nitrophenylglycidate, 19202-48-3; benzoyl *trans*-3-*p*-nitrophenylglycidyl peroxide, 19190-81-9; 2-*t*-butoxy-2-*p*-nitrophenylacetaldehyde, 19202-50-7; 2-*t*-butoxy-2-*p*-nitrophenylethanol, 19190-54-6; 2-*t*-butoxy-2-*p*-nitrophenylethanol phenylurethan derivative, 19190-55-7; phenoxymethyl *p*-nitrobenzoate, 19190-56-8; *p*-nitrobenzoyl *trans*-2-phenylcyclopropylcarboxoyl peroxide, 19202-51-8.

Synthesis of Perfluoroalkyl Vinyl Ether Acids and Derivatives

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Contribution No. 189 from E. I. du Pont de Nemours and Company, Elastomer Chemicals Department, Experimental Station, Wilmington, Delaware 19898

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Potassium salts of certain perfluorodicarboxylic acids have been found to undergo a monodecarboxylation to yield perfluoroalkyl vinyl ether acid salts in low yield. Various carboxyl derivatives were prepared.

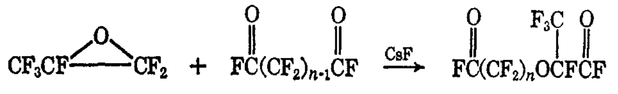
Although alkyl trifluorovinyl ethers, $ROCF{=}CF_2$, in which *R* is a hydrocarbon alkyl group can be prepared by the reaction of an alkali metal alkoxide with tetrafluoroethylene (TFE), this procedure generally fails when an alkali metal perfluoroalkoxide is used. An exception is the reaction of potassium perfluoroisopropoxide with fluorinated cyclobutene to give the vinyl ether.[2] In most cases the fluoroalkoxide anion prefers to lose fluoride ion rather than react with the fluoroolefin. The most convenient preparation of perfluoroalkyl vinyl ethers is by pyrolysis of certain fluorinated ether acid salts *via* the following reaction.

$$R_FOCF(CF_3)CO_2M \xrightarrow{\Delta} R_FOCF{=}CF_2$$[3]

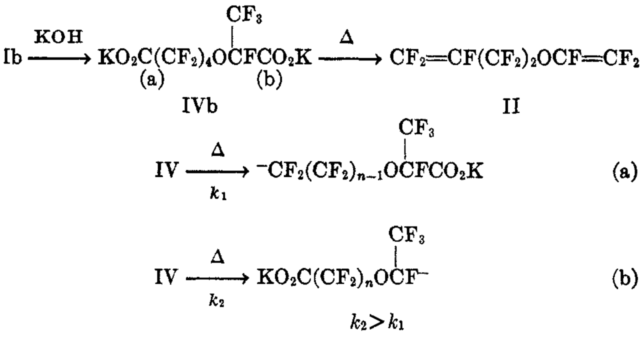
This general procedure has now been refined so that a selective pyrolysis of only one of the carboxyl groups to certain perfluoroalkyldicarboxylic acid salts can be carried out. Thus the reaction can now be used of prepare, although in low over-all yield, functionally substituted perfluoroalkyl vinyl ethers, a new class of compounds. The vinyl ether esters and nitriles can be copolymerized with other fluorinated monomers such as TFE and vinylidene fluoride and other perfluoroalkyl vinyl ethers.

The type of dicarboxylic acid salt used is illustrated in IV, in which the rate of pyrolysis of the carboxyl group on the more substituted α-carbon (b) is faster than the rate of pyrolysis of the other end (a). Pyrolyses of this nature in the perfluorocarbon series are thought to proceed through a carbanion intermediate. The carbanion resulting from pyrolysis at (b) should be more stable due to the delocalizing ability of the α-CF_3 group. A fluorine α to a carbanion is known to have much less delocalizing ability than a fluorine β to the negative charge[4] due to an inductive effect through space.[5]

Compound I is easily prepared by the reaction of hexafluoropropylene epoxide (HFPO)[6] with a diacid fluoride to give the unsymmetrical adduct.[7] This reaction, carried out at −30° in diglyme with cesium fluoride catalyst, involves initial reaction of cesium fluoride with a carbonyl group to give a perfluoroalkoxide, which then attacks the electrophilic center carbon of HFPO to produce I in about 70% yield.



Ia, *n* = 3
b, *n* = 4



$$\mathrm{Ib} \xrightarrow{\mathrm{KOH}} \underset{\text{(a)}}{KO_2C}(CF_2)_4O\underset{\text{(b)}}{\overset{CF_3}{C}}FCO_2K \xrightarrow{\Delta} CF_2{=}CF(CF_2)_2OCF{=}CF_2$$

IVb II

$$\mathrm{IV} \xrightarrow[k_1]{\Delta} {}^-CF_2(CF_2)_{n-1}O\overset{CF_3}{C}FCO_2K \qquad \text{(a)}$$

$$\mathrm{IV} \xrightarrow[k_2]{\Delta} KO_2C(CF_2)_nO\overset{CF_3}{C}F^- \qquad \text{(b)}$$

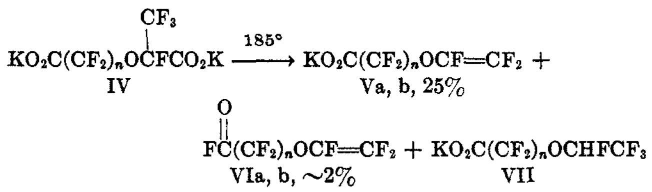
$$k_2 > k_1$$

Evidence of such a difference in the rate of pyrolysis came from the discovery of small amounts of monodecarboxylated product in the pyrolysis of the potassium salt IVb during preparation of the diene II. This product was isolated as the vinyl ether acid, perfluoro-6-oxa-7-octenoic acid (III). The normal temperature

$$CF_2{=}CFO(CF_2)_4CO_2H$$

III

for complete pyrolysis of IVb to the diene II[8] is 200–225°. Infrared and glpc analyses of the product from complete pyrolysis also give evidence of smaller amounts of the internal olefin $CF_3CF{=}CFCF_2OCF{=}CF_2$, which is produced by double-bond migration. For mono-



$$\underset{\mathrm{IV}}{KO_2C(CF_2)_nO\overset{CF_3}{C}FCO_2K} \xrightarrow{185°} \underset{\text{Va, b, 25\%}}{KO_2C(CF_2)_nOCF{=}CF_2} + \underset{\text{VIa, b, }\sim 2\%}{F\overset{O}{\overset{\|}{C}}(CF_2)_nOCF{=}CF_2} + \underset{\mathrm{VII}}{KO_2C(CF_2)_nOCHFCF_3}$$

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[1] Address correspondence to the author at the Stanford Research Institute, South Pasadena, Calif. 91030.

[2] R. W. Anderson, N. L. Madison, and C. I. Merrill, Abstracts, Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967, p 64.

[3] C. G. Fritz and S. Selman, U. S. Patent 3,291,843 (1966).

[4] S. Andreades, *J. Amer. Chem. Soc.*, **86**, 2003 (1964).

[5] A. Streitwieser, Jr., and D. Holtz, *ibid.*, **89**, 692 (1967); A. Streitwieser, Jr., A. P. Marchand, and A. H. Pudjaatmaka, *ibid.*, **89**, 693 (1967).

[6] For a synthesis of HFPO see British Patent 904,877 (1962); *Chem. Eng. News*, **45**, (33), 18 (1967).

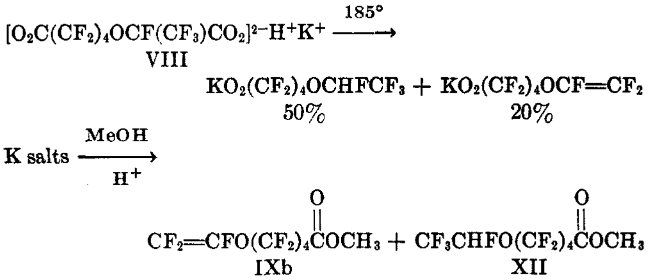
[7] C. G. Fritz and E. P. Moore, U. S. Patent 3,250,807 (1966).

[8] Compound II was first synthesized by this method by Dr. Charles G. Fritz, Plastics Department, E. I. duPont de Nemours & Co., Inc.

decarboxylation a lower temperature was called for. Pyrolysis of IVb at 185–200° gave the monodecarboxylated potassium salt Vb as the major product and in about 15–25% conversion. The pyrolysis was carried out under vacuum and the major product, being nonvolatile, remained behind in the reaction flask. The reaction can be halted when the volatile materials due to double decarboxylation (II) begin to collect in a cold trap connected to the pyrolysis flask.

A volatile by-product of this reaction is the vinyl ether acid fluoride VI, which is produced in low yield. Formation of acid fluorides and anhydrides has been previously reported during pyrolysis of fluorinated acid salts.[9] A more common by-product is the hydro ether VII, which arises from reaction of the carbanion (b) with traces of water of hydration in the potassium salt. Preparation of the dipotassium salt by neutralization of the dibasic acid with aqueous potassium hydroxide invariably gave a 2–5% conversion to the hydrocompound along the vinyl ether even after prolonged drying of the potassium salt (2–3 days under vacuum at up to 120°). Some pyrolysis may have occurred during the drying operation to give the hydro compound. To avoid contamination of the product by the hydro compound, it was necessary to prepare the dipotassium salt IV from the dimethyl ester by saponification with anhydrous potassium hydroxide in anhydrous methanol. Removal of the methanol solvent under vacuum could be done at a lower temperature and was more efficient than removal of water. Less than 1% of hydro compound was produced on pyrolysis after this procedure.

Although the pyrolysis of the dipotassium salt gave a low yield (18–25%) of the vinyl ether potassium salt, it was found that pyrolysis of the half-neutralized dibasic acid (VIII) at 185° gave a 70% conversion to monodecarboxylated product, about 70% of which was the hydro ether potassium salt and about 30% was the vinyl ether.



$$\underset{\text{VIII}}{[O_2C(CF_2)_4OCF(CF_3)CO_2]^{2-}H^+K^+} \xrightarrow{185^\circ} \underset{50\%}{KO_2(CF_2)_4OCHFCF_3} + \underset{20\%}{KO_2(CF_2)_4OCF{=}CF_2}$$

$$\text{K salts} \xrightarrow[H^+]{\text{MeOH}} \underset{\text{IXb}}{CF_2{=}CFO(CF_2)_4\overset{\overset{\displaystyle O}{\|}}{C}OCH_3} + \underset{\text{XII}}{CF_3CHFO(CF_2)_4\overset{\overset{\displaystyle O}{\|}}{C}OCH_3}$$

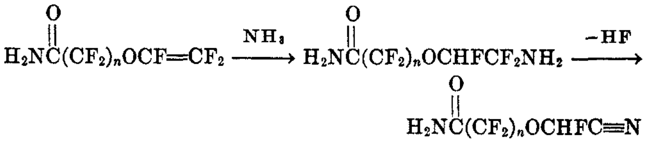
The vinyl ether acid salts were converted to their methyl esters for distillation and identified by ^{19}F nmr and by their infrared spectra. The infrared spectrum shows the vinyl ether unsaturation at 5.42 μ as a medium intensity band and the ester carbonyl at 5.6 μ. Fluorine nmr at 56.4 MHz showed the vinylic fluorine (a) of methyl perfluoro-6-oxa-7-octenoate (IXb) to

IXb

be two doublets centered at 117 ppm (referred to $CFCl_3$) with $J_{ab} = 88$ Hz and $J_{ac} = 66$ Hz. The fluorine at b occurs as four triplets at 124.6 ppm but is partly hidden by the CF_2 group at f with J_{bc} equal to 116 Hz and J_{bd} equal to 6 Hz. The fluorine at c was expected to be farther downfield due to the very electrophilic character of the CF_2O group and it occurs at 138.2 ppm as four triplets with $J_{cd} = 6$ Hz.

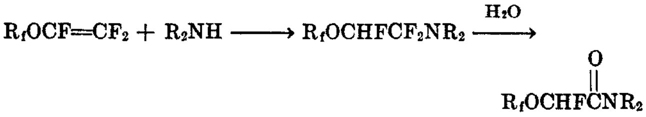
Other work done in these laboratories and elsewhere[10] has shown that the center for nucleophilic attack on the vinyl ether double bond is the terminal carbon. Thus the carbon next to oxygen has more delocalizing ability and fluorine c should be found far downfield. These absorptions are typical of all the perfluoroalkyl vinyl ethers that have been prepared to date. The CF_2O group of IXb occurs at 86.8 ppm, the CF_2 group e at 127 ppm, the CF_2 at f occurs at 125 ppm, and the CF_2 next to the carbonyl at 111 ppm. A number of derivatives of the pyrolysis products were prepared. The amide is easily prepared from the vinyl ether ester by reaction with ammonia. Addition of a stoichiometric amount of ammonia will give only the vinyl ether amide.

Addition of excess ammonia will presumably result in addition of ammonia across the vinyl ether double bond, loss of HF, and production of an amide nitrile.



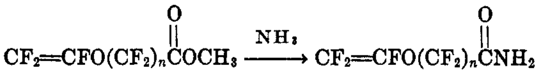
$$H_2N\overset{\overset{\displaystyle O}{\|}}{C}(CF_2)_nOCF{=}CF_2 \xrightarrow{NH_3} H_2N\overset{\overset{\displaystyle O}{\|}}{C}(CF_2)_nOCHFCF_2NH_2 \xrightarrow{-HF} H_2N\overset{\overset{\displaystyle O}{\|}}{C}(CF_2)_nOCHFC{\equiv}N$$

Reaction of the vinyl ether with a secondary amine gives an adduct which is hydrolytically unstable and is converted to an amide on contact with water.[8]



$$R_fOCF{=}CF_2 + R_2NH \longrightarrow R_fOCHFCF_2NR_2 \xrightarrow{H_2O} R_fOCHF\overset{\overset{\displaystyle O}{\|}}{C}NR_2$$

The vinyl ether nitrile can be prepared in good yield in the conventional manner by reaction of the amide with phosphorus pentoxide at 160°.[11] The infrared spectrum of the nitrile XI shows the nitrile group at 4.4 μ and the double bond at 5.42 μ. The over-all yield of XIb beginning with perfluoroglutaryl fluoride was only about 6%.



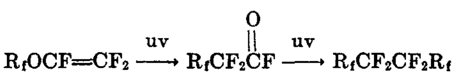
$$CF_2{=}CFO(CF_2)_n\overset{\overset{\displaystyle O}{\|}}{C}OCH_3 \xrightarrow{NH_3} CF_2{=}CFO(CF_2)_n\overset{\overset{\displaystyle O}{\|}}{C}NH_2$$

Xa, $n = 3$
b, $n = 4$

$$X \xrightarrow{P_2O_5} CF_2{=}CFO(CF_2)_nC{\equiv}N$$

XIa, b

Perfluorinated vinyl ethers are stable compounds with no known toxic properties. However, exposure to ultraviolet light will cause isomerization to the acid fluoride which then undergoes homolytic cleavage of



$$R_fOCF{=}CF_2 \xrightarrow{uv} R_fCF_2\overset{\overset{\displaystyle O}{\|}}{C}F \xrightarrow{uv} R_fCF_2CF_2R_f$$

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[9] J. D. La Zerte, L. J. Hals, T. S. Reid, and G. H. Smith, *J. Amer. Chem. Soc.*, **75**, 4525 (1953).

[10] A. V. Tumanova, *et al.*, *Zh. Obshch. Khim.*, **35**, 399 (1965); *Chem. Abstr.* **62**, 13148e (1965).

[11] The nitrile XIb was prepared by Dr. Almut F. Breazeale, Elastomer Chemicals Department, E. I. du Pont de Nemours & Co., Inc.

the CF_2-COF bond to form products of radical coupling.[12]

Experimental Section

All ^{19}F nmr spectra were taken with a Varian Associates A-56/60 spectrometer at 56.4 MHz using $CFCl_3$ as an internal standard. Infrared spectra were taken with a Perkin-Elmer Infracord spectrophotometer. Melting and boiling points are uncorrected. Perfluoroglutaryl chloride and perfluorosuccinic acid were obtained from Peninsular Chemresearch, Inc. Perfluorosuccinyl chloride was prepared from the potassium salt by reaction with PCl_5. Hexafluoropropylene epoxide (HFPO) was obtained from Plastics Department, E. I. du Pont de Nemours & Co. It is also available from Peninsular Chemresearch.

Preparation of Starting Materials.—Perfluoroglutaryl and succinyl fluorides were prepared from the corresponding acid chlorides by reaction with sodium fluoride in tetramethylene sulfone.[12] A typical example is as follows. Into a 2-l. three-neck flask fitted with mechanical stirrer, dropping funnel, and take-off condenser attached to a short Vigreux column were added 500 ml of tetramethylene sulfone and 200 g (5.3 mol) of sodium fluoride and warmed to 60°. Perfluoroglutaryl chloride (400 g, 1.44 mol) was added at such a rate as to maintain the head temperature at 50° or less. The perfluoroglutaryl fluoride was distilled, bp 47–49°, 315 g (90%). The yield of perfluorosuccinyl fluoride (bp 18–19°) was 80%.

Perfluoro-2-methyl-3-oxaoctanedioyl Fluoride (Ib).—A dry 1-l. three-neck flask, fitted with a mechanical stirrer and with fittings wired down to contain 5–10 psig, was charged with 427 g of perfluoroglutaryl fluoride under dry nitrogen, 150 ml of diglyme, and 30 g of cesium fluoride. The vessel and contents were cooled to −30° in a Dry Ice–acetone bath and evacuated to about 25 mm. The mixture was stirred vigorously and 335 g of hexafluoropropylene epoxide (HFPO) was condensed into the flask. The temperature was gradually raised to maintain pressure between 0 and 5 psig for about 8 hr until at room temperature no excess pressure remained in the flask. Distillation of the reaction mixture at 1 atm under dry nitrogen yielded perfluoro-2-methyl-3-oxaoctanedioyl fluoride, bp 108°, in 75% yield based on the perfluoroglutaryl fluoride; nmr of **Ib**: −21.6 (1 F, C–COF), −23.8 (1 F, O–C–COF), the CF_2O group forms an AB system at 80.5 and 87.5 (J = 148 Hz), 84.5 (3 F, CF_3), 120 (2 F, $O{=}CCF_2$), 125 (2 F, $O{=}CCCF_2$), 127 (2 F, $O{=}CCCCF_2$), 146 ppm (1 F, OCF).

A more convenient procedure is to maintain the reaction flask at or above room temperature and at 1 atm of pressure and to lead the HFPO into the flask from a stainless steel cylinder at a rate sufficient to maintain a good reflux from a condenser kept at Dry Ice temperature. The reaction is somewhat exothermic and was cooled in a water bath to keep the temperature down to an arbitrary 50–55°. The advantage of this method is a shorter reaction time (~2 hr).

Perfluoro-2-methyl-3-oxaheptanedioyl Fluoride (Ia).—The adduct was prepared in good yield by condensing 270 g (1.62 mol) of HFPO in an evacuated and dry 1-l. three-neck flask kept at −30° and containing 315 g (1.62 mol) of perfluorosuccinyl fluoride, 50 ml of diglyme, and 10 g of cesium fluoride. The HFPO was added over a 1.5-hr period and the contents were stirred vigorously with a mechanical stirrer. Pressure inside the flask was kept between −10 and +5 psig for about 18 hr. Glpc analysis showed very little starting material and one product peak. The fluorocarbon layer was distilled to give 453.5 g (1.26 mol) of perfluoro-2-methyl-3-oxaheptanedioyl fluoride, bp 86° (80%).

The dipotassium salt IVa was prepared from the diacid fluoride by the addition of KOH in excess water. Phenolphthalein was used to determine the end point. Thorough drying of the salt under vacuum at 100° for 2–3 days was required before pyrolysis.

Dipotassium Perfluoro-2-methyl-3-oxaoctanedioate (IVb). A. IVb from the Acid.—A two- or threefold excess of water was cautiously added to the warm (about 50°) diacid fluoride Ib in a polypropylene beaker. Some of the HF which was formed and excess water were removed under vacuum. The acid was dissolved in water and neutralized to the phenolphthalein end point with aqueous potassium hydroxide. The salt was then dried thoroughly on a rotovac under vacuum at about 100° for several days. It was ground into a fine powder several times during the drying process.

B. From the Ester.—Into an open polyethylene bottle under an atmosphere of dry nitrogen was charged 443 g of perfluoro-2-methyl-3-oxaoctanedioyl fluoride. The bottle and contents were warmed to about 50° and 50 ml of methanol was added slowly and cautiously with occasional stirring in 0.5 hr. The bottle and contents were warmed on a steam bath for several hours at atmospheric pressure to remove excess HF, then stored overnight over sodium fluoride. The liquid was distilled on an 18-in. spinning band column at reduced pressure to yield 462 g of dimethyl perfluoro-2-methyl-3-oxaoctanedioate, bp 112° (1.5 mm). The dimethyl ester was then mixed with an approximately equal volume of methanol, and several drops of phenolphthalein solution and methanolic anhydrous KOH were added to the ester at a rate sufficient to maintain a temperature of 40–50° until the phenolphthalein end point was reached. Solvent was removed by heating *in vacuo* at 50–65° for 1 week. The hydroscopic salt was ground several times during the drying period into a finer mesh and stored as a fine powder under dry nitrogen in preparation for pyrolysis.

Potassium Perfluoro-6-oxa-7-octenoate (Vb). A. Pyrolysis of Dipotassium Perfluoro-2-methyl-3-oxaoctanedioate (IVb) Prepared from the Acid.—Pyrolysis of 250 g of the salt was carried out with 40–50-g batches of the finely ground dipotassium salt IVb in a 250-ml three-neck flask under vacuum. The flask was connected in series to a Dry Ice trap and liquid nitrogen trap and the vacuum pump. The flask was then immersed in a silicone oil bath preheated to 195°. The powder was frequently agitated to prevent caking on the bottom of the flask. At this temperature, CO_2 evolution could be observed by its solidification in the liquid nitrogen trap. The temperature was raised slowly until, after 2–4 hr, it stood at 210°. At this point a small amount of liquid began to collect in the Dry Ice trap. This liquid is largely the diene II and results from decarboxylation at both ends of the molecule. Heating was then discontinued.

B. Pyrolysis of IVb Prepared from the Ester.—A sample of 41.5 g of the dipotassium salt IVb prepared under anhydrous conditions from the ester was pyrolyzed in the same manner as described above. However, after immersion of the salt in the oil bath at 190°, the salt fused into a crusty mass. It was cooled and reground into a fine powder. After this, the salt remained as a powder during pyrolysis. The fine powder is necessary to prevent complete pyrolysis and to ensure good heat transfer. Heating was continued at 190–204° for 3.5 hr.

Methyl Perfluoro-6-oxa-7-octenoate (IXb). A.—The brown solid after pyrolysis of 250 g of IVb (prepared from the acid of Ib) was dissolved in water and acidified with concentrated HCl solution to separate the fluorocarbon acid. The water layer was extracted with ether and the ether extract was combined with the acid layer and filtered. The acid was then mixed with excess methanol and sulfuric acid and refluxed for 2 hr. The lower ester layer was separated, dried over anhydrous magnesium sulfate, and distilled into two fractions: 36 g of bp 146–150° and 6 g of by 150–156°. Also approximately 10% of the ester of the unreacted dibasic acid was recovered.[13] The product composition was analyzed using a glpc column of Dow Corning FS 1265 fluid on firebrick at 100°. The first fraction consisted of 80% of IXb and 20% of XII; the second fraction contained 65% of XII. Samples for analysis were obtained from further distillation. Yields were about 18% of IXb and 6% of XII. Infrared of IXb showed 3.4 (w), 5.45 m (C=C), 5.6 s (C=O), 7.0 m, 7.5 s, 7.7 s, 8.5 sb, 9.6 m, 10.5 m, 11.4 m, 12.6 m, 13.3 m, and 14.1 m μ. *Anal.* Calcd for $C_8H_3O_3F_{11}$: C, 26.98; H, 0.84; F, 58.69. Found: C, 27.1; H, 1.0; F, 59.7.

Nmr of XII showed that the OCF_2 group forms an AB system at 86.5 and 88.5 ppm (J = 150 Hz) and peaks at 86.6 (3 F, CF_3), 120 (2 F, $CF_2C{=}O$), 125 (2 F, $CF_2CC{=}O$), 127 (2 F, $OCCF_2$), 148 ppm (1 F, J_{HF} = 52 Hz, CHF). *Anal.* Calcd for $C_8H_4O_3F_{12}$: C, 25.5; H, 1.1; H, 60.6. Found: C, 24.9; H, 1.3; F, 58.8.

From 575 g of the dipotassium salt pyrolyzed (IVb), 31 g of cold-trap condensate was accumulated. Distillation under a dry nitrogen atmosphere yielded 7.3 g (2.1% conversion) of perfluoro-6-oxa-7-ocetenoyl fluoride (VIb), bp 90–91°, as well as some of the diene, II. Identification was inferred from the infrared and nmr spectra and by reaction with methanol to give an ester with infrared spectrum identical with that of IXb:

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[12] J. F. Harris, Jr., *J. Org. Chem.*, **30**, 2182 (1965).

[13] These are over-all yields based on the amount of dipotassium salt pyrolyzed.

infrared, 5.3 ($C=O$) s, 5.4 ($C=C$) w, 7.5 s, 7.8 s, 8.4 vsb, 9.0 m, 9.8 m, 11.3 m, 11.7 m, 12.5 m, 13.2 m, and 14.0 m μ; nmr, −21.6 (1 F, COF), 87 (2 F, OCF_2), 117 (2 d, 1 F, J = 86, 66 Hz, $CF=CO$), 120 (2 F, $CF_2C=O$), 125 (4 t, 1 F, J = 112, 86, 6 Hz, $CF=CO$, *trans*), 125 (2 F, $OCCCF_2$), 127 (2 F, $OCCF_2$), 139 ppm (4 t, 1 F, J = 112, 66, 6 Hz, $C=CFO$).

B.—The brown solid after pyrolysis of 41.5 g of IVb (prepared from the diester under anhydrous conditions) was worked up as described above and distilled to give 7.7 g of vinyl ether ester IXb, bp 144°, 25% conversion, and 8.6 g of unpyrolyzed ester was recovered. Glpc analysis of the product showed only 0.4 area % of the saturated ester XII.

Pyrolysis of Dipotassium Perfluoro-2-methyl-3-oxaheptanedioate (IVa).—The dry potassium salt, prepared from Ia *via* the aqueous procedure described above for IVb, was pyrolyzed in 50–75-g batches in a 500-ml round-bottom flask at a temperature of 190–198° and about 1 mm. The flask was connected to a Dry Ice trap, a manometer, and a pump. Frequent agitation of the finely ground salt was necessary to prevent it from caking too much. Heating was continued for 2–3 hr and about 2–3 g of a yellow liquid collected in the Dry Ice trap during each run. The end of the reaction could be approximated by the amount of liquid collected which is a crude measure of the amount of twice-decarboxylated product forming. At temperatures above 198° the salt melted. In order to decarboxylate one end of the potassium salt and not the other, the pyrolysis must be run at the lowest temperature possible, and at 190° a satisfactory rate of CO_2 evolution was obtained. As the reaction proceeded, the temperature was raised slowly to 198°. Evolution of CO_2 is noticeable due to agitation of the powder by the escaping gas. At 198°, after 2–3 hr, this agitation had diminished: potassium salt pyrolyzed, 460 g (1.06 mol); pyrolysis residue (crude product), 362.4 g; recovered in Dry Ice trap, 37.4 g; estimated CO_2 lost (1.06 mol), 46.6 g; unaccounted loss during pyrolysis, 13 g.

Methyl Perfluoro-5-oxa-6-heptenoate (IXa).—A sample of 317 g of the crude pyrolysis product was taken up in water and concentrated HCl was added. The lower organic acid layer was separated and dried by distilling off a benzene–water azeotrope, and then excess methanol and excess concentrated sulfuric acid were added and refluxed for 7 hr. The product was washed with water and distilled with benzene to dryness. Distillation under reduced pressure gave 41 g (18%) of the vinyl ether ester, bp 61–62° (51 mm) (contained about 10% of the saturated hydro ester), and about 2 g of the saturated ester, $CH_3O_2C(CF_2)_3$-$OCHFCF_3$. Twenty-one per cent of the starting material was recovered as the dimethyl ester and the diacid. Infrared of IXa showed 3.3 w, 5.45 m, 5.6 s, 6.95 m, 7.5 sb, 8.5 vsb, 9.3 m, 10.2 m, 10.9 m, 12.2 m, 12.5 m, 12.9 w, 13.4 m, and 13.9 m μ; nmr, 87 (2 F, OCF_2), 117 (2 d, 1 F, J = 88, 66 Hz, $CF=CO$), 121 ppm (t, 2 F, $CF_2C=O$), 124.5 (4 t, 1 F, J = 110, 88, 6 Hz, $CF=CO$, *trans*), 128 (2 F, $OCCF_2$), 142 ppm (4 t, 1 F, J = 110, 66, 6 Hz, $C=CFO$).

Anal. Calcd for $C_7H_3O_3F_9$: C, 27.46; H, 0.98; F, 55.87. Found: C, 27.5; H, 1.02; F, 55.9.

From 460 g of dipotassium salt IVa which was pyrolyzed, there was recovered 37.4 g of liquid from the Dry Ice trap which was distilled to give 7.4 g (2.5%) of perfluoro-5-oxa-6-heptenoyl fluoride (VIa), bp 70°. Identification was inferred from the infrared and nmr spectra and by reaction with methanol to give an ester with infrared spectrum identical with IXa: infrared, 5.3 s ($C=O$), 5.4 m ($C=C$), 7.4 s, 7.7 s, 8.4 vsb, 8.8 s, 9.4 m, 10.4 m, 10.8 m, 12.3 m, 13.0 m, 13.9 m, and 14.5 m μ; nmr, −21.6 (1 F, COF), 87 (2 F, OCF_2), 117 (2 d, 1 F, J = 88, 66 Hz, $CF=CO$), 121 (2 F, $CF_2C=O$), 124 (4 t, 1 F, J = 110, 88, 6 Hz, $CF=CO$ *trans*), 129 (2 F, $OCCF_2$), 139 ppm (4 t, 1 F, J = 110, 66, 6 Hz, $C=CFO$).

Pyrolysis of the Half-Neutralized Perfluoro-2-methyl-3-oxaoctanedioic Acid (VIII).—The finely powdered salt was pyrolyzed at a bath temperature of 185–190° with frequent agitation to prevent caking as for the dipotassium salt. At 185° a melt formed which immediately gave off CO_2, leaving a solid residue. After about 2 hr, CO_2 evolution had ceased. Preparation of the esters as described above gave a 70% yield of monodecarboxylated esters which consisted of 27% of IXb and 73% of XII.

Perfluoro-5-oxa-6-heptenamide (Xa).—One gram of anhydrous ammonia (0.06 mol) was condensed in a graduated cold trap and allowed to evaporate into a 250-ml three-neck flask containing 35 ml of anhydrous ether and 18.3 g (0.06 mol) of the vinyl ether ester IXa at −30°. The vinyl ether had been purified by distillation to remove the saturated ester. The contents were stirred magnetically and the flask was evacuated before addition of the ammonia. The uptake of ammonia was complete in 5 min and the flask was allowed to warm to room temperature. The solvent was removed under vacuum and a white solid remained. Crystallization from benzene gave 13 g (73%) of white crystals. The melting point of 64.5–65.5° was determined after a second crystallization and sublimation; infrared, 3.0 m, 5.4 m, 5.9 sb μ ($C=O$).

Anal. Calcd for $C_6H_2F_9O_2N$: C, 24.7; H, 0.7; N, 4.8. Found: C, 24.8; H, 0.9; N, 4.27.

Preparation of the next higher homolog, perfluoro-6-oxa-7-octenamide (Xb), was accomplished in the same manner to give a 75% yield of white solid, mp 89.5–91.5°.

Anal. Calcd for $C_7H_2F_{11}O_2N$: C, 24.6; H, 0.6; N, 4.1; F, 61.3. Found: C, 24.4; H, 0.8; N, 3.8; F, 62.1.

Perfluoro-1-cyano-5-oxa-6-heptene (XIb).—Twelve grams (0.04 mol) of the amide Xb was thoroughly mixed with 8 g (0.056 mol) of phosphorus pentoxide in a drybox and placed in a 300-ml round-bottom flask. A steam-heated reflux condenser was attached in order to keep the amide (mp 90°) from crystallizing high up on the walls of the flask. A Dry Ice trap was attached, the flask was placed in an oil bath previously heated to 140°, and the heat was gradually increased to 160°. After 2 hr, 2 g of fresh P_2O_5 was added and heating was continued for 2 hr more. The flask was swept clean of product by evacuation and the crude nitrile was distilled to give 7.1 g (65%) of vinyl ether nitrile, bp 89–91°. Glpc analysis showed this material to contain 17 area % of the saturated ether nitrile derived from XII and 83% of XIb. Infrared of an 83:17 mixture showed 4.4 m, 5.45 m, and 7.7–8.8 vsb μ; nmr, 87 (2 F, OCF_2), 108 (2 F, $CF_2C\equiv N$), 117 (2 d, 1 F, J = 83, 64 Hz, $CF=CO$), 125 (5 F, 2 multiplets, $CF=CO$, $OCCF_2CF_2$), 138 ppm (4 t, 1 F, J = 108, 64, 6 Hz, $C=CFO$).

Anal. Calcd for $C_7F_{11}ON$: C, 26.02; F, 64.69; N, 4.33. Found: C, 26.2; H, 0.3; F, 64.7; N, 4.62.

Registry No.—Ia, 19190-57-9; Ib, 13140-22-2; IXa, 19190-61-5; IXb, 19190-58-0; Xa, 19190-59-1; Xb, 19190-60-4; XIb, 19237-73-1; XII, 19190-62-6; dimethyl perfluoro-2-methyl-3-oxaoctanedioate, 16835-45-3.