125. *The Reactions of Fluorocarbon Radicals. Part IV. The Synthesis of 3 : 3 : 3-Trifluoropropyne.*

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Interaction of trifluoroiodomethane and acetylene gives mainly 3 : 3 : 3-trifluoro-1-iodopropene, dehydroiodination of which yields 3 : 3 : 3-trifluoropropyne, the first of a new class of compound with perfluoroalkyl groups adjacent to an acetylenic residue. The hydrogen atom is acidic, and copper, silver, and mercuric trifluoromethylacetylides have been prepared. The last compound is a stable low-melting solid. Oxidation of the fluoroalkyne affords trifluoroacetic acid, and hydrogenation and chlorination give 1 : 1 : 1-trifluoropropane and 1 : 1 : 2 : 2-tetrachloro-3 : 3 : 3-trifluoropropane respectively.

In order to study the effect of strongly electronegative fluorocarbon groups on organic functional groups, compounds of the type RX are required where R is the fluorocarbon group linked directly to X, a potentially reactive group such as $\cdot CO_2H$, $\cdot OH$, $\vdots CO$, $\cdot CHO$, $\cdot NH_2$, $\cdot C{\equiv}CH$, and $\cdot MgX$. The syntheses of fluoroalkyl iodides, RI, have enabled methods to be developed for the preparation of compounds of the type $R{\cdot}CO_2H$, $R{\cdot}MgX$ (Haszeldine, *J.*, 1950, 2789; *Nature*, in the press), $R{\cdot}OH$, and $R{\cdot}NH_2$. The present communication is concerned with the synthesis of a compound of the type $R{\cdot}C{\equiv}CH$, where $R = CF_3$.

In Part II (*J.*, 1950, 3037) it was shown that trifluoroiodomethane and acetylene underwent an addition-polymerisation to give the compounds $CF_3{\cdot}[CH{:}CH]_n{\cdot}I$ ($n = 1$ and 2). Trifluoropropyne (trifluoromethylacetylene) has now been synthesised from 3 : 3 : 3-trifluoro-1-iodopropene by dehydroiodination :

$$CF_3{\cdot}CH{:}CHI \xrightarrow{-HI} CF_3{\cdot}C{\vdots}CH$$

this was most conveniently effected by powdered potassium hydroxide, sodamide and alcoholic potassium hydroxide being less satisfactory. The fluoroalkyne (first described in *Nature*, 1950, **165**, 152) is a colourless gas, b.p. —48°, and the effect of structure on the boiling points of 1 : 1 : 1-trifluoropropane derivatives is illustrated in the following table.

Compound.	B. p.	Compound.	B. p.
$CF_3{\cdot}CH_2{\cdot}CH_3$	—13°	$CH_3{\cdot}CH_2{\cdot}CH_3$	—42°
$CF_3{\cdot}CH{:}CH_2$ *	—22	$CH_3{\cdot}CH{:}CH_2$	—48
$CF_3{\cdot}C{\vdots}CH$	—48	$CH_3{\cdot}C{\vdots}CH$	—23

* Haszeldine, *J.*, 1950, 3037. Henne and Waalkes, *J. Amer. Chem. Soc.*, 1946, **68**, 496, report b. p. —17° to —19° and Robbins, *J. Pharmacol.*, 1946, **86**, 197, reports b. p. —24°.

The difference in boiling point of trifluoropropane and trifluoropropene is 9°, a value comparable with that for propane and propylene (6°). On passing from trifluoropropane to trifluoropropyne, however, a *decrease* in boiling point of 35° is found as compared with an increase of 20° for propane to propyne. In the butane series, Henne and Finnegan (*J. Amer. Chem. Soc.*, 1949, **71**, 298) have attributed the decrease in boiling point of 50° on passing from $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}CF_3$ (b. p. 25°) *via* $CF_3{\cdot}CH{:}CH{\cdot}CF_3$ (b. p. 33°) to $CF_3{\cdot}C{\vdots}CCF_3$ (b. p. —25°) to the absence of hydrogen bonding.

That the compound obtained by dehydroiodination of 3 : 3 : 3-trifluoro-1-iodopropene was actually trifluoromethylacetylene was proved by the following reactions. Oxidation with alkaline permanganate gave trifluoroacetic acid, hydrogenation gave the known compound $CF_3{\cdot}CH_2{\cdot}CH_3$, and addition of chlorine gave the hitherto unknown compound 1 : 1 : 2 : 2-tetrachloro-3 : 3 : 3-trifluoropropane, with physical properties similar to its known $C_3HF_3Cl_4$ isomers as shown in the second table. The close similarity in the physical properties of other highly halogenated propanes is also revealed in this table. It will be noted that the freezing or melting point is the property most sensitive to structural isomerism, and that compounds containing hydrogen are liquids which tend to give glasses on cooling. The parallelism between melting point and the asymmetrical distribution of fluorine and chlorine in chlorofluoro-compounds has been noted by Henne, Renoll, and Leicester (*J. Amer. Chem. Soc.*, 1939, **61**, 938).

Compound.	B. p.	n_D.	F. p.	Compound.	B. p.	n_D.	F. p.
$C_3HF_3Cl_4$.							
$CFCl_2{\cdot}CF_2{\cdot}CHCl_2$...	127°	$1{\cdot}4189^{25}$	—[1]	$CF_3{\cdot}CHCl{\cdot}CCl_3$ ...	125·1°	$1{\cdot}4180^{24}$	—[4]
$CF_2Cl{\cdot}CHCl{\cdot}CFCl_2$	128·7	$1{\cdot}4157^{25}$	Glass[2]	$CF_3{\cdot}CCl_2{\cdot}CHCl_2$ ...	126—126·5	$1{\cdot}4195^{25}$	—[5]
$CF_2Cl{\cdot}CFCl{\cdot}CHCl_2$	129·8	$1{\cdot}4197^{20}$	Glass[3]				
$C_3F_3Cl_5$.							
$CFCl_2{\cdot}CF_2{\cdot}CCl_3$ ...	154·5	$1{\cdot}4394^{20}$	$<-80°$[3]	$CFCl_2{\cdot}CFCl{\cdot}CFCl_2$	154·7	$1{\cdot}4387^{20}$	Glass[7]
	152—154	$1{\cdot}4389^{20}$	—[6]	$CF_2Cl{\cdot}CFCl{\cdot}CCl_3$...	153·3	$1{\cdot}4392^{20}$	−14·8[2]
	155·5—157	$1{\cdot}4399^{25}$	55—56[1]	$CF_2Cl{\cdot}CCl_2{\cdot}CFCl_2$	152·3	$1{\cdot}4396^{20}$	− 4·9[2]
				$CF_3{\cdot}CCl_2{\cdot}CCl_3$	153·1	—	109[8, 5]
$C_3F_4Cl_4$.							
$CCl_3{\cdot}CF_2{\cdot}CF_2Cl$ ...	112·0—112·5	$1{\cdot}3961^{20}$	—[9]	$CF_2Cl{\cdot}CFCl{\cdot}CFCl_2$	112·5	$1{\cdot}3960^{20}$	−58[10]
				$CF_2Cl{\cdot}CCl_2{\cdot}CF_2Cl$	112·0	$1{\cdot}3958^{20}$	−42·9[2]
	114·5	$1{\cdot}3974^{25}$	—[1]	$CF_3{\cdot}CFCl{\cdot}CCl_3$ ...	112·5	$1{\cdot}4002^{20}$	12·1[10]
$CFCl_2{\cdot}CF_2{\cdot}CFCl_2$...	112·5—115	$1{\cdot}3980^{25}$	—[1]	$CF_3{\cdot}CCl_2{\cdot}CFCl_2$ ...	112·4	—	41·7[8]

[1] Coffman, Cramer, and Rigby, *J. Amer. Chem. Soc.*, 1949, **71**, 979. [2] Henne and Renoll, *ibid.*, 1939, **61**, 2489. [3] Henne and Ladd, *ibid.*, 1938, **60**, 2491. [4] McBee, Truchan, and Bolt, *ibid.*, 1948, **70**, 2023. [5] This paper. [6] Henne and Renoll, *J. Amer. Chem. Soc.*, 1937, **59**, 2434. [7] Henne and Newby, *ibid.*, 1948, **70**, 130. [8] Henne and Whaley, *ibid.*, 1942, **64**, 1157. [9] McBee, Henne, Hass, and Elmore, *ibid.*, 1940, **62**, 3340. [10] Henne and Haeckl, *ibid.*, 1941, **63**, 3476.

A hydrogen atom on a carbon atom adjacent to a perfluoroalkyl group is resistant to halogenation, and the chlorination of $CF_3{\cdot}CHCl{\cdot}CCl_3$ or $CF_3{\cdot}CH_2{\cdot}CCl_3$, for example, is achieved only with difficulty, even on irradiation with ultra-violet light. The compound obtained by addition of two molecules of chlorine to trifluoromethylacetylene contains a hydrogen atom on a carbon atom once removed from the trifluoromethyl group, and further chlorination was readily achieved in ultra-violet light of moderate intensity. The product, $CF_3{\cdot}CCl_2{\cdot}CCl_3$, was identical with that obtained on prolonged chlorination of the hydrogenated acetylene, and also with the compound prepared by complete chlorination of a known specimen of 1 : 1 : 1-trifluoropropane, obtained by interaction of trifluoroiodomethane and ethylene (Haszeldine, *J.*, 1949, 2856). Henne and Whaley have also prepared $CF_3{\cdot}CCl_2{\cdot}CCl_3$ (see table) and report the same physical properties. The reactions described above establish the carbon skeleton and presence of a triple bond and a trifluoromethyl group.

The hydrogen atom of trifluoromethylacetylene is, as expected, markedly acidic, and can be replaced by metals to yield fluoroacetylides. Treatment with ammoniacal cuprous chloride or silver nitrate affords copper or silver trifluoromethylacetylide, both derivatives being soluble in organic solvents. Mercuric trifluoromethylacetylide is obtained as a low-melting crystalline solid when trifluoromethylacetylene is treated with alkaline potassium mercuri-iodide. The fluoroacetylides are reconverted into the fluoroalkyne when treated with acids, thus showing that they are true acetylides and not addition products. This is of particular importance for the mercury compound, since it is conceivable that addition of mercury salts across the triple bond could also occur.

It is noteworthy that the acetylides formed from trifluoromethylacetylene, unlike those formed from acetylene, are not of complex composition and do not retain water or groups or anions which were linked to the metal in the original salt. Trifluoromethylacetylene yields much more complex products of variable composition when treated with neutral or acid solutions of copper, silver, or mercury salts. These products are insoluble in water and many organic solvents, and do not yield trifluoromethylacetylene quantitatively with acid.

When mercuric trifluoromethylacetylide is treated with iodine, a compound believed to be 3 : 3 : 3-trifluoro-1-iodopropyne, with a characteristic odour like that of di-iodoacetylene, is produced.

The homologues of trifluoromethylacetylene, $C_2F_5{\cdot}C{:}CH$ and $C_3F_7{\cdot}C{:}CH$, have recently been synthesised (Haszeldine and Leedham, unpublished). The influence of the perfluoroalkyl group on the reactivity of the triple bond in ionic and free-radical addition reactions and on reactions involving the acetylenic hydrogen atom is expected to be marked, and is being investigated.

EXPERIMENTAL.

Preparation of 3 : 3 : 3-*Trifluoro*-1-*iodopropene*.—This compound was prepared by interaction of trifluoroiodomethane and acetylene at 200—220°, and constituted 70—80% of the product. Further examination of the higher-boiling material has revealed the presence of small amounts of *trans*- and possibly *cis*-di-iodoethylene in addition to the compounds previously isolated. The *trans*-isomer (Found :

C, 8·6; H, 0·8; I, 89·7. Calc. for $C_2H_2I_2$: C, 8·6; H, 0·7; I, 90·7%) was recrystallised from aqueous ethanol, giving needles, m.p. 72—73°; Keiser (*Amer. Chem. J.*, 1899, **21**, 265) gives m. p. 73°.

Dehydroiodination of 3 : 3 : 3-*Trifluoro*-1-*iodopropene.*—The fluoroiodopropene (24 g.) was added to a large excess of dried, powdered potassium hydroxide (150 g.) in a 100-ml. flask fitted with a reflux condenser connected *via* rubber tubing to a trap cooled by liquid air. The temperature was gradually raised from 120° to 150° (bath-temp.) during 6 hours, at the end of which most of the olefin had disappeared. The flask was disconnected and heated *in vacuo* for recovery of unchanged 3 : 3 : 3-trifluoro-1-iodopropene (2 g.).

The material which had passed through the reflux condenser during the dehydroiodination was transferred to a vacuum system where it was fractionated. A small amount (0·1 g.) of entrained 3 : 3 : 3-trifluoro-1-iodopropene was thereby removed from the 3 : 3 : 3-*trifluoropropyne* (6·6 g., 70%) (Found : C, 39·4; H, 1·2; F, 60·1%; *M*, 94. C_3HF_3 requires C, 38·3; H, 1·1; F, 60·6%; *M*, 94), b. p. −48° to −46°. The analysis of the fluoroalkyne for carbon and hydrogen was somewhat difficult since it tended to explode and flash along the combustion tube when mixed with oxygen and heated; a slow stream of the organic compound with a large excess of oxygen was finally used for combustion.

In repeat experiments, and with quantities of fluoroiodopropene up to 30 g., 68—75% yields of trifluoromethylacetylene were obtained. The dehydroiodination could also be effected by heating small amounts of 3 : 3 : 3-trifluoro-1-iodopropene with powdered potassium hydroxide at 120—180° in Carius tubes.

Properties of 3 : 3 : 3-*Trifluoropropyne.*—The fluoroalkyne is a colourless gas, with an odour like that of acetylene, whose vapour pressure determined over the range −135° to −60° is represented by the equation $\log_{10} p = 7{\cdot}8808 - 1124/T$, whence the calculated boiling point is −48·3°. Trouton's constant is 22·8, and the latent heat of vaporisation is 5140 cals./mole.

Copper derivative. Trifluoromethylacetylene (0·1 g.) was shaken in a sealed tube with a filtered solution of cuprous chloride in ammonium hydroxide. An immediate khaki-coloured precipitate was produced which, if left overnight, darkened to a brown solid. A freshly prepared specimen of the copper derivative was removed by filtration, washed with water, and dried *in vacuo* over silica gel. When heated gently, *cuprous trifluoromethylacetylide* (Found : C, 22·8; F, 36·1; Cu, 40·8. C_3F_3Cu requires C, 23·0; F, 36·4; Cu, 40·6%) slowly decomposed; rapid heating brought about the vigorous decomposition of larger quantities with occasionally a slight explosion.

Analysis for carbon was carried out by carefully heating a small specimen in a standard combustion tube, and fluorine was determined after sodium fusion. Analysis for copper was most conveniently effected after dissolution and warming of the acetylide in dilute nitric acid; identification of the evolved gas as trifluoromethylacetylene proved that the copper derivative was a true acetylide. Copper trifluoromethylacetylide was soluble in alcohol and ether, and was not contaminated by chlorine-containing compounds.

Silver derivative. An immediate white precipitate was produced when trifluoromethylacetylene was shaken with ammoniacal silver nitrate. The precipitate, removed by filtration and washed with water, was shown to be *silver trifluoromethylacetylide* (Found : C, 17·4; F, 27·9; Ag, 54·1. C_3F_3Ag requires C, 17·9; F, 28·4; Ag, 53·7%). Analysis for silver was carried out after warming with dilute nitric acid and removal and identification of the evolved trifluoromethylacetylene. Fluorine was determined after sodium fusion, and carbon by careful combustion in oxygen. Silver trifluoromethylacetylide is a white solid which changes to a fawn colour when kept in a desiccator or on exposure to light. When heated rapidly it decomposes violently, but a steady decomposition occurs when it is heated slowly and metallic silver is left; this gives an alternative method of analysis (Found : Ag, 54·5%).

When trifluoromethylacetylene is shaken with a neutral or slightly acid silver nitrate solution, the white precipitate so obtained is much more complex; it is only slightly soluble in organic solvents and contains traces of apparently combined water and of anions from the aqueous solution.

Mercuric derivative. Mercuric chloride (33 g.) and potassium iodide (82 g.) were dissolved in water (80 ml.) and 10% potassium hydroxide (60 ml.) was added. After filtration, a portion of the clear yellow solution (10 ml.) was shaken with trifluoromethylacetylene (0·4 g.) in a sealed tube. A colourless oil was immediately formed as a lower layer, and to remove inorganic salts this was thoroughly washed with water by centrifugation and decantation. The oil, which had a strong odour of trifluoromethylacetylene, was transferred to a short-path still and heated to 60° under 400 mm. The crude acetylide crystallised on the cold finger of the short-path still in the form of needles, m.p. 39—41°. Further sublimation at atmospheric pressure gave *mercuric trifluoromethylacetylide* (Found : C, 18·6; F, 29·1; Hg, 51·4. C_6F_6Hg requires C, 18·6; F, 29·5; Hg, 51·9%) as a white crystalline solid, m. p. 44—45°, which did not contain traces of iodine or chlorine.

In further experiments, the acetylide, after thorough washing with water, was dissolved in ether, removal of which gave the crude crystalline acetylide, m. p. 39—41°. The use of a large excess of potassium iodide in making the mercuri-iodide reduced the yield of the acetylide. In some instances the acetylide was precipitated as a solid, and it was found preferable to melt the compound by gentle warming so that it could be washed efficiently with water. Mercuric trifluoromethylacetylide liberated trifluoromethylacetylene when warmed with mineral acids. When the theoretical amount of iodine dissolved in hexane was added to the acetylide, the colour was immediately reduced in intensity. Evaporation of a portion of the solution gave a residue which contained mercuric iodide and had an odour very similar to the characteristic odour of di-iodoacetylene and $-C{\vdots}CI$ compounds in general. The isolation of this compound, believed to be 3 : 3 : 3-trifluoro-1-iodopropyne, in a pure state was not attempted.

Oxidation of 3 : 3 : 3-*Trifluoropropyne.*—The fluoroalkyne (1 g.) was readily oxidised by alkaline potassium permanganate to give trifluoroacetic acid (cf. Haszeldine, *J.*, 1950, 2789, and Part II, *loc. cit.*).

The acid was not isolated as such but was esterified and converted into the amide (0·25 g.), m. p. 74°, for identification.

Hydrogenation of 3 : 3 : 3-*Trifluoropropyne.*—The alkyne (4·0 g.) was heated with hydrogen (80 atm.) to a final temperature of 80° in the presence of Raney nickel. The product was 1 : 1 : 1-trifluoropropane (3·9 g.) (Found : *M*, 98. Calc. : *M*, 98), b. p. —12°. The hydrogenated material showed no reaction with chlorine in the dark at 40° and was not unsaturated. When it was sealed with excess of chlorine in a silica tube and exposed to ultra-violet radiation, a slow reaction occurred and after 3 days 1 : 1 : 1 : 2 : 2-pentachloro-3 : 3 : 3-trifluoropropane (3·7 g.) (Found : Cl, 64·8. Calc. for $C_3Cl_5F_3$: Cl, 65·6%), m. p. 108—109°, b. p. (micro) 155° (cf. table above), and a mixture of 1 : 1-dichloro-3 : 3 : 3-trifluoropropane and 1 : 1 : 1-trichloro-3 : 3 : 3-trifluoropropane were isolated. A specimen of 1 : 1 : 1-trifluoropropane prepared from 1 : 1 : 1-trifluoro-3-iodopropane (Haszeldine, *loc. cit.*) reacted in an analogous manner and gave a specimen of the pentachlorotrifluoropropane whose m. p. was not changed on admixture with the compound obtained by chlorination of the hydrogenated trifluoromethylacetylene.

Addition of Chlorine to Trifluoromethylacetylene.—Trifluoromethylacetylene (2·0 g.) was sealed in a tube with a slight excess of chlorine (3·1 g.), and the mixture allowed to warm to room temperature. After 24 hours at 50° in the dark, the tube was opened and the contents were given a preliminary distillation to remove material with b. p. $<0°$; no alkyne or hydrogen chloride, but only a trace of chlorine was recovered. The material, b. p. $>0°$, was distilled at atmospheric pressure to give : (1) a small amount (0·1 g.) of liquid, b. p. 55—60°, n_D^{25} 1·366, which was probably $CF_3{\cdot}CCl{:}CHCl$ (Henne, Whaley, and Stevenson, *J. Amer. Chem. Soc.*, 1941, 3478, report b. p. 53·7°, n_D^{20} 1·3670); (2) 1 : 1 : 2 : 2-*tetrachloro*-3 : 3 : 3-*trifluoropropane* (3·6 g.; 72%) (Found : C, 15·8; H, 0·7; Cl, 60·1. $C_3HCl_4F_3$ requires C, 15·3; H, 0·4; Cl, 60·2%), b. p. 126—126·5°, n_D^{25} 1·4195; (3) still residue (1·0 g.).

The tetrachlorotrifluoropropane was mixed with a 20% excess of chlorine in a Pyrex tube and exposed to ultra-violet radiation (*i.e.*, of wave-length >2900 A.) (chlorination of a mixture of $CF_3{\cdot}CH_2{\cdot}CHCl_2$ and $CF_3{\cdot}CH_2{\cdot}CCl_3$ proceeded extremely slowly under such conditions); after 4 hours the excess of chlorine was allowed to evaporate and the contents of the tube were taken up in ether, evaporation of which gave 1 : 1 : 1 : 2 : 2-pentachloro-3 : 3 : 3-trifluoropropane (2·2 g.) (Found : C, 13·5; Cl, 65·3. Calc. for $C_3Cl_5F_3$: C, 13·3; Cl, 65·6%) as a white crystalline solid, purified by sublimation, m. p. 109°, unaltered by admixture with the pentachlorotrifluoropropane prepared by exhaustive chlorination of 1 : 1 : 1-trifluoropropane.

Professor A. L. Henne reports (private communication) that trifluoromethylacetylene has now been prepared from $CF_3{\cdot}CBr{:}CH_2$ and that the b. p. of the compound so obtained confirms that of the compound reported in *Nature* (*loc. cit.*).

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[*Received, November* 14*th*, 1950.]