[Contribution from the Department of Chemistry, Cornell University, Ithaca, N. Y.]
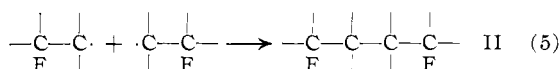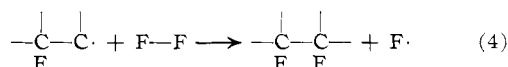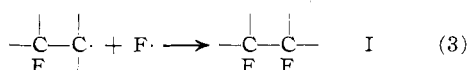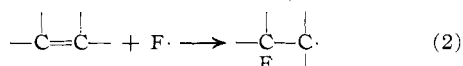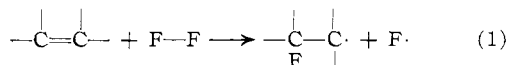
The Mechanism of Fluorination. IV.[1] The Effect of Temperature and of Fluorine Concentration upon the Olefin Dimerization Reaction. A New Fluorination Apparatus[2]

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The interrelated effects of temperature and fluorine concentration on fluorine–olefin reactions have been investigated with some perhaloolefins. Reactions were carried out at low temperatures in a new apparatus which was equipped with a novel high speed nickel gauze stirrer, gas disperser. Reproducible results were obtained with weight recoveries of 95% or better. With $CF_3CF=CFCF_3$, increasing the effective fluorine concentration greatly reduced the formation of dimer addition product relative to simple addition product. Lowering the reaction temperature had a similar effect due to reduction in the rate of the fluorine–olefin free radical initiation reaction. Related experiments with $CClF=CClF$, $CF_2=CCl_2$, and $CF_2=CClF$, and a mixture of $CF_3CF=CFCF_3$ and $CClF=CClF$, are also reported. With $CF_2=CClF$ the fluorine–olefin reaction was diffusion rate-controlled at temperatures as low as $-150°$. The observed effects of reaction conditions on product composition, are shown to be consistent with the general free radical mechanism previously presented for fluorine–olefin reactions[1] and to provide a guide for the choice of synthesis conditions. The liquid phase fluorination procedure described is considered suitable for general use.

Under controlled conditions in the liquid phase the reaction of fluorine with a perhaloolefin has been shown to yield principally simple addition product I and dimer addition product II. Such reactions characteristically take place with great ease at low temperatures in the absence of light or a catalyst and give yields of dimer addition products which may exceed 50%. The following general free radical reaction mechanism has been proposed to account for the available experimental observations.[1] The most striking feature of this mechanism is the initiation step which produces a free fluororadical and a fluorine atom. Its ready occurrence in both the liquid and vapor phases accounts for the unique reaction pattern observed.[3]

$$-C=C- + F-F \longrightarrow -\underset{F}{\underset{|}{C}}-\underset{|}{C}\cdot + F\cdot \qquad (1)$$

$$-C=C- + F\cdot \longrightarrow -\underset{F}{\underset{|}{C}}-\underset{|}{C}\cdot \qquad (2)$$

$$-\underset{F}{\underset{|}{C}}-\underset{|}{C}\cdot + F\cdot \longrightarrow -\underset{F}{\underset{|}{C}}-\underset{F}{\underset{|}{C}}- \quad I \qquad (3)$$

$$-\underset{F}{\underset{|}{C}}-\underset{|}{C}\cdot + F-F \longrightarrow -\underset{F}{\underset{|}{C}}-\underset{F}{\underset{|}{C}}- + F\cdot \qquad (4)$$

$$-\underset{F}{\underset{|}{C}}-\underset{|}{C}\cdot + \cdot\underset{|}{C}-\underset{F}{\underset{|}{C}}- \longrightarrow -\underset{F}{\underset{|}{C}}-\underset{|}{C}-\underset{|}{C}-\underset{F}{\underset{|}{C}}- \quad II \qquad (5)$$

By-products which correspond to disproportionation of the free radicals of reaction 5 and reaction of the new olefin thus produced are also usually formed from chlorofluoroolefins.[1]

The general fluorine–olefin free radical reaction mechanism is pictured in Fig. 1 at the liquid–gas interface. For the present discussion it is especially important to see that the proportion of simple addition product, formed by the free radical chain fluorination steps 2 and 4, relative to the dimer addition product, formed by free radical coupling (5), will be expected to increase rapidly with the concentration of fluorine at the reaction site. With olefins which are highly reactive with fluorine the diffusion controlled reactions shown within the dotted circle of Fig. 1 are postulated to account largely for the isolated products. Fluorine is consumed by reaction with the olefin at a rate com-

parable to or greater than the rate of diffusive mixing and the formation of dimer addition product is favored. The virtual elimination of the chain propagation steps is required for a high yield of dimer addition product. With olefins of low reactivity an appreciable fluorine concentration can be obtained in the liquid phase and the formation of dimer addition product is inhibited.

In general, the formation of polymers higher than dimers due to free radical–olefin reactions, (6) in Fig. 1, has not been observed during the fluorination of perhaloolefins. Combination or fluorination of free radicals which diffuse away from their initial sites is usually much more probable than their addition to olefin. However, very low yields of solid polymer have been isolated from the fluorination of chlorotrifluoroethylene[6] and we have recently obtained a series of polymeric products from the fluorination of perfluoro-2-butyne.[2]

In the present paper we present work on the fluorination of some liquid perhaloolefins with a new "microbubble" reaction apparatus designed to give high rates of mixing with temperature control. The interrelated effects of temperature and fluorine concentration on the composition of reaction products are examined as a test of reaction mechanism and in order to provide a guide for the choice of synthesis condition. This work is part of a continuing effort to develop the organic chemistry of elemental fluorine and to devise convenient techniques for its use.[7]

Apparatus.—The bringing of gaseous fluorine into reaction with liquid organic compounds under controlled conditions which can be evaluated in terms of reaction mechanism presents some unusual problems. In particular, fluorine–olefin reactions are highly exothermic, take place spontaneously on mixing, and in most cases are sufficiently rapid to be diffusion rate controlled. In order to avoid excessive local temperature rise with appreciable rates of conversion, very rapid mixing of the gaseous and liquid phases is required. It was considered that an ideal reactor for the present study would disperse the fluorine-containing gas phase into very small or micro bubbles so as to create a large number of isolated but equivalent reaction systems, each with a large surface to volume ratio and small heat of reaction, at a rate which was fast in terms of the rate of reaction.

The fluorination apparatus shown in Fig. 2 was designed in an attempt to meet the above specification and for convenient use at low temperatures. It was

(1) Preceding paper: W. T. Miller, Jr., and S. D. Koch, Jr., J. Am. Chem. Soc., 79, 3084 (1957).

(2) Presented at the Second International Symposium on Fluorine Chemistry, Estes Park, Colo., July, 1962.

(3) Compounds of fluorine, such as those with halogen or oxygen, in which the fluorine is weakly bonded can also form free radicals by reaction with olefinic bonds. For example, chlorine trifluoride has been shown to promote the free radical chlorination of $CCl_2=CCl_2$ at 0–10°,[4] similarly to elemental fluorine.[5]

(4) W. G. Nilson, M.S. Thesis, Cornell University, 1951.

(5) W. T. Miller, Jr., S. D. Koch, Jr., and F. W. McLafferty, J. Am. Chem. Soc., 78, 4992 (1956).

(6) R. L. Ehrenfeld, Ph.D. Thesis, Cornell University, 1948.

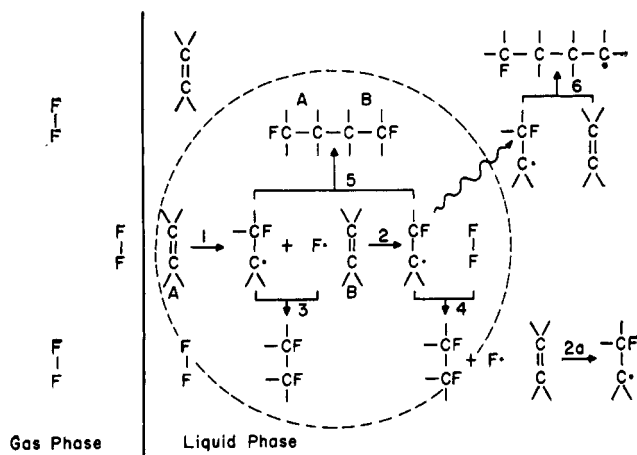(7) We view fluorine as a versatile gaseous free radical initiator as well as fluorination reagent.[5]

Figure 1.

Figure 2.

simple to construct and manipulate, permitted visual observation, and was easily fitted into an ordinary dewar container for cooling. The important innovation of the new apparatus is the use of a high speed, 3500 r.p.m., nickel wire gauze stirrer which rapidly sweeps the reactant gas stream away from the inlet tube and disperses it.[8] Under the conditions described, well controlled reactions took place leading to specific products. Total weight recoveries of 95% or better were obtained.[9] We regard the present apparatus and reaction procedures as suitable for general use.

The reaction picture shown in Fig. 1 for liquid phase reactions applies ideally to systems of negligible vapor pressure. At reaction temperatures where the olefin has an appreciable vapor pressure or under conditions of local temperature rise reaction with vaporizing olefin becomes highly significant.[10] The vapor phase reaction gives more simple addition product relative to dimer addition product,[1] and more by-products are formed because of temperature rise in the vapor phase. With concentrated fluorine and particularly with olefins of relatively high vapor pressure, an uncontrolled reaction tends to take place at the initial point of mixing even though the average liquid temperature may be well controlled. In order to minimize or avoid this effect, lowering the reaction temperature, dilution of the fluorine, or the use of inert solvents for the olefin all can be utilized in addition to rapid mechanical mixing. However, very high dilutions limit the possible variations in reaction conditions and may be impractical for synthetic work.

Perfluoro-2-butene.—As shown above, for the product composition of fluorine–olefin reactions to be sensitive to the rate of fluorine addition the general free radical reaction mechanism requires the rate of reaction 1 to be comparable to the rate of mixing. A similar olefin reactivity is necessary in order for the product composition to be sensitive to temperature, with a constant rate of fluorine addition, due to change in the rate of reaction 1.

Perfluoro-2-butene was chosen for study on the basis of preliminary experiments with fluorine at $-75°$. These showed that its reactivity fell between that of very reactive olefins such as $CClF=CClF$, $CF_2=CCl_2$, and $CF_2=CClF$, which give high yields of fluorine

dimer addition products, and relatively unreactive ones such as $CF_3CCl=CClCF_3$ and $CF_2CF_2CF_2CCl=CCl$, which have not been shown to form dimers. Perfluorocyclobutene had also been shown to exhibit an intermediate range of reactivity.[1]

With perfluoro-2-butene at $-75°$ more than 99% of the fluorination product was found to consist of the simple addition and dimer addition products, CF_3CF_2-CF_2CF_3 and $CF_3CF_2CF(CF_3)CF(CF_3)CF_2CF_3$.[11] On passing 11:1 N_2/F_2 slowly into the pure olefin, the molar ratio of C_4- to C_8-product obtained was 3.7, A-I, Table I. However, when pure fluorine was added rapidly to a dilute solution of olefin in trichlorofluoromethane solution, conditions designed to increase the concentration of fluorine in solution, the molar ratio of C_4- and C_8-product was 28, A-VI. Results for reactions carried out under a range of conditions are summarized in Table I. In all cases the rate of fluorine addition was proportional to the ratio of C_4- to C_8-product formed. Almost all of the fluorine was ab-

TABLE I

FLUORINATION OF PERFLUORO-2-BUTENE

Reacn. no.	Rate of F_2 addn., g./hr.	Molar ratio, CCl_3F/C_4F_8	Molar ratio, C_4F_{10}/C_8F_{18}
A-I[a]	0.83	c	3.7
II[a]	1.3	c	4.2
III[b]	3.4	1	12
V[b]	5.0	13	21
VI[b]	7.0	13	28
B-VIII[a]	0.8	c	40

Approximate C_4F_8 conversion: [a] 20%. [b] 100%; A, $-75°$. B, $-120°$. [c] Pure C_4F_8.

(8) The speed and effectiveness of gas–liquid mixing was confirmed by stroboscopic examination. About 10 ml. of gas was maintained as a dispersion around the nickel gauze stirrer with the 100-ml. size reactor of Fig. 2.

(9) For references to other fluorination apparatus see: J. M. Tedder, "Advances in Fluorine Chemistry," Vol. 2, ed. by M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworths, London, 1961, p. 112.

(10) It was early recognized that fluorine tends to react with liquid organic compounds "in the gas phase and at the liquid surface"[11]: W. T. Miller, J. Am. Chem. Soc., **62**, 341 (1940).
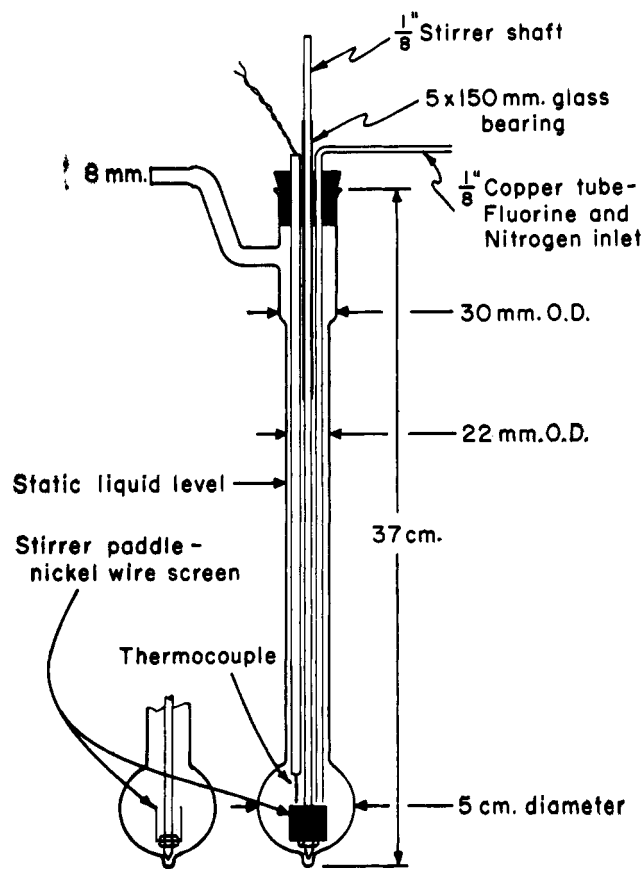
(11) The alkene and alkane fluorine disproportionation products, $CF_3CF=CFCF_3$ and $CF_3CF_2CF_2CF_3$, would be undetectable. However, no evidence has been found for the disproportionation of free perfluoro radicals at low temperatures.

sorbed even though local concentration changes were brought about.

At $-120°$ with pure $CF_3CF{=}CFCF_3$ and 8:1 N_2/F_2 and a low olefin conversion, the molar ratio of C_4- to C_8-product was 40 (B-VIII). This result is consistent with the expected effect of an increased average fluorine concentration due to a reduced rate for reaction 1. It also indicated that the effect of fluorine concentration on product composition was much greater than that of olefin concentration. The free fluoro radicals produced react rapidly with fluorine but do not react with the olefin at an appreciable rate. On the other hand, the fluorine atom–olefin reaction (2), which yields a free fluoro radical, is extremely fast under all conditions and hence insensitive to olefin concentration.

It is considered that the above results are fully consistent with the general mechanism pictured in Fig. 1 in which reaction is initiated by the molecular free radical reaction 1. Similar experimental results are predictable for other olefins although the temperature range within which large changes in product composition can be observed will be expected to vary with olefin reactivity.

1,2-Dichlorodifluoroethylene and Perfluoro-2-butene.—The fluorination of a mixture of two olefins has been shown to yield the mixed dimers which are required if the fluorine atoms produced by reaction 1 add indiscriminately to both olefins (2) to yield pairs of free radicals which then combine (5).[1] Ideally an equimolar mixture of two symmetrical olefins, A and B, should yield a molar amount of mixed dimer AB, equal to the sum of the yields of the two self-dimers AA and BB, and the molar ratio of AA to BB should equal the relative reactivities of the two olefins with fluorine.

In order to test the above conclusion with the more quantitative procedures developed in the present work, a reaction was carried out with 1,2-dichlorodifluoroethylene, A, and perfluoro-2-butene, B. Both olefins yield fluorine dimer addition products but $CClF{=}CClF$ is the more reactive. At $-75°$ an equimolar mixture of the two olefins diluted with CCl_3F yielded $CClF_2CClFCCClFCClF_2$, AA, $CF_3CF_2CF(CF_3)CF(CF_3)CF_2CF_3$, BB, and $CClF_2CClFCF(CF_3)CF_2CF_3$, AB, in the molar proportions of 2.5 to 1.0 to 3.9. These results are consistent with expectations taking into account the greater reactivity of $CClF{=}CClF$ in reaction 1 and its consequent faster removal from the reaction system. The ratio of the dimer of $CClF{=}CClF$ to the dimer of $CF_3CF{=}CFCF_3$ was presumably somewhat less than the reactivity ratio of the two olefins.

Chlorofluoroethylenes.—1,2-Dichlorodifluoroethylene, 1,1-dichlorodifluoroethylene, and chlorotrifluoroethylene were all found to be appreciably more reactive with fluorine than $CF_3CF{=}CFCF_3$ with the order of reactivity indicated as $CClF{=}CClF < CF_2{=}CCl_2 < CF_2{=}CClF$. At $-75°$ with 8:1 N_2/F_2, local reaction temperatures tended to rise sharply as shown by the formation of chlorine disproportionation by-products.[12] At lower temperatures by-product formation was largely eliminated and very high yields of dimer-addi-

(12) By-product formation has been observed previously with $CClF{=}CClF$ and $CF_2{=}CClF$ in metal U-type reactors.[13,14] The complex product mixture obtained at 0° from $CClF{=}CClF$, b.p. 22°, suggested an uncontrolled reaction in the vapor phase. Only 6.5% dimer was isolated. On the other hand, at $-55°$ smaller amounts of by-products were formed and a 30% yield of dimer was obtained.[13] With $CF_2{=}CClF$, b.p. $-27°$, the product mixture obtained with Dry Ice cooling, from which only 18% dimer was isolated, also implies a predominantly vapor phase reaction.[14] Vapor phase temperatures up to 35° have been observed for this reaction.

(13) W. T. Miller, Jr., R. L. Ehrenfeld, J. M. Phelan, M. Prober, and S. K. Reed, *Ind. Eng. Chem.*, **39**, 401 (1947).

(14) W. T. Miller, Jr., Natl. Nuclear Energy Ser., Div. VII, I, "Prepn., Properties and Technol. of Fluorine and Org. Fluorine Compds.," ed. by C. Slesser and S. R. Schram, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, Chapter 32.

tion products were formed. Results are summarized in Table II.

1,2-Dichlorodifluoroethylene yielded 52% dimer addition product at $-110°$, reaction II. At $-133°$ with the addition of an equimolar quantity of CCl_2F_2 to lower the freezing point, the yield of dimer obtained was reduced to 31% and the yield of simple addition product sharply increased (IV). The change in product composition was considered to be due largely to a reduction in the rate of reaction 1 on going from -110 to $-133°$, a result analogous to the change in product composition observed with $CF_3CF{=}CFCF_3$ on going from -75 to $-120°$.

TABLE II

FLUORINATION OF CHLOROFLUOROETHYLENES[a]

Reacn. no.	Temp., °C.	Molar ratio $C_2F_2X_4/C_4F_2X_8$	Yield dimer, %[e]
$CClF{=}CClF$-I[b]	-75	0.8	35
II[b]	-110	0.5	52
IV[b,d]	-133	2	31
$CF_2{=}CCl_2$-I[b]	-110	0.3	77
II[c]	-110	0.3	79
$CF_2{=}CClF$-I[b]	-110	2	14
II[b]	-150	0.7	48
IV[c]	-150	0.4	64

[a] Rate of F_2 addn., 0.8 g./hr.; olefin conversions, <35%. [b] 8:1 N_2/F_2. [c] 45:1 N_2/F_2. [d] An equimolar mixture with CCl_2F_2. [e] Based on F_2 utilized.

With very dilute fluorine, 80:1 N_2/F_2, 0.3 g. of F_2/hr., at $-110°$, without mechanical stirring, a 67% yield of dimer was formed from $CClF{=}CClF$. It is to be expected that the lowest olefin vapor pressure and the most dilute fluorine should give the highest yield of dimer so long as reaction 1 remains diffusion rate controlled.

1,1-Dichlorodifluoroethylene was shown to be more reactive with fluorine than 1,2-dichlorodifluoroethylene at $-110°$. With 8:1 and 45:1 N_2/F_2, 77 and 79% of $CF_3CCl_2–CCl_2CF_3$[15] was formed, the highest yields of a fluorine dimer addition product which have been observed (reactions I and II). The easier formation of the fluoro free radical $CF_3CCl_2·$ as compared with $CClF_2CClF·$ (or $CCl_2FCF_2·$) is consistent with the extra stability of the $CF_3–$ group and with the free radical stabilizing effect of chlorine. This order is also favored by the relative stabilities of $CF_2{=}CCl_2$ and $CClF{=}CClF$.[16] The insensitivity of the yield of dimer addition product to the N_2/F_2 ratio suggests that it will be impossible to obtain significantly higher yields of a fluorine dimer addition product owing to the occurrence of reaction 3.

Chlorotrifluoroethylene was the most volatile and reactive olefin studied with the new reactor. With concentrated fluorine, flaming was observed at $-150°$. With 8.5:1 N_2/F_2 an apparently well controlled reaction took place at $-110°$. However, the formation of approximately 50% of by-products indicated excessive local temperatures.[12] At $-150°$ the formation of by-products was almost eliminated and a 48% yield of dimer addition product obtained (II). Highly dilute fluorine, 45:1 N_2/F_2, was completely absorbed at $-150°$ with the formation of a 64% yield of $CF_3CClFCClF-CF_3$[15] (IV).

(15) The dimer addition products $CF_3CCl_2CCl_2CF_3$ and $CF_3CClFCCl-FCF_3$ contained small amounts of isomeric impurities, presumably due to a lack of complete specificity for reaction 2.

(16) The enhanced stability of $-CF_2–$ and $CF_3–$ groups and the destabilization of CF_2–olefins are of great importance to carbon–fluorine chemistry. For collected thermodynamic data and discussion see: C. R. Patrick, "Advances in Fluorine Chemistry," Vol. 2, ed. by M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworths, London, 1961, p. 1; W. M. D. Bryant, *J. Polymer Sci.*, **56**, 277 (1962).

The observed greater reactivity of CF_2=CClF with fluorine as compared with CF_2=CCl$_2$ would not be predicted on the basis of the free radical stabilizing effects of the halogens, Cl > F. The determinative factor appears to be the relative olefin stabilities.[16,17] On this basis CF_2=CF$_2$ would be expected to be even more reactive with fluorine than CF_2=CClF and possibly to react with oxygen to yield free radicals at moderate temperatures.[18] The observed lower reactivity of CF_3CF=CFCF$_3$ is consistent with the above considerations.

The reactions of the chlorofluoroethylenes with fluorine strikingly demonstrated the ease with which reaction 1 can take place at extremely low temperatures. The available results point to the feasibility of studying other reactions of liquid organic compounds with fluorine at very low temperatures where their vapor pressures are negligible and the control of reaction conditions is greatly facilitated.[19]

Reaction Conditions for the Fluorine–Olefin Dimerization Reaction.

For the production of a high yield of dimer addition product, reaction 1 must be fast relative to the rate of mixing of fluorine with the olefin and the use of dilute fluorine is favorable. Provided that reaction 1 remains fast, the reaction temperature should be as low as possible. With a very low olefin vapor pressure highly diluted fluorine can be utilized effectively with simple apparatus.

For the production of simple addition product, a reaction temperature at which reaction 1 is slow relative to the rate of mixing and, provided that the temperature is adequately controlled, the use of concentrated fluorine are favorable. Very dilute solutions of olefins can be utilized and vapor phase reaction techniques[13] can be applied.

It should be emphasized that for the controlled fluorination of liquid olefins it is desirable to operate with a low olefin vapor pressure. Fortunately, this factor becomes more favorable for higher molecular weight compounds.

Experimental

Apparatus and General Procedure.—Commercial tank fluorine (Allied Chemical Corp.,) was utilized[20] consisting of 99.2% F$_2$, 0.7% O$_2$, and 0.1% CO$_2$.[21] The total amount of fluorine added to each reaction was determined by pressure difference with the 2-l. brass tank buret previously described.[5] The rate of fluorine addition was controlled with a chlorofluorocarbon oil[22] bubble counter.[4] Metered nitrogen was added to the fluorine stream through a T-connection and the resulting mixture passed into the reaction vessel through a $^1/_8$ in. copper tube. A side vent valve was utilized to adjust the gas flows before starting a reaction.

Fluorinations were carried out in reaction vessels of the design shown in Fig. 2 except for some preliminary experiments. Their total lengths were 37 cm. with useful liquid capacities of 100 (Fig. 2) and 300 ml., respectively. The neck diameter of the 300-ml. apparatus was uniformly 30 mm. o.d. The stirrer shaft was $^1/_8$-in. drill rod with the lower end pointed for a bearing and threaded to hold the U-shaped impeller. The impellers were formed from 16 × 38 mm. and 25 × 58 mm. pieces of 40 mesh nickel wire gauze (Newark Wire Co.). The stirrer shaft, lubricated and sealed with chlorofluorocarbon oil, was turned by a motor with a rated speed of 3500 r.p.m. A stirrer speed of 1550 r.p.m. gave appreciably less effective absorption. The glass stirrer bearing, thermocouple tube, and copper inlet tube were mounted in a precisely drilled and fitted rubber stopper. The exposed copper

constantan thermocouple was sealed into the glass support with epoxy cement. The gas inlet tube was positioned with its tip as near to the rotating gauze stirrer as possible, <1 mm., and was supported against lateral movement by a spring wire clamp. The clamp was fitted around the inlet tube slightly below the liquid level and pressed against the apparatus wall. The gas inlet and thermocouple tubes functioned as baffles to limit vortex formation.

During reactions the liquid temperature was recorded continuously. For reactions at ca. −75° the fluorination apparatus was placed directly in a Dry Ice–trichloroethylene bath contained in a 0.5-gal. tall-form strip-silvered dewar. For reactions at lower temperatures the bulb of the fluorination apparatus was about one-half covered with 2 mm. lead and copper shot in the same container and the opening at the top of the dewar filled with loosely packed glass wool. Liquid nitrogen was then added in small increments as required to reach and maintain the desired temperature using an auxiliary thermocouple placed directly in the metal shot to facilitate control. Temperatures down to −150° were easily reached and maintained to within ±2°.

Preliminary experiments at temperatures below −75° were carried out without mechanical stirring using 2 × 37 cm. test tubes.

The reactant olefin or olefin–solvent mixtures were transferred to the fluorination apparatus as liquids with nitrogen pressure using a closed system. The reactant system was flushed with nitrogen with stirring before and after adding fluorine. Reactions took place smoothly under all of the conditions utilized for study but with measured temperature increases of from 0.5 to 6.0°. Even when "flaming" was produced by feeding concentrated fluorine into CF_2=CClF, the over-all temperature did not rise greatly. The absorption of fluorine in most cases was >99%. Excess fluorine was determined iodometrically. In the experiments where all of the perfluoro-2-butene was consumed, the end point of the reaction was marked by the sudden appearance of unabsorbed fluorine and a drop in temperature. The 100-ml. reactor was utilized unless otherwise stated.

After completion of reactions the colorless reaction products were transferred for distillation within a closed system with weight recoveries ordinarily >95%.

All products were initially separated into material boiling above and below 25° with a 1.2 × 30 cm. low temperature distillation column packed with $^1/_8$-in. nickel Podbielniak Heli-Pak. The same column was used for further fractionation of the low boiling material. The higher boiling material was normally fractionated with a 1.2 × 12 cm. Vigreux column for g.l.c. analyses and with a 0.6 mm. × 18 in. spinning-band column (Nester and Faust) for the isolation of pure materials. Boiling points were uncorrected but were determined within the range of 738 to 748 mm. pressure.

The compositions of distilled fractions were determined by isolation and characterization of pure materials and by gas–liquid phase chromatographic analysis, g.l.c. Mixtures of closely boiling saturated and unsaturated compounds were also separated in the form of their dihalides.

Gas–liquid chromatographic analyses were carried out with an F and M Scientific Glassware Co. chromatograph using helium as the carrier gas and a 0.25 in. × 15 ft. coiled copper tube column packed with 30% dioctyl phthalate on 30–60 mesh Chromosorb W (Johns Manville). Relative areas were determined with a Disc Chart integrator. Factors for the conversion of relative areas to molar concentrations were determined with known mixtures of authentic compounds.[23] The largest corrections were about 5%.

Except for $CF_3CF_2CF(CF_3)CF(CF_3)CF_2CF_3$ and CF_3CF_2CF-$(CF_3)CClFCCl_2$, the properties of all the reaction products had been previously reported and pure samples were available for comparison of spectra and other properties and for the preparation of known mixtures for the standardization of the g.l.c. procedures.

Percentage yields of products are expressed as the percentage of the total fluorine utilized which they contain. Olefin was accounted for as reaction products and as recovered olefin. Olefin conversion is the percentage of the olefin charged which was not recovered unchanged and includes losses as well as the olefin converted into isolated products.

Perfluoro-2-butene.—The butene, b.p. 0.0°, was washed with concentrated H$_2$SO$_4$ and redistilled from P$_2$O$_5$. Solvent chlorotrifluoromethane (Matheson), b.p. 23.0°, was treated with excess 5% aqueous KMnO$_4$ at 25° for 24 hr. with mechanical shaking or with fluorine at −78° for 2 hr. in the micro-bubble apparatus and redistilled from P$_2$O$_5$.

The fluorination products obtained from CF_3CF=CFCF$_3$ under various conditions are summarized in Table III.

$CF_3CF_2CF(CF_3)CF(CF_3)CF_2CF_3$.—A redistilled sample of the dimer addition product, C_8F_{18}, b.p. 103.0–104.5, n^{20}D 1.282, was saturated to KMnO$_4$ in acetone. Its infrared spectrum had

(17) J. R. Lacher, J. J. McKinley, C. Walden, K. Lea, and J. D. Park, J. Am. Chem. Soc., **71**, 1334 (1949).

(18) Reference 5, footnote 29.

(19) The formation of free radicals by reaction of molecular fluorine with solid butadiene at −196° has been shown by e.p.r. measurements: G. A. Kapralova and A. E. Shilov, Kinetika i Kataliz, **2**, 362 (1961).

(20) The apparatus for handling fluorine was patterned after that described earlier.[5,14] Hoke, M.-343, 0.25-in. Teflon-packed Monel valves were utilized with 0.25-in. copper tubing and flare fittings.

(21) Determined by absorption of the fluorine with mercury and mass spectrometric analysis of the residual gas. We are grateful to Professor R. F. Porter for the mass spectrometric analyses.

(22) Polychlorotrifluoroethylene oil, MFL.[14]

(23) A. I. M. Keuleman, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1959, p. 32.

TABLE III

$CF_3CF = CFCF_3{}^a$

Reacn. no.	C_4F_8, mole	F_2, mole	N_2/F_2 ratio	N_2, ml./min.	Time, hr.	Temp., °C.	C_4F_{10}, mole	C_8F_{18}, mole	Olefin[e] acctd. for, %
I[b]	0.790	0.164	11	100	7.5	−77	0.090	0.033	79
II[b]	.780	.200	6	75	6.0	−77	.139	.032	84
III[c,f]	.453[g]	.410	2	65	4.5	−75	.373	.030	95
IV[c,l]	.415[h]	.370	2	[m]	8.0	−77	.326	.025	91
V[c,n]	.227[i]	.219	o	[p]	1.67	−72	.190	.009	92
VI[c,n]	.235[j]	.232	o	[p]	1.25	−72	.210	.007	96
VII[b]	.743	.153	9	75	7.75	−120	.144	.003	89
VIII[d]	.776	.125	8	75	6.0	−120	.106	.003	89
IX[p,o]	.520[k]	.05[r]	2	40	12.0		.380	.036	86

[a] 100-ml. reactor, 3500 r.p.m. motor, complete F_2 absorption except as noted. [b–d] Approximate C_4F_8 conversion: [b] 20%, [c] 100% [d] 15%. [e] Unreacted C_4F_8 determined as $CF_3BrFCBrFCF_3$. [f] An immiscible C_8F_{18} layer was formed. [g–k] Plus CCl_3F, moles: [g] 0.452, [h] 0.480, [i] 3.08, [j] 3.15, [k] 1.18. [l] Motor speed 1550 r.p.m. [m] 80 ml./min. N_2 for 1 hr. gave 82% F_2 absorption, 40 ml./min. N_2 for 7 hr. gave 95% F_2 absorption. [n] 300-ml. reaction vessel. [o] Pure F_2. [p] 40 ml./min. N_2 introduced at outlet of reaction vessel to sweep unreacted F_2 into aqueous KI. [q] U-type reactor,[12] Dry-Ice cooling. [r] 87% F_2 absorption.

TABLE IV

Reacn. no.	C_2X_4, moles	F_2, mole	Time, hr.	Temp., °C.	$C_2F_2X_4$, mole	$C_4F_2X_8$, mole	Yield, $C_2F_2X_4$, %	Yield, $C_4F_2X_8$, %	By-prod. acctd. for, %
				$CClF = CClF{}^a$					
I	1.05	0.124	5.75	−77	0.036	0.043	29	35	23[b]
II	1.07	.116	5.25	−110	.031	.061	27	52	4[c]
III	1.07	.138	6.25	−110	.043	.071	31	51	5[d]
IV	0.577[e]	.132	6.0	−133	.082	.041	62	31	2[f]
V[g]	0.676	.050[h]	6.5	−107	[i]	.034	[i]	67	[i]
				$CF_2 = CCl_2{}^a$					
I	1.03	0.140	6.5	−110	0.035	0.107	23	77	<1
II	1.06	.135	6.0	−110	.031	.107	21	79	<1
IIII[g]	1.13	.100[h]	7.3	−110	[i]	.079	[i]	79	[i]
				$CF_2 = CClF{}^a$					
I	1.25	0.143	6.5	−110	0.042	0.020	29	14	17[j]
II	1.26	.166	5.25	−150	.038	.056	33	48	1
III	1.23	.133	6.25	−150	[i]	.058	[i]	44	[i]
IV	1.21	.144[k]	6.5	−150	.038	.092	26	64	<1
V[g]	0.860	.100[l]	6.25	−155	[i]	.063	[i]	63	<[i]

[a] 100-ml. reaction vessel, 3500 r.p.m. motor; complete F_2 absorption; 20 to 35% olefin conversion; 90% olefin acctd. for; 8:1 N_2/F_2, 75 ml./min. N_2 except as noted. [b] CF_3CClF_2, 0.010 mole; $CClF_2CCl_2F$, 0.026 mole; $CF_2=CClF$, 0.004 mole. [c] CF_3CClF_2, 0.001 mole; $CClF_2CCl_2F$, 0.004 mole. [d] CF_3CClF_2, 0.003 mole; $CClF_2CCl_2F$, 0.003 mole. [e] Plus 0.585 mole of CCl_2F_2. [f] $CClF_2CCl_2F$, 0.003 mole. [g] Test tube reactor. [h] 420 ml./min. N_2, 80:1 N_2/F_2. [i] Not determined. [j] $C_2Cl_2F_4$, 0.010 mole; $C_4Cl_3F_7$, 0.004 mole; CF_3CF_3, 0.009 mole. [k] 400 ml./min. N_2, 45:1 N_2/F_2. [l] 420 ml./min. N_2, 70:1 N_2/F_2.

strong peaks at 7.52, 8.0 (broad), 9.03, 9.20, 10.35, 10.90, 11.38, 11.72, 13.43, 13.67. and 13.88 μ. Its F^{19} n.m.r. spectrum showed four peaks at +71.8, 82.9, 115, and 181 p.p.m. from CCl_3F with relative peak areas of 3:3:2:1, a result which supports the expected structure perfluoro-3,4-dimethylhexane.[24]

Anal.[26] Calcd. for C_8F_{18}: C, 21.9; F, 78.1. Found: C, 21.9; F, 78.2.

Perfluoro-2-butene and 1,2-Dichlorodifluoroethylene.—A mixture of 0.357 mole of C_4F_8 with 0.345 mole of $CClF=CClF$ and 0.350 mole of CCl_3F was treated with 0.200 mole of F_2, 10.5:1 N_2/F_2 (100 ml./min. N_2), during 8.75 hr. at −77° to yield 167.5 g. of colorless product.

Analysis of the reaction product yielded: C_4F_{10}, 0.002 mole; $CClF_2CClF_2$, 0.071 mole; $CF_3CF_2CF(CF_3)CF(CF_3)CF_2CF_3$, 0.016 mole; $CClF_2CClFCClFCClF_2$, 0.040 mole; $CF_3CF_2CF(CF_3)CClFCClF_2$, 0.062 mole; CF_3CClF_2, 0.001 mole; $CClF_2CClF_2$, 0.006 mole; $CF_3CF=CFCF_3$, 0.206 mole, isolated as $C_4Cl_2F_8$; $CClF=CClF$, 0.122 mole, isolated as $C_2Cl_2F_4$; CCl_3F, 0.290 mole; $C_4Cl_4F_6/C_8F_{18}/C_6Cl_2F_{12}$, 2.5:1.0:3.9; 94% yield of all fluorinated products; 85% C_4F_8, 95% $C_2Cl_2F_2$, 83% CCl_3F accounted for.

$CF_3CF_2CF(CF_3)CClFCClF_2$.—The three dimer addition products could be only partly separated by distillation. However, 16.6 g. of the mixed dimer addition product, $C_8Cl_2F_{12}$, was obtained from the fraction b.p. 106.0–114.4° with a 0.6 in. × 15 ft. dioctyl phthalate g.l.c. column at 100°. Distillation yielded 13.5 g., b.p. 114.5°, $n^{20}D$ 1.3207, which was saturated to $KMnO_4$. Its infrared spectrum had strong peaks at 7.45, 8.1 (broad), 8.45, 9.05, 9.32, 10.82, 11.42, 12.37, 12.70, 13.00, 13.41, 13.75, 13.94, and 14.15 μ. Its F^{19} n.m.r. spectrum showed six peaks at

62.8, 69.3, 80.6, 116, 125, and 172 p.p.m. from CCl_3F with relative peak areas of 1:3:3:2:2:1 supporting the expected structure 1,2-dichloroperfluoro-3-methylpentane.

Anal. Calcd. for $C_6Cl_2F_{12}$: C, 18.9; Cl, 18.6; F, 62.5; mol. wt., 371. Found: C, 19.0; Cl, 18.4; F, 62.4; mol. wt., 371, 374.

Chlorofluoroethylenes.—Fluorination results for the chlorofluoroethylenes are given in Table IV.

1,2-Dichlorofluoroethylene.—The $CClF=CClF$, b.p. 21.5–22.3°,[27] was prepared by dechlorination[28] of commercial CCl_2FCCl_2F (du Pont). Preferential reaction with alcoholic sodium ethoxide at 20° was utilized to remove $CF_2=CCl_2$.[29] Solvent CCl_2F_2 (Matheson) was washed with 96% H_2SO_4 before use.

1,1-Dichlorodifluoroethylene.—The $CCl_2=CF_2$ (Matheson), b.p. 20.0°, was distilled from P_2O_5.

$CF_3CCl_2CCl_2CF_3$. Analysis of the dimer addition product, b.p. 129–131°, m.p. 50–65°, by g.l.c. showed 90% $CF_3CCl_2CCl_2CF_3$ and 10% of material presumed to be $CF_3CCl_2CF_2CCl_2F$; reported[32] for $CF_3CCl_2CCl_2CF_3$, b.p. 131°, m.p. 83–84°.

Chlorotrifluoroethylene.—Polymerization grade $CF_2=CClF$ (du Pont) was passed through silica gel to remove traces of inhibitor before use. Very vigorous reactions were observed in chlorinating $CF_2=CClF$ in sealed ampoules to separate CF_3CClF_2.

(24) Previously reported[25] for the isomeric perfluoro-n-octane, b.p. 103.3°, $n^{20}D$ 1.2820.

(25) R. N. Haszeldine and F. Smith, J. Chem. Soc., 603 (1951).

(26) Analyses by Galbraith Laboratories, Inc., Knoxville, Tenn.

(27) Prepared by E. Sommerfeld.

(28) E. G. Locke, W. R. Brode, and A. L. Henne, J. Am. Chem. Soc., 56, 1726 (1934).

(29) M. D. Hurwitz, Ph.D. Thesis, Cornell University, 1948.

(30) Chlorine telomers of $CF_2=CClF$ with the general formula $Cl(CF_2-CClF)_nCl$ are readily formed with low chlorine concentrations and high intensity illumination.[6] This reaction has been developed as a preparative procedure for $CClF_2CClFCF_2CCl_2F$, b.p. 134°.[31]

(31) Unpublished work: W. T. Miller, Jr., A. H. Fainberg, P. Resnick, and J. Arnold.

(32) A. L. Henne, J. B. Hinkamp, and W. L. Zimmerschied, J. Am. Chem. Soc., 67, 1907 (1945).

Small amounts of CCl$_2$F$_2$, CCl$_3$F, CCl$_2$FCCl$_2$F, and CClF$_2$CCl-FCF$_2$CCl$_2$F[30] were formed.

CF$_3$CClFCClFCF$_3$.—Analysis of the dimer addition product b.p. 62.0°, n^{20}D 1.3104, 1.3096, by g.l.c. with dioctyl phthalate and hexadecane columns at 25° indicated a pure material and its infrared spectrum was identical with that of authentic CF$_3$CClF-CClFCF$_3$; reported[32] b.p. 62.9°, n^{20}D 1.3100. However, its F[19]

n.m.r. spectrum showed unexpected peaks by comparison with authentic CF$_3$CClFCClFCF$_3$.

Hexachlorocyclopropane[1]

BY STEPHEN W. TOBEY AND ROBERT WEST

The synthesis of hexachlorocyclopropane (1) is described, and its physical and spectral properties are presented. Compound 1 is unreactive toward most nucleophilic reagents and is readily attacked by zinc in alcohols to provide cis-2,3-dichloroacrylate (6), 3,3-dichloroacrylate (7), 2-chloro-3-alkoxyacrylate (8), and dialkylmalonate (9) esters. The reaction probably proceeds via tetrachlorocyclopropene (10) as an intermediate.

Until quite recently the lack of a synthetic route leading to highly halogenated three-membered ring compounds in reasonable yield has been a serious obstacle to a study of their properties. With the discovery in these laboratories[1,2] that completely chlorinated cyclopropanes and cyclopropenes can be obtained rather simply and in good yield from dichlorocarbene (:CCl$_2$) and chlorinated olefins, a detailed study of the chemical reactions of these compounds was undertaken. This paper describes the synthesis and physical properties of hexachlorocyclopropane (1) and discusses its known chemical reactions.

1
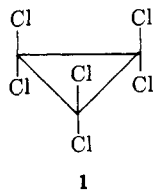
When the work described herein was begun the most highly chlorinated cyclopropane reported was 1,1,2,2-tetrachlorocyclopropane (2), obtained by Stevens during a study of the chlorination of cyclopropane.[3] The only totally halogenated three-membered ring compound reported was hexafluorocyclopropane (3). This compound is formed in small amounts when Teflon is pyrolytically decomposed[4] and when CF$_2$=CF$_2$ is passed over a hot filament.[5] The production of 3 under these conditions can be rationalized in terms of addition of :CF$_2$ to CF$_2$=CF$_2$. That generation of 3 by this mechanism is feasible has been amply demonstrated by a number of workers. Decomposition of CF$_3$Sn(CH$_3$)$_3$,[6a] CF$_3$Fe(CO)$_4$I,[6b] or (CF$_3$)$_3$PF$_2$[6c] at 100–150° in the presence of CF$_2$=CF$_2$ provides 3 in high yield.

The successful synthesis of hexafluorocyclopropane via a carbene mechanism suggested that an attractively straightforward synthesis of 1 might involve addition

of :CCl$_2$[7] to CCl$_2$=CCl$_2$. However, the addition of :CCl$_2$ to olfins is well known to be highly sensitive to the electron density in the π-system of the acceptor,[8] making addition to CCl$_2$=CCl$_2$ inherently unfavorable. Furthermore, unlike :CF$_2$, :CCl$_2$ is most conveniently generated in a liquid phase via CCl$_3$$^-$. These two latter species are known to undergo a variety of rapid degradations when in contact with the reagents from which they are made.[9] Addition of the :CCl$_2$ to a double bond must always compete with these reactions.

With the above difficulties in mind, and in the absence of any information on the chemical stability of 1, synthesis under mild conditions was first attempted. Decarboxylation of CCl$_3$CO$_2$$^-$ Na$^+$ in 1,2-dimethoxyethane to provide :CCl$_2$[10] with CCl$_2$=CCl$_2$ acceptor provided white, crystalline hexachlorocyclopropane, but in below 1% yield. That this procedure does give 1 in 0.3% yield has been independently verified by Moore and co-workers,[11] although Wagner implies this synthesis fails completely.[12]

After preliminary experiments on 1 obtained by the above method demonstrated that it was relatively inert toward strong base, other known successful :CCl$_2$ syntheses requiring the presence of alkoxide and such materials as CCl$_3$COCCl$_3$,[13a] CCl$_3$CO$_2$Et,[13b] and CHCl$_3$[13c,d] were tried on a small scale. Gas chromatographic analyses of the product mixtures showed consistently low yields of 1 (<1%). The formation of some 1 in every reaction, but always in microscopic amounts, indicated that :CCl$_2$ was being formed, but that further degradation took place more readily than addition to CCl$_2$=CCl$_2$.

A study of reaction variables led ultimately to a more satisfactory synthesis of 1, involving a new method for the generation of :CCl$_2$. The procedure consists of stirring a dilute solution of CHCl$_3$ in CCl$_2$=CCl$_2$ over fused 85% KOH at 100–110°. The method is emi-

(1) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, Abstracts of Papers, p. 95Q.

(2) S. W. Tobey and R. West, Tetrahedron Letters, 1179 (1963).

(3) P. G. Stevens, J. Am. Chem. Soc., 68, 620 (1946). On further chlorination of 2 Stevens obtained mainly octachloropropane, but also a small quantity of a crystalline product, m.p. 102–102.5°, which showed some hydrogen content. This compound was probably hexachlorocyclopropane.

(4) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 2.

(5) J. Harmon, U. S. Patent 2,404,374 (1946); cf. Chem. Abstr., 40, 7234² (1946).

(6) (a) H. C. Clark and C. J. Willis, J. Am. Chem. Soc., 82, 1888 (1960); (b) R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, ibid., 83, 3604 (1961); (c) W. Mahler, Inorg. Chem., 2, 230 (1963).

(7) For the purposes of this discussion, those reactions listed in the literature as involving "dichlorocarbene" will be called :CCl$_2$ reactions. This is done with the realization that, depending on the particular mode of production, the dichlorocarbene may or may not ever exist as "free" :CCl$_2$.

(8) (a) P. S. Skell and A. Y. Garner, J. Am. Chem. Soc., 78, 5430 (1956); (b) W. von E. Doering and W. A. Henderson, ibid., 80, 5274 (1958).

(9) (a) J. Hine, ibid., 72, 2438 (1950); (b) W. M. Wagner, "Trichloromethyl Anions in Neutral Aprotic Media," University of Leiden, The Netherlands, October, 1962, Introduction and Chapter 4.

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(13) (a) P. K. Kadaba and J. O. Edwards, J. Org. Chem., 25, 1431 (1960); (b) W. E. Parham and E. E. Schweizer, ibid., 24, 1733 (1959); (c) H. E. Winberg, ibid., 24, 264 (1959); (d) W. von E. Doering and A. K. Hoffman, J. Am. Chem. Soc., 76, 6162 (1954).