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(54) Title: PROCESS FOR THE PREPARATION OF FLUOROOLEFINS			
(57) Abstract			
<p>This invention concerns processes for the preparation of fluoroolefins, including a process for the deiodofluorination of an iodine containing fluorocarbon comprising contacting said iodine containing fluorocarbon with a fluoroolefin capable of picking up the elements of iodine monofluoride in the presence of an aluminum chlorofluoride catalyst.</p>			

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TITLE

PROCESS FOR THE PREPARATION OF FLUOROOLEFINS

FIELD OF THE INVENTION

5 This invention concerns processes for the preparation of fluoroolefins.

TECHNICAL BACKGROUND

U.S. Patent No. 3,377,390 discloses compounds of the formula R_fIF_x where x is an integer of two or four. This patent discloses that a compound of the formula R_fIF_x will initiate telomerization of perfluoroalkyl iodides with certain olefins.

U.S. Patent No. 3,557,224 discloses a process for the manufacture of perfluoroalkyl iodide telomers from the corresponding monomers by telomerizing a perfluoroalkyl iodide with a perfluoroethylene or a perfluoropropylene containing at least one Cl atom in the presence of a catalyst.

U.K. Patent No. 1,443,444 discloses a process for preparing bromine containing telomers.

20 SUMMARY OF THE INVENTION

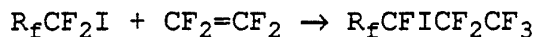
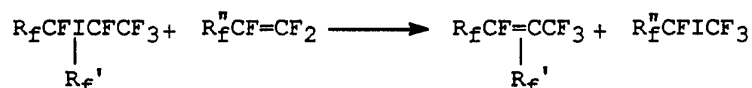
This invention provides a process for the preparation of perfluorinated olefins of the structure $R_fCF=CFCF_3$ by the reaction of perfluoroalkyliodides of the structure R_fCF_2I , wherein R_f is $C_nF_{2n}F$, wherein n is 1 to 12, with perfluoroolefins in the presence of an aluminum chlorofluoride catalyst.

Included herein is a process for the preparation of perfluorobutene-2 by the dimerization of tetrafluoroethylene, in the presence of an aluminum chlorofluoride/perfluoroalkyl iodide catalyst system.

This invention also provides a process for the deiodo fluorination of an iodine containing fluorocarbon comprising contacting said iodine containing fluorocarbon with a fluoroolefin capable of picking up the elements of iodine monofluoride in the presence of an aluminum chlorofluoride catalyst (ACF).

DETAILED DESCRIPTION OF THE INVENTION

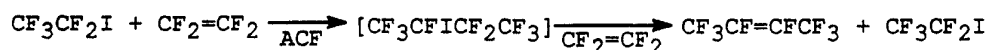
The processes of the present invention are illustrated by the following equations.

5 Equation 110 Equation 2

wherein R_f in Equations 1 and 2 is $C_nF_{2n}F$ where n is 1-12, $R_{f'}$ is selected from F and $C_nF_{2n}F$ and $R_{f''}$ is selected from F and CF_3 .

The iodine-containing starting compound is believed to add across the double bond of tetrafluoroethylene (TFE). The secondary perfluoroalkyl iodide formed in Equation 1 reacts, as shown in Equation 2, with a second molecule of TFE or with hexafluoropropene to generate the product olefin and a molecule of short-chain perfluoroalkyl iodide, $R_{f''}CFICF_3$ ($R_{f''} = CF_3$ or F). Perfluoroalkyl iodide generated in this reaction of perfluoroalkyl iodide with TFE (Eq 2, $R_{f'} = F$) competes with starting iodide R_fCF_2I in the reaction with TFE.

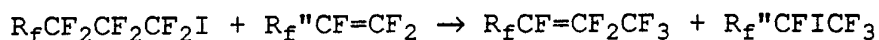
The special case of equation 1 and 2 is the case where R_fCF_2I is perfluoroethyl iodide. This reaction generates perfluoroethyl iodide (see Eq 3) and the process becomes catalytic in perfluoroethyl iodide.

Equation 3

The process of Eq. 2, which involves the transfer of iodine monofluoride from a perfluoroalkyl iodide,

can be carried out independently of Eq. 1 with primary or secondary perfluoroalkyl iodides using TFE or hexafluoropropylene (HFP) as perfluoroolefin (Eq. 2 and 4).

5 Equation 4



wherein R_f in Equation 4 is $C_nF_{2n}F$ where n is 1-12 and
 10 R_f'' is F or CF_3 .

The discussion below summarizes the embodiments exemplified in certain examples; however, the invention is not meant to be limited to these examples as equivalents are also intended to be included.

15 In Example 1, illustrating equations 1 and 2, R_f is CF_3 ; and thus R_fCF_2I is perfluoroethyl iodide. This is the special case cited above.

In Example 2, illustrating equations 1 and 2, R_f is $n-C_3F_7$, R_f' is F and thus $R_f'CF=CF_2$ is TFE. Because
 20 only 0.06 mole of perfluoro- n -butyl iodide is present versus 0.5 mole of TFE, and because perfluoroethyl iodide reacts faster than perfluoro- n -butyl iodide, the predominant products arise from the generated perfluoroethyl iodide competing successfully with
 25 perfluoro- n -butyl iodide. The major product is perfluorobutene-2.

In Example 3, as compared to Example 2, the molar ratio of perfluoro- n -butyl iodide to TFE is increased 2.1 times. Here, the products reflect less successful
 30 competition between perfluoroethyl iodide and perfluoro- n -butyl iodide. A major product is perfluoroethyl iodide and the amount of perfluoro-hexenes is increased.

In Example 4, perfluoro- n -butyl iodide ($R_f =$
 35 $n-C_3F_7$) and hexafluoropropene (R_f' in $R_f'CF=CF_2$ is CF_3) yield perfluoro-butene-2 and perfluoroisopropyl iodide. This is an example of Equation 4 of this invention.

In Example 5, perfluoro-n-hexyliodide ($R_f = n-C_5F_{11}$) with hexafluoropropene yields perfluorohexene-2 and perfluorohexene-3 (in the ratio of 23:77) and perfluoroisopropyl iodide. This is an example of
5 Equation 4.

Example 6, demonstrates scaled-up synthesis and isolation of perfluorobutene-2.

The process of equation 2 can be operated together with equation 1 or independently of equation 1.

10 For the process of Equation 2 practiced independently of Equation 1 or the process of Equation 4, solvents or diluents may be employed in the present process. The solvent or diluent should not be reactive in the process or lead to the deactivation of
15 the aluminum chlorofluoride catalyst. Said solvents or diluents can be perfluoroalkanes or perfluoro-cycloalkanes, for example, perfluorocyclobutane or the cyclic dimer of hexafluoropropene, i.e., the isomeric perfluorodimethylcyclobutanes; perfluoroethers or
20 perfluoro tertiary amines. Preferred on the basis of ready availability is the cyclic dimer of hexafluoropropene.

The temperature employed in the process of the present invention ranges from about 20 degrees to about
25 200 degrees centigrade. The preferred temperature range is about 50°C to 150°C.

Reaction time is not critical and ranges from about 2 to about 24 hours. Overnight reactions, i.e., about 16 hours, are convenient.

30 Pressure of the reaction is not critical. Autogenous pressures are usually employed.

Since the reaction conditions are heterogeneous, some degree of agitation is usually applied.

The reaction is carried out in the presence of an
35 aluminum halide Lewis acid catalyst, wherein the aluminum halide is a mixed halide containing F and at least one of Cl, Br or I. Preferred catalysts are of the structure AlF_nCl_{3-n} , wherein n is from 0.05 to

2.95. Preferably n is from 2.5 to 2.95. Fluorinated aluminum chloride catalysts can be prepared by the reaction of AlCl_3 and CFCl_3 according to the method described in U.S. Patent No. 5,162,594, column 4, line 5 35-57, which is hereby incorporated by reference. Catalysts may be preformed or may be generated in situ.

Since the catalyst is water sensitive, reagents and equipment should be dried before use.

The proportion of catalyst to $\text{R}_f\text{CF}_2\text{I}$ is 0.1 to 20 10 weight percent.

Product can be isolated by conventional means, for example, fractionation.

When the processes of Equations 1 and 2 are carried out sequentially, the temperature range of 15 -10°C to 200°C is employed. Where R_f'' is F, a preferred temperature range is about -10°C to 100°C . Where R_f'' is CF_3 , the preferred temperature range is 50°C to 150°C .

Reaction time is not critical and ranges from 20 about 2 to about 24 hours. Overnight reactions, i.e., about 16 hours, are convenient.

Solvents or diluents may be employed in the present process. The solvent or diluent should not be reactive in the process or lead to the deactivation of 25 the aluminum chlorofluoride catalyst. Said solvents or diluents can be perfluoroalkanes or perfluorocycloalkanes, for example, perfluorocyclobutane or the cyclic dimer of hexafluoropropene, i.e., the isomeric perfluorodimethylcyclobutanes; perfluoroethers or 30 perfluoro tertiary amines. Preferred on the basis of ready availability is the cyclic dimer of hexafluoropropene.

Pressure of the reaction is not critical. Autogenous pressures are usually employed.

35 Since the reaction conditions are heterogeneous, some degree of agitation is usually applied.

The reaction is carried out in the presence of an aluminum halide Lewis acid catalyst, wherein the

aluminum halide is a mixed halide containing F and at least one of Cl, Br or I. Preferred catalysts are of the structure AlF_nCl_{3-n} , wherein n is from 0.05 to 2.95. Preferably n is from 2.5 to 2.95. Fluorinated aluminum chloride catalysts can be prepared by the reaction of $AlCl_3$ and $CFCl_3$ according to the method described in U.S. Patent No. 5,162,594, column 4, line 35-57, which is hereby incorporated by reference. Catalysts may be preformed or may be generated in situ.

Since the catalyst is water sensitive, reagents and equipment should be dried before use.

The proportion of R_fCF_2I to $R_fCF=CF_2$ is between 1:1 and 1:1000 on a molar basis. The amount of AlF_nCl_{3-n} to R_fCF_2I is between 0.1 and 20% on a weight basis.

This process provides a practical route to the highly desirable fluoroolefin of the structure $CF_3CF=CFCF_3$ (perfluorobutene-2). Such olefins are used as intermediates for synthesis of the environmentally friendly HFC's.

Product can be isolated by conventional means, for example, fractionation. In the case of perfluorobutene-2, it is advantageous to use a solvent capable of coordinating or complexing one of the components, perfluoroethyl iodide or perfluorobutene-2, preferentially during isolation. Useful solvents are acetonitrile, dimethylformamide, dimethylacetamide, glymes, hexamethylphosphoramide, aromatic hydrocarbons, dinitriles such as adiponitrile, and ureas. Preferred solvents are acetonitrile, dimethylformamide, dimethylacetamide, glymes, adiponitrile, benzene and toluene.

This invention further provides an azeotrope of perfluorobutene-2 and perfluoroethyliodide in the ratio of 85:15 and a process for preparing said azeotrope. Also provided is a method for breaking said azeotrope by distillation from a mixture containing a solvent

capable of forming a complex with perfluoroethyl iodide or perfluorobutene-2 as discussed above.

EXAMPLES

Catalyst Preparation - AlCl_3 + CFCl_3

5 500 g (3.75 mol) of AlCl_3 (Aldrich-99% pure) was stirred mechanically under N_2 in a r.b. flask fitted with a -80°C condenser while 1750 mL (~2625 g, 19 mol) of CFCl_3 was added over a 1.5-hr period. Reaction is very exothermic in the early stages, so addition of
10 CFCl_3 was slow at first in order to keep the temperature below 65°C , then rapid. The resulting suspension was stirred an additional 3 hrs while volatiles (CF_2Cl_2) were allowed to escape through the warmed condenser. The condenser was then replaced with
15 a simple stillhead, and most of the CCl_4 was distilled under reduced pressure [mainly bp 38°C (200 mm)]. Finally, the last traces of volatiles were removed by warming the residual solid to $30\text{--}35^\circ\text{C}$ at 0.05 mm.

The sealed r.b. flask was transferred to a dry box
20 and unloaded into a Teflon® FEP bottle; 340 g of rather finely divided yellow-green solid. Portions of the catalyst were weighed out in the dry box as needed and taken out in plastic bottles with pressure-seal caps.

Analysis for fluorine of the products from
25 preparation of this type indicated the composition to be $\text{AlF}_{2.9}\text{Cl}_{0.1}$, AlF_xCl_y ; $x = 2.8\text{--}2.9$, $y = 0.2\text{--}0.1$.

EXAMPLE 1

Preparation of perfluorobutene-2 (from perfluoroethyl iodide and TFE)

30 A 240 mL Hastelloy shaker tube was flushed with nitrogen, then loaded with 5 g of aluminum chlorofluoride catalyst, cooled to -78°C , evacuated and loaded with 40g (0.16 mole) of perfluoroethyl iodide and 40 g (0.4 mole) of tetrafluoroethylene. The
35 reaction vessel was allowed to warm and kept on a shaker at $25\text{--}30^\circ\text{C}$ at autogenous pressure. Significant pressure drop (approximately 150 psi) was observed in the first 2 hours. After 18 hours, the pressure tube

was unloaded. The product, 55g, was collected in a -78°C cold trap. According to ^{19}F NMR, it was a mixture of 41% of perfluoroethyl iodide (recovered starting material) and 59% of perfluorobutene-2, mixture of cis and trans isomers in a 3:2 ratio. The calculated yield of perfluorobutene-2 based on converted perfluoroethyl iodide was 82.5%.

EXAMPLE 2

Preparation of perfluorobutene-2

10 (from perfluorobutyl iodide and TFE)

A 240 mL Hastelloy shaker tube was flushed with nitrogen, then loaded with 5 g of aluminum chlorofluoride catalyst, cooled to -78°C, evacuated and loaded with 20 g (0.06 mole) of perfluorobutyl iodide and 50 g (0.5 mole) of tetrafluoroethylene. The reaction vessel was allowed to warm and kept on a shaker at 25-30°C at autogenous pressure. Significant pressure drop (approximately 150 psi) was observed in the first 2 hours. After 18 hours, the pressure tube was unloaded. The product, 40 g, was collected in a -78°C cold trap. According to ^{19}F NMR, it was a mixture of 90% of perfluorobutene-2, mixture of cis and trans isomers in a 3:2 ratio and 10% of perfluoroethyl iodide. The calculated yield of perfluorobutene-2 based on converted perfluorobutyl iodide was 72%. According to ^{19}F NMR, the main component (about 70%) of the residue (15 g) was a mixture of perfluorohexene-2, (minor) and perfluorohexene-3.

EXAMPLE 3

30 Reaction of perfluorobutyl iodide with TFE

A 240 mL Hastelloy shaker tube was flushed with nitrogen, then loaded with 5 g of aluminum chlorofluoride catalyst, cooled to -78°C, evacuated and loaded with 34 g (0.1 mole) of perfluorobutyl iodide and 40 g (0.4 mole) of tetrafluoroethylene. The reaction vessel was allowed to warm and kept on a shaker at 25-30°C at autogenous pressure. Significant pressure drop (approximately 150 psi) was observed in

the first 2 hours. After 18 hours, the pressure tube was unloaded. The crude product, 58 g, was collected in a -78°C cold trap. According to ^{19}F NMR, it was a mixture of 40% of perfluoroethyl iodide, 25% of
5 perfluorobutene-2, 20% of perfluorohexene-3, 10% of perfluorobutyl iodide and 5% of perfluorohexene-2. The calculated yield of perfluorohexenes based on converted perfluorobutyl iodide was 51%. The calculated yield of perfluorobutene-2 based on converted perfluorobutyl
10 iodide was 38%.

EXAMPLE 4

Reaction of perfluorobutyl iodide with hexafluoropropene

A 240 mL Hastelloy shaker tube was flushed with
15 nitrogen, then loaded with 3.5 g of aluminum chlorofluoride catalyst, cooled to -78°C, evacuated and loaded with 34.6 g (0.1 mole) of perfluorobutyl iodide and 15 g (0.1 mole) of hexafluoropropene. The reaction vessel was heated to 80°C and kept on a shaker at 80°C
20 autogenous pressure for 24 hours. After 24 hours, the contents of the first shaker tube was transferred to a second shaker tube containing 3.5 g of aluminum chlorofluoride catalyst. Additional hexafluoropropene, 7.5 g 0.05 mole, was added and the tube was shaken at
25 80°C for 48 hours. The crude product was according to gas chromatography and ^{19}F NMR, a mixture of perfluorobutene-2 and perfluoroisopropyl iodide. Upon distillation, 10 g of material with boiling point -3 to +2°C was obtained that was according to ^{19}F NMR 97%
30 pure perfluorobutene-2, mixture of cis and trans isomers in a 81:19 ratio. The residue (33 g) according to ^{19}F NMR contained 71% of perfluoroisopropyl iodide, 13% of perfluorobutene-2 and 16% of perfluorobutyl iodide starting material and a small amount of 2-
35 iodoperfluorobutane as a contaminant. The calculated yield of perfluorobutene-2 was 84%, the calculated yield of perfluoroisopropyl iodide was 80%.

EXAMPLE 5Reaction of perfluoro-n-hexyliodide
with hexafluoropropene

Perfluoro-n-hexyl iodide, 4.5 g (0.01 mole) and
5 0.5 g of aluminum chlorofluoride catalyst were placed
in a heavy walled Pyrex® glass sample tube equipped
with a Teflon® stopcock. The sample tube was evacuated
at -196°C and 1.5 g (10 mmole) of hexafluoropropene was
added through the vacuum line. The sample tube was
10 placed in a shielded heater and heated to 75°C for 10
hours. The tube was cooled to 0°C, opened and the
reaction mixture was poured into water. The organic
(lower) layer was separated and dried over phosphorous
pentoxide. The product, 5.8 g was a mixture of 49% of
15 perfluoroisopropyl iodide, 48% of a mixture of
perfluorohexene-2 and perfluorohexene-3 (in the ratio
of 23:77) contaminated with a small amount of (2-3%) of
an unidentified product, probably 3-iodo perfluoro-n-
nonane. The calculated yield of perfluorohexenes was
20 93%; the calculated yield of perfluoroisopropyl iodide
was 95%.

EXAMPLE 6Preparation of perfluorobutene-2 by catalytic
dimerization of TFE

25 The reaction was scaled up in a 1L Hastelloy
stirred autoclave which was loaded with 20 g ACF and
100 g of C₂F₅I. TFE was added at 30-35°C in 20 to 30 g
increments. After addition of 400-600 g of TFE the
clave was unloaded, a new portion (100 g) of C₂F₅I was
30 added and the cycle was repeated. Using 20 g of ACF
and 200 g total of C₂F₅I, 980 g of TFE was consumed in
this reaction.

The distillation of crude prouct gave 650 g of an
azeotropic mixture comprising 85% of CF₃CF=CFCF₃ and
35 15% of C₂F₅I (b.p. 0-1°C), and 220 g of higher b.p.
material.

The yield of CF₃CF=CFCF₃ was 57%. The separation
of CF₃CF=CFCF₃ and C₂F₅I was achieved by distillation

of a mixture with dry dimethylacetamide. After the first distillation [350 g of mixture of $\text{CF}_3\text{CF}=\text{CFCF}_3/\text{C}_2\text{F}_5\text{I}$ (85:15); 200 mL $(\text{CH}_3)_2\text{NC}(\text{O})\text{CH}_3$] 253 g of $\text{CF}_3\text{CF}=\text{CFCF}_3$ containing 2% of $\text{C}_2\text{F}_5\text{I}$ was obtained.

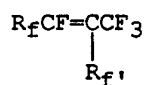
- 5 Second distillation [300 g of 98:2 mixture of $\text{CF}_3\text{CF}=\text{CFCF}_3$ and $\text{C}_2\text{F}_5\text{I}$, 100 mL of $(\text{CH}_3)_2\text{NC}(\text{O})\text{CH}_3$] gave 210 g of perfluorobutene-2 (trans:cis = 4:1), containing, according to GC, 0.2% of $\text{C}_2\text{F}_5\text{I}$.

- 10 The product with higher b.p. obtained in this reaction (220 g) was distilled giving 143 g of material with b.p. 50-52°C and 24 g of residue. According to ^{19}F NMR the main fraction was a mixture of the following compounds: $\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)\text{C}_2\text{F}_5$ cis 38%, trans 9.5%; $\text{CF}_3\text{CF}=\text{CFC}_3\text{F}_7$ cis 2%, trans 7%, $\text{C}_2\text{F}_5\text{CF}=\text{CFC}_2\text{F}_5$ cis 15 5%, trans 29%; $\text{CF}_3\text{CFICF}_2\text{CF}_3$ 9.5%.

What is claimed is:

1. A process for the deiodofluorination of an iodine-containing fluorocarbon comprising:
contacting an iodine-containing fluorocarbon with
5 a fluoroolefin that is capable of picking up the elements of iodine monofluoride, in the presence of an aluminum chlorofluoride catalyst.
2. The process of Claim 1 wherein the iodine containing fluorocarbon is of the structure
10 $R_fCFICFR_f'CF_3$ or $R_fCF_2CF_2CF_2I$ wherein R_f is $C_nF_{2n}F$, wherein n is 1 to 12 and R_f' is F or $C_nF_{2n}F$.
3. The process of Claim 1 wherein the fluoroolefin is of the structure $R_f''CF=CF_2$, wherein R_f'' is selected from the group consisting of F and
15 CF_3 .
4. The process of claim 1 conducted in the presence of solvents or diluents that do not react with the reactants, catalyst or products.
5. The process of claim 4 wherein the solvent or
20 diluent is selected from the group consisting of perfluoroalkanes, perfluoroethers and perfluoro tertiary amines.
6. The process of claim 1 wherein the solvent or diluent is the cyclic dimer of hexafluoropropene.
- 25 7. The process of claim 1 conducted at 20 degrees to about 200 degrees centigrade.
8. The process of claim 7 wherein the temperature range is about 50°C to 150°C.
9. The process of claim 1 wherein the aluminum
30 catalyst is a mixed halide containing F and at least one of Cl, Br or I.
10. The process of Claim 9 wherein the catalyst is AlF_nCl_{3-n} , wherein n is from 0.05 to 2.95.
11. The process of Claim 10 wherein n is from 2.5
35 to 2.95.
12. The process of Claim 10 wherein the proportion of catalyst to R_fCF_2I is 0.1 to 20 weight percent.

13. A process for the preparation of perfluorinated olefins of the structure



5

wherein $R_{f'}$ is selected from the group consisting of F and $C_nF_{2n}F$ comprising:

- (a) reacting perfluoroalkyl iodide of the structure R_fCF_2I with at least two moles
 10 tetrafluoroethylene in the presence of an aluminum chlorofluoride catalyst, where R_f is $C_nF_{2n}F$, where n is 1-12 and $R_{f'}$ is selected from the group consisting of F and $C_nF_{2n}F$ where n is 1-12.

14. A process according to Claim 13 wherein the
 15 product is perfluorobutene-2.

15. A process for the preparation of perfluorobutene-2 comprising dimerization of tetrafluoroethylene in the presence of an aluminum chlorofluoride/pentafluoroethyl iodide catalyst.

20 16. The process of claim 13 conducted in the presence of a solvent or diluent that is not reactive with reactants, catalyst or products.

25 17. The process of claim 13 wherein the solvent or diluent is selected from the group consisting of perfluoroalkanes, perfluoroethers and perfluoro tertiary amines.

18. The process of claim 13 wherein the solvent or diluent is the cyclic dimer of hexafluoropropene.

30 19. The process of claim 13 conducted at -10 degrees to about 200 degrees centigrade.

20. The process of claim 19 wherein the temperature range is about -10 to 100°C wherein $R_{f'}=F$.

21. The process of claim 19 wherein the temperature range is about 50 to 150°C wherein $R_{f'}=CF_3$.

35 22. The process of claim 13 wherein the aluminum catalyst is a mixed halide containing F and at least one of Cl, Br and I.

23. The process of Claim 13 wherein the catalyst is $\text{AlF}_n\text{Cl}_{3-n}$, wherein n is from 0.05 to 2.95.

24. The process of Claim 23 wherein n is from 2.5 to 2.95.

5 25. A process for the isolation of pure $\text{CF}_3\text{CF}=\text{CFCF}_3$ from an azeotropic mixture $\text{CF}_3\text{CF}=\text{CFCF}_3 / \text{C}_2\text{F}_5\text{I}$ (85:15) comprising distillation from a mixture containing a solvent capable of giving a complex with $\text{C}_2\text{F}_5\text{I}$ or perfluorobutene-2.

10 26. The process in Claim 25 where the solvent is acetonitrile, dimethylformamide, dimethylacetamide, glymes, adiponitrile, benzene and toluene.

27. An azeotropic mixture of perfluorobutene-2 and perfluoroethyl iodide in the ratio of 85:15.

15 28. The process of claim 13 wherein the proportion of $\text{R}_f\text{CF}_2\text{I}$ to $\text{R}_f'\text{CF}=\text{CF}_2$ is between 1:1 and 1:100% on a molar basis and the amount of $\text{AlF}_n\text{Cl}_{3-n}$ relative to $\text{R}_f\text{CF}_2\text{I}$ is between 0.1 and 20% on a weight basis.

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/US 96/10865

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C17/23 C07C21/18 C07C17/278 C07C17/04 C07C17/281
C07C17/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 192 274 (C.F. BARANAUCKAS ET AL) 29 June 1965 see the whole document	1
A	--- JOURNAL OF ORGANIC CHEMISTRY, vol. 34, 1969, EASTON US, pages 864-869, XP002015492 P. TARRANT ET AL.: "The peroxide-initiated addition of some polyfluorochloro- and polyfluorobromoalkanes to some hydrocarbon olefins" see page 868	1
A	--- WO,A,95 16656 (DU PONT) 22 June 1995 see claims -----	13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

9 October 1996

Date of mailing of the international search report

15.10.96

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Bonnevalle, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/10865

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3192274	29-06-65	NONE	
WO-A-9516656	22-06-95	EP-A- 0734368	02-10-96