595. *Reactions of the Perfluoroalkyl Radicals.*

By (Miss) J. Banus, H. J. Emeléus, and R. N. Haszeldine.

The absorption spectra of trifluoroiodomethane and pentafluoroiodoethane are continuous in the near ultra-violet, and irradiation is believed to yield the trifluoromethyl and pentafluoroethyl radicals. The increase in the rate of photodecomposition of trifluoroiodomethane by the addition of oxygen, chlorine, cyanogen, or ethylene is attributed to the reaction of the added substance with one of the products of homolytic fission of the fluoro-iodide. Semi-quantitative observations on the quantum yields of certain of these reactions are recorded. The reactions of the CF_3 radical, produced thermally or photochemically, with ethyl alcohol, hexane, or water yields fluoroform whilst chlorotrifluoromethane is formed by reaction with carbon tetrachloride. The mercurials $C_2F_5{\cdot}HgX$ (X = F, Cl, Br, and OH) and $Hg(C_2F_5)_2$ have been synthesised.

The preparation of trifluoroiodomethane and pentafluoroiodoethane has been described recently (Banks, Emeléus, Haszeldine, and Kerrigan, *J.*, 1948, 2188; Emeléus and Haszeldine, *J.*, 1949, 2948). It is believed that these fluoro-iodides yield the free perfluoroalkyl radicals when heated above 100° or when irradiated with ultra-violet light, and this view is consistent with the synthesis of trifluoromethylmercuric iodide and bistrifluoromethylmercury from trifluoroiodomethane (Emeléus and Haszeldine, *J.*, 1949, 2953). Other reactions of trifluoroiodomethane and pentafluoroiodoethane initiated by heat or by light have now been studied, and the results obtained lend further support to the postulation of homolytic fission of the carbon–iodine bonds in these compounds.

The absorption spectra of trifluoroiodomethane and pentafluoroiodoethane are similar to those of methyl and ethyl iodides in the near ultra-violet. Both fluoro-iodides show continuous absorption with maxima in each case at *ca.* 2680 A. Chloro- and bromo-trifluoromethane, on the other hand, do not absorb above 2300 A.

Irradiation of trifluoroiodomethane in the vapour phase produced very little decomposition, and the quantum yield was found to be less than 0·002. This value is similar to those for the alkyl iodides (West and Ginsburg, *J. Amer. Chem. Soc.*, 1934, **56**, 2626; West and Schlesinger, *ibid.*, 1938, **60**, 981). The only decomposition products detected were iodine, hexafluoroethane, and traces of silicon tetrafluoride formed by reaction of the trifluoromethyl radical with the vessel. The rate of decomposition was greatly increased by the addition of substances capable of reaction with the primary photo-dissociation products, $CF_3{\cdot}$ and ${\cdot}I$, and so preventing primary recombination. Thus, in the presence of oxygen, the quantum yield was increased to 0·7—0·8, and carbonyl fluoride and iodine were formed. Complete separation and identification of the products was not achieved and the mechanism of the oxidation of the trifluoromethyl radical is not yet clear. It may proceed *via* a peroxide (*e.g.*, CF_3O_2) as postulated by Blaedel, Ogg, and Leighton (*ibid.*, 1942, **64**, 2499) for the photo-oxidation of methyl iodide which yields formaldehyde, paraformaldehyde, methylal, and iodine. The first of these products is the analogue of carbonyl fluoride.

Irradiation of trifluoroiodomethane and chlorine gave a quantitative yield of chlorotrifluoromethane. The rate on irradiation was about ten times that of the slow dark reaction. Iodine trichloride was deposited on the walls of the reaction vessel in the early stages, but if the ratio of chlorine to trifluoroiodomethane was less than 2 : 1 the iodine trichloride was gradually converted into iodine monochloride and eventually into iodine as the reaction proceeded. Since light which can be absorbed by chlorine was not excluded, this reaction can involve the interaction of a trifluoromethyl radical and chlorine, or the attack of a chlorine atom on trifluoroiodomethane, or both.

Cyanogen and trifluoroiodomethane under similar conditions gave cyanogen iodide and hexafluoroethane, and trifluoroacetonitrile was not formed. Pentafluoroiodoethane yielded cyanogen iodide and perfluorobutane. Cyanogen itself absorbs only below 2240 A. (Hogness and Liu Sheng Ts'Ai, *ibid.*, 1932, **54**, 123), and it is apparent that the reactions of the perfluoroalkyl radicals with cyanogen are too endothermic to proceed under the conditions used, and that combination of these radicals with cyanogen radicals does not occur. That trifluoroacetonitrile was not formed and subsequently destroyed was shown by the facts that the pure compound was not photolysed, nor did mixtures of it with iodine react on irradiation.

The photochemical reaction of trifluoroiodomethane with ethylene proceeds under the conditions employed with a quantum yield of approximately four, a value which is in agreement with the formation of short-chain polymers of the type $CF_3\cdot[CH_2\cdot CH_2]_n\cdot I$ (Haszeldine, *J.*, 1949, 2856).

The trifluoromethyl radical is sufficiently reactive to abstract hydrogen from water at elevated temperatures. In the presence of mercury, mercuric hydroxide is also produced, and the reaction may be represented as:

$$CF_3\cdot + H_2O \longrightarrow CF_3H + \cdot OH \xrightarrow{Hg} Hg(OH)_2$$

Organic liquids undergo reaction with trifluoroiodomethane when heated to 200°. Thus, ethyl alcohol gives fluoroform and acetaldehyde, possibly derived as follows:

$$CF_3\cdot + CH_3\cdot CH_2\cdot OH \longrightarrow CHF_3 + CH_3\cdot\dot{C}H\cdot OH$$
$$2CH_3\cdot\dot{C}H\cdot OH \longrightarrow CH_3\cdot CH_2\cdot OH + CH_3\cdot CHO$$

Acetaldehyde is also formed from trifluoroiodomethane and ether. The trifluoromethyl radical abstracts hydrogen from *n*-hexane to give fluoroform and hexene; the reaction may be represented by the equations:

$$CF_3\cdot + C_6H_{14} \longrightarrow CHF_3 + C_6H_{13}\cdot$$
$$2C_6H_{13}\cdot \longrightarrow C_6H_{14} + C_6H_{12}$$

An unidentified liquid of high boiling point containing fluorine and idodine was also formed in this reaction, and may have been an adduct of trifluoroiodomethane and hexene (cf. Haszeldine, *loc. cit.*).

The addition of mercury in these reactions decreased the temperature required to cause an appreciable thermal reaction. Mercury greatly increased the quantum yield in the decomposition of trifluoroiodomethane at room temperature, and irradiation of solutions of trifluoroiodomethane in organic liquids at room temperature in the presence of mercury brought about marked reaction. Ethyl alcohol, ether, and hexane, for example, gave fluoroform in almost theoretical yield. Clearly, the function of the mercury was to prevent primary recombination of the trifluoromethyl radial and the iodine atom.

The trifluoromethyl radical was also found to be capable of abstracting chlorine from carbon tetrachloride, and chlorotrifluoromethane and hexachloroethane were formed in good yield. The less reactive hydrocarbon free radicals (triphenylmethyl, benzyl, *tert.*-butyl, etc.) will not abstract chlorine in this way, whereas the free methyl and phenyl radicals do so (Kharasch, Kane, and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 1621).

In the course of this work bispentafluoroethylmercury, the free base pentafluoroethylmercuric hydroxide and some of its salts have been synthesised from pentafluoroiodoethane. Photolysis of the dimercurial was shown to yield perfluorobutane and mercury, whilst reaction with chlorine gave chloropentafluoroethane and mercuric chloride.

Thus, it is now known that free perfluoroalkyl radicals will abstract an electropositive element such as hydrogen from aliphatic compounds, or an electronegative element such as chlorine from halogenated solvents, and that they will combine with mercury. In these respects they clearly resemble the hydrocarbon free radicals.

EXPERIMENTAL.

Quantum yields were measured with a standard apparatus, with a uranyl oxalate actinometer and a mercury lamp operated on a stabilised voltage. The quartz reaction vessel (2 cm. long, 8 cm. in diameter) was kept at 25° and pressure changes were read to 0·1 mm. with a Bourdon gauge. Light of wave-length >4000 A. was eliminated by a filter containing saturated solutions of nickel and cobalt sulphates, and in studying the photo-oxidation of trifluoroiodomethane light below 2400 A. was absorbed by a 50% aqueous solution of acetic acid. Under the conditions used, absorption by the reactants or by the actinometer solution was always complete. Irradiation times of 30—80 minutes were used for actinometric purposes, and in quantum-yield determinations the procedure was to measure the iodine liberated, or the pressure change, for the first 10—20% of the total reaction. The limitations of the measurements are pointed out where necessary. To identify the products, a cylindrical quartz bulb (*A*) of 260-ml. capacity, fitted with tap and joint for attachment to the vacuum system, and sealed quartz or, occasionally, Pyrex tubes were used.

Absorption Spectra of Trifluoroiodomethane and Pentafluoroiodoethane.—A Hilger Spekker photometer and medium quartz (E3) spectrograph with a tungsten-steel spark and 5-cm. cells were used. Chlorotrifluoromethane and bromotrifluoromethane did not absorb above 2350 A. Trifluoroiodomethane pressures of 32·8, 50·6, and 82·1 mm., and pentafluoroiodoethane pressures of 25·5 and 49·5 mm., gave molar extinction coefficients of 16·7 and 16·4 at 19° respectively. The absorption maximum for both fluoro-iodides is at 2680 A. and the long wave-length limits appear to be *ca.* 3170 and 3270 A.

Photo-dissociation and Photo-oxidation of Trifluoroiodomethane.—Trifluoroiodomethane vapour (0·094 g.; $p = 101$ mm.) was irradiated for 26 hours. The pressure decrease was 0·5 mm. and iodine was detected by the starch–iodine reaction. If this pressure change is significant, it represents on the basis of the light absorbed ($2·9$—$3·3 \times 10^{-6}$ N.) a quantum yield of *ca.* 0·002. Irradiation for longer periods (in *A* and in sealed tubes) showed that the photo-decomposition yielded iodine, hexafluoroethane, and traces of silicon tetrafluoride.

The quantum yield when *A* was half filled with mercury was *ca.* 0·1 initially and fell steadily as the reaction proceeded and the mercury surface became covered with mercury iodides and trifluoromethylmercuric iodide.

Trifluoroiodomethane (1·123 g.; $p = 404·5$ mm.) and oxygen (0·115 g.; $p = 253·5$ mm.) were irradiated in *A* for 40 hours. The volatile products contained unchanged fluoroiodide (0·509 g.), oxygen (0·066 g.), carbon dioxide (0·003 g.), and carbonyl fluoride (0·215 g.) (Found : *M*, 68. Calc. for COF_2 : *M*, 66). The fluorine content, after absorption in alkali, was equivalent to 0·210 g. of carbonyl fluoride. In this experiment the fluorine balance in the analysis of the reaction products was incomplete by 60 mg. In further experiments the carbonyl fluoride was characterised tensimetrically in a silica apparatus to prevent partial conversion into silicon tetrafluoride and carbon dioxide by attack on the soda-glass vacuum-system. The vapour-pressure data agreed with values calculated from the equation of Ruff and Miltschitzky (*Z. anorg. Chem.*, 1934, **156**, 155).

The quantum yield was determined in two experiments by irradiating trifluoroiodomethane and oxygen, each at a pressure of 150 mm., and determining the iodine liberated. Values of 0·54 and 0·57 were thereby obtained. Since the exact nature of the products is unknown, the pressure decrease in the reaction could not be used to determine the quantum yield. Determination of the fluorine in the volatile reaction products other than trifluoroiodomethane gave quantum yields of 0·52, 0·49, and 0·55 in successive experiments.

Reaction of Trifluoroiodomethane with Chlorine.—A dark reaction was observed when trifluoroiodomethane (0·287 g.; $p = 300$ mm.) and chlorine (0·102 g.; $p = 324$ mm.) were mixed. After 1 hour the pressure had decreased by 5·2 mm. and after 40 hours by 12·7 mm. The rapid photochemical reaction was shown to yield tensimetrically pure chlorotrifluoromethane. Needle-shaped crystals of iodine trichloride separated initially and these changed to impure liquid iodine monochloride as the reaction proceeded. A mixture of trifluoroiodomethane (0·746 g.; $p = 264·6$ mm.) and chlorine (0·274 g.; $p = 268·2$ mm.) in *A* gave chlorotrifluoromethane (0·256 g.) and unchanged fluoro-iodide (0·240 g.) after irradiation for 20 hours. With a pressure of chlorine twice that of the fluoro-iodide, complete conversion into chlorotrifluoromethane was attained after 32 hours, and only iodine trichloride (Found : I, 53·7. Calc. for ICl_3 : I, 54·5%) was present.

The quantum yield, measured in a sealed cell by determination of the iodine liberated, was approximately 1·5.

Irradiation of Trifluoroiodomethane and Pentafluoroiodoethane with Cyanogen.—There was no detectable dark reaction when trifluoroiodomethane (0·903 g.; $p = 320$ mm.) was mixed with cyanogen (0·213 g.; $p = 295$ mm.) in *A*. Small white crystals could be seen after exposure to light for 15 minutes and these increased in quantity during 24 hours' irradiation at the end of which the pressure was 540 mm. The solid was identified as cyanogen iodide. No free iodine or paracyanogen was observed. The volatile reaction products were removed and shown to be hexafluoroethane (0·19 g.) and a mixture of trifluoroiodomethane and cyanogen. In subsequent experiments cyanogen was removed by treatment with alkali, and the hexafluoroethane formed (60—70% yield) was found to be equivalent to the trifluoroiodomethane decomposed. Hexafluoroethane (*M*, 138; b. p. −78°) was identified tensimetrically by comparison with the data of Pace and Aston (*J. Amer. Chem. Soc.*, 1948, **70**, 566). Irradiation of pentafluoroiodoethane and cyanogen similarly yielded perfluorobutane (*M*, 239; b. p. −2°) identified tensimetrically by using the data of Fowler *et al.* (*Ind. Eng. Chem.*, 1947, **39**, 376).

Photochemical Reaction between Trifluoroiodomethane and Ethylene.—The approximate quantum yield was determined by the irradiation of a mixture of trifluoroiodomethane (0·141 g.; $p = 150$ mm.) and ethylene (0·020 g.; $p = 150$ mm.) for 40 minutes, a decrease in pressure of 46 mm. being observed. Oily globules were deposited in the vessel during the reaction. Unchanged trifluoroiodomethane and ethylene were removed and the total iodine in the residue was determined after hydrolysis with alkali of the organic iodo-compounds which constitute the polymer. The quantum yield was 3·4; with an ethylene pressure of 300 mm. the value was 4·6. Similarly, trifluoroiodomethane and propylene gave quantum yields between 5 and 7.

Reaction of Trifluoroiodomethane with Ethyl Alcohol and Hexane.—These experiments were carried out in sealed tubes of *ca.* 50-ml. capacity. Volatile reaction products such as fluoroform were identified tensimetrically and by molecular-weight determination.

Trifluoroiodomethane (1·0 g.) heated with ethyl alcohol (20 ml.) at 180° for 24 hours gave a 30% yield of fluoroform. The residual liquid had a yellow colour, an acid reaction, and gave the qualitative reactions of an aldehyde. Acetaldehyde was shown to be present (the semicarbazone, recrystallised from ethyl alcohol, had m. p. 162—163°; the 2 : 4-dinitrophenylhydrazone, recrystallised from ethyl alcohol, had m. p. 163°; the dimedone derivative had m. p. 140°; literature values are 163°, 164·5°, and 140° respectively).

Trifluoroiodomethane (1·5 g.) and *n*-hexane (10 ml.), which contained no hexene, were heated for 24 hours at 205° and gave fluoroform (13%) and unchanged fluoroiodide (76%). Small amounts of silicon tetrafluoride and carbon dioxide were produced. The residual liquid from five such experiments was combined and distilled through an efficient column. The fraction, b. p. 62—68·5°, had n_D^{21} 1·391 and was unsaturated. Determination of the unsaturation by the bromate–bromide method (Lucas and Pressman, *Ind. Eng. Chem. Anal.*, 1938, **10**, 140) showed that 35% of the hexene which could theortically be produced by the mechanism discussed earlier was present. Physical data for the isomeric hexenes are: hex-1-ene, b. p. 63·5°, n_D^{20} 1·3877; hex-2-ene, b. p. 68·1°, n_D^{20} 1·3928; hex-3-ene, b. p. 66·8°, n_D^{20} 1·3942. When the unchanged *n*-hexane had been removed, there was a residue of an unidentified, high-boiling organic liquid which contained fluorine and iodine. Three further experiments at 220° gave a 60% yield of fluoroform. The hexene fraction from the residual liquid was shaken with bromine and the dibromohexanes isolated by distillation. Found: b. p. 85—90°/20 mm., n_D^{25} 1·502; physical data for the dibromohexanes are b. p. 89—90°/18 mm., n_D^{20} 1·5024; b. p. 90°/16 mm., n_D^{20} 1·5025; b. p. 80—81°/13 mm., n_D^{20} 1·5045.

Sealed-tube Reactions of Trifluoroiodomethane in the Presence of Mercury.—Mercury (1 ml.), trifluoroiodomethane (2·0 g.), and ethyl alcohol (20 ml.) were exposed to ultra-violet light in a Pyrex tube for 3 days at room temperature whilst the tube was agitated in a Vibro-shaker. Mercuric iodide was precipitated, the liquid became brown, and fluoroform was isolated in 93% yield. Acetaldehyde was shown to be present in the residual liquid by the reactions described earlier.

A mixture of trifluoroiodomethane (2·0 g.), mercury (1 ml.), and ethyl alcohol (20 ml.) was heated to 180° for 24 hours in the absence of light and gave a 65% yield of fluoroform.

Hexane (10 ml.), mercury (2 ml.), and trifluoroiodomethane (3·0 g.), heated to 205° for 30 hours, gave a 61% yield of fluoroform, and no fluoro-iodide was recovered. Hexane, an unidentified high-boiling compound containing iodine and fluorine (possibly the adduct of trifluoroiodomethane and hexene) and hexene (identified as described earlier) were isolated. When hexane (10 ml.), mercury (2 ml.), and trifluoroiodomethane in a sealed silica tube were exposed to ultra-violet light at room temperature for 3 days with vigorous shaking, mercuric iodide was deposited and hexene was formed; fluoroform was isolated in 90% yield.

After trifluoroiodomethane (1·0 g.) and water (5 ml.) had been heated to 150° and exposed to ultra-violet radiation for 8 days more than 90% of the fluoro-iodide was recovered unchanged; only a small amount of iodine was liberated. Trifluoroiodomethane (1·5 g.), water (5 ml.), and mercury (2 ml.) were shaken vigorously in a sealed tube at 260° for 24 hours. Fluoroform was isolated in 63% yield. The residual liquid contained mercuric iodide and a white suspension which was separated by decantation. The suspension, combined with that from three further experiments, each with 3·0 g. of trifluoroiodomethane, was centrifuged and filtered, and the light brown solid was dried in a vacuum desiccator (yield, 0·3 g.). This solid, which contained no fluorine, yielded mercuric oxide on being heated to 200°, and after dissolution in nitric acid was found to contain 83·7% of mercury [Calc. for $Hg(OH)_2$: Hg, 85·9%].

Irradiation of Mixtures of Trifluoroiodomethane and Carbon Tetrachloride.—Carbon tetrachloride (5 ml.) was heated with mercury (0·5 ml.) and trifluoroiodomethane (3·0 g.) at 200° for 24 hours. Little reaction occurred and 94% of the fluoro-iodide was recovered. The recovery of fluoro-iodide was only 33% after heating of a similar reaction mixture to 260° for 24 hours. In this case chlorotrifluoromethane (*M*, 103; b. p. −80°) was isolated from the volatile products in 60% yield and identified tensimetrically after removal of traces of silicon tetrafluoride. The solid reaction products contained hexachloroethane, but control experiments showed that this compound was also formed by the interaction of carbon tetrachloride and mercury under these conditions. There was no appreciable reaction when carbon tetrachloride and mercury in a silica tube were exposed to ultra-violet radiation for 7 days at room temperature, but, after trifluoroiodomethane (3·0 g.), carbon tetrachloride (5 ml.), and mercury (2 ml.) had been vigorously shaken and exposed to ultra-violet radiation for the same period, hexachloroethane was isolated in 70% yield based on the chlorotrifluoromethane formed. The volatile products contained trifluoroiodomethane (69% recovery), chlorotrifluoromethane (17% yield), and a small amount of a mixture of carbon dioxide and silicon tetrafluoride removed by treatment with aqueous alkali.

Synthesis of Bispentafluoroethylmercury.—This was prepared from pentafluoroiodoethane by the method developed for bistrifluoromethylmercury (Emeléus and Haszeldine, *loc. cit.*). Cadmium (3 g.) was heated with mercury (20 ml.) to form an amalgam, pentafluoroiodoethane (6·0 g.) was added, and the sealed tube containing the mixture was rocked at 30° for 14 days with occasional agitation to homogenise the amalgam. The unchanged fluoroiodide (4%) was removed and the solid formed extracted with ether. Evaporation of the ether and sublimation of the residue at 70°/760 mm. gave *bispentafluoroethylmercury*, m. p. (sealed tube) 106—107°, in 60% yield [Found: F, 43·0; Hg, 45·6%; *M* (ebullioscopic), 431. $C_4F_{10}Hg$ requires F, 43·3; Hg, 46·3%; *M*, 439]. When heated to 250° for 16 hours, the dimercurial gave perfluorobutane (40% yield).

Synthesis of Salts of the General Formula C_2F_5HgX.—Pentafluoroethylmercuric iodide was prepared in 88% yield by the method described previously (Emeléus and Haszeldine, *loc. cit.*). A reaction temperature of 240° for 12 hours was found convenient. The melting point was 98° (sealed tube) but traces of mercury iodides formed during purification or on storage appreciably altered the melting point, which, however, remained sharp. A similar effect is observed with other trifluoromethyl and pentafluoroethyl mercurials, and also with some methyl mercurials. This effect renders the melting points quoted here somewhat uncertain.

Pentafluoroethylmercuric hydroxide. Pentafluoroethylmercuric iodide (5·74 g.) was dissolved in water and shaken with excess of moist silver oxide for 24 hours. Silver iodide and unchanged silver oxide were removed by filtration, and the filtrate was evaporated to dryness at room temperature *in vacuo*. The residual solid was heated in a short-path still, first at 80° to remove unchanged mercuri-iodide (40%), and then at 100° *in vacuo* to obtain the hygroscopic *pentafluoroethylmercuric hydroxide*, m. p. 220—225° (sealed tube), in 40% yield [Found: F, 27·0; Hg, 58·0%; *M* (ebullioscopic), 348. C_2HOF_5Hg requires F, 28·2; Hg, 59·7%; *M*, 337]. There was a non-volatile residue (10%) which was possibly the oxide or carbonate.

Pentafluoroethylmercuric bromide, chloride, and fluoride. An aqueous solution of pentafluoroethylmercuric hydroxide (1·0 g.) was neutralised with hydrobromic acid and extracted with ether. After being dried, the ether was evaporated at atmospheric pressure and the residual solid sublimed to give *pentafluoroethylmercuric bromide* (0·84 g., 70%), m. p. 78—79° (sealed tube) [Found: Hg, 48·9; Br, 20·9%; *M* (ebullioscopic), 392. C_2BrF_5Hg requires Hg, 50·0; Br, 20·0%; *M*, 400]. A further quantity (0·12 g.; total yield, 80%) of the mercuribromide was obtained by evaporation of the aqueous solution *in vacuo* and sublimation of the residual solid.

Pentafluoroethylmercuric chloride, m. p. 103—104° (sealed tube), was similarly prepared in 76% yield [Found: Cl, 10·4; Hg, 58·1%; *M* (ebullioscopic), 347. C_2ClF_5Hg requires Cl, 10·0; Hg, 56·6%; *M*, 355·5].

Pentafluoroethylmercuric fluoride, m. p. 99—100° (sealed tube), was obtained in only 15% yield by the procedure described above [Found: F, 31·8; Hg, 59·0%; *M* (ebullioscopic), 331. C_2F_6Hg requires F, 33·6; Hg, 59·3%; *M*, 339]. Further amounts of this compound were not obtained by evaporation of the aqueous solution.

Photochemical Reactions of Bispentafluoroethylmercury.—The dimercurial (0·468 g.) was irradiated in an evacuated silica Carius tube for 7 days. Mercury (92% of theory) was formed, and perfluorobutane, identified tensimetrically as described above, was isolated in 80% yield. Small amounts of carbon dioxide and silicon tetrafluoride were also detected and some dimercurial (0·008 g.) was recovered. When the dimercurial (1·12 g.) and chlorine (1·20 g.) were similarly irradiated for 5 days a 33% yield of chloropentafluoroethane (Found: *M*, 155. Calc. for C_2ClF_5: *M*, 154·5), b. p. −38° (Locke, Brode, and Henne, *J. Amer. Chem. Soc.*, 1934, **56**, 1726, report b. p. −38°), was obtained, together with unchanged mercurial.

The authors record their gratitude to Dr. F. S. Dainton for providing facilities for the photochemical studies. One of them (J. B.) is indebted to Newnham College, Cambridge, for College and Bathurst Studentships, and to Imperial Chemical Industries Limited for a maintenance grant.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, August* 10*th*, 1950.]