tions. For 7 and 24 hr., respectively, about 16 and 62% of the sample was oxidized by the periodate.

Oxidation of Ia proceeded at an even slower rate than did *trans*-Ib. For 7 and 24 hr., respectively, about 10 and 42% of the sample was oxidized by the periodate.

Acid-Catalyzed Additions. A.—Equimolar quantities of N,N'-dimethylurea and aqueous 40% glyoxal at pH 2 and 4 were allowed to stand 30–60 hr. at RT. Crystals were obtained by chilling or samples were withdrawn and evaporated to dryness using vacuum only, and the infrared spectra were obtained. In both cases the spectra of the residue or the crystalline product indicated that *trans*-Ib was the major or only product. This procedure was repeated using urea and glyoxal. Again, spectra indicated that the desired dihydroxy derivative, Ia, was the major product. Some higher melting products were also isolated in both cases, especially if delays occurred in the isolation of the products.

B.—From glyoxal and N,N'-dimethylurea using the conditions of Nematollahi and Ketcham[6b] for the synthesis of II ($R = CH_3$) and III ($R = C_6H_5$), the glycoluril (II, $R = CH_3$), m.p. 224–226°, lit.[6b] m.p. 225–227°, was the sole product isolated (lit.[12] m.p. 44–45° for N,N'-dimethylhydantoin).

N.m.r. Spectral Data.—Once isolation of products (including isomers) was completed, these compounds, in addition to 2-imidazolidinone, were dissolved in D_2O and their proton n.m.r. spectra were obtained (see Table I). Spectra were obtained of the reactants in aqueous solution before and after addition of the products (Ia and the Ib isomers) to determine which, if any, of the protons of Ia and Ib were free of interference from the other materials. These preliminary experiments suggested that the methyl protons of N,N'-dimethylurea and Ib could be used to follow the addition reaction to glyoxal. The similar reaction with urea was not followed because the signal from the ring protons of Ia and the adjacent region of the spectrum were not free of interference from signals from water and glyoxal.

Under basic conditions the methyl peak of N,N'-dimethylurea was a doublet separated by a distance of 0.07 p.p.m. Proceeding downfield from these peaks, the methyl peak of *cis*-Ib was a distance of 0.05 p.p.m. and the similar peak of *trans*-Ib was a distance of another 0.05 p.p.m., all peaks being in a 0.17-p.p.m. range. Under acidic conditions the methyl peak of N,N'-dimethylurea was a singlet. Proceeding downfield the methyl peak of *cis*-Ib was a distance of about 0.08 p.p.m. and the similar peak of *trans*-Ib was a distance of another 0.05 p.p.m., all peaks being in a 0.13-p.p.m. range. From these preliminary experiments it was possible to follow the reaction of N,N'-dimethylurea and glyoxal in aqueous solutions at various pH values and to follow the rates of conversion of the pure geometric isomers into an equilibrium mixture of more than 95% *trans*.

The addition reactions were carried out by altering the pH of the 40% glyoxal with either 6 *N* HCl or solid $NaHCO_3$. An equimolar amount of N,N'-dimethylurea was added to the glyoxal. The stirred solution was maintained at room temperature. A final, slight adjustment of the pH was then made. An aliquot was withdrawn and placed in the instrument as rapidly as possible. A sweep of 0.7–0.8 p.p.m. was obtained over the region of the spectrum of the methyl protons. Reactions were considered to be essentially complete when an estimated 5% or less of the urea remained. Using these procedures the following results were obtained.

pH 2.0.—The reaction was 50% completed in 35–50 min., essentially complete in 2 hr. All of the N,N'-dimethylurea reacted in 20 hr., but other products were forming at this time. The contribution to the spectra from the *cis* isomer was very small except at the beginning of the reaction.

pH 4.0.—The reaction was 50% completed in about 3.3 hr., essentially complete in 7.5 hr. All of the N,N'-dimethylurea reacted in 27 hr. Very little *cis* isomer was noted and no other products were observed forming.

pH 8.3.—The reaction was 50% completed after 35–45 min., essentially complete in about 3 hr. The *cis–trans* ratio was about 1:1 at the start of the reaction, but decreased as the reaction proceeded. No other products were observed forming.

Similar procedures were used to determine the rates at which the pure isomers were converted at various pH values to the equilibrium mixture. The conversion was considered to be essentially completed after three partial spectra appeared equivalent.

pH 2.0.—Pure *cis* was converted to the equilibrium mixture in 4–5 min.

pH 3.9.—Pure *cis* was converted 50% in 35 min. and was converted to the equilibrium mixture in 4 hr.

pH 8.6, 10.0, and in Distilled Water.—Pure *cis* was converted to the equilibrium mixture in 24 hr. (20% NaOH was used to obtain pH 10).

pH 2.4.—Pure *trans* was converted to the equilibrium mixture in 5 min.

pH 8.3.—Pure *trans* was converted to the equilibrium mixture in 2 hr.

Acknowledgment.—The authors wish to express their appreciation to P. J. Murphy, Jr., and G. Bremenstul for assistance in laboratory procedures and to S. A. Miles and E. R. McCall for assistance in obtaining the spectral data.

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[12] H. Biltz and R. Lemberg, *Ann.*, **432**, 137 (1923).

The Photolysis of Polyfluoroacyl Fluorides, Chlorides, and Bromides

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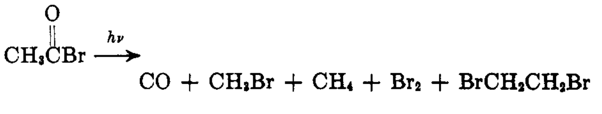
The photolysis of polyfluoroacyl fluorides yields largely fluoroalkanes resulting from the combination of two fluoroalkyl radicals together with ethers formed by addition of two fluoroalkyl radicals to the carbonyl group of the acyl fluoride. Photolysis of polyfluoroacyl chlorides and bromides leads to the formation of decarbonylation products, *i.e.*, polyfluoroalkyl chlorides and bromides, as the major products. When they are irradiated in the presence of terminal fluoro olefins, a variety of products, including oxetanes, fluoroalkyl bromides or chlorides, and polyfluoroalkanes, are formed.

Although photolyses of aliphatic aldehydes and ketones, including fluorinated ones,[1,2] have been studied extensively, there have been relatively few studies of the effects of ultraviolet radiation upon the related acyl halides. From the vapor phase photolysis of acetyl bromide, Etzler and Rollefson[3] obtained carbon monoxide and methyl bromide as major products and small quantities of ethylene bromide, methane, and bromine by what appeared to be a nonchain process (eq. 1). Similarly, the major products from the photolysis of acetyl iodide or acetyl chloride were the methyl



$$CH_3\overset{\overset{O}{\|}}{C}Br \xrightarrow{h\nu} CO + CH_3Br + CH_4 + Br_2 + BrCH_2CH_2Br \quad (1)$$

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[1] R. E. Dodd and J. W. Smith, *J. Chem. Soc.*, 1465 (1957).

[2] P. B. Ayscough and E. W. R. Steacie, *Can. J. Chem.*, **34**, 103 (1956).

[3] (a) D. H. Etzler and G. K. Rollefson, *J. Am. Chem. Soc.*, **61**, 800 (1939); (b) D. H. Etzler and G. K. Rollefson, *J. Chem. Phys.*, **6**, 653 (1938).

TABLE I

ULTRAVIOLET IRRADIATION OF POLYFLUOROACYL HALIDES

Halide, g. (mole)	Irradiation period, days	Product (%)
Chlorides		
$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}Cl$, 50 (0.22)	7	$n\text{-}C_3F_7Cl$ (V) (81) $n\text{-}C_6F_{14}$ (I) (4)
$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}Cl$, 55 (0.238) + $CF_2{=}CF(CF_2)_2H$, 40 (0.219)	6	$n\text{-}C_6F_{14}$ (I) (23) $n\text{-}C_3F_7[CF_2CF(CF_2)_2H]Cl$ (26) $Cl[CF_2CF(CF_2)_2H]_2Cl$ (26)
$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}Cl$, 50 (0.215) + $CF_2{=}CFC_5F_{11}$, 80 (0.229)	5	$n\text{-}C_3F_7[CF_2CF(C_5F_{11})]Cl$ (44) $Cl[CF_2CF(C_5F_{11})]_2Cl$ (27)
$n\text{-}C_7F_{15}\overset{O}{\overset{\|}{C}}Cl$, 87 (0.21)	7	$n\text{-}C_7F_{15}Cl$ (67) $n\text{-}C_{14}F_{30}$ (5.1)
$Cl\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}Cl$, 58 (0.206)	7	$Cl(CF_2)_3Cl$ (VI) (71) $Cl(CF_2)_6Cl$ (VII) (11)
Bromides		
$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}Br$, 22.5 (0.081)	7	$n\text{-}C_3F_7Br$ (94)
$H(CF_2)_4\overset{O}{\overset{\|}{C}}Br$, 28.95 (0.094)	7	$H(CF_2)_4Br$ (XV) (93)
Fluorides		
$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}F$, 68.0 (0.314)	7	$n\text{-}C_6F_{14}$ (I) (58) $(n\text{-}C_3F_7)_2CFOC_3F_7\text{-}n$ (II) ($\sim$10)
$n\text{-}C_7F_{15}\overset{O}{\overset{\|}{C}}F$, 25.0 (0.06)	6	$n\text{-}C_{14}F_{30}$ (58)
$Cl(CF_2)_8\overset{O}{\overset{\|}{C}}F$, 8.6 (0.0179)	2	$Cl(CF_2)_{16}Cl$ (81)
$H(CF_2)_4\overset{O}{\overset{\|}{C}}F$, 30 (0.12)	7	$H(CF_2)_8H$ (56)
$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}F$, 32.0 (0.148) + $n\text{-}C_7F_{15}\overset{O}{\overset{\|}{C}}F$, 40.0 (0.096)	8	$n\text{-}C_6F_{14}$ (I) (62) $n\text{-}C_{10}F_{22}$ (17 based on $n\text{-}C_3F_7COF$, 26 based on $n\text{-}C_7F_{15}COF$) $n\text{-}C_{14}F_{30}$ (33)

halide and carbon monoxide together with unidentified materials. From the photolysis of chlorodifluoroacetyl fluoride, Haszeldine and Nyman[4] obtained mainly 1,2-dichlorotetrafluoroethane and dichlorodifluoromethane with small amounts of several other materials including carbonyl fluoride, carbonyl chloride fluoride, and silicon tetrafluoride (eq. 2).

$$ClCF_2\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} ClCF_2\,CF_2Cl + Cl_2CF_2 + Cl\overset{O}{\overset{\|}{C}}F + COF_2 + SiF_4 \quad (2)$$

This paper reports a study of the liquid phase irradiation of polyfluoroacyl fluorides, chlorides, and bromides alone, and in the presence of terminal fluoro olefins. The results of the experiments are discussed below and are tabulated in Table I.

The ultraviolet spectral data for n-perfluorobutyryl bromide, chloride, and fluoride are tabulated in Table II. In all cases there is a relatively low intensity peak in the 2000–3000-Å. region which may be the n–π^* transition band. A progression to lower wave lengths is apparent as the electronegativity of the halide substituent increases.

TABLE II

ULTRAVIOLET SPECTRA OF PERFLUOROBUTYRYL HALIDES

	λ_{max} (cyclohexane), mμ (ϵ)	λ_{max} (gas phase), mμ (ϵ)
$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}Br$	217 (692) 273 (56)	
$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}Cl$	259 (46.5) 266 (46)	258 (38) 266 (37)
$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}F$		215 (66)

Results and Discussion

Polyfluoroacyl Fluorides.—The photolyses of polyfluoroacyl fluorides lead primarily to the formation of polyfluoroalkanes. For example, from the irradiation of perfluorobutyryl fluoride, the major product isolated was perfluoro-n-hexane (I) (eq. 3). In addition, a higher boiling fraction was obtained from which was

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[4] R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 1084 (1959).

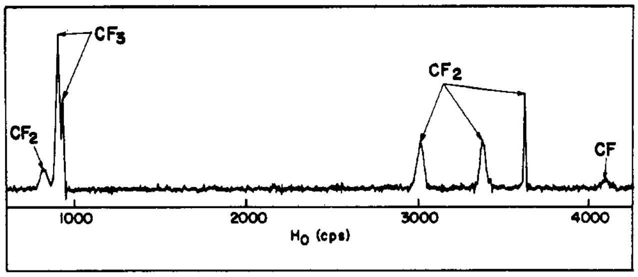
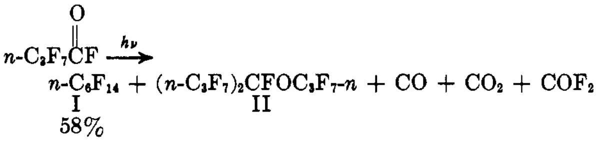
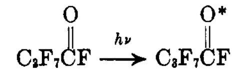


Figure 1.—The F^{19} n.m.r. spectrum of 4-perfluoroheptyl perfluoropropyl ether (see Experimental).

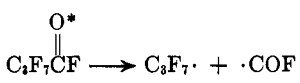


$$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} \underset{\substack{I\\58\%}}{n\text{-}C_6F_{14}} + \underset{II}{(n\text{-}C_3F_7)_2CFOC_3F_7\text{-}n} + CO + CO_2 + COF_2 \qquad (3)$$

isolated an ether of structure II. According to an infrared analysis, the composition of the effluent gases was 5-15% COF_2, traces of SiF_4 and C_3F_7H, and the remainder CO and CO_2. These results are consistent with the scheme proposed in eq. 4-9. In this scheme

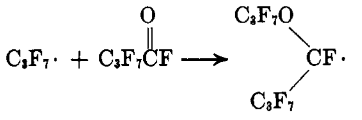


$$C_3F_7\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} C_3F_7\overset{O^*}{\overset{\|}{C}}F \qquad (4)$$

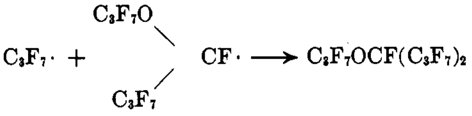


$$C_3F_7\overset{O^*}{\overset{\|}{C}}F \longrightarrow C_3F_7\cdot + \cdot COF \qquad (5)$$

$$2C_3F_7\cdot \longrightarrow n\text{-}C_6F_{14} \qquad (6)$$



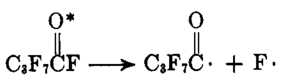
$$C_3F_7\cdot + C_3F_7\overset{O}{\overset{\|}{C}}F \longrightarrow \overset{C_3F_7O}{\underset{C_3F_7}{CF\cdot}} \qquad (7)$$



$$C_3F_7\cdot + \overset{C_3F_7O}{\underset{C_3F_7}{CF\cdot}} \longrightarrow C_3F_7OCF(C_3F_7)_2 \qquad (8)$$

$$\cdot COF \longrightarrow COF_2 + CO \qquad (9)$$

the photoexcited acyl fluoride molecule cleaves to give a perfluoropropyl radical and a fluoroformyl radical. Since no perfluoropropane was observed among the reaction products, it follows that the perfluoropropyl radical does not abstract a fluorine atom from the acyl fluoride. It is also probable that the alternative mode of cleavage of the excited acyl fluoride molecule to give a fluoroacyl radical and a fluorine atom (eq. 10) does



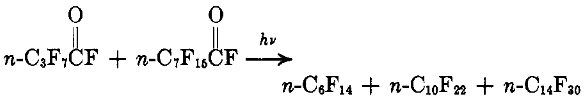
$$C_3F_7\overset{O^*}{\overset{\|}{C}}F \longrightarrow C_3F_7\overset{O}{\overset{\|}{C}}\cdot + F\cdot \qquad (10)$$

not occur.[5] To a major extent the perfluoropropyl radical reacts with another such radical to give perfluorohexane (eq. 6). It also attacks a molecule of the acyl fluoride, presumably at the oxygen, to give the radical III which eventually combines with another perfluoropropyl radical to give the ether II (eq. 7 and 8).[6] The structure of this ether was deduced from the fluorine n.m.r. spectrum (Figure 1). The pertinent features of the spectrum are the CF_2 resonance at 835 c.p.s. and the CF resonance at 4090 c.p.s., both of which are shifted to lower than normal field by the adjacent oxygen.[7]

$$\underset{III}{C_3F_7OCFC_3F_7}$$

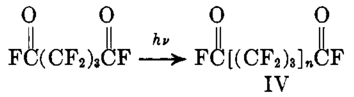
The fate of the COF radical produced in the photolysis is indicated by the detection of CO_2, CO, and COF_2 in the effluent gases. The radical may disproportionate directly to COF_2 and CO as indicated in eq. 9, or possibly it dimerizes to give oxalyl fluoride which then undergoes disproportionation. The CO_2 and SiF_4 presumably arise by reaction of COF_2, oxalyl fluoride, or the COF radical with the walls of the reaction vessel.

From the irradiation of a mixture of perfluorobutyryl fluoride and perfluorooctanoyl fluoride, perfluoro-*n*-hexane, -decane, and -tetradecane were isolated in roughly statistical amounts (eq. 11).



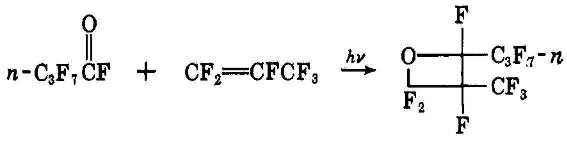
$$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}F + n\text{-}C_7F_{15}\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} n\text{-}C_6F_{14} + n\text{-}C_{10}F_{22} + n\text{-}C_{14}F_{30} \qquad (11)$$

Irradiation of perfluoroglutaryl fluoride led to the formation of materials which were solids at room temperature. The nature of these materials was not extensively investigated, but it seems most likely that they are largely long-chain dicarboxylic acid fluorides represented by structure IV (eq. 12).



$$F\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}F \xrightarrow{h\nu} \underset{IV}{F\overset{O}{\overset{\|}{C}}[(CF_2)_3]_n\overset{O}{\overset{\|}{C}}F} \qquad (12)$$

The irradiation of mixtures of polyfluoroacyl fluorides and fluoro olefins leads primarily to the formation of oxetanes; for example, perfluorobutyryl fluoride and hexafluoropropylene give the *cis* and *trans* isomers of 2-perfluoro-*n*-propyl-3-trifluoromethyltetrafluorooxetane (eq. 13). Virtually no other products are formed. This reaction and several analogous examples have been reported previously.[7]



(13)

Polyfluoroacyl Chlorides.—The irradiation of a polyfluoroacyl chloride leads to decarbonylation resulting primarily in the formation of a polyfluoroalkyl chloride. For example, perfluorobutyryl chloride gave an 81% yield of 1-chloroheptafluoropropane (V) and 4% of perfluoro-*n*-hexane (I) (eq. 14). Carbon monoxide was

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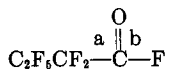
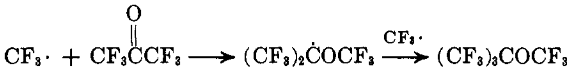
[5] From a consideration of bond energies one would expect that bond a



$$C_2F_5CF_2\overset{a}{—}\overset{O}{\overset{\|}{C}}\overset{b}{—}F$$

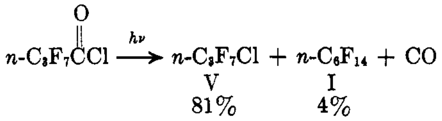
would be considerably weaker than bond b, although apparently no measurements have as yet been made on these bonds in a perfluoroacyl fluoride.

[6] A. S. Gordon [*J. Chem. Phys.*, **36**, 1330 (1962)] has reported the formation of perfluoro-*t*-butyl methyl ether in the photolysis of perfluoroacetone. This ether is formed by the addition of two trifluoromethyl radicals to the carbonyl group of hexafluoroacetone.



$$CF_3\cdot + CF_3\overset{O}{\overset{\|}{C}}CF_3 \longrightarrow (CF_3)_2\dot{C}OCF_3 \xrightarrow{CF_3\cdot} (CF_3)_3COCF_3$$

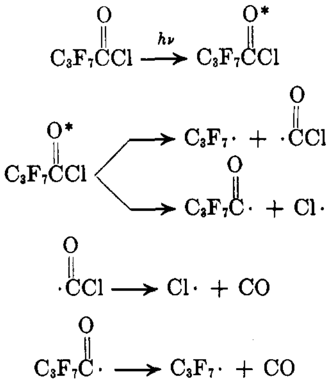
[7] Comparable shifts were observed for CF and CF_2 groups adjacent to oxygen in highly fluorinated oxetanes: J. F. Harris and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 1553 (1962).



$$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}Cl \xrightarrow{h\nu} \underset{\substack{V\\81\%}}{n\text{-}C_3F_7Cl} + \underset{\substack{I\\4\%}}{n\text{-}C_6F_{14}} + CO \quad (14)$$

detected in the off-gases, although it was not determined quantitatively. The photolysis of perfluoro-*n*-octanoyl chloride is completely analogous, giving 1-chloroperfluoroheptane accompanied by a small amount of perfluoro-*n*-tetradecane.

The course considered most likely for these reactions (eq. 15–21) begins with a cleavage of an excited acyl chloride molecule in one or both of the ways indicated in eq. 16 and 17. This is followed by decarbonylation of the carbonyl fragment(s), and reaction of the perfluoroalkyl radical primarily with a chlorine atom to give V, and to a lesser extent with another perfluoroalkyl radical to give I.[8] No quantum yields were measured, but, in view of the results of attempts to initiate this reaction by X-ray irradiation and with a free-radical catalyst, it seems unlikely that a chain process as depicted in eq. 22 and 23 is occurring.[9] It appears



$$C_3F_7\overset{O}{\overset{\|}{C}}Cl \xrightarrow{h\nu} C_3F_7\overset{O^*}{\overset{\|}{C}}Cl \quad (15)$$

$$C_3F_7\overset{O^*}{\overset{\|}{C}}Cl \longrightarrow C_3F_7\cdot + \cdot\overset{O}{\overset{\|}{C}}Cl \quad (16)$$

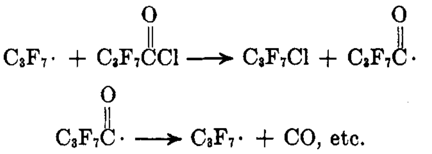
$$C_3F_7\overset{O^*}{\overset{\|}{C}}Cl \longrightarrow C_3F_7\overset{O}{\overset{\|}{C}}\cdot + Cl\cdot \quad (17)$$

$$\cdot\overset{O}{\overset{\|}{C}}Cl \longrightarrow Cl\cdot + CO \quad (18)$$

$$C_3F_7\overset{O}{\overset{\|}{C}}\cdot \longrightarrow C_3F_7\cdot + CO \quad (19)$$

$$C_3F_7\cdot\ Cl\cdot \longrightarrow C_3F_7Cl \quad (20)$$

$$2C_3F_7\cdot \longrightarrow n\text{-}C_6F_{14} \quad (21)$$

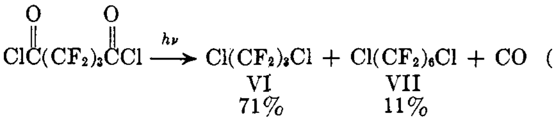


$$C_3F_7\cdot + C_3F_7\overset{O}{\overset{\|}{C}}Cl \longrightarrow C_3F_7Cl + C_3F_7\overset{O}{\overset{\|}{C}}\cdot \quad (22)$$

$$C_3F_7\overset{O}{\overset{\|}{C}}\cdot \longrightarrow C_3F_7\cdot + CO, \text{ etc.} \quad (23)$$

that a perfluoroalkyl radical is thus unable to abstract a chlorine atom from a perfluoroacyl chloride molecule, at least under the conditions of these experiments, whereas it is well known that it can abstract an aldehydic hydrogen atom from a perfluoro aliphatic aldehyde.[1]

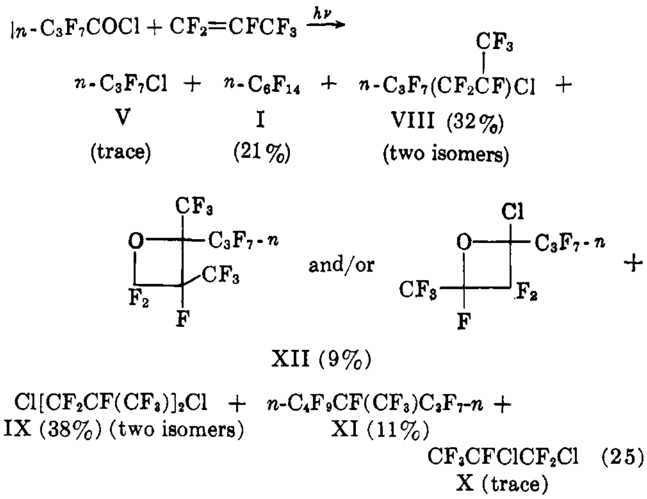
The photolysis of hexafluoroglutaryl chloride apparently proceeds in a manner analogous to that of monobasic acyl chlorides yielding 1,3-dichlorohexafluoropropane (VI) as the major product along with some 1,6-dichloroperfluorohexane (VII) (eq. 24). As



$$Cl\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}Cl \xrightarrow{h\nu} \underset{\substack{VI\\71\%}}{Cl(CF_2)_3Cl} + \underset{\substack{VII\\11\%}}{Cl(CF_2)_6Cl} + CO \quad (24)$$

expected, the relative proportion of the product resulting from dimerization of radicals is significantly larger than for monobasic acyl chlorides. No products with more than six carbons were isolated, and no perfluorocyclopropane was found.

Irradiation of polyfluoroacyl chlorides in the presence of terminal fluoro olefins results in the formation of a variety of products. For example, the reaction of perfluorobutyryl chloride and hexafluoropropylene



n-C$_3$F$_7$COCl + CF$_2$=CFCF$_3$ $\xrightarrow{h\nu}$

n-C$_3$F$_7$Cl + n-C$_6$F$_{14}$ + n-C$_3$F$_7$(CF$_2$CF(CF$_3$))Cl +
V (trace) I (21%) VIII (32%) (two isomers)

XII (9%)

Cl[CF$_2$CF(CF$_3$)]$_2$Cl + n-C$_4$F$_9$CF(CF$_3$)C$_3$F$_7$-n +
IX (38%) (two isomers) XI (11%)

CF$_3$CFClCF$_2$Cl (25)
X (trace)

yielded at least ten products (eq. 25).[10] In contrast to the reactions of fluoroacyl fluorides with terminal fluoro olefins (in which 1:1 adducts were virtually the exclusive products) only small yields of 1:1 adducts were found. There were also relatively small amounts of the products obtained from the photolysis of the acyl chloride itself. The bulk of the products obviously arises from sequences beginning with additions of the acyl chloride photolysis fragments (*i.e.*, the chlorine atom and the perfluoropropyl radical) to the olefin.

The relative amounts of I and V (products of the photolysis of the acyl chloride alone) obtained in this experiment are of interest. In the presence of the olefin, only a trace of V is formed, whereas a substantial amount of I is obtained, just the reverse of the results of the photolysis of the acyl chloride alone. This indicates that the chlorine atom reacts much more readily with the olefin than does the perfluoropropyl radical; *i.e.*, the fluoro olefin is a much better scavanger of the chlorine atom than of the perfluoropropyl radical. From the addition of the photolysis fragments to the olefin, the radicals XIIIa and XIIIb are formed from the chlorine atom (Scheme I, step A) and XIVa and XIVb from the perfluoropropyl radical (step E). Since it has been shown that radicals can add to both double

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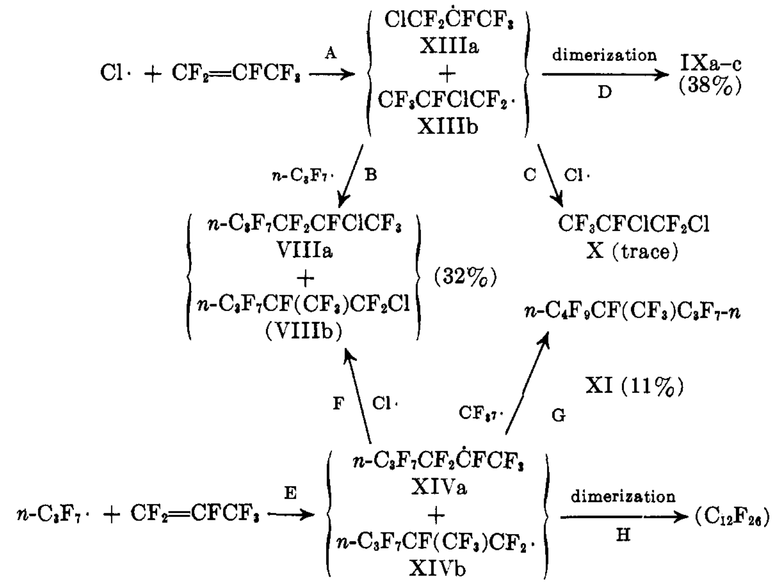
[8] One might expect to find reactions of the perfluorobutyryl radical with a perfluoropropyl radical or with another acyl radical to form a ketone or an α-diketone. However, in view of the probable extremely short lifetimes of perfluoroacyl radicals, these events are considered to be highly unlikely: P. B. Ayscough and E. W. R. Steacie, *Proc. Roy. Soc.* (London), **A234**, 476 (1956).

[9] It has generally been found that free-radical chain reactions which can be initiated by ultraviolet radiation or conventional free-radical catalysts can also be initiated with irradiation by X-rays: A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, Inc., New York, N. Y., 1960. For a reaction to be considered a chain process, the determined value of *G* (the number of molecules changed per 100 e.v. of energy absorbed in the system) must be no less than about 10. In the above case, X-ray irradiation did produce the products obtained in the ultraviolet experiment, but in such small quantity that *G* was virtually zero. Similarly, only traces of the products were formed when the reaction was attempted using 5 mole % of di-*t*-butyl peroxide at 135°.

[10] The yields were estimated from gas chromatography analysis, and were based upon the perfluorobutyryl chloride consumed. The sum of the yield estimates is over 100% since there is some double counting; *i.e.*, some products contain only the Cl from the acyl chloride (*e.g.*, IX), while others contain only the C$_3$F$_7$ group (*e.g.*, I and XI). Appropriate grouping of the figures accounts for 73% of the C$_3$F$_7$ groups and 79% of the Cl atoms.

SCHEME I

REACTIONS OF CHLORINE ATOMS AND PERFLUOROPROPYL RADICALS WITH HEXAFLUOROPROPYLENE

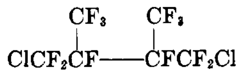


bond carbons of hexafluoropropene,[11] it seems likely that all four radicals are indeed formed.

Reactions of the radicals XIIIa and XIIIb with perfluoropropyl radicals lead to VIIIa and VIIIb which are major products (step B). Although the gas chromatography columns used did not give sufficient separation for isolation of the two isomers in pure form, it was possible to determine that both were present by the fluorine n.m.r. spectrum (Figure 2) which contained two sets of resonances with reasonable chemical shifts. By comparing the areas of the two peaks corresponding to the CF groups, the composition of this fraction was estimated to be 39% VIIIa and 61% VIIIb.[12]

$n\text{-}C_3F_7CF_2CFClCF_3$ VIIIa $n\text{-}C_3F_7CF(CF_3)CF_2Cl$ VIIIb

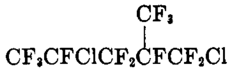
Dimerization of the radicals XIIIa and XIIIb could lead to three compounds, IXa, IXb, and IXc, and, from the higher boiling portion of this reaction mixture, materials with a molecular formula corresponding to


$ClCF_2\overset{CF_3}{C}F\text{—}\overset{CF_3}{C}FCF_2Cl$

IXa

$CF_3CFClCF_2CF_2CFClCF_3$

IXb


$CF_3CFClCF_2\overset{CF_3}{C}FCF_2Cl$

IXc

IX were isolated in considerable yield. A gas chromatogram of the fractions comprised of these compounds contained two peaks and fractions corresponding to each were obtained by preparative-scale gas chromatography. The F^{19} n.m.r. pattern (Figure 2) of one of these fractions (b.p. 114–115°) contained only three peaks indicating a symmetrical structure (IXa or IXb), and since the CF_2 resonance occurred at low field (actually in the normal CF_3 region of the spectrum) this material was assigned structure IXa, in which the chlorine atoms are on the CF_2 groups. The F^{19} pattern of the other fraction contained all of the resonances expected for structure IXc, with reasonable chemical shifts, but there was an additional resonance which does not seem to fit, and thus definite assignment cannot be made at this point. This fraction may be a mixture of IXc and IXb.[13]

Another possible reaction for the radicals XIIIa and XIIIb is with the chlorine atom to give 1,2-dichlorohexafluoropropane (X) (step C). However since the chlorine atom is efficiently scavanged by the olefin, this is not an important process and only a trace of X was found in the product.

As mentioned above, step E leading to XIVa and XIVb is not so efficient as step A, and thus the quantities of products derived from these radicals relative to those stemming from XIIIa and XIIIb are expected to be considerably less. Possible reactions for XIVa and XIVb include combination with chlorine atom to give VIIIa and VIIIb (step F), but this route is probably only a minor source of these compounds. Reaction with the perfluoropropyl radical (step G) yields the perfluorocarbon XI which was found in 11% yield. From dimerization of XIVa and XIVb, C_{12} perfluorocarbons would be expected (step H). No such compounds were isolated. Similarly, reaction of XIVa and XIVb with XIIIa and XIIIb would lead to chloroperfluorononanes none of which were found among the identified products; however, they may have been formed in small amount since the gas chromatogram of the reaction mixture indicated the presence of several additional unidentified substances in low yield.

Two fractions were obtained which, according to analytical results, were 1:1 adducts of the acyl chloride and hexafluoropropylene. Since the infrared spectra of these two materials indicated only trace amounts of

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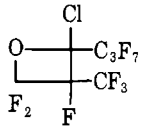
(11) J. F. Harris and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961); F. W. Stacey and J. F. Harris, *J. Org. Chem.*, **27**, 4089 (1962).

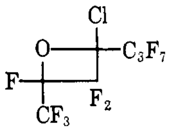
(12) The specific assignment was possible since one of the CF peaks was shifted downfield almost into the normal CF_2 region. This is obviously the CF to which the chlorine is attached.

(13) These same materials have also been obtained in the photoreaction of trifluoromethanesulfenyl chloride with hexafluoropropylene: J. F. Harris, *J. Am. Chem. Soc.*, **84**, 3148 (1962). Although in one case there was some difference in the boiling point and refractive index, the F^{19} n.m.r. patterns of the two fractions obtained in the instant work were identical with those of the materials obtained earlier.

carbonyl compounds, it is concluded that they must be oxetanes resulting from cycloaddition reactions. The complexity of the F^{19} n.m.r. patterns of these fractions indicated that each probably contained more than one compound, and structures could thus not be assigned. They are no doubt isomers (*cis* and *trans*) of structure XIIa and/or XIIb.[14]

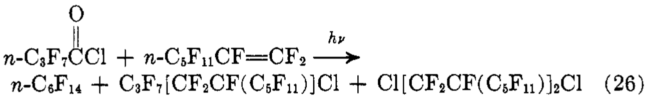


XIIa

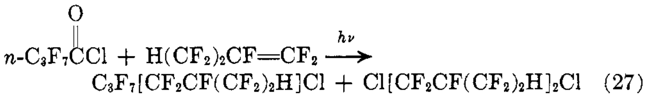


XIIb

Two other fluoro olefin–polyfluoroacyl chloride reactions (eq. 26 and 27) were carried out, and, although a searching analysis of the reaction products was not made, it was established that the main products in each case were analogous to the main fractions of the reaction just discussed. In these cases, too, the products are no doubt mixtures of isomers.

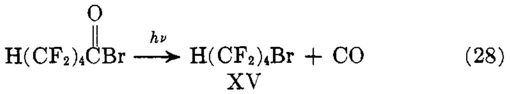


$$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}Cl + n\text{-}C_5F_{11}CF{=}CF_2 \xrightarrow{h\nu} n\text{-}C_6F_{14} + C_3F_7[CF_2CF(C_5F_{11})]Cl + Cl[CF_2CF(C_5F_{11})]_2Cl \tag{26}$$



$$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}Cl + H(CF_2)_2CF{=}CF_2 \xrightarrow{h\nu} C_3F_7[CF_2CF(CF_2)_2H]Cl + Cl[CF_2CF(CF_2)_2H]_2Cl \tag{27}$$

Polyfluoroacyl Bromides.—From the photolyses of polyfluoroacyl bromides only the decarbonylation products, polyfluoroalkyl bromides, were isolated. For example, from 5-H-octafluorovaleryl bromide, 4-H-octafluorobutyl bromide (XV) was obtained in 93% yield (eq. 28).[15]



$$H(CF_2)_4\overset{O}{\overset{\|}{C}}Br \xrightarrow{h\nu} \underset{XV}{H(CF_2)_4Br} + CO \tag{28}$$

A gas chromatogram of the crude reaction mixture indicated that there may be a trace of 1,8-di-H-perfluorooctane present. Similarly, from the photolysis of perfluorobutyryl bromide, a 94% yield of perfluoropropyl bromide was isolated. The reaction path for these photolyses may be the same as that outlined for the acyl chlorides (eq. 15–21). However, here a chain reaction (analogous to eq. 22 and 23) involving abstraction of a bromine atom by a fluoroalkyl radical is a greater possibility than in the acyl chloride reactions, in view of the relatively weaker C–Br bond. No data bearing on the chain nature of these reactions have been obtained.

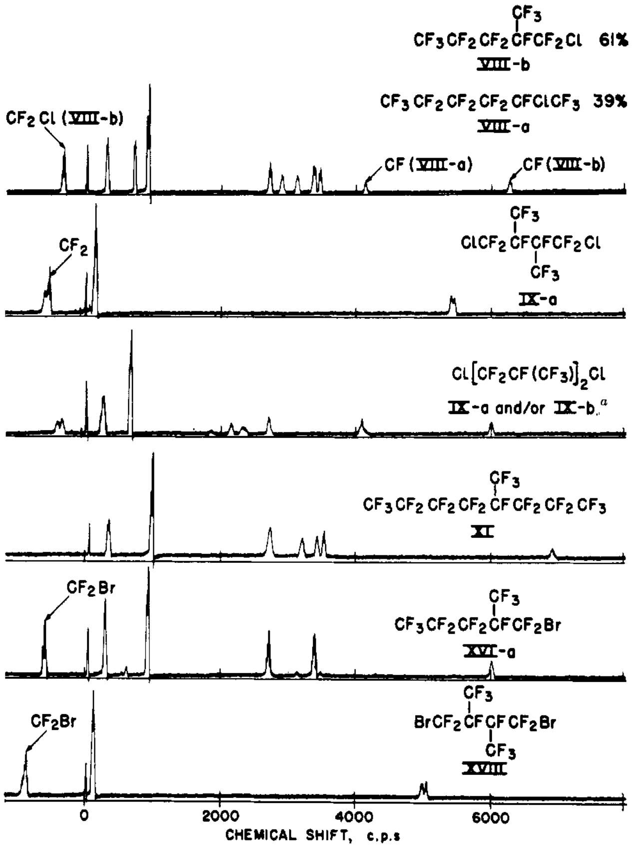


Figure 2.—The fluorine n.m.r. spectra of VIII, IX, XI, XVI, and XVIII at 56.4 Mc. (see Experimental).

[a] This designation should be IX-b and/or IX-c.

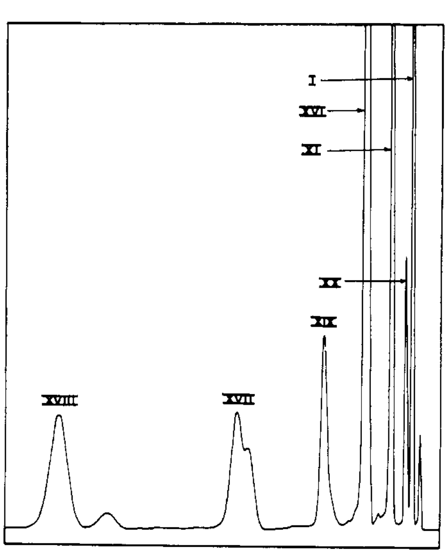


Figure 3.—A gas chromatogram of a crude reaction mixture from the irradiation of *n*-heptafluorobutyryl bromide and hexafluoropropene.

The irradiation of a mixture of perfluorobutyryl bromide and hexafluoropropylene led, as in the corresponding chloride reaction, to a variety of products, several of which have been isolated and identified (eq. 29, Figure 3). The reaction mixture was not investigated so thoroughly as the analogous acyl chloride reaction product, and yields were not determined. A qualitative picture of the relative amounts of the major products can be obtained from Figure 3. It is obvious from the nature of the products that the steps

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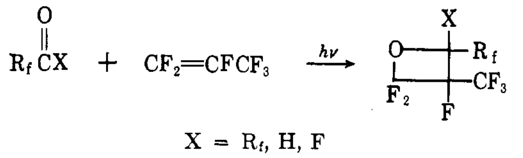
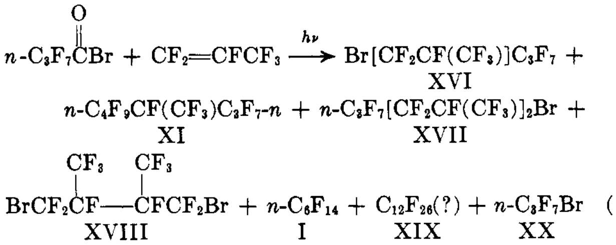
[14] It has previously been shown that polyfluoroacyl fluorides, polyfluoro ketones, and polyfluoroaldehydes react with hexafluoropropylene under irradiation with ultraviolet light to give, as the major products, oxetanes in which the CF_2 group from hexafluoropropylene is adjacent to oxygen.[7]



X = R_f, H, F

[15] J. D. LaZerte, W. H. Pearlson, and E. A. Kauck [U. S. Patent 2,704,776 (1955); *Chem. Abstr.*, **50**, 2650 (1956)] have reported that the vapor phase pyrolysis of trifluoroacetyl bromide at 650° also gives only carbon monoxide and the fluoroalkyl bromide.



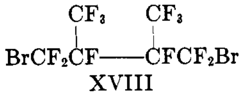
$$n\text{-}C_3F_7\overset{O}{\overset{\|}{C}}Br + CF_2{=}CFCF_3 \xrightarrow{h\nu} \underset{XVI}{Br[CF_2CF(CF_3)]C_3F_7} + \underset{XI}{n\text{-}C_4F_9CF(CF_3)C_3F_7\text{-}n} + \underset{XVII}{n\text{-}C_3F_7[CF_2CF(CF_3)]_2Br} + \underset{XVIII}{BrCF_2\overset{CF_3}{\overset{|}{C}}F{-}\overset{CF_3}{\overset{|}{C}}FCF_2Br} + \underset{I}{n\text{-}C_6F_{14}} + \underset{XIX}{C_{12}F_{26}(?)} + \underset{XX}{n\text{-}C_3F_7Br} \quad (29)$$

involved here are analogous to those encountered in the acyl chloride–hexafluoropropylene reaction (Scheme I), and that most of the products obtained stem from radicals produced by addition of a bromine atom and a perfluoropropyl radical to the olefin. As in the acyl chloride–hexafluoropropylene reaction, the products of the photolysis of the acyl halide alone, *i.e.*, XX and perfluorohexane (I), were formed, but in this case the proportion of the perfluoropropyl halide (XX) relative to perfluorohexane was higher than in the acyl chloride experiment.

The most prevalent product was XVI (the analog of VIII in the acyl chloride reaction). Examination of the fluorine n.m.r. pattern (Figure 2) of this fraction isolated by preparative-scale gas chromatography indicated that, in contrast to the corresponding fraction from the perfluorobutyryl chloride–hexafluoropropylene reaction, it was composed almost entirely of one isomer. In view of the low-field position of one of the CF_2 resonances and the normal position of the CF resonance, it was concluded that this major component was XVIa in which the bromine is attached to the CF_2 of hexafluoropropylene. The spectrum contained several small peaks which, if they were due to XVIb, indicated the presence of <10% of this isomer.

$$\underset{XVIa}{BrCF_2CF(CF_3)C_3F_7\text{-}n} \qquad \underset{XVIb}{n\text{-}C_3F_7CF_2CFBrCF_3}$$

A single compound corresponding in composition to 1:2 bromine–hexafluoropropylene (analog of IX in the acyl chloride reaction) was isolated; from the simplicity of the n.m.r. pattern and the low-field position of the CF_2 resonance, it was concluded that the material was XVIII. Neither of the other possible isomers of

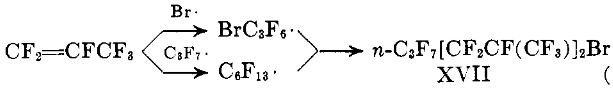


$$BrCF_2\overset{CF_3}{\overset{|}{C}}F{-}\overset{CF_3}{\overset{|}{C}}FCF_2Br$$

XVIII

XVIII was isolated. As in the acyl chloride reaction, the perfluoroalkane XI was obtained in modest yield. Another perfluoroalkane was also obtained (peak XIX in Figure 3) which according to a mass spectral analysis was a C_{12} compound. Not enough was isolated for further characterization.

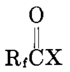
A major product of the reaction was a perfluoroalkyl bromide fraction, whose analysis corresponded to $C_9F_{19}Br$ (XVII), which could have arisen by the sequence shown in eq. 30. Several isomers of XVII are



$$CF_2{=}CFCF_3 \; \begin{array}{l} \xrightarrow{Br\cdot} BrC_3F_6\cdot \\ \xrightarrow{C_3F_7\cdot} C_6F_{13}\cdot \end{array} \; \longrightarrow \underset{XVII}{n\text{-}C_3F_7[CF_2CF(CF_3)]_2Br} \quad (30)$$

possible, and it was obvious from the shape of the peak corresponding to XVII in the gas chromatogram that at least two were present. As stated above, the analogous products were not found in the acyl chloride–hexafluoropropylene reaction mixture. No 1:1 adducts were isolated but it should be emphasized that there were several low-yield materials apparent from the gas chromatogram that were not identified.

The differences in behavior exhibited by the three types of acyl halides upon irradiation can be related to the relative strengths of the C–X bonds in these compounds. In the photolysis of the acyl fluorides, in



$$R_f\overset{O}{\overset{\|}{C}}X$$

which this bond is the strongest, no products are found whose formation would demand its rupture to yield a fluorine atom. Similarly, in the irradiation with fluoro olefins no such evidence is seen; in fact, no fragmentation of any kind apparently occurs, only cycloaddition products being formed. Thus, the photoexcited acyl fluoride molecule is resistant to any fragmentation long enough for a bimolecular reaction with olefin to occur virtually exclusively. The irradiation of the acyl chlorides yields products which do require rupture of the C–X bond, although in the presence of fluoro olefins modest yields of cycloadducts are also obtained. In the reactions of the bromides, in which the C–X bond is weakest, no products are found which require the survival of the C–X bond.

Experimental

The fluorine spectra were obtained by means of a high-resolution n.m.r. spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at approximately 9988 gauss. The spectra were measured in terms of displacement in cycles per second from the fluorine resonance of *sym*-difluorotetrachloroethane as an external standard. The resonance of the standard is evident in each spectrum.

A. Photolysis of Polyfluoroacyl Halides.—All of these reactions were carried out in essentially the same manner. Details for the photolysis of perfluorobutyryl chloride follow. The results of the other photolysis experiments are tabulated in Table I. Analytical data are given in Tables III–VI.

The reactor consisted of a vertical quartz tube (2 × 10 in.) fitted with a magnetic stirrer, a gas inlet adaptor, and a large acetone–Dry Ice cooled condenser vented through a Dry Ice cooled trap, the exit of which was fitted with a T-tube through which a slow stream of nitrogen was passed. The ultraviolet radiation source consisted of a helix-shaped (4 × 2.5 in.) low-pressure mercury resonance lamp constructed of 37-mm. quartz tubing and powered by a 5000 v., 60-ma. transformer. The lamp was fitted around the quartz reactor so that its radiation impinged primarily upon the liquid portion of the reaction mixture.

Dry nitrogen was passed through the assembled apparatus for several minutes, and then 50 g. (0.215 mole) of perfluorobutyryl chloride was poured into the reactor quickly. The condenser and the trap were filled with coolant and the mixture was irradiated at reflux for 7 days. At the end of this time the mixture was distilled through a low-temperature still. There was obtained 35.5 g. (81%) of 1-chloroheptafluoropropane distilling at −2.5°, lit.[16] b.p. −2°.

There was a residue of 1.97 g. (4%) which was shown by F^{19} n.m.r. spectroscopy to be largely perfluoro-*n*-hexane. The F^{19} n.m.r. spectrum and the boiling point served to identify 1-chloroheptafluoropropane.

B. Irradiation of a Mixture of Perfluorobutyryl Chloride and Hexafluoropropylene.—A mixture of 62 g. (0.268 mole) of perfluorobutyryl chloride and 35 g. (0.234 mole) of hexafluoropropylene was irradiated in the manner described in A for 3 days. By this time there was very little reflux indicating that most of the hexafluoropropylene had been consumed. An examination of the crude reaction mixture by gas chromatography

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(16) M. Hauptschein, E. A. Nodiff, and A. V. Grosse, *J. Am. Chem. Soc.*, **74**, 1347 (1952).

TABLE III

PROPERTIES OF COMPOUNDS

Compd.	B.p., °C. (mm.)	Formula	n_D (°C.)	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found	Fluorine, % Calcd.	Fluorine, % Found
n-$C_{10}F_{22}$	147–154	$C_{10}F_{22}$		22.3	22.6					77.7	77.1
n-$C_{14}F_{30}$	98–99 (13)	$C_{14}F_{30}$		22.8	23.2					77.2	77.0
$Cl(CF_2)_{16}Cl$	M.p. 138.5–139.5	$C_{16}Cl_2F_{32}$		22.1	22.3			8.1	7.9	69.8	70.3
$H(CF_2)_8H$	134–138	$C_8H_2F_{16}$		23.9	24.2	0.5	0.7			75.6	74.9
n-$C_7F_{15}Cl$	96–108, mostly 108	C_7ClF_{15}						8.8	9.1	70.4	71.3
								Bromine, %			
$H(CF_2)_4Br$ (XV)	66	C_4HBrF_8		17.1	17.1	0.4	0.4	28.4	29.0	54.1	53.9
$(n$-$C_3F_7)_2CFOC_3F_7$-n (II)	134–136	$C_{10}F_{22}O$		21.7	22.1					75.5	74.8
$C_3F_7[CF_2CF(CF_2)_2H]Cl$	120–124	C_7HClF_{14}	1.3032 (23)	21.8	22.3	0.3	0.4	9.2	9.3	68.7	67.6
$Cl[CF_2CF(CF_2)_2H]_2Cl$	184–190	$C_8H_2Cl_2F_{14}$	1.3400 (23)	22.1	22.5	0.5	0.7	16.3	14.7	61.2	61.4
$C_3F_7[CF_2CF(C_5F_{11})]Cl$	84.5–92 (62)	$C_{10}ClF_{21}$						6.4	6.4	72.0	71.7
$Cl[CF_2CF(C_5F_{11})]_2Cl$	109–116 (13)	$C_{14}F_{28}Cl_2$	1.3217 (25)	21.8	22.3			9.2	8.2	68.9	69.9

TABLE IV

PRODUCTS FROM IRRADIATION OF n-HEPTAFLUOROBUTYRYL CHLORIDE AND HEXAFLUOROPROPYLENE

Structure	B.p., °C.	$n^{25}D$	Formula	Carbon, % Calcd.	Carbon, % Found	Chlorine, % Calcd.	Chlorine, % Found	Fluorine, % Calcd.	Fluorine, % Found	Mol. wt. Calcd.	Mol. wt. Found
VIIIa (39%) VIIIb (61%)	79–84	< 1.300	C_6ClF_{13}	20.3	20.3	10.0	10.4	69.7	70.5		
XII, g.c. cut 1	98–98.5	< 1.300	$C_7ClF_{13}O$			9.3	9.6	64.6	64.1		[a]
XII, g.c. cut 2	100[b]	< 1.300	$C_7ClF_{13}O$	22.0	22.2	9.3	9.4	64.5	65.9		
XI	125		C_9F_{20}	22.2	22.4	0	0.2	77.8	77.7		
IXa	114–115[b]	1.3210	$C_6Cl_2F_{12}$			18.6	19.0	62.5	60.1	371	334, 325
IXb and/or C	112[b]	1.3126	$C_6Cl_2F_{12}$			18.6	19.1	62.5	61.5	371	366, 386

[a] A mass spectrographic analysis of this material gave a small parent peak at 382 and a series of peaks corresponding to ions logically derived from the 1:1 adduct. [b] Infrared spectra of these materials indicated the presence of just trace amounts of carbonyl-containing impurities.

using a Silicone-200-on-firebrick column indicated the presence of at least 10 compounds in addition to a considerable quantity of unreacted perfluorobutyryl chloride and also some hexafluoropropylene. The mixture was distilled through a small spinning-band still, and 13 fractions boiling from 0 to 122° (76.78 g.) were collected. There was a residue of 2.56 g. During the distillation of the first fraction (b.p. 0–25°, 1.22 g.), there collected in the Dry Ice cooled trap connected to the still 8.00 g. of material, which was shown by gas chromatography to be largely hexafluoropropylene and a small amount of 1-chloroheptafluoropropane. The first fraction and the second fraction (b.p. 25–45°, 27.28 g.) were shown to be almost entirely perfluorobutyryl chloride. The subsequent fractions were all mixtures of materials according to gas chromatograms. The yields of the products were estimated from the gas chromatograms and are given in the discussion section. Appropriate fractions were combined, and pure samples of all of the major products were obtained by preparative scale gas chromatography. The properties of these products are given in Table IV. Details of the gas chromatography analyses are given in Table V.

C. **Irradiation of a Mixture of Perfluorobutyryl Bromide and Hexafluoropropylene.**—A mixture of 35.42 g. (0.128 mole) of perfluorobutyryl bromide and 40 g. (0.267 mole) of hexafluoropropylene was irradiated in the manner described in A for 5 days. The reactor was cooled, the Dry Ice condenser was removed, and the reactor was then connected to a Dry Ice cooled trap and allowed to warm to room temperature. The condensed volatiles weighed 16 g. and were shown to be largely hexafluoropropylene by gas chromatography. The residue, 48.25 g., was examined by gas chromatography (Figure 3) and shown to consist of several materials. This mixture was combined with another similar reaction mixture and distilled through a small spinning-band still. The fraction boiling at 32–90° was shown to consist of perfluoro-n-hexane, perfluorobutyryl bromide, and 1-bromoheptafluorobutane. The next fraction boiled at 90–100° and was shown by analysis and F^{19} n.m.r. spectroscopy to be largely XVII. From the remaining material (b.p. 120–159°) four fractions were obtained by preparative-scale gas chromatography. The properties of these materials are given in Table VI. Details of the gas chromatography analyses are given in Table V.

TABLE V

PREPARATIVE GAS CHROMATOGRAPHY SEPARATION[a] OF PRODUCTS FROM IRRADIATION OF PERFLUOROBUTYRYL CHLORIDE AND PERFLUOROBUTYRYL BROMIDE WITH HEXAFLUOROPROPYLENE

Reaction product	Column temp., °C.	Helium flow rate, cc./min.	Retention time, min.
VIIIa + VIIIb	50	400	13.4
1:1 adducts			
XII, cut 1	50	400	16.4
XII, cut 2	50	400	21.2
IXa	50	400	38.7
IXb and c	50	400	46.5
XI	75	790	5.0
XVII	109	435	14.2
XVIII	109	435	32.7

[a] The column used was 20% of the diglyceride of ω-trifluorohexanoic acid on Chromosorb, 12 ft. × 0.75 in.

D. **Irradiation of Perfluoroglutaryl Fluoride.**—Perfluoroglutaryl fluoride (40.52 g., 0.166 mole) was irradiated as described in A for 4 days. At the end of this time, the reaction mixture was completely solid. Two kinds of white solid were evident: (a) hard brittle material stuck to the sides of the reaction tube, and (b) somewhat mushy solid from the center portion of the reactor. The total yield of recovered solid was 26.2 g. The two solids were exposed to air for several days during which they fumed. After the fuming was over, solid a melted at 190–300°, and solid b melted at 100–195°.

E. **X-Ray Irradiation of Perfluorobutyryl Chloride.**—Perfluorobutyryl chloride (51.9 g., 0.223 mole) contained in a 100-ml. stainless steel pressure vessel was irradiated with X-rays for 5 hr. at an average dose rate of about 30,000 rads/min.[17] Upon

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(17) The X-rays were generated by impinging 3-Mv. electrons from a Van de Graaff accelerator on a water-cooled gold target mounted beneath the window of the electron tube. Dose rates were determined by ferrous sulfate dosimetry.

TABLE VI

PRODUCTS FROM IRRADIATION OF *n*-HEPTAFLUOROBUTYRYL BROMIDE AND HEXAFLUOROPROPYLENE

Compd.	B.p., °C.	Formula	Carbon, %		Bromine, %		Fluorine, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
XVII	154–155	C_9BrF_{19}	19.7	19.4	14.6	14.9	65.7	65.4
XVIII	132–145	$C_6Br_2F_{12}$	15.7	15.4	34.7	34.0	49.6	48.5
XVI	90–100	C_6BrF_{13}			20.0	20.9	61.9	61.6

bleeding of the vessel through a small Dry Ice cooled trap there collected less than 0.5 ml. of condensate. The residue was examined by gas chromatography and shown to be almost entirely perfluorobutyryl chloride. The chromatogram indicated the presence of just traces of *n*-perfluorohexane and 1-chloroheptafluoropropane.

F. Preparation of Starting Materials. 1. **5-H-Octafluorovaleryl Bromide.**[18]—Benzoyl bromide (120 g., 0.648 mole) was placed in a flask fitted with a paddle stirrer, thermometer, addition funnel, and short-path still head. The still head was connected to an ice-cooled receiver and then to a Dry Ice cooled trap. 5-H-Octafluorovaleric acid[19] (100 g., 0.406 mole) was added during 0.5 hr. The mixture was heated to 150° and then the system was evacuated with a water pump until no more material collected in the receiver. The contents of the trap and receiver were combined and distilled through a small spinning-band still. There was thus obtained 42.43 g. (34%) of 5-H-octafluorovaleryl bromide distilling at 100–103° (mostly 103°).

Anal. Calcd. for C_5HBrF_8O: C, 19.4; H, 0.3; Br, 25.9; F, 49.2. Found: C, 19.9; H, 0.8; Br, 26.0; F, 49.3.

2.—**Perfluorobutyryl bromide** was prepared in the manner described in 1 from 186 g. (1.0 mole) of benzoyl bromide and 140 g. (0.64 mole) of perfluorobutyric acid (Columbia Organic Chemicals Co.). There was obtained 74.3 g. (41%) of perfluorobutyryl bromide distilling at 55–57°; lit.[20] b.p. 52–54° (748 mm.).

3.—**Perfluorobutyryl chloride** was obtained from Columbia Organic Chemicals Co., and **perfluoroglutaryl chloride** was obtained from Hooker Electrochemical Co., Inc. Each was redistilled before use.

4. **Perfluorooctanoyl Chloride.**—A mixture of 200 g. (0.494 mole) of perfluorooctanoic acid (Columbia Organic Chemicals Co.) and 200 g. (1.02 moles) of α,α,α-trichlorotoluene was refluxed for 5 hr. Upon distillation of the reaction mixture through a spinning-band still, there was obtained 179.4 g. (86%) of perfluorooctanoyl chloride distilling at 134–135°, n^{25}_{D} 1.3080; lit.[21] b.p. 129–130°, n^{25}_{D} 1.3025.

5.—**5-H-Octafluorovaleryl chloride** was prepared in the manner described in 4 from 300 g. (1.53 mmoles) of α,α,α-trichlorotoluene and 200 g. (0.81 mole) of 5-H-octafluorovaleric acid. Upon distillation there was obtained 185.5 g. (86%) of 5-H-octafluorovaleryl chloride distilling at 83–85°; lit.[22] b.p. 84.6–86.6°.

6. **Perfluorooctanoyl Fluoride.**[23]—A mixture of 164 g. (0.396 mole) of perfluorooctanoic acid and 50 g. (0.46 mole) of sulfur tetrafluoride was heated in a stainless steel autoclave at 60° for 9 hr. The reaction mixture was placed in a plastic container, and diluted with 150 ml. of pentane; then 20 g. (0.48 mole) of dry powdered sodium fluoride was added. The mixture was stirred for 0.25 hr., filtered, and distilled through a spinning-band still. There was obtained 87.4 g. (53%) of perfluorooctanoyl fluoride distilling at 108°.

Anal. Calcd. for $C_8F_{16}O$: C, 23.1; F, 73.1. Found: C, 23.6; F, 72.9.

7. **5-H-Octafluorovaleryl Fluoride.**—A mixture of 100 g. (0.378 mole) of 5-H-octafluorovaleryl chloride, 30 g. (0.714 mole) of powdered sodium fluoride, and 100 ml. of tetramethylene sulfone was heated in an autoclave at 100° for 2 hr. and then at 125° for 4 hr. Upon distillation of the reaction mixture through a spinning-band still, there was obtained 42.9 g. (46%) of 5-H-octafluorovaleryl fluoride distilling at 60–61°.

Anal. Calcd. for C_5HF_9O: C, 24.2; H, 0.4; F, 68.9. Found: C, 24.6; H, 0.6; F, 67.0.

8.—**Perfluorobutyryl fluoride** was prepared from perfluorobutyric acid and carbonyl fluoride as described by Fawcett, Tullock, and Coffman.[24]

9.—**Perfluoroglutaryl fluoride** was prepared in the manner described in 6 above from 100 g. (0.416 mole) of perfluoroglutaric acid (Columbia Organic Chemicals Co.) and 115 g. (1.07 moles) of sulfur tetrafluoride (9 hr. at 75°). After work-up there was obtained 40.2 g. (40%) of perfluoroglutaryl fluoride distilling at 46–47°.[25]

10.—**ω-Chloroperfluorononanoyl fluoride** was prepared as described previously.[26]

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[18] This procedure was adapted from that described by J. M. Tinker [U. S. Patent 2,257,868 (1941); *Chem. Abstr.*, **36**, 495 (1942)].

[19] This acid was prepared by permanganate oxidation of the corresponding alcohol according to the procedure described by K. L. Berry [U. S. Patent 2,559,629 (1951); *Chem. Abstr.*, **46**, 3063 (1952)].

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[21] M. Hauptschein, J. F. O'Brien, C. S. Stokes, and R. Filler, *J. Am. Chem. Soc.*, **75**, 87 (1953).

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[23] This procedure is similar to that described by W. R. Hasek, W. C. Smith, and V. A. Engelhardt [*J. Am. Chem. Soc.*, **82**, 543 (1960)].

[24] F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *ibid.*, **84**, 4275 (1962).

[25] Previously reported: b.p. 41–47° [R. D. Smith, F. S. Fawcett, and D. D. Coffman, *ibid.*, **84**, 4285 (1962)]; b.p. 47–48° [R. F. Sweeney and C. Woolf, U. S. Patent 3,018,306 (1962); *Chem. Abstr.*, **56**, 15363 (1962)].

[26] N. O. Brace and W. B. McCormack, *J. Org. Chem.*, **26**, 5098 (1961).

Hydrogen Sulfide Adducts of Chloral, Fluoroaldehydes, and Fluoro Ketones[1]

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Under pressure, hydrogen sulfide reacts with chloral and fluorinated aldehydes and ketones to form 1:1 adducts. The stabilities and some chemical properties of these adducts were investigated.

The reactions of hydrogen sulfide with carbonyl compounds have yielded a variety of products including *gem*-dithiols, trithianes, thiocarbonyl compounds, unsaturated sulfides, enethiols, saturated thiols, hydroxy sulfides, and polysulfides.[2] The nature of the product (or products) obtained depends largely upon the structure of the carbonyl substrate and the reaction conditions employed. It seems logical that the initial molecular product formed in many, if not all, of these reactions is the simple addition product, an olthiol (I),

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[1] A communication of this work has appeared: J. F. Harris, Jr., *J. Org. Chem.*, **25**, 2259 (1960).

[2] E. Campaigne, in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p. 134.