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SHORT COMMUNICATION

Fluoroacyl Hypochlorites and Ester Derivatives

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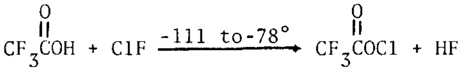
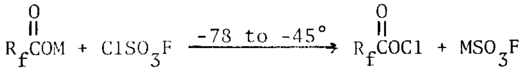
Recently Des Marteau [1] reported the preparation and isolation of CF_3CO_2Cl (and CF_3SO_3Cl) by the low temperature reaction of the corresponding acids with ClF.



$$CF_3\overset{\overset{O}{\|}}{C}OH + ClF \xrightarrow{-111\ \text{to}\ -78°} CF_3\overset{\overset{O}{\|}}{C}OCl + HF$$

In this paper we would like to report the results of an independent simultaneous study. In our study, the chlorinating agent employed was chlorine fluorosulfate [2] and either the acid or its alkali metal salt were used as substrates.



$$R_f\overset{\overset{O}{\|}}{C}OM + ClSO_3F \xrightarrow{-78\ \text{to}\ -45°} R_f\overset{\overset{O}{\|}}{C}OCl + MSO_3F$$

$R_f = CF_3, ClCF_2 \quad M = H, Na$

For cases where a volatile acyl hypochlorite is formed, the use of $ClSO_3F$ instead of ClF allows easier product separation because the by-product HSO_3F is much less volatile than HF. When salts are employed, essentially no separation problems are encountered since the by-products are solids. Although the reaction of ClF and acid salts was not tested, based on our experience [3] $ClSO_3F$ is superior to ClF in chlorinating anionic species. In our preparations using $ClSO_3F$ somewhat higher reaction temperatures were employed than those reported for ClF [1]. Complete reaction of the $ClSO_3F$ occurred. The product acyl hypochlorite was essentially the only volatile product formed and it was purified by fractional condensation in a vacuum line with about 10% material loss due to decomposition during handling.

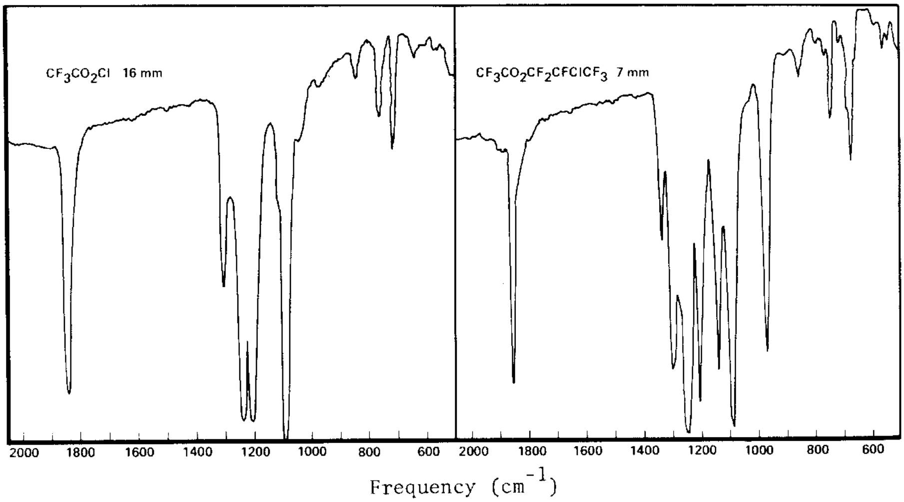
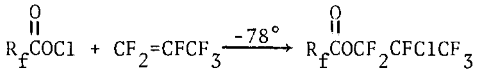


Figure 1. Gas Phase Infrared Spectra

The properties observed for CF_3CO_2Cl agree well with those given by Des Marteau [1]. In addition, it was found that adequate passivation of container surfaces and pretreatment with the compound itself permitted reproducible gas phase infrared spectra to be obtained. The spectrum is shown in Fig. 1 and the observed bands are consistent with an acyl hypochlorite structure. Comparison with related species allows assignment of particular bands. Thus, the band at 1844 cm^{-1} is clearly the C=O stretch which occurs at 1852 cm^{-1} in $CF_3CO_2CF_3$[4]. The three bands at 1308, 1241. and 1206 cm^{-1} are C-F stretching modes typically noted for CF_3 compounds as strong bands in this area [5,6]. The intense band at 1093 cm^{-1} is the C-O stretch which occurs in the range of 1109-1120 cm^{-1} in a series of $R_fCO_2R_f^1$ esters [7] while the weak band at 844 cm^{-1} is the C-C stretching vibration which is normally weak and occurs in the 800-900 cm^{-1} region in similar compounds [5,6]. Of the remaining two bands, the one at 719 cm^{-1} can be assigned to the Cl-O stretching mode based on Des Marteau's observation of an intense polarized Raman band at 716 cm^{-1} and by comparison with other hypochlorites [8]. Finally, then, the medium weak 765 cm^{-1} absorption is ascribed to the CF_3 deformation mode which is in agreement with the 693-781 cm^{-1} range reported [5,6] for similar compounds.

A reaction typical of positively polarized chlorine species [9] is their addition across C=C bonds. Such derivative forming reactions are useful for the characterization of these species and in the present case also serve as a very convenient synthetic method for fluorocarbon esters.



$$R_fC(O)Cl + CF_2{=}CFCF_3 \xrightarrow{-78^\circ} R_fC(O)OCF_2CFClCF_3$$

$R_f{=}CF_3$, $ClCF_2$

The infrared spectrum of a typical ester is shown in Fig. 1 and its ^{19}F nmr spectrum is given in Fig. 2. Although two isomeric addition products

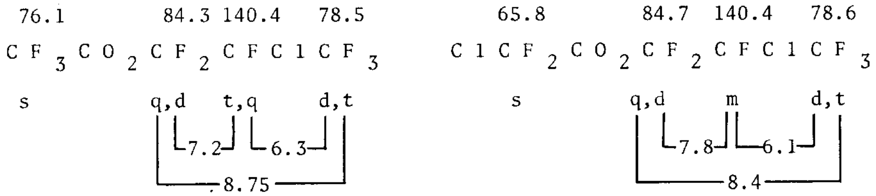


Figure 2. ^{19}F Chemical Shift in ppm Upfield Relative to $CFCl_3$ Internal Reference; S, singlet; d, doublet; t, triplet; q, quartet; m, multiplet

are theoretically possible, only the one expected for a directed, polar addition was found in each reaction. Controlled hydrolysis of $CF_3CO_2CF_2CFClCF_3$ in $CFCl_3$ solution proceeds according to:

$$\begin{array}{l} CF_3CO_2CF_2CFClCF_3 + H_2O \rightarrow CF_3CO_2H + [CF_3CFClCF_2OH] \\ \hspace{14em}\downarrow -HF \\ \hspace{14em} CF_3CFClC(O)F \end{array}$$

Although hydrolytically unstable, these esters are stable at ambient temperature and can be stored in glass.

EXPERIMENTAL

Caution: Fluoroacyl hypochlorites are explosives, possibly even in the gas phase, and should be handled with appropriate safety precautions.

Volatile materials were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps, 316 stainless steel bellows seal valves and a Heise Bourdon tube-type pressure gauge. Transfers outside the vacuum line were carried out in a drybox. Infrared spectra were obtained using 5 cm path stainless steel cells with AgCl windows and a PE Model 283 spectrophotometer. Mass spectra were measured with an EAI Quad 300 quadrupole spectrometer and ^{19}F nmr spectra were determined with a Varian EM390 spectrometer operating at 84.6 MHz. Fluorocarbon starting materials were purchased from PCR Inc. and $ClSO_3F$ was prepared as reported [2].

CF_3CO_2Cl. A 30 ml stainless steel cylinder containing CF_3CO_2Na (5.24 mmol) was cooled to -196° and loaded with freshly purified $ClSO_3F$ (2.93 mmol). The reaction cylinder was then maintained at -45° for 16 hr. The volatile products were separated by fractional condensation through a series of U traps cooled to -78, -112, and -196°. All material passed the -78° trap while the -196° trap contained 0.6 mmol of a mixture of CF_3Cl, CO_2, COF_2 and Cl_2. The material retained at -112° was a very pale yellow liquid. Removal of part of this material to another trap followed by careful warming resulted in decomposition to an equimolar mixture of CF_3Cl and CO_2. The observed weight change (38 mg) of the solids in the cylinder agreed well with that calculated (41 mg) for the conversion of 2.93 mmol CF_3CO_2Na to $NaSO_3F$. On one occasion, a sample of CF_3CO_2Cl, when allowed to warm to a temperature resulting in 40 mm vapor pressure, exploded in the vacuum line forming mainly CF_3Cl and CO_2 but also some COF_2, CF_4, C_2F_6, and Cl_2. In carefully passivated IR cells which were pretreated with some CF_3CO_2Cl, a reproducible infrared spectrum of this acyl hypochlorite was obtained, cm^{-1}; 1844(S), 1308(M), 1241(S), 1206(S), 1093(S), 844(W), 765(W) and 719(MW): Fig. 1. Decomposition rates varied considerably from minutes to hours depending on the sample. The primary decomposition product in the cells was CF_3CO_2H indicating incomplete passivation despite the precautions taken.

$ClCF_2CO_2Cl$. Chlorodifluoroacetic acid (2.80 mmol) was placed in a 30 ml stainless steel cylinder. After cooling to -196° and evacuating, $ClSO_3F$ (2.91 mmol) was condensed in and the reaction allowed to proceed at -45°

for two days. Separation of the products was effected by keeping the cylinder at -30° (to retain HSO_3F) and pumping the volatile materials through U traps cooled to -78 and -196°. The latter contained 0.24 mmol of Cl_2 and SO_2F_2, while the former contained the pale yellow liquid $ClCF_2CO_2Cl$. A sample of $ClCF_2CO_2Cl$, allowed to stand at ambient temperature in the vacuum line for two hours, was found to have completely decomposed to an equimolar mixture of CF_2Cl_2 and CO_2. On one occasion a sample of $ClCF_2CO_2Cl$ warmed to about 0° exploded when a valve was opened rapidly to allow it to expand. This contained explosion produced primarily CF_2Cl_2 and CO_2, but also some COF_2 and Cl_2.

$\underline{CF_3CO_2CF_2CFClCF_3}$. To a 2.03 mmol sample of CF_3CO_2Cl contained in a U-trap at -78°, hexafluoropropylene (2.72 mmol) was slowly added. After several hours the mixture was warmed to ambient temperature for 1 hour prior to fractional condensation through traps cooled to -78 and -196°. The -196° fraction consisted of one mmol C_3F_6 and 0.27 mmol each of CF_3Cl and CO_2. The material retained at -78° was a colorless liquid and was identified as $CF_3CO_2CF_2CFClCF_3$ (1.70 mmol, 84% yield) on the basis of its vapor density molecular weight (297 found vs. 298.5 g/mol calculated), and controlled hydrolysis to a 1:1 mixture of $CF_3CFClCFO$ [10] and CF_3CO_2H. Its spectroscopic properties confirmed this identification: infrared, cm^{-1}; 1856 (S), 1335 (M), 1297 (S), 1249 (VS), 1205 (S), 1137 (S), 1088 (VS), 970 (S), 850 (W), 740 (W), 671 (MW): mass spectrum, 40 ev; m/e (assign., rel. intens.) 298 (M, 0.01), 279 (M-F, 0.03), 263 (M-Cl, 0.03), 244 (M-F, Cl, 0.05) 229 ($M-CF_3$, 0.14), 185 (C_3F_6Cl, 4.7), 166 (C_3F_6O, 0.04), 163 ($C_3F_5O_2$, 0.06), 135 (C_2F_5O, C_2F_4Cl, 6.8), 131 (C_3F_5, 1.0), 119 (C_2F_5, 0.3), 116 (C_2F_3Cl, 1.8), 113 ($C_2F_3O_2$, 0.6), 109 (C_3F_3O, 0.1), 100 (C_2F_4, 3.3), 97 (C_2F_3O, 30), 94 ($C_2F_2O_2$, 0.7), 85 (CF_2Cl, 17), 81 (C_2F_3, 0.5), 78 (C_2F_2O, 0.9), 69 (CF_3, 100), 66 (COF_2, 1.7), 51 (CFCl, 0.6), 50 (CF_2, 3.6), 47 (COF, 3.5), 44 (CO_2, 3.6): ^{19}F nmr; Fig. 2.

$\underline{ClCF_2CO_2CF_2CFClCF_3}$. Using the above described conditions, $ClCF_2CO_2Cl$ (2.30 mmol) was reacted with C_3F_6 (2.46 mmol) to furnish 0.60 mmol each of CF_2Cl_2 and CO_2 together with 0.76 mmol of unreacted C_3F_6. The colorless liquid $ClCF_2CO_2CF_2CFClCF_3$ (1.70 mmol, 74% yield) was identified spectroscopically: infrared, cm^{-1}; 1856 (S), 1300 (MS), 1270 (MS), 1238(VS), 1193 (S), 1135 (S), 1096 (VS), 985,975 (S, doublet), 848 (W), 736 (W), 690 (W, br), 617 (W): mass spectrum, 40 ev; m/e (assign., rel. intens.) 314 (M, 0.05), 295 (M-F, 0.03), 279 (M-Cl, 0.02), 245 ($M-CF_3$, 0.02), 229 ($M-CF_2Cl$, 0.15), 185 (C_3F_6Cl, 31), 166 (C_3F_6O, 0.41), 150 (C_3F_6, 3.1), 147 (C_3F_5O, 0.5), 135 (C_2F_4Cl, 12), 131 (C_3F_5, 2.4), 116 (C_2F_3Cl, 3.8), 113 ($C_2F_3O_2$, 2.9), 100 (C_2F_4, 7), 97 (C_2F_3O, 22), 94 (C_2F_2O, 3.5), 85 (CF_2Cl, 100), 78 (C_2F_2O, 6), 69 (CF_3, 55), 66 (CFCl, 6), 50 (CF_2, 12), 47 (COF, 10), 44 (CO_2, 24): ^{19}F nmr; Fig. 2.

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