733. *Mixtures of Halogens * and Halogen Polyfluorides as Effective Sources of the Halogen Monofluorides in Reactions with Fluoro-olefins.*†

By R. D. CHAMBERS, W. K. R. MUSGRAVE, and J. SAVORY.

Mixtures containing bromine trifluoride and bromine, or iodine pentafluoride and iodine, can be effective sources of " bromine fluoride " and " iodine fluoride," respectively; they are useful for the preparation of bromo- and iodo-fluoroalkanes; similarly, a mixture of bromine and chlorine acts as a source of bromine chloride. Hexafluoropropene yielded the new fluorohalogenoalkanes $CF_3{\cdot}CFBr{\cdot}CF_3$ and $CF_3{\cdot}CFI{\cdot}CF_3$; the addition of iodine bromide and iodine chloride to chlorotrifluoroethylene has been investigated; and addition of interhalogen compounds to fluoro-olefins is discussed.

BROMINE TRIFLUORIDE and iodine pentafluoride are extremely reactive and have been used alone for the preparation of bromo-[1,2a] and iodo-fluoroalkanes. Banks *et al.*[2a] prepared trifluoroiodomethane and pentafluoroiodoethane by the reaction of iodine pentafluoride with carbon tetraiodide and tetraiodoethylene, and Emeléus and Haszeldine[2b] obtained pentafluoroiodoethane from 1,2-di-iodotetrafluoroethane. The reactions of bromine trifluoride and iodine pentafluoride with fluoro-olefins, however, have not been investigated

---

* Halogen, in the sense used in this paper, does not include fluorine.

† Preliminary communication, *Proc. Chem. Soc.*, 1961, 113.

[1] Nutting and Petrie, U.S.P., 1,961,622/1934.

[2] (*a*) Banks, Emeléus, Haszeldine, and Kerrigan, *J.*, 1948, 2188; (*b*) Emeléus and Haszeldine, *J.*, 1949, 2948.

extensively whereas reactions between other, much less reactive interhalogen compounds and fluoro-olefins are quite well known. Simons and Brice[3] investigated some reactions of iodine pentafluoride and higher iodine fluorides with fluoro-olefins at 175—250°, in the gas phase, for the purpose of preparing fluorocarbon iodides. The yields, although not stated, are necessarily limited by the fact that only one of the fluorine atoms in a particular molecule of iodine pentafluoride can react to yield fluorocarbon iodide; two remaining molecules of fluorine per molecule of iodine pentafluoride are then available for reaction with the fluorocarbon iodide, thus reducing the yield: $R_fI + 3F_2 \longrightarrow R_fF + IF_5$.

It has now been found that yields of fluorocarbon bromides and iodides obtained by reaction of fluoro-olefins with bromine trifluoride and iodine pentafluoride, in the liquid phase, under autogenous pressure, may be substantially increased by the addition of a quantity of bromine or iodine, as the situation requires, sufficient to make the mixtures equivalent to the halogen monofluoride.‡ "Bromine fluoride" and "iodine fluoride" reacted with hexafluoropropene, giving 2-bromoheptafluoropropane (I) and heptafluoro-2-iodopropane (II) respectively. That the compounds had structures (I) and (II) and not (III; X =

$CF_3\cdot CFBr\cdot CF_3$	$CF_3\cdot CFI\cdot CF_3$	$CF_3\cdot CF_2\cdot CF_2X$
(I)	(II)	(III)

Br or I), was deduced from their ^{19}F resonance spectra, both of which consisted of a low-field doublet and a high-field septet, and the intensity distribution was consistent with structures (I) and (II). Further evidence was provided by the observed chemical shifts. Heptafluoro-2-iodopropane (II) was easily coupled on irradiation with ultraviolet light in the presence of mercury and gave an excellent yield (96·5%) of a new fluorocarbon, perfluoro-2,3-dimethylbutane, $(CF_3)_2CF\cdot CF(CF_3)_2$. Hydrolysis of the iodide (II) by potassium hydroxide in acetone proceeded at room temperature and gave the known 2*H*-heptafluoropropane (75%), $CF_3\cdot CHF\cdot CF_3$, proving conclusively the assigned structure (II).

Trifluoromethyl-, pentafluoroethyl-, and heptafluoropropyl-lithium derivatives and Grignard reagents have been reported but only the heptafluoropropyl compounds seem to have been established with absolute certainty.[4] Heptafluoro-2-iodopropane is equally capable of yielding organometallic derivatives; $(CF_3)_2CF\cdot Li$ and $(CF_3)_2CF\cdot MgBr$ can be formed by exchange reactions at low temperature, and $(CF_3)_2CF_2ZnI$ by reaction with zinc in dioxan. The behaviour of these compounds will be described later.

Fluoroalkyl and halogenofluoroalkyl bromides and iodides and bromoundecafluorocyclohexane have been prepared from the olefins tetrafluoroethylene, hexafluoropropene, 1,1-difluoroethylene, chlorotrifluoroethylene, and perfluorocyclohexene, according to the general reaction:

$$CFZ{:}CXY + MF \longrightarrow M\cdot[CFZ\cdot CXY]\cdot F$$

where $M = Br$ or I; $XY = F_2$, F/CF_3, or F/Cl: $Z = F$

or $M = I$: $XY = H_2$; $Z = F$

or $M = Br$: $ZY = [CF_2]_2\cdot \quad \cdot[CF_2]_2$: $X = F$

The reactions are included in Table 1. Thus, mixtures of bromine trifluoride and bromine, or of iodine pentafluoride and iodine, are effective sources of bromine fluoride and iodine fluoride, respectively. We also found, as have other workers,[5] that a mixture of chlorine and bromine can be an effective source of bromine chloride, and one of the products obtained by the reaction of "bromine fluoride" with chlorotrifluoroethylene, $CF_2Cl\cdot CF_2Br$, was conveniently synthesised by the reaction of an equimolar mixture of bromine and chlorine with tetrafluoroethylene: $Cl_2 + Br_2 + 2C_2F_4 \longrightarrow 2CF_2Cl\cdot CF_2Br$.

‡ These mixtures are often referred to as "bromine fluoride" and "iodine fluoride" in this paper.

[3] Simons and Brice, U.S.P. 2,614,131/1952.

[4] See Lagowski, *Quart. Rev.*, 1959, **13**, 240, for a review of these derivatives.

[5] Buckles, Forrester, Burham, and McGee, *J. Org. Chem.*, 1960, **25**, 24.

Only very recently[6] has iodine monofluoride been prepared, although Durie[7] earlier observed it spectroscopically. Bromine fluoride has never been isolated but conductometric measurements by Quarterman *et al.*[8] provide evidence for its formation when bromine is dissolved in bromine trifluoride. Many complicated reaction schemes, involving the self-ionisation of the halogen fluorides,[9] may be devised to account for the reactions between bromine trifluoride plus bromine, and iodine pentafluoride plus iodine, with fluoro-olefins but the mode of addition is most easily explained in terms of the formation of halogen monofluorides:

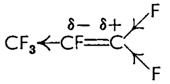
TABLE 1.

Olefin	Reaction	Products
$CF_2{:}CF_2$	$I_2 + IF_5$	C_2F_5I (86%)
$CF_2{:}CF_2$	$Br_2 + BrF_3$	C_2F_5Br
$CF_2{:}CF_2$	$Br_2 + Cl_2$	$CF_2Cl{\cdot}CF_2Br$
$CF_3{\cdot}CF{:}CF_2$	$I_2 + IF_5$	$CF_3{\cdot}CFI{\cdot}CF_3$ (99%)
$CF_3{\cdot}CF{:}CF_2$	$Br_2 + BrF_3$	$CF_3{\cdot}CFBr{\cdot}CF_3$ (45·5%)
$CF_2{:}CH_2$	$I_2 + IF_5$	$CF_3{\cdot}CH_2I$ (86%)
$CF_2{:}CFCl$	$I_2 + IF_5$	$CF_2I{\cdot}CF_2Cl$ (45%) + $CF_3{\cdot}CFClI$ (37%)
$CF_2{:}CFCl$	$Br_2 + BrF_3$	$CF_2Br{\cdot}CF_2Cl$ (73%) + $CF_3CFClBr$ (13%)
$CF_2{:}CFCl$	ICl	$CF_2I{\cdot}CFCl_2$ (29%) + $CF_2Cl{\cdot}CFClI$ (57%)
$CF_2{:}CFCl$	IBr	$CF_2I{\cdot}CFClBr$ (14%) + $CF_2Br{\cdot}CFClI$ (44%)
cyclo-C_6F_{10}	$Br_2 + BrF_3$	cyclo-$C_6F_{11}Br$ (78%)
$CCl_2{:}CCl_2$	$I_2 + IF_5$	$CCl_2F{\cdot}CCl_2F$ (51%)
$CF_2{:}CCl_2$	$I_2 + IF_5$	$CF_3{\cdot}CFCl_2$ (25%) + $CF_2I{\cdot}CCl_2F$ (31%) + $CF_3{\cdot}CCl_2I$ (23%)

$$IF_5 + 2I_2 \rightleftharpoons 5IF$$

$$\overset{\delta+}{I}—\overset{\delta-}{F} + \overset{\delta+}{CF_2}{=}\overset{\delta-}{CF}{\cdot}CF_3 \longrightarrow CF_3{\cdot}CFI{\cdot}CF_3$$

Many workers have shown that nucleophilic addition to fluoro-olefins occurs very easily and that olefins containing a terminal difluoromethylene group are the most reactive;[10] the nucleophile invariably becomes attached to the difluoromethylene group. This situation can be rationalised by considering the ability of fluorine atoms in a difluoromethylene group to " back-donate " non-bonding *p*-electrons to the olefinic double bond. In hexafluoropropene the effect of this " back-donation " and the strong inductive effect of the trifluoromethyl are complimentary:



This has been confirmed by the addition of ionic reagents to hexafluoropropene; hydrogen fluoride gives $CF_3{\cdot}CHF{\cdot}CF_3$[11] and the base-catalysed addition of methanol yields $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}OMe$.[12] Similarly 1,1-difluoroethylene, $\overset{\delta+}{CF_2}{=}\overset{\delta-}{CH_2}$, yields $CF_2Br{\cdot}CH_2I$ with iodine bromide[13] and chlorotrifluoroethylene, $\overset{\delta+}{CF_2}{=}\overset{\delta-}{CFCl}$, yields products of the form $CF_2R{\cdot}CHFCl$ (where R = $^-$OAlk,[14] F^-,[11] etc.).

" Bromine fluoride " and " iodine fluoride " gave specific addition products $CF_3{\cdot}CFX{\cdot}CF_3$ (X = Br or I) with hexafluoropropene, and 1,1-difluoroethylene gave exclusively $CF_3{\cdot}CH_2I$ with " iodine fluoride." However, chlorotrifluoroethylene yielded

---

[6] Schmeisser and Scharf, *Angew. Chem.*, 1960, **72**, 324.

[7] Durie, *Proc. Roy. Soc.*, 1951, *A*, **207**, 388.

[8] Quarterman, Hyman, and Katz, *J. Phys. Chem.*, 1957, **61**, 912.

[9] See Clark, *Chem. Rev.*, 1958, **58**, 869, for a discussion of the self-ionisation of interhalogen compounds.

[10] Miller and Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 4164, and references cited therein.

[11] Miller, Fried, and Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3094.

[12] Knunyants, Shchekotikhim, and Folkin, *Izvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1953, 282.

[13] Haszeldine and Steele, *J.*, 1954, 923.

[14] Miller, Fager, and Griswold, *J. Amer. Chem. Soc.*, 1948, **70**, 431.

mixtures of the isomers $CF_3\cdot CFClX$ and $CF_2X\cdot CF_2Cl$ (X = Br or I); this was particularly surprising since it has been reported that iodine bromide and iodine chloride add specifically to the olefin. Barr *et al.*[15a] claimed that $CF_2Cl\cdot CFClI$ was the only product from iodine chloride and chlorotrifluoroethylene, and Haszeldine[15b] supported this conclusion since the iodide, on fluorination and subsequent dehalogenation, yielded tetrafluoroethylene; it was also claimed[15b] that iodine bromide and chlorotrifluoroethylene yielded $CF_2Br\cdot CFClI$ but no $CF_2I\cdot CFClBr$. Since the addition of " bromine fluoride " and " iodine fluoride " to chlorotrifluoroethylene was not specific this was an apparent contradiction to the view that reactions of these mixtures with fluoro-olefins involve the monofluorides.

However, the reactions of chlorotrifluoroethylene with iodine bromide and chloride have been reinvestigated and we have found that a substantial amount of both possible isomers was obtained in each case:

$$2CF_2{:}CFCl + 2IX \longrightarrow CF_2X\cdot CFClI + CF_2I\cdot CFClX \quad (X = Br \text{ or } Cl)$$

The reactions were carried out in an autoclave under conditions similar to those used by Haszeldine;[15b] $CF_2Cl\cdot CFClI$ and $CF_2I\cdot CFCl_2$ were separable by gas chromatography, and $CF_2I\cdot CFCl_2$ (together with $CF_3\cdot CCl_2I$) was obtained independently from the reaction between " iodine fluoride " and 1,1-dichlorodifluoroethylene. When a mixture of $CF_2Cl\cdot CFClI$ and $CF_2I\cdot CFCl_2$ was irradiated with ultraviolet light, in the presence of mercury, $CF_2Cl\cdot CFClI$ quickly reacted to give coupled products, whereas $CF_2I\cdot CFCl_2$ was relatively unchanged. Only partial separation of the peaks could be obtained when $CF_2Br\cdot CFClI$ and $CF_2I\cdot CFClBr$ were examined by gas chromatography but, by collecting early and late cuts as the components emerged from the detector, two fractions with equivalent analysis but different infrared spectra were isolated. The isomers were distinguished by irradiation with ultraviolet light, in the presence of mercury: $CF_2Br\cdot CFClI$ coupled rapidly, leaving $CF_2I\cdot CFClBr$ relatively unchanged; the carbon–iodine bond in a group $-CFClI$ is much weaker than the corresponding bond in $-CF_2I$.

The " halogen monohalides " react with fluoro-olefins which contain no other halogen, to give products which can be predicted by a consideration of the polarisation resulting from a difference in electronegativity between the halogens in the halogen halide, and of the point at which the nucleophile usually becomes attached to the fluoro-olefin. However, this situation does not apply when other halogens are present in the olefin; a steric factor appears to operate. Crowding will exist in a group $-CFXY$ (X = Cl: Y = Br or I) and there will be a consequent tendency to resist its formation. Thus, this steric factor encourages the formation of $CF_2I\cdot CFClY$ (Y = Br, Cl, or F) from chlorotrifluoroethylene when other considerations predict only $CF_2Y\cdot CFClI$; 1,1-dichlorodifluoroethylene yielded $CF_2I\cdot CFCl_2$ and $CF_3\cdot CCl_2I$ with " iodine fluoride " when only $CF_3\cdot CCl_2I$ might have been predicted. Probably this steric factor accounts for the fact that $CFCl_2\cdot CFCl_2$, and not $CFCl_2\cdot CCl_2I$, was isolated on reaction between " iodine fluoride " and tetrachloroethylene.

EXPERIMENTAL

Unless otherwise stated, pressure reactions were performed in a stainless-steel autoclave (527 ml.). Gases were handled by standard high-vacuum techniques; molecular weights were determined by Regnault's method. Analytical-scale vapour-phase chromatography was carried out in a Griffin–George's mark II B apparatus. A preparative-scale gas-chromatography unit for separating up to 10-g. quantities was constructed in the laboratory, involving a glass tube 5 m. in length and of 22 mm. internal diameter, containing the appropriate stationary phase supported on 44—60 mesh Celite. The detector involved a slight modification of that described by Musgrave,[16] by allowing part of the gas-stream from the column to by-pass the detector. A Grubb–Parsons type G.S.2A infrared spectrophotometer was used.

---

[15] (*a*) Barr, Gibson, and Lafferty, *J. Amer. Chem. Soc.*, 1951, **73**, 1352; (*b*) Haszeldine, *J.*, 1952, 4423.

[16] Musgrave, *Chem. and Ind.*, 1959, 46.

General Note on Reactions of a Mixture of Iodine Pentafluoride and Iodine with Fluoro-olefins.—The molecular proportions used in these reactions were those required by the scheme $5C{:}C + IF_5 + 2I_2 \longrightarrow 5CI{\cdot}CF$. Yields are based on the amount of olefin which reacted.

Tetrafluoroethylene.—Teflon was pyrolysed at 550—600°/5 mm., giving tetrafluoroethylene (95%) which was purified by low-temperature distillation. An autoclave was charged with iodine pentafluoride (44·4 g., 0·2 mole), iodine (102 g., 0·4 mole), and tetrafluoroethylene (100 g., 1·0 mole) and then rotated for 10 hr. without heating. The autoclave was vented through cold traps to condense volatile material, leaving unchanged iodine and a residual liquid. Fractionation of the volatile material and distillation of the residue afforded pentafluoroiodoethane (152 g., 86%) (Found: F, 38·2; I, 51·8%; *M*, 245·3. Calc. for C_2F_5I: F, 38·6; I, 51·6%; *M*, 245·9), and recovered tetrafluoroethylene (28·5 g.). A small amount of high-boiling material was obtained as residue, which was probably the di-iodide $CF_2I{\cdot}CF_2I$.

1,1-*Difluoroethylene.*—An autoclave, charged with iodine pentafluoride (18 g., 0·081 mole), iodine (40 g., 0·157 mole), and 1,1-difluoroethylene (25 g., 0·390 mole), was rotated for 15 hr. at 103°. The autoclave was vented through cold traps but no gaseous material was collected. The remaining liquid was washed free from iodine with dilute aqueous sodium thiosulphate, dried ($CaCl_2$), and distilled, giving 1,1,1-trifluoro-2-iodoethane (70 g., 85·5%) (Found: I, 61·3%; *M*, 209. Calc. for $C_2H_2F_3I$: I, 61·4%; *M*, 210), b. p. 54·8°, n_D^{25} 1·3980 (lit.,[17a] 55°, 1·3981). Confirmation of structure was obtained by preparing an authentic sample, according to the method of Henne, Alm, and Smook [17b] from 2,2,2-trifluoroethanol (treatment of the toluene-*p*-sulphonate with sodium iodide). The authentic 1,1,1-trifluoro-2-iodoethane had an infrared spectrum identical with that of the reaction product, which was therefore not a mixture containing 1,1,2-trifluoro-1-iodoethane.

Hexafluoropropene.—An autoclave, charged with iodine pentafluoride (29·5 g., 0·132 mole), iodine (67 g., 0·264 mole), and hexafluoropropene (100 g., 0·660 mole), was rotated for 24 hr. at 150°. No gaseous material was vented from the autoclave; the residue was washed with aqueous alkaline thiosulphate, dried, and distilled, yielding *heptafluoro-2-iodopropane* (196 g., 99%) (Found: F, 44·6; I, 42·9. C_3F_7I requires F, 44·9; I, 42·8%), b. p. 38°, n_D^{20} 1·32631. Gas chromatography indicated that only one isomer was present; strong bands in its infrared spectrum at 7·75, 8·00, 8·42, 8·88, 10·40, 11·20, 13·25, 13·95, and 14·2 (doublet) distinguish $CF_3{\cdot}CFI{\cdot}CF_3$ from $CF_3{\cdot}CF_2{\cdot}CF_2I$, whose infrared spectrum is well known.[18]

Proof of Structure of Heptafluoro-2-iodopropane.—^{19}F *Resonance spectra.* The spectra of liquid C_3F_7Br and C_3F_7I were determined by using a Varian 4300-B nuclear magnetic resonance spectrometer operating at 40 Mc./sec. Both spectra consisted of a low-field doublet and a high-field septet. The intensity distribution between the multiplets is consistent with the compounds' being 2-bromoheptafluoropropane and heptafluoro-2-iodopropane. Further evidence for their identity is provided by the chemical shifts; these were measured from trifluoroacetic acid (used as an external reference) to the centres of the multiplets:

	Doublet ($CF_3{\cdot}CF{\cdot}CF_3$ group) (cycles/sec.)	Septet (·CF· group) (cycles/sec.)	Coupling constants (cycles/sec.)
C_3F_7Br	32	2600	8·9
C_3F_7I	−82	2790	12·9

Hydrolysis. Heptafluoro-2-iodopropane (4·5 g., 15·2 mmoles), potassium hydroxide (3·5 g., 62·2 mmoles), and acetone (10 ml.), sealed under vacuum, were shaken at room temperature. Reaction was complete after 30 min.; the products were separated by fractionation *in vacuo*, yielding 2*H*-heptafluoropropane (1·95 g., 75%), identified by its infrared spectrum.[19]

*Coupling Reaction: Preparation of Perfluoro-*2,3-*dimethylbutane.*—Heptafluoro-2-iodopropane (10 g., 0·0338 mole) and mercury (60 g.), contained in a Carius tube, sealed under vacuum, was irradiated with ultraviolet light and shaken for 3 days. The products were removed from the tube under a vacuum and separated by gas chromatography (tritolyl phosphate at 80°) into recovered heptafluoro-2-iodopropane (0·3 g.) and perfluoro-2,3-dimethylbutane (5·5 g., 96·5%) (Found: F, 78·4%; *M*, 337·5. Calc. for C_6F_{14}: F, 78·7%; *M*, 338), b. p. 60·0°/756 mm., n_D^{20} 1·31483.

---

[17] (*a*) Tiers, Brown, and Reid, *J. Amer. Chem. Soc.*, 1953, **75**, 5978; (*b*) Henne, Alm, and Smook, *ibid.*, 1948, **70**, 1968.

[18] " Fluorine Chemistry," ed. Simons, Academic Press, New York, 1954, Vol. II, p. 475.

[19] Ref. 18, p. 472.

Chlorotrifluoroethylene.—1,1,2-Trichlorotrifluoroethane was dechlorinated by zinc dust in ethanol.[20] The chlorotrifluoroethylene so produced was purified by distillation. An autoclave was charged with iodine pentafluoride (35 g., 0·158 mole), iodine (80·5 g., 0·317 mole), and chlorotrifluoroethylene (92·5 g., 0·794 mole) and rotated for 4 hr. without heating. The reaction was almost quantitative, giving a liquid product which, after being washed with alkaline thiosulphate, dried, and distilled, yielded a fraction, b. p. 53—57°, corresponding to chlorotetrafluoroiodoethane (171 g., 82%) (Found: F, 29·4. Calc. for C_2ClF_4I: F, 29·0%). Analytical gas chromatography (tritolyl phosphate at 42°) showed the presence of two components and these were separated by collecting samples over several runs. The first component (55% of the mixture) was 1-chlorotetrafluoro-2-iodoethane (Found: F, 29·5. Calc. for C_2ClF_4I: F, 29·0%), b. p. 57·6°, $n_D^{18·5}$ 1·395 (lit.,[21] 56·5°, 1·393). An authentic sample of 1-chlorotetrafluoro-2-iodoethane was prepared by reaction of iodine monochloride and tetrafluoroethylene in an autoclave at 50—60°; the infrared spectrum and retention time were identical with those of the above sample. The second component (45% of the mixture) was therefore 1-*chlorotetrafluoro*-1-*iodoethane* (Found: F, 28·7. C_2ClF_4I requires F, 29·0%), b. p. 57·7°, n_D^{25} 1·3900; its infrared spectrum contained strong bands at 7·80, 8·15, 8·25, 8·42, 8·85, 9·12, 10·88, 11·69 (sh), 11·88, 13·78, 13·82, and 13·92 μ (triplet).

The second component, $CF_3{\cdot}CFClI$, liberated iodine on exposure to air and light much more readily than the first.

1,1-*Dichlorodifluoroethylene.*—An autoclave charged with iodine pentafluoride (7·3 g., 0·033 mole), iodine (16·8 g., 0·066 mole), and 1,1-dichlorodifluoroethylene (22·0 g., 0·165 mole) was rotated for 6 hr. at 170°. After treatment with aqueous alkaline thiosulphate, the mixture was fractionated *in vacuo*, yielding 1,1-dichlorotetrafluoroethane (5·9 g., 25%) and recovered 1,1-dichlorodifluoroethylene (3·49), which were purified by gas chromatography (Found: F, 44·4; Cl, 41·3%; *M*, 171. Calc. for $C_2Cl_2F_4$: F, 44·5; Cl, 41·5%; *M*, 171), and a less volatile liquid fraction (21 g.). Gas chromatography showed that this material consisted of two components which were separable on the preparative-scale apparatus. The first component (57% of the mixture) was identified as 1,1-*dichlorotrifluoro*-2-*iodoethane* (12 g., 31%) (Found: F, 20·7. $C_2Cl_2F_3I$ requires F, 20·4%), b. p. 98°/763 mm., n_D^{20} 1·44450. The infrared spectrum was identical with that of one of the isomers obtained from the addition of iodine monochloride to chlorotrifluoroethylene (see below), containing strong bands at 8·41, 8·60, 9·00, 9·82, 9·95 (sh), 11·07, and 13·30 μ. The second component (43% of the mixture) must then be 1,1-dichlorotrifluoro-1-iodoethane (9 g., 23%) (Found: F, 20·6. $C_2Cl_2F_3I$ requires F, 20·4%): its infrared spectrum contained strong bands at 8·06, 8·20, 11·89, 12·78, and 14·32 μ. On exposure to air or sunlight $CCl_2I{\cdot}CF_3$ liberated iodine much more quickly than $CCl_2F{\cdot}CF_2I$.

Tetrachloroethylene.—An autoclave was charged with iodine pentafluoride (44·4 g., 0·20 mole), iodine (101·6 g., 0·40 mole), and tetrachloroethylene (165·9 g., 1·00 mole) and rotated for 12 hr. at 110°. When the autoclave was vented, it was observed that the reaction had not proceeded sufficiently, so the recovered material was replaced, and the autoclave was resealed and rotated at 190° for a further 4 hr. After the removal of iodine, the products were distilled through a concentric-tube column (20 theoretical plates), and a fraction of b. p. 92—93° (41·5 g., 51%) was collected, corresponding to tetrachloro-1,2-difluoroethane (Found: F, 18·8; Cl, 69·1. Calc. for $C_2Cl_4F_2$: F, 18·6; Cl, 69·6%), b. p. (centre cut) 93·0° (lit.,[22] 93·0°). The residue (100 g.) consisted of unchanged tetrachloroethylene.

General Note on Reactions of Fluoro-olefins with a Mixture of Bromine Trifluoride and Bromine.—The molecular proportions used in these reactions were those required by the scheme $3C{:}C + BrF_3 + Br_2 \longrightarrow 3CF{\cdot}CBr$.

Tetrafluoroethylene.—An autoclave charged with tetrafluoroethylene (16·9 g., 0·169 mole), bromine trifluoride (7·7 g., 0·0562 mole), bromine (9 g., 0·0563 mole), and 1,1,2-trichlorotrifluoroethane (230 g.), as diluent, was rotated for 2 hr. without heating (a previous reaction, without diluent, was very vigorous, causing decomposition and formation of carbon tetrafluoride). Gaseous material vented from the autoclave, and that produced by refluxing the solvent, consisted of tetrafluoroethylene (2 g.) and bromopentafluoroethane (2 g.,) (Found: F, 47·7; Br, 39·5%; *M*, 201. Calc. for C_2BrF_5: F, 47·7; Br, 40·2%; *M*, 199) (correct infrared

---

[20] Buxton, Ingram, Smith, Stacey, and Tatlow, *J.*, 1952, 3830.

[21] Haszeldine, *J.*, 1953, 2075.

[22] Miller, *J. Amer. Chem. Soc.*, 1940, **62**, 341.

spectrum [23]). No further amount of bromopentafluoroethane could be obtained from the residual solvent by distillation but separation of an aliquot part by preparative-scale gas chromatography (tritolyl phosphate at 20°) showed that a considerable quantity of bromopentafluoroethane (18 g.) remained inseparable from the solvent.

Hexafluoropropene.—An autoclave charged with hexafluoropropene (25 g., 0·167 mole), bromine trifluoride (7·5 g., 0·055 mole), and bromine (9 g., 0·056 mole) was rotated for 2 hr. without heating. The gaseous products were distilled at atmospheric pressure, yielding 2-*bromoheptafluoropropane* (16 g., 45·5%), contaminated with a small amount of hexafluoropropene. A pure sample was obtained by preparative-scale gas chromatography (tritolyl phosphate at 20°) (Found: F, 53·8; Br, 31·2%; *M*, 248. C_3BrF_7 requires F, 53·4; Br, 32·1%; *M*, 248·9). Strong infrared bands at 7·74, 8·07, 8·81, 10·38, 10·73, 13·17 (sh), 13·23, 13·30 (sh), 13·92 (sh), and 14·00 μ distinguished this compound from 1-bromoheptafluoropropane.[18] The structure of this compound was also confirmed by ^{19}F resonance measurements (see under heptafluoro-2-iodopropane). The remaining gaseous material (3·8 g., condensing at −183°) was unchanged hexafluoropropene.

Chlorotrifluoroethylene.—An autoclave charged with bromine trifluoride (20·5 g., 0·148 mole), bromine (24 g., 0·150 mole), chlorotrifluoroethylene (145 g.), and 1,1,2-trichlorotrifluoroethane (154 g.) was rotated for 2 hr. without heating. Unchanged chlorotrifluoroethylene (7 g.) was vented from the autoclave and separation of aliquot parts of the residue by both preparative and analytical-scale gas chromatography (dinonyl phthalate at 50°) showed, apart from the solvent peak, a single peak of material whose analyses indicated bromochlorotetrafluoroethane (72 g., 86%) (Found: F, 34·9%; *M*, 216·7. Calc. for C_2ClBrF_4: F, 35·3%; *M*, 215·4). The infrared spectrum contained, not only the bands corresponding to 2-bromo-1-chlorotetrafluoroethane (prepared from tetrafluoroethylene and a mixture of bromine and chlorine; see below), but also strong bands at 7·74, 8·02, 8·15 (doublet), 10·73, 11·39, 13·16, 13·25, and 13·33 μ (triplet) that were attributed to 1-bromo-1-chlorotetrafluoroethane. The relative proportions of these isomers were estimated by using a calibration graph drawn for the infrared absorption bands at 9·62 and 11·10 μ in the spectrum of $CF_2Br{\cdot}CF_2Cl$. The mixture contained 85% of $CF_2Cl{\cdot}CF_2Br$. Distillation of the solvent residue through a packed column (80 cm.) yielded a fraction, b. p. 21—23°, which was pure bromochlorotetrafluoroethane (mixture of isomers).

Synthesis of 2-*Bromo*-1-*chlorotetrafluoroethane.*—An autoclave, charged with bromine (65 g., 0·813 mole), chlorine (29 g., 0·817 mole), and tetrafluoroethylene (81·7 g., 0·817 mole), was rotated for 2 hr. without heating. The contents of the autoclave were vented through cooled traps, and products were separated from unchanged tetrafluoroethylene by fractionation *in vacuo*. Gas chromatography (tritolyl phosphate at 42°) showed that the product contained 3 components, which were then separated. One of these components was 2-bromo-1-chlorotetrafluoroethane (Found: F, 34·7%; *M*, 216·8. Calc. for C_2ClBrF_4: F, 35·3%; *M*, 215·4), $\nu_{max.}$ (strong) 7·92, 8·40, 8·79, 9·62, 11·10, 11·35 (sh), and 12·32 μ. The other two components were not investigated but were probably $CF_2Cl{\cdot}CF_2Cl$ and $CF_2Br{\cdot}CF_2Br$.

Decafluorocyclohexene.—An autoclave (10 ml. capacity), charged with decafluorocyclohexene (6·5 g., 24·8 mmoles), bromine trifluoride (1·13 g., 8·25 mmoles), and bromine (1·32 g., 8·26 mmoles), was shaken for 26 hr. at 265°. Bromoundecafluorocyclohexane (7 g., 78%) was obtained (Found: F, 57·6; Br, 23·2. Calc. for C_6BrF_{11}: C, 57·9; Br, 22·2%), b. p. 92°/735 mm. (lit.,[24] 90—92°), having n_D^{20} 1·32206.

Addition of Iodine Monochloride to Chlorotrifluoroethylene.—An autoclave charged with iodine monochloride (28 g., 0·172 mole) and chlorotrifluoroethylene (20 g., 0·172 mole) was rotated for 3 hr. at 45°. A purple liquid (45 g.) was recovered from the autoclave; this liquid was washed with aqueous alkaline thiosulphate, dried ($MgSO_4$), and distilled; the bulk of the material boiled at 97—101° (41 g.). Gas chromatography showed that the distillate consisted almost entirely of two components (33% and 67%) whose retention times did not differ sufficiently to allow complete separation. However, pure samples of each component were obtained by collecting early and late cuts corresponding to the chromatogram. That complete separation had been achieved could be observed from the infrared spectra which differed completely: the first component (Found: F, 19·6. Calc. for $C_2Cl_2F_3I$: F, 20·4%) had a spectrum identical with that of 1,1-dichlorotrifluoro-2-iodoethane, being one of the isomers obtained from the addition of iodine pentafluoride and iodine to 1,1-dichlorodifluoroethylene (see above). The

---

[23] Ref. 18, p. 474.

[24] Lazerte, Pearlson, and Kauck, U.S.P. 2,647,933/1953.

second component was therefore 1,2-*dichlorotrifluoro*-1-*iodoethane* (Found: F, 19·8. $C_2Cl_2F_3I$ requires F, 20·4%); the infrared spectrum of $CFClI{\cdot}CF_2Cl$ contained strong bands at 8·34, 8·48 (doublet), 8·60 (sh), 9·06, 9·68, 11·49, 12·01, 12·50, and 13·52 μ. This was confirmed by irradiating a mixture of $CFCl_2{\cdot}CF_2I$ and $CFClI{\cdot}CF_2Cl$ with ultraviolet light, in the presence of mercury: the isomer to which the formula $CFClI{\cdot}CF_2Cl$ has been assigned, coupled very rapidly, leaving $CFCl_2{\cdot}CF_2I$ relatively unchanged.

Addition of Iodine Monobromide to Chlorotrifluoroethylene.—An autoclave charged with iodine monobromide (142 g., 0·686 mole) and chlorotrifluoroethylene (81 g., 0·695 mole) was rotated for 2 hr. at 100°. The products were washed with aqueous alkaline thiosulphate and distilled under reduced pressure, giving a colourless distillate (168 g.) which rapidly liberated iodine on exposure to light. Preparative-scale gas chromatography showed that the distillate contained 1,2-dibromo-1-chlorotrifluoroethane (38 g.) (Found: F, 20·2. Calc. for $C_2Br_2ClF_3$: F, 20·6%), and two other components (24% and 76%) with similar retention times. A pure sample of the last component was collected (tritolyl phosphate at 110°) which was 2-*bromo*-1-*chlorotrifluoro*-1-*iodoethane*, $CFClI{\cdot}CF_2Br$ (Found: F, 17·3. C_2BrClF_3I requires F, 17·6%), having strong infrared bands at 8·39 (sh), 8·48, 9·05, 9·88, 11·43 (sh), 11·54, 12·00, 12·09 (doublet), 13·02, and 14·20 μ. The other isomer, 1-*bromo*-1-*chlorotrifluoro*-2-*iodoethane*, $CFClBr{\cdot}CF_2I$, was obtained by irradiating a portion of the mixture with ultraviolet light, in the presence of mercury: $CFClI{\cdot}CF_2Br$ reacted very quickly, leaving unchanged $CFClBr{\cdot}CF_2I$ which was isolated by gas-chromatography (tritolyl phosphate at 130°) (Found: F, 18·0. C_2BrClF_3I requires F, 17·6%), b. p. 120·1°/768 mm.; $CFClBr{\cdot}CF_2I$ had strong infrared bands at 8·30, 8·45, 8·60 (doublet), 9·02, 9·30 (sh), 9·42, 11·30, 11·58, 12·03, 13·40, 13·51, and 14·17 μ.

Halogen Analyses.—These were carried out by the biphenyl–sodium method of decomposition;[25] it is ideal for application to halogen-containing gases.[26]

We thank Dr. L. H. Sutcliffe of the University of Liverpool for the nuclear magnetic resonance measurements, and the Department of Scientific and Industrial Research for a Maintenance Allowance (to J. S.).

THE UNIVERSITY, SOUTH ROAD, DURHAM.

[*Received, April 17th*, 1961.]

---

[25] Johncock, Musgrave, and Wiper, *Analyst*, 1959, **84**, 245.
[26] Chambers, Musgrave, and Savory, *Analyst*, 1961, **86**, 356.