

669. *Reactions of Fluorocarbon Radicals. Part VII.* Addition to Trifluoromethyl-substituted Acetylenes.†*

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The addition of HX to 3 : 3 : 3-trifluoropropyne and hexafluorobut-2-yne yields $\text{CF}_3\cdot\text{CH}\cdot\text{CHX}$ (X = F, Cl, Br, I, CN, OMe, OEt, NEt₂) and $\text{CF}_3\cdot\text{CH}\cdot\text{CX}\cdot\text{CF}_3$ (X = Cl, Br, OMe, OEt, NEt₂). Addition tends to stop at this stage, but under more stringent conditions $\text{CF}_3\cdot\text{CH}_2\cdot\text{CHX}_2$ and $\text{CF}_3\cdot\text{CH}_2\cdot\text{CX}_2\cdot\text{CF}_3$ (X = Ome, OEt) are formed. Hydrogenolysis of the vinylic ethers $\text{CF}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{OR}$ and $\text{CF}_3\cdot\text{CH}\cdot\text{C}(\text{OR})\cdot\text{CF}_3$ or hydrolysis of the dialkoxy-compounds $\text{CF}_3\cdot\text{CH}_2\cdot\text{CH}(\text{OR})_2$ and $\text{CF}_3\cdot\text{CH}_2\cdot\text{C}(\text{OR})_2\cdot\text{CF}_3$ yields $\beta\beta\beta$ -trifluoropropaldehyde and hexafluorobut-2-one. Hydrolysis of 1-cyano-3 : 3 : 3-trifluoropropene gives $\gamma\gamma\gamma$ -trifluorocrotonic acid, independently synthesised by the interaction of trifluoriodomethane and acrylonitrile followed by treatment with alkali. The addition of hydrogen bromide in ultra-violet light to trifluoropropyne and hexafluorobut-2-yne is reported.

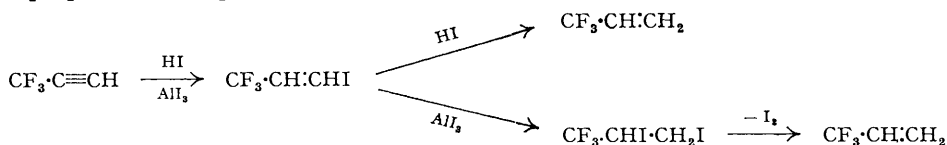
The importance of hyperconjugated structures of the type $\text{F}-\text{CF}_2\cdot\text{C}\cdot\text{C}\angle$ in olefinic and acetylenic fluorine compounds is discussed.

As part of a general study of the influence of perfluoroalkyl groups on the properties of adjacent organic functional groups, an investigation has been made of ionic and free-radical addition reactions to 3 : 3 : 3-trifluoropropyne and to hexafluorobut-2-yne, compounds in which the functional group is $-\text{C}\equiv\text{C}-$. When X = F, Cl, Br, I, addition of HX to trifluoropropyne gave $\text{CF}_3\cdot\text{CH}\cdot\text{CHX}$, *i.e.*, addition was opposite to that in propyne. The reaction when X = F, Cl, or Br took place smoothly and without catalysts; the addition of hydrogen chloride and bromide was particularly rapid. Use of an excess of hydrogen halide did not bring about the addition of 2 mols. under moderate conditions. Boron trifluoride (when X = F) or aluminium halides (X = Cl or Br) catalysed the addition reactions, and the addition of hydrogen bromide, for example, could thereby be brought about at a lower temperature. The use of aluminium tri-iodide was necessary to effect addition of hydrogen iodide at room temperature. At higher temperatures, and in presence of an excess of hydrogen iodide, were obtained aluminium fluoride, 3 : 3 : 3-trifluoro-1-iodopropene, 3 : 3 : 3-trifluoropropene, and unidentified higher-boiling products. The

* Part VI, preceding paper.

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formation of the trifluoropropene may be attributed to the reduction of 3 : 3 : 3-trifluoro-1-iodopropene or, less probably, to elimination of iodine from a di-iodide :

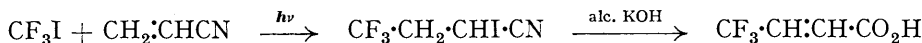


Addition of iodine to 3 : 3 : 3-trifluoropropene to give a stable di-iodide could not be achieved.

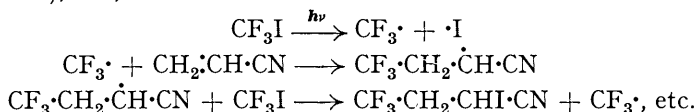
The addition of hydrogen bromide under the influence of ultra-violet radiation was carried out with conditions such that the ionic reaction could not occur; the product was exclusively 1-bromo-3 : 3 : 3-trifluoropropene. Trifluoropropyne thus yields the same product from the ionic or the free-radical addition of hydrogen bromide.

The addition of hydrogen cyanide to trifluoropropyne was slow with the temperature and catalyst used, but a satisfactory yield of $\gamma\gamma\gamma$ -trifluorocrotonic acid was obtained by hydrolysis of the addition product. The structure of the fluorocrotonic acid is supported by its infra-red spectrum. Thermal decomposition of the sodium salt of the acid in ethylene glycol containing boric acid gave the expected 3 : 3 : 3-trifluoropropene, but even when the olefin was removed from the reaction medium as rapidly as possible, appreciable attack on the allylic trifluoromethyl group was apparent. Application of the simultaneous iodination and decarboxylation technique (Haszeldine, *J.*, 1951, 584) to silver $\gamma\gamma\gamma$ -trifluorocrotonate yielded exclusively 3 : 3 : 3-trifluoro-1-iodopropene, $\text{CF}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Ag} \xrightarrow{\text{I}_2} \text{CF}_3\cdot\text{CH}\cdot\text{CHI} + \text{CO}_2 + \text{AgI}$, thereby eliminating the possibility of formation of 2-cyano-3 : 3 : 3-trifluoropropene by the interaction of trifluoropropyne and hydrogen cyanide.

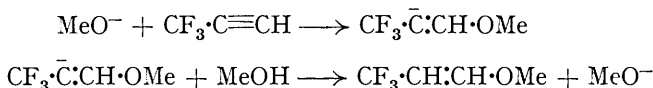
An independent synthesis of $\gamma\gamma\gamma$ -trifluorocrotonic acid was made by the addition of trifluoroiodomethane to acrylonitrile under the influence of ultra-violet light, followed by dehydroiodination and hydrolysis of the idonitrile :



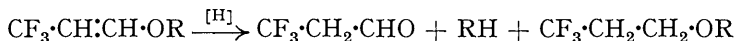
The photochemical addition reaction probably proceeds by the free-radical chain mechanism (Haszeldine, *J.*, 1949, 2856; 1950, 2037; preceding paper; Haszeldine and Steele, *Chem. and Ind.*, 1951, 684), *viz.*,



Treatment of trifluoropropyne with methyl or ethyl alcohol in the presence of the corresponding alkoxide yields the 1-alkoxy-3 : 3 : 3-trifluoropropenes by nucleophilic attack, *e.g.*,

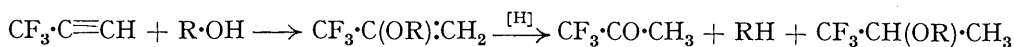


The structures of the vinylic ethers were proved by treatment with hydrogen under pressure in presence of Raney nickel: partial hydrogenation to the known 1-alkoxy-3 : 3 : 3-trifluoropropanes occurred, but the main reaction was hydrogenolysis to methane or ethane and 3 : 3 : 3-trifluoropropaldehyde :



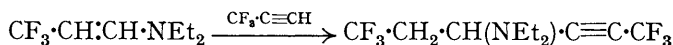
The aldehyde was identified and estimated as its 2 : 4-dinitrophenylhydrazone, and the absence of trifluoroacetone was shown by removal of the aldehyde as the dimedone derivative followed by testing with 2 : 4-dinitrophenylhydrazine. The absence of trifluoroacetone and of the known isomeric 2-ethoxy-3 : 3 : 3-trifluoropropane, whose boiling

point differs appreciably from that of the 1-ethoxy-compound, proved that the alternative reaction



did not occur. The 1-alkoxy-3 : 3 : 3-trifluoropropenes gave $\beta\beta\beta$ -trifluoropropaldehyde and the alkyl iodide on treatment with hydriodic acid, and trifluoroacetone could not be detected.

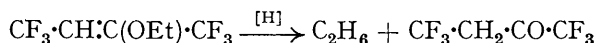
As with the addition of hydrogen halide, the addition of the alcohols tended to stop with the formation of the vinyl compound, even in the presence of excess of alcohol. The addition of a second mol. of an alcohol was effected at higher temperatures, but was accompanied by appreciable conversion of the trifluoromethyl groups into fluoride. The dialkoxy-compound was not isolated in the pure state but was immediately hydrolysed with sulphuric acid to give only 3 : 3 : 3-trifluoropropaldehyde, the formation of which proves that the addition of the second mol. of alcohol gave 1 : 1-diethoxy-3 : 3 : 3-trifluoropropane. By a similar nucleophilic attack on trifluoropropyne was obtained a moderate yield of 1-diethylamino-3 : 3 : 3-trifluoropropene; the direction of addition was assumed by analogy with the alcohol addition reactions. An unidentified by-product from the interaction of trifluoropropyne and diethylamine contained a triple bond, and by analogy with the work of Rose and Gale (*J.*, 1949, 793) on phenylacetylene may be formed as follows :



The reaction of hydrogen halide ($\text{X} = \text{Cl}, \text{Br}$) with hexafluorobut-2-yne was slow in the absence of an aluminium halide catalyst. In both cases addition tended to stop at the 2-halogeno-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene stage even in the presence of excess of hydrogen halide; aluminium fluoride was also formed, and it is possible that this may be the active catalyst. By contrast, the photochemical addition of hydrogen bromide was rapid and almost quantitative. Reaction again stopped at the 2-bromohexafluorobut-2-ene stage, and the only by-product was 2 : 3-dibromohexafluorobut-2-ene. There was no reaction between hydrogen bromide and hexafluorobut-2-yne in the dark.

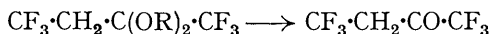
Although the aluminium halide-catalysed addition of hydrogen halide was slow, nucleophilic attack on hexafluorobut-2-yne occurs very readily. The addition of both methanol and ethanol in presence of their respective alkoxides took place below 0° and yielded the vinyl ethers. Fluoride was again formed by attack on the trifluoromethyl groups. A recent patent by Chaney (*Chem. Abs.*, 1951, 45, 2015) also describes the addition of ethanol to hexafluorobut-2-yne.

The vinyl ethers yielded trifluoroacetic acid on oxidation and gave dibromides. The ethyl ether underwent catalytic hydrogenolysis :



at higher temperatures than required for 1-ethoxy-3 : 3 : 3-trifluoropropene, but the formation of the hydrogenated ether was not observed. The ketone was also formed by the interaction of the 2-alkoxy-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutenes and hydriodic acid.

Addition of methanol or ethanol to the 2-alkoxyhexafluorobut-2-enes was achieved more readily than with the corresponding alkoxytrifluoropropene, and yielded the 2 : 2-dialkoxyhexafluorobutanes, small amounts of which were obtained during the initial formation of the 2-alkoxyhexafluorobutenes from hexafluorobutyne. The direction of addition of the second molecule of alcohol was proved by the formation of 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutan-2-one on treatment of the dialkoxy-compounds with sulphuric acid :

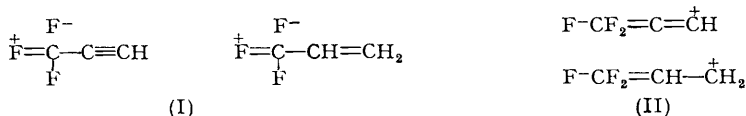


This route is more convenient than the original procedure for the butanone (Henne, Schmitz, and Finnegan, *J. Amer. Chem. Soc.*, 1950, 72, 4195).

Secondary amines also undergo ready reaction with hexafluorobut-2-yne; *e.g.*, diethylamine gave 2-diethylaminohexafluorobut-2-ene, $\text{CF}_3\cdot\text{CH}:\text{C}(\text{NEt}_2)\cdot\text{CF}_3$, and the addition of a second mol. of the amine could not be effected under moderate conditions.

Discussion.—The addition of HX to trifluoropropyne to give exclusively $\text{CF}_3\cdot\text{CH}\cdot\text{CHX}$ indicates that the polarisation of the alkyne molecule during ionic reactions is $\text{F}_3\text{C}\leftarrow\text{C}\equiv\text{CH}$. The reversal of polarisation compared with that of propyne is similar to that for 3 : 3 : 3-trifluoropropene, deduced from the direction of addition of hydrogen fluoride, chloride, and bromide and of alcohols (unpublished data; see also Henne and Kaye, *ibid.*, p. 3369).

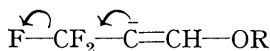
Two main effects must be distinguished in considering the effect of a trifluoromethyl group on an adjacent unsaturated group such as $-\text{C}\equiv\text{CH}$ or $-\text{CH}:\text{CH}_2$, *viz.*, (a) the powerful inductive effect of the trifluoromethyl group, which may be deduced from the fact that trifluoroacetic acid is appreciably stronger than trichloroacetic acid, and (b) resonance effects. Concerning (b), double-bonded structures of type (I) affect only the trifluoromethyl group, but hyperconjugation (no-bond resonance) structures of type (II) involve the unsaturated system, and it is considered that, owing to the extreme negativity of fluorine, such resonance structures make a much greater contribution to the real resonance level than do hyperconjugation structures in hydrocarbon compounds (*e.g.*, $\text{H}^+\text{CH}_2:\text{C}:\bar{\text{C}}\text{H}$). Although the inductive and hyperconjugation effects often act in the same direction concerning reactions involving addition to the unsaturated linkage (*e.g.*, with trifluoropropyne), the possible importance of hyperconjugation effects in the interpretation of the reactions of organic fluorine compounds does not seem to have been fully appreciated.



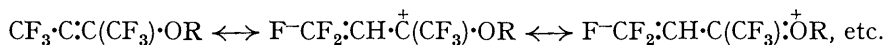
The trifluoromethyl group exerts a marked immobilising or deactivating effect on the unsaturation electrons of the adjacent double or triple bonds towards electrophilic attack; the (assumed) electrophilic additions of hydrogen chloride or bromide to trifluoropropyne proceed readily in absence of a catalyst, but qualitatively are slower than with propyne. The use of aluminium halides is not essential (as with 3 : 3 : 3-trifluoropropene) to bring about reaction. The increased deactivation to electrophilic attack in hexafluorobut-2-yne is revealed by the necessity to use a catalyst to effect addition of hydrogen chloride or bromide at moderate temperatures. Only the mono-addition product is formed from trifluoropropyne and hexafluorobut-2-yne in presence of excess of hydrogen halide, and it is evident that the trifluoromethyl groups deactivate the double bond more than the triple bond towards electrophilic attack.

Decreased activity to electrophilic attack is accompanied by increased susceptibility to nucleophilic attack, and the reactions of alcohols or of amines with the triple bond in the perfluoroalkylacetylenes occur almost as readily as with the polyfluoro-olefins such as tetrafluoroethylene or chlorotrifluoroethylene. The reactions tend to stop with the formation of the mono-addition compound, again indicating the greater influence of trifluoromethyl groups on double compared with triple bonds.

The formation of fluoride ion during reaction may occur by direct attack on the trifluoromethyl groups of the alkynes, or by loss of fluoride from the intermediate ion



in a manner outlined earlier for perfluoroalkyl carbanions (Haszeldine, *Nature*, 1951, 168, 1028). Attack on the trifluoromethyl groups of the vinyl ethers is also possible, since hyperconjugation structures make an important contribution to resonance :



The addition of the second molecule of alcohol gives the products expected from the above effects, *e.g.*, $\text{CF}_3\cdot\overset{\curvearrowright}{\text{C}}\text{H}=\text{CH}\cdot\overset{\curvearrowleft}{\text{O}}\text{R} \longrightarrow \text{CF}_3\cdot\text{CH}_2\cdot\text{CH}(\text{OR})_2$. Qualitatively, base-

catalysed addition of one and two molecules of an alcohol, or of one molecule of diethylamine, takes place more readily with hexafluorobutene than with trifluoropropene, presumably because of the increased electron withdrawal from the unsaturated link.

The hydrogenolysis which occurs with the vinyl ethers is similar to that observed with compounds of the type $R \cdot CO \cdot CR' : CH \cdot OEt$ (R , aromatic or aliphatic) (Kötz and Schaeffer, *J. pr. Chem.*, 1913, **196**, 604; Baker and Weiss, *J. Amer. Chem. Soc.*, 1944, **66**, 343; Baker and Schlesinger, *ibid.*, 1946, **68**, 2009). Although hydrogenation accompanies hydrogenolysis in the case of 1-alkoxy-3 : 3 : 3-trifluoropropene, the reaction does not proceed *via* the 1-alkoxy-3 : 3 : 3-trifluoropropane, since this was shown to be stable under the conditions used. Furthermore, the ready hydrogenolysis cannot be correlated completely with the electron drain from the oxygen by the effects outlined earlier, since hydrogenolysis of 2-ethoxy-1 : 1 : 1 : 4 : 4-hexafluorobutene is more difficult and is not accompanied by hydrogenation.

EXPERIMENTAL

Preparation of Trifluoropropene and Hexafluorobut-2-yne.—Trifluoropropene was prepared from trifluoroiodomethane by the methods of Parts IV and V (*loc. cit.*). Hexafluorobut-2-yne was obtained from the addition product of trifluoroiodomethane and 3 : 3 : 3-trifluoropropene, by the bromination, dehydrobromination, and debromination sequence described by Haszeldine (*J.*, 1952, 2504). Unless otherwise stated, reactions were carried out in sealed Pyrex tubes of ca. 50 ml. capacity.

Addition of Hydrogen Halides to Trifluoropropene.—(a) *Hydrogen fluoride.* Into a cooled nickel bomb of 30-ml. capacity was distilled anhydrous hydrogen fluoride (10 ml.) and trifluoropropene (0.94 g.). The bomb was sealed, warmed to room temperature, and kept for 48 hours, the temperature then being raised to 60° for 4 hours. After cooling, the reaction products were distilled into water, and the residual volatile material condensed, washed with water, and transferred to a vacuum system. Fractionation gave 1 : 3 : 3 : 3-tetrafluoroprop-1-ene (1.05 g., 92%) (Found: C, 31.8; H, 2.2%; M , 114. $C_3H_2F_4$ requires C, 31.6; H, 1.75%; M , 114), b. p. -16°. The structure of this compound is known by independent synthesis from vinyl fluoride and trifluoroiodomethane followed by dehydroiodination (Steele, unpublished results). Use of boron trifluoride as catalyst brought about the addition reaction at a lower temperature.

(b) *Hydrogen chloride.* Pure dry hydrogen chloride (0.38 g.) was condensed into a Pyrex Carius tube of 50-ml. capacity containing trifluoropropene (0.94 g.). On warming to room temperature an immediate reaction was apparent, and after 2 hours the tube was opened and the contents were fractionated *in vacuo* to give hydrogen chloride (0.01 g.) and 1-chloro-3 : 3 : 3-trifluoropropene (1.30 g., 100%) (Found: M , 130.5. Calc. for $C_3H_2ClF_3$: M , 130.5), b. p. 21°. The b. p. reported in Part V (*loc. cit.*) was 21°, and the b. p. of 2-chloro-3 : 3 : 3-trifluoropropene was 14—15°. Use of a 100% excess of hydrogen chloride at room temperature gave only 1-chloro-3 : 3 : 3-trifluoropropene, and a dichloro-compound could not be detected.

(c) *Hydrogen bromide.* Anhydrous hydrogen bromide (0.82 g.) and trifluoropropene (0.94 g.) were condensed in a Carius tube. No reaction was observed after 4 hours below -15° (cf. the photochemical addition, below), but after 2 hours at 0° complete reaction had occurred and no unchanged trifluoropropene was detected. The product of reaction was exclusively 1-bromo-3 : 3 : 3-trifluoropropene (1.75 g., 100%) (Found: M , 174. Calc. for $C_3H_2BrF_3$: M , 175), b. p. 40°. The b. p.s of 1-bromo- and 2-bromo-3 : 3 : 3-trifluoropropene are 41° and 33.5° (Part V, *loc. cit.*).

The above experiment was repeated in the presence of aluminium tribromide (0.1 g.) at -25°. Reaction was complete after 4 hours and the product was again exclusively 1-bromo-3 : 3 : 3-trifluoropropene (91% yield). A control experiment showed that aluminium tribromide did not bring about rearrangement of 3 : 3 : 3-trifluoropropene or of 1-bromo-3 : 3 : 3-trifluoropropene under the conditions used. Use of a 300% excess of hydrogen bromide in the absence of aluminium tribromide gave only 1-bromo-3 : 3 : 3-trifluoropropene at room temperature.

(d) *Hydrogen iodide.* The interaction of anhydrous hydrogen iodide (1.38 g.) and trifluoropropene (0.94 g.) at room temperature was very slow in the absence of catalysts. Thermal reaction in a sealed tube at 100° gave a 65% yield of 3 : 3 : 3-trifluoro-1-iodopropene, b. p. 70—71°. Additional material boiling over the range 67—74° was also obtained, however, and could not be resolved into definite fractions by distillation.

When the experiment was repeated in the presence of aluminium tri-iodide (0.25 g.), steady

reaction took place at room temperature and, after 24 hours, fractionation gave trifluoropropyne (17%), hydrogen iodide (19%), and a clean-cut fraction (1.74 g., 80%) of 3 : 3 : 3-trifluoro-1-iodopropene, b. p. 70.5°. The b. p. of this compound recorded in Part II (Haszeldine, *J.*, 1950, 3037) was 70.2°, and since the b. p. of the isomeric 3 : 3 : 3-trifluoro-2-iodopropene is unknown, identity was confirmed by comparison of infra-red spectra.

A similar experiment using a 100% excess of hydrogen iodide at 100° in the presence of aluminium tri-iodide gave 3 : 3 : 3-trifluoro-1-iodopropene (20%), 3 : 3 : 3-trifluoropropene (8%), unidentified higher-boiling material containing free iodine, aluminium trifluoride, and unchanged aluminium tri-iodide.

Addition of Hydrogen Cyanide to Trifluoropropyne.—Trifluoropropyne (0.94 g.) was sealed in a Carius tube with anhydrous hydrogen cyanide (0.81 g.), potassium cyanide (0.1 g.), potassium chloride (0.2 g.), cuprous chloride (0.8 g.), and water (10 ml.), and heated to 110° for 24 hours. Unchanged trifluoropropyne (48%) was recovered. A similar experiment carried out at 120° for 36 hours gave 36% recovered trifluoropropyne. The combined liquid phase was filtered through glass-wool, treated with an excess of 10% sodium hydroxide solution, and slowly heated under reflux to 80°. After filtration the solution was acidified (sulphuric acid) and continuously extracted by ether for 24 hours. After drying (Na_2SO_4), the ether was removed and the residual solid was fractionally recrystallised from light petroleum to give $\gamma\gamma\gamma$ -trifluorocrotonic acid (1.01 g., 62%) (Found: C, 34.1; H, 2.3%; equiv., 140. $\text{C}_4\text{H}_3\text{O}_2\text{F}_3$ requires C, 34.3; H, 2.1%; equiv., 140), m. p. 51°.

The infra-red spectrum of $\gamma\gamma\gamma$ -trifluorocrotonic acid shows a sharp band at 3.26 μ due to the vinylic hydrogen atoms, and strong bands at 7.67, 7.87, and 8.76 μ attributed to carbon-fluorine stretching vibrations. The *trans* $\cdot\text{CH}\cdot\text{CH}\cdot$ group is revealed by bands at 6.00 and 10.28 μ (cf. Haszeldine, *Nature*, 1951, **168**, 1025; *J.*, 1952, 2504), and the carboxyl group produces bands at 3.85 μ (bonded OH group), 5.85 μ (C=O) and 5.93 μ (dimer). Corresponding bands in crotonic acid are 6.06 and 10.31 μ ($\cdot\text{CH}\cdot\text{CH}\cdot$) and 3.85 and 5.85 μ (CO_2H). Other strong bands in the spectrum of trifluorocrotonic acid are at 10.8, 11.54, 13.98, and 14.10 μ .

Decarboxylation of $\gamma\gamma\gamma$ -Trifluorocrotonic Acid.—(a) *Of the sodium salt.* The fluorocrotonic acid was converted into its sodium salt (0.40 g.), which was placed in a flask containing ethylene glycol (15 ml.) and boric acid (2 g.) (cf. Auerbach, Verhoek, and Henne, *J. Amer. Chem. Soc.*, 1950, **72**, 299) and fitted with a reflux condenser leading to traps cooled by liquid air. The temperature was raised from 150° to 200° during 4 hours, and by controlled pumping a vigorous reflux was maintained and the volatile products of reaction removed from the reaction vessel. These were then passed through 15% sodium hydroxide, and the residual gas, dried by distillation *in vacuo*, was found to be 3 : 3 : 3-trifluoropropene (0.99 g., 41%).

(b) *Of the silver salt by iodine.* The silver salt (1.23 g.), prepared from the acid by treatment with silver oxide and carbonate, was dried *in vacuo* and mixed with dry powdered iodine (3 g.). The mixture was then rapidly heated in a silica trap at a pressure of *ca.* 10 mm., so that the reaction products collected in an adjacent trap cooled in liquid air. After removal of the carbon dioxide by allowing the trap to warm to room temperature, the excess of iodine was removed by treatment with thiosulphate, and the liquid distilled to give only 3 : 3 : 3-trifluoro-1-iodopropene (0.83 g., 76%). The absence of isomers was shown by examination of the infra-red spectrum.

Alternative Synthesis of $\gamma\gamma\gamma$ -Trifluorocrotonic Acid.—Acrylonitrile (0.53 g.) was sealed with excess of trifluoroiodomethane (8.5 g.) in a Pyrex tube which was then irradiated by ultra-violet light for 48 hours. The excess of trifluoroiodomethane was removed, and unchanged acrylonitrile (*ca.* 0.01 g.) was distilled from the residual liquid *in vacuo*. The $\gamma\gamma\gamma$ -trifluoro- α -iodobutyronitrile was not isolated in the pure state but was separated from a trace of poly(acrylonitrile) by semimicro-distillation *in vacuo*, and treated immediately with a 5% excess of 10% alcoholic potassium hydroxide, initially at room temperature and finally at 50° for 1 hour. After acidification with excess of dilute sulphuric acid, ether extraction followed by crystallisation from light petroleum gave $\gamma\gamma\gamma$ -trifluorocrotonic acid (1.02 g., 72%), m. p. 50.5–51°.

There was no reaction between trifluoroiodomethane and acrylonitrile in the absence of light.

Photochemical Addition of Hydrogen Bromide.—Hydrogen bromide (0.82 g.) and trifluoropropyne (0.94 g.) were sealed *in vacuo* in a carefully cleaned Pyrex test-tube which was then allowed to warm to -60° at which temperature it was maintained by partly surrounding the reaction vessel by solid carbon dioxide. After 36 hours in the dark the contents of the tube were transferred to a vacuum system without allowing the temperature to rise above -40° ; fractionation *in vacuo* showed that no reaction had occurred.

The experiment was repeated in the same vessel but with irradiation from a Hanovia ultra-violet lamp at a distance of 2 ft. The temperature was kept at $-60^{\circ} \pm 5^{\circ}$ throughout, and after 8 hours the reaction tube was immersed in a bath at -40° , opened, and the volatile reaction products removed by pumping; only a trace of hydrogen bromide was found, and distillation of the product with b. p. $>0^{\circ}$ showed it to be exclusively 1-bromo-3:3:3-trifluoropropene, b. p. $39.5-40^{\circ}$, n_D^{20} 1.357 (see above). A second control experiment was then made in the same tube at -60° and confirmed the absence of reaction in the dark.

Addition of Methanol and Ethanol to Trifluoropropyne.—A Carius tube of 100-ml. capacity was charged with methanol (25 ml.) and sodium (0.5 g.) and, after completion of reaction, was cooled in liquid air. Trifluoropropyne (1.88 g.) was then added, and the tube sealed *in vacuo*. When the tube was allowed to warm, reaction became apparent at *ca.* -20° , and this temperature was therefore maintained for 3 hours, after which no unchanged trifluoropropene could be recovered. The contents of the tube were treated with water (20 ml.) and then dilute hydrochloric acid until almost neutral. The lower layer was then removed, washed with water, dried (P_2O_5), and distilled to give 3:3:3-trifluoro-1-methoxypropene (2.32 g., 92%) (Found: C, 38.0%; *M*, 124. $C_4H_5OF_3$ requires C, 38.1%; *M*, 126), b. p. $83-84^{\circ}$. A test for fluoride on the aqueous solution was positive.

A similar experiment with ethanol instead of methanol at -5° to -10° gave 1-ethoxy-3:3:3-trifluoropropene (2.55 g.; 91%) (Found: C, 42.6%; *M*, 138. $C_5H_7OF_3$ requires C, 42.9%; *M*, 140), b. p. 103° , n_D^{25} 1.349. A. L. Henne and M. Nager have independently obtained this compound by a similar route (personal communication).

The alkoxy-3:3:3-trifluoropropenes gave a positive unsaturation test with potassium permanganate, and on oxidation with alkaline permanganate afforded trifluoroacetic acid, characterised as its amide, in yields of 58 and 62%. The compounds absorbed bromine to give higher-boiling liquids which were not characterised further.

When heated under reflux with an excess of constant-boiling hydriodic acid, 1-methoxy- and 1-ethoxy-3:3:3-trifluoropropene (0.71 g.; 0.81 g.) gave 57 and 61% yields of $\beta\beta\beta$ -trifluoropropaldehyde; methyl and ethyl iodide were also formed.

Hydrogenation of 1-Alkoxy-3:3:3-trifluoropropenes.—A series of Carius tubes were charged with 3:3:3-trifluoro-1-methoxypropene (1.25 g.), hydrogen (0.1 g.), Raney nickel (0.3 g.), and ethanol (4 ml.), and were heated to $10-15^{\circ}$ for 1 hour. The volatile products were found to be methane (80% of theory) (Found: *M*, 16. Calc. for CH_4 : *M*, 16) and hydrogen. The contents of the tubes were poured into water (30 ml.) and filtered, and a small lower layer was removed and examined later. The aqueous solution showed positive tests for an aldehyde, which was shown to be $\beta\beta\beta$ -trifluoropropaldehyde (79% yield) by formation of its 2:4-dinitrophenylhydrazone, m. p. $150.5-151^{\circ}$, mixed m. p. $150-151^{\circ}$. Henne, Pelley, and Alm (*J. Amer. Chem. Soc.*, 1950, **72**, 3370) report m. p. $150-151^{\circ}$.

The experiment was repeated under the same conditions and the yield of 3:3:3-trifluoropropaldehyde (82%) was estimated by formation of its dimedone, m. p. 114° (Part VI, *loc. cit.*). Treatment of the solution after dimedone formation with 2:4-dinitrophenylhydrazine gave only a trace of the 2:4-dinitrophenylhydrazone of the aldehyde, m. p. 150° , and no evidence for the 2:4-dinitrophenylhydrazone of 1:1:1-trifluoroacetone (m. p. $138-139^{\circ}$). The lower layer obtained on pouring the filtered hydrogenation mixture into water was combined with that from the first experiment, washed, dried, and distilled to give 3:3:3-trifluoro-1-methoxypropane (15% yield) (Found: C, 37.9%; *M*, 128. Calc. for $C_4H_7OF_3$: C, 37.5%; *M*, 128), b. p. $54.5-55.5^{\circ}$. Henne and Smook (*J. Amer. Chem. Soc.*, 1950, **72**, 4378) report b. p. 54.8° .

The hydrogenation of 3:3:3-trifluoro-1-methoxypropene (1.25 g.) in a small autoclave under 10 atm. of hydrogen and with freshly-prepared Raney nickel gave a theoretical yield of methane; the yield of 3:3:3-trifluoropropaldehyde was 91%.

Under similar conditions in an autoclave, 1-ethoxy-3:3:3-trifluoropropene (1.41 g.) gave a 98% yield of ethane (Found: *M*, 30. Calc. for C_2H_6 : *M*, 30) and an 89% yield of trifluoropropaldehyde. The reaction of the ether (2.31 g. total) with hydrogen in sealed tubes by the method described above but with methanol as solvent gave ethane (78%), 3:3:3-trifluoropropaldehyde (74%), and 1-ethoxy-3:3:3-trifluoropropane (18%) (Found: C, 42.0%; *M*, 140. Calc. for $C_5H_9OF_3$: C, 42.3%; *M*, 142), b. p. $72-73.5^{\circ}$. Henne and Smook (*loc. cit.*) report b. p. 72.2° for the last compound and $63-64^{\circ}$ for the isomeric 2-ethoxy-3:3:3-trifluoropropane. The yield of 3:3:3-trifluoropropaldehyde was estimated by 2:4-dinitrophenylhydrazone formation from an aliquot and the absence of 1:1:1-trifluoroacetone was shown by tests with 2:4-dinitrophenylhydrazine solution after precipitation of the dimedone derivative.

Under identical conditions, 1-methoxy- and 1-ethoxy-3 : 3 : 3-trifluoropropane showed no reaction with hydrogen and Raney nickel.

Addition of Ethanol to 1-Ethoxy-3 : 3 : 3-trifluoropropene.—(i) There was no indication of the addition of 2 mols. of ethanol to trifluoropropyne at 0° in the presence of sodium ethoxide, even after 7 days. (ii) To pure 1-ethoxy-3 : 3 : 3-trifluoropropene (1.70 g.) was added ethanol (25 ml.) containing sodium ethoxide (4 g.), and the reaction tube was then heated to 80° for 1.5 hour. No volatile products were obtained. The contents of the tube were poured into water to dissolve the precipitated sodium fluoride, and neutralised with sulphuric acid, and the lower layer removed. Distillation *in vacuo* gave a trace of unchanged 1-ethoxy-3 : 3 : 3-trifluoropropene and a residual liquid of higher b. p. Sulphuric acid (1 : 1) was added to the latter, and the mixture was heated to 40° at atmospheric pressure. The evolved gas was passed into 2 : 4-dinitrophenylhydrazine solution, and after 1 hour the temperature of the distilling flask was slowly raised to 120°. After the flask had been swept out with nitrogen, the precipitated 2 : 4-dinitrophenylhydrazone, recrystallised from ethanol, had m. p. 150—151°. The yield of $\beta\beta\beta$ -trifluoropropaldehyde was 28%. Dilution of the sulphuric acid in the distilling flask gave no indication of the presence of residual organic material, and the material evolved by the sulphuric acid treatment reacted completely with the 2 : 4-dinitrophenylhydrazine solution. The sodium fluoride produced by reaction corresponded to *ca.* 50% of the ethoxy-trifluoropropene taken.

Addition of Diethylamine to 3 : 3 : 3-Trifluoropropyne.—Trifluoropropyne (0.94 g.) was sealed with cuprous chloride (0.02 g.) and diethylamine (3 ml.), kept at room temperature for 4 hours, and slowly heated to 100°. Unchanged trifluoropropyne (0.11 g.) was recovered, and after pouring into water (fluoride present), distillation of the lower layer *in vacuo* gave 1-diethylamino-3 : 3 : 3-trifluoropropene (28%) (Found: N, 8.3%; *M*, 161. $C_7H_{12}NF_3$ requires N, 8.4%; *M*, 167), b. p. *ca.* 40°/105 mm. The still residue (0.4 g.) was qualitatively examined by infra-red spectroscopy in the 4 μ region and showed a band at 4.65 μ ascribable to a $C\equiv C$ stretching frequency. Decomposition occurred on attempted distillation.

Addition of Hydrogen Halides to Hexafluorobut-2-yne.—(a) *Hydrogen chloride.* Hexafluorobutyne (0.81 g.) was sealed with a 20% excess of hydrogen chloride in a tube containing aluminium trichloride (0.1 g.). After being at room temperature for 3 hours, the tube was heated to 50° for 30 minutes, cooled, and opened. The non-gaseous products were transferred *in vacuo* to a distilling flask and fractionated to give 2-chloro-1 : 1 : 1 : 4 : 4-hexafluorobut-2-ene (65% yield) (Found: C, 24.0; H, 0.3%; *M*, 195. Calc. for C_4HClF_6 : C, 24.2; H, 0.5%; *M*, 198.5), b. p. 34—35°. Henne, Hinkamp, and Zimmerschied (*J. Amer. Chem. Soc.*, 1945, 67, 1907) report b. p. 34.4° (see also Haszeldine, *J.*, 1952, 2504).

In another experiment with a 200% excess of hydrogen chloride, only the monochloro-hexafluorobutene was isolated. Small amounts of material of higher b. p. were present in both experiments but could not be resolved into definite components on the scale used. Aluminium trifluoride was formed during reaction. Antimony pentachloride was also used to catalyse the addition of hydrogen chloride.

A further experiment on the same scale, with a 20% excess of hydrogen chloride in the absence of aluminium trichloride, gave a 78% yield of the chlorohexafluorobutene after 24 hours' heating at 100°.

Control experiments with hexafluorobut-2-yne and the 2-halogenohexafluorobut-2-enes showed that aluminium chloride or bromide did not bring about appreciable rearrangement under the conditions used.

(b) *Hydrogen bromide.* Hexafluorobut-2-yne (0.82 g.) and hydrogen bromide (20% excess) were sealed with aluminium bromide (0.1 g.) and left in the dark at 30° for 7 days. After removal of the excess of hydrogen bromide, distillation of the liquid products of reaction gave 2-bromo-1 : 1 : 1 : 4 : 4-hexafluorobut-2-ene (68%), b. p. 54—56°, and unidentified material of higher b. p. Aluminium fluoride was found to be present.

(c) *Hydrogen bromide under the influence of ultra-violet light.* There was no reaction between hexafluorobut-2-yne (0.81 g.) and hydrogen bromide (20% excess) after 24 hours in the dark at room temperature. Irradiation of the Pyrex tube with a Hanovia lamp brought about a rapid reaction, and after 2 hours the contents were distilled to give unchanged hexafluorobutyne (8%), hydrogen bromide, 2-bromo-1 : 1 : 1 : 4 : 4-hexafluorobut-2-ene (87%) (Found: C, 20.0; H, 0.3. Calc. for C_4HBrF_6 : C, 19.8; H, 0.4%), b. p. 55° (Haszeldine, *J.*, 1952, 2504, reports b. p. 55°), and a small amount (*ca.* 5%) of 2 : 3-dibromohexafluorobut-2-ene, b. p. 105—107° (Haszeldine, *loc. cit.*, reports b. p. 105°).

Addition of Methanol and Ethanol to Hexafluorobut-2-yne.—Methanol (15 ml.), in which

sodium (0.75 g.) had been dissolved, was sealed in a tube with hexafluorobutene (1.51 g.), and set aside at 0° for 48 hours, then at 30° for 1 hour; 10% of the butyne was recovered unchanged, and after dilution by water, the reaction mixture was acidified with sulphuric acid, and the lower layer removed, washed, dried, and distilled to give 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-methoxybut-2-ene (61% yield) (Found: C, 30.6; H, 1.8%; *M*, 195. $C_5H_4OF_6$ requires C, 30.9; H, 2.1%; *M*, 194), b. p. 55—57°, and a small amount of liquid with higher b. p. which was probably the ketal (see below). A qualitative test for fluoride ion was strongly positive.

Under similar conditions ethanol gave a 57% yield of 2-ethoxy-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (Found: C, 34.4%; *M*, 205, 204. $C_6H_6OF_6$ requires C, 34.6%; *M*, 208), b. p. 72.5—73°; 8% of the hexafluorobutene was recovered, and fluoride ion was again present. Oxidation with alkaline potassium permanganate yielded trifluoroacetic acid. The 2-methoxy- and 2-ethoxy-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-enes absorbed bromine quantitatively to give 2 : 3-dibromo-1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-methoxybutane (Found: C, 16.8. $C_5H_4Br_2F_6$ requires C, 16.9%), b. p. 58—59°/25 mm., n_D^{20} 1.408, and 2 : 3-dibromo-2-ethoxy-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (Found: C, 19.9. $C_6H_6Br_2F_6$ requires C, 19.6%), b. p. 72—73°/32 mm., n_D^{20} 1.409, respectively. The 2-methoxy- and 2-ethoxy-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutenes (1.0 g.) were heated in sealed tubes with constant-boiling hydriodic acid to give 51 and 55% yields of 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutan-2-one, identified as described below.

Hydrogenation of 2-Ethoxy-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene.—Ethoxyhexafluorobutene (2.31 g.) was sealed in a small autoclave with hydrogen (10 atm.), Raney nickel (0.15 g.), and methanol (10 ml.), set aside for 0.5 hour, then heated to 120° for 0.5 hour. The pressure of hydrogen was maintained at 10 atm. throughout. The gaseous products were removed and found to contain ethane (88% of theory). The contents of the autoclave were added to water (20 ml.), and after filtration, addition of semicarbazide gave the semicarbazone of 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutan-2-one (58% yield). The yield was estimated from the weight of semicarbazone, and is therefore probably lower than the true yield of ketone. The semicarbazone (Found: N, 17.8. Calc. for $C_5H_5N_3OF_6$: N, 17.7%), recrystallised from methanol, had m. p. 123°. Henne, Schmitz, and Finnegan (*loc. cit.*) report m. p. 122°. There was no indication of the formation of 2-ethoxy-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane.

Addition of Methanol and Ethanol to 2-Alkoxy-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-enes.—Ethoxyhexafluorobutene (1.65 g.) was sealed in a Carius tube with ethanol (10 ml.) containing sodium ethoxide (1 g.) and heated to 70° for 1 hour. After dilution with water and acidification with sulphuric acid, the lower layer was distilled to give 2 : 2-diethoxy-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (59% yield) (Found: C, 38.0. $C_8H_{11}O_2F_6$ requires C, 38.0%), b. p. 135°, n_D^{20} 1.342. A qualitative test on the solution for fluoride was positive.

The diethoxyhexafluorobutane (0.51 g.) was heated under reflux with sulphuric acid (50%), and the volatile products condensed in semicarbazide solution to give the semicarbazone of 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutan-2-one (53% yield), m. p. 122—123°.

In a similar manner, the interaction of 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-methoxybut-2-ene (1.01 g.) and methanol in the presence of sodium methoxide gave 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2 : 2-dimethoxybutane (53%) (Found: C, 31.8. $C_6H_8O_2F_6$ requires C, 31.9%), b. p. 50°/100 mm. Hydrolysis of this compound by the method described above gave 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutan-2-one in 48% yield. In both cases the hydrolysis was accompanied by appreciable decomposition, and it is possible that the use of dilute acid would give better results.

Addition of Diethylamine to Hexafluorobut-2-yne.—Diethylamine (5 ml.) and hexafluorobutene (1.42 g.) were sealed in a Carius tube which, after 4 days, was heated to 50° for 5 hours. Treatment with excess of water caused separation into two layers, and after being washed and dried the lower layer was distilled to give 2-diethylamino-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (57% yield) (Found: N, 6.0. $C_8H_{11}NF_6$ requires N, 6.0%), b. p. 72—74°/150 mm., 123°/760 mm. (micro), n_D^{20} 1.371.

Analysis for Carbon and Hydrogen.—These were determined by pyrolysis of the fluorine compound in a silica tube packed with silver vanadate and heated to 800°.