241. *The Addition of Free Radicals to Unsaturated Systems. Part II*. Radical Addition to Olefins of the Type* $R\cdot CH{:}CH_2$.

By R. N. Haszeldine and B. R. Steele.

The formation of $CF_3\cdot CH_2\cdot CHIR$ and not $CF_3\cdot CHR\cdot CH_2I$ by the addition of trifluoroiodomethane to $R\cdot CH{:}CH_2$ ($R = Me$, Cl, F, CO_2Me, CF_3, or CN), shows that orientation in radical addition reactions does not depend on the polarisation of the double bond, but on other factors such as radical stability.

Methods for the replacement of iodine in fluoro-iodo-compounds by chlorine, bromine, or hydrogen are described, and infra-red and ultra-violet spectra are recorded.

In attempting to determine how the direction of addition of a radical to an unsaturated system $RR'C{:}CR''R'''$ is influenced by the nature of R, R', R'', and R''', olefins of the type $R\cdot CH{:}CH_2$ have been studied. The olefins chosen ($R = Me$, Cl, F, CO_2Me, CN, and CF_3) show a wide range of reactivity to electrophilic and nucleophilic attack by reagents A^+B^-, each yielding substantially one product. The direction of addition of A^+B^- is not the same in each case: some give $CHRA\cdot CH_2B$, others $CHRB\cdot CH_2A$. For addition to $R\cdot CH{:}CH_2$, inductive and hyperconjugation effects are operative when $R = Me$, induction and back-co-ordination must be considered when $R = Cl$ or F, and when $R = CO_2Me$ or CN effects due to induction and conjugation may be of importance.

The direction of addition of the trifluoromethyl radical derived from trifluoroiodomethane to these olefins has been established (for a preliminary note see *Chem. and Ind.*, 1951, 684). The reactions were carried out in the vapour phase where possible, with light of wave-length >3000 Å, which only the fluoroiodide can absorb. The reactants were carefully purified so that addition reactions catalysed by traces of peroxides present in the olefin, or involving an ionic mechanism, can be excluded; in no instance was a dark reaction observed.

Propylene reacts smoothly with trifluoroiodomethane on exposure to ultra-violet light, and yields only one product, 1 : 1 : 1-trifluoro-3-iodobutane (I) whose identity is proved by its dehydroiodination to 1 : 1 : 1-trifluorobut-2-ene (III), b. p. 20°, and not to the known isomer (IV), b. p. 6·4° (Swarts, *Bull. Soc. chim. Belg.*, 1927, **36**, 191).

$CF_3\cdot CH_2\cdot CHI\cdot CH_3$ (I)

$CF_3\cdot CH{:}CH\cdot CH_3$ (III)

$CF_3\cdot CH_2\cdot CH{:}CH_2$ (V)

$CF_3\cdot CH(CH_3)\cdot CH_2I$ (II)

$CF_3\cdot C(CH_3){:}CH_2$ (IV)

$CF_3\cdot CH_2\cdot CHCl\cdot CH_3$ (VI)

Dehydroiodination of (I), which could give (III) or (V), yields only (III), and the absence of (V) (b. p. 10·6°; prepared by two independent routes by Leedham and Steele, unpublished work) is shown by comparison of infra-red spectra. The formation of only (III) affords another example of the marked directing influence of a polyfluoro-group on dehydrohalogenation reactions, caused by the increased acidic character of the α-hydrogen

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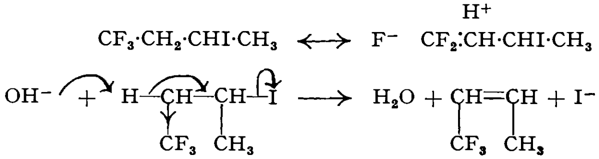
* Part I, Haszeldine, *J.*, 1952, 2504.

atom by hyperconjugation and inductive effects (cf. Haszeldine, *J.*, 1951, 2495; *Nature*, 1951, **168**, 1028). The infra-red spectrum of (III) (C.S. 1*) shows C–H stretching vibrations at 3·27 μ, and 3·38 and 3·49 μ (doublet), ascribed to the $-CH=$ and CH_3 groups respectively; the strong band at 10·4 μ caused by the carbon–hydrogen out-of-plane bending mode in *trans*-olefins (see Part I), and the C:C stretching vibration at 5·90 μ fully support structure (III). Comparison of the ultra-violet spectra of (III) and its perfluoro-analogue, octafluorobut-2-ene (Haszeldine, *J.*, 1952, 4423), reveals the marked shift to shorter wave-length produced by substitution of hydrogen by fluorine (Table 1).



$$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3 \longleftrightarrow \overset{H^+}{F^- \quad CF_2{:}CH{\cdot}CHI{\cdot}CH_3}$$

$$OH^- + H{-}\underset{\displaystyle CF_3}{\underset{|}{CH}}{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}I \longrightarrow H_2O + \underset{\displaystyle CF_3}{\underset{|}{CH}}{=}\underset{\displaystyle CH_3}{\underset{|}{CH}} + I^-$$

TABLE 1.

	Extinction coefficients		
mμ :	230	220	210
$CF_3{\cdot}CH{:}CH{\cdot}CH_3$	7·8	17·8	37·8
$CF_3{\cdot}CF{:}CF{\cdot}CF_3$	2·2	4·6	11·6

TABLE 2.

	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
$CF_3{\cdot}CH_2{\cdot}CHClI$ ...	272	430	230	125
$CF_3{\cdot}CH_2{\cdot}CHIF$ ...	260	340	214	46
$CF_3{\cdot}(CH_2{\cdot}CHF)_2{\cdot}I$	258	430	222	100
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$	264	435	220	28

Treatment of (I) with chlorine gave (VI) whose physical properties agreed with those reported for 3-chloro-1 : 1 : 1-trifluorobutane; the isomeric 1-chloro-3 : 3 : 3-trifluoro*iso*butane derived from (II) is unknown, but would be expected to have an appreciably lower boiling point. Reduction of (I) with zinc and hydrochloric acid yielded 1 : 1 : 1-trifluorobutane, whose b. p. (16·7°) was close to the recorded value (18°).

The above evidence established that the CF_3 radical attacks the terminal methylene group in propylene. The following general mechanism is suggested (R = Me) :

Initiation : $CF_3I \longrightarrow CF_3{\cdot} + {\cdot}I$
Propagation : $CF_3{\cdot} + R{\cdot}CH{:}CH_2 \longrightarrow R{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CF_3$
$R{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CF_3 + R{\cdot}CH{:}CH_2 \longrightarrow R{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CHR{\cdot}CH_2{\cdot}CF_3$
Transfer : $R{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CF_3 + CF_3I \longrightarrow R{\cdot}CHI{\cdot}CH_2{\cdot}CF_3 + CF_3{\cdot}$

If it is assumed that the chain-transfer step is equally efficient for the reaction of trifluoroiodomethane with propylene and 3 : 3 : 3-trifluoropropene (see below), then the rates of reaction are $CH_3{\cdot}CH{:}CH_2 > CF_3{\cdot}CH{:}CH_2$. The orientation in radical addition to propylene is in accord with work on the peroxide-catalysed addition of hydrogen bromide, hydrogen sulphide, thiols, bromodichloromethane, and dibromodichloromethane, α-bromo-esters, sodium hydrogen sulphite, and sulphuryl chloride (see Hey, *Ann. Reports*, 1944, **41**, 186, and Kharasch *et al.*, 1946—1951, for references). Addition of hydrogen halide under conditions favouring an ionic reaction yields the *iso*propyl derivative and indicates a polarisation $\overset{\delta+}{CH_3}{\rightarrow}\overset{\delta-}{-CH}{:}CH_2$.

Irradiation of vinyl chloride and trifluoroiodomethane gives high yields of only one product (VII). As with propylene, only traces of iodine are liberated if the liquid reaction products are shielded from ultra-violet light. The absence of the possible isomer (VIII) was shown by the following reactions : (*a*) Dehydroiodination gave the known 1-chloro-3 : 3 : 3-trifluoropropene (IX), b. p. 21°, and not the known isomer (X), b. p. 14—15° (Haszeldine, *J.*, 1951, 2495). The infra-red spectrum of (IX) (C.S. 2) suggests its formulation as mainly the *trans*-isomer, since olefinic C–H vibrations are apparent at 3·25 and

$CF_3{\cdot}CH_2{\cdot}CHClI$	$CF_3{\cdot}CHCl{\cdot}CH_2I$	$CF_3{\cdot}CH{:}CHCl$	$CF_3{\cdot}CCl{:}CH_2$
(VII)	(VIII)	(IX)	(X)

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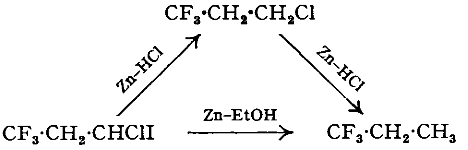
* Spectra thus designated have been deposited with the Chemical Society (cf. *Proc.*, 1952, 164), and photocopies may be obtained from the General Secretary. The C.S. number must be cited in such requests.

10·70 μ, and the C:C stretching vibration is at 6·06 μ, with a side band at 5·90 μ. (*b*) Treatment of (VII) with chlorine gave the 1 : 1-dichloride (XI), b. p. 72·4°, shown to be different from, and not contaminated by, the 1 : 2-dichloride (XII), b. p. 76·7°, which would have been obtained from (VIII). The infra-red spectra of (XI) (C.S. 3) and (XII) (C.S. 4) (prepared by

$$\text{(XI)}\quad CF_3{\cdot}CH_2{\cdot}CHCl_2 \qquad\qquad CF_3{\cdot}CHCl{\cdot}CH_2Cl\quad\text{(XII)}$$

addition of chlorine to 3 : 3 : 3-trifluoropropene) are readily distinguished by the pattern of the C–F stretching vibrations in the 7·5—9 μ region, and by the presence or absence of the strong band at 10·6 μ (XII), and of the strong bands at 12·95 and 14·6 μ (XI). (*c*) Reaction of the vinyl chloride–trifluoroiodomethane addition product with zinc and ethanol failed to yield the 3 : 3 : 3-trifluoropropene which would be readily obtained from (VIII); instead, reduction of (VII) to 1 : 1 : 1-trifluoropropane was observed. (*d*) Similar reduction was noted on treatment of (VII) with zinc and hydrochloric acid, and under the conditions used 3-chloro-1 : 1 : 1-trifluoropropane was also isolated :



The formation of only 1 : 1 : 1-trifluoropropane (C.S. 5) would not distinguish between (VII) and (VIII), but the intermediate chloro-compound isolated can be derived only from (VII). The chloro-compound is readily distinguished from its isomer ($CF_3{\cdot}CHCl{\cdot}CH_3$, b. p. 30·0°) by its infra-red spectrum (C.S. 6), its b. p. (45°), and by its ready dehydrochlorination to 3 : 3 : 3-trifluoropropene (cf. $CF_3{\cdot}CHCl{\cdot}CH_3$; Haszeldine, *J.*, 1951, 2495).

3-Chloro- and 3-bromo-1 : 1 : 1-trifluoropropane (C.S. 7) are readily prepared from 1 : 1 : 1-trifluoro-3-iodopropane (C.S. 8) by reaction with chlorine or bromine in Pyrex vessels.

The photochemical reaction of trifluoroiodomethane with vinyl chloride in the liquid phase is more rapid than in the vapour phase, but iodine is liberated by photolysis of (VII). A thermal reaction causes substantial decomposition of (VII) to 3-chloro-1 : 1 : 1-trifluoropropane, probably by hydrogen abstraction from a hydrogen-containing molecule, RH :

$$CF_3{\cdot}CH_2{\cdot}CHClI \xrightarrow{\text{Heat}} CF_3{\cdot}CH_2{\cdot}CHCl{\cdot} \xrightarrow{\text{RH}} CF_3{\cdot}CH_2{\cdot}CH_2Cl\ (+\ R{\cdot})$$

Hydrogen chloride and polymeric products were also obtained, suggesting that a vinyl chloride polymer $CF_3{\cdot}[CH_2{\cdot}CHCl]_n{\cdot}I$, formed initially, decomposed by dehydrochlorination.

The polarisation of vinyl chloride during reactions involving ionic intermediates can be represented as $\overset{\delta+}{CHCl}{:}\overset{\delta-}{CH_2}$, *e.g.*, in addition of hydrogen chloride, bromide, and iodide, Friedel–Crafts addition of alkyl halides (Schmerling, *J. Amer. Chem. Soc.*, 1946, **68**, 1650; Kharasch *et al.*, *ibid.*, 1934, **56**, 712; *J. Org. Chem.*, 1939, **4**, 429). The direction of addition of the trifluoromethyl radical established above is in accord with the peroxide-catalysed addition of hydrogen bromide to give 1-bromo-2-chloroethane, of hydrogen sulphide to give 2-chloroethanethiol and 2 : 2′-dichlorodiethyl sulphide, of 2-mercaptoethanol to yield 2-chloroethyl 2′-hydroxyethyl sulphide, and of sulphuryl chloride to give 2 : 2-dichloroethanesulphonyl chloride (Vaughan, Rust, and Evans, *loc. cit.*; Fuson and Ziegler, *J. Org. Chem.*, 1946, **11**, 510; Kharasch and Zavist, *loc. cit.*; Yakubovich and Zinov'ev, *loc. cit.*).

Vinyl fluoride reacts with trifluoroiodomethane much faster than does vinyl chloride, and yields (XIII) (C.S. 9) with small amounts of the di-addition product (XV) (C.S. 10).

$$\underset{\text{(XIII)}}{CF_3{\cdot}CH_2{\cdot}CHFI} \qquad \underset{\text{(XIV)}}{CF_3{\cdot}CHF{\cdot}CH_2I} \qquad \underset{\text{(XV)}}{CF_3{\cdot}CH_2{\cdot}CHF{\cdot}CH_2{\cdot}CHFI}$$

That the mono-addition product is (XIII) and not (XIV) is shown by treatment with zinc and dilute acid to give 1 : 1 : 1 : 4-tetrafluoropropane (XVI) (C.S. 11), identical with the compound obtained by halogen replacement in 1 : 1 : 1-trifluoro-3-iodopropane, or by addition of hydrogen fluoride to 3 : 3 : 3-trifluoropropene :

$$\begin{array}{l} CF_3{\cdot}CH_2{\cdot}CHFI \xrightarrow{Zn-HCl} \\ CF_3{\cdot}CH_2{\cdot}CH_2I \xrightarrow[Hg_2F_2]{} \end{array} \underset{(XVI)}{CF_3{\cdot}CH_2{\cdot}CH_2F} \xleftarrow{HF} CF_3{\cdot}CH{:}CH_2$$

Dehydroiodination of (XIII) gave 1 : 3 : 3 : 3-tetrafluoropropene, identical with the compound obtained by addition of hydrogen fluoride to 3 : 3 : 3-trifluoropropyne (Haszeldine, *J.*, 1952, 3490). The infra-red spectrum of the tetrafluoropropene (C.S. 12) shows olefinic C–H absorption at 3·21 and 10·8 μ, and the C:C stretching vibration at 5·90 μ has been moved to lower wave-length relative to that of 1-chloro-3 : 3 : 3-trifluoropropene (see above). The additional band at 5·68 μ may be caused by *cis-trans*-isomerism.

The ultra-violet spectrum of (XV) (Table 2) shows that the alternative formula $CF_3{\cdot}CH_2{\cdot}CHF{\cdot}CHF{\cdot}CH_2I$, containing the CH_2I as distinct from the CHFI chromophore, can be eliminated. This is supported by comparison of the infra-red spectra of (XIII) and (XV), and by the stability of (XV) to water, since compounds with adjacent CHF groups are very unstable and yield CH:CF or C:C by loss of hydrogen fluoride.

Thus addition of the $CF_3{\cdot}CH_2{\cdot}CHF{\cdot}$ radical to a second molecule of vinyl fluoride follows the same orientation as for addition of $CF_3{\cdot}$ to vinyl fluoride. This strongly suggests that polyvinyl fluoride has formula $[{\cdot}CH_2{\cdot}CHF{\cdot}CH_2{\cdot}CHF{\cdot}]$.

Trifluoroiodomethane reacts rapidly with methyl acrylate in the liquid phase to give high yields of the mono-addition compound (XVII), and material of higher boiling point, of general formula (XVIII), partly resolved into its individual members. The direction of addition of the trifluoromethyl radical is established by the conversion of (XVII) (C.S. 13), by zinc and hydrochloric acid, into γγγ-trifluorobutyric acid, identical with material independently synthesised by the sequence :

(XVII) $CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CO_2Me$ $\qquad$ $CF_3{\cdot}[CH_2{\cdot}CH(CO_2Me)]_n{\cdot}I$ (XVIII)

$$CF_3I + C_2H_4 \xrightarrow{Heat} CF_3{\cdot}CH_2{\cdot}CH_2I \xrightarrow[CO_2]{Mg-Et_2O;} CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$

Examination of the infra-red and ultra-violet spectra of the higher-boiling material shows conclusively that it has structure (XVIII). There is a marked similarity in the infra-red spectra of the fractions where in (XVIII) *n* changes from 1 to 4. The presence of the CO_2Me group is shown by the C:O stretching absorption at 5·75 μ. The ultra-violet spectra (Table 3) show that the C–I chromophore is present, and thus eliminate the possibility that the compound $(CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2Me)_2$, formed by combination of two resonance-stabilised $CF_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2Me$ radicals, is a major reaction product.

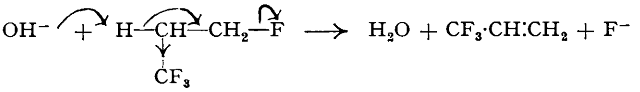
TABLE 3.

	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CO_2Me$	279	390	249	240
$CF_3{\cdot}[CH_2{\cdot}CH(CO_2Me)]_2{\cdot}I$	278	345	251	240
$CF_3{\cdot}[CH_2{\cdot}CH(CO_2Me)]_4{\cdot}I$	270	280	252	253

The addition of hydrogen bromide to acrylic acid yields only one product, β-bromopropionic acid, whether peroxides or antioxidants are added (Walling, Kharasch, and Mayo, *J. Amer. Chem. Soc.*, 1939, **61**, 2693). Thus, it is not known whether the same compound is formed by a reaction involving free radicals as by one involving ionic intermediates, or whether one of the reactions proceeds so much faster than the other that only one product is formed. Studies on the addition of thiols suggest that the RS· radical and the RS⁻ ion become attached to the methylene group in methyl acrylate (Kharasch and Fuchs, *J. Org. Chem.*, 1948, **13**, 97). The present investigation shows quite clearly that free-radical attack takes place on the methylene group.

Results of preparative importance which have emerged during the present work are the ready conversion, in high yield, of fluoro-iodo-compounds into their fluoro-chloro-, or fluoro-bromo-analogues by reaction with chlorine or bromine on exposure to light of wavelength >3000 Å, and their conversion into the fluoro-hydrogeno-compounds by reaction with zinc in hydrochloric acid or ethanol. These techniques considerably simplify structural determinations. The conversion of $>CHI$ into $>CH_2$ takes place smoothly with zinc and acid or ethanol (*e.g.*, I, XVII), but compounds of the type $>CXI$ can yield $>CHX$ or $>CH_2$. Thus, when X = Cl (VII), only the $>CH_2$ compound is obtained with zinc and ethanol, whereas with zinc and hydrochloric acid equal amounts of the $>CHCl$ and $>CH_2$ compounds are obtained. When X = F (XIII), reaction stops at the $>CHF$ stage, indicating that the CH_2F bond is more stable than the CH_2Cl bond in this type of reaction.

The compound $CF_3{\cdot}CH_2{\cdot}CH_2F$ is the first of the type $R{\cdot}CH_2{\cdot}CH_2F$ (R = polyfluoroalkyl) to be prepared, and it is of interest to ascertain whether the lone C–F bond is appreciably stabilised by the CF_3 group compared with an alkyl fluoride and with the compounds $CF_3{\cdot}CH_2{\cdot}CH_2X$ (X = Cl, Br, I). The marked increase in stability of X in compounds of the type $CF_3{\cdot}CHX{\cdot}CH_3$, with X adjacent to the CF_3 group, relative to those of type $CF_3{\cdot}CH_2{\cdot}CH_2X$ (X = Cl, Br, I), has been noted earlier (Haszeldine, *J.*, 1951, 2495). The increased stability of the CH_2F group relative to the CH_2Cl group indicated above, is not shown to as marked an extent in dehydrohalogenation reactions, since the fluoro- and chloro-compounds both readily yield 3 : 3 : 3-trifluoropropene by reaction with ethanolic potassium hydroxide at room temperature. Thus, for the reaction



$$OH^- + H{-}\underset{\underset{CF_3}{\downarrow}}{CH}{-}CH_2{-}F \longrightarrow H_2O + CF_3{\cdot}CH{:}CH_2 + F^-$$

the acidity of the α-hydrogen atom, increased by the inductive effect of the trifluoromethyl group, and the high solvation energy of the fluoride ion, substantially overcome the expected retardation caused by the difference in the C–F and C–Cl bond energies.

Hydrogen abstraction by the CF_3 radical occurs to a very small extent, and is detected only with propylene, where the resonance stability of the allyl radical becomes important :

$$CF_3{\cdot} + CH_3{\cdot}CH{:}CH_2 \longrightarrow CF_3H + \dot{C}H_2{\cdot}CH{:}CH_2$$

The C–I bond in the addition products containing negative atoms or groups on the same carbon atom, e.g., (VII), (XIII), and particularly (XVII), is susceptible to homolysis, but under optimum conditions no iodine is liberated if the reaction products are shielded from the light, thus showing the efficiency of the chain-transfer step (see mechanism above).

Attack of the CF_3 radical on the olefins $R{\cdot}CH{:}CH_2$ (R = Me, Cl, F, CO_2Me) reported above, and on $R{\cdot}CH{:}CH_2$ (R = CF_3, CN; Haszeldine, Part I, *loc cit.*; *J.*, 1952, 3490), is, within the accuracy of the experiments (*ca.* 5%), *exclusively* on the $:CH_2$ group, and the general mechanism outlined above is suggested. Since in ionic reactions $R{\cdot}CH{:}CH_2$ has a polarisation $R{\cdot}\overset{\delta-}{C}H{:}\overset{\delta+}{C}H_2$ (R = CO_2Me, CF_3, CN) or $R{\cdot}\overset{\delta+}{C}H{:}\overset{\delta-}{C}H_2$ (R = Me, Cl, F), it is evident that the nature of R, and hence the apparent polarisation of the double bond, is of little importance in determining orientation in free-radical attack. This becomes particularly clear by comparison of $CF_3{\cdot}CH{:}CH_2$ and $CH_3{\cdot}CH{:}CH_2$, where the inductive and hyperconjugative (but no mesomeric) effects, which act in the *same* direction and determine the polarisation during ionic attack given above, apparently have no influence in *orientation* in radical attack although they do influence the *rate* of reaction. The situation is more complicated with vinyl chloride and fluoride, where inductive ($X{\leftarrow}CH{:}CH_2$) and back-co-ordination ($\overset{+}{X}{:}CH{\cdot}\overset{-}{C}H_2$) effects act in *opposite* directions, and with acrylonitrile and methyl acrylate, where attack on a conjugated system may be influenced by mesomeric effects. Although the *assumption* that the overall polarisation of the double bond on approach of a neutral CF_3 radical can be inferred from orientation in ionic reactions may well be unjustified, it is unlikely that the direction of radical addition to olefins of such different types should be the same if ionic influences were involved.

If orientation in free-radical addition reactions is governed by the stability of the intermediate free radical, then it follows that the secondary radicals $CF_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}$, $CF_3{\cdot}CH_2{\cdot}CHCl{\cdot}$, $CF_3{\cdot}CH_2{\cdot}CHF{\cdot}$, $CF_3{\cdot}CH_2{\cdot}CH(CF_3){\cdot}$, $CF_3{\cdot}CH_2{\cdot}CH(CO_2Me){\cdot}$, and $CF_3{\cdot}CH_2{\cdot}CH(CN){\cdot}$ are more stable than the primary radicals $CF_3{\cdot}CH(CH_3){\cdot}CH_2{\cdot}$, $CF_3{\cdot}CHCl{\cdot}CH_2{\cdot}$, $CF_3{\cdot}CHF{\cdot}CH_2{\cdot}$, $(CF_3)_2CH{\cdot}CH_2{\cdot}$, $CF_3{\cdot}CH(CO_2Me){\cdot}CH_2{\cdot}$, and $CF_3{\cdot}CH(CN){\cdot}CH_2{\cdot}$.

It might be argued that steric factors were controlling the orientation in radical addition, but this seems unlikely to cause such great specificity in orientation. Studies in this connection and the factors which affect the stability of free radicals will be discussed in detail in a later communication in this series.

EXPERIMENTAL

Preparation of Materials and General Technique.—Trifluoroiodomethane (*J.*, 1951, 584) was thoroughly washed with 33% aqueous sodium hydroxide and purified by repeated distillation *in vacuo*. Vinyl chloride and fluoride, propene, and methyl acrylate were commercial specimens purified by repeated distillation *in vacuo* or through a packed column in nitrogen, and checked for purity by their infra-red spectra. Extreme precautions were taken to prevent peroxide formation, and once pure the chemicals were manipulated in a vacuum-system.

The reaction vessels were of Pyrex (30- or 300-ml. capacity) or silica (50-ml. capacity), and were placed 10 cm. from a Hanovia ultra-violet lamp used without the Woods filter. The reaction tubes were connected to a vacuum-system by pressure tubing for filling and emptying, and were sealed *in vacuo*. Thermal reactions were carried out in furnaces controlled to ±3°.

Reaction of Trifluoroiodomethane with Propene.—There was no reaction when trifluoroiodomethane (24·7 g., 0·126 mol.) and propene (5·3 g., 0·126 mol.) were sealed in a Pyrex tube and kept in the dark for 14 days. The tube was then exposed to ultra-violet light with the base of the vertical tube shielded to prevent reaction in the liquid phase or photolysis of the reaction products. A slow reaction occurred during 14 days, and fractionation *in vacuo* then gave unchanged reactants (14·6 g., 49%) [Found: *M*, 121. Calc. for $C_3H_6 + CIF_3$ (1 : 1): *M*, 119], liquid products (see below), and a fraction (0·94 g.) which when sealed with bromine (3 ml.) in a Carius tube for 4 days gave propylene dibromide and fluoroform (0·060 g., 1% based on trifluoroiodomethane used) (Found: *M*, 69. Calc. for CHF_3: *M*, 70), identified tensimetrically. The liquid products were shaken with mercury to remove a small amount of iodine and distilled to give 1 : 1 : 1-*trifluoro-3-iodobutane* (14·9 g., 98%), b. p. 103·5°/763 mm., n_D^{20} 1·4277 (Found: C, 19·8; H, 2·5%; *M*, 240. $C_4H_6F_3I$ requires C, 20·2; H, 2·5%; *M*, 238). Ultra-violet spectrum: Table 2.

There was no apparent reaction when alcoholic potassium hydroxide (30 ml. of 10%) was slowly added to 1 : 1 : 1-trifluoro-3-iodobutane (1·70 g.), cooled in ice, and stirred for 2 hours. Heating at 80° during 4 hours caused precipitation of potassium iodide, and distillation of the gas evolved and collected in traps cooled by liquid nitrogen gave 1 : 1 : 1-*trifluorobut-2-ene* (0·61 g., 77%), b. p. 20° (Found: C, 43·1; H, 4·6%; *M*, 109. $C_4H_5F_3$ requires C, 43·6; H, 4·5%; *M*, 110).

Chlorine (0·55 g.) and 1 : 1 : 1-trifluoro-3-iodobutane (1·68 g.), sealed in a Pyrex tube and exposed to sunlight for 2 hours, then to ultra-violet light for 1 hour, gave, after shaking with mercury to remove iodine and chlorine, 3-chloro-1 : 1 : 1-trifluorobutane (0·97 g., 93%) (Found: C, 32·5; H, 4·2. Calc. for $C_4H_6ClF_3$: C, 32·7; H, 4·1%), b. p. 65·4—66·0°, n_D^{20} 1·3438. Henne and Hinkamp (*J. Amer. Chem. Soc.*, 1945, **67**, 1197) reported b. p. 65·3°, n_D^{20} 1·3433.

To zinc dust (4 g.) and dilute hydrochloric acid (30 ml.) was added 1 : 1 : 1-trifluoro-3-iodobutane (1·37 g.), and the mixture heated under reflux for 4 hours. The volatile products were distilled *in vacuo* to give 1 : 1 : 1-trifluorobutane (0·46 g., 71%) (Found: *M*, 111. Calc. for $C_4H_7F_3$: *M*, 112), b. p. 18°. Henne and Hinkamp (*loc. cit.*) reported b. p. 16·7°.

Interaction of Trifluoroiodomethane and Vinyl Chloride.—(a) *Photochemical, vapour-phase.* Trifluoroiodomethane (25·5 g., 0·13 mol.) and vinyl chloride (8·2 g., 0·13 mol.), sealed in a Pyrex tube, showed no reaction after 15 days in the dark at room temperature. The liquid reactants were then shielded from light, and the vapour phase exposed to ultra-violet light for 14 days. The liquid reaction products, coloured slightly pink by liberated iodine, collected in the shielded portion of the tube. Distillation gave unchanged reactants (16·6 g., 50%) (Found: *M*, 132. Calc. for equimolar amounts of reactants: *M*, 129), and a liquid product, distilled through a small column to give 3-chloro-1 : 1 : 1-trifluoro-3-iodopropane (16·8 g., 97%), b. p. 120°, n_D^{20} 1·453 (Found: C, 14·4; H, 1·3%; *M*, 260. Calc. for $C_3H_3ClIF_3$:

C, 14·0; H, 1·2%; *M*, 258·5). Haszeldine (*J.*, 1951, 2495) reports b. p. 119°, n_D^{20} 1·450. Ultra-violet spectrum: Table 2. Fluoroform was not a product of reaction.

(b) *Photochemical, liquid phase.* Vinyl chloride (2·3 g.) and trifluoroiodomethane (7·0 g.) were sealed in a Pyrex tube, and only the liquid phase was irradiated for 4 days. Much more iodine was liberated than in the vapour-phase reaction, but distillation of the deep red liquid gave 3-chloro-1 : 1 : 1-trifluoro-3-iodopropane (4·4 g., 47%) (identical with that obtained above), unchanged reactants (3·5 g., 38%), and a fraction, b. p. 45—90° (0·80 g.).

(c) *Thermal.* Preliminary experiments in Carius tubes showed that trifluoroiodomethane (2·0 g.) and vinyl chloride (0·6 g.) failed to react below 220° in the dark; at 230° liquid products, iodine, and iodine monochloride were formed, and at 240° copious liberation of iodine was apparent.

Trifluoroiodomethane (37·9 g.) and vinyl chloride (14·8 g.), heated to 230—235° for 4 days in an autoclave (300 ml.), yielded hydrogen chloride (3·5 g., 18% based on vinyl chloride), a mixture of unchanged trifluoroiodomethane (22·4 g., 59%) and vinyl chloride (1·7 g., 11%) (Found: *M*, 187. Calc. for CF_3I: *M*, 196. Calc. for C_2H_3Cl: *M*, 62·5), and the following liquid fractions: (*a*) b. p. 45—50°, n_D^{20} 1·352, 4·5 g.; (*b*) b. p. 50—110°, n_D^{20} 1·409, 3·4 g.; (*c*) 110—120°, n_D^{20} 1·432, 1·3 g. Redistillation of (*a*) gave 3-chloro-1 : 1 : 1-trifluoropropane (Found: C, 27·2; H, 2·8%; *M*, 131. Calc. for $C_3H_4ClF_3$: C, 27·2; H, 3·0%; *M*, 132·5), b. p. 45·8—46·4°/773 mm., n_D^{20} 1·339, identified by comparison of its infra-red spectrum with that of a known specimen, and by the ready dehydrochlorination of a 2·0-g. sample by alcoholic potassium hydroxide (40 ml. of 10%) at 20—40° during 4 hours to give 1 : 1 : 1-trifluoropropene (1·04 g., 72%) (Found: *M*, 96·5. Calc. for $C_3H_3F_3$: *M*, 96). Henne and Whaley (*J. Amer. Chem. Soc.*, 1942, **64**, 1157) report b. p. 45·1°, n_D^{20} 1·3350, for 3-chloro-1 : 1 : 1-trifluoropropane. Infra-red spectroscopic examination of (*c*) showed that it was mainly 3-chloro-1 : 1 : 1-trifluoro-3-iodopropane.

3-Bromo- and 3-chloro-1 : 1 : 1-trifluoropropane are obtained in 80—90% yield by treatment of 1 : 1 : 1-trifluoro-3-iodopropane (1·5 g.) with a slight excess of bromine or chlorine in a Pyrex vessel exposed to ultra-violet light.

(d) *Reactions of* 3-*chloro*-1 : 1 : 1-*trifluoro*-3-*iodopropane.* The compound (1·16 g.) reacted immediately with chlorine (0·353 g.) in a Pyrex tube at room temperature. Iodine monochloride was liberated, and after 12 hours in the dark was removed with the excess of chlorine by shaking the whole with mercury. Distillation gave 3 : 3-dichloro-1 : 1 : 1-trifluoropropane (0·59 g., 80%), b. p. 72·8—73·4°/766 mm., n_D^{20} 1·363 (Found: C, 21·3; H, 1·8%; *M*, 166. Calc. for $C_3H_3Cl_2F_3$: C, 21·6; H, 1·8%; *M*, 167). Henne and Whaley (*loc. cit.*) report b. p. 72·4°, n_D^{20} 1·3631.

For comparison, 2 : 3-dichloro-1 : 1 : 1-trifluoropropane (1·45 g., 83%) b. p. 76·6—77·2°, n_D^{20} 1·367, was prepared by addition of chlorine (0·75 g.) to 1 : 1 : 1-trifluoropropene (1·0 g.; prepared by dehydroiodination of 1 : 1 : 1-trifluoro-3-iodopropane). Henne and Whaley (*loc. cit.*) report b. p. 76·7°, n_D^{20} 1·3671.

To ice-cold 3-chloro-1 : 1 : 1-trifluoro-3-iodopropane (1·8 g.) was added 10% ethanolic potassium hydroxide (40 ml.), potassium iodide being precipitated. After 2 hours the mixture was acidified (dilute hydrochloric acid), then a large excess of water was added. The volatile products were transferred to a vacuum-system and distilled, to give 1-chloro-3 : 3 : 3-trifluoropropene (0·74 g., 82%), b. p. 20·8° (Found: *M*, 129·5. Calc. for $C_3H_2ClF_3$: *M*, 130·5). Haszeldine (*loc. cit.*) reports b. p. 21°.

Reduction of 3-chloro-1 : 1 : 1-trifluoro-3-iodopropane (1·3 g.) with zinc dust (4 g.) and dilute hydrochloric acid (25 ml.) at *ca.* 80° for 4 hours gave, as products carried through a reflux condenser into a liquid air trap: (*a*) 3-chloro-1 : 1 : 1-trifluoropropane (0·225 g., 34%) and 1 : 1 : 1-trifluoropropane (0·065 g., 13%) as a mixture (*M*, 125) which could not be separated by distillation, but which infra-red spectroscopic examination showed to contain only the two components (*M*, 132·5 and 98 respectively); (*b*) 1 : 1 : 1-trifluoropropane (0·105 g., 21%) (Found: *M*, 98·5), b. p. −13°. The total yield of 1 : 1 : 1-trifluoropropane is thus 34%. Attempts to bring about a reduction to only 3-chloro-1 : 1 : 1-trifluoropropane failed.

Treatment of 3-chloro-1 : 1 : 1-trifluoro-3-iodopropane (1·14 g.) with zinc (4 g.) and refluxing ethanol (30 ml.) for 6 hours, followed by addition of an excess of water to the flask and fractionation of the combined volatile products *in vacuo*, gave 1 : 1 : 1-trifluoropropane (0·22 g., 51%) and no 3 : 3 : 3-trifluoropropene.

Interaction of Trifluoroiodomethane and Vinyl Fluoride.—Vinyl fluoride (4·07 g.) and trifluoroiodomethane (17·4 g.) were sealed in a Pyrex vessel and the vapour phase was irradiated for 14 days. The unchanged reactants (5·0 g., 23%) (Found: *M*, 120. Calc. for equimolar mixture of CF_3I and C_2H_3F : *M*, 121) were separated in a vacuum-system from the colourless liquid products, distillation of which gave 1 : 1 : 1 : 3-*tetrafluoro*-3-*iodopropane* (13·9 g., 84%), b. p. 86·2°/757 mm., n_D^{20} 1·4024 (Found : C, 14·7; H, 1·5%; *M*, 240. $C_3H_3F_4I$ requires C, 14·9; H, 1·2%; *M*, 242), and 1 : 1 : 1 : 3 : 5-*pentafluoro*-5-*iodopentane* (1·5 g., 7%), b. p. 64°/20 mm., n_D^{20} 1·421 (Found : C, 20·2; H, 2·0. $C_5H_6F_5I$ requires C, 20·8; H, 2·0%).

Reduction of 1 : 1 : 1 : 3-tetrafluoro-3-iodopropane (1·9 g.) at 70° for 4 hours with zinc dust (4 g.) and dilute hydrochloric acid (30 ml.) gave as volatile product 1 : 1 : 1 : 3-*tetrafluoropropane* (0·72 g., 79%), b. p. 29·4°/761 mm., 23·0°/590 mm. (Found : C, 31·3; H, 3·4%; *M*, 116·5. $C_3H_4F_4$ requires C, 31·0; H, 3·4%; *M*, 116).

Ethanolic potassium hydroxide (15 ml. of 10%), slowly added to 1 : 1 : 1 : 3-tetrafluoro-3-iodopropane (2·5 g.), caused only a slight precipitation of potassium iodide at room temperature. After 4 hours' heating at 60°, an excess of water was added, and the combined volatile products, which had passed through a reflux water condenser and collected in liquid oxygen-cooled traps, were distilled *in vacuo*, to give 1 : 3 : 3 : 3-*tetrafluoropropene* (0·94 g., 80%), b. p. $-16°$ (Found : C, 31·3; H, 1·9%; *M*, 115. $C_3H_2F_4$ requires C, 31·6; H, 1·8%; *M*, 114).

Alternative Synthesis of 1 : 1 : 1 : 3-*Tetrafluoropropane*.—To mercurous fluoride (5·0 g.), thoroughly dried in a platinum dish at 110°, in a 10-ml. Pyrex flask, was added 1 : 1 : 1-trifluoro-3-iodopropane (2·0 g.) (Haszeldine, *J.*, 1949, 2856), and the mixture was heated at 120° under reflux for 5 hours. The volatile products were distilled to give 1 : 1 : 1 : 3-tetrafluoropropane (0·42 g., 41%), b. p. 29° (Found : *M*, 116. Calc. for $C_3H_4F_4$: *M*, 116), shown to be identical with the material obtained above by comparison of their infra-red spectra.

Dehydrofluorination of 1 : 1 : 1 : 3-*Tetrafluoropropane*.—The compound (0·280 g.) shaken with 10% ethanolic potassium hydroxide (3 ml.) in a sealed tube at 20° for 24 hours gave 3 : 3 : 3-trifluoropropene (0·219 g., 94%) (Found : *M*, 96. Calc. for $C_3H_3F_3$: *M*, 96), identified tensimetrically.

Interaction of Trifluoroiodomethane and Methyl Acrylate.—No dark reaction was detected. Methyl acrylate (2·0 g., 0·023 mol.) and trifluoroiodomethane (7·2 g., 0·036 mol.) were sealed in a Pyrex tube and irradiated for 4 days at a distance of 8 cm. from the ultra-violet source. Under these conditions, with most of the trifluoroiodomethane present in the liquid phase, the time of irradiation is critical, and if prolonged, breakdown of the products occurs. Distillation gave unchanged trifluoroiodomethane (5·2 g., 72%), methyl acrylate (1·0 g., 50%), and *methyl* $\gamma\gamma\gamma$-*trifluoro*-α-*iodobutyrate* (2·6 g., 88%), b. p. 82°/42 mm., n_D^{20} 1·440 (Found : C, 21·5; H, 2·3. $C_5H_6O_2F_3I$ requires C, 21·3; H, 2·1%). The iodo-ester readily liberates iodine on exposure to light and is preferably distilled at $\ngtr 110°$ in nitrogen.

In a second experiment, methyl acrylate (8·38 g., 0·098 mol.) and trifluoroiodomethane (17·9 g., 0·091 mol.) were irradiated in a Pyrex vessel for 6 days, to give methyl $\gamma\gamma\gamma$-trifluoro-α-iodobutyrate and 6 g. of a polymer distilled through a Vigreux column : (*a*) b. p. 112°/3 mm., n_D^{20} 1·447 (Found : C, 31·5; H, 3·1%), and (*b*) b. p. 138° ± 2°/0·1 mm., n_D^{20} 1·443 (Found : C, 39·0; H, 4·2%). Compounds of general formula $CF_3\cdot[CH_2\cdot CH(CO_2Me)]_n\cdot I$ have analysis : $n = 1$, C 21·3, H 2·1; $n = 2$, C 29·4, H 3·3; $n = 3$, C 34·4, H 4·0; $n = 4$, C 37·8, H 4·4%. Calc. for $[CF_3\cdot CH_2\cdot CH(CO_2Me)]_2$: C, 38·7; H, 3·9%.

Methyl $\gamma\gamma\gamma$-trifluoro-α-iodobutyrate (0·65 g.) was heated under reflux with zinc dust (2 g.) and 50% sulphuric acid until the zinc dissolved. Ether extraction followed by drying ($MgSO_4$) and distillation gave $\gamma\gamma\gamma$-trifluorobutyric acid (0·32 g., 48%), b. p. 70°/12 mm., which crystallised. Comparison of its infra-red spectrum with that of a genuine specimen confirmed its identity.

Ultra-violet Absorption Spectra.—A Beckman DU and a Unicam instrument were used to obtain the data shown in Table 1 (vapours), and Tables 2 and 3 (ethanolic solutions).

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