540. *Addition of Free Radicals to Unsaturated Systems. Part XIV.* The Direction of Radical Addition to Trifluoroethylene.*

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Radical attack on trifluoroethylene is 80% on the CHF group and 20% on the CF_2 group; attack by an atom is 60% on the CHF group and 40% on the CF_2 group. This is the first time that anything other than exclusive radical attack on one carbon of an unsymmetrical olefin has been reported. Polytrifluoroethylene thus contains units such as $-CHF{\cdot}CF_2{\cdot}CHF{\cdot}CF_2-$, $-CHF{\cdot}CF_2{\cdot}CF_2{\cdot}CHF-$, and $-CF_2{\cdot}CHF{\cdot}CHF{\cdot}CF_2-$; each unit is flanked by itself or by one of the other units, and the last of these units in particular explains why the polymer is thermally less stable than poly-1 : 1-difluoroethylene. Proofs of structure are given for the reaction products from trifluoroiodomethane and trifluoroethylene, and for those from hydrogen bromide and trifluoroethylene. (*cis* + *trans*)-1 : 2-Difluoroethylene has been prepared. Comments are made on earlier reports on the direction of radical addition to trifluoroethylene.

It was pointed out earlier [1] that the order of free-radical stability is, in general, primary $-CH_2{\cdot} <$ secondary $>CH{\cdot} <$ tertiary $\geqslant C{\cdot}$ where the terms primary, secondary, and tertiary refer not to the carbon skeleton but to the number of atoms or groups other than hydrogen attached to the carbon atom formally carrying the lone electron. Use of this simple rule enables clear predictions to be made for the direction of addition of an atom or radical to a wide variety of olefins [2] of the type $CH_2{:}CHX$, $R{\cdot}CH{:}CX_2$, $CH_2{:}CX_2$, $CHX{:}CX_2$, $R{\cdot}CX{:}CHX$, $R{\cdot}CX{:}CHR'$, etc., by consideration of the relative stabilities of the possible free-radical intermediates. The rule is of widespread application, but as was pointed out earlier [1] there might be certain secondary free radicals which would be more stable than certain tertiary free radicals; such a situation could arise when the secondary radical contains atoms (*e.g.*, Cl or Br) or groups (*e.g.*, aryl, carboxyl, nitrile) which have a powerful stabilising effect on the radical, whereas the tertiary radical under consideration has atoms (*e.g.*, F) or groups (*e.g.*, alkyl, perfluoroalkyl) which have a relatively weak stabilising effect on a radical. In such special circumstances there will be some overlap between the two classes of radical, and we have therefore sought for examples. A clear-cut example was chloro-1 : 1-difluoroethylene [2] where radical or atom attack is exclusively on the CF_2 group, *i.e.*, stability of $R{\cdot}CF_2{\cdot}CHCl{\cdot} >$ stability of $R{\cdot}CHCl{\cdot}CF_2{\cdot}$.

The stabilising power of fluorine in this connection is only weak, and the direction of atomic and radical addition to trifluoroethylene was therefore examined, since here there was a possibility that the two possible radicals $R{\cdot}CHF{\cdot}CF_2{\cdot}$ and $R{\cdot}CF_2{\cdot}CHF{\cdot}$ would have an approximately equal stability, with the first somewhat more stable than the second. It

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* Part XIII, *J.*, 1957, 2193.

[1] Haszeldine, *J.*, 1953, 3565, 3761.

[2] Part XIII, where references to preceding papers are given.

was thus expected that a mixture would arise by free-radical addition, and this is as found experimentally with the trifluoromethyl radical or the bromine atom as the attacking entities. Radical attack is approximately 80% on the CHF group and 20% on the CF_2 group, and atomic attack is approximately 60% on the CHF group and 40% on the CF_2 group. This is the first time that anything other than exclusive or predominant (>95%) radical or atomic attack on one carbon of an unsymmetrical olefin has been reported. The homopolymer of trifluoroethylene thus contains both head to head, and tail to tail units, *e.g.*, $-CHF\cdot CF_2\cdot CF_2\cdot CHF\cdot CHF\cdot CF_2-$.

Trifluoroiodomethane and trifluoroethylene do not react in the dark, but when irradiated with light of wavelength >3000 Å give high yields of the monoaddition product $CF_3\cdot[C_2HF_3]\cdot I$. The reaction is faster in silica vessels, which transmit light of wavelength >2200 Å, and if an excess of trifluoroiodomethane is used the product is again mainly $CF_3\cdot[C_2HF_3]\cdot I$. Use of an excess of trifluoroethylene leads to the formation of polymer $CF_3\cdot[C_2HF_3]_n\cdot I$ where $n = 2, 3, 4$ . . . etc., as noted for the reaction between trifluoroiodomethane and tetrafluoroethylene.[1] Trifluoroethylene is a reactive olefin in this sense, but less so than tetrafluoroethylene, and it is thus easier to control the chain propagation step :

$$
\begin{aligned}
CF_3\cdot + CHF{:}CF_2 &\longrightarrow CF_3\cdot[C_2HF_3]\cdot \quad \text{Initiation}\\
CF_3\cdot[C_2HF_3]\cdot + CHF{:}CF_2 &\longrightarrow CF_3\cdot[C_2HF_3]_n\cdot \quad \text{Propagation}\\
CF_3\cdot[C_2HF_3]_n\cdot + CF_3I &\longrightarrow CF_3\cdot[C_2HF_3]_n\cdot I + CF_3\cdot \quad \text{Transfer}
\end{aligned}
$$

The monoaddition product can be prepared in 85% yield; that it contains both 1 : 1 : 1 : 2 : 3 : 3- (I) (80%) and 1 : 1 : 1 : 2 : 2 : 3-hexafluoro-3-iodopropane (II) (20%) was shown as follows.

Photochemical chlorination of the monoaddition product under conditions chosen to effect replacement of hydrogen as well as of iodine by chlorine gave a mixture of the two dichlorides[3] 1 : 2- (III) and 1 : 1-dichlorohexafluoropropane (IV). These cannot be separated easily by distillation, but can be detected readily by means of their infrared spectra. Compound (III) was prepared for comparison by the reaction of hexafluoropropene with chlorine, and (IV) is the product obtained earlier[3] by the action of chlorine on the reaction product from trifluoroiodomethane with chlorotrifluoroethylene :

$CF_3\cdot CHF\cdot CF_2I$	$CF_3\cdot CF_2\cdot CHFI$	$CF_3\cdot CFCl\cdot CF_2Cl$	$CF_3\cdot CF_2\cdot CFCl_2$
(I)	(II)	(III)	(IV)

$$CF_3I + CF_2{:}CFCl \longrightarrow CF_3\cdot CF_2\cdot CFClI \xrightarrow{Cl_2} CF_3\cdot CF_2\cdot CFCl_2$$

It has also been prepared by the sequence

$$C_2F_5\cdot CH_2\cdot OTs \xrightarrow{KF} C_2F_5\cdot CH_2F \xrightarrow{Cl_2} C_2F_5\cdot CFCl_2$$
$$(Ts = p\text{-}C_6H_4Me\cdot SO_2)$$

The dichlorides react differently on controlled treatment with zinc and ethanol: (III) gives hexafluoropropene, and (IV) gives 1-chloro-1 : 2 : 2 : 3 : 3 : 3-hexafluoropropane (V), both in high yield (*ca.* 85%). The olefin (b. p. −29°) and the reduction product (V) (b. p. 20°)[3] are readily separated by distillation, so the zinc–ethanol reaction provides a means of determining the amounts of (III) and (IV) in a mixture.

The formation of a mixture of (I) and (II) was confirmed by treatment of the mixture with bromine under conditions such that only iodine is replaced by bromine. 1-Bromo-1 : 1 : 2 : 3 : 3 : 3- (VI) and 1-bromo-1 : 2 : 2 : 3 : 3 : 3-hexafluoropropane (VII) were thus obtained. A sample of the former was available from the reaction of hydrogen bromide

$CF_3\cdot CF_2\cdot CHFCl$	$CF_3\cdot CHF\cdot CF_2Br$	$CF_3\cdot CF_2\cdot CHFBr$
(V)	(VI)	(VII)

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[3] Haszeldine and Steele, *J.*, 1953, 1592.

with hexafluoropropene,[4] a reaction which cannot yield (VII). Infrared spectroscopy of the mixed bromo-compounds prepared from $CF_3\cdot[C_2HF_3]\cdot I$ revealed the extra bands caused by (VII), a sample of which was synthesised by bromination of 1 : 1 : 1 : 2 : 2 : 3-hexafluoropropane.

Trifluoroethylene does not react with hydrogen bromide in the dark, even at 100° or in the presence of a solvent such as acetic acid; reaction involving ionic intermediates is thus slow. Photochemical reaction

$$Br\cdot + CHF{:}CF_2 \longrightarrow C_2HBrF_3\cdot \xrightarrow{HBr} C_2H_2BrF_3$$

is rapid at room temperature and gives the monoaddition product $H\cdot[C_2HF_3]\cdot Br$, which has been shown to be a mixture of the two possible isomers (VIII) and (IX). These isomers differ in boiling point by 15° and on a larger scale can be separated by distillation. On a smaller scale, reaction of the mixture with zinc and ethanol gave (*cis* + *trans*)-1 : 2-difluoroethylene (from VIII) and 1 : 1-difluoroethylene (from IX) in amounts showing that attack by the bromine atom had occurred on the CHF group of trifluoroethylene to an extent of 58% and on the CF_2 group to an extent of 42%. This ratio was substantially unaffected by use of light of wavelength >3000 Å instead of >2200 Å to initiate the reaction.

$CHFBr\cdot CHF_2$	$CF_2Br\cdot CH_2F$	$CF_2Br\cdot CH_2I$	$CF_3\cdot CH_2F$
(VIII)	(IX)	(X)	(XI)

It was shown earlier[5] that 1-bromo-1 : 1-difluoro-2-iodoethane (X) with mercurous fluoride gives exclusively 1 : 1 : 1-trifluoro-2-iodoethane, and it might have been expected that (IX) would similarly yield 1 : 1 : 1 : 2-trifluoroethane (XI) more rapidly than (VIII) would yield 1 : 1 : 2 : 2-tetrafluoroethane. Examination of infrared spectra showed that preferential replacement of the bromine in (IX) was occurring, but since replacement did not occur exclusively with one of the isomers, this method for determination of the relative proportions of the isomers in $H\cdot[C_2HF_3\cdot]Br$ was unsatisfactory.

When taken in conjunction with the evidence derived from the trifluoroiodomethane reaction, it is clear that the formation of a mixture of isomers by photochemical reaction of hydrogen bromide with trifluoroethylene provides strong evidence that atomic attack occurs on both the CHF and the CF_2 group, and the possibility of a concurrent ionic reaction ($\overset{\delta-}{C}HF{=}\overset{\delta+}{C}F_2 \longrightarrow CH_2F\cdot CF_2Br$) can be neglected.

The direction of ionic attack on trifluoroethylene is shown by its reaction with iodine monochloride to give only 1-chloro-1 : 1 : 2-trifluoro-2-iodoethane (XII). The absence of the other isomer (XIII) was shown by comparison of the infrared spectrum of the product with that of an authentic sample of 1-chloro-1 : 2 : 2-trifluoro-2-iodoethane prepared by reaction of hydrogen iodide with chlorotrifluoroethylene; this last reaction could not produce (XII). The presence of (XIII) in amounts greater than 5% would have been detected spectroscopically. Hydrogen chloride reacts with trifluoroethylene only at 240° in absence of a catalyst to give 1-chloro-1 : 1 : 2-trifluoroethane (XIV), b. p. 12°. Its known isomer 1-chloro-1 : 2 : 2-trifluoroethane (XV) has b. p. 17°. Zinc and ethanol convert (XIV) into 1 : 1-difluoroethylene; under similar conditions (XV) would be reduced or would yield 1 : 2-difluoroethylene. The identification of the products from trifluoroethylene and iodine monochloride or hydrogen chloride thus shows that reactions of this olefin involving ionic intermediates give only one product, whereas radical addition gives two.

$CF_2Cl\cdot CHFI$	$CF_2I\cdot CHFCl$	$CF_2Cl\cdot CH_2F$	$CHF_2\cdot CHFCl$
(XII)	(XIII)	(XIV)	(XV)

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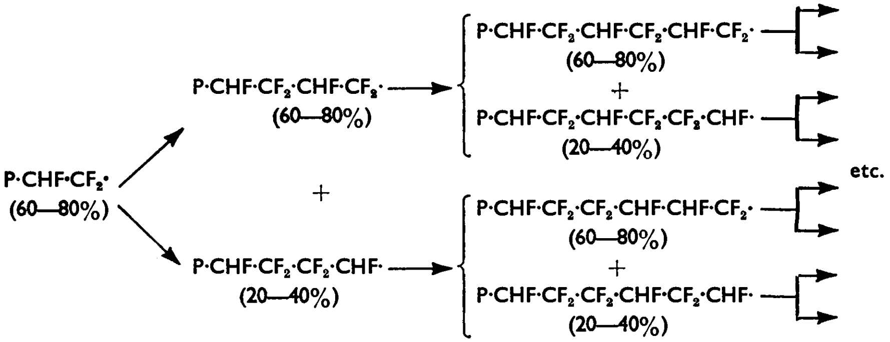
[4] Haszeldine, *J.*, 1953, 3559.

[5] Haszeldine and Steele, *J.*, 1954, 923.

Tarrant and Lilyquist [6] concluded recently that reaction of 1 : 2-dibromo-1-chlorotrifluoroethane with trifluoroethylene gave the compound $CF_2Br\cdot CFCl\cdot CHF\cdot CF_2Br$, since hydrogen bromide could be removed from the product to give olefins. 1 : 2-Dichloro-1-iodotrifluoroethane was similarly considered [6] to give the compound $CF_2Cl\cdot CFCl\cdot CHF\cdot CF_2I$ since dehydroiodination gave the known 3 : 4-dichlorohexafluorobut-1-ene, which in turn yielded hexafluorobuta-1 : 3-diene (40%) on dehalogenation.

Tarrant, Lovelace, and Lilyquist [7] reported that dibromodifluoromethane and trifluoroethylene gave the compounds $CF_2Br\cdot CHF\cdot CF_2Br$ and $CF_2Br\cdot[CHF\cdot CF_2]_2\cdot Br$ since the dibromopropane gave 3-bromopentafluoroprop-1-ene in 59% yield by reaction with aqueous potassium hydroxide. The evidence presented is clearly insufficient to show that only one isomer is produced during these free-radical reactions, and the possibility of the other isomer's being present was ignored. It is most unlikely that the $CF_2Br\cdot CFCl\cdot$, $CF_2Cl\cdot CFCl\cdot$, or $CF_2Br\cdot$ radicals would react at all differently from the $CF_3\cdot$ radical or the bromine atom as far as attack on trifluoroethylene is concerned, particularly since it has already been shown [3, 8] that the $CF_3\cdot$ and the $CF_2Cl\cdot CFCl\cdot$ radical are closely similar in their attack on chlorotrifluoroethylene. The products reported by the above authors are thus not pure compounds but mixtures of $R\cdot CHF\cdot CF_2X$ (*ca.* 80%) and $RCF_2\cdot CHFX$ (*ca.* 20%), and of $R\cdot CHF\cdot CF_2\cdot CHF\cdot CF_2X$ (*ca.* 64%), $R\cdot CHF\cdot CF_2\cdot CF_2\cdot CHFX$ (*ca.* 16%), $R\cdot CF_2\cdot CHF\cdot CF_2\cdot CHFX$ (*ca.* 4%), and $R\cdot CF_2\cdot CHF\cdot CHF\cdot CF_2X$ (*ca.* 16%), where $R =$ $CF_2Br\cdot CFCl$, $CF_2Cl\cdot CFCl$, or CF_2Br, and $X =$ Br or I.

Polytrifluoroethylene.—Homopolymerisation of trifluoroethylene initiated by a free radical P will give both $P\cdot CHF\cdot CF_2\cdot$ (60—80%) and $P\cdot CF_2\cdot CHF\cdot$ (20—40%). The subsequent growth of these radicals by combination with further molecules of trifluoroethylene can be represented as follows :



with a similar sequence initiated by radical $P\cdot CF_2\cdot CHF\cdot$.

The decreasing order of thermal stability for fluoro-polymers is polytetrafluoroethylene > poly-1 : 1-difluoroethylene > polytrifluoroethylene > polyethylene > polyvinyl fluoride.[9] It is known that compounds which contain only one fluorine on a carbon atom split off hydrogen fluoride much more readily than compounds which contain two or more fluorine atoms on the same carbon atom. It is thus not unexpected that polyvinyl fluoride, which consists entirely of $-CH_2\cdot CHF\cdot CH_2\cdot CHF-$ units,[2] should be thermally less stable than polyethylene or poly-1 : 1-difluoroethylene,[5] which contains only $-CH_2\cdot CF_2\cdot CH_2\cdot CF_2-$ units. The apparently anomalous position [9] of polytrifluoroethylene in the stability sequence can now be explained. This polymer is not made up of only $-CHF\cdot CF_2\cdot CHF\cdot CF_2-$ units arranged as $[-CHF\cdot CF_2\cdot CHF\cdot CF_2-]_n$ as hitherto assumed; such units would be thermally more stable than $-CH_2\cdot CF_2\cdot CH_2\cdot CF_2-$ units, since the hydrogen

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[6] Tarrant and Lilyquist, *J. Amer. Chem. Soc.*, 1955, **77**, 3640.
[7] Tarrant, Lovelace, and Lilyquist, *ibid.*, 1955, **77**, 2783.
[8] Haszeldine, *J.*, 1955, 4291, 4302.
[9] Madorsky, Hart, Straus, and Sedlak, *J. Res. Nat. Bur. Standards*, 1953, **51**, 327.

of a $-CF_2\cdot CHF\cdot CF_2-$ group is split off as proton or atom with less readiness than the hydrogen of a $-CF_2\cdot CH_2\cdot CF_2-$ group which tends towards the polyethylene type. The $-CHF\cdot CF_2\cdot CF_2\cdot CHF-$ units in polytrifluoroethylene, if flanked by CF_2 groups, would similarly be at least as stable as $-CH_2\cdot CF_2\cdot CH_2\cdot CF_2-$ units. It is the $-CHF\cdot CHF-$ groups in the $-CF_2\cdot CHF\cdot CHF\cdot CF_2-$ units (flanked by CF_2 or CHF groups) in polytrifluoroethylene which are the main cause of thermal instability, since hydrogen fluoride is readily eliminated to give groups such as $-CF_2\cdot CF{:}CH\cdot CF_2-$ which then break down further.

It can thus be predicted that the polymer $[-CHF\cdot CHF-]_n$ prepared from the new fluoro-olefin 1 : 2-difluoroethylene described above will show relatively poor thermal stability for a fluoro-polymer, *i.e.*, will be less stable than polyethylene.

EXPERIMENTAL

Preparation of Trifluoroethylene.—The olefin, prepared in 85% yield by the dehalogenation with zinc and ethanol of 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane, was purified by distillation *in vacuo* (Found : *M*, 82. Calc. for C_2HF_3 : *M*, 82); its purity was checked by means of its infrared spectrum.

Reaction of Trifluoroiodomethane with Trifluoroethylene.—*In the dark.* There was no reaction when trifluoroiodomethane (8·0 g.) and trifluoroethylene (2·4 g.) were sealed in a Pyrex tube and kept in the dark for 6 weeks.

In ultraviolet light. (a) *In Pyrex vessels.* The olefin (1·6 g., 0·02 mole) and trifluoroiodomethane (9·0 g., 0·046 mole) in a 150-ml. Pyrex tube were exposed to ultraviolet light for 3 weeks with the lower portion of the tube shielded. Distillation of the combined products from several such reactions gave, per experiment, unchanged reactants (8·6 g., 81%) and liquid products (1·9 g.), which were redistilled to give $CF_3\cdot[C_2HF_3]\cdot I$ (1·7 g., 85% based on trifluoroethylene consumed) as a 4 : 1 mixture, b. p. 62—63°, n_D^{20} 1·355, of 1 : 1 : 1 : 2 : 3 : 3-hexafluoro-3-iodopropane and 1 : 1 : 1 : 2 : 2 : 3-hexafluoro-3-iodopropane (Found : C, 12·8; H, 0·4%; *M*, 274. Calc. for C_3HIF_6 : C, 12·9; H, 0·4%; *M*, 278). A small amount (*ca.* 0·1 g.) of material of higher b. p. was also isolated. The $CF_3\cdot[C_2HF_3]\cdot I$ had ultraviolet spectra : Vapour, $\lambda_{max.}$ 268 (ε 190); $\lambda_{min.}$ 227 (ε 23). In light petroleum, $\lambda_{max.}$ 268 (ε 255); $\lambda_{min.}$ 223 (ε 50).

(b) *In silica vessels with an excess of trifluoroiodomethane.* Trifluoroiodomethane (16·1 g., 0·083 mole) and trifluoroethylene (1·21 g., 0·015 mole) were exposed to ultraviolet light for 4 days in a 200-ml. silica vessel with the lower portion shielded. Distillation gave trifluoroiodomethane (13·0 g.), $CF_3\cdot(C_2HF_3)\cdot I$ (3·5 g., 85%), b. p. 62—63°, and a fraction with a higher b. p. (0·7 g.). Infrared spectroscopy showed that the $CF_3\cdot(C_2HF_3)\cdot I$ fraction had the same composition as that obtained in (a) above.

(c) *In silica vessels with an equimolar ratio.* Trifluoroiodomethane (6·5 g., 0·033 mole) and trifluoroethylene (2·5 g., 0·031 mole), treated as in (b) above, gave trifluoroiodomethane (3·5 g.) and liquid products (4·7 g.). Redistillation of the liquid products gave the 1 : 1 addition product $CF_3\cdot(C_2HF_3)\cdot I$ (3·5 g., 41%), b. p. 61—66°, shown by infrared spectroscopy to be identical with the material obtained as in (a) and (b) above, and $CF_3\cdot[C_2HF_3]_2\cdot I$ (0·8 g., 7%), b. p. 112—118° (mainly 115—116°), n_D^{20} 1·370 (Found : C, 16·1; H, 0·7. Calc. for $C_5H_2IF_9$: C, 16·7; H, 0·6%). The last material, a mixture of the compounds $CF_3\cdot CHF\cdot CF_2\cdot CHF\cdot CF_2I$ (mainly) and $CF_3\cdot CHF\cdot CF_2\cdot CF_2\cdot CHFI$, $CF_3\cdot CF_2\cdot CHF\cdot CHF\cdot CF_2I$, and $CF_3\cdot CF_2\cdot CHF\cdot CF_2\cdot CHFI$, was characterised by infrared bands at 7·20, 7·75, 8·25, 8·36, 9·00, 10·41, 11·84, and 14·50 μ. A small amount of polymer remained in the distillation flask.

Reaction of the 1 : 1 *Addition Product* $CF_3\cdot(C_2HF_3)\cdot I$ *with Chlorine.*—In a typical experiment, the adduct (1·45 g.) was sealed with chlorine (2·0 g.) and water (0·5 ml.) in a 20-ml. silica vessel and exposed to ultraviolet light for 14 days. After reaction with mercury to remove the iodine chlorides and the excess of chlorine, the volatile products were distilled *in vacuo* to give $CF_3\cdot(C_2ClF_3)\cdot Cl$ (0·99 g., 86%) (Found : *M*, 221. Calc. for $C_3Cl_2F_6$: *M*, 221). Infrared spectroscopy showed that this material was 1 : 2- (*ca.* 80%) and 1 : 1-dichlorohexafluoropropane (*ca.* 20%). The characteristic infrared bands for $CF_3\cdot CFCl\cdot CF_2Cl$ (C.S. 37) * are 7·80, 8·07, 8·84, 9·34, 9·58, 10·31, 11·75, and 13·76 μ, and for $CF_3\cdot CF_2\cdot CFCl_2$ (C.S. 36) are 7·55, 8·07, 8·25, 8·97, 11·03, 11·93, and 13·54 μ.

* See *J.*, 1955, 4500, 4501.

In a typical experiment, the mixture of dichlorides (0·99 g.), stirred with zinc dust (4 g.) and ethanol (5 ml.) in a sealed vessel at 40° for 24 hr., yielded volatile products fractionated *in vacuo* to give hexafluoropropene (0·455 g., 67%) (Found : *M*, 150. Calc. for C_3F_6 : *M*, 150) and 1-chloro-1 : 2 : 2 : 3 : 3 : 3-hexafluoropropane (0·132 g., 16%) (Found : *M*, 184. Calc. for C_3HClF_6 : *M*, 186·5), identified by means of their infrared spectra.[3]

The above reactions were repeated with the adduct (1·02 g.) derived from experiments in Pyrex vessels. The dichlorides (0·68 g., 85%) gave hexafluoropropene (0·34 g., 72%) and 1-chloro-1 : 2 : 2 : 3 : 3 : 3-hexafluoropropane (0·08 g., 14%).

Reaction of the toluene-*p*-sulphonate of pentafluoropropanol (4·8 g.) with potassium fluoride[2, 10] (100% excess) in refluxing diethylene glycol monobutyl ether (50 ml.) for 8 hr. gave 1 : 1 : 1 : 2 : 2 : 3-hexafluoropropane (67%) (Found : *M*, 152. Calc. for $C_3H_2F_6$: *M*, 152), collected in a trap cooled by liquid oxygen then fractionated *in vacuo*. A sample (2·1 g.) prepared in this way was sealed with chlorine (20% excess) and water (2 ml.) in a 15-ml. Pyrex tube and exposed to ultraviolet radiation for 10 days, giving 1 : 1-dichlorohexafluoropropane (Found : *M*, 221) in 84% yield. Its infrared spectrum agreed with that reported earlier.[3]

Reaction of the 1 : 1 *Addition Product* $CF_3\cdot(C_2HF_3)\cdot I$ *with Bromine*.—The adduct (2·0 g.) was sealed in a Pyrex tube with bromine (1·6 g.) and exposed to ultraviolet light for 8 days to give a mixture (1·58 g., 92%) of 1-bromo-1 : 1 : 2 : 3 : 3 : 3- and 1-bromo-1 : 2 : 2 : 3 : 3 : 3-hexafluoropropane, b. p. 35° (Found : *M*, 232. Calc. for C_3HBrF_6 : *M*, 231). Comparison of the infrared spectra of this material and of pure 1-bromo-1 : 1 : 2 : 3 : 3 : 3-hexafluoropropane[4] revealed the extra bands at 7·45, 9·09, 9·60, 13·3, and 14·1 μ caused by the 1-bromo-1 : 2 : 2 : 3 : 3 : 3-hexafluoropropane.

Exposure of 1 : 1 : 1 : 2 : 2 : 3-hexafluoropropane (2·6 g.), bromine (60% of theory for complete bromination), and water (1 ml.), in a 10-ml. silica tube, to ultraviolet light for 9 days gave 1-*bromo*-1 : 2 : 2 : 3 : 3 : 3-*hexafluoropropane* (76%) (Found : C, 15·6; H, 0·5%; *M*, 231. C_3HBrF_6 requires C, 15·6; H, 0·4%; *M*, 231), b. p. 35°.

Reaction of Trifluoroethylene with Hydrogen Bromide.—(a) *In the dark*. There was no reaction when trifluoroethylene (0·55 g.) and hydrogen bromide (0·55 g.) were kept in the dark in a Pyrex tube for 14 days.

(b) *Thermal*. The reaction mixture of (a) was heated at 100° for 2 days in the dark without reaction. Reaction occurred only at 200° and after 5 days gave unchanged reactants and a 50% yield of a mixture of 1-bromo-1 : 2 : 2- and 1-bromo-1 : 1 : 2-trifluoroethane.

No reaction was detected when hydrogen bromide (0·50 g.), trifluoroethylene (0·50 g.), and glacial acetic acid (4 ml.) were kept in the dark for 2 days.

(c) *Photochemical*. In a typical small-scale experiment, trifluoroethylene (1·58 g., 0·019 mole) and hydrogen bromide (1·56 g., 0·019 mole) were sealed in a silica tube and exposed to light. An immediate reaction was apparent and after 30 min. distillation gave a mixture (3·07 g., 98%) (vapour pressure 760 mm. at 34°) of 1-bromo-1 : 2 : 2- and 1-bromo-1 : 1 : 2-trifluoroethane (Found : C, 15·0; H, 1·9%; *M*, 164. Calc. for $C_2H_2BrF_3$: C, 14·7; H, 1·2%; *M*, 165). Henne and Renoll[11] report b. p. 40—41°/735 mm. for 1-bromo-1 : 2 : 2-trifluoroethane, and Swarts[12] reports b. p. 25° for 1-bromo-1 : 1 : 2-trifluoroethane.

An experiment on a larger scale with trifluoroethylene (8·05 g.) and hydrogen bromide (8·02 g.), irradiated for 1 hr., gave a mixture (15·8 g., 98%) of the bromo-compounds. This was separated by distillation into 1-bromo-1 : 1 : 2- (38%) and 1-bromo-1 : 2 : 2-trifluoroethane (53%) with an intermediate fraction which spectroscopic examination showed to have essentially the same composition as the original mixture. If the intermediate fraction is assumed to contain 53% of $CHFBr\cdot CHF_2$ and 38% of $CF_2Br\cdot CH_2F$, the photochemical reaction of hydrogen bromide with trifluoroethylene has thus produced 57% of $CHFBr\cdot CHF_2$ and 43% of $CF_2Br\cdot CH_2F$. These figures agree well with the analysis based on zinc and ethanol treatment (see below) used for experiments carried out on a smaller scale.

Reaction of the 1 : 1 *Addition Product* $C_2H_2F_3Br$ *with Zinc and Ethanol*.—The adduct (3·39 g.) was sealed in a Pyrex tube with zinc dust (10 g.) and ethanol (5 ml.) and heated in a rotating furnace at 85° for 24 hr. The volatile products were washed with water and distilled repeatedly *in vacuo* through traps cooled to −95°, −140°, and −183°. The fraction which condensed at

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[10] Tiers, Brown, and Reid, *J. Amer. Chem. Soc.*, 1953, **75**, 5978; Edgell and Parts, *ibid.*, 1955, 77, 4899.

[11] Henne and Renoll, *ibid.*, 1936, **58**, 887.

[12] Swarts, *Bull. Acad. roy. Belg.*, 1911, 563.

−140° was (cis + trans)-1 : 2-*difluoroethylene* (0·683 g., 51%), b. p. −28° (isoteniscope) (Found : F, 58·8%; *M*, 64. $C_2H_2F_2$ requires F, 59·3%; *M*, 64), shown to be free from 1 : 1-difluoroethylene by infrared spectroscopy. Spectroscopic examination of the fraction which condensed at −183° (0·600 g., 45%) showed that it was 1 : 1-difluoroethylene contaminated with a small amount of one of the isomers of 1 : 2-difluoroethylene (Found : *M*, 64. Calc. for $C_2H_2F_2$: *M*, 64). The mixture was therefore sealed with chlorine (0·66 g.) and allowed to warm from −80° to 20° during 12 hr., then exposed to light for 2 hr. Distillation gave the mixed dichlorides (1·23 g., 98%) shown by infrared spectroscopy to contain 1 : 2-dichloro-1 : 1-difluoroethane (*ca.* 90%) and 1 : 2-dichloro-1 : 2-difluoroethane (10%).

1 : 2-Difluoroethylene (0·65 g.), prepared as above, was sealed with chlorine (0·72 g.) and, to prevent an explosive reaction, was allowed to warm from −80° to room temperature during 12 hr. The reaction was completed by exposure to ultraviolet light for 1 hr. Distillation gave 1 : 2-dichloro-1 : 2-difluoroethane (1·36 g., 99%), b. p. 58°, n_D^{20} 1·376. Henne and Waalkes[13] report b. p. 59°, n_D^{20} 1·391.

A known specimen of 1 : 2-dichloro-1 : 1-difluoroethane was prepared by reaction of 1 : 1-difluoroethylene (1·2 g.) and chlorine (1·04 g.) in the dark for 12 hr. followed by exposure to ultraviolet light for 2 hr. The product (1·96 g., 98%) had b. p. 47°. Henne and Hubbard[14] report b. p. 46·8°, n_D^{20} 1·3619.

The above experiments show that the mixture of difluoroethylenes obtained from the reaction of the addition product $C_2H_2F_3Br$ with zinc and ethanol contained 56% of 1 : 2-difluoroethylene and 41% of 1 : 1-difluoroethylene, *i.e.*, $CHF{:}CHF$ to $CF_2{:}CH_2$ = 1·36 to 1, and $CHFBr{\cdot}CHF_2$ to $CF_2Br{\cdot}CH_2F$ = 58 to 42.

1 : 2-Difluoroethylene shows infrared bands at 3·19 (C–H), 5·76, 5·83 (strong doublet, C:C stretch.), 6·25, 6·33 (weak doublet), 7·22, 7·26, 7·33 (triplet), 7·86, 7·97, 8·78, 8·85, 8·95 (triplet), 9·77, 10·00, 12·83, 13·00, 13·23 μ (triplet).

Reaction of the 1 : 1 *Addition Product* $C_2H_2F_3Br$ *with Mercurous Fluoride.*—The adduct (1·65 g.) was sealed in a Pyrex tube with mercurous fluoride (5 g.) and heated at 120—140° for 2 days. Distillation gave unchanged starting material (1·26 g., 77%) and a mixture of 1 : 1 : 1 : 2- and 1 : 1 : 2 : 2-tetrafluoroethane (0·163 g., 70%), b. p. −24° (Found : *M*, 101·5. Calc. for $C_2H_2F_4$: *M*, 102). The infrared spectrum of the recovered bromo-compounds was slightly different from that of the starting material, *i.e.*, preferential replacement of bromine by fluorine in one isomer was occurring to a limited extent.

Reaction of Trifluoroethylene with Hydrogen Chloride.—The olefin (1·35 g., 0·0165 mole) and anhydrous hydrogen chloride (0·61 g., 0·0167 mole), heated to 200° for 2 days, showed no reaction, but after 2 days at 240° gave 1-*chloro*-1 : 1 : 2-*trifluoroethane* (0·64 g., 33% conversion), b. p. 12° (Found : C, 20·6; H, 2·1%; *M*, 119. $C_2H_2ClF_3$ requires C, 20·3; H, 1·7%; *M*, 118·5). Swarts[15] reports b. p. 17° for the isomer 1-chloro-1 : 2 : 2-trifluoroethane.

The structure of the product from hydrogen chloride and trifluoroethylene was shown by treatment of a sample (0·53 g.) with zinc dust (3 g.) and ethanol (5 ml.) in a sealed Pyrex tube at 80—90° for 8 hr. Only 1 : 1-difluoroethylene (85% yield), shown by spectroscopic examination to be uncontaminated by 1 : 2-difluoroethylene, 1 : 2 : 2-trifluoroethane, or vinyl fluoride, was produced.

Reaction of Trifluoroethylene with Iodine Monochloride.—The olefin (1·33 g., 0·016 mole) and iodine monochloride (2·05 g., 0·013 mole), set aside for 12 hr., gave unchanged olefin (0·33 g.) and 1-*chloro*-1 : 1 : 2-*trifluoro*-2-*iodoethane* (2·95 g., 97%), b. p. 82—83°, n_D^{20} 1·433 (Found : C, 9·7; H, 0·7. C_2HClIF_3 requires C, 9·8; H, 0·4%). Ultraviolet spectrum in light petroleum : $\lambda_{max.}$ 265 (ε 295); $\lambda_{min.}$ 218 (ε 45); cf. $CF_2I{\cdot}CHFCl$ in light petroleum : $\lambda_{max.}$ 269 (ε 290), $\lambda_{min.}$ 223 (ε 40).

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[13] Henne and Waalkes, *J. Amer. Chem. Soc.*, 1945, **67**, 1639.

[14] Henne and Hubbard, *ibid.*, 1936, **58**, 404.

[15] Swarts, Mémoires couronnés et autre Mémoires publiés par l'Academie royale de Belgique, 1901, 61; *Zent.*, 1903, I, 13.