CARBON FORMATION

The carbon formed in these experiments was, surprisingly, an activated char. It had decolorizing properties. Its density was a function of the temperature of the reaction, higher temperature producing a more dense form. It was not contaminated with tarry substances. Tars were not found as products from the oxidation of either aromatic or aliphatic substances. All of the organic compound may be converted to carbon without gaseous products, depending only upon the use of sufficient oxygen. In most of the experiments reported in Table I, only a relatively small amount of oxygen was present in the vessel and the reaction proceeded only as far as this was used.

LITERATURE CITED

(1) Simons, J. H., and Lewis, C. J., *J. Am. Chem. Soc.*, 60, 492 (1938)
(2) Simons, J. H., and Passino, H. J., *Ibid.*, 62, 1624 (1940).

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PROPERTIES OF FLUOROCARBONS

Aristid V. Grosse[1] **and George H. Cady**[2]
WAR RESEARCH LABORATORIES, COLUMBIA UNIVERSITY, NEW YORK, N. Y.

THE main chemical characteristic of fluorocarbons is due to the great stability of the C—F bond. Thus, particularly in contrast to chlorocarbons, they show remarkable thermal stability and molecules with long carbon chains, similar to those of hydrocarbons and their derivatives, are possible. They are furthermore characterized by their great chemical inertness and resistance to oxidation. The physical properties of fluorocarbons are compared with those of hydrocarbons of the same carbon structure, and a number of regularities observed. Their boiling points and volatilities are close together, but the fluorocarbons have about double the density of hydrocarbons and remarkably low indices of refraction. On the basis of present information, it is not premature to conclude that we are confronted here with a vast new field of inorganic "organic chemistry", a field potentially as immense in size and as varied, both in compounds and reactions, as that of ordinary organic chemistry.

IN THE fall of 1941 work was started at Columbia, and extended to various other universities, having as its objective the development of certain liquid and solid compounds with special properties required by the Atomic Energy Project. From the behavior of those fluorocarbons, C_xF_y, which were described by Simons (*26*), Grosse suggested in 1940 that compounds of this chemical type might be satisfactory for the intended purpose. A few cubic centimeters of a mixture of liquid fluorocarbons, practically all of the available supply, were secured from Simons, tested (*8*), and found to be satisfactory. Further intensive research was indicated.

As the result of a great cooperative effort by both university and industrial laboratories, a large number of new compounds containing only carbon and fluorine (fluorocarbons) were discovered. A large amount of data on their properties has accumulated, and the purpose of this paper is to compare the fluorocarbons with hydrocarbons of the same carbon skeleton.

On the basis of information now available, it is not premature to conclude that we are confronted here with a vast new field of inorganic "organic chemistry", which is potentially as immense and as varied as that of ordinary organic chemistry. If we consider, in addition, the mixing of fluorocarbon compounds or their radicals with classical organic compounds or their respective radicals these potentialities become staggering. (Approximately 10^6 organic compounds are now known; in view of the stability of fluorocarbons and their derivatives, a similar number is possible. The number of possible "mixed" compounds is thus 10^{12}.)

At the time that work on the fluorocarbons was started, only the first gaseous members of the fluorine paraffin series—namely, CF_4, C_2F_6, C_3F_8, and C_4F_{10}—and $CF_2{=}CF_2$, were known as pure compounds, and some information was available on one or two pure liquid fluorocarbons. By the summer of 1942 a large number of pure, liquid fluoroparaffins and -naphthenes, both mono- and bicyclic, were available.

The first practical and general way to produce them was the CoF_3 method of Fowler and associates (*6*) at Johns Hopkins. This was followed shortly after by Columbia's catalytic method and later by others.

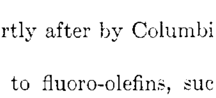
The first references to fluoro-olefins, such as $CF_2{=}CF_2$, are found in early papers by Otto Ruff and A. L. Henne. Since then our knowledge of fluoro-olefins has substantially increased. Fluorodiolefins, such as fluorobutadiene (C_4F_6), were first isolated by W. T. Miller, and cyclo-olefins, such as fluorocyclobutene (C_4F_6), by Henne. Representatives of fluoroaromatics, such as hexafluorobenzene (C_6F_6), have been synthesized by E. T. McBee and co-workers.

Table I lists all fluorocarbons known to date with their physical properties.

NOMENCLATURE OF FLUOROCARBONS

The classical nomenclature becomes cumbersome, particularly for compounds containing many atoms of fluorine and only a few of hydrogen. For example, $CF_3—CFH—CF_2—CF_2—CF_2—CF_2—CF_2—H$ would be called 1,1,1,2,3,3,4,4,5,5,6,6,7,7-tetradecafluoroheptane.

We have found it convenient to use the Greek letter phi as a symbol to indicate complete substitution of all hydrogen atoms attached to carbon by fluorine in the compound following the symbol. For example, Φ-heptane is C_7F_{16}, and the hydrofluorocarbon mentioned above is 1,6-dihydro-Φ-heptane. Similarly Φ-cyclohexane, pronounced phi-cyclohexane, is:



Bigelow's $C_6F_{11}H$ would be named monohydro-Φ-cyclohexane, whereas its regular Geneva organic name would be 1,2,2,3,3,4,4,5,5,6,6-undecafluorocyclohexane. Further examples are Φ-benzoic acid (C_6F_5COOH), Φ-ethyl alcohol (C_2F_5OH), and Φ-ethyl-Φ-benzoate ($C_6F_5—COOC_2F_5$). The letter Φ was chosen as the Greek equivalent for the Latin F, symbol of the element.

We believe that this departure from organic nomenclature is warranted, particularly since we do not consider this new field of chemistry a part of regular organic chemistry.

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[1] Present address, Houdry Process Corporation, Marcus Hook, Pa.
[2] Present address, University of Washington, Seattle, Wash.

CHEMICAL PROPERTIES

The saturated fluorocarbons—that is, the fluoroparaffins (C_nF_{2n-2}) and the fluoronaphthenes, monocyclic (C_nF_{2n}) and bicyclic (C_nF_{2n-2})—may be produced in good yields (from 50–95%) by two general methods. The first was Fowler's two-step method (*6*). The compound to be fluorinated is vaporized, diluted with nitrogen, and passed over a bed of CoF_3 at 200–350° C. Substitution takes place according to the general equation:

$$>C—H + 2CoF_3 \longrightarrow >C—F + 2CoF_2 + HF$$

The degree of substitution depends on contact time, temperature, and structure of the compound. The second step consists in reconversion of CoF_2 to CoF_3 by passage of elementary fluorine at 200–250° C. MnF_3, CeF_4, and AgF_2 may be used in a similar manner, and the latter modification was worked out later at Purdue by McBee, Hass, and co-workers.

A second method, developed at Columbia (*5*), is a continuous one-step catalytic process. Vapors of the substance to be fluorinated and fluorine are each diluted with nitrogen and mixed gradually, in the range 150–325° C., over catalyst consisting of fine copper turnings or ribbon covered with a thin layer of silver fluorides. Substitution takes place according to the general equation:

$$>C—H + F_2 \longrightarrow >C—F + HF$$

These general methods permit direct conversion of a saturated hydrocarbon to a fluorocarbon of substantially the same carbon structure, but depend on the use of expensive elementary fluorine. Parallel to these, specialized methods were developed for the stepwise conversion of hydrocarbons to fluorocarbons by way of the much less expensive chlorination and anhydrous hydrogen fluoride treatment.

The conversion of benzotrichloride (obtained by direct chlorination of toluene) with hydrogen fluoride to benzotrifluoride, without or with catalysts ($SbCl_5$ or SbF_3), was previously established. Similarly, the xylenes and mesitylene could be chlorinated and then converted with hydrogen fluoride to bis(trifluoromethyl)-benzenes ("hexafluoroxylenes", *17*) and tris(trifluoromethyl)-benzenes ("nonafluoromesitylene"), respectively. All these partially fluorinated compounds can be readily fluorinated by the two general methods (*2*), referred to previously, to completely fluorinated products with much greater yields than the original hydrocarbons.

In addition to the increase in yield, an advantage is the great decrease in elementary fluorine consumption (i.e., 6 moles fluorine for nonafluoromesitylene with a loss of only 1.5 moles as hydrogen fluoride compared to 15 moles fluorine for mesitylene with a loss of 9 moles as hydrogen fluoride).

In addition, paraffins can be converted substantially to fluorocarbons (*19*). For instance, *n*-heptane can be chlorinated photochemically and in the liquid phase (*19*) up to $C_7H_4Cl_{12}$. When treated with hydrogen fluoride, the latter yields $C_7H_4F_6Cl_6$. Much higher fluorine substitution is possible (*1*) by intermittent chlorination during hydrogen fluoride treatment—namely, up to an average composition of $C_7H_2F_{10.5}Cl_{1.5}$. Final treatment of this compound by the two general methods gives Φ-heptane; thus, consumption of elementary fluorine has been reduced from 16 moles per mole heptane (Equation 1 below) to only 3.75 moles.

The saturated fluorocarbons are characterized by great stability and inertness toward even the most reactive chemicals. This is to be expected in view of the strength of the C—F bond and the large heat of formation of fluorocarbons.

The direct substitution of hydrogen by fluorine in an organic molecule is an extremely exothermic reaction, and it is remarkable that high yields of completely fluorinated products with an intact carbon structure may be obtained. This may best be illustrated by citing heptane as an example. Using bond strength data of both Pauling and Rice, the heat of reaction for Equation 1,

$$C_7H_{16} + 16F_2 \longrightarrow C_7F_{16} + 16HF \qquad (1)$$

has been calculated as 1660 kg.-cal. per mole (Pauling data) or 1600 kg.-cal. per mole (Rice data). In comparison, the heat of formation of water, 68 kg.-cal. per mole, appears insignificant.

The saturated fluorocarbons are attacked by the most reactive substance known—elementary fluorine—to yield CF_4 as the final stable fluorination product. With Pauling's bond energy values, it is evident that the reactions will be highly exothermic. Taking Φ-heptane as an example, the heat of reaction ΔH should be:

$$C_7F_{16} + 6F_2 \longrightarrow 7\ CF_4;\quad \Delta H = -551 \text{ kg.-cal.}$$

$$(16\ C—F \text{ bonds} + 6\ C—C \text{ bonds}) + 6\ F—F \text{ bonds} \longrightarrow 28\ C—F \text{ bonds}$$

$$2064 \text{ kg.-cal.} + 381 \text{ kg.-cal.} \longrightarrow 2996 \text{ kg.-cal.}$$

In view of this highly negative value, ΔF (the free energy decrease) should also be negative. Mixtures of fluorine and Φ-heptane vapors do explode violently when ignited by a spark discharge, as found by Cady. It is therefore to be expected that fluorocarbons will burn in fluorine, and vice versa, if admitted through a jet and ignited. Consequently precautions are necessary in handling fluorocarbons in the presence of free fluorine.

The fluorocarbons are readily attacked by metallic sodium and potassium at temperatures around and above 400° C., as mentioned by Simons (*26*).

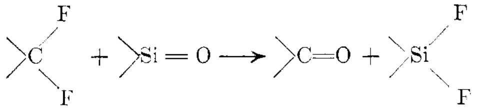
SATURATED FLUOROCARBONS

The following results were obtained, using Φ-heptane and Φ-cyclohexane as representatives of their respective classes. These results may be generalized and are believed to be typical of the saturated fluorocarbons, unless special structural features interfere.

The fluorocarbons are thermally very stable. They can be heated to 400–500° C. even in the presence of possible catalytic material, such as finely divided CaF_2, without cracking. At red heat, however, decomposition to carbon and CF_4 takes place. Probably other products are also formed, in amounts depending on temperature, pressure, and time conditions.

Solubilities of fluorocarbons in various solvents are discussed later in the paper.

Fluorocarbons react with finely divided silica at temperatures above 400° C., forming carbon dioxide and SiF_4 and perhaps oxyfluorides, according to the scheme:



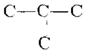
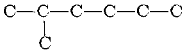
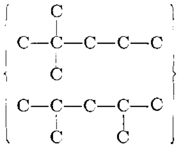
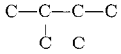
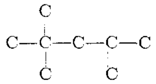
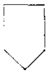
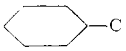
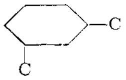
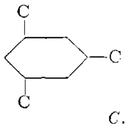
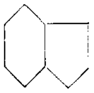
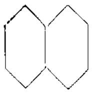
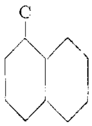
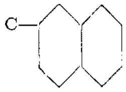
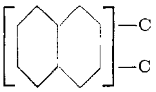
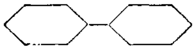
$$>CF_2 + >Si=O \longrightarrow >C=O + >SiF_2$$

Fluorocarbons are not attacked by nitric acid, concentrated (96%) and fuming sulfuric acid, nitrating mixture, acid chromate, and permanganate solutions. The reaction product of the fluorination of benzene (i.e., Φ-cyclohexane) may be easily separated from the last traces of unreacted benzene by nitrating the latter with nitrating mixture and separating the dinitrobenzene from the volatile C_6F_{12}.

Fluorocarbons are stable toward air and do not burn by themselves. They crack, however, in the flame of a Bunsen burner. They do not decolorize bromine water and are stable against bromine and iodine.

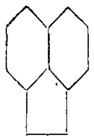
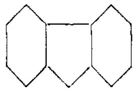
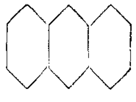
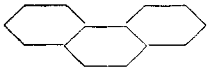
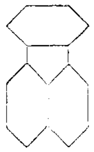
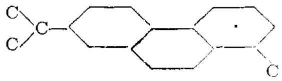
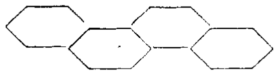
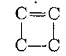
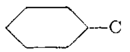
Fluorocarbons react in the presence of catalysts with hydrogen under pressure at higher temperatures. For instance, Φ-methylcyclohexane (boiling at 75.5° C.) reacts with hydrogen under about 100 atmospheres and at 450° C. for 22 hours, in the presence of $NiCr_2O_3$ and NiF_2 as catalyst, in a steel bomb. A few moles of hydrogen fluoride form per mole of C_7F_{14}. At the same time no noticeable cracking to gases takes place. Higher boiling material (i.e., from 75° to 95° C.) forms, having lower density, higher refractive indices, and higher specific refraction than the original (Table II).

TABLE I. LIST OF ISOLATED FLUOROCARBONS KNOWN TO DATE

Name	Formula	C Skeleton	Melting Point, ° C.	Boiling Point at 760 Mm., ° C.	Density (t° C.)	Refractive Index (t° C.)	Viscosity at 99.5° C., Millipoises	Appearance at Room Temp.	Literature Reference
A. Φ-PARAFFINS									
Φ-Methane	CF_4	C	−184	−128	1.96 (−184)	....	....	Colorless gas	*(24)*
Φ-Ethane	C_2F_6	C—C	−100.6	−78.2	1.85 (−78)	....	....	Colorless gas	*(24)*
Φ-Propane	C_3F_8	C—C—C	−183	−38	1.45 (0.2)	....	....	Colorless gas	*(26)*
Φ-*n*-Butane	C_4F_{10}	C—C—C—C	Glass	−4.7	1.47 (20)	....	....	Colorless gas	*(26)*
Φ-Isobutane	C_4F_{10}	 $C-\underset{C}{\underset{\mid}{C}}-C$	Glass	+3.0	....	....	....	Colorless gas	*(26)*
Φ-*n*-Heptane	C_7F_{16}	C—C—C—C—C—C—C	[a]	82	1.7038 (30)	1.2572 (30)	....	Colorless liquid	*(6, 9)*
Φ-Methylhexane and dimethylpentanes	C_7F_{16}	 $C-\underset{C}{\underset{\mid}{C}}-C-C-C-C$	.....	.....	....	....	....	Colorless liquid	*(9)*
Φ-2,2- & 2,4-Dimethylpentanes	C_7F_{16}	 $\left\{\begin{matrix} C-\overset{C}{\overset{\mid}{\underset{C}{\underset{\mid}{C}}}}-C-C-C \\ C-\underset{C}{\underset{\mid}{C}}-C-\underset{C}{\underset{\mid}{C}}-C \end{matrix}\right\}$	.....	.....	....	....	....	Colorless liquid	*(9)*
Φ-2,2,3-Trimethylbutane	C_7F_{16}	 $C-\underset{C}{\underset{\mid}{C}}-\underset{C}{C}-C$	.....	+82	1.7535 (30)	1.2676 (30)	....	Colorless liquid	*(6, 9)*
Φ-2,2,4-Trimethylpentane	C_8F_{18}	 $C-\overset{C}{\overset{\mid}{\underset{C}{\underset{\mid}{C}}}}-C-\underset{C}{\underset{\mid}{C}}-C$	.....	+104	1.8002 (30)	1.2733 (30)	....	Colorless liquid	*(9)*
Φ-*n*-Hexadecane (cetane)	$C_{16}F_{34}$	$C-(C)_{14}-C$	+115	+240	....	....	....	Colorless plates sol. in hot CCl_4	*(9)*
Φ-Tetraisobutane	$C_{16}F_{34}$	....		≃110[b]	1.98 (25)	1.324 (25)	32	....	*(5)*
Solid from high boiling fractions of *n*-heptane fluorinations	C_xF_y	....	+93	≃+85[c]	....	....	....	Thin colorless plates from ether	*(9)*
B. MONOCYCLIC Φ-NAPHTHENES									
Φ-Cyclopentane	C_5F_{10}		−12	22	1.64 (30)	1.24 (30)	....	Colorless liquid	*(24)*
Φ-Cyclohexane	C_6F_{12}		+50	52	1.684 (30)	1.2685 (30)	....	White glistening compact crystals	*(3)*
Φ-Methylcyclohexane	C_7H_{14}		.....	76	1.7779 (30)	1.2762 (30)	....	Colorless liquid	*(9)*
Φ-Dimethylcyclohexanes[d]	C_8F_{16}		.....	100	1.8270 (30)	1.2858 (30)	....	Colorless liquid	*(9)*
Φ-1,3,5-Trimethylcyclohexane	C_9F_{18}		.....	123	1.8676 (30)	1.2930 (30)	....	Colorless liquid	*(6)*
C. BI-, TRI-, AND TETRACYCLIC Φ-NAPHTHENES									
Φ-Indan	C_9F_{16}		−8 to −15	116–117	1.8838 (20)	1.3033 (20)	....	Colorless liquid	*(16)*
Φ-Naphthalane	$C_{10}F_{18}$		−7 to −10	140[e]	1.9456 (20)	1.3118 (20)	....	Colorless liquid	*(16)*[f]
Φ-1-Methylnaphthalane	$C_{11}F_{20}$		<−75	161	1.9606 (20)	1.3168 (20)	....	Colorless liquid	*(16)*
Φ-2-Methylnapthalane	$C_{11}F_{20}$		<−60	160–161	1.9632 (20)	1.3164 (20)	....	Colorless liquid	*(16)*
Φ-Dimethylnaphthalanes	$C_{12}F_{22}$		−30 to −40	177–179	1.9759 (20)	1.3200 (20)	....	Colorless liquid	*(16)*
Φ-Dicyclohexyl	$C_{12}F_{22}$		+75	.....	....	....	....	White glistening compact crystals	*(3)*

(Continued on page 370)

TABLE I. LIST OF ISOLATED FLUOROCARBONS KNOWN TO DATE (*Continued*)

Name	Formula	C Skeleton	Melting Point, ° C.	Boiling Point at 760 Mm., ° C.	Density (t° C.)	Refractive Index (t° C.)	Viscosity at 99.5° C., Millipoises	Appearance at Room Temp.	Literature Reference
Φ-Acenaphthane	$C_{12}F_{20}$		2 to 0	173	1.9883 (20)	1.3292 (20)	....	Colorless liquid	*(16)*
Φ-Fluorane	$C_{13}F_{22}$		< −40	190	.9819 (20)	1.3264 (20)	....	Colorless liquid	*(16)*
Φ-Anthracane	$C_{14}F_{24}$		76–81	211–213[g]	....	....	22.4	Colorless glistening crystals	*(5, 16)*
Φ-Phenanthrane	$C_{14}F_{24}$		< −40	205–206	2.0197 (20)	1.3315 (20)	....	Colorless liquid	*(16)*
Φ-Fluoranthane	$C_{16}F_{26}$		−30 to −36	235–239	2.0598 (20)	1.3460 (20)	....	Colorless liquid	*(16)*
Φ-Retane (Φ-1-methyl-7-isopropylphenanthrane)	$C_{18}F_{32}$		.....	≃135[b]	2.05 (30)	1.343 (25)	≃60	Colorless oil	(5)
Φ-Chrysane	$C_{18}F_{30}$		.....	≃135[b]	2.06 (25)	1.344 (25)	≃60	Colorless oil	(5)
			D. Φ-OLEFINS (SRAIGHT, MONO- AND DI-, AND CYCLICS)						
Φ-Ethylene	C_2F_4	—C=C—	−142.5	−76.3	1.616 (−100); 1.368 (−40)	....	....	Colorless, odorless gas[i]	Benning *(23)*; *(15)* *(25)*
Φ-Polyethylene	$(C_2F_4)_n$	$—(C—C)_n—$	[h]	.....	2.2–2.3	1.37–1.38	....	White insol., solid	Benning *(23)*
Φ-Butadiene	C_4F_6	C=C—C=C	.....	−6.6	....	....	....	Gas	*(20)*
Φ-Butadiene dimer	C_8F_{12}	?	.....	+98–100	....	....	....	Liquid	*(20)*
(Satd. dimer)	C_8F_{12}	?	+40	.....	....	....	....	Solid	*(20)*
(Satd. trimer)	C_8F_{18}	?	.....	64–66[b]	....	....	....	Liquid	*(20)*
Φ-Cyclobutene	C_4F_6		−60.37	+1.13	....	....	....	Gas	*(12)*
			E. Φ-AROMATICS						
Φ-Benzene	C_6F_6		−13 to −11	81.0–82.0[j]	1.612	1.3760	....	Colorless liquid	*(18)*
Φ-Toluene	C_7F_8		< −70	103.5[k]	1.660	1.3664	....	Colorless liquid	*(18)*

[a] Crystallizes in dry ice in colorless large plates. [b] At 10 mm. mercury. [c] At 5 mm. mercury.

[d] Mixture of ortho, meta, and para isomers. [e] 20° C. at 10 mm. [f] Additional data from Hass and Weber, quoted from Grosse and Cady *(9)*: absolute viscosity at 24.6° C. = 53.39 and at 99.3° C. = 11.61 millipoises; average molecular weight = 462; specific refraction, experimental = 0.101, calculated = 0.100_3; molecular refraction, experimental = 46.71, calculated = 46.32.

[g] ≃ 90° C. at 10 mm. [h] Solid-phase transition at 320–327° C.; decomposed above 400° C.

[i] Critical temp. = +33.3° C.; critical pressure = 38.9 atm.; critical density = 0.58; dielectric constant at 28° C. = 1.0017; thermal conductivity at 30° C. = 0.000037 cal./sq. cm./sec./° C./cm. Vapor pressure (log p), atm.: from −76.3° to 0° C., $5.6210 - 875.14/T$, and from 0° to +33.3° C., $5.5906 - 866.84/T$. (Data of A. F. Benning, cited by Renfrew and Lewis, *23*.)

[j] At 743 mm. mercury. [k] At 740 mm. mercury.

Neither fractions 1, 2, or 3 nor the residue (Table II) reacted with 5% bromine in CCl_4, whereas $CF_2{=}CF_2$ rapidly decolorized it. This fact indicates the absence of unsaturated fluorocarbons. All four fractions, but not the original C_7F_{14}, precipitate manganese dioxide from neutral 2% potassium permanganate; this is similar to the behavior of hydro-Φ-heptanes obtained in the catalytic fluorination of Φ-heptane.

At present all these facts may best be interpreted by assuming that substitutions of fluorine by hydrogen have taken place with the formation of hydrogen fluoride and hydro-Φ-methylcyclohexanes. The splitting of the ring, although less likely, is not excluded.

The fluorocarbons are stable toward dilute and concentrated alkali, at both room temperature and around 100° C. Hydrofluorocarbons, however, do react with concentrated alkali at elevated temperatures. For instance, hydro-Φ-n-heptane, of the composition n-$C_7F_{12\cdot7}H_{3\cdot3}$, mostly dissolves in a fourfold volume of aqueous 40% potassium hydroxide on heating for 45 hours at 90° C., and forms an opaque, deep brown solution. About 5 moles of fluoride ion per mole of hydrofluorocarbon were split off. Pure Φ-n-heptane under identical conditions gives only a slight reaction, with no trace of coloration.

FLUORO-OLEFINS

Φ-Olefins are just as stable as the saturated compounds as far as the C—F bond is concerned, but show, as would be expected, the typical double-bond behavior. They add chlorine and bromine with great heat evolution to form colorless dichlorides or dibromides. These, in turn, can readily be converted back to Φ-olefins with zinc; thus a general method for preparation of Φ-olefins is provided.

Table II. Distillation of Products of Hydrogenation of Φ-Methylcyclohexane

(Charge, 18.5 grams; pressure, 766 mm.)

Fraction	Boiling Range, ° C.	Weight Grams	Weight %	n_D^{30}	d_4^{30}	Sp. Refraction	Composition[a]
1	75.8-77.4	5.9	32	1.2811	1.7544	0.100_0	$C_7F_{13.5}H_{0.5}$
2	77.4-78.9	5.5	30	1.2822	....	....	....
3	78.9-92.5	4.7	25	1.2918	1.7316	0.104_8	$C_7F_{12.5}H_{1.5}$
Residue	92.5	1.0	5.5	....	....	....	....
Loss	..	1.4	7.5	....	....	....	....
Original C_7F_{14}	75.5	...	..	1.2761	1.7779	0.0973	C_7F_{14}

[a] Assuming no double bonds are present; calculation of composition is discussed elsewhere (*7*).

A general procedure for obtaining mixed chlorofluorocarbons is the in-line dimerization reaction of Miller and associates (*21*). Halo-olefins add fluorine, at relatively low temperatures, under liquid-phase conditions, in two ways, as illustrated for CFCl=CFCl:

$$CFCl{=}CFCl + F_2 \longrightarrow CF_2Cl{-}CF_2Cl \qquad (2)$$

$$2CFCl{=}CFCl + F_2 \longrightarrow CF_2Cl{-}CFCl{-}CFCl{-}CF_2Cl \qquad (3)$$

Reaction 2 is normal addition; reaction 3, which is favored by lower temperatures, gives a dimer. Dechlorination of this dimer with zinc and alcohol led Miller and co-workers (*20*) to the highly reactive Φ-butadiene, $CF_2{=}CF{-}CF{=}CF_2$.

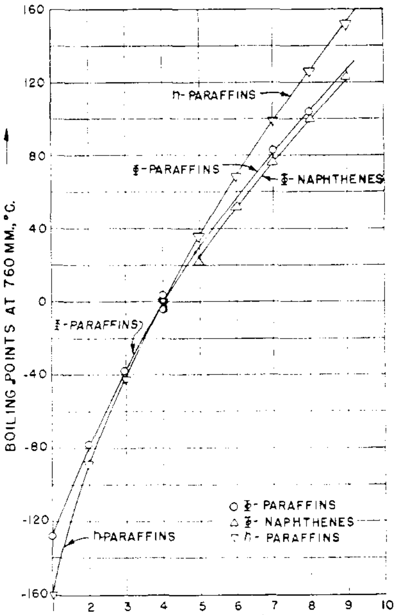
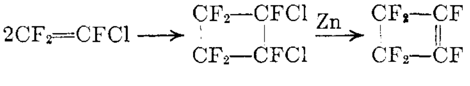


Figure 1. Boiling Points Plotted against Number of Carbon Atoms

Cyclic dimerization is also possible, and Henne and Ruh (*12*) thus obtained the cyclic olefin,



$$2CF_2{=}CFCl \longrightarrow \begin{matrix} CF_2{-}CFCl \\ | \quad\quad | \\ CF_2{-}CFCl \end{matrix} \xrightarrow{Zn} \begin{matrix} CF_2{-}CF \\ | \quad\quad \| \\ CF_2{-}CF \end{matrix}$$

Φ-cyclobutene, isomeric with Φ-butadiene.

Φ-Ethylene can be obtained by noncatalytic pyrolysis of CF_2Cl_2 in an inert reaction tube above 650° C. (*22*).

The Φ-olefins are readily polymerized, like their hydrocarbon counterparts. Φ-Ethylene is polymerized by BF_3 slowly during a period of days, at room temperature, to a white, inert, highly insoluble and temperature-stable polymer $(C_2F_4)_n$. A similar polymer, Teflon, has been disclosed (*4*), and its properties have been described in detail (*23*). Columbium fluoride, CbF_5, will polymerize Φ-ethylene rapidly, in the course of a few minutes, as $AlCl_3$ does ordinary ethylene (*14*) to a similar polymer.

Φ-Ethylene is slowly absorbed at room temperature by fuming (15% SO_3) sulfuric acid. Ordinary concentrated sulfuric acid (96%) will not absorb it at a noticeable rate.

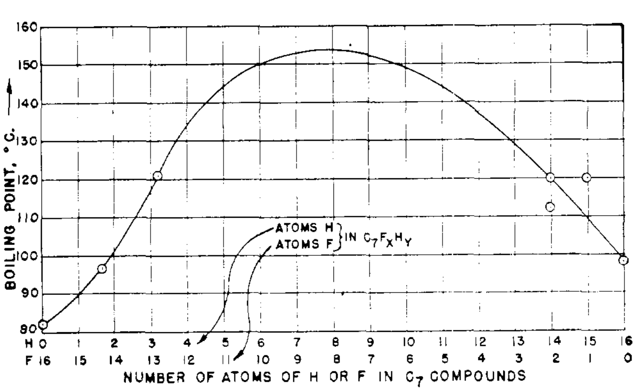
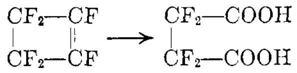


Figure 2. Boiling Points of Hydro-Φ-*n*-Heptanes

Permanganate oxidation splits the olefin at the double bond; for instance, Φ-cyclobutene gives Φ-succinic acid (*12, 13*):



$$\begin{matrix} CF_2{-}CF \\ | \quad\quad \| \\ CF_2{-}CF \end{matrix} \longrightarrow \begin{matrix} CF_2{-}COOH \\ | \quad\quad\quad \\ CF_2{-}COOH \end{matrix}$$

FLUOROAROMATICS

Φ-Aromatics were obtained by McBee, Lindgren, and Ligett (*18*) by reacting bromine trifluoride and hexachlorobenzene, respectively, with pentachlorobenzotrifluoride, $C_6Cl_5{-}CF_3$. A complex mixture of a large variety of possible perhalogenated fluorochlorobromonaphthenes is produced; this mixture can be satisfactorily separated by precision fractionation. By dechlorination or debromination with zinc and alcohol, referred to previously, Φ-benzene (C_6F_6) and Φ-toluene ($C_6F_5{-}CF_3$) were produced and isolated in pure form (Table I).

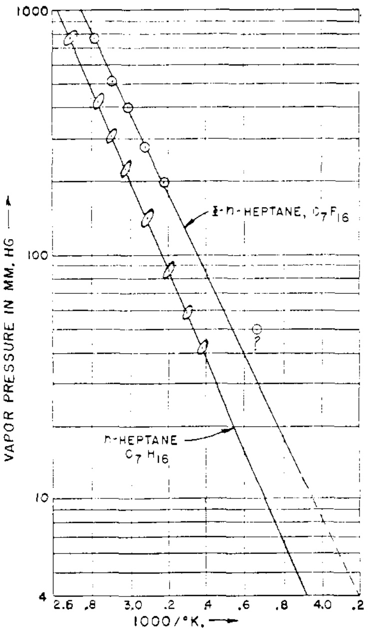
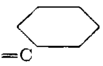


Figure 3. Vapor Pressures of Φ-*n*-Heptane and *n*-Heptane

PHYSICAL PROPERTIES

BOILING POINTS. Table I gives these values. Figure 1 compares the boiling points of Φ-paraffins with those of normal paraffins. Up to the C_4 group the fluorocarbons are less volatile than the paraffins, but become markedly more volatile above the butane range.

As Simons pointed out, the volatility of fluorocarbons is remarkable, particularly if one considers their high molecular weight as compared to hydrocarbons of the same number of carbon atoms. Evidently the molecular attraction forces are very low, and in this respect the fluorocarbons approach the noble gases. The following brief comparison illustrates this point:

Formula		Fluorocarbon (X = F)		Hydrocarbon (X = H)	
		B.P. at 760 mm., ° C.	Mol. wt.	B.P. at 760 mm., ° C.	Mol. wt.
n-C_7X_{16}		82	388	98	100
C_6X_{12}		52	300	80	84
C_2X_4, C=C		−78	100	−104	28

The increment per CF_2 group in a homologous series, both of Φ-paraffins and Φ-naphthenes, in the gasoline range, is 20° to 25° C. and is not substantially different from the hydrocarbon increment. This is illustrated by the following comparison:

Paraffins		Δ			Δ
Φ-Heptane	82°		n-Heptane	99°	
		22° C.			27° C.
Φ-Octane	104°		n-Octane	126°	

Naphthenes		Δ			Δ
Φ-Cyclohexane	52°		Cyclohexane	81.2°	
		24° C.			19° C.
Φ-Methylcyclohexane	76°		Methylhexane	100.3°	
		24° C.			20° C.
Φ-Dimethylcyclohexane	100°		Dimethylhexane	119–121°	
		23° C.			19° C.
Φ-1,3,5-Trimethylcyclohexane	123°		1,3,5-Trimethylcyclohexane	139–141°	

On the basis of Figure 1, the boiling points of the still unknown Φ-n-pentane (C_5F_{12}) and Φ-n-hexane (C_6F_{14}) are expected to lie between 25–30° and at about 60° C., respectively.

The boiling point of Φ-paraffins and Φ-naphthenes of the same number of carbon atoms are quite close. The loss of 2 atoms of fluorine in the ring formation causes a decrease of only 6° in the case of C_7, and 4° in the case of C_8.

Boiling point data on isomers are available only on several Φ-heptanes (C_7F_{16}) as follows:

Φ-Heptanes	B.P. at 760 Mm., ° C.	B.P. of Corresponding Hydrocarbons, ° C.
Normal	82	98
Mixt. of Φ-methylhexanes and Φ-dimethylpentanes	80–84	90.0–91.8
Mixt. of Φ-2,2- and Φ-2,4-dimethylpentanes	82	79.1–89.7
Φ-2,2,3-Trimethylbutane	82	79

The boiling points of all isomers are, for all practical purposes, identical; the range in the hydrocarbon series is 21°. As Cady emphasizes, this is to be expected in view of the extraordinarily low molecular attractive forces in fluorocarbons.

The knowledge of boiling point of incompletely fluorinated heptanes is important for the purification of Φ-heptanes. Boiling points of hydro-Φ-heptanes lie above the value for C_7F_{16} and also C_7H_{16}. The semihydrofluoroheptanes (i.e., $C_7F_8H_8$) should boil around 150° C. Evidently hydrogen bonding is responsible for this phenomenon. Figure 2 illustrates the change in boiling point with number of substituting hydrogen or fluorine atoms, respectively. This graph is based on the following experimental values:

	B.P. at 760 Mm., ° C.
Fraction $C_7F_{14.3}H_{1.7}$	91–100
Fraction $C_7F_{13.7}H_{2.3}$	100–112
Fraction $C_7H_{12.7}H_{3.3}$	112–130
2,2-Difluoroheptane	111.8
1,1-Difluoroheptane	119.7
1-Fluoroheptane	120.4

VAPOR PRESSURES. Research on the determination of vapor pressures of various fluorocarbons is in progress at Columbia. However, no data are available as yet. R. D. Fowler at Johns Hopkins obtained the following results on Φ-n-heptane:

Temp., ° C.	0	41.3	51.4	61.5	69.6	81.7
Vapor pressure, mm. Hg	50	191.3	272.3	393.5	502.2	760.0

Figure 3 compares these results with those on the corresponding hydrocarbon. The slopes of the two curves seem to be about the same.

MELTING POINTS. Only a few data are available, and as usual they show less regularity than do boiling point data.

Comparison of the melting points of symmetrical compounds, such as Φ-cyclohexane, and of straight-chain derivatives leads to the tentative conclusion that fluorocarbons melt substantially higher than the corresponding hydrocarbons, except possibly Φ-methane. All known values are compared below:

Fluorocarbons	M.P., ° C.	Δ	M.P., ° C.	Hydrocarbons
Φ-Methane	−184	−1	−183	Methane
Φ-Ethane	−100.6	+81	−172.0	Ethane
Φ-Propane	−183	+4	−187.1	Propane
Φ-n-Heptane	−78	+13	−90.6	n-Heptane
Φ-n-Cetane	+115	+98	+18.13	n-Cetane
Φ-Cyclopentane	−12	+81	−93.3	Cyclopentane
Φ-Cyclohexane	+50	+43	+6.5	Cyclohexane
Φ-Dicyclohexyl	+75	+55	+20	Dicyclohexyl

The main reason for this effect is probably the much higher atomic mass of fluorine as compared to hydrogen.

DENSITY AND MOLAR VOLUMES. Table I and Figure 4 correlated our density data. Both in Φ-paraffin and naphthene series the densities increase regularly with the number of carbon atoms (Figure 4). The increase per carbon atom is, however, much larger than in hydrocarbon series. For instance, the increase from C_6F_{12} (d_4^{20} = 1.711) to C_9F_{18} (d_4^{20} = 1.891) is large in comparison to the change from C_6H_{12}(d_4^{20} = 0.780) to C_9H_{18} (d_4^{20} = 0.773).

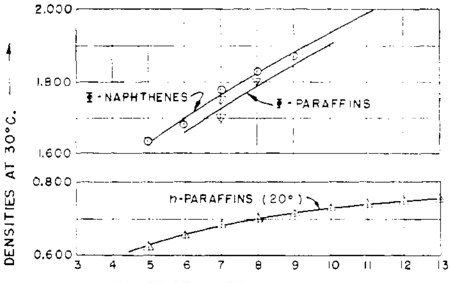


Figure 4. Densities of Fluorocarbons

REFRACTIVE INDEX AND MOLECULAR REFRACTION. The refractive indices of fluorocarbons are lower than those of any other known type of compounds, owing to the very low value of the atomic refraction of fluorine. For this reason they are outside the range of usual refractometers, and we have reverted to the classical method of determining the angle of minimum deflection for their determination. Table I gives our results, a comparison with hydrocarbons is made in Figure 5 and illustrates the difference mentioned. The refractive indices of Φ-naphthenes increase regularly with the number of carbon atoms. As expected, the refractive indices of the corresponding paraffins lie lower.

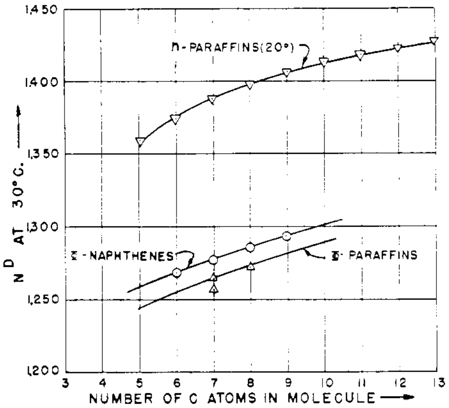


Figure 5. Refractive Indices of Fluorocarbons

From the data available, the atomic refraction of fluorine was calculated by the method described earlier (7). At present the best value for AR_F is 1.23 (±0.01). The molecular refraction, MR, of any saturated fluoro- or hydrofluorocarbon of the formula $C_kF_mH_n$ may now be calculated from the expression:

$$MR = 2.418k + 1.25m + 1.100n$$

where $AR_C = 2.418$ and $AR_H = 1.100$ are the well known Eisenlohr values for carbon and hydrogen.

In contrast to other elements, the atomic refraction of fluorine is not a constant. It changes as follows with the number of fluorine atoms per molecule, in the gasoline range:

No. of F Atoms per Mol.	AR_F	Source of Value
1	0.95	Grosse, Wackher, & Linn (*11*)
2	0.99	Grosse & Linn (*10*)
3	1.02	A. L. Henne (personal communication to authors)
4	1.08	
5	1.14	
Φ-compounds	1 23	This report

TEMPERATURE COEFFICIENTS OF DENSITY AND OF REFRACTIVE INDEX. Fluorocarbons change density rapidly with temperature, more so than any other well known type of compound. The ratio dD/dt for Φ-*n*-heptane (C_7F_{16}) and Φ-1,3,5-trimethylcyclohexane (C_9F_{18}) is −0.0027 and −0.0023 gram/(cc.)(° C.) in the range 0° to 65° and 0° to 75° C., respectively (Figure 6). These coefficients are based on the following experimentally determined density values:

Φ-*n*-Heptane		Φ-1,3,5-Trimethylcyclohexane	
° C.	G./cc.	° C.	G./cc.
0.0	1.7740	0.0	1.9484
27.0	1.7019	28.0	1.8848
63.2	1.6031	76.0	1.7710

For comparison the coefficient for *n*-heptane in the same temperature range is −0.00084 gram/(cc.)(° C.) or approximately three times as small.

The temperature coefficient for refractive index has not yet been determined experimentally. However, since the molecular or specific refraction should be temperature independent, at least in the first approximation, $\Delta n_D/\Delta t$ can be calculated by means of the equation:

$$\frac{n^2_{t_1} - 1}{n^2_{t_1} + 2} \times \frac{1}{d_{t_1}} = \frac{n^2_{t_2} - 1}{n^2_{t_2} + 2} \times \frac{1}{d_{t_2}}$$

where n_{t_1}, d_{t_1}, and n_{t_2}, d_{t_2} are the refractive index and density, respectively, at t_1 and t_2° C.

For Φ-*n*-heptane and Φ-perhydromesitylene, we obtain in the temperature range 25–50° C.:

$$\Delta n/\Delta t = -0.00045 \text{ and } -0.00040$$

These values have been adopted throughout this paper.

VISCOSITY. The absolute viscosities of Φ-*n*-heptane and Φ-1,3,5-trimethylcyclohexane have been determined. They are substantially higher than those of the corresponding hydrocarbons. Their temperature coefficients are also much greater. Figure 7 illustrates these relations for n-C_7F_{16} and n-C_7H_{16}.

The viscosity of n-C_7F_{16} and C_9F_{18} was determined with an Ostwald viscometer, which was calibrated using water at two temperatures and the expression:

$$\eta = c_1 dT - c_2 (d/T)$$

where η = viscosity, millipoises
d = density, grams/cc.
T = time, seconds

The measurements on water were made at 23.35° and 39.64° C. The data are: (1) t = 23.35° C., d = 0.99748 (literature), η = 9.30 millipoises (literature) ±0.1%. (2) t = 39.64° C.

TABLE III. VISCOSITY DATA[a]

Compound	Observed Temp., ° C.	Observed Time, sec.	Density, Grams/Cc.	η (Calcd.), Millipoises
Φ-*n*-Heptane	0.42	81.42	1.7740	13.67
	27.5	54.18	1.6990	8.61
	32.1	51.19	1.6875	8.05
	38.2	47.28	1.6700	7.33
	45.0	43.54	1.5620	6.64
Φ-1,3,5-Trimethylcyclohexane	0.28	202.05	1.9445	37.49
	35.7	97.66	1.8630	17.27
	62.2	66.24	1.8040	11.25
	94.6	45.68	1.7300	7.32

[a] Errors in these measurements: for temperature, ±0.1° C.; for η, ±0.2%; for time, about 0.2% (maximum deviation, 0.6%).

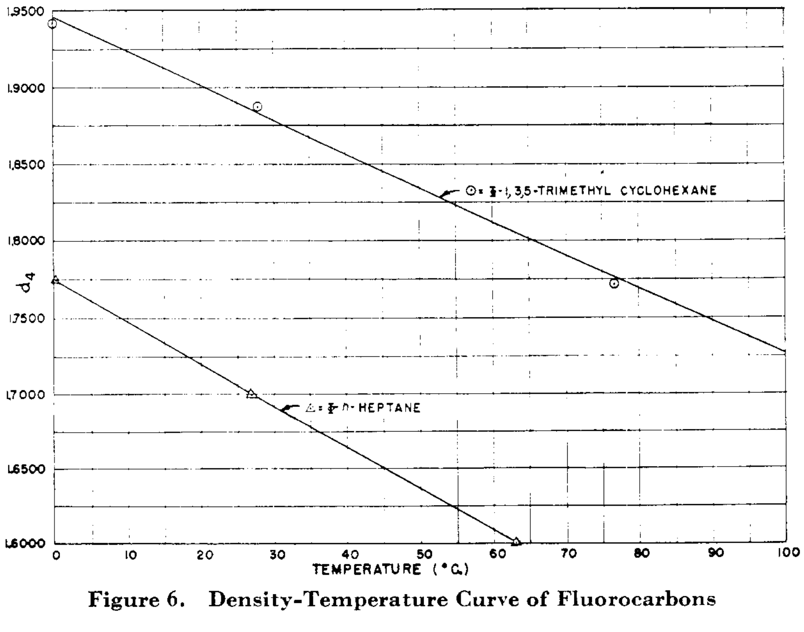


Figure 6. Density-Temperature Curve of Fluorocarbons

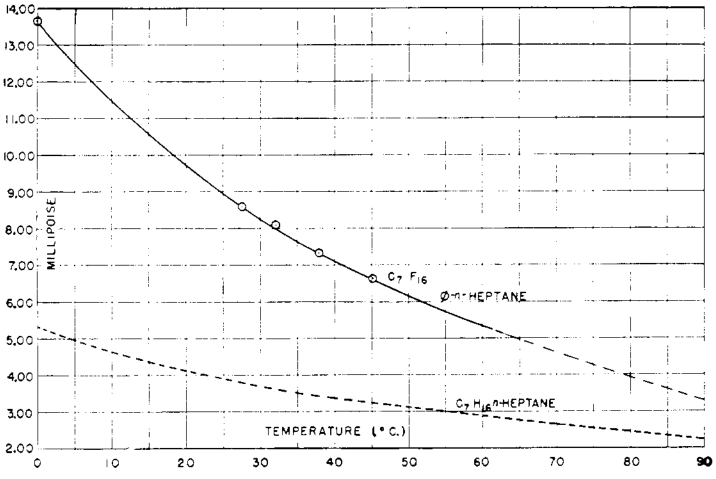


Figure 7. Viscosity-Temperature Curve of Fluorocarbons

d = 0.99238 (literature), η = 6.58 millipoises (literature) ±0.1%, and $T_{\text{obsvd.}}$ = 70.30 seconds. The calculated constants are: c_1 = 0.09556 and c_2 = 6.151. Results are given in Table III.

RAMAN SPECTRA. Raman spectra of two isomeric heptanes, Φ-*n*-C_7F_{16} and Φ-2,2,3-trimethylbutane, were taken by E. Rosenbaum of the Sun Oil Research Laboratories. The Raman shifts were not evaluated, but the difference in the spectra definitely eliminates the possibility of any identity of the two Φ-heptanes. Raman spectra data were desirable since no chemical reactions are available at this time to distinguish between isomers of saturated fluorocarbons.

SOLUBILITY. The liquid saturated fluorocarbons are substantially insoluble in water, alcohols, and hydrocarbons. They show appreciable solubility and, at higher temperatures, miscibility with chlorocarbons. They are completely miscible in ether and in some partly fluorinated hydrocarbons, such as C_6H_5—CF_3. Some preliminary quantitative data are available on Φ-cyclohexane (Table IV), Φ-heptane, and some hydro-Φ-heptane fractions (Table V).

TABLE IV. SOLUBILITY OF Φ-CYCLOHEXANE[a] IN ORGANIC SOLVENTS

(Boiling point, 45.2–53.4° C.; solid to about 90% at room temperature; n_D^{30} of fraction used, 1.2622)

		n_D^{30} of:		Δn_D of:		
C_6F_{12}, Cc.	Solvent, Cc.	Pure solvent	Upper layer satd. with C_6F_{12}	Solution	Pure liquids	Approx. % C_6F_{12} Dissolved at 27° C.
2	Acetone, 2	1.3540	1.3470	0.0070	0.0920	8
1	$CHCl_3$[b], 2	1.4389	1.4060	0.0329	0.1767	19
2	Benzene[c], 2	1.4934	1.4889	0.0045	0.2312	2
2	CCl_4[d], 2	1.4545	1.4532	0.0013	0.1923	0.7[f]
1	Trichloroethylene[e], 2	1.4715	1.4709	0.0006	0.2093	0.2
1	Ether $(C_2H_5)_2O$	Completely miscible at 27° C.				
1	C_6H_5—CF_3	Completely miscible at 27° and 0° C.				

[a] Insoluble in water and methanol.
[b] Completely miscible on heating to about 50° C.
[c] Solubility increases on warming to 50° C., although two layers remain; no cooling, turbidity in both layers.
[d] Separated into two layers at 0° C.; completely miscible at 27° C.; $n_D^{28.5}$, 1.3657.
[e] Completely miscible on warming to about 50° C.
[f] 0.7% soluble at 0° C.; completely miscible at 27° C.

TABLE V. SOLUBILITY OF Φ-*n*-HEPTANE AND HYDRO-Φ-HEPTANES

		Solubility, G./G. of Solvent	
	Temp., ° C.	In anhydrous HF	In H_2O
Φ-Heptane[a]	0	3.14	0.23
	−78	0.4	...
Trihydro-Φ-heptane (b.p. 121.6–130.0° C.)	0	10	...
Monohydro-Φ-heptane (b.p. 90–122° C.)	25	...	0.3

[a] The solubility of Φ-heptane in anhydrous HF is small but not negligible. It is significant that trihydro-Φ-heptane is much more soluble. In its presence the solubility of Φ-heptane is increased, and this fact should be taken into account in recovering the latter from the reaction products.

CONCLUSION

The substantial amount of knowledge now available on the main classes of fluorocarbons form the skeleton around which the chemistry of their various derivatives will develop in the future. At present little is known about Φ-acids, Φ-alcohols, Φ-amines, or Φ-ketones, etc. There is no doubt, however, that these will prove even more interesting than their parent substances, and various new reactions will be discovered in this fertile field.

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