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The Addition of Free Radicals to Unsaturated Systems. Part XV.¹ Further Investigation of the Direction of Radical Addition to Chloro-1,1-difluoroethylene

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Photochemical reaction of chloro-1,1-difluoroethylene with trifluoroiodomethane gives a 92% yield of the 1:1 adducts 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane and 2-chloro-1,1,1,3,3-pentafluoro-3-iodopropane in the ratio 92:8. The major by-product is 1,1-difluoroiodoethylene. Reaction at 225° gives a low yield of the same 1:1 adducts (ratio 98:2). Irradiation of 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane gives as major products trifluoroiodomethane, chlorotrifluoromethane, and 1,1-difluoroiodoethylene. The photochemical reaction of hydrogen bromide with chloro-1,1-difluoroethylene results in the exclusive formation of 1-bromo-2-chloro-1,1-difluoroethane.

IN the course of this series of investigations into the direction of free-radical additions to olefins bidirectional addition is sometimes observed, although addition to one end of the olefin usually predominates greatly unless the olefin and the attacking radical are chosen to maximise bidirectional addition; even then it is rare to find less than 80-90% of the radical attack on one end of the olefin. Thus although trifluoroiodomethane reacts to

¹ Part XIV, R. N. Haszeldine and B. R. Steele, J. Chem. Soc., 1957, 2800.

give a 1:1 adduct from the olefins $CF_3 \cdot CF \cdot CF_2$,² ČHF:CF₂,¹ or ČH₂:CHF,^{3,4} predominantly by attack on the carbon indicated, modern techniques reveal the presence of 10-20% of the other 1:1 adduct. Similar bidirectional free-radicaladdition of hydrogen bromide to hexafluoropropene⁵ and trifluoroethylene¹ takes place. Bidirectional addition may be interpreted on the basis that the two possible intermediate radicals (I) and (II) have similar stabilities, provided that other factors can be neglected:

$$R \cdot + CAB CXY \longrightarrow RCAB \dot{C}XY + RCXY \dot{C}AB$$
(I)
(II)

Since chlorine is more efficient at stabilising a radical than is fluorine or hydrogen, the radicals CF₃·CF₂·CHCl· and CF_3 ·CHCl·CF₂· possibly produced by attack on chloro-1,1-difluoroethylene might be sufficiently similar in stability to enable bidirectional addition to this olefin to be achieved. If this could occur to a major extent, the olefin, like trifluoroethylene and hexafluoropropene. would be useful in studies on the variation of the extent of bidirectional radical addition with the type of attacking radical. Earlier we reported ⁶ that the photochemical addition-reactions of trifluoroiodomethane or hydrogen bromide gave only the 1:1 adducts derived from exclusive initial radical-attack at the CF_2 group of the olefin, but since the earlier study was carried out before the availability of g.l.c. and n.m.r. spectroscopy as analytical tools, it was possible that the 1:1 adducts derived from radical attack at the CHCl group of the olefin could have remained undetected. The photochemical reactions of trifluoroiodomethane and of hydrogen bromide with chloro-1,1-difluoroethylene were therefore reinvestigated in order to confirm the earlier results, and to examine the effect of variation in the conditions on the direction of addition.

Trifluoroiodomethane.-The photochemical reaction of trifluoroiodomethane with chloro-1,1-difluoroethylene (2:1 molar ratio) gave two 1:1 adducts in the ratio 90:10; these were separated by g.l.c. and identified as 3-chloro-1,1,1,2,2-pentafluoro-3-iodopropane (III) and 2-chloro-1,1,1,3,3-pentafluoro-3-iodopropane (IV) respectively. The formation of (III) as major product is thus in agreement with the earlier report, but the formation of the small amount of (IV) is reported for the first time.

² R. N. Haszeldine, J. Chem. Soc., 1953, 3559; J. Brown and R. N. Haszeldine, unpublished results cited in J. Chem. Soc., 1963, 1083.

³ T. J. Dougherty, *J. Amer. Chem. Soc.*, **1964**, **86**, 460. ⁴ R. N. Haszeldine, D. W. Keen, and A. E. Tipping, unpublished results.

The structure of (III) follows from spectroscopic and chemical evidence. (a) The n.m.r. spectrum of (III) is of the ABPX₃ type, and the two non-equivalent fluorine nuclei of a CF₂ group form the AB portion of the spec-The absence of coupling between the three trum. equivalent fluorines (F_x) and F_A or F_B is in accord with the presence of a $CF_{3(X)}$ · $CF_{A}F_{B}$ grouping,⁷ and the absence of $\mathrm{HF}_{\mathtt{X}}$ coupling shows that the $\mathrm{F}_{\mathtt{X}}$ fluorines and the hydrogen atom are not on adjacent carbon atoms. Chemical shifts are in good agreement with the proposed structure and also with those for similar compounds.8

(b) The photochemical reaction of (III) with chlorine gave the dichloro-compound (V), the ¹⁹F n.m.r. spectrum of which showed the presence of two different types of fluorine nuclei (intensities 3:2) in which a small coupling constant (0.4 c./sec.) confirmed that these were adjacent to one another. The ¹H n.m.r. spectrum appeared as a triplet caused by coupling of the hydrogen nucleus to two identical fluorine nuclei in the CF₂·CHCl₂ group. Strong peaks in the mass spectrum at m/e 83, 85, and 87 (100%) correspond to the ion $CHCl_2^+$ [peaks at m/e85 and 87 (70%) are also due to the rearranged ion CF_2Cl^+], and the peak at m/e 119 (10%) corresponds to the ion CF₃·CF₂⁺.

(c) The absence of reaction when (III) was treated with powdered potassium hydroxide in vacuo suggests that the hydrogen and iodine atoms are not on adjacent carbon atoms.

The structure of (IV) follows from the following. (a) Its n.m.r. spectrum was of the $ABPX_3$ type and the single proton appeared as a sextet ($J_{\rm HF}$ 7.4 c./sec.) which infers the presence of five adjacent fluorine atoms. The reasonably large splitting (ca. 11.5 c./sec.) between three identical fluorine atoms (F_x) and two non-identical fluorine atoms F_A and F_B confirms the absence of the CF₃·CF₂ grouping.

(b) The photochemical reaction with chlorine gave a dichloro-compound which had an i.r. spectrum identical to that of compound (VI) prepared by the reaction of chlorine with 1,1,3,3,3-pentafluoropropene.⁶

The n.m.r. spectrum of compound (VI) was very similar to that of the parent iodo-compound, and the mass spectrum showed strong peaks at m/e 98 and 100 (22%), corresponding to the ion CF₂·CHCl⁺ and/or $CF_2Cl \cdot CH^+$, and m/e 85 and 87 (100%), corresponding to the ion CF₂Cl⁺.

(c) Reaction of (IV) with powdered potassium hydroxide in vacuo gave 2-chloropentafluoropropene (91%), the n.m.r. spectrum of which was identical to that reported.⁹ The formation of this olefin in good yield

⁵ F. W. Stacey and J. F. Harris, J. Org. Chem., 1962, 27, 4089. ⁶ R. N. Haszeldine and B. R. Steele, J. Chem. Soc., 1957, 2193.

L. Petrakis and C. H. Sederholm, J. Chem. Phys., 1961, 35.

1243. ⁸ N. Muller, P. C. Lauterbur, and G. F. Svatos, J. Amer.

⁹ J. D. Swalen and C. A. Reilly, J. Chem. Phys., 1961, 34, 2122.

rules out the possibility that the minor adduct is 3-chloro-1,1,1,3,3-pentafluoro-2 iodopropane, or 3-chloro-1,1,1,2,3pentafluoro-2-iodopropane formed *via* rearrangement of an intermediate radical:

$$\begin{array}{c} CF_3 \cdot CHCl \cdot \dot{C}F_2 \longrightarrow \\ CF_3 \cdot \dot{C}H \cdot CF_2 Cl \xrightarrow{CF_3 I} CF_3 \cdot CHI \cdot CF_2 Cl \\ CF_3 \cdot CF_2 \cdot \dot{C}HCl \longrightarrow \\ CF_3 \cdot \dot{C}F \cdot CHFCl \xrightarrow{CF_3 I} CF_3 \cdot CFI \cdot CHFCl \end{array}$$

A series of reactions with only low olefin conversion was then carried out to determine accurately the 1:1adduct ratio; the short irradiation time diminished the possibility of further reactions of the primary products. The results of this series of reactions are shown in Table 2.

The 1:1 adduct ratio was not affected markedly by the time of irradiation, and although little or no telomer was formed, the yield of the 1:1 adducts (65-75%)showed that other products were being formed. However, when an etched silica reaction-tube was used to diminish the intensity of radiation, the yield of the 1:1 adducts rose to 92%, and the ratio of 1:1 adducts in this reaction, where side-reactions are at a minimum, is (III): (IV) 92:8.

A major by-product, separated by g.l.c., was identified as 1,1-difluoroiodoethylene since its i.r. spectrum contained all the major bands reported ¹⁰ for the spectrum of 1,1-difluoroiodoethylene, and its ¹H and ¹⁹F n.m.r. spectra were very similar to those obtained with chloro-1,1-difluoroethylene. The H-F coupling constants found (*trans* 27·3, *cis* 2·1 c./sec.) are much smaller than expected for a geminal H-F coupling, and so the two fluorine nuclei are on the same carbon atom. Formation of 1,1-difluoroiodoethylene was not accompanied by the production of chlorotrifluoromethane, *under these particular conditions*, so that abstraction of chlorine from chloro-1,1-difluoroethylene by a trifluoromethyl radical:

$$CF_3 \cdot + CF_2 \cdot CHCl \longrightarrow CF_2 \cdot CH + CF_3 Cl$$

$$CF_2 \cdot CH \cdot + CF_3 I \longrightarrow CF_2 \cdot CHI + CF_3 \cdot CF$$

does not occur to any appreciable extent.

It is unlikely that chlorotrifluoromethane is first formed then reacts further, so homolytic fission of C-Cl in chloro-1,1-difluoroethylene is presumably involved:

$$CF_{2}:CHCI \xrightarrow{u.v.} CF_{2}:\dot{C}H + CI \cdot$$

$$CF_{2}:\dot{C}H + CF_{3}I \longrightarrow CF_{2}:CHI + CF_{3} \cdot$$

$$CF_{2}:\dot{C}H + I_{2} \longrightarrow CF_{2}:CHI + I \cdot$$

Experiments carried out to give complete conversion of olefin into products, followed by further photolysis of the products *in situ* resulted in a decrease in the yield of the iodo-olefin (Table 1). Thus *under these conditions* either the difluoroiodoethylene photolyses faster than it is formed from the 1:1 adducts or it is not formed at all *via* the 1:1 adducts.

Finally, these experiments showed that over-exposure

of the reaction mixture to radiation increased the yield of material of higher b.p., presumed to contain telomer:

$$CF_{3} \cdot CF_{2} \cdot CHCII \xrightarrow{u.v.} CF_{3} \cdot CF_{2} \cdot CHCI \cdot \underbrace{\stackrel{i \ CF_{2} \cdot CHCI}{\underset{ii \ CF_{3} \cdot CF_{2} \cdot CHCII}} }_{CF_{3} \cdot CF_{2} \cdot CHCI \cdot CF_{2} \cdot CHCII \ etc.}$$

It is to be expected that as the amount of olefin decreases during the reaction, trifluoroiodomethane competes less successfully for it than the more readily photolysed (III), the concentration of which is steadily increasing; telomer formation should thus increase towards the end of the reaction. The material of higher b.p. will also contain dimer:

$$CF_3 \cdot CF_2 \cdot CHCII \longrightarrow CF_3 \cdot CF_2 \cdot CHCl \cdot \longrightarrow (CF_3 \cdot CF_2 \cdot CHCl)_2$$

The mixture of 1:1 adducts [91% (III), 9% (IV)] was next irradiated on its own, and *under these conditions* 1,1-difluoroiodoethylene was a major product (44%), together with chlorotrifluoromethane (63%), trifluoroiodomethane (31%), a small amount of chloro-1,1-difluoroethylene, and several minor components. The mixture of 1:1 adducts recovered (74%) had an isomer ratio of 92% (III) and 8% (IV) thus showing that (III) had not rearranged to (IV) under these conditions. The reaction products thus imply:

$$CF_{3} \cdot CF_{2} \cdot CHCII \xrightarrow{u.v.} CF_{3} \cdot CF_{2} \cdot CHCI \cdot \longrightarrow CF_{3} \cdot + CF_{2} \cdot CHCI \cdot \longrightarrow CF_{3} \cdot + CF_{2} \cdot CHCI \cdot CF_{3} \cdot CF_{2} \cdot CHCI \cdot CF_{3} \cdot CF_{2} \cdot CHCI \cdot + CF_{2} \cdot CH \cdot := CF_{2} \cdot CHI \cdot CF_{2} \cdot CHI \cdot CF_{3} \cdot CF_{2} \cdot CHCII \cdot CF_{3} \cdot CF_{2} \cdot CHCII \cdot CF_{3} \cdot CF_{2} \cdot CHCI \cdot + CF_{3}I + CF_{3} \cdot CF_{2} \cdot CHI \cdot + CF_{3}CI \cdot CF_{3} \cdot + CF_{2} \cdot CHI \cdot + CF_{3}CI \cdot CF_{3} \cdot + CF_{2} \cdot CHI \cdot CF_{3} \cdot + CF_{2} \cdot CHI \cdot CF_{3} \cdot CF_{3} \cdot CF_{2} \cdot CHI \cdot CF_{3} \cdot CF_{3} \cdot CF_{2} \cdot CHI \cdot CF_{3} \cdot CF_{3$$

At present, however, no conclusions can be drawn concerning the relative importance of these.

The 1:1 adducts were also formed in low yield (13%)[ratio (III): (IV), 98:2] from a thermal reaction of trifluoroiodomethane with chloro-1,1-difluoroethylene. Such a low yield of adducts means the isomer ratio has little or no mechanistic significance.

Hydrogen Bromide.—Only unchanged reactants were obtained from the attempted reaction of hydrogen bromide with chloro-1,1-difluoroethylene in the dark at room temperature either alone or in the presence of a trace of bromine which sometimes catalyses ionic addition of hydrogen bromide to fluoro-olefins. A photochemical reaction in silica was rapid and complete conversion of the olefin occurred in 20 min. Only one adduct (97%) was formed (g.l.c. and n.m.r.) and this had an ¹⁰ M. Hauptschein, A. H. Fainberg, and M. Braid, J. Org. Chem., 1958, 23, 322.

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i.r. spectrum identical to that reported ⁶ for the spectrum of 1-bromo-2-chloro-1,1-difluoroethane. The ¹H and ¹⁹F n.m.r. spectra were in complete agreement with the structure CF₂Br·CH₂Cl and the chemical shifts correlate reasonably well with those reported; ¹¹ triplet splitting was observed for both the hydrogen and the fluorine nuclei. In the mass spectrum of the adduct bands were observed at m/e 129 and 131 (8%) corresponding to the ion CF₂Br⁺ and at m/e 49 and 51 (11%) corresponding to the ion CH₂Cl⁺; these also confirm the structure CF₂Br·CH₂Cl for the adduct. olefin (4.83 g., 49.2 mmoles) and trifluoroiodomethane (19.76 g., 100.7 mmoles) gave (i) unchanged trifluoroiodomethane (11.15 g., 56.9 mmoles, 56%), (ii) chlorotrifluoromethane (0.63 g., 5.9 mmoles, 12%) (Found: M, 106. Calc. for CClF₃: M,104.5) shown by i.r. spectroscopy to be contaminated with small amounts of hexafluoroethane and trifluoromethane, (iii) a higher-boiling fraction (9.48 g.) shown by g.l.c. (2 m.D.D.P. at 102°) to contain two major and twelve minor components, and (iv) a non-volatile residue (3.0 g.).

The two major components of fraction (iii) were separated by g.l.c. $(2 \text{ m.D.D.P. at } 95^{\circ})$ and identified as 3-chloro-

The reac	tion of trifluoroiodomet	hane with chloro-1,1	-difluoroe	thylene wi	th complete ole	fin conversion
Irradiation			1:1 Add	luct ratio		
time (hr.)	Olefin conversion (%)	1 : 1 Adducts (%)	(III)	(IV)	CF2:CHI (%)	Non-volatiles * (%)
72	100	75	89	11	12	t
96	100	60	83	17	12	÷
150	100	34	72	28	1	16
192	100	37	51	49	1	21
330	100	23	35	65	0	33
	* Calculated for a 2 : 1	l adduct, which is not	necessaril	v the case.	† Not determin	ned.

TABLE 1

TABLE 2

Th	ne reaction of	trifluoroiodometh	ne with ch	loro-1,1-diflu	loroethylene	with lov	v olefin	conversion
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Distance from	Irradiation	Olefin					
lamp (cm.)	time (hr.)	conversion (%)	1 : 1 Adducts (%)	(III)	(IV)	CF2:CHI (%)	Non-volatiles (%)
50	4	7	71	91	9	10	0
10	8	28	65	90	10	11	Trace
50	8	14	71	90	10	6	0
100	16	10	76	87	13	8	0
15 *	24	34	92	92	8	4	0
			* Etched tube u	sed.			

The unidirectional addition of bromine atom agrees with the earlier report,⁶ and contrasts with the 90:10bidirectional addition of trifluoromethyl radical. Further discussion of the significance of these results is deferred to a later paper.

EXPERIMENTAL

Org.

Volatile materials were manipulated in a conventional high-vacuum apparatus to avoid contact with air or moisture. Photochemical reactions (Hanovia S 500 lamp) were carried out in 350-ml. silica tubes and thermal reactions in 300-ml. Dreadnought glass tubes, unless stated to the contrary. Pure products were separated either by repeated fractional condensation *in vacuo* or by g.l.c. [Perkin-Elmer 451 or 452 instruments using columns packed with dodecyl phthalate (D.D.P., 30%) on Celite], and were examined by i.r. spectroscopy (Perkin-Elmer 21 instrument with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R.10 instrument operating at 60-00 Mc./sec. for ¹H and 56·46 Mc./sec. for ¹⁹F), mass spectroscopy (A.E.I. MS./2H instrument), or u.v. spectroscopy (Unicam SP 700 spectrophotometer).

Chloro-1,1-difluoroethylene was prepared in 70% overall yield by the photochemical addition of hydrogen bromide to 1,1-dichlorodifluoroethylene followed by debromochlorination of the adduct.⁶

Photochemical Reaction of Chloro-1,1-difluoroethylene with Trifluoroiodomethane.—(a) With complete olefin conversion. In a typical experiment the vapour-phase irradiation (150 hr.) at a distance of 10—15 cm. of a mixture of the 1,1,1,2,2-pentafluoro-3-iodopropane (III) ($3\cdot56$ g., $12\cdot1$ mmoles, 24% yield) (Found: C, $12\cdot0$; H, $0\cdot3\%$; M, 294. C₃HClF₅I requires C, $12\cdot2$; H, $0\cdot3\%$; M, 295), b.p. (isoteniscope) 95·1° (lit., 6 102°); λ_{max} (vapour) 278 mµ (ϵ 600), λ_{min} , 226—227 mµ (ϵ 14); i.r. bands at $3\cdot30$ w, $7\cdot27$ m, $7\cdot47s$, $7\cdot68$ m, $7\cdot83s$, $8\cdot05s$, $8\cdot15s$, $8\cdot29s$, $8\cdot70s$, $8\cdot82s$, $9\cdot00s$, $9\cdot38m$, $9\cdot75s$, $12\cdot05s$, $12\cdot65m$, $12\cdot76m$, $12\cdot85m$, $14\cdot05m$, $14\cdot18s$, $14\cdot25s$, and $14\cdot30s$ µ and 2-chloro-1,1,1,3,3-penta-fluoro-3-iodopropane (IV) ($1\cdot38$ g., $4\cdot7$ mmoles, 10% yield) (Found: C, $12\cdot4$; H, $0\cdot4\%$; M, 293. C₃HClF₅I requires C, $12\cdot2$; H, $0\cdot3\%$; M, 295), b.p. (isoteniscope) 98·6°; i.r. bands at $3\cdot38w$, $7\cdot47s$, $7\cdot93s$, $8\cdot06s$, $8\cdot21s$, $8\cdot30s$, $8\cdot69m$, $8\cdot74m$, $9\cdot12s$, $9\cdot32m$, $9\cdot37m$, $9\cdot75s$, $10\cdot27s$, $11\cdot12w$, $11\cdot47m$, $11\cdot69m$, $12\cdot12m$, $12\cdot65m$, $12\cdot84m$, $13\cdot60w$, and $14\cdot22m$ µ.

The results from further reactions carried out on a similar scale are shown in Table 1.

(b) Low olefin conversion. In a typical experiment the vapour-phase irradiation (4 hr.) at a distance of 50 cm. of a mixture of the olefin (2.64 g., 26.8 mmoles) and trifluoroiodomethane (10.50 g., 53.6 mmoles) gave (i) unchanged olefin (2.46 g., 25.0 mmoles, 93%), (ii) unchanged trifluoroiodomethane (10.11 g., 51.7 mmoles, 96%), and (iii) a higherboiling fraction (0.46 g.) shown by g.l.c. (2 m.D.D.P. at 95°) to contain the 1:1 adduct (III) (0.34 g., 1.16 mmoles, 65% yield), the 1:1 adduct (IV) (0.03 g., 0.12 mmole, 6% yield), an olefin later identified as 1,1-difluoroiodoethylene (0.03 g., 0.18 mmoles, 10%), and three other unidentified components.

¹¹ J. Lee and L. H. Sutcliffe, Trans. Faraday Soc., 1959, 55, 880.

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Further reactions carried out on a similar scale varying the reaction time and the distance from the lamp are shown in Table 2.

(c) In an etched tube. The vapour-phase irradiation (24 hr.) in a very etched tube at a distance of 10-15 cm. of a mixture of the olefin (2.05 g., 20.8 mmoles) and trifluoroiodomethane (7.76 g., 39.6 mmoles) gave (i) unchanged olefin (1.34 g., 13.6 mmoles, 66%), (ii) unchanged trifluoroiodomethane (6.24 g., 31.8 mmoles, 80%), (iii) a lowboiling fraction (0.09 g., 0.7 mmole; M, 128) shown by its i.r. spectrum to be a mixture of hexafluoroethane and

Reactions of 3-Chloro-1,1,1,2,2-pentafluoro-3-iodopropane (III).--(a) Photolysis. The halopropane (0.71 g., 2.43 mmoles) contaminated with its isomer (IV) (0.07 g., 0.24 mmole), sealed in a 100-ml. silica tube and the vapourphase irradiated (24 hr.), gave (i) a mixture (0.08 g., 0.58 mmole; M, 136) shown by its i.r. spectrum to contain chlorotrifluoromethane (0.04 g., 0.39 mmole, 63%) and trifluoroiodomethane (0.04 g., 0.19 mmole, 31%) contaminated with a trace of chloro-1,1-difluoroethylene, (ii) a higher-boiling fraction (0.70 g.) shown by g.l.c. (2 m.D.D.P. at 102°) to contain unchanged (III) (0.55 g.,

		¹⁹ F 1	N.m.r. spectra	a: assignments and	chemical	shifts			
			Group I		_		Group 2		
Compound	Intensity	Shift (p.p.m.)	Multiplicity	Coupling constant (c./sec.)	Intensity	Shift (p.p.m.)	Multiplicity	Coupling (c./	constant sec.)
$CF_3 - CF_2 \cdot CHCII$ (X) (AB)	3	0.7	S		1 (A)	24.6	dd	A–B	$265 \\ 4.6$
. , . ,					1 (B)	37.0	dd	B-A	$265 \\ 18.0$
$\begin{array}{c} CF_3 - CF_2 \cdot CHCl_2 \\ (X) (A) \end{array}$	3	3.0br	s		2	44 •0	dq	A–H A–X	$8.8 \\ 0.4$
CF ₃ -CHCl-CF ₂ I (AB)	3	-14.0	td	$\begin{array}{c} 11 \cdot 3 \\ 7 \cdot 05 \end{array}$	1 (A)	-27.6	qd		$11.6 \\ 8.2$
					1 (B)	-28.4	qd		$11.0 \\ 8.5$
CF ₃ -CHCl-CF ₂ Cl (AB)	3	-7.6	td	11·1 5·7	1 (A)	-19.8	$\mathbf{q}\mathbf{d}$		$11.3 \\ 7.6$
					1 (B)	-20.4	qd		$11.4 \\ 6.3$
CF ₂ Br-CH ₂ Cl		$-24 \cdot 8 br$	t	12.0					
	1 (X)	-1.7	dd	X-A 27·3 X-H 23·1					
F I (A)	1 (A)	-6.0	dd	A-X 27·3 A-H 2·1					
F H	1 (X)	12.0	dd	X-A 42·3 X-H 16·6					
F Cl	1 (A)	16.3	dd	A-X 42·3 A-H 1·0					

TABLE 3

Negative values are to low field.

chlorotrifluoromethane contaminated with a trace of trifluoromethane, and (iv) a higher-boiling fraction (2.21 g)shown by g.l.c. (2 m.D.D.P. at 96°) to contain 1:1 adduct (III) (1.80 g., 6.12 mmoles, 85%), 1:1 adduct (IV) (0.15 g., 0.50 mmole 7%), 1,1-difluoroiodoethylene (0.05 g., 0.29 mmole, 4%) (Found: C, 12.7; H, 0.5%; M, 190. Calc. for C_2HF_2I : C, 12.6; H, 0.5%; M, 190) identified by a comparison of its i.r. spectrum with that reported,¹⁰ and five unidentified minor components.

Thermal Reaction of Chloro-1,1-difluoroethylene with Trifluoroiodomethane.-The olefin (1.50 g., 15.2 mmoles) and trifluoroiodomethane (5.93 g., 30.3 mmoles), heated at 225° (20 hr.), gave (i) unchanged olefin (0.78 g., 7.9 mmoles, 52%) (ii) unchanged trifluoroiodomethane (5.08 g., 25.9mmoles, 85%), and (iii) a higher-boiling fraction (0.45 g.) shown by g.l.c. (2 m.D.D.P. at 95°) to contain 1:1 adduct (III) (0.25 g., 0.85 mmole, 12%), 1:1 adduct (IV) (0.03 g., 0.01 mmole, <1%), and seven unidentified components. Free iodine and a black tar formed a layer on the inside of the reaction tube; this was not investigated further.

1.89 mmoles, 78% recovered), unchanged (IV) (0.05 g., 0.16 mmole, 67% recovered), 1,1-difluoroiodoethylene (0.05 g., 0.27 mmole, 44%), and five minor unidentified components, and (iii) a trace of non-volatile material.

(b) With chlorine. The halopropane $(0.525 \text{ g}_{...} 1.78)$ mmoles) and chlorine (1.26 g., 17.8 mmoles), sealed in a 100-ml. silica tube and irradiated (36 hr.), gave, after shaking with mercury to remove excess of chlorine, 3,3-dichloro-1,1,1,2,2-pentafluoropropane (V) (0.334 g., 1.65 mmoles, 93%) (Found: C, 17.6; H, 0.5%; M, 201. Calc. for C₃HCl₂F₅: C, 17.7; H, 0.5%; M, 203); the i.r. spectrum was similar to that reported,⁶ the main difference being the absence of a strong band at 10.06μ ; g.l.c. (2) m.D.D.P. at 70°) showed only one peak.

(c) With potassium hydroxide. The halopropane (0.423 g.)1.44 mmoles) condensed onto powdered potassium hydroxide (ca. 5 g.) in vacuo and left at 20° (20 min.) gave only unchanged (III) (0.416 g., 1.41 mmoles, 98%).

Reactions of 2-Chloro-1,1,1,3,3-pentafluoro-3-iodopropane (IV).—(a) With chlorine. The halopropane (0.256 g., 0.87 mmole) and chlorine (0.63 g., 8.9 mmoles), sealed in a

There was no reaction at 195° (100 hr.).

¹ H N.n	n.r. spectra	a: chemical shi	ifts	
	Chemical shift		Cour	oling tant
Compound	τ	Multiplicity	(c./s	ec.)
$CF_3 \cdot CF_2 \cdot CHCII$ (X) (AB)	4.04	dd		18·0 4·6
$\begin{array}{c} CF_3 \cdot CF_2 \cdot CHCl_2 \\ (X) (A) \end{array}$	$4 \cdot 12$	t	H–A	8.8
CF ₃ ·CHCl·CF ₂ I (X) (AB)	$5 \cdot 12$	Sextet		7.4
$\begin{array}{ll} CF_3 \cdot CHCl \cdot CF_2Cl \\ (X) & (AB) \end{array}$	5.48	dquintet		7.5
CF ₂ Br•CH ₂ Cl	5.92	t		12.0
F (X) F (A)	5.27	dd	H–X H–A	$23 \cdot 1 \\ 2 \cdot 1$
F (X) F CC F C1	5·20	dd	H–X H–A	16·6 1·0

TABLE 4

¹⁹F Chemical shifts which have been established for various groups are as follows:

	Chemical shift	Reported	
	(p.p.m.) (present	chemical shift	
Group	work)	(p.p.m.)	Ref.
CF₃·C←	-14.0 to 3.0	-19.7 to 11.9	8
$-CF_2-$	24.6 to 44.0	21.9 to 57.8	8
-CF ₂ I	ca28	ca20	12
-CF,Cl	ca20	ca15 to -5	12
-CF,Br	-24.8	-22.0 to -13.0	11, 13

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g., 0.64 mmole), condensed in vacuo onto powdered potassium hydroxide (ca. 5 g.) and left at 20° (20 min.) with occasional shaking, gave (i) unchanged (IV) (0.085 g., 0.29 mmole, 45% recovered) and (ii) 2-chloropentafluoropropene (0.053 g., 0.32 mmole, 91%) (Found: C, 21.3%; M, 166. Calc. for C₃ClF₅: C, 21.6%; M, 166) identified by a comparison of its ¹⁹F n.m.r. spectrum with that reported.9

Reaction of Hydrogen Bromide with Chloro-1,1-difluoroethylene.—(a) In the dark. The olefin (2.14 g., 21.7 mmoles) and hydrogen bromide (3.52 g., 43.4 mmoles), sealed in a 300-ml. Pyrex tube and left in the dark (21 days) gave only unchanged reactants. The addition of bromine (0.5 g)to the reactants again resulted in no reaction after 56 days in the dark.

(b) Photochemically. The olefin (2.17 g., 22.0 mmoles) and hydrogen bromide (3.56 g., 44.0 mmoles) irradiated (20 min.) in the vapour phase, gave (i) unchanged hydrogen bromide (1.74 g., 21.5 mmoles, 49% recovered) (Found: M, 80. Calc. for HBr; M, 81), and (ii) a higher-boiling fraction (3.94 g.) which was shown by g.l.c. (2 m.D.D.P. at 70°) to contain 3 minor unidentified components with short g.l.c. retention times and 1-bromo-2-chloro-1,1-difluoroethane (3.85 g., 21.5 mmoles, 97%) (Found: C, 13.1; H, 1.0%; M, 179. Calc. for C₂H₂BrClF₂: C, 13.4; H, 1.1%; M, 179).

N.m.r. Spectra.—The chemical shifts in Table 3 were recorded using trifluoroacetic acid as external reference for ¹⁹F and in Table 4 using tetramethylsilane as internal reference for ¹H.

Mass-spectral Data.-The main mass-spectral bands for the compounds prepared are shown in Table 5.

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TABLE 5

Main	mass-spectral	bands
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Intensity				Intensity				
M e	(III)	(IV)	Assignment	M e	(V)	(VI)	Assignment	
296, 294	67	100	Parent+	206, 204, 202	26	7	Parent+	
259	1	39	C ₃ HF ₅ I+	186, 184, 182		22	C ₃ F ₄ Cl ₉ +	
190	4	19	C,HF,I+	169, 167	10	51	C₄H¯F₅Čl+	
177	4 *	10	CF _• I+	119	10		C _s F₅+	
169, 167	50	67	C ₂ ĤF₅Cl+	112		6	C,F,+	
164, 162		25	IČl+	100, 98	4.5	22	C,HF,Cl+	
131, 129	1	10	C,HF,Cl+	87, 85	70	100	CF _• Cl ⁺	
127	17	46	I+	87, 85, 83	100		CHCl.+	
113	6	59	$C_{a}HF_{a}^{+}$	69	37	54	CF ₃ +	
112		34	$C_{3}F_{4}^{+}$	69, 67	19 *	10 *	CH [*] FCI+	
87, 85	13 *	41 *	Ċ Ĕ ,Ĉl+					
69	100	75	CF ₃ +					
31	1	9	CF^+	;	* Rearrange	ment ions		
	CF.Br·CH	Cl.						
182, 180, 178		3	Parent ⁺					
131, 129		8	CF _a Br+					
101, 99	10	0	C _a H _a F _a Cl+					
81, 79		5	Br+					
64		4·5	C.H.F.+					
51, 49	1	1	CH,ČI+					

100-ml. silica tube and irradiated (40 hr.), gave, after removal of excess chlorine by shaking with mercury in 2,3-dichloro-1,1,1,3,3-pentafluoropropane (VI) (0.173 g., 0.85 mmole, 98%) (Found: C, 17.8; H, 0.5%; M, 202. Calc. for C₃HCl₂F₅: C, 17.7; H, 0.5%; M, 203) identified by a comparison of its i.r. spectrum with that reported ⁶ and with that of a sample prepared by the ad-

The compound CF2:CHI showed one major peak at m/e 190 (100%) due to the parent ion.

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vacuo, dition of chlorine to 1,1,3,3,3-pentafluoropropene.

(b) With potassium hydroxide. The halopropane (0.187 7 c