226. *The Reactions of Highly Fluorinated Organic Compounds. Part I. The Preparation and Reactions of Some Chloroundecafluoro*cyclo*hexanes.*

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The fluorination of *o*-dichlorobenzene in the vapour phase with cobaltic fluoride gave mainly chloroundecafluoro*cyclo*hexane and 1 : 2-dichlorodecafluoro*cyclo*hexane. The former was obtained also by a similar fluorination of chlorobenzene. Chloroundecafluoro*cyclo*hexane, when treated with lithium aluminium hydride, gave the corresponding fluoro-hydrocarbon, undecafluoro*cyclo*hexane, by exchange of hydrogen for chlorine. This reacted with aqueous alkali, being converted by loss of hydrogen fluoride into perfluoro*cyclo*hexene. From this olefin the dibromo- and dichloro-addition products were prepared, and oxidation afforded perfluoroadipic acid which was converted into certain derivatives.

The reaction of organic compounds in the vapour phase with certain transition-element fluorides in which the metal exerts its highest valency state is a convenient method for effecting full fluorination of organic structures. The method has been used fairly extensively for the conversion of hydrocarbons into fluorocarbons, cobaltic fluoride being the

fluorinating agent most widely employed (Fowler *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 292; Benner *et al.*, *ibid.*, p. 329; Burford *et al.*, *ibid.*, p. 319; Irwin *et al.*, *ibid.*, p. 350; Haszeldine and Smith, *J.*, 1950, 3617; Barber, Burger, and Cady, *J. Amer. Chem. Soc.*, 1951, **73**, 4241; Barbour, Barlow, and Tatlow, *J. Appl. Chem.*, in the press). Other metallic fluorides used for fluorocarbon synthesis have been silver difluoride (McBee and Bechtol, *Ind. Eng. Chem.*, 1947, **39**, 380), manganese trifluoride and cerium tetrafluoride (Fowler *et al.*, *ibid.*, p. 343), and lead tetrafluoride (McBee and Robb, U.S.P. 2 533 132; *Chem. Abs.*, 1951, **45**, 2975).

Compounds containing elements in addition to carbon and hydrogen have been fluorinated by this general method; thus, vapour-phase fluorination of amines and of pyridine derivatives with cobalt trifluoride to give perfluoro-amines has been reported (Thompson and Emeléus, *J.*, 1949, 3080: Haszeldine, *J.*, 1950, 1638, 1966; *J.*, 1951, 102), and by the use of the same reagent the compound CSF_8 has been produced from methanethiol and carbon disulphide (Silvey and Cady, *J. Amer. Chem. Soc.*, 1950, **72**, 3624). All these derivatives are chemically inert and in this respect resemble the fluorocarbons. Attempts to fluorinate methyl alcohol (Kellogg and Cady, *ibid.*, 1948, **70**, 3986) and aliphatic ketones (Holub and Bigelow, *ibid.*, 1950, **72**, 4879) with cobaltic fluoride were unsuccessful.

As part of our general study of highly fluorinated organic compounds, we wished to investigate certain perfluorinated chloro-derivatives and to examine their reactions. Some results obtained a few years ago suggested that when chlorofluorocarbon mixtures were fluorinated in the vapour phase by means of cobaltic fluoride, removal of the whole of the chlorine was difficult; similar observations have been made by Couper *et al.* (*Ind. Eng. Chem.*, 1947, **39**, 346), and by McBee *et al.* (*ibid.*, p. 310). Accordingly, we decided to attempt to synthesise the desired perfluorinated chloro-compounds by treatment of chlorohydrocarbons, having the same carbon skeletons, in the vapour phase with cobalt trifluoride. This paper describes the preparation, from chlorobenzene and *o*-dichlorobenzene, of chloroundecafluoro*cyclo*hexane and 1 : 2-dichlorodecafluoro*cyclo*hexane, together with certain reactions of chloroundecafluoro*cyclo*hexane. While the work was in progress, Lindgren and McBee (U.S.P. 2 480 081; *Chem. Abs.*, 1950, **44**, 2020) described the fluorination of *o*-dichlorobenzene with silver difluoride and with manganese trifluoride to give the same two products though apparently in somewhat less pure forms than ours, and McBee, Robb, and Ligett (U.S.P. 2 493 007; *Chem. Abs.*, 1950, **44**, 5375) claimed that chlorine was retained in organic structures during fluorinations with cerium tetrafluoride.

For the fluorination of chloro-compounds we found that the apparatus and conditions of reaction which were most suitable were those already used by us for fluorocarbon production (see Barbour, Barlow, and Tatlow, *loc. cit.*). The reaction vessel which we have developed for carrying out vapour-phase fluorinations with cobaltic fluoride is a horizontal electrically-heated nickel tube in which the cobalt trifluoride (*ca.* 3500 g.) is gently stirred during the reaction. To obtain the maximum yields of fully fluorinated products careful control of the reaction conditions, particularly temperature, is necessary. When chlorobenzene was fluorinated with cobaltic fluoride, chloroundecafluoro*cyclo*hexane and perfluoro*cyclo*hexane were formed. The maximum yields (*ca.* 14%) of the former were obtained when the chloro-compound (input rate 22 g./hr.) was fluorinated at 350°, care being taken to avoid temperature increases in the reaction zone. At lower reaction temperatures, increased proportions of partly fluorinated material were found in the products; below 300°, recycling of the crude product through the fluorination apparatus was necessary, and much lower overall yields were obtained. When chlorobenzene was fluorinated at 350° at higher input rates, the temperature of the reaction zone unavoidably increased, owing to the faster reaction rate, and again low yields of chloroundecafluoro*cyclo*hexane resulted. It was found that in the fluorination of *o*-dichlorobenzene, perfluoro*cyclo*hexane and three chlorofluoro*cyclo*hexanes were produced; the best reaction conditions found were almost the same as for chlorobenzene. *o*-Dichlorobenzene gave, on fluorination, chloroundecafluoro*cyclo*hexane in rather better yields (*ca.* 16%) than those obtained from chlorobenzene, the expected 1 : 2-dichlorodecafluoro*cyclo*hexane in about equal yields, and in addition small yields (*ca.* 4%) of trichlorononafluoro*cyclo*hexane. Thus, *o*-dichlorobenzene is by far the better starting material for the synthesis of chlorofluoro*cyclo*hexanes.

As in the case of chlorobenzene, lower reaction temperatures gave rise to less completely fluorinated products.

Much of the chlorine present in the chlorobenzenes was retained in the molecules during the fluorination process, though a proportion was eliminated, perfluoro*cyclo*hexane being present in all products, and chloroundecafluoro*cyclo*hexane resulting from the fluorination of *o*-dichlorobenzene. Part of the displaced chlorine was present in the elemental form in the cooled traps in which the reaction products were collected. It is noteworthy, however, that the eliminated chlorine, either in the elementary form or as chlorine fluorides, is capable of re-entering the organic structures, as shown by the formation of trichlorononafluoro*cyclo*hexane during the fluorination of *o*-dichlorobenzene, and of dichlorodecafluoro*cyclo*hexanes during the fluorination of chlorobenzene, though in the latter case no pure compound was isolated. Careful temperature control during the fluorination, the use of low feed rates, and the utilisation of less than 50% of the "available fluorine" of the reactor were necessary in order to get maximum yields of the desired products. The avoidance of recycling stages is also advantageous, since in fluorinations of this type, though yields are calculated most conveniently from the amount of organic starting material employed, the fluorine consumption, and the number of runs which can be carried out in a cobaltic fluoride reactor in a given time, are usually the most important factors.

The chlorofluoro*cyclo*hexanes obtained are all low-melting volatile solids, which are rather more soluble in the common organic solvents than are fluorocarbons. It is interesting that many of the saturated highly-fluorinated *cyclo*hexane derivatives have melting points above room temperature, and exist as low-boiling solids. This fact makes fractional distillation and other operations difficult in certain cases.

Some of the reactions of chloroundecafluoro*cyclo*hexane and of compounds derived from it are described below. Further reactions, including those of 1 : 2-dichlorodecafluoro*cyclo*hexane and the trichlorononafluoro*cyclo*hexane which were obtained, will be reported later.

Preliminary investigations, in which the monochloro-compound was treated under drastic conditions with a number of reagents which react readily with alkyl halides, showed, as expected, that these fluoro-derivatives were very stable. Aqueous alkalis, metallic salts such as acetates, cyanides, nitrites, and iodides, and metals such as sodium and magnesium could not be induced to react except under extreme conditions of temperature and pressure in certain cases, in which complete degradation resulted. It was found, however, that reaction with lithium aluminium hydride occurred readily, much chloride ion but no fluoride ion being detected after the addition of water to the reaction mixture.

The reactions of lithium aluminium hydride with hydrocarbon-type chloro-, bromo-, and iodo-derivatives have been studied recently, and, in general, with primary and secondary aliphatic halides the halogen atom is replaced by hydrogen, the order of reactivity being iodides > bromides > chlorides (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3738; Johnson, Blizzard, and Carhart, *ibid.*, p. 3664; Trevoy and Brown, *ibid.*, 1949, **71**, 1675). Bromo*cyclo*hexane gives *cyclo*hexane in poor yield only, and chloro*cyclo*hexane does not react (Johnson, Blizzard, and Carhart, *loc. cit.*).

The reaction of chloroundecafluoro*cyclo*hexane with lithium aluminium hydride in ethereal solution resulted in replacement of the chlorine atom by a hydrogen atom, the fluorinated structure remaining intact and the product being undecafluoro*cyclo*hexane, a compound already reported by Fukuhara and Bigelow (*J. Amer. Chem. Soc.*, 1941, **63**, 2792) who obtained it from the vapour-phase fluorination of benzene by fluorine–nitrogen mixtures in a vessel packed with copper gauze. It is also one of the products of the vapour-phase fluorination of benzene by cobaltic fluoride at temperatures below those necessary for fluorocarbon production (Barbour, Mackenzie, Stacey, and Tatlow, unpublished work). The ready replacement of chlorine by hydrogen in the reaction of chloroundecafluoro*cyclo*hexane with lithium aluminium hydride is rather surprising, in view of the general stability of chloro-fluoro-compounds and the failure of chloro*cyclo*hexane to give a similar reaction.

Little has been reported so far about the reactions of highly fluorinated compounds retaining a few hydrogen atoms in the molecule. We found that undecafluoro*cyclo*hexane

reacted readily with concentrated aqueous alkali to give perfluoro*cyclo*hexene by elimination of a molecule of hydrogen fluoride. This olefin was reported recently by Brice and Simons (*J. Amer. Chem. Soc.*, 1951, **73**, 4017), being a product of the decomposition of undecafluoro-*cyclo*hexanecarboxylic acid in aqueous solution.

Perfluoro*cyclo*hexene possesses an unreactive double bond and undergoes the expected addition reactions only with difficulty. For instance, it reacts with chlorine only in a sealed tube; the dichloro-addition product was identical with the material obtained from the fluorination experiments with *o*-dichlorobenzene. Brice and Simons (*loc. cit.*) obtained the same dichloro-addition product. They mention the lack of reactivity of the olefin and failed to get a dibromide. We obtained this 1 : 2-dibromodecafluoro*cyclo*hexane by reaction of bromine with the olefin whilst the mixture was irradiated with light from a mercury-vapour lamp. Further, by oxidation of the olefin with aqueous potassium permanganate, perfluoroadipic acid was obtained, and was identified as the free acid and as the dianiline salt. McBee, Wiseman, and Bachman (*Ind. Eng. Chem.*, 1947, **39**, 415) obtained crude perfluoroadipic acid by fluorination of hexachlorobenzene with antimony pentafluoride to give 1 : 2-dichloro-octafluoro*cyclo*hex-1-ene, followed by oxidation of this olefin, but they did not isolate the acid itself, only derivatives. We prepared the diethyl ester and the diamide of perfluoroadipic acid; they were identical with those described by the above authors.

Further reactions of perfluorinated chloro-, polyfluoro-, and perfluoro-olefin derivatives of the *cyclo*hexane series are now being studied. A similar series of conversions proceeding in an analogous fashion to that described above has been carried out already starting from 1 : 2-dichlorodecafluoro*cyclo*hexane. It would appear that reactions of these types offer novel routes for the synthesis of many new fluorinated compounds of known constitution. These reactions enable the convenient cobaltic fluoride fluorination method, and related processes, to be employed for the production of highly fluorinated compounds which are starting points for general synthetic chemistry, and from which a variety of derivatives, hitherto inaccessible, may be made. Previously, by the use of this type of fluorination process, only chemically inert materials have been produced. Several new perfluorinated chloro-compounds have been made already, and the further reactions of these derivatives are being examined.

Experimental

Apparatus and Procedure for Fluorinations.—(a) *Cobalt trifluoride reactor.* The fluorination unit and the cell for generation of fluorine which were used in this investigation are described by Barbour, Barlow, and Tatlow (*loc. cit.*). The cobalt trifluoride reactor was a horizontal nickel tube (3′ 6″ long; $3\frac{3}{8}$″ internal diam.) fitted with a coaxial nickel stirrer shaft carrying paddles and driven at approx. 4 revs./min. The vessel was heated by seven electrical heaters, each controlled by a Simmerstat or a variable transformer. Temperatures were measured by chromel–alumel thermocouples. One of these was enclosed in a long, thin, copper tube which could be moved along inside the stirrer shaft, which was made of stout nickel tube. Temperature readings could thus be taken inside the reactor body; other thermocouples brazed on to the reactor shell gave the temperatures of the body itself. Organic materials were fed into the apparatus from a constant-rate dropper. Liquid displaced by a piston, lowered by a synchronous electric motor, ran down a heated sloping inlet tube into the reactor. After passage over the cobaltic fluoride, the products passed up a short exit tower fitted with baffle plates and were condensed in copper vessels cooled by solid carbon dioxide–alcohol. The reactor was charged with about 3500 g. of cobalt trifluoride, the " available " fluorine being approx. 575 g.

(b) *Distillation.* Fractional distillations were carried out by using glass vacuum-jacketed columns 1′ and 2′ long. When necessary, side-heaters of the type designed by Massingham (*Chem. and Ind.*, 1951, 31) were employed. Still-heads were of the simple manually-operated type incorporating capillary taps. The most suitable column packing was found to be Dixon gauze cylinders (Dixon, *J. Soc. Chem. Ind.*, 1949, **68**, 88), size $\frac{1}{16}$″ × $\frac{1}{16}$″, made of nickel gauze (100 mesh; 42 s.w.g.). Take-off rates were usually of the order of 10 c.c./hr., and the ratios of material condensed on the total condenser to that taken off were about 20 : 1 on the rises and 10 : 1 on the flats of the distillation curves. Difficulty was experienced with the low-boiling materials which were solids at normal temperatures, and to collect such products it was necessary

to use a cooled receiver almost totally enclosed, and to warm the side-arm of the still-head by means of an electric lamp or a small heater to prevent crystallisation. Removal of perfluoro*cyclo*hexane (which sublimes at 52—53°) from the products of fluorination experiments was best accomplished by using an unjacketed column (which could be heated quickly if necessary to avoid blockages) and a simple direct take-off with no reflux. The yields of various fractions recorded below are minimum values only, since combination of intermediate fractions from different experiments followed by re-fractionation gave further quantities of pure materials.

Fluorination of Chlorobenzene.—The general method was the same as that described for the fluorination of hydrocarbons by Barbour, Barlow, and Tatlow (*loc. cit.*). The best conditions appeared to be as follows.

Chlorobenzene (110·0 g.; input rate 22 g./hr.) was passed into the cobalt trifluoride reactor, which was kept throughout at 350°, temperature increases due to the heat of reaction being avoided by adjustment of the heater controls and removal of lagging segments if necessary. After completion of the addition, the apparatus was swept out with a stream of nitrogen, and the fluorinated product was poured into ice-water, separated, washed with water, dried (P_2O_5), and filtered. The crude products (430 g.) from two such experiments were combined and fractionated. Two pure compounds were obtained: perfluoro*cyclo*hexane, subliming at 52—53°, and chloroundecafluoro*cyclo*hexane (89·2 g., 14%) which crystallised spontaneously, b. p. 79·4—80·1°/754 mm., m. p. 30—31°, n_D^{40} 1·301 (Found: C, 22·6; Cl, 11·7; F, 65·9%; *M*, 318. Calc. for C_6ClF_{11}: C, 22·8; Cl, 11·2; F, 66·0%; *M*, 316·5). Lindgren and McBee (*loc. cit.*) gave b. p. 76·9—77·0° and m. p. 24—26° for this compound.

Other experiments gave the following results: chlorobenzene (220 g.), fluorinated in two experiments at 250° (input rate 22 g./hr.), yielded C_6ClF_{11} (55·1 g., 9%) after recycling of the product under the same conditions; chlorobenzene (220 g.), fluorinated in two experiments at 300° (input rate 22 g./hr.), yielded C_6ClF_{11} (77·7 g., 13%); and chlorobenzene (110 g.) at 350° (input rate 33 g./hr.) yielded C_6ClF_{11} (17·5 g., 6%).

Fluorination of o-Dichlorobenzene.—By the same general method as in the case of chlorobenzene, *o*-dichlorobenzene (139 g.; input rate 26 g./hr.) was fluorinated at 350°, care being taken to avoid temperature increases. The crude product (445 g.) from two such experiments, after being washed with water, dried (P_2O_5), and filtered, was fractionated. After removal of perfluoro*cyclo*hexane, three pure crystalline compounds were isolated: chloroundecafluoro*cyclo*hexane (96·0 g., 16%), b. p. 79·0—79·7°/746 mm., n_D^{45} 1·297, m. p. 30—31°, identical with the specimen already mentioned; 1 : 2-dichlorodecafluoro*cyclo*hexane (98·8 g., 16%), b. p. 109·6—110·2°/756 mm., m. p. 39—41°, n_D^{45} 1·332 (Found: C, 21·7; Cl, 21·9; F, 57·6%; *M*, 334. Calc. for $C_6Cl_2F_{10}$: C, 21·6; Cl, 21·3; F, 57·1%; *M*, 333); and *trichlorononafluoro*cyclo*hexane* (27·5 g., 4%), b. p. 140·7—141·2°/758 mm., m. p. 32·5—33·5°, n_D^{45} 1·363 (Found: C, 20·4; Cl, 30·6; F, 49·6%; *M*, 348. $C_6Cl_3F_9$ requires C, 20·6; Cl, 30·45; F, 48·9%; *M*, 349·5). Lindgren and McBee (*loc. cit.*) gave b. p. 107·5—107·7°, m. p. 12—14°, and n_D^{20} 1·3413 for 1 : 2-dichlorodecafluoro*cyclo*hexane, and Brice and Simons (*loc. cit.*) recorded b. p. 108°, m. p. 18·5—20°, n_D^{20} 1·338—1·339. Lindgren and McBee (*loc. cit.*) mentioned a trichlorononafluoro*cyclo*hexane, b. p. 144—148°, obtained by treatment of hexachlorobenzene with lead tetrafluoride.

o-Dichlorobenzene (278 g.), fluorinated in two experiments at 300° (input rate 26 g./hr.), yielded C_6ClF_{11} (41·1 g., 7%), $C_6Cl_2F_{10}$ (77·2 g., 12%), and $C_6Cl_3F_9$ (17·4 g., 3%). The amount of crude product was greater than in the other experiment but the intermediate fractions distilling between the pure components comprised a much higher proportion of the material, suggesting that fluorination was incomplete.

*Undecafluoro*cyclo*hexane from Chloroundecafluoro*cyclo*hexane.*—A suspension of powdered lithium aluminium hydride (2·1 g.) in dry ether (120 c.c.) was stirred mechanically and cooled in water whilst a solution of chloroundecafluoro*cyclo*hexane (50·0 g.) in dry ether (50 c.c.) was added slowly, during 1 hour, the reaction being carried out under anhydrous conditions in a vessel fitted with a reflux condenser cooled by solid carbon dioxide above the usual water condenser. Heat was evolved and a bulky white precipitate was formed. The reaction mixture was stirred at room temperature for 1 hour further and was then refluxed for 2 hours. With great care, 50% sulphuric acid (20 c.c.) was added dropwise, the reaction mixture being cooled in ice. Initially, there was a vigorous reaction with a rapid refluxing of the ether. Water (130 c.c.) was then added and, when dissolution was complete, the ethereal layer was separated, the aqueous layer was extracted with fresh portions of ether, and the combined ethereal layers were washed with water, dried ($MgSO_4$), filtered, and fractionated through a 1′ column. After removal of ether there was obtained undecafluoro*cyclo*hexane (26·4 g., 59%), which crystallised on cooling,

b. p. 63·0—63·5°/757 mm., n_D^{50} 1·275, m. p. 46—48° (Found: C, 25·9; H, 0·4; F, 73·6%; *M*, 283. Calc. for C_6HF_{11}: C, 25·55; H, 0·35; F, 74·1%; *M*, 282). Fukuhara and Bigelow (*loc. cit.*) recorded b. p. 62° for this compound and said that it consisted of high- and low-melting isomers, m. p.s 41—43° and −16° to −14°, in a mobile equilibrium. We obtained no evidence of a low-melting isomer.

*Non-reactivity of Chloroundecafluoro*cyclo*hexane.*—No exchange of the chlorine atom for other radicals could be effected when chloroundecafluoro*cyclo*hexane was treated with any of the following reagents: aqueous sodium hydroxide, potassium or silver acetates in glacial acetic acid, aqueous-alcoholic sodium or cuprous cyanides, magnesium turnings in dry ether, phenylmagnesium bromide, molecular sodium, or sodium iodide in acetone. In general, the starting material was recovered unchanged, but in some cases complete degradation occurred under very drastic conditions.

*Perfluoro*cyclo*hexene from Undecafluoro*cyclo*hexane.*—Undecafluoro*cyclo*hexane (85·0 g.) was refluxed for 4 hours with potassium hydroxide (50·0 g.) in water (100 c.c.). The mixture was then allowed to cool, and the lower liquid layer was separated, washed with water, and dried (P_2O_5). Fractionation yielded perfluoro*cyclo*hexene (65·0 g., 82%), b. p. 52·0—53·0°/750 mm., n_D^{15} 1·296 (Found: C, 27·4; F, 72·2%; *M*, 257. Calc. for C_6F_{10}: C, 27·5; F, 72·5%; *M*, 262). Brice and Simons (*loc. cit.*) gave b. p. 51—52°/728 mm., n_D^{20} 1·292—1·293, for this compound.

1 : 2-*Dibromodecafluoro*cyclo*hexane from Perfluoro*cyclo*hexene.*—The olefin (2·60 g.) and bromine (1·63 g.) were refluxed together for 60 hours whilst exposed to the light from a mercury-vapour lamp. After being washed with sodium thiosulphate solution, the organic layer solidified, and was washed with water. After being dried (P_2O_5) and filtered whilst warm, the product was distilled from a small flask, giving 1 : 2-*dibromodecafluoro*cyclo*hexane* (1·30 g., 31%), b. p. 139·0—140·5° (a colourless liquid which crystallised), m. p. 31·0—32·5°, n_D^{45} 1·367 (Found: Br, 37·0; F, 44·9%; *M*, 420. $C_6Br_2F_{10}$ requires Br, 37·9; F, 45·0%; *M*, 422).

1 : 2-*Dichlorodecafluoro*cyclo*hexane from Perfluoro*cyclo*hexene.*—The olefin (4·51 g.) and liquid chlorine (*ca.* 1·5 c.c.) were heated for 40 hours in a sealed tube by means of a mercury-vapour lamp. The product was washed with dilute aqueous potassium hydroxide, then with water, and was dried (P_2O_5). Distillation from a small flask afforded 1 : 2-dichlorodecafluoro-*cyclo*hexane (3·22 g., 56%), b. p. 108·0—109·0°/752 mm., n_D^{45} 1·331, which crystallised on cooling, m. p. 36—37° (Found: Cl, 21·2; F, 57·4. Calc. for $C_6Cl_2F_{10}$: Cl, 21·3; F, 57·1%). A mixture with the specimen mentioned previously had m. p. 38—40°.

*Perfluoroadipic Acid from Perfluoro*cyclo*hexene.*—The olefin (20·0 g.), potassium permanganate (100·0 g.), and water (300 c.c.) were heated at 100° for 24 hours in a rocking autoclave. The reaction mixture was filtered, and the filtrate was treated with sulphur dioxide until the excess of permanganate had been reduced, and then refiltered. The filtrate was acidified with concentrated sulphuric acid (50 c.c.) and was then extracted continuously with ether. The ethereal extracts were filtered and distilled to remove ether. After being dried for 15 minutes at 100°/16 mm., and then overnight *in vacuo* over phosphoric oxide, the residual white solid (19·5 g.) was recrystallised from benzene, giving the strongly acidic *perfluoroadipic acid* (15·4 g., 70%) as white, very hygroscopic needles, m. p. 133—134° (after being dried at 60° *in vacuo* over P_2O_5) [Found: C, 24·7; H, 0·8 (after correction for the water absorbed before the combustion); F, 52·5%; equiv., 145. $C_6H_2O_4F_8$ requires C, 24·8; H, 0·7; F, 52·4%; equiv., 145]. Owing to the ready hydration of this acid, pure specimens have low m. p.s after only short exposure to the atmosphere, and drying of the m. p. tubes containing the samples is advisable.

With aniline in ethereal solution perfluoroadipic acid gave the *dianilinium* salt, m. p. 212° (after recrystallisation from acetone–chloroform) [Found: C, 45·4; H, 3·6; F, 32·0%; equiv. (by titration with NaOH), 235. $C_{18}H_{16}O_4N_2F_8$ requires C, 45·4; H, 3·4; F, 31·9%; equiv., 238].

The Diamide of Perfluoroadipic Acid.—The acid (10·0 g.) was refluxed for 24 hours with ethyl alcohol (50 c.c.) and concentrated sulphuric acid (0·1 c.c.). After removal of excess of alcohol by distillation, the residue was distilled under diminished pressure to give diethyl perfluoroadipate (8·5 g., 71%), b. p. 110—111°/16 mm., n_D^{20} 1·3546 (Found: C, 33·9; H, 3·0; F, 44·3. Calc. for $C_{10}H_{10}O_4F_8$: C, 34·7; H, 2·9; F, 43·9%).

The diester (2·00 g.) was dissolved in anhydrous ether (20·0 c.c.) and ammonia was passed through the cooled solution until precipitation was complete. The diamide (1·65 g., 99%) had m. p. 237°, unchanged by recrystallisation from ethyl alcohol (Found: C, 25·3; H, 1·3; F, 53·3. Calc. for $C_6H_4O_2N_2F_8$: C, 25·0; H, 1·4; F, 52·75%). McBee, Wiseman, and Bachman (*loc. cit.*) recorded b. p. 70—71°/2·5 mm., n_D^{20} 1·3541, for the diester, and m. p. 237° for the diamide.

Analysis.—Carbon and hydrogen determinations were carried out by the method of Belcher

and Goulden (*Mikrochem. Mikrochim. Acta*, 1951, **36/37**, 679), fluorine determinations by the method of Belcher and Tatlow (*Analyst*, 1951, **76**, 593), and molecular-weight measurements by a modified Victor Meyer process.

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