536. *Organic Fluorides. Part IV. Fluorination of Hydroaromatic Hydrocarbons by Use of a Gold Catalyst.*

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Vapour-phase fluorination using a gold catalyst gives better yields of fluorocarbons from hydroaromatic hydrocarbons than from the parent aromatic hydrocarbons. Ethyl*cyclo*hexane was found to be the best hydrocarbon for the preparation of a C_8F_{16} fluorocarbon.

IN Part III (*J.*, 1950, 2689) the optimum conditions for the fluorination of aromatic hydrocarbons were determined. From the point of view of fluorine economy, it is apparent that since hydroaromatic hydrocarbons will consume more fluorine than unsaturated or aromatic hydrocarbons during complete fluorination, it would be advantageous to use the unsaturated compounds. The experiments recorded herein prove, however, that higher yields of fluorocarbons are obtained from hydroaromatic than from aromatic hydrocarbons (Table I). Hence, as far as fluorination is concerned, the double bond in aromatic as well as in aliphatic hydrocarbons is a position of weakness (cf. Part I, *J.*, 1949, 3021). The results also show that, under the conditions employed in this work, fluorination of hydroaromatic hydrocarbons is attended by less decomposition and less polymerisation than is the case with aromatic hydrocarbons. These results should be compared with those of Cady *et al.* (*Ind. Eng. Chem.*, 1947, **39**, 290), published since this work was completed, which indicated that aromatic hydrocarbons give higher yields of fluorocarbons than the paraffinic hydrocarbons when fluorinated in the vapour phase in the presence of silver-plated copper turnings.

TABLE I.

The effect of unsaturation upon the yield of fluorocarbon.

Hydrocarbon.	Fluorocarbon.	Yield, %.
Ethylbenzene	Perfluoroethyl*cyclo*hexane	9·6
Ethyl*cyclo*hexane	,,	21
Mesitylene	Perfluoro-1 : 3 : 5-trimethyl*cyclo*hexane	5·9
1 : 3 : 5-Trimethyl*cyclo*hexane	,,	11·2
m-Xylene	Perfluoro-1 : 3-dimethyl*cyclo*hexane	4·5
1 : 3-Dimethyl*cyclo*hexane	,,	15·4
Tetrahydronaphthalene	Perfluorodecahydronaphthalene	11·4
Decahydronaphthalene	,,	18·8

The rôle played by the gold-plated copper turnings in vapour-phase fluorination is not immediately apparent. Before the recent fluorination studies (see Parts I, II, and III of this series; Cady *et al.*, *loc. cit.*), it was recorded by Fredenhagen and Cadenbach (*Ber.*, 1934, **67**, 928) that the presence of copper, iron, silver, or cerium filling agents gave improved yields during fluorination. This improvement was ascribed to the dispersion of the reactants and no catalytic effect was suspected. Bigelow and his co-workers then confirmed and extended the beneficial effect of copper gauze during fluorination. The view has been advanced that the reaction is the vapour phase involves free radicals (Bigelow *et al.*, *J. Amer. Chem. Soc.*, 1937, **59**, 198; 1938, **60**, 427; 1939, **61**, 3552; 1940, **62**, 267, 1171, 3302; 1941, **63**, 788, 2792; *Ind. Eng. Chem.*, 1947, **39**, 360; Miller, *J. Amer. Chem. Soc.*, 1940, **62**, 341), and that it is a catalytic one (Cady *et al.*, *loc. cit.*; Part I, *loc. cit.*). Moreover, the elements which aid fluorination, such as gold, silver, copper, cobalt, etc., show variable valency, and the higher fluorides of some of these metals are themselves capable of acting as fluorinating agents (McBee and Bechtol, *Ind. Eng. Chem.*, 1947, **39**, 380; Fowler *et al.*, *ibid.*, pp. 292, 343). This would, therefore, lead to the suggestion that, in part, the rôle of the catalyst is that of a halogen carrier and that its action is due to the formation of the higher fluoride, which in contact with hydrocarbon vapour effects the introduction of fluorine into the molecule. Examination of the gold catalyst after several experiments, however, has repeatedly shown that the metal surface is only slightly attacked and little increase in weight takes place. Since auric fluoride is readily detectable by its orange colour (Moissan, *Compt. rend.*, 1889, **109**, 807), it seems that there is not the complete conversion which might be expected if the gold (as a fluoride) is acting solely as a halogen carrier. Whatever the exact rôle of the gold may be, it is certainly an important one, for in time it is slowly attacked and the auric and copper fluorides are gradually carried to the base of the reaction vessel by the gas streams, a development accompanied by diminishing yields of fluorocarbon.

At the time (1940—1946) when this and the preliminary work (Parts I and II) was being carried out, it seemed that, although a vast improvement had been brought about by the use of gold and silver as catalysts, vapour-phase procedures involving the direct use of elementary fluorine were unlikely to become generally useful or economical on a large scale. Since that time no experimental evidence has been produced which would justify any alteration of this view. In a forthcoming communication, however, it will be shown that the indirect use of fluorine for the fluorination of hydrocarbons by cobalt trifluoride affords better yields of fluorocarbons (see also Fowler *et. at., loc. cit.*).

EXPERIMENTAL.

Apparatus and Procedure.—The apparatus used for this work has been fully described in Part III (*loc. cit.*). The catalyst was replaced when its activity (tested against benzene or heptane as described in Parts I and III) was seen to be reduced. The procedure adopted was the same as that for the work in Part III.

(A) *Fluorination of* 1 : 3-*Dimethyl*cyclo*hexane.*—This was best accomplished by treating the hydrocarbon (17 g.) at the rate of 2 c.c./hr. (reservoir temp. 75°) with fluorine (13 g./hr.) at 200°. The hydrocarbon was diluted with 19 l. of nitrogen/hr. and the fluorine with 18 l. of nitrogen/hr. The yield of crude fluorocarbon (22 g.) corresponded to a recovery of 129%. Fractional distillation gave: fraction 1, (decomposition products), 6·3 g., b. p. 40—95°; fraction 2 (perfluorodimethyl*cyclo*hexane), 9·9 g., b. p. 95—105°; fraction 3 (hydrofluorocarbon), 4·7 g., b. p. 105—170°. No polymer was obtained in this experiment but it was produced when a high rate of addition of hydrocarbon and a high nitrogen dilution of the reactants were employed. The yield of fluorocarbon formed from the saturated hydrocarbon was much greater than that produced from the parent aromatic hydrocarbon (see Part III). This observation, hitherto unknown, was substantiated by the experiments recorded below. Purification of 28·1 g. of the crude fluorocarbon (fraction 2) obtained in this way gave perfluoro-1 : 3-dimethyl*cyclo*hexane (24·2 g.), b. p. 101·5°, D_4^{25} 1·828 g./c.c., n_D^{25} 1·283, γ^{25} 15·1 dynes/cm., η^{25} 19·3 millipoises.

(B) *Fluorination of Ethyl*cyclo*hexane.*—This proved to be the best hydrocarbon for producing C_8F_{16} by the vapour-phase catalytic procedure. Treatment of ethyl*cyclo*hexane (24 g.) [added at the rate of 2·7 c.c./hr.) (reservoir temp. 105°) and diluted with 10 l. of nitrogen/hr.] with fluorine (15 g./hr. diluted with 10 l. of nitrogen/hr.) gave 78·1 g. of crude product, 29·2 g. of which collected in traps *A* and *B* and 48·9 g. in the U-tubes. Distillation of the U-tube condensate gave: fraction 1, 9·3 g. (decomposition products) b. p. 20—95°; fraction 2, crude perfluoroethyl*cyclo*hexane, 27·4 g., b. p. 95—105°; fraction 3, hydrofluorocarbon, 10·4 g., b. p. 105—170°. The distillation residue of polymeric material was 0·5 g., b. p. >170°. The " recovery " was approximately 200%. Purification of a total of 161 g. of fraction 2 obtained in this way afforded perfluoroethyl*cyclo*hexane (121 g.; yield 75—80% of ethyl*cyclo*hexane), b. p. 101·5°, f. p. −60°, D_4^{25} 1·826, n_D^{25} 1·283. After a number of experiments the polymeric material which collected in traps *A* and *B* was fractionated to give stable colourless fluoro-oils of the same type as those isolated previously in much greater quantity from ethylbenzene.

(C) *Fluorination of* 1 : 3 : 5-*Trimethyl*cyclo*hexane.*—A typical experiment was carried out at 200° by treating the hydrocarbon (14 g.) (3·5 c.c./hr.) (reservoir temp. 125°) diluted with 16 l. of nitrogen/hr. with fluorine (15 g./hr. diluted with 14 l. of nitrogen/hr.). This procedure afforded 7·2 g. in traps *A* and *B* and 16·3 g. in the U-tubes. The latter gave: fraction 1, decomposition products, 3·7 g., b. p. 40—120°; fraction 2, crude C_9F_{18}, 7·9 g., b. p. 120—128°: fraction 3, hydrofluorocarbon, 2·6 g., b. p. 128—170°: fraction 4, polymeric material, 0·7 g., b. p. >170°. These figures correspond to a recovery of 106%. Refractionation of polymeric material corresponding to fraction 4 gave oils of the usual type, and from the reactor a small amount of a wax-like polymer was recovered.

Table II shows a detailed analysis of these results and those on the fluorination of mesitylene. The advantage of using the hydroaromatic hydrocarbon for fluorination instead of the corresponding aromatic hydrocarbon is quite apparent though the difference is not as marked as with ethylbenzene and ethyl*cyclo*hexane. Purification of fraction 2 in the usual way yielded perfluoro-1 : 3 : 5-trimethyl*cyclo*hexane, b. p. 124·6°, D_4^{25} 1·89, n_D^{25} 1·294.

TABLE II.

Material fluorinated.	$\frac{\text{Wt. } C_9F_{18}}{\text{Wt. hydrocarbon}} \times 100.$	C_9F_{18} in total distillate (%).	Decomposition products (b. p. 40—124°) in crude yield (%).	Hydrofluorocarbon (b. p. 125—170°) in crude yield (%).
Trimethyl*cyclo*hexane	26	26	36	24
Mesitylene *	10	11	52	26

* Results from Part III (*loc. cit.*).

(D) *Fluorination of Tetrahydronaphthalene.*—Under the best conditions for the fluorination (temp. 360°; hydrocarbon 3 c.c./hr. diluted with 15 l. of nitrogen/hr.; temp. of reservoir 185°; fluorine 14 g./hr. diluted with 10 l. of nitrogen/hr.), 20 g. of tetrahydronaphthalene gave 24·4 g. of crude fluorocarbon which upon distillation yielded: fraction 1, decomposition products, 7·0 g., b. p. 40—135°; fraction 2, crude perfluorodecahydronaphthalene, 9·2 g., b. p. 135—146°; fraction 3, hydrofluorocarbon, 5·9 g., b. p. 146—210°. It was noted as in previous fluorinations that increasing the nitrogen dilution of the hydrocarbon produced more hydrofluorocarbon and polymeric material.

Purification of the crude fluorocarbon corresponding to fraction 2 (51·4 g.) yielded perfluorodecahydronaphthalene (10·2 g.), b. p. 142°, f. p. −15°, D_4^{25} 1·919, n_D^{25} 1·309, γ^{25} 18·4, η^{25} 51·1 (Found: C, 25·4; F, 73·7%; *M*, 454: Calc. for $C_{10}F_{18}$: C, 26·0; F, 74·0%; *M*, 462). McBee and Bechtol (*loc. cit.*) give b. p. 140°, f. p. −7° to −10°, D_4^{20} 1·9456, n_D^{20} 1·3118 for this compound (cf. Musgrave and Smith, *J.*, 1949, 3021).

The series of experiments carried out with this compound showed that much more decomposition occurred with tetrahydronaphthalene than with either benzene or toluene. Some polymerisation also occurred, and the product collected in trap *A* afforded the usual fractions of colourless fluoro-oils (b. p. 150—240°/10 mm.) and a glassy solid, b. p. 240—300°/10 mm.

(E) *Fluorination of Decahydronaphthalene.*—In one of a series of experiments fluorine (14 g./hr.) diluted with 10 l. of nitrogen/hr. was allowed to react with decahydronaphthalene (2 g./hr.) diluted with 10 l. of nitrogen/hr. at 370° during 12 hours. The crude fluorocarbon (32·8 g.) collected in the U-tubes was washed with water, dried (phosphoric oxide) and distilled to give: fraction 1, decomposition products, 8·3 g., b. p. 40—135°; fraction 2, crude perfluorocarbon, 15·1 g., b. p. 135—146°; fraction 3, hydrofluorocarbon, 6·7 g., b. p. 146—210°; fraction 4, polymer, 0·15 g., b. p. >210°. The crude perfluorodecahydronaphthalene formed 63% of the weight of the starting product; this should be compared with the best figure of 46% produced during the fluorination of tetrahydronaphthalene. When purified in the manner described in Part III, the perfluorodecahydronaphthalene had the same properties as those described in Section D (Found: F, 73·6. Calc. for $C_{10}F_{18}$: F, 74·0%).

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