(12) UK Patent Application (19) GB (11) 2 056 445 A

(21) Application No **8024976**
(22) Date of filing **30 Jul 1980**
(30) Priority data
(31) **54/102749**
(32) **14 Aug 1979**
(33) **Japan (JP)**
(43) Application published
18 Mar 1981
(51) **INT CL³**
C07C 53/50
(52) Domestic classification
C2C 20Y 21X 304 311 315 316 31X 31Y 364 366 36Y 410 41Y 443 444 449 44X 500 50Y 565 567 607 624 628 634 659 65Y 73Y 771 AB CW HJ YC
(56) Documents cited
None
(58) Field of search
C2C
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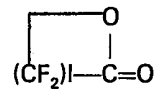
(54) **Iodoacyl fluorides**

(57) An ω-iodoacyl fluoride having the formula

$$ICF_2CF_2O(CF_2)_nCOF$$

(n is an integer from 1 to 8) is produced by reacting a perfluorolactone having the formula



(l is the same as n and is an integer of 2 to 4) and/or a perfluorodiacyl fluoride having the formula

$$FOC(CF_2)_{m-1}COF$$

(m is the same as n and is an integer of 1 to 8) as a starting material with tetrafluoroethylene in an addition reaction in the presence of a fluorine anion source and an iodine source in an aprotic polar solvent.

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SPECIFICATION

Process for producing ω-iodoacyl fluoride

The present invention relates to a process for producing an ω-iodoacyl fluoride. More particularly, it relates to a novel process for producing an ω-iodoacyl fluoride having a group of formula ICF_2CF_2O— which is convertible into a perfluorovinyl ether group (CF_2=CFO—) by a de-IF reaction.

The ω-iodoacyl fluoride having the formula

$$ICF_2CF_2O(CF_2)_nCOF$$

(n is an integer of 1 to 8) which is produced by the process of the present invention is remarkably useful as an intermediate which can be convertible into various useful fluorinated compounds by utilizing the reactivity of the terminal groups of —I and —COF.

For example, this compound can be converted into a perfluorovinyl ether, having an ester group and having the formula:

$$CF_2=CFO(CF_2)_n—COOR$$

(n is defined above and R represents a C_1—C_{10} straight or branched alkyl group) by a de-IF reaction and an esterification. The resulting vinyl ether is useful as a main source for polymers having the ester group in a side chain.

The ω-iodoacyl fluoride can be used as a telogen in a telomerization with a perfluoroalkenexide or a fluoroolefin as a taxogen or can be used in a deiodocoupling reaction as a source for producing inert liquids useful as functional oils and insulating oils having high heat resistance and high chemical resistance.

As a process for producing ω-iodoacyl fluoride having a terminal group of formula ICF_2CF_2O—, it has been proposed to react difluoroiodoacetyl fluoride as a starting material with tetrafluoroethyleneoxide (British Patent No. 1,038,190).

The known process can not be used for producing a compound having the formula

$$ICF_2CF_2O(CF_2)_nCOF$$

wherein n is 2 or more. In the process for producing perfluoro(3-oxa-5-iodopentanoyl fluoride) having the formula

$$ICF_2CF_2OCF_2COF$$

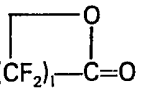
difluoroiodacetyl fluoride having an iodine atom has to be used as the starting material. Therefore, it is not easy to carry out the reaction smoothly during the addition of tetrafluoroethyleneoxide and it is not possible to prevent side reactions producing compounds having different members of molecules of tetrafluoroethyleneoxide added.

The inventors have studied the above-mentioned problems and ways of overcoming them and have found that ω-iodoacyl fluoride can be obtained in high yield by a reaction of a specific perfluorolactone and/or a perfluorodiacyl fluoride with tetrafluoroethylene.

The present invention provides a process for producing an ω-iodoacyl fluoride having the formula

$$ICF_2CF_2O(CF_2)_nCOF$$

wherein an integer from 1 to 8 which comprises reacting a perfluorolactone having the formula



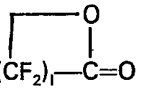
(l is the same as n and is an integer of 2 to 4) and/or a perfluorodiacyl fluoride having the formula

$$FOC(CF_2)_{m-1}COF$$

(m is the same as n and is an integer of 1 to 8) as a starting material with tetrafluoroethylene in an addition reaction in the presence of a fluorine anion source and an iodine source in an aprotic polar solvent.

It is important to use the specific perfluorolactone and/or perfluorodiacyl fluoride defined above as the starting material.

The perfluorolactones used in the process of the present invention are compounds having the formula



(l is an integer from 2 to 4).

These perfluorolactones can be produced by reacting C_3—C_5 α,ω-diiodperfluoroalkane with an oxidizing acid such as fuming sulfuric acid. (Japanese Unexamined Patent Publication No. 23020/1977) or by reacting a fluorinated compound having the formula

$$I(CF_2)_lCOX$$

(l is as defined above; X represents a halogen atom or a group of formula —OR or —NR^1R^2 wherein R, R^1 and R^2 each represent a hydrogen atom or a C_1—C_{10} alkyl group) with an oxidizing acid such as a fuming sulfuric acid. (Japanese Unexamined Patent Publication No. 39665/1977.)

The perfluorodiacyl fluorides used in the present invention are compounds having the formula

$$FOC(CF_2)_{m-1}COF$$

(m is an integer from 1 to 8).

These diacyl fluorides can be produced by reacting α,ω-diiodoperfluoralkane having the formula

$I(CF_2)_{m+1}I$

with an oxidizing acid. (Japanese Unexamined Patent Publication No. 23020/1977), or by fluorinating a corresponding hydrocarbon-type diacyl halide by electrolysis.

From the viewpoint of easy availability of starting materials and usefulness of the products, it is preferable to use perfluoro-γ-butyrolactone and/or perfluorosuccinyl fluoride or oxalyl difluoride as the starting material, thus producing perfluoro (5-oxa-7-iodoheptanoyl fluoride).

In the process of the present invention, it is preferable to carry out the addition reaction under substantially anhydrous conditions. When water is present in the reaction, hydrolysis of the —COF group occurs as a side-reaction and lowers the yield of the desired acyl fluoride.

In the process of the present invention, it is important to carry out the addition reaction in an aprotic polar solvent. In a protic solvent, a hydrogen extraction reaction occurs which decreases the yield of ω-iodoacyl fluoride. In a non-polar solvent, the required fluorine anion is not separated from its source so that the reaction cannot proceed.

Suitable solvents include sulfolane, diglyme, tetraglyme, dimethylformamide, dimethylsulfoxide, dioxane and benzonitrile. The solvent is usually used of 5 : 1 to 50 : 1 preferably 3 : 1 to 10 : 1 by weight based on the starting material.

The fluorine anion sources suitable for use in the present invention include alkali metal fluorides, ammonium fluoride and silver fluoride. From the point of view of reactivity and commercial availability, it is preferable to use an alkali metal fluoride such as potassium fluoride. When oxalyl fluoride is used as the starting material, a high yield of the desired product can be provided by using a combination of an alkali metal fluoride and silver fluoride. In such a case, it is preferable to incorporate a crown ether such as 18-crown-6, dicyclohexyl-18-crown-6 or dibenzo-18-crown-6 which increases the yield. The fluorine anion source is preferably used as a molar ratio of 0.2 : 1 to 5 : 1 based on the starting material.

The iodine sources used in the process of the present invention are preferably iodine itself or an iodine halide such as iodine chloride or iodine bromide.

The iodine source is preferably used at a molar ratio of 0.2 : 1 to 5 : 1 based on the starting material.

The addition reaction of the present invention can be carried out under various conditions and in various ways. It is preferable to select the conditions for the reaction according to the type of starting material used and the product to be obtained.

A reaction temperature is usually in the range of −20°C to +150°C preferably 0°C to 100°C in order to give a smooth reaction.

The pressure at which tetrafluoroethylene is changed into the system is preferably in the range of 0 to 20 kg/cm^2 gauge.

The fluorine anion source, the solvent, the starting material, the iodine source and tetrafluoroethylene are preferably charged in this order with thorough stirring in each stage, to increase the yield.

The reaction time is usually in a range of 5 to 50 hrs., preferably 8 to 20 hrs.

The recovery of the product from the reaction mixture can be carried out by any suitable conventional method. A process comprising fine distillation followed by a simple distillation is found to be particularly suitable.

The present invention will be illustrated by the following examples which are provided for purposes of illustration only and are not construed as limiting the scope of the present invention.

EXAMPLE 1

In a 200 ml autoclave lining with Hastelloy steel which was dried, 9.0 g of potassium fluoride dried by heating it at 450°C for 5 hrs. was charged and evacuated and then, 100 g of diglyme dried with molecular sieve was charged under a reduced pressure and the mixture was stirred at the ambient temperature for 1 hr. Then, 2.96 g of perfluoro-γ-butyrolactone was charged and the mixture was stirred for about 8 hrs. at the ambient temperature and then the reactor was released under nitrogen gas flow, and 78.5 g of solid iodine was charged. The reactor was cooled to −30°C and evacuated.

The temperature in the reactor was raised to the ambient temperature. The mixture was stirred for 1 hr. Tetrafluoroethylene was fed through a holder connected to the reactor into the reactor. Tetrafluoroethylene was additionally fed into the reactor so as to maintain the pressure of 0 to 2 kg/cm^2 gauge and the mixture was continuously stirred for 15 hrs. at the ambient temperature to carry out the addition reaction. During the reaction 19.9 g of tetrafluoroethylene was fed.

According to a gas chromatography and a ^{19}F—NMR spectrum analysis, it was confirmed that the reaction mixture includes 46.1 g of perfluoro(5-oxa-7-iodoheptanoyl fluoride) was the object product and 1.2 g of 1,4-bis(2-iodotetrafluoroethoxy)perfluorobutane $(ICF_2CF_2OCF_2CF_2)_2$ and 0.6 g of 1,2-diiodoperfluoroethane (ICF_2CF_2I) as by-products.

The reaction mixture was simply distilled to separate a fraction containing most of the object product from most of the solvent and the unreacted iodine and then, the object product was finely distilled to obtain 42.0 g of perfluoro(5-oxa-7-iodoheptanoyl fluoride) having a purity of 99%.

The resulting perfluoro(5-oxa-7-iodoheptanoyl fluoride) was a transparent liquid having a boiling point of 50°C/80 mmHg. The product was identified by the following data.

Elementary Analysis:

$C_5F_{11}O_2I$

	C	F	I
Found (%)	16.42	47.91	28.94
Calculated (%)	16.38	47.50	28.84

IR Spectrum:

The absorption for —COF group was observed at $1880^{cm^{-1}}$.

^{19}F—NMR Spectrum:

(a) (b) (c) (d) (e) (f)

$ICF_2CF_2OCF_2CF_2CF_2COF$

Chemical shifts of ^{19}F-nuclear (based on CCl_3F: solvent of $CDCl_3$)

(a) −65.4 ppm;
(b) −83.9 ppm;
(c) −85.8 ppm;
(d) −127.0 ppm;
(e) −118.9 ppm;
(f) +24.7 ppm.

EXAMPLE 2

In accordance with the process of Example 1, an addition reaction was carried out by charging 71.8 g of potassium fluoride, 66.3 g of diglyme, 194.3 g of perfluoro-γ-butyrolactone and 524 g of iodine in a 1.5 liter autoclave made of stainless steel and feeding 118.0 g of tetrafluoroethylene under a pressure of 3 to 5 kg/cm^2 gauge at a reaction temperatore of 0°C.

As a result, 333 g of perfluoro(5-oxa7-iodoheptanoyl fluoride), 15.7 g of 1,4-bis(2-iodotetrafluoroethoxy) perfluorobutane and 30.4 g of 1,2-diiodoperfluoroethane were obtained.

EXAMPLE 3

In accordance with the process of Example 1, an addition reaction was carried out by charging 13.5 g of potassium fluoride, 100 g of diglyme, 30.7 g of perfluoro-γ-butyrolactone and 78.5 g of iodine and feeding 18.2 g of tetrafluoroethylene under a pressure of 3 to 5 kg/cm^2 gauge at a reaction temperature of 0°C. As a result, 41.0 g of perfluoro(5-oxa-7-iodoheptanoyl fluoride), 4.0 g of 1,4-bis(2-iodotetrafluoroethoxy) perfluorobutane and 5.7 g of 1,2-diiodoperfluoroethane were obtained.

EXAMPLE 4

In accordance with the process of Example 1, an addition reaction was carried out except using 30.0 g of perfluorosuccinyl fluoride instead of perfluoro-γ-butyrolactone and feeding 11.2 g of tetrafluoroethylene under a pressure of 0—1 kg/cm^2 gauge for 7 hrs. As a result, 21.2 g of perfluoro(5-oxa-7-iodoheptanoyl fluoride), 1.0 g of 1,4-bis(2-iodotetrafluoroethoxy) perfluorobutane and 0.4 g of 1,2-diiodoperfluoroethane were obtained.

EXAMPLE 5

In accordance with the process of Example 1, an addition reaction was carried out except using 30.0 g of a mixture of perfluoro-γ-butyrolactone and perfluorosuccinyl fluoride at a molar ratio of 85 : 15 instead of perfluoro-γ-butyrolactone and feeding 20.0 g of tetrafluoroethylene for 10 hrs.

As a result, 45.2 g of perfluoro(5-oxa-7-iodoheptanoyl fluoride), 1,4-bis(2-iodotetrafluoroethoxy) perfluorobutane and 0.6 g of 1,2-diiodoperfluoroethane were obtained.

EXAMPLE 6

In a 200 ml autoclave made of stainless steel, 25.0 g of potassium fluoride dried at 450°C for 5 hrs. was charged and evacuated and 100 g of tetraglyme dried with molecular sieve was charged in suction and the mixture was stirred for about 1 hr. at the ambient temperature and then 19.9 g of oxalyl fluoride was charged and the mixture was stirred for 1 day at the ambient temperature. The pressure in the reactor was released under nitrogen gas flow and 110 g of solid iodine and 27.0 g of silver fluoride were charged. The reactor was cooled to −30°C and evacuated.

The temperature in the reactor was raised to the ambient temperature and the mixture was stirred for 1 hr. and heated to 70°C. Tetrafluoroethylene was fed through a holder connected to the reactor into the reactor. Tetrafluoroethylene was additionally fed into the reactor so as to maintain the pressure of 13 to 15 kg/cm^2 gauge and the mixture was stirred at 70°C for about 10 hrs. to perform the addition reaction. During the reaction, 45 g of tetrafluoroethylene was fed.

The reaction mixture was distilled to separate about 4 g of perfluoro(3-oxa-5-iodopentanoyl fluoride)($ICF_2CF_2OCF_2COF$). The compound is a pale pink liquid having a boiling point of 26 to 27°C/100 mmHg which was identified by the following data of the GC—MS analysis.

GC—MS Data:

M peak:	340
(M—I) peak:	213($FOCCF_2OCF_2CF_2$)
	227(ICF_2CF_2)
	97(CF_2COF)
	47(COF).

EXAMPLE 7

In a 1.5 l autoclave made of stainless steel, 190 g of a dry potassium fluoride and 25 g of dicyclohexyl-18-crown-6 were charged and evacuated and 850 ml of dried tetraglyme was charged in suction and the mixture was stirred at the ambient temperature for about 1 hr. and then, 160 g of oxalyl fluoride was charged and the mixture was stirred. The reactor was released under nitrogen gas flow and 950 g of solid iodine and 65 g of silver fluoride was charged. The reactor was cooled at −30°C and evacuated and then heated to the ambient temperature and the mixture was stirred for about 1 hr.

An addition reaction was carried out at a reaction temperature of 40 to 42°C by feeding

350 g of tetrafluoroethylene under a pressure of 5 to 6 kg/cm^2 gauge for 6 hrs.

The unreacted tetrafluoroethylene was discharged and the reaction mixture was analyzed by a gas chromatography. It was confirmed a conversion of oxalyl fluoride was 60.4% and 37.2 g of perfluoro(3-oxa-5-iodopentanoyl fluoride), 147.9 g of 1,2-bis(2-iodotetrafluoroethoxy) perfluoroethane and 35.6 g of 1,2-diiodoperfluoroethane were obtained.

EXAMPLE 8

In a 200 ml autoclave made of Hastelloy C, 5.5 g of a dry potassium fluoride was charged and evacuated and 100 g of dried tetraglyme was charged in suction and the mixture was stirred at the ambient temperature for about 1 hr. and 30 g of perfluorosuberic fluoride was charged and the mixture was stirred for about 8 hrs. The reactor was released under nitrogen gas flow and 39 g of solid iodine was charged. The reactor was cooled to −30°C and evacuated and then heated to the ambient temperature and the mixture was stirred for about 1 hr.

An addition reaction was carried out at a reaction temperature of 0 to 5°C by feeding 10.0 g of tetrafluoroethylene under a pressure of 0 to 2 kg/cm^2 gauge for 8 hrs. After the reaction, the reaction mixture was distilled to obtain 10 g of a fraction containing perfluoro(9-oxa-11-iodoundecanoyl fluoride) ($ICF_2CF_2O(CF_2)_7COF$) as a main component which had a boiling point of 69—71°C/40 mmHg.

The compound was identified by the following data of the GC—MS analysis.

GC—MS Data:

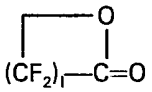
M peak:	640
(M—I) peak:	513 ($FOC(CF_2)_7OCF_2CF_2$)
	227 (ICF_2CF_2)
	97 (CF_2COF)
	47 (COF).

CLAIMS

1. A process for producing ω-iodoacyl fluoride having the formula

$$ICF_2CF_2O(CF_2)_nCOF$$

wherein n is an integer from 1 to 8 which comprises reacting a perfluorolactone having the formula



(l is the same as n and is an integer of 2 to 4) and/or a perfluorodiacyl fluoride having the formula

$$FOC(CF_2)_{m-1}COF$$

(m is the same as n and is an integer of 1 to 8) as a starting material with tetrafluoroethylene in an addition reaction in the presence of a fluorine anion source and an iodine source in an aprotic polar solvent.

2. A process according to Claim 1 wherein perfluoro(5-oxa-7-iodoheptanoyl fluoride) is produced by using perfluoro-γ-butyrolactone and/or perfluorosuccinyl fluoride as the starting material.

3. A process according to Claim 1 wherein perfluoro (3-oxa-5-iodopentanoyl fluoride) is produced by using oxalyl fluoride as the starting material.

4. A process according to Claim 3 wherein the fluorine anion source is a combination of an alkali metal fluoride and silver fluoride.

5. A process according to Claim 4 wherein a crown ether is incorporated in the reaction mixture.

6. A process according to Claim 1 or Claim 2 wherein the fluorine anoine source is selected from alkali metal fluorides, ammonium fluoride and silver fluoride.

7. A process according to any preceding Claim wherein the addition reaction is carried out under substantially and anhydrous conditions.

8. A process according to any preceding Claim wherein the iodine source is iodine or an iodine halide.

9. A process according to Claim 1 substantially as herein described with reference to any one of the examples.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.