Tetrahedron Letters,Vol.24,No.12,pp 1217-1220,1983 0040-4039/83/121217-04$03.00/0
Printed in Great Britain

THE THERMAL ISOMERIZATION OF 2-FLUORO-1-METHYLENECYCLOPROPANE

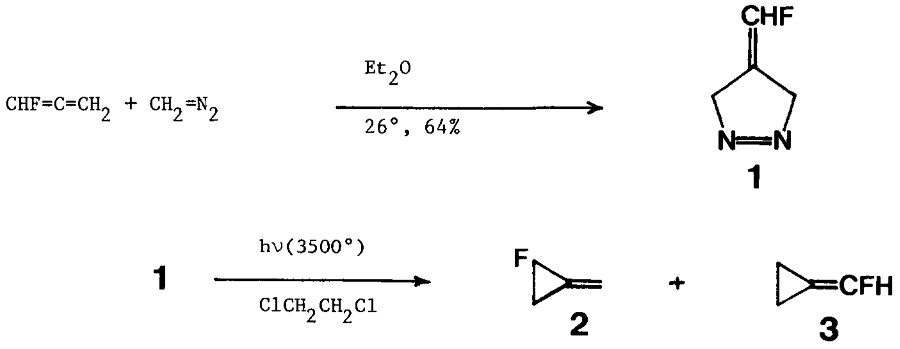
William R. Dolbier, Jr.* and Conrad R. Burkholder
Department of Chemistry, University of Florida
Gainesville, FL 32611

Summary: The thermodynamics of the thermal equilibration of 2-fluoro-1-methylenecyclopropane and 1-(fluoromethylene)cyclopropane are presented and discussed.

The kinetic effect of *gem*-difluoro substituents on the thermal chemistry of cyclopropane compounds has been probed exhaustively in recent years with the result that such effects are quite predictable.[1] Recently the first data have appeared[2] which provide evidence as to the *thermodynamic* effect of *gem*-difluoro substitution on cyclopropane stability, with the indication being that an additional strain of 12-14 kcal/mole can be attributed to the presence of the fluorine substituents. A slightly lower value (11.7 kcal/mole) was estimated on the basis of 4-31G calculations.[3]

In contrast to the considerable understanding of *gem*-difluoro systems, very little is known about monofluorocyclopropanes. Recently we reported the thermodynamic effects of *single* fluorine substituents at alkylic, allylic and vinylic sites to be neither unusual nor dramatic, in contrast to effects at the respective multi-fluorine-substituted sites.[4,5] We would like to report at this time our first examination of a monofluorocyclopropane system the fluoromethylenecyclopropane thermal isomerization, in which one observes no dramatic special thermodynamic effects due to the fluorine substituent.

A mixture of the isomeric fluoromethylenecyclopropanes 2 and 3 was obtained from the photolysis of 4-(fluoromethylene)-1-pyrazoline, 1[6] which could itself be obtained from the facile cycloaddition of fluoroallene[7] with diazomethane.

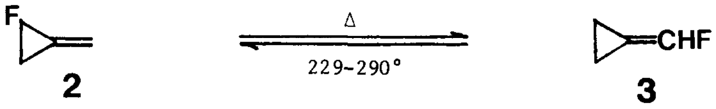


65 : 35

The isomers **2** and **3** were characterized spectroscopically.[8]

2-Fluoro-1-methylenecyclopropane, **2**, and 1-(fluoromethylene)cyclopropane, **3**, were found to smoothly interconvert at temperatures greater than 220°. Equilibrium constants were obtained for five temperatures as seen in the Table, and a plot of K versus 1/T provided the thermodynamic values indicated.

(1)



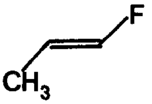
$\Delta H° = -2.6 \pm 0.06$ kcal/m. $\Delta S° = 1.0 \pm 0.02$ e.u.

Table. Equilibrium Data for the Fluoromethylenecyclopropane System.

Temp°C	229.0	243.0	257.2	277.0	289.6
K_{eq}	7.70	7.19	6.77	6.19	5.82

From the comparison of the above thermodynamic results with those for the analogous simple allylic-vinylic isomerization (eq. 2)[5], it would appear that there is nothing unusual about the fluoromethylenecyclopropane system. Using our previously determined group equivalent values[5] and those of Benson[9], and assuming the C(F)(C)(C_d) value to be -49.2,[10] one can calculate the heats of formation of **2** and **3** to be 3.5 and 2.8 kcal/m respectively, values which predict a ΔH° of -0.7 kcal/mole for their equilibration. Assuming no other unrecognized stabilizing or de-stabilizing interactions to be present in **2** or **3** (a dubious assumption) one could estimate the excess strain in **2** due to the fluorine substituent to be about 2 kcal/mole. This compares with an estimate of 4.5 kcal/mole based upon the calculated heat of hydrogenation of fluorocyclopropane.[3]

(2) $CH_2{=}CH{-}CH_2F \underset{\Delta}{\overset{I_2}{\rightleftharpoons}}$

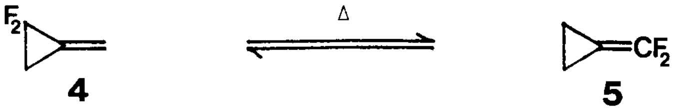


$\Delta H° = -2.7$ kcal/mole

$\Delta S° = 1.7$ e.u.

It is interesting to compare the thermodynamics of this monofluoro system with the analogous *gem*-difluoro system. The fact that **5** is favored *less* than **3** in its equilibration with **4** might appear suprising since, for example, the related rearrangement of dimethymethylenecyclopropane system (ΔH = 1.2 kcal/mole)[11] *is about twice as exothermic as that of the*

(3)



$\Delta H° = -1.9$ kcal/mole

monomethyl system ($\Delta H = 0.5$ kcal/mole).[12] However the relative exothermicities of the 2 ⇌ 3 and 4 ⇌ 5 systems can be understood if one recognizes that the variation in incremental geminal stabilization for fluorine is quite great,[5,3] with these IGSTAB's being relatively, alkyl >> cyclopropyl > vinyl, such that the net effect on going from the 2 ⇌ 3 system to the 4 ⇌ 5 system is a slight favoring of the cyclopropane-substituted isomer, in spite of the fact that the incremental strain in 4 is much greater than that in 2.

As in the case of the *gem*-difluoro-substituted system, 4,[13] there is no dramatic kinetic effect in the isomerization of 2. Details on the kinetic aspects of general substituent effects on methylenecyclopropane rearrangements will be discussed in a forthcoming full paper.

Acknowledgement. The authors acknowledge with thanks the support of this research in part by the National Science Foundation.

References and Footnotes

1. Dolbier, W.R., Jr. Acc. Chem. Res. 1981, 14, 195.
2. Roth, W.R.; Kirmse, W.; Hoffman, W.; Lennartz, H.-W. Chem. Ber. 1982, 115, 2508.
3. Greenberg, A.; Liebman, J.F.; Dolbier, W.R., Jr. Medinger, K.S.; Skancke, A. Tetrahedron, in press
4. Dolbier, W.R., Jr.; Medinger, K.S. Tetrahedron, 1982, 38, 2411.
5. Dolbier, W.R., Jr.; Medinger, K.S.; Greenberg, A.; Liebman, J.F. Tetrahedron 1982, 38, 2415.
6. The pyrazoline was very labile, but capable of purification by distillation under reduced pressure: bp 59-60° (23 mm); IR(CCl_4), 1710(s) (C = CHF), 1545 cm^{-1} (m) (N=N); ^1H NMR (300 MHz) ($CDCl_3$) δ6.67 (d of pent, 1H, J = 2.7, J_{FH} = 83.9Hz), 5.16 (t, 2H, J = 2.8 Hz), 5.06 ppm (t, 2H, J = 2.8 Hz); ^{19}F NMR (94.1 MHz). Φ121.7 (d of pent, J_{FH} = 3, J_{FH} = 84 Hz); mass spectrum gave M^+ 100.04442 ± 0.00195 (19.5 ppm), calcd for $C_4H_5N_2F$ 100.04368, dev - 0.00075 (7.5 ppm).
7. Dolbier, W.R., Jr.; Burkholder, C.R.; Piedrahita, C.A. J. Fluorine Chem. 1982, 20, 637.
8. 2: ^1H NMR (100 MHz, $CDCl_3$), δ5.86 (M, 1H), 5.61 (M, 1H), 4.92 (d of M, 1H, J_{FH} = 68.6 Hz), 1.65 - 1.45 ppm. (M, 2H); ^{19}F NMR (94.1 MHz), Φ169.6 (d of M, J_{FH} = 68.6 Hz); mass spect. gave M^+ 72.03732 ± 0.00107 (14.8 ppm); calcd for C_4H_5F 72.03753 dev - 0.0002 (2.9 ppm). 3: IR (CCl_4), 1790 cm^{-1} (s) (C=CHF); ^1H NMR (100 MHz, $CDCl_3$), δ6.88 (d of pent, 1H, J_{FH} = 91.5; J = 2.2 Hz), 1.27 ppm (d of d, 4H, J_{FH} = 4.6, J = 2.2Hz); ^{19}F NMR (94.1 MHz, $CDCl_3$), Φ130.6 (d of pent, J_{FH} = 91.5, J_{FH} = 4.6 Hz); mass spect, gave M^+ 72.03751 + 0.00083 (11.5 ppm), calcd for C_4H_5F 72.03753, dev - 0.00002 (0.2 ppm).

9. Benson, S.W. Thermochemical Kinetics (2nd Edn.) Wiley, New York (1976).

10. Based upon the published heat of formation of 2-fluoropropane (-70.1 kcal/mole); Jorgenson, W.L.; Cournoyer, M.E. J. Am. Chem. Soc. **1978**, 100, 5278.

11. Crawford, R.J.; Cameron, D.M.; Tokunaga, H. Can. J. Chem. **1974**, 52, 4025.

12. Chesick, J.P. J. Am. Chem. Soc. **1963**, 85, 2720.

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

(Received in USA 29 November 1982)