SYNTHESIS OF PERFLUORO(POLYETHER) DIFUNCTIONAL COMPOUNDS

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SUMMARY

   Omega-iodoperfluoro(polyether) esters $IR_fOR_fCO_2R$* have been synthe-
sized by two procedures. These iodoesters have been reacted via zinc
coupling reactions to yield alpha, omega-perfluoro(polyether) diesters.
The diesters serve as convenient starting materials for the synthesis of a
variety of other difunctional compounds of high molecular weight and
exhibiting a variation of oxygen-carbon ratio.

INTRODUCTION

   Perfluoro(polyether) difunctional compounds, XR_fOR_fX where X is a
functional group e.g., $-CO_2H$, $-CONH_2$, $-CN$, $-C(=NH)OR$ etc., have been
used in the synthesis of various polymeric systems. The resulting polymers
have in many instances shown improved thermo-oxidative properties over
conventional state of the art polymers.[1] Our study on the synthesis
of well defined, rather than polymeric perfluoro(polyether) difunctional
compounds, was prompted by a need for such compounds in order to determine
property-structure correlation on various polymeric systems. The procedures
employed in our study involved the synthesis of omega-iodoperfluoro(poly-
ether) esters ($IR_fOR_fCO_2R$) followed by zinc coupling to yield a variety of

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*The symbol $-R_fOR_f-$ is used to designate the general structure of a
 perfluoro(polyether) group.

perfluoro(polyether) diesters ($RO_2CR_fOR_fR_fOR_fCO_2R$). From these diesters other difunctional compounds e.g., diamides, dinitriles and diimidate esters could be prepared by use of conventional reactions.
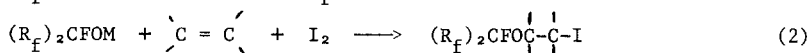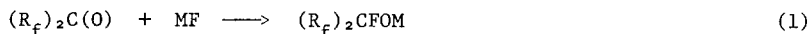

RESULTS AND DISCUSSION


Synthesis of $IR_fOR_fCO_2R$
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The available methods for the preparation of perfluoroalkyl iodides fall generally into two classes: (a) decarboxylation of metal salts of perfluoroacids in the presence of iodine[2−5] and (b) addition of the elements of iodine and fluorine across the double bond of perfluoroolefins.[6,7]

Hexafluoropropylene oxide (HFPO, $CF_3\overline{CFCF_2}O$) oligomers, $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)C(O)F$ can be readily converted by these methods to secondary perfluoroalkylene oxide iodides.[8] Application of the above methods to the preparation of perfluoroalkyl iodides bearing a second functional group, i.e., an ester or an acyl halide is not feasible since under the usual reaction conditions such groups do not remain intact.

Evans and coworkers[9,10] reported an interesting reaction between cesium or potassium alkoxide of a perhalogenated ketone, an olefin and iodine.

$$(R_f)_2C(O) \;+\; MF \;\longrightarrow\; (R_f)_2CFOM \tag{1}$$

$$(R_f)_2CFOM \;+\; \overset{}{C} = \overset{}{C} \;+\; I_2 \;\longrightarrow\; (R_f)_2CFO\overset{|}{C}\text{-}\overset{|}{C}\text{-}I \tag{2}$$
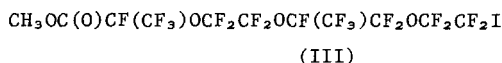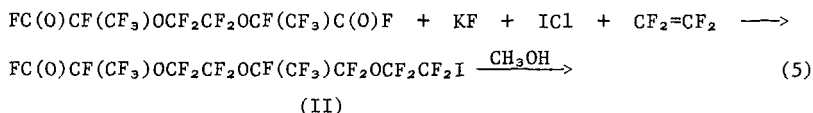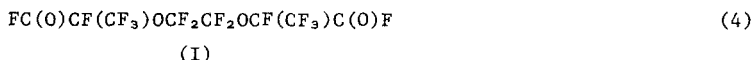
This reaction has been extended to HFPO oligomer acyl fluorides and tetrafluoroethylene oxide acyl fluorides and constitutes a rather unique method for the preparation of primary perfluoro(polyether) iodides.[8]

$$R_fOR_fOCFXC(O)F \;+\; MF \;+\; ICl \;+\; CF_2 = CF_2 \;\longrightarrow\;$$

$$R_fOR_fOCFXCF_2OCF_2CF_2I \tag{3}$$
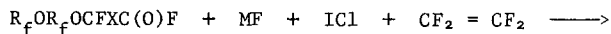
where $X = CF_3$ or F, $M = Cs$ or K

We have found that with diacyl fluorides, $F(O)CR_fOR_fC(O)F$, the reaction as described by equation 3 gives a mixture of 1:1 adduct (omega-iodoacyl fluoride) and a 2:1 adduct (alpha, omega-diiodide). Using a limited amount of KF, the reaction can be directed to yield the omega-iodoacyl fluoride as the major product. This type of reaction is feasible only with symmetrical alpha, omega-diacyl fluorides, e.g., compound I. Compound II was prepared in this manner and isolated as the methyl ester III.

$$\overset{\overset{\textstyle O\,O}{\textstyle \|\ \|}}{FCCF} \ + \ 2CF_3\overline{CFCF_2O} \ \xrightarrow{\ CsF\ }$$

$$FC(O)CF(CF_3)OCF_2CF_2OCF(CF_3)C(O)F \tag{4}$$
$$(I)$$

$$FC(O)CF(CF_3)OCF_2CF_2OCF(CF_3)C(O)F \ + \ KF \ + \ ICl \ + \ CF_2=CF_2 \ \longrightarrow$$

$$FC(O)CF(CF_3)OCF_2CF_2OCF(CF_3)CF_2OCF_2CF_2I \ \xrightarrow{\ CH_3OH\ } \tag{5}$$
$$(II)$$

$$CH_3OC(O)CF(CF_3)OCF_2CF_2OCF(CF_3)CF_2OCF_2CF_2I$$
$$(III)$$

By the same process $FC(O)(CF_2)_3C(O)F$ can be converted in good yields to $ROC(O)(CF_2)_4OCF_2CF_2I$ (IV, R = C_2H_5).

In contrast to other methods, the experimental conditions as described by equation 5 are mild and an omega ester functional group present in the molecule is not affected. Thus, ester containing acyl fluorides, which can be synthesized conveniently, may be used to prepare omega ester perfluoro-alkylene ether iodides.

$$CH_3OC(O)(CF_2)_3C(O)F \ + \ (n+1) \ CF_3\overline{CFCF_2O} \ \xrightarrow{\ CsF\ }$$
$$(V)$$

$$CH_3OC(O)(CF_2)_4O[CF(CF_3)CF_2O]_nCF(CF_3)C(O)F \tag{6}$$
$$(VI \ n = 1) \qquad (VII \ n = 2)$$

$$CH_3OC(O)(CF_2)_4O[CF(CF_3)CF_2O]_nCF(CF_3)C(O)F \ + \ KF \ + \ ICl \ + \ CF_2=CF_2$$

$$\longrightarrow \ CH_3OC(O)(CF_2)_4O[CF(CF_3)CF_2O]_nCF(CF_3)CF_2OCF_2CF_2I$$
$$(VIII \ n = 1) \qquad (IX \ n = 2) \tag{7}$$
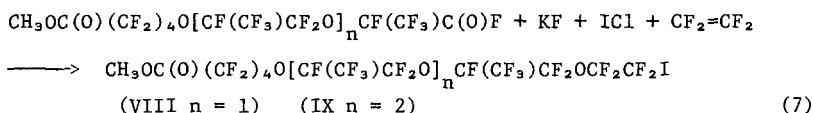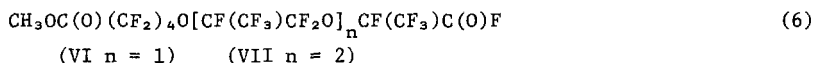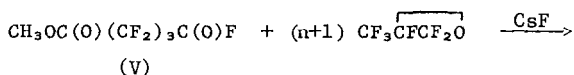
The above two methods as described by equations 6 and 7 offer procedures for the synthesis of a variety of $ROC(O)R_fOR_fI$.

Zinc Coupling Reactions

C_3F_7I has been reacted with metallic zinc under various conditions[11-13] to yield C_6F_{14} as one of the products. Subsequently, a perfluoroalkyl iodide containing a functional group, $I(CF_2)_3CO_2R$, has been coupled to yield an alpha, omega difunctional perfluoroalkane.[14-15] These investigations, as well as our own studies, have shown that zinc coupling reactions are sensitive to solvent, temperature and nature of the zinc. For high molecular weight
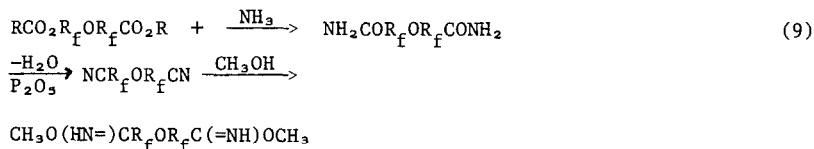
$IR_fOR_fCO_2R$ compounds, we have found that 1,1,2-trifluorotrichloroethane was found to be a better solvent than methylene chloride which was previously reported. Higher reaction temperature and improved solubility were realized. Particle size of the zinc metal seemed to govern the inductive period of the coupling reaction. A 40 mesh zinc was found to be desirable. A number of $IR_fOR_fCO_2R$ compounds were coupled to yield the diesters in moderate to high yields (see Table 1).

$$IR_fOR_fCO_2R \ + \ Zn \ \longrightarrow \ RCO_2R_FOR_fR_fOR_fCO_2R \tag{8}$$
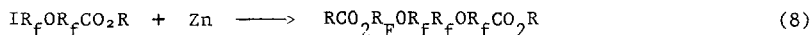
In all coupling reactions, small quantities of the reduction product $HR_fOR_fCO_2R$ were found. Reduction products (R_fH) from previous R_fI zinc coupling reactions have also been noted. Under our experimental conditions, it appeared that as the rate of the coupling reaction decreased, which was evident in higher molecular weight $IR_fOR_fCO_2R$, the yields of the $HR_fOR_fCO_2R$ increased while the yield of the coupled products $RCO_2R_fOR_fR_fOR_fCO_2R$ decreased.

Synthesis of XR_fOR_fX

The $RCO_2R_fOR_fR_fOR_fCO_2R$ compounds synthesized as described above (Table 1) are convenient compounds for synthesis of other difunctional compounds, X = amides, nitriles, imidate esters, etc. through conventional reactions, e.g.

$$RCO_2R_fOR_fCO_2R \ + \ \xrightarrow{NH_3} \ NH_2COR_fOR_fCONH_2 \tag{9}$$

$$\xrightarrow[P_2O_5]{-H_2O} NCR_fOR_fCN \xrightarrow{CH_3OH}$$

$$CH_3O(HN=)CR_fOR_fC(=NH)OCH_3$$

These difunctional compounds (Tables II and III) which ranged in molecular weight from 720 to 1744 can all be isolated in high purity as shown by gas chromatography and other analysis. The high boiling dinitriles and imidate esters are thermally stable and can be distilled under reduced pressure undecomposed. Application of some of these difunctional compounds as intermediates in polymer studies has been described elsewhere.[1]

TABLE I

PERFLUOROPOLYETHER DIESTERS $RCO_2R_fOR_fCO_2R$*

	R_fOR_f	R	% Yield	B.P. °C/mm	M.W. Calc'd Found	C Calc'd Found	H Calc'd Found
X	A	C_2H_5	86	113/0.5	$\frac{778}{778}$	$\frac{27.8}{27.5}$	$\frac{1.30}{1.20}$
XI	B	CH_3	68	126/0.008	$\frac{1414}{1395}$ (M-F)	$\frac{23.8}{23.3}$	$\frac{0.43}{0.41}$
XII	C	CH_3	51	197/0.24	$\frac{1746}{1727}$ (M-F)	$\frac{23.4}{23.7}$	$\frac{0.35}{0.27}$
XIII	D	CH_3	81	118/0.12	$\frac{1114}{1095}$ (M-F)	$\frac{23.7}{23.8}$	$\frac{0.54}{0.95}$

A = $(CF_2)_4O(CF_2)_4O(CF_2)_4$

B = $(CF_2)_4O[CF(CF_3)CF_2O]_2(CF_2)_4[OCF_2CF(CF_3)]_2O(CF_2)_4$

C = $(CF_2)_4O[CF(CF_3)CF_2O]_3(CF_2)_4[OCF_2CF(CF_3)]_3O(CF_2)_4$

D = $F(CF_3)COCF_2CF_2OCF(CF_3)CF_2O(CF_2)_4OCF_2CF(CF_3)OCF_2CF_2OCF(CF_3)$

* All new compounds

TABLE II

DIFUNCTIONAL PERFLUOROPOLYETHERS $XR_fOR_fX^*$

R_fOR_f	X	% Yield	B.P. °C/mm	M.W. Calc'd / Found	C Calc'd / Found	H Calc'd / Found	N Calc'd / Found
XIV	A	$H_2N(CO)$	98	m.p. 158°	$\frac{720}{720}$	$\frac{23.4}{23.2}$	$\frac{0.56}{0.38}$	$\frac{3.89}{3.89}$
XV	A	CN	96	125°/105	$\frac{684}{684}$	$\frac{24.6}{24.6}$	$\frac{0}{0}$	$\frac{4.09}{3.80}$
XVI	A	$CH_3O(HN=)C$	78	100°/0.42	$\frac{748}{748}$	$\frac{25.7}{25.7}$	$\frac{1.08}{1.11}$	$\frac{3.74}{3.83}$
XVII	B	$H_2N(CO)$	98	not analyzed				
XVIII	B	CN	71	123°/0.10	$\frac{1348}{1329}$ (M-F)	$\frac{23.1}{22.9}$	–	$\frac{2.07}{2.20}$
XIX	B	$CH_3O(HN=C)$	86	136°/0.02	$\frac{1412}{1412}$	$\frac{23.8}{24.2}$	$\frac{0.57}{0.65}$	$\frac{1.98}{1.98}$

A = $(CF_2)_4O(CF_2)_4O(CF_2)_4$

B = $(CF_2)_4O[CF(CF_3)CF_2O]_2(CF_2)_4[OCF_2CF(CF_3)]_2O(CF_2)_4$

* All new compounds

TABLE III

DIFUNCTIONAL PERFLUOROPOLYETHERS XR_fOR_fX*

	R_fOR_f	X	% Yield	B.P. °C/mm	M.W. Calc'd/Found	C Calc'd/Found	H Calc'd/Found	N Calc'd/Found
XX	C	$H_2N(CO)$	85	not analyzed				
XXI	C	CN	61	158°/0.18	1680/1661 (M-F)	22.9/22.9	-	1.67/1.67
XXII	C	$CH_3O(HN=)C$	75	204°/0.95	1744/1743 (M-H)	23.4/23.5	0.46/0.41	1.61/1.49
XXIII	D	$H_2N(CO)$	93	not analyzed				
XXIV	D	CN	72	156°/45	1048/1029 (M-F)	22.9/22.7	--	2.67/2.73
XXV	D	$CH_3O(HN=)C$	64	105°/0.19	1112/1112	23.8/23.7	0.72/0.90	2.52/2.51

C = $(CF_2)_4O[CF(CF_3)CF_2O]_3(CF_2)_4[OCF_2CF(CF_3)]_3O(CF_2)_4$

D = $F(CF_3)COCF_2CF_2OCF(CF_3)CF_2O(CF_2)_4OCF_2CF(CF_3)OCF_2CF_2OCF(CF_3)$
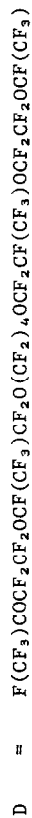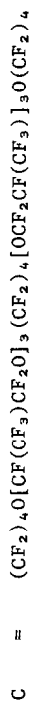
* All new compounds

EXPERIMENTAL

Gas chromatography analyses were performed in an F & M Model 700 instrument using a 6 ft., 12% SE-30 on Chromosorb W column and a 12 ft., 10% Apiezon L on Chromosorb W. Mass spectral analyses were performed on a CEC-21-110B mass spectrometer. All products were characterized by infrared analysis, ^{1}H and ^{19}F nuclear magnetic resonance analysis. The NMR data are not reported in this paper.

Preparation of $FC(O)CF(CF_3)OCF_2CF_2OCF(CF_3)C(O)F$ (I)[16,17]

Oxalyl fluoride (100 g, 1.06 mole) was added to a slurry of CsF (15 g, 0.10 moles) in anhydrous tetraglyme (150 ml). The mixture was cooled to 0°C and hexafluoropropylene oxide was added through a vacuum manifold. The progress of the reaction was followed by frequent sampling and gas chromatographic analysis (GC analysis). When the product was maximized as indicated by GC analysis, the reaction mixture was allowed to warm to room temperature and the lower fluorocarbon layer was phase separated. Distillation gave the product (I), b.p. 102-103°C, 187 g in 40.3% yield (based on oxalyl fluoride).

Preparation of $CH_3OC(O)CF(CF_3)OCF_2CF_2OCF(CF_3)CF_2OCF_2CF_2I$ (III) (nc)

Dry KF (8.7 g, 0.15 moles) and tetraglyme (110 ml) were placed into a 500 ml Fisher-Porter pressure bottle. The bottle was evacuated and the bis-acylfluoride I (73 g, 0.17 mole) was added through a syringe to the stirred mixture. The reaction mixture was cooled in an ice bath while ICl (25 g, 0.15 mole) was added by a syringe through the rubber septrum of the Fisher-Porter reaction bottle. After the exothermic reaction subsided, the ice bath was removed and the system was connected through copper tubing to a cylinder of tetrafluoroethylene (TFE). The reaction bottle was pressurized with TFE at 60 psi. The course of the reaction was followed by a decrease of TFE pressure. The excess TFE was vented, the volatile products, mostly CF_2ICF_2Cl, were removed under vacuum and an excess of CH_3OH was added to the remaining mixture. The reaction mixture was poured into water, the excess iodine destroyed with a $NaHSO_3$ solution and the lower fluorocarbon layer separated. Distillation gave the product III, b.p. 101-102°C/12 mm (30.3 g, yield 50.7%). Analysis: Found: C, 19.26; H, 0.29; I, 18.18. $C_{11}F_{18}H_3O_5I$

requires C, 19.30; H, 0.44; I, 18.57. Mass spectral analysis: 684 $(M)^+$, 665 $(M-F)^+$ and 557 $(M-1)^+$. IR and ^{19}F NMR were consistent with the structure.

Preparation of $C_2H_5OC(O)(CF_2)_4OCF_2CF_2I$ (IV) (nc)

In a similar manner as described above from $FC(O)(CF_2)_3C(O)F$, KF, ICl and $CF_2=CF_2$, except that C_2H_5OH instead of CH_3OH was added prior to hydrolysis of the reaction mixture, the product IV was isolated b.p. 47-50°/0.5 mm. Analysis: Found: C, 20.92; H, 0.90; I, 24.46. $C_9F_{12}H_5O_3I$ requires C, 20.95; H, 0.98; I, 24.59. Mass spectral analysis: 516 $(M)^+$, 487 $(M-C_2H_5)^+$, 471 $(M-OC_2H_5)^+$, 243 $(I(CF_2)_2O)^+$ and 227 $(I(CF_2)_2)^+$. IR and ^{19}F NMR were consistent with the structure.

Addition of HFPO to $CH_3OC(O)(CF_2)_3C(O)F$ (V)

$CH_3OC(O)(CF_2)_3C(O)F$ (128 g, 0.54 mole) was added to a slurry of CsF (9.2 g, 0.06 mole) in tetraglyme (100 ml). The mixture was cooled to 0°C and hexafluoropropylene oxide (HFPO) (340 g, 2.05 moles) was added through a vacuum manifold at such a rate that the reaction temperature was main-tained between 0-5°C and the pressure did not exceed 700 mm Hg. The lower fluorocarbon layer was separated and subjected to fractional distillation giving two principal reaction products, [VI (n=1); VII (n=2)] $CH_3OC(O)(CF_2)_4O$ $[CF(CF_3)CF_2O]_nCF(CF_3)C(O)F$; VI, b.p. 61-63°C/0.5 mm (87.7 g, yield 27.6%) and VII, b.p. 66°C/0.04 mm (91.3 g, yield 22.4%).

Preparation of $CH_3OC(O)(CF_2)_4OCF(CF_3)CF_2OCF(CF_3)CF_2OCF_2CF_2I$ (VIII) (nc)

KF (10 g, 0.16 mole), tetraglyme (100 ml) and $CH_3OC(O)(CF_2)_4OCF$ $(CF_3)CF_2OCF(CF_3)C(O)F$ (VI) (54 g, 0.09 mole) and ICl (30 g, 0.18 mole) were charged into a 500 ml Fisher-Porter pressure bottle as described above. Tetrafluoroethylene was pressured into the reaction bottle at 60 psi while the mixture was stirred at ambient temperature. The reaction was terminated when the decrease in TFE pressure essentially ceased. The reaction mixture, after venting the excess TFE, was poured into water, excess iodine destroyed with $NaHSO_3$ solution and the product extracted with $F_2CClCFCl_2$. Distillation gave the iodoester product VIII (n=1), b.p. 90-93°C/0.6 mm (34.3 g, yield 45.1%). Analysis: Found: C, 20.36; H, 0.29; I, 13.62. $C_{14}F_{24}H_3O_5I$ requires C, 20.14; H, 0.36, I, 15.23. Mass spectral analysis: 834 $(M)^\top$, 815 $(M-19)^+$ and 707 $(M-I)^+$. IR and ^{19}F NMR were consistent with the structure.

The iodoester product IX, b.p. 102-104°C/0.4 mm was prepared similarly in a 50.8% yield. Analysis: Found: C, 20.54; H, 0.10; I, 12.17. $C_{17}F_{30}H_3O_6I$ requires C, 20.40; H, 0.30; I, 12.70. Mass spectral analysis; 1000 $(M)^+$ very weak, 873 $(m-I)^+$ and 773 $(M-CF_2CF_2I)^+$. IR and ^{19}F NMR were consistent with the structure.

Synthesis of $C_2H_5OC(O)(CF_2)_4O(CF_2)_4O(CF_2)_4C(O)OC_2H_5$ (X) (nc)

A mixture of the iodoester $ICF_2CF_2O(CF_2)_4CO_2C_2H_5$ (IV) (30.04g, 0.059 mole), 40 mesh zinc (12.0 g, 0.184 mole), acetic anhydride (36.0 g, 0.353 mole) and $F_2CClCFCl_2$ (90 ml) were heated under a nitrogen atmosphere to reflux temperature (ca. 54°) with stirring for a period of 24 hours. During this time a white precipitate formed. The reaction mixture was cooled, filtered, the filtrate was hydrolyzed and dried ($MgSO_4$). Gas chromatography analysis of the organic layer indicated two reaction products A and B in the area ratio of 7:90. The reaction mixture was distilled to yield the diester X (Component B), b.p. 113°C/0.5 mm (19.8 g, 86.5% yield). (See Table I). The forerun from the distillation was subjected to preparative gas chromatography separation to yield component A. Mass spectral analysis, ^1H and ^{19}F NMR analysis of this component were consistent with the structure $H(CF_2)_2O(CF_2)_4C(O)OC_2H_5$.

The other $IR_fOR_fCO_2R$ compounds (III, VIII and IX) were zinc coupled by the procedure described above except the reaction times were longer and the reactions were assumed completed when the GC analysis of reaction samples indicated maximum diester formation. See Table I. In each case the minor reduced product $HR_fOR_fCO_2R$ was isolated by preparative column chromatography and characterized by mass spectral, ^1H and ^{19}F NMR.

Synthesis of $NH_2(O)C(CF_2)_4O(CF_2)_4O(CF_2)_4C(O)NH_2$ (XIV) (nc)

An excess of ammonia was bubbled through an ether-1,1,2-trichloro-trifluoroethane solution (200 ml) of (X) (19.6 g, 0.025 mole). The solvents were removed from the reaction leaving a white solid which on repeated washing with 1,1,2-trichlorotrifluoroethane yielded 17.7g of the diamide product, m.p. 157-158°C. (See Table II).

Synthesis of $NC(CF_2)_4O(CF_2)_4O(CF_2)_4CN$ (XV) (nc)

The diamide XIV (16.6g., 0.023 mole) was mixed with an excess of phosphorus pentoxide, placed in a distillation flask and heated to 210°C

for two hours. The reaction mixture was cooled, a vacuum of 105 mm was applied and heat was reapplied. The fraction boiling 125°C at 105 mm was collected (15.3g. 96% yield). (See Table II).

Synthesis of $CH_3O(NH)C(CF_2)_4O(CF_2)_4O(CF_2)_4C(NH)OCH_3$ (XVI) (nc)

Approximately 0.1 gram of sodium was dissolved in anhydrous methanol (50 ml). To this solution was added the dinitrile XV (13.0g, 0.019 mole). The reaction was stirred at room temperature for approximately 18 hours. On adding water to the methanol solution, a heavy lower organic layer was formed, phase separated, dried and distilled. The product distilled at 99-100°C at 0.42 mm. (78% yield). (See Table II).

TABLE IV

INFRARED ANALYSIS (cm^{-1})

Compound	C-H		C=O	NH$_2$	C≡N	C=N-H	C≡N-
X	2985		1785				
XI	2970,	2860	1790				
XII	2970,	2860	1790				
XIII	2970,	2860	1795				
XIV			1685, 1715	3380, 3200			
XV					2260		
XVI	2990,	2940				3310,3230	1685
XIX	2955,	2860				3365, 3300	1685
XXI					2260		
XXII	2955,	2860				3365, 3300	1685
XXIV					2270		
XXV	2955,	2860				3365, 3300	1685

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