321. The Addition of Free Radicals to Unsaturated Systems. Part III.* Chlorotrifluoroethylene.†

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The direction of addition of the trifluoromethyl radical to chlorotrifluoroethylene has been established. Photochemical reaction of trifluoroiodomethane with chlorotrifluoroethylene yields only compounds of general formula $CF_3\cdot[C_2ClF_3]_n\cdot I$, the value of n depending on the ratio of reactants, with a maximum of 85% of the compound where $n = 1$. The constitution of the compound with $n = 1$ is unambiguously shown to be exclusively $CF_3\cdot CF_2\cdot CFClI$, this contradicting Henne and Kraus's results (*J. Amer. Chem. Soc.*, 1951, **73**, 1791). This compound yields perfluorohex-3-ene by intermolecular removal of iodine followed by dechlorination, and $CF_3\cdot CF{:}CHF$ by reduction followed by dehalogenation; mechanisms are suggested for these reactions. The compounds where $n = 1$—5 have been separated and characterised, and their constitution as $CF_3\cdot[CF_2\cdot CFCl]_n\cdot I$ proved. Polychlorotrifluoroethylene (Kel-F) is thus formed by head-to-tail polymerisation of chlorotrifluoroethylene. Ultra-violet and infra-red spectra are presented and their diagnostic value is discussed.

THE direction of addition of a free radical to chlorotrifluoroethylene cannot be predicted in a satisfactory manner by any of the current theories; so, as part of a systematic investigation on free-radical addition reactions, the attack of a trifluoromethyl radical

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has been studied. Photolysis of trifluoroiodomethane was used for preparation of the trifluoromethyl radical; the reasons for the choice of this radical and the basic assumptions made in this type of study have been outlined earlier (Part I, *J.*, 1952, 2504).

Trifluoroiodomethane and chlorotrifluoroethylene react smoothly on exposure to ultra-violet light and yield products of general formula $CF_3\cdot[C_2ClF_3]_n\cdot I$. The value of n depends on the relative amounts of the reactants and to aid determination of orientation conditions have been chosen so that the compound where $n = 1$ is obtained in high yield (*ca.* 85%).

The compound where $n = 1$ might be (I) or (II), but the following evidence shows that only (I) is formed (to the extent of at least 95%).

(I) $CF_3\cdot CF_2\cdot CFClI$ $\qquad$ $CF_3\cdot CFCl\cdot CF_2I$ (II)

The product readily liberates iodine on exposure to light, and photochemical chlorination gives a high yield of the dichloride (III): (II) would have given (IV) by this procedure. Compounds (III) (b. p. 35°, n_D^{20} 1·305) and (IV) (b. p. 34·7°, n_D^{20} 1·3029) cannot be distinguished by boiling point or refractive index, but comparison of the infra-red spectrum of (III) with that of a known sample of (IV), prepared from hexafluoropropene and chlorine, readily distinguishes the two isomers.* Further, with zinc and ethanol (IV) readily yields hexafluoropropene, whereas (III) does not (see below).

$CF_3\cdot CF_2\cdot CFCl_2$	$CF_3\cdot CFCl\cdot CF_2Cl$	$CF_3\cdot CF_2\cdot CHFCl$	$C_2F_5\cdot CFCl\cdot CFCl\cdot C_2F_5$
(III; C.S. 36)	(IV; C.S. 37)	(V; C.S. 38)	(VI; C.S. 39)

With bromine trifluoride, a vigorous fluorinating agent found very suitable for the replacement of iodine by fluorine in polyhalogeno-iodides, the compound where $n = 1$ yields 1-chloroheptafluoropropane, identical with a specimen prepared from heptafluorobutyric acid (Haszeldine, *J.*, 1951, 584; 1952, 4259) by comparison of infra-red spectra (C.S. 40.) This again establishes the configuration as (I), since (II) would have yielded 2-chloroheptafluoropropane,

The compound (I; $n = 1$) (C.S. 41) undergoes a complex reaction with zinc and ethanol, mainly replacement of iodine by hydrogen, to give (V), but spectroscopic examination in the 5·5—6·5-μ region reveals that two olefins, neither being hexafluoropropene, are formed in *ca.* 10% yield. Removal of the unsaturated material by treatment with chlorine left (V), whose infra-red spectrum proves that hydrogen is present (typical sharp C–H stretching absorption at 3·34 μ). The dichloride (III) fails to liberate hexafluoropropene on treatment with zinc and ethanol, which proves that (IV) is absent: (IV) gave more than 90% of hexafluoropropene under identical conditions. Somewhat surprisingly, (III) is not inert to zinc and ethanol, and like (I) yields mainly (V); spectroscopic examination shows that only one of the two olefins is present.

The unsaturated material formed from (I) yields two dichlorides. The first, $C_6F_{12}Cl_2$, b. p. 111°, is shown to be 3 : 4-dichlorododecafluorohexane (VI) by means of its infra-red spectrum; the second is 2 : 3-dichloro-1 : 1 : 1 : 2 : 3-pentafluoropropane (VII), identified *via* its dechlorination product (IX). These compounds clearly arise from (I), (*a*) by a coupling reaction, $CF_3\cdot CF_2\cdot CFClI \xrightarrow{\text{Zn-EtOH}} [CF_3\cdot CF_2\cdot CFCl]_2 \xrightarrow{\text{Zn-EtOH}} C_2F_5\cdot CF{:}CF\cdot C_2F_5$, and (*b*) by reduction to (V) followed by removal of chlorine and fluorine. The dichloride (VI) was synthesised by photolysis of (I) in the presence of mercury:

$CF_3\cdot CFCl\cdot CHFCl$	$C_2F_5\cdot CF{:}CF\cdot C_2F_5$	$CF_3\cdot CF{:}CHF$	$CF_3\cdot CF{:}CFCl$
(VII)	(VIII; C.S. 42)	(IX; C.S. 43)	(X)

$$CF_3\cdot CF_2\cdot CFClI \xrightarrow{h\nu,\ Hg} CF_3\cdot CF_2\cdot CFCl\cdot \longrightarrow \text{(VI)}$$

Dechlorination of (VI) with zinc and ethanol yields perfluorohex-3-ene (VIII) {(II) would have given $[CF_3\cdot CFCl\cdot CF_2]_2$ by this sequence}. The infra-red spectrum of (VIII) has a C=C stretching vibration at 5·84 μ, showing that at least some of the *cis*-isomer is present; the marked shift to longer wave-length of the C=C vibration relative to that in octafluorobut-2-ene (5·77 μ; Haszeldine, *J.*, 1952, 4423) can be attributed to the replace-

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* Copies of infra-red spectra designated by C.S. nos. have been deposited with the Chemical Society (cf. *Proc.*, 1952, 164), and photocopies may be obtained from the General Secretary. The C.S. no. must be cited in such requests.

ment of the trifluoromethyl group by the heavier and less electronegative pentafluoroethyl group. Comparison of the spectrum of (VIII) with the spectra of the materials obtained by reaction of (I) or (III) with zinc and ethanol showed that (VIII) was formed from (I) but not from (III). This is not unexpected, since the coupling reaction to give (VI), which must precede the formation of (VIII), will clearly occur much more readily with (I), which contains a carbon–iodine bond, than with (III), which contains a carbon–chlorine bond.

The coupling of compounds containing carbon–iodine bonds can be achieved photochemically, mercury being used to remove iodine atoms, or by the use of zinc and dioxan, which favours intermolecular dehalogenation rather than intramolecular dehalogenation or reduction (Haszeldine, *J.*, 1952, 4423). Application of the zinc–dioxan technique to (I) gave (VIII), with only traces of (V). It is emphasised that, to get preferential coupling instead of reduction, the reaction with zinc and dioxan must be carried out at as low a temperature as possible. After coupling has occurred, dehalogenation of the new compound can be effected *in situ* by raising the temperature to the boiling point :

$$\text{(I)} \xrightarrow[20^\circ]{\text{Zn-dioxan}} \text{(VI)} \xrightarrow[100^\circ]{\text{Zn-dioxan}} \text{(VIII)}.$$

The isolation of (IX) after reaction of zinc and ethanol with (III) or (V) shows that its formation from (I) proceeds *via* (V). This is the first recorded instance of the removal of fluorine from a CF_2 group under such relatively mild conditions. Perfluoropropane and 1-chloroheptafluoropropane are stable to zinc and ethanol at 300°, but heptafluoro-1-iodopropane yields hexafluoropropene and heptafluoropropane at 200°. If the first step of the dehalogenation reaction $\cdot CF_2\cdot CFXX' \longrightarrow \cdot CF{:}CFX'$ involves loss of X as X^-, or conversion of $\cdot CF_2\cdot CFXX'$ into $\cdot CF_2\cdot CFX'\cdot ZnX$, then the ease of reaction will clearly be in the order $X = I > Br > Cl > F$. The nature of X′ is also important in so far as it facilitates loss of X as X^-. The dehalogenation reaction should proceed most readily with $X = H > Br > Cl > F$, and this is in accord with the absence of $CF_3\cdot CF{:}CFCl$ as a reaction product of (I) or (III) with zinc and ethanol. Dehalogenation does not occur until the terminal CHFCl group has been formed by reduction. Pentafluoropropene reacts readily with chlorine, to give the dichloride (VII). That the pentafluoropropene obtained from (I) contains no hexafluoropropene is shown by examination of infra-red spectra.

The boiling points of the fluoropropenes (Table 1) show that concentration of fluorine atoms at one end of the molecule, or on the minimum number of carbon atoms, gives the lower boiling point in any particular pair of isomers (cf. $CF_3\cdot CF{:}CH_2$, $CF_3\cdot CH{:}CHF$; $CF_3\cdot CH{:}CF_2$, $CF_3\cdot CF{:}CHF$); this effect has been noted earlier with bromo- and chloro-fluoropropenes (Haszeldine, *J.*, 1951, 2495).

TABLE 1. *Boiling points.*

$CF_3\cdot CF{:}CF_2$ [1]	−29°	$CF_3\cdot CH{:}CHF$ [3]	−16°	$CF_3\cdot CF{:}CHF$ [2]	−18·5°
$CF_3\cdot CF{:}CH_2$ [1]	−28·3°	$CF_3\cdot CH{:}CF_2$ [1]	−21·0°	$CF_3\cdot CH{:}CH_2$ [4]	−22°

[1] Henne and Waalkes, *J. Amer. Chem. Soc.*, 1946, **68**, 496. [2] This paper. [3] Haszeldine and Steele, *J.*, 1953, 1199. [4] Haszeldine, *J.*, 1951, 2495.

The evidence summarised above clearly establishes the orientation in the addition of trifluoroiodomethane to chlorotrifluoroethylene. With a chain mechanism similar to that proposed for the interaction of trifluoroiodomethane and tetrafluoroethylene (Haszeldine, *J.*, 1949, 2856), *viz.*,

$$CF_3I \xrightarrow{h\nu} CF_3\cdot + I\cdot.$$

Initiation : $CF_3\cdot + CF_2{:}CFCl \longrightarrow CF_3\cdot CF_2\cdot CFCl\cdot$

Propagation : $CF_3\cdot CF_2\cdot CFCl\cdot + CF_2{:}CFCl \longrightarrow CF_3\cdot CF_2\cdot CFCl\cdot CF_2\cdot CFCl\cdot$ etc.

Transfer : $CF_3\cdot CF_2\cdot CFCl\cdot + CF_3I \longrightarrow CF_3\cdot CF_2\cdot CFClI + CF_3\cdot \longrightarrow$ etc.

the propagation step to give $CF_3\cdot[CF_2\cdot CFCl]_n\cdot I$ competes with the chain-transfer step which gives the compound where $n = 1$. Since collision with a trifluoroiodomethane molecule is necessary to cause chain transfer, it is to be expected that a high

$CF_3I : C_2ClF_3$ ratio will favour formation of (I), and a low ratio polymer formation. This is true for any addition–polymerisation reaction of the type given above, but the ease of polymerisation of the olefin, also a major factor, often prevents control of the products being achieved merely by changing the ratio of the reactants. With chlorotrifluoroethylene and trifluoroiodomethane, however, appreciable control is possible in this way. When $CF_3I : C_2ClF_3$ is $>5 : 1$, only (I; $n = 1$) (85—90%) and (XI; $n = 2$) (10—15%) are formed, but as the ratio is decreased (*e.g.*, 1 : 1), compounds where $n > 1$ (*e.g.*, $n = 1$—5) are obtained; a moderate excess of chlorotrifluoroethylene (1 : 2) gives products with $n > 12$, and with a high $C_2ClF_3 : CF_3I$ ratio, a Kel-F type solid polymer is produced (see Table 3). In the compound (I; $n = 1$), the carbon–iodine bond is readily broken homolytically by ultra-violet light, and yields a $CF_3\cdot CF_2\cdot CFCl\cdot$ radical which, although less reactive than a $-CF_2\cdot$ radical, can initiate a chain reaction with chlorotrifluoroethylene. To obtain high yields of (I), therefore, the reaction products must be removed from the reaction zone and shielded from light.

Since a quantitative yield of (I) cannot be obtained even with a large excess of trifluoroiodomethane, it becomes essential to determine the constitution of the compounds where $n = 2, 3, 4$, etc., since it could be argued that if the $CF_3\cdot$ radical attacked the CFCl group of chlorotrifluoroethylene and gave $CF_3\cdot CFCl\cdot CF_2\cdot$, then this radical, being more reactive than the $CF_3\cdot CF_2\cdot CFCl\cdot$ radical, would combine with a second molecule of chlorotrifluoroethylene at a much greater rate. This could mean that the compound where $n = 1$ was $CF_3\cdot CF_2\cdot CFClI$, whereas the compounds where $n = 2, 3, 4$, etc., were $CF_3\cdot CFCl\cdot CF_2\cdot[C_2ClF_3]_{n-1}\cdot I$ or mixtures containing compounds having this general formula. Such a possibility would not alter the conclusion that the main attack of the $CF_3\cdot$ radical was on the CF_2 group of chlorotrifluoroethylene, but it would invalidate the statement that attack was exclusively on this group.

The compounds where $n > 1$ isolated from the reaction of trifluoroiodomethane with chlorotrifluoroethylene have been separated. That where $n = 2$ could have four possible formulæ (XI—XIV). The ultra-violet spectrum (Table 2) provides strong evidence that the CFClI chromophore is present, since the CF_2I chromophore is characterised by $\lambda_{max.}$ 250—251 mμ, whereas the CFClI chromophore has $\lambda_{max.}$ 261—262 mμ. Marked similarities can also be observed in the infra-red spectra of the compounds where $n = 1$ and 2. The compound where $n = 1$ has been proved to be (I); photochemical reaction of (I) with chlorotrifluoroethylene yields compounds $CF_3\cdot CF_2\cdot CFCl\cdot[C_2ClF_3]_m\cdot I$; in the liquid phase, with a high ratio (I) : C_2ClF_3, the compound where $m = 1$ can be isolated in *ca.* 50% yield.

TABLE 2. *Absorption spectra in ethanol.*

	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε		$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
$CF_3\cdot CF_2\cdot CFClI$ ...	262	315	235	240	$CF_3\cdot[CF_2\cdot CFCl]_5\cdot I$	Infl. 250—270	450	—	—
$CF_3\cdot[CF_2\cdot CFCl]_2\cdot I$	267·5	400	238·5	230					
$CF_3\cdot[CF_2\cdot CFCl]_3\cdot I$	268	450	245	380	$CF_2Cl\cdot CFClI$ [1] ...	261	295	233	195
$CF_3\cdot[CF_2\cdot CFCl]_4\cdot I$	262	470	250	420	$CF_2Cl\cdot CF_2I$ [2]	251·5	280	225·5	185
					$CF_3\cdot CF_2\cdot CF_2I$ [3] ...	250·5	230	225·5	150

[1] Haszeldine, *J.*, 1952, 4423. [2] *Nature*, 1950, **166**, 192. [3] *J.*, 1952, 3423.

$$CF_3\cdot CF_2\cdot CFCl\cdot \xrightarrow{C_2ClF_3} CF_3\cdot CF_2\cdot CFCl\cdot[C_2ClF_3]_m\cdot \xrightarrow{CF_3\cdot CF_2\cdot CFClI} CF_3\cdot CF_2\cdot CFCl\cdot[C_2ClF_3]_m\cdot I$$

Infra-red spectroscopic examination shows that the compounds where $m = 1, 2$, or 3 are identical with the compounds where $n = 2$ (C.S. 44), 3, or 4 derived from trifluoroiodomethane and chlorotrifluoroethylene. Since the compound with $m = 1$ (*i.e.*, $n = 2$) derived from (I) can be only (XI) or (XII), depending on the direction of addition to chlorotrifluoroethylene, the possible formulæ (XIII) and (XIV) can be discarded.

(XI) $CF_3\cdot CF_2\cdot CFCl\cdot CF_2\cdot CFClI$ $CF_3\cdot CF_2\cdot CFCl\cdot CFCl\cdot CF_2I$ (XII)
(XIII) $CF_3\cdot CFCl\cdot CF_2\cdot CF_2\cdot CFClI$ $CF_3\cdot CFCl\cdot CF_2\cdot CFCl\cdot CF_2I$ (XIV; C.S. 46)

Now treatment of the compound where $n = 2$ with chlorine yields a trichloride, *A*, which must be (XV) or (XVI). The latter, which contains chlorine on adjacent carbon atoms, would yield a perhalogeno-olefin on treatment with zinc and ethanol, just as (IV) readily gives hexafluoropropene. Reaction of the trichloride, *A*, with zinc and ethanol yields an olefin C_5HClF_8, whose infra-red spectrum reveals a vinylic carbon–hydrogen bond, and two bands in the C=C stretching vibration region, at 5·56 and 5·78 μ, closely

(XV; C.S. 45) $CF_3{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl_2$ $CF_3{\cdot}CF_2{\cdot}CFCl{\cdot}CFCl{\cdot}CF_2Cl$ (XVI)
(XVII) $CF_3{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}CHFCl$ $CF_3{\cdot}CF_2{\cdot}CFCl{\cdot}CF{:}CHF$ (XVIII; C.S. 46)

similar to those of 1 : 2 : 3 : 3 : 3-pentafluoropropene (IX). The absence of perhalogeno-olefin thus eliminates (XVI), and as in the reaction of 1 : 1-dichlorohexafluoropropane with zinc and ethanol discussed earlier, the olefin C_5HClF_8 is clearly derived from (XV) by reduction of the $CFCl_2$ group to CHFCl—this gives (XVII), small amounts of which were isolated—followed by removal of fluorine and chlorine from adjacent carbon atoms to give ${\cdot}CF{:}CHF$, as in XVIII.

The 1 : 2-addition product of trifluoroiodomethane and chlorotrifluoroethylene is thus (XI).

The ultra-violet spectra of the compounds where $n = 3$, 4, or 5 (Table 2) are very similar to that of the compound where $n = 2$, and reveal the presence of the CFClI chromophore. As the chain length increases, so the minimum moves to longer wave-length, and the maximum to longer and then to somewhat shorter wave-length. When $n = 5$, the absorption of the CFClI chromophore is submerged in the general absorption of the $[CF_2{\cdot}CFCl]_n$ chain, and only an inflection is apparent. The infra-red spectra of compounds where $n = 3$—6 are also very similar and show that each contains $[CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl]_x$ groups.

The results thus show that free-radical attack on chlorotrifluoroethylene is exclusively on the CF_2 group. It follows that polychlorotrifluoroethylene (" Kel-F ") is formed by head-to-tail addition, $nCF_2{:}CFCl \xrightarrow{R\cdot} R{\cdot}[CF_2{\cdot}CFCl]_x \cdots$, after initiation by a radical R·.

Henne and Kraus (*J. Amer. Chem. Soc.*, 1951, **73**, 1791) have reported that chlorotrifluoroethylene with bromotrichloromethane or trifluoroiodomethane yields $CCl_3{\cdot}CFCl{\cdot}CF_2Br$ or $CF_3{\cdot}CFCl{\cdot}CF_2I$ (II) respectively. Our results contradict this. Henne and Kraus argued that the trifluoroiodomethane addition product was (II), since on treatment with zinc and ethanol a gas of b. p. —28° was isolated without liberation of fluoride ion; the gas combined with chlorine to give a compound, b. p. 35°, n_D^{20} 1·3041, with properties said to agree with those of (IV). The pure 1 : 1-addition compound was, however, not isolated and there was no proof that (I) was not formed during reaction. The conditions used by these authors would favour polymerisation, but it now seems probable that the 1 : 1-addition product obtained in low yield was actually (I), and that the compound considered to be hexafluoropropene (b. p. —28°) was in fact 1 : 2 : 3 : 3 : 3-pentafluoropropene (b. p. —18·5°) obtained by reduction of (I) to (V) and dehalogenation, and that the dichloride was (VII) and not (IV).

The evidence for the bromotrichloromethane reaction product rested upon the following sequence (Henne and Kraus, *loc. cit.*):

$$C_3BrCl_4F_3\ (CCl_3{\cdot}CFCl{\cdot}CF_2Br) \xrightarrow[100^\circ]{SbF_3Cl_2} C_3Cl_3F_5\ (CF_3{\cdot}CFCl{\cdot}CFCl_2) \xrightarrow[150^\circ]{SbF_3Cl_2} C_3Cl_2F_6\ (CF_3{\cdot}CFCl{\cdot}CF_2Cl)$$

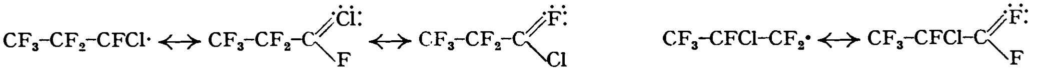
Treatment of the final product $C_3Cl_2F_6$ with zinc and ethanol gave a gas, b. p. —29°, considered to be hexafluoropropene. However, it has recently been shown (Haszeldine, *J.*, 1953, 922) that $CF_3{\cdot}$ and $CCl_3{\cdot}$ radicals behave similarly in addition reactions, and it is thus probable that the bromotrichloromethane addition product is $CCl_3{\cdot}CF_2{\cdot}CFClBr$, and that rearrangement has taken place during treatment with antimony trifluoride. Dr. W. T. Miller has stated (personal communication) that re-investigation of the bromotrichloromethane reaction reveals that the product is $CCl_3{\cdot}CF_2{\cdot}CFClBr$. All apparent differences between trifluoroiodomethane and bromotrichloromethane are thus removed. Further, the photochemical reaction of hydrogen bromide with chlorotrifluoroethylene has shown that the bromine atom, like the $CF_3{\cdot}$ and the $CCl_3{\cdot}$ radical, becomes attached to the CF_2 group (B. R. Steele, unpublished results).

In addition reactions involving ionic intermediates the negative substituent becomes attached to the CF_2 group of chlorotrifluoroethylene, indicating a polarisation $\overset{\delta+}{CF_2}{:}\overset{\delta-}{CFCl}$

(*e.g.*, iodine halides; Haszeldine, *J.*, 1952, **4423**; alcohols and amines, 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). One would thus predict that addition of a polyhalide CX_3Y in presence of aluminium chloride would yield $CX_3{\cdot}CFCl{\cdot}CF_2Y$ ($CX_3Y \xrightarrow{AlCl_3} [CX_3]^+[AlCl_3Y]^- \xrightarrow{CF_2:CFCl} [CX_3{\cdot}CFCl{\cdot}CF_2]^+ \longrightarrow CX_3{\cdot}CFCl{\cdot}CF_2Y$), and the earlier report (Coffman, Cramer, and Rigby, *ibid.*, 1949, **71**, 979) indicating the reverse addition with carbon tetrachloride has recently been corrected by Henne and Kraus (*ibid.*, 1951, **73**, 5303) (*i.e.*, $CCl_4 \longrightarrow CCl_3{\cdot}CFCl{\cdot}CF_2Cl$). Thus, addition of CX_3Y under conditions favouring radical intermediates gives an orientation different from that observed with ionic intermediates, and suggests that the $CX_3{\cdot}$ radical should not be regarded as an electrophilic reagent (cf. Part I, *J.*, 1952, 2504).

As observed with a series of olefins $R{\cdot}CH{:}CH_2$ (Part II, *loc. cit.*), attack of the $CF_3{\cdot}$ radical is on the carbon atom most open to attack for steric reasons. In fact, all radical addition reactions so far encountered could be explained on this simple concept. Until further evidence becomes available, however, this is accepted only with reserve, since it is difficult to explain the marked specificity of attack on olefins such as vinyl fluoride (Part II, *loc. cit.*) on purely steric grounds.

For attack of a CF_3 radical on chlorotrifluoroethylene, formation of the strong $CF_3{-}CF_2$ bond, as found in fluorocarbons, might be favoured over the (presumably) weaker $CF_3{-}CFCl$ bond, thereby favouring the formation of the intermediate $CF_3{\cdot}CF_2{\cdot}CFCl{\cdot}$ radical rather than the $CF_3{\cdot}CFCl{\cdot}CF_2{\cdot}$ radical. Other factors can, however, influence radical stability, *e.g.*, the relative contributions of resonance structures of the type



A full discussion of such factors is deferred.

EXPERIMENTAL

Trifluoroiodomethane was prepared from silver trifluoroacetate (Haszeldine, *J.*, 1951, 584) and was purified by distillation *in vacuo* (Found : *M*, 196. Calc. for CF_3I : *M*, 196). Chlorotrifluoroethylene was a commercial specimen, purified by repeated distillation *in vacuo*, and shown by its infra-red spectrum to be pure (Found : *M*, 116·5. Calc. for C_2ClF_3 : *M*, 116·5).

Irradiations were carried out in sealed Pyrex (300 ml.) or silica (50 ml.) tubes, with extreme precautions to remove air, moisture, etc., which might inhibit or promote peroxide-catalysed or ionic reactions. Other reactions were in 30-ml. Pyrex tubes. A Hanovia lamp without the Wood's filter was the source of ultra-violet radiation.

Distillations were made in an apparatus, which will be described later, designed to reduce handling losses to a minimum.

Interaction of Trifluoroiodomethane and Chlorotrifluoroethylene.—(a) *In silica vessels with a molar ratio ca.* 5 : 1. Trifluoroiodomethane (15·4 g., 0·079 mole) and chlorotrifluoroethylene (2·0 g., 0·017 mole) were sealed *in vacuo* and irradiated at a distance of 8 cm., the liquid phase being shielded. Reaction in the vapour phase gave colourless liquids, which collected in the shielded portion of the tube. After 4 days, fractionation in a vacuum gave unchanged trifluoroiodomethane (12·4 g., 80%) (Found : *M*, 196), and a more volatile fraction (0·15 g.) which passed through a trap cooled to −140° and condensed in a trap at −183° Spectroscopic examination of the latter fraction showed it to be a mixture of hexafluoroethane and chlorotrifluoromethane (approx. 1 : 1). The last two compounds were isolated only when irradiation was prolonged and trifluoroiodomethane was in excess, and involve radical combination and abstraction of chlorine from the polymer. The liquid products (4·8 g.) were distilled, to give 1-*chlorohexafluoro*-1-*iodopropane* (4·0 g., 84% based on trifluoroiodomethane used, 75% based on chlorotrifluoroethylene), b. p. 58°/330 mm., n_D^{20} 1·381 (Found : C, 11·4. C_3ClF_6I requires C, 11·5%), and 1 : 3-*dichlorononafluoro*-1-*iodopentane* (0·6 g., 9% based on trifluoroiodomethane used), b. p. 68°/32 mm., n_D^{20} 1·400 (Found : C, 13·8. $C_5Cl_2F_9I$ requires C, 13·9%). The reactions of this compound are described below. Only traces of material of higher molecular weight remained.

(b) *In silica vessels with a molar ratio ca.* 1 : 1. Chlorotrifluoroethylene (8·6 g., 0·074 mole) and trifluoroiodomethane (18·4 g., 0·094 mole), irradiated as in (a), gave unchanged trifluoroiodomethane (8·7 g., 47%) and liquid products faintly coloured with iodine. Distillation gave 1-chlorohexafluoro-1-iodopropane (9·8 g.), b. p. 60°/340 mm., n_D^{20} 1·381, 1 : 3-dichlorononafluoro-1-iodopentane (4·5 g.), b. p. 72°/34 mm., n_D^{20} 1·400, and a residue (3·0 g.) [shown later by combination with similar material to contain 1 : 3 : *5-trichlorododecafluoro-*1*-iodoheptane* (*ca.* 1·5 g.), b. p. 74—6°/14 mm., n_D^{20} 1·402 (Found: C, 14·8. $C_7Cl_3F_{12}I$ requires C, 15·4%)], 1 : 3 : 5 : 7*-tetrachloropentadecafluoro-*1*-iodononane* (*ca.* 0·9 g.), b. p. 110°/9 mm., n_D^{20} 1·405 (Found: C, 16·2. $C_9Cl_4F_{15}I$ requires C, 16·3%), and a residual fraction, 1 : 3 : 5 : 7 : 9*-pentachloro-octadecafluoro-*1*-iodoundecane* (*ca.* 0·5 g.) (Found: C, 16·8. $C_{11}Cl_5F_{18}I$ requires 16·9%).

The compounds $CF_3{\cdot}[C_2ClF_3]_n{\cdot}I$ are readily decomposed by light or on contact with oxygen, yielding iodine and solid products; they must be stored in sealed containers in the dark.

(c) *In silica vessels, with an excess of chlorotrifluoroethylene.* Chlorotrifluoroethylene (6·1 g., 0·052 mole) and trifluoroiodomethane (6·1 g., 0·027 mole), irradiated as in (a), gave unchanged trifluoroiodomethane (1·1 g., 18%) (distilled in a vacuum system), liquids (10·5 g.), which on distillation through a short column gave fractions with b. p.s identical with those obtained as in (b) (n = 1—5: 4·0, 2·2, 1·4, 0·5, and 0·3 g. respectively), and a glass-like residue (1·3 g.) containing an average of eleven units of chlorotrifluoroethylene (Found: C, 18·9. Calc. for $C_{23}Cl_{11}F_{36}I$: C, 18·7%).

The yields of the compounds $CF_3{\cdot}[C_2ClF_3]_n{\cdot}I$ in experiments (a), (b), and (c) are shown in Table 3, and their ultra-violet spectra in Table 2.

TABLE 3.

	Yield (%) based on $CF_2{:}CFCl$			Yield (%) based on CF_3I		
n	(a)	(b)	(c)	(a)	(b)	(c)
1	75	44	25	84	63	50
2	16	29	20	9	21	20
3	—	11	15	—	5	10
4	—	7	6	—	4	4
5	—	4	3	—	1	2
Res.	—	—	20	—	—	3

(d) *In Pyrex vessels.* Trifluoroiodomethane (14·5 g., 0·075 mole) and chlorotrifluoroethylene (7·3 g., 0·063 mole) were sealed in a Pyrex tube, and the vapour phase was irradiated at a distance of 8 cm. for 7 days, the liquid phase being shielded. A small amount of solid polymer was formed on the side of the tube nearest the lamp. The unchanged reactants (15·3 g., 70%) (Found: M, 170) were distilled in a vacuum, and the liquid products (4·7 g.) yielded 1-chlorohexafluoro-1-iodopropane (3·0 g., 45% based on trifluoroiodomethane used), b. p. 67°/500 mm., 1 : 3-dichlorononafluoro-1-iodopentane (0·7 g., 14%), b. p. 46°/10 mm., n_D^{20} 1·400 [shown by their infra-red spectra to be identical with the fractions obtained as in (a) above], and material of higher b. p. (0·4 g.).

Chlorination of 1*-Chlorohexafluoro-*1*-iodopropane.*—The compound (3·3 g.) was sealed in a Pyrex tube with an excess of chlorine (1·29 g.) and exposed to ultra-violet light for 2 days. Mercury was then added to remove the chlorine and iodine chlorides, the volatile products were transferred to a vacuum system, and distillation gave 1 : 1-dichlorohexafluoropropane (1·74 g., 75%), b. p. 35° (Found: M, 222. Calc. for $C_3Cl_2F_6$: M, 221). Henne and Waalkes (*J. Amer. Chem. Soc.*, 1945, **67**, 1639) report b. p. 35°.

For comparison 1 : 2-dichlorohexafluoropropane was prepared in 90% yield by reaction of chlorine (0·55 g.) with hexafluoropropene (0·80 g.) in a Pyrex tube exposed to light, followed by treatment with mercury and fractionation *in vacuo* (Found: M, 222). The 1 : 2-dichloro-compound has a characteristic absorption band at 11·75 μ which is absent from the spectrum of 1 : 1-dichlorohexafluoropropane.

Conversion of 1*-Chlorohexafluoro-*1*-iodopropane into* 1*-Chloroheptafluoropropane.*—Dropwise addition of an excess of bromine trifluoride to 1-chlorohexafluoro-1-iodopropane (1·05 g.), contained in a platinum crucible fitting inside a Pyrex flask which was cooled to *ca.* −80°, gave volatile products collected in a trap cooled by liquid nitrogen. These were washed with 30% aqueous sodium hydroxide to remove traces of bromine and silicon tetrafluoride, and were distilled *in vacuo*, giving 1-chloroheptafluoropropane (0·52 g., 75%) (Found: M, 202. Calc. for C_3ClF_7: M, 204·5).

An authentic specimen of 1-chloroheptafluoropropane (b. p. −1°) was prepared by interaction of silver heptafluorobutyrate (2·0 g.) and an excess of chlorine at 100° for 12 hours. The gas was washed with 30% aqueous sodium hydroxide, and distilled, to give 1-chloroheptafluoropropane (1·01 g., 79%) (Found: M, 206).

*Preparation of Perfluorohex-*3*-ene from* 1*-Chlorohexafluoro-*1*-iodopropane.*—(a) *By photo-*

chemical reaction with mercury, etc. The compound (4·0 g.), sealed and vigorously shaken with mercury (11 g.) in a silica tube for 7 days with exposure to ultra-violet light, gave 3 : 4-*dichlorododecafluorohexane* (1·60 g., 68%), b. p. 110—112°, n_D^{20} 1·324 (Found: C, 18·7. $C_6Cl_2F_{12}$ requires C, 19·4%). This (0·80 g.) was heated in a Carius tube with zinc dust (5 g.) and alcohol (10 ml.) at 110° for 24 hours, to give a volatile product which was washed with water and distilled, yielding *perfluorohex-3-ene* (0·37 g., 58%), b. p. 49° (Found: C, 24·3; *M*, 300. C_6F_{12} requires C, 24·0%; *M*, 300).

(b) *By reaction with zinc and dioxan.* The chlorofluoroiodopropane (2·0 g.) was sealed with zinc dust (5 g.) and dioxan (5 ml.), shaken vigorously, and slowly heated during 48 hours to 110°. The volatile products were washed with water, dried, and distilled in a vacuum, giving perfluorohex-3-ene (0·52 g., 54%) and 1-chloro-1 : 2 : 2 : 3 : 3 : 3-hexafluoropropane (0·13 g., 11%). Infra-red spectroscopic examination showed that the former was identical with the material obtained in (a) above, and the latter with the compound described below.

Reaction of 1-*Chlorohexafluoro*-1-*iodopropane with Zinc and Ethanol.*—A solution of the iodo-compound (4·7 g.) in ethanol (10 ml.) was slowly added to a well-stirred mixture of zinc dust (50 g.) and refluxing ethanol (100 ml.) to give, by a slow reaction requiring 40 hr. for completion, volatile products passing through the reflux water-condenser. These were washed with water and distilled *in vacuo*, to give a fraction (1·90 g.) condensing at −95°, shown by infra-red spectroscopic examination to be 1-chloro-1 : 2 : 2 : 3 : 3 : 3-hexafluoropropane contaminated by olefinic compounds. The material was sealed with an excess of chlorine (0·7 g.) for 2 days and redistilled, to give pure 1-*chloro*-1 : 2 : 2 : 3 : 3 : 3-*hexafluoropropane* (1·70 g., 60%), b. p. 20° (Found: C, 19·4; H, 0·3%; *M*, 187. C_3HClF_6 requires C, 19·4; H, 0·5%; *M*, 186·5), and two dichlorides; the first dichloride (0·24 g.), on fractionation in a micro-distillation apparatus, gave 3 : 4-dichlorododecafluorohexane (*ca.* 9%), b. p. 110°, n_D^{20} 1·323, identical with the material obtained earlier; the second (*ca.* 0·1 g.) was shown to be 1 : 2-dichloro-1 : 2 : 3 : 3 : 3-pentafluoropropane (see below). Infra-red spectroscopic examination showed that hexafluoropropene was not present in the olefinic compounds mentioned above (see also 1 : 2 : 3 : 3 : 3-pentafluoropropene, below)

Reaction of Dichlorohexafluoropropanes with Zinc and Ethanol.—Zinc dust (4 g.), ethanol (8 ml.), and 1 : 1-dichlorohexafluoropropane (1·37 g.) were sealed together and stirred at 50° for 16 hr. The volatile products were then washed with water, dried (phosphoric anhydride), and distilled *in vacuo*, to give 1-chloro-1 : 2 : 2 : 3 : 3 : 3-hexafluoropropane (0·937 g., 80%) (Found: *M*, 185. Calc. for C_3HClF_6: *M*, 186·5) (identified tensimetrically and by its infra-red spectrum) and 1 : 2 : 3 : 3 : 3-pentafluoropropene (0·10 g., 12%) (Found: *M*, 131), b. p. −18·5° (shown to be identical with the material described below by comparison of infra-red spectra).

Similar treatment of 1 : 2-dichlorohexafluoropropane (0·95 g.) at 40° for 18 hr. gave hexafluoropropene (0·58 g., 90%) (Found: *M*, 149. Calc. for C_3F_6: *M*, 150), identified tensimetrically.

Preparation of 1 : 2 : 3 : 3 : 3-*Pentafluoropropene.*—1-Chloro-1 : 2 : 2 : 3 : 3 : 3-hexafluoropropane (0·644 g.), heated and shaken at 120° for 7 days with zinc dust (4 g.) and ethanol (10 ml.), gave 1 : 2 : 3 : 3 : 3-pentafluoropropene (0·240 g., 53%), b. p. −18·5° (Found: C, 27·6%; *M*, 131·5. C_3HF_5 requires C, 27·3% *M*, 132); a small amount of hydrogen was formed during reaction.

The infra-red spectrum of the pentafluoropropene shows the vinylic C–H stretching vibration at 3·18 μ and the C=C stretching vibration at 5·74 μ; the weak band at 5·56 μ may be caused by *cis–trans*-isomerism. Hexafluoropropene has the strong C=C stretching absorption at 5·56 μ, but the strong doublet at 12·97—13·05 μ readily enables even small amounts of the olefin to be detected when mixed with 1 : 2 : 3 : 3 : 3-pentafluoropropene.

Reaction of the pentafluoropropene with a slight excess of chlorine in a sealed tube gave 1 : 2-dichloro-1 : 2 : 3 : 3 : 3-pentafluoropropane (80%), b. p. 56°, n_D^{16} 1·339.

Reaction of 1-*Chlorohexafluoro*-1-*iodopropane with Chlorotrifluoroethylene.*—(a) *With excess of* 1-*chlorohexafluoro*-1-*iodopropane.* The iodo-compound (2·0 g., 0·0064 mole) was sealed in a 10-ml. silica tube with chlorotrifluoroethylene (0·277 g., 0·0024 mole) and the *liquid* phase was irradiated for 18 hr., the vapour phase being shielded. Fractionation gave unchanged chlorotrifluoroethylene (0·060 g., 22%) and a liquid coloured with iodine (cf. vapour-phase reaction where photolysis of reaction products is negligible). The liquid was shaken with sodium thiosulphate solution and distilled from phosphoric anhydride, to give unchanged 1-chlorohexafluoro-1-iodopropane (1·0 g.), b. p. 58°/330 mm., 3 : 4-dichlorododecafluorohexane (0·2 g.), b. p. 50°/200 mm. (formed by dimerisation of $CF_3{\cdot}CF_2{\cdot}CFCl{\cdot}$ radicals), 1 : 3-dichlorononafluoro-1-iodopentane (0·4 g., 50% based on C_2ClF_3 used), b. p. 70°/34 mm., and material

(0·2 g.) of higher b. p. Infra-red spectroscopic examination showed that these fractions were identical with the materials obtained as above.

(b) *With an excess of chlorotrifluoroethylene.* The iodo-compound (2·0 g., 0·0064 mole) and chlorotrifluoroethylene (1·4 g., 0·012 mole) were exposed to ultra-violet light, as in (a), for 4 days, giving unchanged 1-chlorohexafluoro-1-iodopropane (0·5 g.), 1 : 3-dichlorononafluoro-1-iodopentane (0·4 g., 8% based on C_2ClF_3), b. p. 78°/37 mm., 1 : 3 : 5-trichlorododecafluoro-1-iodoheptane (*ca.* 0·5 g., 15% based on C_2ClF_3), b. p. 72°/17 mm., 1 : 3 : 5 : 7-tetrachloropentadecafluoro-1-iodononane (*ca.* 0·7 g., 26% based on C_2ClF_3), b. p. 110°/10 mm., and 1 : 3 : 5 : 7 : 9-pentachloro-octadecafluoro-1-iodoundecane (*ca.* 1·0 g., 43% based on C_2ClF_3). These fractions were shown by their infra-red spectra to be identical with materials obtained from trifluoroiodomethane and chlorotrifluoroethylene.

Reaction of 1 : 3-*Dichlorononafluoro*-1-*iodopentane with Zinc and Ethanol.*—The compound (1·79 g.) was stirred with zinc dust (4 g.) and ethanol (15 ml.) for 4 hr. at 0—4°. Filtration followed by addition of water gave a lower layer, b. p. <120°, which was shaken with mercury and exposed to ultra-violet light to remove unchanged iodo-compound. Distillation then gave 1 : 3-dichloro-1 : 2 : 2 : 3 : 4 : 4 : 5 : 5 : 5-nonafluoropentane, b. p. 103° (micro), n_D^{20} 1·334 (Found: C, 20·7. $C_5HCl_2F_9$ requires C, 19·8%), shown by its infra-red spectrum and analysis to be slightly contaminated with the chloro-octafluoropentene. The infra-red spectrum showed bands at 3·38 and 3·5 μ (C–H stretching) 7·50, 8·06, 8·25, 8·68 (w), 8·85 (w), 9·08 (w), 9·40 (w), 9·65 (w), 10·50, 11·45, 12·57, 13·15 (w), 13·23, 14·04, 14·65 and 15·32 μ.

Preparation of 1 : 1 : 3-*Trichlorononafluoropentane and its Reaction with Zinc and Ethanol.*—1 : 3-Dichlorononafluoro-1-iodopentane (2·0 g.) was sealed in a small Pyrex tube with chlorine (0·35 g.), and exposed to ultra-violet light for 2 days, and then shaken with mercury. Distillation gave 1 : 1 : 3-*trichlorononafluoropentane* (1·10 g., 70%), b. p. 119°, n_D^{20} 1·345 (Found: C, 17·6. $C_5Cl_3F_9$ requires C, 17·8%).

The trichloride (0·66 g.) was sealed with zinc dust (2 g.) and ethanol (10 ml.) and stirred at 110° for 24 hr., to give, after filtration and precipitation of the organic phase by addition of an excess of water, 3-*chloro*-1 : 2 : 3 : 4 : 4 : 5 : 5 : 5-*octafluoropent*-1-*ene* (0·24 g., 50%), b. p. 67°, n_D^{20} 1·306 (Found: C, 24·6; H, 0·7%; *M*, 245. $C_5Cl_2F_8$ requires C, 24·2; H, 0·4%; *M*, 248·5), and a compound of higher b. p., probably 1 : 3-dichloro-1 : 2 : 2 : 3 : 4 : 4 : 5 : 5 : 5-nonafluoropentane (0·07 g., 12%) (as obtained earlier from the 1 : 3-dichlorononafluoro-1-iodopentane).

Infra-red and Ultra-violet Spectra.—These were determined by use of a Perkin–Elmer Model 21 instrument with rock-salt optics, and of a Unicam Ultra-violet Spectrophotometer.

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