715. *Organic Fluorides. Part V. Fluorination of Hydrocarbons with Cobalt Trifluoride.*

By R. N. Haszeldine and F. Smith.

The fluorination of hydrocarbons is more readily achieved by the use of cobalt trifluoride than by treatment with fluorine in the presence of a catalyst. The control of the conditions is not as critical, and polymerization and decomposition are greatly reduced. Higher yields of fluorocarbons are obtained from unsaturated than from saturated hydrocarbons.

Previous investigations have shown that hydrocarbons can be completely fluorinated in the vapour phase by the action of fluorine diluted with nitrogen in the presence of a " catalyst " such as gold-plated (*J.*, 1949, 3026; 1950, 2689, 2787) or silver-plated copper turnings (Cady *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 290). Since the catalytic method required careful control and at best gave relatively poor yields of the required fluorocarbon as well as undesirable decomposition and polymeric products, attention was directed to the development of a method of indirect fluorination by the use of metallic fluorides. This development was based on the observations of previous workers that fluorides of zinc, mercury, antimony, and silver can be used to replace other halogen atoms by fluorine, and that some metal fluorides such as cerium tetrafluoride (Löw, *Ber.*, 1881, **14**, 1145, 2441) and lead tetrafluoride (Brauner, *J.*, 1882, **41**, 68; 1894, **65**, 393) evolve fluorine when heated (see Ruff, " Die Chemie des Fluors," Julius Springer, Berlin, 1920).

In the present communication it is shown that cobalt trifluoride can be used for the smooth conversion of saturated and unsaturated hydrocarbons into the corresponding fluorocarbons. Cobalt trifluoride is obtained from the difluoride, dichloride, or oxide by the action of fluorine at 250—300°, and contains one atomic proportion of fluorine available for the fluorination of hydrocarbons by either substitution or both substitution and addition. The energy liberated during fluorination with cobalt trifluoride is less than that evolved when gaseous fluorine is used; the reaction is therefore less violent, decomposition and polymerisation are reduced, and the yields of fluorocarbon are much improved. Silver difluoride was found better for the stabilisation of fluoro-oils in the liquid phase, but caused more decomposition during vapour-phase fluorination than did cobalt trifluoride. Furthermore, silver difluoride, being deliquescent and unstable in moist air, was not as convenient to handle (cf. McBee and Bechtol, *Ind. Eng. Chem.*, 1947, **39**, 380). Also, when prepared from silver chloride by the action of elementary fluorine it was obtained as a hard non-porous solid which offered very little surface area compared with the powdery cobalt trifluoride prepared as described above. The experiments recorded herein, and those of Fowler *et al.* (*ibid.*, p. 343) (see also Benner *et al.*, *ibid.*, p. 329) published after this work was done, demonstrate that cobalt trifluoride is a good fluorinating agent. The fluorides of manganese and cerium have also been used with some success (Fowler *et al.*, *loc. cit.*) and it seems desirable that other fluorides as well as mixtures of two or more of them with and without inert diluents should be examined to see whether still further improvement is possible.

The apparatus used for fluorination with cobalt trifluoride consisted of an electrically heated reactor attached to a condensing system very similar to that used for catalytic fluorination (see Parts I, III, and IV). Since the reaction is a surface one, the cobalt trifluoride was packed in thin layers. In early experiments the reactor consisted of a horizontal nickel tube in which the cobalt trifluoride was placed on metal trays. Later, a series of three reactors adjusted to temperatures of 250°, 300°, and 350°, respectively, was employed. The most efficient reactor consisted of a vertical cylindrical apparatus (see figure) in which there was placed a large number of nickel trays each containing a thin layer of cobalt trifluoride.

The use of an inert gas such as nitrogen to transport the hydrocarbon proved unsatisfactory since the contact time was reduced and fluorination did not proceed to completion. Furthermore, a carrier gas increased the entrainment of finely divided cobalt trifluoride and this eventually blocked the exit tube. The product to be fluorinated was, therefore, added as a liquid and vapourized immediately upon entering the reactor.

The main factors affecting the yield of fluorocarbons were similar to those found important in the catalytic process, namely, reaction temperature, vapour velocity, and the nature of the compound to be fluorinated, but they were neither as well defined nor as critical as with the catalytic method. The cobalt trifluoride method has been used to produce perfluoro-compounds from aliphatic and alicyclic hydrocarbons and from aromatic hydrocarbons containing one or two ring systems. The optimum conditions for complete fluorination were determined as in the case of the catalytic process. A temperature of 350° was suitable for the fluorination of most hydrocarbons while the best yields of hydrofluorocarbons required for polymerisation tests were obtained at about 250°.

The catalytic method of fluorination using elementary fluorine caused considerable cleavage of carbon–carbon double bonds when applied to unsaturated aliphatic or aromatic compounds, and it was shown that the use of dimethyl*cyclo*hexane instead of xylene as starting material led to greatly improved yields of perfluorodimethyl*cyclo*hexane. This effect was not observed in the cobalt trifluoride process. In fact, the contrary applied; *e.g.*, dimethyl*cyclo*hexane gave rise to 62% of its weight, whereas xylene yielded 96% of its weight, of perfluorodimethyl*cyclo*hexane. This significant observation was confirmed with ethylbenzene and ethyl*cyclo*hexane, the former giving a considerably higher yield of perfluoroethyl*cyclo*hexane. Further, ethylbenzene is somewhat better than xylene as a starting product for the production of a C_8F_{16} compound.

It then became of interest to ascertain the better procedure for conversion of ethylbenzene into perfluoroethyl*cyclo*hexane. The first procedure was to pass ethylbenzene over cobalt trifluoride at 350° to complete the fluorination as far as possible by one treatment; small amounts of hydrofluorocarbon could be recycled. In the second procedure the ethylbenzene was allowed to react with cobalt trifluoride first at 250° to give mainly hydrofluorocarbon together with small amounts of completely fluorinated product, and then at 350° to complete the fluorination. A comparison showed that the one-step process was the better. Similar results were obtained with xylene.

The cobalt trifluoride method, like the catalytic method of fluorination, was not particularly successful in the conversion of *o*-xylene into perfluoro-1 : 2-dimethyl*cyclo*hexane and only small yields of product were obtained (cf. Fowler *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 292). Cobalt trifluoride converted mesitylene and *ψ*-cumene into perfluoro-1 : 3 : 5- and -1 : 2 : 4-trimethyl*cyclo*hexane, respectively. Although the physical properties of the latter were approximately the same as those of the former product the compound was not isolated in a pure state. Cobalt trifluoride produced perfluoromethyl*cyclo*hexane from toluene and benzotrifluoride, and perfluoromethyl-4-*iso*propyl*cyclo*hexane from *p*-cymene, but the method was not so satisfactory with *n*-propyl- and *n*-butyl-*cyclo*hexane, although even in these cases products with approximately the expected properties resulted.

The melting point of naphthalene precluded its use alone but a solution of it in tetrahydronaphthalene was suitable for fluorination. Having a low m. p. (35°), 2-methylnaphthalene could be added directly to the reactor. In both cases the yields of the corresponding perfluorocarbon were satisfactory.

The decomposition products resulting from the action of cobalt trifluoride on xylene contained small amounts of perfluoro*cyclo*hexane and perfluoromethyl*cyclo*hexane.

Cleavage of methyl groups also took place during the fluorination of trimethylbenzenes since perfluoromethyl*cyclo*hexane and perfluorodimethyl*cyclo*hexane were identified in the reaction products. It is thus apparent that even under the improved conditions of fluorination provided by cobalt trifluoride, it is difficult to avoid some cleavage of side-chain methyl groups. There is thus an analogy between fluorination and photochemical chlorination of alkylbenzenes (where the alkyl group is not methyl) inasmuch as both reactions involve free radicals and bring about side-chain halogenolysis.

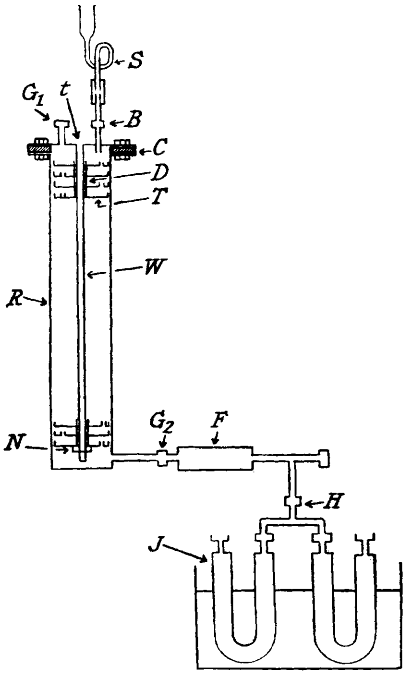
The paraffin hydrocarbons (*e.g.*, 2 : 2 : 3-trimethylbutane, *n*-octane, *n*-nonane) underwent smooth fluorination with cobalt trifluoride to perfluoro-derivatives. Perfluorononane was also produced by simultaneous cleavage as a by-product in the fluorination of *n*-decene. Fluorination of either *n*-decane or *n*-decene provided crystalline perfluorodecane, the crystalline form of which appears to be common to the higher members of the perfluoro-paraffin series.

As the paraffin series of hydrocarbons is ascended the yields of perfluoro-compounds tend to be lower, but, in spite of this, crystalline perfluoro-derivatives of *n*-undecane, *n*-dodecane, and *n*-hexadecane (cetane) were isolated. Fluorination of cetane was accompanied by some central cleavage of the molecule giving perfluoro-octane.

EXPERIMENTAL.

Apparatus.—(a) *Horizontal reactor.* This was made from a nickel tube (30″ × 3″) and was heated electrically. The cobalt trifluoride was placed in two pairs of trays placed one above the other. The trays were shaped to fit the tube and nickel deflector plates directed the vapours on to the cobalt trifluoride. After fluorination, 175 g. of fluorine were available for reaction.

(b) *Graded-temperature horizontal reactors.* Three reactors were joined in series and each could be adjusted to any desired temperature. The first two were 28″ × 2½″ and the third was 36″ × 1¾″. The three reactors were fitted with deflector plates and trays carrying cobalt trifluoride capable of providing 200 g. of available fluorine.



(c) *Vertical reactor* (see figure). This proved to be the most efficient type of static apparatus. It consisted of a vertical copper or, preferably, nickel tube 36″ × 4½″, closed by a nickel or copper plate *C* bolted to a flange and sealed with a copper–asbestos gasket. Into the upper plate were welded two copper tubes (G_1 and *B*). The nickel trays *T* which carried the cobalt trifluoride were fixed on a central tube (*W*) which served both as a support for the trays and as a thermometer-well (*t*). The trays fitted snugly to the side of the reactor and each was drilled with a ½″ hole. Into each hole a ½″ length of steel tube was inserted to retain the cobalt salt and to provide a passage for the gas. The closely packed trays were separated by short lengths of steel tube *D* which fitted over *W*. The trays and distance pieces were held in place by a nut *N* screwed to the bottom of *W*. Each tray was arranged so that the holes were as far apart horizontally as possible thereby forcing the gases to travel the maximum distance over the cobalt salt. The trays carried 850 g. of cobalt difluoride which when fully fluorinated provided 170 g. of available fluorine.

Traps. The trap system used to collect the fluorinated products from any of the three types of reactor consisted of a small horizontal nickel tube *F* (5″ × 1″) to collect high-boiling products, and two copper U tubes *J* arranged in parallel and cooled in solid carbon dioxide and ethanol. All connections used in these reactors were made with ⅜″ copper tubing.

Procedure.—With the vertical reactor, the hydrocarbon was added from a 10-c.c. microburette into a glass tube *S* joined to *B* with a copper–glass joint. The tube *S* acted as a liquid seal and as a manometer to indicate blockages in the system. With tube *B* closed and a temperature of 300°, fluorine was introduced through *G*, until the cobalt difluoride had been completely converted into trifluoride and fluorine issued freely from the exit tube. The excess of fluorine was then swept out with a slow stream of dry nitrogen. The trap system was connected at G_2, and seal *S* at *B*, and the reactor was adjusted to the desired temperature.

After each fluorination the product collected in the trap system was washed with water to remove acid, and then with ethanol to remove hydrofluorocarbon. The latter was recovered by pouring the alcoholic extract into water. The alcohol-soluble and the alcohol-insoluble fractions were washed with water, dried, and distilled. The alcohol-soluble products consisted of a mixture of hydrofluorocarbons containing the same number of carbon atoms as, or fewer than, the hydrocarbon subjected to fluorination. The alcohol-insoluble fraction consisted mainly of fully fluorinated compounds together with a small amount of hydrofluorocarbon. The fully fluorinated compounds were separated by distillation into decomposition products and the required fluorocarbon. The latter was then purified as described in Part III (*J.*, 1950, 2689). At the end of an experiment, the cobalt trifluoride was regenerated with fluorine at 300°.

Fluorination in the Horizontal Reactor.—(a) *Technical xylene.* The preliminary experiments were conducted with xylene, since perfluorodimethyl*cyclo*hexane had already been prepared by the action of fluorine on xylene and on dimethyl*cyclo*hexane in the presence of gold-plated copper turnings (Part III).

The temperature was not very critical since the yields at 340° and 360° were almost the same, but below 340° the yield of hydrofluorocarbon increased and above 360° there was more decomposition. The best yields were produced when the hydrocarbon was added slowly. High rates of addition or intermittent additions gave poor yields of perfluorodimethyl*cyclo*hexane.

The results of numerous experiments showed that the optimum conditions were : temp. 350°, rate of addition of xylene 5—10 c.c./hour. Under these conditions 37 g. of xylene added in 8 hours gave 90 g. of crude fluorocarbon (efficiency,[1] 64 : recovery,[2] 229). Fractional distillation of the crude product yielded 47 g. of crude perfluorodimethyl*cyclo*hexane, b. p. 98—102°. The purification of 384 g. of crude C_8F_{16} obtained in this way afforded pure perfluorodimethyl*cyclo*hexane (317 g.), 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. These constants are in good agreement with those recorded for material prepared by the catalytic method (Part III).

(a′) *Preparation and recycling of partly fluorinated xylene.* When xylene (59 g.) was passed at 20 c.c./hour through the reactor at 250°, a crude yield corresponding to an efficiency of 65—70% was obtained which afforded 74·5 g. of partly fluorinated product, b. p. >105°, corresponding to $C_8H_8F_8$ by refractometric analysis. When freshly prepared, this hydrofluorocarbon was homogeneous but on storage a small upper layer of material, with a low degree of fluorination, separated.

Partly fluorinated product from 100 g. of xylene was then re-fluorinated at 350° and the condensate separated by distillation into (*a*) crude perfluorodimethyl*cyclo*hexane, C_8F_{16}, (*b*) hydrofluorocarbon, and (*c*) decomposition products. The process of recycling the hydrofluorocarbon was repeated twice, giving a total of 110 g. of C_8F_{16}.

Fluorination of 100 g. of xylene at 350° followed by two re-treatments of the partly fluorinated material at 350° gave a total of 125 g. of C_8F_{16}. It will be seen that this direct procedure gave a better yield than the above indirect method, and one stage less was required to accomplish it.

(b) o-*Xylene.* *o*-Xylene (35 g.), fluorinated at 250° during 3 hours, gave a crude product (73·5 g.) of which a portion (65 g.) was re-treated at 12 c.c./hour at 350°. The crude product (59·8 g.) gave upon distillation fractions : (1) 6·8 g., decomposition products, b. p. 30—100°; (2) 15·1 g., crude perfluoro-1 : 2-dimethyl*cyclo*hexane, b. p. 100—102°; (3) 33 g., partly fluorinated material, b. p. 102—150°. The wide boiling range of the required perfluorocarbon, fraction 2, indicated that the latter was less pure than the C_8F_{16} previously prepared from technical xylene. The boiling range of fraction 2 was not narrowed after it had been treated with uranium hexafluoride, and the physical constants of the perfluoro-1 : 2-dimethyl*cyclo*hexane (b. p. 100—102°, n_D^{25} 1·284, d_4^{25} 1·824, γ_4^{25} 15·5 dynes/cm.) are therefore quoted with reserve (cf. Fowler *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 375).

(c) 1 : 3-*Dimethyl*cyclo*hexane.* Experiments carried out in the manner already described showed that a relatively slow addition of the hydrocarbon (10 c.c./hour) and a temperature of 350° gave the best results. The recovery and efficiency were about the same as those obtained during the fluorination of *m*-xylene, but the percentage of C_8F_{16} was appreciably less. After recovery of some perfluorodimethyl*cyclo*hexane from the decomposition products the total crude C_8F_{16} (79·7 g.), on purification, yielded perfluorodimethyl*cyclo*hexane (59·8 g.), corresponding to 62% by weight of the dimethyl*cyclo*hexane used and to 34% by weight of the total fluorocarbon produced.

Comparison of these results with those obtained by the fluorination of xylene shows the advantage of using an aromatic compound. More of the desired perfluorodimethyl*cyclo*hexane is produced, less decomposition occurs, and less cobalt trifluoride is required to carry out the reaction. These results are in direct contrast with those obtained by vapour-phase catalytic fluorination (see *J.*, 1950, 2689, 2787).

(d) *Ethylbenzene.* This was an alternative to xylene for the production of a C_8F_{16} fluorocarbon, and a considerable number of experiments was carried out in order to ascertain its usefulness as a starting product. Variation of the rate of hydrocarbon addition did not affect either the efficiency or the recovery. The optimum yield was produced on addition of 10 c.c./hour at 350°. Fractional distillation of the products from 116 g. of ethylbenzene afforded 100 g. of perfluoroethyl*cyclo*hexane (85% by weight of the ethylbenzene used). The purified product had b. p. 101·5°, f. p. −60°, d_4^{25} 1·826, n_D^{25} 1·283.

Partial fluorination of 100 g. of ethylbenzene at 250° followed by two re-treatments at 350° gave 127 g. of crude fluorocarbon from which 114 g. of perfluoroethyl*cyclo*hexane were obtained. Fluorination of 100 g. of ethylbenzene at 350° followed by two re-treatments of the partly fluorinated hydrocarbon gave 170 g. of crude fluorocarbon which in turn afforded 150 g. of perfluoroethyl*cyclo*hexane.

Comparison of these results with those from the xylene experiments [(b) above] demonstrates (see table below) that ethylbenzene is better than xylene for preparation of a C_8F_{16} fluorocarbon.

	Yield of C_8F_{16} (g.) by :	
Starting material (100 g.).	initial fluorination at 350° and 2 recycles at 350°.	initial fluorination at 250° and 2 recycles at 350°.
Xylene	125	110
Ethylbenzene	150	114

(e) *Ethyl*cyclo*hexane.* This proved to be inferior to ethylbenzene for the preparation of a C_8F_{16} fluorocarbon. Thus at 350° ethyl*cyclo*hexane (15 g.), added at 20 c.c./hour, gave a crude fluorinated product (40 g., efficiency 75) which on fractional distillation afforded fractions (*a*) decomposition products, 7·8 g., (*b*) crude perfluoroethyl*cyclo*hexane, C_8F_{16}, 15·5 g., b. p. 100—102°, and (*c*) hydrofluorocarbon, 11 g., recovery 227. Purification of crude perfluoroethyl*cyclo*hexane (72·5 g.) yielded the pure fluorocarbon (46·0 g.).

---

[1] $$\text{“ Efficiency ”} = \frac{\text{Wt. of crude fluorocarbon condensate}}{\text{Theoretical wt. of product}} \times 100.$$

[2] $$\text{“ Recovery ”} = \frac{\text{Wt. of total fluorocarbon distillate}}{\text{Wt. of hydrocarbon}} \times 100.$$

(f) *Mesitylene.* At the optimum temperature of 350° and with a low addition rate (5 c.c./hour) mesitylene (44 g.) gave a crude fluorinated product (120 g., efficiency 73) of which 86% was insoluble in ethanol and from which crude perfluorotrimethyl*cyclo*hexane (73·5 g.), b. p. 120—128°, was separated by distillation (the recovery was 257). At 250° the chief product was hydrofluorocarbon which could be converted into perfluorotrimethyl*cyclo*hexane by recycling it at 350°. (Yield, 75% by weight of the original mesitylene.) Pure perfluoro-1 : 3 : 5-trimethyl*cyclo*hexane (110 g.) obtained from 205 g. of crude material had b. p. 124·6°, f. p. *ca.* −56°, n_D^{25} 1·294, d_4^{25} 1·890, γ^{25} 17·2 dynes/cm., η^{25} 22·4 millipoises. Cady and Grosse (*Ind. Eng. Chem.*, 1947, **39**, 367) give b. p. 123°, d^{30} 1·8676, n_D^{30} 1·2930, $\eta^{35\cdot7}$ 17·27 millipoises, and Fowler *et al.* (*ibid.*, p. 375) give b. p. 125·18°, d^{20} 1·9025, n^{20} 1·2995.

Fractional distillation of the decomposition products (32·7 g. from 44 g. of mesitylene) furnished small amounts of perfluoromethyl*cyclo*hexane (b. p. 75—77°, d_4^{25} 1·78, n_D^{25} 1·2765, γ^{25} 13·7 dynes/cm.) and of perfluorodimethyl*cyclo*hexane (b. p. 100—102°, n_D^{25} 1·283, γ^{25} 15·2 dynes/cm.). A third component distilling at about 50° crystallised in the condenser and was believed to be perfluoro*cyclo*hexane, but insufficient material was available for its identity to be established completely.

(g) *ψ-Cumene.* The results were similar to those with mesitylene. Fractional distillation of the crude product (efficiency 66, recovery 231) at 350° (addition 9 c.c./hour) failed to yield a fraction with a well defined b. p., the best material boiling between 123° and 125°. The material was evidently fully fluorinated since no change in physical properties, including the specific refraction, occurred after treatment with uranium hexafluoride. The fraction of fluorinated product believed to be perfluoro-1 : 2 : 4-trimethyl*cyclo*hexane had b. p. 123—125°, n_D^{25} 1·295, d_4^{25} 1·888, γ^{25} 17·3 dynes/cm., η^{25} 22·5 millipoises. With the exception of the b. p. these properties correspond closely to those of perfluoro-1 : 3 : 5-trimethyl*cyclo*hexane. It is of interest that the two-degree range in the b. p. was also exhibited by a sample of this material made by the action of fluorine on *ψ*-cumene in the presence of a gold catalyst (Part III).

Fluorination with the Graded-temperature Reactor.—(a) *Octane.* When *n*-octane (33 g.) was passed at 9 c.c./hour through the reactors adjusted to 250°, 300°, and 350°, a crude product (29·7 g.) was obtained. Distillation of this material gave decomposition material, b. p. 30—102°, followed by crude C_8F_{18} fluorocarbon, b. p. 102—106°. Purification of crude perfluoro-octane (60·8 g.) obtained in this way gave perfluoro-octane (42·3 g.), b. p. 103·3°, n_D^{25} 1·272, d_4^{25} 1·776, γ^{25} 13·7 dynes/cm., η^{25}, 14·9 millipoises (Found : C, 21·3 ; F, 78·0% ; *M*, 433. Calc. for C_8F_{18} : C, 21·9 ; F, 78·0% ; *M*, 438).

(b) *Dodecane.* This was prepared from the corresponding secondary alcohol by dehydration with syrupy phosphoric acid and hydrogenation of the dodecene over Raney nickel. With the three reactors adjusted to 280°, 330°, and 380° successively, 29 g. of dodecane gave 15·8 g. of solid (collected in trap *F*) and 18·2 g. (collected in the U tubes) (efficiency, 32).

Fractional distillation of the combined products followed by treatment with uranium hexafluoride and a further fractional distillation gave perfluorododecane (15·5 g.). This was further purified by recrystallisation from carbon tetrachloride. The perfluorododecane had b. p. 178°, m. p. 74—75°, $d_4^{113\cdot5}$ 1·670, $\gamma^{113\cdot5}$ 10·6 dynes/cm., η^{80} 13·1 millipoises (Found : C, 22·3 ; F, 77·1. Calc. for $C_{12}F_{26}$: C, 22·6 ; F, 77·4%).

(c) 2-*Methylnaphthalene.* The m. p. (35°) of this hydrocarbon was low enough to enable the substance to be added from a microburette which was gently warmed. The best results were obtained with the three reactors adjusted successively to 250°, 320°, and 380° ; 2-methylnaphthalene (36 g.), added at 7 g./hour, gave a crude yield of 63·4 g. (efficiency, 50). The alcohol-insoluble component, amounting to 95% of the total yield, showed that fluorination was almost complete. Distillation of the crude fluorocarbon gave fractions : (1) decomposition products, 11·2 g., (2) $C_{11}F_{20}$, b. p. 155—165°, 49·0 g., and (3) hydrofluorocarbon, 1·8 g. (recovery, 173).

Purification of 203 g. of crude $C_{11}F_{20}$ yielded perfluoro-2-methyldecahydronaphthalene (101 g.), b. p. 160·5°, n_D^{25} 1·312, d_4^{25} 1·945, γ^{25} 19·2 dynes/cm., η^{25} 53·6 millipoises (Found : C, 25·8 ; F, 73·9. Calc. for $C_{11}F_{20}$: C, 25·8 ; F, 74·2%). McBee and Bechtol (*Ind. Eng. Chem.*, 1947, **39**, 380) record b. p. 160—161°, f. p. $< -60°$, n_D^{20} 1·3164, d_4^{20} 1·9632.

Fluorination with the Vertical Reactor.—(a, i) *Toluene.* When toluene (31 g.) was introduced at 9 c.c./hour into the reactor adjusted to 300°, a crude product (76·1 g., efficiency 64) was obtained of which 91% was insoluble in alcohol. Distillation gave fractions : (1) decomposition products, 16·5 g., (2) crude perfluoromethyl*cyclo*hexane, 53 g., b. p. 74—78°, and (3) hydrofluorocarbon, 6·0 g. (recovery, 243).

(a, ii) *Benzotrifluoride.* At 350°, benzotrifluoride (49 g.) added at 12 c.c./hour gave a crude product (89·6 g., efficiency, 79), 93% of which was insoluble in ethanol. Distillation of the crude product gave fractions : (1) decomposition products, 123 g., (2) perfluoromethyl*cyclo*hexane, 72·0 g., b. p. 74—78°, and (3) hydrofluorocarbon, 3·6 g.

Purification of product, b. p. 74—78° (224 g.), obtained from toluene or benzotrifluoride afforded perfluoromethyl*cyclo*hexane, C_7F_{14} (163 g.), b. p. 76·2°, f. p. −37°, n_D^{25} 1·276, d^{25} 1·786, γ^{25} 13·8 dynes/cm., η^{25} 15·6 millipoises (Found : F, 75·7% ; *M*, 348. Calc. for C_7F_{14} : F, 76·0% ; *M*, 350).

(b) n-*Propyl*cyclo*hexane.* This was fluorinated to confirm the observation made with the perfluoro-derivatives of mesitylene and *ψ*-cumene that isomeric C_9F_{18} fluorocarbons show only slight difference in their physical properties. The fluorination was best carried out at 380° and with an addition rate of 3 c.c./hour.

Under optimum conditions *n*-propyl*cyclo*hexane (23 g.) afforded a crude product (61·3 g., efficiency 75) of which 60% was insoluble in alcohol and gave, on distillation, fractions : (1) decomposition products, 3·1 g., (2) crude perfluoro-*n*-propyl*cyclo*hexane, 33·0 g., b. p. 120—127°, and (3) hydrofluorocarbon, 19 g. (recovery, 246). The partly fluorinated product (fraction 3) was readily converted into the C_9F_{18} fluorocarbon by re-cycling it.

Purification of a total of 125 g. of crude fluorocarbon gave *perfluoro*-n-*propyl*cyclo*hexane*, C_9F_{18}, b. p. 123—126°, n_D^{25} 1·293, d_4^{25} 1·888, γ^{25} 17·2 dynes/cm. (Found : C, 23·5%; *M*, 445. C_9F_{18} requires C, 24·0%; *M*, 450).

(c) n-*Butyl*cyclo*hexane*. The passage of *n*-butyl*cyclo*hexane (23 g.) at 3·5 c.c./hour into the reactor at 350° yielded a crude product (66·5 g., efficiency 64) of which 56% was insoluble in alcohol. Distillation of the crude product gave fractions : (1) decomposition products, 7·9 g., (2) crude perfluoro-*n*-butyl*cyclo*hexane, 34·4 g., b. p. 142—149°, and (3) hydrofluorocarbon, 23·9 g. (recovery, 288). Recycling of fraction 3 and other experiments gave more of the $C_{10}F_{20}$ fluorocarbon which was purified to give *perfluoro*-n-*butyl*cyclo*hexane*, $C_{10}F_{20}$ (53 g.), b. p. 145—147°, n_D^{25} 1·298, d_4^5 1·899, γ^{25} 17·7 dynes/cm. (Found : *M*, 496. $C_{10}F_{20}$ requires *M*, 500).

(d) p-*Cymene*. When *p*-cymene (23 g.) was passed at 3 c.c./hour through the reactor adjusted to 350°, the crude fluorinated product amounted to 54·8 g. (efficiency, 65), and of this 72% was insoluble in ethanol. Fractional distillation of the product gave fractions : (1) decomposition products, 6·8 g., (2) crude perfluoro-1-methyl-4-*iso*propyl*cyclo*hexane, 34·2 g., b. p. 143—148°, and (3) hydrofluorocarbon, 7·2 g. (recovery, 210).

Thus an increase in hydrocarbon addition caused a decrease in the yield of the $C_{10}F_{20}$ fluorocarbon, and an increase in the amount of the hydrofluorocarbon and of the decomposition products.

Purification of 268 g. of crude $C_{10}F_{20}$ yielded *perfluoro*-1-*methyl*-4-iso*propyl*cyclo*hexane* (137 g.), b. p. 146·5°, f. p. *ca.* —45°, n_D^{25} 1·2965, d_4^{25} 1·902, γ^{25} 17·5 dynes/cm., η^{25} 29·5 millipoises (Found : C, 23·4; F, 75·5%; *M*, 497. $C_{10}F_{20}$ requires C, 24·0; F, 76·0%; *M*, 500).

(e) *Naphthalene and tetrahydronaphthalene*. A saturated solution of naphthalene in tetrahydronaphthalene was used. The results demonstrated that high yields of the required fluorocarbon are obtained at 350° even when the rate of addition of hydrocarbon is relatively rapid (16 c.c./hour) compared with the optimum rate for other hydrocarbons. With these conditions the hydrocarbon mixture (47 g.) gave a crude product (132 g., efficiency, 85) 90% of which was insoluble in ethanol. Fractional distillation gave fractions : (1) decomposition products, 29·2 g., (2) crude perfluorodecahydronaphthalene, $C_{10}F_{18}$, 90·0 g., b. p. 135—146°, and (3) hydrofluorocarbon, 7·6 g. (recovery, 270). Purification of a total of 311 g. of fraction 2 gave perfluorodecahydronaphthalene, $C_{10}F_{18}$ (161 g.), b. p. 141·9°, f. p. —14°, n_D^{25} 1·3085, d_4^{25} 1·920, γ^{25} 18·3 dynes/cm., η^{25} 51·4 millipoises (cf. Grosse and Cady, *Ind. Eng. Chem.*, 1947, **39**, 367).

(f) 2 : 2 : 3-*Trimethylbutane*. The highest yield of fluorocarbon was obtained at 350° and with an addition rate of 5 c.c./hour. Thus the trimethylbutane (16 g.) yielded a crude product (44·0 g., efficiency 71), 96% of which was insoluble in ethanol. Distillation of the alcohol-insoluble portion gave fractions : (1) decomposition products (1·7 g.), and (2) crude perfluorotrimethylbutane, 41·5 g., b. p. 78—85° (recovery, 290). Treatment of 117 g. of fraction 2 with uranium hexafluoride followed by fractional distillation gave pure perfluorotrimethylbutane, b. p. 82·2°, f. p. —80°, n_D^{25} 1·267, d_4^{25} 1·741, η^{25} 9·1 millipoises (Found : C, 21·1; F, 77·9%; *M*, 388. Calc. for C_7F_{16} : C, 21·65; F, 78·35%; *M*, 388). Cady and Grosse, *loc. cit.*, record b. p. 82°, d^{30} 1·7535, n_D^{30} 1·2676.

(g) *Nonane*. This was prepared by hydrogenation of nonene, which was produced from nonyl alcohol by dehydration with boiling syrupy phosphoric acid. The best yields of perfluorononane were obtained at 350° with an addition rate of 5·5 c.c./hour. In this manner nonane (23 g.) afforded a crude fluorocarbon (65 g., efficiency, 75) 50% of which was insoluble in alcohol. Distillation of the crude material gave fractions : (1) decomposition products, 6·1 g., (2) crude perfluorononane, 30·0 g., b. p. 122—127°, and (3) hydrofluorocarbon, 25·0 g. (recovery, 265).

During the experiments which afforded these results it was observed that a slight increase in temperature coupled with a corresponding increase in the rate of hydrocarbon addition caused little change in the yield of the derived perfluorononane although more decomposition occurred. Lower reaction temperatures (300°) resulted in a decrease in the yield of perfluorononane and an increase in that of hydrofluorocarbon (fraction 3). At the optimum temperature (350°) a decrease in the rate of addition of hydrocarbon causes more decomposition. The partly fluorinated materials (fraction 3) can be recycled (5 c.c./hour) at 350° to give additional amounts of perfluorononane.

Purification of crude perfluorononane (295 g., 177% by weight of the nonane used) yielded perfluorononane (125 g.), b. p. 125·3°, f. p. —16°, n_D^{25} 1·276, d_4^{25} 1·799, γ^{25} 14·4 dynes/cm., η^{25} 18·1 millipoises. It is believed that these figures are more accurate than those quoted previously (Musgrave and Smith, *J.*, 1949, 3021) (Found : C, 22·0; F, 77·3%; *M*, 483. Calc. for C_9F_{20} : C, 22·1; F, 77·9%; *M*, 488).

(h) n-*Decane*. The decane was prepared from *sec.*-decyl alcohol by the method used for preparing nonane from nonyl alcohol. Under optimum conditions (380° and 3 c.c./hour), decane (24 g.) gave a crude product (49·4 g.; efficiency, 55) 76% of which was insoluble in ethanol. Distillation of the fluorocompound gave fractions : (1) decomposition products, 15·7 g., (2) perfluorodecane, 25·5 g., b. p. 140—147°, and (3) hydrofluorocarbon, 1·3 g. (recovery, 177).

Decreasing the temperature by 20—30° or increasing the rate of hydrocarbon addition to 4—6 c.c./hour reduced the efficiency and increased the yield of hydrofluorocarbon. On raising of the temperature to 400° and of the rate of addition to 16 c.c./hour the efficiency fell to 32 and the recovery to 110, while the yield of crude perfluorodecane was reduced by 40%.

For decene at 380° the efficiency (65) with an addition rate of 9 c.c./hour compared favourably with the best efficiencies recorded for decane.

Purification of the crude fluorocarbon (fraction 2; 209 g. total) from either decane or decene afforded *perfluorodecane*, $C_{10}F_{22}$, b. p. 143·9—144·6°, which crystallised spontaneously. After recrystallisation from carbon tetrachloride it had b. p. 144·2°, m. p. 36°, n_D^{45} 1·271, d_4^{45} 1·770, γ^{45} 13·5 dynes/cm., η^{35} 20·5 millipoises (Found : C, 22·2; F, 77·4%; *M*, 529. $C_{10}F_{22}$ requires C, 22·3; F, 77·7%; *M*, 538).

The decomposition products obtained on fluorination of decene contained perfluorononane (b. p. 125—126°, n_D^{25} 1·276, d_4^{25} 1·798), cleavage having occurred at the double bond.

(i) *Undecane.* This hydrocarbon was prepared from undecyl alcohol by dehydration followed by hydrogenation. The fluorination of undecane is not efficient. A reaction temperature of 390° and a rate of addition of 18 c.c./hour was least unsatisfactory. The efficiency was 47 and all the crude product was insoluble in ethanol. Combination of a low temperature and a rapid rate of addition of hydrocarbon favour the formation of hydrofluorocarbon.

Under optimum conditions, 14 g. of undecane gave 48·1 g. of crude product which upon fractional distillation yielded 16·1 g. of decomposition products and 30 g. of crude perfluoroundecane, $C_{11}F_{24}$, b. p. 154—168° (recovery, 171). When purified, 132 g. of crude perfluoroundecane yielded *perfluoroundecane* (61 g.), b. p. 160·8°, m. p. 57—58°, n_D^{70} 1·268, d_4^{70} 1·745, γ^{70} 12·7 dynes/cm., η^{60} 16·4 millipoises (Found : C, 22·1; F, 77·2. $C_{11}F_{24}$ requires C, 22·45; F, 77·55%).

(j) *Cetane.* The maximum yield of perfluorocetane was produced at 400° with an addition rate of 8 c.c./hour (efficiency, 50). Most of the crude perfluorocetane was condensed in the trap *F*, but usually a portion passed through it and was condensed in the U-tubes *J* as a semi-solid, and was extracted with perfluoroheptane. Cetane (24 g.) yielded 45 g. of crude fluorocarbon.

After a preliminary distillation, the crude perfluorocetane was treated with uranium hexafluoride either in a Carius tube at 150° or in perfluoroheptane solution on the boiling water-bath. Both procedures gave only a slight green coloration due to uranium tetrafluoride, thus indicating that the product was almost completely fluorinated. A solution of the product in perfluoroheptane was washed with water, dried, and fractionally distilled. The required perfluorohexadecane (perfluorocetane) had b. p. 233°, m. p. 125—126° (from perfluoroheptane followed by carbon tetrachloride) (Found : C, 22·7; F, 76·8. Calc. for $C_{16}F_{34}$: C, 22·9; F, 77·1%). Fowler *et al.* (*loc. cit.*) and Burford *et al.* (*Ind. Eng. Chem.*, 1947, **39**, 319) quote b. p. 238—240°.

The fluorination of cetane is accompanied by central cleavage of the molecule since perfluoro-octane (b. p. 103—104°, n_D^{25}, 1·272, d_4^{25} 1·78, γ^{25} 13·7 dynes/cm.) was identified amongst the products.

The authors are indebted to the late Professor Sir Norman Haworth, F.R.S., and to Professor M. Stacey, F.R.S., for their interest in this work during the period 1940—1946. They also thank the Director General of Scientific Research for permission to publish it.

THE CHEMISTRY DEPARTMENT, THE UNIVERSITY, BIRMINGHAM. [*Received, June* 24*th*, 1950.]