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668. *Reactions of Fluorocarbon Radicals. Part VI.* The Hydration of Trifluoromethyl- and Pentafluoroethyl-substituted Acetylenes.*

By R. N. HASZELDINE and K. LEEDHAM.

The synthesis of 3 : 3 : 4 : 4 : 4-pentafluorobut-1-yne (pentafluoroethylacetylene) by reaction of pentafluoroiodoethane with acetylene, followed by dehydroiodination, is reported. Mercury-catalysed hydration of 3 : 3 : 3-trifluoropropyne at room temperature yields 1 : 1 : 1-trifluoroacetone and 3 : 3 : 3-trifluoropropaldehyde in the ratio of 2 : 1; at higher temperatures the ketone and βββ-trifluoropropionic acid are formed. The pentafluorobutyne similarly yields 3 : 3 : 4 : 4 : 4-pentafluorobutan-2-one and ββγγγ-pentafluorobutyric acid. A mechanism for the hydration of acetylenes is proposed and discussed, and infra-red and ultra-violet spectra of certain fluorine compounds are presented.

SYNTHESES for 3 : 3 : 3-trifluoropropyne were described in Parts IV and V (Haszeldine, *J.*, 1951, 588, 2495). The present communication (see Abstracts 120th Meeting Amer. Chem. Soc., New York, Sept. 1951, 7K) is concerned with the synthesis of 3 : 3 : 4 : 4 : 4-pentafluorobut-1-yne and with the hydration of this and of 3 : 3 : 3-trifluoropropyne.

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* Part V, Haszeldine, *J.*, 1951, 2495.

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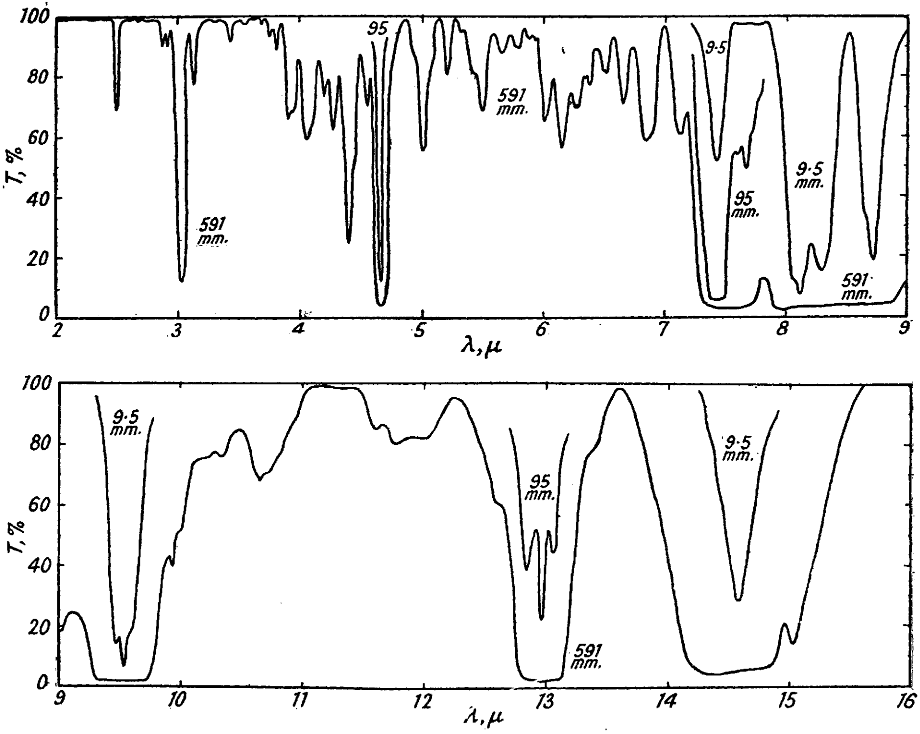
Pentafluoroiodoethane and acetylene do not react in the dark at room temperature, but on exposure to ultra-violet light a smooth reaction occurs to yield compounds of the general formula $C_2F_5{\cdot}[CH{:}CH]_n{\cdot}I$:

$$C_2F_5{\cdot} + CH{:}CH \longrightarrow C_2F_5{\cdot}CH{:}CH{\cdot} \xrightarrow{C_2F_5I} C_2F_5{\cdot}CH{:}CHI + C_2F_5{\cdot}, \text{ etc.}$$

The compound where $n = 1$, *viz.*, 3 : 3 : 4 : 4 : 4-pentafluoro-1-iodobut-1-ene, is the main product, but small amounts of the compound where $n = 2$, *viz.*, 5 : 5 : 6 : 6 : 6-pentafluoro-1-iodohexa-1 : 3-diene, have been isolated and characterised. The interaction of pentafluoroiodoethane and acetylene takes place in absence of light at 210—240° and yields similar products.

Dehydroiodination of 3 : 3 : 4 : 4 : 4-pentafluoro-1-iodobut-1-ene with powdered potassium hydroxide gives pentafluorobut-1-yne, from which copper, silver, and mercuric acetylides are prepared in the standard manner. The infra-red spectrum of pentafluorobutyne is shown in Fig. 1. The acetylenic carbon–hydrogen and the C≡C stretching frequencies are at 3·01 and 4·66 μ (cf. trifluoropropyne 3·01, 4·65 μ; propyne 2·96, 4·625 μ).

FIG. 1. 3 : 3 : 3 : 4 : 4-*Pentafluorobutyne* (*vapour in* 50 *mm. cell*).



Details for the preparation of 3 : 3 : 3-trifluoropropyne from trifluoroiodomethane in 56% yield by the sequence

$$\begin{tikzcd}
CF_3I \arrow[r, "C_2H_4"] & CF_3{\cdot}CH_2{\cdot}CH_2I \arrow[r, "-HI"] & CF_3{\cdot}CH{:}CH_2 \arrow[r, "Br_2"] & CF_3{\cdot}CHBr{\cdot}CH_2Br \arrow[d, "-HBr"] \\
CF_3{\cdot}C{:}CH & CF_3{\cdot}CBr{:}CHBr \arrow[l, "Zn,\ EtOH"'] & CF_3{\cdot}CBr_2{\cdot}CH_2Br \arrow[l, "-HBr"'] & CF_3{\cdot}CBr{:}CH_2 \arrow[l, "Br_2"']
\end{tikzcd}$$

are given in the Experimental section. This route is applicable to the higher fluoro-iodides and on an autoclave scale provides the most convenient method for the preparation of larger quantities of the (perfluoroalkyl)acetylenes.

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The ionic addition of HX (X = F, Cl, Br, I, OMe, OEt, NR_2) to trifluoropropyne has been found to yield $CF_3\cdot CH{:}CHX$ (see following paper), *i.e.*, a reversal of the direction of addition compared with propyne, and indicating a polarisation $F_3C\leftarrow\overset{\delta-}{C}\equiv\overset{\delta+}{C}H$. Thus, trifluoropropyne might be expected to yield an aldehyde on hydration :

$$CF_3\cdot C\vdots CH \xrightarrow{H_2O} CF_3\cdot CH{:}CH\cdot OH \longrightarrow CF_3\cdot CH_2\cdot CHO$$

rather than the ketone usually obtained by hydration of 1-alkynes.

The trifluoropropyne and pentafluorobutyne are recovered unchanged from dilute sulphuric acid even after being heated to 120°, indicating that, as in trifluoropropene, the perfluoroalkyl group tends to deactivate the adjacent unsaturated linkage. The hydration of trifluoropropyne proceeds smoothly at room temperature, however, when mercuric sulphate is added to the sulphuric acid, and after several days a mixture of βββ-trifluoropropaldehyde and 1 : 1 : 1-trifluoroacetone is produced :

$$CF_3\cdot C\vdots CH \longrightarrow CF_3\cdot CH_2\cdot CHO + CF_3\cdot CO\cdot CH_3$$

This can be separated by conversion of the aldehyde into the dimedone derivative and of the residual ketone into the 2 : 4-dinitrophenylhydrazone. The ratio of aldehyde : ketone is 1 : 2.

The mercury-catalysed hydration thus yields mainly the ketone and not the aldehyde expected from the polarisation. With other acetylenes the hydration product is that predicted on general grounds. Thus, αβ-acetylenic acids or nitriles give the corresponding β-keto-acids [$R\cdot\overset{\delta+}{C}\equiv\overset{\delta-}{C}\cdot CO_2H \longrightarrow R\cdot CO\cdot CH_2\cdot CO_2H$, where R = alkyl, Ph, p-$NO_2\cdot C_6H_4$, p-$Br\cdot C_6H_4$, o-$NH_2\cdot C_6H_4$, or Cl (Zernik, *Apoth. Ztg.*, 1904, **20**, 382; *Chem. Zent.*, 1905, I, 1728; Moureu and Delange, *Compt. rend.*, 1901, **132**, 1121; 1903, **136**, 552, 753; *Bull. Soc. chim.*, 1903, **29**, 648, 666, 676; Reimer and Tobin, *J. Amer. Chem. Soc.*, 1941, **63**, 2490)], and hydration of acetylenic ketones gives β-diketones [$R\cdot CO\cdot\overset{\delta-}{C}\equiv\overset{\delta+}{C}R' \longrightarrow R\cdot CO\cdot CH_2\cdot COR'$, where R and R′ = alkyl, aryl, etc. (Nef, *Annalen*, 1899, **308**, 277; Yvon, *Compt. rend.*, 1925, **180**, 748; Moureu and Delange, *Bull. Soc. chim.*, 1901, **25**, 306; *Ann. Chim.*, 1914, **2**, 277; Fuson, Ullyot, and Hickson, *J. Amer. Chem. Soc.*, 1939, **61**, 410; Morton, Hassan, and Calloway, *J.*, 1934, 883)]. Similarly, alkoxyacetylenes give the expected ester [*e.g.*, $Bu\cdot\overset{\delta-}{C}\equiv\overset{\delta+}{C}OPh \longrightarrow Bu\cdot CO_2Ph$ (Jacobs, Cramer, and Weiss, *J. Amer. Chem. Soc.*, 1940, **62**, 1849)]. With monosubstituted acetylenes, the hydration of 1-alkynes invariably yields the 2-ketone, and alkoxyacetylenes give the ester [$H\overset{\delta-}{C}\equiv\overset{\delta+}{C}\cdot OR \longrightarrow CH_3\cdot CO_2R$, R = Et, Bu (Jacobs, Cramer, and Hanson, *ibid.*, 1942, **64**, 223)] whether water, sulphuric acid, or sulphuric acid in the presence of mercuric sulphate be used as hydrating agent. It is thus significant that the monosubstituted acetylene, ethynyl phenyl ketone, is hydrated to 1-phenylpropane-1 : 2-dione in the presence of mercuric sulphate [$Ph\cdot CO\cdot C\vdots CH \longrightarrow Ph\cdot CO\cdot CO\cdot CH_3$ (Bowden, Braude, and Jones, *J.*, 1946, 945)], despite the α-carbonyl group which would be expected to favour the formation of the 1 : 3-dione. The hydration of ethynyl phenyl ketone clearly resembles that of $R\cdot C\vdots CH$ (R = CF_3, C_2F_5), and the following general scheme is advanced to explain the apparent anomaly.

It is suggested that two competing reactions are involved in the hydration of $R\cdot C\vdots CH$ (R = CF_3, C_2F_5, COPh, etc.). (*a*) The aldehyde is formed *via* an intermediate complex formed by addition of HgY_2 (Y = HSO_4, say, in acid solution) followed by addition of water and loss of HgY_2 (cf. Hennion, Vogt, and Nieuwland, *J. Org. Chem.*, 1936, **1**, 159). The direction of addition of HgY_2 is determined by the group R :

$$R\cdot\overset{\delta-}{C}\equiv\overset{\delta+}{C}H \xrightarrow{HgY_2} R\cdot C(HgY){:}CHY \xrightarrow[-HgY_2]{+H_2O} R\cdot CH{:}CH\cdot OH \longrightarrow R\cdot CH_2\cdot CHO$$

(*b*) A compound of the type $R\cdot C\vdots C\cdot HgY$, or the mercuric acetylide, is postulated as the initial reversible step, which is followed by the rapid addition of HgY_2. The direction of addition of HgY_2 is now reversed compared with (*a*), since the mercury attached

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directly to the acetylenic carbon atom will exert a greater influence on the unsaturation electrons of the triple bond than will the fluorine atoms on a carbon atom once removed from the triple bond, and the ketone is produced regardless of the nature of R :

$$R{\cdot}C{\vdots}CH \rightleftharpoons R{\cdot}\overset{\delta+}{C}{\equiv}\overset{\delta-}{C}{\cdot}HgY \xrightarrow{HgY_2} R{\cdot}CY{:}C(HgY)_2 \xrightarrow[HgY_2]{H_2O,HY} R{\cdot}C(OH){:}CH_2 \longrightarrow R{\cdot}CO{\cdot}CH_3$$

Schemes (*a*) and (*b*) would yield the same product, the ketone, when R = alkyl or an electron-supplying group.

A white solid complex is formed as soon as the (perfluoroalkyl)acetylenes and mercuric sulphate are mixed in presence of sulphuric acid, but attempts to purify and analyse the complex (which is not the known low-melting mercuric perfluoroalkylacetylide) have been unsuccessful. Since the acetylenic hydrogen atom is essential in scheme (*b*), the hydration of 1 : 1 : 1-trifluorobut-2-yne is being investigated, since this should yield 4 : 4 : 4-trifluorobutan-2-one ($CF_3{\cdot}C{\vdots}C{\cdot}CH_3 \longrightarrow CF_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3$).

The hydration of the (perfluoroalkyl)acetylenes has also been investigated at higher temperatures. When traces of mercuric sulphate were used at 130°, complete reduction to mercury took place, at which stage the hydration stopped. Trifluoroacetone and traces of βββ-trifluoropropionic acid were formed, but 3 : 3 : 3-trifluoropropaldehyde could not be detected. When an excess of mercuric sulphate was used as catalyst at 135°, the trifluoropropyne underwent rapid and complete reaction, and free mercury was not evident. The volatile reaction products were 1 : 1 : 1-trifluoroacetone, fluoroform, and carbon dioxide; 3 : 3 : 3-trifluoropropaldehyde was not detected, but the aqueous solution contained βββ-trifluoropropionic acid, characterised as its nitron salt and as the urea derivative (I; R = NMe_2, R′ = CF_3). The nitron salts are readily obtained from fluoro-acids of general formula $CF_3{\cdot}[CF_2]_n{\cdot}[CH_2]_m{\cdot}CO_2H$ (*m* = 0 or 1), which are appreciably stronger acids than their hydrocarbon analogues. Since the nitron salts decompose on heating, they are best characterised by their infra-red spectra (*e.g.*, see Fig. 2). Fluoro-acids of the above formula with $m \gg 1$ are more readily characterised by their ready reaction with carbodi-imines (II) (Schall, *J. pr. Chem.*, 1901, **64**, 261; Zetzsche, Lüscher, and Meyer, *Ber.*, 1938, **71**, 1088; Zetzsche and Röttger, *ibid.*, 1940, **73**, 50, introduced this reagent for the characterisation of carboxylic acids). Derivatives of sharp m. p. and characteristic infra-red spectra are obtained. Comparison of the urea derivative (I; R = NMe_2, R′ = CF_3) with a specimen obtained from βββ-trifluoropropionic acid prepared by the sequence (Haszeldine, *Nature*, 1951, **168**, 1028)

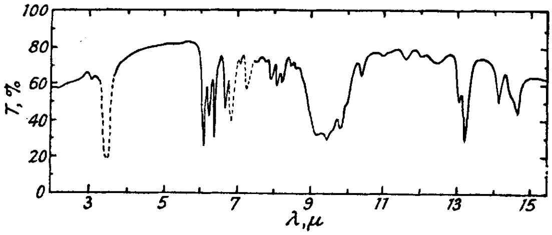

FIG. 2. *Nitron derivative of* $CF_3{\cdot}CH_2{\cdot}CO_2H$.

(I) p-$R{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}N(CO{\cdot}CH_2R'){\cdot}C_6H_4R$-$p$ $\qquad$ $C({:}N{\cdot}C_6H_4R$-$p)_2$ (II)

$$CF_3I \longrightarrow CF_3{\cdot}CH_2{\cdot}CH_2I \longrightarrow CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}MgI \longrightarrow CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH \longrightarrow CF_3{\cdot}CH_2{\cdot}CO_2H$$

confirmed the identity of the hydration product from trifluoropropyne.

Pentafluorobutyne similarly showed no reaction with dilute sulphuric acid at 110° but on addition of an excess of mercuric sulphate the alkyne was rapidly converted into 3 : 3 : 4 : 4 : 4-pentafluorobutan-2-one, carbon dioxide, and pentafluoroethane. The fluoroketone, which readily forms a hydrate, was characterised by its 2 : 4-dinitrophenylhydrazone. The presence of ββγγγ-pentafluorobutyric acid in the aqueous phase was shown by the formation of the urea derivative (I; R = NMe_2, R′ = C_2F_5). Salt formation between the

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βββ-trifluoropropionic or ββγγγ-pentafluorobutyric acids and the dimethylamino-group, in preference to acyl-urea formation, can be excluded, since the infra-red spectra of derivatives (I) show the acyl carbonyl band at 5·81 μ, and the strong band at 4·77 μ present in the spectrum of the parent carbodi-imine (II; R = NMe_2) is no longer apparent.

The formation of trifluoropropionic and pentafluorobutyric acids is attributed to the thermal oxidation of the aldehydes whose presence can be demonstrated at lower temperatures and may be associated with the formation of mercury from mercuric sulphate. The carbon dioxide produced during reaction did not arise by decarboxylation of the fluoro-acids, since 1 : 1 : 1-trifluoroethane and 1 : 1 : 1 : 2 : 2-pentafluoropropane were not isolated.

The infra-red spectra of 1 : 1 : 1-trifluoroacetone and 3 : 3 : 4 : 4 : 4-pentafluorobutan-2-one are shown in Fig. 3. The carbonyl stretching vibrations are at the remarkably low wave-lengths of 5·63 and 5·65 μ (cf. 5·85 μ for an alkyl ketone), providing another example of the shift to lower wave-length of the " characteristic " wave-length of functional groups noted earlier (Haszeldine, *Nature*, 1951, **168**, 1028). The carbon–hydrogen stretching vibration appeared at 3·33 μ in both compounds, and the bands at 7·00 and 7·25 and at 7·03 and 7·30 μ, respectively, may be associated, at least in part, with the carbon–hydrogen bending vibrations of the methyl groups. The pattern of the strong bands in the 8—9 μ region of the spectrum due to the carbon–fluorine stretching vibrations easily distinguishes the homologous ketones.

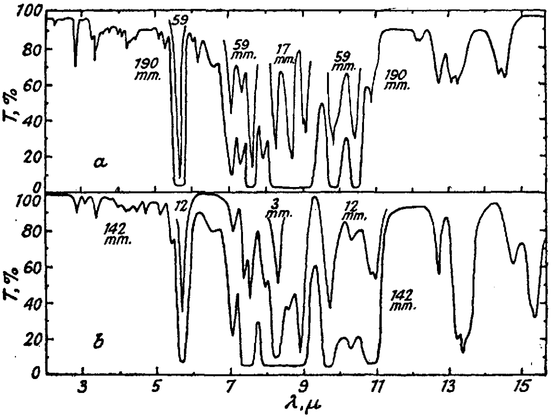

FIG. 3.

(*a*) $CF_3 \cdot CO \cdot CH_3$. *Vapour in* 50-*mm. cell.*
(*b*) $C_2F_5 \cdot CO \cdot CH_3$. *Vapour in* 50-*mm. cell.*

EXPERIMENTAL

Preparation of Trifluoroiodomethane and Pentafluoroiodoethane.—Trifluoroiodomethane was prepared from silver trifluoroacetate and iodine (Haszeldine, *J.*, 1951, 584) in yields of 90—95%, and pentafluoroiodoethane from tetrafluoroethylene by Emeléus and Haszeldine's method (*J.*, 1949, 2948) in 85% yield.

Interaction of Pentafluoroiodoethane and Acetylene.—(a) *Under influence of heat.* Under optimum conditions, pentafluoroiodoethane (3·25 g.) was sealed with acetylene (0·41 g., 20% excess) in a Carius tube of 30-ml. capacity, and heated to 220—260° for 15—20 hours. A cuprene-type polymer was deposited on the walls of the vessel, and *ca.* 10% of the acetylene was found to be unchanged. The liquid products of reaction were shaken with mercury to remove iodine and distilled, to give 3 : 3 : 4 : 4 : 4-*pentafluoro*-1-*iodobut*-1-*ene* (2·60 g., 72%) (Found: C, 17·5; H, 0·7; F, 34·4; I, 46·4%; *M*, 274. $C_4H_2F_5I$ requires C, 17·6; H, 0·7; F, 34·9; I, 46·7%; *M*, 272), b. p. 84·4°, n_D^{25} 1·392. The higher-boiling products from several such experiments were combined and distilled, to give 5 : 5 : 6 : 6 : 6-*pentafluoro*-1-*iodohexa*-1 : 3-*diene* (*ca.* 0·5% yield) (Found: C, 23·6; H, 1·4; I, 41·7. $C_6H_4F_5I$ requires C, 24·2; H, 1·3; I, 42·6%), b. p. 104°/46 mm., *trans*-di-iodoethylene (0·5—1·0%) (Found: C, 9·0; H, 1·0. Calc. for $C_2H_2I_2$: C, 8·6; H, 0·7%), m. p. 72·5—73·5° after recrystallisation from ethanol (Keiser, *J. Amer. Chem. Soc.*, 1899, **21**, 265, reports m. p. 73°), and a fluorine-free oil, immiscible with, and sometimes contaminating, the fluoroiodohexadiene on distillation, which may be *cis*-di-iodoethylene.

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(b) *Under influence of light.* Acetylene (1·55 g., 15% excess) and pentafluoroiodoethane (12·8 g.) were sealed in a series of Pyrex Carius tubes of 50-ml. capacity and irradiated at a distance of 12″ by a Hanovia lamp without the Wood's filter. After 9 days the contents were combined and fractionated, to give unchanged acetylene (6%), unchanged pentafluoroiodoethane (3%), and higher-boiling material (13·0 g.), 57% of which was 3 : 3 : 4 : 4 : 4-pentafluoro-1-iodobutene.

Preparation of Pentafluorobutyne.—Dry, powdered potassium hydroxide (50 g.) was added to a 250-ml. flask fitted with a dropping-funnel and reflux water condenser leading to traps cooled in liquid air. After dropwise addition of a portion of the 3 : 3 : 4 : 4 : 4-pentafluoro-1-iodobut-1-ene (38·6 g.) to the flask, the temperature was slowly raised to 110°, then reduced to 70°, a further portion added, and the temperature raised to 110° again. After 5 hours no refluxing could be observed, and the contents of the flask were heated *in vacuo* to recover unchanged fluoroiodobutene (3·4 g., 9%). The volatile products of the dehydroiodination were purified by fractional condensation *in vacuo*, to give 3 : 3 : 4 : 4 : 4-*pentafluorobut*-1-*yne* (11·8 g., 63·5% based on fluoroiodobutene used) (Found: *M*, 144. C_4HF_5 requires *M*, 144). Its vapour pressure is represented over the temperature range −70° to −12° by the equation log *P* (mm.) = 7·5952 − 1231·7/*T*, whence the b. p. is calculated as −12°, the latent heat of vaporisation as 5640 cals./mole, and Trouton's constant as 21·6.

Copper, Silver, and Mercuric Pentafluorobutynylides.—By the method of Part IV (*J.*, 1951, 588), pentafluorobutyne (0·3—0·5 g.) was converted into the khaki-coloured *cuprous pentafluorobutynylide* (Found: Cu, 30·9. C_4F_5Cu requires Cu, 30·8%), the white *silver* analogue (Found: Ag, 42·8. C_4F_5Ag requires Ag, 43·1%), and the white, crystalline *mercuric* derivative (Found: C, 20·0; Hg, 41·2. $C_8F_{10}Hg$ requires C, 19·8; Hg, 41·2%), m. p. *ca.* 25° after sublimation at 100°/760 mm. The fluoro-alkyne was liberated quantitatively on heating of the acetylides with 5N-nitric acid.

Preparation of Trifluoropropyne.—(*a*) Trifluoroiodomethane was converted into trifluoropropyne by the method of Part IV in yields of 70%. (*b*) Route IV [6(*a*) and (*b*)] of Part V was modified as follows: Trifluoroiodomethane (0·33 mol.) was converted into 1 : 1 : 1-trifluoro-3-iodopropane (82% yield based on fluoro-iodide used) by reaction with ethylene (0·33 mol.) at 275° for 15 hours in a 300-ml. autoclave. The fluoroiodopropane (113 g., 0·51 mol.) was added dropwise during 2·5 hours to alcoholic potassium hydroxide (60 g., 1·1 mol., in 300 ml. of ethanol), and the evolved 3 : 3 : 3-trifluoropropene led into a 500-ml. silica flask containing bromine (103 g., 25% excess) and exposed to ultra-violet light. The excess of bromine was removed (sodium hydrogen sulphite) and the solution dried (P_4O_{10}); distillation gave 2 : 3-dibromo-1 : 1 : 1-trifluoropropane (120 g., 92·5%), b. p. 116°. To the stirred dibromide (110 g., 0·43 mol.), cooled to −5°, was slowly added ice-cold alcoholic potassium hydroxide (26 g., 0·46 mol., in 65 ml. of ethanol). Phenolphthalein was used to follow the course of reaction to avoid high local concentrations of alkali. After being stirred for 1 hour the reaction mixture was acidified (hydrochloric acid) and diluted with water to dissolve the potassium bromide, and the lower layer washed, dried (P_4O_{10}), and distilled, to give 2-bromo-3 : 3 : 3-trifluoroprop-1-ene (70·1 g., 91·5%), b. p. 33·8°. The volatile product formed during the dehydrohalogenation was 3 : 3 : 3-trifluoropropyne (0·2 g.). The bromotrifluoropropene (15·3 g., 0·09 mol.) was treated with bromine (16·5 g., 0·1 mol.) in a silica flask irradiated by ultra-violet light and fitted with a reflux condenser cooled to −78°, until no further refluxing was apparent. After cooling to 10°, the reaction mixture was treated with ice-cold alcoholic potassium hydroxide (5·6 g., 0·1 mol., in 15 ml. of ethanol) in the manner just described, and the lower layer after acidification was distilled, to give 1 : 2-dibromo-3 : 3 : 3-trifluoroprop-1-ene (17·8 g., 0·07 mol., 87%), b. p. 96°, and recovered 2-bromo-3 : 3 : 3-trifluoroprop-1-ene (1·22 g., 0·007 mol.). Dehalogenation of the 1 : 2-dibromo-3 : 3 : 3-trifluoropropene (17·8 g., 0·07 mol.) was effected by its addition during 5 hours to zinc (14 g.) in ethanol (60 ml.) at the reflux temperature; the yield of 3 : 3 : 3-trifluoropropyne was 93% (6·38 g., 0·068 mol.). The overall yield from 1 : 1 : 1-trifluoro-3-iodopropane was thus 70%.

Hydration of Trifluoropropyne.—(1) *In absence of a catalyst.* 3 : 3 : 3-Trifluoropropyne (1·14 g.) was sealed in a Carius tube with 10% sulphuric acid (5 ml.) and heated at 100° for 45 hours but was substantially unchanged.

(2) *In presence of mercuric sulphate.* (a) *Catalytic amounts.* 3 : 3 : 3-Trifluoropropyne (2·25 g., 0·024 mol.) was heated at 130° for 15 hours with mercuric sulphate (0·2 g., 0·0007 mol.). Mercury (0·096 g. ≡ 75% of the mercuric sulphate added) was liberated, 77% (1·74 g.) of the trifluoropropyne was recovered unchanged, and 1 : 1 : 1-trifluoroacetone (0·51 g., 19% yield, 84% based on acetylene used) (identified as described below) were formed. The aqueous

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solution contained a trace of βββ-trifluoropropionic acid (see below), but 3 : 3 : 3-trifluoropropaldehyde could not be detected.

(b) *Excess of mercuric sulphate at room temperature.* The trifluoropropyne (1·05 g., 0·011 mol.) and mercuric sulphate (6·54 g., 0·022 mol.), shaken at room temperature for 148 hours with 15% sulphuric acid (5 ml.), gave unchanged trifluoropropyne (0·11 g., 10%), and a fraction *A* (Found: *M*, 113. Calc. for $C_3H_3OF_3$: *M*, 112). Carbon dioxide was not detected (see below). A 10% aliquot of fraction *A* gave a mixture of 2 : 4-dinitrophenylhydrazones melting over the range 125—128° and this could not be separated by fractional crystallisation on a micro-scale. The remainder of the gaseous fraction was shaken in a sealed tube for 24 hours with excess of a 2% aqueous dimedone solution, residual gaseous material *B* (*M*, 112) returned to the vacuum system, and the solid product removed by filtration. Treatment of the diluted, filtered aqueous solution from the hydration with an aqueous dimedone solution gave a small quantity of solid after 24 hours. The combined white solid was washed with water and recrystallised from aqueous ethanol, to give the *dimedone* derivative of 3 : 3 : 3-trifluoropropaldehyde (1·05 g.) (Found: C, 61·2; H, 6·5. $C_{19}H_{25}O_4F_3$ requires C, 61·0; H, 6·5%), m. p. 115°. The yield of 3 : 3 : 3-trifluoropropaldehyde was thus 28% based on the trifluoropropyne used.

A 20% aliquot of the gas *B* was treated for 24 hours with 2 : 4-dinitrophenylhydrazine. The solid formed was combined with a small amount arising by similar treatment of a 20% aliquot of the dimedone-treated hydration solution, and recrystallised from aqueous ethanol, to give the 2 : 4-dinitrophenylhydrazone of 1 : 1 : 1-trifluoroacetone (0·357 g.), m. p. 138—139° (see below). The yield of trifluoroacetone based on trifluoropropyne used was thus 61%, and the yields of aldehyde and ketone account for 89% of the fluoro-acetylene used.

The residual 80% aqueous aliquot was distilled, and the distillate extracted continuously by ether overnight. Tests for βββ-trifluoropropionic acid were negative. A small amount of mercury (<0·1 g.) had been liberated during the hydration.

(c) *Excess of mercuric sulphate at high temperatures.* 3 : 3 : 3-Trifluoropropyne (1·75 g., 0·019 mol.), mercuric sulphate (12·6 g.; 0·043 mol.), and 10% sulphuric acid (5 ml.) were heated in a Carius's tube at 135° for 15 hours to give: carbon dioxide (0·26 g., equiv. to 32% of trifluoropropyne), fluoroform (0·02 g.), and 1 : 1 : 1-trifluoroacetone (0·37 g., 18%) (Found: *M*, 114. Calc. for $C_3H_3OF_3$: *M*, 112), b. p. 22·0°. This gave a 2 : 4-dinitrophenylhydrazone (Found: N, 19·6. Calc. for $C_9H_7N_4O_4F_3$: N, 19·2%), m. p. 138·5—139·0°. Ultra-violet absorption in ethanol: $\lambda_{max.}$ 338, 256, and 218 mμ; ε 20,200, 11,700, and 13,050, respectively. Swarts (*Bull. Acad. roy. Belg.*, 1927, **13**, 175) reports b. p. 21·9° for the ketone, and Henne, Newman, Quill, and Staniforth (*J. Amer. Chem. Soc.*, 1947, **69**, 1819) report m. p. 139° for the 2 : 4-dinitrophenylhydrazone.

The filtered, pale brown aqueous solution was extracted by ether (50 ml.), and the extracts were dried ($MgSO_4$) and distilled, to give a pale yellow oil (0·52 g.) with an odour similar to that of the higher perfluoro-acids. Treatment of the oil with water gave an insoluble polymeric residue (*ca.* 0·1 g.) which was soluble in alcohol. A dimedone derivative could not be prepared before or after heating of the polymer with sodium carbonate solution. The water-soluble material was shown to be βββ-trifluoropropionic acid (*ca.* 22% yield): a specimen of the crude acid dissolved in ether and treated with an excess of an ethereal solution of *NN'*-bis-*p*-dimethylaminophenylcarbodi-imine (kindly given by Dr. H. G. Khorana) gave a precipitate, which was recrystallised from ethanol, giving NN'-*bis*-p-*dimethylaminophenyl*-N-3 : 3 : 3-*trifluoropropionylurea* (Found: N, 13·5. $C_{20}H_{23}N_4O_2F_3$ requires N, 13·7%), m. p. 155°, identical in m. p. and infra-red spectrum with the derivative prepared from a known specimen of βββ-trifluoropropionic acid. An aqueous solution of the crude βββ-trifluoropropionic acid was also added in slight excess to a 6% solution of nitron in 10% acetic acid to give the βββ-*trifluoropropionate* (Found: N, 12·9. $C_{23}H_{19}N_4O_2F_3$ requires N, 12·7%) as an off-white solid, recrystallised from aqueous ethanol and characterised by its infra-red spectrum. The aqueous solution of crude βββ-trifluoropropionic acid gave a negative test for aldehyde.

A similar experiment with the trifluoropropyne (2·2 g., 0·023 mol.), mercuric sulphate (7·86 g., 0·027 mol.), and 10% sulphuric acid (5 ml.), heated at 140° for 15 hours, gave a 16% yield of trifluoroacetone.

Hydration of Pentafluorobutyne.—No reaction was detected when the pentafluorobutyne (2·4 g.) was shaken with 10% sulphuric acid (5 ml.) at 110° for 28 hours, but pentafluorobutyne (4·33 g., 0·03 mol.), mercuric sulphate (16·6 g., 0·056 mol.), and 10% sulphuric acid (5 ml.), heated at 110° for 16 hours, gave carbon dioxide (0·14 g.; equiv. to 13% of the butyne), unchanged fluoro-acetylene (0·07 g.; 16%), pentafluoroethane (0·07 g.) (Found: *M*, 121. Calc. for C_2HF_5: *M*, 120) (identified by its infra-red spectrum), and 3 : 3 : 4 : 4 : 4-*pentafluoro-*

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butan-2-one (0·78 g., 16%) (Found : *M*, 162. $C_4H_3OF_5$ requires *M*, 162), b. p. 39·5—40°. This ketone readily formed a hydrate which could be reconverted into the ketone by distillation from phosphoric oxide.

The 2 : 4-*dinitrophenylhydrazone* (Found : N, 16·0. $C_{10}H_7O_4N_4F_5$ requires N, 16·4%), m. p. 99°, was recrystallised from aqueous ethanol, and had absorption maxima in ethanol at 336, 256, and 220 mμ (ε 20,100, 11,600, and 12,900, respectively). The ketone and the 2 : 4-dinitrophenylhydrazone were further characterised by their infra-red spectra.

Ether-extraction of the aqueous phase from the hydration gave crude ββγγγ-pentafluorobutyric acid (*ca.* 1·4 g., 17%), which with an ethereal solution of *NN'*-bis-*p*-dimethylaminophenylcarbodi-imine gave the corresponding urea as a white solid, m. p. 151°, characterised by its infra-red spectrum.

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