849. *Fluoro-olefins. Part I. The Synthesis of Hexafluorobuta-1 : 3-diene.*

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A general method for the synthesis of fluorohalogenobutadienes * is described and illustrated by the conversion of chlorotrifluoroethylene into hexafluorobuta-1 : 3-diene in 80% yield. Addition of iodine monochloride or monobromide to chlorotrifluoroethylene gives chlorofluoro- and bromochlorofluoroiodo-compounds, which react readily with mercury in ultra-violet light or with zinc in dioxan, to yield hexafluoro-1 : 2 : 3 : 4-tetrahalogenobutanes. Dehalogenation of the last compounds with zinc and ethanol affords hexafluorobutadiene. Syntheses of certain fluoro- and fluorohalogeno-butenes, including octafluorobut-2-ene, are described, and infra-red and ultra-violet spectra are presented and discussed.

TETRAFLUOROETHYLENE is of great value in synthetic organic fluorine chemistry and is finding industrial application. Potentially as important is hexafluorobuta-1 : 3-diene, but the only synthesis for this compound yet described is that by Miller *et al.* (*Ind. Eng. Chem.*, 1947, **39**, 401). Direct fluorination of 1 : 2-dichlorodifluoroethylene at −78° gave a fluorine-containing dimer $C_4Cl_4F_6$, in 44% optimum yield, as well as the expected dichlorotetrafluoroethane; dechlorination of the compound $C_4Cl_4F_6$ afforded hexafluorobutadiene. The disadvantages of this method are that elementary fluorine is required, the yield of $C_4Cl_4F_6$ is low, and by-products such as chloropentafluoroethane, 1 : 1 : 2-trichlorotrifluoroethane, 1 : 2-difluorotetrachloroethane, a pentachloropentafluorobutane, and a hexachlorotetrafluorobutane, are produced. Using hexafluorobutadiene prepared in this way, Miller and his co-workers (*loc. cit.*; Prober and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 598) have shown the potential interest of hexafluorobutadiene and have reported its polymerisation initiated by heat or by fluorine. Since the work reported below was completed, Miller ("Preparation and Properties and Technology of Fluorine and Organic Fluoro-compounds," Editors Glasser and Schram, McGraw Hill, 1951, pp. 567—685) has reported an alternative procedure developed during the recent war for the preparation of hexafluorobutadiene from chlorotrifluoroethylene involving pyrolysis at 500°, to give 3 : 4-dichlorohexafluorobut-1-ene, followed by dechlorination. The yields by this procedure are apparently low (30—40%).

A simple general method for the conversion of suitable fluoroethylenes into dienes is now illustrated by the preparation of hexafluorobutadiene from commercially available chlorotrifluoroethylene.

Addition of iodine monochloride or monobromide to chlorotrifluoroethylene gives 1 : 2-dichloro- (I) and 1-bromo-2-chloro-1 : 1 : 2-trifluoroiodoethane (II) in almost quantitative yield. The reaction takes place readily under slight pressure in absence of a solvent, or somewhat more slowly when the chlorotrifluoroethylene is passed through a suspension of the iodine halide in solvents such as carbon tetrachloride, 1 : 1 : 2-trichlorotrifluoroethane, 1 : 2-dibromo-1-chlorotrifluoroethane, or any fluoro- or fluorohalogeno-compound of suitable boiling point. The use of (I) or (II) as reaction media is also convenient, since the necessity for subsequent efficient fractional distillation is thereby removed. As might be expected the addition of iodine chloride occurs at a much lower temperature than that of iodine bromide. The only by-product is the compound in which the iodine atom in (I) or (II) has been replaced by chlorine or bromine. This is ascribed either to the reaction of chlorotrifluoroethylene with chlorine or bromine (formed by dissociation of the iodine halide into iodine and halogen), or to the secondary reaction of (I) or (II) with the iodine halide or halogen. The by-products 1 : 1 : 2-trichlorotrifluoroethane and 1 : 2-dibromo-1-chlorotrifluoroethane are dehalogenated to chlorotrifluoroethylene in almost theoretical yield, so that the preparation of (I) and (II) is essentially quantitative.

$CClF_2{\cdot}CClIF$	$CBrF_2{\cdot}CClIF$	$CIF_2{\cdot}CCl_2F$	$CClF_2{\cdot}CHClF$
(I)	(II)	(III)	(IV)

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* Used in this sense, "halogen" excludes fluorine.

The constitution of (I) follows from its conversion into the known 1 : 2-dichlorotetrafluoroethane and thence into tetrafluoroethylene [(I) $\longrightarrow (CClF_2)_2 \longrightarrow C_2F_4$; cf. the possible isomer (III) which would yield 1 : 1-dichlorotetrafluoroethane], by mild treatment with cobalt trifluoride. It is confirmed by conversion of (I) into (IV) by irradiation in a solvent from which hydrogen is readily abstracted by the fluorohalogeno-radical:

$$\text{(I)} \xrightarrow[\text{Hg}]{\text{Light}} CClF_2{\cdot}CClF{\cdot} \xrightarrow{\text{RH}} \text{(IV)} \qquad (+\ R{\cdot})$$

Zinc and ethanol removed chlorine from (IV), to give the known trifluoroethylene [cf. (III) which would yield 1 : 1-dichloro-1 : 2 : 2-trifluoroethane; this compound is probably inert to zinc under the conditions used, but if anything would give 1-chloro-1 : 2-difluoroethylene]. Barr, Gibson, and Lafferty (*ibid.*, 1951, **73**, 1352) have recently described the preparation of (I), but assigned the structure only by analogy.

The structure of (II) was proved in a similar manner. Reaction with cobalt trifluoride gave 1-bromo-2-chlorotetrafluoroethane, and thence tetrafluoroethylene by removal of equimolar amounts of bromine and chlorine. The possible isomer (V) would have given 1-bromo-1-chlorotetrafluoroethane. Irradiation of (II) in a hydrogen-containing organic solvent gave (VI), which was converted into trifluoroethylene by removal of equimolar amounts of bromine and chlorine [(V) would have given 1-bromo-1-chloro-1 : 2 : 2-trifluoroethane].

$$\text{(V)} \quad ClF_2{\cdot}CClBrF \qquad\qquad CBrF_2{\cdot}CHClF \quad \text{(VI)}$$

The direction of addition of I^+X^- to chlorotrifluoroethylene is in agreement with the addition of alcohols and amines under conditions favouring ionic reactions (Hanford and Rigby, U.S.P. 2,409,274/1946; Miller, Fager, and Griswold, *J. Amer. Chem. Soc.*, 1948, **70**, 431; Young and Tarrant, *ibid.*, 1949, **71**, 2432; Pruett *et al.*, *ibid.*, 1950, **72**, 3646). In all instances the negative substituent becomes attached to the $:CF_2$ group; this may be attributed to importance of resonance forms $\overset{-}{F}\ \overset{+}{CF}{:}CClF \longleftrightarrow CF_2{:}CClF \longleftrightarrow \overset{+}{F}{:}CF{\cdot}\overset{-}{C}ClF$ giving a polarisation $\overset{\delta+}{CF_2}{:}\overset{\delta-}{CClF}$.

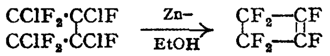
Photochemical chlorination or bromination of (I) yielded 1 : 1 : 2-trichloro- and 1-bromo-1 : 2-dichloro-trifluoroethane, and of (II) yielded 1-bromo-2 : 2-dichloro- and 1 : 2-dibromo-1-chloro-trifluoroethane. (I) readily combines with mercury in ultra-violet light, to give 1 : 2-dichloro-1 : 2 : 2-trifluoroethylmercuric iodide. Irradiation under more stringent conditions gives the mercuric iodide only transiently, if at all, and the 1 : 2-dichloro-1 : 1 : 2-trifluoroethyl radical dimerises to give 1 : 2 : 3 : 4-tetrachlorobutane in high yield:

$$CClF_2{\cdot}CClIF \xrightarrow[\text{Light}]{\text{Hg,}} (CClF_2{\cdot}CClF)_2 \qquad \text{(VII)}$$

The butane (VII) is also formed by photolysis of the mercuri-iodide in an inert solvent (perfluoromethyl*cyclo*hexane). Dimerisation of the bromo-compound (II) similarly yields 1 : 4-dibromo-2 : 3-dichlorohexafluorobutane. Thus the replacement of fluorine in the trifluoromethyl or pentafluoromethyl radicals (which dimerise with difficulty and are often preferentially decomposed on the glass or silica of the containing vessel) by chlorine or bromine gives radicals of decreased activity and longer life, which dimerise readily. Dehalogenation of the hexafluoro-1 : 2 : 3 : 4-tetrahalogenobutanes to hexafluorobuta-1 : 3-diene is almost quantitative.

Conversion of (I) into hexafluorobutadiene is more conveniently effected by the preferential coupling by intermolecular deiodination when a concentrated solution of (I) in dioxan is treated at low temperatures with zinc. Under such conditions the intramolecular dehalogenation of (I) to chlorotrifluoroethylene occurs to only a slight extent. By increasing the temperature, (VII) can then be converted *in situ* into hexafluorobutadiene.

The possibility of hexafluoro*cyclo*butene formation from (VII) by the sequence:



can be eliminated, since the products absorb two molecules of chlorine or bromine to give the hexafluoro-1 : 2 : 3 : 4-tetrahalogenobutanes. Furthermore, the presence of two conjugated double bonds in the diene, which readily decolorises acetone–permanganate, is shown by the ultra-violet and the infra-red spectrum. The considerably more powerful absorption of hexafluorobutadiene is apparent from the Table where it is compared with four mono-olefins containing only carbon and fluorine.

Extinction coefficients.

λ(mμ) :	230	225	220	215	210	206
$CF_2{:}CF\cdot CF{:}CF_2$	250	430	760	1350	2130	2800
$CF_3\cdot CF{:}CF\cdot CF_3$	2·2	3·2	4·6	6·8	11·6	—
$CF_2{:}CF_2$	0·3	1·0	2·1	3·8	6·0	10·0
$CF_3\cdot CF{:}CF_2$	0·03	0·06	0·08	0·14	0·30	0·65
$\overline{CF_2\cdot CF{:}CF\cdot CF_2}$	—	0·02	0·04	0·08	0·13	0·18

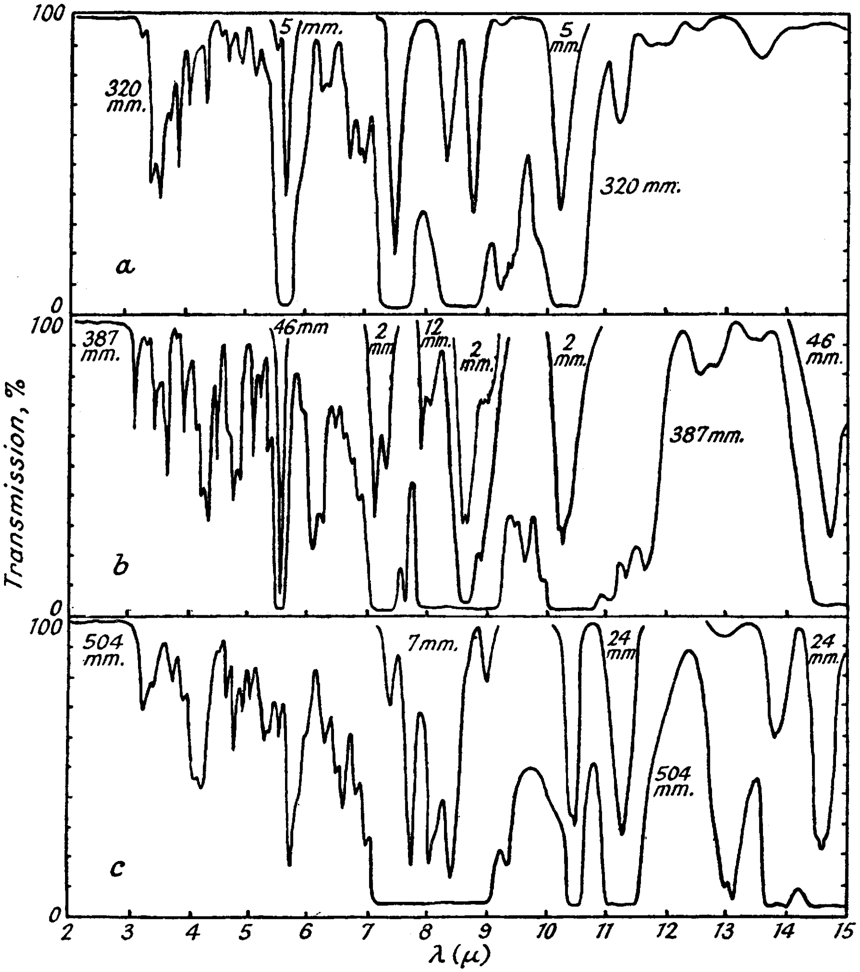
The most significant point in the Table is that the intensity of absorption of hexafluorobutadiene is much less than that of butadiene ($\lambda_{max.}$ 217 mμ, $\varepsilon = 21{,}000$; Smakula, *Angew. Chem.*, 1934, **47** 657) or of hexachlorobutadiene ($\lambda_{max.}$ 251·5 mμ, $\varepsilon = 4400$; $\lambda_{max.}$ 222 mμ, $\varepsilon = 17{,}800$; $\lambda_{min.}$ 244·5 mμ, $\varepsilon = 4200$). Thus replacement of hydrogen by chlorine produces an extra band at longer wave-length, although there is still the "typical" butadiene band at 220 mμ with ε *ca.* 20,000, whereas on replacement of hydrogen by fluorine the butadiene band at 220 mμ is considerably displaced to a lower wave-length. This, and the reduction in intensity of absorption, indicate that the unsaturation electrons in hexafluorobutadiene are much more localised and are available for conjugation to a much smaller extent than might have been expected.

Butadiene shows C═C absorption in the infra-red at 6·24 and 6·30 μ (doublet), a marked shift to longer wave-length compared with ethylene (6·16 μ); the replacement of hydrogen by chlorine to give hexachlorobutadiene causes a further displacement to 6·39 μ. The C═C absorption in hexafluorobutadiene (Fig. 1*a*) is, for a diene, at the remarkably low wave-length of 5·65 μ, and comparison with that in tetrafluoroethylene (5·35 μ; Torkington and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 236) and with the C═C absorption at 5·56 μ in compounds of the type $R\cdot CF{:}CF_2$ (R = H, Cl, CF_3, or C_2F_5) (unpublished data; see below) reveals that the conjugation effect exists, but is small. The spectrum of hexafluorobutadiene is of great value for characterisation, and that of the isomeric hexafluoro*cyclo*butene (Fig. 1*b*) is sufficiently different to render feasible its detection as impurity in the diene.

Octafluorobut-2-ene has been prepared from chlorotrifluoroethylene or hexafluorobutadiene *via* 1 : 4-dichlorohexafluorobut-2-ene. The last compound is obtained by partial dechlorination of 1 : 2 : 3 : 4-tetrachlorohexafluorobutane with zinc and dioxan; dehalogenation is slow at room temperature, and under vigorous reflux yields only hexafluorobutadiene, but with suitable intermediate conditions moderate yields of the dichloro-compound may be obtained. The 1 : 4-dichlorohexafluorobut-2-ene absorbs chlorine or bromine, to give the hexafluorotetrahalogenobutanes (which readily give hexafluorobutadiene with zinc and ethanol), and on oxidation yields chlorodifluoroacetic acid; treatment with zinc and ethanol or with zinc alone fails to give hexafluorobutadiene. The possible alternative products of the zinc–dioxan dehalogenation, 1 : 2-dichlorohexafluoro*cyclo*butane and 3 : 4-dichlorohexafluorobut-1-ene, can thus be eliminated. The chlorine atoms in 1 : 4-dichlorohexafluorobut-2-ene, like other allylic halogen atoms in the system $C{:}C\cdot CF_2X$, are much more reactive to bases, amines, ammonia, etc., than is the chlorine atom in, say, chloroheptafluoropropane. In particular, treatment under mild conditions with antimony trifluoride gives a high yield of octafluorobut-2-ene [$(CClF_2\cdot CClF)_2 \longrightarrow (CClF_2\cdot CF{:})_2 \longrightarrow (CF_3\cdot CF{:})_2$], the structure of which was proved by its reaction with chlorine and bromine and by its oxidation to 1·5 mols. of trifluoroacetic acid.

The boiling points of octafluoro-but-1-ene, -but-2-ene, and -*iso*butene are very similar, but these compounds are readily distinguished from each other and from others of similar boiling point (*e.g.*, perfluoro-*n*-butane, hexafluoro*cyclo*butene, hexafluorobutadiene) by their infra-red spectra. That of octafluorobut-2-ene is shown in Fig. 1*c* and, if the band at 5·77 μ is attributed to the C=C stretching vibration, it follows that the but-2-ene contains at least some of the *cis*-isomer. This interpretation is supported by the band at 5·74 μ in perfluoro*cyclo*hexene where *cis*-configuration is essential; the low value of 5·59 μ for hexafluoro*cyclo*butene is attributed to ring strain. As might be expected from the fact that they contain three fluorine atoms attached to the double bond, the C=C stretching absorption in octafluorobut-1-ene and hexafluoropropene is at 5·56 μ, nearer to that of tetrafluoroethylene.

FIG. 1*a*—*c*.



a, CF_2:CF·CF:CF_2, *vapour in* 50 *mm. cell.*
b, CF_2·CF:CF·CF_2, ,, 100 ,,
c, CF_3·CF:CF·CF_3, ,, 50 ,,

The addition of bromine or chlorine to hexafluorobutadiene under conditions favouring a free radical reaction proceeds stepwise. At room temperature one molecule of bromine is absorbed to give, quantitatively, a mixture (*A*) of 1 : 4-dibromohexafluorobut-2-ene and 3 : 4-dibromohexafluorobut-1-ene. Photochemical chlorination at low temperature similarly yields a mixture of 1 : 4-dichlorohexafluorobut-2-ene and 3 : 4-dichlorohexafluorobut-1-ene, but 1 : 2 : 3 : 4-tetrachlorohexafluorobutane and unchanged hexafluorobutadiene were also detected; the rates of addition of chlorine to hexafluorobutadiene and to one, or both, of the dichlorohexafluorobutenes are clearly comparable. The hexafluoro-1 : 4- and

-3 : 4-dihalogenobutenes are easily distinguished by infra-red spectroscopy. In the following Table are given the C═C stretching vibrations of olefins containing the $\cdot CF{:}CF_2$ or $\cdot CF{:}CF\cdot$ groups. It is evident that compounds containing a double bond of the first type have a band at *ca.* 5·56 μ, whereas those with a double bond of the second type have a band at *ca.* 5·77 μ. Considering now the compound $CXF_2\cdot CXF\cdot CF{:}CF_2$, it can be predicted that it will show a band in the C═C stretching region at *ca.* 5·60 μ, the increase in wave-length being due to replacement of the C_2F_5 group by the heavier and less electronegative $CClF_2\cdot CClF$ group. Similarly, the C═C stretching vibration in $(CXF_2\cdot CF{:})_2$ would be predicted at *ca.* 5·80 μ. The mixture of the dibromo-compounds shows bands at 5·62 and 5·85 μ, and of the dichloro-compounds show bands at 5·61 and 5·84 μ.

	$CF_2{:}CClF$	$CF_2{:}CHF$	$CF_2{:}CF\cdot CF_3$	$CF_2{:}CF\cdot C_2F_5$	$(CF_2{:}CF)_2$	$(CF_3\cdot CF{:})_2$
λ (μ)	5·57	5·57	5·56	5·56	5·65	5·77

Treatment of the mixture (*A*) (X = Br) with zinc and ethanol converted the 3 : 4-dibromo-compound present into hexafluorobutadiene. The unchanged material then showed only one band in the C═C stretching region, at 5·85 μ, and was the 1 : 4-dibromo-compound; treatment with antimony trifluorodichloride converted it into octafluorobut-2-ene. The ratio of 3 : 4- to 1 : 4-addition products was approximately 2 : 3. Reversal of the procedure, *i.e.*, treatment of the mixture of dibromohexafluorobutenes first with antimony trifluorodichloride, then with zinc and ethanol, gave a ratio of 1 : 1, so that isomerisation may take place during reaction :

$$\begin{tikzcd}
Br\cdot + C_4F_6 \arrow[r] & CBr_2F\cdot\dot{C}F\cdot CF{:}CF_2 \arrow[r, "Br_2"] \arrow[d, leftrightarrow] & CBrF_2\cdot CBrF\cdot CF{:}CF_2 \arrow[d, shift right, "(Zn\text{-}EtOH)"'] \\
& CBrF_2\cdot CF{:}CF\cdot CF_2\cdot \arrow[r, "Br_2"] & CBrF_2\cdot CF{:}CF\cdot CBrF_2 \arrow[u, shift right, "(SbF_3Cl_2)"']
\end{tikzcd}$$

Application of the dehalogenation technique to the mixture of dichlorohexafluorobutenes similarly removed the 3 : 4-dichloro-compound, and the residual dichloro-compound (C═C stretching vibration 5·84 μ) was easily converted into octafluorobut-2-ene; the ratio of hexafluoro-3 : 4- to -1 : 4-dihalogenobutenes was 1 : 2. Some 1 : 2 : 3 : 4-tetrachlorohexafluorobutane was formed during the initial reaction with chlorine, however, so this ratio may be nearer to 3 : 4, since it is to be expected that a compound $CXF_2\cdot CXF\cdot CF{:}CF_2$ will be more susceptible to radical attack than will $(CXF_2\cdot CF{:})_2$.

EXPERIMENTAL

Addition of Iodine Monochloride to Chlorotrifluoroethylene.—Chlorotrifluoroethylene (11·65 g., 0·10 mole) was condensed into an evacuated steel bomb (capacity 300 ml.), fitted with a needle valve and pressure gauge and containing iodine monochloride (20 g., 0·12 mole). The bomb was sealed and warmed to 35—40° to melt the iodine monochloride. An exothermic reaction set in on shaking, and the pressure reached a maximum of 9 atm. before dropping rapidly to 1 atm. The initial reaction was complete after 10 minutes, and after 2 hours the contents of the bomb were removed by pumping through a trap cooled in liquid air. All the chlorotrifluoroethylene had been converted into a liquid product which, after treatment with sodium thiosulphate to remove traces of iodine, was dried (P_2O_5) and distilled, giving 1 : 1 : 2-trichlorotrifluoroethane (1%), b. p. 47·5—48·0°, n_D^{25} 1·355 (Locke, Brode, and Henne, *J. Amer. Chem. Soc.*, 1934, **56**, 1726, report b. p. 47·6, n_D^{25} 1·3557), and 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (27·1 g., 97%), b. p. 99—99·5°, n_D^{20} 1·449, a colourless liquid becoming pink on exposure to light (Found : C, 8·7; I + Cl, 70·9%; *M*, 275, 280. Calc. for $C_2Cl_2IF_3$: C, 8·6; I + Cl, 71·0%; *M*, 279). Ultra-violet absorption spectrum in ethanol : Max., 261 mμ, ε = 295; Min. 233 mμ, ε = 190. Barr *et al.* (*loc. cit.*) reported b. p. 43—44°/100 mm., n_D^{25} 1·4474, for the compound obtained by the interaction of iodine chloride and chlorotrifluoroethylene.

On a larger scale, the bomb containing iodine monochloride (54 g., 0·33 mole) was evacuated, heated to 30°, and connected by a flexbile-metal pressure-tube to a cylinder of chlorotrifluoroethylene. The olefin was slowly admitted to the continuously shaken bomb, at such a rate that the temperature did not rise above 40°, until no more was absorbed (2 hours). The excess of chlorotrifluoroethylene was removed, and the residue on distillation gave 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (89·2 g., 96%). A small amount of iodine was left in the bomb.

In a reaction at atmospheric pressure, chlorotrifluoroethylene was passed by means of dispersion disc into a stirred suspension of iodine monochloride (16·2 g., 0·10 mole) in 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (80 ml.) at 45—50°. The unchanged olefin was recycled, and after 4 hours no further absorption occurred. After removal of iodine with sodium thiosulphate, the yield of distilled 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane was 87%, and of 1 : 1 : 2-trichlorotrifluoroethane 6%.

The 1 : 1 : 2-trichlorotrifluoroethane formed as a by-product was reconverted into chlorotrifluoroethylene in 95% yield by treatment with zinc and ethanol.

Proof of Structure of 1 : 2-*Dichloro*-1 : 2 : 2-*trifluoroiodoethane*.—(*a*) The iodo-compound (4·0 g.) was added dropwise during 1 hour to cobalt trifluoride (50 g.) in a horizontal copper reaction vessel at 190°. The volatile products were washed with water and fractionated *in vacuo*, to give chloropentafluoroethane (7%), b. p. −37° (Found : C, 15·3%; *M*, 155. Calc. for C_2ClF_5 : C, 15·5%; *M*, 154·5) (Calfee, Fukuhara, Young, and Bigelow, *J. Amer. Chem. Soc.*, 1940, **62**, 267, report b. p. −38°), and 1 : 2-dichlorotetrafluoroethane (72%), b. p. 4° (Found : *M*, 170. Calc. for $C_2Cl_2F_4$: *M*, 171) (Locke, Brode, and Henne, *loc. cit.*, report b. p. 3·5°), shown to be free from isomers by its infra-red spectrum and by treatment with zinc and ethanol at 90° in a sealed tube to give tetrafluoroethylene (96%) identified by infra-red spectroscopy.

(*b*) Irradiation for 7 days of an ethanolic solution (10 ml.) of pyrogallol (0·3 g.) and 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (6·1 g.) shaken vigorously at 120° in a silica tube containing mercury (10 ml.) gave, on distillation, 1 : 2-dichloro-1 : 2 : 2-trifluoroethane (47%), b. p. 28·5° (Found : *M*, 152. Calc. for $C_2HCl_2F_3$: *M*, 153) (Henne and Ladd, *ibid.*, 1936, **58**, 402, report b. p. 28°). When this was heated with zinc and ethanol to 80° (sealed tube), chlorine (96%), and no fluorine, was removed to give trifluoroethylene, identified by infra-red spectroscopy.

Photochemical Chlorination and Bromination of 1 : 2-*Dichloro*-1 : 2 : 2-*trifluoroiodoethane*.—When exposed to ultra-violet radiation for 3 days, the iodo-compound (2·1 g.) and excess of chlorine in a silica vessel gave 1 : 1 : 2-trichlorotrifluoroethane (77%), b. p. 47—48° (Found : *M*, 186. Calc. for $C_2Cl_3F_3$: *M*, 187·5). Similar treatment of 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane with bromine yielded 1-*bromo*-1 : 2-*dichlorotrifluoroethane* (80%), b. p. 71·5—72·0° (Found : C, 10·1; Br + Cl, 65·1%; *M*, 231. $C_2Cl_2BrF_3$ requires C, 10·3; Br + Cl, 65·1%; *M*, 232).

Interaction of 1 : 2-*Dichloro*-1 : 2 : 2-*trifluoroiodoethane and Mercury*.—Mercury (10 ml.) and 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (12·0 g.) were sealed in an evacuated 100-ml. silica tube which was then shaken horizontally (vibro-shaker). Intimate mixing of the mercury and iodo-compound was thereby obtained, and on exposure to ultra-violet light from a Hanovia arc situated 5 cm. from the reaction vessel, mercuric iodide was rapidly deposited. Use of an excess of mercury prevents coating of the walls of the vessel by mercuric iodide. After 48 hours the liquid mixture was transferred by heating and pumping to a cooled trap, then distilled to give unchanged 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (5%), b. p. 99—100°, 1 : 2 : 3 : 4-*tetrachlorohexafluorobutane* (82%, calc. on iodo-compound), b. p. 134·0—134·5°, 75°/106 mm., n_D^{23} 1·382 (Found : C, 15·6; Cl, 46·4. $C_4Cl_4F_6$ requires C, 15·8; Cl, 46·7%), and an unidentified by-product (*ca.* 7%), b. p. *ca.* 95°/30 mm., n_D^{23} 1·394. Miller *et al.* (*Ind. Eng. Chem.*, 1947, **39**, 401) refer to 1 : 2 : 3 : 4-tetrachlorohexafluorobutane but record no physical data.

A similar experiment, carried out in a silica tube which was rocked gently during reaction, gave an 85% yield of 1 : 2 : 3 : 4-tetrachlorohexafluorobutane (89%, calc. on the iodo-compound used) after 48 hours.

With the tube stationary during irradiation, the mercury–organic liquid interface became covered with mercuric iodide and, after 48 hours, the liquid reaction products consisted of 1 : 2 : 3 : 4-tetrachlorohexafluorobutane (71%) and unchanged 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (5%). The ethereal extract of the solid products yielded, after removal of the ether and sublimation of the residual solid, 1 : 2-*dichloro*-1 : 2 : 2-*trifluoroethylmercuric iodide* (12%) (Found : C, 5·2; I, 26·0. $C_2Cl_2IF_3Hg$ requires C, 5·0; I, 26·5%), white plates recrystallised from chloroform to m. p. 92—94° and with an odour similar to that of trifluoromethylmercuric iodide (Emeléus and Haszeldine, *J.*, 1949, 2948). On exposure to ultra-violet light while suspended in perfluoromethyl*cyclo*hexane, the mercurial (2·3 g.) was converted into mercuric iodide and 1 : 2 : 3 : 4-tetrachlorohexafluorobutane (61%).

Preparation of Hexafluorobutadiene.—To a well-stirred suspension of zinc dust (100 g.) in ethanol (100 ml.) heated under an efficient water condenser leading to traps cooled in liquid air, was added dropwise during 5 hours 1 : 2 : 3 : 4-tetrachlorohexafluorobutane (30·4 g., 0·1 mole) in ethanol (10 ml.). Steady gas evolution took place, and after a further 2 hours the contents of the liquid-air traps were passed through 5% sodium hydroxide and distilled *in vacuo*, to give hexafluorobutadiene (15·7 g., 98%), b. p. 5·8° (Found: C, 29·5; F, 70·2%; *M*, 162. Calc. for C_4F_6: C, 29·6; F, 70·4%; *M*, 162). Prober and Miller (*loc. cit.*) report b. p. 6·5—7·5°.

For comparison of infra-red spectra, hexafluoro*cyclo*butene, b. p. 1·2°, was synthesised by cyclisation of chlorotrifluoroethylene at 200° in an autoclave, followed by dechlorination of the 1 : 2-dichlorohexafluoro*cyclo*butane with zinc and boiling ethanol. Harmon, U.S.P. 2,433,844/1948, reports b. p. 1·1°.

Conversion of 1 : 2-*Dichloro*-1 : 2 : 2-*trifluoroiodoethane into Hexafluorobutadiene.*—To a vigorously stirred suspension of zinc (30 g.) in dioxan (35 ml.) at 25—30° was slowly added 25% of a solution of 1 : 2-dichloro-1 : 2 : 2-trifluoroiodoethane (17·0 g.) in dioxan (10 ml.). After a further 20 minutes, the temperature was slowly raised to 50° (or to 100° to produce hexafluorobutadiene), and, after cooling to 25° again, a second 25% of the iodo-compound solution was slowly added. This cycle of operations was repeated until complete addition of the chlorofluoroiodide had been achieved. The volatile products at this stage were chlorotrifluoroethylene (40%) and a trace of hexafluorobutadiene. Care must be taken with the intermolecular deiodination carried out in this way. If the temperature is too low, or the solution of iodo-compound too dilute, little deiodination occurs initially and when the temperature is raised a very vigorous reaction sets in which leads to almost complete chlorotrifluoroethylene formation. If the temperature is too high, intramolecular dehalogenation occurs to the exclusion of intermolecular deiodination. The intramolecular dehalogenation is favoured in ethanolic solution, and the use of dioxan, benzene, or a higher alcohol is advantageous for coupling.

The 1 : 2 : 3 : 4-tetrachlorohexafluorobutane formed by the intermolecular deiodination is converted into hexafluorobutadiene *in situ* under reflux. The total yield of hexafluorobutadiene, separated from chlorotrifluoroethylene in a vacuum system, is 60%.

Synthesis of Octafluorobut-2-ene.—1 : 2 : 3 : 4-Tetrachlorohexafluorobutane (6·10 g.) was treated with zinc powder (20 g.) and anhydrous dioxan (50 ml.) at 55—70° under a reflux condenser at such a temperature that the required product distilled off as soon as formed. After 2 hours the distillate was shaken with water; the gaseous product was hexafluorobutadiene (15%), and removal and distillation of the lower layer from the aqueous medium gave 1 : 4-*dichlorohexafluorobut*-2-*ene* (2·46 g., 40%), b. p. 65·0—65·5°, n_D^{25} 1·339 (Found: C, 20·7; Cl, 30·4%; *M*, 232. $C_4Cl_2F_6$ requires C, 20·6; Cl, 30·5%; *M*, 233), shown by infra-red spectroscopy to be free from 3 : 4-dichlorohexafluorobut-1-ene. The dioxan solution was filtered, excess of water was added, and the lower layer separated, dried, and distilled, to give unchanged 1 : 2 : 3 : 4-tetrachlorohexafluorobutane (35%), which did not react with zinc and dioxan at room temperature during 48 hours. When the chloro-compound was added during 10 hours to zinc and refluxing dioxan, 95% of hexafluorobutadiene was formed.

With alkaline potassium permanganate (*J.*, 1950, 2789), 1 : 4-dichlorohexafluorobut-2-ene (2·1 g.) gave chlorodifluoroacetic acid (1·3 mols.), b. p. 122°, characterised as its amide (Swarts, *Bull. Acad. roy. Belg.*, 1906, **50**, 42; 1907, **52**, 339).

Dropwise addition of 1 : 4-dichlorohexafluorobut-2-ene (2·3 g.) in ethanol (5 ml.) to zinc powder (10 g.) and refluxing ethanol (20 ml.) failed to yield hexafluorobuta-1 : 3-diene after 3 hours. Traces of a compound believed to be 1 : 1 : 2 : 3 : 4 : 4-hexafluorobut-2-ene were formed by reduction.

On reaction in ultra-violet light with a slight excess of chlorine, 1 : 4-dichlorohexafluorobut-2-ene (1·7 g.) gave a quantitative yield of 1 : 2 : 3 : 4-tetrachlorohexafluorobutane, identical with the compound described earlier. An excess of bromine similarly yielded 2 : 3-*dibromo*-1 : 4-*dichlorohexafluorobutane* (95%), b. p. 172—173°/760 mm., 78°/21 mm., n_D^{25} 1·425 (Found: C, 12·4; Br + Cl, 58·9. $C_4Br_2Cl_2F_6$ requires C, 12·2; Br + Cl, 58·8%), which on treatment with zinc and refluxing ethanol gave 95% of hexafluorobutadiene.

Antimony trifluoride (18 g.) and chlorine (0·5 g.) were sealed in a Carius tube, shaken vigorously, and heated gently until a homogeneous mass was obtained. The tube was opened and resealed with 1 : 4-dichlorohexafluorobut-2-ene (3·1 g.) condensed in from a vacuum system. Reaction was apparent at room temperature and was completed by 30 minutes' shaking and heating at 40°. The gaseous reaction product was octafluorobut-2-ene (2·26 g., 85%), b. p. 0·9° (Found: C, 24·0%; *M*, 199. Calc. for C_4F_8: C, 24·0%; *M*, 200). Henne and Newby (*J. Amer. Chem. Soc.*, 1948, **70**, 130) report b. p. 0·4—3·0°. With alkaline potassium permanganate this gave trifluoroacetic acid (1·5 mols.) identified as its amide. Octafluorobut-2-ene reacts quantitatively with chlorine or bromine on exposure to ultra-violet light, to give the dichloride, b. p. 63—64°, n_D^{25} 1·308 (Henne and Newby, *loc. cit.*, report b. p. 62·9°), and the *dibromide*, b. p. 96°, n_D^{25} 1·357 (Found: Br, 44·2. $C_4Br_2F_8$ requires Br, 44·4%). Minnesota Mining and Manufacturing Co. find b. p. 93° (personal communication).

Interaction of Iodine Bromide and Chlorotrifluoroethylene.—Chlorotrifluoroethylene (11·65 g.) and iodine monobromide (23 g.) in a steel bomb (capacity, 300 ml.) were heated from 30° to 100° during 2 hours. Preliminary experiments had shown that there was incomplete reaction at 60° for a similar period, but that reaction was essentially complete at 80° in 6 hours. Distillation gave unchanged chlorotrifluoroethylene (2%), 1 : 2-dibromo-1-chlorotrifluoroethane (4%), b. p. 92—92·5°, n_D^{25} 1·425 (Found : C, 8·6. Calc. for $C_2Br_2ClF_3$: C, 8·7%) (Locke, Brode, and Henne, *loc. cit.*, report b. p. 92·9°, n_D^{25} 1·4272), and 1-*bromo*-2-*chloro*-1 : 1 : 2-*trifluoroiodoethane* (84%), b. p. 82°/195 mm., n_D^{25} 1·482 (Found : C, 7·5; F, 17·4. $C_2ClBrIF_3$ requires C, 7·4; F, 17·6%). The last compound is partly decomposed by distillation at atmospheric pressure but can be distilled in the dark under partial vacuum as a colourless liquid which readily liberates iodine on exposure to light. Absorption spectrum in ethanol: Max. 267 mμ, ε = 370; Min. 241 mμ, ε = 280.

The structure of the bromo-iodo-compound was proved as follows. (*a*) Passage, during 4 hours, of 1-bromo-2-chloro-1 : 1 : 2-trifluoroiodoethane (4·9 g.) over cobalt trifluoride (50 g.) at 200° gave, after washing with water and distillation *in vacuo*, chloropentafluoroethane (12%) (Found : *M*, 156. Calc. for C_2ClF_5 : *M*, 154·5) and 1-*bromo*-2-*chlorotetrafluoroethane* (68%), b. p. 25·5° (Found : C, 11·4%; *M*, 216. C_2ClBrF_4 requires C, 11·1%; *M*, 215·5). When shaken with zinc (5 g.) and ethanol (20 ml.) in a sealed tube at 80°, 1-bromo-2-chlorotetrafluoroethane (2·4 g.) was converted into tetrafluoroethylene (95%), identified spectroscopically. The ethanolic solution contained bromide and chloride (98%) in a ratio of 1·03 : 1·00. (*b*) Irradiation by a Hanovia lamp of mercury (10 ml.) and a solution of 1-bromo-2-chloro-1 : 1 : 2-trifluoroiodoethane (5·1 g.) in ethanol (3 ml.) and light petroleum (2 ml.; b. p. 100—120°) containing pyrogallol (0·2 g.) in a silica tube shaken vigorously and heated at 120—150° for 48 hours gave 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane (53%), b. p. 52·8°, n_D^{25} 1·368 (Found : C, 12·1%; *M*, 196. Calc. for $C_2HClBrF_3$: C, 12·1%; *M*, 197·5). Park, Sharrah, and Lacher (*J. Amer. Chem. Soc.*, 1949, **71**, 2339) report b. p. 46°/619 mm. Treatment with zinc and ethanol removed bromine and chlorine (and no fluorine), in a 1 : 1 ratio, from 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane, to give trifluoroethylene (91%), b. p. −55° (Found : *M*, 82. Calc. for C_2HF_3 : *M*, 82), identified by infra-red spectroscopy. Swarts (*Bull. Acad. roy. Belg.*, 1899, **37**, 357) reports b. p. −51°.

After exposure to ultra-violet radiation for 8 hours in a silica tube, 1-bromo-2-chloro-1 : 1 : 2-trifluoroiodoethane (4·2 g.) and chlorine (100% excess) gave 1-*bromo*-2 : 2-*dichlorotrifluoroethane* (83%), b. p. 70—71° (Found : C, 10·6%; *M*, 232. $C_2Cl_2BrF_3$ requires C, 10·3%; *M*, 232). Similarly, photochemical bromination gave 1 : 2-dibromo-1-chlorotrifluoroethane, b. p. 92° (76%).

Conversion of 1-*Bromo*-2-*chloro*-1 : 1 : 2-*trifluoroiodoethane into Hexafluorobutadiene.*—Mercury (10 ml.) and 1-bromo-2-chloro-1 : 1 : 2-trifluoroiodoethane (16·2 g.) were sealed in a silica tube which was shaken vigorously and exposed to ultra-violet radiation for 3 days. The liquid products were separated from mercuric iodide by heating and pumping into a trap cooled in liquid air, and then distilled, to give 1 : 4-*dibromo*-2 : 3-*dichlorohexafluorobutane* (14·8 g., 75%), b. p. 75°/20 mm., n_D^{20} 1·427 (Found : C, 12·3; Br + Cl, 58·6. $C_4Br_2Cl_2F_6$ requires C, 12·2; Br + Cl, 58·8%), and unchanged 1-bromo-2-chloro-1 : 1 : 2-trifluoroiodoethane (<1%).

The 1 : 4-dibromo-2 : 3-dichlorohexafluorobutane (7·9 g.) dissolved in ethanol (10 ml.) was added as fast as possible to zinc powder (20 g.) in boiling ethanol (50 ml.); after 6 hours the volatile products were washed with water and fractionated *in vacuo*, to give hexafluorobutadiene (3·05 g., 92%), b. p. 5·5—6·0°, whose identity was confirmed by its infra-red spectrum.

Bromination and Chlorination of Hexafluorobutadiene.—Treatment of hexafluorobutadiene (4·0 g.) with a 5% excess of bromine at 120° with exposure to ultra-violet light gave 1 : 2 : 3 : 4-*tetrabromohexafluorobutane* (theoretical yield), b. p. 130°/70 mm., 105°/40 mm., *ca.* 210°/760 mm., n_D^{25} 1·464 (Found : C, 10·2; Br, 65·9. $C_4Br_4F_6$ requires C, 10·0; Br, 66·4%), reconverted into the diene by zinc and refluxing ethanol. Irradiation of the fluorodiene at room temperature with 1·0 mol. of bromine gave mixed dibromohexafluorobutenes, b. p. 99—100°, n_D^{25} 1·394, which on further reaction with bromine gave 1 : 2 : 3 : 4-tetrabromohexafluorobutane, identical with that described above; similarly, 1 mol. of chlorine was absorbed to give a mixture of dibromodichlorohexafluorobutanes. When the dibromohexafluorobutene mixture (4·31 g.) was added to zinc and refluxing dioxan, the yield of hexafluorobutadiene, identified spectroscopically, after 12 hours was 37%. The dioxan solution was freed from zinc by filtration, then treated with an excess of water, and the precipitated oil was dried, distilled, and heated at 40° with an excess of freshly prepared antimony trifluoride to which chlorine had been added (Sb^{III} : Sb^{V} = 1 : 1). The gaseous products, washed with 10% aqueous sodium hydroxide and distilled *in* *vacuo*, gave octafluorobut-2-ene (49%, based on original mixture), identified by spectroscopic examination of the dibromide. When the above procedure was reversed, unchanged dibromohexafluorobutene being removed from the fluorinating agent by pumping and then subjected to treatment with zinc and dioxan, the yield of octafluorobut-2-ene was 41% and of hexafluorobutadiene was 44%.

When mixed with a 5% excess of dry chlorine in a silica vessel, heated to 40°, and exposed to ultra-violet radiation for 3 minutes, hexafluorobutadiene (3·1 g.) was converted quantitatively into 1 : 2 : 3 : 4-tetrachlorohexafluorobutane, b. p. 134°, shown by infra-red spectroscopy to be identical with that described earlier.

Hexafluorobutadiene (4·4 g.) and 50% of the chlorine required for saturation were condensed into a silica tube which, after being sealed and vigorously shaken, was exposed to ultra-violet radiation and allowed to warm to room temperature. Reaction was complete in 2 minutes, and gave unchanged hexafluorobutadiene (15%), 1 : 2 : 3 : 4-tetrachlorohexafluorobutane (17%), and a mixture (61%) of 3 : 4-dichlorohexafluorobut-1-ene and 1 : 4-dichlorohexafluorobut-2-ene (b. p. 64·5—65·5°, n_D^{20} 1·341). Treatment of this mixture of chlorofluorobutenes with zinc and boiling ethanol gave hexafluorobutadiene (31%), and treatment with antimony trifluorodichloride gave octafluorobut-2-ene (61%). The mixture of chlorofluorobutenes absorbed chlorine quantitatively to give 1 : 2 : 3 : 4-tetrachlorohexafluorobutane, shown, by infra-red spectroscopy, to be identical with that described above; it absorbed bromine quantitatively to give a mixture of dibromodichlorohexafluorobutanes converted into hexafluorobutadiene by zinc and refluxing ethanol.

Since the above work was complete, Miller (*op. cit.*) has listed compounds prepared by his group by alternative unpublished procedures. These include $(CClF_2{\cdot}CClF)_2$, b. p. 134·5—134·6°/700 mm., n_D^{20} 1·3853; $(CBrF_2{\cdot}CBrF)_2$, b. p. 118—122°/60 mm., n_D^{20} 1·467, $(CF_3{\cdot}CBrF)_2$, b. p. 96°, n_D^{20} 1·3574; and $(CClF_2{\cdot}CF{:})_2$, b. p. 64—66°.

Absorption Spectra.—Silica gas cells (10 cm. and 4 cm.) were used and the extinction coefficient, ε, was calculated from the equation $\varepsilon = 760\, D \times 22{\cdot}4 \times 290/273pl$ where D = optical density, p = gas pressure (mm.), and l = cell length (cm.). No great accuracy is claimed for the ε values of hexafluorobutadiene, owing to possible errors in measuring the low pressures required.

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