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REACTION OF PHOSPHORUS PENTACHLORIDE WITH PERHALO CARBONYL-CONTAINING COMPOUNDS*

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SUMMARY

The reaction between PCl_5 and the carbonyl oxygen in a variety of perfluoro compounds containing the carbonyl functional group, e.g. $R_fC(O)R_f'$, $R_fC(O)X$ or $XC(O)R_fC(O)X$, where X = Cl, F, OH, NH_2, and ONH_4 has led to a convenient synthesis procedure for fluorochloro compounds. Monoketones, e.g. $R_fC(O)R_f'$, yield $R_fCCl_2R_f'$ compounds, while the diketones, e.g. $R_fC(O)(CF_2)_nC(O)R_f'$, also react to yield the fluorochloro compounds. When n = 3, $R_fCCl_2(CF_2)_3CCl_2R_f'$ is produced in quite high yields (65 percent); however, when n = 2, the principal product is a cyclic fluorodichloroether compound while the fluorotetrachloro compound is the minor product. The $R_fC(O)X$ and $XC(O)R_fC(O)X$ compounds produce R_fCCl_3 and $Cl_3CR_fCCl_3$ respectively in high yields. Reaction temperature and pressure are important factors for high yield synthesis.

INTRODUCTION

The reaction of PCl_5 with hydrocarbon ketones or aldehydes will produce gem-dichlorohydrocarbon compounds in high yield. As an example, norcamphor dichloride has been prepared in 92 percent yield by the action of norcamphor with PCl_5 at room temperature for one day [1]. One might expect that the reaction between PCl_5 and perfluoro carbonyl-containing compounds should be more difficult

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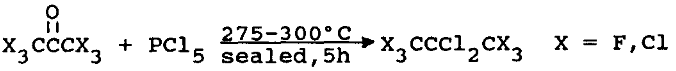
than that of hydrocarbon ketones due to electronic and/or steric effects of the perfluoroalkyl group. For example, in earlier studies Farah and Gilbert [2] reported the reaction of perhaloacetones with PCl_5 to yield the corresponding dichlorides



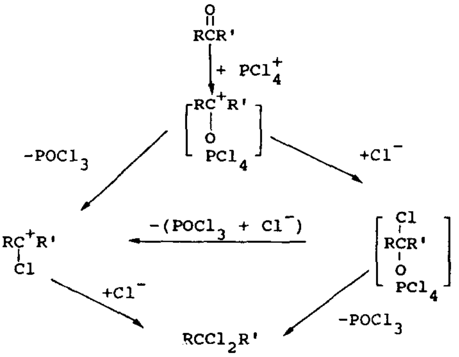
$$X_3C\overset{O}{\overset{\|}{C}}CX_3 + PCl_5 \xrightarrow[\text{sealed, 5h}]{275\text{-}300^\circ C} X_3CCCl_2CX_3 \qquad X = F, Cl \qquad (1)$$

$F_3CCCl_2CF_3$ (31 percent), $F_3CCCl_2CF_2Cl$ (50 percent), $ClF_2CCCl_2CCF_2Cl$ (61 percent), $ClF_2CCCl_2CFCl_2$ (48 percent), $Cl_2FCCCl_2CFCl_2$ (62 percent) and $Cl_3CCCl_2CCl_3$ (85 percent). From these results it can be seen that perfluoroacetone is more difficult to chlorinate by PCl_5.

In our current studies we have re-examined in more detail the previously reported [2] reactions between PCl_5 and perhalo carbonyl-containing compounds with the objective of providing an improved synthesis procedure of the geminal dichloro and terminal trichloro perfluoroalkanes.

RESULTS AND DISCUSSION

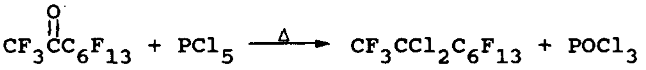
The mechanism of the reaction between phosphorus pentachloride with hydrocarbon ketones [3,4] or perhaloacetones at 275-300°C [2] has been suggested to proceed according to the reactions shown in Scheme 1.



Scheme 1

When R and R' are strong electron withdrawing groups, the electron density at the carbonyl oxygen is reduced which subsequently inhibits the attack by a chlorophosphonium ion, PCl_4^+. In addition the leaving ability of the $POCl_3$ would be reduced. For this reason the perfluoroalkyl ketones are not readily chlorinated by PCl_5 using experimental conditions for hydrocarbon ketones.

In our present study we have examined in detail the chlorination of $R_f\overset{\overset{O}{\|}}{C}R_f'$ where R = CF_3, R' = C_6F_{13}. The reactions were carried out under various experimental conditions of temperature,



$$CF_3\overset{\overset{O}{\|}}{C}C_6F_{13} + PCl_5 \xrightarrow{\Delta} CF_3CCl_2C_6F_{13} + POCl_3 \qquad (2)$$

time and concentration of reactants. Table 1 is a summation of the yield of the reaction product, $CF_3CCl_2C_6F_{13}$, found based on variations of the above mentioned experimental conditions.

Temperature Effect

From the experimental results (see Table 1, exp. 1, 2, and 3), it can be seen that the $CF_3CCl_2C_6F_{13}$ gave an extremely low yield at 150°C for 3 h. At 250°C the yield of 2,2-dichloroperfluorooctane increased to 25 percent. Increasing the reaction temperature however also increased the amount of decomposition products. At 300°C the products of decomposition increased to 36 percent. The structures of these compounds were identified by GC/MS as CF_3CCl_3, C_2Cl_4, $C_6F_{13}CCl_3$ and C_2Cl_6. A reaction temperature between 250 and 275°C gave the highest yields of the dichloroperfluoro compound.

Time Effect

At 250°C and 120 psi (see Table 1, exp. 2, 4, and 5), the chlorination of $CF_3C(O)C_6F_{13}$ by PCl_5 was time dependent. For

TABLE 1

Reaction of $CF_3C(O)C_6F_{13}$ with PCl_5

	Conditions			Concentrations[a] (mole/liter)			GC Area %		
								Products	
Experiment	Time (day)	Temp. (°C)	Pressure (psi)[d]	[A]	x [B]	= Product	Unreacted $CF_3C(O)C_6F_{13}$	$CF_3CCl_2C_6F_{13}$	Others[e]
1	3h	150[b]	70	0.17	0.96	0.16	98	trace	-
2	3h	250[b]	120	0.17	0.96	0.16	62	25	3
3	3h	300[b]	180	0.17	0.96	0.16	33	27	36
4	2	250[b]	120	0.17	0.96	0.16	35	55	8
5	3	250[b]	120	0.17	0.96	0.16	24	65	9
6	2	250[c]	60	0.06	0.37	0.02	95	3	trace
7	2	250[c]	150	0.12	1.71	0.21	29	67	2
8	2	250[c]	250	0.21	2.57	0.54	17	80	trace
9	2	250[c]	260	0.26	2.67	0.69	5	92	trace

[a] [A] and [B] represent the concentrations of $CF_3C(O)C_6F_{13}$ and PCl_5, respectively.

[b] In 20 ml reaction vessel, accuracy, ±20°C.

[c] In 450 ml reaction vessel, accuracy, ±5°C.

[d] Reaction pressure of the vessel, psi = pounds per square inch.

[e] The structures of the compounds were determined by GC/MS, they included CF_3CCl_3, C_2Cl_4, $C_6F_{13}CCl_3$ and C_2Cl_6.

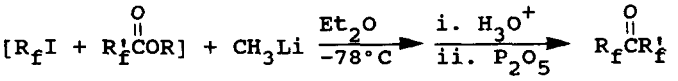
3 h, 2 and 3 days reaction times, the yields of 2,2-dichloroperfluorooctane were 25, 55, and 65 percent, respectively. After three days the rate of chlorination was extremely slow.

Concentration/Pressure Effect

The reactants, $CF_3C(O)C_6F_{13}$ and PCl_5, and products $CF_3CCl_2C_6F_{13}$ and $POCl_3$, are in the gas phase at ≥250°C (see Equation 2). The rate of formation of $CF_3CCl_2C_6F_{13}$ is found to obey the rate equation as follows: $d[CF_3CCl_2C_6F_{13}]/dt = k[CF_3C(O)C_6F_{13}]\cdot[PCl_5]$. At constant reaction volume and temperature, the reaction pressure in the vessel is proportional to the product of concentration of the reactants. From the experimental results (see Table 1, exp. 4, 6, 7, 8, and 9), it can be seen that increasing the products of [A] x [B] from 0.02, 0.16, 0.21, 0.54, to 0.69 $(\text{mole/liter})^2$ or the reaction pressures from 60, 120, 150, 250, to 260 psi at the same reaction time and temperature, increased the yield of 2,2-dichloroperfluorooctane from 3, 55, 67, 80, to 92 percent, respectively. Therefore the product of the reactants concentration or the reaction pressure is an important factor for producing high yields.

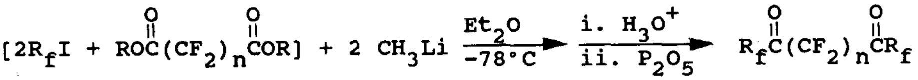
Synthesis of Perfluoroalkyl Monoketones and Diketones

In our present study we have synthesized the perfluoroalkyl monoketones and diketones, by the <u>in-situ</u> reaction which we have previously reported [5] and summarized by equations 3 and 4.



$$[R_fI + R_f'\overset{O}{\overset{\|}{C}}OR] + CH_3Li \xrightarrow[-78°C]{Et_2O} \xrightarrow[ii.\ P_2O_5]{i.\ H_3O^+} R_f\overset{O}{\overset{\|}{C}}R_f' \qquad (3)$$

$R_f = C_6F_{13}$, C_8F_{17}; $R_f' = CF_3$, CF_2Cl, C_3F_7; $R = CH_3$, C_2H_5



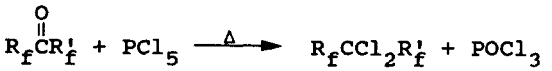
$$[2R_fI + RO\overset{O}{\overset{\|}{C}}(CF_2)_n\overset{O}{\overset{\|}{C}}OR] + 2\ CH_3Li \xrightarrow[-78°C]{Et_2O} \xrightarrow[ii.\ P_2O_5]{i.\ H_3O^+} R_f\overset{O}{\overset{\|}{C}}(CF_2)_n\overset{O}{\overset{\|}{C}}R_f$$

$R_f = C_2F_5$, C_3F_7; $R = CH_3$, C_2H_5; $n = 2,3$ (4)

The lithium-iodine exchange reaction, producing the perfluoroalkyllithium intermediate, is much faster than the addition of methyllithium to the carbonyl group of the ester. The transient R_fLi which is produced first, is unstable at -78°C, however it can be used as an intermediate if it is prepared by this in-situ process and allowed to react with a substrate (ester) immediately. This suggests that the rate of R_fLi decomposition is slower than the reaction between R_fLi and the ester. This observation was noted previously by McBee and coworkers [9]. The characterization of perfluoroalkyl monoketones and diketones, is listed in Table 2. In our earlier studies [5,6] we have shown that highly fluorinated carbonyl compounds tend to retain water and form stable hydrate derivatives quite readily. The perfluoroalkyl monoketones and diketones prepared in this study likewise form the hydrate in air quite readily. These hydrates can easily be dehydrated by reaction with P_2O_5 at reflux temperature.

Synthesis of gem-dichloroperfluoroalkanes

As mentioned above, the gem-dichloroperfluoroalkanes were synthesized by the reaction between perfluoroalkyl monoketone and PCl_5 (see Table 1) in high yields (see Equation 5). The



$$R_f\overset{\overset{\displaystyle O}{\|}}{C}R'_f + PCl_5 \xrightarrow{\Delta} R_fCCl_2R'_f + POCl_3 \qquad (5)$$

$$R_f = CF_3,\ CF_2Cl,\ C_3F_7;\ R'_f = C_6F_{13},\ C_8F_{17}$$

optimum reaction conditions for maximum yield are as follows: concentration of monoketone, ~0.3 mole/liter, excess PCl_5, ~3.0 moles/liter; pressure of vessel, ~260 psi; time of reaction, 2-3 days. Excess PCl_5 was recycled to be used for subsequent chlorinations. In most instances the isolated yields are more than 80 percent, except in the case of $C_3F_7CCl_2C_6F_{13}$ where the reaction conditions were 275°C, ~380 psi, and three days reaction time in order to reach the highest yield obtained of 55 percent.

TABLE 2

Characterization of Perfluoroalkyl Monoketones and Diketones

Compound	Isolated Yield (%)	b.p. (°C)	IR,[b] C=O (cm^{-1})	M.S.[c]	Combustion Data (Calc'd/Found) C	H
$CF_3C(O)C_6F_{13}$ (n.c.)	72	97	1800	$416(M^{+})$	23.09 22.92	0 0.09
$CF_3C(O)C_8F_{17}$ (n.c.)	77	136	1799	$516(M^{+})$	23.27 23.10	0 0.11
$CF_2ClC(O)C_6F_{13}$ (n.c.)	89	121	1798	$433,435(M^{+})$	22.21[a] 22.08	0 0.11
$C_3F_7C(O)C_6F_{13}$ (n.c.)	80	137	1795	$516(M^{+})$	23.27 23.14	0 0.08
$C_2F_5C(O)(CF_2)_3C(O)C_2F_5$ (n.c.)	72	111	1790	$325(M-C_2F_5)^{+}$	23.34 23.20	0 0.04
$C_3F_7C(O)(CF_2)_3C(O)C_3F_7$ (n.c.)	75	73/35 mmHg	1790	$375(M-C_3F_7)^{+}$,[d] $347(C_3F_7C(O)(CF_2)_3)^{+}$	24.28 24.13	0 0.06
$C_2F_5C(O)(CF_2)_2C(O)C_2F_5$ (n.c.)	67	91	1790	$394(M^{+})$,[d] $275(M-C_2F_5)^{+}$	24.38 24.26	0 0.08

[a] For Cl: Calculated, 8.20; found, 8.01.

[b] Neat liquid, capillary film between NaCl plates.

[c] Determined by electron impact; the highest mass in the fragmentation for diketones are reported in the Table.

[d] Very weak peaks.

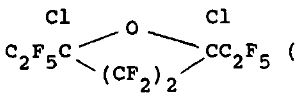
It is difficult at this time to provide an acceptable explanation of this anomaly. The IR spectra data and ^{19}F NMR chemical shifts of polychloroperfluoro compounds are shown in the experimental section. The characterization of these products is listed in Table 3.

Synthesis of $C_2F_5CCl_2(CF_2)_3CCl_2C_2F_5$

The $R_fCCl_2(CF_2)_nCCl_2R_f$ were synthesized by the same procedure as for the $R_fCCl_2R_f'$ except at higher reaction temperature (275°C) and longer reaction time (seven days). The yield of the desired product, tetrachloroperfluoroalkane, depends on the number of CF_2 groups (n). When n = 3, the linear fluorotetrachloroalkane, e.g. $C_2F_5CCl_2(CF_3)_3CCl_2C_2F_5$, is produced in reasonable yields (65 GC area percent); however, when n = 2, the principal product is the cyclic dichlorofluoroether compound (74 GC area percent) - see Scheme 2. This result is similar to the data described for the fluorination of $HO_2C(CH_2)_nCO_2H$ by sulfur tetrafluoride [7]. A possible mechanism for the formation of both linear and cyclic compounds is suggested in Scheme 2. When n = 2, the cyclic ether intermediate is quite stable at 275°C, however when n = 3, the linear ketone intermediate is more stable than the cyclic ether intermediate. The structure of the cyclic dichlorofluoroether compound was confirmed by MS and ^{19}F NMR spectra and its infrared spectrum shows the absence of a carbonyl peak. In Figure 1 the mass spectrum of a linear dichlorofluoroketone, $C_2F_5C(O)(CF_2)_3CCl_2C_2F_5$ (compound A), obtained as a by-product in the synthesis of the linear tetrachloroperfluoroalkane (see Table 3), is compared to the mass spectrum of the cyclic ether (compound B). The linear ketone has the fragments m/e = 201 $(C_2F_5CCl_2)^+$, 297 $(C_2F_5C(O)CF_2CF_2CF_2)^+$ and 351 $(M-C_2F_5C(O))^+$. If compound B were a linear ketone, comparable fragment peaks at m/e = 201 $(C_2F_5C(O))^+$, 247 $(C_2F_5C(O)CF_2CF_2)^+$ and 301

TABLE 3

Characterization of Polychloroperfluoro Compounds

Compound	Yield, % Isolated (GC area)	b.p. (°C)	M.S.[a] (m/e)	Combustion Data (Calc'd/Found)		
				C	F	Cl
$CF_3CCl_2C_6F_{13}$ (n.c.)	81(92)	144	401,403$(M-CF_3)^+$	20.40/20.26	64.54/64.08	15.05/14.99
$CF_3CCl_2C_8F_{17}$ (n.c.)	84(92)	95/30 mmHg	501,503$(M-CF_3)^+$	21.03/20.76	66.55/66.01	12.42/12.41
$CF_2ClCCl_2C_6F_{13}$ (n.c.)	82(92)	81/30 mmHg	451,453$(M-Cl)^+$	19.71/19.52	58.47/58.12	21.82/21.66
$C_3F_7CCl_2C_6F_{13}$ (n.c.)	55(65)	82/20 mmHg	401,403$(M-C_3F_7)^+$	21.03/20.76	66.55/66.08	12.42/12.10
$C_2F_5CCl_2(CF_2)_3CCl_2C_2F_5$ (n.c.)[b]	60(65)	104/20 mmHg	433,435,437, 439$(M-C_2F_5)^+$	19.52/19.40	54.88/54.39	25.60/25.28
 (n.c.)	74(74)	139	413,415$(M-Cl)^+$ 329,331$(M-C_2F_5)^+$	21.40/21.14	59.24/58.48	15.79/15.34
$CCl_3(CF_2)_3CCl_3$ (n.c.)	85(93)	35(m.p.)	349,351,353, 355$(M-Cl)^+$	15.53/15.89	29.47/28.89	55.00/54.71
$[CCl_3CF_2CF_2]_2O$ (n.c.)	64(92)	76/2.4 mmHg	415,417,419 $(M-Cl)^+$	15.92/15.96	33.57/33.89	46.98/46.92
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CCl_3$ (n.c.)	24(51)	88/30 mmHg	533,535$(M-C)^+$	18.98/19.08	56.67/56.29	18.68/18.29

[a] Determined by electron impact.

[b] By-product $C_2F_5C(O)(CF_2)_3CCl_2C_2F_5$ (28 GC area percent), the chemical structure was identified by MS (see Figure 1, A) and IR spectrum ($V_{C=O}$ = 1785 cm^{-1}) only.

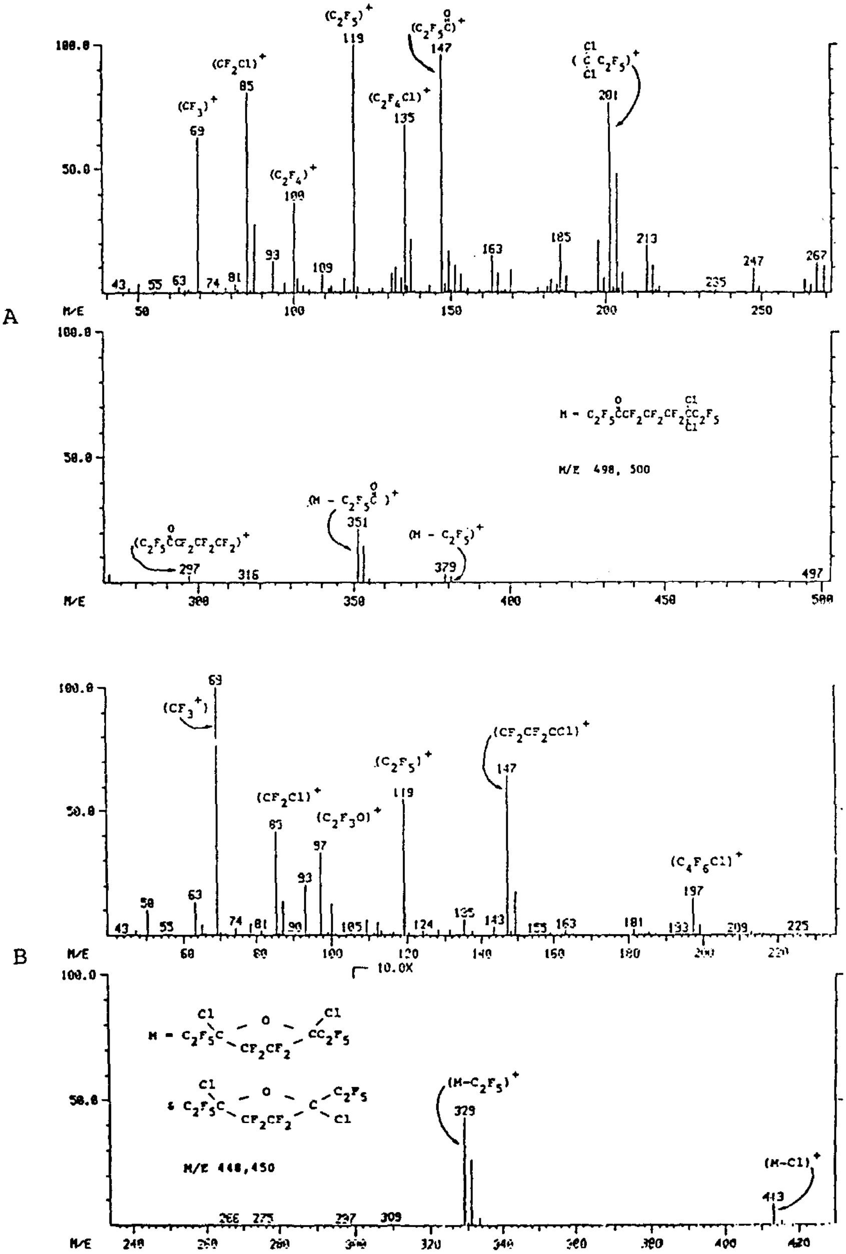
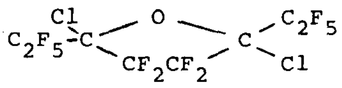
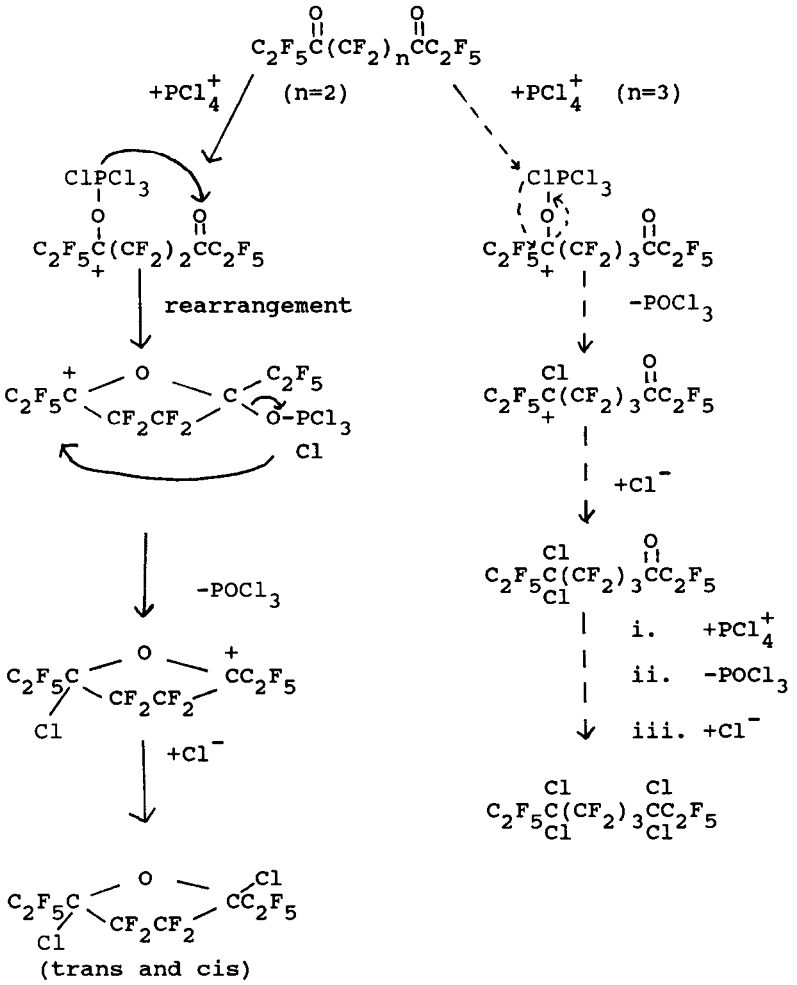


Fig. 1. Mass spectra of compounds A - $C_2F_5C(O)(CF_2)_3CCl_2C_2F_5$ and B -



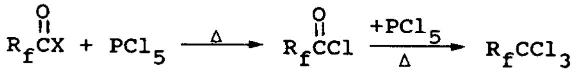


Scheme 2

$(M-C_2F_5C(O))^+$ would be expected in the mass spectrum of compound B. The mass spectrum of compound B does not show these fragments. The peak at m/e = 147 is assigned to the fragment $(C_2F_4CCl)^+$ in the mass spectrum of compound B. The ratio of the relative intensity of the 147 to 149 peak is 3.7. This is close to the expected ratio of 3 for the relative natural abundance of Cl^{35}/Cl^{37}. Although the fragment $(C_2F_4CCl)^+$ might also be expected in the mass spectrum of compound A, the observed ratio of relative intensity of the 147 to 149 peak is 5.8 in the spectrum for compound A. The m/e = 147 peak is therefore assigned to $(C_2F_5C(O))^+$ in compound A. The presence of both cis and trans forms of the cyclic ether compound was confirmed by ^{19}F NMR (see experimental section). However, the present results do not allow us to assign which peaks belong to which isomer (cis or trans). The characterization of these products is listed in Table 3.

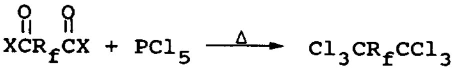
Synthesis of R_fCCl_3 and $Cl_3CR_fCCl_3$

The perfluorotrichloro and hexachloroperfluoro compounds, e.g. $C_7F_{15}CCl_3$ and $Cl_3CCF_2CF_2CCl_3$, had been synthesized from perfluoroalkyl iodides and anhydrous aluminum chloride in ~55 percent yield [10]. In the present study we have synthesized R_fCCl_3 and $Cl_3CR_fCCl_3$ compounds by procedures similar to those described for the gem-dichloroperfluoroalkanes (see Experimental Section). The reactions between perfluoro carbonyl-containing compounds and PCl_5 are shown in Equations 6 and 7. The yields by GC area percent are between 85 and 93 except in the case of n-$C_7F_{15}C(O)NH_2$ and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$. The major products of the chlorination of a perfluoroalkyl amide,



$$R_f\overset{O}{\overset{\|}{C}}X + PCl_5 \xrightarrow{\Delta} R_f\overset{O}{\overset{\|}{C}}Cl \xrightarrow[\Delta]{+PCl_5} R_fCCl_3 \qquad (6)$$

R_f = n-C_3F_7, n-C_7F_{15}, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$
X = Cl, F, OH, NH_2, ONH_4



$$X\overset{O}{\overset{\|}{C}}R_f\overset{O}{\overset{\|}{C}}X + PCl_5 \xrightarrow{\Delta} Cl_3CR_fCCl_3 \qquad (7)$$

R_f = $-(CF_2)_3-$, $-CF_2CF_2OCF_2CF_2-$
X = Cl, OH

e.g. n-$C_7F_{15}C(O)NH_2$, are n-$C_7F_{15}CCl_3$ (42 GC area percent) and n-$C_7F_{15}C \equiv N$ (42 GC area percent). These results are consistent with previously reported studies on the reaction of PCl_5 with $CF_3C(O)NHCH_3$ [8]. The physical properties of n-$C_3F_7CCl_3$, n-$C_7F_{15}CCl_3$ and n-$C_7F_{15}C \equiv N$ were compared to known samples and confirmed by GC/MS analysis.

The chlorination of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ yields the trichloro compound (at 250°C for seven days) only in 51 GC area percent. The CF_3 group present on the α-carbon to the carbonyl group provides steric hindrance to the chlorination and could account for the lower yields obtained.

Experimentally we have found that the best conditions for the chlorination of perfluorocarbonyl containing compounds are: (a) reaction temperatures of 250-275°C; (b) high concentration of reactants (ketone >0.3 mole/liter, excess PCl_5 of >3 moles/liter); (c) high reaction pressures of at least 300 psi; and (d) reaction times of three to seven days. In addition, reduction of electron density at the carbonyl group reduces the rate of chlorination of the perhalocarbonyl compounds.

EXPERIMENTAL

General Comments

All reactions were carried out in flame-dried 20 ml and 450 ml stainless steel high pressure reactors. The 20 ml reactor was a high pressure, lined reactor vessel-model LRA (LECO Corp., Bellefonte, PA). The 450 ml reactor was a 4562 mini reactor with 4842 controller (Parr Instrument Company, Moline, IL). The various perfluoro compounds used as starting materials were commercially available through PCR/SCM Specialty Chemicals, Gainesville, FL. The PCl_5 and CH_3Li were purchased from Aldrich Chemical Company, Inc., Milwaukee, WI. All new compounds were characterized by GC, IR, MS, ^{19}F NMR and combustion analysis.

Infrared spectra were recorded on a Perkin-Elmer Model 600 computing infrared spectrophotometer. Gas chromatographic analyses (GC) were performed on a Perkin-Elmer Sigma 1 chromatograph using a six-foot stainless steel column (1/4" o.d.) packed with 10 percent SE-30 on Chromosorb W. Mass spectra were obtained on a duPont Model 21-490 mass spectrometer used in the electron impact mode. ^{19}F NMR spectra were recorded on an XL-100-15 spectrometer using $CFCl_3$ for reference in $CDCl_3$ solvent. All boiling points are uncorrected. All the perfluoroalkyl ketones and chlorofluoro compounds were prepared following typical procedures.

Typical Procedure for Preparation of Perfluoroalkyl Ketones

To a diethyl ether solution (1000 ml) of n-$C_6F_{13}I$ (55.4 g, 0.124 mol) and $CF_3C(O)OC_2H_5$ (16.8 g, 0.118 mol) was slowly added CH_3Li (82.9 ml of 1.5 M diethyl ether solution, 0.124 mol) at -78°C over a period of 30 minutes. After an additional 30 minutes, the reaction mixture was hydrolyzed with conc. HCl (30 ml). The mixture was then poured into 2N HCl (600 ml), phase separated and dried over $MgSO_4$. Diethyl ether and low boiling compounds were removed with a compact distilling apparatus. Distillation of the crude product from phosphorus pentoxide (4 g) on a spinning band column gave $CF_3C(O)C_6F_{13}$, 35.2 g, 72 percent isolated yield. The yield, b.p., MS and analysis data of monoketones and diketones are listed in Table 2.

Typical Procedures for Preparation of Chlorofluoro Compounds

A mixture of $CF_3C(O)C_6F_{13}$ (49.0 g, 0.118 mol) and PCl_5 (250 g, 1.20 mol) was placed in a 450 ml stainless steel reactor under dry N_2 atmosphere. The reactor was heated at 250°C (±5°C). The pressure in the reactor was between 260 and 280 psi. After two days the reactor was cooled to room temperature and the liquid part of the reaction mixture was hydrolyzed with crushed ice (~50 g) in an ice-water bath. The lower layer was withdrawn and washed with water (3x35 ml). The organic phase contained two liquid layers and a white solid. The results obtained by GC/MS analysis are as follows: bottom layer (50 g) - $CF_3CCl_2C_6F_{13}$ (93 percent), $CF_3C(O)C_6F_{13}$ (two percent), $C_2F_3Cl_3$ (one percent), $C_6F_{13}CCl_3$ (one percent), and C_2Cl_6 (two percent); top layer (4 g) - $CF_3CCl_2C_6F_{13}$ (45 percent), $CF_3C(O)C_6F_{13}$ (45 percent), $C_2F_3Cl_3$ (two percent), $C_6F_{13}CCl_3$ (two percent), and C_2Cl_6 (three percent); white solid (2 g) - C_2Cl_6 (96 percent), $CF_3CCl_2C_6F_{13}$ (one percent) and $CF_3C(O)C_6F_{13}$ (one percent). Excess PCl_5 in the reactor may be reused three additional times for additional chlorinations of the ketone following the above described procedure. The organic phases from the quadruple chlorinations were combined to give 205 g (92 GC area percent) of the desired product. Distillation of combined crude products yielded $CF_3CCl_2C_6F_{13}$ (179 g, 81 percent isolated). The yield, b.p., MS and analysis data of the new chlorofluoro compounds are summarized in Table 3.

IR Spectra

They were obtained as neat liquids, capillary film, between NaCl plates.

C-F stretching vibration: 1400-1100 cm^{-1} (vs)
C-Cl stretching vibration: 1000-900 cm^{-1} (s)

^{19}F NMR Spectra

^{19}F NMR (282.31 MHz), chemical shifts (ppm), solvent $CDCl_3$, internal reference $CFCl_3$.

(a) $\underline{CF_3CCl_2C_6F_{13}}$: -74.5 (septet, CF_3 next to CCl_2), -110.0, -117.2, -122.1, -123.0, -126.8 (multiplet, 5 CF_2), -81.7 (triplet, CF_3 next to CF_2).

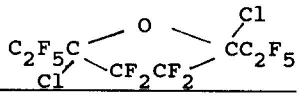
(b) $CF_3CCl_2C_8F_{17}$: -74.6 (septet, CF_3 next to CCl_2), -110.1, -117.3, -122.1, -122.1, -122.5, -123.3, -126.9 (multiplet, 7 CF_2), -81.9 (triplet, CF_3 next to CF_2).

(c) $CF_2ClCCl_2C_6F_{13}$: -59.3 (multiplet, CF_2 next to CCl_2), -107.7, -116.9, -122.1, -123.0, -126.7 (multiplet, 5 CF_2), -81.6 (triplet, CF_3 next to CF_2).

(d) $C_3F_7CCl_2C_6F_{13}$: -81.8 (triplet, 2 CF_3), -108.3, -108.9, -116.5, -120.9, -122.1, -123.1, -126.8 (multiplet, 7 CF_2).

(e) $C_2F_5CCl_2(CF_2)_3CCl_2C_2F_5$: -76.7 (singlet, 2 CF_3), -108.7 (broad, 2 CF_2), -111.3 (unresolved multiplet, CF_2), -112.6 (unresolved multiplet, 2 CF_2).

(f) cis,trans-



: -78.0 (singlet, 2 CF_3 -78 percent of one isomer), -78.1 (singlet, 2 CF_3 -22 percent of the other isomer), -105, -117, -119, -121.5, -126.7 (doublet - half of AB pattern, 4 CF_2).

(g) $CCl_3(CF_2)_3CCl_3$: -109.8 (multiplet, middle CF_2), -110.0 (distorted triplet, 2 CF_2).

(h) $[CCl_3CF_2CF_2]_2O$: -77.2 (singlet, 2 CF_2 next to oxygen), -113.6 (singlet, 2 CF_2 next to CCl_3).

(i) $(CF_3)_2CFOCF(CF_3)CF_2OCF(CF_3)CCl_3$: -73.33 (doublet-doubled, CF_3 next to CCl_3), -80.4 (quartet-doubled, CF_3 next to CF_2), -81.5 (AB pattern - nonequivalent F's, CF_2O), -82.0 (doublet-doubled, 2 CF_3), -130.1 (multiplet, 2 CF), -145.6 (multiplet, CF).

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