ELECTROPHILICITY OF PERFLUOROISOBUTYLENE AND

METHYL PERFLUOROMETHACRYLATE

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Methyl perfluoromethacrylate (I) reacts with nucleophiles (alcohol, trimethyl phosphite, DMF, peracids*) more rapidly than perfluoroisobutylene (II) [1]. Even weakly nucleophilic carboxylic acids readily add to ester (I) in the absence of base catalysts [1], whereas with (II) this reaction proceeds only in the presence of a tertiary amine [3]. These facts together with the unusual cleavage of the phosphoranes (RO)₃PFCF = C(CF₃)CO₂R on heating have been attributed to the greater electrophilicity of the β carbon in the CF = C-CO₂R system by comparison with CF = C-CF₃ [1].

The greater ease of the reactions of (I) can, in principle, be accounted for by at least three factors: 1) the higher positive charge on the carbon of the CF_2 group; 2) the greater stabilization of the carbanion by the COOR group relative to CF_3 ; and 3) "intramolecular base catalysis" [1]. Here we describe attempts to clarify the causes of the differences in reactivity of ester (I) and olefin (II) by physical and theoretical methods.

The ¹³C chemical shifts of the equivalent C atoms in (I) and (II) (Table 1) are almost identical; i.e., the method is not sensitive enough to measure the differences in electron density distribution in these molecules.

We would expect to find correlations between the charge on the β carbon in (I) and (II) and the acceptor properties of the CF =C(CF₃)CO₂R and CF =C(CF₃)₂ units toward the benzene ring. We therefore recorded the ¹⁹F NMR spectra of the appropriate meta- and para-substituted fluorobenzenes (IIIb, c) and (IVb, c), prepared by reactions of (I) and (II) with arylmagnesium bromides:

$$\begin{array}{rl} \mathrm{CF}_2 = \mathrm{C}(\mathrm{CF}_3)\mathrm{CO}_2\mathrm{Me} + \mathrm{YC}_6\mathrm{H}_4\mathrm{MgBr} \rightarrow \mathrm{YC}_6\mathrm{H}_4\mathrm{CF} = \mathrm{C}(\mathrm{CF}_3)\mathrm{CO}_2\mathrm{Me} \\ & (\mathrm{III}) \end{array}$$

$$\begin{array}{r} \mathrm{Y} = \mathrm{H} \ (\mathrm{IIIa}), \ m\text{-}\mathrm{F} \ (\mathrm{IIIb}), \ p\text{-}\mathrm{F} \ (\mathrm{IIIc}). \end{array}$$

$$\mathrm{CF}_2 = \mathrm{C} \ (\mathrm{CF}_3)_2 + \mathrm{YC}_6\mathrm{H}_4\mathrm{MgBr} \rightarrow \mathrm{YC}_6\mathrm{H}_4\mathrm{CF} = \mathrm{C} \ (\mathrm{CF}_3)_2 \\ & (\mathrm{II}) \end{array}$$

$$\begin{array}{r} \mathrm{Y} = \mathrm{H} \ (\mathrm{IVa}), \ m\text{-}\mathrm{F} \ (\mathrm{IVb}), \ p\text{-}\mathrm{F} \ (\mathrm{IVc}) \end{array}$$

Table 2 summarizes the fluorine chemical shifts in the fluorophenyl substituents of (IIIb, c) and IVb, c), together with the substituent constants σ_I and σ_R calculated from Eqs. (1) and (2) [4]:

$$\sigma_I = \frac{0.6 - \delta_m}{7.1} \tag{1}$$

$$\sigma_R = \frac{\delta_m - \delta_p}{29.5} \tag{2}$$

The negative inductive effect of the CF_3 group is known to be stronger than that of the CO_2R group whereas its resonance effect is weaker.⁺ Thus σ_T of the CF_3 and CO_2Et groups is

*In contrast to the normal Prilezhaeva reaction [2] the peracid acts as a nucleophile in the epoxidation of ester (I) [1].

+The electronic effects of fluorine-containing units have been reviewed [5].

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Com- pound		CF		F: CX		CF3		со	Me	
	x	8	J	8	J	8	J	8	8	J
(I) (II)	CO2Me CF3	160 dd 159t	305, 314 307	85 m 85 tt	19.1 36,8	120 q 120 q	270 271	158 brs –	51 q 	148 -

TABLE 1. ¹³C NMR Spectra of the Compounds $CF_2 = CXCF_3$ (I) and (II)*

*Chemical shifts, δ , from TMS as external standard; coupling constants J, Hz. Spectra were recorded by P. V. Petrovskii on a Bruker HX-90 (22.63 MHz).

TABLE 2. Electronic Effect of Unsaturated Units

Unit		Solvent	8 [*] m	δ_p^{\bullet}	σΙ	σ _R
$CF = C(CF_3)_2$ $CF = C(CF_3)CO_2Me^{\dagger}$ $H C = C \begin{pmatrix} CF_3 \\ H \end{pmatrix}$ $H C = C \begin{pmatrix} CO_2Me \\ H \end{pmatrix}$	[5,6]	cyclohexane * n-heptane n-hexane	-2,3 -1,8 -0,75 -0,25	8,4 -6,8 -3,00 2,52	0,41 0,34 0,19 0,12	0,21 0,17 0,08 0,08
			•	-	•	

*Chemical shifts of the fluorophenyl $\frac{4'9}{F}$ nuclei in the m- and p-substituted fluorobenzenes after extrapolation to infinite dilution relative to fluorobenzene, which was used as external standard. Spectra were recorded on a Perkin-Elmer R-20 (56.46 MHz).

[†]The chemical shifts of the fluorophenyl ¹⁹F nuclei of the cis and trans isomers are almost identical — the separate signals could not be detected in the spectra of mixtures; the average values are quoted here.

0.41 and 0.11, respectively, while σ_R is 0.10 and 0.19 [4]. Our results unexpectedly revealed that both the inductive and the resonance constants of the CF =C(CF₃)₂ substituent are higher than those of CF =C(CF₃)CO₂Me. However, in compounds (III) and (IV), which contain these substituents, the C =C double bond is displaced from the plane of the aromatic ring as a result of steric hindrances due to the presence of the bulky groups. In view of this we decided to compare the effect of the trans-CH =CHCF₃ and trans-CH =CHCO₂Me units in the less sterically hindered compounds FC₆H₄CH =CHCF₃ and FC₆H₄CH =CHCO₂Me (V).

The electronic effects of the trans-CH =CHCF₃ unit have been examined earlier [5, 6]. We prepared the fluorocinnamate esters m-FC₆H₄CH =CHCO₂Me (Va) and p-FC₆H₄CH =CHCO₂Me (Vb) (cf. [7]) and examined their ¹⁹F NMR spectra. We found that $\sigma_{\rm I}$ of the trans-CH =CHCO₂Me substituent is slightly less than $\sigma_{\rm I}$ of trans-CH =CHCF₃, while these substituents have the same $\sigma_{\rm R}$ (Table 2).

Thus the ¹⁹F chemical shifts of the fluorophenyl substituent imply that in this case the total electron-accepting effect of the unsaturated unit containing CO₂Me on the aromatic ring is also lower than that of the equivalent unit containing CF₃, while the method is not sensitive enough to distinguish the π -electronic effects. However, this method seems unreliable as regards clarification of the electronic effects of the CH = CHX units (X = CF₃, CO₂Me). Equation (2) provides a poor fit even in the case of such "simple" electron-accepting substituents ($\sigma_R > 0$) as NO₂, CHO, and COMe [4], and for more complex units additional effects that cause deviations from linearity are possible.*

^{*}Our values of σ_I and σ_R for the trans-CH = CHCO₂Me substituent differ considerably from those calculated from the equations σ_I (trans-CH = CHCO₂Me) = 0.01 + 0.41 σ_I (CO₂Me) and σ_R (trans-CH = CHCO₂Me) = -0.03 + 0.96 σ_R (CO₂Me) [4, 5].

TABLE 3. Atomic Populations in Methyl Perfluoromethacrylate (I) and Perfluoroisobutylene (II)



(atoms equivalent by symmetry are not numbered)

Atom	1	EHV	1		CNDO/2				
	(I)	(11)		(1)	(11)		
	σ+π	π	σ+π	π	σ+π	π	σ+π	π	
C^{i}	+1,479	+0,240	+1,340	+0,100	+0,496	+0,141	+0,508	+0,141	
C2 C3	-0,252 +1.944	-0.174 +0.697	-0,321 +1.946	+0.208	+0.649	+0.256	+0.654	+0,250	
Č4	+1.308	+0,363	-	_	+0,425	+0,182		_	
\tilde{C}^5	+0.281	-0,076	-	-	+0,122	+0,010			
F1	-0,543	+0,081	-0,561	+0,066	-0,156	+0,065	-0,154	+0,064	
\mathbf{F}^{2}	-0,542	+0,083	-0,561	+0,066	-0,160	+0,065	-0,154	+0,064	
F^{3}	-0,631	-	-0,631	-	-0,215	-	-0,210	_	
F^4	-0,632	+0,021	-0,632	+0,021	-0,202	+0,034	-0,204	+0,033	
H1	+0,072			- 1	+0,023	-	- 1	· -	
H^2	+0,051		-	-	+0,005	—		-	
0 ¹	-1,189	-0,747	-	-	-0,317	-0,340		-	
O^2	-0,764	+0,163	-	- 1	-0,231	+0,122	— -		

TABLE 4. Total Bond Populations in Methyl Perfluoromethacrylate (I) and Perfluroisobutylene (II) (EHM Calculation)

Bond	(I)	(II)	Bond	(I)	(11)	
$\begin{array}{c} C^{1}-C^{2}\\ C^{2}-C^{3}\\ C^{2}-C^{4}\\ C^{1}-F^{1}\\ C^{1}-F^{2}\\ C^{3}-F^{3} \end{array}$	1,235 0,813 0,986 0,484 0,483 0,438	1,307 0,816 	$\begin{array}{c} C^{3}-F^{4}\\ C^{4}-O^{1}\\ C^{4}-O^{2}\\ C^{5}-O^{2}\\ C^{5}-H^{4}\\ C^{5}-H^{2} \end{array}$	0,440 0,872 0,726 0,494 0,842 0,827	0,439 	

Quantum-chemical calculations provide the most direct method of finding atomic charges in a molecule. We have carried out calculations on (I) and (II) using the extended Hückel method (EHM) in the valence approximation. Examination of the molecular diagrams (Tables 3 and 4) reveals that the positive charge on the β carbon in ester (I) (+1.479e) is much greater than that in (II) (+1.340e) and that this difference is entirely due to the difference in the π -electron charges (+0.240e and +0.100e, respectively), i.e., to the difference in the -M effects of the CO₂Me and CF₃ groups. The greater mesomeric acceptor ability of the CO₂Me group is also apparent in the reduction in the negative π -electron charge on the α carbon in ester (I) relative to (II) (-0.174e and -0.208e).

Since EHM does not explicitly include electron-electron interactions, we carried out an MO LCAO SCF calculation on (I) and (II), using the CNDO/2 method (Table 3). The greater mesomeric acceptor ability of the CO_2Me group is also apparent in this calculation: the total negative π -electron charge on this group (-0.054e) is more than three times that on the CF₃ (-0.016e). However, the sensitivity of the method was not enough to detect the differences in the mesomeric effect of these groups on the β carbon.* In this calculation the greater

*The stronger –I effect of the CF₃ group is apparent in the slight increase in the positive σ -electron charge on the β carbon in (II) (+0.367e) by comparison with (I) (+0.355e).

TABLE 5. Compounds $YC_6H_4CF = CXCF_3$ (III), (IV)

Compound	x	Y	bp, °C (p, mm Hg)	Yield of impure pro- duct, %
(IIIa)	CO2Me	H	118-125 (20)	38
(IIIb)	CO2Me	<i>m</i> -F	100-106 (10)	35
(IIIc)	CO2Me	<i>p</i> -F	108-114 (14)	24
(IVa)	CF3	H	74-79 (40) [14]	55
(IV b)	CF3	<i>m</i> -F	73-75 (40)	22
(IVc)	CF3	<i>p</i> -F	76-77 (40)	27



$$\begin{array}{c} H_4 \\ F \\ C = C \\ Z \end{array}$$
 (III)

1	T٦	7)	
۰.	<u>+ 1</u>		

Com-			z	Chemical shifts, ppm					Coupling constants, J, Hz		
pound	X	. Y		FC.H.	CF≓	CF. (X)	C F; (Z)	trans- CF,CF	CIS— CF3CF	CF ₃ CF ₃	
(IIIa) (IIIb) (IIIc) (IVa) (IVb) (IVc)	CF, CO:Me CF, CO:Me CF, CG, CF, CF, CF,	H H m-F p-F p-F H m-F p-F	CO,Me CF: CO,Me CF: CP: CF: CF: CF: CF:		-8,6 q +4,5 q +5,6 q +5,8 q -7,6 q -14,3 m -12,1 m -12,9 m	-21,4 d -21,2 d -21,0 d 21,7 dq 20,5 dq 20,4 dq	19,1d 18,8 d 18,8 d 19,2 dq 18,1 dq 18,2dq	10,7 9,8 10,4 9,7 9,5 9,5	20,8 20,8 20,8 20,8 24,2 24,9 23,7		

-M effect of the CO₂Me group has a considerable effect only on the nearest atom of the trio $F-C=C \leftrightarrow F=C-\overline{C}$, bonded to it, reducing the negative π -electron charge on the α carbon from -0.236e in (II) to -0.202e in ester (I).

Thus the EHM and particularly the CNDO/2 calculations reveal that the CO₂Me group reduces the negative π -electron charges on the α carbon far more than does the CF₃ group. This difference in the delocalizing and stabilizing effect of the groups will be even more pronounced when the negative charge on the α carbon is increased. Consequently, the carbanions formed in the reactions of nucleophiles with methyl perfluoromethacrylate should be considerably more stable than the analogous carbanions derived from perfluoroisobutylene. There are also other results that imply that replacement of the CF₃ group in CF₃CXY carbanions by CO₂R promotes the stabilization of the carbanions.*

Consequently, the greater reactivity of methyl perfluoromethacrylate toward nucleophiles is obviously due not so much to the electron density deficiency on the β carbon as to the distinctive tendency of the alkoxycarbonyl group to stabilize the intermediate carbanions or carbanion-like transition states.

We do not exclude the possibility that the greater reactivity of methyl perfluoromethacrylate relative to perfluoroisobutylene stems from the peculiar nucleophilic assistance from the O atom of the alkoxycarbonyl group; in the case of N,N-dialkylperfluoromethacrylamides there are compelling arguments in favor of the involvement of the CONR₂ group in this "intramolecular base catalysis" [1].

EXPERIMENTAL

The EHM calculations on (I) and (II) used Clementi and Raimondi's parametrization [9, 10], while the CNDO/2 calculation was carried out in Pople's parametrization [11]. The geometries were chosen on the basis of published figures [12, 13].

^{*}This is apparent in the increase in the acidity of the corresponding carbon acids. Thus the dissociation constant increases by a factor of 60 on going from $O_2NCH_2CF_3$ to $O_2NCH_2CO_2Me$ but by a factor of almost 700 on going from $O_2NCHFCF_3$ to $O_2NCHFCO_2Et$ [8].

m/e (intensity, %)									
:	X=CO ₂ Me			Suggested					
Y=H (III.a)	$\begin{array}{c c} \mathbf{Y} = \mathbf{H} \\ \textbf{(III.a)} \\ \textbf{(IIIb)} \\ \textbf{(IIIb)} \\ \textbf{(IIIc)} \end{array}$		Y=H (IVa)	Y=m-F (IVb)	Y=p-F (IVC)	assignment			
248 (62) 247 (28) 229 (2) 227 (0) 217 (74) 209 (0) 198 (1) 189 (2) 179 (1) 169 (22) 139 (31) 127 (100) 120 (12) 69 (5) 59 (5)	$\begin{array}{c} 266 (38) \\ 265 (7) \\ 247 (1) \\ 245 (0) \\ 235 (53) \\ 227 (0) \\ 216 (0) \\ 207 (2) \\ 197 (0) \\ 187 (11) \\ 157 (31) \\ 145 (100) \\ 138 (11) \\ 69 (6) \\ 59 (7) \end{array}$	266 (34) 265 (3) 247 (1) 245 (0) 235 (44) 227 (0) 216 (0) 207 (1) 197 (0) 187 (12) 157 (25) 145 (100) 138 (11) 69 (5) 59 (5)	$\begin{array}{c} 258(100)\\ 257(10)\\ 239(21)\\ 237(9)\\ \hline \\ 219(15)\\ 208(7)\\ 189 \\ 189 \\ 169(37)\\ 139(2)\\ 127(19)\\ 120(8)\\ 69 \\ 69 \\ 16) \end{array}$	$\begin{array}{c} 276 (100) \\ 275 (7) \\ 257 (24) \\ 255 (5) \\ \hline \\ 237 (19) \\ 226 (7) \\ 207 \\ 207 \\ 207 \\ 187 (28) \\ 157 (2) \\ 145 (46) \\ 138 (9) \\ 69 \\ 69 \\ 69 \\ 19 \end{array}$	$\begin{array}{c} 276 (100) \\ 275 (8) \\ 257 (29) \\ 255 (4) \\ - \\ 237 (13) \\ 226 (10) \\ 207 \\ 207 \\ 137 (29) \\ 157 (2) \\ 145 (50) \\ 138 (8) \\ 69 \\ 69 \\ 69 \\ 17 \end{array}$	$\begin{array}{c} M^{+} \\ M^{+}-H \\ M^{+}-F \\ M^{+}-MeO \\ M^{+}-F-HF \\ M^{+}-CF_{2} \\ M^{+}-X \\ M^{+}-CF_{3} \\ M^{+}-X-HF \\ M^{+}-X-CF_{2} \\ YC_{6}H_{4}CF_{2}^{+} \\ M^{+}-X-CF_{3} \\ CF_{3}^{+} \\ X^{+} \end{array}$			

TABLE 7. Mass Spectra of the Compounds $YC_6H_4CF = CXCF_3$ (III) and (IV)

Spectra were recorded on: PMR: a Perkin-Elmer R-12 (60 MHz), with TMS as external standard; ¹⁹F NMR: Hitachi H-60 (56.46 MHz), with CF₃COOH as external standard. Mass spectra were derived with a Varian MAT CH-8 at 70 eV.

Arylperfluoroisobutylenes (IVa-c). Phenylperfluoroisobutylene (IVa) was prepared after [14]. Fluorophenylperfluoroisobutylenes (IVb, c) were prepared in the same way.

Methyl α -Trifluoromethyl- β -fluoro- β -arylacrylates (IIIa-c). To a solution of (I) (3.19 g) in absolute ether (15 ml) was slowly added with stirring and cooling (~0°C) a solution of p-fluorophenylmagnesium bromide, prepared from p-fluorobromobenzene (2.94 g) and Mg (0.45 g) in absolute ether (20 ml). The mixture was warmed with stirring to ~20°C. After 1 h it was poured onto ice and ether was added. The ethereal layer was separated, washed with H₂O, and dried over CaCl₂. After stripping of the ether, vacuum distillation gave impure ester (IIIc). Preparative GLC (QF-1 column, 4 m ×25 mm, 180°C) gave pure ester (IIIc).

Esters (IIIa, b) were prepared in the same way.

Table 5 summarizes the yields and boiling points of the products, Table 6 their ¹⁹F NMR spectra, and Table 7 their mass spectra.

<u>Methyl Fluorocinnamates (Va, b)</u>. Dry HCl was passed through a suspension of m-fluorocinnamic acid (1.25 g) [7] in absolute MeOH (6 ml) until saturation. The resulting solution was kept at ~20°C for several days. The solvent was stripped off under vacuum and the residue was treated with ice and extracted with benzene. The benzene extract was washed with saturated NaHCO₃ solution and with H₂O and dried over MgSO₄. Fractional distillation gave ester (Va) (0.88 g, 65%), bp 124-128°C (11 mm), mp ~30°C. PMR spectrum (δ): 3.25 s (Me), 6.3-7.1 m (C₆H₄), 6.00 and 7.17 (CH =CH, AB system, J =16.0 Hz). ¹⁹F NMR spectrum: +33.7 m (FC₆H₄). Mass spectrum (here and subsequently we quote m/e, intensity, suggested assignment): 180, 52%, M⁺; 149, 100%, M⁺ - MeO; 121, 40%, M⁺ - CO₂Me; 101, 33%, M⁺ - CO₂Me - HF.

The same method gave ester (Vb), bp 123-125°C (11 mm), mp 38-41°C. PMR spectrum (δ , CC1₄): 3.77 s (Me), 6.8-7.7 m (C₆H₄), 6.32 and 7.63 (CH = CH, AB system, J = 16.5 Hz). ¹⁹F NMR spectrum (CC1₄): +30.0 m (FC₆H₄). Mass spectrum: 180, 60%, M⁺; 149, 100%, M⁺ - MeO; 121, 40%, M⁺ - CO₂Me; 101, 27%, M⁺ - CO₂Me - HF.

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CONCLUSIONS

l. Interaction of m- and p-fluorophenylmagnesium bromide with perfluoroisobutylene or with methyl perfluoromethacrylate gives the corresponding arylperfluoroisobutylenes and methyl α -trifluoromethyl- β -fluoro- β -arylacrylates.

2. Examination of the ¹⁹F NMR spectra of substituted m- and p-fluorobenzenes reveals that the unsaturated units $CF = C(CF_3)X$ and trans-CH = CHX have a greater deshielding effect on the fluorine nucleus in C_6H_4F when $X = CF_3$ than when $X = CO_2Me$.

3. Extended Hückel and CNDO/2 calculations on methyl perfluoromethacrylate and perfluoroisobutylene reveal that the negative π -electron charge on the "central" carbon atom is more efficiently delocalized by the methoxycarbonyl group than the trifluoromethyl.

4. The higher electrophilicity of methyl perfluoromethacrylate relative to perfluoroisobutylene stems from the greater ability of the alkoxycarbonyl group to stabilize the intermediate carbanion or the carbanion-like transition state in the reaction with the nucleophile.

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