distillation and ether was distilled off as stirring was continued until the residue became very viscous. Anhydrous, thiophene-free benzene (45 ml) was added, and 15 ml of liquid were removed by distillation. An additional 45 ml of benzene was added and the reflux condenser was replaced. The mixture was refluxed with vigorous stirring for a few minutes and cooled to 5°, and a solution of 8.3 g (0.11 mol) of freshly distilled acetyl chloride in 25 ml of dry benzene was added during 2–3 min. After addition, the mixture was stirred at room temperature for 18 hr. It was then poured into 150 g of crushed ice containing 75 ml of 25% (v/v) sulfuric acid, and the resulting two-phase mixture was stirred for 5 min. The dark brown benzene layer was separated, and the water layer was extracted with two 30-ml portions of benzene. The combined benzene layers were washed successively with 45 ml of saturated sodium chloride solution, 45 ml of saturated sodium bicarbonate solution, 45 ml of water, and 25 ml of saturated sodium chloride solution. The benzene layer was dried over anhydrous sodium sulfate and the benzene was removed on a flash evaporator at room temperature. The dark residue was distilled *in vacuo* to give 14.0 g (56%) of 2,3,4,5,6-pentafluoroacetophenone: bp 65–66° (5 mm); pmr δ 2.67 (5, CH$_3$); 2,4-dinitrophenylhydrazone mp 156–157°.

Dibenzoylmethane.—Dibenzoylmethane, mp 77–78°, was prepared according to the procedure described by Sieglitz and Horn.[9]

Pentafluorodibenzoylmethane (2). **Enamine Method.**—A mixture of 174 g (2.0 mol) of morpholine, 120 g (1.0 mol) of acetophenone, and 8.6 g (0.05 mol) of *p*-toluenesulfonic acid in 250 ml of toluene was heated under reflux for 72 hr. The water which formed was collected in a Dean–Stark trap and removed from the system. After completion of the reaction, the toluene was removed *in vacuo* and the residue was vacuum distilled to give the enamine in low yield. A large amount of viscous tar remained in the distillation flask.

A mixture of 3.22 g (0.014 mol) of pentafluorobenzoyl chloride and 5.3 g (0.028 mol) of α-(4-morpholino)styrene in 100 ml of dry dioxane was stirred overnight in a dry nitrogen atmosphere, at room temperature. The reaction mixture was filtered and the residue was washed with ether. The organic layers were combined, mixed with 75 ml of 10% hydrochloric acid, and heated under reflux for 4 hr. The aqueous solution was then diluted with water to a volume of *ca.* 1 l. and the ether layer was separated and combined with three 100-ml extracts of the aqueous layer. The ethereal solution was dried over Na$_2$SO$_4$ and evaporated *in vacuo* to give a red oil which later solidified. Two recrystallizations of the oil from methanol gave 1.1 g (25%) of colorless needles: mp 118°; uv $\lambda_{\max}^{\mathrm{EtOH}}$ 333 nm (log ϵ 4.28) and 246 (3.82); ir (CCl$_4$) 1645 (s), 1598 (br s), and 1568 cm^{-1} (br s); pmr (CCl$_4$) 386 Hz (t, J = 1.5 Hz, vinyl CH).

Anal. Calcd for C$_{15}$H$_7$F$_5$O$_2$: C, 57.34; H, 2.25. Found: C, 57.23; H, 2.35.

Pentafluorodibenzoylmethane (2). **Anselme's Method.**[7]—This diketone, mp 118°, was prepared in 60% yield from pentafluoroacetophenone and methyl benzoate, according to the procedure described above for bis(pentafluorobenzoyl)methane.

Enol Contents of 1,3 Diketones.—The percentage of enol in the following 1,3 diketones was determined by titration with standard sodium methoxide solution, according to a known procedure.[13] The results follow: C$_6$H$_5$COCH$_2$COC$_6$H$_5$, 100%; C$_6$F$_5$COCH$_2$COC$_6$H$_5$ (2), 93%; C$_6$F$_5$COCH$_2$COCH$_3$ (8), 100%; C$_6$F$_5$COCH$_2$COC$_6$F$_5$ (3), 98.8%.

Registry No.—**1**, 3516-87-8; **2**, 23074-28-4; **3**, 23074-29-5; **4**, 2251-50-5; **5**, 4487-61-0; pentafluorobenzoic acid, 602-94-8; ethyl 3-hydroxy-3-pentafluorophenylpropionate, 23115-90-4; 2,4-dinitrophenylhydrazone of pentafluoroacetophenone, 858-82-2; 2,3,4,5,6-pentafluoroacetophenone, 652-29-9.

Acknowledgment.—This research was supported by Grant GM-12146 from the National Institutes of Health.

Liquid Fluorocarbon from Hexafluoropropene by an Electrical Discharge Process[1a]

ELIZABETH S. LO[1b] AND S. W. OSBORN

Research Department of Thiokol Chemical Corporation, Trenton, New Jersey 08607

Received July 25, 1969

A mixture of liquid fluorocarbons derived from C$_3$F$_6$ was prepared by an electrical discharge process. The gas-phase discharge was initiated at 150–800 Torr in concentric quartz tube reactors at 15–60° using field strengths of 9–13 kV/mm and alternating current at 1.4 or 10 kc/sec. The liquid discharge product contained substantial quantities of linear and branched fluoro alkanes as well as unsaturated (olefinic) fractions. No small-ring components were found. Carbon numbers of the products were shown to be random rather then multiplets of the monomer units. Base-catalyzed reaction of the liquid fluorocarbon with alcohol gave three fractions: (1) unsaturated ethers, (2) nonreactive fluoro alkanes, and (3) small amounts of perfluoroalkyl carboxylic acids. One of the sources of the carboxylic acids could be the stable free radicals shown by epr measurement (10^{21}–10^{17} spins/cc) to be present in the discharge products. A radical mechanism was suggested in which C$_3$F$_6$ was fragmented by the discharge process into reactive radicals which combined with each other and with neutral molecules to form higher molecular weight fractions. The fact that many linear alkanes were found indicated that difluorocarbene (:CF$_2$) was involved in the chain-extension process. A significant amount of F radical was also postulated to explain the formation of alkanes. Perfluorodienes were suggested as reaction intermediates for the presence of many identified olefinic groups. Halogenation of the discharge product proceeded readily with elemental fluorine, but not with chlorine or bromine trifluoride.

Reports in the literature concerning electrical discharge of gaseous fluorocarbons[2–5] have described only the discharge at low pressure. The present investigation was made at higher pressures and the electrical conditions were milder than those of previous workers. The products obtained with hexafluoropropene were predominantly liquids. Instrumental and chemical analyses indicated that the liquid product (herein called liquid fluorocarbon) contained perfluoro alkanes as well as unsaturated fractions.[2]

Results and Discussion

Hexafluoropropene was converted into a mixture of gaseous (3–10%) and liquid fluorocarbons in quantita-

---

(1) (a) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968. (b) To whom inquires should be addressed: 102 Maclean Circle, Princeton, N. J. 08540.

(2) (a) P. B. Weisz, *J. Phys. Chem.*, **59**, 464 (1955); (b) P. B. Weisz, *et al.*, U. S. Patent 2,676,145 (1954).

(3) J. Goodman, *J. Polym. Sci.*, **44**, 551 (1960).

(4) A. Bradley and J. P. Hammes, *J. Electrochem. Soc.*, **110**, No. 1, 15 (1963).

(5) Y. Kometani, A. Katsushima, T. Fukui, and K. Nakamura, Japanese Patent 10,989 (1965).

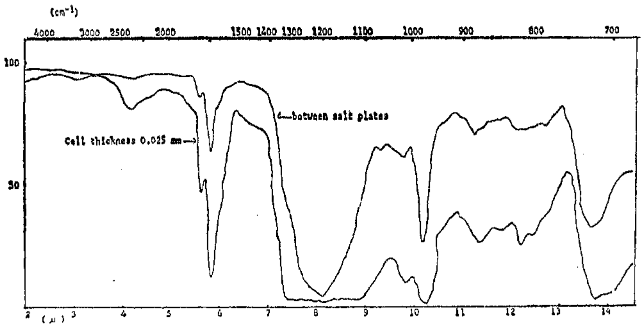

Figure 1.—Infrared spectrum of the liquid fluorocarbon from hexafluoropropene by the electrical discharge process.

tive yield[6] by passing the monomer through an electrical discharge cell. The discharge was initiated across gaseous gaps of 1.5–2.0 mm at monomer pressures of 150–800 Torr, total applied voltages of 12–24 kV (rms), and AC currents at 1.4–10 kc/sec.[6] Within these diversified reaction conditions, the crude products showed the same general infrared spectrum (Figure 1). Molecular weight distribution of the products, however, varied, as shown by the fractional distillation results (Table I). The major components of the gaseous fraction identified by instrumental analyses were $F(CF_2)_nF$ (n = 1, 2, 3, 4, 5), $(CF_3)_3CF$, $CF_3CF{=}CF_2$, and CO_2. In addition, the following components were sought, but were not observed by any of the analytical methods: $CF_2{=}CF_2$, $c\text{-}C_3F_6$, $CF_2{=}CFCF{=}CF_2$, $CF_3CF_2CF{=}CF_2$, $c\text{-}C_4F_8$,[7] $(CF_3)_2C{=}CF_2$, CF_3OF, CF_3CFO, CO, F_2,[7] SiF_4,[7] and COF_2.[7]

Table I

Physical Properties of Liquid Fluorocarbon Prepared at Two Different Frequencies (1.4 and 10 kc/sec)

Bp, °C	Wt %	η at 20° cSt	$n^{15}D$	ρ at 22°
A. Frequency, 1.4 kc/sec; Energy Input/mol of Reactant (kcal/mol), 1320				
→100	10	0.56	<1.3	1.6888
100–150	34	1.01	<1.3	1.7820
150–200	30	3.96	1.3132	1.8730
>200	17	35.5	1.3262	1.9119
Gaseous products	9	. . .	. . .	. . .
B. Frequency, 10 kc/sec; Energy Input/mol of Reactant (kcal/mol), 3010				
→100	6	0.60	<1.3	1.5926
100–150	17	1.05	<1.3	1.6903
150–200	38	2.77	1.3069	1.8557
>200	31	55.4	1.3254	1.9186
Gaseous products	8	. . .	. . .	. . .

The low-boiling liquids were further fractionated by gas chromatography. Many linear and branched alkanes were separated and identified (Table II). There were also many unsaturated fluorocarbons present in this fraction, as shown by the infrared spectrum. Small amounts of perfluorohexene and perfluoroheptene were identified by mass and infrared spectroscopy. The fact that most of the larger peaks in the gaseous and low-boiling fractions were identified as saturated fluorocarbons showed that these components were much less reactive toward further discharge reactions than were the olefinic components.

Table II

Major Components Identified[a] from the Low-Boiling Liquid Fluorocarbon[b]

Structures	%[c]
$n\text{-}C_5F_{12}$	6.19
$i\text{-}C_5F_{12}$	2.05
$n\text{-}C_6F_{14}$	9.31
$i\text{-}C_6F_{14}$	24.30
$(CF_3)_2CFCF(CF_3)_2$	17.75
$(CF_3)_2CF(CF_2)_3CF_3$	6.92
$(i\text{-}C_3F_7)_2CF_2$	12.20
Other C_7F_{16} isomers	8.61
Unidentified (many peaks)	12.67

[a] By mass infrared, and ^{19}F nmr spectroscopy. [b] This fraction (57%) was collected at 35–150° from the fractional distillation of a liquid fluorocarbon having a viscosity of 1.8 cSt at 20°. [c] Area measurement by gas chromatographic analysis.

No carbon deposit was found in either the discharge cell or the liquid fluorocarbon. The yield of the liquid fluorocarbon was quantitative; however, it varied with the electrical power input to the system within constant-temperature or constant-pressure limits. Viscosity of the product was more effected by temperature than by applied voltage (Table III).

Table III

Effect of Discharge Condition on Yield and Viscosity of Product

Temp of electrode, °C Inner	Temp of electrode, °C Outer	Monomer pressure, mm	Operating voltage, kV (rms)	Power,[a] W	Energy input per mol of C_3F_6 charged, kcal/mol	Yield,[b] g	η at 20°, cSt
18	11	260	18.0	499	1182	193	2.05
21	11	260	16.9	353	870	185	1.99
20	11	260	15.8	252	784	164	1.87
19	10	260	14.5	238	835	130	1.71
52	36	260	18.0	481	1303	156	4.01
52	36	260	15.9	363	1257	132	3.67
52	37	260	15.0	264	992	121	3.46
53	37	260	14.5	247	1030	109	3.17
27	13	150	18.0	418	1616	118	2.89
27	13	150	16.5	378	1616	107	2.86
28	13	150	15.0	302	1403	98	2.72
28	13	150	14.0	265	1297	93	2.25
52	37	150	18.0	378	2534	68	8.27
52	37	150	16.5	319	2107	69	7.74
52	37	150	15.0	258	1645	72	5.65
52	37	150	14.0	227	1567	66	4.9

[a] The frequency of all the experiments was set at 1.4 kc/sec. [b] The time for all the experiments was 3.5 hr. The yield is quantitative; *i.e.*, the amount of C_3F_6 consumed was the same as the gram yield of each experiment.

The C_6 and C_9 fractions of the liquid fluorocarbon were compared with the dimers and trimers of C_3F_6 prepared in dimethylaniline and methanol.[8] None of the isomers prepared by that method was found in the liquid fluorocarbon of the present process.

Base-catalyzed reaction of the liquid fluorocarbon with alcohol showed the presence of three types of structures: perfluoro alkanes, perfluoro olefins, and a

---

[6] S. W. Osborn, E. Broderick, E. L. Kutch, M. Kawahata, and J. C. Fraser, presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1968, Abstracts, p Fluo. 1 (to be published).

[7] Present in the electrical discharge product of tetrafluoroethylene: E. S. Lo, unpublished data.

[8] W. J. Brehm, *et al.*, U. S. Patent 2,918,501 (1959).

small third fraction. The olefins were isolated as unsaturated ethers.[9,10] The third fraction was identified as carboxylic acids. The carboxylic acids can also be obtained by treating the liquid fluorocarbon with aqueous alkali. Since the discharge product showed no OH absorption in its infrared spectrum, the carboxylic acids must result from the hydrolysis of some precursors in the discharge product. Epr study[11] of the liquid fluorocarbon indicated the presence of stable fluorocarbon radicals. The electron spin densities range from 10^{21} to 10^{17} spins/cc. High spin densities have also been observed in the radio-frequency discharge with benzene.[12] These radicals were known to chemisorb oxygen readily.[12,13] Mass spectroscopy of an air-exposed liquid fluorocarbon sample indicated the presence of SiF_4, CO_2, and oxygen-containing components such as $C_4F_7O^+$, $C_2F_3O^+$, and $C_2F_2O^+$. Hydrolysis of these radicals would be expected to produce carboxylic acids.

Another precursor of these carboxylic acids may be oxygen-containing fragments present in the discharge product. The source of oxygen is not clear, but it could be the Pyrex discharge cell, since the cell was slightly etched after the discharge reaction.

About 98% of the unsaturation shown by infrared spectrum could be effectively removed by elemental fluorination. Prolonged fluorination, even at higher temperature, did not saturate the liquid fluorocarbon further. Infrared analyses during the fluorination process indicated the presence of a small new peak at 5.3 μ (–FC=O), which appeared at the beginning of fluorination and remained at the same intensity until the end of the process. This acyl fluoride peak could result from oxygen, chemisorbed by the stable fluorocarbon radicals.

Halogenation of the liquid fluorocarbon was sluggish. Both vapor-phase chlorination[14] and bromine trifluoride addition reactions succeeded only partially in reducing the unsaturation present in the liquid fluorocarbon.

Mechanism of Reaction.—Both ionic[2,15] and free-radical[12,16,17] mechanism have been proposed for the reactions involved in electrical discharge processes. The reaction path of the discharge process is not only influenced by applied electrical fields, but also by the temperature of the gas plasma, which is often much higher[18] than the wall temperature of the reactor. The present study is made at much higher monomer pressures than those used by previous workers.[2–5] The interaction of electrons and molecular assembly, therefore, is much greater than that encountered in low-pressure discharges. In the present systems, it is possible to consider reaction paths otherwise unavailable in normal thermal or regular free-radical systems.

The dissociation of C_3F_6 to excited free radicals and the combination of these radicals with each other and with C_3F_6 (Scheme I) could account for a number of components identified. The fact that many linear alkanes were present suggested the presence of difluorocarbene (:CF_2). The large number of branched alkanes found also indicated the presence of the isopropyl radicals, which could easily be formed from the fluorine radicals and the C_3F_6 molecules. The larger amounts of branched alkanes (Table II) further indicated the abundance of the isopropyl radicals and thus of the fluorine radicals in the discharge system.

SCHEME I

SUGGESTED MECHANISM OF REACTION FOR THE ELECTRICAL DISCHARGE PROCESS

A. Initial Reactions

$$\begin{gathered}
CF_3CF{=}CF_2 \longrightarrow \cdot CF_3 + \cdot CF{=}CF_2 \\
CF_3CF{=}CF_2 \longrightarrow CF_3\dot{C}{=}CF_2 + \cdot F \\
\cdot CF_3 \longrightarrow :CF_2 + \cdot F
\end{gathered}$$

B. Radical Reactions

$$\begin{gathered}
\cdot CF_3 + n(\cdot CF_2) + \cdot F \text{ (or } \cdot CF_3) \longrightarrow CF_3(CF_2)_nF^{a,b} \\
\cdot F + CF_2{=}CFCF_3 \longrightarrow (CF_3)_2\dot{C}F \xrightarrow{\cdot CF_3} (CF_3)_3CF^{a} \\
2(CF_3)_2\dot{C}F \longrightarrow (CF_3)_2CFCF(CF_3)_2{}^{a,c} \\
\Big\downarrow {\scriptstyle :CF_2} \\
(i\text{-}C_3F_7)_2CF_2{}^{a} \\
(CF_3)_2\dot{C}F + n(:CF_2) + \cdot F \text{ (or } \cdot CF_3) \longrightarrow (CF_3)_2CF(CF_2)_nF^{d} \\
2\cdot CF{=}CF_2 \longrightarrow CF_2{=}CFCF{=}CF_2 \\
\cdot CF{=}CF_2 + CF_3\dot{C}{=}CF_2 \longrightarrow CF_2{=}CFC(CF_3){=}CF_2
\end{gathered}$$

C. Polymerization

$$\cdot F \text{ (or } \cdot CF_3) + \text{“dienes”} + n(:CF_2) + mCF_3CF{=}CF_2 \longrightarrow \begin{array}{c}\text{liquid fluorocarbon polymers} \\ \text{(containing terminal and internal –C=C–)}\end{array}$$

[a] Identified; see text. [b] Alkanes from methane to hexane were individually identified. [c] Dresdner, *et al.*, described the formation of $(CF_3)_2CFCF(CF_3)_2$ by radicals coupling: R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Amer. Chem. Soc.*, **82**, 5831 (1960). [d] Isopentane, isohexane, and isoheptane were isolated and identified.

Dienes have not been identified among the gaseous and low-boiling fractions of the discharge products; however, their presence as intermediates in the discharge system is considered possible. The following groups were identified by ^{19}F nmr in the liquid fluorocarbon: $CF_3\overset{|}{C}{=}$, $(CF_3)_2C{=}$, $CF_3CF{=}$, $CF_2{=}CF–$, $–CF{=}C(CF_3)–$, $–CF{=}CF–$, $CF_3CF_2–$, $(CF_3)_2CF–$, and $CF_3\overset{|}{C}F–$. Many of these olefinic groups could result from 1,2 or 1,4 radical addition to the appropriate diene. Perfluorobutadiene is "polymerized" readily to a viscous liquid under similar discharge conditions.[19] The absence of 1,3-dienes among the identified components is probably due to their much greater reactivity in the discharge system.

Alkanes are not necessarily the ultimate product of the present discharge process. Perfluoropropane[19] gives a small amount of liquid fluorocarbon after several hours of discharge under the same electrical conditions

---

(9) J. D. Park, W. M. Sweeney, S. L. Hopwood, Jr., and J. R. Lacher, *J. Amer. Chem. Soc.*, **78**, 1685 (1956).

(10) E. S. Lo, U. S. Patent 2,975,163 (1961).

(11) Determined by Dr. J. J. Downs and Dr. T. Woodhouse, Midwest Research Institute, Kansas City, Mo.

(12) D. D. Neiswender, "Chemical Reactions in Electrical Discharges," Advances in Chemistry Series, No. 80, American Chemical Society, Washington, D. C., 1969, p 338.

(13) H. N. Rexroad and W. Gordy, *J. Chem. Phys.*, **30**, 399 (1959).

(14) By E. Broderick.[6]

(15) J. Morris and A. Charlesby, *Eur. Polym. J.*, **2**, 177 (1966).

(16) M. Burton and J. L. Magee, *J. Chem. Phys.*, **23**, 2194, 2195 (1955).

(17) R. R. Williams, Jr., *J. Phys. Chem.*, **63**, 776 (1959); **66**, 372 (1962), and references cited therein.

(18) (a) J. D. Cobine, "Gas Conductors," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, Chapter 9; (b) C. G. Found, *Trans. Illum. Eng. Soc.*, **33**, 161 (1938).

(19) E. S. Lo, unpublished data.

used to synthesize the liquid fluorocarbon. This experiment, as well as previous work,[2,4] indicates that alkanes are much more stable than olefins under discharge conditions. Nevertheless if alkanes remain in the discharge zone, further dissociation of carbon–carbon and carbon–fluorine bonds are likely to occur.

Some of the groups identified in the liquid fluorocarbon may also be explained by an ionic mechanism, especially the branched unsaturated olefinic groups. However, none of the products is unequivocally the product of an ionic mechanism, as indicated by the absence of the dimers and trimers of C_3F_6 prepared by the ionic method.[8] There is a possibility that both the ionic and the radical mechanisms could exist in an electrical discharge process and that one could be made to predominate over the other by changing monomer pressure, temperature, and electrical conditions. The present study, however, seems to indicate that higher monomer pressures favor the radical mechanism.

Experimental Section

The Electrical Discharge Cell.—The electrical discharge cell used was similar to a Siemens ozonizer and has been described in the literature.[2,6] Typical reactions were carried out as follows. The glassware was dried and assembled, then evacuated and refilled two times with N_2 and then with C_3F_6. Hexafluoropropene was led into the evacuated assembly at the desired pressure. High-voltage electrical power was applied to the reactor. Within minutes, oil droplets streamed down the reactor wall were collected in the receiver. The yield was quantitative; *i.e.*, the loss of monomer weight from the tank was the same as the weight of the product.

To collect the dissolved gaseous components, a small, evacuated trap kept closed during the discharge process was placed between the pump and the discharge cell. At the end of the reaction, the C_3F_6 supply valve was closed. The trap cooled in liquid N_2 was opened to the system. Gaseous components were collected for analyses before the system was opened to air.

Spectra.—Proton and ^{19}F nmr data were obtained with Varian DP-60 high-resolution nmr spectrometer. Gas chromatographic data were obtained with a Nester–Faust preparatory gas chromatograph. The analytical columns (0.25 in. × 24 ft) were packed with silicone stationary phases, either SF96 on Chromosorb P or UCW98 on Chromosorb G. Infrared spectra were run on a Beckman IR-2 spectrophotometer. Mass spectrograms were obtained using a Bendix time-of-flight mass spectrometer.

Materials.—Perfluoropropene (Thiokol Chemical Corp.) and trifluoroethanol (Pennsalt Chemical Corp.) were of 99+% purity. Elemental fluorine and bromine trifluoride were from Matheson Scientific, Inc., and were used without further purification.

Reaction of Liquid Fluorocarbon with Trifluoroethanol.—Liquid fluorocarbon (80 g) was dropped slowly into a solution of CF_3CH_2OH (160 g) and KOH (10 g) at 50°. The reaction was slightly exothermic. After 5 hr at 50°, the solution was distilled. The distillate contained two immiscible, colorless liquids: the top layer (CF_3CH_2OH) and the lower layer (36 g, fraction a). The residue also contained two liquid layers and solid inorganic salts. The salts were identified as KF and K_2CO_3. The yellow lower layer (44 g, fraction b) was the alcohol reaction product. The brown, alcoholic upper layer was poured into 5% sulfuric acid and a small amount of pale yellow liquid (3 g, fraction c) was precipitated.

Fraction a.—The major components in this fraction were saturated perfluorocarbons. Proton nmr gave no signal, indicating the absence of CH groups. The infrared spectrum showed no absorption at 2750–3500 and 1450–2000 cm^{-1}, indicating the absence of both CH and C═C, respectively. ^{19}F nmr, however, indicated the presence of a small amount of unsaturation owing to $(CF_3)_2C=$ and $CF_3C=$ groups. This discrepancy is common in the analyses of fluoro olefins, especially olefins having internal trans unsaturation.[8] The density of fraction a at 20° was 1.855. Ninety-five per cent of the liquid boiled at 93–108° and 5% boiled above 180°.

Fraction b.—The major components in this fraction were the ethers of fluoro olefins.[9,10] Typical CH absorption at 2850–2950 cm^{-1} and strong C═C absorption at 1650 cm^{-1} were observed in the ir. Some of these unsaturated ethers were the result of multiple substitution by alkoxide groups.

Fraction c.—A minor component (2–5%) was also obtained by reacting the liquid fluorocarbon with 8% aqueous KOH solution. Its neutralization equivalent varied from 350 to 800. A broad absorption at 2750–3500 cm^{-1} (hydroxy) and a sharp absorption at 1725 cm^{-1} (carbonyl) indicated a carboxylic acid structure. The surface tension of an aqueous solution (0.025%) of the potassium salt of fraction c was 24.4 dynes/cm.

Fluorination of Liquid Fluorocarbon with F_2.—Fluorination with elemental F_2 was done in a barricaded cell with a protective window and remotely controlled valves.[20] For room-temperature fluorination, a dried glass reactor equipped with a condenser was used. For high-temperature fluorination, a stainless steel or monel cylinder heated by a remotely controlled thermal tape was used instead. A bubbler with Kel-F oil was attached to the exit side of the condenser to measure the gas flow. Occasional accumulation of F_2 in the system often resulted in flame or even explosion.

Liquid fluorocarbon (200 g) was placed in a 500-cc flask. Nitrogen was passed through the system for 30 min, then F_2 was added slowly to the N_2 stream. There was usually a noticeable exotherm which could be controlled by the F_2 flow rate. After fluorination with N_2–F_2 (1:1) for 2 hr, the amount of F_2 in the gas mixture was increased slowly by gradually turning off the N_2. The exotherm still had to be watched closely to prevent flaming or explosion. Fluorination took about 20 hr, and the system was then purged with nitrogen for 1 hr before being opened to air. The yield was 190.5 g. About 98% of the unsaturation in the infrared spectrum had been removed; however, a small amount of unsaturation persisted. Also a new peak at 5.3 μ appeared at the beginning of the fluorination period and remained at the same intensity until the end of the process.

Fluorination at higher temperature (120–180°) in a stainless steel cylinder shortened the time required for saturation of double bonds, but also resulted in some carbon–carbon bond cleavage. It was more difficult to control the exothermic reaction at higher temperature. Often carbonaceous materials were carried into the Kel-F bubbler. For fluorination of the liquid fluorocarbon, high temperatures did not offer appreciable advantage.

Vapor-Phase Chlorination.[14]—Liquid fluorocarbon (150 g) was placed in a flask connected to a gas inlet and a hot tube packed with 0.25 in. Berl Saddles. The temperature of the hot tube was automatically controlled at 250°. Chlorine gas was bubbled through the liquid fluorocarbon maintained at 100°. The product was collected in a cooled receiver at the other end of the heated tube and weighed 93 g. It contained 14% Cl. The infrared spectrum indicated that a substantial amount of unsaturation still remained.

Reaction of Liquid Fluorocarbon with BrF_3 in Br_2.—The liquid fluorocarbon (300 g) was dropped into a solution containing BrF_3 (33 g) and Br_2 (77 g) during 45 min. The reaction was mildly exothermic. After 1 hr, the temperature dropped from 45 to 25°. The brown solution was washed with 10% $NaHSO_3$ and water and dried over $MgSO_4$. The yield was 291 g. The resulting fluorocarbon liquid contained 6.6% Br. The infrared spectrum indicated reduction of the unsaturation peak at 5.8 μ, but a new peak at 5.35 μ was introduced.

Registry No.—Hexafluoropropene, 116-15-4.

Acknowledgments.—The authors are indebted to Dr. J. D. Readio for the instrumental analyses, Mr. E. Kutch for the synthesis of the liquid fluorocarbon, and Mr. J. Magazzu for laboratory assistance.

---

(20) Fluorine was handled according to the procedures described in the Matheson Gas Data Book, 4th ed, p 237, 1966.