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FLUORIDE ION CATALYZED ISOMERIZATION OF 2-ARYL-F-BUTENES [1]

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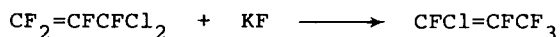
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SUMMARY

A kinetic study of the fluoride ion catalyzed isomerization of a series of 2-aryl-F-1-butenes shows the reactions to be pseudo first order in olefin at constant fluoride ion concentration. The resultant Hammett plot is non-linear with a concave downward break near $\sigma=0$. A two step mechanism involving formation of a carbanionic intermediate is proposed. A change in the rate limiting step causes the break in the Hammett plot. Carbanion trapping experiments are also reported.

INTRODUCTION

The initial investigation of the reaction of fluoride ion with 3,3-dichloro-F-propene demonstrated that the reaction proceeded via attack of fluoride on the difluoromethylene olefinic carbon with an allylic shift of the double bond and elimination of chloride ion [2].

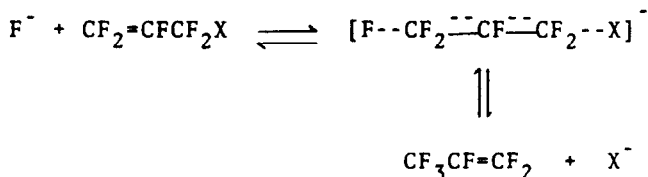


The report of the incorporation of ^{18}F into F-propene that had been passed over alkali metal fluorides containing ^{18}F , also suggested possible displacement of fluoride in an isomerization reaction [3].

Several fluoride ion catalyzed isomerizations have now been observed [4]. Tetraethylammonium fluoride in chloroform

isomerized F-1-heptene to its internal isomers [5]. F-1-Heptene has also been isomerized in the gas phase over alkali or alkaline earth metal fluorides [6]. F-2-Pentyne was isolated in 95% yield from the cesium fluoride catalyzed isomerization of F-1,4-pentadiene [7,8]. The reaction was shown to proceed via F-1,3-pentadiene and F-2,3-pentadiene. Isomerization of 2-phenyl-F-1-butene with fluoride ion yielded cis- and trans-2-phenyl-F-2-butene [9].

The initial proposed mechanism was an SN2' process, implying a concerted attack of fluoride and elimination of halide [2,5], giving transitory existence to a species with

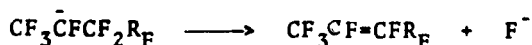
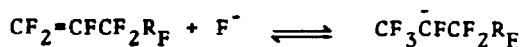


the charge distributed over five atoms.

To date the isomerizations have generally been referred to as proceeding via an SN2' mechanism, although it has not been demonstrated that this type of transition state is involved. Indeed, certain reactions of this type have been shown to involve second order kinetics [2,10]. However, the meager kinetic evidence only indicates that both reacting species are present in the transition state. This does not constitute evidence for a concerted reaction. Slow or reversible formations of an intermediate are equally plausible explanations for the second order kinetics.

The very existence of any SN2' mechanism has been seriously questioned [11]; the major objection is the requirement of nucleophilic attack on an unactivated carbon-carbon double bond. This objection should not be a factor in the fluoroolefin systems, however, due to their known reactivity with a large variety of nucleophiles.

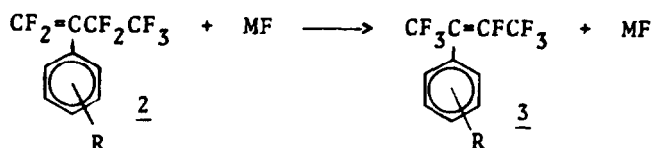
Since the formation of a carbanion from fluoroolefin and fluoride ion is a vital force in synthetic fluoro-organic chemistry, a viable alternative mechanism would be formation of a carbanionic intermediate with subsequent elimination of



halide. Slow or reversible formation of the carbanion would satisfy a second order rate law. The formation of a discrete carbanion in the isomerization has probably received little attention due to the very limited success in trapping carbanions from isomerizable olefins [12,13]. If β -elimination of fluoride from the carbanion occurs at a greater rate than reaction of carbanion with electrophilic substrate, the less reactive internal olefin will be produced.

A third possibility involving a six-membered cyclic transition state has also been suggested for reaction with metal fluorides [9]. This mechanism would display second order kinetics and a high negative entropy of activation.

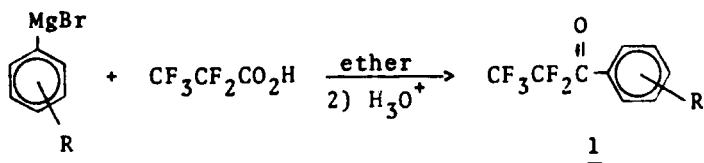
This study was undertaken in an attempt to determine the type of transition state or intermediate that is involved in this type of isomerization. The system chosen for study was the isomerization of 2-aryl-F-1-butene to the corresponding



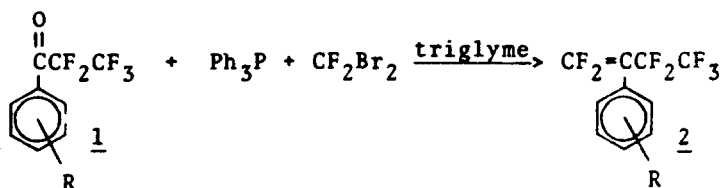
2-aryl-F-2-butene. Thus, a kinetic study of the reaction of several substituted olefins with different R substituents would allow construction of a Hammett plot. The direction and magnitude of the slope of the Hammett plot would indicate the susceptibility of the reaction to substituent effects [14]. In addition, several carbanion trapping experiments were carried out.

RESULTS AND DISCUSSION

The 1-aryl-F-1-propanones (1), needed for the synthesis of the butenes, were prepared from the corresponding aryl Grignard reagent by the literature method [15,16]. The

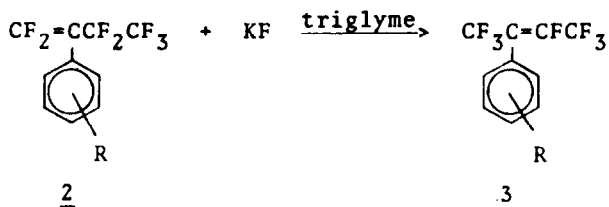


1-aryl-F-1-butenes(2) were then prepared by the method of Naae



and Burton [17]. The ketones(1)and olefins(2) prepared were those with the following substituents: (a) H; (b) 4-CH₃; (c) 3-CH₃; (d) 4-F; (e) 4-Cl; (f) 3-CF₃; (g) 4-CF₃. The compounds were characterized by their spectral properties given in Tables I and II.

The internal olefin isomers were prepared by isomerization of 2 with potassium fluoride in triglyme. This system allowed a convenient rate of reaction that could be monitored by glpc. As soon as the 2-aryl-F-1-butene(2) had been consumed, the reaction was quenched by addition of hydrochloric acid. This procedure gave the trans- and cis-isomers in an approximately 2:1 ratio. If the reaction was not quenched at this time,



equilibration of the isomers occurred to give higher trans/cis ratios that were unsuitable for isolation of the cis-isomer[9].

The olefins were easily separated by glpc on a column of 15% 20M Carbowax on 80-100 mesh Chromasorb P (acid washed) [18].

They eluted in the order: 3(trans), 2, 3(cis). The internal isomers prepared were then isolated by preparative glpc. The trans-CF₃C=CCF₃ interaction (1.1-1.4 Hz) was always less than the corresponding cis coupling (10.1-11.3 Hz). Similarly, the trans-CF₃C=CF couplings (10.1-11.3 Hz) were smaller than the coupling for the cis arrangement (22.6-25.7 Hz). The magnitudes of these couplings are in agreement with literature values for similar interactions [19]. The spectral properties of the trans- and cis-2-aryl-F-2-butenes(3) are given in Tables III and IV, respectively.

The isomerizations were performed in dimethylformamide (DMF). Low temperatures were required to give a convenient rate of reaction. The reactions were carried out as described in the Experimental section and monitored by glpc. Consumption of olefin(2), plotted as ln A vs t (A=area ratio of 2 to internal standard, t in seconds), was found to be linear to complete consumption of the terminal olefin. Since fluoride ion is not consumed in the reaction, the slope of the plot gives k_{ex} , a pseudo first order rate constant.

$$\text{Rate} = k_{ex} [2]$$

Determination of k_{ex} was by a least squares determination of the slope, performed by computer [20]. Estimates of errors were obtained from the program as standard deviation of the fit.

The initial kinetic data was collected using Method A. Two solutions of Et₄NF in DMF were used. The data, collected at -35° is reported in Table V as k_{ex} . The second order rate constants calculated from k_{ex} and the fluoride concentration are also shown. For the cases studied, k_{calc} was within experimental error when fluoride was varied by a factor of 2. This data suggests a first order dependence on fluoride ion and a second order rate law of

$$\text{Rate} = k_{calc} [2] [F^-]$$

Elemental analysis of the Et₄NF used then indicated that it was largely bifluoride, which is much less reactive than fluoride [4]. The two solutions used to collect the data in

TABLE I

Properties of 1-Aryl-F-1-propanones

	Yield %	bp °C (mm)	μ (C=O) -1 cm	Mass Spectral Data m/e (Relative intensity)
<u>1b</u>	34	68(2)	1711	P 238(6), 120(10), 119(100), 91(79), 89(10), 65(27), 63(10)
<u>1c</u>	30	60(1)	1706	P 238(4), 120(10), 119(100), 91(75), 89(11), 65(30), 63(13)
<u>1d</u>	32	54(5)	1727	P 242(4), 124(34), 123(52), 96(21), 95(73), 94(19), 75(100), 74(19), 69(36), 51(15), 50(29)
<u>1e</u>	30	73(5)	1718	P 260(2), 258(5), 141(34), 139(100), 113(18), 111(58), 76(11), 75(36), 74(10), 50(19)
<u>1f</u>	36	64(4)	1731	No P, 273(11), 214(15), 174(10), 173(100), 145(90), 95(15), 75(14)
<u>1g</u>	32	57(4)	1729	No P, 273(30), 174(41), 173(100), 143(36), 145(88), 126(30), 125(43), 95(73), 75(67), 69(30), 50(48)

	^1H NMR δ (ppm)		^{19}F NMR δ^* (ppm)		ArCF ₃ F	
	2,6-H	4,5(3,5)-H	CH ₃	CF ₂		CF ₃
<u>1b</u>	7.8-8.1 m	7.1-7.4 m	2.38 s	116.1 s	82.3 s	
<u>1c</u>	8.1-8.4 m	7.7-7.9 m	2.39 s	115.6 s	81.6 s	
<u>1d</u>	7.9-8.3 m	7.0-7.4 m		116.0 q 1 Hz	82.2 t 1 Hz	100.2 m
<u>1e</u>	7.8-8.2 m	7.2-7.7 m		116.6 q <1 Hz	82.5 t <1 Hz	
<u>1f</u>	8.0-8.4 m	7.4-8.0 m		116.4 q 1 Hz	82.2 t 1 Hz	63.9 s
<u>1g</u>	8.0-8.3 m	7.6-7.9 m		116.5 s	82.1 s	64.3 s

TABLE II

Properties of 2-Aryl-F-1-butenes

	Yield %	bp °C (mm)	ν (C=C) cm ⁻¹	m/e (Relative intensity)	Mass Spectral Data
<u>2b</u>	49	67-68(13)	1721	273(14), 151(20)	P 272(100), 253(13), 203(36), 183(26), 153(16), 133(41), 101(15)
<u>2c</u>	40	65-66(13)	1718	273(13), 153(19)	P 272(100), 253(13), 203(53), 183(41), 182(16), 134(27), 133(58), 101(15)
<u>2d</u>	35	55-55(15)	1721	277(9), 138(27)	P 276(65), 237(12), 207(100), 187(50), 158(24), 137(24), 69(12)
<u>2e</u>	38	95-96(46)	1723	P 294(33), 188(25)	292(100), 257(12), 225(19), 223(56), 203(22), 187(17), 138(30), 75(11), 69(11)
<u>2f</u>	33	52-53(16)	1733	P 326(48), 207(16)	307(28), 287(11), 258(13), 257(100), 237(25), 188(23), 187(29), 169(20), 138(14), 69(19)
<u>2g</u>	35	65-66(13)	1718	P 326(47), 207(13)	307(25), 287(10), 258(12), 257(100), 237(24), 188(22), 187(27), 169(19), 138(14), 69(17)

^1H NMR δ (ppm)	CH_3	^{19}F NMR δ^* (ppm)	$ \begin{array}{c} \text{2 } \text{CF}_2\text{CF}_3 \\ \diagup \quad \diagdown \\ \text{3F} \quad \text{C}=\text{C} \quad \text{Ar} \\ \diagdown \quad \diagup \\ \text{4F} \end{array} $	F^2 , ddq (J_{23} , J_{24})	F^3 , dtq (J_{34})	F^4 , dt	$\text{ArCF}_3(\text{F})$
Ar		F^1 , dt (J_{12} , J_{13})					
<u>2b</u>	7.18 s	2.33 s	84.6 (2.3, 7.5)	111.9 (24.6, 8.1)	75.1 (8.2)	73.8	
<u>2c</u>	7.0-7.3 m	2.33 s	84.3 (2.5, 8.1)	111.6 (25.2, 8.5)	74.9 (8.5)	73.2	
<u>2d</u>	6.8-7.5 m		84.6 (1.9, 6.1)	111.9 (20.5, 6.3)	74.1 (6.2)	72.8	111.7 m
<u>2e</u>	7.1-7.5 m		85.3 (2.2, 7.2)	112.7 (21.1, 8.0)	74.5 (6.1)	73.2	
<u>2f</u>	7.4-7.7 m		84.3 (2.4, 7.6)	111.5 (24.4, 8.1)	72.7 (4.7)	71.3	63.2 s
<u>2g</u>	7.2-7.8 m		84.8 (2.3, 7.5)	112.1 (23.2, 8.0)	73.3 (5.0)	72.2	63.9 s

TABLE III

Properties of trans-2-Aryl-F-2-butenes

	$\mu(\text{C}=\text{C})$ cm ⁻¹	Mass Spectral Data	
		m/e	(Relative intensity)
<u>3b</u>	1700	273(14), P 272(100), 271(17), 253(17), 203(26) 183(39), 134(38), 133(38), 91(15)	
<u>3c</u>	1707	273(13), P 272(100), 253(18), 203(38), 183(54) 134(19), 133(39)	
<u>3d</u>	1706	277(12), P 276(100), 257(23), 237(21), 207(94), 187(89), 138(30), 69(16)	
<u>3e</u>	1705	P 294(35), 292(100), 273(14), 257(12), 225(15), 223(47), 205(11), 203(29), 188(42), 187(28), 169(17), 69(14)	
<u>3f</u>	1702	P 326(78), 307(39), 287(17), 258(13), 257(100), 237(38) 207(13), 188(24), 187(33), 169(30), 164(14), 69(24)	
<u>3g</u>	1707	P 326(78), 307(44), 287(20), 258(12), 257(100), 237(39), 207(12), 188(24), 187(32), 169(31), 164(16), 69(21)	

^1H NMR δ (ppm)	^{19}F NMR ϕ^* (ppm)	Chemical Structure	Ar	CH_3	F^1 , dq (J_{12})	F^2 , dq (J_{23})	F^3 , qq (J_{13})	$\text{ArCF}_3(\text{F})$
7.16 s	61.9 (1.4)			2.37 s	61.9 (1.4)	66.6 (7.7)	116.0 (25.7)	
7.0-7.4 m	61.6 (1.2)			2.35 s	61.6 (1.2)	66.6 (7.3)	116.1 (24.4)	
6.9-7.4 m	61.9 (1.2)				61.9 (1.2)	66.5 (6.6)	114.3 22.8	110.4 m
7.1-7.6 m	61.6 (1.3)				61.6 (1.3)	66.4 (7.5)	113.9 25.6	
7.4-7.8 m	61.5 (1.1)				61.5 (1.1)	66.5 (6.5)	113.3 22.6	63.6 s
7.2-7.8 m	61.4 (1.2)				61.4 (1.2)	66.5 (7.5)	113.7 25.1	63.8 s

TABLE IV

Properties of cis-2-Aryl-F-2-butenes

	μ (C=C) cm ⁻¹	Mass Spectral Data m/e (Relative intensity)
<u>3b</u>	1687	273(19), P 272(100), 271(22), 253(25), 203(38), 183(53), 182(16), 151(17), 134(23), 133(50), 91(18)
<u>3c</u>	1689	273(12), P 272(100), 253(18), 203(36), 183(54), 134(20), 133(40)
<u>3d</u>	1682	277(11), P 276(100), 257(20), 237(20), 207(90), 187(83), 138(25), 69(15)
<u>3e</u>	1695	P 294(32), 292(100), 273(15), 225(16), 223(43), 205(28), 188(33), 187(26), 169(16)
<u>3f</u>	1686	P 326(74), 307(37), 287(18), 258(11), 257(100), 237(36), 207(11), 188(21), 187(27), 169(24), 164(13), 69(18)
<u>3g</u>	1693	P 326(72), 307(37), 287(18), 257(100), 237(33), 188(21), 187(25), 169(27), 69(19)

^1H NMR δ (ppm)	^{19}F NMR δ^* (ppm)		Chemical Structure			
	Ar	CH_3	F^1 , dq (J_{12})	F^2 , dq (J_{23})	F^3 , qq (J_{13})	ArCF ₃ (F)
<u>3b</u>	7.22 s	2.38 s	58.1 (11.2)	66.7 (6.8)	112.7 (11.2)	
<u>3c</u>	7.0-7.4 m	2.38 s	58.2 (11.3)	66.7 (7.0)	112.5 (11.3)	
<u>3d</u>	7.0-7.4 m		58.4 (11.2)	67.3 (6.7)	111.8 (11.2)	110.8 m
<u>3e</u>	7.1-7.6 m		58.1 (10.9)	66.9 (6.5)	111.3 (10.9)	
<u>3f</u>	7.4-7.8 m		58.0 (10.1)	66.8 (6.1)	111.0 (10.1)	63.5 s
<u>3g</u>	7.2-7.8 m		57.9 (11.3)	66.8 (6.7)	110.4 (11.3)	63.7 s

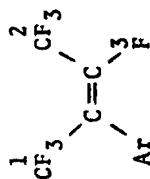


Table V were prepared using the same batch of suspected Et_4NF . The ratio of fluoride between the sets remains the same although the actual fluoride concentration is not known. The difficulty in obtaining pure Et_4NF and its highly hygroscopic nature led to the use of cesium fluoride as a fluoride ion source.

Since cesium fluoride is not greatly soluble in DMF, a saturated solution of CsF/DMF was prepared. To avoid the presence of excess solid cesium fluoride, the supernatant liquid was carefully withdrawn via syringe and stored separately until used. By this Method B, a series of isomerizations were carried out using an aliquot of the solution for each experiment. Three sets of k_{ex} were obtained for several of the olefins from three separate solutions. The k_{ex} s are reported in Table VI. It was found that the agreement was good, indicating that reproducible fluoride concentrations were obtained in the solutions. However, the isomerizations of olefins 2f and 2g were so rapid at -35° that monitoring of the progress of the reaction became difficult.

Thus Method B was abandoned in favor of Method C. Two sets of data from two separate CsF/DMF solutions were collected by Method C. The temperatures for the two sets were slightly different. The k_{ex} s obtained are presented in Table VII. Each k_{ex} represents a plot with 4-5 separate kinetic runs. The k_{ex} s for the two sets agree quite well considering the small difference in temperature.

The k_{ex} s from the -33° data set are plotted in Figure 1 as $\log k_{\text{ex}}$ vs σ . The Hammett plot is non-linear and appears to consist of two separate lines. The line through the four points of lowest σ has a slope (rho value) of 6.7 ± 1.0 . The line through the points of higher σ , exhibits a slope (rho value) of 1.3 ± 0.2 .

A point on each portion of the line (2b and 2e) was then chosen for a temperature study to determine the activation parameters of the isomerizations. Using Method C, triplicate determinations of k_{ex} were made at -23° and -13° , using three separate solutions. The k_{ex} s obtained are presented in Table VIII. The k_{ex} s needed for the study were calculated from the

TABLE V

Method A: Et₄NF/DMF

R	[Et ₄ NF] M	k _{ex} (std. dev.) sec ⁻¹	k _{calc} lit/mole/sec
4-CH ₃ (2b)	0.009	1.74 x 10 ⁻⁶ (0.08)	1.93 x 10 ⁻⁴
	0.020	3.04 x 10 ⁻⁶ (0.11)	1.52 x 10 ⁻⁴
4-CF ₃ (2g)	0.009	5.93 x 10 ⁻⁴ (0.94)	6.59 x 10 ⁻²
	0.020	3.87 x 10 ⁻³ (0.46)	1.93 x 10 ⁻¹

TABLE VI

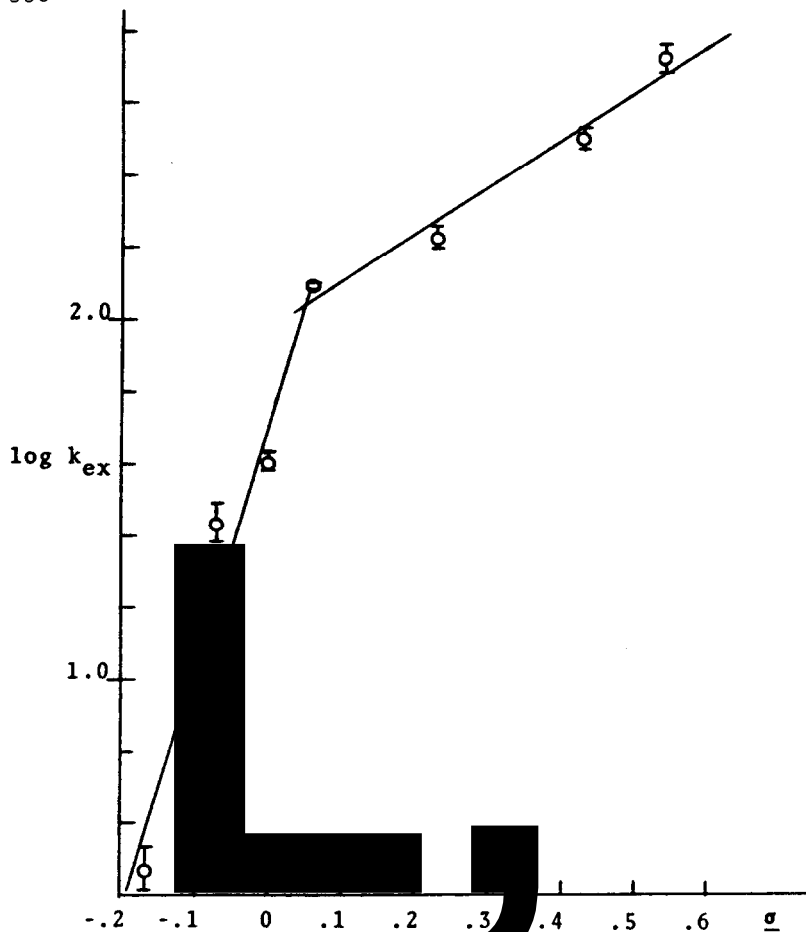
Method B: CsF/DMF

R	Temp.	k _{ex} x 10 ⁴ (std. dev.) sec ⁻¹		
		-35°	-35°	-33°
4-CH ₃		1.95(0.25)	0.93(0.07)	3.27(0.32) 3.98(0.26)
3-CH ₃		15.0(3.3)	9.45(0.30)	33.7(4.5) 31.3(2.7)
-H		15.2(1.5)	9.67(0.74)	
4-F			16.2(1.0)	164(7.0)
4-Cl		128(7.0)	132(31) 93.0(21)	

TABLE VII

Method C: CsF/DMF

R	Temp.	k _{ex} x 10 ⁴ (std. dev.) sec ⁻¹		
		-35°	-33°	-33°
4-CH ₃		1.79(0.03)	2.97(0.39)	4.33
3-CH ₃		12.6(2.0)	27.0(3.0)	
-H		19.2(2.4)	40.0(2.3)	
4-F		62.1(9.9)	124(3.0)	
4-Cl		106(7.0)	167(12)	270(28)
3-CF ₃		163(5.1)	317(20)	
4-CF ₃			526(48)	

Fig.1 Hammett Plot: Log k_{ex} vs σ TABLE VIII
Method C: CsF/DMF Temperature Study

Temp.	$k_{ex} \times 10^3$ (std. dev.) sec ⁻¹	$k_{ex} \times 10^2$ (std. dev.) sec ⁻¹
	-23°	-13°
4-CH ₃	0.93(0.11)	0.30(0.03)
	0.92(0.11)	0.33(0.02)
	2.18(0.43)	0.49(0.05)
4-Cl	44.4(4.1)	11.3(2.0)
	41.5(1.9)	9.2(0.9)
	55.1(4.6)	14.3(2.2)

second order rate law. The fluoride ion concentration in each solution was determined spectrophotometrically [21]. It was found to be identical for all the solutions, being $7.9 \times 10^{-4} \text{M}$.

$$\text{Rate} = k_{\text{calc}} [2] [\text{F}^-]$$

$$= k_{\text{ex}} [2]$$

$$k_{\text{calc}} = k_{\text{ex}} / [\text{F}^-]$$

The activation parameters were determined by use of the absolute rate equation [22]. Thus, a plot of $\ln k_2/T$ vs $1/T$ will yield a line of slope = $-\Delta H^\ddagger/R$ and intercept = $\Delta S^\ddagger/R + \ln k/h$.

$$k_2 = \frac{kT}{h} \exp \frac{-\Delta H^\ddagger}{RT} \exp \frac{\Delta S^\ddagger}{R}$$

$$\ln \frac{k_2}{T} = \frac{-\Delta H^\ddagger}{R} \frac{1}{T} + \frac{\Delta S^\ddagger}{R} + \ln \frac{k}{h}$$

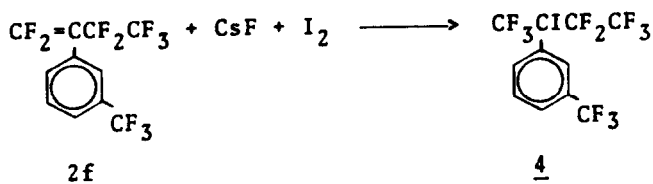
The data was least squares fit by computer [23] and gave the following results with computer estimates of the standard deviation of the fit: 2b, $\Delta H^\ddagger = 14.0(1.9)$ kcal/mole, $\Delta S^\ddagger = -1.3(3.9)$ eu; 2e, $\Delta H^\ddagger = 10.0(1.2)$ kcal/mole, $\Delta S^\ddagger = -9.9(2.4)$ eu.

During the isomerizations the trans/cis ratios were also monitored. The ratio was observed to increase slowly throughout the isomerization of 2. Plots of the trans/cis ratio vs time (as half lives of the isomerization) were found to be linear through 10-12 half lives. The ratio then leveled off to an equilibrium value. Equilibrium was reached over a period of time corresponding to 15-17 half lives of the isomerization. The values of the trans/cis ratios at equilibrium and extrapolated to time zero are presented in Table IX.

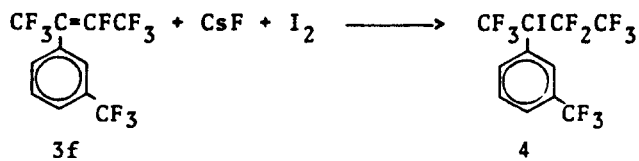
Several experiments were carried out in an attempt to chemically trap a carbanion intermediate. 2-[3-(F-Methylphenyl)]-F-1-butene(2f) was used in most of these reactions, due to its greater reactivity with fluoride ion. When the isomerization was carried out with cesium fluoride in triglyme or DMF in the presence of excess iodine, nearly quantitative yields of the carbanion trapping product were formed. However, it was found that the trapping product was formed equally

TABLE IX
trans/cis Ratios of 2-Aryl-F-2-butenes

R	t ₀	Equilibrium
4-CH ₃	3.1	9.9
3-CH ₃	2.7	8.1
-H	2.8	9.3
4-F	3.7	9.8
4-Cl	3.7	9.6
3-CF ₃	4.6	8.4
4-CF ₃	3.8	7.6



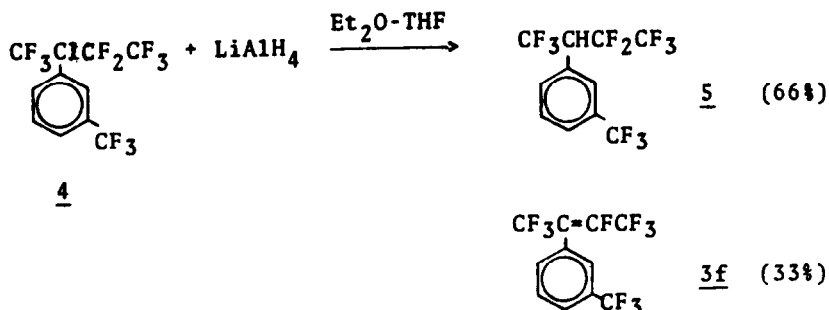
as well by the addition of iodine to the mixture after isomerization was complete. These reactions took place readily at



room temperature.

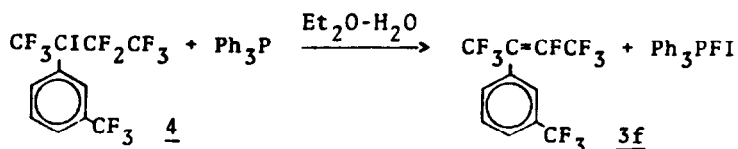
The 2-iodo-2-[3-(F-methyl)phenyl]-F-butane(4) that was formed was not thermally stable. Attempted distillation or analysis by glpc gave only evidence of the trans-and cis-2-aryl-F-2-butenes(3f). The iodide was extracted into ether, and the excess iodine was destroyed with sodium bisulfite. It was best to use cold aqueous bisulfite, since the heat generated led to some decomposition of the aryl iodide. The individual fluorines of the CF₂ group in 2-iodo-2-[3-(F-methyl)phenyl]-F-2-butane(4) were nonequivalent. The two fluorines absorbed at 98.4 ppm and 103.7 ppm; a geminal fluorine-fluorine coupling constant of 282 Hz was observed.

The iodide was further characterized by its reaction with lithium aluminum hydride (LiAlH_4). Reaction of an ether solution of the iodide with LiAlH_4 led to 5 in 66% yield. The 2-aryl-F-2-butenes(3f) were also observed (33%) by ^{19}F NMR. 2-Hydril-2-[3-(F-methyl)phenyl]-F-butane(5) was isolated by preparative glpc and identified by its IR, ^1H and ^{19}F NMR and mass spectral data.

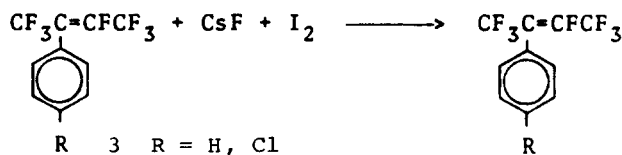


The ^{19}F NMR spectrum also showed the non-equivalency of the CF_2 fluorines. The geminal fluorine-fluorine coupling was 256 Hz. The ^1H NMR exhibited a doublet-doublet-quartet signal at δ 4.12 ppm consistent with the assigned structure. A molecular ion (m/e 346, 41% of base) was observed in the mass spectrum. The IR showed no olefinic unsaturation.

The iodide was rapidly dehalogenated by triphenylphosphine to yield the 2-aryl-F-2-butenes. In the presence of water, the reaction again yielded the olefins.

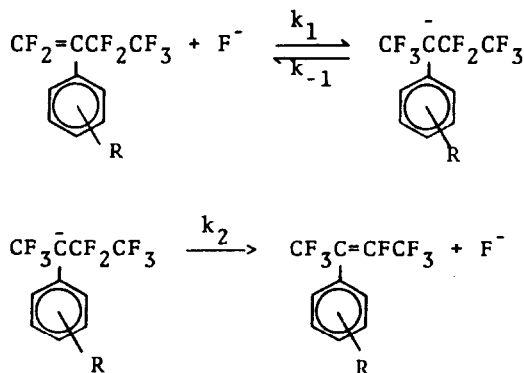


Attempts to prepare a similar iodide by reaction of cesium fluoride and iodine with 3a and 3e were unsuccessful. Only the internal olefin isomers were observed.



Only isomerization to 3f was observed from reactions of 2f with fluoride ion and methyl iodide, dimethylcarbonate or carbonyl fluoride. Although some consumption of olefin was observed, no volatile products were formed. Extended reaction of 3f also failed to give carbanion trapping products.

The kinetic data is consistent with a two step mechanism which involves formation of a reaction intermediate. A carbanionic intermediate is proposed. A slow or reversible formation of the intermediate is consistent with the overall second order kinetics of the reaction. The non-linear Hammett plot also indicates formation of an intermediate, with a change in the rate limiting step across the series 2a-2g [24].



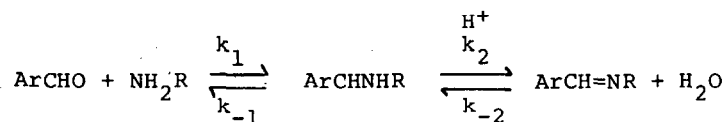
Two possibilities need to be considered. If the formation of the intermediate is rate determining ($k_2 > k_1$), then $k = k_1$. If the second step of the mechanism (β -elimination of fluoride) is rate limiting, then $k = k_1 k_2 / (k_{-1} + k_2)$.

The following interpretation of the Hammett plot is proposed. When the R substituent is hydrogen or electron donating ($\sigma \leq 0$), the formation of the intermediate is rate limiting. Thus $k_{\text{ex}} = k_1 [\text{F}^-]$ and the Hammett rho value in this region

should indicate the degree of bond formation and bond breaking that has occurred in the intermediate. The very high positive value of rho (+6.7) indicates that bond formation far exceeds bond breaking in the intermediate. The fact that rho is positive shows that the formation of the intermediate is favored by electron withdrawal. Thus the rho value favors formation of a high degree of negative charge on the benzylic carbon atom in the intermediate. The rho value can be compared with those obtained from studies of other benzylic carbanions; that is a +4.0 rho value in the deuterium-hydrogen exchange of 2-hydril-2-aryl-F-propanes [25] and the detritration of α -tritiotoluenes [26].

When R is electron withdrawing ($\sigma > 0$), k_2 becomes rate limiting. Since k is now a composite of several rate constants ($k = k_1 k_2 / (k_{-1} + k_2)$), the significance of the rho value is much less obvious. The effect of σ on k will be determined by its relative effects on k_1 , k_{-1} , and k_2 . The rho value of +1.3 simply implies that the isomerization is accelerated by electron withdrawal, although the effect is greatly subdued compared to the $\sigma \leq 0$ cases.

A non-linear Hammett plot with a concave downward break has been interpreted as a change in the rate-determining step [24,27,28,29,30,31]. In the formation of semicarbazones from benzaldehydes, the proposed mechanism involves reversible formation of an adduct followed by acid catalyzed dehydration. The



equilibrium constant ($K = k_1/k_{-1}$) and k_2 was determined at neutral pH. The rho value for K was +1.81 and for k_2 , -1.74. The overall rate constant was a composite given by $k = k_2 K$ and a rho value of +0.07 was observed, indicating virtual cancellation of the substituent effects. When the pH was lowered to 1.75, k_1 became rate limiting and a rho of +0.91 was obtained. At the intermediate pH of 3.9, a break in the Hammett plot occurred near $\sigma = 0$. A shift in the rate determining step was proposed [30].

Other examples include reaction of aromatic aldehydes with *n*-butylamine to form Schiff bases [28] and the cyclodehydration of 2-phenyltriarylcarbinols [31]. These cases give Hammett plots in which ρ changes from positive to negative as σ increases. They are interpreted as an indication of two step mechanism with a shift in the rate limiting step.

The effects of the substituents on the k 's are easily rationalized. An increase in σ (greater electron withdrawal from the system) will increase the susceptibility of the olefin to nucleophilic attack and serve to increase k_1 . By the same token, k_{-1} and k_2 will be decreased since the anionic intermediate will be stabilized relative to a substituent of less positive σ . Thus in the cases of $\sigma \leq 0$ (e.g. 4-CH₃), rate limiting attack occurs at the terminal carbon to form a carbanion. The presence of an electron donating substituent on the ring causes a relative destabilization of the anion which rapidly β -eliminates fluoride ion, with formation of the more stable internal isomers. When $\sigma > 0$ (e.g. 4-CF₃), the already activated double bond is made even more electrophilic by the presence of an electron withdrawing substituent on the phenyl ring. This not only increases the rate of fluoride attack, but produces a carbanion that is stabilized by the same electron withdrawal. This stabilization reduces the driving force for β -elimination, with a subsequent reduction of its rate. The break in the Hammett plot then occurs at the point where k_1 is no longer rate limiting.

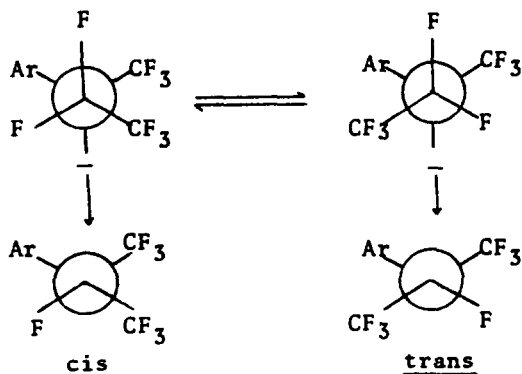
The alternative explanation for a non-linear Hammett plot is a change in mechanism. However a shift in mechanism, as opposed to a shift in the rate limiting step, introduces a new reaction path and results in a rate minimum (i.e. Hammett plot concave upward) [24,27].

The high positive ρ value at $\sigma < 0$ and the much lower ρ value for $\sigma > 0$ might suggest a change in mechanism from anion formation to an SN2' process. The ρ values might be expected to be consistent with the amounts of bond making and bond breaking that has taken place in the intermediate and transition state involved. This possibility is discarded since it is totally inconsistent with the Hammett plot required for a change in mechanism. If such a system was involved, it is ex-

pected that the roles would be reversed. That is, anion formation at high ρ and the SN2' process at low ρ . Indeed, this would then yield a concave upward Hammett plot.

The nearly zero entropy of activation for the isomerization of 2b argues against formation of a highly ordered SN2' or cyclic transition state. Reactions that have been classified as SN2' substitutions generally exhibit ΔS^\ddagger in the range of -20 to -43 eu [32]. A more highly negative ΔS^\ddagger would also be expected for a cyclic transition state [33]. What ΔS^\ddagger might indicate is that cesium fluoride is still appreciably associated in DMF. Freedom created by breakage of the double bond of the olefin may be compensated by increased solvent ordering around the now free cesium ion. The activation entropy for 2e was determined from k_{calc} , which is a composite of several rate constants. It does not indicate entropy changes in the formation of a transition state leading to the intermediate.

The initial trans/cis ratios are kinetic ratios of products. They show that β -elimination of fluoride to form the trans olefin is 2.7-4.6 times faster than elimination to form the cis olefin. Assuming the energetically more favorable trans elimination [9], it is easily seen from the Newman projections why the kinetic ratio favors formation of the trans olefin. Elimination to the cis isomer requires the bulky F-methyl groups in a gauche arrangement. Rotation moves the F-methyls into a lower energy anti arrangement. The observation that the kinetic ratio for phenyl substituents of $\rho \leq 0$ are generally lower than for $\rho > 0$ probably indicates decreased selectivity due to decreased stability of the anion.

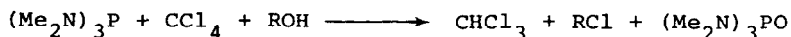


The trans/cis ratios increased steadily throughout the isomerization. Apparently the internal isomers can compete effectively for the fluoride ion present. At seven half-lives of the isomerization (99% reaction), the ratios were 55-75% of the equilibrium values, increasing with increasing σ . This shows that increasing σ apparently has a greater effect on equilibration than it has on the isomerization. This would indicate a shift back to rate controlling fluoride attack in the equilibration reaction. The steadily increasing ratio was not observed when the isomerization was carried out with potassium fluoride in diglyme [9]. In that system the initial ratio did not increase appreciably during the isomerization. Prolonged reaction times were required to effect equilibrium. This is probably a manifestation of the marked decrease in reactivity of this system. The greatly decreased reactivity is shown by the isomerization requiring 4 hours at 100° [9].

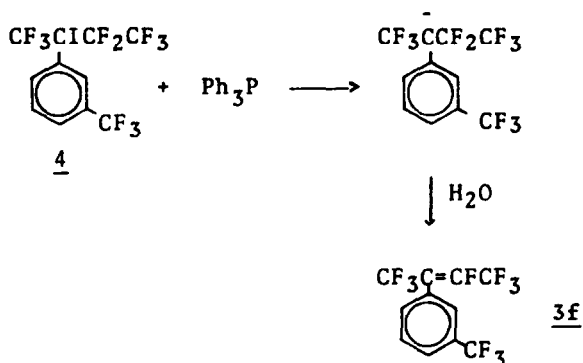
The equilibrium trans/cis ratios simply reflect the relative thermodynamic stabilities of the two isomers. These stabilities are best explained by electrostatics repulsion of the large F-methyl groups.

The successful reaction of 3f with fluoride and iodine shows that an anion is generated of sufficient lifetime to allow its reaction with substrate. The fact that the anions could not be trapped from 3a or 3e most likely indicates that β -elimination from the anion is more rapid than reaction of the anion. This supports the position that k_{-1} and k_2 would be decreased by an increase in σ .

The reactions of phosphines with highly activated halogen compounds have been shown to proceed via abstraction of positive halogen and formation of a carbanion [34,35]. The dehalogenation of 4 by triphenylphosphine in the presence of water



would be expected to proceed similarly. The failure of the anion generated to be protonated by water indicates a very facile β -elimination. However, in this system, the β -elimination of fluoride may be greatly aided by formation of the phosphorus-fluorine bond.



The corresponding anion from F-2-butene has been successfully reacted with carbonyl fluoride [36] and with the nitrogen containing F-aromatics [37]. The markedly decreased reactivity of the anions from 3 apparently reflects the decreased nucleophilicity of the anion by withdrawal of electron density into the ring. The anions from 3 that would be expected to be most nucleophilic (those of low σ), exhibit too short a lifetime to react with an electrophile.

EXPERIMENTAL

The melting points were obtained in capillary tubes and are corrected. The boiling points are uncorrected. They were determined during fractional distillation by means of a partial immersion thermometer. Boiling points of known compounds were in good agreement with reported values. The infrared spectra were recorded on either a Perkin-Elmer Model 21 or a Beckman IR 20-A spectrophotometer using a neat film between sodium chloride plates. ¹H NMR spectra were recorded on a Varian A-60 NMR spectrometer. Tetramethylsilane (TMS) was employed as an internal reference. Chemical shifts are reported in δ values downfield from TMS. ¹⁹F NMR spectra were obtained with a Varian HA-100 NMR spectrometer operated at 94.075 MHz. Chemical shifts are reported in ϕ^* values upfield from the fluorotrichloromethane standard. Area ratios were determined by cutting out and weighing the peaks from a photocopy of the spectrum. Mass spectra were obtained with a Hitachi-Perkin-Elmer RMU-6E mass spectrometer. Analysis by

glpc was performed on a Hewlett-Packard 5750 dual column chromatograph equipped with thermal conductivity detectors. Helium was used as the carrier gas. Column A was a 10 ft x 0.25 in copper column packed with 15% w/w 20M Carbowax on 80-100 mesh Chromasorb P. Column B was a 10 ft x 0.5 in stainless steel column of 30% w/w 20M Carbowax on 100-200 mesh Chromasorb P. Fluoride analysis was carried out with a Cary Model 11 Recording Spectrophotometer by preparing a standard curve, measuring the absorbance of solutions of known fluoride concentration containing Amadac-F concentrate (Burdick and Jackson). The unknown fluoride solution (2.0 ml) was diluted to 50.0 ml with 5.0 ml of Amadac-F concentrate and water and the absorbance compared to the standard curve [21]

Materials

Triglyme (Ansul Ether 161) was dried by distillation at reduced pressure from a sodium-benzophenone ketyl. Dimethylformamide was stirred for several days over barium oxide, decanted from the excess oxide under a nitrogen atmosphere and fractionally distilled. The DMF was then stored over Type 4A molecular sieve under nitrogen. Potassium fluoride (Baker Anhydrous) was used as purchased. Cesium fluoride (Ozark Mahoning) was vacuum dried at room temperature and stored over phosphorus pentoxide in a desiccator.

Tetraethylammonium Fluoride

$\text{Et}_4\text{N}^+\text{OH}^-$ (25% in water) was neutralized and made acidic (pH 2) with 48% HF. Most of the water was removed on a rotary evaporator and the syrup dissolved in methylene chloride. Excess lithium hydride was added and the mixture filtered via a nitrogen pressure apparatus. Evaporation of the methylene chloride from the filtrate provided the hygroscopic Et_4NF , mp 110-112° (reported for Et_4NF , 115-116°) [5].

Anal. Calcd for $\text{C}_8\text{H}_{20}\text{NF}$: C, 64.37; H, 13.39; N, 9.39.
 Found: C, 56.32; H, 13.18; N, 8.25. Calcd for $\text{C}_8\text{H}_{21}\text{NF}_2$: C, 56.75; H, 12.53; N, 8.27.

Preparation of F-Alkylketones(1)

The ketones were prepared from the Grignard reagent and the corresponding acid by the method of Dishart and Levine [15], modified by Herkes and Burton [16]. 1-Phenyl-F-1-propanone, 44% yield, bp 49-50° (5 mm) was previously reported (literature 62-63° (22 mm)) [16]. Properties of the 1-aryl-F-1-propanones are summarized in Table I.

Preparation of 2-Aryl-F-1-butenes(2)

The 2-aryl-F-1-butenes were prepared by the method of Naae and Burton [17]. 2-Phenyl-F-1-butene was isolated in 47% yield, bp 49-50° (15 mm) (literature bp 138-139(737)) [16]. Properties of the butenes are reported in Table II.

Preparation and Isolation of cis- and trans-2-Aryl-F-2-butenes(3)

To potassium fluoride slurried in 5 ml of triglyme was added one ml of the corresponding 2-aryl-F-1-butene. The isomerization was monitored by glpc (Column A), observing the loss of terminal olefin and the consequent appearance of the internal isomers. When the isomerization was complete, the reaction was quenched with 5 ml 3N HCl. Quenching at this time gave trans/cis ratios of 1.5-2 [9]. Longer reaction times gave higher trans/cis ratios. The products were extracted into 10 ml of diethyl ether and the ether extract washed with two equi-volume portions of water. The ether solution was dried over Type 4A molecular sieve, most of the ether removed by distillation and the isomeric olefins isolated by preparative glpc (Column A). The isomers were identified by IR, ¹H and ¹⁹F NMR and mass spectral analysis. The spectral properties of the trans- and cis-2-aryl-F-2-butenes are reported in Tables III and IV, respectively. Trans- and cis-2-phenyl-F-2-butenes have been previously reported [9] and were identified in this study by comparison of the IR, ¹H and ¹⁹F NMR spectra with those of the authentic materials.

Isomerization of 2-Aryl-F-1-butenes(2) with Tetraethylammonium Fluoride in Dimethylformamide(DMF): Method A

A solution of $\text{Et}_4\text{NF}/\text{DMF}$ was prepared by transferring Et_4NF to a preweighed 100 ml volumetric flask in a dry nitrogen atmosphere. Determination of the gross weight was followed by addition of 1.0 ml of chlorobenzene internal standard and dilution to the mark with DMF while at the required reaction temperature. The stock solution was stored at the reaction temperature.

The apparatus used involved a 125 ml two neck glass reaction vessel with septum port, a mechanical stirrer and a nitrogen inlet. The apparatus was thoroughly cleaned, oven dried, assembled while hot and flushed with dry nitrogen. Then, 10 ml of the $\text{Et}_4\text{NF}/\text{DMF}$ solution was syringed into the vessel. The vessel was then submerged in a Wilkins-Anderson Co. Lo-Temp Bath at the desired temperature. After allowing 20 minutes for temperature equilibration, 0.10 ml of the olefin was syringed into the vigorously stirred mixture.

The reaction was monitored by withdrawal of 0.25 ml of the mixture into a syringe which contained 0.25 ml of 3N HCl, thereby quenching the aliquot. This aliquot was stored in a capped vial until 0.25 ml of hexane was added and the mixture vigorously shaken. After separation into two phases, the hexane layer was analyzed by glpc (Column A) vs the chlorobenzene internal standard.

Isomerization of 2-Aryl-F-1-butenes with Cesium Fluoride in Dimethylformamide(DMF): Method B

Cesium fluoride was stirred with 100 ml of DMF at room temperature for 24 hours. After standing for one hour, 80 ml of supernatant liquid was withdrawn via syringe and stored under nitrogen. In a kinetic experiment, 5.0 ml of this solution was combined with 0.05 ml of chlorobenzene in the apparatus described for Method A. Addition of 0.05 ml of olefin initiated the reaction, which was monitored and analyzed as previously described.

Isomerization of 2-Aryl-F-1-butenes with Cesium Fluoride in
Dimethylformamide (DMF): Method C

Cesium fluoride was stirred with DMF at room temperature for 24 hours. The solution was allowed to stand for one hour, the excess cesium fluoride settling to the bottom. The supernatant liquid was then withdrawn via syringe and stored under nitrogen in a tightly septum capped bottle.

For a kinetic run, 2.0 ml of the solution was placed in the apparatus used in Method A. After allowing at least 20 minutes for temperature equilibration, 0.05 ml of an equi-volume mixture of the olefin and chlorobenzene was injected into the reaction solution. At the appropriate time, 0.3 ml of 3N HCl was injected to quench the isomerization. A 0.5 ml aliquot of the quenched mixture was then placed in a vial with 0.5 ml of water. Addition of 0.5 ml of hexane was followed by glpc analysis (Column B) of the hexane layer. The procedure was then repeated using the same olefin-chlorobenzene mixture.

Reaction of 2-[3-(F-Methyl)phenyl]-F-1-butene (2f) with Cesium
Fluoride and Iodine

To a stirred solution of 6.3 g (41 mmole) of cesium fluoride and 15.1 g (59 mmole) of iodine in 15 ml of triglyme was added 7.6 g (23 mmoles) of 2f. After 24 hours at room temperature, ^{19}F NMR analysis of the reaction mixture indicated that the olefin had been consumed, and the observed ^{19}F NMR signals were assigned to 2-iodo-2-[3-(F-methylphenyl)-F-butane (4) as follows: (1) ϕ^* 59.2 (3F, CF_3CI complex m), (2) ϕ^* 98.4 (1F, CFF , d 282 Hz to F^3 , q 6.3 Hz to F^1), (3) ϕ^* 103.7 (1F, CFF , d to F^2 , q 9.1 Hz to F^1), (4) ϕ^* 76.0 (3F, CF_3CF_2 , q 5.7 Hz to F^1), (5) ϕ^* 62.8 (3F, CF_3Ar , s). Attempted flash distillation of 4 from the reaction mixture (0.5 mm) yielded a ~ 50:50 mixture of 4 and cis- and trans-3f. The reaction mixture from a similar reaction was poured into cold sodium bisulfite solution and stirred until the iodine color disappeared. The product was extracted into 60 ml diethyl ether, the ether extract washed with two equal volume portions of water and

dried over Type 4A molecular sieve. After removal of the ether by distillation, attempted distillation of the product at reduced pressure (1 mm) led only to recovery of the internal olefins.

Reaction of 2-Iodo-2-[3-(F-methyl)phenyl]-F-butane(4) with Lithium Aluminum Hydride

An ether solution of 4 was prepared as described in the preceding section. To 6 ml of ether solution of 4 at 0° was slowly added one ml of 1.8M lithium aluminum hydride in tetrahydrofuran. When addition was complete, the mixture was allowed to warm to room temperature. ¹⁹F NMR analysis after 4 hours revealed a 33% yield of cis- and trans-3f and a 66% yield of 2-hydril-2-[3-(F-methyl)phenyl]-F-butane(5). 5 was isolated by preparative glpc on Column B: mass spectrum, m/e (relative intensity), P 346(41); 327(21), 307(14), 277(9), 257(12), 227(100), 208(13), 177(64), 69(8); IR (neat) 1455(w), 1325(s), 1250-1130(s), 1097(m), 1087(m), 1022(m), 927(w), 846(w), 798(m), 742(w), 707(s), 670(w); ¹H NMR (CDCl₃) δ 4.12 (1 H, CH, q 8 Hz to F¹, d 9 Hz to F², d 18 Hz to F³), δ 7.5-7.8 (4 H, Ar, m); ¹⁹F NMR (CDCl₃) (1) φ* 63.4 (3 F, CF₃CH, complex m), (2) φ* 115.0 (1 F, CFF, d 256 Hz to F³, q 12.6 Hz to F¹, d to H), (3) φ* 119.9 (1 F, CFF, q 7.5 Hz to F¹, d to F², d to H), (4) φ* 82.7 (3 F, CF₃CF₂, q 1.3 Hz to F¹); (5) φ* 63.5 (3 F, ArCF₃, s).

Reaction of 2-Iodo-2-[3-(F-methyl)phenyl]-F-butane(4) with Triphenylphosphine

An ether solution of 4 was prepared as previously described. The ether solution was added to triphenylphosphine in an NMR tube. Rapid formation of a precipitate was observed. ¹⁹F NMR analysis showed a 70% yield of 3f (cis and trans) vs an internal standard (C₆F₆). Addition of 3 ml of an ether solution of 4 to 5 ml of triglyme containing 2.0 g (7.5 mmoles) triphenylphosphine and 0.3 g (17 mmoles) of water resulted in formation of 3f (cis and trans). No 5 was formed.

Reaction of 2-[3-(F-Methyl)phenyl]-F-2-butene with Cesium Fluoride and Iodine

To 0.7 g (4.5 mmoles) of cesium fluoride slurried in one ml of triglyme was added 0.3 g (one mmole) of 2f. After allowing sufficient time for isomerization to be complete, 1.0 g (4.0 mmoles) of iodine was added. After 4 hours, ^{19}F NMR analysis showed a small amount of 3f (trans) remaining with nearly quantitative formation of 4.

1.6 g (4.8 mmoles) of 2f was added to a slurry of cesium fluoride in 5 ml of dimethylformamide. When isomerization was complete, 2.7 g (10 mmoles) of iodine was added. Subsequent ^{19}F NMR analysis showed no 3f present and a 98% yield of 4 vs an internal standard (C_6F_6).

Reaction of 2-(4-Chlorophenyl)-F-2-butene(3e) with Cesium Fluoride and Iodine

Isomerization of 0.33 g (1.1 mmole) of 2e in cesium fluoride-triglyme followed by addition of iodine did not produce the corresponding iodide. Only 3e (cis and trans) were observed by ^{19}F NMR. Heating had no effect on the reaction.

Reaction of 2-Phenyl-F-2-butene (2a) with Cesium Fluoride and Iodine

Reaction of 0.17 g (0.66 mmole) of 2a with 0.15 g (1.0 mmole) of cesium fluoride in one ml of triglyme followed by addition of 0.3 g (1.2 mmoles) of iodine led only to the formation of 32 (cis and trans). Extended heating at 60° had no effect.

Reaction of 2-[3-(F-Methyl)phenyl]-F-1-butene(2f) with Tetraethylammonium Fluoride and Dimethylcarbonate

In 20 ml of DMF were combined 2.2 g (15 mmoles) of tetraethylammonium fluoride, 1.4 g (15 mmoles) of dimethylcarbonate and 3.3 g (10 mmoles) of the olefin. After heating at 50° for

34 hours, glpc analysis (Column A) showed no consumption of dimethylcarbonate. Isomerization of 3f was observed with a 30% loss of olefin. No other volatile products were observed.

Reaction of 2-[3-(F-Methyl)phenyl]-F-1-butene(2f) with Tetraethylammonium Fluoride and Methyl Iodide

Combined in 15 ml of DMF were 2.1 g (10 mmoles) of tetraethylammonium fluoride, 1.4 g (10 mmoles) of methyl iodide and 1.6 g (5.0 mmoles) of the olefin. Heating the mixture to 50-60° for 48 hours led to isomerization to 3f with a 30% loss of the olefins. No other volatile products were observed by glpc (Column A).

Reaction of 2-[3-(F-Methyl)phenyl]-F-2-butene(3f) with Cesium Fluoride and Carbonyl Fluoride

Into a 500 ml stainless steel pressure vessel was charged 1.9 g (12 mmoles) of cesium fluoride, 7.6 g (23 mmoles) of the olefins and 5 ml of acetonitrile. The vessel was sealed, cooled in liquid nitrogen and 14 g (212 mmoles) of carbonyl fluoride condensed into the vessel. After warming to room temperature, the vessel was heated to 50° for 10 hours and at 100° for 40 hours. The pressure vessel was then cooled to 0° and vented. ¹⁹F NMR analysis of the vessel contents showed only the presence of the original olefins.

ACKNOWLEDGEMENTS

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