

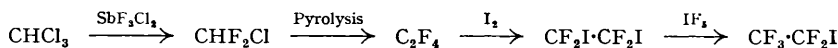
315. The Reactions of Fluorocarbon Radicals. Part IX.* Synthesis and Reactions of Pentafluoropropionic Acid.

By R. N. HASZELDINE and K. LEEDHAM.

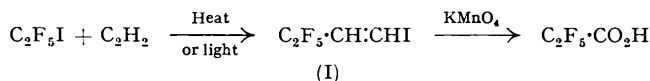
Interaction of pentafluoridoethane and acetylene yields 3 : 3 : 4 : 4 : 4-pentafluoro-1-iodobut-1-ene, oxidised to pentafluoropropionic acid, from which the derivatives C_2F_5X [$X = CO_2Na, CO_2K, CO_2Ag, CO_2Me, CO_2Et, CO \cdot NH_2, CN, COCl, CO_2 \cdot CH \cdot CH_2, CH_2 \cdot OH, CHO, CH(OH)_2, CH_2 \cdot NH_2, CH_2 \cdot NCO, \text{ and } CO \cdot O \cdot CO \cdot C_2F_5$] have been prepared; their infra-red spectra are discussed. The decomposition of salts of perfluoro-carboxylic acids under a variety of conditions is considered.

THE synthesis of pentafluoropropionic acid first recorded in *Nature* (1950, 166, 192) and presented in abstract at the 120th Meeting, Amer. Chem. Soc., New York, 1951, is now reported in detail.

The synthesis described earlier (Emeléus and Haszeldine, *J.*, 1949, 2953) for pentafluoroiodoethane :



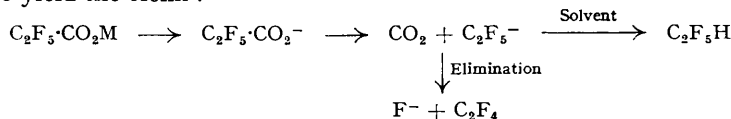
is readily applied on a larger scale and forms a convenient route to this compound. Reaction of the fluoro-iodide with acetylene under conditions favouring a free-radical chain reaction (Part VI, *J.*, 1952, 3483) gives a high yield of the addition compound (I), oxidation of which with alkaline potassium permanganate gives pentafluoropropionic acid :



This strong acid boils some 45° lower than propionic acid (141°), and is conveniently characterised by its infra-red spectrum or by the spectrum of the solid nitron pentafluoropropionate. Small amounts of the acid present in aqueous solution are readily detected and estimated as the nitron salt. A urea derivative could not be obtained by reaction with carbodi-imines (Part VI, *loc. cit.*).

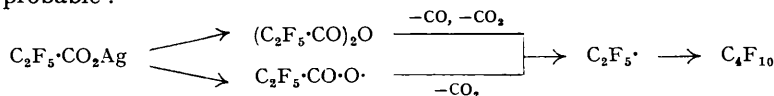
Pentafluoropropionic acid may also be obtained by two alternative routes : electrolysis of propionyl fluoride in anhydrous hydrogen fluoride, followed by hydrolysis of the pentafluoropropionyl fluoride (Minnesota Mining and Manufacturing Co., personal communication), and carboxylation of pentafluoropropylmagnesium iodide ($C_2F_5I \longrightarrow C_2F_5 \cdot MgI \longrightarrow C_2F_5 \cdot CO_2H$; unpublished, this laboratory).

Sodium, potassium, and silver salts, methyl and ethyl esters, the amide, the nitrile, and the acid chloride were obtained by slight modification of standard techniques. Decomposition of salts of perfluoroalkancarboxylic acids, $CF_3 \cdot [CF_2]_n \cdot CO_2M$, can yield, depending on the conditions and on the nature of M, the hydrogeno-compound, $CF_3 \cdot [CF_2]_n \cdot H$, the olefin, $CF_3 \cdot [CF_2]_{n-2} \cdot CF \cdot CF_2$, or the fluorocarbon, $CF_3 \cdot [CF_2]_{2n} \cdot CF_3$, the last two reactions having no parallel in the hydrocarbon series. Aqueous solutions of sodium or potassium pentafluoropropionate, particularly if sodium or potassium hydroxide or carbonate is added, yield pentafluoropropane at 150–200°; decarboxylation is particularly efficient in boiling ethylene glycol. Pyrolysis (250°) of the anhydrous salts yields tetrafluoroethylene, carbon dioxide, and alkali-metal fluoride (Haszeldine, *J.*, 1952, 4259). It is believed that in both instances fluorocarbanion formation occurs, followed by rapid abstraction of hydrogen from the solvent or, where this is impossible, stabilisation by elimination to yield the olefin :

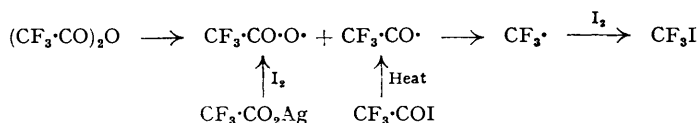


* Part VIII, *J.*, 1953, 922.

(cf. the reactions of perfluoroalkyl Grignard reagents, *J.*, 1952, 3423). Aqueous solutions of silver pentafluoropropionate similarly yield pentafluoropropane at 200°, but when this salt is heated in the dry state at 300° perfluoro-*n*-butane (mainly) and perfluoropropionic anhydride are formed. Pyrolysis of silver heptafluorobutyrate similarly yields perfluoro-*n*-hexane (75—85%) and perfluorobutyric anhydride (10—20%). The anhydrides are possibly precursors of the fluorocarbons, since the yields of the former increase when the pyrolysis products are removed from the seat of reaction as rapidly as possible, and pyrolysis of perfluoropropionic anhydride yields perfluoro-*n*-butane. Free-radical mechanisms seem probable :



It was shown earlier that perfluoroacetic anhydride was obtained when silver trifluoroacetate was heated with phosphorus or sulphur, and that heating perfluoroacetic anhydride and iodine gave trifluoroiodomethane, also obtained by pyrolysis of trifluoroacetyl iodide or by interaction of iodine and silver trifluoroacetate (*J.*, 1951, 584; 1952, 4259).



Silver pentafluoropropionate, like silver trifluoroacetate and silver perchlorate, is readily soluble in ether and benzene.

Interaction of pentafluoropropionic acid and acetylene gave vinyl pentafluoropropionate, hydrogenation of which yielded ethyl pentafluoropropionate. Reduction of the acid with lithium aluminium hydride gave pentafluoropropanol and pentafluoropropaldehyde hydrate. Oxidation of the alcohol to pentafluoropropionic acid is difficult and is best effected by potassium permanganate. The aldehyde hydrate can be distilled without decomposition, and fails to yield a 2 : 4-dinitrophenylhydrazone unless a dehydrating agent, *e.g.*, sulphuric acid, is present. Treatment of the hydrate with phosphoric anhydride gave the volatile pentafluoropropaldehyde. Application of the lithium aluminium hydride technique to pentafluoropropionamide yielded pentafluoro-*n*-propylamine which, like trifluoroethylamine, gives a stable diazo-compound, C₂F₅·CHN₂ and can be converted into the isocyanate by reaction with carbonyl chloride.

	X :	CO ₂ H	CO ₂ Me	CO ₂ Et	CO·NH ₂
C.S. no.		14	15	16	17
C ₂ F ₅ X		5·62 (5·48)	5·59	5·56	5·84 6·13
CH ₃ ·[CH ₂] _n ·X		5·83	5·7—5·8	5·7—5·8	2 bands 5·9—6·2
	X :	COCl	CHO	CO·O·COC ₂ F ₅	
C.S. no.		18		19	
C ₂ F ₅ X		5·51	5·73	5·33	5·51
CH ₃ ·[CH ₂] _n ·X		5·55—5·60	5·8—5·9	5·4—5·5 †	5·6—5·7 †

† For (CH₃·[CH₂]_n·CO)₂O.

The infra-red spectra of the derivatives * are more useful for identification than are their other physical properties. The carbonyl stretching absorptions shown in the Table reveal the strong inductive effect of the fluoro-group, since a marked shift to shorter wavelength of the "characteristic" vibration of the hydrocarbon analogues is apparent.

The amide N—H stretching vibrations are at 2·97 and 3·13 μ, and the C=N stretching vibration appears at 4·41 μ (cf. CH₃·[CH₂]_{2n}·CN, 4·44 μ) (the spectrum of C₂F₅·CN has C.S. no. 20*). It is evident that correlation rules for the characteristic frequencies of specific groups in fluorocarbon derivatives can be drawn up, but will differ from the rules applicable to hydrocarbon derivatives, and will prove equally useful in qualitative analysis.

* Some of the spectra have been deposited with the Chemical Society (cf. *Proc.*, 1952, 164), and photocopies may be obtained from the General Secretary. Identifying C.S. numbers are listed in the Table and must be cited in requests for photocopies.

EXPERIMENTAL

Pentafluoroiodoethane.—To a stainless-steel autoclave (300 ml.) were added dry iodine (210 g., 0.83 mol.), α -pinene stabiliser (0.25 ml.), and tetrafluoroethylene (20 g., 0.2 mol.), air being excluded. After 24 hr. at the optimum temperature of 150°, the gaseous and the liquid products were pumped from the autoclave and after addition of a further 20 g. of tetrafluoroethylene the heating was repeated. Eighty grams of tetrafluoroethylene were thus treated without recharging with iodine. The maximum pressure was 30 atm. at 100°. At >150° or higher initial pressures of tetrafluoroethylene, cyclic dimerisation, polymerisation, and formation of carbon occur. Distillation gave tetrafluoro-1 : 2-di-iodoethane (200 g., 76%), tetrafluoroethylene (*ca.* 20%), and octafluorocyclobutane (*ca.* 2%).

To iodine pentafluoride (700 g.) in a 2-l. nickel vessel with flanged top and nickel, reflux water-condenser leading *via* rubber tubing to traps cooled in liquid air, was added tetrafluoroiodoethane (10 g.). The temperature was slowly raised until reaction began (*ca.* 90°), and further tetrafluoroiodoethane (90 g.) was added dropwise during 5 hr., the temperature being kept at 90—100°. The reaction was thus readily controlled, and the yield of pentafluoroiodoethane, washed with aqueous alkali to remove traces of iodine, etc., was 85% (Found : *M*, 246. Calc. for C_2F_5I : *M*, 246) : this had b. p. 13°. Emeléus and Haszeldine (*loc. cit.*) report b. p. 13°.

Preparation and Oxidation of 3 : 3 : 4 : 4 : 4-Pentafluoro-1-iodobut-1-ene.—This material was prepared in 72% yield by interaction at 240° for 20 hr. of pentafluoroiodoethane (3.25 g.) and acetylene (0.41 g.) in a 30-ml. Carius tube (Part VI, *loc. cit.*).

In a typical experiment the pentafluoroiodobutene (20.8 g.) was added dropwise during 5 hr. to a stirred solution of potassium permanganate (62.4 g.) and potassium hydroxide (4.53 g.) in water (300 ml.), and the whole heated at 90°. After final heating at 120° for 1½ hr. droplets were no longer apparent in the condenser, and the solution was acidified (H_2SO_4), treated with sulphur dioxide, made alkaline (KOH), concentrated until potassium sulphate was deposited on cooling, filtered, acidified (H_2SO_4), and extracted with ether for 48 hr. The ethereal extracts were dried ($MgSO_4$) and distilled, to give an acid fraction, b. p. 109.5—110.5° (3.8 g.), which was exactly neutralised with 10% sodium carbonate solution. After evaporation to dryness, treatment with concentrated sulphuric acid and distillation from a trace of phosphoric anhydride gave *pentafluoropropionic acid* (22%), b. p. 95.5—95.7°, n_D^{20} 1.298 (Found : C, 21.7% ; Equiv., 163.6, 164.1. $C_3HO_2F_5$ requires C, 21.9% ; Equiv., 164.0).

In a second experiment the order of addition was reversed, a hot solution of potassium permanganate (44.0 g.) and potassium hydroxide (2.0 g.) in water (250 ml.) being added during 1.5 hr. to 3 : 3 : 4 : 4 : 4-pentafluoro-1-iodobut-1-ene (9.4 g.) and sodium carbonate (2.0 g.) in water (25 ml.) at 90°. Unchanged olefin was not detected, and after acidification (H_2SO_4), ether-extraction (48 hr.), shaking with mercury to remove iodine, drying, and removal of the ether, followed by treatment as described above, pentafluoropropionic acid was obtained in 30% yield.

Volatile material liberated during the oxidation was shown to be pentafluoroethane (1.0 g.), b. p. -48° (Found : F, 78.2% ; *M*, 122. Calc. for C_2HF_5 : F, 79.2% ; *M*, 120). Young, Fukuhara, and Bigelow (*J. Amer. Chem. Soc.*, 1940, **62**, 1171) report b. p. -48.4°. Fluoride was liberated during the oxidation.

Pentafluoropropionic acid is a strong, hygroscopic acid which fumes in air and has an odour similar to that of heptafluorobutyric acid (Haszeldine, *J.*, 1950, 2789). It is readily soluble in water, ethanol, acetone, carbon tetrachloride, benzene, and ether.

A freshly prepared (6%) solution of nitron in aqueous acetic acid (10%) was slowly added to a solution of pentafluoropropionic acid in water, to give *nitron pentafluoropropionate* (Found : N, 11.8. $C_{23}H_{17}O_2N_4F_5$ requires N, 11.8%), m. p. 204—206° (decomp.) after recrystallisation from aqueous ethanol. The nitron salt is best characterised by its infra-red spectrum (C.S.21 ; see footnote, p. 1549).

Silver, Sodium, and Potassium Pentafluoropropionate.—Neutralisation of aqueous pentafluoropropionic acid with silver oxide or silver carbonate, and evaporation to dryness or extraction with ether followed by evaporation to dryness of the ethereal extracts, yielded colourless, crystalline silver pentafluoropropionate. When heated with an excess of iodine the silver salt gives pentafluoroiodoethane in high yield (Haszeldine, *J.*, 1952, 4259). When heated above its m. p. (245°) at atmospheric pressure silver pentafluoropropionate (2.1 g.) gave perfluoro-*n*-butane (85%), b. p. 1° (Found : *M*, 236. Calc. for C_4F_{10} : *M*, 238), and perfluoropropionic anhydride (10%) (see below). Fowler *et al.* (*Ind. Eng. Chem.*, 1947, **39**, 375) report b. p. -1.7° for perfluoro-*n*-butane. When the salt was heated in a nickel apparatus to

500°/0.1 mm. during 3 hr. the yields of perfluorobutane and anhydride were 74 and 20%. Traces of pentafluoropropionyl fluoride were also obtained.

Pyrolysis of silver heptafluorobutyrate (4.2 g.) (*J.*, 1950, 2789) at 550° during 5 hr. similarly yielded perfluoro-*n*-hexane (81%), b. p. 55–56° (Found: *M*, 335. Calc. for C_6F_{14} : *M*, 338), and perfluorobutyric anhydride (11%), b. p. 107° (Found: *M*, 409. Calc. for $C_8O_3F_{14}$: *M*, 410). Haszeldine (*J.*, 1952, 3423; 1950, 2789) reports b. p. 56° and 108° for these compounds. Pyrolysis *in vacuo* gave perfluorohexane (75%) and the anhydride (16%).

Neutralisation of an aqueous solution of pentafluoropropionic acid with potassium or sodium carbonate, followed by evaporation to dryness, purification by extraction with ethanol and evaporation to dryness of the ethanolic solution, gave *potassium pentafluoropropionate* (Found: *K*, 19.4. $C_3O_2F_5K$ requires *K*, 19.3%) and *sodium pentafluoropropionate* (Found: *Na*, 12.2. $C_3O_2F_5Na$ requires *Na*, 12.4%) as colourless crystals. Pyrolysis of thoroughly dried potassium pentafluoropropionate (2.2 g.) at 250° gave tetrafluoroethylene (80%) (Found: *M*, 100. Calc. for C_2F_4 : *M*, 100) (identified spectroscopically), potassium fluoride, carbon dioxide, and a small amount of carbon.

Ethyl and Methyl Pentafluoropropionate.—Pentafluoropropionic acid (4.80 g.), ethyl alcohol (1.2 g.), and concentrated sulphuric acid (0.2 ml.) were set aside for 8 hr. at room temperature, then heated under reflux for 3 hr. After rapid washing with ice-water and drying (P_2O_5), distillation gave *ethyl pentafluoropropionate* (4.46 g., 79%), b. p. 76.5°/773 mm., n_D^{20} 1.300, (Found: *C*, 31.6; *H*, 3.0. $C_5H_5O_2F_5$ requires *C*, 31.2; *H*, 2.6%).

Methanol similarly gave *methyl pentafluoropropionate* (85%), b. p. 60.5°, n_D^{20} 1.295 (Found: *C*, 28.3%; *M*, 180. $C_4H_3O_2F_5$ requires *C*, 27.6%; *M*, 178).

Pentafluoropropionamide and Pentafluoropropionitrile.—Through an ice-cold ethereal solution of ethyl pentafluoropropionate (2.0 g.) was passed an excess of dry ammonia. Evaporation of the ether followed by sublimation of the residual solid at 60°/760 mm. gave *pentafluoropropionamide* (1.5 g., 88%), m. p. 96° (Found: *C*, 22.3; *H*, 1.7; *N*, 8.7. $C_3H_2F_5ON$ requires *C*, 22.1; *H*, 1.2; *N*, 8.6%).

The amide (1.75 g.), mixed with an excess of phosphoric anhydride (5 g.), was heated under a reflux air-condenser connected to a trap cooled by liquid oxygen. After 30 min.' heating the amide which had sublimed was returned to the reaction vessel with a further quantity of phosphoric anhydride (5 g.). After re-heating, fractionation of the volatile products gave *pentafluoropropionitrile* (1.0 g.), b. p. –35° (Found: *C*, 23.9%; *M*, 145. C_3NF_5 requires *C*, 24.8%; *M*, 145).

Pentafluoropropionyl Chloride.—Benzoyl chloride (6.43 g.) and pentafluoropropionic acid (3.11 g.) were heated under reflux at 150° during 7 hr. to give, as volatile product, *pentafluoropropionyl chloride* (2.82 g., 82%), b. p. 9.4° (Found: *C*, 19.2; *Cl*, 19.4%; *M*, 182.5. C_3OCIF_5 requires *C*, 19.7; *Cl*, 19.45%; *M*, 182.5), purified by fractionation *in vacuo*.

Vinyl Pentafluoropropionate.—Pentafluoropropionic acid (1.9 g.), sealed with its sodium salt (0.2 g.) and an excess of acetylene in a Pyrex tube and heated at 220–240° for 12 hr., gave *vinyl pentafluoropropionate* (75%), b. p. 60°, n_D^{20} 1.310 (Found: *C*, 31.8; *H*, 2.2%; *M*, 190. $C_5H_3O_2F_5$ requires *C*, 31.6; *H*, 1.6%; *M*, 190).

Pentafluoropropaldehyde and Pentafluoropropanol.—To an ice-cold solution of lithium aluminium hydride (0.5 g.) in dry ether (15 ml.) was added pentafluoropropionic acid (1.8 g.) in ether (10 ml.) during 45 min. After 30 min.' stirring, sulphuric acid (2 ml. of concentrated acid in 5 ml. of water) was carefully added and, after separation of the ether, and extraction of the aqueous layer with ether (10 ml.), the combined ethereal extracts were distilled to give a fraction, b. p. 78–82°, which, on redistillation from phosphoric anhydride, gave *pentafluoropropanol* (38%), b. p. 81°, n_D^{15} 1.295 (Found: *C*, 24.0. $C_3H_3OF_5$ requires *C*, 24.0%), and a fraction, b. p. 87–105°, which was taken up in ether and dried ($MgSO_4$). Distillation of the ethereal solution gave the *propaldehyde hydrate* (32%), b. p. 92–94°, m. p. 54–56° (Found: *C*, 21.7; *H*, 2.0. $C_3H_3O_2F_5$ requires *C*, 21.7; *H*, 1.8%), treatment of which with phosphoric anhydride, followed by fractionation *in vacuo*, gave *pentafluoropropaldehyde* (27% overall yield), b. p. 3.5° (Found: *C*, 24.1%; *M*, 147. C_2HOF_5 requires *C*, 24.3%; *M*, 148). The 2:4-dinitrophenylhydrazine had m. p. 129–130° (Found: *N*, 17.0. $C_6H_3O_4N_4F_5$ requires *N*, 17.1%).

*Pentafluoro-*n*-propylamine*.—Treatment of a solution of pentafluoropropionamide (2.6 g.) with lithium aluminium hydride (0.5 g.) by the method given above, but with dibutyl ether in place of diethyl ether, gave, after distillation of the ethereal extracts from calcium oxide, *pentafluoro-*n*-propylamine* (81%), b. p. 51°, n_D^{15} 1.300 (Found: 9.1%; *M*, 149. $C_3H_4NF_5$ requires *N*, 9.4%; *M*, 149). The amine (1.9 g.) was sealed with carbonyl chloride (10% excess) and perfluoro-1:3:5-trimethylcyclohexane (as inert medium) and heated to 100° for 2 hr., to give

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2 : 2 : 3 : 3 : 3-pentafluoropropyl isocyanate (63%), b. p. 74.5°, n_D^{20} 1.339 (Found : N, 8.0%; *M*, 173. $C_4H_2NOF_5$ requires N, 8.0%; *M*, 175).

Perfluoropropionic Anhydride.—Pentafluoropropionic acid (2.2 g.), heated with an excess of phosphoric anhydride to 200° for 24 hr., gave *perfluoropropionic anhydride* (88%), b. p. 68° (Found : C, 23.1%; *M*, 306. $C_6O_3F_{10}$ requires C, 23.2%; *M*, 310).

Pyrolysis of the anhydride at 350° in a platinum-lined tube yielded perfluoro-*n*-butane (65%), carbon dioxide and monoxide, and unchanged anhydride (20%).

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