

## Organic Polyvalent Iodine. Perfluoroalkyl Iodide Polyfluorides.

## I. Preparation and Properties

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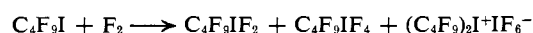
**Abstract:** Perfluoroalkyl iodide difluorides and tetrafluorides ( $R_iIF_2$  and  $R_iIF_4$ ) are new classes of organic polyvalent iodine. They are prepared by fluorination of a perfluoroalkyl iodide with chlorine trifluoride, bromine trifluoride, bromine pentafluoride, or elementary fluorine. The pure difluorides form from excess  $R_iI$  and  $ClF_3$  or occasionally  $F_2$ . The pure tetrafluorides are obtained with  $ClF_3$ ,  $BrF_3$ , or  $BrF_5$  in slight excess. Iodine pentafluoride is ineffective. Safe conditions for synthesis have been devised. The new polyfluorides usually melt near room temperature. They have been characterized by their nmr spectra and elementary analyses. Hydrolysis liberates the two (or four) fluorines on iodine and also half the iodine in water-soluble form. The organic product appears to be an iodonium salt. The fluorination product is occasionally a very high-melting solid, insoluble in common laboratory solvents. The iodonium salt structure  $(R_i)_2I^+IF_n^-$  is assigned from the properties of the solid and X-ray evidence. The  $R_iIF_2$  are moderately stable at room temperature and above. Stability increases with increasing organic chain length. The  $R_iIF_4$  are somewhat less stable. The " $CF_3IF_2$ " prepared by Schmeisser decomposes rapidly at  $0^\circ$ . Thermal decomposition leads to  $R_iI$ ,  $RF_i$ , and some chain degradation.

Fluorine attacks perfluorobutyl iodide rapidly at  $-70^\circ$  with immediate liberation of iodine and perfluorobutane, even when the fluorine is greatly diluted with nitrogen. However, dilution of the iodide with an equal volume of inert solvent prevents the destructive fluorinolysis and permits formation of the unusual products which are the subject of this paper.

Organic compounds containing polyvalent iodine are familiar.<sup>1-3</sup> In most examples, the iodine atom is bonded to an aromatic ring. Examples include the well-known iodoarene dichlorides ( $ArICl_2$ ), iodoarenes ( $ArI=O$ ), iodoxyarenes ( $ArIO_2$ ), diaryliodonium salts ( $Ar_2I^+X^-$ ), iodoso diacylates [ $ArI(OCOR)_2$ ], and several less common types. Very few aliphatic representatives are recorded. Thiele<sup>4a</sup> learned that  $CH_3ICl_2$  decomposed at about  $-30^\circ$  to  $CH_3Cl$ ,  $CH_3I$ , and  $ICl$ . Thiele,<sup>4</sup> Clauss,<sup>5</sup> and Noyes<sup>6</sup> obtained stable chlorovinyl iodide dichlorides and other derivatives; evidently unsaturation stabilizes positive iodine. Lemieux proposed an unstable aliphatic iodo dibromide as an intermediate in cleavage of 2-iodohexopyranosides with bromine.<sup>7</sup> Exner<sup>8a</sup> and Keefer and Andrews<sup>8b</sup> prepared  $\alpha$ -iodosulfone dichlorides  $ArSO_2CH_2ICl_2$ ; their stability is attributed to steric and inductive retardation of  $SN_1$  and  $SN_2$  mechanisms of decomposition.<sup>8b</sup>

We were therefore unprepared for the discovery that the reaction product from diluted perfluorobutyl iodide and fluorine was the new perfluorobutyl iodide difluoride contaminated with varying amounts of per-

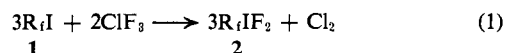
fluorobutyl iodide tetrafluoride and a solid believed to be bis(perfluorobutyl)iodonium hexafluoroiodate.



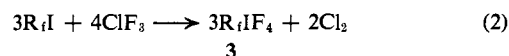
Since the mixture was active in promoting low-temperature telomerization of tetrafluoroethylene with perfluoroalkyl iodides,<sup>9</sup> we began an intensive study of these curious compounds.<sup>10</sup>

## Results and Discussion

**Preparation of Perfluoroalkyl Iodide Polyfluorides.** Not only fluorine but also the chlorine and bromine fluorides<sup>11</sup> are active fluorinators of iodine. Chlorine trifluoride, the most active of these, converts a perfluoroalkyl iodide to the difluoride in virtually quantitative fashion according to eq 1. Larger amounts of



chlorine trifluoride yield the tetrafluoride according to eq 2.



Perfluorobutyl iodide was the favorite substrate for this study because of its convenient boiling ( $69^\circ$ ) and freezing ( $-90^\circ$ ) points; it is easily prepared by the method of Parsons<sup>12,13</sup> and purified by fractional distillation. Perfluoromethyl iodide reacts anomalously (see below), perfluoroethyl iodide (bp  $13^\circ$ ) is inconveniently volatile, perfluoro-*n*-propyl iodide produced from perfluorobutyric acid is expensive, and the higher iodides have increasingly higher melting points. The reactions with halogen fluorides

(9) C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, in press.

(10) The research described in these papers is the subject of U. S. Patent 3,377,390 and corresponding foreign patents.

(11) Recent reviews of interhalogen compounds, including halogen fluorides, include Y. D. Shishkov and A. A. Opalovskii, *Russ. Chem. Rev.*, 760 (1960); H. C. Clark, *Chem. Rev.*, 58, 869 (1958); E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, 3, 133 (1961).

(12) R. E. Parsons, U. S. Patent 3,283,020 (Nov 1, 1966).

(13) R. E. Parsons, U. S. Patent 3,234,294 (Feb 8, 1966).

(1) D. F. Banks, *Chem. Rev.*, 66, 243 (1966).

(2) R. B. Sandin, *ibid.*, 32, 249 (1943); F. M. Beringer and E. M. Gindler, *Iodine Abstr. Rev.*, 3 (3) (1956).

(3) C. Willgerodt, "Die organischen Verbindungen mit mehrwertigem Jod," F. Enke, Stuttgart, 1914.

(4) (a) J. Thiele and W. Peter, *Ber.*, 38, 2842 (1905); *Ann.*, 369, 119 (1909); (b) J. Thiele and H. Haakh, *Ann.*, 369, 131 (1909).

(5) K. Clauss, *Chem. Ber.*, 88, 268 (1955).

(6) L. B. Howell and W. A. Noyes, *J. Am. Chem. Soc.*, 42, 991 (1920).

(7) R. U. Lemieux and B. Fraser-Reid, *Can. J. Chem.*, 42, 539 (1964).

(8) (a) O. Exner, *Collection Czech. Chem. Commun.*, 24, 3567 (1959);

(b) J. L. Cotter, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, 84, 4692 (1962).

may be conducted in neat iodide (depending on its freezing point) or in solution in perfluorohexane or other perfluorocarbon. Chlorofluorocarbons like  $\text{CCl}_3\text{F}$  or  $\text{CClCF}_2\text{CCl}_2\text{F}$  are inert to fluorine but are attacked to some extent by the halogen fluorides.

Perfluorobutyl iodide difluoride is conveniently prepared on a *small* scale (0.05 mol) by adding cold liquid (bp  $12^\circ$ ) chlorine trifluoride all at once to a very small excess of perfluorobutyl iodide at  $-70^\circ$ . The mixture is allowed to warm slowly, and the reaction is complete according to eq 1 when it reaches room temperature. On a larger scale, the reaction is very difficult to control when stoichiometric quantities are employed, and it is advantageous to use a larger excess of the iodide or to operate in perfluorohexane solvent; either of these is readily removed by vacuum pumping. Under the proper conditions, the difluoride rarely contains more than 1–2% of tetrafluoride. The yields are 90–95% based on unrecovered iodide and 110–130%/mol of  $\text{ClF}_3$ . In other words, as much as 87% of the fluorine in  $\text{ClF}_3$  appears in  $\text{C}_4\text{F}_9\text{IF}_2$ . Chlorine monofluoride was never detected in experiments with excess iodide. In one experiment, chlorine was isolated in 62% yield by vacuum-line fractionation of recovered iodide. The loss was probably mechanical because  $\text{C}_4\text{F}_9\text{Cl}$  was not found in the recovered iodide, and no chlorine could be detected in the  $\text{C}_4\text{F}_9\text{IF}_2$ .

Perfluoroethyl, *n*-propyl, and isopropyl iodides may be fluorinated similarly. On a *small* scale, perfluorohexyl iodide reacts controllably with chlorine trifluoride just above its own freezing point; but it is preferable to dissolve it in perfluorohexane or -octane. Perfluorooctyl iodide can be fluorinated at low temperature in perfluorohexane solution; perfluorodecyl iodide and higher homologs crystallize from perfluorohexane at low temperatures, but the finely divided iodide slurries obtained by rapid chilling react quite smoothly.

The perfluoroalkyl iodide tetrafluorides are readily prepared only in solvents. Since the products freeze near room temperature, the stirring required for control is impossible at the low temperatures needed to prevent violent reaction with chlorine trifluoride. On a small scale, the entire quantity of chlorine trifluoride (eq 2) may be added to the solution below about  $-50^\circ$ , and the reaction proceeds smoothly near  $-30^\circ$ . A moderate excess of chlorine trifluoride is not harmful, for it is readily removed by pumping at the close of the reaction. On a larger scale, close attention is required to prevent a surprise runaway reaction. Sometimes a second liquid phase separates; then after an induction period of 20–60 min at  $-20$  to  $-30^\circ$ , an abrupt temperature rise occurs. Prompt application of strong cooling prevents explosions. As the temperature rises past  $0^\circ$ , the product crystallizes from solution; at about  $+15^\circ$  it melts and redissolves. Particularly with excess chlorine trifluoride present, chlorine monofluoride is evolved and caught in a liquid nitrogen trap. When the exothermic reaction does not occur, no chlorine monofluoride is detected; and the inorganic by-product is instead chlorine (and unreacted  $\text{ClF}_3$ ). The nature of this exothermic reaction was studied only incidentally to the desired preparative reaction, so that the conditions which provoke it are not understood. Under some circumstances an unstable complex  $\text{R}_f\text{IF}_3\text{Cl}$  may

form and then disproportionate bimolecularly (?) to  $\text{R}_f\text{IF}_4$ ,  $\text{R}_f\text{IF}_2$ , and  $\text{ClF}$ . Surprisingly, the yield and quality of  $\text{R}_f\text{IF}_4$  are not seriously impaired by the exothermic reaction, though more fluorodeiodination occurs. Because of the high-potential hazard posed by an unexpected runaway reaction, the large-scale preparations are conducted by portionwise addition of chlorine trifluoride.

As an alternative to addition of *liquid* chlorine trifluoride to iodide, a measured quantity of liquid  $\text{ClF}_3$  may be vaporized by a stream of inert gas. The gas mixture is bubbled into the iodide maintained in the range  $-40$  to  $-60^\circ$ . Though this method is not difficult to control with *constant* attention, the instantaneous heat evolution seems to be much *greater* with chlorine trifluoride *vapor* than with relatively massive amounts of the liquid added by the first procedure. Explosions occur in the vapor phase when the gas feed is rapid enough so that unreacted chlorine trifluoride gas bubbles emerge from the liquid. The violence is accompanied by loud reports and flashes of fire; once, the *upper* part of the flask was shattered. This phenomenon is never encountered with addition of liquid chlorine trifluoride to purified iodides. The reason for the different behaviors is not understood. In fluorination with gaseous  $\text{ClF}_3$ , even a deficiency, the tetrafluoride is invariably formed in small amount, increasing at higher fluorination temperatures.

Chlorine monofluoride and chlorine pentafluoride<sup>14</sup> were not studied as fluorinating agents for perfluoroalkyl iodides.

Bromine tri- and pentafluorides are articles of commerce. Apparently all the fluorine atoms in either compound are available for formation of perfluoroalkyl iodide tetrafluorides. The by-product is bromine. Drops of liquid bromine trifluoride (mp  $8^\circ$ ) added to a pure iodide at low temperature freeze and seem not to react. When the mixture warms up, the drops melt and tend to react violently. The violence is less in perfluorohexane solvent. However,  $\text{BrF}_3$  is not very soluble in perfluorohexane and cannot be added in solution. Bromine pentafluoride has a much wider liquid range ( $-61$  to  $+40^\circ$ ); when it is added to excess iodide, neat or a solution in perfluorohexane, it dissolves. Below about  $-50^\circ$ , no bromine is liberated. Above this temperature, a mildly exothermic reaction ensues with liberation of free bromine. With excess iodide, either bromine fluoride yields a roughly equimolar mixture of di- and tetrafluorides. It was never possible to prepare pure difluorides from a bromine fluoride, despite the fact that the bromine fluorides are normally much less reactive than chlorine trifluoride toward other substrates. An unstable dimeric intermediate containing bromine is seemingly formed. When it disproportionates, both di- and tetrafluorides are formed. Tetrafluoride does not react with free iodide to yield 2 mol of difluoride. An excess of bromine fluoride yields the tetrafluorides quantitatively.

Iodine pentafluoride is insoluble in perfluoroalkyl iodides. Neither freshly prepared mixtures nor those which have been allowed to stand show any  $\text{R}_f\text{IF}_n$  signals in the nmr spectrometer. The iodide is slowly attacked by iodine pentafluoride in evacuated, dry

(14) D. Pilipovich, *et al.*, *Inorg. Chem.*, **6**, 1918 (1967), and references cited therein.

Pyrex tubes. The lower  $\text{IF}_3$  layer becomes gummy, and a white solid creeps up the walls of the tube above the liquid level. During this time the pressure within the vessel increases as perfluoroalkanes and other degradation products are created. The white solid probably results from attack on the silica in the glass. It behaves like a lower iodine oxide or oxyfluoride though it could not be purified adequately for consistent analysis. When mixed with water, it dissolves with the formation of free iodine in varying amounts. The organic phase reacts with water to deposit a yellowish solid which may be an iodonium salt; satisfactory analyses could not be obtained.

Iodine heptafluoride was not tested. Iodine mono- and trifluorides are known to be unstable at room temperature.<sup>15</sup> Mixtures of iodine and iodine pentafluoride in composition corresponding either to  $\text{IF}$  or  $\text{IF}_3$  are soluble in perfluorobutyl iodide as red-brown entities. The color is not the brown of iodine in  $\text{IF}_3$ .<sup>16</sup> Surprisingly, the nmr spectra of such solutions show only the known  $\text{IF}_3$  and  $\text{R}_f\text{I}$  resonances. If either  $\text{IF}$  or  $\text{IF}_3$  were present, it does not give rise to a detectable signal. These solutions also do not develop  $\text{R}_f\text{IF}_n$  signals. They decompose rather rapidly to form perfluoroalkanes and lower iodides.

Elementary fluorine destroys neat perfluoroalkyl iodides even at low temperatures and very low mole ratios of fluorine. However, solutions in perfluoro-hexane, octafluorocyclobutane, or fluorotrichloromethane were converted smoothly by fluorine to iodide polyfluorides. We suggest that  $\text{R}_f\text{I}$  exists as loose aggregates  $(\text{R}_f\text{I})_n$  held together by dipole interactions and that these aggregates are broken up by dilution. Sometimes these were the same low-melting solids obtained from the chlorine or bromine fluorides. More often they were high-melting and insoluble yellowish solids (see below).

These results must be contrasted with those of Schmeisser.<sup>17</sup> Perfluoromethyl iodide, when fluorinated in  $\text{CCl}_3\text{F}$  with diluted fluorine at  $-70^\circ$ , was converted to a white solid which decomposed slowly to  $\text{CF}_3\text{I}$ ,  $\text{CF}_4$ ,  $\text{IF}_3$ , and  $\text{I}_2$ . Schmeisser has not reported further details beyond this preliminary communication. In our hands, chlorine trifluoride and perfluoromethyl iodide form a yellowish solid which decomposes fairly rapidly at about  $-10^\circ$ . Visually, except for color, it is similar to the product formed with fluorine. Neither product promotes telomerization to any detectable extent. The thermal instability of this material discouraged further study.

By-products accompany the perfluoroalkyl iodide polyfluorides in small amount, but larger amounts appear at higher temperatures, especially when abrupt exotherms are encountered. The chief by-product is the perfluoroalkane of the same carbon number. It is accompanied by decreasing amounts of lower perfluoroalkanes and perfluoroalkyl iodides. These by-products parallel closely the products obtained when a

perfluoroalkyl iodide polyfluoride is decomposed thermally (see discussion of thermolysis below).

These fluorinating reagents were applied casually to synthesis of aryl iodide difluorides.<sup>18</sup> Addition of a few drops of bromine pentafluoride to a solution of iodobenzene in  $\text{CCl}_3\text{F}$  at  $-50^\circ$  caused an explosion. As was later discovered,  $\text{CCl}_3\text{F}$  is *not* inert to the halogen fluorides, though it is toward fluorine. Fluorine converted iodobenzene in  $\text{CCl}_3\text{F}$  at  $-70^\circ$  to impure iodobenzene difluoride containing some ring fluorine (nonhydrolyzable). No attempt was made to determine optimum conditions nor to purify the product. Preparation of iodobenzene tetrafluoride was not tried.

**Analysis of Perfluoroalkyl Iodide Polyfluorides.** The composition is established by elementary analysis. The atom ratios agree well with the empirical formulas  $\text{R}_f\text{IF}_2$  or  $\text{R}_f\text{IF}_4$ . However, the sum of the C-F-I values does not always reach 100%. The discrepancy is not a result of chlorine or bromine from the halogen fluoride used, since neither element can be detected in these products. It may result from the well-known difficulty of decomposing perfluorinated compounds by standard microanalytical procedures. However, since the atom ratios are satisfactory, it may also result from inclusion of some oxygen from the glass vessels or from traces of moisture. The discrepancies were different in different samples but were not usually large.

Fluorine attached to iodine in  $\text{R}_f\text{IF}_n$  is readily liberated by hydrolysis. In contrast,  $\text{C}_6\text{H}_5\text{IF}_2$  is prepared in aqueous  $\text{HF}$ .<sup>18</sup> Direct addition of water to weighed samples of  $\text{R}_f\text{IF}_n$  is unsatisfactory, since the insoluble solid formed at once coats the sample and prevents complete reaction. The sample is preferably dissolved in methanol and slowly diluted with water to precipitate a solid. Fluoride ion is then determined by titration, and it corresponds well to two (or four) fluorines per iodine. Surprisingly, about half the total iodine is also converted to water-soluble form.<sup>19</sup> No elementary iodine appears. Direct iodometric titration of the hydrolyzates yields the same values as those obtained by reduction to iodide, reoxidation to iodate with bromine, and iodometric titration. Thus, the iodine is liberated in the pentavalent state. Both the difluorides and tetrafluorides appear to yield the same form of inorganic iodine.

The organic hydrolysis product is insoluble in common solvents such as water, methanol, isopropyl alcohol, acetone, benzene, chloroform, trichlorotrifluoroethane, acetonitrile, and dimethyl sulfoxide. On heating, it begins to decompose at  $200\text{--}250^\circ$  into tarry products. Nmr analysis of the solid is not possible. Its infrared spectrum shows the rich variety of intense bands expected for a fluorocarbon structure, along with diffuse absorption in the OH region. Elementary analyses are extremely erratic, reflecting our inability to purify the solid. Element ratios are roughly consistent with two perfluoro groups per iodine atom. Numerous analyses of the product from perfluorobutyl iodide difluoride showed between seven and eight

(15) H. Schmidt and F. Meinert, *Angew. Chem.*, **71**, 126 (1959); **72**, 109, 493 (1960); M. Schmeisser and E. Scharf, *ibid.*, **72**, 324 (1960). See also R. D. Chambers, W. K. R. Musgrave, and J. Savory, *J. Chem. Soc.*, 3779 (1961); M. Hauptschein and M. Braid, *J. Am. Chem. Soc.*, **83**, 2383, 2495 (1961); R. H. Andreatta and A. V. Robertson, *Australian J. Chem.*, **19**, 161 (1966).

(16) E. E. Aynsley, N. N. Greenwood, and D. H. W. Wharmby, *J. Chem. Soc.*, 5369 (1963).

(17) M. Schmeisser and E. Scharf, *Angew. Chem.*, **71**, 524 (1959).

(18) B. S. Garvey, L. F. Halley, and C. F. H. Allen, *J. Am. Chem. Soc.*, **59**, 1827 (1937); W. Bockemüller, *Ber.*, **64**, 522 (1931).

(19) F. Viebock and A. Schwappach, *Ber.*, **63**, 2818 (1930), removed all the iodine from aliphatic iodides with bromine in acetic acid containing sodium acetate. They proposed formation and cleavage of  $\text{RIBr}_3$ .

carbons per iodine and approximately two fluorines per carbon. Replicate analyses of a given sample of hydrolysis product agreed fairly well, but analyses of two separate samples prepared from the same (or different)  $C_4F_9IF_2$  were discordant. Note that iodobenzene difluoride is hydrolyzed reversibly to iodobenzene and HF, not to diphenyliodonium fluoride.

The available information supports but does not prove the formulation of the hydrolysis product as an iodonium salt  $(R_f)_2I^+X^-$ , in which X may be hydroxide, iodate, iodide, fluoride, etc.

**Nuclear Magnetic Resonance.**  $^{19}F$  nmr spectroscopy affords the clearest insight into the structures of the new difluorides and tetrafluorides. The difluorides resonate at very high field, showing that the fluorines are strongly shielded. The tetrafluorides, by contrast, are little shielded and resonate at very low field. Both peaks are well outside the usual range of fluorocarbon resonance, and they are easy to detect. Chemical shifts for the compounds studied most carefully are presented in Table I.

Table I.  $^{19}F$  Chemical Shifts in  $C_mF_{2m+1}IF_n^a$

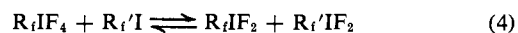
| <i>m</i> | <i>n</i> | $CF_3$ | $CF_2$ | $CF_2$ | $CF_2$ | $IF_n$ |
|----------|----------|--------|--------|--------|--------|--------|
| 4        | 0        | +4.0   | +36.5  | +47.6  | -18.2  |        |
|          | 2        | +3.9   | +40.7  | +48.1  | -2.7   | +91.3  |
|          | 4        | +3.8   | +42.8  | +48.1  | +4.6   | -49.5  |
| $IF_n$   |          |        |        |        |        |        |
| 3        | 0        | +2.2   | +43.6  | -18.8  |        |        |
|          | 2        | +4.0   | +43.0  | +2.9   | +88.7  |        |
|          | 4        | +4.0   | +47.1  | +5.5   | -53.5  |        |
| $IF_n$   |          |        |        |        |        |        |
| 2        | 0        | +8.0   | -13.1  |        |        |        |
|          | 2        | +3.9   | -0.9   | +88.7  |        |        |
|          | 4        | +3.9   | +12.1  | -47.9  |        |        |

<sup>a</sup> Measured neat with a Varian A56-60 nmr spectrometer at 56.4 MHz, probe temperature 35–36°. Shifts relative to trifluoroacetic acid (external), not corrected for solvent or for bulk magnetic susceptibility effects.

Since only a single  $-IF_n$  resonance is observed, the fluorines must be symmetrically arranged with respect to the  $R_f$  group in both classes of polyfluoride. In the tetrafluorides, the geometry is square pyramidal with the  $R_f$  group located in the apical position. If  $R_f$  were equatorial, or if the geometry were trigonal bipyramidal, the four fluorines would have different environments and chemical shifts, contrary to observation.

Nmr spectroscopy is very useful in the analysis of mixtures of difluorides and tetrafluorides, in determination of the amount of unreacted  $R_fI$  or perfluoroalkane solvent, in following rates of decomposition, and in other analytical applications.

Possible exchange reactions were also examined by nmr. As shown by Table I, the homologous iodides, iodide difluorides, and iodide tetrafluorides are all distinguishable. For example, all four components of a mixture of  $C_3F_7I$ ,  $C_3F_7IF_2$ ,  $C_4F_9I$ , and  $C_4F_9IF_2$  can be measured readily. Separate binary mixtures of  $C_3F_7IF_2$  with  $C_4F_9I$  and of  $C_4F_9IF_2$  with  $C_3F_7I$  were inspected by nmr at intervals during several days. At no time did the instrument see any equilibration according to eq 3. Similarly, mixtures of  $C_4F_9IF_4$  in  $C_3F_7I$  showed no evidence for eq 4.



The bridging shown in the following structures apparently does not occur.



Such bridging and exchange are readily detected in the inorganic halogen fluorides and in  $SbF_5$ .<sup>20</sup> Coordinating solvents might be effective promoters, however.

**Behavior in Organic Solvents.** Perfluorobutyl iodide difluoride dissolves without visible reaction in acetonitrile, ethyl acetate, methanol, and trifluoroacetic acid, though the latter two may react to form  $R_fI(OY)_2$  ( $Y = CH_3, COCF_3$ ). In carbon tetrachloride, slow reaction destroys the nmr signal of the  $-IF_2$ ; replacement of chlorine by fluorine would form  $CCl_3F$ , but no new nmr signal was detected. A chloroform (alcohol-free) solution forms a few bubbles, then slowly deposits a white solid. Benzene reacts with bubbling to form a white solid, probably  $C_6H_5I + C_4F_9X^-$ ,<sup>21</sup> which was not further examined. Dimethylformamide, pyridine, and fluorosulfonic acid react to yield, respectively, yellow, amber, and deep green solutions; this may indicate formation of coordination complexes analogous to those known with iodine mono- and trifluorides.<sup>15</sup> Triethylamine reacts violently with neat  $C_4F_9IF_2$  to form a brown oil; a solvent might moderate the reaction. Dimethyl sulfoxide forms a yellow solution which gradually deposits solid. Acetone reacts rapidly to form a black insoluble tar, perhaps as a result of condensation reactions proceeding through the enol form. Detailed study of the coordination chemistry and organic reactions of perfluoroalkyl iodide polyfluorides is contemplated.

**The Solid Isomers.** Most freshly prepared samples of  $R_fIF_2$  are low-melting solids with similar solubility properties. Not infrequently, however, the reaction product appeared as an insoluble, infusible solid which could not be purified. The insolubility precluded nmr and molecular weight measurements. Mass spectrometry yielded cracking patterns resembling those of  $R_fI$  and low-melting  $R_fIF_2$ .

Elementary analyses on several such solids with various perfluoroalkyl groups agreed fairly well with the empirical composition  $R_fIF_n$ , isomeric with those described above. The marked difference in physical properties suggests that the high-melting solids are iodonium salts  $R_2I^+Y^-$ , where  $Y^-$  may be  $IF_4^-$ ,  $IF_6^-$ , or even  $IF_8^-$ . Treatment of these solids with water liberates some fluoride ion, but the insolubility of the material evidently prevents complete reaction.

X-Ray analysis provides evidence for a dimeric structure. The unit cell of  $C_{10}F_{22}$  is 15.5–16.0 Å long, compared to 16.1 Å calculated for a fully extended chain; the unit cell of  $C_{10}F_{21}I$  measures 16.4 Å. How-

(20) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **84**, 1084 (1959); R. J. Gillespie and R. A. Rothenbury, *Chem. Can.*, **15**, [8], 46 (1963).

(21) Iodonium salts are often prepared by reaction of an organic iodine (III) compound with an aromatic hydrocarbon, such as  $ArI=O + Ar'H + acid \rightarrow ArI^+Ar'X^-$ . These syntheses have been developed by F. M. Beringer and coworkers; see ref 1 and 2, and also *J. Am. Chem. Soc.*, **81**, 342 (1959).

ever, the solid " $C_{10}F_{21}IF_2$ " is 30–33 Å long, consistent with its formulation as  $C_{10}F_{21}I^+C_{10}F_{21}Y^-$ . An alternative formulation as a molecule with only ten carbons, but "dimerized" somehow through head-to-head packing induced by fluorine bridges is believed unlikely, because such fluorine bridges are not detected (nmr) in any of the low-melting difluorides or tetrafluorides.

When the low-melting compounds are stored in glass vessels, either neat or in perfluorocarbon solution, solid products are formed which apparently are the same as those sometimes formed directly in the fluorination reaction. The reaction is catalyzed by moisture, because vigorously dried glass is a better vessel for preserving the low-melting products than air-dried glass. The isomerization is slower in Pyrex than in soft glass, which may bespeak base catalysis. For these reasons, polytetrafluoroethylene (PTFE) containers are preferred for storage. Isomerization is retarded strongly by freezing, which may mean that crystals of monomeric  $RIF_2$  do not have a head-to-head orientation of individual chains.

The perfluoroalkyl iodide tetrafluorides have not yielded solid "dimers" in this work. The "dimers" appear not to react with  $ClF_3$  or  $F_2$  to form  $RIF_4$ , perhaps because of their insolubility.

**Thermolysis of Perfluoroalkyl Iodide Polyfluorides.** Most of the  $R_fIF_n$  compounds are moderately stable at room temperature out of contact with moisture and glass. Thus samples of  $C_4F_9IF_2$  stored in a desiccator in PTFE containers deposit only traces of solid during eight weeks at room temperature, while weak nmr signals attributable to fluorinated impurities develop slowly. About 95% of the material survives eight weeks of storage. Samples of  $C_2F_5IF_2$  are less stable, and several per cent decompose per day at room temperature. About 5% of the same preparation decomposes in ten weeks when solidly frozen at  $-20^\circ$ . Casual observation of low-melting  $C_3F_7IF_2$  indicates an intermediate stability. Low-melting  $C_6F_{13}IF_2$  is similar to  $C_4F_9IF_2$ . As noted above, " $CF_3IF_2$ " prepared with fluorine (Schmeisser<sup>16</sup>) or with chlorine trifluoride (the present study) does not survive warming to room temperature.

The corresponding tetrafluorides are much less stable, perhaps by an order of magnitude. Pentafluoroethyl iodide tetrafluoride is about 50% destroyed in 24 hr at room temperature, with weight loss and solid formation. About 5% of  $C_4F_9IF_4$  is degraded in a day.

The thermal stability of the "dimeric" high-melting  $R_fIF_2$  could not be studied for lack of an analytical method.

At high temperatures, the neat compounds decompose more rapidly. A sample of  $C_4F_9IF_2$  in a PTFE beaker inside a glass pressure tube was heated at  $90^\circ$  for 3 hr, then vacuum stripped at  $25^\circ$ . The volatile material was  $IF_5$  containing fluorocarbon impurities; the residue, 85% of the starting material, was virtually pure  $C_4F_9IF_2$ . But after 12 hr at  $100^\circ$ , most of it was destroyed. The products expected by analogy to Schmeisser's discoveries with " $CF_3IF_2$ " were  $C_4F_9I$ ,  $C_4F_{10}$ , and  $IF_5$ . These are indeed the major products, but substantial amounts of (5–20%)  $R_fI$  and  $R_fF$  containing one to three carbons were isolated by gas chromatography and identified by time-of-flight mass spectrometry. The thermolysis experiments were

extended to the di- and tetrafluorides of perfluoroethyl-, -butyl, and -hexyl iodides. The decompositions could be compared by the rates of pressure rise, and they parallel the generalizations for room-temperature stability. The products in every case are  $IF_5$  and its reaction products with glass (the reactions were not studied in metal or all-PTFE apparatus) and  $R_fI$  and  $R_fF$  in roughly equal amounts. Both the iodide and fluorocarbon contain predominately the same number of carbons as the original  $RIF_n$ , but they also contain all of the smaller homologous  $R_fI$  and  $R_fF$  down to  $C_1$ . Each fragmented molecule is about 10–20% of the next larger homolog.

The decomposition mechanism is not known in detail. These results indicate that at one stage, the carbon-iodine bond is broken. The fluoroalkyl fragment may abstract fluorine from another  $R_fIF_2$  to form  $R_fF$  and  $R_fIF\cdot$ , or it may expel a  $CF_2$  group (formally difluorocarbene) to form a shorter fluoroalkyl fragment which has the same options. The  $RIF\cdot$  resulting from fluorine abstraction should disproportionate rapidly to  $RI$  and  $RIF_2$ . The intermediates are more likely radicals than ions in the nonpolar medium, but specific evidence for this statement is not available. The fate of the expelled  $CF_2$  units is uncertain. They do not insert into a C–I bond, for higher homologs are never identified. To a very small extent they may insert into C–F bonds, because some of the trace chromatographic peaks show mass spectral patterns consistent with a branched carbon skeleton. The  $CF_2$  groups do not dimerize to a significant extent because tetrafluoroethylene and hexafluoropropylene could not be detected; at such low concentrations, tetrafluoroethylene does not telomerize significantly.<sup>9</sup> In part, the chain-breaking reactions may result from the attack of  $IF_5$  formed in the primary reaction upon  $RI$ . When an iodide is heated with iodine pentafluoride, a small amount of fragmentation occurs to yield a mixture of homologous  $R_fI$  and  $R_fF$  resembling in product distributions those obtained by heating  $R_fIF_n$ . Likewise, the volatile by-products from  $RIF_n$  preparation always contain traces of fragmentation products, though the amount decreases as the preparation temperature is lowered.

**Other Perfluoroalkyl Iodide Derivatives.** By analogy to the aromatic iodides, such compounds as  $R_fICl_2$ ,  $R_fI=O$ ,  $R_fI(OCH_3)_2$ ,  $R_fI(OCOCH_3)_2$ , etc. might exist. Incidental experiments did not result in isolable compounds. Chlorination of perfluorobutyl iodide at various temperatures produces no definite products. In strong light, perfluoroalkyl chlorides are formed, but in the dark, the iodide remains apparently unchanged. The nmr spectra of chlorinated iodides do not differ from those of the parent iodides; one would expect the  $\alpha$ -fluorine atoms in  $R_fCF_2ICl_2$  to resonate differently from  $R_fCF_2I$ , as is the case in  $R_fCF_2IF_2$  (Table I). Low-temperature distillation of chlorinated iodides yielded unchanged iodides and no residue of dichloride.

Ozone at various temperatures does not form iodoso compounds; no reaction of any sort is detected.<sup>22</sup> Iodoso compounds might be formed during hydrolysis of iodide difluorides; however, the properties of the

(22) C. Harries, *Ber.*, **36**, 2996 (1903), prepared iodosobenzene from iodobenzene and ozone.

Table II. Properties of Perfluoroalkyl Iodide Polyfluorides

| n   | Method <sup>a</sup>                  | Mp, °C <sup>b</sup>   | Formula   | Calcd, <sup>c</sup> % |                |                |      | Found, <sup>c</sup> % |                |                |      |
|---|--------------------------------------|-----------------------|---|-----------------------|----------------|----------------|------|-----------------------|----------------|----------------|------|
|   |                                      |                       |   | C                     | F <sub>t</sub> | F <sub>h</sub> | I    | C                     | F <sub>t</sub> | F <sub>h</sub> | I    |
| A. C <sub>n</sub> F <sub>2n+1</sub> IF <sub>2</sub> |                                      |                       |   |                       |                |                |      |                       |                |                |      |
| 2   | C,V,N<br>C,L,S<br>B,L,N <sup>d</sup> | 18<br>17<br>12-15     | C <sub>2</sub> F <sub>5</sub> IF <sub>2</sub>   | 8.4                   | 46.8           | 13.4           | 44.4 | 8.6                   | 46.7           | 13.5           | 42.9 |
| 3   | C,V,S<br>C,L,N                       | 0                     | Characterized by nmr <sup>e</sup>   |                       |                |                |      |                       |                |                |      |
| 3 <sup>f</sup>                                      | C,V,N                                |                       | Mixture of high- and low-melting forms <sup>e</sup>                                   |                       |                |                |      |                       |                |                |      |
| 4   | C,L,S<br>C,V,N<br>C,L,N              | 15                    | C <sub>4</sub> F <sub>9</sub> IF <sub>2</sub>   | 12.5                  | 54.4           | 9.9            | 33.1 | 12.4                  | 55.3           | 9.0            | 33.3 |
|   | F <sub>2</sub>                       |                       |   |                       |                |                |      |                       | 54.6           | 9.9            |      |
| 6   | C,L,S<br>C,V,N                       | >200 dec<br>35        | C <sub>6</sub> F <sub>13</sub> IF <sub>2</sub>  | 14.9                  | 58.8           | 7.8            | 26.2 | 15.5                  | 58.4           | 7.9            | 25.8 |
| 10  | C,L,S,sl                             | >200 dec <sup>g</sup> | C <sub>10</sub> F <sub>21</sub> IF <sub>2</sub>                                       | 17.5                  | 63.8           | 5.5            | 18.6 | 17.4                  | 61.4           | 5.0            | 19.2 |
| B. C <sub>n</sub> F <sub>2n+1</sub> IF <sub>4</sub> |                                      |                       |   |                       |                |                |      |                       |                |                |      |
| 2   | C,L,S                                | 13                    | C <sub>2</sub> F <sub>5</sub> IF <sub>4</sub> +<br>30% C <sub>6</sub> F <sub>14</sub> | 11.6                  | <i>h</i>       | <i>h</i>       | 27.6 | 11.2                  | <i>h</i>       | <i>h</i>       | 27.5 |
| 4   | C,L,S<br>B,L,S                       | 10                    | C <sub>4</sub> F <sub>9</sub> IF <sub>4</sub>   | 11.4                  | 58.6           | 18.0           | 30.1 | 11.6                  | 58.7           | 16.7           | 30.2 |
| 10  | C,L,S                                | >200 dec              | C <sub>10</sub> F <sub>21</sub> IF <sub>4</sub> <sup>i</sup>                          | 16.6                  | 65.8           |                | 17.6 | 17.1                  | 60.3           |                | 19.7 |

<sup>a</sup> C = ClF<sub>3</sub>; B = BrF<sub>3</sub>; L = liquid reagent; V = reagent vaporized in helium stream; N = neat iodide in excess; S = solvent (perfluorohexane); sl = slurry. <sup>b</sup> Melting point given as temperature at which liquid and solid phases are in equilibrium. Solid is a glassy material, not well-formed crystals. <sup>c</sup> F<sub>t</sub> = total fluorine; F<sub>h</sub> = titratable fluorine after hydrolysis by adding water to a methanol solution. <sup>d</sup> Product was a mixture of difluoride and tetrafluoride. <sup>e</sup> Useful as telomerization catalyst. <sup>f</sup> From 2-iodoperfluoropropane. <sup>g</sup> Apparently contains a little unchanged C<sub>10</sub>F<sub>21</sub>I. <sup>h</sup> Contains 30% of C<sub>6</sub>F<sub>14</sub> (nmr) which could not be removed by pumping without causing decomposition. The analysis refers to this mixture. Consistent fluorine analyses could not be obtained. <sup>i</sup> Contaminated with C<sub>10</sub>F<sub>21</sub>IF<sub>2</sub> and perhaps C<sub>10</sub>F<sub>21</sub>I.

hydrolysate are in better agreement with the iodonium salt formulation, though the structure of the solid is still open to question.

Further study of alcoholysis and acidolysis will be directed at isolating the dialkoxy and diacyloxy derivatives. The coordination chemistry of R<sub>n</sub>IF<sub>n</sub> will be studied.

## Experimental Section

**CAUTION!** Fluorine and the halogen fluorides are extremely dangerous materials and should be handled only in proper equipment by experienced personnel wearing protective clothing. Useful suggestions are provided by the manufacturer, General Chemical Division of Allied Chemical Corp. Chlorine trifluoride, which is readily handled as a liquid, can ignite wood, plastics, and even concrete; it explodes violently in contact with common organic solvents at -100°. The bromine fluorides are slightly less hazardous but still dangerous. Iodine pentafluoride is not so aggressive, but should be handled with respect.

**Apparatus.** Much of the present research was conducted in glass pressure bottles attached to the vacuum line described fully in the following paper.<sup>9</sup> All glassware was dried for at least 24 hr at 200°. Alternatively, a reaction assembly of conventional glassware was flamed vigorously under vacuum. Reagents or solvents were added by vacuum transfer on a small scale or by siphoning through dry tubing from storage bottles for larger scale preparations.

**Materials.** The halogen fluorides and fluorine were obtained from the Matheson Company in cylinders. For safety, the halogen fluorides were transferred from the shipping cylinders into 90-ml nickel or Monel cylinders. These were equipped with degreased needle valves (Whitey, Series 1) of Monel with machined PTFE packing. ClF<sub>3</sub> could be dispensed either as a gas or, by chilling the cylinder, as a liquid. The delivery tubes were carefully degreased and oven dried; they were made of copper or Monel and connected with "Swagelok" fittings.

Pentafluoroethyl iodide was prepared by Parsons' procedure<sup>12</sup> from 1,2-diiodotetrafluoroethane. It was telomerized by Parsons' procedure<sup>13</sup> to a mixture of the even-numbered perfluoroalkyl iodides which was then separated by fractional distillation. Small amounts of the odd-numbered iodides were formed as by-products, perhaps resulting from degradation reactions similar to those

described in the discussion. Perfluoro-*n*-propyl and *n*-heptyl iodides were obtained from Columbia Organic Chemicals Company. Perfluoroisopropyl iodide was prepared from hexafluoropropene.<sup>12</sup> All the iodides were carefully fractionated until no impurities could be detected by gas chromatography (gc) analysis. They were stored in brown bottles over dried granular charcoal to absorb iodine.

Perfluorohexane and perfluorooctane were isolated as by-products from the fractionation of telomers. They were contaminated by 10-20% of perfluorobutyl and hexyl iodides, respectively, which could not be completely separated by distillation. For most purposes these solutions were satisfactory as taken from the still, after gc analysis. Treatment with fluorine or chlorine trifluoride converted the iodides into the less volatile difluorides which were left behind when the perfluoroalkane was vacuum stripped. The perfluoroalkane could then be purified.

The purity of all starting materials was assayed by gc on columns of 5-10% DC-200 silicone oil, on Chromosorb W, AW-DMCS, 6 ft or 14 ft long, using an F & M Model 700 chromatograph. Column temperatures and heating cycles were adjusted to the compounds at hand. Homologous iodides or alkanes could readily be separated.

**Preparation of Perfluoroalkyl Iodide Polyfluorides.** Typical procedures are described. Properties and analyses of the products are presented in Table II.

**Liquid Chlorine Trifluoride.** The storage cylinder was cooled to -50°. A small PTFE beaker was chilled and placed on a balance, and liquid ClF<sub>3</sub> (4.67 g, 0.05 mol) was drained into it from the cylinder. Meanwhile, a solution of 33.4 g (0.075 mol) of perfluoroethyl iodide in 100 ml of perfluorohexane was prepared in a 6-oz pressure bottle and chilled to -70°, with moisture protection. With magnetic stirring, the ClF<sub>3</sub> was added all at once. The bottle was attached to the vacuum line. In some experiments, the mixture was frozen in liquid nitrogen and degassed, then thawed in a -70° bath before it was warmed slowly with stirring. In others, the bottle was evacuated quickly at -70° to about 15 mm pressure, then warmed. The reaction proceeded smoothly and was complete before the mixture reached room temperature. The solvent was stripped into an adjacent bottle on the vacuum line and condensed at -196°. The residue was pumped at 25-30° to remove traces of solvent. In one such experiment, the solid modification of "C<sub>6</sub>-F<sub>13</sub>IF<sub>2</sub>" was obtained, believed to be the iodonium salt. In other similar experiments, the low-melting form was produced. Perfluorooctane can also be used as solvent.



Perfluorobutyl iodide difluoride was prepared similarly in various dilutions by perfluorohexane or simply by using excess iodide. Stirring is *essential*, and magnetic stirring is sufficient on the small scale. The procedure needs slight modification for reactions with perfluoroethyl iodide because of its low boiling point.

The tetrafluorides were prepared similarly using a slight excess of  $\text{ClF}_3$ . Since they are less stable, they were pumped at lower temperatures to remove the solvent.

With higher iodides, such as perfluorodecyl iodide or the mixture of solid telomers obtained as fractionation residues, the iodide was dissolved in perfluorohexane, with heating if necessary; and the mixture was shock cooled in a  $-80^\circ$  bath to precipitate the iodide as a fine slurry. Chlorine trifluoride was added below  $-60^\circ$ , and the mixture was allowed to warm to room temperature. Both the difluorides and tetrafluorides were obtained as high-melting solids, and these were washed with fresh solvent to remove most of the unchanged iodide. The products were collected on a filter in the drybox.

For large-scale work, extra precautions are required. The hood is carefully cleaned to remove combustible materials. All operations are carried out behind a stout safety shield. The operator wears protective clothing, including a face mask, sleeves, and apron of Neoprene synthetic rubber, and leather gloves covered with large Neoprene rubber gloves. Glassware is flame dried under vacuum. Typically, a mixture of 206 g (0.6 mol) of perfluorobutyl iodide and 2614 g of perfluorohexane was chilled in a 3-l., three-necked flask with mechanical stirrer, low-temperature thermometer, and a drying tube. The  $-80^\circ$  bath was removed and replaced by a pan of solid carbon dioxide. **CAUTION!** Liquid  $\text{ClF}_3$  will *explode* if accidentally dropped into  $\text{CO}_2$ -acetone mixtures. Liquid  $\text{ClF}_3$  (about 40 g) was weighed into a PTFE beaker and poured in portions directly onto the stirred liquid through a dry glass funnel. It may react violently if allowed to run down the wall of the flask, probably owing to local overheating. The drying tube was replaced and the flask was surrounded by acetone at  $-70^\circ$ ; the bath was allowed to warm slowly. The solid which formed initially dissolved at about  $-30^\circ$ . The mass was cooled again to about  $-55^\circ$ , the solid  $\text{CO}_2$  bath was installed, and the remainder of the  $\text{ClF}_3$  was added similarly; the total weight of  $\text{ClF}_3$  was 110 g. The mixture was allowed to warm slowly to  $0^\circ$  in an acetone bath. An exothermic reaction can be controlled by adding a large amount of solid  $\text{CO}_2$  to the bath. The perfluorohexane was then stripped *in vacuo* at  $0^\circ$  with stirring. The pasty residue, 216 g, still contained about 15% of perfluorohexane (nmr) but was otherwise pure  $\text{C}_4\text{F}_9\text{IF}_4$ . The analytical sample, mp  $10^\circ$ , was prepared by exhaustive pumping just above the melting point. It decomposes slowly at room temperature and should be stored at  $-20^\circ$  until ready for analysis. The same product was obtained in a similar procedure with bromine pentafluoride.

**Fluorination with Chlorine Trifluoride Vapor.** The chlorine trifluoride was vaporized from the storage cylinder into a chilled receiver through a 0.25 in. copper tube connected with a PTFE "Swagelok" union. The calibrated receiver was fashioned from 16-mm quartz tubing. A head attached with a standard taper joint held the gas inlet and also an outlet tube attached to a drying tube with a union. In early experiments, the receiver was immersed in a bath at  $+13^\circ$  to induce the  $\text{ClF}_3$  to boil out slowly through an empty safety trap and a delivery tube immersed in the perfluoroiodide-solvent mixture at  $-60^\circ$ . Bumping was a problem. In one such experiment, a suckback into the safety trap allowed some organic vapor to permeate back into the liquid  $\text{ClF}_3$ . The reaction was sufficiently vigorous to crack the quartz tube and discharge the  $\text{ClF}_3$  into the solvent bath. The resulting blast prompted a search for a safer method.

Subsequently the quartz receiver was fitted with a capillary sealed through the upper wall of the tube reaching to its bottom. A stream of dry helium was passed through the liquid  $\text{ClF}_3$  maintained at a temperature which afforded the desired vapor pressure. The gas stream was then passed through an empty safety trap into a gas delivery tube dipping well below the surface of the mixture to be fluorinated. It is essential that the  $\text{ClF}_3$  react completely before reaching the vapor space above the reaction mixtures; flashes of fire, loud reports, and one destructive explosion were encountered before the need for this stricture was determined. If the liquid-phase reaction becomes too vigorous, it may be controlled by adding solid carbon dioxide to the bath surrounding the  $\text{ClF}_3$  container. However, the helium flow *must be increased* before such cooling. In one experiment before this was realized, an apparent vapor suckback into the liquid  $\text{ClF}_3$  caused another energetic reaction which cracked the quartz tube. The deafening detonation pulverized the dewar flask containing the carbon dioxide-methanol coolant.

Under proper conditions, small-scale fluorinations with  $\text{ClF}_3$  vapor were performed safely to yield the same products obtained with liquid-phase feed. Strangely, reactions with the vapor were usually much more exothermic and required several times longer than with liquid addition. Attempts to accelerate the process frequently caused uncontrollable exothermic reactions, though no explosions. Based on about 30 experiments with vapor feed and about 50 with liquid feed, the author strongly prefers the liquid feed. For ultimate safety, a remotely controlled, jacketed dropping funnel with some reliable stopcock could be employed. A micrometering pump of some inert metal should serve the purpose.

The writer again urges extreme care in working with chlorine trifluoride, especially on a preparative scale. No personal injuries were sustained in this work because of close attention to proper safety precautions, especially body protection and shielding.

**Fluorination with Fluorine. Apparatus.** The manufacturer's fluorine cylinder was stored outdoors in a steel barricade. The gas was taken through a regulator (Matheson) designed for fluorine service to a remotely operated shutoff valve, through a tower filled with NaF pellets, and thence to a reservoir for storage at 60 psig. A 1-l. stainless steel cylinder served as reservoir for small-scale work, and a pair of interconnected 20-l. vessels fabricated of stainless steel in our shop served for larger scale experiments. Lines led from the reservoirs through valves and flowmeters into tees where nitrogen or other inert gas could be added, and then into a small pipe filled with NaF pellets to insure thorough gas mixing and removal of the last traces of HF. The mixed gas streams were taken through bubblers filled with Krytox perfluorinated ether oil, past a tee leading to a back-pressure relief tube filled with Krytox oil to provide an appropriate pressure head, and finally through an empty vessel (suckback protection) into the reaction mixture itself.

The reservoirs, mixing and measuring equipment, gauges, and valves were contained in a heavy steel barricade with a safety-glass window. The enclosure was ventilated by a powerful blower feeding directly to a *clean* exhaust stack outdoors. The valves were operated from outside the barricade by extension handles. *These must be properly labeled.* The actual reactions were conducted in an adjoining hood with special ventilation and shielding; use of the hood was limited to fluorination work.

After construction was complete, the reservoirs and all measuring equipment were calibrated with nitrogen. The quantity of fluorine delivered to the reaction was measured by pressure drop, demonstrated to be accurate to about 1%.

All equipment was degreased and thoroughly cleaned and dried before assembly. It was then passivated by adding successively stronger fluorine-nitrogen mixtures and allowing each to remain overnight. Finally the apparatus was evacuated and filled with pure fluorine.

The reaction vessels were 6-oz glass pressure bottles fitted with three-hole stoppers machined from solid PTFE. Copper tubes (0.25 in.) carried the gas, and a thermometer was inserted in the third hole. Since elastomeric connections are not permissible with fluorine, 0.25 in. PTFE Swagelok unions screwed finger-tight permitted leak-free assembly. Laboratory glass tubing in millimeter dimensions must be sealed to a short terminus of 0.25 in. glass tubing.

The formidable equipment described permitted safe conduct of many fluorinations, not only of perfluoroalkyl iodides, but also of many other compounds outside the scope of this paper. No explosions were ever encountered in this work with fluorine.

**Fluorinations of Perfluoroalkyl Iodides.** Fluorination of neat iodides, even with strongly diluted and precooled fluorine, always led to immediate production of iodine. At low temperatures, the iodine crystallized at once because of its low solubility in cold  $\text{R}_i\text{I}$ . Therefore, the iodides were always fluorinated in a solvent, usually perfluorohexane, sometimes  $\text{CCl}_3\text{F}$  or perfluorocyclobutane.

Fluorination in solvent could be conducted at  $0^\circ$ , but  $-40^\circ$  minimized solvent evaporation by the nitrogen diluent. The desired quantity of fluorine was added, usually at the rate of 3 g/hr. The reactor contents were stirred magnetically. Most fluorinations yielded the high-melting solid "isomeric" form of  $\text{R}_i\text{IF}_2$  which precipitated in the later stages of the fluorinations. Pure  $\text{R}_i\text{IF}_4$  could not be obtained with  $\text{F}_2$ , since the insoluble solid evidently resisted attack by  $\text{F}_2$ . The fluorination of  $\text{R}_i\text{IF}_2$  with  $\text{F}_2$  has not been studied.

**Acknowledgments.** I am indebted to Dr. J. A. Nelson for his encouragement of this work. R. E. Parsons conducted some large-scale preparations of  $\text{C}_2\text{F}_5\text{IF}_2$

and  $C_4F_9IF_2$  and confirmed many of the observations reported herein. I want to express particular appreciation to Walter G. Barber for his assistance throughout this work. His intrepid handling of  $ClF_3$  demonstrated that even the most dangerous work can be performed safely. Mr. Barber also built the fluo-

rine-handling equipment, with assistance and advice from Edward Hancock, our resourceful mechanic.

Thomas E. Beukelman performed the nmr studies, and I owe a great deal to his imaginative examination of the spectra. Dr. James Proctor conducted the X-ray study of solid  $C_{10}F_{21}IF_2$ .

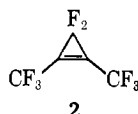
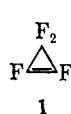
## Fluorocyclopropanes. III. 1,4-Cycloaddition Reactions of Perfluorocyclopropene and 1,2-Bis(trifluoromethyl)-3,3-difluorocyclopropene

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**Abstract:** Perfluorocyclopropene and 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene undergo (a) Diels–Alder reaction with cyclopentadiene to yield *endo*-2,3,3,4-tetrafluorotricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene and *exo*- and *endo*-2,4-bis(trifluoromethyl)-3,3-difluorotricyclo[3.2.1.0<sup>2,4</sup>]oct-6-enes, and with furan to yield 2,3,3,4-tetrafluoro-8-oxatricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene and 2,4-bis(trifluoromethyl)-3,3-difluoro-8-oxatricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene; (b) cycloaddition with quadricyclane to provide 3,4,4,5-tetrafluorotetracyclo[5.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]dec-8-ene and 3,5-bis(trifluoromethyl)-4,4-difluorotetracyclo[5.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]dec-8-ene; and (c) homoconjugate Diels–Alder reaction with norbornadiene to provide 4,5,5,6-tetrafluoropentacyclo[5.3.0.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>]decane and 4,6-bis(trifluoromethyl)-5,5-difluoropentacyclo[5.3.0.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>]decane. The perfluorocyclopropene adducts undergo facile cyclopropyl–allyl rearrangement to yield the corresponding unsaturated fluorocarbons. The 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene adducts are more stable; however, the cyclopentadiene adduct undergoes cyclopropyl–allyl–homovinylcyclopropyl rearrangement. Proton and fluorine nmr spectra are reported and discussed.

Cyclopropenes react with 1,3-dienes to give Diels–Alder adducts.<sup>2–4</sup> Perfluorocyclopropene<sup>5,6</sup> yields a Diels–Alder adduct with 1,3-butadiene, and a 1,2 cycloadduct with tetrafluoroethylene.<sup>6</sup> In this paper we report additional Diels–Alder reactions of perfluorocyclopropene (1) and 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene (2),<sup>7,8</sup> as well as cycloaddition reactions with tetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptane (quadricyclane) and norbornadiene.



### Results

Perfluorocyclopropene and cyclopentadiene gave *endo*-2,3,3,4-tetrafluorotricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene (3) which readily underwent cyclopropyl–allyl rearrangement to 2,2,3,4-tetrafluorobicyclo[3.2.1]octa-3,6-diene

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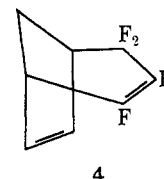
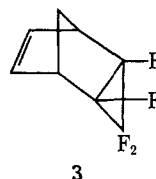
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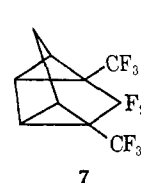
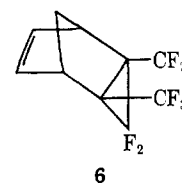
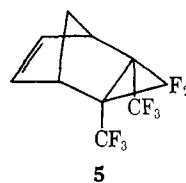
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(9) We designate the isomer with the *endo*-substituted cyclopropane ring as the *endo* isomer in this and subsequent compounds.



(4). Cyclopropene 2 and cyclopentadiene gave both *exo*- and *endo*-2,4-bis(trifluoromethyl)-3,3-difluorotricyclo[3.2.1.0<sup>2,4</sup>]oct-6-enes (5 and 6). The *exo* isomer 5 isomerized to the more stable *endo* isomer 6 on mild



heating (65°); at 200° the cyclopropyl–allyl rearrangement did not occur, rather a cyclopropyl–allyl–homovinylcyclopropyl rearrangement gave 2,4-bis(trifluoromethyl)-3,3-difluorotetracyclo[3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>]octane (7). Furan gave 2,3,3,4-tetrafluoro-8-oxatricyclo[3.2.1.0<sup>2,4</sup>]oct-6-one (8) with 1 and 2,4-bis(trifluoromethyl)-3,3-

