550. *Reactions of Fluorocarbon Radicals. Part V.* Alternative Syntheses for Trifluoromethylacetylene* (3 : 3 : 3-*Trifluoropropyne*), *and the Influence of Polyfluoro-groups on Adjacent Hydrogen and Halogen Atoms.*

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Syntheses of trifluoromethylacetylene from trifluoroacetic acid or trifluoroiodomethane by preparation and dehydrohalogenation or dehalogenation of compounds of the type $CF_3\cdot CH_2\cdot CHXY$, $CF_3\cdot CH{:}CHX$, $CF_3\cdot CX_2\cdot CHY_2$, $CF_3\cdot CX{:}CH_2$, and $CF_3\cdot CX{:}CHY$ (X or Y = halogen other than fluorine) have been investigated. 3 : 3 : 3-Trifluoropropene has proved to be the most convenient intermediate for the preparation of comparatively large amounts of the acetylene. The influence of the trifluoromethyl group on the reactivity of hydrogen and halogen atoms attached directly to it, attached to an adjacent carbon atom, and attached to the carbon atom once removed is considered. The infra-red spectrum of trifluoromethylacetylene is reported.

3 : 3 : 3-TRIFLUOROPROPYNE was first prepared by the interaction of trifluoroiodomethane and acetylene to give 3 : 3 : 3-trifluoro-1-iodopropene, followed by dehydroiodination (Haszeldine, *Nature*, 1950, **165**, 152; *J.*, 1951, 588). The reaction of trifluoroiodomethane with acetylene can be carried out in glass apparatus at pressures of 10—15 atmospheres, and although it constitutes a convenient synthesis for small laboratory-scale quantities of the trifluoromethylacetylene, the dangers associated with acetylene under pressure prevent its convenient application on a large scale. Other syntheses have now been developed, some of which are suitable for the preparation of larger quantities.

Trifluoroacetic acid was used as the source of the CF_3 group, and was converted into trifluoroiodomethane by reaction of the silver salt with iodine (Haszeldine, *Nature*, 1950, **166**, 192; *J.*, 1951, 584). Trifluoroiodomethane, also prepared from carbon tetraiodide (Haszeldine, *J.*, 1950, 3037), was converted by reaction with ethylene into a polymer $CF_3\cdot[CH_2\cdot CH_2]_n\cdot I$, in which the compound with $n = 1$ predominated (Haszeldine, *J.*, 1949, 2856).

$$\begin{tikzcd} CF_3\cdot CO_2H \arrow[r] & CF_3\cdot CO_2Ag \arrow[d] & \\ CI_4 \arrow[r] & CF_3I \arrow[r] & CF_3\cdot CH_2\cdot CH_2I \end{tikzcd}$$

The synthesis of trifluoromethylacetylene from 3 : 3 : 3-trifluoro-1-iodopropane can be performed by four routes.

Route I.—The fluoroiodopropane is converted into a compound of general formula $CF_3\cdot CH_2\cdot CHXY$ (X or Y = Cl, Br, or I), which, on dehydrohalogenation, yields trifluoromethylacetylene. The following reaction schemes were employed for the preparation of $CF_3\cdot CH_2\cdot CHClI$, $CF_3\cdot CH_2\cdot CHBrI$, $CF_3\cdot CH_2\cdot CHCl_2$, $CF_3\cdot CH_2\cdot CHBr_2$, and $CF_3\cdot CH_2\cdot CHClBr$:

$$(1)\ CF_3\cdot CH_2\cdot CH_2I \xrightarrow[\text{chlorination}]{\text{Photochemical}} \underset{\text{Main product}}{CF_3\cdot CH_2\cdot CHClI} + \underset{\text{See (4) below}}{CF_3\cdot CH_2\cdot CH_2Cl} + CF_3\cdot CH_2\cdot CHCl_2 + CF_3\cdot CH_2\cdot CCl_3$$

$$(2)\ CF_3\cdot CH_2\cdot CH_2I \xrightarrow[\text{bromination}]{\text{Thermal}} CF_3\cdot CH_2\cdot CHBrI + \underset{\text{See (4) below}}{CF_3\cdot CH_2\cdot CH_2Br} + CF_3\cdot CH_2\cdot CHBr_2$$

$$\begin{tikzcd} (3a)\ CF_3\cdot CH_2\cdot CH_2I \arrow[r, "Mg-Et_2O"] \arrow[d, "RH-Hg"] & CF_3\cdot CH_2\cdot CH_2\cdot MgI \arrow[r, "H_2O"] & CF_3\cdot CH_2\cdot CH_3 \\ CF_3\cdot CH_2\cdot CH_3 & & \end{tikzcd}$$

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* Part IV, *J.*, 1951, 588.

$$\begin{tikzcd}
(3b)\ \mathrm{CF_3{\cdot}CH_2{\cdot}CH_3} \arrow[r, "\text{Photochemical or}", "\text{thermal chlorination}"'] \arrow[d, "\text{Thermal bromination}"] & \mathrm{CF_3{\cdot}CH_2{\cdot}CHCl_2} + \underset{\text{See (4) below}}{\mathrm{CF_3{\cdot}CH_2{\cdot}CH_2Cl}} + \mathrm{CF_3{\cdot}CH_2{\cdot}CCl_3} \\
\mathrm{CF_3{\cdot}CH_2{\cdot}CHBr_2} + \underset{\text{See (4) below}}{\mathrm{CF_3{\cdot}CH_2{\cdot}CH_2Br}} + \mathrm{CF_3{\cdot}CHBr{\cdot}CH_3} &
\end{tikzcd}$$

$$\begin{tikzcd}
(4)\ \mathrm{CF_3{\cdot}CH_2{\cdot}CH_2I} \arrow[r, "\mathrm{Mg{-}C_6H_6}"] & \mathrm{CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}MgI} \arrow[r, "\mathrm{Cl_2}"] \arrow[d, "\mathrm{Br_2}"] & \mathrm{CF_3{\cdot}CH_2{\cdot}CH_2Cl} \\
& \mathrm{CF_3{\cdot}CH_2{\cdot}CH_2Br} &
\end{tikzcd}$$

$$\mathrm{CF_3{\cdot}CH_2{\cdot}CH_2Cl} \xrightarrow[\text{or } \mathrm{Br_2}\text{, heat}]{\mathrm{Cl_2},\ h\nu,} \mathrm{CF_3{\cdot}CH_2{\cdot}CHCl_2} \text{ or } \mathrm{CF_3{\cdot}CH_2{\cdot}CHClBr}$$

$$\mathrm{CF_3{\cdot}CH_2{\cdot}CH_2Br} \xrightarrow[\text{or } \mathrm{Br_2}\text{, heat}]{\mathrm{Cl_2},\ h\nu,} \mathrm{CF_3{\cdot}CH_2{\cdot}CHClBr} \text{ or } \mathrm{CF_3{\cdot}CH_2{\cdot}CHBr_2}$$

Scheme 1. Photochemical chlorination of 1 : 1 : 1-trifluoro-3-iodopropane gave, under the conditions used, mainly 3-chloro-1 : 1 : 1-trifluoro-3-iodopropane. The structural formula of this product follows from the facts that treatment with zinc and alcohol does not give trifluoropropene and that irradiation with chlorine yields 3 : 3-dichloro-1 : 1 : 1-trifluoropropane and 3 : 3-dichloro-1 : 1 : 1-trifluoro-3-iodopropane. The structural formula of the last compound is, in turn, shown by the fact that irradiation with chlorine in a Pyrex vessel yields only one product, 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane :

$$\begin{tikzcd}
\mathrm{CF_3{\cdot}CH_2{\cdot}CHClI} \arrow[r] & \mathrm{CF_3{\cdot}CH_2{\cdot}CHCl_2} + \mathrm{CF_3{\cdot}CH_2{\cdot}CCl_2I} \arrow[d] \\
& \mathrm{CF_3{\cdot}CH_2{\cdot}CCl_3}
\end{tikzcd}$$

The trichlorotrifluoropropane can be identified by its boiling point, which is appreciably different from that of its isomer 2 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane, and by the fact that treatment with zinc and alcohol does not give 1-chloro-3 : 3 : 3-trifluoropropene.

The structural formula of 3 : 3-dichloro-1 : 1 : 1-trifluoropropane formed by chlorination of 1 : 1 : 1-trifluoro-3-iodopropane and of 3-chloro-1 : 1 : 1-trifluoro-3-iodopropane rests partly on its physical properties, but mainly on the facts that further chlorination gives 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane, and that treatment with zinc and alcohol does not give 3 : 3 : 3-trifluoropropene. The formula of 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane isolated from 1 : 1 : 1-trifluoro-3-iodopropane and chlorine is based upon similar arguments, and that of the fourth product 3-chloro-1 : 1 : 1-trifluoropropane by its boiling point which is 15° higher than that of the possible isomer 2-chloro-1 : 1 : 1-trifluoropropane; furthermore, the formation of the 2-chloro-compound by the chlorination of the 3-iodo-compound is unlikely.

It is evident, therefore, that the chlorination of 1 : 1 : 1-trifluoro-3-iodopropane proceeds by replacement of the hydrogen atom on the carbon carrying the iodine atom, and that this is accompanied either by homolytic fission of the carbon–iodine bond or by replacement of iodine in an iodo-compound by chlorine, *e.g.* :

$$\mathrm{CF_3{\cdot}CH_2{\cdot}CH_2I} \xrightarrow{h\nu} \mathrm{CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}} + {\cdot}\mathrm{I} \xrightarrow{\mathrm{Cl_2}} \mathrm{CF_3{\cdot}CH_2{\cdot}CH_2Cl} + \mathrm{ICl}$$

$$\mathrm{CF_3{\cdot}CH_2{\cdot}CHClI} + \mathrm{Cl_2} \xrightarrow{h\nu} \mathrm{CF_3{\cdot}CH_2{\cdot}CHCl_2} + \mathrm{ICl}$$

Scheme 2. The conditions used for thermal bromination of 1 : 1 : 1-trifluoro-3-iodopropane were more stringent than those for its chlorination, and products (*e.g.*, bromotrifluoromethane) other than those indicated were also formed by decomposition. In general, however, the bromination resembled the chlorination and yielded 3-bromo-1 : 1 : 1-trifluoro-3-iodopropane, whose structure was established by photochemical bromination at room temperature to give 3 : 3-dibromo-1 : 1 : 1-trifluoropropane. The boiling point of the latter compound is sufficiently removed from that of the isomer 2 : 3-dibromo-1 : 1 : 1-trifluoropropane to make identification possible. In addition, it was found that dehydrobromination was readily effected and in good yield, as was observed with the 3 : 3-dibromo-compound prepared by a different route, and that heating with zinc and alcohol did not yield 3 : 3 : 3-trifluoropropene.

Other compounds identified in the product from the thermal bromination of 1 : 1 : 1-trifluoro-3-iodopropane were 1 : 1 : 1-trifluoro-3 : 3-dibromo- and -3-bromo-propane whose boiling point is some 13° higher than that of the 2-bromo-isomer.

Scheme 3. The fluoropropane, $CF_3{\cdot}CH_2{\cdot}CH_3$, was prepared from 1 : 1 : 1-trifluoro-3-iodopropane by reaction in ultra-violet light at room temperature, or at high temperature in an autoclave, with a compound from which the free $CF_3{\cdot}CH_2{\cdot}CH_2$ radicals are capable of abstracting hydrogen atoms. Such compounds are alcohols, ethers, and hydrocarbons, but to avoid side reactions hydrocarbons are preferred. The addition of mercury to remove iodine and so prevent primary recombination facilitates the reaction (Haszeldine, *J.*, 1949, 2856). Small amounts of 3 : 3 : 3-trifluoropropene, possibly formed by disproportionation $2CF_3{\cdot}CH_2{\cdot}CH_2{\bullet} \longrightarrow CF_3{\cdot}CH_2{\cdot}CH_3 + CF_3{\cdot}CH{:}CH_2$ were also identified. A more suitable method for the conversion of 1 : 1 : 1-trifluoro-3-iodopropane into trifluoropropane is by formation and hydrolysis of the Grignard reagent, $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}MgI$ (forthcoming communication).

The reactions illustrated by scheme (3*b*), *i.e.*, the conversion of trifluoropropane into 3 : 3-dichloro- and 3 : 3-dibromo-1 : 1 : 1-trifluoropropane by chlorination or thermal bromination, were first carried out by Henne and by McBee with their respective co-workers. Somewhat different experimental conditions have been used in the present work and the results are now discussed. Henne and Whaley (*J. Amer. Chem. Soc.*, 1942, **64**, 1157) observed that photochemical chlorination of 1 : 1 : 1-trifluoropropane gave 3-chloro-, 3 : 3-dichloro-, and 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane, and intermediate fractions in a weight ratio of 21 : 41 : 26 : 12. Photochemical chlorination at room temperature by the method described in the Experimental section gave a product which contained the above fractions in a weight ratio of 16 : 62 : 14 : 8. Thus, it is possible to chlorinate trifluoropropane to give mainly the mono- and di-chloro-compounds. In accord with Henne and Whaley's results, a negligible amount of the 2-chloro-trifluoropropane was formed. Vapour phase photochemical chlorination at 80—100°, however, gave an appreciable amount of the 2-chloro-1 : 1 : 1-trifluoropropane. The weight ratio of 3-chloro-, 2-chloro-, 3 : 3-dichloro-, and 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane was 55 : 18 : 17 : 2 which is in substantial agreement with McBee and Truchan's results (*J. Amer. Chem. Soc.*, 1948, **70**, 2910), who found a ratio of 58 : 22 : 17 : x (not quoted), by a flow-chlorination technique. Thermal chlorination (420°) of trifluoropropane gave a weight ratio of products of 36 : 3 : 18 : 8, which can be compared with the figures 44 : 12 : 11 : (unknown) calculated from the results of McBee, Hass, Thomas, Toland, and Truchan (*J. Amer. Chem. Soc.*, 1947, **69**, 944) for a similar temperature (380°). The amount of the 2-chloro-1 : 1 : 1-trifluoropropane formed clearly depends on the technique and conditions used. The structural formulæ of the products of chlorination were established by the procedures outlined earlier.

Thermal bromination of trifluoropropane gave 3 : 3-dibromo-1 : 1 : 1-trifluoropropane and two isomeric monobromo-compounds, $CF_3{\cdot}CH_2{\cdot}CH_2Br$ and $CF_3{\cdot}CHBr{\cdot}CH_3$. The amount of the 2-bromo-compound isolated was much less than was found by McBee, Hass, Toland, and Truchan (*Ind. Eng. Chem.*, 1947, **39**, 420) (cf. weight ratios of 3-bromo- : 2-bromo- : 3 : 3-dibromo-compound, 30 : 6 : 64 and 43 : 25 : 32 respectively).

Scheme 4. The 3-bromo- and 3-chloro-1 : 1 : 1-trifluoropropanes produced as by-products in the earlier reactions could also be obtained from the 3-iodo-compound by interaction of the Grignard reagent and bromine or chlorine, and from ethylene by free-radical addition of carbon tetrachloride or bromotrichloromethane to give $CCl_3{\cdot}CH_2{\cdot}CH_2Cl$ or $CCl_3{\cdot}CH_2{\cdot}CH_2Br$, followed by catalysed antimony fluoride fluorination (unpublished). Chlorination or bromination converted these 3-halogeno-fluoropropanes into $CF_3{\cdot}CH_2{\cdot}CHCl_2$, $CF_3{\cdot}CH_2{\cdot}CHBr_2$, or $CF_3{\cdot}CH_2{\cdot}CHClBr$. The 3 : 3-dihalogeno-compounds were formed in good yield by chlorination of the monohalogeno-compounds, whereas thermal bromination brought about some decomposition. The formulæ of the first two compounds were established as described earlier. That of 3-bromo-3-chloro-1 : 1 : 1-trifluoropropane was based on its failure to give 3 : 3 : 3-trifluoropropene with zinc and alcohol (although it was not inert to this reagent), and on its dehydrohalogenation to 1-chloro-3 : 3 : 3-trifluoropropene and trifluoromethylacetylene.

Photochemical chlorination of 3-chloro-1 : 1 : 1-trifluoropropane gave some 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane, and of the 3-bromo-compound gave a small amount of 3-bromo-3 : 3-dichloro-1 : 1 : 1-trifluoropropane in addition to the compounds noted above. The structure of the bromodichloro-compound was established by dehydrobromination to an olefin ($CF_3{\cdot}CH{:}CCl_2$) which was not dechlorinated by zinc and alcohol. The bromodichloro-isomers which could have been formed were $CF_3{\cdot}CCl_2{\cdot}CH_2Br$, which could not undergo dehydrobromination, and $CF_3{\cdot}CHCl{\cdot}CHClBr$. The last compound, on dehydrobromination, would give an olefin ($CF_3{\cdot}CCl{:}CHCl$), which has been found to give trifluoromethylacetylene in small yield when treated with zinc and alcohol.

It will be noted that the chlorination and bromination of $CF_3{\cdot}CH_2{\cdot}CH_2X$ is again markedly directed to the carbon atom which already carries the lone halogen X.

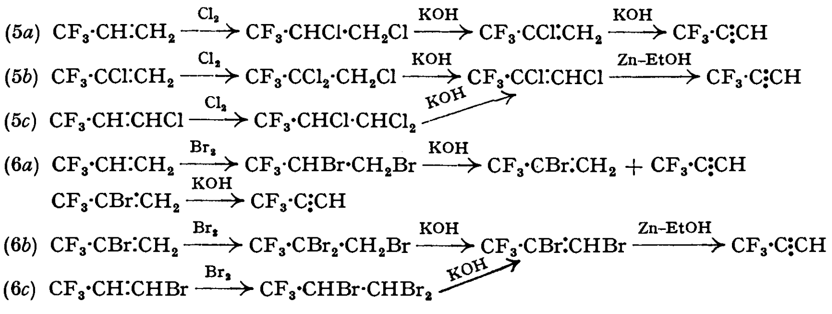
The compounds of formulæ $CF_3{\cdot}CH_2{\cdot}CH_2X$, $CF_3{\cdot}CHX{\cdot}CH_3$, and $CF_3{\cdot}CH_2{\cdot}CHX_2$ obtained by the routes described above were dehydrohalogenated by powdered potassium hydroxide. It was found that reaction occurred most easily and with the best yields when the hydrogen removed was on the carbon atom adjacent to the CF_3 group, and the halogen atom was on the carbon atom once removed, *i.e.*, the most suitable system was $CF_3{\cdot}\overset{|}{C}H{\cdot}\underset{|}{\overset{|}{C}}X$, and X was preferably iodine or bromine. Removal of hydrogen chloride from 2-chloro-1 : 1 : 1-trifluoropropane was achieved in only poor yield, and the chlorine atom is thus stabilised by its position on the carbon atom adjacent to the CF_3 group : the 2-bromo-compound gave only a slightly better yield of 3 : 3 : 3-trifluoropropene. The dehydrohalogenation of a compound such as 2 : 2-dichloro-1 : 1 : 1-trifluoropropane to give trifluoromethylacetylene was not attempted and, in view of the results with the 2-chloro-compound, is unlikely to be a suitable method for the preparation of the acetylene.

Route II.—The second method available for the preparation of trifluoromethylacetylene is by dehydrohalogenation of an olefin $CF_3{\cdot}CH{:}CHX$ (X = Cl, Br, or I). The compound where X = I can be prepared from trifluoroiodomethane and acetylene, but the only convenient method at present available for the synthesis of the compounds where X = Cl and Br is from suitable $CF_3{\cdot}CH_2{\cdot}CHX_2$ compounds. The 1-bromo- and 1-chloro-3 : 3 : 3-trifluoropropenes were isolated as intermediates in the conversion of $CF_3{\cdot}CH_2{\cdot}CHCl_2$, $CF_3{\cdot}CH_2{\cdot}CHBr_2$, $CF_3{\cdot}CH_2{\cdot}CHClBr$, $CF_3{\cdot}CH_2{\cdot}CHBrI$, and $CF_3{\cdot}CH_2{\cdot}CHClI$ into trifluoromethylacetylene; the ease of hydrogen halide removal from these compounds is in the expected order $HI > HBr > HCl$. The structural formulæ of the halogenopropenes follow from the formulæ of the parent compounds : they were readily dehydrohalogenated to give the acetylene in good yield, in contrast to their isomers 2-bromo- and 2-chloro-3 : 3 : 3-trifluoropropene (see below).

Route III.—The third method for the synthesis of trifluoromethylacetylene was from compounds of general formula $CF_3{\cdot}CXX'{\cdot}CHYY'$, by dehalogenation. Suitable compounds of this type have yet to be prepared. 2 : 2 : 3 : 3-Tetrachloro-1 : 1 : 1-trifluoropropane, for example, has been obtained only by addition of chlorine to trifluoromethylacetylene (Haszeldine, *J.*, 1951, 588). Unless X and X′ are bromine or iodine, the yields by this route will be poor, since the stabilising influence of the CF_3 group on X and X′ will render dehalogenation difficult.

Route IV.—The fourth method involves the conversion of the olefin 3 : 3 : 3-trifluoropropene into olefins of the type $CF_3{\cdot}CX{:}CH_2$ or $CF_3{\cdot}CX{:}CHY$, followed by dehydrohalogenation or dehalogenation. The 3 : 3 : 3-trifluoropropene was prepared from the compounds $CF_3{\cdot}CH_2{\cdot}CH_2X$ described earlier, but its preparation need not involve trifluoroiodomethane or trifluoroacetic acid, since $CF_3{\cdot}CH_2{\cdot}CH_2Cl$ and $CF_3{\cdot}CH_2{\cdot}CH_2Br$ can be obtained from 1 : 1 : 1 : 3-tetrachloro-, 3-bromo-1 : 1 : 1-trichloro- (above), or 1 : 1 : 1-trifluoro-propane which last, in turn, can be synthesised from 1 : 1 : 1-trichloropropane, 1 : 1-dichloropropene, or 1 : 1-dichloro*cyclo*propane (McBee, Hass, Thomas, Toland, and Truchan, *loc. cit.*).

The following syntheses were investigated :



$$(5a)\ CF_3{\cdot}CH{:}CH_2 \xrightarrow{Cl_2} CF_3{\cdot}CHCl{\cdot}CH_2Cl \xrightarrow{KOH} CF_3{\cdot}CCl{:}CH_2 \xrightarrow{KOH} CF_3{\cdot}C{\vdots}CH$$

$$(5b)\ CF_3{\cdot}CCl{:}CH_2 \xrightarrow{Cl_2} CF_3{\cdot}CCl_2{\cdot}CH_2Cl \xrightarrow{KOH} CF_3{\cdot}CCl{:}CHCl \xrightarrow{Zn\text{-}EtOH} CF_3{\cdot}C{\vdots}CH$$

$$(5c)\ CF_3{\cdot}CH{:}CHCl \xrightarrow{Cl_2} CF_3{\cdot}CHCl{\cdot}CHCl_2 \xrightarrow{KOH}$$

$$(6a)\ CF_3{\cdot}CH{:}CH_2 \xrightarrow{Br_2} CF_3{\cdot}CHBr{\cdot}CH_2Br \xrightarrow{KOH} CF_3{\cdot}CBr{:}CH_2 + CF_3{\cdot}C{\vdots}CH$$

$$CF_3{\cdot}CBr{:}CH_2 \xrightarrow{KOH} CF_3{\cdot}C{\vdots}CH$$

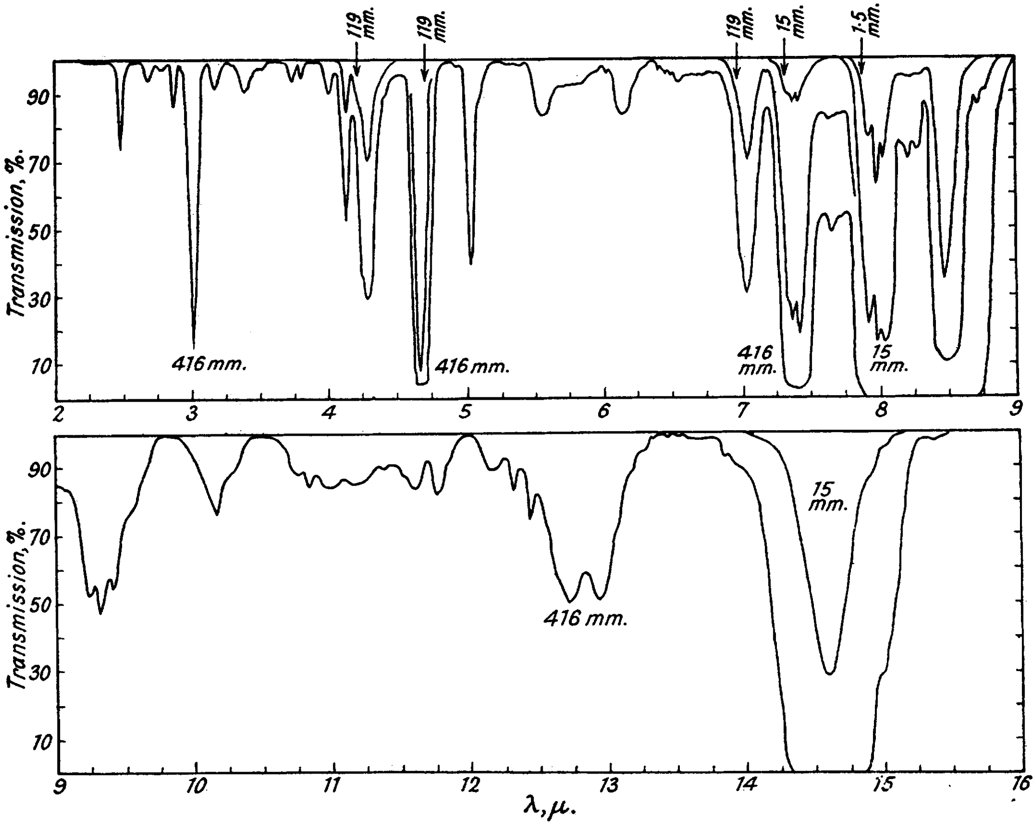
$$(6b)\ CF_3{\cdot}CBr{:}CH_2 \xrightarrow{Br_2} CF_3{\cdot}CBr_2{\cdot}CH_2Br \xrightarrow{KOH} CF_3{\cdot}CBr{:}CHBr \xrightarrow{Zn\text{-}EtOH} CF_3{\cdot}C{\vdots}CH$$

$$(6c)\ CF_3{\cdot}CH{:}CHBr \xrightarrow{Br_2} CF_3{\cdot}CHBr{\cdot}CHBr_2 \xrightarrow{KOH}$$

The photo-catalysed addition of chlorine to 3 : 3 : 3-trifluoropropene gave 2 : 3-dichloro-1 : 1 : 1-trifluoropropane in good yield, but treatment with potassium hydroxide gave mainly a monochloro-trifluoropropene, which, on further treatment with alkali, gave the acetylene in only poor yield. The two $C_3H_2ClF_3$ isomers thus differ greatly in their reactivity to alkali. The structural formula of the $CF_3{\cdot}CH{:}CHCl$ isomer is known by its synthesis from $CF_3{\cdot}CH_2{\cdot}CHX_2$ compounds. It thus follows that the other isomer (obtained from $CF_3{\cdot}CHCl{\cdot}CH_2Cl$) is $CF_3{\cdot}CCl{:}CH_2$, that in the dehydrochlorination of $CF_3{\cdot}CHCl{\cdot}CH_2Cl$ it is the hydrogen atom on thec arbon atom adjacent to the CF_3 group which is removed (in accord with the observations on the ease of dehydrohalogenation of $CF_3{\cdot}CH_2{\cdot}CHX_2$ compounds), and that the chlorine atom in $CF_3{\cdot}CCl{:}CH_2$ resists chemical attack.

An alternative route from 2-chloro-3 : 3 : 3-trifluoropropene to trifluoromethylacetylene is by addition of chlorine to give 2 : 2 : 3-trichloro-1 : 1 : 1-trifluoropropane, followed by dehydrochlorination to give the known dichlorotrifluoropropene, $CF_3{\cdot}CCl{:}CHCl$. The acetylene was obtained from this compound in only poor yield on treatment with zinc and alcohol. The isomeric 1-chlorotrifluoropropene could be chlorinated and dehydrochlorinated (route 5*c*) to give 1 : 2-dichloro-3 : 3 : 3-trifluoropropene in much better yield.

The infra-red spectrum of trifluoromethylacetylene vapour.



The corresponding bromo-compounds were found to give better yields. Treatment of 2 : 3-dibromo-1 : 1 : 1-trifluoropropane with alkali (route 6*a*) gave 2-bromo-3 : 3 : 3-trifluoropropene; some trifluoromethylacetylene was also formed. Further treatment of $CF_3{\cdot}CBr{:}CH_2$ with alkali gave the acetylene in poor yield and the difference in reactivity of the two $C_3H_2BrF_3$ isomers is apparent. Addition of bromine to $CF_3{\cdot}CBr{:}CH_2$ gave the unstable tribromo-compound which, on dehydrobromination, yielded 1 : 2-dibromo-3 : 3 : 3-trifluoropropene. This compound could be debrominated to give trifluoromethylacetylene in almost theoretical yield. Method 6*b* is essentially that used by Henne in his synthesis of the acetylene (private communication). The 1 : 2-dibromotrifluoropropene was also prepared from 1-bromotrifluoropropene by successive bromination and dehydrobromination.

For the preparation of 3 : 3 : 3-trifluoromethylacetylene on a small scale the original method from trifluoroiodomethane and acetylene is most convenient, whereas for larger-scale preparation the syntheses represented by 6*a* and *b* are preferred.

The infra-red spectrum of trifluoromethylacetylene is shown in the diagram. The $C{\equiv}C$ stretching frequency at 4·65 μ. is similar to that in methylacetylene (4·625 μ.; Infra-red absorption spectrogram No. 45 of the American Petroleum Institute, Research Project 44, Nat. Bur. Stand., Washington, D.C.). The acetylenic carbon–hydrogen stretching frequency is at a slightly higher wave-length (3·01 μ.) than in methylacetylene (2·96 μ.). The multiple absorption bands at *ca.* 8·0 and 8·5 μ. are clearly associated with the CF_3 group, and other strong absorption bands can be interpreted in terms of the fundamentals of trifluoromethylacetylene. These results, together with those derived from the potassium bromide region of the spectrum, will be considered in detail in a later communication.

Influence of CF_3 *on Reactivity.*—Since in establishing the formulæ of the compounds described in this paper, no assumptions were made as to the point of attack of halogen atoms, direction of hydrogen halide removal, etc., additional evidence becomes available for the effect of a polyfluoro-group such as CF_3 on nearby hydrogen and halogen atoms. The reactions of three classes of compounds can be distinguished.

(1) When the polyfluoro-group is separated by one or more carbon atoms from the hydrogen or halogen atom under consideration, *e.g.*, $CF_3{\cdot}CH_2{\cdot}\overset{|}{\underset{|}{C}}H$ or $CF_3{\cdot}CH_2{\cdot}\overset{|}{\underset{|}{C}}X$, then it has only a slight influence. This is illustrated by the fact that replacement of the hydrogen atom on the CH_2X group in $CF_3{\cdot}CH_2{\cdot}CH_2X$ by chlorine or bromine can occur, although at a slower rate and under more vigorous conditions than for a normal hydrocarbon. Removal of X from $CF_3{\cdot}CH_2{\cdot}CH_2X$ or $CF_3{\cdot}CH{:}CHX$ as HX can readily be achieved. Again, the C–X bond in the $CF_3{\cdot}CH_2{\cdot}CH_2X$ type of compound can undergo Grignard formation and many nucleophilic reactions (unpublished results).

(2) When the hydrogen atom under consideration is attached to the carbon atom adjacent to the polyfluoro-group, then it is substantially protected from attack by atomic reagents, as first observed by Henne and his co-workers in a series of chlorination experiments (Haeckl and Henne, *J. Amer. Chem. Soc.*, 1941, **63**, 2692; Elmore, Hass, Henne, and McBee, *ibid.*, 1940, **62**, 3340; Henne and Whaley, *loc. cit.*; Henne and Hinkamp, *ibid.*, 1945, **67**, 1195). Thus chlorination of $CF_3{\cdot}CH_2{\cdot}CH_2X$ occurs mainly on the terminal carbon atom, and there is a definite tendency at low temperatures for the halogenation to proceed to the $CF_3{\cdot}CH_2{\cdot}CX_3$ stage before attack on the central CH_2 group begins. The " acidic " nature of the hydrogen atoms on the central carbon atom is revealed by their ready removal as HX. A halogen atom on the carbon atom adjacent to the polyfluoro-group, *e.g.*, $CF_3{\cdot}\overset{|}{C}X{\cdot}\overset{|}{\underset{|}{C}}{-}$, $CF_3{\cdot}CX{:}\overset{|}{\underset{|}{C}}$, is stabilised, and its removal as HX is difficult, although the removal of halogen from adjacent carbon atoms (*e.g.*, $CF_3{\cdot}CX{:}CHX$) can be effected.

(3) When the hydrogen or halogen atom is attached to the carbon atom carrying the fluorine atom, it becomes resistant to chemical attack, as illustrated by the properties of CHF_3, CF_3Cl, CF_3Br, and CF_3I.

EXPERIMENTAL.

Preparation of Trifluoroiodomethane and 1 : 1 : 1-*Trifluoro*-3-*iodopropane.*—Trifluoroiodomethane was prepared either by the interaction of carbon tetraiodide and iodine pentafluoride or from silver trifluoroacetate and iodine as previously described. The reaction of trifluoroiodomethane with ethylene was carried out in sealed tubes or in a small autoclave; the 1 : 1 adduct formed 80—85% of the product.

Chlorination of 1 : 1 : 1-*Trifluoro*-3-*iodopropane.*—Photochemical chlorination was carried out in a silica tube (200-ml. capacity), cooled by running water and fitted with an efficient reflux condenser cooled to 0°. Chlorine was passed through 1 : 1 : 1-trifluoro-3-iodopropane (11·2 g.) at such a rate that the temperature of the liquid in the flask did not rise above 25°, and that the chlorine was largely absorbed. The tube was irradiated by a Hanovia ultra-violet lamp used without the Wood's filter and situated 24″ from the flask. The gases from the condenser were passed through water; when the conditions were carefully controlled, only a trace of organic material was carried through the condenser. When 1·2 mols. of chlorine had been added, the reaction was stopped. A similar experiment in which the fluoroiodopropane in a Pyrex tube was covered by water for the chlorination appeared, on preliminary investigation, to give substantially the same products as in the first experiment. The yields were therefore combined and fractionated to give as main product 3-*chloro*-1 : 1 : 1-*trifluoro*-3-*iodopropane* (11·2 g., 43%) (Found : C, 13·8; H, 1·1; Cl, 13·4; I, 49·2. $C_3H_3ClIF_3$ requires C, 13·9; H, 1·2; Cl, 13·7; I, 49·1%), b. p. 119°, n_D^{20} 1·450. The second product isolated was 3-chloro-1 : 1 : 1-trifluoropropane (2·1 g., 16%) (Found : Cl, 26·5%; *M*, 133. Calc. for $C_3H_4ClF_3$: Cl, 26·8%; *M*, 132·5), b. p. 45—46°, n_D^{25} 1·334. Henne and Whaley, *loc. cit.*, report b. p. 45·1°, n_D^{20} 1·3350, and Henne and Kaye (*J. Amer. Chem. Soc.*, 1950, **72**, 3369) report b. p. 45—46°, n_D^{20} 1·3379, for this compound; its isomer, 2-chloro-1 : 1 : 1-trifluoropropane, has b. p. 30·0°, n_D^{20} 1·3150 (Henne and Whaley, *loc. cit.*).

The third product was also free from iodine and was identified as 3 : 3-dichloro-1 : 1 : 1-trifluoropropane (2·0 g., 12%) (Found : Cl, 41·9%; *M*, 165. Calc. for $C_3H_3Cl_2F_3$: Cl, 42·5%; *M*, 167), b. p. 72—74°, n_D^{25} 1·360. Henne and Whaley (*loc. cit.*) report b. p. 72·4°, n_D^{20} 1·3631. A final product was 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane (2·2 g., 11%) (Found : *M*, 198. Calc. for $C_3H_2Cl_3F_3$: *M*, 201·5), b. p. 93·5—96·5°, n_D^{25} 1·390. Henne and Whaley (*loc. cit.*) report b. p. 95·1°, n_D^{20} 1·3900 for this compound, whose isomer 2 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane has b. p. 106·8°.

The material between the fractions detailed above amounted to 8% of the product and, although it failed to give any definite product, may have contained small amounts of isomers of some of the above compounds.

When 3-chloro-1 : 1 : 1-trifluoro-3-iodopropane (2·6 g.) was treated with chlorine in a sealed silica tube exposed to ultra-violet radiation, 3 : 3-dichloro-1 : 1 : 1-trifluoropropane (0·9 g., 52%) and 3 : 3-*dichloro*-1 : 1 : 1-*trifluoro*-3-*iodopropane* (0·5 g., 17%) (Found : C, 12·1; H, 0·9. $C_3H_2Cl_2IF_3$ requires C, 12·3; H, 0·7%), b. p. 142—143°, were formed. When this last compound (1·5 g.) was irradiated in a Pyrex tube with chlorine, the only product was 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane, b. p. 94—96°, n_D^{22} 1·389.

Bromination of 1 : 1 : 1-*Trifluoro*-3-*iodopropane*.—Thermal bromination was effected by passing the vapour of 1 : 1 : 1-trifluoro-3-iodopropane (11·2 g.) and a slight excess of bromine through a silica tube of 1-cm. internal diameter and 100-cm. length, heated to 380° over a length of 40 cm. The products were condensed in a trap cooled by liquid air, washed with water to remove bromine, hydrogen bromide, and iodine bromide, dried over phosphoric oxide, and distilled in the presence of a globule of mercury, to yield the following products. (*a*) 3-*Bromo*-1 : 1 : 1-*trifluoro*-3-*iodopropane* (2·1 g., 14%) (Found : C, 12·4; Br, 26·2; I, 41·7. $C_3H_3BrIF_3$ requires C, 11·9; Br, 26·4; I, 41·9%), b. p. 139—140°, n_D^{20} 1·487. (*b*) 3-Bromo-1 : 1 : 1-trifluoropropane (1·2 g., 13%) (Found : Br, 44·9%; *M*, 175. Calc. for $C_3H_4BrF_3$: Br, 45·2%; *M*, 177), b. p. 63°, n_D^{25} 1·358. McBee, Hass, Toland, and Truchan (*loc. cit.*) report b. p. 62—62·5°, n_D^{25} 1·3572. The compound contained no iodine and did not show unsaturation to bromine. (*c*) 3 : 3-Dibromo-1 : 1 : 1-trifluoropropane (3·3 g., 26%) (Found : C, 14·2; H, 0·9%; *M*, 250. Calc. for $C_3H_3Br_2F_3$: C, 14·1; H, 1·1%; *M*, 256), b. p. 110—112°, n_D^{25} 1·426. McBee, Hass, *et al.* (*loc. cit.*) report b. p. 111°, n_D^{26} 1·4242. The fraction was free from iodine and was not unsaturated. (*d*) Intermediate fractions, material formed by decomposition (subsequent experiments revealed the presence of bromotrifluoromethane), and higher-boiling compounds, which were not investigated closely.

Photochemical bromination of 3-bromo-1 : 1 : 1-trifluoro-3-iodopropane (1·50 g.) in a Pyrex tube at room temperature gave 3 : 3-dibromo-1 : 1 : 1-trifluoropropane (0·85 g., 68%) (*M*, 252), b. p. 110—112°.

Samples of 3 : 3-dibromo-1 : 1 : 1-trifluoropropane did not give 3 : 3 : 3-trifluoropropene when refluxed with zinc and absolute alcohol for 5 hours.

Preparation of 1 : 1 : 1-*Trifluoropropane*.—Two methods were used : (*a*) 1 : 1 : 1-Trifluoro-3-iodopropane (22·5 g.) was heated to 280—300° for 24 hours in an autoclave with excess of a saturated hydrocarbon of comparable volatility (*e.g.*, hexane, 50 ml.) and mercury (10 ml.). The 1 : 1 : 1-trifluoropropane (5·0 g., 52%), b. p. −13°, was readily separated from unchanged fluoroiodopropane by distillation. Traces of 3 : 3 : 3-trifluoropropene (2—5%) were removed by mixing the material with chlorine in a tube in the dark for 1 hour, followed by washing of the volatile material with alkali and refractionation. (*b*) 1 : 1 : 1-Trifluoro-3-iodopropane (22·5 g.) was converted into the Grignard reagent which, on hydrolysis, gave 1 : 1 : 1-trifluoropropane in 75% yield.

Chlorination and Bromination of 1 : 1 : 1-*Trifluoropropane*.—*Photochemical chlorination.* Water (5 ml.) was added to a silica flask (500 ml.) which was then filled with 1 : 2 molar amounts of the fluoropropane and chlorine to a pressure of 700 mm. The Hanovia lamp was used 2 feet from the flask which was cooled by water. As chlorination proceeded, further portions of 1 : 1 : 1-trifluoropropane and chlorine were added to keep the pressure near 1 atmosphere, and to prevent the chlorine being present in large excess. The liquid which condensed on the walls of the flask was periodically collected in the ice-cooled and shielded base of the flask by warming of the walls. When a total of 33 g. of the fluoropropane had been treated in this way, chlorination was continued in the liquid phase, using the apparatus described earlier, until the amount of chlorine added and the weight of crude product (54 g.) corresponded to the formation of a dichloro-derivative. Distillation then gave (*a*) 3-chloro-1 : 1 : 1-trifluoropropane (8·2 g., 18%) (*M*, 132), b. p. 44—46°, (*b*) 3 : 3-dichloro-1 : 1 : 1-trifluoropropane (31·6 g., 57%) (*M*, 166), b. p. 72—74°, n_D^{25} 1·359, (*c*) 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane (6·8 g., 10%) (Found : Cl, 52·1%; *M*, 200. Calc. for $C_3H_2Cl_3F_3$: Cl, 52·85%; *M*, 201·5), b. p. 95—95·5°, n_D^{25} 1·388, and (*d*) intermediate fractions and residue (4·2 g.). The composition of the product, monochloro : dichloro : trichloro : intermediate fractions is thus 16 : 62 : 14 : 8 by weight. Under the conditions used, the formation of compounds other than the three indicated above seems doubtful.

Chlorination in the vapour phase was also effected in the absence of water in a 1-l. Pyrex flask at 80—100°. The flask, which had a reflux condenser and a cold finger cooled in ice and shielded from the light, was filled with the fluorohydrocarbon and chlorine (molar ratio 1 : 1) and recharged as necessary to keep the pressure near atmospheric. The chlorinated product from a reaction of this type contained a higher percentage of 2-chloro-1 : 1 : 1-trifluoropropane than formerly. This compound, b. p. 29—31°, was separated by distillation (Found : Cl, 26·0%; *M*, 131. Calc. for $C_3H_4ClF_3$: Cl, 26·8%; *M*, 132·5). The yields of 3-chloro-, 2-chloro-, 3 : 3-dichloro-, and 3 : 3 : 3-trichloro-compounds from 20 g. of reacted trifluoropropane were in the ratios 55 : 18 : 17 : 2 by weight.

The first method of photochemical chlorination was used for most of the work described in this paper.

Thermal chlorination. On passage of equimolar amounts of 1 : 1 : 1-trifluoropropane and chlorine through 6 feet of Pyrex tubing (10-mm. internal diameter), heated to 420°, so as to give a contact time of *ca.* 3 seconds, it was found that 40% of the fluorohydrocarbon (20 g.) underwent reaction to give 3-chloro-, 2-chloro-, 3 : 3-dichloro-, and 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane in yields of 36, 3, 18, and 8% by weight respectively. The 2-chloro-compound (*M*, 131·5) had b. p. 29·5—30·5°, n_D^{25} 1·313, and could be dehydrochlorinated to trifluoropropene as described below.

Thermal bromination. 1 : 1 : 1-Trifluoropropane was treated by the method described earlier. The fluoropropane (33 g.) was passed with excess of bromine through the silica tube heated to 380° and, after preliminary fractionation, unchanged fluorohydrocarbon (10 g.) was recycled. The contact time was very approximately 5 seconds. The combined products were washed with water, dried, and distilled, to yield (*a*) 3-bromo-1 : 1 : 1-trifluoropropane (12·1 g., 20%) (*M*, 176), b. p. 62·5—63·0°, n_D^{25} 1·358, (*b*) 3 : 3-dibromo-1 : 1 : 1-trifluoropropane (26·1 g., 31%) (Found : Br, 61·9%; *M*, 252. Calc. for $C_3H_3Br_2F_3$: Br, 62·5%; *M*, 256), b. p. 110—112°, n_D^{25} 1·425, and (*c*) 2-bromo-1 : 1 : 1-trifluoropropane (2·6 g., 4%) (Found : C, 20·6; H, 2·5; Br, 44·6%; *M*, 177. Calc. for $C_3H_4BrF_3$: C, 20·3; H, 2·3; Br, 45·2%; *M*, 177), b. p. 48—50·5°, n_D^{25} 1·350 [Swarts (*Bull. Soc. chim. Belg.*, 1929, **48**, 106) reports b. p. 49° for this compound]. The amount of (*c*) in the product was much less than observed by McBee *et al.*, *loc. cit.*, however: $CF_3{\cdot}CH_2{\cdot}CH_2Br : CF_3{\cdot}CHBr{\cdot}CH_3 : CF_3{\cdot}CH_2{\cdot}CHBr_2$ = 30 : 6 : 64 and 43 : 25 : 32 by weight respectively.

Chlorination and Bromination of 3-*Chloro- and* 3-*Bromo*-1 : 1 : 1-*trifluoropropane*.—The monochloro- and -bromo-compounds were obtained by chlorination and bromination of 1 : 1 : 1-trifluoro-3-iodopropane and of trifluoropropane as described above, and from trifluoropropylmagnesium iodide (unpublished results). The samples prepared by these routes were identical.

Chlorination of 3-chloro-1 : 1 : 1-trifluoropropane (16·7 g.) was carried out in the liquid phase at 20° in the apparatus described above. Chlorine was added until the weight of crude product corresponded approximately to the formation of the dichloro-derivative, and at such a rate that the liquid remained almost colourless throughout. After washing and drying, distillation gave unchanged monochloro-compound (3·5 g.), 3 : 3-dichloro- (12·3 g., 73%), and 3 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane (2·5 g., 12%), identified as above. The still residue (1·9 g.) contained a liquid of b. p. higher than that of the trichloro-derivatives and which may have been 2 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane (b. p. 107°) but was not definitely identified.

Thermal bromination of 3-chloro-1 : 1 : 1-trifluoropropane (6·6 g.) at 400° with a contact time of *ca.* 5 seconds in the apparatus described above gave 3-*bromo*-3-*chloro*-1 : 1 : 1-*trifluoropropane* (4·3 g., 41%) (Found : C, 16·8; H, 1·4; Br, 37·0; Cl, 17·0%; *M*, 209. $C_3H_3BrClF_3$ requires C, 17·0; H, 1·4; Br, 37·8; Cl, 16·8%; *M*, 211·5), b. p. 91—92°, n_D^{25} 1·395. An unidentified dibromochloro-compound ($CF_3{\cdot}CHBr{\cdot}CHClBr$ or $CF_3{\cdot}CH_2{\cdot}CClBr_2$) was also formed in small amount.

When 3-bromo-3-chloro-1 : 1 : 1-trifluoropropane was added to zinc in refluxing absolute alcohol, trifluoropropene was not formed after 6 hours' heating, whereas the compound could be converted into trifluoromethylacetylene by treatment with potassium hydroxide (see below).

Photochemical chlorination of 3-bromo-1 : 1 : 1-trifluoropropane in the silica apparatus described above also yielded 3-bromo-3-chloro-1 : 1 : 1-trifluoropropane (3·6 g., 51%), b. p. 90·5—91·5°, whose structure was proved as above. A further product isolated was 3-*bromo*-3 : 3-*dichloro*-1 : 1 : 1-*trifluoropropane* (1·2 g., 14%) (Found : C, 14·4; H, 0·9; Br, 31·8; Cl, 28·8. $C_3H_2BrCl_2F_3$ requires C, 14·6; H, 0·8; Br, 32·5; Cl, 28·9%), b. p. 115—117°. The structure of this compound (1·8 g.) was shown by its dehydrobromination with powdered potassium hydroxide to the known 1 : 1-dichloro-3 : 3 : 3-trifluoropropene (1·0 g., 83%) (*M*, 164), b. p. 53·5—56·0°, n_D^{25} 1·367 (Henne and Whaley, *loc. cit.*, report b. p. 55·1°, n_D^{20} 1·3690), which did not react with zinc and alcohol to give trifluoropropyne. Isomers of $CF_3{\cdot}CH_2{\cdot}CCl_2Br$ (*e.g.*, $CF_3{\cdot}CHCl{\cdot}CHBrCl$) must therefore have been present in only small amounts in the original material.

Thermal bromination of 3-bromo-1 : 1 : 1-trifluoropropane (5·9 g.) at 400° with a contact time of 2—5 seconds gave 3 : 3-dibromo-1 : 1 : 1-trifluoropropane (3·2 g., 37%), b. p. 110·5—111·5°, which did not give trifluoropropene with zinc and ethyl alcohol. A fraction of higher b. p. (112—118°) (0·8 g.) may have contained 2 : 3-dibromo-1 : 1 : 1-trifluoropropane.

Dehydrohalogenation Reactions.—The dehydro-chlorination or -bromination of the compounds described below was effected by adding the compound to a large excess of finely ground, carefully dried, potassium hydroxide which three-quarters filled a 50-, 100-, 250-, or 500-ml. flask (depending on the amount of material). The flask was fitted with a reflux water-condenser and a Dewar condenser which was cooled to −20° for the preparation of 3 : 3 : 3-trifluoropropene or to −45° for the preparation of 3 : 3 : 3-trifluoropropyne, and was connected to a trap cooled by liquid air for the collection of volatile products. The lower one-third of the flask was placed in an oil-bath and the temperature was slowly raised from room temperature to reflux temperature so that the refluxing liquid percolated through potassium hydroxide of gradually increasing temperature before being vaporised. The reactions were carried out at the lowest possible temperature to prevent attack on the trifluoromethyl group.

3-*Halogeno*-1 : 1 : 1-*trifluoropropanes.* These readily underwent dehydrohalogenation when the temperature was slowly raised to that necessary for reflux. The iodo-, bromo-, and chloro-compounds gave 3 : 3 : 3-trifluoropropene, b. p. −22°, in 70, 65, and 62% yields respectively on a 20-g. scale.

2-*Halogeno*-1 : 1 : 1-*trifluoropropanes.* When heated with powdered potassium hydroxide in a sealed tube at 120—150° for 12 hours, 2-bromo-1 : 1 : 1-trifluoropropane (2·0 g.) gave trifluoropropene (0·4 g., 36%). Similarly, 2-chloro-1 : 1 : 1-trifluoropropane (2·0 g.) gave trifluoropropene (9%) and unchanged chloro-compound (21%) after 24 hours.

The 3 : 3 : 3-trifluoropropene formed in the above reactions was identified by its b. p., molecular weight (96), and infra-red absorption spectrum.

3 : 3-*Dihalogeno*-1 : 1 : 1-*trifluoropropanes*. The first molecule of hydrogen halide was readily removed from the dibromo-compound (13 g.) and subsequent formation of trifluoromethylacetylene was carried out during 8 hours. The contents of the liquid-air trap were then found to contain trifluoromethylacetylene (2·9 g., 62%) and a small amount of 1-*bromo*-3 : 3 : 3-*trifluoropropene* (1·1 g., 12%) (Found : C, 20·6; H, 1·4; Br, 45·0%; *M*, 175. $C_3H_2BrF_3$ requires C, 20·6; H, 1·1; Br, 45·7%; *M*, 175), b. p. 41°.

After 12 hours' refluxing, 3 : 3-dichloro-1 : 1 : 1-trifluoropropane (16·6 g.) similarly yielded trifluoromethylacetylene (4·2 g., 45%) and 1-*chloro*-3 : 3 : 3-*trifluoropropene* (2·1 g., 16%) (Found : Cl, 27·5%; *M*, 129. $C_3H_2ClF_3$ requires Cl, 27·2%; *M*, 130·5), b. p. 21°. Henne and Whaley (*loc. cit.*) state that this dehydrohalogenation can be achieved by alcoholic potassium hydroxide, but give no analytical or physical data for the chlorofluoropropane.

When 3-bromo-3-chloro-1 : 1 : 1-trifluoropropane (2·10 g.) was refluxed over potassium hydroxide for 4 hours, trifluoromethylacetylene (0·52 g., 55%) and 1-chloro-3 : 3 : 3-trifluoropropene (0·1 g., 8%) (*M*, 130) were formed.

3-Chloro-1 : 1 : 1-trifluoro-3-iodopropane similarly yielded the acetylene (0·49 g., 52%) and 1-chloro-3 : 3 : 3-trifluoropropene (0·13 g., 10%) (*M*, 131) after 6 hours. Under the same conditions, 3-bromo-1 : 1 : 1-trifluoro-3-iodopropane (3·00 g.) gave 1-bromo-3 : 3 : 3-trifluoropropene (0·2 g., 11%) (*M*, 173) and trifluoromethylacetylene (0·62 g., 66%).

1-*Chloro and* 1-*bromo*-3 : 3 : 3-*trifluoropropene*. 1-Chlorotrifluoropropene (2·0 g.) gave the acetylene (1·0 g., 70%) after 5 hours, while the bromo-compound (1·3 g.) gave a 72% yield in the same period.

Synthesis of Trifluoromethylacetylene from Trifluoropropene via *Chloro-compounds*.—3 : 3 : 3-Trifluoropropene (14·0 g.) was treated with a slight excess of chlorine in a series of sealed tubes, giving 2 : 3-dichloro-1 : 1 : 1-trifluoropropane (20·1 g., 80%) (Found : C, 22·1; H, 1·7%; *M*, 165. Calc. for $C_3H_3Cl_2F_3$: C, 21·6; H, 1·8%; *M*, 167), b. p. 76·5°, n_D^{25} 1·365. Henne and Whaley report b. p. 76·7°, n_D^{20} 1·3671. In subsequent experiments the olefin and chlorine were mixed in a bulb exposed to daylight; a smooth reaction occurred to give the dichloro-compound in 85% yield.

Treatment of the 2 : 3-dichloro-compound (4·1 g.) with potassium hydroxide for 12 hours gave trifluoromethylacetylene (0·3 g., 12%) and 2-*chloro*-3 : 3 : 3-*trifluoropropene* (1·65 g., 50%) (Found : Cl, 26·9%; *M*, 130. $C_3H_2ClF_3$ requires Cl, 27·2%; *M*, 130·5), b. p. 14—15°. When this compound (2·1 g.) was heated at 130° for 6 hours with powdered potassium hydroxide in a sealed tube, trifluoromethylacetylene was formed in 8% yield. A further experiment in which the chlorofluoropropene was refluxed vigorously at 100-cm. pressure over potassium hydroxide gave the acetylene in 6% yield after 12 hours, with 55% of the chloro-compound (1·1 g.) recovered unchanged.

Treatment of 2-chloro-3 : 3 : 3-trifluoropropene (3·9 g.) with an equivalent amount of chlorine in a sealed tube gave 2 : 2 : 3-*trichloro*-1 : 1 : 1-*trifluoropropane* (5·4 g., 90%) (Found : Cl, 53·1%; *M*, 200. $C_3H_2Cl_3F_3$ requires Cl, 52·9%; *M*, 201·5), b. p. 104—105°, n_D^{25} 1·392. The trichlorofluoropropane (4·8 g.) was refluxed over powdered potassium hydroxide in a flask fitted with a reflux condenser heated to 60° and connected to a trap cooled in liquid air. After 6 hours no further reflux could be observed and the trap was found to contain unchanged trichloro-compound (1·8 g.) and 2 : 3-dichloro-1 : 1 : 1-trifluoropropene (1·2 g., 48%) (Found : C, 21·2; H, 0·8%; *M*, 164. Calc. for $C_3HCl_2F_3$: C, 21·8; H, 0·6%; *M*, 165), b. p. 53—54°, n_D^{25} 1·365. Henne and Whaley (*loc. cit.*) report b. p. 53·7°, n_D^{20} 1·3670.

1 : 2-Dichloro-3 : 3 : 3-trifluoropropene (3·2 g.) was dehalogenated by zinc dust (20 g.) and absolute ethanol (200 ml.) at reflux temperature in a flask fitted with efficient condensers at 15° and —45° and connected to a trap cooled by liquid air. Trifluoromethylacetylene was formed in 15% yield after 40 hours. 40% of the dichloro-compound was recovered unchanged and was re-treated, to give a 25% yield of the acetylene after 120 hours.

1 : 2-Dichloro-3 : 3 : 3-trifluoropropene was also obtained by the addition of chlorine to 1-chloro-3 : 3 : 3-trifluoropropene (2·5 g.), to give 2 : 3 : 3-trichloro-1 : 1 : 1-trifluoropropane (3·4 g., 85%) (Found : *M*, 202. Calc. for $C_3H_2Cl_3F_3$: *M*, 201·5), b. p. 107—107·5°, n_D^{25} 1·398 (Henne and Whaley, *loc. cit.*, report b. p. 106·8°. This compound (3·0 g.) was dehydrochlorinated to the dichlorofluoropropene (2·0 g., 80%). Dehalogenation to the acetylene (18% yield) was effected as described earlier.

Synthesis of Trifluoromethylacetylene from Trifluoropropene via *Bromo-compounds*.—3 : 3 : 3-Trifluoropropene (9·5 g.) was treated with a slight excess of bromine in a series of sealed tubes to give 2 : 3-dibromo-1 : 1 : 1-trifluoropropane (22·1 g., 86%) (Found : C, 14·2%; *M*, 250. Calc. for $C_3H_3Br_2F_3$: C, 14·1%; *M*, 256), b. p. 116°, n_D^{25} 1·427. McBee *et al.* (*loc. cit.*) report b. p. 115·8°, n_D^{10} 1·4281.

The dibromotrifluoropropane (2·6 g.) was readily dehydrobrominated by addition to powdered potassium hydroxide at room temperature and slow increase of the temperature to the reflux point. The reflux condenser was heated to 40°. After 2 hours the volatile products were 2-*bromo*-3 : 3 : 3-*trifluoropropene* (1·1 g., 63%) (Found : C, 20·8; Br, 44·8%; *M*, 175. $C_3H_2BrF_3$ requires C, 20·6; Br, 45·7%; *M*, 175), b. p. 33·5°, n_D^{25} 1·349, and trifluoromethylacetylene (0·04 g., 4%). Further experiments of this type gave yields of 60—65% of the monobromo-compound and 2—8% yields of the acetylene.

The condenser was replaced by two in series at 15° and —40°, respectively. The dibromo-compound (5·2 g.) was slowly heated to reflux with potassium hydroxide, and after 5 hours the volatile products contained 2-bromo-3 : 3 : 3-trifluoropropene (1·6 g., 46%) and the acetylene (0·25 g., 12%).

When 2-bromo-3 : 3 : 3-trifluoropropene (1·7 g.) was vigorously refluxed over potassium hydroxide for 5 hours, a 31% yield of the acetylene was obtained.

Treatment of the 2-bromofluoropropene (5·1 g.) with a slight excess of bromine at 50° in a sealed tube gave 2 : 2 : 3-*tribromo*-1 : 1 : 1-*trifluoropropane* (9·6 g., 98%) (Found: Br, 71·4. $C_3H_2Br_3F_3$ requires Br, 71·6%), b. p. 61°/20 mm., *ca.* 162°/760 mm., n_D^{25} 1·480, as a pale yellow liquid which decomposed appreciably when distilled at atmospheric pressure and slightly when kept at room temperature but could be stored indefinitely at 0°.

The tribromotrifluoropropane (6·7 g.) was dehydrobrominated by addition to powdered potassium hydroxide which had been cooled to −40°. The flask was warmed slowly to a maximum temperature of 140° and a stream of nitrogen passed through it to carry the olefin formed through a condenser kept at 100° and into a trap cooled by liquid air. In this way was obtained 1 : 2-*dibromo*-3 : 3 : 3-*trifluoropropene* (3·2 g., 63%) (Found: C, 14·1; Br, 62·5%; *M*, 253. $C_3HBr_2F_3$ requires C, 14·2; Br, 63·0%; *M*, 254), b. p. 96·5—97·0°, n_D^{25} 1·430. The absence of 1-bromo-3 : 3 : 3-trifluoropropyne, which might result by removal of 2 mols. of hydrogen bromide, was shown by infra-red spectroscopy.

The 1 : 2-dibromo-3 : 3 : 3-trifluoropropene was also prepared from 1-bromo-3 : 3 : 3-trifluoropropene. Addition of bromine to the monobromo-compound (1·75 g.) in a sealed tube gave 2 : 3 : 3-*tribromo*-1 : 1 : 1-*trifluoropropane* (3·2 g., 95%) (Found: Br, 71·0. $C_3H_2Br_3F_3$ requires Br, 71·6%), b. p. 167—168°, 70°/30 mm., n_D^{25} 1·483. Dehydrobromination of this (2·8 g.) was effected as described for its isomer and gave the same olefin, 1 : 2-dibromo-3 : 3 : 3-trifluoropropene (1·6 g., 75%) (*M*, 250), b. p. 95—97°, n_D^{25} 1·431, free from acetylenic compounds.

The 1 : 2-dibromopropene (12·7 g.) was debrominated with zinc dust (20 g.) and absolute ethanol (200 ml.) under a reflux condenser kept at −40°. The reaction was complete after 6 hours. The yield of trifluoromethylacetylene was 4·5 g. (96%)

Purity of Trifluoromethylacetylene.—Samples of the acetylene prepared by the routes described above were tested for purity by boiling-point and molecular-weight determinations, formation of copper and silver derivatives, and examination of the residual gaseous material, and by the infra-red spectrum.

Infra-red Spectrum.—This was measured on a Perkin–Elmer Model 21 Double-beam instrument with a rock-salt prism. Gas pressures in a 5-cm. gas cell with rock-salt windows were measured to 0·5 mm.

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