Free-radical Additions to Unsaturated Systems. Part XVII.[1] Reaction of Trifluoroiodomethane with Mixtures of Ethylene and Vinyl Fluoride and of Ethylene and Propene

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The thermal reaction of trifluoroiodomethane with vinyl fluoride gives a high yield of a mixture of the two isomeric 1 : 1 adducts 1,1,1,3-tetrafluoro-3-iodopropane and 1,1,1,2-tetrafluoro-3-iodopropane in the ratio 89 : 11. Reaction of trifluoroiodomethane with propene at 200° gives a high yield of a mixture of the 1 : 1 adducts 1,1,1-trifluoro-3-iodobutane and 1-iodo-2-trifluoromethylpropane in the ratio 90 : 10. Thermal reactions of trifluoroiodomethane at 200° with the olefins trifluoroethylene, hexafluoropropene, and vinyl chloride give appreciable amounts of 2 : 1 and higher telomers in addition to the 1 : 1 adducts. The extent of telomer formation is much reduced in the case of trifluoroethylene when the reaction is carried out in the presence of added iodine. Competitive reactions of trifluoroiodomethane with mixtures of ethylene and vinyl fluoride or of ethylene and propene show that the reactivity of the olefins towards trifluoromethyl radical attack is in the order: propene > ethylene > vinyl fluoride.

EARLY work on the direction of addition of a trifluoromethyl radical to an olefin of the type $RCH{:}CH_2$ showed that attack was predominantly at the terminal CH_2 group; attack at the CH group was not detected.[2] Other unsymmetrical olefins, *e.g.* trifluoroethylene,[3-5] gave products which resulted from initial bidirectional radical addition. The availability of g.l.c. and n.m.r. as analytical techniques now allows isomer ratios to be determined with greater precision, and the thermally initiated addition reactions of trifluoroiodomethane with the unsymmetrical olefins vinyl fluoride and propene have thus been re-investigated. Competitive reactions between the iodo-compound and mixtures of ethylene and vinyl fluoride and of ethylene and propene have also been carried out.

Vinyl Fluoride.—The *photochemical* addition of trifluoroiodomethane gave predominant and apparently exclusive (±5%) addition to the CH_2 group of the olefin.[2] More recently the *benzoyl peroxide-initiated* addition of trifluoroiodomethane has been reported[6] to give a 1 : 1 adduct fraction and higher telomers. The ^{19}F n.m.r. spectrum of the 1 : 1 adduct fraction showed the presence of the two isomeric 1 : 1 adducts, 1,1,1,3-tetrafluoro-3-iodopropane (I) and 1,1,1,2-tetrafluoro-3-iodopropane (II), but these were not separated. Bidirectional addition has also been observed[7] in the photochemical reaction of hydrogen bromide with this olefin, although the possibility of a competing ionic reaction has always to be considered in such experiments.

It has now been found that the *thermal* addition of the iodo-compound to vinyl fluoride (3 : 1 molar ratio) at 200° gives a mixture of 1 : 1 adducts (96%). Higher telomers were not detected, and this removes a source of possible error in the earlier work,[2,6] where telomer formation was observed; formation of telomer might remove one of the radicals $CF_3{\cdot}CH_2{\cdot}\dot{C}HF$ or $CF_3{\cdot}CHF{\cdot}\dot{C}H_2$ more rapidly than the other, thus affecting the ratio of (I) to (II). The mixture of 1 : 1 adducts, separated by g.l.c., was identified by physical means (n.m.r., mass spectroscopy, *etc.*) as the isomers (I) (86%) and (II) (10%). It was also shown that under the conditions of the reaction the major product (I) did not isomerise to the adduct (II); the results of a number of experiments showed the minor isomer (II) to comprise, on

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[1] Part XVI, R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1969, 991.

[2] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1953, 1199.

[3] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1957, 2800.

[4] J. F. Harris and F. W. Stacey, *J. Amer. Chem. Soc.*, 1961, **83**, 840; 1963, **85**, 749.

[5] R. Fields, H. Goldwhite, R. N. Haszeldine, and J. Kirman, *J. Chem. Soc.* (*C*), 1966, 2075.

[6] T. J. Dougherty, *J. Amer. Chem. Soc.*, 1964, **86**, 460.

[7] P. I. Abell, *Trans. Faraday Soc.*, 1964, **60**, 2214.

average, 11% of the 1 : 1 adduct mixture. These results indicate an initial bidirectional addition of trifluoromethyl radicals to the olefin.

$$CF_3I \longrightarrow CF_3\cdot + I\cdot$$

$$CF_3\cdot + CH_2{:}CHF \longrightarrow \begin{cases} CF_3\cdot CH_2\cdot \dot{C}HF \xrightarrow{CF_3I} CF_3\cdot CH_2\cdot CHFI \quad \text{(I)} \\ CF_3\cdot CHF\cdot \dot{C}H_2 \xrightarrow{CF_3I} CF_3\cdot CHF\cdot CH_2I \quad \text{(II)} \end{cases}$$

The rate of initial attack of the benzoyl peroxide-generated trifluoromethyl radical on the CH_2 group of the olefin was eleven times greater than attack on the CHF group;[6] this corresponds to the formation of 8—9% of the intermediate radical $CF_3\cdot CHF\cdot\dot{C}H_2$, in reasonable agreement with the 10% yield of the minor isomer (II) found for thermal reaction.

Further confirmation of the structures of the adducts (I) and (II) was provided by their dehydroiodination with powdered potassium hydroxide *in vacuo* to give a mixture of *cis*- and *trans*-1,2,2,2-tetrafluoropropene (97%) and 2,3,3,3-tetrafluoropropene (95%), respectively.

$$CF_3\cdot CH_2\cdot CHFI \xrightarrow{KOH} CF_3\cdot CH{:}CHF$$

$$CF_3\cdot CHF\cdot CH_2I \xrightarrow{KOH} CF_3\cdot CF{:}CH_2$$

Propene.—The majority of free-radical additions to propene, including that of *photochemically produced* trifluoromethyl radicals from trifluoroiodomethane,[2] involve attack on the terminal CH_2 group. However, the additions of the radicals $CH_3\cdot$,[8,9] $CH_3\cdot CH_2\cdot$,[10] and $CH_3\cdot\dot{C}HOH$,[11] and of hydrogen atoms,[12] although predominantly on the CH_2 group, show detectable competing attack on CH.

The *thermal* addition of trifluoroiodomethane to propene (3 : 1 molar ratio) at 200° (18·5 hr.) gave a 99% yield of the isomers 1,1,1-trifluoro-3-iodobutane (III) and 1-iodo-2-trifluoromethylpropane (IV) in the ratio of 89 : 11. The isomers were separated by g.l.c. and identified by physical methods and by their dehydroiodination to a mixture of *cis*- and *trans*-1,1,1-trifluorobut-2-ene (98%) and 2-trifluoromethylpropene (100%), respectively. It was also found that isomer (III), when heated under the conditions of the experiment, rearranged slowly to isomer (IV) (3·5% in 17 hr.). For this reason the percentage of the minor product (IV) in the 1 : 1 adduct mixture varied with time but it was always in the range 9—11%.

$$CF_3\cdot + CH_2{:}CH\cdot CH_3 \longrightarrow CF_3\cdot CH_2\cdot\dot{C}H\cdot CH_3 \text{ and } CF_3\cdot CHMe\cdot\dot{C}H_2$$

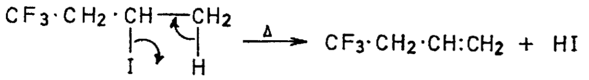
$$CF_3\cdot CH_2\cdot\dot{C}H\cdot CH_3 \xrightarrow{CF_3I} \underset{\text{(III)}}{CF_3\cdot CH_2\cdot CHI\cdot CH_3} \xrightarrow{KOH} CF_3\cdot CH{:}CH\cdot CH_3$$

$$CF_3\cdot CHMe\cdot\dot{C}H_2 \xrightarrow{CF_3I} \underset{\text{(IV)}}{CF_3\cdot CHMe\cdot CH_2I} \xrightarrow{KOH} CF_3\cdot CMe{:}CH_2$$

It has been reported[13] that the addition of trifluoroacetonitrile to propene at 400—420° gives a mixture (52—80%) of the two isomers $CF_3\cdot CH_2\cdot CH(CN)\cdot CH_3$ and $CF_3\cdot CHMe\cdot CH_2\cdot CN$ in the ratio 89 : 11, fortuitously identical with the ratio obtained for trifluoromethyl radical attack in the present work.

At 250° the products were trifluoromethane (4·5%), the adduct (III) (5%), a mixture of 4,4,4-trifluorobut-1-ene and 1,1,1-trifluorobutane (*ca.* 80—90%), and a residue of iodine and carbonaceous material. Thus at this temperature extensive dehydroiodination of the initially formed 1 : 1 adducts occurs, accompanied by reduction of unchanged adducts with hydrogen iodide.

The observation that adduct (III) is dehydroiodinated thermally to give the terminal olefin $CF_3\cdot CH_2\cdot CH{:}CH_2$, but is dehydroiodinated with base to give the internal olefin $CF_3\cdot CH{:}CH\cdot CH_3$ may be interpreted as follows. Base removes the most acidic hydrogen, *i.e.* that adjacent to the CF_3 group, whereas thermal dehydroiodination involves cleavage of the C–H bond of lowest dissociation energy, *i.e.* that in CH_3 and not that adjacent to CF_3.



$$CF_3\cdot CH_2\cdot CH{-}CH_2 \xrightarrow{\Delta} CF_3\cdot CH_2\cdot CH{:}CH_2 + HI$$

The very high yields of a 90 : 10 ratio of isomeric 1 : 1 adducts obtained from vinyl fluoride or from propene give a measure of the relative overall rates of formation of the isomers. This leads to a quantitative measure of the relative rates of formation of each of the pairs of radicals [$CF_3\cdot CH_2\cdot\dot{C}HF$ and $CF_3\cdot CHF\cdot\dot{C}H_2$, and $CF_3\cdot CH_2\cdot\dot{C}H\cdot CH_3$ and $CF_3\cdot CHMe\cdot\dot{C}H_2$], and hence a measure of the relative stabilities of each pair of radicals provided that the radicals are formed irreversibly or nearly so.

Since the isomer ratio was the same for both olefins it follows that the difference in stability between the radicals $CF_3\cdot CH_2\cdot\dot{C}HF$ and $CF_3\cdot CHF\cdot\dot{C}H_2$ is approximately the same as that between the radicals $CF_3\cdot CH_2\cdot\dot{C}H\cdot CH_3$ and $CF_3\cdot CHMe\cdot\dot{C}H_2$, and it would be interesting to examine the products from radical additions to the olefin $CHF{:}CH\cdot CH_3$ in which the CHF group could be directly compared with the $CH\cdot CH_3$ group. It is to be expected that bidirectional addition would be observed even though the only reported radical addition, that

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[8] F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 95.

[9] M. Miyoshi and R. K. Brinton, *J. Chem. Phys.*, 1962, **36**, 3019.

[10] O. Beeck and F. F. Rust, *J. Chem. Phys.*, 1941, **9**, 480.

[11] V. O. Vorob'eo and G. I. Nikishin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1966, 138.

[12] J. N. Bradley, W. H. Melville, and J. C. Cobb, *Proc. Roy. Soc.*, 1956, *A*, **236**, 339.

[13] G. J. Janz, N. A. Gac, A. R. Monahan, and W. J. Leahy, *J. Org. Chem.*, 1965, **30**, 2075.

of dibromodifluoromethane, is said to result in exclusive attack on the terminal CHF group.[14]

Other Olefins.—The thermal reaction of trifluoroiodomethane with ethylene gave a high yield (98% at 200°) of the 1 : 1 adduct 1,1,1-trifluoro-3-iodopropane; 2 : 1 or higher telomers were not detected. Ethylene was thus chosen as the standard olefin for competitive reactions with trifluoroiodomethane. The thermal reactions of trifluoroiodomethane with vinyl chloride, trifluoroethylene, and hexafluoropropene were also investigated, but the formation of 2 : 1 and higher telomers could not be suppressed completely, even by increasing the ratio of trifluoroiodomethane to olefin. With trifluoroethylene the 1 : 1 adduct fraction (52%) contained the isomers $CF_3{\cdot}CHF{\cdot}CF_2I$ and $CF_3{\cdot}CF_2{\cdot}CHFI$ in the ratio 68 : 32 as compared with a ratio of 74 : 26 obtained from the ultraviolet-initiated addition;[3] hexafluoropropene gave a 1 : 1 adduct fraction (82%) which contained the isomers $CF_3{\cdot}CF_2{\cdot}CFI{\cdot}CF_3$ and $(CF_3)_2CF{\cdot}CF_2I$ in the ratio 82 : 18 as compared with a ratio of 80 : 20 obtained from the ultraviolet-initiated addition.[15]

We considered that, because iodine is a highly efficient chain-transfer agent, the addition of iodine to the reactants might prevent the formation of 2 : 1 and higher telomers, since the reaction of the intermediate radical with iodine to give the 1 : 1 adduct could take place more readily than reaction with a further molecule of olefin. Provided that the rate-determining step is the initial radical addition to the olefin, then the means by which the 1 : 1 adduct is formed from an intermediate radical, be it by transfer with iodine, or with trifluoroiodomethane, would not matter. The overall rate would be lower, however, since iodine abstraction from trifluoroiodomethane leads to continuation of the reaction chain *via* the CF_3 radical:

$$CF_3{\cdot}[\text{olefin}]{\cdot} + CF_3I \longrightarrow CF_3{\cdot}[\text{olefin}]{\cdot}I + CF_3{\cdot}$$

whereas abstraction of iodine atom from iodine leads to chain termination:

$$CF_3{\cdot}[\text{olefin}]{\cdot} + I_2 \longrightarrow CF_3{\cdot}[\text{olefin}]{\cdot}I + I{\cdot}$$

$$2I{\cdot} \longrightarrow I_2$$

Furthermore, an excess of molecular iodine during reaction should diminish the concentration of CF_3 radicals:

$$CF_3{\cdot} + I_2 \longrightarrow CF_3I + I{\cdot} \longrightarrow I_2$$

An addition reaction between trifluoroiodomethane and trifluoroethylene in the presence of added iodine gave a higher yield of 1 : 1 adducts (78%) than in the reaction without iodine, and only 4% of 2 : 1 and higher telomers were detected (compared with 30% with no iodine present); a tar which contained some iodine was also obtained. The ratio of isomers $CF_3{\cdot}CHF{\cdot}CF_2I$ and $CF_3{\cdot}CF_2{\cdot}CHFI$ in the 1 : 1 adduct fraction was 89 : 11.

Competitive Reactions.—These were carried out between ethylene and vinyl fluoride and between ethylene and propene at 200°, with equimolar amounts of the olefins and a CF_3I : total olefin ratio of 3 : 1. The reaction time was also varied for each pair of olefins in order to obtain a range of olefin conversions.

If the requirements listed previously for the bidirectional addition to an olefin are met, and the concentration of trifluoromethyl radicals is low and constant throughout the reaction, the initial additions of trifluoromethyl radicals to competing olefins A and B can be represented as:

$$CF_3{\cdot} + A \xrightarrow{k_A} CF_3{\cdot}A{\cdot}$$

$$CF_3{\cdot} + B \xrightarrow{k_B} CF_3{\cdot}B{\cdot}$$

giving the rate constant ratio as

$$K = \frac{k_A}{k_B} = \frac{\log\,[A_0]/[A_F]}{\log\,[B_0]/[B_F]} \qquad \text{(i)}$$

where A_0 and A_F are, respectively, the initial and final concentrations of olefin A, and similarly for B. The relationship (i) is valid only as long as side reactions such as telomerisation and hydrogen abstraction are low, *e.g.*

$$CF_3{\cdot}A{\cdot} + A \longrightarrow CF_3{\cdot}A{\cdot}A{\cdot} \longrightarrow \text{2 : 1 and higher telomers}$$

$$R{\cdot} + \text{olefin} \longrightarrow RH + \text{other products}$$

where R· is any radical present in the system.

Evidence has been presented previously[16] to show that under the conditions used the addition of trifluoromethyl radicals to the olefins propene and vinyl fluoride is irreversible, and in the present work the extent of side reactions was shown to be low under the conditions employed; some hydrogen abstraction did occur (2—3%) but no telomers were detected.

The evaluation of relative reactivities from expression (i) requires the measurement, after reaction, of unchanged olefins. Instead it was found to be easier for analytical reasons to measure the quantities of 1 : 1 adducts formed (g.l.c.). Since the yields of 1 : 1 adducts from the olefins used had been previously shown to be almost quantitative (⩾96%), and a check of olefins recovered against 1 : 1 adducts formed in one of the competitive reactions from each olefin pair showed good agreement, it was possible to use the modified expression:

$$\frac{k_A}{k_B} = \frac{\log\,[A_0]/[A_0 - P_A]}{\log\,[B_0]/[B_0 - P_B]} \qquad \text{(ii)}$$

where P_A and P_B are the concentrations of 1 : 1 adducts

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[14] P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Amer. Chem. Soc.*, 1955, **77**, 2783.

[15] R. N. Haszeldine, *J. Chem. Soc.*, 1953, 3559; J. Brown and R. N. Haszeldine, unpublished results.

[16] J. M. Pearson and M. Szwarc, *Trans. Faraday Soc.*, 1964, **60**, 553.

CF_3·A·I and CF_3·B·I formed respectively from olefins A and B. The modified expression (ii) was found to hold, since the relative reactivities for the pairs of olefins agreed very closely at different olefin conversions. The results shown in Tables 1A and B give the relative reactivities of the olefins towards the highly electrophilic trifluoromethyl radicals: propene (1·46) > ethylene (1·00) > vinyl fluoride (0·25). This order is in accord with the inductive effects of the substituent R in the olefin RCH:CH_2.

There are no reported results with which the relative reactivities found can be directly compared. However, rate constants have been reported for the reaction of trifluoromethyl radicals, produced by the thermal decomposition of trifluoroacetonitrile at 440°, with ethylene [17] and vinyl fluoride.[17] A comparison of these results gives a value of 0·15 for *k*(vinyl fluoride)/*k*(ethylene), which agrees, qualitatively, with the present results. Similarly the relative reactivities of various olefins towards trifluoromethyl radicals as compared with the case of hydrogen abstraction from iso-octane by these radicals have been reported.[16] From these results the following relative reactivities of the olefins at 180° in the gas phase can be calculated: *k*(vinyl fluoride)/*k*(ethylene) = 0·17; *k*(propene)/*k*(ethylene) = 1·12. Also from the results of similar work [18] in the liquid phase at 65° a value of 1·40 for *k*(propene)/*k*(ethylene) can be calculated. These results are again in qualitative agreement with the results of the present investigation.

TABLE 1A

Competitive reactions of ethylene and vinyl fluoride with trifluoroiodomethane at 200°

Reaction time (hr.)	Vinyl fluoride: Initial reactant (mmoles)	Vinyl fluoride: Final adduct (mmoles)	Vinyl fluoride: Conversion (%)	Ethylene: Initial reactant (mmoles)	Ethylene: Final adduct (mmoles)	Ethylene: Conversion (%)	*k*(vinyl fluoride)/*k*(ethylene)
4	6·979	0·036	0·5	6·961	0·142	2·0	0·24
17	7·490	4·198	56	7·425	7·132	96	0·25
			(98% yield)			(100% yield)	

TABLE 1B

Competitive reactions of ethylene and propene with trifluoroiodomethane at 200°

Reaction time (hr.)	Propene: Initial reactant (mmoles)	Propene: Final adduct (mmoles)	Propene: Conversion (%)	Ethylene: Initial reactant (mmoles)	Ethylene: Final adduct (mmoles)	Ethylene: Conversion (%)	*k*(propene)/*k*(ethylene)
6·5	7·505	0·565	7·2	7·482	0·372	5·4	1·52
13	7·560	4·190	54	7·530	3·190	44	1·46
16	7·831	4·800	64	7·482	3·650	49	1·40
			(99% yield)			(99% yield)	

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture. Products were separated either by repeated fractional distillation *in vacuo* or by preparative scale g.l.c. [Perkin-Elmer 116, 451, or 452 instruments or an Aerograph Autoprep; columns (2 m. or 8 m.) of Silicone MS550 oil (30%) on Celite unless stated to the contrary]. The identities of products were established by molecular weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometer model 21 with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 spectrometer operating at 56·46 Mc./sec. for ^{19}F and 60·0 Mc./sec. for ^{1}H), mass spectrometry (A.E.I. MS/2H spectrometer with a resolution of 1 in 700), g.l.c., and u.v. spectroscopy (Unicam SP 700 instrument over the range 200—800 mμ).

Trifluoroiodomethane, trifluoroethylene, and propene were prepared and purified by known methods; the other olefins were commercial samples adequately purified.

All reactions were carried out in sealed Dreadnought tubes (350 ml.) unless stated to the contrary.

The Reactions of Trifluoroiodomethane with Olefins.—(a) *With ethylene.* Ethylene (0·424 g., 15·13 mmoles) and trifluoroiodomethane (8·849 g., 45·14 mmoles), heated at 200° (37 hr.), gave (i) a mixture of trifluoromethane (0·038 g., 0·54 mmole, 3·5%) and silicon tetrafluoride (0·012 g., 0·12 mmole), (ii) unchanged ethylene (0·008 g., 0·27 mmole, 2%), (iii) unchanged trifluoroiodomethane (5·77 g., 29·46 mmoles, 65%), (iv) 1,1,1-trifluoro-3-iodopropane (3·284 g., 14·65 mmoles, 98% based on ethylene) (Found: C, 16·3; H, 1·9%; *M*, 225. Calc. for $C_3H_4F_3I$: C, 16·1; H, 1·8%; *M*, 224), and (v) a residue of iodine (0·10 g.).

A second reaction carried out with a 2 : 1 molar ratio of reactants at 265° (48 hr.) gave the 1 : 1 adduct (64%), together with trifluoromethane (*ca.* 20%) and a compound thought to be 3,3,3-trifluoropropene.

(b) *With vinyl fluoride.* The olefin (0·717 g., 15·60 mmoles) and trifluoroiodomethane (8·99 g., 45·9 mmoles), heated at 200° (48 hr.), gave (i) trifluoromethane (0·010 g., 0·14 mmole, 0·5%), (ii) a mixture (6·35 g., 33·3 mmoles; *M*, 191) shown by i.r. spectroscopy and g.l.c. (8 m. column at 20°) to consist of unchanged trifluoroiodomethane (6·31 g., 32·2 mmoles, 70%) and unchanged olefin (0·051 g., 1·10 mmoles, 7%), (iii) a 1 : 1 adduct fraction (3·375 g.,

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[17] G. J. Janz and J. B. Flannery, *J. Phys. Chem.*, 1966, **70**, 2061.

[18] A. P. Stefani, L. Herk, and M. Szwarc, *J. Amer. Chem. Soc.*, 1961, **83**, 4732.

13·95 mmoles, 96% based on olefin) (Found: *M*, 239. Calc. for $C_3H_3F_4I$: *M*, 242), and (iv) a trace of iodine.

The 1 : 1 adduct fraction was shown by g.l.c. (8 m. column at 50°) to be a mixture of two components in the ratio 89 : 11; these were separated and identified as 1,1,1,3-*tetrafluoro*-3-*iodopropane* (I) (3·01 g., 12·45 mmoles, 86%) (Found: C, 14·9; H, 1·0%. $C_3H_3F_4I$ requires C, 14·9, H, 1·25%), $\lambda_{max.}$ (i.r.) 3·33w, 3·37w, 6·95m, 7·02m, 7·25s, 7·45s, 7·76s, 7·92s, 8·30s, 8·57vs, 8·90s, 9·10s, 9·80m, 10·07s, 11·35s, 11·44s, 11·90m, 14·04s, and 14·10s μ, $\lambda_{max.}$ (u.v.; vapour) 262 (ε 225), $\lambda_{min.}$ 218 (ε 144) mμ, and 1,1,1,2-*tetrafluoro*-3-*iodopropane* (II) (0·36 g., 1·48 mmoles, 10%) (Found: C, 15·1; H, 1·4%), $\lambda_{max.}$ (i.r.) 3·37w, 7·01w, 7·29s, 7·78s, 8·46s, 8·74s, 8·97m, 10·19m, 11·66m, and 14·12m μ, $\lambda_{max.}$ (u.v.; vapour) 262—263 (ε 197), $\lambda_{min.}$ 218 (ε 9) mμ. The photochemical product reported [2] to be adduct (I) is now known [19] to be a mixture of adducts (I) and (II) with the former predominating.

(c) *With propene.* The olefin (0·596 g., 14·2 mmoles) and trifluoroiodomethane (8·160 g., 41·6 mmoles), heated at 200° (18·5 hr.) gave (i) a mixture of trifluoromethane (0·02 g., 0·27 mmole, 2%) and silicon tetrafluoride (0·008 g., 0·10 mmole), (ii) unchanged propene (0·070 g., 1·7 mmoles, 12%), (iii) unchanged trifluoroiodomethane (5·52 g., 28·2 mmoles, 68%), (iv) a 1 : 1 adduct fraction (2·952 g., 12·4 mmoles, 99% based on propene) (Found: C, 20·4; H, 2·6%; *M*, 236. Calc. for $C_4H_6F_3I$: C, 20·2; H, 2·6%; *M*, 238), and (v) a residue of iodine (0·02 g.).

The 1 : 1 adduct fraction was shown by g.l.c. (8 m. column at 50°) to be a mixture of two components in the ratio 89 : 11 (in subsequent experiments the ratio varied from 89 : 11 to 91 : 9); these were separated by g.l.c. and identified as (i) 1,1,1-*trifluoro*-3-*iodobutane* (III) (2·63 g., 11·05 mmoles, 88% based on propene) (Found: C, 20·5; H, 2·5%), $\lambda_{max.}$ (i.r.) 3·33m, 3·38m, 3·46w, 6·85m, 6·96m, 7·20m, 7·30s, 7·45s, 7·60m, 7·83s, 7·95vs, 8·17m, 8·38s, 8·55vs, 8·82s, 8·97s, 9·16s, 10·00m, 12·05m, and 14·70w μ, $\lambda_{max.}$ (u.v.; vapour) 264—265 (ε 400), $\lambda_{min.}$ 217 (ε 20) mμ, and (ii) 1-*iodo*-2-*trifluoromethylpropane* (IV) (0·32 g., 1·36 mmoles, 11% based on propene) (Found: C, 20·3; H, 2·6%), $\lambda_{max.}$ (i.r.) 3·32m, 3·36m, 3·44w, 6·80m, 6·95m, 7·18m, 7·37s, 7·62s, 7·89vs, 8·17s, 8·40s, 8·80s, 9·03s, 9·77m, 9·88s, 10·30m, 12·98m, and 14·09m (triplet) μ, $\lambda_{max.}$ (u.v.; vapour) 259—260 (ε 240), $\lambda_{min.}$ 223—224 (ε 90) mμ.

The photochemical product reported [2] to be adduct (III) is now known [19] to be a mixture of adducts (III) and (IV) in the ratio *ca.* 95 : 5.

A further reaction carried out at 250° (48 hr.) with a 2 : 1 molar ratio of reactants gave the 1 : 1 adduct (III) (5%), trifluoromethane (4·5%), a mixture of 4,4,4-trifluorobut-1-ene and 1,1,1-trifluorobutane (*ca.* 80—90%), and a residue of iodine and carbonaceous material.

(d) *With perfluoropropene.* The olefin (1·780 g., 11·9 mmoles) and trifluoroiodomethane (11·75 g., 60·0 mmoles), heated at 200° for 233 hr. in a bulb (5·6 l.), gave (i) unchanged trifluoroiodomethane (11·60 g., 59·2 mmoles, 98·5%), (ii) unchanged olefin (1·68 g., 11·2 mmoles, 94%), and (iii) a mixture (0·191 g.) shown by g.l.c. (8 m. column at 100°) to consist of 1 : 1 addition products (0·173 g., 0·50 mmoles, 72% based on olefin) and higher telomers [0·018 g., 0·033 mmole, 11% based on olefin and calculated on the basis that the second and third peaks were 2 : 1 adducts and later peaks (three) were 3 : 1 adducts]. The 1 : 1 adduct peak was shown by g.l.c. (8 m. column at 20°) to contain the two isomers nonafluoro-2-iodobutane and hexafluoro-1-iodo-2-trifluoromethylpropane in the ratio 79 : 21.

A similar reaction with a 3 : 1 ratio of reactants gave the two isomeric 1 : 1 adducts (86%) in a ratio of 82 : 18, together with telomers (8% based on olefin).

(e) *With vinyl chloride.* The olefin (0·375 g., 6·0 mmoles) and trifluoroiodomethane (10·60 g., 54·1 mmoles), heated at 200° (24 hr.), gave (i) a mixture (0·24 mmole) of trifluoromethane and silicon tetrafluoride (i.r.), (ii) unchanged trifluoroiodomethane (9·60 g., 49·0 mmoles, 91%), (iii) unchanged olefin (0·063 g., 1·01 mmoles, 17%), (iv) 3-chloro-1,1,1-trifluoro-3-iodopropane (0·816 g., 3·16 mmoles, 63% based on olefin) (Found: C, 13·9; H, 1·2%; *M*, 262. Calc. for $C_3H_3ClF_3I$: C, 14·1; H, 1·2%; *M*, 259), identified by i.r. spectroscopy, and (v) a liquid residue which was extracted from the reaction tube with light petroleum (b.p. 30—40°). The ether was removed *in vacuo* and the residue (0·121 g.) was shown by g.l.c. (2 m. column at 60°) to contain a small quantity of 3-chloro-1,1,1-trifluoro-3-iodopropane, the remainder being higher molecular weight telomers (Found: C, 20·1; H, 2·1%. Calc. for $CF_3\cdot[C_2H_3Cl]_{2\cdot42}\cdot I$: C, 20·2; H, 2·1%).

(f) *With trifluoroethylene.* The olefin (1·23 g., 15·0 mmoles) and trifluoroiodomethane (8·86 g., 45·3 mmoles), heated at 200° (72 hr.), gave (i) unchanged olefin (0·390 g., 4·76 mmoles, 32%), (ii) unchanged trifluoroiodomethane (7·15 g., 36·5 mmoles, 81%), (iii) a mixture (1·477 g., 5·3 mmoles, 52% based on olefin) (Found: *M*, 278. Calc. for C_3HF_6I: *M*, 278) of the two isomeric 1 : 1 adducts 1,1,1,2,3,3-hexafluoro-3-iodopropane and 1,1,1,2,2,3-hexafluoro-3-iodopropane, identified by i.r. spectroscopy, (iv) a mixture (0·271 g.) shown by g.l.c. (2 m. column at 75°) to contain 2 : 1 and higher telomers contaminated with a small quantity of the 1 : 1 adducts, and (v) a residue (0·457 g.) shown by g.l.c. (2 m. column at 175°) to contain 2 : 1 and higher telomers. In a similar experiment with a reactant ratio of 14 : 1, g.l.c. examination of the adducts showed the presence of 2 : 1 and higher telomers (19% by weight) and 1 : 1 adducts (81% by weight) with a 1 : 1 adduct isomer ratio of 68 : 32 of 1,1,1,2,3,3-hexafluoro-3-iodopropane to 1,1,1,2,2,3-hexafluoro-3-iodopropane.

(g) *With trifluoroethylene in the presence of iodine.* The olefin (1·130 g., 13·8 mmoles), trifluoroiodomethane (8·20 g., 41·8 mmoles), and iodine (2·0 g., 7·9 mmoles) were heated at 200° (72 hr.). The products, shaken with excess of mercury *in vacuo* to remove iodine, gave (i) unchanged olefin (0·918 g., 11·2 mmoles, 82%), (ii) unchanged trifluoroiodomethane (7·47 g., 38·1 mmoles, 91%), and (iii) a mixture (0·584 g.) shown by g.l.c. (2 m. column at 74°) to contain 1,1,1,2,2,3-hexafluoro-3-iodopropane (0·499 g., 1·79 mmoles, 69% based on olefin), 1,1,1,2,3,3-hexafluoro-3-iodopropane (0·062 g., 0·22 mmole, 9% based on olefin), and higher telomers (0·023 g.).

Pyrolysis of 1,1,1,3-*Tetrafluoro*-3-*iodopropane.*—Pyrolysis of the propane at 200° (16 hr.) gave only unchanged reactant (100%); the isomer 1,1,1,2-tetrafluoro-3-iodopropane was not detected.

Reaction of 1,1,1,3-*Tetrafluoro*-3-*iodopropane with Potassium Hydroxide.*—The propane (0·108 g., 0·445 mmole), condensed, *in vacuo*, on to an excess of finely powdered,

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[19] R. Gregory, R. N. Haszeldine, and A. E. Tipping, unpublished results.

TABLE 2

Vapour pressure data

Compound	Range measured	A	B	L_V	T	B.p.
$CF_3{\cdot}CH_2{\cdot}CHFI$ *	28—83°	7·442	—1630	7469	20·9	84·2°
$CF_3{\cdot}CHF{\cdot}CH_2I$	22—83	7·045	−1486	6819	19·1	83·8
$CF_3{\cdot}CH_2{\cdot}CHMeI$ †	31—98	7·389	−1690	7721	20·6	101·6
$CF_3{\cdot}CHMe{\cdot}CH_2I$	25—95	7·176	−1586	7273	19·7	96·0

* Lit.,[2] b.p. 86·2°/757 mm. (probably for mixture of isomers $CF_3{\cdot}CH_2{\cdot}CHFI$ and $CF_3{\cdot}CHF{\cdot}CH_2I$). † Lit.,[2] b.p. 103·5°/763 mm. (probably for mixture of isomers $CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$ and $CF_3{\cdot}CHMe{\cdot}CH_2I$).

dry potassium hydroxide (*ca.* 10 g.) and heated at 60—70° (10 min.), gave a mixture of *cis*- and *trans*-1,3,3,3-tetrafluoropropene [2] (0·049 g., 0·43 mmole, 97%) (Found: C, 31·8; H, 1·8%; *M*, 114. Calc. for $C_3H_2F_4$: C, 31·6; H, 1·8%; *M*, 114), identified by i.r. and n.m.r. spectroscopy.

Reaction of 1,1,1,2-*Tetrafluoro*-3-*iodopropane with Potassium Hydroxide.*—The propane (0·041 g., 0·17 mmole) heated with an excess of potassium hydroxide, as in the previous experiment, gave (i) unchanged propane (0·014 g., 0·06 mmole, 34%) and (ii) 2,3,3,3-tetrafluoropropene (0·026 g., 0·11 mmole, 95%) (Found: C, 31·9; H, 1·8%; *M*, 113. Calc. for $C_3H_2F_4$: C, 31·6; H, 1·8%; *M*, 114), $\lambda_{max.}$ 3·22w and 3·32w (C–H str.), 5·89s (C:C str.), 7·18s, 7·35s, 7·42s, 8·26s, 8·40s, 8·45s, 8·60s, 9·01s, 9·07s, 10·53 and 10·59m (doublet), 11·20s (triplet), 11·82m, 12·96m, and 14·38m (triplet) (CF_3 def.) μ, identified by n.m.r. spectroscopy.

Pyrolysis of 1,1,1-*Trifluoro*-3-*iodobutane.*—The butane was sealed in two ampoules (*ca.* 10 ml. capacity), one of which was stored at −196° in the dark and the other heated at 200° (17 hr.). Examination of the products from each tube by g.l.c. (8 m. column at 58°) showed that the tube kept at −196° contained only unchanged reactant, but that the tube heated at 200° contained unchanged reactant (96·5%) and 1-iodo-2-trifluoromethylpropane (3·5%).

Reaction of 1,1,1-*Trifluoro*-3-*iodobutane with Potassium Hydroxide.*—The butane (0·489 g., 2·05 mmoles), condensed, *in vacuo*, on to an excess of finely powdered, dry potassium hydroxide and heated at 60—70° (10 min.) with shaking, gave a mixture of *cis*- and *trans*-1,1,1-trifluorobut-2-ene [2] (0·222 g., 2·02 mmoles, 98%) (Found: C, 43·4; H, 4·5%; *M*, 110. Calc. for $C_4H_5F_3$: C, 43·6; H, 4·6%; *M*, 110), identified by i.r. and n.m.r. spectroscopy.

Reaction of 1-*Iodo*-2-*trifluoromethylpropane with Potassium Hydroxide.*—The propane (0·038 g., 0·16 mmole) treated with potassium hydroxide as in the previous experiment, gave (i) unchanged propane (0·013 g., 0·05 mmole, 33%) and (ii) 2-trifluoromethylpropene (0·012 g., 0·11 mmole, 100%) (Found: C, 43·6; H, 4·5%; *M*, 109. Calc. for $C_4H_5F_3$: C, 43·6; H, 4·6%; *M*, 110), $\lambda_{max.}$ 3·21w, 3·35m, 3·39m, 3·46w, 5·92m (double bond str.), 6·85m, 7·08m, 7·40s, 7·85s, 8·45vs, 8·67vs, 8·73vs, 9·04m. 9·09m, 9·27m, 9·91m, 9·95m, 10·69s (triplet), 11·35m, 13·58m (triplet),

TABLE 3

Main mass spectral bands

$CF_3{\cdot}CH_2{\cdot}CH_2I$

m/e	Abundance (%)	Ion
224	100	M^+
141	6·3	CH_2I
128	9·8	HI
127	12	I
97	19	$C_3H_4F_3$
77	20	$C_3H_3F_2$
69	9·8	CF_3
51	7·5	CHF_2
47	4·2	C_2H_4F
40	3·9	C_3H_4
28	10	C_2H_4
27	8·1	C_2H_3

$CF_3{\cdot}CH_2{\cdot}CHFI$

m/e	Abundance (%)	Ion
242	100	M^+
159	27	CHFI
153	2·1	C_2H_2I
127	31	I
115	100	$C_3H_3F_4$
95	5·1	$C_3H_2F_3$
69	23	CF_3
65	4·0	$C_2H_3F_2$
64	3·4	$C_2H_2F_2$
51	43	CHF_2
27	7·2	C_2H_3

$CF_3{\cdot}CHF{\cdot}CH_2I$

m/e	Abundance (%)	Ion
242	100	M^+
173	4·5	C_2H_3FI
172	12	C_2H_2FI
141	7·9	CH_2I
127	14	I
115	15	$C_2H_3F_4$
95	4·2	$C_3H_2F_3$
69	12	CF_3
65	19	$C_2H_3F_2$
51	22	CHF_2

$CF_3{\cdot}CH_2{\cdot}CH_2Cl$

m/e	Abundance (%)	Ion
260, 258	33	M^+
177, 175	9·8	CHClI
133, 131	100	$C_3H_3ClF_3$
127	20	I
87, 85	7·7	$CClF_2$
77	5·3	$C_2H_3F_2$
69	22	CF_3
69, 67	36	CHClF
32	14	CHF
27	8·4	C_2H_3

$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$

238	57	M^+
155	11	C_2H_4I
127	18	I
111	100	$C_4H_6F_3$
91	54	$C_4H_5F_2$
71	8·9	C_4H_4F
47	6·3	C_2H_4F
41	12	C_3H_5
39	11	C_3H_3

$CH_3{\cdot}CH(CF_3){\cdot}CH_2I$

238	100	M^+
141	11	CH_2I
127	17	I
111	84	$C_4H_6F_3$
91	64	$C_4H_5F_2$
71	11	C_4H_4F
65	19	$C_2H_3F_2$
47	79	C_2H_4F
41	17	C_3H_5
39	14	C_3H_3

$CF_3{\cdot}CH{:}CHF$

114	71	M^+
113	33	C_3HF_4
95	52	$C_3H_2F_3$
75	11	C_3HF_2
69	100	CF_3
64	82	$C_2H_2F_2$
51	17	CHF_2
45	17	C_2H_2F
31	20	CF

$CF_3{\cdot}CF{:}CH_2$

114	100	M^+
113	34	C_3HF_4
95	65	$C_3H_2F_3$
75	17	C_3HF_2
69	97	CF_3
64	90	$C_2H_2F_2$
51	9·9	CHF_2
45	60	C_2H_2F
31	25	CF

$CH_3{\cdot}CH{:}CH{\cdot}CF_3$

110	97	M^+
95	25	$C_3H_2F_3$
91	22	$C_4H_5F_2$
77	31	$C_3H_3F_2$
69	28	CF_3
64	53	$C_2H_2F_2$
59	16	C_3H_4F
46	19	C_2H_3F
41	100	C_3H_5
39	55	C_3H_3

$CF_3{\cdot}CMe{:}CH_2$

110	100	M^+
95	50	$C_3H_2F_3$
91	15	$C_4H_5F_2$
90	12	$C_4H_4F_2$
69	60	CF_3
65	20	$C_2H_3F_2$
64	35	$C_2H_2F_2$
59	15	C_3H_4F
41	93	C_3H_5
39	59	C_3H_3

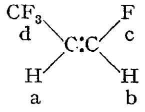
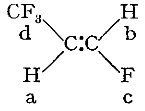
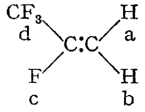
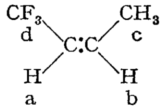
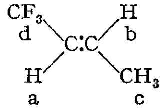
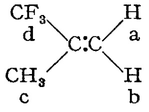
14·30m, 14·55m (triplet), and 14·80m μ, identified by n.m.r. spectroscopy.

Vapour Pressure Equations.—The constants A and B for the vapour pressure equation log p (mm.) = A + B/T, the b.p., latent heat of vaporisation [L_V(cal. mole^{-1})] and Trouton's constant [T(cal. mole^{-1} deg.$^{-1}$)] for the 1 : 1 adducts prepared are shown in Table 2.

Mass Spectral Data.—The major mass spectral bands and assignments are shown in Table 3. All the spectra agree with the structures proposed, but a number of rearrangement ions are observed and in certain cases these are of high abundance, *e.g.* CHF_2^+, *m/e* 51, from $CF_3\cdot CH_2\cdot CHFI$, $CF_3\cdot CHF\cdot CH_2I$, and $CF_3\cdot CH{:}CHF$; $C_2H_4F^+$, *m/e* 47, from $CF_3\cdot CH_2\cdot CHI\cdot CH_3$ and $CH_3\cdot CH(CF_3)\cdot CH_2I$; $C_2H_2F_2^+$, *m/e* 64 from $CF_3\cdot CH{:}CHF$, $CF_3\cdot CF{:}CH_2$, $CH_3\cdot CH{:}CH\cdot CF_3$, and $CH_2{:}C(CF_3)\cdot CH_3$; and $CHFCl^+$, *m/e* 69 and 67 from $CF_3\cdot CH_2\cdot CHClI$. In addition low-intensity peaks were observed in the spectra of the adducts $CF_3\cdot CH_2\cdot CH_2I$, $CF_3\cdot CH_2\cdot CHFI$, and $CF_3\cdot CHF\cdot CH_2I$ which correspond to the replacement of a hydrogen atom in the adducts by a trifluoromethyl group. In the adduct $CF_3\cdot CH_2\cdot CHClI$ a peak was observed at *m/e* 292 (*ca.* 10% of base peak)

TABLE 4

N.m.r. spectra

Compound	Absorption type	Intensity	τ	p.p.m.	Splitting	J (c./sec.)
$CF_3\cdot CHH\cdot CHFI$ e a b c d	ab	2	6·88		Complex m	
	c	1	2·97		ddd	H_c–F_d 50·7
	d	1		66·6	dddq	F_d–F_e 7·6
	e	3		−13·6	Overlapping ddd	
$CF_3\cdot CHF\cdot CHHI$ e c d a b	ab	2	6·63		Complex m	
	c	1	5·21		ddqd	H_c–F_d 44·9
	d	1		115·8	Complex m	F_d–F_e 11·5
	e	3		1·4	dddd	
$CF_3\cdot CHH\cdot CHI\cdot CH_3$ e a b c d	ab	2	7·21		Complex m	
	c	1	5·66		Overlapping qdd	
	d	3	8·00		dq	
	e			−11·7	dd	
$CF_3\cdot CH(CH_3)\cdot CHHI$ e c d a b	a	1	6·53		dd	H_a–H_b 9·9
	b	1	7·03		Overlapping dd	
	c	*ca.* 1	6·7—7·8		Broad complex m	
	d	3	8·72		d	H_d–H_c 6·8
	e			−3·0	d	F_e–H_c 8·4
	a	1	4·87		dqd	H_a–H_b 5·7
	b	1	3·37		dd	H_a–F_c 36·7
	c	1		35·8	ddq	H_a–F_d 7·5
	d	3		−17·6	ddd	H_b–F_c 77·5
						F_c–F_d 17·3
						F_d–H_b 0·4
	a	1	4·41		ddq	H_a–F_c 14·8
	b	1	2·84		ddq	H_a–H_b 11·5
	c	1		46·0	ddq	H_a–F_d 6·7
	d	3		−14.4	ddd	H_b–F_c 78·0
						H_b–F_d 2·15
						F_c–F_d 8·75
	a	1	4·83		dd	H_a–F_c 43·5
	b	1	4·90		ddq	H_a–H_b 4·5
	c	1		47·8	ddq	H_b–F_c 13·6
						H_b–F_d 1·7
	d	3		−1·8	ddd	F_c–F_d 9·6
						F_d–H_a 0·5
	a		*			
	b } *		*			
	c		*			
	d			−19·8	dq	F_d–H_a 8·5
						F_d–H_c 2·8
	a	1	4·40		dqq	H_a–H_b 15·9
	b	1	3·58		dqq	H_a–H_c 1·5
	c	3	8·21		dqd	H_a–F_d 6·0
						H_b–H_c 6·3
	d			−13·5	dqd	H_b–F_d 2·1
						H_c–F_d 2·6
	a	1	4·40		Complex m	
	b	1	4·71		Broad complex m	
	c	3	8·11		Complex m	
	d			−4·2	ddq	F_d–H_b 1·5
						F_d–H_a 1·1
						F_d–H_c 0·4

* Spectrum of a mixture of the *cis*- and *trans*-isomers; the chemical shifts for a, b, and c were masked by those for a, b, and c in the major, *trans*-isomer.

which corresponds to replacement of a chlorine atom in the adduct by a trifluoromethyl group.

Interesting metastable peaks were observed in the spectra of the compounds $CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$ (*m/e* 74·6 and 55·4), $CF_3{\cdot}CHMe{\cdot}CH_2I$ (*m/e* 74·6 and 55·4), and $CF_3{\cdot}CH{:}CH{\cdot}CH_3$ (*m/e* 55·4), which result from the following transitions:

$$\underset{111}{C_4H_6F_3^+} \longrightarrow \underset{91}{C_4H_5F_2^+} + HF$$

$$\underset{91}{C_4H_5F_2^+} \longrightarrow \underset{71}{C_4H_4F^+} + HF$$

N.m.r. Spectra.—The data in Table 4 were recorded with tetramethylsilane as internal reference for ^1H and trifluoroacetic acid as external reference for ^{19}F. The ^{19}F n.m.r. spectrum of a mixture of the 1 : 1 adducts $CF_3{\cdot}CH_2{\cdot}CHFI$ and $CF_3{\cdot}CHF{\cdot}CH_2I$ has been reported [6] previously and the chemical shifts are in good agreement with those found in the present work. ^{19}F and ^1H chemical shifts which have been established for various groups are shown in Table 5.

TABLE 5

Group chemical shifts

Group	Observed chemical shift * (present work)	Reported chemical shift	Ref.
$CF_3{\cdot}C$	−13·6 to +1·4	−15·2 to +11·9	20, 21
CHF	115·8	107·3 to *139·1*	*20*
CHFI	66	52·2 to 90·2	20
$CF_3{\cdot}CH{=}$	−19·8 to −13·5	−20·0 to −14·8	20
$C\mathit{F}_3{\cdot}CF{=}$	−1·8	−11·7 to −1·0	21
$CF_3{\cdot}C\mathit{F}{=}$	47·8	*ca.* 50	22
CHF=	46·0 and 35·8	*ca.* 42 and 36	22
CHI	5·66	5·76	23
CH_2I	6·53 to 7·03	6·42 to 6·80	23

* In p.p.m. except for CHI and CH_2I (τ value).

The n.m.r. spectra of ethylene,[24] 3,3,3-trifluoropropene,[25] and propene [26] have been reported; on the basis of these spectra, and on the assumption of additive substituent effects, the observed vinylic hydrogen chemical shifts in *trans*-$CF_3{\cdot}CH{:}CH{\cdot}CH_3$ are close to those expected, but for the compounds *cis*- and *trans*-$CF_3{\cdot}CH{:}CHF$ and $CF_3{\cdot}CF{:}CH_2$ the observed chemical shifts are to lower field than expected, owing perhaps to only a weak electromeric effect from the vinylic fluorine atom.

We thank Dr. W. T. Flowers for help with the mass spectra, Dr. M. G. Barlow for help with the n.m.r. spectra, and the D.S.I.R. for a research studentship (to D. W. K.).

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[20] Unpublished data from this department.

[21] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' vol. 2, Pergamon, Oxford, 1966, ch. 2.

[22] M. G. Barlow, unpublished results.

[23] G. V. D. Tiers, reported in ref. 23, Appendix B.

[24] C. N. Banwell and N. Sheppard, *Mol. Phys.*, 1960, **3**, 351.

[25] A. A. Bothner-By, S. Castellano, and H. Gunther, *J. Amer. Chem. Soc.*, 1965, **87**, 2439.

[26] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, 1961, **83**, 231.