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(54) Titre : HYDROFLUOROETHERS COMPORTANT AU MOINS UN GROUPEMENT TERMINAL -OCFX'CH₃
HYDROGENE, DANS LEQUEL X'=F, CF₃, ET LEUR PROCEDE DE PREPARATION

(54) Title: HYDROFLUOROETHERS HAVING AT LEAST ONE HYDROGENATED -OCFX'CH₃, END GROUP WHEREIN
X'=F, CF₃ AND THEIR PREPARATION PROCESS

(57) Abrégé/Abstract:

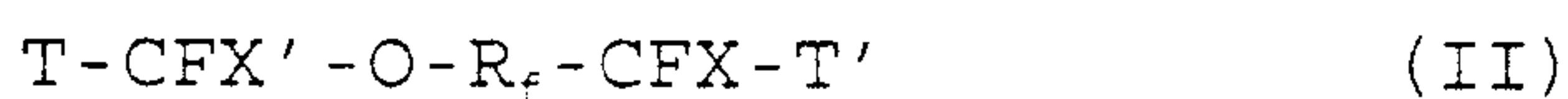
Hydrofluoroethers of formula: T-CFX'-O-R_f-CFX-T' (II) wherein: T = CH₃; X, X', equal to or different from each other, are selected between F, CF₃; T00' = F, Cl, H, C₁-C₃ perfluoroalkyl, CH₃, CH₂OH, COCl, CHO, CO₂H; R_f is a perfluoroalkylene or a perfluoropolyoxyalkylene and respective preparation process by reduction with hydrogen in the presence of a platinum catalyst supported on metal fluorides of the corresponding compounds with at least one -COCl end group.



HYDROFLUOROETHERS HAVING AT LEAST
ONE HYDROGENATED -OCFX'CH₃ END GROUP
WHEREIN X' = F, CF₃ AND THEIR PREPARATION PROCESS

ABSTRACT

Hydrofluoroethers of formula:



wherein:

T = CH₃;

X, X', equal to or different from each other, are selected between F, CF₃;

T00' = F, Cl, H, C₁-C₃ perfluoroalkyl, CH₃, CH₂OH, COCl, CHO, CO₂H;

R_f is a perfluoroalkylene or a perfluoropolyoxyalkylene and respective preparation process by reduction with hydrogen in the presence of a platinum catalyst supported on metal fluorides of the corresponding compounds with at least one -COCl end group.

Description of the industrial invention in the name of:

SOLVAY SOLEXIS S.p.A., of Italian nationality, with head office in Milano, Via Turati, 12.

* * * * *

The present invention relates to hydrofluoroethers characterized in having at least one hydrogenated $-OCFX'CH_3$ end group wherein $X' = F, CF_3$, and their preparation process.

More specifically, the preparation process relates to the reduction with H_2 , in the presence of platinum catalysts (Pt), of the corresponding fluorinated acylchloride precursors.

Hydrofluoroethers prepared by direct fluorination with F_2 or electrochemical fluorination of an ether compound or by alkylation of fluorinated alcohols are known.

In patent application WO 99/47,480 it is shown that hydrofluoroethers can be obtained by alkylation of fluorinated carbonyl compounds. The above methods employ starting compounds having a low molecular weight with a number of carbon atoms equal to or lower than 12, besides they give low yields and selectivity, and do not give hydrofluoroethers having at least one $OCFX'CH_3$ end group with $X' = F, CF_3$.

More specifically patent application WO 99/47,480 describes an alkylation process of perfluorinated carbonyl compounds in the presence of a Lewis acid, for example SbF_5 . Although in the general formula:



wherein

- R_f is a fluorinated C_1-C_{15} alkyl, optionally substituted and optionally containing heteroatoms in the chain as N, O, S;
- R is a C_1-C_{10} alkyl, optionally substituted,
- x ranges from 1 to 3,

a great number of potential hydrofluoroethers is contained, really by the process only hydrofluoroethers having end groups different from $-OCFX'CH_3$, are obtainable. See the Examples of patent application WO 99/47,480. Therefore the compounds having $-OCFX'CH_3$ termination have not been prepared and no indication about how to prepare them is given. Accordingly the skilled man in the art on the basis of the aforesaid patent and of the common general knowlegde is unable to prepare the compounds of the present invention.

Generally the reaction described in patent application WO 99/47,480 proceeds with very low conversions when R_f is branched. The reaction shows the limitation that to obtain acceptable conversions it is necessary to use CH_3F as alkylating agent, has the drawback to require the use of Lewis acids which are aggressive and need the use of pressure resistant equipments built in special substances. Furthermore HF forms, producing further problems in the equipment choice.

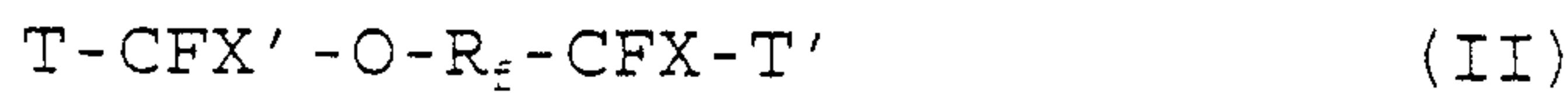
Since the alkylation reaction is an equilibrium reaction, it does not allow the obtainment of hydrofluoro-ethers with a high yield.

The Applicant has furthermore found that by using a Lewis acid as SbF_5 , in the ratios suggested by patent application WO 99/47,480 and by following the same modalities suggested by the same, no hydrofluoroethers are obtained starting from precursors having a perfluoropolyether structure, in particular containing $-OCF_2O-$ sequences; besides the use of SbF_5 amounts higher than those suggested causes the almost total degradation of the initial perfluoropolyether structure without obtaining however hydrofluoroethers (see the comparative Examples).

The need was therefore felt to obtain hydrofluoroethers by a process avoiding the prior art inconveniences and limitations.

It has been found a hydrogenation process of fluorinated precursors containing acylchloride groups carried out in the presence of platinum catalysts which allows to obtain hydrofluoroethers characterized in having at least one $-OCFX'CH_3$ end group and quantitative conversions with selectivity even of the order of 70%.

An object of the present invention are therefore hydrofluoroethers of formula:



wherein:

$T = CH_3$;

X, X' , equal to or different from each other, are selected from F, CF_3 ;

$T' = F, Cl, H, C_1-C_3$ perfluoroalkyl, $CH_3, CH_2OH, COCl, CHO, CO_2H$;

R_f is selected from:

- C_2-C_{15} perfluoroalkylene;
- $-(C_2F_4O)_m(CF_2CF(CF_3)O)_n(CF_2O)_p(CF(CF_3)O)_q-$

wherein

the sum $n+m+p+q$ ranges from 2 to 200, the $(p+q)/(m+n+p+q)$ ratio is lower than or equal to 10:100, preferably comprised between 0.5:100 and 4:100, the n/m ratio ranges from 0.2 to 6, preferably from 0.5 to 3; m, n, p, q are equal to or different from each other and when m, n range from 1 to 100, preferably from 1 to 80, then p, q range from 0 to 80, preferably from 0 to 50; the units with n, m, p, q indexes being statistically distributed along the chain;

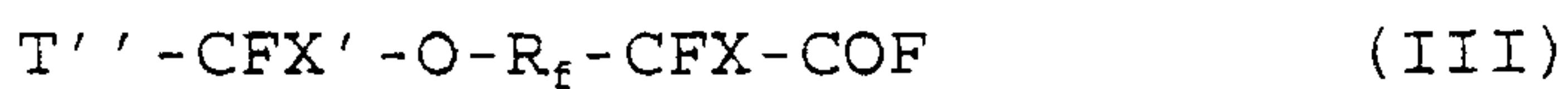
- $-(CF_2CF_2CF_2O)_r-$ wherein r ranges from 2 to 200,
- $-(CF(CF_3)CF_2O)_s-$ wherein s ranges from 2 to 200,

The preferred structures of the perfluoroxyalkylene chain R_f are selected from the following:

- $(CF_2CF_2O)_m - (CF_2O)_p -$,
- $(CF_2CF(CF_3)O)_n - (CF_2O)_p - (CF(CF_3)O)_q$

wherein the indexes have the above meanings.

A further object of the present invention is the preparation process of the formula (II) compounds comprising the reduction of the formula (III) corresponding precursors:



wherein

T'' is $-COCl$,

$T''' = F, C_1-C_3$ perfluoroalkyl, $COCl, H, Cl$,

X, X', R_f are as defined in formula (II),

carried out with gaseous hydrogen in the presence of a catalyst formed by supported platinum, preferably on metal fluorides, preferably in the presence of inert solvents, at a temperature in the range $20^\circ C - 150^\circ C$, preferably $80^\circ C - 120^\circ C$, at a pressure between 1 and 50 atm, preferably between 1 and 10 atm.

The formula (III) compounds having at least one $-COCl$ end group are known, preparable for example by reaction of the corresponding PFPEs having $-COF$ or $-COOH$ end groups with inorganic chlorides or chlorinating agents such as thionyl chloride; preferably they are prepared according to what described in Italian patent applications MI2002A 001733 and MI2002A 001734 filed at the same time as the present

application, and herein incorporated by reference, by a solid-liquid reaction between a large excess of inorganic chloride, CaCl_2 and a PFPE acylfluoride, at a temperature higher than 100°C , under strong stirring or alternatively a PFPE acylfluoride can be hydrolyzed obtaining the corresponding carboxylic acid which is subsequently treated with SOCl_2 , in the presence of a tertiary amine, at a temperture in the range $50-100^\circ\text{C}$, obtaining the corresponding acylchloride.

The formula (II) hydrofluoroethers can alternatively be obtained from the corresponding PFPEs having at least one $-\text{CHO}$ or $-\text{CH}(\text{OH})\text{O}(\text{CH}_2)_t\text{R}$ end group wherein $t = 0$ or 1 and R is a $\text{C}_1\text{-C}_{10}$ alkyl group, H , or R_f .

The process can be carried out in a continuous or discontinuous way.

The metal fluorides are preferably selected from the group formed by CaF_2 , BaF_2 , MgF_2 , AlF_3 ; more preferably CaF_2 .

The Pt concentration on the support is comprised beteeen 0.1% and 10% with respect to the total weight of the catalyst, preferably between 1% and 2% by weight.

The used catalyst amount is in the range 1%-100% by weight with respect to the weight of the formula (III) compound, preferably 10%-100% by weight.

The inert solvents can for example be linear or cyclic perfluorinated ethers such for example perfluorotetra-

hydrofuran, perfluorotetrahydropyran, or their mixtures.

The invention hydrofluoroethers having at least one $-\text{OCFX}'\text{CH}_3$ end group with $\text{X}' = \text{F, CF}_3$, can be used as refrigerants, solvents in cleaning processes of printed circuits, and degreasing in vapour phase of metal components as substituents of CFCs, HCFCs and PFCs, resulted harmful for the ozone layer or show a high GWP (greenhouse potential).

Besides they found application for the wide range of utilization temperatures as substituents of HFCs which in some cases have a limited application as refrigerants due to their very low boiling temperature or their very high freezing point.

The following Examples are given for illustrative and not limitative purposes of the present invention.

EXAMPLES

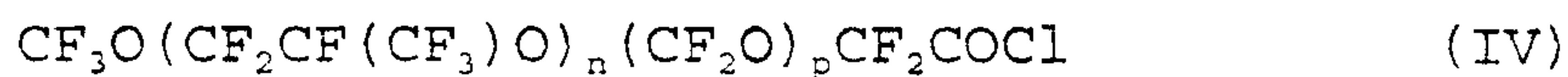
EXAMPLE 1

In a 1,000 ml flask, equipped with mechanical stirrer, bubbling pipe to introduce hydrogen/nitrogen, condenser with a bubble-counter

36.7 g of Pt supported on CaF_2 (Pt = 1.5% by weight), 400 ml of mixture 1:1 of perfluorobutyltetrahydrofuran and perfluoropropyltetrahydropyran (D100), are introduced.

By external heating with thermostated oil bath, the solvent is brought to the boiling temperature (100°C), then

hydrogen is fed at atmospheric pressure at a flow-rate of 20 l/h, and 36.7 g of perfluoropolyether (PFPE) acylchloride of formula (IV)

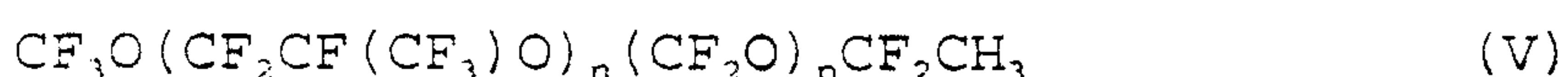


wherein n/p = 25 and n, p are integers such that the number average molecular weight is 400, are fed by dropping funnel in 30 minutes.

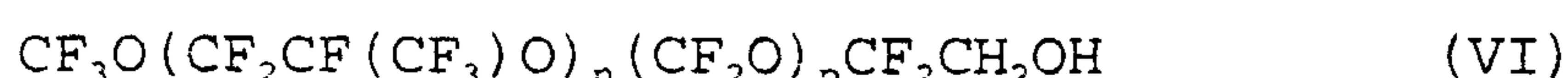
When the PFPE-COCl feeding is over, the reduction is let complete for 15 minutes in hydrogen flow.

It is then cooled to room temperature in nitrogen flow. The raw reaction compound is filtered to recover the catalyst.

The NMR (¹⁹F and ¹H) analysis of the compound shows a 100% conversion of the starting PFPE-acylchloride and a yield in formula (V) hydrofluoroether of 60% by moles:



The NMR analysis shows furthermore the presence of the alcoholic compound of structure (VI) in an amount equal to 40% by moles:



To separate the hydrofluoroether (V) from the alcohol (VI), the raw reaction compound is chromatographed on silica gel using D 100 as eluent. From the extract, after solvent distillation, 18 g of a compound are obtained which by the NMR (¹⁹F and ¹H) analysis shows to be the hydrofluoroether of

formula (V) .

EXAMPLE 2

In the same equipment of the Example 1
 32.5 g of Pt supported on CaF_2 (Pt = 1.5%) ,
 150 ml of D100, are introduced.

One operates as described in the Example 1, by feeding
 38.9 g of PFPE-acylchloride of formula (VII) :

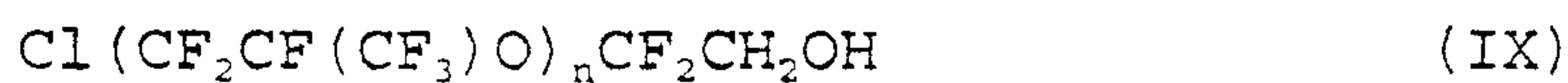


wherein $n = 3$ and the number average molecular weight equal to
 647.

The NMR (^{19}F and ^1H) analysis of the compound shows a 100%
 conversion of the starting PFPE-acylchloride and a yield of
 70% by moles in hydrofluoroether of formula (VIII) :



The NMR analysis shows furthermore the presence of the
 alcohol compound in an amount equal to 30% by moles, having
 structure (IX) :



To separate the hydrofluoroether from the alcohol, the
 raw reaction compound is chromatographed on silica gel using
 D 100 as eluent. From the extract, after solvent distillation,
 23 g of a compound are obtained which by the NMR (^{19}F and ^1H)
 analysis shows to be the hydrofluoroether of formula (VIII) .

The experimentation is repeated with the same modalities

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feeding each time 38 g of the acylchloride of the Example 2 by using the same catalyst of the preceding test.

After a cycle of 10 consecutive tests no variation of the reaction conversion and selectivity has been obtained and therefore no catalyst deactivation was evident.

EXAMPLE 3

In a 100 ml flask equipped with mechanical stirrer, bubbling pipe to introduce hydrogen/nitrogen, condenser with bubble-counter,

1 g of Pt supported on C (Pt = 5%) ,

40 ml of D100, are introduced.

One operates as described in the Example 1, by feeding 3.54 g of PFPE-acylchloride of the Example 2.

The NMR (¹⁹F and ³H) analysis of the compound shows a partial conversion of the starting PFPE-acylchloride (53% by moles) and the converted compound shows to be a mixture of compounds of which the formula (VIII) hydrofluoroether forms the 64% by moles.

The difference to 100 is constituted by the acid of formula (X) :



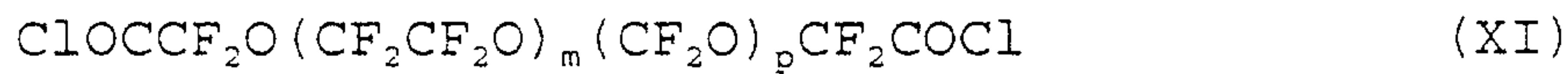
EXAMPLE 4

In the same equipment of the Example 1
30.4 g of Pt on CaF₂ (Pt = 1.5%) ,

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150 ml of D100, are introduced.

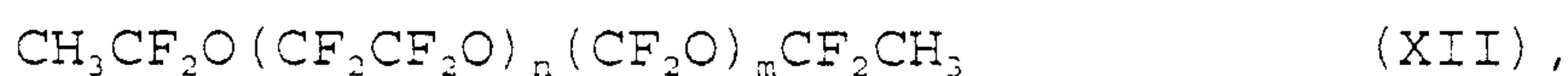
One operates as described in the Example 1, by feeding 35.2 g of PFPE-acylchloride of formula (XI) :



wherein $m/p = 1$ and m, p are such that the number average molecular weight is 2,030.

The NMR (^{19}F and ^1H) analysis of the compound shows a 100% conversion of the starting PFPE-acylchloride obtaining a reaction mixture which on an average has 60% by moles of $-\text{CF}_2\text{CH}_3$ end groups, 32% of $-\text{CF}_2\text{CH}_2\text{OH}$ end groups, 8% of $-\text{CF}_2\text{CO}_2\text{H}$ end groups.

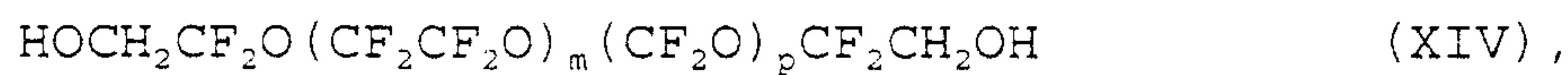
From the mixture, after chromatography on silica and solvent distillation, 5.8 g of hydrofluoroether of formula:



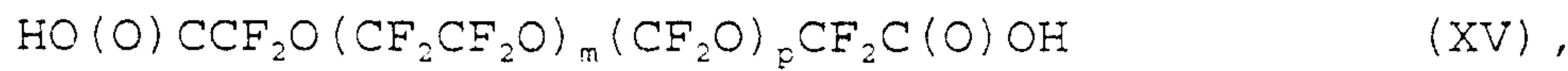
12 g of PFPE of formula:



9.7 g of PFPE-alcohol of formula:



and 2.4 g of PFPE-acid of formula (XV) :



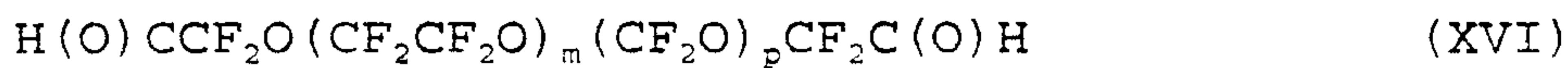
are obtained.

EXAMPLE 5

In the same equipment of the Example 3
3.26 g of Pt on CaF_2 (Pt = 1.5%) ,

40 ml of D100, are introduced.

One operates as described in the Example 1, by feeding 3.21 g of PFPE-aldehyde of formula (XVI):



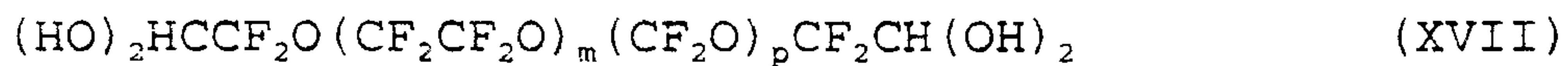
wherein $m/p = 1$ and m, p are such that the number average molecular weight is 2,000.

The NMR (^{19}F and ^1H) analysis of the compound shows a 100% conversion of the starting PFPE-aldehyde with the obtainment of a reaction mixture which on an average has 30% by moles of $-\text{CF}_2\text{CH}_3$ end groups and 70% of $-\text{CF}_2\text{CH}_2\text{OH}$ groups.

EXAMPLE 6

In the same equipment of the Example 3
2.9 g of Pt on CaF_2 (Pt = 1.5%),
40 ml of D100, are introduced.

One operates as described in the Example 1, by feeding 2.48 g of hydrated PFPE-aldehyde of formula:



wherein $m/p = 1$ and m, p are such that the number average molecular weight is 2,000.

The NMR (^{19}F and ^1H) analysis of the compound shows a 100% conversion of the starting hydrated PFPE-aldehyde with the obtainment of a reaction mixture which on an average has 14% by moles of $-\text{CF}_2\text{CH}_3$ end groups and 86% of $-\text{CF}_2\text{CH}_2\text{OH}$ groups.

EXAMPLE 7 (comparative)

In the same equipment of the Example 3
 4 g of Pt on CaF_2 (Pt = 1.5%),
 40 ml of D100, are introduced.

By operating as described in the Example 1, 4 g of PFPE-alcohol of formula:



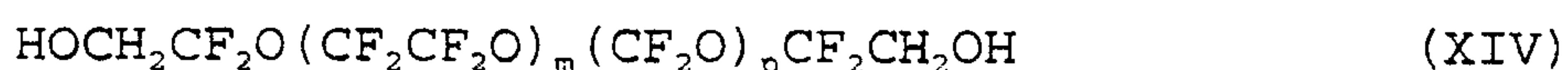
are fed, wherein $n = 3$ and number average molecular weight equal to 604.

The compound NMR (^{19}F and ^1H) shows that no reaction has taken place, only the PFPE-alcohol of formula (IX) being present.

EXAMPLE 8 (comparative)

In the same equipment of the Example 3
 4 g of Pt on CaF_2 (Pt = 1.5%),
 40 ml of D100, are introduced.

By operating as described in the Example 1, 4 g of PFPE-alcohol of formula:



are introduced, wherein $m/p = 1$ and m, p are such that the number average molecular weight is 2,000.

The NMR (^{19}F and ^1H) of the compound shows that no reaction has taken place, only the PFPE-alcohol of formula (XIV) being present.

EXAMPLE 9 (comparative)

In the same equipment of Example 3
 60 mg of Pt black,
 40 ml of D100, are introduced.

By operating as described in the Example 1, 4 g of PFPE-acylchloride of formula (VII) of the Example 2, are introduced.

The NMR (^{19}F and ^1H) of the compound shows that no reaction has taken place, only the PFPE-acylchloride of formula (VII) being present.

EXAMPLE 10 (comparative)

A 250 ml AISI 316 reactor equipped with magnetic stirring, bubbling pipe, thermocouple for the temperature reading and manometer, is dried at 70°C under vacuum for 7 hours. It is then transferred in dry-box and fed with:
 47 mg of SbF_5 ,

10 g of PFPE-acyl fluoride of formula:

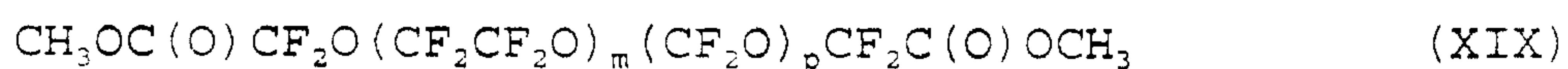


wherein $m/p = 2.13$ and m, p such that the number average molecular weight is 1,529.

The reactor is reassembled in the dry-box and cooled to -80°C. After the reactor has been put under vacuum, 1.82 g of gaseous CH_3CF_3 are fed. Then one operates by letting the reaction mixture reach the room temperature, then heating it

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to 30°C and leaving it for 45 minutes at said temperature. The reactor is then cooled again to -30°C and after 20 minutes the reaction mixture is quenched by the addition of 8 g of anhydrous methanol. It is brought to room temperature, then the reaction raw compound is discharged from the reactor. The methanol excess is removed by distillation at reduced pressure. 8.9 g of a compound are obtained, which at the ¹⁹F and ¹H NMR analysis shows to be only a PFPE-ester of formula:



i.e. the reaction compound between the starting PFPE-acylfluoride and the methyl alcohol.

Therefore no formation of hydrofluoroether has been noticed.

EXAMPLE 11 (comparative)

In the same equipment of the Example 10 and proceeding as described in the Example 10, the acid catalyst amount is increased by feeding:

2.2 g of SbF_5 ,

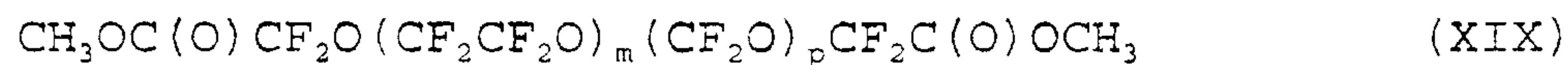
10.5 g of PFPE-acylfluoride of the Example 10.

It is cooled to -80°C noticing a residual pressure of 1.5 bar. One proceeds however as described in the Example 10 by feeding 1.82 g of CH_3CF_3 . A further pressure increase is observed. After quenching with methanol at low temperature, it is let reach again the room temperature. The gas is sampled

and is analyzed by gas-mass. It shows to be constituted by a mixture of decomposition compounds of the PFPE-acylfluoride chain, having low number average molecular weight (MW \leq 500).

None of these shows hydrofluoroether structure with $-\text{OCF}_2\text{CH}_3$ end groups.

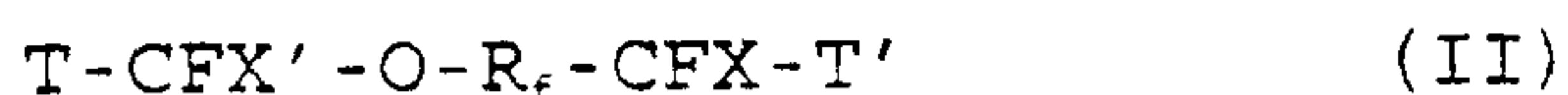
The liquid reaction mass gives only 2.5 g of PFPE-ester of formula:



wherein $m/p = 5$ and m, p are such that the number average molecular weight is 1,371.

CLAIMS

1. Hydrofluoroethers of formula:



wherein:

$T = CH_3$;

X, X' , equal to or different from each other, are selected between F, CF_3 ;

$T' = F, Cl, H, C_1-C_3$ perfluoroalkyl, $CH_3, CH_2OH, COCl, CHO, CO_2H$;

R_f is selected from:

- C_2-C_{15} perfluoroalkylene;

- $-(C_2F_4O)_m(CF_2CF(CF_3)O)_n(CF_2O)_p(CF(CF_3)O)_q-$

wherein

the sum $n+m+p+q$ ranges from 2 to 200,

the $(p+q)/(m+n+p+q)$ ratio is lower than or equal to 10:100, preferably comprised between 0.5:100 and 4:100, the n/m ratio ranges from 0.2 to 6, preferably from 0.5 to 3; m, n, p, q are equal to or different from each other and when m, n range from 1 to 100, preferably from 1 to 80, then p, q range from 0 to 80, preferably from 0 to 50; the units with n, m, p, q indexes being statistically distributed along the chain;

- $-(CF_2CF_2CF_2O)_r-$ wherein r ranges from 2 to 200,

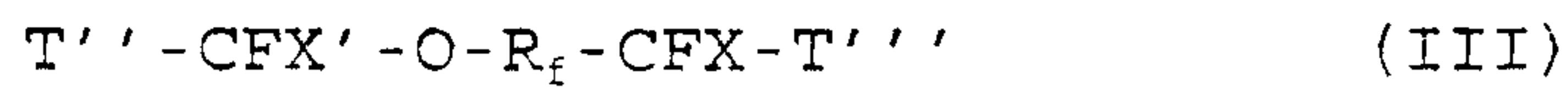
- $-(CF(CF_3)CF_2O)_s-$ wherein s ranges from 2 to 200,

2. A process according to claim 1, wherein R_f is selected from the following structures:

- $(CF_2CF_2O)_m-(CF_2O)_p-$,

- $(CF_2CF(CF_3)O)_n-(CF_2O)_p-(CF(CF_3)O)_q$

3. A process for the preparation of the formula (II) compounds of claim 1 comprising the reduction of the formula (III) corresponding precursors:



wherein:

$T'' = COCl$,

$T''' = F, C_1-C_3$ perfluoroalkyl, $COCl$, H , Cl ,

X, X', R_f are as defined in formula (II) of claim 1, carried out with gaseous hydrogen in the presence of a catalyst formed by supported platinum, preferably on metal fluorides, preferably in the presence of inert solvents, at a temperature in the range $20^\circ C-150^\circ C$, preferably $80^\circ C-120^\circ C$, at a pressure between 1 and 50 atm, preferably between 1 and 10 atm.

4. A process according to claim 3, wherein the metal fluorides are selected from the group formed by CaF_2 , BaF_2 , MgF_2 , AlF_3 , more preferably CaF_2 .

5. A process according to claims 3-4, wherein the Pt concentration on the support is comprised between 0.1%

and 10% with respect to the total weight of the catalyst, preferably between 1% and 2% by weight.

6. A process according to claims 3-5, wherein the catalyst is used in an amount in the range 1%-100%, preferably 10%-100% by weight with respect to the weight of the formula (III) compound.

7. A process according to claims 3-6, wherein the inert solvent is selected among perfluorotetrahydrofuran, perfluorotetrahydropyran, or their mixtures.