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The kinetic and thermodynamic influence of fluorine versus methyl substituents in methylenecyclopropane rearrangements

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Abstract

A comprehensive review of the kinetic and thermodynamic influences of methyl and fluorine substituents on the methylenecyclopropane rearrangement is presented. In spite of a superficial similarity of the overall influence of these two substituents, methyl's effect derives largely from the incremental nature of its radical- and alkene-stabilizing, and steric impact, while fluorine's effect derives from its large and non-incremental influence on the strain of cyclopropane coupled with its similarly variable effect on the stability of alkenes and free radicals.

Keywords: Kinetic influence; Thermodynamic influence; Fluorine substituents; Methyl substituents; Methylene cyclopropane rearrangements; NMR spectroscopy

1. Introduction

If one examines carefully the literature of methylenecyclopropane (MCP) rearrangements, one finds a remarkable similarity in both the kinetic and the thermodynamic impact of methyl and fluorine substituents on these mechanistically well-understood thermal, homolytic isomerizations.

In this paper we present a comprehensive review and discussion of the relative kinetic influence of methyl and fluorine substituents on the methylenecyclopropane rearrangement, such data being gleaned both from the literature and from our own recent results. We also present kinetic data which, for such rearrangements, indicates (a) the relative propensity for fluorine- versus methyl-substituted carbons to migrate to the *exo* position and (b) the stereochemistry of single methyl rotation in such migration processes. We also discuss the thermodynamic influence of methyl and fluorine substituents on methylenecyclopropane equilibria.

The mechanism of the methylenecyclopropane rearrangement has been examined in detail over the last 25 years [1], with the 'pivot mechanism' being first presented and defined by Doering and Roth in 1970 [2]. The energetics of the reaction are accommodated by a non-concerted mechanism in which the half-way stage is best represented by a structure such as **I**, "which is a planar allyl radical, to the central carbon atom of which there is attached a free radical in its perpendicular and non-bonding arrangement" [2]. One obtains this diradical intermediate by a 90° rotation about the C_3–C_1 axis, and the intermediate proceeds on to product by a 90° rotation of the C_4–C_1 axis. Doering proposed that the carbon atom (C_1 or C_3) which bears the substituent(s) which more highly stabilize a free radical will assume the role of pivot in this mechanism.

2. New results

Kinetic and thermodynamic studies of the MCP rearrangements of two previously unstudied molecules were carried out and the results of these studies correlated with all available published data related to the thermal rearrangements of

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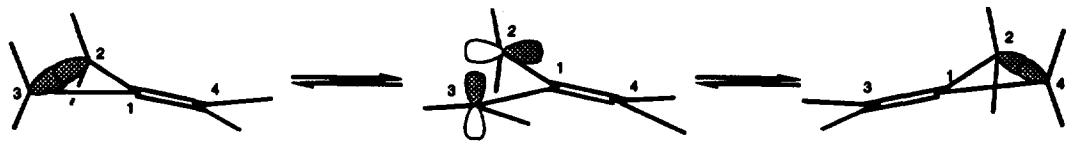

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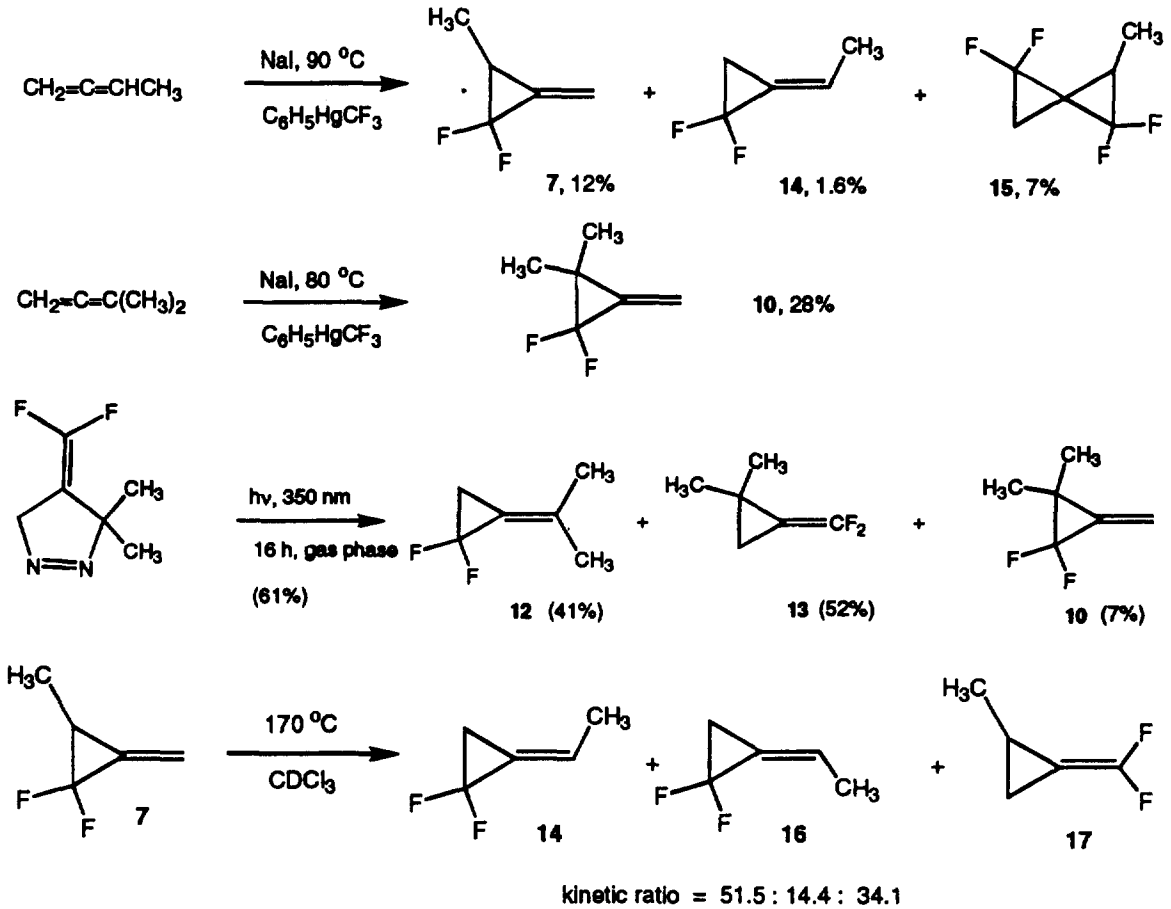


methyl- and/or fluorine-substituted methylenecyclopropanes.

2.1. Synthesis

1,1-Difluoro-2-methyl-3-methylenecyclopropane (**7**) and 1,1-difluoro-2,2-dimethyl-3-methylenecyclopropane (**10**) were synthesized via addition of difluorocarbene to 1,2-butadiene and 3-methyl-1,2-butadiene, respectively, using Seyferth's method [3]:

Substrate **10**, along with its isomers, 1,1-difluoro-2-(1-methylethylidine)cyclopropane (**12**) and 2-(difluoromethylene)-1,1-dimethylcyclopropane (**13**), was formed from the photolysis of 4-(difluoromethylene)-4,5-dihydro-3,3-dimethyl-3*H*-pyrazole [4]:

2.2. Thermal isomerizations

The rate of rearrangement of **7** to a mixture of **14, 16** and **17** was determined to be 7.2×10^{-5} s^{-1} in the gas phase at 169.0 °C, whereas the kinetic product ratios were determined by solution thermolysis at 170.5 °C. At equilibrium, only 1.3% of **7** remained.

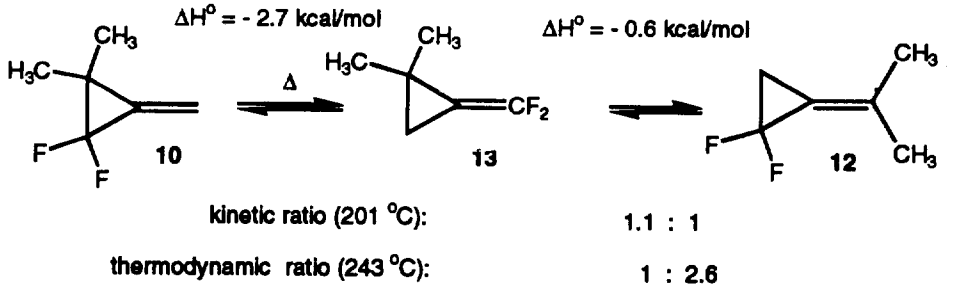
The thermal isomerization of **10** was studied kinetically at 200.8 °C, with a rate of 1.47×10^{-3} s^{-1} being observed, whereas the equilibrium between **10** and its isomers, **12** and **13**, was studied over a range of temperatures between 200 °C and 278 °C.

3. Discussion

3.1. Kinetic influence

Table 1 provides a summary of all available kinetic data for methylenecyclopropane rearrangements which have fluorine and/or methyl substituents at the 2- and/or 3-positions.

From this table it can be seen that, from a kinetic point of view, fluorine and methyl substituents have a very similar impact upon the rates of rearrangement of ring-substituted methylenecyclopropanes, with such rates increasing progressively as one increases the total number of F or Me substituents. It is seen, for example, that one ring methyl or fluorine substituent lowers the $\Delta G^{\neq}$ value by ~2 kcal mol^{-1} compared to the parent MCP system. The apparent identity of $\Delta G^{\neq}$ for substrates **2, 3, 4** and **6**, wherein singly-substituted and geminally substituted MCPs rearrange at virtually identical rates, is probably an anomaly in that the related degenerate rearrangement of entry **5** indicates that C–C bond cleavage for the *gem*-dimethyl case does indeed give rise to



an incremental 2.4 kcal mol^{-1} lowering of activation barrier. Although the rates of the analogous degenerate rearrangements of neither monofluoro nor monomethyl MCPs have been determined, LeFevre and Crawford did point out that the deuterated isomers of **2** did not equilibrate at temperatures where the equilibration of **5** was measured [12].

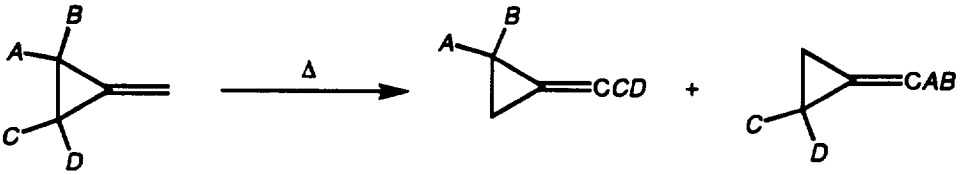
Three substituents (i.e., **7** and **8**) give rise to an additional ~1 kcal mol^{-1} lowering of $\Delta G^{\neq}$, while four methyls (**9**) or two methyls and two fluorines (**10**) lower $\Delta G^{\neq}$ by only a bit more (< 1 kcal mol^{-1}). 2,2,3,3-Tetrafluoro-MCP (**11**) is anomalously reactive, with such reactivity appearing to derive from some type of ground-state thermodynamic destabilization of **11** [11].

Except for this latter example, the relative influence of ring-substituted methyl and fluorine substituents on the thermal reactivity of MCP appears to be comparable. There are two factors by which substituents are known to influence the rate of cleavage of a cyclopropane ring. Either the ground state of the cyclopropane can be *raised* by an increase in the strain of the system due to the substituent(s), or the product of the homolytic cleavage (the trimethylene diradical) can be *stabilized* by the substituent(s). It is clear that the nature of the influence of fluorines is different from that of methyl substituents in that geminal fluorine substituents have been demonstrated to increase the strain of the cyclopropane ring by ~12 kcal mol^{-1} [13], but they would appear to provide little if any stabilization to a radical. Indeed, Borden et al. have calculated (SDQ-CI/6-31G*) that 1,1-difluorotrimethylene (0, 90 conformer) has virtually the same heat of formation as the 2,2-difluoro isomer [14]. Single fluorine substituents provide some radical stabilization, but probably not as much as a methyl group [15].

3.2. Migrating group competition

Consistent with the above factors which are generally accepted to be involved in the mechanism for MCP rearrangements, the data in Table 2 indicate that in those cases where there is a choice (i.e., compounds **5, 7, 8** and **10**), the most radical-stabilizing (and in this case also most sterically-demanding) methylene group will remain orthogonal and will become the pivot carbon in the Doering orthogonal trimethylenemethane intermediate.

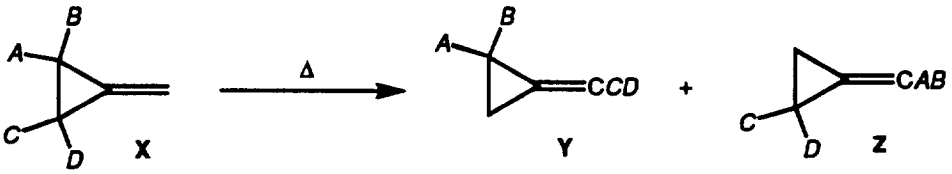
Table 1
Rate data (s^{-1}) for methyl- and fluorine-substituted methylenecyclopropane rearrangements



Compd.	A	B	C	D	Temp. (°C)	Rate, $10^5 k$	$\Delta G^{\neq}$ (kcal mol^{-1})	Ref.
1	H	H	D	D	180	0.054	39.9	[5]
2	CH_3	H	H	H	180	0.35	38.2	[6]
3	F	H	H	H	247	150	37.7	[a]
4	CH_3	CH_3	H	H	180	0.34	38.3	[5]
5	CH_3	CH_3	D	D	180	4.5	35.9	[5]
6	F	F	H	H	193	2.13	37.7	[8]
7	F	F	CH_3	H	169	7.2	34.6	this work
8	CH_3	CH_3	CH_3	H	170	7.2	34.7	[9]
9	CH_3	CH_3	CH_3	CH_3	180	25.7	33.8	[10]
10	F	F	CH_3	CH_3	201	147	34.3	this work
11	F	F	F	F	150	234	30.3	[11]

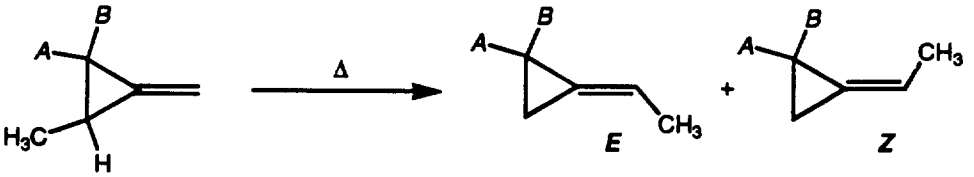
[a] Approximated from the measured half-life of **3** (7.7 min at 247 °C) obtained during studies of its thermal equilibration [7].

Table 2
Relative migratory propensity of methyl- and fluorine-substituted carbons



Compd.	A	B	C	D	Temp. (°C)	Y/Z	Ref.
5	CH_3	CH_3	D	D	180	13.2	[5]
7	F	F	CH_3	H	170	1.5	this work
8	CH_3	CH_3	CH_3	H	170	2.4	[9]
10	CH_3	CH_3	F	F	201	1.1	this work

Table 3
Rotational stereochemistry for methyl migration



Compd.	A	B	Temp. (°C)	E/Z	Ref.
7	F	F	170	3.6	this work
8	CH_3	CH_3	170	14.5	[10]

Table 4
Thermodynamic data for methyl- and fluorine-substituted methylenecyclopropane rearrangements

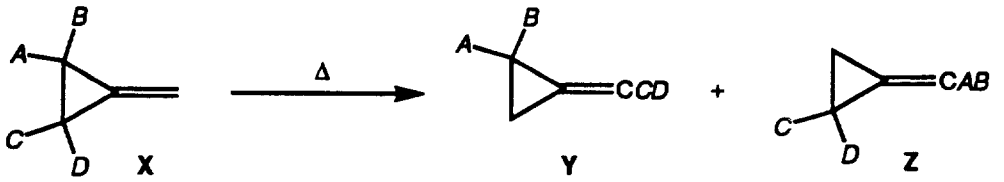
Compd.	A	B	C	D	Temp. (°C)	%X	%Y	%Z	Ref.
2	CH_3	H	H	H	210	43.5		56.5	[6]
3	F	H	H	H	243	12		88	[7]
4	CH_3	CH_3	H	H	236	22		78	[5]
6	F	F	H	H	236	16.4		83.6	[8]
7	F	F	CH_3	H	169	1.3	64.6	34.1	this work
8	CH_3	CH_3	CH_3	H	170	1.9	22.6	75.5	[9]
9	CH_3	CH_3	CH_3	CH_3	237	0.3		99.7	[10]
10	F	F	CH_3	CH_3	243	2.0	71.1	26.9	this work
11	F	F	F	F	150	–		~100	[11]

Earlier results by LeFevre and Crawford demonstrated that a CH_2 migrates 13.2-times faster than a dimethyl-substituted methylene (compare **4** and **5**) [5], and a comparison of the data for **7** and **8** indicates that the monomethyl-substituted carbon of **8** has a slightly greater preference for migration than that of **7**, a result consistent with both the greater radical stabilizing ability and the greater bulk of a $C(Me)_2$ group versus a CF_2 group. In the case of **10**, little preference is shown, which may reflect an energetic trade-off between the methyl's radical stabilizing ability versus the inclination for CF_2 to remain at the pivot position where it can maintain its preferential pyramidal geometry [14].

3.3. Steric impact on methyl group rotation

Another result of this difference in size of a methyl versus a fluorine substituent is the significantly greater preference for outward rotation exhibited by the single methyl substituent in the rearrangement of **8** in comparison to **7** (see Table 3).

There can be no doubt that the relative rotational propensities exhibited within both of these systems are strongly influenced by the steric size of the substituents which are vicinal to the rotating methyl substituent.



3.4. Thermodynamics

Lastly, Table 4 provides a summary of the thermodynamic data which are available for these systems. As expected, one sees a thermodynamic preference for mono- and di-substituted carbons to occupy the vinylic rather than a cyclopropyl site, and in situations where methyl-substituted carbons compete with fluorine-substituted (i.e., **7** and **10**), one sees a preference for the methyl-substituted carbons to occupy the vinylic site.

The overt similarity of the overall thermodynamic impacts of methyl and fluorine substituents on the above MCP equilibria is deceptive in nature, as is indicated by the comparison of the effects of single and geminal methyl and fluorine substitution on alkene stability given below:

$$CH_2{=}CH{-}CH_2F \underset{\Delta H^0 = -3.3 \text{ kcal mol}^{-1}}{\rightleftharpoons} (Z)\text{-}CHF{=}CHCH_3 \quad [16] \quad (1)$$

$$CH_2{=}CH{-}CHF_2 \underset{\Delta H^0 = +2.5 \text{ kcal mol}^{-1}}{\rightleftharpoons} CF_2{=}CH{-}CH_3 \quad [16] \quad (2)$$

$$CH_2{=}C(CH_3)CH_2CH_3 \underset{\Delta H^0 = -1.6 \text{ kcal mol}^{-1}}{\rightleftharpoons} CH_3CH{=}C(CH_3)_2 \quad [17] \quad (3)$$

$$CH_2{=}C(CH_3)CH(CH_3)_2 \underset{\Delta H^0 = -1.5 \text{ kcal mol}^{-1}}{\rightleftharpoons} (CH_3)_2C{=}C(CH_3)_2 \quad [17] \quad (4)$$

The similar influence of one versus two methyl groups on the enthalpy of the hypothetical alkene isomerizations given in Eqs. (3) and (4) is consistent with their similar preference for the alkene position in the MCP equilibria of compounds **2** and **4**, and this is also consistent with the lack of effect of methyl substituents on cyclopropane ring strain. The methyl systems thus allow a very straightforward correlation and understanding of the results. On the other hand, one can see a significant difference in influence of one versus two fluorines reflected in the thermodynamics of the actual equilibria given in Eqs. (1) and (2), where one fluorine is seen to stabilize an alkene while two fluorines destabilize relative to the allylic position. This phenomenon, which seems to derive from unique incremental geminal stabilizations of two or three fluorines on a *saturated* carbon, has been described before [16]. Thus, the fact that the thermodynamics of the MCP equilibria of mono- and difluoro-substituted MCPs **3** and **6**, which like the methyl systems are also almost identical, must derive from counterbalancing differences in the strain imparted to the cyclopropanes by one and geminal fluorines. Unfortunately there are no thermodynamic data indicating what are the specific strains of a monofluorocyclopropane or a tetrafluorocyclopropane.

4. Experimental details

4.1. Preparation of 1,1-difluoro-2,2-dimethyl-3-methylenecyclopropane (10)

Into a 10 ml glass tube containing 3.8 g (11.0 mmol) of $PhHgCF_3$ [3], 4.00 g (26.7 mmol) of dried NaI and 30 mg of tetra-n-butylammonium iodide was condensed 1.4 g (20.6 mmol) of 3-methyl-1,2-butadiene. The tube was sealed under vacuum and heated at 80 °C for 16.5 h. The tube was cooled and opened. Vacuum-transfer gave 1.7 g of a liquid which was subjected to preparative GC (20 ft × 0.25 in, 15% ODPN, ambient temperature, 30 ml min^{-1}) to give 0.815 g of recovered 3-methyl-1,2-butadiene and 0.368 g (28%) of **10**, b.p. 63.5–63.8 °C. IR (gas) (cm^{-1}): 3100; 3008; 2983; 2955; 2895; 1853 (w); 1762 (m); 1450; 1332; 1243; 1172 (s); 990; 924; 881. ^1H NMR (60 MHz, $CDCl_3$) δ: 5.91 (t, 1H, J_{HF} = 1.6 Hz); 5.61 (t, 1H, J_{HF} = 2.3 Hz); 1.24 (t, 6H, J_{HF} = 2.2 Hz) ppm. ^{19}F NMR (100 MHz, $CDCl_3$) ϕ: −139.9 (complex m) ppm. HRMS: Calc. for $C_6H_8F_2$, 118.059 41. Found, 118.059 08. The order of elution was 3-methyl-1,2-butadiene first followed by **10**.

4.2. Preparation of 1,1-difluoro-2-(1-methylethylidene)cyclopropane (12), 1,1-difluoro-2,2-dimethyl-3-methylenecyclopropane (10) and 2-(difluoromethylene)-1,1-dimethylcyclopropane (13)

Photolysis of 200 mg (1.37 mmol) of 4-(difluoromethylene)-4,5-dihydro-3,3-dimethyl-3*H*-pyrazole [4] in a 500 ml gas sample bulb for 16 h using a Rayonet Photoreactor (350 nm) gave 98 mg (61%) of crude photolysis mixture which was subjected to preparative GC (20 ft × 0.25 in, 15% ODPN, ambient temperature, 30 ml min^{-1}) to give 17 mg (11%) of **12**. IR (gas) (cm^{-1}): 2990; 2955; 2930; 1854 (w); 1784 (m); 1458; 1414; 1330; 1202 (s); 1130; 1061. ^1H NMR (60 MHz, $CDCl_3$) δ: 1.9 (m) ppm. ^{19}F NMR (100 MHz, $CDCl_3$) ϕ: −130.6 (complex m) ppm. HRMS: Calc. for $C_6H_8F_2$, 118.059 4. Found, 118.059 0.

The reaction also gave 4 mg (2%) of **10**, identical to **10** prepared by addition of difluorocarbene to 3-methyl-1,2-butadiene, and 22 mg (14%) of **13**. IR (gas) (cm^{-1}): 3062;

2980; 2940; 2885; 1840 (s); 1440; 1316; 1230 (s); 1140. ^{1}H NMR (60 MHz, $CDCl_3$) δ: 1.43 (m) ppm. ^{19}F NMR (100 MHz) ϕ: −86.6 (dt, 1F, J_{FF}=73.2 Hz and J_{HF}=4.1 Hz); 90.9 (d, 1F, J_{FF}=73.2 Hz) ppm. HRMS: Calc. for $C_6H_8F_2$, 118.059 41. Found: 118.059 48. The combined yield of isolated products was 27%. The order of elution was **13, 10** then **12**.

4.3. Preparation of 1,1-difluoro-2-methyl-3-methylenecyclopropane (7), (E)-1,1-difluoro-2-ethylidenecyclopropane (14) and 1,1,4,4-tetrafluoro-2-methylspiropentane (15)

To a thick-walled, glass tube were added 3.806 g (11 mmol) of $PhHgCF_3$ [18] and 4.005 g (26.7 mmol) of dried NaI. Into the tube was condensed 0.7622 g (20.6 mmol) of 1,2-butadiene and the tube was sealed under vacuum. The tube was heated in an oil bath at 90 °C for 22 h, then cooled and opened. The volatile materials were transferred on the vacuum line to a flask which was stored on Dry Ice.

Analysis by GC (10 ft×0.25 in, 20% SE-30, ambient temperature) was performed using a syringe cooled with powdered Dry Ice to make the injections. Five major peaks were observed. The order of elution was: 1,2-butadiene, then **7, 14, 15** and finally benzene. The products were isolated by preparative GC using the same column (45 ml min^{-1}).

A total of 141 mg (12%) of **7** was obtained. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 5.93 (m, 1H); 5.63 (q, 1H, J=2.4 Hz); 2.12 (complex m, 1H); 1.20 (dq, 3H, J_d=6.6. Hz and J_q=1.5 Hz) ppm. ^{19}F NMR (188 MHz, $CDCl_3$) ϕ: −129.3 (ddm, 1F, J_{FF}=175.6 Hz and J_{HF}=12.1 Hz); −143.9 (dm, 1F, J_{FF}=175.6 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 134.0 (t, quat, J_{CF}=7.1 Hz); 110.8 (d, $=CH_2$, J_{CF}=1.9 Hz); 108.2 (t, CF_2, J_{CF}=292.0 Hz); 24.1 (dd, CH, J_{CF}=11.2 and 13.2 Hz); 10.4 (t, CH_3, J_{CF}=2.9 Hz) ppm. MS (70 eV): 104 (M^+, 68%); 103 (77); 89 (24); 76 (45); 65 (21); 53 (75); 40 (100); 39 (78). HRMS: Calc. for $C_5H_6F_2$, 104.043 7. Found: 104.027 2.

There was also obtained 18 mg (1.6%) of **14**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.47 (m, 1H); 1.86–1.92 (m, 5H) ppm. ^{19}F NMR (188 MHz, $CDCl_3$) ϕ: −130.2 (hextet, J=2.7 Hz) ppm. MS (70 eV): 104 (M^+, 73%); 103 (41); 84 (39); 77 (41); 64 (47); 53 (46); 39 (100). HRMS: Calc. for $C_5H_6F_2$, 104.043 7. Found: 104.027 6.

Also obtained was 62 mg (7%) of **15**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.6–2.24 (m, 3H); 1.18, 1.28 (two m, CH_3, ratio 29:71) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) ϕ: major isomer (74%): −133.1 (dm, 1F, J_{FF}=155 Hz); −133.4 (dm, 1F, J_{FF}=155 Hz); −135.2 (dddt, 1F, J_{FF}=155.0 Hz, J_d=18.5 and 8.6 Hz, J_t=2.4 Hz); −145.9 (ddm, 1F, J_{FF}=155.0 Hz and J_d=19.3 Hz); minor isomer (17%): −132.8 to −133.7 (resonances obscured by major isomer, 2F); −137.7 (ddd, 1F, J_{FF}=157.4 Hz, J_d=19.6 and 9.3 Hz); −146.7 (dt, 1F, J_{FF}=156 Hz and J_t=7.3 Hz); impurity (9%): −141.6 (dt, 1F, J_{FF}=169.3 Hz and J_t=9.1 Hz); −144.0 (non-first-order AB pattern, 2F); −149.2 (dt, 1F, J_{FF}=169.6 Hz and J_t=7.6 Hz) ppm. GC–MS (70 eV): 153 (M^+, 7%); 139 (10); 115 (8); 103 (36); 90 (71); 85 (100); 75 (60); 64 (85); 39 (43).

Table 5
Product ratios from from thermolysis of 7 in $CDCl_3$ at 170.5 °C determined by integration of the ^{19}F NMR spectrum

Time (h)	%7	%14	%16	%17	14:16
1.00	81.7	8.5	2.4	7.5	3.6
1.50	74.6	12.1	3.3	10.1	3.7
6.00	28.4	38.9	11.0	21.7	3.6

4.4. Thermolysis of 1,1-difluoro-2-methyl-3-methylenecyclopropane (7) to give (E)-1,1-difluoro-2-ethylidenecyclopropane (14) (Z)-1,1-difluoro-2-ethylidenecyclopropane (16) and 1-methyl-2-(difluoromethylene)cyclopropane (17)

Into a thick-walled, 5-mm NMR tube was added a solution of **7** in $CDCl_3$. The tube was sealed and then heated in a thermostatically controlled oil bath at 170.5 °C. After periods of 1.00, 1.50 and 6.00 h, the solution was analyzed by ^{19}F NMR spectroscopy to determine the amounts of starting material and products by integration.

Thermolysis gave **14** which had fluorine resonances identical to the material isolated from the reaction of difluorocarbene with 1,2-butadiene.

Also observed in the reaction mixture was **16**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.02 (m, 1H); 2.0–1.0 (obscured by other resonances, 5H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) ϕ: −131.9 (m) ppm.

In addition, there was observed in the reaction mixture **17**. ^{19}F NMR (282 MHz, $CDCl_3$) ϕ: −87.2 (dq, 1F, J_{FF}=71.0 Hz and J_q=4.1 Hz); −89.7 (dqq, 1F, J_{FF}=71.0 Hz and J_q=4.4, 1.7 Hz) ppm.

The ratios of starting material **7** and products **14, 16** and **17** from integration of the ^{19}F NMR spectra are listed in Table 5. After heating for 102 h, the sample decomposed.

Thermolysis of **7** was carried out in the gas phase by expanding the gas into a well-conditioned thermolysis vessel at 169 °C. Gaseous samples were taken periodically and the amounts of products were determined by GC using gas injection (18 ft×0.125 in, 5% ODPN). A rate constant of 7.2×10^{-5} s^{-1} was obtained at 169 °C for the disappearance of **7**. After equilibrium had been obtained, there was 1.3% of **7**, 64.4% of **14** and **16**, and 34% of **17**.

4.5. Thermolysis of 1,1-difluoro-2,2-dimethyl-1-methylenecyclopropane (10)

Thermolysis of **10** was carried out in the gas phase by expanding 10 mm of **10** into a well-conditioned thermolysis vessel at 200 °C to 279 °C. Gaseous samples were taken periodically and the amounts of products were determined by

Table 6
Equilibrium constants for **10,12** and **13** in the gas phase

Temp. (°C)	*K* (**13/10**)	*K* (**13/12**)	*K* (**10/12**)
278.7	13.5	0.379	0.0281
256.7	15.1	0.370	0.0245
243.7	15.8	0.366	0.0231
221.5	18.0	0.357	0.0199
200.2	20.3	0.347	0.0171

Table 7
Thermodynamic ΔH^0 and ΔS^0 values for the gas-phase equilibrium of **10, 12** and **13**

Reaction	ΔH^0 (kcal mol^{-1})	ΔS^0 (eu)
12 → **10**	3.25 ± 0.07	-1.2 ± 0.03
10 → **13**	-2.68 ± 0.07	0.32 ± 0.03
12 → **13**	0.58 ± 0.01	-0.89 ± 0.01

GC using gas injection (ODPN column). The products were **12** and **13**. A rate constant of $1.47 \pm 0.01 \times 10^{-3}$ s^{-1} was obtained at 200.8 °C.

The equilibrium was also studied. Starting with **10**, the equilibrium ratio at 243.7 °C was 72.0% of **12**, 1.7% of **10** and 26.3% of **13**. The equilibrium was verified by thermolysis of **12** at 244.0 °C for 60 min to give 72.1% of **12**, 1.6% of **10** and 26.3% of **13**. The equilibrium constants for **10, 12** and **13** starting with pure **10** are presented in Table 6. The ΔH^0 and ΔS^0 values for the equilibrium are reported in Table 7.

5. Conclusions

The overall influence of a methyl substituent on the kinetics and thermodynamics of methylenecyclopropane rearrangements can be understood in terms of its well-documented radical-stabilizing and alkene-stabilizing effects, combined with its steric impact. Although the effect of fluorine substituents is superficially similar to that of methyl, unlike methyl the overall influence of multiple fluorine substitution is presently not nearly so well understood. Like methyl, a single fluorine substituent stabilizes an alkene and appears to be slightly radical stabilizing. However, a CF_2 group would appear to thermodynamically detest a trigonal state [18,19]. Thus, geminal fluorine substituents do not stabilize alkenes or radicals, with the latter assuming a pyramidal arrangement to gain back some stability, and the former losing stabilization because of their enforced planarity. Also, just as importantly, unlike methyl substituents, fluorine substituents have a significant and non-additive incremental effect upon the ring strain of a cyclopropane ring, one which except for CF_2 is not quantitatively defined. Therefore, at present there are neither enough thermochemical data nor theoretical insight available for one to completely dissect the kinetic and thermodynamic results which derive from fluorinated MCB systems.

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