

## EUROPEAN QUALIFYING EXAMINATION 2001

### PAPER B CHEMISTRY

This paper comprises:

- |                                   |                   |
|-----------------------------------|-------------------|
| * Description of the Application  | 2001/B(C)/e/1-9   |
| * Communication                   | 2001/B(C)/e/10    |
| * Document DI (State of the Art)  | 2001/B(C)/e/11    |
| * Document DII (State of the Art) | 2001/B(C)/e/12-13 |

**DESCRIPTION OF THE APPLICATION**

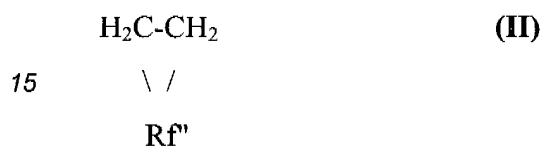
The present invention relates to certain fluorinated hydrocarbons, their preparation by catalytic hydrogenation of appropriate olefins, and to the use of these fluorinated hydrocarbons in cleaning fluids and as working fluids for heat pump systems.

5 The compounds of the present invention are those of the formula



wherein **Rf** is a monovalent fluorinated hydrocarbon radical or the two **Rf** groups taken together  
10 are a divalent fluorinated hydrocarbon radical.

In the latter case, the compounds of the formula (I) are cyclic compounds of the type



where **Rf''** means the divalent fluorinated hydrocarbon radical.

20 Preferred divalent fluorinated hydrocarbon radicals are those of the formula



where n is an integer of at least 2.

25

An example of the monovalent radical **Rf** is the trifluoromethyl radical (ie  $-\text{CF}_3$ ); examples of the divalent fluorinated hydrocarbon radicals **Rf''** are  $-\text{CF}_2-\text{CF}_2-$  and  $-\text{CF}_2-\text{CF}_2-\text{CF}_2-$ .

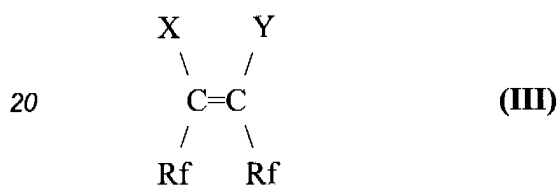
Examples of compounds of formula (I) are

$F_3C-CH_2-CH_2-CF_3$  , ie 1,1,1,4,4,4-hexafluorobutane,

5 
$$\begin{array}{c} H_2C-CH_2 \\ | \quad | \\ F_2C-CF_2 \end{array}$$
 , ie 1,1,2,2-tetrafluorocyclobutane, and

10 
$$\begin{array}{c} H_2C-CH_2 \\ / \quad \backslash \\ F_2C \quad CF_2 \\ \backslash \quad / \\ CF_2 \end{array}$$
 , ie 1,1,2,2,3,3-hexafluorocyclopentane.

15 The compounds of the formula (I) and (II) can be produced by a process which comprises catalytically hydrogenating an olefinic compound of the formula



wherein

25 **X** is hydrogen, fluorine, chlorine, or bromine;  
**Y** is fluorine, chlorine, or bromine; and  
**Rf** is as defined above.

30 Compounds of formula (III) where at least one of the radicals **X** and **Y** is chlorine are preferred because they are more readily available.

Suitable preferred olefinic starting compounds of the formula (III) include, for example, 1,1,1,4,4,4-hexafluoro-2-chloro-2-butene; 1,1,1,4,4,4-hexafluoro-2,3-dichloro-2-butene; 3,3,4,4-tetrafluoro-1-chlorocyclobutene; 3,3,4,4-tetrafluoro-1,2-dichlorocyclo-butene; 3,3,4,4,5,5-hexafluoro-1-chlorocyclopentene; 3,3,4,4,5,5-hexafluoro-1,2-dichloro-cyclopentene; and 1,1,1,4,4,4-hexafluoro-2-bromo-3-chloro-2-butene.

These starting compounds are known in the prior art. They can be synthesised, using, for example, the method according to H. L. Henne et al, J. Am. Chem. Soc., 67, 1235 (1945), and 73, 1103 (1951).

10

Suitable hydrogenation catalysts for the process according to the invention include metals or metal-containing materials. Suitable examples include palladium, platinum and nickel. Preference is given to Raney nickel or palladium on carbon. All the catalysts mentioned above are known and have been described in the prior art, see eg EP-A-0 315 783.

15

In general, the amount of catalyst is not critical. For example, 1 to 100% by weight of catalyst, based on the weight of the compound of formula (III), can be used.

As mentioned above, those compounds of formula (III) where at least one of the radicals X and Y is chlorine are the preferred starting materials. However, the use of such chlorinated starting materials generally gives rise to chlorinated by-products in the reaction mixture. These are difficult to separate from the desired product and are harmful to the ozone layer.

If chlorinated by-products are to be avoided, the process should be conducted in the presence of a base.

Suitable bases for the process according to the invention include a wide range of inorganic and organic basic compounds. Examples of such bases include the oxides, hydroxides, carbonates and bicarbonates of alkali metals and alkaline-earth metals, as well as tertiary amines. Preferred bases include potassium hydroxide, sodium hydroxide, sodium bicarbonate ( $\text{NaHCO}_3$ ), magnesium hydroxide, triethylamine and pyridine.

The bases can be used in various amounts. Preferably, 1.8 to 3 equivalents of base per mole of compound of the formula (III) are used.

The hydrogenation according to the invention can be carried out at various pressures and temperatures. Suitable pressures are 1 to 200 bar and suitable temperatures are 0 °C to 200 °C. Pressures of 1 to 60 bar and temperatures of 20 °C to 60 °C are preferred.

The process according to the invention may be carried out in the presence of a solvent. Suitable solvents include, for example, alcohols such as methanol and ethanol, ethers such as tetrahydrofuran and diglyme, aromatics such as toluene, and alkanolic acids such as acetic acid.

The reaction mixture can, for example, be worked up by first filtering off any solids present and then stripping (ie distilling off) the solvent from the filtrate. It can also be worked up by pouring the reaction mixture freed from the catalyst onto ice water, separating the resulting organic phase, and then fractionally distilling this organic phase.

The process according to the invention has several advantages. For example, the process requires no starting materials and reagents which are difficult to obtain, it affords pure products in good yield, and it provides an economical route to fluorinated, chlorine-free, hydrocarbons.

The present compounds are useful in cleaning fluids and as working fluids for heat pumps. Working fluids for heat pumps are fluid media in heat pumps which absorb heat while evaporating and give off heat while condensing.

The boiling points of the preferred compounds are as follows:

Compound of the formula	Chemical name	Boiling point
Rf-CH <sub>2</sub> -CH <sub>2</sub> -Rf ( <b>I</b> )		at 1013 hPa
-----		
5 (a) each Rf = -CF <sub>3</sub>	1,1,1,4,4,4-hexafluorobutane	25-26 °C
(b) both Rf taken together are a divalent radical Rf'		
10 of the formula		
-CF <sub>2</sub> -CF <sub>2</sub> -	1,1,2,2-tetrafluorocyclobutane	50-51 °C
-CF <sub>2</sub> -CF <sub>2</sub> -CF <sub>2</sub> -	1,1,2,2,3,3-hexafluorocyclopentane	87-88 °C
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15 For some applications the boiling point of 1,1,2,2,3,3-hexafluorocyclopentane is too high. We found out that this compound forms azeotropic mixtures with lower alkanols (ie C<sub>1</sub>- to C<sub>4</sub>- alkanols). The boiling points of these mixtures are considerably lower than that of the pure 1,1,2,2,3,3-hexafluorocyclopentane.

20 An azeotrope is an admixture of two or more liquid compounds which has a constant boiling point and behaves like a single substance in that the vapor produced by partial evaporation or distillation has the same composition as the liquid, ie the admixtures distil without a substantial change in composition.

25 Azeotropes which are mixtures of 1,1,2,2,3,3-hexafluorocyclopentane with an alcohol selected from the group consisting of methanol and ethanol are preferred.

The composition may be defined as an azeotrope of its components, say component A and component B, since the very term "azeotrope" is at once both definitive and limitive, requiring that effective amounts of A and B form this unique composition of matter which is an admixture having a constant boiling point. The composition of an azeotrope of A and B varies depending on temperature and/or pressure. Therefore, compositional ranges, rather than fixed compositions, are often used to define azeotropes.

In accordance with this invention, compositions which are binary mixtures of from 65 to 75 weight percent 1,1,2,2,3,3-hexafluorocyclopentane and from 35 to 27 weight percent methanol are characterized as azeotropes in that mixtures within this range exhibit a substantially constant boiling point. Also, in accordance with this invention, compositions which are binary mixtures of  
5 from 71 to 79 weight percent 1,1,2,2,3,3-hexafluorocyclopentane and from 29 to 21 weight percent ethanol are characterized as an azeotrope in that mixtures within this range exhibit a substantially constant boiling point.

1,1,2,2,3,3-hexafluorocyclopentane, its azeotropes with methanol and ethanol, and other mixtures  
10 of this invention are useful eg as working fluids in heat pumps and as fluids for cleaning solid surfaces. Applications include the removal of flux and flux residues from printed circuit boards.

The compositions of the invention may be used as solvents in conventional apparatus, employing conventional operating techniques. The cleaning action of the solvent may be enhanced by  
15 conventional means (eg heating, agitation, etc.). In some applications (eg removing certain tenacious fluxes from soldered components) it may be advantageous to use ultrasound in combination with the solvent.

The azeotropes of the present invention permit easy recovery and reuse of the solvent from  
20 defluxing operations because of their azeotropic nature. As an example, compositions provided in accordance with this invention can be used in cleaning processes such as those described in US-A-3 881 949 and US-A-4 715 900.

The azeotropes of the instant invention can be prepared by any convenient method including  
25 mixing or combining the desired amounts of the components. A preferred method is to weigh out the desired amount of each component and thereafter to combine them in an appropriate container.

### Example 1

In a stainless steel autoclave, 40 g of 1,1,1,4,4,4-hexafluoro-2-chloro-2-butene in 300 ml of ethanol were hydrogenated with hydrogen in the presence of 12 g of potassium hydroxide and 25 g of Raney nickel for 3 hours at 20 °C and another hour at 100 °C at a pressure of from 30 to 40 bar. The solid components were then removed from the reaction mixture by filtration and the remaining liquid was distilled to give 16 g of 1,1,1,4,4,4-hexafluorobutane having a boiling point of 25 °C - 26 °C at 1013 mbar. The mass spectrum showed the molecular ion at m/e 166.

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### Example 2

In a 1.3 l stainless steel autoclave, 245 g (1 mol) of 1,2-dichloro-3,3,4,4,5,5-hexafluoro-cyclopentene were hydrogenated at 60 °C to 70 °C with the addition of 202 g (2 mol) of triethylamine in 200 ml of toluene and in the presence of 20 g of Raney nickel. Over a period of 12 hours, the theoretical amount of hydrogen was absorbed at a hydrogen pressure of 40 to 50 bar. The reaction mixture was filtered and the methanolic solution was diluted with 400 ml of water. The lower organic phase was separated, washed with 100 ml of 5% aqueous hydrochloric acid, and dried over sodium sulphate. Distillation gave 107 g (60% yield) of 1,1,2,2,3,3-hexafluorocyclopentane having a boiling point of 87 °C - 88 °C at 1013 mbar. The mass spectrum showed the molecular ion at m/e 178.

20

### Example 3

Example 2 was repeated with the exception that the 1,2-dichloro-3,3,4,4,5,5-hexafluoro-cyclopentene was replaced by 197 g (1 mol) of 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene. Distillation gave 69 g (54% yield) of 1,1,2,2-tetrafluorocyclobutane having a boiling point of 50 °C - 51 °C at 1013 mbar. The mass spectrum showed the molecular ion at m/e 128.

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Example 4

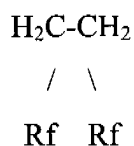
25 grams of 1,1,2,2,3,3-hexafluorocyclopentane and 10 grams of methanol were combined and the mixture was distilled using a tube column of the type commercially available from Ace Glass of Vineland, N.J. A constant boiling azeotrope was formed which had a boiling point of 61.1 °C. Gas chromatographic analysis showed the azeotrope consisted of 69.4% of 1,1,2,2,3,3-hexafluorocyclopentane and 30.6% of methanol by weight.

10 Example 5

10 grams of 1,1,2,2,3,3-hexafluorocyclopentane and 2 grams of ethanol were combined in a flask and distilled using a tube column of the type commercially available from Ace Glass of Vineland, N.J. A constant boiling azeotrope was formed which had a boiling point of 71 °C. Gas chromatographic analysis showed the azeotrope consisted of 75.4% 1,1,2,2,3,3-hexafluorocyclopentane and 24.6% ethanol by weight

**Claims**

1. Compounds of the formula



wherein **Rf** is a monovalent fluorinated hydrocarbon radical or the two **Rf** groups taken together are a divalent fluorinated hydrocarbon radical.

2. A process for preparing the compounds of claim 1, which process comprises catalytically hydrogenating an olefinic compound of the formula



wherein **X** is hydrogen, fluorine, chlorine, or bromine; **Y** is fluorine, chlorine, or bromine; and **Rf** is defined as above.

3. A process according to claim 2 wherein the olefinic compound is 1,1,1,4,4,4-hexafluoro-2-chlorobutene; 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene; 3,3,4,4,5,5-hexafluoro-1,2-dichlorocyclopentene; 1,1,1,4,4,4-hexafluoro-2,3-dichlorobutene; or 1,1,1,4,4,4-hexafluoro-2-bromo-3-chlorobutene.

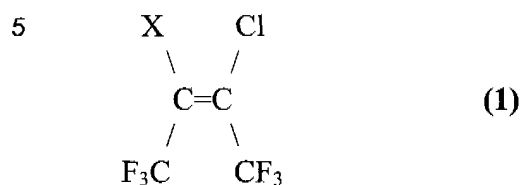
## COMMUNICATION

1. The subject-matter of claims 1 to 3 is not novel. See document **DI** which describes the hydrogenation of compounds of present formula **(III)** to yield 1,1,1,4,4,4-hexafluorobutane; see also document **DII** which discloses the hydrogenation of compounds of present formula **(III)** to yield 1,1,2,2,3,3-hexafluorocyclopentane. Each of the documents thus discloses the subject-matter of present claims 1 to 3.
2. If you wish to maintain the application, you are invited to submit claims which take the aforementioned objections into account and comply with the requirements of the EPC, especially with regard to novelty, inventive step, clarity, disclosure in the application as originally filed and, if necessary, unity (Art. 54 (1) and (2), 56, 84, 123 (2) and 82 EPC).
3. In your reply, you should also identify the difference between the new claims and the state of the art and its significance, and present the invention in such a way that both the technical problem to be solved vis-à-vis the state of the art and the solution found (see Rule 27(1)(c) EPC and Guidelines C-IV, 9.5), as well as your position on the question of inventive step, can be understood.
4. According to the Guidelines (C-III, 4.4) an independent claim should specify clearly all the essential features needed to define the invention, ie each independent claim must indicate all the features necessary to solve the problem on which the invention is based.
5. Your attention is drawn to the fact that the application may not be amended in such a way that its subject-matter extends beyond the content of the application as filed (Art. 123(2) EPC). Therefore, and also in view of the Guidelines E-II, 1 and C-VI, 5.4, you should explain from where in the original application documents the new features in any newly formulated claim have been directly and unambiguously derived.
6. It is suggested not to file an adapted description until the Examining Division has indicated that the amended claims are allowable.

**DOCUMENT DI (State of the Art)**

Palladium-catalyzed hydrogenation of fluoroalkenes

Fluoroalkenes of the formula



where X means H (compound **(1a)**) or Cl (compound **(1b)**) were hydrogenated over Pd/C in methanol or ethanol as the solvent to give mixtures of  $\text{F}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CF}_3$  (**(2)**) and  $\text{F}_3\text{C}-\text{CH}_2-\text{CHCl}-\text{CF}_3$  (**(3)**). The hydrogenation of compound **(1a)** yielded a mixture containing 84 mole % of **(2)** and 16 mole % of **(3)**. **(2)** was isolated by means of high performance liquid chromatography (HPLC). Boiling point: 25 °C.

**DOCUMENT DII (State of the Art)**

The present application relates to a new fluorine-substituted hydrocarbon compound, a process for making it and its use in cleaning compositions or as working fluids in heat pumps.

5 Various organic solvents have been used as cleaning liquids for the removal of contaminants from contaminated articles and materials. Certain fluorine containing organic compounds such as 1,1,2-trichloro-1,2,2-trifluoroethane are useful for cleaning organic polymers and plastics which may be sensitive to other more common and more powerful solvents such as trichloroethylene or perchloroethylene. Recently, however, there have been efforts to reduce the use of certain compounds such as trichlorotrifluoroethane because of their potential to deplete ozone.

10

A novel fluorohydrocarbon compound, 1,1,2,2,3,3-hexafluorocyclopentane is provided in accordance with this invention. The designation of this compound in conventional nomenclature for halogen-substituted hydrocarbons containing fluorine is C456ff. C456ff may be prepared by mixing together 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene (available commercially), Raney nickel or Pd on 15 carbon (commercially available catalysts), and excess hydrogen gas and reacting the mixture at a temperature of 0° C to 200 °C and a pressure of from 1 bar to 60 bar for from about 5 to 30 hours. The hydrogenation may take place in a solvent. It can be carried out in a pressure vessel such as an autoclave. Generally, after completion of the reaction, the crude product is filtered to remove the catalyst, washed with water, treated with magnesium sulfate to remove excess water, then distilled to 20 give C456ff. The product contained traces of 1,1,2,2,3,3-hexafluoro-5-chloro-cyclopentane. C456ff is a liquid under normal conditions and is useful as a solvent for cleaning contaminants from solid substrates.

C456ff is useful in a wide variety of processes for cleaning solid surfaces. Applications include 25 removal of flux and flux residues from printed circuit boards.

C456ff may be used as a solvent in conventional apparatus, employing conventional operating techniques. The cleaning action of this solvent may be enhanced by conventional means (eg heating, agitation, etc.). In some applications (eg removing certain tenacious fluxes from soldered components) it may be advantageous to use ultrasound in combination with the solvent.

5

### Example

1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene (215 g) was added to a 400 ml autoclave along with 5% palladium on carbon (1 g). The autoclave was cooled, evacuated, and pressurized with  
10 hydrogen to 4.5 bar at room temperature. It was then heated to 100 °C, and the hydrogen pressure was adjusted to 35 bar. It was held at 100 °C for 12 hours with periodic additions of hydrogen to maintain a pressure of 35 bar. The autoclave was then cooled and bled of excess hydrogen. The product was filtered to remove the catalyst, washed with 20 ml of water, and dried over MgSO<sub>4</sub>. This reaction gave approximately 10 ml of clear liquid. GC/IR: 2900 m, 1190 vs. Mass Spect.:  
15 178 (molecular ion), 95 and 64 (major peaks).

### **Claims**

1. 1,1,2,2,3,3-hexafluorocyclopentane
2. A process for cleaning a solid surface which comprises treating said surface with a composition comprising an effective amount of 1,1,2,2,3,3-hexafluorocyclopentane.
3. The process of claim 2 wherein the solid surface is a printed circuit board contaminated with flux and flux residues.
4. Use of 1,1,2,2,3,3-hexafluorocyclopentane as a working fluid or as a component in working fluids in heat pump systems.