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Reactions of Alkanoyl Fluorides with *F*-Isopropyl and *F*-1-Chloroethyl Anions

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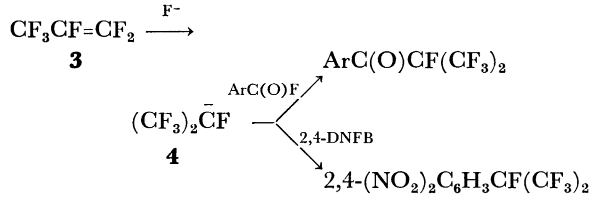
Reactions between alkanoyl chlorides and *F*-propene or *F*-chloroethene with fluoride ion were investigated. While alkyl (*F*-isopropyl) ketones and 1-(*F*-isopropyl)alkenol esters were formed in the former case, 1-(*F*-1-chloroethyl)alkenol esters were exclusively obtained in the latter case. Reaction mechanisms are discussed.

Some sorts of perfluoroalkenes are readily attacked by a fluoride ion affording perfluoroalkyl anions, which are used as a versatile nucleophile. A number of reactions of *F*-tert-butyl anion (**2**), the most stable perfluoroalkyl anion formed from *F*-2-methylpropene (**1**) and a fluoride ion, have been widely investigated by I. L. Knunyants and his coworkers.[1)]

$$\underset{\mathbf{1}}{(CF_3)_2C{=}CF_2} + F^- \longrightarrow \underset{\mathbf{2}}{(CF_3)_3\bar{C}} \xrightarrow{RX} (CF_3)_3C\text{-}R$$

F-Propene (**3**), a monomer which is handled much more safely than *F*-isobutene, also gives *F*-isopropyl anion (**4**) by the action of a fluoride ion in an aprotic solvent. This carbanion is trapped readily by strong electrophiles such as 2,4-dinitrofluorobenzene[2)] and aroyl fluorides,[3,4)] giving organic molecules carrying *F*-isopropyl group.



Alkanoyl fluorides as an electrophile, however, react with *F*-isopropyl anion not to give a single product. The reaction accompanies *O*-acylation and is more complicated than that of aroyl fluorides.

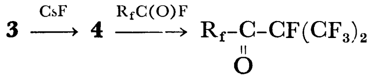
Although *F*-chloroethene (**5**), on the other hand, is less susceptible to the attack of a fluoride ion than *F*-propene, it is known to give *F*-1-chloroethyl anion (**6**) at higher temperatures. Some 1-chlorotetrafluoroethylated products such as triazine derivatives were reported to be formed.[5)] We now wish to reveal the details of the reactions of alkanoyl fluorides with *F*-isopropyl and *F*-chloroethyl anions.

$$\underset{\mathbf{5}}{ClCF{=}CF_2} + F^- \longrightarrow$$

$$\underset{\mathbf{6}}{ClF\bar{C}\text{-}CF_3} \xrightarrow{sym\text{-}C_3N_3F_3} C_3N_3F_2(CClFCF_3)\ etc.$$

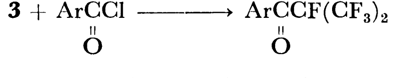
Results and Discussion

Reactions of F*-Propene with Alkanoyl Chlorides in the Presence of Fluoride Ion.* An earlier report[6)] revealed that *F*-propene reacts with perfluoroalkanoyl fluorides in the presence of cesium fluoride affording *F*-alkyl isopropyl ketones.



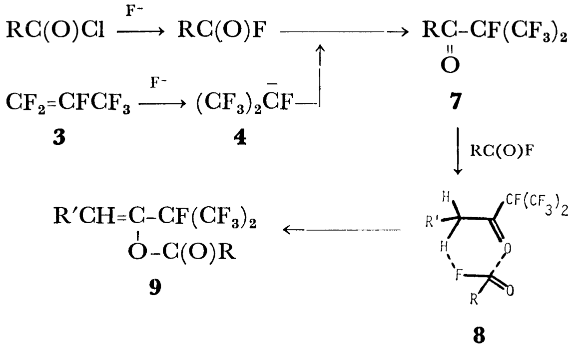
$$\mathbf{3} \xrightarrow{CsF} \mathbf{4} \xrightarrow{R_fC(O)F} R_f\text{-}\underset{\underset{O}{\|}}{C}\text{-}CF(CF_3)_2$$

In our previous paper, it was reported that *F*-propene and an aroyl chloride in the presence of potassium fluoride in *N*,*N*-dimethylformamide gave aryl (*F*-isopropyl) ketones in a good yield.[3)]



$$\mathbf{3} + Ar\underset{\underset{O}{\|}}{C}Cl \xrightarrow{KF/DMF} Ar\underset{\underset{O}{\|}}{C}CF(CF_3)_2$$

However, alkanoyl chlorides and *F*-propene in potassium fluoride-*N*,*N*-dimethylformamide system gave alkanoyl fluorides and *F*-propene oligomers[7)] as main products. When the reaction was carried out in potassium fluoride–diglyme system, a mixture of an *F*-isopropyl ketone (**7**) and an enol ester (**9**) were obtained. The reactions were carried out at 120—130 °C, and potassium fluoride was used in excess, so that the chloride had been converted to the fluoride prior to the reaction with *F*-isopropyl anion **4**.



The enol ester **9** should be formed by the reaction of *F*-isopropyl ketone **7** with one more molecule of the alkanoyl fluoride. However, it was surprising to know that a nearly 1:1 mixture of **7** and **9** was always formed even by allowing a large excess amount of *F*-propene to react. This means that the formation of **9** from **5** undergoes as fast as the preceeding ketone formation. Another feature of this acylation was that the *O*-acylation giving **9** occurred exclusively and no *C*-acylated products were observed.

These facts can be explained by assuming a direct attack of acyl fluoride to the ketone **7**. Thus the α-hydrogen atoms of the alkyl group of **7** should be highly activated by the strong electron-withdrawing *F*-2-methylpropanoyl group, and they would readily accept the negative fluorine atom of the acyl fluoride. This H–F bond formation would assist the nucleophilic attack of the carbonyl oxygen of **7** to the carbonyl carbon of acyl fluoride to give *O*-acylated product **9**, through a six-membered cyclic transition state (**8**). The structures of enol esters **9** were elucidated from the ^1H and ^{19}F NMR spectral data (Table 1), though it was unable to determine whether these are in *E*-

TABLE 1. PHYSICAL PROPERTIES OF KETONES, $\mathrm{R\text{-}C(O)\text{-}CF(CF_3)}$ (**7**)

Compd **7**	Bp	IR	NMR				Found (Calcd)(%)	
	θ_b/°C	C=O	^{19}F(δ)$^{a)}$		^{1}H(δ)			
R	(mmHg)**	$\tilde{\nu}$/cm^{-1}	C$\underline{\mathrm{F}}_3$($J_{\mathrm{F-F}}$)	C$\underline{\mathrm{F}}$	C(O)C$\underline{\mathrm{H}}$($J_{\mathrm{H-F}}$)	C(O)-C-R′(H)	C	H
Me	53—54	1760	−3.0 d (5.6)	104m	2.47 d, 3H(5.9)	—	28.16(28.32)	1.52(1.43)
Et	66—69	1755	−2.4 d (6.0)	107m	2.90 m, 2H(3.0)	1.23 t, 3H	31.68(31.87)	2.36(2.23)
n-Pr	49—50(140)	1755	−3.0 d (5.6)	107m	2.75 m, 2H(3.9)	1.73 m, 2H 1.0 t, 3H	35.32(35.01)	3.06(2.94)
i-Pr	89—90	1745	−3.8 d (6.2)	108m	3.28 m, 1H(2.9)	1.20 d, 6H	34.86(35.01)	2.78(2.94)
n-Bu	48—49(55)	1755	−2.5 d (6.2)	107m	2.72 m, 2H(3.6)	0.98 t, 3H 1.1—1.85, 4H	37.96(37.81)	3.62(3.57)
t-Bu	49—51(130)	1730	−4.0 d (6.0)	105m	—	1.30 br, 9H	37.86(37.81)	3.62(3.57)
n-$\mathrm{C_5H_{11}}$	75—77(90)	1755	−2.5 d (6.2)	111m	2.70 m, 2H(3.5)	0.90 t, 3H 1.1—1.8, 6H	40.86(40.31)	4.24(4.13)

a) δ ppm from ext. $\mathrm{CF_3CO_2H}$ in $\mathrm{CCl_4}$. ** 1 mmHg≈133.322 Pa.

TABLE 2. PHYSICAL PROPERTIES OF ENOL ESTERS, $\mathrm{R'CH{=}\underset{\substack{|\\ OC(O)R}}{C}CF(CF_3)_2}$ (**9**)

Compd **9**		Bp	IR $\tilde{\nu}$/cm^{-1}		NMR			Found (Calcd)(%)	
		θ_b/°C			^{19}F(δ)$^{a)}$		^{1}H(δ)		
R	R′	(mmHg)	C=O	C=C	C$\underline{\mathrm{F}}_3$($J_{\mathrm{F-F}}$)	C$\underline{\mathrm{F}}$	=C-H($J_{\mathrm{H-F}}$)	C	H
Et	Me	58—60(25)	1785	1695	−2.5 d (6.4)	101m	6.03m (3.0)	38.53(38.31)	3.16(3.22)
n-Pr	Et	49—50(10)	1790	1690	−2.0 d (6.2)	101m	5.93m (3.3)	42.48(42.59)	4.42(4.22)
n-Bu	*n*-Pr	49—51(1.5)	1780	1685	−2.0 d (6.2)	101m	5.93m (3.0)	46.21(46.16)	5.11(5.07)
n-$\mathrm{C_5H_{11}}$	*n*-Br	105—108(14)	1785	1690	−2.0 d (7.1)	102m	5.90m (3.0)	49.36(49.18)	5.56(5.78)

a) Table 1, footnote a).

TABLE 3. PHYSICAL PROPERTIES OF ENOL ESTERS, $\mathrm{R'\text{-}CH{=}\underset{\substack{|\\ OC(O)R}}{C}\text{-}CClF\text{-}CF_3}$ (**10**)

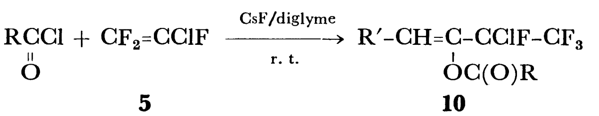
Compd **10**		Bp	Yield	IR $\tilde{\nu}$/cm^{-1}		NMR			Found (Calcd)(%)	
		θ_b/°C				^{19}F(δ)$^{a)}$		^{1}H(δ)		
R	R′	(mmHg)	%	C=O	C=C	C$\underline{\mathrm{F}}_3$($J_{\mathrm{F-F}}$)	C$\underline{\mathrm{F}}$Cl	=C-$\underline{\mathrm{H}}$($J_{\mathrm{H-F}}$)	C	H
Et	Me	53—55(19)	83	1785	1690	3.0 d (6.6)	50.7m	6.07m (1.9)	39.23(38.65)	4.01(3.65)
n-Pr	Et	68—70(18)	90	1780	1675	3.5 d (6.6)	50.7m	5.97m (1.7)	43.88(43.42)	4.79(4.74)
n-Bu	*n*-Pr	57(1)	81	1780	1680	3.0 d (6.6)	50.5m	5.99m (1.8)	47.08(47.30)	5.48(5.62)
n-$\mathrm{C_5H_{11}}$	*n*-Bu	69—72(2)	63	1780	1675	2.8 d (6.6)	50.5m	6.02m (1.8)	49.65(50.53)	5.88(6.36)

a) Table 1, footnote a).

or *Z*-form.

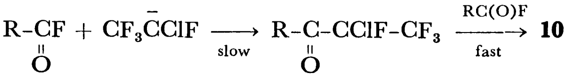
Reactions of F-*Chloroethene with Alkanoyl Chlorides in the Presence of Fluoride Ion.* The reaction of alkanoyl chlorides with *F*-chloroethene in the presence of potassium fluoride did not undergo smoothly as those with *F*-propene. This should be ascribed to the difficulty of formation of *F*-1-chloroethyl anion **6** compared with *F*-isopropyl anion **4**. Since the chlorine atom is less electronegative than trifluoromethyl group, the anion **6** should be less stable than **4**.

$$\underset{\mathbf{6}}{\mathrm{CF_3\overset{-}{C}ClF}} < \underset{\mathbf{4}}{\mathrm{CF_3\overset{-}{C}FCF_3}}$$



$$\underset{\mathbf{5}}{\mathrm{R\underset{\substack{\|\\ O}}{C}Cl}} + \mathrm{CF_2{=}CClF} \xrightarrow[\text{r. t.}]{\text{CsF/diglyme}} \underset{\mathbf{10}}{\mathrm{R'\text{-}CH{=}\underset{\substack{|\\ OC(O)R}}{C}\text{-}CClF\text{-}CF_3}}$$

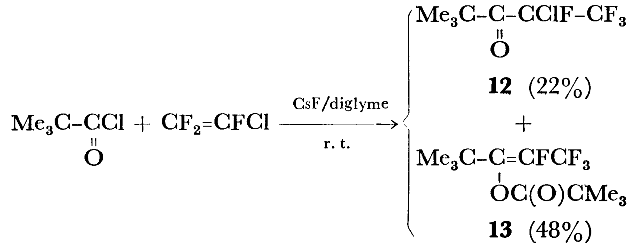
When cesium fluoride instead of potassium fluoride was used in the reaction, the corresponding enol esters (**10**) were obtained in good yields even at room temperatures (Table 2). Cesium fluoride is known as a stronger source for fluoride ions than potassium fluoride in an aprotic solvent.[8] Hence CsF accelerated the formation of *F*-chloroethyl anion **6** which reacted with an alkanoyl fluoride in a similar manner as *F*-isopropyl anion **4**. In this case, however, no formation of the *F*-chloroethyl ketone (**11**) was ob-



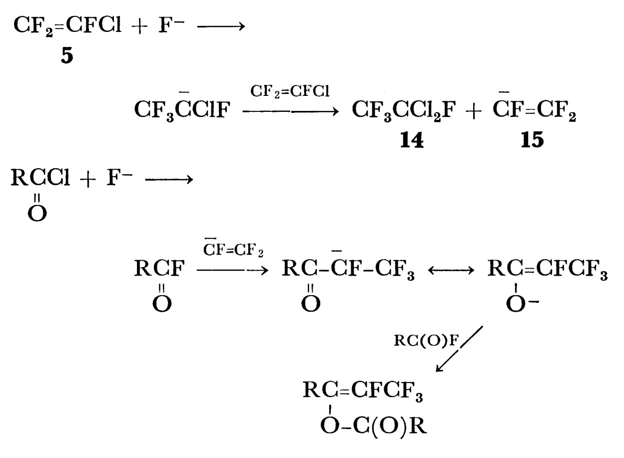
$$\mathrm{R\text{-}\underset{\substack{\|\\ O}}{C}F} + \underset{\mathbf{6}}{\mathrm{CF_3\overset{-}{C}ClF}} \xrightarrow[\text{slow}]{} \underset{\mathbf{11}}{\mathrm{R\text{-}\underset{\substack{\|\\ O}}{C}\text{-}CClF\text{-}CF_3}} \xrightarrow[\text{fast}]{\mathrm{RC(O)F}} \mathbf{10}$$

served. This should be ascribed to the much slower first-step reaction of *F*-chloroethyl anion with alkanoyl fluoride compared with the following *O*-acylation.

When 2,2-dimethylbutanoyl chloride, which has no α-hydrogen atoms, was allowed to react with *F*-chloroethene, a kind of enol ester(**13**) carrying no chlorine atom was formed together with *F*-chloroethyl ketone (**12**). Although the formation of **13** seemed to be strange, it was rationalized by considering the formation of *F*-ethenyl anion(**15**) from *F*-chloroethene, followed by the addition of acyl fluoride.[5,9] Actually we observed the formation of 1,1-dichlorotetrafluoroethane **14** when *F*-chloroethene (**5**) was treated in cesium fluoride–diglyme system and no oligomerization of **5** occurred.



$$\mathrm{Me_3C\text{-}\underset{\overset{\|}{O}}{C}Cl + CF_2{=}CFCl \xrightarrow[\text{r.t.}]{\text{CsF/diglyme}} \left\{\begin{array}{l} Me_3C\text{-}\underset{\overset{\|}{O}}{C}\text{-}CClF\text{-}CF_3 \\ \quad \mathbf{12}\ (22\%) \\ \quad + \\ Me_3C\text{-}\underset{\overset{|}{OC(O)CMe_3}}{C}{=}CFCF_3 \\ \quad \mathbf{13}\ (48\%) \end{array}\right.}$$



$$\mathrm{\underset{\mathbf{5}}{CF_2{=}CFCl} + F^- \longrightarrow}$$

$$\mathrm{CF_3\overset{-}{C}ClF \xrightarrow{CF_2=CFCl} \underset{\mathbf{14}}{CF_3CCl_2F} + \underset{\mathbf{15}}{\overset{-}{C}F{=}CF_2}}$$

$$\mathrm{R\underset{\overset{\|}{O}}{C}Cl + F^- \longrightarrow}$$

$$\mathrm{R\underset{\overset{\|}{O}}{C}F \xrightarrow{\overset{-}{C}F=CF_2} R\underset{\overset{\|}{O}}{C}\text{-}\overset{-}{C}F\text{-}CF_3 \longleftrightarrow R\underset{\overset{|}{O^-}}{C}{=}CFCF_3 \xrightarrow{RC(O)F} R\underset{\overset{|}{O\text{-}C(O)R}}{C}{=}CFCF_3}$$

Experimental

*Heptyl (*F*-Isopropyl) Ketone (**7**, R=*n*-C_7H_{15}) and 1-(*F*-Isopropyl)-1-hexenyl Octanoate (**9**, R=*n*-C_7H_{15}, R′=*n*-C_6H_{13}).* Into a mixture of octanoyl chloride (1.63 g, 10 ml), calcine-dried potassium fluoride (3.50 g, 60 mmol) and freshly dried diglyme (10 ml) in a pressure-vessel, liquefied *F*-propene (3.0 g, 20 ml) was introduced at −70 °C. The vessel was brought to room temperature, and heated for 2 h in an oil bath kept at 120—130 °C with magnetic stirring. The reaction mixture was poured onto water and an oily material was extracted with diethyl ether. After the solvent was removed, the residue was subjected to vacuum distillation. **7** (R=*n*-C_7H_{15}), bp 59—62 °C/12 mmHg, and **9** (R=*n*-C_7H_{15}, R′=*n*-C_6H_{13}), bp 150—152 °C/11 mmHg, were obtained in yields of 48 and 20%, respectively.

Other *F*-isopropyl ketones (**7**) and enol esters (**9**) were prepared in a similar manner.

*1-(*F*-1-Chloroethyl)-1-propenyl Propionate (**10**, R=Et, R′=Me).* Propionyl chloride (1.85 g, 20 mmol), calcine-dried cesium fluoride (7.5 g, 50 mmol) and freshly dried diglyme (20 ml) were put in a pressure-vessel, and liquefied chlorotrifluoroethene (4.8 g, 40 mmol) was introduced at −70 °C. The mixture was stirred for 48 h at room temperature, and worked up as described above. The enol ester **10** (R=Et, R′=Me), bp 68—70 °C/18 mmHg, was obtained in 83% yield.

Other enol esters **10** were prepared in a similar manner.

*Reaction between 2,2-Dimethylpropionyl Chloride and *F*-Chloroethene with a Fluoride Ion.* When 2,2-dimethylpropionyl chloride and *F*-chloroethene were allowed to react in a similar manner, following two products were obtained.

*t-Butyl (*F*-1-Chloroethyl) Ketone (**12**):* Bp 45—46 °C/46 mmHg, 22%. IR: 1730, 1745 cm^{-1} (C=O). ^{19}F NMR: δ 2 (d, CF_3), 57 (br, CF) ppm; $J_{F-F}=5.6$ Hz. ^{1}H NMR: δ 1.34 (d); $J_{H-F}=1.7$ Hz. Too much volatile to be analyzed.

*1-t-Butyl-2,3,3,3-tetrafluoro-1-propenyl 2,2-Dimethylpropionate (**13**):* Bp 67—68 °C/13 mmHg, 48%. IR: 1765 (C=O), 1690 (C=C) cm^{-1}. ^{19}F NMR: δ −9 (d, CF_3), 71 (m, F) ppm, $J_{F-F}=1.7$ Hz. ^{1}H NMR: δ 1.29 (s, 9H), 1.25 (d, 9H), $J_{H-F}=1.7$ Hz. Found: C, 53.72; H, 6.47%. Calcd for $C_{12}H_{18}F_4O_2$: C, 53.33; H, 6.67%.

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