Free Radical Addition to Olefins. Part XVIII.† Addition of Chloroiodo- and Di-iodo-methane to Fluoroalkenes

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The free-radical addition of chloroiodo- and di-iodo-methane to ethylene, vinyl fluoride, 1,1-difluoroethylene, trifluoroethylene, tetrafluoroethylene, and hexafluoropropene, has been investigated in sealed-tube experiments employing di-t-butyl peroxide as initiator. The main reaction products were 1 : 1 adducts derived from chloromethyl and iodomethyl radicals respectively. The addition of bromotrichloromethane to hexafluoropropene has been examined under similar experimental conditions. The relative rates of addition of chloromethyl radicals to the alkenes, and the orientation ratios for the unsymmetrical alkenes have been estimated. It is shown that the orientation of radical addition can be successfully accommodated within the 'Patterns of Reactivity' scheme developed for polymer radical reactions.

THE peroxide initiated addition of bromoform to fluoroalkenes at temperatures of *ca.* 150° leads to products derived from tribromomethyl and dibromomethyl radicals.[1] Similarly the photolysis of bromodichloromethane yields products derived from dichloromethyl radicals and also bromodichloromethyl radicals.[2] This dual behaviour is due to competition between hydrogen and halogen transfer in the chain-propagating step, and it is probable that it is general for trihalogenomethanes of the type CHX_2I or CHX_2Br at temperatures above 100°. Hardly any investigations of the free-radical reactions of dihalogenomethanes have been reported,[3] and we therefore embarked on a study of the peroxide-initiated addition of chloroiodo- and di-iodo-methane to a series of fluoroalkenes in order to determine if they also act as dual radical sources. Another primary objective of the study was to obtain orientation data for chloro- and iodo-methyl radicals with unsymmetrical olefins. This type of information is scarce for less electrophilic radicals and yet it is necessary if a more balanced view of the radical addition reaction with olefins is to be built up.

TABLE 1

Relative yields [a] of products from reactions of CH_2ClI with fluoroalkenes at 150°

Alkene *E*	Me_2CO	CH_3I	$ClCH_2CH_2Cl$	Cl*E*I	CH_2Cl*E*I	CH_2Cl*E'*I	Telomer
$CH_2=CH_2$		3.7	1.4	0.3	63.6		
$CH_2=CHF$	7.0	3.3	0.9	0.1	12.5	2.2	
$CH_2=CF_2$	5.4	3.4	0.2	<0.1	3.1	0.4	0.6
$CHF=CF_2$	3.5	3.2	0.4	<0.1	5.4	5.6	2.8
$CF_2=CF_2$			<0.1	<0.1	27.0		11.3 [b]
$CF_3CF=CF_2$	3.5	3.1	<0.1	0.1	4.1	0.8	

Traces of CH_3Cl were formed in all experiments.

[a] Yields as mol % relative to CH_2ClI remaining at end of experiment. [b] Yields of individual telomers: $CH_2Cl[CF_2CF_2]_nI$; $n = 2$, 4.1%; $n = 3$, 3.5; $n = 4$, 2.2; $n = 5$, 0.5; $n = 6$, 0.1; $n = 7$, 0.1; $H(CF_2CF_2)_2CHCl[CF_2CF_2]_nI$; $n = 1$, 0.6%; $n = 2$, 0.2.

TABLE 2

Relative yields of products from reactions of CH_2I_2 with fluoroalkenes at 150°

	No ethylene present			Competition with ethylene			
Alkene *E*	CH_2I*E*I %	CH_2I*E'*I %	Telomer %	$CH_2ICH_2CH_2I$ %	CH_2I*E*I %	CH_2I*E'*I %	Telomer %
$CH_2=CHF$				100	526		71
$CH_2=CF_2$	100	10.2		100	157	19.5	110
$CHF=CF_2$	100	92.7		100	267	267	398
$CF_2=CF_2$			*a*				*a*
$CF_3CF=CF_2$	100	16.5	33				*a*

Acetone and methyl iodide were produced in all experiments.

[a] Main product polymer.

RESULTS AND DISCUSSION

The relative yields of the main products from the reactions of chloroiodomethane and di-iodomethane with the fluoroalkenes are given in Tables 1 and 2. Di-t-butyl

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† Part XVII, J. P. Sloan, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1975, 1846.

[1] D. S. Ashton, D. J. Shand, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1975, 320.

[2] J. C. Gibb, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1974, 807.

[3] W. E. Hanford and R. M. Joyce, U.S.P. 2,440,800 (*Chem. Abs.*, 1947, **42**, 6373).

peroxide decomposes at 150° to give methyl radicals and acetone, and the methyl radicals initiate the reaction by abstracting iodine from the dihalogenomethane [reactions (1)—(3)]. Acetone and methyl iodide should be formed in equal amounts if methyl radicals are only consumed in reaction (1). In fact there was always a slight excess of acetone (see Table 1) suggesting that a small proportion of the methyl radicals take part in other reactions including addition to the alkene and combination.

$$CH_3\cdot + CH_2XI \longrightarrow CH_3I + CH_2X\cdot \tag{1}$$

$$CH_2X\cdot + E \longrightarrow CH_2XE\cdot \tag{2}$$

$$CH_2XE\cdot + CH_2XI \longrightarrow CH_2XEI + CH_2X\cdot \tag{3}$$

$$E = \text{fluoroalkene}$$

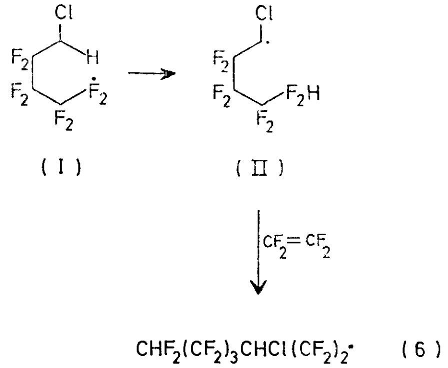
The only chain-carrying radicals were chloromethyl from chloroiodomethane and iodomethyl from di-iodomethane. No adducts derived from other radicals were detected so that hydrogen abstraction from the dihalogenomethane is not competitive with iodine abstraction and neither compound acts as a dual radical source under the conditions of the present experiments. Traces of methyl chloride detected in the reactions with chloroiodomethane indicate that some chlorine abstraction occurs [reaction (4)] but this reaction was of negligible importance compared with iodine abstraction. Another

$$CH_3\cdot + CH_2ClI \longrightarrow CH_3Cl + CH_2I\cdot \tag{4}$$

minor process gave rise to products of the type Cl*E*I, presumably from addition of traces of chlorine atoms to the fluoroalkenes. The identification of the dimer of chloromethyl radicals in most of the reactions suggests that the main termination process (5) involves combination of this radical:

$$CH_2Cl\cdot + CH_2Cl\cdot \longrightarrow ClCH_2CH_2Cl \tag{5}$$

The extent of telomer formation increased with increasing fluorine content of the fluoroethylene with both dihalogenomethanes. In the reactions to which ethylene was added, telomer formation increased, cross-telomers of the type $CH_2IECH_2CH_2I$ forming more readily than normal 2:1 telomers, because the adduct radicals $CH_2IE\cdot$ add more rapidly to ethylene than to the fluoroalkene *E*. An interesting feature of the results was the formation of small yields of telomers of structure $H[CF_2CF_2]_2CHCl[CF_2CF_2]_nI$ from the reaction of chloroiodomethane with tetrafluoroethylene. The mechanism probably involves a 1,5-hydrogen shift by intramolecular hydrogen abstraction in the 2:1 telomer radical (I) giving the rearranged radical (II) which can itself telomerize or react with the dihalogenomethane [reaction (6)]. The first member of this series of telomers ($n = 0$) was not detected, but since the rearranged products account for <8% of the total products from radical (I), the trace amounts expected for this telomer were probably below the limits of detection. Chain branching in telomerizations of ethylene has been ascribed to 1,5-hydrogen shifts of this type.[4,5]



The main products of the reactions were 1 : 1 adducts of the dihalogenomethane with the fluoroalkene, except in the reaction of di-iodomethane with tetrafluoroethylene which showed extensive polymerization. The orientation ratios O_r can be calculated from the yields of CH_2XEI (initial addition to the least substituted end of the alkene) and $CH_2XE'I$ (initial addition to the most substituted end) [equation (7)]. The orientation ratios

$$O_r = k'_2/k_2 = [CH_2XE'I]_f/[CH_2XEI]_f \tag{7}$$

obtained for chloro- and iodo-methyl radicals are compared with those for some related radicals in Table 3.

TABLE 3

Orientation of addition of halogenoalkyl radicals to fluoroalkenes at 150°

Radical	$CH_2{=}CHF$ O_r	$CH_2{=}CF_2$ O_r	$CHF{=}CF_2$ O_r	$CF_2{=}CFCF_3\cdot$ O_r	Ref.
$CH_2F\cdot$	0.29	0.45	2.04		1
$CH_2Cl\cdot$	0.18	0.14	1.03	0.19	*a*
$CH_2I\cdot$		0.10	0.93	0.16	*a*
$CCl_3\cdot$	0.070	0.012	0.29	<0.02	6, *b*

[a] This work. [b] J. M. Tedder and J. C. Walton, *Trans. Faraday Soc.*, 1966, **62**, 1859.

The orientation ratios show a uniform decrease along the series of radicals $CH_2F\cdot$, $CH_2Cl\cdot$, $CH_2I\cdot$ for each fluoroalkene. Chloromethyl radicals, like fluoromethyl radicals, show a slight preference for addition to the more substituted end of trifluoroethylene, but iodomethyl radicals show the more usual orientation of preferential addition to the least substituted end. Comparison of the O_r values of chloro- and trichloro-methyl radicals shows that the latter, larger, and more electronegative radical is much more selective. The photolytic addition of trichloromethyl radicals to hexafluoropropene in the gas phase gave none of the adduct from the CF_3CF-end,[6] whereas $CH_2Cl\cdot$, $CH_2I\cdot$, and $CF_3\cdot$[7] radicals all show

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[4] R. Kh. Freidlina, *Adv. Free-Radical Chem.*, 1965, **1**, 224; A. B. Terent'ev and R. Kh. Freidlina, *Izvest. Akad. Nauk, S.S.S.R., Ser khim.*, 1966, 1854.

[5] R. Kh. Freidlina, A. B. Terent'ev, M. Ya. Khorlina, and S. N. Aminov, *Zhur. Vsesoyuz Khim. Obshch. Im. D.T. Mendeleeva*, 1966, **11**, 211.

[6] J. M. Tedder and J. C. Walton, *Trans. Faraday Soc.*, 1967, **63**, 2678.

[7] R. N. Haszeldine, *J. Chem. Soc.*, 1953, 3559.

appreciable attack at this position. In an effort to detect the reverse adduct from $CCl_3\cdot$ radicals a sealed-tube experiment was carried out with CCl_3Br and hexafluoropropene, and the products together with their yields (mol %) relative to the unused CCl_3Br were as follows:

Product	Me_2CO	CH_3Br	$CHCl_3$	$CF_3CFBrCF_2Br$	$CCl_3CF_2CFBrCF_3$	CH_3COCH_2Br	C_2Cl_6
%	2.2	2.0	1.0	0.3	2.4	0.2	1.0

If formed the reverse adduct must have been present in <0.1% yield.

The mechanism of the reaction is clearly very similar to that given above; $CCl_3\cdot$ radicals are the main chain carriers and they add to the alkene and abstract hydrogen from acetone and other compounds. The presence of the dibromide $CF_3CFBrCF_2Br$ suggests that small amounts of bromine atoms are also formed.

The trends in the orientation ratios can be interpreted in terms of steric and polar effects, and the orientation ratios for chloro- and iodo-methyl radicals conform with the correlations of log O_r with radical diameter (d_c) and with radical diameter modified by a polar term ($d_c + 1.0 \sum_\alpha \sigma_I$) described previously.[1] The full range of orientation ratios do not correlate well with the inductive substituent constants of the radicals $\sum_\alpha \sigma_I$,[1] but significant correlations are observed between log O_r and the Taft σ^0 constants of the radicals for the data from each fluoroethylene (and with Hammett σ constants which are virtually identical with σ^0 values for these radicals except for fluorine atoms). The σ^0 constant of a radical is defined as the algebraic sum of the substituent constants of the groups attached to the radical centre.

In the 'Patterns' approach developed by Bamford and Jenkins for interpreting polymer radical reactivities,[8] the specific velocity constant k_s for a radical reaction is given by equation (8) where $k_{3,T}$ is the rate constant of

$$\log k_s = \log k_{3,T} + \alpha\sigma + \beta \qquad (8)$$

the abstraction reaction of the radical with toluene, σ is the substituent constant of the radical, and α and β are constants for a given olefin. A simple extension of this approach in which α, β characterise one end of the olefin

$$\log O_r = \log k'_2/k_2 = \sigma\,(\alpha' - \alpha) + \beta' - \beta \qquad (9)$$

and α', β' characterise the other end leads to expression (9) for the orientation ratio. The values of $\alpha' - \alpha$ and $\beta' - \beta$ were determined from the gradients and intercepts of the plots of log O_r against σ^0, and are given as 'experimental' results in Table 4. A plot of log O_r against $\sigma^0\,(\alpha' - \alpha) + \beta' - \beta$ is shown in the Figure.

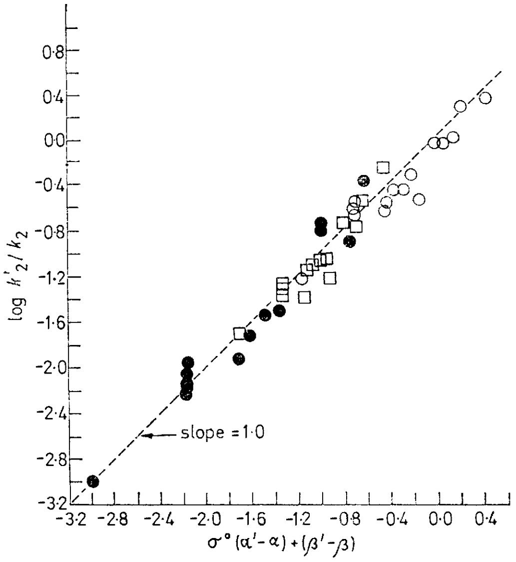
Effectively this amounts to a correlation of log O_r against σ^0, the $\alpha' - \alpha$ and $\beta' - \beta$ values serving to bring the results from the three alkenes into a single straight line the correlation coefficient of which was 0.98. The α and β values of these fluoroalkenes have not been determined independently from polymerization studies, but Bamford and Jenkins have shown that the α value of an olefin is related to its polarity by the approximate empirical equation: $\alpha = -5.3\ \sigma$, where σ here refers to the substituent constant of the adduct radical formed from the olefin. The α values calculated from this expression (see Table 4) are in reasonable agreement with the experimental values.

The 'Patterns' approach developed by Bamford and Jenkins for polymerization in solution can thus be adapted to the problem of orientation of radical addition to olefins in the gas phase with considerable success. The correlations indicate that both the polarity of the olefin and the polar character of the radical are important.

TABLE 4

Comparison of experimental and calculated olefin reactivity constants

Olefin	$(\beta' - \beta)_{expt}$	$(\alpha' - \alpha)_{expt}$	$(\alpha' - \alpha)_{calc.}$
$CH_2{=}CHF$	−0.46	−0.99	−0.90
$CH_2{=}CF_2$	−0.25	−2.18	−1.80
$CHF{=}CF_2$	0.44	−1.28	−0.90



Correlation of the logarithms of the orientation ratios with σ^0 constants of the radicals. ○, trifluoroethylene; □, vinyl fluoride; ●, 1,1-difluoroethylene

An attempt was made to measure the relative rates of addition of iodomethyl radicals to the fluoroalkenes by adding ethylene as a competitor to the reaction mixture. Unfortunately this increased the extent of telomerization to such an extent that the results are worthless for kinetic purposes. An estimate of the relative rates of addition of chloromethyl radicals to the alkenes can be obtained by summing the yield of adducts (including

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[8] C. H. Bamford and A. D. Jenkins, *Trans. Faraday Soc.*, 1963, **59**, 530; A. D. Jenkins, *Adv. Free-Radical Chem.*, 1967, **2**, 139.

both adducts from an unsymmetrical olefin) and telomers for each alkene and comparing this with the corresponding yield for ethylene. The relative rates found in this way are: $CH_2{=}CH_2$, 1.0; $CH_2{=}CHF$, 0.2; $CH_2{=}CF_2$, 0.06; $CHF{=}CF_2$, 0.2; $CF_2{=}CF_2$, 0.6; $CF_3CF{=}CF_2$, 0.08. The relative rates of addition to the fluoroethylenes initially decrease as the number of fluorine substituents in the fluoroethylene increases, and then subsequently increase to tetrafluoroethylene. Iodomethyl radicals also follow the same trend, as Table 2 shows, although no quantification is possible. Similar behaviour has been observed for a variety of halogenoalkyl radicals,[1] and for hydrogen atoms.[9]

EXPERIMENTAL

Materials.—Chloroiodomethane was prepared by refluxing CH_2Cl_2 with KI in acetone for three weeks. The product was distilled and purified by preparative g.l.c. to give material of $>99.6\%$ purity. Di-iodo- and bromotrichloromethane were commercial materials redistilled before use. Di-t-butyl peroxide was washed with iron(II) sulphate, several times with water, and distilled under reduced pressure. The fluoroalkenes were commercial materials, dried and trap-to-trap distilled and degassed before use; g.l.c. showed no impurities.

Method.—Materials were handled on a conventional vacuum line. Measured amounts of the polyhalogenomethane, di-t-butyl peroxide, and the appropriate alkene were distilled into a thick Pyrex tube (*ca*. 100 ml) and thoroughly degassed. The tube was sealed under vacuum and transferred to a furnace at $150 \pm 4°$ where reaction occurred for a timed interval. The mixture was cooled in liquid nitrogen, the tube opened, and the contents analysed directly, or after dissolving in acetone or methylene dichloride.

Analysis.—Product identification was achieved by coupled g.l.c.–mass spectrometry of the reaction mixture using a Pye 104 gas chromatograph with 15 ft columns of 10% w/w Embaphase silicone oil, 15% dinonyl phthalate, or 15% tritolyl phosphate on Chromosorb G, coupled *via* a single stage Bieman separator to an A.E.I. MS902 mass spectrometer. The mass spectra of the adducts are given in Supplementary Publication No. SUP 21538 (6 pp.).* Wherever possible products were then separated by preparative g.l.c. on a Pye 105 instrument.

^1H and ^{19}F n.m.r. spectra were recorded on the products at room temperature using CCl_4 solutions in microcells containing traces of Me_4Si and CCl_3F as internal standards. A Varian HA-100 instrument was employed, and in several instances the time-averaging facility was used.

Quantitative analysis was achieved using Griffin and George gas density balance chromatographs employing the same columns as in the mass spectral analyses. Peak areas were measured with a DuPont 310 curve resolver. Most reactions were run in duplicate as a check on the consistency of the results and the analysis figures are average values estimated to be accurate to within $\pm 5\%$.

Reaction of Chloroiodomethane with Ethylene.—Chloroiodomethane (6.1 mmol), ethylene (3.6 mmol), and di-t-butyl peroxide (0.064 mmol) were reacted at 150° for 16 h. Five products were observed on the g.l.c. trace: peak 1, CH_3COCH_3 (structure established by m.s. and retention time R_t); peak 2, CH_3I (m.s., R_t); peak 3, CH_2ClCH_2Cl (m.s., R_t); peak 4, $ClCH_2CH_2I$ (m.s.); peak 5 $CH_2ClCH_2CH_2I$ (m.s.). Traces of CH_3Cl were also detected. The relative yields of the products are given in Table 1.

Reaction of Chloroiodomethane with Vinyl Fluoride.—Chloroiodomethane (5.9 mmol), vinyl fluoride (3.6 mmol), and di-t-butyl peroxide (0.064 mmol) were reacted at 150° for 12 h. Six products were observed on the g.l.c. trace: peak 1, CH_3COCH_3 (m.s., R_t); peak 2, CH_3I (m.s., R_t); peak 3, CH_2ClCH_2Cl (m.s., R_t); peak 4, C_2H_3FClI (m.s.); peak 5, CH_2ClCH_2CHFI (m.s., n.m.r.); peak 6, CH_2ClCHF-CH_2I (m.s., n.m.r.). The structure $CH_2ClCH_cH_bCH_aF$ for peak 5 was confirmed by the ^1H n.m.r. spectrum, δ 2.5—3.1 (2 H, m), 3.4—3.8 (2 H, m), and 6.95 (1 H, dt, J_{H_aF} 50.0, $J_{H_aH_b} = J_{H_aH_c} = 6.5$ Hz), and by the ^{19}F n.m.r. spectrum, ϕ 143.6 (8 lines, J_{FH_a} 50.0, J_{FH_b} 21.5, J_{FH_c} 15.0 Hz). The structure $CH_2ClCH_aFCH_2I$ for peak 6 was confirmed by the ^1H n.m.r. spectrum δ 3.6 (4 H, *ca*. 8 lines, $J_{CH_2Cl,H_a} \approx J_{CH_2,I,H_a} = 15.5$, $J_{CH_2Cl,F} \approx J_{CH_2I,F} = 17.5$ Hz) and 4.58 (1 H, d quintet, J_{H_aF} 46.2, $J_{H_a,\,CH_2Cl} = J_{H_aCH_2I} = 5.5$ Hz), and by the ^{19}F n.m.r. spectrum, ϕ 170.2 (d quintet, J_{FH_a} 46.2, $J_{F_aCH_2Cl} = J_{F_aCH_2I} = 17.5$ Hz). The relative yields of the products are given in Table 1; traces of CH_3Cl were also detected.

Reaction of Chloroiodomethane with 1,1-*Difluoroethylene*.—Chloroiodomethane (5.4 mmol), 1,1-difluoroethylene (3.6 mmol), and di-t-butyl peroxide (0.064 mmol) were reacted at 150° for 16 h. Six products were observed on the g.l.c. trace: peak 1, CH_3COCH_3 (m.s., R_t); peak 2, CH_3I (m.s., R_t); peak 3, CH_2ClCH_2Cl (m.s., R_t); peak 4, CH_2ClCH_2-CF_2I (m.s., n.m.r.); peak 5, $CH_2ClCF_2CH_2I$ (m.s., n.m.r.); peak 6, $CH_2Cl(CH_2CF_2)_2I$ (m.s.). The ^1H n.m.r. spectrum confirmed structure for peak 4 δ 2.6—3.1 (2 H, m), and 3.65 (2 H, t, J 8.0 Hz), as did the ^{19}F n.m.r. spectrum, ϕ 37.9 (t, J 14.2 Hz). The ^1H n.m.r. spectrum (time averaged) for peak 5 confirmed the structure, δ 3.9 (2 H, t, J 13.5 Hz) and 4.2 (2 H, t, J 11.0 Hz). Traces of CH_3Cl and $C_2H_2F_2ClI$ were also identified.

Reaction of Chloroiodomethane with Trifluoroethylene.—Chloroiodomethane (6.0 mmol), trifluoroethylene (3.6 mmol), and di-t-butyl peroxide (0.064 mmol) were reacted at 150° for 16 h. The g.l.c. trace showed seven products: peak 1, CH_3COCH_3 (m.s., R_t); peak 2, CH_3I (m.s., R_t); peak 3, CH_2ClCH_2Cl (m.s., R_t); peak 4, $CH_2ClCHFCF_2I$ (m.s., n.m.r.); peak 5, CH_2ClCF_2CHFI (m.s., n.m.r.); peak 6 and 7 were 2:1 telomers $CH_2Cl(CHFCF_2)_2I$. The ^1H n.m.r. spectrum confirms the structure $CH_2ClCHF_aCF_bF_cI$ for peak 4, δ 3.6—3.9 (2 H, m), δ 4.5 (1 H, dd quartet, J_{HF_a} 48.0, J_{HF_b} 3.0, $J_{HF_c} = J_{HH} = 8.5$ Hz), as did the ^{19}F n.m.r. spectrum, ϕ 184.4 (m) and 54.5 (AB, each component 4 lines, $J_{F_bF_c} = J_{F_cF_b} = 198.5$, $J_{F_bF_a}$ 21.0, J_{F_bH} 7.5, $J_{F_cF_a}$ 22.0, J_{F_cH} 8.5 Hz). The ^1H n.m.r. spectrum confirmed the structure $CH_2ClCF_bF_cCHF_aI$, δ 3.9 (2 H, t, further split, J 12.5 Hz) and 7.0 (1 H, 8 lines, J_{HF_a} 47.5, J_{HF_b} 11.0, J_{HF_c} 8.5 Hz), as did the ^{19}F n.m.r. spectrum, ϕ 166.3 (dt, J_{F_aH} 47.0, $J_{F_aF_b} = J_{F_aF_c} = 21.5$ Hz) and 109.3 (m).

Reaction of Chloroiodomethane with Tetrafluoroethylene.—Chloroiodomethane (6.1 mmol), tetrafluoroethylene (3.6 mmol), and di-t-butyl peroxide (0.064 mmol) were reacted at 150° for 18 h. The product was dissolved in acetone and on

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue. Items less than 10 pp. are supplied as full-size copies.

[9] J. P. Kilkoyne and K. R. Jennings, *J.C.S. Faraday I*, 1974, 379.

analysis showed 10 peaks (acetone was probably also a product): peak 1, CH_3I (m.s., R_t); peak 2, $CH_2ClCF_2CF_2I$ (m.s.); peak 3, $CH_2Cl(CF_2CF_2)_2I$; peak 4, $H(CF_2CF_2)_2CHCl(CF_2CF_2)I$ (m.s.); peak 5, $CH_2Cl(CF_2CF_2)_3I$ (m.s.); peak 6, $H(CF_2CF_2)_2CHCl(CF_2CF_2)_2I$ (m.s.); peak 7, $CH_2Cl[CF_2CF_2]_4I$ (m.s.); peak 8, $CH_2Cl[CF_2CF_2]_5I$ (R_t); peak 9, $CH_2Cl[CF_2CF_2]_6I$; peak 10 $CH_2Cl[CF_2CF_2]_7I$. A plot of log R_t against carbon number was found to be linear for the first four members of the series of telomers $CH_2Cl[CF_2CF_2]_nI$ which were positively identified from their mass spectra. The last three members of this series, *i.e.* $n = 5$—7 were too weak for mass spectral analysis, but comparison of their retention times with the correlation established for the first four provided good confirmation of their structures.

Reaction of Chloroiodomethane with Hexafluoropropene.—Chloroiodomethane (5.6 mmol), hexafluoropropene (3.6 mmol), and di-t-butyl peroxide (0.064 mmol) were reacted at 150° for 16 h. Seven products were observed: peak 1, CH_3COCH_3 (m.s., R_t); peak 2, CH_3I (m.s., R_t); peak 3, $CF_3CFClCF_2I$ (m.s.); peak 4, CF_3CFICF_2Cl (m.s.); peak 5, CH_2ClCH_2Cl (m.s., R_t); peak 6, $CH_2ClCF(CF_3)CF_2I$ (m.s.); peak 7, $CH_2ClCF_2CFICF_3$ (m.s., n.m.r.). The ^1H n.m.r. spectrum of peak 7 showed a signal at δ 3.8—4.3 (m); the ^{19}F n.m.r. spectrum supported the structure $CH_2ClCF_aF_b$-CF_cICF_3, ϕ 143.7 (m), 105.6 (AB, each component a multiplet which simplified to a quartet on spin decoupling the CF_3 group, J 15.5 Hz), and 73.6 (six lines, $J_{CF_3F_c} = J_{CF_3F_b} = 12.2$, $J_{CF_3F_a}$ 8.0 Hz).

Reaction of Bromotrichloromethane with Hexafluoropropene.—Bromotrichloromethane (5.7 mmol), hexafluoropropene (3.6 mmol), and di-t-butyl peroxide (0.064 mmol) were reacted at 150° for 16 h. The following products were observed: peak 1, CH_3Br (m.s.); peak 2, CH_3COCH_3 (m.s., R_t); peak 3, $CF_3CFBrCF_2Br$ (m.s.); peak 4, $CCl_3CF_2CFBrCF_3$ (m.s., n.m.r.); peak 5, C_2Cl_6 (m.s., R_t). $CHCl_3$ and CH_3COCH_2Br were also observed. Analysis on several columns of differing polarity showed only one adduct, and this was separated by preparative g.l.c. and the ^{19}F n.m.r. spectrum confirmed the structure $CCl_3CF_cF_bCF_aBrCF_3$, ϕ 133.3 (F_a, m), 104.7 (F_b, 16 lines, $J_{F_bF_c}$ 254, $J_{F_bF_3}$ 18.5, $J_{F_bF_a}$ 7.5 Hz), 93.0 (F_c, 10 lines, $J_{F_cF_b}$ 254, $J_{F_cF_3} = J_{F_cF_a} = 7.5$ Hz), and 76.0 (F_3, 8 lines, $J_{F_3F_b}$ 18.5, $J_{F_3F_c}$ 7.5, $J_{F_3F_a}$ 9.5 Hz). No signals attributable to the reverse adduct, $CCl_3CF(CF_3)CF_2Br$, were detected.

Reaction of Di-iodomethane with Alkenes.—Di-iodomethane (3.7 mmol), the alkene (3.6 mmol), and di-t-butyl peroxide (0.064 mmol) were reacted at 150° for 18 h. A second experiment was carried out for each alkene in which ethylene (0.51 mmol) was added as a reference olefin. Acetone and methyl iodide were identified as products in each reaction, but were not quantitatively analysed.

Vinyl fluoride. Two compounds were observed and were shown by m.s. to be 1:1 adducts $C_3H_5FI_2$, but they could not be separated by g.l.c. on a variety of columns of different polarity. In the reaction with added ethylene the adduct $CH_2ICH_2CH_2I$ was identified together with a cross-telomer, $C_5H_9FI_2$.

1,1-*Difluoroethylene.* Acetone and methyl iodide were identified together with $CH_2ICH_2CF_2I$ (m.s.) and $CH_2ICF_2CH_2I$ (m.s.). In the runs with added ethylene considerable amounts of telomers $C_5H_8F_2I_2$ were also observed.

Trifluoroethylene. $CH_2ICH_aFCF_2I$ was identified by m.s. and the structure confirmed by the ^1H n.m.r. spectrum which was very similar to that of $CH_2ClCHFCF_2I$, δ 2.5—3.1 (2 H, m) and 3.7 (1 H, m). $CH_2ICF_bF_cCHF_aI$ was identified by m.s. and the structure confirmed by the ^1H n.m.r. spectrum (very similar to that of CH_2ClCF_2CHFI), δ 3.95 (2 H, t, J 13 Hz) and 7.15 (1 H, dt, J_{HF_a} 46, $J_{HF_b} = J_{HF_c} = 8.5$ Hz). In the run with added ethylene considerable quantities of 2:1 telomers $C_5H_7F_3I_2$ were observed.

Tetrafluoroethylene. Reactions in the presence and absence of ethylene resulted in a solid mass of polymer which was not further analysed.

Hexafluoropropene. The two 1:1 adducts $CH_2ICF(CF_3)CF_2I$ (m.s.) and $CH_2ICF_2CFICF_3$ (m.s.) were identified together with a third product $C_4H_3F_6I_2$.

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