5), 149 (0.5), 130 (4), 115 (5), 81 (27), 77 (8), 41 (98), 28 (100).

3-(*Trifluoromethyl*)-1,5-*hexadiene*, **1d**. The mixture of **2d** and **3d** was pyrolyzed at 350° for 5 min and the product, **1d**, separated by preparative glpc on column 4: NMR, ϕ71.5 (d, $J_{FH(3)} = 8.7$ Hz); δ4.8–6.1 (6H, m), 2.0–3.2 (3H, m); IR (gas), 3100, 3000, 2995, 1860, 1650, 1430, 1360, 1310, 1260 (s), 1190 (s), 1125 (s), 990, 925 (s), 720 cm^{-1}; Mass spectrum gave M$^+$ 150.0647 ± 0.0024 (14.9 ppm), Calc. for $C_7H_9F_3$: 150.0656, deviation = 0.0009 (6 ppm); *m/e* (relative intensity): 150 (0.1) 135 (5), 122 (4), 115 (4), 90 (3), 81 (29), 41 (100).

Equilibration of **1d**, **2d** *and* **3d**. **1d** was pyrolyzed in a well-conditioned glass vessel from 321.2° to 408.0° and the mixture of **2d** and **3d** was pyrolyzed at 408.0°. The resulting equilibrium mixtures were analysed on column 4. The values are listed in Table 1. The mass balance was 96.4% using pentane as an internal standard. The correlation coefficient for the van't Hoff plot of the data was 0.999.

5,7-*Dibromo*-7-*difluoro*-1-*heptene*, **5**. 3.6 g benzoyl peroxide, 30 g 1,5-hexadiene, and 115 g Br_2F_2C were placed in a dry 250 ml autoclave. It was heated with rocking at 100° for 6.5 h. Distillation yielded unreacted starting material and 29.3 g of **5**, b.p. 69–70, at 4 mm, 27% yield: NMR, ϕ43.3 (t, $J_{FH(6)} = 13.6$ Hz); δ5.3–6.2 (1H, m), 4.8–5.3 (2H, m), 4.2 (1H, p, $J_{H(5)H(4)} = 6$ Hz, $J_{H(5)H(6)} = 6$ Hz), 2.7–3.5 (2H, m), 1.7–2.7 (4H, m). IR 3100, 2995, 2930, 2860, 1650, 1450, 1435, 1200 (s), 1100 (s), 1000 (s), 920 (s), 760, 635, 550 cm^{-1}; Mass spectrum gave M$^+$ 289.9122 ± 0.00418 (14.4 ppm), calculated for $C_7H_{10}F_2Br_2$: 289.9118, deviation = 0.00042 (1.5 ppm); *m/e* (relative intensity): 294 (0.1), 292 (0.4), 290 (0.1), 252 (0.4), 67 (25), 55 (11), 28 (100).

7-*Bromo*-7,7-*difluoro*-1,5-*heptadiene*, **6**. A 3-necked 250 ml flask was equipped with an addition funnel and a distillation take-off with a 6 in. vigreux column. 10 g KOH (pellets) was placed in the flask and 16.4 g **5** was placed in the addition funnel. The pressure was reduced to 30 mm and the flask was heated to 120°. **5** was slowly added and a mixture of **5** and **6** was distilled out. Redistillation of the distillate yielded 6.8 g **6**, b.p.$_{15}$55°, and 4.3 g **5**. Yield based on amount of **5** used was 77.3%, **6** was 95% *trans* isomer and 5% *cis* isomer as determined by glpc and ^{19}F NMR: NMR, ϕ(**6**-*cis*) 39.3 (2F, 2m, $J_{FH(6)} = 13.8$ Hz), ϕ(**6**-*trans*) 44.6, (2F, dd, $J_{FH(6)} = 9.0$ Hz, $J_{FH(5)} = 1.4$ Hz); δ5.3–6.7 (3H, m) 4.8–5.3 (2H, m), 2.1–2.5 (4H, broad s); IR, 3095, 2995, 2940, 2860, 1740, 1730, 1675, 1650, 1450, 1350, 1300, 1230 (s), 1190, 1090, 920 (s), 735 cm^{-1}; Mass spectrum gave insufficient parent ion for exact mass: *m/e* (relative intensity): 212 (0.2), 210 (0.2), 171 (1), 169 (1), 131 (38), 111 (13), 90 (38), 41 (53), 28 (100).

7,7-*Difluoro*-1,5-*heptadiene*, **3c**. In a 25 ml flask, 3.5 g of tri-n-butyltin hydride and 2 g of **6** was stirred for 4 h at room temp. The mixture was flash vacuum distilled and preparative glpc on column 2 yielded 0.5 g **3c** for a 42% yield. **3c**, b.p. 120–122°, was shown on column 4, to be composed of 95% **3c** and 5% **2c**: NMR, ϕ (**3c**) 110.3 (2F, 2m, $J_{FH(7)} = 59.5$ Hz), ϕ(**2c**) 111.4 (2F, ddt, $J_{FH(7)} = 56.0$ Hz, $J_{FH(6)} = 8.2$ Hz); δ5.9 (1H, td, $J_{H(7)F} = 59.5$ Hz, $J_{H(7)H(6)} = 5$ Hz), 5.2–6.4 (3H, m), 4.8–5.2 (2H, m), 2.0–2.4 (4H, broad s); IR (gas), 3095, 2995, 2940, 2860, 1680, 1645, 1395, 1145, 1130, 1020 (s), 970, 915 cm^{-1}; The mass spectrum gave insufficient parent ion for exact mass: *m/e* (relative intensity): 132 (0.3), 131 (0.2), 117 (1), 104 (5), 97 (3), 91 (4), 81 (69), 72 (14), 59 (6), 41 (100).

3-*Difluoromethyl*-1,5-*hexadiene*, **1c**. **3c** was pyrolyzed at 350° for 5 min, which yielded an equilibrium mixture of **3c**, **2c** and **1c**. Several runs were combined and separated by preparative glpc on column 2. NMR, ϕ123.5 (dd, $J_{FH(7)} = 56.7$ Hz, $J_{FH(3)} = 15.1$ Hz); δ5.74 (1H, td, $J_{H(7),F} = 56.7$ Hz, $J_{H(7)H(3)} = 3.5$ Hz), 4.7–6.1 (6H, m), 2.0–3.0 (3H, m); IR (gas), 3095, 2998, 2940, 1645, 1450, 1425, 1380, 1140, 1090, 1050, 720 cm^{-1}; The mass spectrum gave insufficient parent ion for exact mass: *m/e* (relative intensity); 131 (0.2), 104 (3), 91 (3), 81 (80), 77 (6), 72 (16), 53 (11), 51 (13), 41 (100).

Equilibration of **1c**, **2c** *and* **3c**. **1c** was pyrolyzed in a well-conditioned pyrex vessel at temp from 309.9° to 409.0°. **2c** and **3c** were pyrolyzed at 409.0°. The resulting equilibrium mixtures were analyzed on column 4. The equilibrium values are listed in Table 2. The mass balance was 97.6%, using pentane as the internal standard. The correlation coefficient for the van't Hoff plot of the equilibrium data was 0.999.

Acknowledgements—We wish to acknowledge with thanks the support of this research in part by the National Science Foundation. We also wish to thank Professors Joel Liebman and Art Greenberg for numerous stimulating discussions relating to the data.

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