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A NEW SYNTHESIS OF PERFLUOROACYL HALIDES AND ANHYDRIDES FROM PERFLUOROCARBOXYLATE SALTS. A SYNTHETIC STUDY

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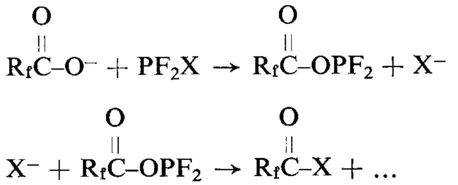
SUMMARY

The nucleophilic cleavage of difluorophosphine esters of perfluorocarboxylic acids by halide ions to form acyl halides has not been previously reported. Furthermore, the reactions between halophosphoryldifluorides or the anhydrides, $P_2O_5F_2$ and $P_2O_3F_4$, and perfluorocarboxylate salts produce acyl halides or acyl anhydrides, respectively.

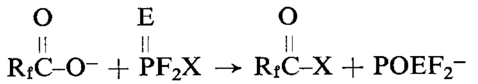
INTRODUCTION

Phosphorus(III) difluoride halides and phosphorus(V) oxy- and thiodifluoride halides (halide = Cl^-, Br^-, I^-) have been used to prepare perfluoroacyl halides from perfluorocarboxylate salts. An intermediate ester is formed in the case of reaction (1)[1] and the reactions are summarized as follows:



$$R_f\overset{O}{\overset{\|}{C}}\text{–}O^- + PF_2X \rightarrow R_f\overset{O}{\overset{\|}{C}}\text{–}OPF_2 + X^- \qquad (1)$$

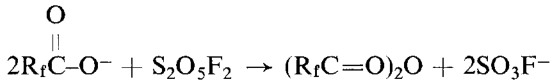
$$X^- + R_f\overset{O}{\overset{\|}{C}}\text{–}OPF_2 \rightarrow R_f\overset{O}{\overset{\|}{C}}\text{–}X + \ldots$$



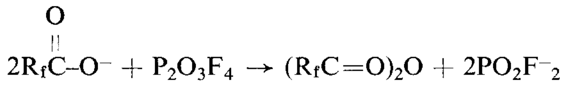
$$R_f\overset{O}{\overset{\|}{C}}\text{–}O^- + \overset{E}{\overset{\|}{P}}F_2X \rightarrow R_f\overset{O}{\overset{\|}{C}}\text{–}X + POEF_2^- \qquad (2)$$

(where $R_f = CF_3$ and C_2F_5; X = Cl, Br, I and E = O, S).

On the other hand, when pyrosulfuryl difluoride or pyrophosphoryl tetrafluoride is used as a substrate, reaction with the perfluorocarboxylate salt produces the carboxyl anhydride.



$$2R_f\overset{\overset{O}{\|}}{C}\text{–}O^- + S_2O_5F_2 \rightarrow (R_fC{=}O)_2O + 2SO_3F^- \qquad (3)$$



$$2R_f\overset{\overset{O}{\|}}{C}\text{–}O^- + P_2O_3F_4 \rightarrow (R_fC{=}O)_2O + 2PO_2F^-_2 \qquad (4)$$

EXPERIMENTAL

Reagents

The sodium and silver perfluorocarboxylate salts were procurred from Peninsular Chem. Research, Inc. Pyrophosphoryl tetrafluoride[2], pyrosulfuryl difluoride[3], chlorodifluorophosphine[4], bromodifluorophosphine[5], iododifluorophosphine[6], chlorothiophosphoryldifluoride[7], chlorophosphoryldifluoride[8] and bromophosphoryldifluoride[8] were prepared by known procedures. Before their use, the fluorocarboxylate salts were finely ground and heated under dynamic vacuum at 55° for 2–3 h.

Apparatus

Standard high-vacuum technique using a Pyrex glass system was employed throughout. Glass stopcocks were lubricated with Kel-F No. 90 grease (3M Co.). The reactions were carried out in 100 ml Pyrex flasks fitted with a Teflon stopcock (Fischer and Porter Co.).

Infrared spectra were taken in the gas phase with a Perkin–Elmer 621 instrument with the samples being contained in a Pyrex cell (10 cm path length) equipped with NaCl windows.

General procedure

In a typical procedure the perfluorocarboxylate salt was dried. To the salt was added the fluorophosphorus compound and, in some cases, a solvent. The mixture was allowed to warm. The course of the reaction was monitored by observation of the infrared spectra. An example is the following:

Silver perfluoroacetate (2.01 mmole) and bromophosphoryldifluoride (2.01 mmole) were added together in the reactor, cooled to −196°. The mixture was allowed to warm slowly to *ca.* −40° and the reaction was quenched by rapid cooling to −196°. The products were passed through traps set at −80° and −126°, respectively. The former retained 0.15 mmoles of $(CF_3CO)_2O$ and the latter CF_3COBr (1.7 mmole, 85% yield). The silver difluorophosphate remaining in the reactor was identified by its infrared spectrum. Table 1 lists the reactions in which perfluoroacyl halides and anhydrides are formed. The products were separated by trap-to-trap distillation in the manner illustrated above.

TABLE 1

REACTIONS OF PERFLUORO-ORGANIC CARBOXYLATE SALTS AND THE PREPARATION OF PERFLUORO-ORGANIC ACYL HALIDES AND ANHYDRIDES

Reactants (mmoles)	Reaction conditions	Product mixture (mmoles)
PF_2Cl, $CF_3C(O)O^-Na^+$ (2.41) (2.41)	Neat, warmed to ambient temperature in 20 min	$CF_3C(O)OPF_2$ (quantitative)
PF_2Br, $CF_3C(O)O^-Na^+$ (1.41) (1.41)	Same as above	$CF_3C(O)OPF_2$, $CF_3C(O)Br$, (1.13) (trace) $(CF_3C(O))_2O$, PF_3 (trace quantities)
PF_2Br, $CF_3C(O)O^-Na^+$ (1.49) (2.98)	Same as above	$CF_3C(O)OPF_2$, $(CF_3C(O))_2O$, (1.10) (0.067) $CF_3C(O)Br$, PF_2OPF_2, PF_3 (0.22) (trace quantities)
PF_2Br, $CF_3C(O)O^-Na^+$ (1.54) (1.54)	Stirred in 5 ml of CH_3CN for 5 min	$CF_3C(O)Br$, PF_3 (1.48) (trace)
PF_2I, $CF_3C(O)O^-Na^+$ (2.41) (2.89)	Neat, warmed to room temperature in 20 min	$CF_3C(O)OPF_2$, $CF_3C(O)I$ (2.05) (trace) PF_3, PF_2OPF_2 (trace quantities)
$CF_3C(O)OPF_2$, NaCl (1.53) (6.0)	Stirred in 5 ml of CH_3CN for 1 h	$CF_3C(O)Cl$, $CF_3C(O)OPF_2$ (0.50) (*ca.* 1)
$CF_3C(O)OPF_2$, NaI (1.33) (1.52)	Neat, 2 h at ambient temperature	$CF_3C(O)I$, PF_3, PF_2OPF_2 (0.266)
$CF_3C(O)OPF_2$, $CsPS_2F_2$ (*ca.* equal quantities)	Neat, 2 h at ambient temperature Nitrobenzene, 45 min at ambient temperature CH_2Cl_2, 45 min at ambient temperature	Unreacted $CF_3C(O)OPF_2$, PF_3 ? Unidentified products Unidentified products
$CF_3C(O)OPF_2$, $\Phi_4AsPOSF_2$ (*ca.* equal quantities)	Neat, several hours at ambient temperature	PF_3 ?
POF_2Cl, $CF_3C(O)O^-Na^+$ (1.83) (1.91)	Neat, 15 min at ambient temperature	$CF_3C(O)Cl$ (1.37)
POF_2Cl, $CF_3C(O)O^-Na^+$ (2.06) (5.25)	Stirred in 5 ml of CH_3CN for 15 min	$CF_3C(O)Cl$ (1.47)

TABLE 1 *(continued)*

Reactants (mmoles)	Reaction conditions	Product mixture (mmoles)
POF_2Cl, $CF_3C(O)O^-Na^+$ (1.06) (1.06)	Stirred in 5 ml of nitrobenzene in the presence of 1.25 mmoles of $AlCl_3$ for 15 min	$CF_3C(O)Cl$ (0.80)
POF_2Cl, $CF_3CF_2C(O)O^-Na^+$ (2.43) (2.43)	Neat, warmed to room temperature in 15 min	$CF_3CF_2C(O)Cl$ (1.70)
POF_2Br, $CF_3C(O)O^-Ag^+$ (2.0) (2.1)	Neat, warmed to —40° in 10 min	$CF_3C(O)Br$, $(CF_3C(O))_2O$ (1.7) (0.2)
PSF_2Cl, $CF_3C(O)O^-Ag^+$ (0.066) (0.71)	Neat, warmed to ambient temperature in 20 min	No reaction
PF_3, $CF_3C(O)O^-Na^+$ (0.78) (0.78)	Refluxed 14 h in CH_3CN	No reaction
$CF_3C(O)OH$, $(CH_3)_2NPF_2$ (9.14) (5.0)	Neat, warmed to room temperature in 5 min	PF_3, PF_2OPF_2
$CF_3C(O)OPF_2$, O_2 (1.22) (0.61)	70° for 14 h	POF_3
$CF_2C(O)OPF_2$, S (4.12) ~1 g	150° for 1 week	$(CF_3C(O))_2O$
$CF_3C(O)OPF_2$, Cl_2 (1.52) (1.52)	4 min at ambient temperature	$CF_3C(O)Cl$, POF_2Cl (1.31) (1.50)
$CF_3CF_2C(O)O^-Na^+$, (1.53) $CF_3CF_2C(O)Cl$ (1.38)	Neat, room temperature for 4 h	$(CF_3CF_2C(O))_2O$ (0.76)
$S_2O_5F_2$, $CF_3CF_2C(O)O^-Na^+$ (2.39) (4.78)	Stirred in 1 ml of CH_3CN for 15 min	$(CF_3CF_2C(O))_2O$ (quantitative)
$S_2O_5F_2$, $CF_3C(O)O^-Na^+$ (2.74) (2.74)	Neat, 4 h at room temperature	$(CF_3C(O))_2O$, $S_2O_5F_2$ (1.37) (1.35)
$P_2O_3F_4$, $CF_3CF_2C(O)O^-Na^+$ (1.88) (3.75)	Neat, 30 min at room temperature	$(CF_3CF_2C(O))_2O$ (quantitative)
$S_2O_5F_2$, $CH_3C(O)O^-Na^+$ (11.5) (11.5)	Neat, heated at 85° for 18 h	$S_2O_5F_2$, SO_2F_2 (trace)

RESULTS AND DISCUSSION

Phosphorus pentahalides or trihalides have normally been used to prepare perfluoroaliphatic acyl halides by their action on carboxylic acids or their salts. These syntheses frequently require prolonged time periods and/or heating[9], and the yields range from poor to good. We have now found that the neat reactions of phosphorus(V) oxy- and thio-difluoride halides with either the sodium or silver salts of perfluoro-acetic or -propionic acids give generally good yields of the corresponding acyl halides rapidly at or below room temperature, although similar reactions involving the phosphorus(III) difluoride halides proceed more slowly. Even the presence of a chloride-ion acceptor, $AlCl_3$, in the reaction involving POF_2Cl did not decrease the yield of the acyl halide. In some cases involving the phosphorus(III) and -(V) difluorides, small yields of the acyl anhydrides are also produced.

The reactions between the anhydrides of fluorosulfuric and difluorophosphoric acids, $S_2O_5F_2$ and $P_2O_3F_4$, respectively, and perfluorinated aliphatic carboxylate salts lead extensively to the corresponding perfluorocarboxylic acid anhydrides. The reactions may proceed by the following courses.

$$R_fC(O)O^- + S_2O_5F_2 \rightarrow R_fC(O)OSO_2F$$
$$R_fC(O)OSO_2F + R_fC(O)O^- \rightarrow (R_fCO)_2O + SO_3F^-$$
$$R_fC(O)O^- + P_2O_3F_4 \rightarrow R_fC(O)OPOF_2$$
$$R_fC(O)OPOF_2 + R_fC(O)O^- \rightarrow (R_fCO)_2O + PO_2F_2^-$$

Both SO_3F^- and $PO_2F_2^-$ were identified by their infrared spectra. It appears that this method of preparing anhydrides is restrictive because the reaction between $S_2O_5F_2$ and $Na^+CH_3COO^-$ under the conditions given did not lead to acetic anhydride. Instead, small quantities of SO_2F_2 were formed from the decomposition of $S_2O_5F_2$ under prolonged heating. Although the action of acyl halides on carboxylic acids or their salts produces anhydrides, the synthesis of $(CF_3CF_2CO)_2O$ has not been reported by this procedure (Table 1).

It is interesting to note that while compounds of the type PF_2X react with perfluorocarboxylate salts to give the intermediate $R_fC(O)OPF_2$, compounds of the type $P(E)F_2X$ do not react with the same carboxylate salts to give an intermediate mixed anhydride. The $R_fC(O)OPF_2$ slowly disappears when the reaction is allowed to progress under heat conditions, but rapidly disappears in the presence of a solvent. Attempts were made to prepare the intermediate $R_fC(O)OP(E)F_2$ by other routes. One method involved the oxidation of the phosphorus(III) of $R_fC(O)OPF_2$ to the phosphorus(V) of the mixed anhydride, but the reactions with both oxygen and sulfur were unrewarding. Another trial involving a nucleophilic displacement on $R_fC(O)OPF_2$, similar to the halide reactions but using $CsPS_2F_2$, was also unsuccessful. The reaction with chlorine, indeed, does oxidize the phosphorus but the acyl halide and POF_2Cl are quantitatively produced.

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