516. *Organic Fluorides. Part III. Fluorination of Aromatic Hydrocarbons by Use of a Gold Catalyst.*

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The action of fluorine upon aromatic hydrocarbons in the vapour phase in the presence of a gold catalyst and an inert gas affords fluorocarbons. The latter contain only carbon and fluorine and are believed to possess the same carbon skeleton as the parent hydrocarbon.

In Part I (Musgrave and Smith, *J.*, 1949, 3021) it was demonstrated that fluorination of hydrocarbons in the presence of a silver catalyst is greatly facilitated by carrying out the reaction at elevated temperatures (200—300°), and in Part II (*idem, ibid.*, p. 3026) the evidence indicated that, among several metals examined, gold was the most effective catalyst for the vapour-phase fluorination of benzene. This communication and Part IV (*J.*, 1950, paper no. 536) deal with the application of these findings to the fluorination of a number of aromatic and alicyclic hydrocarbons. By controlling the conditions fluorocarbons can be produced in yields not previously attainable by other direct fluorination techniques which employed lower temperatures (Bockemüller, *Annalen*, 1933, **506**, 20; Fredenhagen and Cadenbach, *Ber.*, 1934, **67**, 928; Bigelow *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 4614; see also Bigelow, *Chem. Rev.*, 1947, **40**, 51).

This investigation was made in order to determine the effects of temperature, rate of addition of fluorine and hydrocarbon, and dilution of fluorine and of hydrocarbon with nitrogen upon the yield of fluorocarbon, and to obtain sufficient pure material to enable the physical properties of the fluorocarbons to be studied.

The general effects of the variables were as follows: An increase in the nitrogen dilution favoured the production of hydrofluorocarbon, and a decrease in nitrogen dilution increased the decomposition. When the reaction temperature was increased the yield of the required fluorocarbon rose to a maximum and then fell as decomposition proceeded more rapidly. Increasing the amount of fluorine caused extensive degradation and a consequent reduction in the yield of the required fluorocarbon. Decreasing the rate of hydrocarbon addition resulted occasionally in an increase in the yield of fluorocarbon with little increase in the amount of decomposition, and an increase in the rate of addition sometimes gave an increase in hydrofluorocarbon with little alteration in the yield of fluorocarbon. The latter effect was of value since the hydrofluorocarbon could be recycled.

Most hydrocarbons upon fluorination give rise to varying amounts of polymeric products, some of which appear to have possibilities as lubricants and insulators. This polymer formation is controllable to a certain degree by the choice of starting material and by the reaction conditions. Unsaturated hydrocarbons appeared to polymerise to a somewhat greater extent than the corresponding saturated hydrocarbon (cf. McElvain and Langston, *J. Amer. Chem. Soc.*, 1944, **66**, 1749; see Part IV) and it was also observed that high addition rates and high nitrogen dilution favoured polymerisation.

It was shown that perfluoro*cyclo*hexane is readily obtained from benzene at 280° (cf. Part I). At lower temperatures the yield of perfluoro*cyclo*hexane was greatly reduced. This was expected from the pioneering experiments of Bigelow and Fukuhara, who obtained small amounts of perfluoro*cyclo*hexane by the action of fluorine diluted with nitrogen upon benzene at 90° in the presence of copper gauze (*J. Amer. Chem. Soc.*, 1941, **63**, 2792).

Perfluoromethyl*cyclo*hexane was produced by fluorination of toluene at 250°. It was obtained in still higher yields from benzotrifluoride, a result probably due to the fact that benzotrifluoride is more stable than toluene under the conditions of fluorination. Similar results have already been reported by Cady and his co-workers (*Ind. Eng. Chem.*, 1947, **39**, 290).

Fluorocarbons of the formula C_8F_{16} were obtained by fluorination of technical xylene, *o*-xylene, *m*-xylene, bistrifluoromethylbenzene, and ethylbenzene. Although good yields were produced from technical xylene, the most readily available hydrocarbon which would give rise to C_8F_{16}, better yields resulted from the *m*- than from the *o*-isomer and still higher yields were produced from ethylbenzene.

Contrary to expectation, the fluorination of 1 : 3-bistrifluoromethylbenzene appeared to indicate that this was not a good starting material for the preparation of C_8F_{16} since extensive polymerisation occurred.

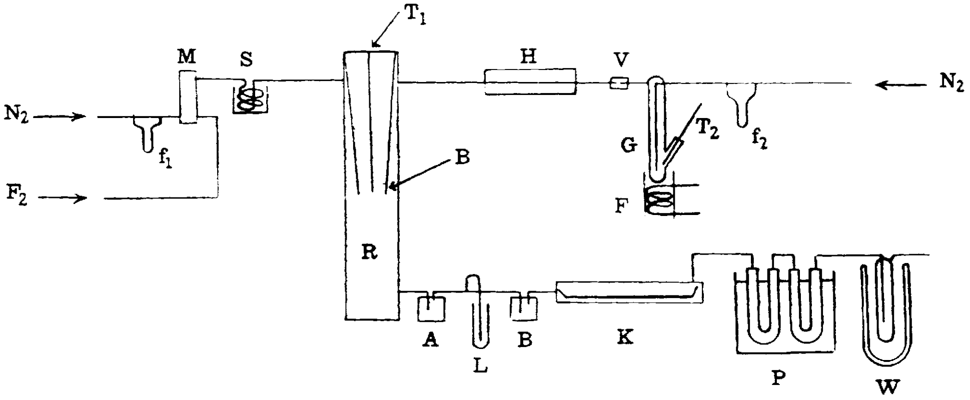
Mesitylene proved to be a convenient substance for the production of C_9F_{18} but it suffered more decomposition than either xylene or toluene. *ψ*-Cumene, less symmetrical and presumably less stable than mesitylene during fluorination, gave a poor yield of C_9F_{18}.

The isomeric C_8F_{16} fluorocarbons, which are believed to have the same carbon skeleton as the parent hydrocarbons from which they were prepared, were found to display very similar physical properties. A similar relationship existed in the C_9F_{18} series (see also Grosse and Cady, *Ind. Eng. Chem.*, 1947, **39**, 367; Fowler *et al.*, *ibid.*, p. 375), and although more refined techniques may reveal significant differences in the physical properties of these isomeric fluorocarbons, it is already apparent that the intermolecular forces in these substances are very small compared with those in normal organic compounds, whilst the intramolecular forces are very high. Fluorocarbons should, therefore, prove to be valuable for the study of the internal structure of organic molecules.

EXPERIMENTAL.

Apparatus.—This is represented diagrammatically in the figure. It was operated as described in Part I (*loc. cit.*).

Procedure.—The optimum conditions were determined by keeping the fluorine generation constant and investigating in turn the effect of reaction temperature, hydrocarbon addition, and nitrogen dilution of fluorine and of hydrocarbon. Unless stated otherwise, the product collected in the U tubes P was washed, dried, and distilled through an efficient fractionating column. Products collected in trap A were usually distilled separately.



f_1 *and* f_2. *Pyrex flow-meters.*
M. *Mixing chamber for fluorine and nitrogen.*
S. *Copper spiral for preheating the fluorine–nitrogen mixture.*
R. *Steel reaction vessel* (34″ × 3″) *filled with gold-plated copper turnings.*
T_1. *Thermometer pocket.*
B. *Nickel baffle plate, extending* $\frac{1}{3}$ *length of R; lower half drilled with* $\frac{1}{32}$″ *holes* $\frac{1}{2}$″ *apart.*
H. *Furnace for preheating hydrocarbon–nitrogen mixture.*
V. *Copper–glass ground joint.*
G. *Graduated 50-c.c. Pyrex vessel carrying a thermometer,* T_2.
F. *Silica tube furnace for heating the hydrocarbon reservoir.*
A *and* B. *Traps for the condensation of polymeric material.*
L. *Copper tube dipping into " Cerechlor " or a fluorinated oil to act as a safety valve.*
K. *Potassium fluoride scrubber (removed during preparation of high-boiling fluorocarbons).*
P. *Two copper* U *tubes joined in series and cooled by a mixture of solid carbon dioxide and alcohol.*
W. *Liquid-air trap to condense any volatile decomposition products.*

Preliminary experiments were carried out with each compound to find the approximate b. p. of the required fluorocarbon. An arbitrary temperature range covering this value was adopted, and the yield of product distilling in this range was used to compare the efficiency of the various experiments. The distillate with b. p. below that of the fluorocarbon was termed " decomposition products," and that with boiling point greater than that of the fluorocarbon was termed " partially fluorinated " or " hydrofluorocarbon " material.

Benzene was fluorinated from time to time to make sure that there was no leakage in the apparatus and that the catalyst was fully active.

Results.—(A) *Fluorination of benzene.* (*a*) When benzene (added at 4 c.c./hr.) was diluted with nitrogen (10 l./hr.) and treated with fluorine (15 g./hr.) diluted with nitrogen (10 l./hr.) the optimum temperature was found to be approx. 280° by the following results :

Temp.	200°	250°	280°	300°	350°
$\text{" Recovery "} = \dfrac{\text{Wt. of crude fluorocarbon (b. p. 48—58°)}}{\text{Wt. of benzene}} \times 100$ ...	101	151	153	143	118

(*b*) With this optimum temperature (280°), a benzene addition of 4 c.c./hr. diluted with nitrogen (10 l./hr.), and a fluorine addition of 15 g./hr., the following results were obtained upon varying the dilution of fluorine with nitrogen :

N_2 Dilution of F_2 (l./hr.)	2	6	8	10	15
" Recovery "	51	90	155	153	102

These results showed that a 40% yield of perfluoro*cyclo*hexane could be produced from benzene under the following optimum conditions: temp. 280°; benzene 4 c.c./hr. diluted with 10 l. of nitrogen/hr.; fluorine, 15 g./hr., diluted with 8 l. of nitrogen/hr.

Purification of the fluorocarbon as described later gave perfluoro*cyclo*hexane, m. p. 51°, b. p. 52°, D_4^{25} 1·72 g./c.c. (Found : C, 23·8; F, 75·6%; *M*, 299. Calc. for C_6F_{12} : C, 24·0; F, 76·0%; *M*, 300). Bigelow and Fukuhara (*J. Amer. Chem. Soc.*, 1941, **63**, 2792) quote m. p. 48—49°, b. p. 50°, D^{30} 1·684 for this compound, and Christoffers, Lingafelter, and Cady (*ibid.*, 1947, **69**, 2502) give m. p. 58·2° (sealed tube), sublimes 51°/760 mm., D^{23} 1·93.

Partially fluorinated benzene. A high nitrogen dilution was found to be a major factor in forming hydrofluorocarbons. The following experiment with benzene is typical of many carried out to prepare hydrofluorocarbons. Nitrogen (13 l./hr.) was bubbled through benzene so that the latter was carried into the reactor (adjusted to 280°) at the rate of 5·5 c.c./hr. Fluorine (15 g./hr.) diluted with nitrogen (17 l./hr.) was also introduced into the reactor. After 4 hours, the combined crude yield (28·7 g.) gave upon fractional distillation : fraction 1 (decomposition products), 8·3 g., b. p. 25—48° ; fraction 2 (crude perfluoro*cyclo*hexane), 7·5 g., b. p. 48—58° ; fraction 3 (partially fluorinated benzene), 10·6 g. (40% of total), b. p. 58—150°.

The partially fluorinated benzene fraction was a complex mixture which could not be separated easily into its constituents by fractional distillation. Examination of the fractions from a distillation of hydrofluorobenzene material (in which partial separation had been effected) indicated, however, that as the percentage of fluorine increased the b. p.s of the compounds steadily increased to a maximum, after which they steadily fell to a value below that of the parent hydrocarbon. Finally, a minimum value was reached when the material was completely fluorinated thus :

Fraction.	B. p.	F (%).*	*M* (Regnault method).	Fraction.	B. p.	F (%).*	*M* (Reguault method).
1	60—70°	70·4	270	3	100—110°	56·7	190
2	90—100	66·3	240	4	120—140	36·1	128

* Fluorine analyses were carried out by decomposing the fluorocarbon with potassium and precipitating the fluoride as calcium fluoride. This gave reproducible results but invariably they were slightly low. The molecular weights were usually determined in a Regnault bulb, but for compounds of high b. p. an ebullioscopic method was used.

The calculated analytical data for some partially fluorinated benzenes are as follows : $C_6H_5F_3$, F, 42·5% ; *M*, 134. $C_6H_6F_6$, F, 59·4% ; *M*, 192. $C_6H_3F_9$, F, 69·5% ; *M*, 246. C_6F_{12}, F, 76·0% ; *M*, 300. In view of the probable contamination from partially fluorinated and polymeric compounds arising from the fragmentation of the parent hydrocarbon, the correlation of the experimental analytical figures with possible empirical formulæ for hydrofluorobenzenes must be treated with reserve.

Examination of polymeric material. Distillation of the combined still residues from a series of experiments gave a range of products varying from a colourless mobile liquid (b. p. 140—160°/10 mm.) to a thick opaque oil (b. p. 200—240°/10 mm.).

(B) *Fluorination of Benzotrifluoride.*—Under the optimum conditions (temp. 200° ; F_2, 13 g./hr. ; benzotrifluoride addition (5 c.c./hr. ; N_2 dilution of F_2, 15 l./hr. ; N_2 dilution of benzotrifluoride, 10 l./hr.), benzotrifluoride (72 g.) yielded a crude product (84·1 g.) which gave upon fractional distillation : fraction 1, decomposition products, 18·7 g., b. p. 30—72° ; fraction 2, perfluoromethyl*cyclo*hexane, 50·5 g. (" recovery " 70%), b. p. 72—78° ; fraction 3, partially fluorinated product, 12·1 g., b. p. 78—150°.

Fractional distillation of crude fluorocarbon (117 g.) corresponding to fraction 2, followed by purification as described later, gave perfluoromethyl*cyclo*hexane (82·7 g.), b. p. 76·2°, f. p. —38°, n_D^{25} 1·276, D_4^{25} 1·784 g./c.c., γ^{25} 13·8 dynes/cm., η^{25} 15·6 millipoises (Found : C, 23·7 ; F, 75·5% ; *M*, 347. Calc. for C_7F_{14} : C, 24·0 ; F, 76·0% ; *M*, 350). Grosse and Cady (*loc. cit.*) give b. p. 76°, D^{30} 1·7779, n_D^{30} 1·2762, and Fowler *et al.* (*loc. cit.*) give b. p. 76·32°, D^{20} 1·7994, n_D^{20} 1·2815, γ^{20} 15·4 for this substance.

From a number of experiments it was observed that an increase in the nitrogen dilution of the hydrocarbon gave a higher yield of hydrofluorocarbon and polymeric materials.

Fractional distillation of the decomposition products, fraction 1 (b. p. 30—72°), showed that the bulk of the material had b. p. 48—60°. A pure compound could not be isolated but it is believed that the fluorocarbon, b. p. 48—60°, was mainly a mixture of perfluoro*cyclo*hexane and perfluorohexane, since the analysis of the decomposition material shows that it consists largely of completely fluorinated compounds (Found : F, 76·2% ; *M*, 309. Calc. for C_6F_{12} : F, 76·0 ; *M*, 300. Calc. for C_6F_{14} : F 78·7% ; *M*, 338).

A parallel series of experiments with toluene showed that the optimum fluorination temperature was 250°.

(C) *Fluorination of Xylene* (*Technical*).—The optimum conditions were found to be : temp. 200°, xylene addition 4 c.c./hr., diluted with 14 l. of nitrogen/hr. ; and fluorine 15 g./hr., diluted with 9 l. of nitrogen/hr. Under these conditions xylene (40 g.) gave a product (48·8 g.) in the U-tubes from which perfluorodimethyl*cyclo*hexane (12 g.) (" recovery " 27·5%), b. p. 95—100°, was separated by fractional distillation. Purification of 101 g. of this crude fluorocarbon afforded 67 g. of perfluorodimethyl*cyclo*hexane, b. p. 101·5°, f. p. —55°, D_4^{25} 1·829, n_D^{25} 1·283, γ^{25} 15·1 dynes/cm., η^{25} 19·3 millipoises (Found : C, 24·0 ; F, 75·7% ; *M*, 395. Calc. for C_8F_{16} : C, 24·0 ; F, 76·0 ; *M*, 400). Grosse and Cady (*loc. cit.*) give b. p. 100°, D^{30} 1·8270, n_D^{30} 1·2858 ; Fowler *et al.* (*loc. cit.*) record b. p. 101·5—102·4°, D^{20} 1·8530, n_D^{20} 1·2902, γ^{20} 16·3 dynes/cm. Both groups of workers believed the products to be a mixture of isomers.

Experiments were carried out on the recycling of the hydrofluorocarbon fraction (b. p. 105—170°). " Recovery " figures of 70—80% showed that good yields of fluorocarbon could be produced in this way. As with the parent hydrocarbon, the reaction temperature was found to be critical since at 250° the decomposition products amounted to 41% of the total distillate while at 200° they amounted to 20% ; moreover, the perfluorodimethyl*cyclo*hexane increased from 34% at 250° to 40% at 200°.

It is noteworthy that the hydrofluorocarbon produced in these experiments underwent partial polymerisation simply on heating, as indicated by a marked increase in its b. p.

Examination of polymeric material. The fraction, b. p. >170°, from the fluorination of 414 g. of xylene was divided into two portions (*a*) and (*b*). Each was freed from an upper tarry layer by extraction with ether and then distilled. Portion (*a*) gave : fraction 1 (decomposition products, formed either on storage or by heat during distillation), 24·3 g., b. p. 70—95°; fraction 2 (a pale yellow thin oil), 18·0 g., b. p. (bath temp.) 170—210°/10 mm.; fraction 3 (a pale yellow viscous oil), 18·0 g., b. p. (bath temp.) 210—260°/10 mm. (*M*, ebullioscopic, 620—650).

Portion (*b*) gave: fraction 1 (decomposition products), 5·7 g., b. p. 70—90°; fraction 2 (colourless thin oil), 15·7 g., b. p. (bath temp.) 100—170°/10 mm.; fraction 3 (colourless oil), 31·7 g., b. p. (bath-temp.) 170—210°/10 mm. [Found: C, 44·4; H, 2·1; F, 53·0%; *M* (ebullioscopic), 437. Calc. for $C_{16}H_8F_{12}$: C, 44·9; H, 1·8; F, 53·3%; *M*, 428]. The compounds may be dimers of partly fluorinated xylenes, *e.g.* $(CH_3{\cdot}C_6F_4{\cdot}CHF_2)_2$ or $[C_6H_4(CF_3)_2]_2$—it is evident from the molecular weight and C and F figures that the material is neither a completely fluorinated hydrocarbon nor a partly fluorinated xylene; fraction 4 (colourless viscous oil), 8·7 g., b. p. (bath temp.) 210—260°/10 mm.; fraction 5 (yellow glass), 10·0 g., b. p. (bath temp.) 260—300°/10 mm.

The difference in the products of distillation of the two samples is explained by the fact that portion (*a*) had been left for several weeks before distillation, during which time some decomposition had occurred.

The amount of oily material distilling in the range 170—210°/10 mm. was relatively large in both distillations, but in spite of repeated distillation, a definite fraction of perfluoro-oil could not be separated.

Examination of decomposition products. Refractionation of the combined decomposition products from the 414 g. of xylene gave: fraction 1, 4·0 g., b. p. 30—50°; fraction 2, 88·3 g., b. p. 55—95°; fraction 3, perfluorodimethyl*cyclo*hexane, 12·6 g., b. p. 95—105°; still residue, 5·1 g. Fraction 2, which had F, 76·1%, and an average *M* of 340, appeared to contain mainly cyclic perfluoro-compounds and perfluoroparaffins, but fractional distillation failed to give any one component.

(D) *Fluorination of* 1 : 3-*Bistrifluoromethylbenzene.*—This substance, prepared by the hydrofluorination of 1 : 3-bistrichloromethylbenzene, was fluorinated at 200°, the optimum temperature for the fluorination of xylene. The hexafluoroxylene (62 g.) was carried from a reservoir (temp. 90°) at 7 c.c./hr. in a stream of nitrogen (25 l./hr.) into the reactor at the same time that fluorine (10 g./hr.) diluted with nitrogen (16 l./hr.) was also added. Fractional distillation of the crude fluorocarbon (79·2 g.) yielded: fraction 1, (decomposition products) 15·6 g., b. p. 30—95°; fraction 2, crude perfluorodimethyl*cyclo*hexane (10·3 g.), b. p. 95—105°; fraction 3 (partly fluorinated material) (27·9 g.), b. p. 105—170°; fraction 4 (polymeric material), 11 g., b. p. >170°.

When the nitrogen dilution of the fluorine was increased from 16 to 22 l./hr. the crude yield (76·1 g. from 69 g. of starting product) was almost the same, but both the yield of decomposition product (8·2 g.) and that of crude perfluorodimethyl*cyclo*hexane (4·8 g.) fell while the yield of polymer (27 g.) increased.

Refractionation of the combined decomposition products and the crude desired fluorocarbon gave perfluoro-1 : 3-dimethyl*cyclo*hexane (14 g. or 11% of the hexafluoroxylene used). Comparison of this with the total polymer (56·2 g. or 43% of the hexafluoroxylene) showed that vapour-phase fluorination of hexafluoroxylene under the conditions specified resulted mainly in polymerisation (cf. Cady *et. al.*, *loc. cit.*).

(E) *Fluorination of* o-*Xylene.*—Only small yields of perfluoro-1 : 2-dimethyl*cyclo*hexane could be produced by fluorination of *o*-xylene at 200°. The main products were those of decomposition and partial fluorination. A decrease in the rate of addition of hydrocarbon reduced polymer formation but neither the " recovery " nor the yield of perfluorodimethyl*cyclo*hexane was improved. Redistillation of the combined fractions of perfluorodimethyl*cyclo*hexane and decomposition fragments (from 122 g. of *o*-xylene) afforded perfluoro-1 : 2-dimethyl*cyclo*hexane (4·6 g.). Although this fraction cannot be considered pure, its physical properties, b. p. 100—102°, n_D^{25} 1·285, D_4^{25} 1·825 g./c.c., corresponded closely to those of perfluoro-1 : 3-dimethyl*cyclo*hexane (Fowler *et al.*, *loc. cit.*, record b. p. 102·6°, D^{20} 1·8672, n_D^{20} 1·2923 for perfluoro-1 : 2-dimethyl*cyclo*hexane).

(F) *Fluorination of* m-*Xylene.*—By analogy with previous experiments with the xylenes (Sections C and E) the reaction temperature was adjusted to 200°. The flow of fluorine, and its dilution with nitrogen were kept fairly constant so that the effect of varying the rate of addition of xylene and its dilution with nitrogen could be ascertained. The best yields of perfluoro-1 : 3-dimethyl*cyclo*hexane were obtained when xylene was transported from the reservoir (adjusted to 105—110°) at 3—4 c.c./hr. in a stream of nitrogen (18 l./hr.). Thus *m*-xylene (77 g.) afforded 22 g. of product in traps *A* and *B* and 83·8 g. in the U-tubes. Distillation of the U-tube product gave: fraction 1, decomposition products (40 g.), b. p. 40—95°; fraction 2, crude perfluoro-1 : 3-dimethyl*cyclo*hexane (23·6 g.), b. p. 95—105°; fraction 3, hydrofluorocarbon (9·3 g.), b. p. 105—170°; fraction 4, polymeric material (1·1 g.), b. p. >170°.

Purification of fraction 2 gave rise to perfluoro-1 : 3-dimethyl*cyclo*hexane, b. p. 101·5°, f. p. −56°, D^{25} 1·829 g./c.c., n_D^{25} 1·283, γ^{25} 15·1 dynes/cm., η^{25} 19·3 millipoises (Fowler *et al.*, *loc. cit.*, record b. p. 102·12°, n_D^{20} 1·2908, D^{20} 1·8560 for this fluorocarbon). After the fluorination of 296 g. of the xylene, the reactor was dismantled, and a thick viscous colourless oil (15 g.) extracted from it and purified by distillation in high vacuum (Found: F, 74·1%). As far as viscosity, and stability to heat, fluorine, and uranium hexafluoride are concerned, this oil compared favourably with similar fluoro-oils prepared later by liquid-phase polymerisation of hydrofluorocarbons.

During the course of the experiments it was found that polymer formation was favoured by a high rate of addition of *m*-xylene.

(G) *Fluorination of Ethylbenzene.*—By following the procedure already outlined above, the optimum conditions were found to be: temp. 200°; ethylbenzene addition, 5·5 c.c./hr., diluted with 25 l. of nitrogen/hr.; fluorine, 24 g./hr., diluted with 14 l. of nitrogen/hr. Under these conditions 52 g. of ethylbenzene furnished 24·2 g. of crude perfluoro-derivative, b. p. 100—103°, which upon purification yielded ***perfluoroethyl*****cyclo*****hexane***, b. p. 101·5°, f. p. −60°, D_4^{25} 1·826 g./c.c., n_D^{25} 1·283, γ^{25} 15·0 dynes/cm., η^{25} 19·1 millipoises (Found: F, 75·7%; *M*, 396. C_8F_{16} requires F, 76·0%; *M*, 400).

(H) *Fluorination of Mesitylene.*—Under the optimum conditions (temp. 230°; mesitylene addition 4 c.c./hr. diluted with 11 l. of nitrogen/hr.; fluorine addition 17 g./hr. diluted with 9 l. of nitrogen/hr.), 42 g. of mesitylene yielded 12·4 g. of crude perfluorocarbon, b. p. 120—128°. Purification of 63 g. of product obtained in this way gave perfluoro-1 : 3 : 5-trimethyl*cyclo*hexane, b. p. 124·6°, f. p. −56°, D_4^{25} 1·890 g./c.c., n_D^{25} 1·294, γ^{25} 17·2 dynes/cm., η^{25} 22·4 millipoises. Grosse and Cady (*loc. cit.*) give b. p. 123°, n_D^{30} 1·2930, D^{30} 1·8676, and Fowler *et al.* (*loc. cit.*) give b. p. 125·18°, n_D^{20} 1·2995, D^{20} 1·9025 for this compound (Found : C, 23·5; F, 75·8%; *M*, 443. Calc. for C_9F_{18} : C, 24·0; F, 76·0%; *M*, 450).

Considerable polymerisation took place during these experiments. Distillation of 124 g. of this material collected in traps *A* and *B* from 10 experiments gave :

Fraction.	Wt. (g.).	B. p. (bath temp.)/10 mm.	F (%).	*M* (ebull.).
1. Colourless oil	11·2	120—160°	—	—
2. Colourless viscous oil	59·1	160—210	68·2	520
3. Colourless very viscous oil	27·0	210—260	—	—
4. Colourless very viscous oil	14·2	260—300	59·7	580
5. Pale yellow glass	2·0	>300	—	—

(J) *Fluorination of ψ-Cumene.*—This hydrocarbon gave poor results compared with mesitylene; considerable decomposition occurred and tar-like material as well as fluorocarbon collected in the U-tubes. Treatment of 124 g. of *ψ*-cumene (at the rate of 4 c.c./hr. diluted with 20 l. of nitrogen/hr.) with fluorine (20 g./hr. diluted with 14 l. of nitrogen/hr.) at 230° furnished a U-tube condensate which upon distillation gave : fraction 1 (decomposition products), 19·4 g., b. p. 40—124°; fraction 2, *perfluoro-1 : 2 : 4-trimethyl*cyclo*hexane*, 5·2 g., b. p. 124—126° (Found : F, 75·6%; *M*, 445. C_9F_{18} requires F, 76·0%; *M*, 450); fraction 3, hydrofluorocarbon, 16·5 g., b. p. 126—170°. Since the perfluoro-1 : 2 : 4-trimethyl*cyclo*hexane amounting to 4% by weight of the hydrocarbon fluorinated boiled over the range 124—126°, its properties (D_4^{25} 1·881, n_D^{25} 1·296, γ^{25} 17·5 dynes/cm., η^{25} 22·5 millipoises) are quoted with reserve. It is to be noted, however, that these physical properties closely resemble those of perfluoro-1 : 3 : 5-trimethyl*cyclo*hexane.

Purification of Fluorocarbons.—The physical properties quoted above (and of which use will be made in a later communication) were determined on samples which had been washed with water, alcohol (to remove hydrofluorocarbon), water, and dried (phosphoric oxide); they were then distilled, and the fluorocarbon collected over a close range, treated with uranium hexafluoride either in a closed Pyrex vessel on a hot water-bath or by refluxing the fluorocarbon with the hexafluoride until no more green tetrafluoride was produced. The fluorocarbon was then washed, dried, and distilled through an efficient column.

The authors express their thanks to (the late) Sir Norman Haworth, F.R.S., and Professor M. Stacey, F.R.S., for their interest in this work. They also thank the Director General of Scientific Research for permission to publish.

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[*Received, February* 16*th*, 1950.]