

Description

BACKGROUND OF THE INVENTION

5 1. Field of the Invention:

This invention concerns a process for the production of polyfluoroolefins by the catalytic addition of polyfluoroallylic fluorides to fluoroethylenes. 1:1 and 1:2 Adducts such as F-pentene-2 and F-heptene-3 can be formed selectively and reduced further to dihydro- or trihydropolyfluoroalkanes, which are useful as HFC
 10 cleaning agents. Higher boiling products, e.g., boiling points above 100 °C, are useful as solvents and stable liquids, particularly after the double bond has been saturated by hydrogenation, fluorination, or chlorination.

2. Technical Review:

15 Various catalysts for the addition of polyfluoroallylic fluorides to fluoroethylenes are known.

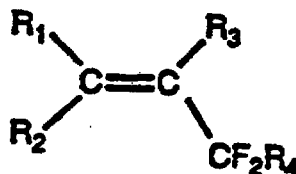
G.G. Belen'kii, E.P. Lur'e, and L.S. German, UDC 66.095.253:547.413, Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow (1975) use SbF₅ as a catalyst for carrying out the alkylation of the fluoro derivatives of ethylene using perfluoropropylene and 2-H-perfluoropropylene.

20 Chang-Ming Hu, Hui Liu and Ze-Qi Xu, Reactions of Perchlorofluoro Compounds VI Rearrangement of Higher Perchlorofluoroolefins and Their Reactions with Nucleophiles and Electrophiles (Journal of Fluorine Chemistry, 46 (1990) 491-506), teaches the alkali fluoride on induced formation of a TFE/HFP adduct.

The present invention employs an aluminum halide to catalyze the addition of an allyl fluoride to fluoroethylene.

25 SUMMARY OF THE INVENTION

The present invention provides a process for the manufacture of polyfluoroolefins having at least 5 carbon atoms comprising reacting a first polyfluoroolefin of the structure

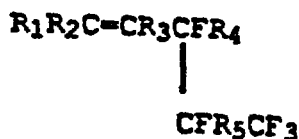


where:

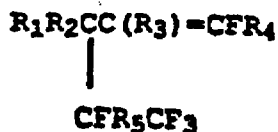
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- R₁ is F, Cl, H or R_f;
 - R₂ is F, Cl, H or R_f;
 - R₃ is F, Cl, or H;
 - R_f is a C₂ to C₁₂ perfluoroalkyl, optionally containing 1 H or 1 Cl;
 - R₄ is F or R_f or where R₄ together with R₂ is -(CF₂)_n; wherein n is 1, 2 or 3; with a second polyfluoroolefin of structure R₅CF=CF₂ and where
 - R₅ is F, H, or Cl;

in the presence of a catalyst of the structure AlX₃ wherein X is one or more of F, Cl or Br, provided that X cannot be entirely F; wherein said process is carried out within a temperature range of -20 °C to 150 °C.

The invention also concerns the production of olefins of the structures

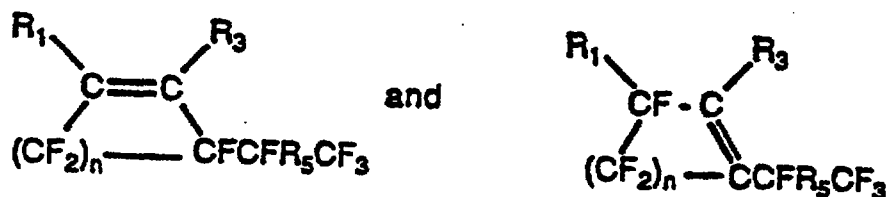


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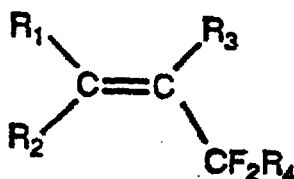


or structures derived therefrom by further "migration" of the double bond. By "migration" is meant a shift in the double bond position in the molecule accompanied by relocation of fluorine.

The invention also concerns olefins of the structures:



or rearrangement Products resulting from a shift of the double bond. (These later olefins result where R_4 , together with R_2 is $-(CF_2)_n$ in the starting

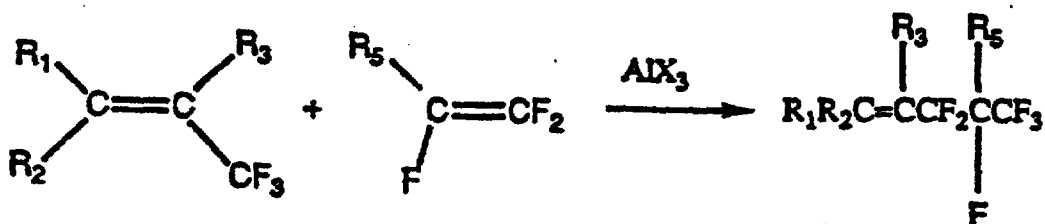


compound) where n is 1, 2 or 3.

Specific compositions in accordance with the present invention are claimed in Claims 28-30.

DETAILED DESCRIPTION OF THE INVENTION

The equation for the addition reaction which is claimed is as follows (where R_4 is F):



where R_1 , R_2 , R_3 and R_5 are as defined in the Summary of the Invention.

The allylic fluoride may either have the structure shown or be capable of rearranging to that structure by fluorine atom migration in the presence of a catalyst.

The product may also either have the structure shown or a structure resulting from fluorine atom migration. In some cases isomeric products, such as



are formed.

The catalyst used is of the structure AlX_3 , where X is one or more of F, Cl or Br, with a proviso that X cannot be entirely F. Active catalyst can be preformed, as in most examples, or can be formed *in situ* by partial halogen-F exchange with allylic fluoride, as in Examples 9 and 20. Preferred catalysts are AlF_xCl_y - (mixed aluminum halide), where the total number of atoms of halide, x plus y equals 3, where x ranges from 0 to about 2.95 and y ranges from 3 to about .05. The AlF_xCl_y , where y is greater than 0, may be prepared by pretreating AlCl_3 with reactive C-F compounds such as $\text{CF}_3\text{CF}=\text{CF}_2$, CFCl_3 or CHFCl_2 .

Temperatures range from -20°C to 150°C , depending on the reactivity of the reagents but are preferably in the range of 20°C to 85°C . Pressures may vary from less than 101.3 KPa (1 atm) to over 5.1 MPa (50 atm), but a preferred range is from 101.3 KPa (1 atm) to 2 MPa (20 atm). Times for batch reactions may vary from about 5 min. to about 2 days depending on batch size. Times for a continuous reaction may vary from about 1/2 to 120 min. Times for the reaction vary depending upon the identity of the reactants, the temperature, pressure and amount of catalyst.

The reaction is best conducted in a liquid phase and can be carried out in several modes; batchwise with addition of reactants and catalyst to a reactor cold and warming to reaction temperature; semibatch by injection of one or both reactants optionally containing catalyst into a vessel containing catalyst and or the other reagent at reaction temperature; or continuous by passing the reactants (preferably at least partly liquified, optionally with catalyst) through a reaction zone, which also optionally contains catalyst. The catalyst must be present in the reactant mixture or the reaction zone but may be present in both places. Reactant mole ratios of allylic fluoride (e.g., HFP) to fluoroolefin (e.g., TFE) can vary from 5:1 to 1:50. Ratios in the 5:1 to 1:1 range are generally used when high yields of one to one adducts are desired. Ratios from 1:1 to 1:50 are used when multiple additions of fluoroethylene are desired to form one-to-two and higher adducts, especially when the fluoroolefin is tetrafluoroethylene (TFE). Catalyst loadings in a batch reaction can be from about 0.5 to about 20 wt-%, preferably 2-8 wt-%, of the total charge of reactants.

Solvents are generally not essential, but a liquid phase is useful to facilitate reaction of low-boiling materials that are not condensed under reaction conditions. Solvents are also useful for controlling any initial exotherm when a catalyst, such as aluminum chloride, is used in a large scale reaction. Relatively inert materials which may be used as solvents include hexafluorobenzene, F-n-hexane, $\text{ClCF}_2\text{CF}_2\text{Cl}$, SO_2ClF , $\text{CF}_3\text{CF}_2\text{CHCl}_2$, $\text{ClCF}_2\text{CF}_2\text{CHFCl}$, $\text{CF}_3\text{CHFCHFCF}_2\text{CF}_3$, $\text{CF}_3\text{CHFCH}_2\text{CF}_2\text{CF}_3$, $\text{CF}_3\text{CH}_2\text{CHFCH}_2\text{CF}_3$, $\text{ClCF}_2\text{CFCl}_2$, CF_3CCl_3 , $\text{CF}_3\text{CCl}_2\text{CF}_3$, CF_3CHCl_2 , F-1,2-dimethylcyclobutane, $\text{CCl}_2=\text{CCl}_2$, $\text{CCl}_2=\text{CHCl}$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CHFCF}_3$, $(\text{CF}_3)_2\text{C}=\text{CFCF}_2\text{CF}_3$, $(\text{CF}_3)_2\text{CFCF}=\text{CFCF}_2$, F-pentene-2, F-heptene-3, F-heptene-2, and C_nF_{2n} , where n is 5 to 15. Highly fluorinated olefins are preferred solvents and perfluoroolefins, C_nF_{2n} , wherein n is 5 to 15 are most preferred. F-pentene-2, for example, is especially preferred for the reaction in which it is also the product, i.e. the condensation of $\text{CF}_3\text{CF}=\text{CF}_2$ with $\text{CF}_2=\text{CF}_2$, since the reaction mixture can be over 95% C_5F_{10} , and therefore easily purified. Selectivity in this procedure is high because $\text{CF}_3\text{CF}=\text{CF}_2$ is much more reactive than $\text{CF}_3\text{CF}=\text{CFCF}_2\text{CF}_3$ and, when present, reacts with $\text{CF}_2=\text{CF}_2$, almost exclusively.

Table I shows various examples and reaction conditions. It should be noted that some of the entries in Table I, in which large excesses of tetrafluoroethylene (TFE) over hexafluoropropene (HFP) were used, resulted in appreciable condensation of TFE with itself to yield even numbers of carbon atoms in product fluoroolefins. Also, as multiple additions of TFE to HFP increase in number, branching in the product olefins becomes more pronounced. Thus, C_5F_{10} and C_7F_{14} are linear products, C_9F_{18} is mainly linear, $\text{C}_{11}\text{F}_{22}$ and higher have increasing amounts of structures of the type $(\text{R}_1)_2\text{C}=\text{CFR}_1$. These mixtures of high-boiling liquids are converted to even higher boiling, stable liquids by hydrogenation, chlorination or fluorination.

The synthesis described herein can be used to form 1:1 and 1:2 adducts such as F-pentene-2 ($\text{CF}_3\text{CF}=\text{CFCF}_2\text{CF}_3$) and F-heptene-3/F-heptene-2 mixtures which can be reduced to form HFC cleaning agents. It can also be used to form higher adducts useful as a source of unreactive solvents, vapor degreasing agents, and stable liquids by chlorination, fluorination or hydrogenation of the double bond.

EXAMPLESCatalyst preparation - $\text{AlCl}_3 + \text{CF}_3\text{CF}=\text{CF}_2$

5 A slurry of 100 g (0.75 mol) of AlCl_3 (Aldrich, 99.9% pure) in 100 mL of CCl_4 was stirred under nitrogen under a -80°C condenser while 20 g (0.13 mol) of $\text{CF}_3\text{CF}=\text{CF}_2$ was bled in over 1.75 hr. Some unreacted hexafluoropropene, which was present at the end and caused the temperature to drop to 5°C , was bled off, and the mixture was warmed to 40°C . Another addition of 11 g (0.07 mol) of $\text{CF}_3\text{CF}=\text{CF}_2$ over a 1 hr period
 10 resulted in an exotherm to 50°C . Continued slow addition at 50 - 65°C of 42 g (0.28 mol) of $\text{CF}_3\text{CF}=\text{CF}_2$ finally resulted in persistent reflux of unreacted $\text{CF}_3\text{CF}=\text{CF}_2$. The reaction mixture was transferred to a dry box, where it was filtered. The filter cake was rinsed with 2 X 50 mL of dry CCl_4 , then dried under vacuum to afford 84.7 g of greenish, free-flowing powder.

Catalyst Preparation - $\text{AlCl}_3 + \text{CFCl}_3$

15 500 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 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)
 20 were allowed to escape through the warmed condenser. The condenser was then replaced with a simple stillhead, and most of the CCl_4 was distilled under reduced pressure [mainly bp 38°C (1961 Pa (200 mm))]. Finally, the last traces of volatiles were removed by warming the residual solid to 30 - 35°C at 0.5 Pa (0.05 mm).

The sealed r.b. flask was transferred to a dry box and unloaded into a Teflon® FEP bottle; 340 g of
 25 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.

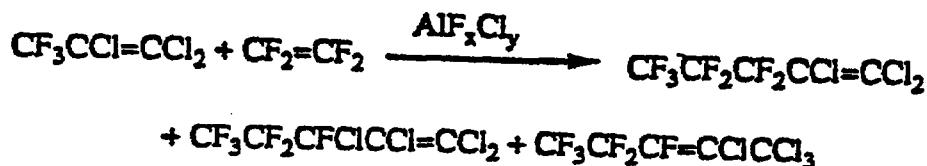
Analysis for fluorine of the products from preparation of this type indicated the composition to be $\text{AlF}_{2.9}\text{Cl}_{0.1}$, AlF_xCl_y ; $X = 2.8$ - 2.9 , $\text{Cl} = 0.2$ - 0.1 .

30 EXAMPLE 1

A 400-mL metal tube charged with 16.4 g of fluoridated AlCl_3 ($\text{AlCl}_3 + \text{CFCl}_3$), 100 g (0.5 mol) of 1,1,2-trichloro-3,3,3-trifluoropropene, and 50 g (0.50 mol) of tetrafluoroethene was agitated at 25°C for 1.5 hr. Fractionation of the liquid product mixture gave 25.4 g (25%) of recovered $\text{CF}_3\text{CCl}=\text{CCl}_2$, then 42.3 g (38%
 35 yield) of F -1,1,2-trichloropentene-1, bp 63 - 66°C , 980 Pa (100 mm), identified by IR, NMR and GC/MS. Further fractionation afforded 23.3 g (15%) of an isomeric mixture of F -1,1,2-tetrachloropentene-1 and F -1,1,1-2-tetrachloropentene-2, bp 86 - 89°C , 980 Pa (100 mm), identity indicated by IR, NMR and GC/MS. Some higher boiling 2:1 adducts were also present.

The equation for the reaction is shown below:

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EXAMPLE 2

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A 400-mL metal tube charged at -20°C with 8.0 g of $\text{AlF}_{2.8}\text{Cl}_{0.2}$ (prepared from $\text{AlCl}_3 + \text{CFCl}_3$), 75 g (0.50 mol) of hexafluoropropene (HFP), and 50 g (0.50 mol) of tetrafluoroethylene (TFE) was shaken for 30 min. while the temperature rose sickly to 20°C and the pressure dropped to 55 KPa (8 psi). Distillation of the product afforded 88.0 g (70%) of F -pentene-2, b.p. 23 - 26°C , identified by IR, NMR and GC/MS. NMR
 55 showed the product to be 89% *trans*-isomer and 11% *cis*-isomer.

EXAMPLE 3**Reaction of $\text{CF}_3\text{CF}=\text{CF}_2/\text{CF}_2=\text{CF}_2$ in 1:2 Ratio**

- 5 A 400-mL metal tube charged cold with 3 g of AlF_xCl_y (fluorinated aluminum chloride catalyst prepared by treating aluminum chloride with CFCI_3), 40 g (0.27 mol) of hexafluoropropene, and 50 g (0.50 mol) of tetrafluoroethylene was agitated at 25 °C for 2 hr and at 80 °C for 4 hr. Analysis of the liquid product, 73 g, by GC and MS indicated the presence of 28.2 g (42%) of perfluoro-pentene-2, 42.2 g (48%) of perfluoroheptene isomers, 2.7 g (4%) of perfluorononene isomers, <0.7 g (1%) of $\text{C}_{11}\text{F}_{22}$ isomers, and
- 10 traces of higher oligomers, with very small amounts of perfluorohexene and perfluorooctene also detected. Fractionation afforded 21.9 g (32%) of perfluoropentene-2, bp 24-26 °C, followed by 34.1 g (39%) of perfluoroheptenes, bp 69.5-71 °C. Analysis of a center cut, bp 70.9 °C, by IR and NMR showed the major component to be *trans*-perfluoroheptene-3 with only small amounts of other isomers present. Continued fractionation afforded 1.2 g (2%) of perfluorononenes, bp 66-68 °C, 1471 Pa (150 mm), shown by IR and
- 15 NMR to consist mainly of *trans*-perfluorononene-4 and *trans*-perfluorononene-3.

EXAMPLE 4**Reaction of $\text{CF}_3\text{CF}=\text{CF}_2/\text{CF}_2=\text{CF}_2$ in 1:4 Ratio**

- 20 A 400-mL tube charged cold with 5.0 g of AlF_xCl_y , 40 g (0.27 mol) of hexafluoropropene, and 50 g (0.50 mol) of tetrafluoroethylene was shaken at 25 °C for 30 min. while the pressure dropped to 0 Pa (0 psi). Another 50 g (0.50 mol) of tetrafluoroethylene was added, and the mixture was agitated for 4 hr at 25 °C while the pressure again fell to 0 Pa (0 psi). Analysis of the liquid product, 122 g, by GC and MS indicated
- 25 the presence of 34.5 g (37% yield) of perfluoroheptenes, 59.0 g (49% of perfluorononenes, 22.2 g (15%) of perfluoroundecenes, and 2.0 g (1%) of perfluorotridecenes, with 0.5-1% of perfluoroolefins having even numbers of carbon atoms C_6F_{12} , C_8F_{16} and $\text{C}_{10}\text{F}_{20}$ also detected. Distillation afforded a series of fractions, bp 66 °C, 101.3 KPa (1 atm) to 66 °C, 177 Pa (18 mm), which were characterized by GC, IR and NMR analysis. Product boiling at 71-72 °C was shown to consist of straight-chain *trans*-perfluoroheptene-3 and
- 30 *trans*- and *cis*-perfluoroheptene-2, with very small amounts of branched olefins (e.g., $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)=\text{CFCF}_2\text{CF}_3$) present. Product with bp 74-80 °C, 1961 Pa (200 mm) was found to be mainly straight-chain *trans*-perfluorononene-4 and *trans*-perfluorononene-3, with perhaps 50% of branched perfluorononenes present in a fraction bp 74 °C, 1961 Pa (200 mm) dropping to about 5% branched olefins in fractions bp 76-80 °C, 1961 Pa (200 mm). The mixed perfluoroundecenes with bp 70-77 °C, 490 Pa (50 mm) were shown to
- 35 be mainly branched structures of the type $(\text{R}_1)_2\text{C}=\text{CFR}_1$, with linear olefins $\text{R}_1\text{CF}=\text{CFR}_1$ as minor components.

EXAMPLE 20

- 40 **Reaction of Equimolar $\text{CF}_3\text{CF}=\text{CF}_2$ with $\text{CF}_2=\text{CF}_2$ with AlCl_3 Catalyst in $\text{CCl}_2=\text{CCl}_2$ Solvent**

- A tube charged cold with 5.0 g of aluminum chloride, 100 mL of tetrachloroethylene, 75 g (0.50 mol) of hexafluoropropene, and 50 g (0.50 mol) of tetrafluoroethylene was shaken at 25-30 °C for 4 hr while the pressure dropped to 476 KPa (69 psi). The reaction mixture was then heated at 60 °C for 10 hr while the
- 45 pressure fell to 310 KPa (45 psi). The liquid product, two phases, was distilled to give a foreshot of 4 mL followed by 58.4 g (47%) of perfluoropentene-2, bp 10-25 °C, nearly 100% pure by GC.

Tetrachloroethylene is a preferred solvent because of its availability, relative inertness under reaction conditions, and ease of separation from low boiling 1:1 and 1:2 adducts.

- 50 **EXAMPLE 21**

Addition of $\text{CF}_2=\text{CF}_2$ to F-Cyclopentene

- A 1-L. stirred autoclave was charged with 30 g of AlF_xCl_y and 118 g (0.56 mol) of F-cyclopentene. Tetrafluoroethylene (47.3 g, 0.47 mol) was pressured in and the vessel was heated slowly with stirring to
- 55 80 °C, where reaction rate was appreciable Tetrafluoroethylene was added in portions at 80 °C until a total of 114.4 g (1.14 mol) had been added over 14 hr. Reaction was continued another 7 hr. Volatiles obtained by beating the crude reaction product at 100 °C, 2.9 Pa (0.3 mm) were 122.6 g of liquid. Fractionation

afforded 96.2 g (55%) of F-1-ethylcyclopentene, bp 64-66 °C, identified by IR and NMR analysis.

EXAMPLE 22

5 Addition of $\text{CF}_2 = \text{CF}_2$ to $\text{F}(\text{CF}_2)_4\text{CH} = \text{CH}(\text{CF}_2)_4\text{F}$

A metal tube charged with 5 g of AlF_3Cl_3 , 50 g (0.50 mol) of $\text{CF}_2 = \text{CF}_2$, and 139 g (0.30 mol) of $\text{F}(\text{CF}_2)_4\text{CH} = \text{CH}(\text{CF}_2)_4\text{F}$ was shaken at 25 °C for 17 hr. The reaction mixture was filtered and distilled to give 90.5 g (54%) of 1:1 adducts, bp 60-63 °C, 196 Pa (20 mm), identified by GC/MS. The major isomer, about 95% of the total, was shown to be

$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF} = \text{CHCH}(\text{CF}_2\text{CF}_3)\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ by IR and NMR analysis.

EXAMPLE 23

15 Use of $\text{CF}_3\text{CF} = \text{CF}(\text{CF}_2\text{CF}_3)$ as Solvent

A 400-mL metal tube charged with 5.0 g AlF_3Cl_3 , 49.5 g of $\text{CF}_3\text{CF} = \text{CF}(\text{CF}_2\text{CF}_3)$, 75 g (0.50 mol) of $\text{CF}_3\text{CF} = \text{CF}_2$, and 50 g (0.50 mol) of $\text{CF}_2 = \text{CF}_2$ was agitated as it warmed over 0 °C. From a peak pressure, 894 KPa (115 psig) at 16 °C, the pressure fell rapidly to 163 KPa (9 psig), while a slight exotherm carried the temperature to 28 °C before subsiding to 22 °C, all in 1 hr. Heating at 60 °C produced no further sign of reaction. GC analysis of the crude product, 169 g, indicated that 110.1 g (88%) of C_5F_{10} had been formed. Only small amounts of by-products such as hexafluoropropene dimer were present.

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TABLE I

Example	Cat. (wt. %)	Reactants (molar ratio)	Temp (°C) (Time (hr.))	Pressure Range kPa (psig)	Products (% yield)
1	AlF ₃ Cl ₃ (10)	CF ₃ CCl-CCl ₂ + CF ₂ =CF ₂ (1:1)	25° (1.5)	1246-143 (166-6)	F(CF ₂) ₅ CCl-CCl ₂ (38%), F(CF ₂) ₂ CFClCCl-CCl ₂ + F(CF ₂) ₂ CF-CClCCl ₂ (15%)
2	AlF ₃ Cl ₃ (6)	CF ₃ CF=CF ₂ + CF ₂ =CF ₂ (1:1)	0-20° (0.5)	down to 156 (down to 8)	89:11 <i>trans/cis</i> -F(CF ₂) ₂ CF-CF ₂ (70%), trace HFP dimer
3	AlF ₃ Cl ₃ (3)	CF ₃ CF=CF ₂ + CF ₂ =CF ₂ (1:2)	25° (2), 80° (4)	1935-570, 763-446 (266-68), (96-50)	F(CF ₂) ₂ CF-CF ₂ (32%), F(CF ₂) ₃ CF-CF(CF ₂) ₂ F (39%), F(CF ₂) ₃ CF-CF(CF ₂) ₂ F + F(CF ₂) ₄ CF-CF(CF ₂) ₃ F + others (2%)
4	AlF ₃ Cl ₃ (5)	CF ₃ CF=CF ₂ + CF ₂ =CF ₂ (1:4)	11-25° (0.5, 4) (2 TFE additions)(138-0), (173-0)	1053-0 1294-0	C ₇ F ₁₄ (37%), C ₉ F ₁₈ (49%), C ₁₁ F ₂₂ (15%), small amounts other olefins and solid polymer
5	AlF ₃ Cl ₃ (3)	CF ₃ CF-CF ₂ CF ₃ +CF ₂ =CF ₂ (1:1) Carried out semibatch with TFE added continuously.	35-40° (4)	377-515 (40-60)	C ₇ F ₁₄ (78%), C ₉ F ₁₈ (60)

Example	Cat (wt. %)	Reactants (molar ratio)	Temp (°C) (Time (hr.))	Pressure Range kPa (psig)	Products (% yield)
6	AlF ₃ Cl ₃ (3)	CF ₃ CH=CH ₂ + CF ₂ =CF ₂ (1:1)	25° (2), 60° (4)	1687-2859 (230-400)	F(CF ₂) ₃ CH=CH ₂ (low, mainly CF ₃ CH=CH ₂ dimers
7	AlF ₃ Cl ₃ (4)	 + CF ₂ =CF ₂ (1:2)	80° (3)	2404-232 (334-19)	1:1 adducts (36%), 2:1 adducts (32%)
8	AlF ₃ Cl ₃ (3)	CF ₃ CCl=CClCF ₃ + CF ₂ =CF ₂ (0.8:1)	80° (2)	2494-336 (347-34)	F(CF ₂) ₃ CCl=CClCF ₃ (48%), F(CF ₂) ₃ CCl=CCl(CF ₂) ₃ F (20%)
9	AlCl ₃ (2)	CF ₃ CF=CF ₂ + CF ₂ =CF ₂ (1:1)	25° (0.5), 40° (2)	1756, down to 336 (240, down to 34)	F(CF ₂) ₃ CF=CF ₂ (47), small ante. high boilers
10	AlF ₃ Cl ₃ (2)	CF ₃ CF=CF ₂ + CF ₂ =CF ₂ (1:1)	12-26° (4)	1501-343 (203-35)	F(CF ₂) ₃ CF=CF ₂ (69%)
11	AlF ₃ Cl ₃ (4)	CF ₃ CH=CF ₂ + CF ₂ =CF ₂ (1:1)	25° (3.5)	1156-0 (153-0)	CF ₃ CH=CF ₂ CF ₂ CF ₃ (80%), F(CF ₂) ₃ CF=CH(CF ₂) ₃ F (low), plus others

Example	Cat. (wt. %)	Reactants (molar ratio)	Temp (°C) (Time (hr.))	Pressure Range kPa (psig)	Products (b yield)
12	AlF ₃ Cl ₃ (4)	CF ₃ CF=CF ₂ + CF ₂ =CFCl (1:1)	25° (4)	687-225 (85-18)	CF ₃ CF ₂ CF=CClCF ₂ (36%), along with CF ₃ CF ₂ CCl=CClCF ₂ , F(CF ₂) ₃ CF=CClCF ₂ CF ₃ , F(CF ₂) ₃ CCl=CClCF ₂ (18%) and others
13	AlF ₃ Cl ₃ (4)	CF ₃ CF=CF ₂ + CF ₂ =CF ₂ (1:10)	4-25° (3, 18)	1149-232, 1756-108	C ₇ F ₁₄ , C ₈ F ₁₈ , C ₁₁ F ₂₂ and C ₁₃ F ₂₆ as major series, (2 TFE additions) (152-19), (240-1)
14	AlF ₃ Cl ₃ (5)	CF ₃ CF=CF ₂ + CF ₂ =CF ₂ (1:30)	25° (4), 50° (1)	1239-246, 1335-405	C ₈ F ₁₆ , C ₁₀ F ₂₀ , and solid polymer also formed C ₈ F ₁₂ to C ₁₃ F ₂₆ liquids + 12%
15	AlF ₃ Cl ₃ (6)	C ₇ F ₁₄ isomers + CF ₂ =CF ₂ (1:7)	25° (10), 50° (6)	1466-0 (198-0), constant	C ₈ F ₁₂ (11), C ₈ F ₁₄ (14), C ₈ F ₁₆ (16), C ₈ F ₁₈ (32), C ₁₀ F ₂₀ (30), C ₁₁ F ₂₂ (30), C ₁₂ F ₂₄ (30), C ₁₃ F ₂₆ (21) plus polymer

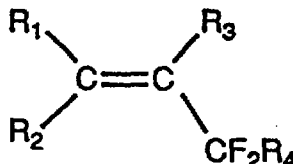
Example	Cat. (wt. %)	Reactants (molar ratio)	Temp (°C) (Time (hr.))	Pressure Range kPa (psig)	Products (% yield)
16	AlF ₃ Cl ₃ (5)	(CF ₃) ₂ CFCF-CFCF ₃ + CF ₂ -CF ₂ (1:3)	10-25° (6)	1204-0 (160-0)	1:1 adducts (32%), 2:1 (54%), 3:1 (10%)
17	AlF ₃ Cl ₃ (6)	CF ₃ CF-CF ₂ (C ₆ F ₆ solvent)	25° (4), 85° (10)	(no readings)	(CF ₃) ₂ C-CFCF ₂ CF ₃ (20%), (CF ₃) ₂ CFCF-CFCF ₃ (2%)
18	AlF ₃ Cl ₃ (5)	(CF ₃) ₂ C-CFCF ₂ CF ₃ + CF ₂ -CF ₂ (1:3)	16-25° (8)	1329-0 (178-0)	CF ₃ CF ₂ CF ₂ C(CF ₃)-CFCF ₂ CF ₃ (2%), considerable poly(TFE) C ₃ F ₁₀ (1%) + C ₇ F ₁₄ (1%)
19	AlBr ₃ (7)	CF ₃ CF-CF ₂ + CF ₂ -CF ₂ (1:1)	25-60° (8)	1618-3652 (220-515)	CF ₂ CF-CFCF ₂ CF ₃ (47%)
20	AlCl ₃ (4)	CF ₂ CF-CF ₂ + CF ₂ -CF ₂ (1:1)	25-30° (4) 60° (10)	see text	
21	AlF ₃ Cl ₃ (13)	F-cyclopentene, CF ₂ -CF ₂ (1:2)	80° (21)	no readings	F-1-ethylcyclopentene (55%)
22	AlF ₃ Cl ₃ (2.6)	F(CF ₃) ₂ CH-CH(CF ₃) ₂ + CF ₂ -CF ₂ (3:5)	25° (17)	no readings	CF ₃ (CF ₂) ₂ CF-CH(CF ₃)CF ₃ (CF ₂) ₃ CF ₃ + isomers (54%) C ₃ F ₁₀ (88%)
23	AlF ₃ Cl ₃ (4)	CF ₃ CF-CF ₂ ' + CF ₂ -CF ₂ (1:1)	see text	793 (115 psi) → 9	

Although preferred embodiments of the invention have been described hereinabove, it is to be understood that there is no intention to limit the invention to the precise constructions herein disclosed, and it is to be further understood that the right is reserved to all changes coming within the scope of the invention as defined by the appended claims.



Claims

1. A process for the manufacture of polyfluoroolefins having at least 5 carbon atoms comprising reacting a first polyfluoroolefin of the structure



where:

- 15 R_1 is F, Cl, H or R_f ;
 R_2 is F, Cl, H or R_f ;
 R_3 is F, Cl or H;
 R_f is a C_2 to C_{12} perfluoroalkyl, optionally containing 1 H or 1 Cl;
 R_4 is F or R_f or where R_4 together with R_2 is $-(CF_2)_n-$; wherein n is 1, 2 or 3;
- 20 with a second polyfluoroolefin of structure $R_5CF=CF_2$ and where
 R_5 is F, H or Cl;
 in the presence of a catalyst wherein the catalyst is of the structure AlX_3 wherein X is one or more of F, Cl or Br, provided that X cannot be entirely F; wherein said process is carried out within a temperature range of $-20^\circ C$ to $150^\circ C$.
- 25 2. The process of Claim 1 wherein the temperature is $0^\circ C$ to $100^\circ C$.
3. The process of Claim 1 carried out at 101.3 KPa (1 atm.) pressure.
- 30 4. The process of Claim 1 carried out in a batch process for 5 min. to 2 days.
5. The process of Claim 1 carried out in a continuous process for 1/2 min. to 120 min.
6. The process of Claim 1 wherein the reactants and catalyst are placed batchwise in a cold reactor then
- 35 warmed to reaction temperature.
7. The process of Claim 1 wherein the reaction is carried out semibatchwise by injection of one or both reactants into a vessel containing catalyst at reaction temperature.
- 40 8. The process of Claim 1 wherein the reaction is carried out semibatchwise by injection of one reactant and catalyst into a vessel containing the other reactant or containing the other reactant and additional catalyst.
9. The Process of Claim 1 wherein the process is run as a continuous reaction by passing the reactants
- 45 through a reaction zone containing catalyst.
10. The Process of Claim 9 wherein the reactants are at least partly liquid.
11. The process of Claim 1 wherein the process is run as a continuous reaction by passing at least partially
- 50 liquid reactants containing catalyst through a reaction zone.
12. The process of Claim 10 wherein the at least partially liquid reactants also contain catalyst.
13. The process of Claim 1 carried on in a solvent.
- 55 14. The process of Claim 13 wherein the solvent is selected from hexafluorobenzene, F-n-hexane, $ClCF_2CF_2Cl$, SO_2ClF , $CF_3CF_2CHCl_2$, $ClCF_2CF_2CH_2Cl$, $CF_3CHFCH_2CF_2CF_3$, $CF_3CHFCH_2CF_2CF_3$, F-pentene-2, $CF_3CH_2CH_2CF_2CF_3$, $ClCF_2CF_2Cl$, CF_3CCl_3 , $CF_3CCl_2CF_3$, CF_3CHCl_2 , perfluoro-1,2-



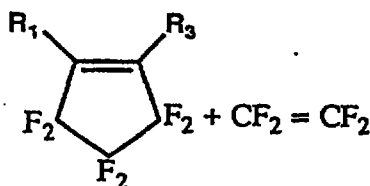
dimethylcyclobutane, $\text{CCl}_2 = \text{CCl}_2$, $\text{CCl}_2 = \text{CHCl}$, C_nF_{2n} wherein n is 5 to 15 and $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}[\text{CF}(\text{CF}_3)-\text{CF}_2\text{O}]_n\text{CHF}_2\text{CF}_3$.

15. The process of Claim 13 wherein the solvent is C_nF_{2n} , wherein n is 5 to 15.

16. Process of Claim 14 wherein the solvent is $\text{CF}_2\text{CF} = \text{CFCF}_2\text{CF}_3$.

17. Process of Claim 14 wherein the solvent is F-pentene-2.

18. The process of Claim 1 wherein the reactants are:



where:

R_1 is F, Cl, H or R_f ; and

R_3 is F, Cl, H or R_f .

19. The process of Claim 1 wherein the first fluoroolefin is hexafluoropropene (HFP) and the second polyolefin is tetrafluoroethylene (TFE).

20. Process of Claim 19 wherein an excess of TFE over HFP is used.

21. The process of Claim 1 wherein an excess of first polyfluoroolefin over second polyfluoroolefin is used.

22. The process of Claim 19 wherein the ratio of HFP to TFE varies from 5:1 to 1:50.

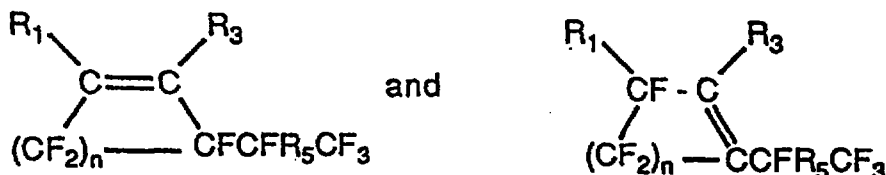
23. The process of Claim 22 wherein the ratio of HFP to TFE is from 1:2 to 1:50 and wherein some of the product fluoroolefins contain even numbers of carbon atoms.

24. The process of Claim 22 wherein the ratio of HFP to TFE is from 2:1 to 1:50 and wherein some of the product fluoroolefins contain branching.

25. The process of Claim 1 wherein the catalyst is AlCl_3 .

26. The process of Claim 1 wherein the catalyst is AlF_xCl_y , wherein the total number of halide atoms x plus y equals 3, and wherein x ranges from 0 to 2.95 and y ranges from 3 to .05.

27. Isomeric compositions of the structures:



wherein R_1 , R_3 , R_5 , and n are as defined in Claim 1.

28. Liquid phase mixtures comprising perfluorinated olefins of the formula C_mF_{2m} where m is an integer from 9 to 15, as prepared by the process of Claim 19.

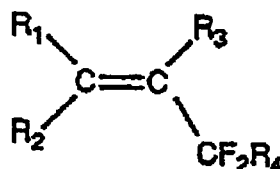


29. A composition of the structure $\text{CF}_3\text{CCl}=\text{CClCF}_2\text{CF}_2\text{CF}_3$.

30. A composition of the structure $\text{CF}_3\text{CF}_2\text{CF}_2\text{CCl}=\text{CClCF}_2\text{CF}_2\text{CF}_3$.

5 Patentansprüche

1. Verfahren zur Herstellung von Polyfluorolefinen mit wenigstens 5 Kohlenstoffatomen, umfassend die Umsetzung eines ersten Polyfluorolefins der Struktur



worin

R_1 für F, Cl, H oder R_1 steht,

R_2 für F, Cl, H oder R_1 steht,

R_3 für F, Cl oder H steht,

R_1 für ein C_2 - bis C_{12} -Perfluoralkyl steht, das gegebenenfalls 1 H oder 1 Cl enthält,

R_4 für F oder R_1 steht oder worin R_4 zusammen mit R_2 $-(\text{CF}_2)_n$ - bedeutet, worin n für 1, 2 oder 3 steht,

mit einem zweiten Polyfluorolefin der Struktur $\text{R}_5\text{CF}=\text{CF}_2$ worin

R_5 für F, H oder Cl steht,

in Gegenwart eines Katalysators, worin der Katalysator die Struktur AlX_3 besitzt, worin X eines oder mehrere von F, Cl oder Br bedeutet, mit der Maßgabe, daß X nicht ausschließlich F bedeuten kann, wobei das genannte Verfahren innerhalb eines Temperaturbereichs von -20°C bis 150°C durchgeführt wird.

2. Verfahren nach Anspruch 1, bei dem die Temperatur 0°C bis 100°C beträgt.

3. Verfahren nach Anspruch 1, durchgeführt bei einem Druck von 101,3 KPa (1 atm.).

4. Verfahren nach Anspruch 1, durchgeführt als diskontinuierlicher Prozeß für 5 Minuten bis 2 Tage.

5. Verfahren nach Anspruch 1, durchgeführt in einem kontinuierlichen Verfahren für 1/2 Minute oder 120 Minuten.

6. Verfahren nach Anspruch 1, bei dem die Reaktanden und der Katalysator chargenweise in einen kalten Reaktor gegeben und anschließend auf die Reaktionstemperatur aufgeheizt werden.

7. Verfahren nach Anspruch 1, bei dem die Reaktion halbdiskontinuierlich durch Einleiten von einem oder beiden Reaktanden in ein Reaktionsgefäß, das den Katalysator bei Reaktionstemperatur enthält, durchgeführt wird.

8. Verfahren nach Anspruch 1, bei dem die Reaktion halbdiskontinuierlich durch Einleiten eines Reaktanden und eines Katalysators in ein Reaktionsgefäß, das den anderen Reaktanden oder den anderen Reaktanden und zusätzlichen Katalysator enthält, durchgeführt wird.

9. Verfahren nach Anspruch 1, bei dem das Verfahren als kontinuierliche Reaktion betrieben wird, indem die Reaktanden eine katalysatorhaltige Reaktionszone durchlaufen.

10. Verfahren nach Anspruch 9, bei dem die Reaktanden wenigstens teilweise flüssig sind.

11. Verfahren nach Anspruch 1, bei dem das Verfahren als kontinuierliche Reaktion betrieben wird, indem die wenigstens teilweise flüssigen Reaktanden, die den Katalysator enthalten, eine Reaktionszone



durchlaufen.

12. Verfahren nach Anspruch 10, bei dem die wenigstens teilweise flüssigen Reaktanden ebenfalls Katalysator enthalten.

13. Verfahren nach Anspruch 1, das in einem Lösungsmittel durchgeführt wird.

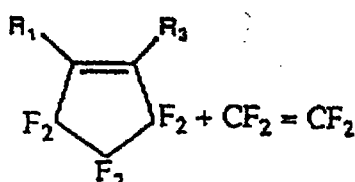
14. Verfahren nach Anspruch 13, bei dem das Lösungsmittel ausgewählt wird aus Hexafluorbenzol, F-n-Hexan, $\text{ClCF}_2\text{CF}_2\text{Cl}$, SO_2ClF , $\text{CF}_3\text{CF}_2\text{CHCl}_2$, $\text{ClCF}_2\text{CF}_2\text{CHFCl}$, $\text{CF}_3\text{CHFCHFCF}_2\text{CF}_3$, $\text{CF}_3\text{CHFCH}_2\text{CF}_2\text{CF}_3$, F-Penten-2, $\text{CF}_3\text{CH}_2\text{CHFCF}_2\text{CF}_3$, $\text{ClCF}_2\text{CFC}_2$, CF_3CCl_3 , $\text{CF}_3\text{CCl}_2\text{CF}_3$, CF_3CHCl_2 , Perfluor-1,2-dimethylcyclobutan, $\text{CCl}_2 = \text{CCl}_2$, $\text{CCl}_2 = \text{CHCl}$, C_nF_{2n} , worin n für 0 bis 15 steht, und $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CHFCF}_3$.

15. Verfahren nach Anspruch 13, bei dem das Lösungsmittel C_nF_{2n} ist, worin n für 0 bis 15 steht.

16. Verfahren nach Anspruch 14, bei dem das Lösungsmittel $\text{CF}_2\text{CF} = \text{CFCF}_2\text{CF}_3$ ist.

17. Verfahren nach Anspruch 14, bei dem das Lösungsmittel F-Penten-2 ist.

18. Verfahren nach Anspruch 1, bei dem die Reaktanden



sind, worin

R_1 für F, Cl, H oder R_f steht, und

R_3 für F, Cl, H oder R_f steht.

19. Verfahren nach Anspruch 1, bei dem das erste Fluorolefin Hexafluorpropen (HFP) und das zweite Polyolefin Tetrafluorethylen (TFE) ist.

20. Verfahren nach Anspruch 19, bei dem ein Überschuß an TFE gegenüber HFP verwendet wird.

21. Verfahren nach Anspruch 1, bei dem ein Überschuß des ersten Polyfluorolefins gegenüber dem zweiten Polyfluorolefin verwendet wird.

22. Verfahren nach Anspruch 19, bei dem das Verhältnis von HFP zu TFE von 5:1 bis 1:50 variiert.

23. Verfahren nach Anspruch 22, bei dem das Verhältnis von HFP zu TFE 1:2 bis 1:50 beträgt und bei dem ein Teil der Produkt-Fluorolefine eine gradzahlige Anzahl von Kohlenstoffatomen enthalten.

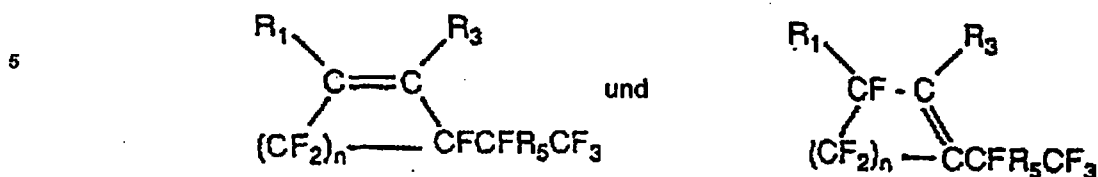
24. Verfahren nach Anspruch 22, bei dem das Verhältnis von HFP zu TFE 2:1 bis 1:50 beträgt und bei dem ein Teil der Produkt-Fluorolefine eine Verzweigung enthalten.

25. Verfahren nach Anspruch 1, bei dem der Katalysator AlCl_3 ist.

26. Verfahren nach Anspruch 1, bei dem der Katalysator AlF_xCl_y ist, bei dem die Gesamtzahl von Halogenatomen, x plus y, 3 entspricht und bei dem x im Bereich von 0 bis 2,95 und y im Bereich von 3 bis 0,05 liegen.



27. Isomere Zusammensetzungen der Strukturen



worin R_1 , R_3 , R_5 und n die bei Anspruch 1 gegebenen Definitionen besitzen.

28. Flüssigphasen-Gemische, umfassend perfluorierte Olefine der Formel C_mF_{2m} , worin m eine ganze Zahl von 9 bis 15 bedeutet, wie durch das Verfahren von Anspruch 19 hergestellt.

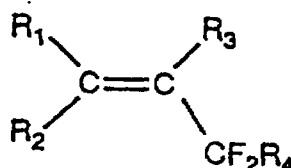
29. Zusammensetzung der Struktur $CF_3CCl = CCICF_2CF_2CF_3$.

30. Zusammensetzung der Struktur $CF_3CF_2CF_2CCl = CCICF_2CF_2CF_3$.

20 Revendications

1. Un procédé pour la production d'oléfines polyfluorées ayant au moins 5 atomes de carbone, consistant à faire réagir une première oléfine polyfluorée de la structure

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où :

R_1 est F, Cl, H ou R_1 ;

R_2 est F, Cl, H ou R_1 ;

R_3 est F, Cl ou H ;

R_1 est un groupe perfluoroalkyle en C_2 à C_{12} , contenant facultativement 1 H ou 1 Cl ;

R_4 est F ou R_1 , ou bien R_4 joint à R_2 est $-(CF_2)_n-$ où n est 1, 2 ou 3 ;

avec une seconde oléfine polyfluorée de structure $R_5CF = CF_2$ et où

40

R_5 est F, H ou Cl ;

en présence d'un catalyseur, le catalyseur ayant la structure AlX_3 où X est l'un ou plusieurs de F, Cl ou Br, à condition que les X ne soient pas tous F ; ledit procédé étant exécuté dans un intervalle de température de $-20^\circ C$ à $150^\circ C$.

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2. Le procédé de la revendication 1, dans lequel la température est de $0^\circ C$ à $100^\circ C$.

3. Le procédé de la revendication 1, exécuté à une pression de 101,3 kPa.

4. Le procédé de la revendication 1, exécuté en opération discontinue pendant 5 minutes à 2 jours.

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5. Le procédé de la revendication 1, exécuté en opération continue pendant 1/2 min à 120 min.

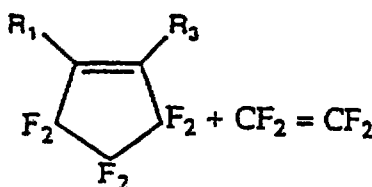
6. Le procédé de la revendication 1, dans lequel les corps réagissants et le catalyseur sont placés en charges discontinues dans un réacteur froid, puis chauffés à la température de réaction.

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7. Le procédé de la revendication 1, dans lequel la réaction est conduite en mode semi-discontinu par injection de l'un ou chacun des deux corps réagissants dans un récipient contenant un catalyseur à la température de réaction.



8. Le procédé de la revendication 1, dans lequel la réaction est conduite en mode semi-discontinu par injection d'un corps réagissant et du catalyseur dans un récipient contenant l'autre corps réagissant ou contenant l'autre corps réagissant et un supplément de catalyseur.
- 5 9. Le procédé de la revendication 1, dans lequel le procédé est conduit comme une réaction continue en faisant passer les corps réagissants à travers une zone réactionnelle contenant le catalyseur.
10. Le procédé de la revendication 9, dans lequel les corps réagissants sont au moins partiellement liquides.
- 10 11. Le procédé de la revendication 1, dans lequel le procédé est conduit comme une réaction continue en faisant passer les corps réagissants au moins partiellement liquides contenant un catalyseur à travers une zone réactionnelle.
- 15 12. Le procédé de la revendication 10, dans lequel les corps réagissants au moins partiellement liquides contiennent également un catalyseur.
13. Le procédé de la revendication 1, exécuté dans un solvant.
- 20 14. Le procédé de la revendication 13, dans lequel le solvant est choisi parmi l'hexafluorobenzène, le F-n-hexane, $\text{ClCF}_2\text{CF}_2\text{Cl}$, SO_2ClF , $\text{CF}_3\text{CF}_2\text{CHCl}_2$, $\text{ClCF}_2\text{CF}_2\text{CHFCl}$, $\text{CF}_3\text{CHFCHFCF}_2\text{CF}_3$, $\text{CF}_3\text{CHFCH}_2\text{CF}_2\text{CF}_3$, le F-pentène-2, $\text{CF}_3\text{CH}_2\text{CHFCF}_2\text{CF}_3$, $\text{ClCF}_2\text{CFCl}_2$, CF_3CCl_3 , $\text{CF}_3\text{CCl}_2\text{CF}_3$, CF_3CHCl_2 , le perfluoro-1,2-diméthylcyclobutane, $\text{CCl}_2 = \text{CCl}_2$, $\text{CCl}_2 = \text{CHCl}$, C_nF_{2n} où n est de 5 à 15 et $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CHFCF}_3$.
- 25 15. Le procédé de la revendication 13, dans lequel le solvant est C_nF_{2n} où n est de 5 à 15.
16. Procédé de la revendication 14, dans lequel le solvant est $\text{CF}_2\text{CF}=\text{CFCF}_2\text{CF}_3$.
- 30 17. Procédé de la revendication 14, dans lequel le solvant est le F-pentène-2.
18. Le procédé de la revendication 1, dans lequel les corps réagissants sont :



ou :

R_1 est F, Cl, H ou R_4 ; et
 R_3 est F, Cl, H ou R_4 .

- 45 19. Le procédé de la revendication 1, dans lequel la première oléfine fluorée est l'hexafluoropropène (HFP) et la seconde oléfine polyfluorée est le tétrafluoréthylène (TFE).
20. Procédé de la revendication 19, dans lequel on utilise un excès de TFE par rapport à HFP.
- 50 21. Le procédé de la revendication 1, dans lequel utilise un excès de la première oléfine polyfluorée par rapport à la seconde oléfine polyfluorée.
22. Le procédé de la revendication 19, dans lequel le rapport de HFP à TFE varie entre 5:1 et 1:50.
- 55 23. Le procédé de la revendication 22, dans lequel le rapport de HFP à TFE est de 1:2 à 1:50, et dans lequel certaines des oléfines fluorées produites contiennent des nombres pairs d'atomes de carbone.

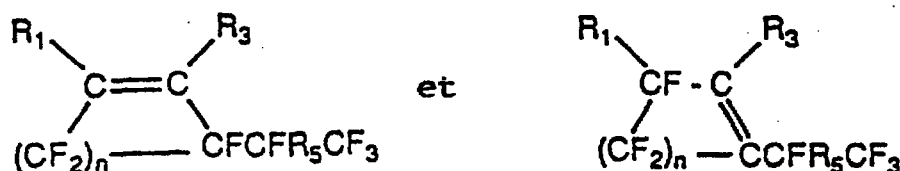


24. Le procédé de la revendication 22, dans lequel le rapport de HFP à TFE est de 2:1 à 1:50 et dans lequel certaines des oléfines fluorées produites comportent une ramification.

25. Le procédé de la revendication 1, dans lequel le catalyseur est AlCl_3 .

26. Le procédé de la revendication 1, dans lequel le catalyseur est AlF_xCl_y , où le nombre total d'atomes d'halogénure x plus y est égal à 3, et où x est de 0 à 2,95 et y est de 3 à 0,05.

27. Compositions isomères des structures :



où R_1 , R_3 , R_5 et n sont tels que définis dans la revendication 1.

28. Mélanges en phase liquide comprenant des oléfines perfluorées de la formule C_mF_{2m} où m est un nombre entier de 9 à 15, tels que préparés par le procédé de la revendication 19.

29. Une composition de la structure $\text{CF}_3\text{CCl}=\text{CClCF}_2\text{CF}_2\text{CF}_3$.

30. Une composition de la structure $\text{CF}_3\text{CF}_2\text{CF}_2\text{CCl}=\text{CClCF}_2\text{CF}_2\text{CF}_3$.