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SYNTHESIS OF NEW HIGH PERFORMANCE LUBRICANTS AND SOLID LUBRICANTS

Progress Report

April 1992 - March 1993

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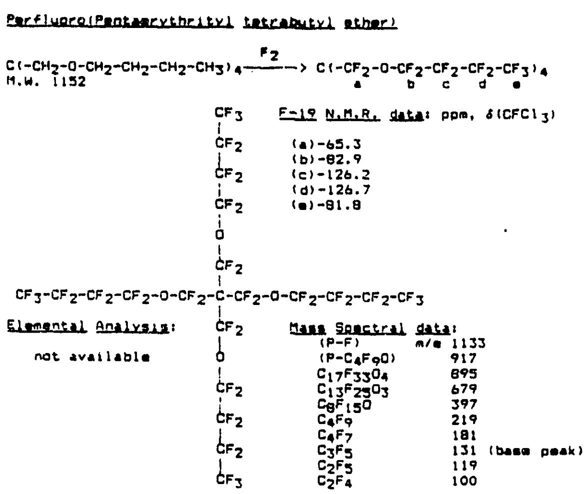
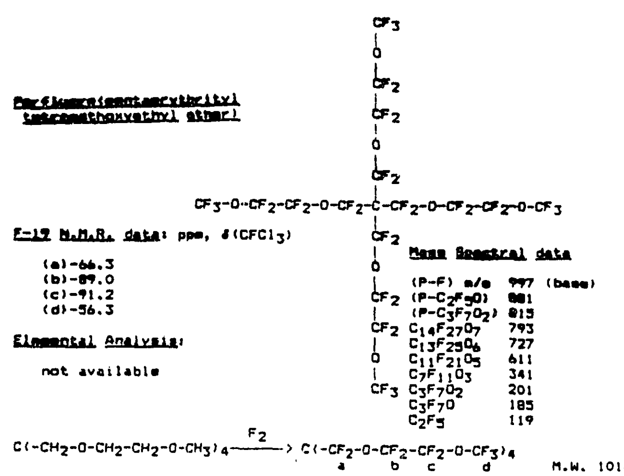
SYNTHESIS OF NEW HIGH PERFORMANCE LUBRICANTS AND SOLID LUBRICANTS

Technical Progress Report

In our second year of funding we began the testing phase of a number of new classes of lubricants. Three different testing collaborations have already begun and a fourth one is in the works with Dr. Stephen Hsu of the National Institute of Standards and Technology with whom we had established a working relationship after meeting at the Automotive and Technology Development Coordination Meeting held in November 2-5, 1992 in Dearborn, Michigan. Dr. Hsu also plans to test some of the same materials for us that Shell Development is studying.

With Dr. Bill Jones of NASA, we are studying the effects of branching on high temperature lubricant properties in perfluoropolyethers. Initially Bill Jones is comparing the lubrication and physical properties of perfluoro-tetraglyme and the following two spherical perfluoropolyethers. Note that one contains a fluorocarbon chain and the other one contains a fluorocarbon ether chain. The synthesis of these was reported in the last progress report.





With Professor Patricia Thiel of Iowa State University, we are working on studies of perfluoromethylene oxide ethers and have prepared a series of four of these polyethers to study in collaboration with her research group. These are model compounds which correspond to structures proposed on the bottom of page 17 and top of page 18 of our research proposal:

$(-CF_2O-CF_2CF_2CF_2-O-)_n$

$(-CF_2O-CF_2CF_2CF_2CF_2-O-)_n$

$(-CF_2-C(CF_3)(F)-OCF_2-O-)_n$

$(-C(CF_3)(CF_3)-O-CF_2-O-)_n$

These perfluoromethylene oxide ethers have the best low temperature properties of any known lubricants. Thiel's group is studying their interactions with metals under extreme conditions.

Thirdly, we have also begun an interaction with Dr. August Birke of Shell Development Company in Houston for whom we have already prepared samples of the chlorine-substituted fluorocarbon polyether lubricants whose structures appear on page 54 of our research proposal. Each of these four structures is thought to have potential as lubricant additives to motor oils. Each of the following structures is completely soluble in hydrocarbon motor oils and hydrocarbon polyalphaolefins.

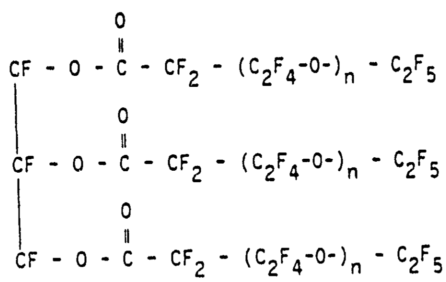
$ClCF_2CF_2(-CF_2CF(CF_2Cl)O-)_nCF_2CF_2CF_2Cl$ Type I

$ClCF_2CF_2O(-CF(CF_2Cl)O-)_nCF_2CF_2Cl$ Type III

$(ClCF_2)_2CFO(-CF_2CF(CF_2Cl)O-)_nCF_2CF_2CF_2Cl$ Type II

$R_fO(-C(F)(OCF_2Cl)-CF_2O-)_nOR_f$ Type IV

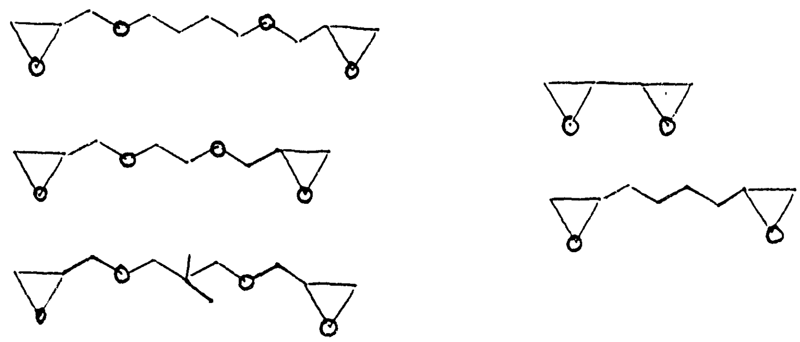
We also have underway syntheses of other fluorine-containing branched ether lubricants. These new materials which are also promising as antifriction additives for motor oils appear ahead of the perfluoro additives as Appendix I to the progress report. Additionally for Birke and Shell Development we have at their request prepared the novel compound perfluoro salicylic acid. This synthesis was suggested by the Shell staff who thought that esters of perfluoro salicylic acid might be an excellent antifriction additive for motor oil fuels. One of the best additives currently used in motor oils is the hydrocarbon ester of salicylic acid.



where n is varied to produce fluids and solids with different properties

Dr. Kuangsen Sung of our research group has succeeded in preparing the first example of glycerin-based perfluoropolyester structures and specifically has succeeded in preparing the glyceride ester of perfluoro stearic acid, $CF_3(CF_2)_{16}COOH$. We shall be submitting this new class of branched perfluorocarbon esters for testing shortly.

We also have achieved success with synthesis of perfluoro epoxy ether chains, a class of compounds that have never been previously prepared:



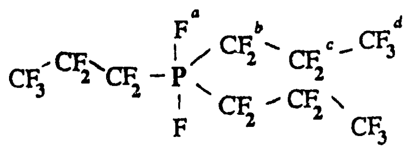
Additionally with Dr. Bill Jones of NASA we are testing a new class of antifriction additives for perfluoropolyether lubricants, the perfluorophosphoranes. We have made quite a number of these and will shortly be submitted these to Dr. Jones for screening. The first structure appears below and the rest of the new structures constitute Appendix II.

<u>^{19}F NMR Chemical Shifts</u>

a - 47.5 ppm (d of mult.)
b -110.3 ppm (d of t)
c -125.7 (s)
d - 82.2 (s)

<u>Coupling Constants</u>

$^{1}J_{PF}$=1041 Hz
$^{2}J_{FCP}$= 124 Hz



<u>^{31}P NMR Chemical Shift</u>

-41.8 ppm (t of sept.)

<u>High Resolution Mass Analysis</u>

$C_9F_{22}P^+$ Calculated: 556.938635
Observed : 556.937623

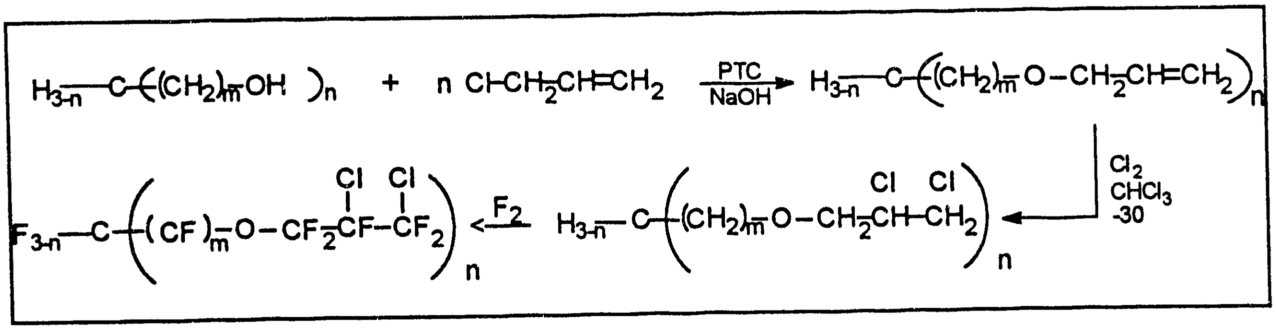
<u>Low Resolution Mass Spectrum Fragments</u>

Fragment	m/z
$FP(C_3F_7)_3^+$	557
$F_2P(C_3F_7)_2^+$	407
$F_3P(C_3F_7)^+$	257
F_4P^+	107
$C_3F_7^+$	169

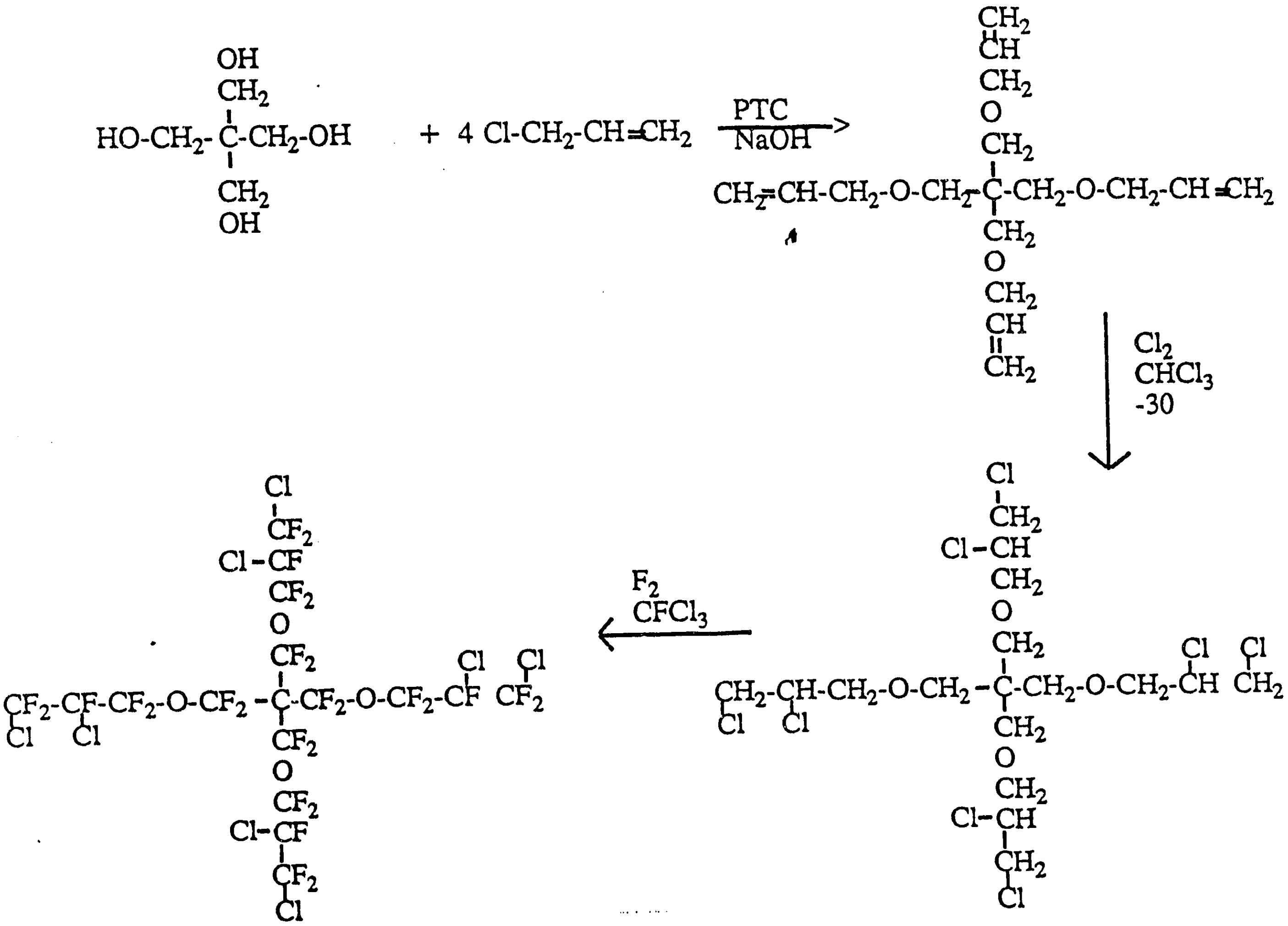
There are successes in many other areas to report but we lack the space here to do so. This has been a very successful year in our program.

APPENDIX I

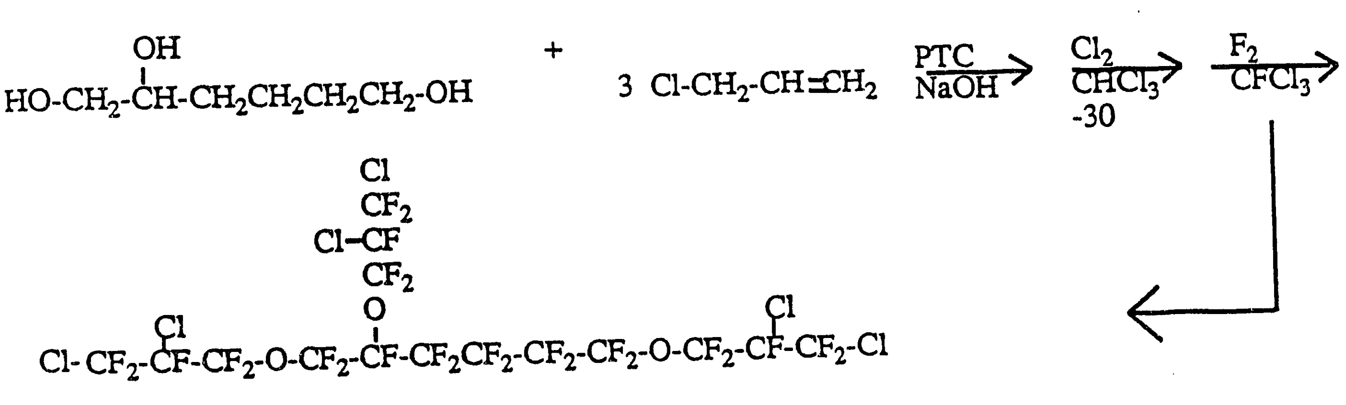
General Scheme



Representative examples:

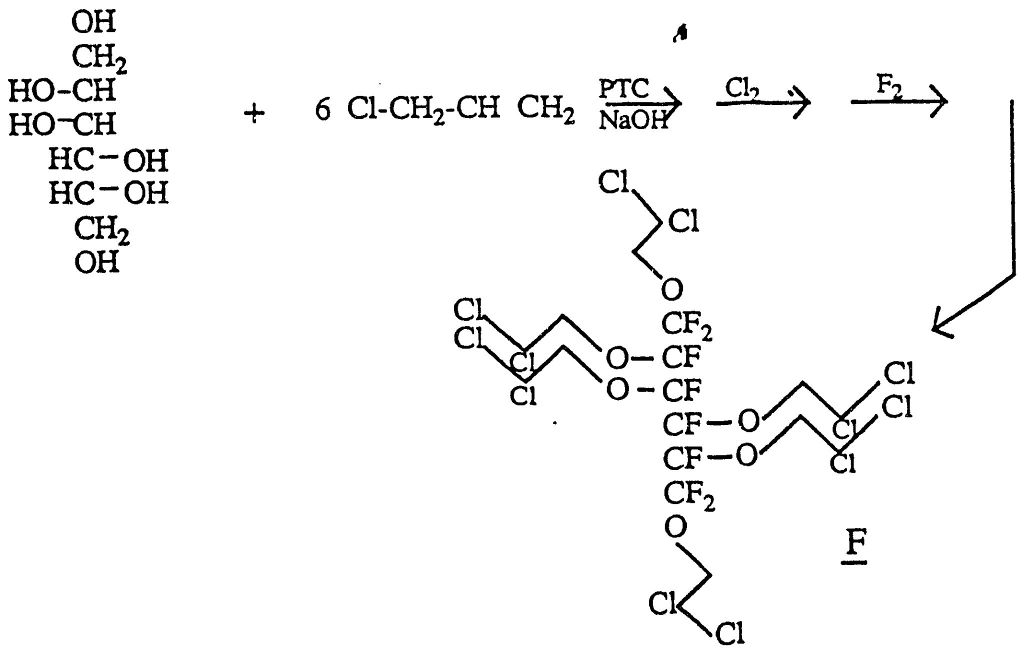


C.I. Mass Spec. Parent - F m/e = 1065

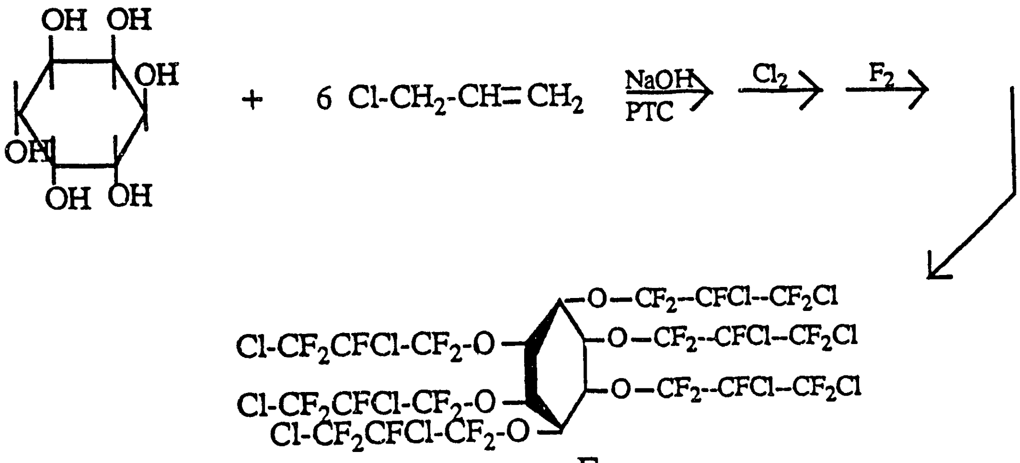


C.I. Mass Spec. Parent -F m/e =916

Variations in the polyhydrolic starting materials will provide a variety of chlorofluorocarbon ether structures. Synthesis of the following compounds is underway.



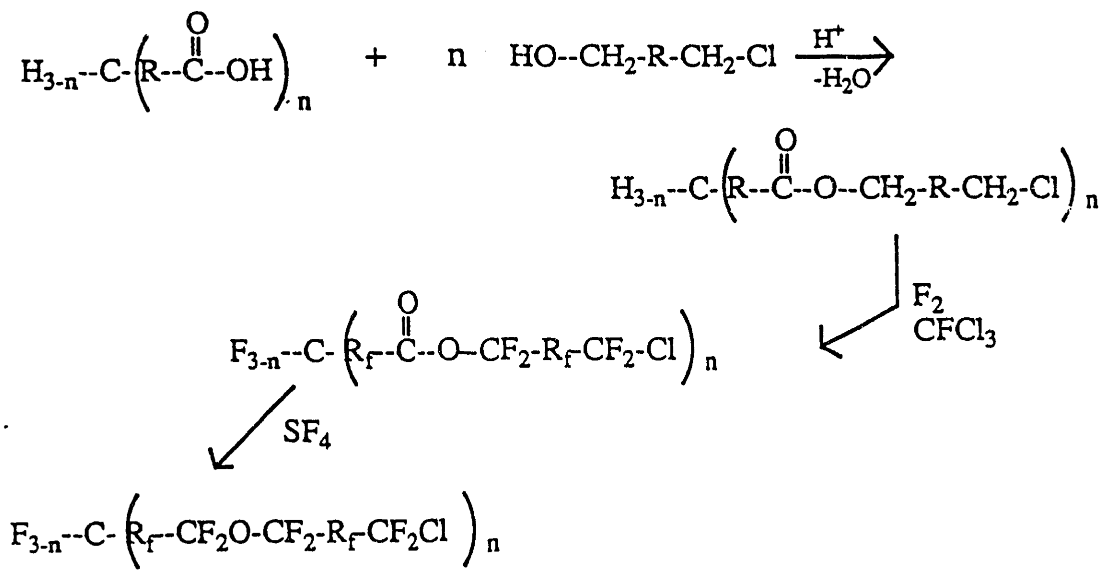
F



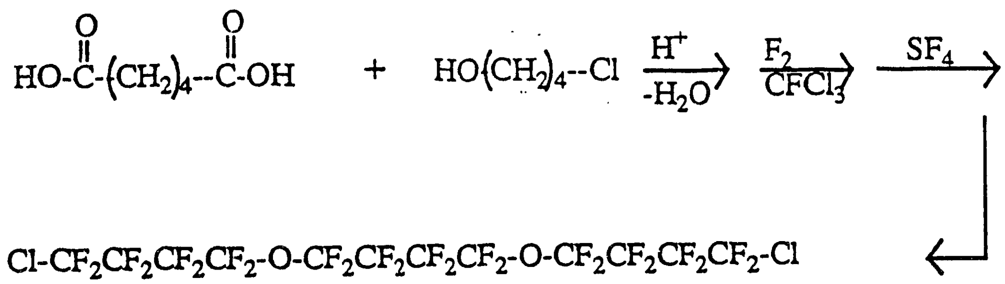
F

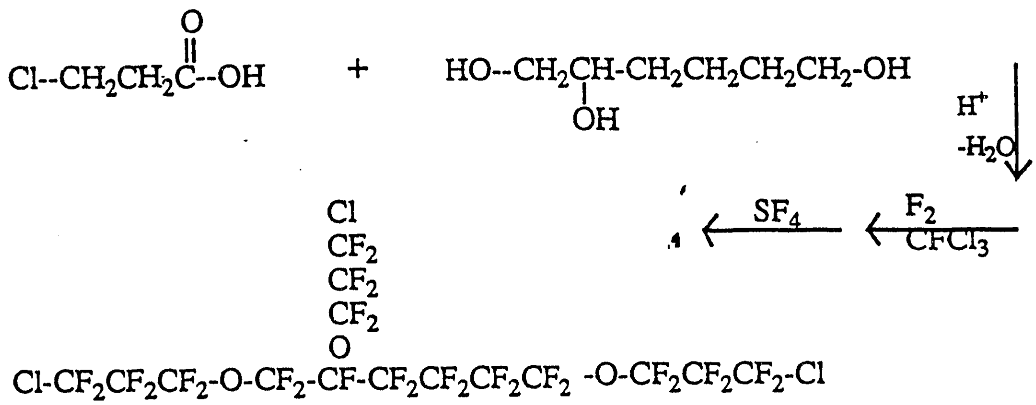
Approach II : Conversion of Perfluoroësters to Perfluoroethers using SF_4 is well known. Synthesis of chlorine containing fluoroesters followed by their conversion to ethers will provide for a variety of chlorinated fluoroethers, and will also provide a great deal of control over chlorine content and location. The synthesis of such molecules is underway.

General Scheme



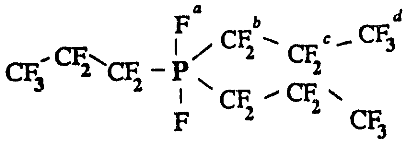
Representative examples:





Cl--CH2CH2C(=O)--OH
+
HO--CH2CH(OH)-CH2CH2CH2CH2-OH
H+
-H2O
F2
CFCl3
SF4
Cl
CF2
CF2
CF2
O
Cl-CF2CF2CF2-O-CF2-CF-CF2CF2CF2CF2 -O-CF2CF2CF2-Cl

APPENDIX II



^{19}F NMR Chemical Shifts

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c -125.7 (s)
d - 82.2 (s)

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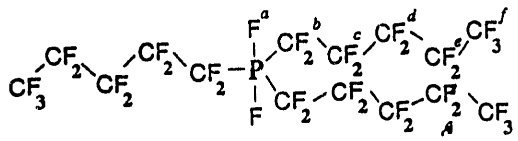
$F_3P(C_3F_7)^+$	257
F_4P^+	107
$C_3F_7^+$	169



^{19}F NMR Chemical Shifts

a - 46.8 ppm (d of mult.)
b -108.8 ppm (d)
c -120.7 (s)
d - 123.4 (s)
e -127.4 (s)
f - 82.5 (s)

Coupling Constants

$^{1}J_{PF}$=1050 Hz
$^{2}J_{FCP}$= 126 Hz

^{31}P NMR Chemical Shift

-37.6 ppm (t of sept.)

High Resolution Mass Analysis

$C_{15}F_{34}P^+$ Calculated: 856.919474
Observed : 856.918693

Low Resolution Mass Spectrum Fragments

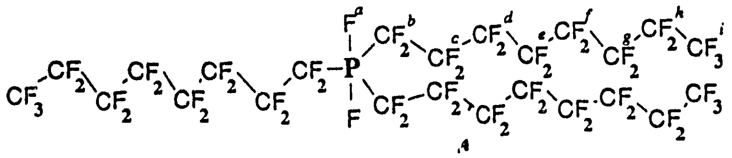
Fragment	m/z
$FP(C_5F_{11})_3^+$	857
$F_2P(C_5F_{11})_2^+$	607
$F_3P(C_5F_{11})^+$	357
F_4P^+	107
$C_5F_{11}^+$	269

^{19}F NMR Chemical Shifts

a - 46.9 ppm (d of mult.)
b -109.1 ppm (d)
c -120.8 (s)
d - 122.8 (s)
e -123.1 (s)
f -123.4 (s)
g -124.3 (s)
h -128.0 (s)
i - 83.3 (s)

Coupling Constants

$^1J_{PF}$=1060 Hz
$^2J_{FCP}$= 123 Hz



^{31}P NMR Chemical Shift

-38.0 ppm (t of sept.)

High Resolution Mass Analysis

$C_{24}F_{53}P^-$ Calculated: 1325.889136
Observed : 1325.888968

Low Resolution Mass Spectrum Fragments

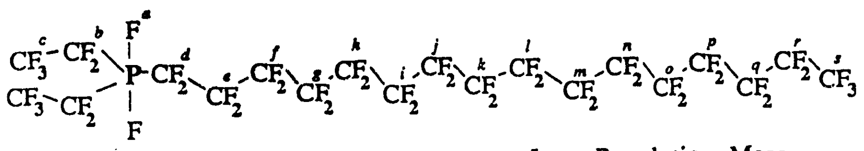
Fragment	m/z
$F_2P(C_8F_{17})_3^-$	1326
$FP(C_8F_{17})_3^+$	1307
$F_2P(C_8F_{17})_2^+$	907
$F_3P(C_8F_{17})^+$	507
F_4P^+	107
$C_8F_{17}^+$	419

^{19}F NMR Chemical Shifts

a - 48.6 ppm (d of mult.)
b -113.3 ppm (d)
c - 81.5 (s)
d - 117.2 (d)
e-p -121.9 (s)
q -123.0 (s)
r -126.6 (s)
s - 81.7 (s)

Coupling Constants

$^1J_{PF}$=1030 Hz
$^2J_{FCP}$= 112 Hz
$^2J_{FCP}$= 91 Hz



^{31}P NMR Chemical Shift

-43.8 ppm (t of sept.)

High Resolution Mass Analysis

$C_{20}F_{44}P^+$ Calculated: 1106.903506
Observed : 1106.906923

Low Resolution Mass Spectrum Fragments

Fragment	m/z
$FP(C_2F_5)_2(C_{16}F_{33})^+$	1107
$F_2P(C_2F_5)(C_{16}F_{33})^+$	1007
$F_2P(C_2F_5)_2^+$	307
$F_3P(C_2F_5)^+$	207
$F_3P(C_{16}F_{33})^+$	907
F_4P^+	107
$C_{16}F_{33}^+$	819
$C_2F_5^+$	119

^{19}F NMR Chemical Shifts

a - 18.7 ppm (d of mult.)

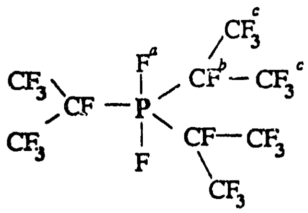
b -176.7 ppm (d)

c - 71.0 (s)

Coupling Constants

$^{1}J_{PF}$=1015 Hz

$^{2}J_{FCP}$= 99 Hz



^{31}P NMR Chemical Shift

-29.0 ppm (t of q)

Low Resolution Mass Spectrum Fragments

Fragment	m/z
$FP(C_3F_7)_3^+$	557
$F_2P(C_3F_7)_2^+$	407
$F_3P(C_3F_7)^+$	257
F_4P^+	107
$C_3F_7^+$	169

^{19}F NMR Chemical Shifts

a - 50.2 ppm (d of mult.)

b -114.7 ppm (d)

c - 83.1 (s)

d - 114.1 (d)

e - 84.9 (s)

f - 90.0 (t)

g - 88.9 (s)

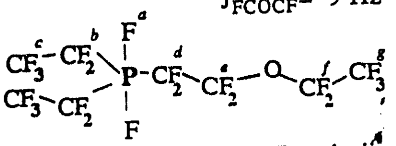
Coupling Constants

$^{1}J_{PF}$=1007 Hz

$^{2}J_{FCP}$= 122 Hz

$^{2}J_{FCP}$= 112 Hz

$^{4}J_{FCOCF}$= 9 Hz



^{31}P NMR Chemical Shift

-45.3 ppm (t of sept.)

High Resolution Mass Analysis

$C_8F_{20}OP^+$ Calculated: 522.936743

Observed : 522.935822

Low Resolution Mass Spectrum Fragments

Fragment	m/z
$F_2P(C_2F_5)_2(C_4F_9O)^-$	542
$FP(C_2F_5)_2(C_4F_9O)^+$	523
$F_2P(C_2F_5)(C_4F_9O)^+$	423
$F_2P(C_2F_5)_2^+$	307
$F_3P(C_2F_5)^+$	207
$F_3P(C_4F_9O)^+$	323
F_4P^+	107
$C_4F_9O^+$	235
$C_2F_5^+$	119

^{19}F NMR Chemical Shifts

a - 83.6 ppm (s)

b -114.9 ppm (d)

c - 49.8 (d of mult.)

d -110.0 (d)

e -120.6 (s)

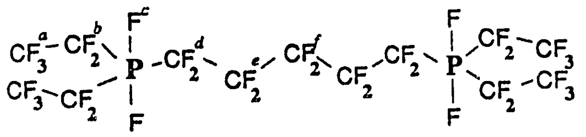
f -128.2 (s)

Coupling Constants

$^{2}J_{FCP}$= 122 Hz

$^{1}J_{PF}$= 1019 Hz

$^{2}J_{FCP}$= 125 Hz



^{31}P NMR Chemical Shift

-44.0 ppm (t of sept.)

High Resolution Mass Analysis

$C_{13}F_{33}P_2^+$ Calculated: 844.894834

Observed : 844.894530

^{19}F NMR Chemical Shifts

a - 83.6 ppm (s)

b -115.0 ppm (d)

c - 50.5 (d of mult.)

d -114.0 (d)

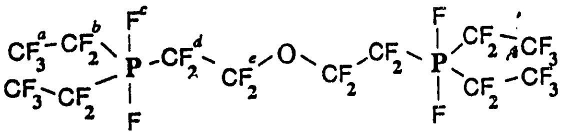
e - 84.3 (s)

Coupling Constants

$^{2}J_{FCP}$= 122 Hz

$^{1}J_{PF}$= 1008 Hz

$^{2}J_{FCP}$= 123 Hz



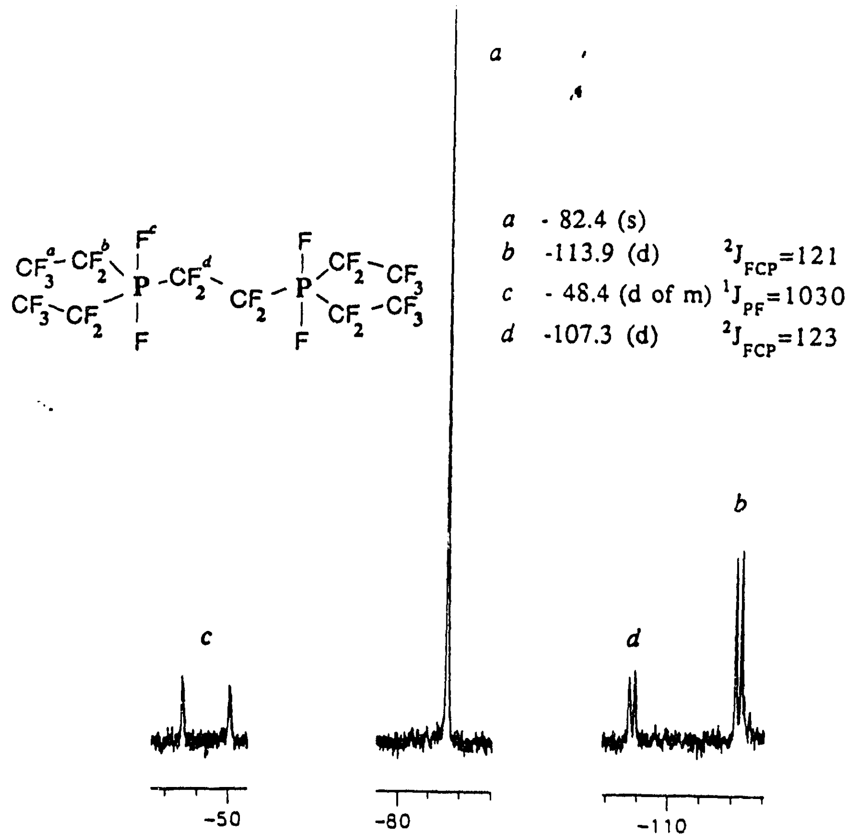
^{31}P NMR Chemical Shift

-45.2 ppm (t of sept.)

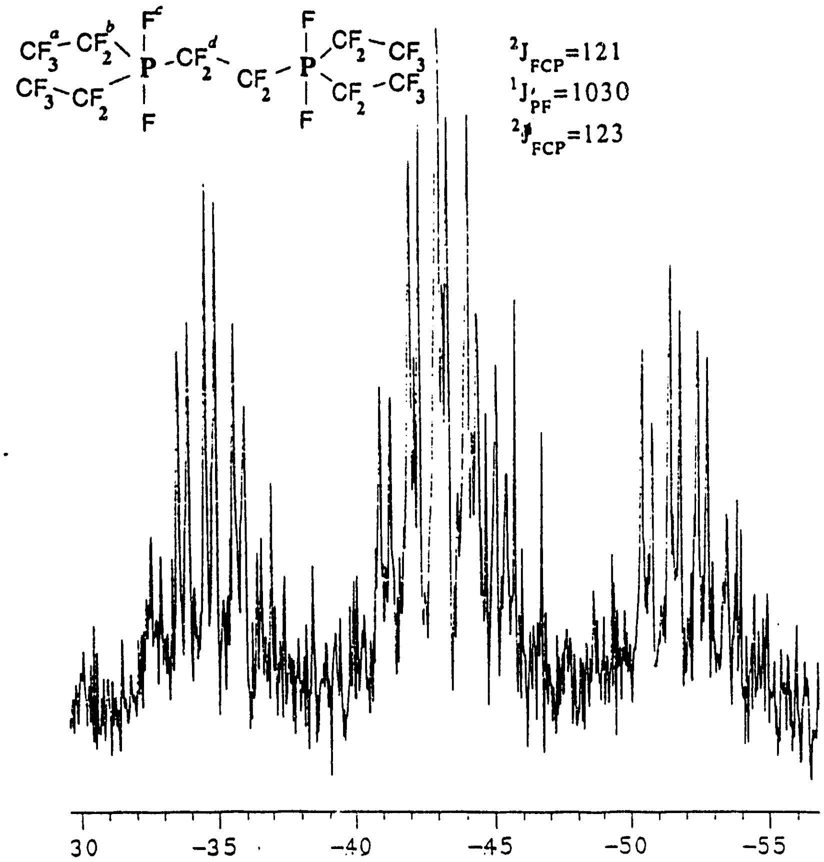
High Resolution Mass Analysis

$C_{12}F_{32}OP_2^-$ Calculated: 829.891345

Observed : 829.893040

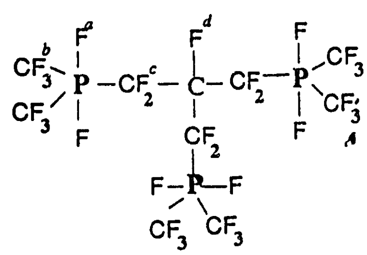


^{19}F NMR of 1,2-bis(difluorobis(pentafluoroethyl)-phosphorano)tetrafluoroethane



31P NMR of 1,2-bis(difluorobis(pentafluoroethyl)-phosphorano)tetrafluoroethane

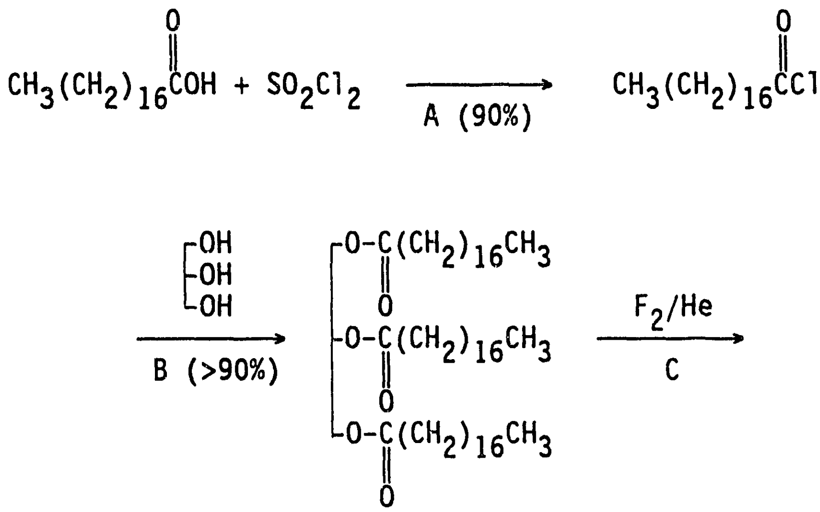
^{19}F NMR Chemical Shifts	Coupling Constants
a - 55.2 ppm (d of mult.)	$^1J_{PF}$= 1068 Hz
b - 64.7 ppm (d)	$^2J_{FCP}$= 162 Hz
c -109.7 (d)	$^2J_{FCP}$= 122 Hz
d -177.0 (s)	



^{31}P NMR Chemical Shift	High Resolution Mass Analysis
-49.5 ppm (t of mult.)	$C_{10}F_{30}P_3^-$ Calculated: 782.873388
	Observed : 782.869965

APPENDIX III

Preparation of perfluorinated triglyceride



Procedure A: Thionyl chloride (50 g, 0.42 mole) was added to a one-neck 500 ml flask. Stearic acid (100 g, 0.35 mole) was dissolved in 50 ml of CH_2Cl_2. The solution was added to the thionyl chloride slowly. After complete addition, the mixture was refluxed for two hours. After pumping off unreacted SO_2Cl_2, the residue was sublimated at 50 °C to get pure acid chloride in 90% yield.

Procedure B: 80 g of $CH_3(CH_2)_{16}C(=O)Cl$ was added slowly to a mixture of 6.7 g glycerin and 80 ml pyridine at room temperature under an argon atmosphere. Two hours after addition of the acid chloride, the mixture was acidified by 10% of H_2SO_4. After filtration, the precipitate was washed with saturated $NaHCO_3$(aq) until it is neutral. The solid triglyceride was dried at 80 °C under high vacuum for 12 hours. The yield is higher than 90%.

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