636. *Organic Fluorides. Part I. Fluorination of Hydrocarbons.*

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An apparatus is described for the direct fluorination of hydrocarbons to give fluorocarbons (perfluorocarbons) by a vapour-phase catalytic method. Reference is made to the necessary conditions for successful fluorination. Copper and silver which act as catalysts in fluorination are believed to participate to some extent in the form of higher fluorides as halogen carriers. The large metal surface offered by the catalyst also dissipates the heat of the reaction and reduces decomposition.

The fluorocarbons are unique in the field of organic chemistry. Composed of carbon and the most electronegative element fluorine, they display a stability approaching that of the so-called rare gases. These substances display remarkable physical properties. Except with respect to density there is little resemblance between fluorocarbons and other halogen derivatives of carbon.

Fluorination of organic substances by means of fluorine was early demonstrated to be a violent reaction usually involving degradation (Bockemüller, *Annalen*, 1933, **506**, 20) and not infrequently accompanied by explosions (Moissan, *Ann. Chim. Phys.*, 1891, [vi], **24**, 224; Moissan and Chavanne, *Compt. rend.*, 1905, **140**, 407; Meslans, *Ann. Chim. Phys.*, 1894, [vii], **1**, 346). The main product of the reaction was carbon tetrafluoride (Humiston, *J. Physical Chem.*, 1919, **23**, 572; Damiens and Lebeau, *Compt. rend.*, 1926, **182**, 134; 1930, **191**, 939). No intermediate fluorinated products were identified. It was because of the danger which attended experiments with fluorine that attention was given to indirect methods of fluorination such as that discovered by Swarts (*Bull. Acad. roy. Belg.*, 1936, [v], **22**, 781) in which chloro- or bromo-derivatives or organic compounds were treated with metal fluorides (see Henne, Gilman's " Organic Chemistry," 2nd edn., Vol. II. p. 944, John Wiley and Sons, New York, 1943); such methods, however, are tedious and do not lead to complete fluorination.

Small yields of some of the lower fluorocarbons have been produced by treatment of carbon, impregnated with a mercuric salt, with fluorine (Simons and Block, *J. Amer. Chem. Soc.*, 1939, **61**, 2962; cf. Ruff and Keim, *Z. anorg. Chem.*, 1930, **192**, 249) and they may also be produced together with polymeric fluorocarbons by the fluorination of metal carbides such as CaC_2, ThC_2, UC_2 (Smith, unpublished). More recently the ingenious procedure of fluorinating organic compounds by adding them to a mixture of potassium fluoride and hydrogen fluoride undergoing carefully controlled electrolysis has been reported by Simon and his co-workers (Amer. Chem. Soc. Meeting, Portland, Oregon, 1948), but most progress has been made in recent years with the vapour-phase fluorination of organic compounds, a study of which forms the subject of this paper (see Bigelow, *Chem. Reviews*, 1947, **40**, 51; Smith, *Ann. Reports*, 1947, **44**, 86).

This work shows that a surprising improvement in the yields of fluorocarbons results when fluorine and a hydrocarbon react in the vapour phase at higher temperatures in the presence of large surface areas of metal such as is offered by small pieces or turnings. This conclusion has also been reported by Cady *et al.* (*Ind. Eng. Chem.*, 1947, **39**, 290). Fluorocarbon yields of 50—80% have been recorded for the direct fluorination of hydrocarbons using silver-plated copper turnings. Further, the catalytic activity of metals in fluorination is not confined to one or two elements, for, in addition to copper and silver, cobalt, nickel, and gold may also be used (see succeeding paper). The effectiveness of all of them may reside partly in their conversion by fluorine into a fluoride which acts as the fluorinating agent (Bigelow, Calfie, and Miller, *J. Amer. Chem. Soc.*, 1937, **59**, 198; Cady *et al.*, *loc. cit.*), but it is difficult to see how this can be the complete explanation for in the case of copper for example the amount of fluoride formed on the surface is very small.

Several conditions appear to be necessary for the successful fluorination of hydrocarbons using good-quality fluorine: (*a*) the catalyst, *e.g.*, silver-plated copper turnings must be pre-treated with fluorine to remove organic contaminants and to produce a surface layer of metal fluoride before any hydrocarbon is admitted to the reaction vessel; (*b*) the reactants should be diluted with nitrogen, and each of the mixtures should be preheated to a temperature approximating to the value found to give the highest yields of fluorocarbon from the particular hydrocarbon under examination: (*c*) slightly more than the theoretical amount of fluorine should be used; (*d*) premature interaction of fluorine and hydrocarbon should be avoided by the insertion of baffle plates, suitably placed near the inlets in order to deflect the reactants downwards so that they intermingle relatively slowly—if the fluorination occurs prematurely, *i.e.*, as soon as the reactants enter the reaction vessel the yield of the desired fluorocarbon is negligible, since most of the hydrocarbon is converted either into carbon tetrafluoride or into a mixture of the latter and a viscous oily polymeric fluorocarbon; the latter may be produced especially at lower temperatures in such an amount as to cover the surface of the catalyst, in which condition all catalytic activity is lost (see Cady *et al., loc. cit.*); (*e*) once the catalyst has been used it should be disturbed as little as possible so as to avoid dislodging the surface film of metallic fluoride; mechanical shaking or rapid flow of gases should be avoided; this is especially true with silver- or gold-plated copper turnings.

The results of these preliminary experiments seemed to indicate that as the boiling points of the hydrocarbons increased the optimum reaction temperature for fluorocarbon formation should also be increased. Thus *n*-heptane gave good yields at 150°, whilst octene was best transformed into *perfluoro-octane* at 200° and tetrahydronaphthalene gave maximum yields of perfluorodecalin at 350—380°.

Fluorination of ethylenic hydrocarbons was characterised by a tendency for cleavage to take place, especially at the double bond; thus octene afforded perfluoroheptane in addition to perfluoro-octane.

Fluorocarbons are the most stable organic substances known, approaching the stability of the rare gases. They are stable to boiling strong acids and alkalis and to the halogens, chlorine and bromine, but when heated with fluorine they undergo degradation to give fluorocarbons containing fewer carbon atoms than the original material. When heated with sodium or potassium, complete decomposition occurs giving carbon and the alkali-metal halide (Elving and Ligett, *Ind. Eng. Chem., Anal.*, 1942, **14**, 449). Fluorocarbons also react with sodium in liquid ammonia at room temperature (Miller, Hunt, and McBee, *ibid.*, 1947, **19**, 148). They are relatively thermostable but at red-heat undergo " cracking." Above 400° they are reported to react with silica giving carbon dioxide and silicon tetrafluoride (Rice and White, *J. Amer. Chem. Soc.*, 1947, **69**, 267; McKenna and Teston, *Ind. Eng. Chem., Anal.*, 1947, **19**, 193). Pressure hydrogenation of fluorocarbons at 400° appears to replace some fluorine to give hydrofluorocarbons, but no hydrogenolysis appears to occur (Grosse and Cady, *Ind. Eng. Chem.*, 1947, **39**, 367).

Fluorocarbons also have unique physical properties, displaying remarkably low values for surface tension, boiling point, viscosity, and refractive index. The densities are high, and the compounds are characterised by a low solubility in the usual organic solvents. They are miscible with each other and dissolve in ether and in some chlorofluorocarbons. Such peculiar properties are probably due to the operation of low intermolecular and high intramolecular forces (see Grosse and Cady, *ibid.*, 1947, **39**, 367; McBee and Bechtol, *ibid.*, p. 380; Fowler *et al.*, *ibid.*, p. 375).

EXPERIMENTAL.

Apparatus. The apparatus used is similar to that used by Cady *et al.* (*loc. cit.*) at about the same time.

The electrically-heated reaction vessel *C* in which fluorinations were conducted consisted of a piece of cylindrical iron pipe approx. 27 in. long and 2 in. in diameter. A narrow (0·5 in. diam.) iron or nickel tube, closed at the lower end, was brazed into the lid of *C* to act as a thermometer well. The lid of *C* was threaded (flanged joints are better) so that it could be removed to make inspections and adjustments. Two short (3—4 in.) ⅜-in. copper tubes were brazed into *C* (1 in. below the lid) opposite each other to serve as inlets. The fluorine, previously mixed with nitrogen (regulated with a glass flowmeter f_1) in the copper vessel *A* (8 in. high and 2 in. in diameter), was preheated, by passing it through a spiral copper tube B_1 (8—10 spirals, each 4 in. in diameter) heated in a sand-bath, before it entered *C*. The hydrocarbon was carried from the graduated glass reservoir *D* in a current of nitrogen regulated by the glass flowmeter f_3. The hydrocarbon–nitrogen mixture which could be diluted further by nitrogen passing through the glass flowmeter f_2, was passed through the copper coil B_2, similar to B_1, to be preheated in sand before entering *C*.

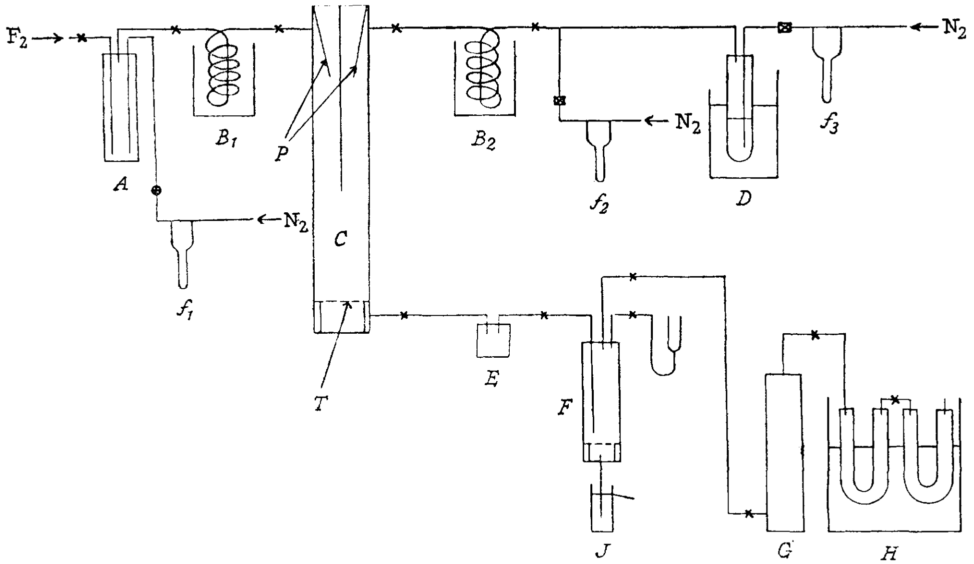
Copper baffle plates *P* were inserted in the top of *C* to deflect the reactants downwards into the main body of the catalyst. The exit from *C* consisted of a ⅜-in. copper tube (3—4 in. in length) inserted 1·5 in. from the bottom of *C* and beneath a shallow perforated tray *T*; this arrangement of the exit below the tray supporting the turnings avoided blockage of the exit which occurs when the tube is placed in the bottom of *C* and there is no tray to support the catalyst. The bottom of *C* was closed by a steel screw-cap or flanged plate. The reaction products from *C*, consisting of fluorocarbon compounds, hydrogen fluoride, excess of fluorine, and nitrogen, passed, through a small steel cylindrical vessel *E* (4 in. high and 2½ in. in diameter) in which high-boiling products were collected, to the base of a copper cylinder *F* (12 by 2·5 in.) down which water trickled over copper turnings to remove hydrogen fluoride and then through a tower *G* containing calcium chloride into two U-tubes *H* in which the product was condensed at −78° (solid carbon dioxide and alcohol). In later experiments the water tower *F* and the drying tower *G* were discarded, and both the product and hydrogen fluoride were condensed in wide copper U-tubes cooled in solid carbon dioxide–alcohol. All connections to the vessels, *A*, *C*, *E*, *F*, and *G* were brazed. " Cerechlor " was used in the flowmeters but this was replaced by a suitable fluorocarbon as soon as this material became available from this and subsequent fluorination studies.

The amount of fluorine generated was calculated from the current in the fluorine cell on the assumption that the efficiency was approximately 65%. In the early stages of this work a low-temperature (10—15°) cell was used but this was replaced by a medium-temperature (100°) fluorine generator; this type of cell fitted with a carbon anode impregnated with copper and excluded from atmospheric moisture is believed to be the most satisfactory cell to operate (Pinkston, *Ind. Eng. Chem.*, 1947, **39**, 255).

Before assembling the apparatus for fluorinations, each piece of it was tested for leaks and, when assembled, the apparatus was re-checked for leaks by passing a known amount of hydrocarbon in a stream of nitrogen through the apparatus and collecting it in the U-tube receivers. Failure to obtain an almost complete recovery of the hydrocarbon was taken to indicate the presence of leaks. Any leaks on the fluorine side of the apparatus between *C* and the fluorine generator were detected by means of potassium iodide paper during a preliminary low fluorine generation.

The amount of fluorine, to be used in slight excess, was based upon the amount of hydrocarbon being carried out of the graduated vessel *D* by the current of nitrogen. This hydrocarbon input was ascertained approximately by disconnecting the copper tube just before it entered *C* and passing nitrogen through *D* and noting the rate of evaporation of the hydrocarbon. The rate of evaporation of hydrocarbon, and consequently of its introduction into *C*, could be regulated by varying the temperature of *D* and the rate at which nitrogen bubbled through the hydrocarbon.

Before the commencement of each fluorination, the reactor *C* was adjusted by a " Variac " transformer to the temperature required for fluorination and undiluted fluorine was then passed into *C* in order to dry the apparatus and generate the surface film of metal fluoride. When not in use the reactor *C* was adjusted to about 150°, and while still containing some fluorine it was closed off from the rest of the apparatus. This insured that the catalyst remained dry and in an active state. When once charged with catalyst the reactor *C* was not disturbed more than was necessary.



× *Brass unions.* ⊕ *Metal-glass joint.* ⊠ *Rubber joint.*

RESULTS.

Perfluoroheptane.—Experiment I. The catalyst for this experiment consisted of 4 kg. of copper turnings plated electrically with silver. The reaction vessel was adjusted to 150° and fluorine was introduced from a medium-temperature fluorine generator at the rate of 6 g. per hour (this was estimated from a current efficiency in the fluorine cell of 65%). When fluorine was issuing freely from the exit of the reaction vessel (disconnected at this point for convenience), the fluorine stream was diluted with nitrogen (9 l. per hour). The hydrocarbon was passed into the vessel in a current of nitrogen (10 l. per hour). Heptane (19 c.c.), introduced during 17 hours, gave a crude product (23·6 g.) which was collected in the U-tubes cooled in carbon dioxide–alcohol. The crude product was washed with water, dried (K_2CO_3), and distilled, giving fractions: (i) decomposition products (2·6 g.), b. p. 30—80°, (ii) perfluoroheptane (16 g.), b. p. 80·5—83°, and (iii) partly fluorinated heptane (3·8 g.), b. p. 83—120°.

Experiments II—V. In these, fluorine generated at 12 g. per hour (current in cell, 30 amp.) was diluted with nitrogen (direct from cylinder) (23·5 l. per hour), while the heptane was diluted with 11·5 l. of the nitrogen per hour. The results and those of experiment I were as follows:

Experiment:	I.	II.	III.	IV.	V.
Reaction temp. (° c.)	150	150	150	150	150
Reaction time (hrs.)	17	28	28	28	28
F_2 (g. per hr.)	6	12	12	12	12
N_2 dilution of F_2 (l. per hr.)	9	23·5	23·5	23·5	23·5
Heptane total (c.c.)	19	62	86·5	72	57
N_2 dilution of heptane (l. per hr.)	10	11·5	11·5	11·5	11·5
Yield of fluorocarbon (crude), g.	23·6	80	96	76	33
$\frac{\text{Wt. of fluorocarbon} \times 100}{\text{Wt. of heptane}}$	181	189	162	155	85

Fractional distillation of the crude product (dried over phosphoric oxide) gave fractions: (iv) decomposition products (48 g.), b. p. 60—80°, (v) perfluoroheptane (150 g.), b. p. 81—83°, and (vi) partly fluorinated heptane (53·5 g.), b. p. 83—130°. Redistillation of fraction (v) gave perfluoroheptane, b. p. 82°, n_D^{20} 1·272, d_{20}^{20} 1·69, γ^{20} (surface tension) 13·6 dynes per cm., η^{20} 1·05 × 10^{-2} c.g.s. units. Refluorination of fraction (vi) gave 34 g. of crude product from which by fractional distillation a further 21 g. of perfluoroheptane (b. p. 81—83°) were obtained together with 10 g. of partly fluorinated material. Thus, 277·5 c.c. of *n*-heptane afforded 171 g. of perfluoroheptane (Found: F, 78·5. Calc. for C_7F_{16}: F, 78·35%).

When the reaction vessel was not in use, it was tightly stoppered with blank unions whilst still containing some fluorine; it was never left exposed to the air. If the catalyst was set aside for any length of time, its activity was usually ascertained by the fluorination of a small sample of some hydrocarbon. In one such experiment 13 g. of heptane afforded 25 g. of crude perfluoroheptane.

Perfluoro-octane.—Experiment I. Octene (prepared from technical octanol by dehydration with boiling phosphoric acid) underwent smooth fluorination by the aforementioned procedure. Introduced during 23 hours in a current of nitrogen (9·5 l. per hour), octene (24 g.) reacted at 155° with fluorine, generated at 6 g. per hour and diluted with nitrogen (11 l. per hour) to give crude perfluoro-octane which was neutralised with potassium carbonate and filtered (yield, 25 g.). Fractional distillation gave fractions: (i) degradation products (6·5 g.), b. p. 70—102°, (ii) perfluoro-octane (8·5 g.), b. p. 103—105°, and (iii), partly fluorinated octane (5·1 g.), b. p. 105—150°.

Experiment II. In another experiment conducted as above, 30 g. of octene gave 24 g. of crude product.

Experiment III. In one of several other experiments with the temperature of the reaction vessel adjusted to 200°, 37 g. of octene, fluorinated during 25·5 hours, gave 58 g. of crude perfluoro-octane.

The crude material from experiments II and III yielded upon fractional distillation fractions: (iv) decomposition products (30·5 g.), b. p. 60—100°, (v) perfluoro-octane (35·5 g.), b. p. 100—110°, and (vi) partly fluorinated octane (15 g.), b. p. 110—150°. Refractionation of fraction (v) gave *perfluoro-octane* (30·5 g.), b. p. 104°, n_D^{20} 1·282, d_{20}^{20} 1·73, γ^{22} 15·3, η^{20} 1·63 × 10^{-2} (Found: F, 77·7. C_8F_{18} requires F, 78·1%).

Refractionation of 20 g. of the decomposition products [fraction (iv)] gave fractions: (*a*) (2 g.), b. p. 33°, (*b*) (3·5 g.), b. p. 60—63, (*c*) (2·5 g.), b. p. 71—75°, and (*d*) (11·6 g.), b. p. 81—83°. The lower-boiling materials decolorised bromine water and alkaline potassium permanganate, indicating the presence of unsaturated products (cf. Henne and Ruh, *J. Amer. Chem. Soc.*, 1947, **69**, 279). Fraction (*d*) did not react with bromine or potassium permanganate. Its b. p. (81—83°) and mol. wt. (360; by Victor Meyer's method) suggested that it was perfluoroheptane arising by cleavage at the double bond and simultaneous fluorination.

Perfluorononane.—This was prepared by the fluorination of nonene by the method already described. The nonene reservoir was heated to 59° in order to facilitate the introduction of the hydrocarbon into the fluorination vessel without the use of excessive amounts of nitrogen. The results are tabulated below.

Experiment:	I.	II.	III.	IV.	V.
Reaction temp. (° c.)	200	200	225	270	235
Reaction time (hrs.)	16	21·5	16·5	16·25	31·5
F_2 (g. per hr.)	6	6	6	6	6
N_2 dilution of F_2 (l. per hr.)	14	14	14	14	14
Nonene, total (c.c.)	10	19	21	25	59
N_2 dilution of nonene (l. per hr.)	11·5	11·5	11·5	11·5	11·5
Product (g.) collected in:					
Trap E	—	1·8	3·3	1·5	0·95
Trap J	—	1·5	1·9	2·3	3·0
U-Tubes	3·5	13	19	19·5	40
Total	3·5	16·3	24·2	23·3	43·95
$\frac{\text{Wt. of total fluorocarbon} \times 100}{\text{Wt. of nonene}}$	48·8	119	160	130	104

The low yield of fluorinated product obtained in experiment I is probably due to the use of a large excess of fluorine.

In experiments I, II, III, and IV distillation of the product which was collected in the U-tubes gave fractions: (i) decomposition products (20·6 g.), b. p. 40—115°, (ii) crude perfluorononane (15·1 g.), b. p. 115—130°, and (iii) partly fluorinated nonane (10·1 g.), b. p. 130—220°. Fraction (i) contained unsaturated substances since it decolorised bromine and alkaline potassium permanganate.

In experiment V distillation of the product (40 g.) which had collected in the U-tubes gave fractions: (iv) decomposition products (13·4 g.), b. p. 40—115°, (v) perfluorononane (19 g.), b. p. 115—130°, and (vi) partly fluorinated nonane (5·5 g.), b. p. 130—220°. Redistillation of the combined fractions (ii) and (v) gave fractions: (*a*) (7·4 g.), b. p. 119—122·5°, (*b*) perfluorononane (20·5 g.), b. p. 122·5—123·5°, and (*c*) (4·6 g.), b. p. 123·5—127°.

Perfluorononane [fraction (*b*)] had n_D^{20} 1·281, d_{20}^{20} 1·80, γ^{22} 15·3, η^{20} 20 × 10^{-2} (Found: F, 77·5. C_9F_{20} requires F, 77·9%).

Fraction (vi) was redistilled and a portion collected at 160°. The profound influence of residual hydrogen upon the b. p. is indicated by this fraction (Found: C, 21·4; H, 1·7; F, 76·1%).

Redistillation of the material collected, from experiments II—V, in trap J (the latter was not used for experiment I) gave fractions: (*a*) (0·8 g.), perfluorononane, b. p. 122—124°, (*b*) (4·5 g.) partly fluorinated nonane, b. p. 125—220°, (*c*) (0·5 g.), a viscous liquid, b. p. 160°/10 mm. (Found: F, 76·2%), and (*d*) (0·4 g.), a viscous liquid, b. p. 205°/10 mm. (Found: F, 78·9%). Fractions (*c*) and (*d*) appeared to be perfluoro-polymers probably arising, as will be demonstrated in a later paper, from the polymerisation of hydrofluorocarbons.

Distillation of the material collected in trap E gave more of the viscous high-boiling perfluoro-polymer.

Perfluorodecahydronaphthalene.—A series of experiments were carried out with tetrahydronaphthalene using silver-plated copper turnings. The hydrocarbon was heated to 185° and introduced into the reaction vessel in a current of nitrogen preheated in a copper coil at 200°; the fluorine was similarly diluted with nitrogen and preheated. The temperature of the reaction vessel was varied in order to ascertain the optimum temperature. The results were as follows :

Experiment :	I.	II.	III.	IV.	V.
Reaction temp. (° c.)	200	300	350	380	350
Reaction time (hrs.)	17·5	18·5	11	11	45·5
F_2 (g. per hr.)	6	6	12	8	14
N_2 dilution of F_2 (l. per hr.)	9	9	13·5	13·5	16·0
Tetralin (total, c.c.)	25	25	25	17	83
N_2 dilution of tetralin (l. per hr.)	13	13	7	7	9
Product (g.) collected in :					
Trap E	—	—	trace	trace	1·6
Trap J	—	—	9·8	1·5	22·6
U tubes	1·8	6·0	24·0	15·0	70·0
Total	1·8	6·0	33·8	16·5	92·4
$\frac{\text{Total wt. of fluorocarbon} \times 100}{\text{Wt. of hydrocarbon}}$	7·3	24·5	138·0	99·0	117

Fractionation of the product from the U*-tubes.* The combined material (109 g.) from experiments III, IV, and V was washed with water until neutral, dried ($MgSO_4$), and distilled giving fractions : (i) decomposition products (unsaturated) (76·5 g.), b. p. 30—135°, (ii) perfluorodecahydronaphthalene (16 g.), b. p. 135—140°, and (iii) partly fluorinated decahydronaphthalene (9·3 g.), b. p. 140—230°.

Fractional distillation of the product from experiments III, IV and V collected in trap J (the water trap) gave fractions : (iv) crude perfluorodecahydronaphthalene (8·4 g.), b. p. 135—140°, (v) partly fluorinated decahydronaphthalene (9·1 g.), b. p. 140—230°, (vi) a viscous liquid (6·9 g.), b. p. 165—175°/10 mm. (Found : F, 76·2%), (vii) a viscous liquid, partly crystalline (4·4 g.), b. p. 195—205°/10 mm. (Found : F, 75·2%), (viii) a viscous liquid, b. p. 210—235°/10 mm., which crystallised almost completely (Found : F, 76·4%), and (ix) a glassy solid, b. p. 170—180°/0·07 mm. (Found : F, 74·7%). Fractions (vi), (vii), (viii), and (ix) appeared to be polymeric.

The fractions (ii) and (iv) of fairly pure perfluorodecahydronaphthalene were combined and redistilled, giving perfluorodecahydronaphthalene (20·8 g.), b. p. 138°, n_D^{20} 1·315, d_{20}^{20} 1·90, η^{20} 4·75 × 10^{-2}, γ^{20} 19·25 (by Sugden's method) (Found : F, 73·8. Calc. for $C_{10}F_{18}$: F, 74·0%).

Fractionation of high-boiling material collected in trap E. The combined material from experiments III, IV, and V gave upon distillation fractions (*a*) glassy (1·0 g.), b. p. 190—200°/0·07 mm. (Found : F, 75·6%), and (*b*), a glassy material, 1·5 g., b. p. 215—225°/0·07 mm. (Found : F, 75·95%). These materials were evidently polymeric.

Fluorination of Dodecene.—The technique employed was the same as for the fluorination of tetrahydronaphthalene. The results are given in the following table :

Experiment :	I.	II.	III.	IV.
Reaction temp. (° c.)	200	300	350	380
Reaction time (hrs.)	17	19	22·5	21·5
F_2 (g. per hr.)	6	6	12	12
N_2 dilution of F_2 (l. per hr.)	14	14	17	17
Dodecene (total, c.c.)	14	29	47	48
N_2 dilution of dodecene	7	7	10	10
Product (g.) collected :				
Trap J	0·4	0·9	—	—
U-tubes	3·5	9·5	24·6	21·5
Total	3·9	10·4	24·6	21·5
$\frac{\text{Total wt. of fluorocarbon} \times 100}{\text{Wt. of hydrocarbon}}$	36	46·5	67·6	58

The products from the U-tubes were combined, washed with water, dried, and distilled, giving fractions : (i) a colourless unsaturated liquid (52·7 g.), b. p. 30—165° (ii) crude perfluorododecane (2·8 g.), b. p. 165—180°, and (iii) partly fluorinated dodecane (1·1 g.), b. p. >180°.

The fluorination of dodecene was thus attended by extensive degradation and in an attempt to minimise this, further experiments (V—VII) in which nitrogen dilution of the reaction mixture was greater were carried out; the results are given below :

Experiment :	V.	VI.	VII.	
Reaction temp. (° c.)	340	340	380	
Reaction time (hrs.)	20	19	18	
F_2 (g. per hr.)	12	12	12	
N_2 dilution of F_2 (l. per hr.)	22	31·5	35	
Dodecene (total, c.c.)	35	38	77	
N_2 dilution of dodecene (l. per hr.)	9	9	9	
Product (g.) collected :				
Trap J	2·5	—	9·9	(unchanged dodecene)
U-tubes	10	9·8	11·5	
Total	12·5	9·8	11·5	
$\frac{\text{Total wt. of fluorocarbon} \times 100}{\text{Wt. of dodecene}}$	46·2	33·4	19·3	

Fractionation of the product from these three experiments gave fractions: (*a*) fluorinated degradation products (27 g.), b. p. 40—165° (unsaturated), (*b*) colourless liquid, probably impure perfluorododecane (3·4 g.), b. p. 165—180°, which could not be resolved into a product of constant b. p., and (*c*) partly fluorinated dodecane (1·7 g.), b. p. >180°.

In order to ascertain that the catalyst, used in this series of fluorinations of dodecene, was still of good quality and in an active condition a sample of benzene was fluorinated. The fluorine generated at 12 g. per hour was diluted with 17 l. of N_2 per hour while benzene (28 c.c.) admitted in 11 hours was diluted with 7 l. of N_2 per hour. The reaction conducted at 180° gave 42 g. of crude perfluoro*cyclo*hexane which upon washing, drying, and distillation gave perfluoro*cyclo*hexane, b. p. 51°, m. p. 52°. The catalyst was therefore active.

There seemed to be no indication that long-chain unsaturated hydrocarbons could be fluorinated by this catalytic vapour-phase method, and another procedure had to be devised, as will be reported later.

The fluorocarbons obtained in the above series of experiments could be recovered unchanged after being boiled with strong acids and with strong alkalis.

Measurement of the Refractive Index.—This could not be done for the fluorocarbons by means of the Abbé refractometer since the lower limit of the scale was 1·3. For these preliminary experiments a small air cell was made from three discs (1-cm. diam.) of microscope cover slips. In one of these discs a hole (0·3 mm.) was drilled. This perforated disc was sealed between the other two of the same size with a solution of cellulose acetate in acetone. The small air cell was fixed to a wire support attached to a goniometer platform and adjusted so that it rotated about an axis perpendicular to a parallel beam of sodium light from a Webski slit. The light from the slit passed through the cell, and an image of it could be seen in the telescope of the goniometer (focused at infinity). The crosswire of the telescope was arranged to bisect the image of the slit.

The air cell was then immersed in the fluorocarbon, contained in a small cubic copper container, in two opposite sides of which were glass panels through which light could pass. Rotation of the cell in one direction caused one half of the image to disappear; this was the position for total internal reflection. The reading on the goniometer platform was noted. The cell was rotated in the opposite direction until the other half of the image of the slit disappeared. The reading of the platform was again noted. It can readily be shown that the cosecant of half of the angle through which the air-cell was rotated to give the two extreme positions of extinction gives the refractive index of the fluorocarbon. The instrument was calibrated by using liquids of known refractive index.

Unless stated otherwise, surface tensions were measured by a DuNuoy tensiometer and are quoted with reserve. The densities were determined in a pyknometer and the viscosities in a viscometer of the Ostwald type.

Determination of Fluorine in Organic Fluorides [with J. C. TATLOW].

The compound was heated with sodium at 400—500° in a simplified form of Parr bomb made of nickel (cf. Elving and Ligett, *Ind. Eng. Chem., Anal.*, 1942, **14**, 449; Kimball and Tufts, *ibid.*, 1947, **19**, 150; Hunt, McBee, and Miller, *ibid.*, p. 148; Bigelow *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 267; Schumb and Radimer, *Ind. Eng. Chem., Anal.*, 1948, **20**, 871). The sodium fluoride formed in the fusion was titrated with thorium nitrate, sodium alizarinsulphonate being used as indicator (Armstrong, *Ind. Eng. Chem.*, 1936, **8**, 384; Rowley and Churchill, *ibid.*, 1937, **9**, 551). The difficulty in determining the end-point was largely surmounted by filtering the thorium tetrafluoride after most of the thorium nitrate had been added and completing the titration with the clear filtrate.

More recently it has been shown by Stross (*Metallurgia*, 1947, **36**, 346) and confirmed by one of us (W. K. R. M.) that the addition of a protective colloid such as starch presents the precipitation of thorium tetrafluoride and the premature appearance of a pink colour. This appears to be the best solution to the problem of the exact determination of the end-point (cf. Matuszak and Brown, *Ind. Eng. Chem., Anal.*, 1945, **17**, 100).

Compounds containing chlorine as well as fluorine can be analysed for both halogens by the above method, the chloride being determined in the presence of fluoride by titration with silver nitrate using dichloro-R-fluorescein as an adsorption indicator (Kolthoff, Lauer, and Sunde, *J. Amer. Chem. Soc.*, 1929, **51**, 3273).

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