594. *The Reactions of Fluorocarbon Radicals. Part II. The Reaction of Trifluoroiodomethane with Acetylene.*

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The interaction of trifluoroiodomethane and acetylene under the influence of heat or of ultra-violet radiation yields 3 : 3 : 3-trifluoro-1-iodoprop-1-ene and probably higher members of the series $CF_3{\cdot}[CH{:}CH]_n{\cdot}I$. The oxidation of 3 : 3 : 3-trifluoro-1-iodopropene to trifluoroacetic acid provides an example of a general method for the synthesis of fluoro-acids, $R{\cdot}CO_2H$, from the fluoroalkyl iodides RI. The use of chlorine trifluoride to prepare iodine pentafluoride and bromine trifluoride is described.

THE reaction of the free trifluoromethyl radical, formed by the homolytic fission of the carbon–iodine bond in trifluoroiodomethane, with ethylene and with tetrafluoroethylene was described in Part I (*J.*, 1949, 2856). The reaction of trifluoroiodomethane with unsaturated compounds has now been extended to the acetylene series, and an addition-polymerisation reaction has been found to occur with acetylene itself.

There was no reaction between trifluoroiodomethane and acetylene in the dark at room temperature, but a smooth reaction took place on heating the mixture in the absence of light or on its exposure to ultra-violet radiation. The main constituent of the product was 3 : 3 : 3-trifluoro-1-iodoprop-1-ene, but small amounts of higher-boiling products including a compound believed to be 5 : 5 : 5-trifluoro-1-iodopenta-1 : 3-diene were also isolated.

The thermal reaction between trifluoroiodomethane and acetylene was carried out in sealed tubes at temperatures above 200°. The fluoroalkyl iodide was slowly and almost quantitatively converted into a liquid contaminated with traces of free iodine. A reaction temperature above 250° brought about fission of the carbon–iodine bond in the addition products and consequent formation of by-products; a cuprene-type fluorine-free polymer derived solely from the acetylene is also formed at these higher temperatures.

The majority of the experiments described in this communication, however, involved the use of ultra-violet light to initiate the reaction between trifluoroiodomethane and acetylene. Reaction occurred in Pyrex as well as in silica vessels, but the latter were preferred since, although a small amount of iodine was liberated, the reaction was appreciably faster. Increasing the pressure of both the reactants increased the rate of reaction but did not appreciably alter the composition of the liquid products, which appear to consist mainly of compounds with one trifluoromethyl group and one iodine atom per molecule. The reaction mechanism suggested is therefore :

$$CF_3I + h\nu \longrightarrow CF_3{\cdot} + {\cdot}I$$
$$CF_3{\cdot} + CH{\equiv}CH \longrightarrow CF_3{\cdot}CH{=}CH{\cdot} \text{ (chain initiation)}$$
$$CF_3{\cdot}CH{=}CH{\cdot} + CF_3I \longrightarrow CF_3{\cdot}CH{=}CHI + CF_3{\cdot} \text{ (chain termination)}$$

Chain propagation,

$$CF_3{\cdot}CH{=}CH{\cdot} + CH{\equiv}CH \longrightarrow CF_3{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}, \text{ etc.,}$$

probably occurs, but has yet to be proved conclusively. Chain termination by abstraction of an iodine atom from a molecule of trifluoroiodomethane by a growing radical chain is in accord with the liberation of only traces of molecular iodine, with the absence of compounds of the type $CF_3{\cdot}[CH{=}CH]_n{\cdot}CF_3$, and with the absence, under optimum conditions, of compounds of general formula $CF_3{\cdot}[CH{=}CH]_n{\cdot}CH{=}CH_2$ (n = 0, 1, 2, etc.) formed by chain termination involving hydrogen abstraction. The addition of two molecules of trifluoroiodomethane to acetylene occurred to only a very slight extent, if at all.

Steacie ("Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, 1946, p. 166) has suggested that the polymerisation of acetylene by methyl radicals derived from azomethane at 300° could proceed *via* the primary reactions

$$(a)\quad CH_3{\cdot} + C_2H_2 \longrightarrow CH_4 + C_2H{\cdot}$$
or
$$(b)\quad CH_3{\cdot} + C_2H_2 \longrightarrow CH_3{\cdot}CH{=}CH{\cdot}$$

Since fluoroform was not obtained by the interaction of trifluoroiodomethane and acetylene, it is evident that a reaction of type (*a*) did not occur.

The 3 : 3 : 3-trifluoro-1-iodopropene did not undergo further reaction with acetylene to give higher members of the polymer series under the conditions used. Increasing the temperature above 250° brought about side-reactions by the pyrolysis of the fluoroiodopropene, whereas irradiation of mixtures of this compound and acetylene led to the formation of 3 : 3 : 3-trifluoroprop-1-ene :

$$CF_3{\cdot}CH{=}CHI + RH \longrightarrow CF_3{\cdot}CH{=}CH_2 + R{\cdot} + {\cdot}I$$

where RH is a compound containing hydrogen, probably acetylene. Trifluoropropene was also formed when mixtures of trifluoroiodomethane and acetylene in silica vessels were irradiated for long periods, or when a large excess of acetylene was present during the reaction. In the latter case, the $CF_3{\cdot}CH{=}CH{\cdot}$ radicals were apparently terminated by collision with acetylene molecules instead of by collision with trifluoroiodomethane molecules.

The liquid products other than 3 : 3 : 3-trifluoro-1-iodopropene have received preliminary examination. An unsaturated compound $C_5H_4IF_3$, which yielded trifluoroacetic acid on oxidation, is believed to be $CF_3{\cdot}CH{=}CH{\cdot}CH{=}CHI$, the second member of the polymer series.

The presence of a double bond in 3 : 3 : 3-trifluoro-1-iodopropene is shown by the formation of an unstable solid dichloro-compound on treatment with gaseous chlorine. The addition of bromine to a double bond adjacent to a perfluoroalkyl group is apparently difficult, since a dilute solution of bromine in an organic solvent is not immediately decolorised; a slow reaction involving the liberation of iodine occurs when the mixture is kept. The double bond adjacent to the trifluoromethyl group in 3 : 3 : 3-trifluoro-1-iodopropene is, however, susceptible to oxidation, and treatment with potassium permanganate yielded trifluoroacetic acid, with fluoroform as a by-product. By the series of reactions

$$RI \longrightarrow R{\cdot}CH{=}CHI \longrightarrow R{\cdot}CO_2H$$

it is possible therefore to replace the iodine atom in a fluoroalkyl iodide, RI, by a carboxyl group. This conversion is of interest since it cannot be carried out by direct nucleophilic replacement with metal cyanides, or by the homolytic reaction involving irradiation with cyanogen. Furthermore, it illustrates one of the ways in which the fluoroalkyl iodides may be used in synthetic organic fluorine chemistry.

Most of the trifluoroiodomethane used in connection with the present studies was prepared from carbon tetraiodide and iodine pentafluoride, as described in Part I. Trifluoroiodomethane can also be prepared, in low yield, by the direct interaction of carbon tetraiodide and fluorine diluted by nitrogen. Another and better method which involves the decarboxylation of salts of trifluoroacetic acid with simultaneous iodination has been described recently (Haszeldine, *Nature*, 1950, **166**, 192).

Iodine pentafluoride is normally prepared by the direct combination of fluorine and iodine. An alternative, rapid, and often more convenient method is to treat iodine with chlorine trifluoride; bromine trifluoride may be prepared similarly by the interaction of bromine and chlorine trifluoride. It has been found that chlorine trifluoride dissolves in iodine pentafluoride and in bromine trifluoride, and is not evolved on heating of the mixtures to temperatures above the boiling point of chlorine trifluoride (12°). Liquids which are intermediate in boiling point and are vigorous fluorinating agents are thereby obtained, and are being studied further.

EXPERIMENTAL.

Reaction between Trifluoroiodomethane and Acetylene under the Influence of Heat.—The acetylene used in the experiments described was withdrawn from a commercial cylinder and purified by fractionation *in vacuo.*

Trifluoroiodomethane (4·5 g.) and excess of acetylene (1·0 g.) were condensed *in vacuo* into a Pyrex reaction tube of *ca.* 50-ml. capacity. After 6 hours' heating at 220° in a rocking furnace in the absence of light, 33% of the iodide had reacted. When the time of reaction was extended to 24 hours, 30% of the acetylene, but no trifluoroiodomethane, was recovered unchanged, and a pink liquid (4·6 g.) of b. p. above room temperature was present. The liquid products from thermal experiments of the type described above had the same composition as those from the light-initiated reactions (see below). A temperature of 220—250° brings about a complete conversion of trifluoroiodomethane into polymers.

Reaction of Trifluoroiodomethane and Acetylene in Pyrex Vessels under the Influence of Ultra-violet Radiation.—There was no reaction when trifluoroiodomethane and acetylene were kept in the dark in a sealed tube for several weeks.

When trifluoroiodomethane (4·5 g.) and excess of acetylene (1·0 g.) were shaken at room temperature in a vibro-shaker and irradiated by a Hanovia lamp (with a U-type self-starting arc tube) used without the Wood's filter at a distance of 12″ from the vessel, the majority of the radiation of wave-length below 3000 A. was absorbed by the thick walls of the reaction tube. A slow reaction occurred, and a liquid contaminated by a small amount of iodine collected in the tube. Thirty % of the fluoroiodide was recovered after reaction for 75 hours, and the product (3·5 g.) was retained for later examination.

The time of irradiation required to bring about appreciable reaction in Pyrex vessels varied slightly with the thickness of the vessel (1—2 mm.). In typical experiments, irradiation for 4—5 days converted

70% of the iodide taken (4·5 g.) into polymer (5·0 g.) in 98% yield, assuming that the polymer consisted entirely of the 1 : 1 adduct. The presence of excess of acetylene (up to twice that theoretically required to give a 1 : 1 adduct) did not change the percentage of the 1 : 1 adduct in the polymer. Excess of acetylene was present at the end of such experiments.

The free iodine in the product was removed by shaking it with mercury, and the colourless liquid was fractionally distilled. About 80% of the crude polymer was the 1 : 1 adduct, 3 : 3 : 3-*trifluoro*-1-*iodoprop*-1-*ene* (Found : C, 16·0; H, 1·2; I, 56·7; F, 25·3%; *M*, 220. $C_3H_2IF_3$ requires C, 16·2; H, 0·9 I, 57·2; F, 25·7%; *M*, 222).

From the higher-boiling material a compound $C_5H_4IF_3$, b. p. *ca.* 40°/30 mm., tentatively identified as 5 : 5 : 5-*trifluoro*-1-*iodopenta*-1 : 3-*diene* was isolated (Found : C, 24·7; H, 1·9; I, 50·9%; *M*, 240. $C_5H_4IF_3$ requires C, 24·2; H, 1·6; I, 51·2%; *M*, 248). This compound, amounting to 1—2% of the crude polymer, is unsaturated and can be oxidised by potassium permanganate to trifluoroacetic acid; this suggests that it contains a $CF_3{\cdot}C{\equiv}C$ unit. An unidentified compound, b. p. 130°, n_D^{25} 1·478, was also isolated in small amount.

Reaction of Trifluoroiodomethane and Acetylene in Silica Vessels under the Influence of Ultra-violet Radiation.—More iodine is liberated during reaction in silica than in Pyrex vessels, but never more than 3% of that theoretically possible. Unlike the reaction of trifluoroiodomethane and ethylene (Haszeldine, *loc. cit.*), which proceeds to completion on irradiation, complete conversion of trifluoroiodomethane into polymer in the presence of acetylene is obtained only by prolonged irradiation. It is convenient to irradiate for a time sufficient to bring about 80—85% conversion in order to prevent excessive decomposition.

Typical experiments carried out at room temperature in sealed silica tubes of 100-ml. capacity are recorded in Table I, and illustrate the effect of exposure time on the reaction. CF_3I (4·5 g.) theoretically requires C_2H_2 (0·6 g.) to give a 1 : 1 adduct. Several pairs of experiments were performed with a particular set of reaction conditions to obtain sufficient product for distillation.

TABLE I.

CF_3I (g.).	C_2H_2 (g.).	Time of reaction (hrs.).	CF_3I recovered (%).	C_2H_2 recovered (%).	Polymer (g.).	1 : 1 Adduct in polymer (%).
4·5	0·75	5	75	80	2·40	77
4·5	0·75	5				
4·5	0·75	14	49	47	4·91	84
4·5	0·75	14				
4·5	0·75	48	20	27	8·12	83
4·5	0·75	48				
4·5	0·75	72	15	25	8·55	81
4·5	0·75	72				
4·5	0·75	96	11	14	8·86	78
4·5	0·75	96				

The effect of increasing the pressure in 50-ml.-capacity reaction tubes is shown in Table II. Several experiments were performed with each particular set of reaction conditions, and the theoretical yield of polymer was taken as that for a 1 : 1 adduct. The yield of polymer decreases with increase in pressure; the side-reactions caused by the irradiation of the excess of acetylene also increase, and cuprene is formed on the surface of the silica.

TABLE II.

CF_3I (g.)	4·5	4·5	4·5	4·5	4·5	4·5	4·5
C_2H_2 (g.)	0·6	0·7	0·8	0·9	1·0	1·2	1·5
Time of irradiation (hrs.)	15	15	15	15	15	15	15
CF_3I recovered (%)	53	50	46	43	42	38	35
Yield of polymer (%)	97	97	95	90	86	75	70

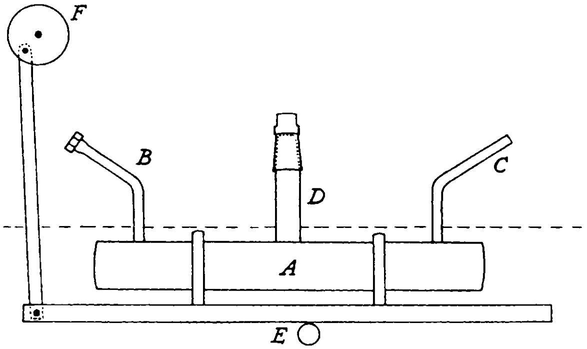
When a large excess of acetylene is present, some 3 : 3 : 3-trifluoroprop-1-ene is formed. The last three experiments in Table II, for example, gave a total of 1·4 g. of this compound (Found : *M*, 96; b. p. −22°. Calc. for $C_3H_3F_3$: *M*, 96. Henne and Waalkes, *J. Amer. Chem. Soc.*, 1946, **68**, 496, report b. p. −17° to −19°, and Robbins, *J. Pharmacol.*, 1946, **86**, 197, reports b. p. −24°). For further identification this was converted into the chloro-adduct, $CF_3{\cdot}CHCl{\cdot}CH_2Cl$, b. p. 75—76°, n_D^{25} 1·367 (Found : Cl, 41·5%; *M*, 165. Calc. for $C_3H_3Cl_2F_3$: Cl, 42·5%; *M*, 167). Henne and Whaley (*J. Amer. Chem. Soc.*, 1942, **64**, 1157) report b. p. 76·7°, n_D^{25} 1·3671.

Properties of 3 : 3 : 3-*Trifluoro*-1-*iodoprop*-1-*ene*.—This compound is a colourless liquid, b. p. 70·2°, n_D^{25} 1·420, with the characteristic odour of iodofluorocarbons. It fails to decolorise bromine immediately in organic solvents, but a slow reaction takes place; aqueous potassium permanganate reacts instantaneously. The presence of a double bond is proved by the addition of chlorine to give an unstable pale yellow solid, m. p. 45—46·5° (forthcoming communication).

Oxidation of 3 : 3 : 3-*Trifluoro*-1-*iodoprop*-1-*ene*.—The fluoroiodopropene (15 g.) was added dropwise during 2 hours to a stirred solution of potassium permanganate (30 g.) and potassium hydroxide (20 g.) in water (200 ml.) at 85—90°. Gaseous products passing through a reflux condenser were collected in a trap cooled by liquid nitrogen. Heating was continued for a further 2 hours with the addition of four 5-ml. portions of water down the condenser to remove oily globules. The volatile product of reaction was fluoroform (0·4 g., 8%; *M*, 70), identified tensimetrically.

The contents of the flask were treated with sulphur dioxide, acidified with sulphuric acid to discharge the carbon dioxide, made alkaline with potassium hydroxide, filtered, and evaporated to 50 ml. The solution was acidified with sulphuric acid and extracted by ether. The ether was removed, the residual acid neutralised to bromothymol-blue with potassium hydroxide, and the solution was evaporated to dryness. The potassium salt of the acid was extracted by hot absolute alcohol (2 × 100 ml.); the solid obtained by removal of the alcohol was heated with absolute ethyl alcohol (3·5 ml.) and concentrated sulphuric acid (2·5 ml.) under reflux at 80° for 4 hours, and then set aside overnight. The contents of the flask were distilled through a short Vigreux column, and the liquid boiling below 70° was dissolved in ether, cooled in ice, and treated with dry ammonia. Evaporation of the ether yielded trifluoroacetamide (3·1 g., 41%) which after purification by sublimation at 60°/760 mm. and recrystallisation from alcohol had m. p. 75° (Gilman and Jones, *J. Amer. Chem. Soc.*, 1943, **65**, 1458, record m. p. 74·5—75·0°). The optimum conditions for the oxidation were not investigated.

Preparation of Trifluoroiodomethane.—The bulk of the trifluoroiodomethane required for the present investigation was prepared by the method described in Part I. The action of fluorine diluted by nitrogen on carbon tetraiodide has also been investigated and found to give trifluoroiodomethane in 30% yield. Fluorine (5 g./hour) diluted by nitrogen (10 l./hour) was passed over carbon tetraiodide (260 g.) spread along a horizontal, water-cooled copper tube. The course of the reaction was followed by the progress of the hot reaction zone along the tube. The exit gases were passed through silica traps cooled to −100° and −130° respectively. When excess of fluorine was observed towards the end of the reaction, the flow of fluorine was reduced to 2 g./hour, and when fluorine again began to pass through the traps the reaction was stopped. The contents of the traps (iodine pentafluoride and trifluoroiodomethane) were passed through dilute alkali, and the fluoroiodo-compound was further purified by distillation. Its vapour pressure and molecular weight agreed with the values recorded earlier. The yield was 29·5 g. (30%).



Preparation of Iodine Pentafluoride.—(a) *By the interaction of iodine and fluorine.* This is conveniently carried out in the apparatus shown in the diagram. *A* is a nickel or stainless steel tube, 15″ long and 1″ in internal diameter. Powdered iodine (300 g.) is added through tube *D*, of ¾″ internal diameter, which is fitted with a cone and socket lubricated with Cereclor. *A* is held on a platform pivoted at *E* and rocked by an eccentric *F*. Water is circulated over *A* continuously. Fluorine (30 g./hour) is passed into *B* by means of flexible steel bellows tubing, and converts the iodine into the pentafluoride in 90% yield. Rocking is essential during the reaction to prevent the formation of an upper layer of colourless iodine pentafluoride which protects unchanged iodine from attack. The reaction is complete when a sample of liquid withdrawn through *D* is colourless. A slight excess of fluorine can be detected at *C* towards the end of the experiment.

(b) *By the interaction of iodine and chlorine trifluoride.* Chlorine trifluoride, now available commercially in cylinders, eliminates the need for elementary fluorine in the laboratory-scale preparation of iodine pentafluoride. Iodine (200 g.) is placed in a nickel (or stainless steel) tube fitted with a flange or, more conveniently, with a large nickel cone and socket, and an inlet tube which reaches almost to its base. The exit tube passes into a fume chamber. Chlorine trifluoride is passed down the inlet tube, slowly at first, then more rapidly once liquid has been formed in the reaction vessel. The initial addition of 10 ml. of iodine pentafluoride enables the chlorine trifluoride addition to be rapid throughout. Heat is evolved, and passage of chlorine trifluoride is continued until a test portion of the liquid is colourless.

Chlorine trifluoride dissolves in iodine pentafluoride and is not evolved on heating the solution to 60—70° (ClF_3 boils at 12°). This phenomenon is being investigated further. In one instance chlorine trifluoride was passed slowly into iodine pentafluoride at 40° until a 30% increase in volume had occurred. The colourless, mobile chlorine trifluoride–iodine pentafluoride mixtures are vigorous fluorinating agents, and dilute solutions of chlorine trifluoride in iodine pentafluoride are of value for experiments in which a liquid fluorinating agent intermediate in reactivity between iodine pentafluoride and the very vigorous chlorine trifluoride or bromine trifluoride is required.

The crude iodine pentafluoride prepared as described above is decanted into a silica tube to separate it from the orange solid (probably iodine trichloride) which has sublimed on to the upper walls of the reaction vessel. The chlorine trifluoride dissolved in the iodine pentafluoride is removed by the addition of iodine in portions until a permanent dark colour is obtained. During this process, small particles of iodine sometimes burn in the vapour above the liquid; cotton wool will also inflame in the vapour.

Iodine pentafluoride prepared in this way contains small amounts of chlorine (probably as dissolved iodine mono- or tri-chloride) which cannot be removed completely by distillation.

Bromine trifluoride also dissolves chlorine trifluoride and the latter is not evolved on heating the solution to temperatures above its b. p. A convenient method for the preparation of bromine trifluoride without resource to elementary fluorine is to pass the theoretical amount of chlorine trifluoride into bromine in a cooled nickel vessel of the type described above. The crude yellow bromine trifluoride can be purified by distillation.

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[*Received, May 25th* 1950.]