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Syntheses by Free-Radical Reactions. XII. Reactions of Fluoroacyl Radicals

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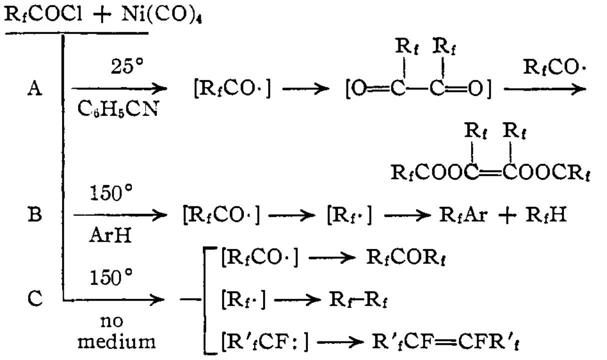
New syntheses of fluorine compounds have been discovered in a study of the chemistry of fluorine-containing radicals generated by reaction of equimolar amounts of a polyfluoroacyl chloride, R_fCOCl, and nickel carbonyl. Reactions catalyzed by benzonitrile at room temperature gave the novel enediol diesters $R_fCOOC(R_f)=C(R_f)OOCR_f$, which could be converted to the corresponding acyloins, 1,2-diketones and 1,2-glycols by alcoholysis, pyrolysis and hydrogenation, respectively. When the fluoroacyl chloride and nickel carbonyl were heated at 150° in an aromatic hydrocarbon, polyfluoroalkyl-substituted aromatic compounds were formed. At 150° in the absence of a medium, the products included polyfluoro ketones, polyfluoroalkanes and polyfluoroölefins.

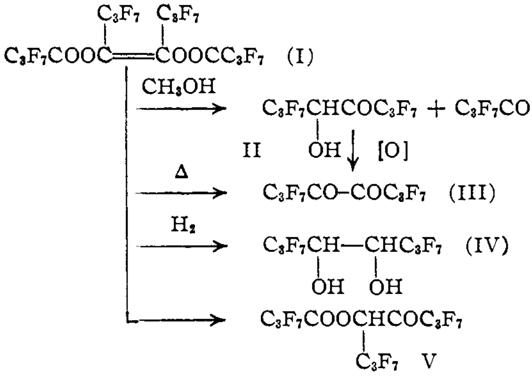
Polyfluoroacyl chlorides and nickel carbonyl have been found to form fluorine-containing products that appear to be derived from polyfluoroacyl radicals,[1] polyfluoroalkyl radicals and polyfluorocarbenes. The nature of the products is determined by the medium and the reaction conditions employed. The equations of Chart I represent the principal transformations.

CHART I



Fluorine-containing Enediol Diesters (A, Chart I) and their Conversion to Acyloins and 1,2-Diketones.—Fluorine-containing enediol diesters and the derived acyloins and 1,2-diketones have not been accessible heretofore. Thus, unsuccessful efforts to prepare the acyloin $CF_3CHOHCOCF_3$ and the 1,2-diketone $CF_3COCOCF_3$ by reaction of sodium with ethyl trifluoroacetate[2] gave ethyl trifluoroacetoacetate and trifluoroethanol. Enediol diesters $R_fCOO\underset{R_f}{C}{=}\underset{R_f}{C}OOCR_f$ (I, R_f = C_3F_7—; Ia, R_f = $H(CF_2)_4$—) have now been prepared from perfluorobutyryl chloride and from 5-hydroöctafluorovaleryl chloride by prolonged reaction with nickel carbonyl in benzonitrile medium at room temperature in 51% and 19% conversions, respectively. The identities of the enediol diesters were established by determination of elemental composition and by infrared and nuclear magnetic resonance spectral analyses. Furthermore, transformation (Chart II) of the enediol diester I by alcoholysis to an acyloin (II), by pyrolysis to a 1,2-diketone (III) and by hydrogenation to a 1,2-glycol (IV) are in accord with the structures assigned the parent enediol diester prepared from perfluorobutyryl chloride. The ester V of the acyloin may have been formed by adventitious hydrolysis of I or by addition of a hydrogen atom to the intermediate $C_3F_7COO\underset{C_3F_7}{C}{=}\underset{C_3F_7}{C}{-}O\cdot$. The perfluoro-4,5-octanedione (III) was further characterized by reaction with *o*-phenylenediamine to obtain 2,3-bis-(perfluoropropyl)-quinoxaline.

CHART II



The function of benzonitrile is not known, but it may reside in the ability of this polar solvent to solvate[3] intermediates in the synthesis. In the absence of benzonitrile, the polyfluoroacyl chlorides in solutions with nickel carbonyl underwent negligible reaction during 48 hours at 25°.

Synthesis of the enediol diesters appears to be dependent upon the formation of polyfluoroacyl radicals[4] ($R_fCO\cdot$) that persist in the medium at ordinary temperature and, like hydrocarbon acyl radicals,[5] react as a unit and do not decarbonylate to a polyfluoroalkyl radical. The polyfluoroacyl radicals, which are presumed to have been formed along with nickel chloride and carbon monoxide as coproducts, yield the enediol diester represented as originating through the 1,2-diketone, the dimer of a polyfluoroacyl radical. Although the forma-

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(1) Several transformations of simple acyl radicals are reported in the literature. For example, S. Winstein and F. H. Seubold, THIS JOURNAL, **69**, 2916 (1947), postulate acyl radicals as intermediates in the conversion of β-phenyl isovaleraldehyde to *t*-butylbenzene and of isovaleraldehyde to isovaleryl chloride.

(2) R. N. Haszeldine, *Nature*, **168**, 1028 (1951); E. T. McBee, O. R. Pierce, H. W. Kilbourne and J. A. Barone, THIS JOURNAL, **75**, 4090 (1953).

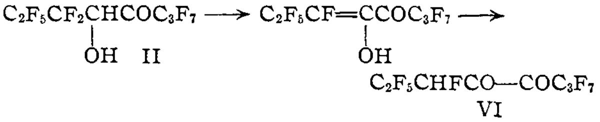
(3) J. E. Leffler and W. B. Bond, *ibid.*, **78**, 335 (1956).

(4) Formation of acyl radicals in this way does not lack precedent. H. Reihlen, A. Gruhl and G. v. Hessling, *Ann.*, **472**, 285 (1929), describe the reaction of nickel carbonyl with acetyl chloride in refluxing petroleum ether at 50° with irradiation from a mercury lamp to obtain a 1:1 complex of nickel chloride and biacetyl.

(5) Richard Cramer, THIS JOURNAL, **79**, 6215 (1957).

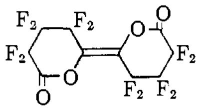
tion of a 1,2-diketone as a reaction product was not proved, its presence seems almost certain because of the intensely yellow-colored, lower-boiling fractions observed during distillation of the enediol diesters. The acyloin ester V and also $H(CF_2)_4COO\underset{(CF_2)_4H}{\underset{|}{C}}HCO(CF_2)_4H$ (Va) which was isolated as a minor product in the synthesis with 5-hydrooctafluorovaleryl chloride may have been derived from the enediol diesters I and Ia by hydrolysis or by abstraction from benzonitrile of a hydrogen atom by the intermediate $R_fCOOC{=}\underset{R_f}{\underset{|}{C}}O\cdot$ radical.

In the preparation of perfluoro-4,5-octanedione (III) by oxidation of 5-hydrotetradecafluoro-5-hydroxy-4-octanone (II) with bismuth triacetate, a surprising side reaction occurred. Evidently the bismuth triacetate was sufficiently basic to effect dehydrofluorination of the acyloin II to form the 1,2-diketone, 3-hydrotridecafluoro-4,5-octanedione (VI). The 1,2-diketone structure VI was confirmed by reaction with *o*-phenylenediamine to obtain a quinoxaline.



$$\underset{\mathrm{II}}{C_2F_5CF_2\underset{OH}{\underset{|}{C}}HCOC_3F_7} \longrightarrow C_2F_5CF{=}\underset{OH}{\underset{|}{C}}COC_3F_7 \longrightarrow \underset{\mathrm{VI}}{C_2F_5CHFCO{-}COC_3F_7}$$

The enediol synthesis has been extended to the use of bifunctional reactants. A dilactone of an enediol appears to have been formed by reaction of perfluoroglutaryl chloride with nickel carbonyl. The elemental composition of the crystalline product and its spectral properties are consistent with the dilactone structure VII, but other possibilities have not been excluded.



VII

Synthesis of Fluoroalkyl-substituted Aromatic Compounds (B, Chart I).—Products quite different from the enediol diesters were formed by reaction of polyfluoroacyl chlorides with stoichiometric amounts of nickel carbonyl at about 150°, a temperature known to effect the decarbonylation of acyl radicals.[1,5] When such reactions were carried out in an aromatic hydrocarbon medium, polyfluoroalkyl-substituted aromatic compounds were obtained. In this synthesis, polyfluoroalkyl radicals formed by decarbonylation of the acyl chloride became, in part, ring substituents and, in part, hydrofluorocarbons. Aromatic compounds so prepared are listed in Table I. The yields ranged from 30–80%, based on the requirement that two moles of polyfluoroacyl chloride were consumed for each mole of fluoroalkylation product formed. When perfluoropropionyl chloride was employed, heptafluoropropane was a coproduct.

$$ArH + R_fCOCl + Ni(CO)_4 \longrightarrow ArR_f + R_fH + NiCl_2 + CO$$

Table I

Fluoroalkylation of Aromatic Compounds

Aromatic reactant and medium (in excess)	Fluoroacyl chloride	Product	Yield, %
C_6H_6	C_3F_7COCl	$C_6H_5C_3F_7$	70–80
$CH_3C_6H_5$	C_3F_7COCl	$CH_3C_6H_4C_3F_7$	70–80
$CF_3C_6H_5$	C_3F_7COCl	$CF_3C_6H_4C_3F_7$	30
BrC_6H_5	C_3F_7COCl	$BrC_6H_4C_3F_7$	30–40
C_6H_6	$H(CF_2)_{10}COCl$	$C_6H_5(CF_2)_{10}H$	80–90

In the perfluoropropylation of benzene, the monosubstituted benzene was the principal product when the mole ratio of benzene to perfluorobutyryl chloride was about 10. When the mole ratio was reduced to about 0.7, the yield of (perfluoropropyl)-benzene was 50%, and bis-(perfluoropropyl)-benzene was obtained in about 10% yield. The fluoroalkylations of toluene, benzotrifluoride and bromobenzene yielded mixtures of isomers which were not separated.

Synthesis of Fluoroölefins (C, Chart I).—When perfluorobutyryl chloride was allowed to react with stoichiometric amounts of nickel carbonyl at 150° in the absence of a medium, fluoroketones, fluoroalkanes and fluoroölefins were formed as judged by chromatographic analysis and use of nuclear magnetic resonance to characterize the products. The products suggest that polyfluoroacyl $R_fCO\cdot$ and polyfluoroalkyl $R_f\cdot$ radicals and polyfluorocarbenes $R'_fCF{:}$ were transitory intermediates that either dimerized or combined with one another. Formation of fluoroketones, fluoroalkanes and fluoroalkenes was confirmed by the isolation of $H(CF_2)_4CO(CF_2)_4H$, $H(CF_2)_8H$ and a mixture of 1,8-dihydrotetradecafluoroöctenes from among the products from 5-hydroöctafluorovaleryl chloride. In reactions involving a mixture of perfluorobutyryl chloride and 11-hydroeicosafluoroundecanoyl chloride both C_{13} and C_{20} fluoroölefins appear to have been formed.

Experimental

Nuclear magnetic resonance spectra of the various products were measured with a Varian high resolution nuclear magnetic resonance spectrometer and associated electromagnet. Fluorine magnetic resonance spectra were obtained at 56.4 Mc. in a field of approximately 14,081 gauss. A capillary of trifluoroacetic acid was placed in each sample, and the spectra were calibrated in terms of displacement in cycles per second (c.p.s.) from the fluorine resonance of trifluoroacetic acid. Except as noted, all peaks were to the high field side. The proton magnetic resonance spectra were similarly measured at 56.4 Mc. in a field strength of 13,244 gauss employing the resonances of acetone or tetramethylsilane as references.

Preparation of an Enediol Diester from Perfluorobutyryl Chloride.—A mixture of 115 g. of perfluorobutyryl chloride,[6] 41 g. of nickel carbonyl and 300 g. of benzonitrile was stirred for 72 hours at 25° under anhydrous conditions. The filtrate from the reaction mixture was distilled to obtain 6 g. (6% of theoret.) of 5-hydrotetradecafluoro-4-oxo-5-octyl perfluorobutyrate (V), a colorless liquid boiling at 64° (18 mm.). The fluorine magnetic resonance spectrum of V consisted of five chemically shifted resonances having intensities in the approximate ratios 9:2:4:4:2, a CF_3–resonance at 264 c.p.s., two overlapping resonances at approximately 2390 c.p.s., and singlet $-CF_2-$ resonances at

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[6] This acyl chloride was prepared conveniently in 90–95% yields by refluxing perfluorobutyric acid in a twofold excess of benzotrichloride and distilling the product. Most of the acid chlorides were prepared in this way.

2792 and 2838 c.p.s. Proton nuclear magnetic resonance analysis showed one kind of hydrogen on saturated carbon.

Anal. Calcd. for $C_{12}F_{21}O_3H$: C, 24.34; H, 0.16; F, 67.38. Found: C, 24.54; H, 0.17; F, 67.48.

On continued distillation there was also obtained 5 g. (5.1% of theoret.) of perfluoro-4-octene-4,5-diol di-(perfluorobutyrate) (I), a colorless liquid boiling at 89° (18 mm.). Infrared analysis of I showed carbonyl absorption at 5.45 μ, and the spectrum suggested a *trans* structure. The fluorine magnetic resonance spectrum of the enediol diester exhibited a CF_3– resonance at 263 c.p.s. and four equal –CF_2– resonances at 2264, 2350, 2826 and 2862 c.p.s.

Anal. Calcd. for $C_{16}F_{28}O_4$: C, 24.37; F, 67.49. Found: C, 24.62; F, 67.49.

A higher conversion to the enediol diester I was obtained by increasing the reaction time. A mixture of 400 g. of benzonitrile, 160 g. of nickel carbonyl and 1,055 g. of perfluorobutyryl chloride was stirred under anhydrous conditions at room temperature for 72 hours. An additional 100 g. of nickel carbonyl was added, and the mixture was stirred for 48 hours more under the same conditions. Another 100-g. portion of nickel carbonyl then was added, and stirring was continued at room temperature for 7 more days. The reaction mixture was filtered to remove nickel chloride. Distillation of the filtrate gave 455 g. (51% conversion) of perfluoro-4-octene-4,5-diol di-(perfluorobutyrate) (I) boiling at 89° (18 mm.).

Preparation of 5-Hydrotetradecafluoro-5-hydroxy-4-octanone (II) by Methanolysis of the Enediol Diester.—Methanol (73 ml.) and 600 g. of perfluoro-4-octene-4,5-diol di-(perfluorobutyrate) (I) were mixed at 25°. As solution took place, an exothermic reaction occurred which heated the mixture to reflux temperature. Distillation of the reaction products gave 270 g. of a mixture of methanol and methyl perfluorobutyrate boiling below 70° (90 mm.) and 272 g. (90% of theoret.) of 5-hydrotetradecafluoro-5-hydroxy-4-octanone (II), a colorless liquid boiling at 70–72° (90 mm.), n^{25}_{D} 1.4940. Infrared analysis showed carbonyl absorption at 5.65 μ and hydroxyl doublet absorption at 2.85 and 2.92 μ. The fluorine magnetic resonance spectrum consisted of a CF_3– resonance at 277 c.p.s. and two sets of quadruplet –CF_2– resonances centered at 2487 and 2528 c.p.s.

Anal. Calcd. for $C_8F_{14}H_2O_2$: F, 67.18. Found: F, 66.81.

Preparation of 4,5-Dihydrotetradecafluoro-4,5-octanediol (IV) by Hydrogenation of the Enediol Diester.—A mixture of tetradecafluoro-4-octene-4,5-diol di-(perfluorobutyrate) (I) (11.2 g.), 105 ml. of acetic acid and 0.2 g. of 10% palladium-on-carbon catalyst was shaken under 40 lb./sq. in. hydrogen pressure at room temperature for 18 hours. The reaction mixture was filtered, the filtrate was diluted with 200 ml. of water saturated with sodium chloride, and the resultant mixture was extracted with about 100 ml. of diethyl ether. After removal of the diethyl ether, there was obtained 4,5-dihydrotetradecafluoro-4,5-octanediol (IV), a colorless liquid boiling at 80° (25 mm.). On standing, the dihydrotetradecafluoroöctanediol solidified. Recrystallization from chloroform gave pure 4,5-dihydrotetradecafluoro-4,5-octanediol in 50% yield as a white crystalline solid melting at 71–73°. The identity of this product among the various possible stereoisomers was not determined. Nuclear magnetic resonance analysis of an acetone solution of the glycol showed the presence of a perfluoropropyl group with CF_3– resonance at 243 c.p.s. and two sets of quadruplet –CF_2– resonances at 1985, 2250, 2643, 2912, and 2420, 2696, 2750, 3026 c.p.s.

Anal. Calcd. for $C_8H_4F_{14}O_2$: F, 66.82. Found: F, 66.42.

Preparation of Perfluoro-4,5-octanedione (III) by Oxidation of the Acyloin II.—Into a flask equipped with a spinning band distillation column were placed 100 g. of 5-hydrotetradecafluoro-5-hydroxy-4-octanone (II), 210 ml. of acetic acid and 66 g. of bismuth triacetate. Distillation gave about 60 g. of product boiling in the range 90–115° (760 mm.). Upon redistillation there was obtained 30 g. of a yellow liquid boiling at 96° which, by gas chromatography, was shown to be an azeotrope of acetic acid and perfluoro-4,5-octanedione. The pure perfluoro-4,5-octanedione (III) was recovered from the azeotrope by shaking with water and distilling the perfluoro-4,5-octanedione from the resultant perfluoro-4,5-octanedione hydrate over phosphorus pentoxide. The perfluoro-4,5-octanedione so obtained was identical in boiling point (95° at 760 mm.), infrared spectrum and fluorine magnetic resonance spectrum with perfluoro-4,5-octanedione prepared by pyrolysis of perfluoro-4-octene-4,5-diol di-(perfluorobutyrate) (I) over glass at 600° and 5 mm. pressure.

The fluorine magnetic resonance spectra of the ketone showed a perfluoropropyl group with resonances at 273, 2380 and 2780 c.p.s. Infrared analysis showed strong carbonyl absorption at 5.65 μ.

Anal. Calcd. for $C_8F_{14}O_2$: F, 67.49. Found: F, 67.45.

The perfluoro-4,5-octanedione was characterized further by conversion to 2,3-bis-(perfluoropropyl)-quinoxaline. Thus, 0.25 g. of *o*-phenylenediamine was added to 0.88 g. of perfluoro-4,5-octanedione. A vigorous reaction ensued. The liquid product was heated with 5.4 g. of acetic anhydride for 1 hour, 7.9 ml. of ethanol was added, and the resultant mixture was heated at steam-bath temperature for 15 minutes. Approximately 20 ml. of water was added, and the lower layer was separated and distilled. There was thus obtained 2,3-bis-(perfluoropropyl)-quinoxaline as a colorless liquid boiling at 75° (3 mm.), n^{25}_{D} 1.4195. The nuclear magnetic resonance spectrum showed a C_3F_7– grouping and aromatic hydrogen. The ultraviolet spectrum showed absorption at 320 mμ (*K* 8.4), 313 mμ (*K* 8.0), and 242.5 mμ (*K* 107).

Anal. Calcd. for $C_{14}H_4F_{14}N_2$: F, 57.05. Found: F, 57.11.

Further distillation of the residue gave 20 g. of a mixture of acetic acid and 3-hydrotridecafluoro-4,5-octanedione (VI) as a yellow liquid boiling at 108–110° (760 mm.). The fluorine magnetic resonance spectrum confirmed the presence of $CF_3CF_2CF_2$– and CF_3CF_2CFH– groups. The spectrum consisted of CF_3– resonances at 288 and 414 c.p.s., singlet –CF_2– resonances at 2396 and 2802 c.p.s., a quadruplet –CF_2– with resonances at 2320, 2619, 2763 and 3089 c.p.s. and a doublet –CFH– centered at 7746 c.p.s.

The identity of the 3-hydrotridecafluoro-4,5-octanedione (VI) was further established by conversion to 2-(perfluoropropyl)-3-(1-hydrohexafluoropropyl)-quinoxaline. Thus, 3 g. of 3-hydrotridecafluoro-4,5-octanedione was added to 0.9 g. of *o*-phenylenediamine. The reaction mixture was heated gently over an open flame, and water was added. The resultant crystalline solid was isolated and sublimed at 100 mm. to obtain 2-(perfluoropropyl)-3-(1-hydrohexafluoropropyl)-quinoxaline as plates melting at 42–43°. Proton nuclear magnetic resonance analyses showed aromatic and saturated hydrogen in a 4/1 ratio. The fluorine magnetic resonance spectrum confirmed the presence of $CF_3CF_2CF_2$– and CF_3CF_2CFH– groups. The spectrum consisted of CF_3– resonances at 170 and 368 c.p.s., singlet –CF_2– resonances at 1657 and 2668 c.p.s., a quadruplet –CF_2– with resonances at 2293, 2583, 2862 and 3174 c.p.s., and a doublet –CFH– centered at 6553 c.p.s. The ultraviolet spectra showed absorption at 314 mμ (*K* 9.5), 242 mμ (*K* 105) and 322 mμ (*K* 10.1).

Anal. Calcd. for $C_{14}H_5F_{13}N_2$: C, 37.50; H, 1.12; F, 55.11. Found: C, 37.79; H, 1.54; F, 55.05.

Preparation of an Enediol Diester (Ia) from 5-Hydrooctafluorovaleryl Chloride.—The synthesis was carried out using 20 g. of benzonitrile, 1,065 g. of 5-hydroöctafluorovaleryl chloride and 160 g. of nickel carbonyl. The mixture was stirred at 25° for 24 hours under anhydrous conditions. An additional 100 g. of benzonitrile was added, and stirring at room temperature was continued for an additional 2 days. Another addition of nickel carbonyl (100 g.) was made, and stirring was continued for 14 days. The nickel chloride formed was removed by filtration. Distillation of the filtrate gave two products, A and B.

Product A (25 g. of 5% conversion) was the ester 1,6,10-trihydrohexadecafluoro-5-oxo-6-decyl 5-hydroöctafluorovalerate (Va) derived from the acyloin. The ester was a colorless liquid boiling at 117° (3–4 mm.). The fluorine magnetic resonance spectrum of 1,6,10-trihydrohexadecafluoro-5-oxo-6-decyl 5-hydroöctafluorovalerate showed six chemically shifted resonances with approximate relative intensities of 6:6:2:4:4:2, a doublet centered at 3467, and singlets at 2968, 2672, 2617 and 2340 c.p.s. (two peaks poorly resolved). The infrared spectrum showed carbonyl absorption at 5.55 and 5.65 μ and saturated CH absorption at 3.35 μ.

Anal. Calcd. for $C_{15}H_4O_2F_{24}$: C, 26.18; H, 0.59; F, 66.40. Found: C, 26.96; H, 0.82; F, 65.14.

Continued distillation of the filtrate gave product B (181 g. or 19.6% of calcd.), the enediol diester 1,10-dihydrohexadecafluoro-5-decene-5,6-diol di-(5-hydroöctafluorovalerate) (Ia) a clear, colorless liquid boiling at 124–129° (3–4 mm.), 167° (20 mm.), n^{25}_D 1.3255. The fluorine magnetic resonance spectrum of the enediol diester Ia exhibited five chemically shifted resonances with relative intensities of 4:4:4:2:2, a doublet centered at 3454 c.p.s., and singlets at 2965, 2631, 2294 and 2207 c.p.s. Infrared analyses showed absorption by carbonyl at 5.45 μ and by saturated CH at 3.35 μ, and the spectrum suggested a *trans* structure. These spectra are in accord with the structure 1,10-dihydrohexadecafluoro-5-decene-5,6-diol di-(5-hydroöctafluorovalerate).

Anal. Calcd. for $C_{20}H_4F_{32}O_4$: C, 26.21; H, 0.44; F, 66.37; mol. wt., 920. Found: C, 25.72; H, 0.64; F, 66.17; mol. wt., 900, 940.

Preparation of 1,6,10-Trihydrohexadecafluoro-6-hydroxy-5-decanone (IIa) by Methanolysis of the Enediol Diester Ia.—A mixture of methanol (15 ml.) and 91 g. of 1,10-dihydrohexadecafluoro-5-decene-5,6-diol di-(5-hydroöctafluorovalerate) (Ia) was stirred at room temperature for 15 minutes. Distillation gave methyl 5-hydroöctafluorovalerate and 45.5 g. (*ca.* 100% yield) of 1,6,10-trihydrohexadecafluoro-6-hydroxy-5-decanone as a clear, colorless liquid boiling at 74–76° (50 mm.).

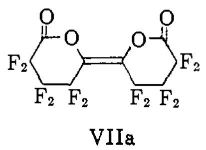
Anal. Calcd. for $C_{10}H_4F_{16}O_2$: C, 26.11; H, 0.88; F, 66.06 Found: C, 26.43; H, 1.04; F, 66.03.

Infrared analysis showed carbonyl, hydroxyl and CH absorption at 5.66, 2.85 and 3.35 μ, respectively. The fluorine magnetic resonance spectrum consisted of a double $-CF_2H$ resonance centered at 3462 c.p.s. (peaks at 3490 and 3434 c.p.s.), singlet $-CF_2-$ resonances at 3108, 2943 and 2662 c.p.s., and quadruplet $-CF_2-$ resonances centered at 2458 and 2459 c.p.s. in the high field side of the reference.

Reaction of Perfluoroglutaryl Chloride with Nickel Carbonyl.—A mixture of perfluoroglutaryl chloride (100 g.), nickel carbonyl (62 g.) and benzonitrile (20 g.) was stirred at room temperature under anhydrous conditions for 3 days. Carbon monoxide slowly evolved, and a precipitate of nickel chloride formed. The reaction mixture was filtered, and the nickel chloride precipitate was washed with diethyl ether. The ether washings were added to the filtrate. Distillation of the combined filtrate and washings afforded 75 g. of recovered perfluoroglutaryl chloride and 4 g. of dodecafluoro-5,6-dihydroxy-*trans*-5-decene-1,10-dioic acid dilactone (VII), *i.e.*, dodecafluorotetrahydro-*trans*-$\Delta^{2,2'}$-bi-2H-pyran-6(5H),6'(5'H)-dione, a clear, colorless liquid boiling at 93–110° (90 mm.). The product, which crystallized from benzene, was sublimed to obtain the purified dilactone as plates melting at 88–90°.

Anal. Calcd. for $C_{10}F_{12}O_4$: C, 29.14; F, 55.32. Found: C, 29.36; F, 55.58.

The fluorine magnetic resonance of the product showed three $-CF_2-$ resonances of equal intensities at 2111, 2592 and 3227 c.p.s. The infrared spectrum showed carbonyl absorption at 5.45 and 5.62 μ. These data are consistent with the structures VII and VIIa. The most likely structure appears to be VII, which is less strained, as judged by molecular models.



VIIa

Preparation of (Perfluoropropyl)-benzene.—A 500-ml. stainless steel reaction vessel charged with 46 g. of perfluorobutyryl chloride, 34 g. of nickel carbonyl and 176 g. of benzene was closed and heated at 150° with agitation for 6 hours. The reaction mixture was cooled, vented through a trap cooled in a solid carbon dioxide–acetone slush to condense the volatile fluorocarbons, filtered to remove the solid products, and the filtrate was fractionally distilled to obtain 18–20 g. (70–80% yield) of (perfluoropropyl)-benzene, boiling at 128°, n^{25}_D 1.3765. The observed infrared and nuclear magnetic resonance analyses were consistent with the assigned structure, and the physical characteristics are similar to those reported in the literature.[7] The contents of the cold trap consisted chiefly of heptafluoropropane which was identified by fluorine magnetic resonance analysis.

Preparation of Isomeric (Perfluoropropyl)-toluenes.—A 500-ml. stainless steel pressure vessel charged with 70 g. of perfluorobutyryl chloride, 50 g. of nickel carbonyl and 174 g. of toluene was closed and heated at 150° with agitation for 12 hours. After cooling, the reaction mixture was filtered, and the filtrate was fractionally distilled to obtain 30 g. (corresponding to a 70% yield) of a mixture of isomeric (perfluoropropyl)-toluenes boiling at 87–89° (100 mm.). Attempts to separate the isomers were unsuccessful. A sample purified by gas chromatography had a refractive index, n^{25}_D 1.3905. The fluorine magnetic resonance spectrum indicated the presence of two isomers in approximately 3:1 ratio. The spectrum consisted of a CF_3- resonance at 199 c.p.s., and two pairs of $-CF_2-$ resonances at 1952 and 2796 c.p.s. and 1699 and 2736 c.p.s., respectively. The proton magnetic resonance spectrum showed two resonances on the low field side of the tetramethylsilane reference: (1) one due to the methyl group, consisting of two components at 121 and 131 c.p.s. in area ratio of about 3:1 presumably arising from the methyl group of two isomers and (2) one resonance due to aromatic hydrogen, consisting of two components at 398 and 410 c.p.s. separated by 12 c.p.s. indicative of a mixture of isomers having slightly separated chemical shifts. The infrared spectrum showed absorption by unsaturated CH at 3.25 μ, by saturated CH at 3.4 μ, and by conjugated carbon–carbon double bonds at 6.2, 6.57 and 6.7 μ.

Anal. Calcd. for $C_{10}H_7F_7$: F, 51.08. Found: F, 50.54.

Preparation of Isomeric (Perfluoropropyl)-(perfluoromethyl)-benzenes.—Perfluorobutyryl chloride (70 g.), nickel carbonyl (35 g.) and (perfluoromethyl)-benzene (180 g.) after 8 hours at 150° in a pressure vessel gave 10 g. (30% yield) of (perfluoropropyl)-(perfluoromethyl)-benzene, boiling at 138°, n^{25}_D 1.3595. The fluorine magnetic resonance spectrum of this product showed a perfluoropropyl group with resonance at 230 c.p.s. (CF_3), 2015 and 2815 c.p.s. (two CF_2 groups) in the high field side and a CF_3- attached to an aromatic nucleus with a resonance at 720 c.p.s. in the low field side relative to trifluoroacetic acid. The latter appeared to consist of two very closely-spaced superimposed peaks.

The infrared spectrum showed absorption at 3.25 μ for unsaturated CH and at 6.1, 6.55 and 6.7 for μ benzenoid carbon–carbon double bonds. The proton magnetic resonance spectrum showed a strong peak at 432 c.p.s. and a weak one at 443 c.p.s., both on the low field side of tetramethylsilane reference, attributed to aromatic hydrogen. A sample purified by gas chromatography was analyzed.

Anal. Calcd. for $C_{10}H_4F_{10}$: F, 60.48. Found: F, 60.03.

Preparation of Isomeric (Perfluoropropyl)-bromobenzenes.—Perfluorobutyryl chloride (46 g.), bromobenzene (100 g.) and nickel carbonyl (35 g.) in a stainless steel container at 150° for 8 hours gave 12 g. or a 30% yield of isomeric (perfluoropropyl)-bromobenzenes, boiling at 174°. A portion of this product, purified further by gas chromatography, was analyzed. Infrared and nuclear magnetic resonance analyses were consistent with the assigned structure. The nuclear magnetic resonance analysis indicated the presence of at least two isomers.

Anal. Calcd. for $C_9H_4F_7Br$: C, 32.26; H, 1.24; F, 40.92. Found: C, 33.59; H, 1.57; F, 40.38.

Preparation of (Perfluoropropyl)-benzene and Bis-(perfluoropropyl)-benzene.—Benzene (22 g.), perfluorobutyryl chloride (93 g.) and nickel carbonyl (35 g.) heated at 150° for 8 hours gave 25 g. (50%) of (perfluoropropyl)-benzene boiling at 128° (n^{25}_D 1.3765) and 4 g. (10%) of bis-(perfluoropropyl)-benzene boiling at 145°. The bis-(perfluoropropyl)-benzene was identified by elemental analysis and by infrared and nuclear magnetic resonance analysis. Although nuclear magnetic resonance analysis showed only one compound, the presence of isomers was not rigorously excluded.

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(7) German Patent 1,049,862, George V. D. Tiers to Minnesota Mining and Manufacturing Co., reports for (perfluoropropyl)-benzene b.p. 132° (760 mm.), n^{25}_D 1.3790.

Anal. Calcd. for $C_{12}H_4F_{14}$: C, 34.80; H, 0.97; F, 64.23. Found: C, 35.64; H, 1.54; F, 62.85.

Preparation of (10-Hydroeicosafluorodecyl)-benzene.—11-Hydroeicosafluoroundecanoyl chloride (56 g.), benzene (174 ml.), and nickel carbonyl (8.5 g.) heated at 150° for 8 hours gave 24 g. (90%) of (10-hydroeicosafluorodecyl)-benzene, boiling at 193° and melting at 43°. The fluorine magnetic resonance spectrum of the fluoroalkylbenzene consisted of five chemically shifted resonances with relative intensities of 2:6:2:2:2, four singlets at 1867, 2507, 2588, 2951 c.p.s. and a doublet centered at 3447 c.p.s. The infrared spectrum showed doubly bonded CH absorption at 3.25 μ, aromatic carbon-carbon double bond absorption at 6.17 and 6.65 μ, and absorption by monosubstituted aromatic bonds at 13.0 and 14.26 μ.

Anal. Calcd. for $C_{16}H_6F_{20}$: C, 33.23; H, 1.05; F, 65.72. Found: C, 33.03; H, 1.31; F, 65.79.

Reaction of 5-Hydroöctafluorovaleryl Chloride with Nickel Carbonyl.[8]—A 500-ml. stainless steel pressure vessel charged with 79 g. of 5-hydroöctafluorovaleryl chloride and 51 g. of nickel carbonyl was heated at 150° with agitation for 4 hours. The products from two runs were combined and washed by agitation with 200 ml. of water. The lower fluorocarbon layer was separated from the aqueous layer, flash-distilled, dried over phosphorus pentoxide, and fractionally distilled to obtain 36 g. of a mixture boiling at 127–152°. Titration of a sample in aqueous ethanol at 0° indicated the presence of free carboxylic acid corresponding to 5.4% (by weight) 5-hydroöctafluorovaleric acid and 31% ketone.

Examination of the mixture by analytical gas chromatography using a 78 × 1/4 inch column packed with 20% fluoroalkyl pyromellitate on 40–60 mesh Columpak operated at 99° and 30 ml./min. helium flow gave the results

Component elution time, min.	Approximate % In eluted material	In orig. sample[a]	Identity later established
8.5	1	1	
9.65	14	13	$H_2C_8F_{14}$ subsequently obtained in admixture with $H(CF_2)_8H$
11.6	48	45	$H(CF_2)_8H$
19.8	35	33	$H(CF_2)_4CO(CF_2)_4H$

[a] Corrected for non-eluted acid content of 5.4%.

Separation of Products.—The mixture was separated by preparative gas chromatography employing a 6 ft. × 3/4 in. diameter column packed with 15% fluoroalkyl pyromellitate on fire brick operated at 100° and 790 ml./min. helium flow. From 16 charges of 0.4 ml. there were obtained 3 fractions at 8.0, 10.5 and 19.25 min. elution time. Fraction 1, in view of its composition as indicated by analytical gas chromatography, was reprocessed with the same column as 4 charges of 0.2 ml. each to give two subfractions 1a and 1b. Fractions 2 and 3 were subjected to simple distillation *in vacuo* to remove entrained column packing liquid.

Examination of Fractions. A. Fraction 1a.—This appeared to contain a 1,8-dihydrotetradecafluoroöctene as judged by the infrared and fluorine magnetic resonance spectra and by elemental analysis. Analytical gas chromatography showed the approximate composition 9% at 8.7 min. elution time, 76% at 10.1 min. and 15% at 11.5 min. Infrared absorption at 5.72μ (C=C stretching) indicated the presence of the —CF= group of a fluoroölefin (possibly the *cis* form). Additional bands were CH absorption at 3.32 μ and major CF absorption at 8.5 and 8.85 μ. The fluorine magnetic resonance measured at 40 Mc./sec. and recalculated to 56.4 Mc. showed 10 peaks, with 2 peaks at 4434 and 4540 indicative of vinyl fluorine of a fluoroölefin.

Anal. Calcd. for $C_8H_2F_{14}$: C, 26.39; H, 0.55. Found: C, 26.09; H, 1.12.

B. Fraction 2.—The data reported suggest that this 11.6-min. component is a mixture comprised chiefly of 1,8-dihydrohexadecafluoroöctane.

Analytical gas chromatography showed fraction 2 to consist of *ca.* 94% of the 11.6-min. component contaminated by *ca.* 6% of the 9.65-min. component. The fluorine magnetic resonance spectrum of this fraction consisted of 5 resonances: (a) two peaks at 3450 (1)[9] and 3395 (1)[9] c.p.s. indicated the presence of a HCF_2– group with the characteristic 55 c.p.s. splitting due to the hydrogen; and (b) three peaks at 2975 (2),[9] 2612 (2)[9] and 2526 (2)[9] c.p.s. indicated the presence of three $-CF_2-$ groups. The proton magnetic resonance consisted of a triplet peak at 185, 236 and 288 c.p.s. to the low field side of acetone as reference, with the 50 c.p.s. splitting typical of the HCF_2 group. The infrared spectrum showed a CH band at 3.32 μ, and major CF absorption at 8.26, 8.43, 8.55 and 8.75 μ.

Anal. Calcd. for $C_8H_2F_{16}$: C, 23.90; H, 0.50; F, 75.61. Found: C, 24.30; H, 0.61; F, 75.26.

C. Fraction 3.—The 19.8-min. component was identified as 1,9-dihydrohexadecafluoro-5-nonanone.

Analytical gas chromatography showed fraction 3 to be essentially one component. The fluorine magnetic resonance spectrum showed four resonances: (a) three single peaks at 2274, 2581 and 2293 c.p.s. due to three CF_2 groups in $-CF_2CF_2CF_2-$ units; and (b) a doublet with components at 3391 and 3447 c.p.s. due to the terminal $-CF_2H$ group with the characteristic 56 c.p.s. splitting by the hydrogen. The proton magnetic resonance spectrum was essentially identical with that of fraction 2 above, *i.e.*, a triplet peak at 188, 238 and 288 c.p.s. on the low field side of acetone. The infrared spectrum showed a strong carbonyl absorption at 5.59 μ as well as CH absorption at 3.32 μ, and major CF absorption at 8.45 and 8.83 μ.

Anal. Calcd. for $C_9H_2F_{16}O$: C, 25.13; H, 0.47; F, 70.68; neut. equiv., 430. Found: C, 25.84; H, 0.76; F, 70.36; neut. equiv., 439 in aqueous ethanol at 0°.

Preparation of 1,20-Dihydroöctatriacontafluoro-10-eicosene.—A stainless steel 500-ml. vessel containing 13 g. of 11-hydroeicosafluoroundecanoyl chloride, 23 g. of perfluorobutyryl chloride and 40 g. of nickel carbonyl was heated at 150° with agitation for 16 hours. The cooled reaction product was shaken with 100 ml. of water, and the lower organic layer was separated and fractionally distilled. There was obtained 2 g. of product melting at 89–91° that possessed the elemental composition and nuclear magnetic resonance spectrum consistent with the structure 1,20-dihydroöctatriacontafluoro-10-eicosene.

Anal. Calcd. for $C_{20}F_{38}H_2$: C, 24.92; H, 0.42; F, 74.66. Found: C, 25.25; H, 0.67; F, 74.31.

Also there was obtained a mixture (6 g.) boiling at 82–96° (10 mm.) that appeared to contain 13-hydropentacosafluoro-3-tridecene, 13-hydropentacosafluoro-2-tridecene and 1-hydroheptacosatridecane as judged by nuclear magnetic resonance analyses.

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(8) J. J. Drysdale, U. S. Patent 2,925,446, February 16, 1960.

(9) Relative areas in parentheses.