United States Patent Office 3,471,484
Patented Oct. 7, 1969

3,471,484

PERFLUORINATED BETA AMINO PROPIONIC ACID FLUORIDES

Richard A. Guenthner, Birchwood, Minn., assignor to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware

No Drawing. Filed May 3, 1965, Ser. No. 452,845
Int. Cl. C07d 87/28, 51/62, 93/10
U.S. Cl. 260—247.2 7 Claims

ABSTRACT OF THE DISCLOSURE

Perfluoro di-N-substituted beta amino propionic acid fluorides are provided by the electrochemical fluorination of di-N-substituted beta amino acid halides.

This invention relates to a process for electro-chemically fluorinating carboxylic acid halides, and to the perfluorinated products resulting therefrom.

In one aspect, the invention relates to the electro-fluorination of di-N-substituted beta amino propionic acid halides in a current-conducting electrolyte solution of anhydrous liquid hydrogen fluoride in a cell containing an electrode pack.

In another aspect, the invention relates to perfluoro (di-N-substituted beta amino propionyl acid fluorides) and derivatives thereof.

The conventional process of producing fluorinated carboxylic acid fluorides from hydrocarbon acid halides is characterized by relatively low yields of perfluorinated carboxylic acid fluoride products because of cyclization and associated chain fragmentation or cleavage and sludge formation on the electrodes of the cell. The art has long sought techniques for selectively controlling the electrofluorination reaction to produce high yields of perfluorinated carboxylic acid fluoride compounds. The present invention provides a new class of the desired perfluorinated compounds which are nitrogen substituted on the beta carbon (relative to the carbonyl group), and a process for producing same.

The general electrochemical process utilized in the present invention is disclosed in Simons U.S. Patent No. 2,519,983; Scholberg et al. U.S. Patent No. 2,717,871; Brice et al. U.S. Patent No. 2,732,398; and pages 417–18 of the book entitled Fluorine Chemistry, volume I, edited by J. H. Simons, published by Academic Press, Inc., 1950. This process utilizes an electrode pack comprising alternating and closely-spaced iron cathode plates and nickel anode plates. Although the theoretical voltage required to obtain fluorine from anhydrous hydrogen fluoride is given in the literature to be 2.77 volts, the processes of this invention are carried out at voltages typically in the range from about 4 to 8 volts direct current, though higher voltages can be employed. The direct current employed can conveniently be in the range of from about 5 to 35 amperes, though those skilled in the art will appreciate that the amperage can be as high as 40,000 amperes or higher in large scale commercial electrolytic cells; the amperage used in any given cell is a function of the size of the cell. A cell can be operated substantially at atmospheric pressures using temperatures ranging from about 0° C. to about 40° C., or at higher temperatures and pressures as those skilled in the art will appreciate.

An object of this invention is to provide a new class of perfluorinated carboxylic acid fluorides.

Another object of this invention is to provide a class of compounds as above described which are perfluoro-di-N-substituted beta amino propinyl acid fluorides).

Another object of this invention is to provide derivatives of the above described class of compounds.

Another object of this invention is to provide a class of compounds having surfactant and other utility made by electrofluorinating di-N-substituted beta amino propionyl halides.

Another object of the present invention is to provide an improvement in the electrochemical process for the production of perfluorinated carboxylic acid fluorides.

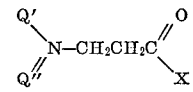
Another object of this invention is to increase the yield of perfluorinated carboxylic acid fluoride obtainable from the electrochemical cell.

Various other objects and advantages of the present invention will become apparent to those skilled in the art from the accompanying description and disclosure.

The present invention resides in the use of carboxylic acid halides substituted by nitrogen in the gamma position (i.e. nitrogen substituted on the beta carbon atom relative to the carbonyl group) and having only methylene groups between the said radical and the nitrogen atom as starting compounds for introduction into the electrochemical cell as described above. Specifically, it has now been discovered that, when a nitrogen atom is so substituted in a carboxylic acid halide before electrofluorination, yields, of the corresponding perfluorinated acid fluorides are unexpectedly increased with minimum cyclization and cleavage.

A preferred class of starting compounds for use in the present invention are di-N-substituted beta amino propionic acid halides of the formula:

(1)



where:

X is halogen;

Q′ can be a straight or branched chain alkyl radical of less than 9 carbon atoms, a cycloalkyl radical of less than 9 carbon atoms, a lower alkylcycloalkyl radical of less than 9 carbon atoms, a phenyl radical, an alkaryl radical of less than 9 carbon atoms, an aralkyl radical of less than 9 carbon atoms;

Q″ can be a straight or branched chain alkyl radical of less than 19 carbon atoms, a cycloalkyl radical of less than 9 carbon atoms, a lower alkylcycloalkyl radical of less than 9 carbon atoms, a phenyl radical, an alkaryl radical of less than 9 carbon atoms, an aralkyl radical of less than 9 carbon atoms, and an ethylene carbonyl halide; and

Q′ and Q″ taken together can be an alkylene diradical whose chain portion is formed by at least 4 and less than 7 carbon atoms, an alkylene oxide diradical whose chain portion is formed by at least 4 and less than 6 carbon atoms, an alkylene sulfide diradical whose chain portion is formed by at least 4 and less than 6 carbon atoms, an alkylene sulfone diradical whose chain portion is formed by at least 4 and less than 6 carbon atoms, and diethylene gamma amino propionyl halide diradical.

In the foregoing definitions of Formula 1 it will be appreciated that when Q′ and Q″ are taken together they form together with the nitrogen atom between them (shown in Formula 1) the indicated various types of heterocyclic diradicals all of which contain the nitrogen atom of Formula 1 as one member of the ring. The alkylene portions of these heterocyclic ring structures can contain one or two alkyl branches substituted on ring carbon atoms such alkyl branches contain one or two carbon atoms each.

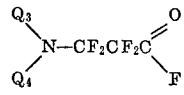
A more preferred class of starting compounds consists of those compounds of Formula 1 where Q′ and Q″ are each a lower alkyl radical (i.e. one containing less than 5 carbon atoms) and Q′ and Q″ together with the

nitrogen atom between them form a morpholine or a piperazine ring structure.

The organic starting material may suitably be initially present in a mixture in the electrolytic solution of hydrogen fluoride in an amount ranging from about 1 to 20 percent by weight. Both the organic starting material and the conventional hydrogen fluoride electrolyte are replenished from time to time as utilized. The exit gas mixture is passed through a refrigerated condenser to condense out most of the hydrogen fluoride vapors that are evolved, and the liquefied hydrogen fluoride is then drained back into the cell.

After being subjected to electrofluorination in accordance with the teachings of this invention, the corresponding perfluoro (di-N-substituted beta amino propionic acid fluorides) are produced. Perfluorinated carboxylic acid fluorides produced from the starting compounds of Formula 1 have the formula

(2)



where:

Q_3 can be a monovalent radical such as a perfluoroalkyl radical of less than 9 carbon atoms, a perfluoro cycloalkyl radical of less than 9 carbon atoms, a lower perfluoroalkylcycloalkyl radical of less than 9 carbon atoms, and a perfluoro ethylene carbonyl fluoride;

Q_4 can be a monovalent radical such as a perfluoroalkyl radical of less than 19 carbon atoms, a perfluorocycloalkyl radical of less than 9 carbon atoms, a lower perfluoroalkylcycloalkyl radical of less than 9 carbon atoms; and

Q_3 and Q_4 taken together are a divalent radical such as a perfluoroalkylene diradical of at least 4 and less than 7 carbon atoms, a perfluoroalkylene oxide diradical of at least 4 and less than 6 carbon atoms, a perfluoroalkylene sulfur tetrafluoride diradical of at least 4 and less than 6 carbon atoms, a perfluoroalkylenesulfone diradical of at least 4 and less than 6 carbon atoms, and perfluoro [beta-(N,N-diethyleneamino) propionyl fluoride] diradical.

In the foregoing definitions of Formula 2 it will be appreciated that when Q_3 and Q_4 are taken together they form the indicated types of perfluorinated heterocyclic radicals all of which contain nitrogen as one member of the ring. The perfluoroalkylene portions of these heterocyclic ring structures can contain one or two perfluoroalkyl branches substituted on ring carbon atoms; such perfluoroalkyl branches can contain one or two carbon atoms each.

A more preferred class of compounds of Formula 2 consists of those where Q_3 and Q_4 are each a lower perfluoroalkyl radical (i.e. one containing less than 5 carbon atoms) and Q_3 and Q_4 together with the nitrogen atom between them form a perfluorinated morpholine or a perfluorinated piperazine ring structure.

The perfluorinated carboxylic acid fluorides of Formula 2 (above) can be converted to the corresponding perfluorinated carboxylic acids by conventional hydrolysis, and to the corresponding esters, alkali metal and ammonium salts by conventional methods well known to those of ordinary skill in the art.

The fluorinated products are insoluble in liquid hydrogen fluoride and either settle to the bottom of the cell, or evolve with the hydrogen fluoride and other gaseous products, depending upon the volatility, and can be readily recovered as above by refrigeration and condensation.

The perfluorinated (di-N-substituted beta amino propionic acid fluorides) of this invention are useful for a number of purposes. Thus, by treatment of the acid fluorides with aqueous alkali metal hydroxides, the corresponding alkali metal salts are obtained. These alkali metal salts are useful as emulsifiers in polymerization systems. By substitution of aqueous ammonium hydroxide, the ammonium salt having similar uses to the metal salts is obtained. The chromium coordination complex of the perfluorinated carboxylic acids of this invention which are useful for the sizing of paper can be prepared by reaction of a perfluoro (di-N-substituted beta aminopropionic) acid with a reactive compound containing trivalent chromium in accordance with the processes described in U.S. Patents 2,693,458 and 2,662,835. The free carboxylic acids derived from Formula 2 compounds can be reduced to the corresponding 1,1-dihydroalcohols by employing the methods described in U.S. Patent No. 2,666,797. These new 1,1-dihydroalcohols are useful as intermediates for the preparation of acrylate and methacrylate esters and their polymers in accordance with the methods of U.S. Patent No. 2,642,416. Valuable cationic surface active agents based on these perfluorinated carboxylic acids can be prepared using the methods described in U.S. Patents Nos. 2,764,602 and 2,764,603. The dicarboxylic acids formed by hydrolysis of the corresponding Formula 2 compounds are useful as components in the manufacture of polyesters by reactions with polyols, particularly diols.

The compounds of Formula 1 can be prepared by any convenient route. Thus, one can use betapropiolactone and acrylonitrile; see the teachings of T. L. Gresham et al. in JACS, 73, 3168 (1951) and the book, The Chemistry of Acrylonitrile, American Cyanamid Company. Also, one can use acrylic acid or an ester of acrylic acid and add the appropriate amine thereto; see the teachings of Reppe et al. in U.S. Patent No. 2,195,974.

The following di-N-substituted beta amino propionic acid halides shown in Table I are useful for the production of the corresponding perfluorinated acid fluorides. Yields generally range up to about 35 weight percent based on organic raw materials used. Procedures and conditions for fluorination can be generally as described below in Example 1. It will be appreciated that in the process of practicing the processes of the present invention one inherently obtains as the product a mixture of perfluorinated isomers. This mixture is then processed further to recover a desired perfluorinated product.

TABLE I

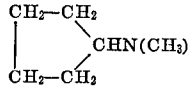
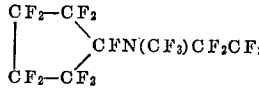
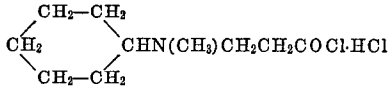
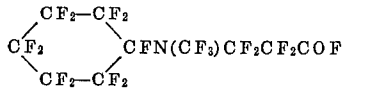
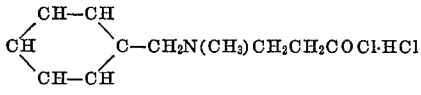
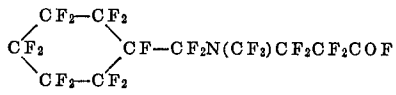
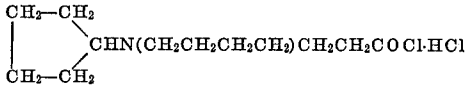
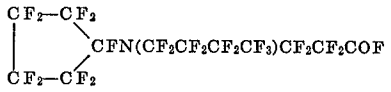
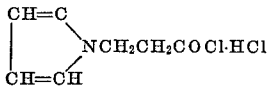
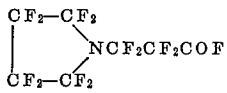
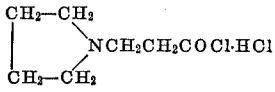
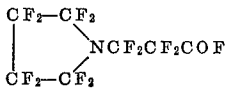
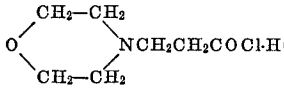
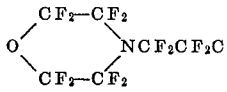
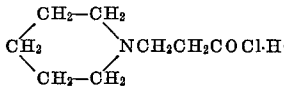
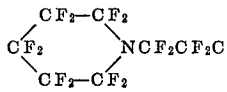
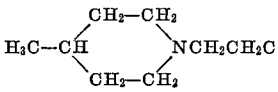
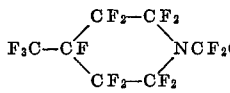
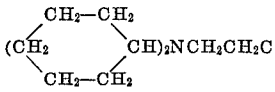
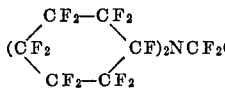
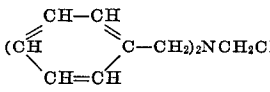
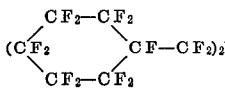
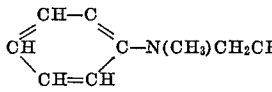
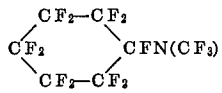
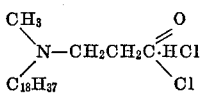
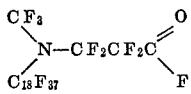
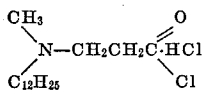
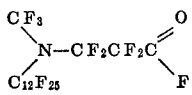
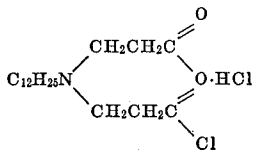
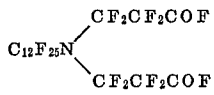
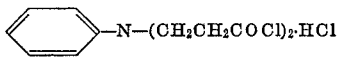
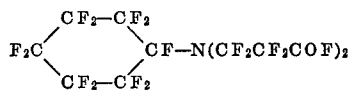
	Starting material	Product
1	$(CH_3)_2CHN(CH_3)CH_2CH_2COCl\cdot HCl$	$(CF_3)_2CFN(CF_3)CF_2CF_2COF$
2	$CH_3CH_2CH_2CH_2N(CH_3)CH_2CH_2COCl\cdot HCl$	$CF_3CF_2CF_2CF_2N(CF_3)CF_2CF_2COF$
3	$(CH_3)_2CHCH_2N(CH_3)CH_2CH_2COCl\cdot HCl$	$(CF_3)_2CFCF_2N(CF_3)CF_2CF_2COF$
4	$(CH_3)_2CHN(C_2H_5)CH_2CH_2COCl\cdot HCl$	$(CF_3)_2CFN(C_2F_5)CF_2CF_2COF$
5		
6	$CH_3CH_2CH_2CH(CH_3)N(CH_3)CH_2CH_2COCl\cdot HCl$	$CF_3CF_2CF(CF_3)N(CF_3)CF_2CF_2COF$
7	$[(CH_3)_2CH]_2NCH_2CH_2COCl\cdot HCl$	$[(CF_3)_2CF]_2NCF_2CF_2COF$

TABLE I—Continued

	Starting material	Product
8		
9	$CH_3CH_2CH_2CH_2N(CH_2CH_2CH_3)CH_2CH_2COCl\cdot HCl$	$CF_3CF_2CF_2CF_2N(CF_2CF_2CF_3)CF_2CF_2COF$
10	$(CH_3)_2CHCH_2N(CH_2CH_2CH_3)CH_2CH_2COCl\cdot HCl$	$(CF_3)_2CFCF_2N(CF_2CF_2CF_3)CF_2CF_2COF$
11		
12	$(CH_3CH_2CH_2CH_2)_2NCH_2CH_2COCl\cdot HCl$	$(CF_3CF_2CF_2CF_2)_2NCF_2CF_2COF$
13	$[(CH_3)_2CHCH_2]_2NCH_2CH_2COCl\cdot HCl$	$[(CF_3)_2CFCF_2]_2NCF_2CF_2COF$
14		
15	$[CH_3(CH_2)_3CH(C_2H_5)CH_2]_2NCH_2CH_2COCl\cdot HCl$	$[CF_3(CF_2)_3CF(C_2F_5)CF_2]_2NCF_2CF_2COF$
16		
17		
18		
19		
20		
21		
22		
23		
24		
25		
26		
27		

The following examples are offered as a better understanding of the present invention and should not be construed as unnecessarily limiting thereto.

EXAMPLE 1

An iron electrochemical cell as described in U.S. Patent No. 2,519,983 containing a set of nickel anodes and iron cathodes, operating at atmospheric pressure and a temperature of about 22° C. is used for this run:

Beta-piperidine propionyl chloride hydrochloride is prepared using the procedure of Gresham et al. in JACS 73, 3168 (1951) as follows:

Six hundred grams of piperidine is added to 500 grams beta-propiolactone with stirring at a temperature of 0–10° C. The reaction is then allowed to stand at room temperature for 16 hours. Five hundred milliliters of isopropyl ether is added followed by nine hundred milliliters of concentrated HCl maintaining the temperature below 30° C. The insoluble hydrochloride salt of the piperidine propionic acid is removed by filtration and dried to yield 885 grams amino acid hydrochloride which has a melting point of 209–212° C.

The amino acid hydrochloride is converted to the acid chloride by addition to twice its weight of thionyl chloride followed by heating at 50° C. for six hours. The excess thionyl chloride is removed under vacuum to leave the solid acid chloride hydrochloride which is slurried in low boiling petroleum ether, filtered and dried. Conversion to the acid chloride is 86 percent. The acid chloride melts at 155°–157° C., and contains 31.4 percent chlorine.

300 grams of 1-piperidine propionyl chloride hydrochloride is dissolved in 2000 grams of anhydrous liquid hydrogen fluoride in the electrochemical cell. The solution is electrolytically conductive. A current density of the order of 20 amperes per square foot of anode surface is obtained at the operating cell voltage in the range of 5–6 volts direct current. During the 87 hour run 790.7 grams of the organic starting material is added to maintain conductivity. Also, anhydrous hydrogen fluoride is added periodically to maintain a fixed level in the cell.

In the course of the run a total of 959.1 grams of liquid perfluorinated product is removed from the bottom of the cell and the condenser trap.

Fractionation of the liquid cell product gives perfluoro [(N-piperidino) beta propionic acid fluoride] having the structural formula c-$C_5F_{10}NC_2F_4COF$. This product has a boiling point of about 110–116° C. at 738 mm. Hg pressure. The yields of perfluorinated acid halides is 37 percent of theory based on current.

The free acid of the above acid halide is isolated from the liquid cell product in the following manner: Two hundred grams of cell product is slowly added to 48 grams sodium hydroxide in 48 grams water to hydrolyze the acid fluoride. The inert fluorocarbons are steam distilled from the salt mixture to a pot temperature of 110° C. Seventy-three grams of fluorocarbons are separated. The salt mixture is acidified with 169 grams H_2SO_4 in 430 grams water. A lower phase of 125 grams of acid is separated from the aqueous sulfuric acid mixture. The acid is further purified by addition to 100 ml. (milliliters) of H_2SO_4 containing 5 percent free SO_3 followed by distillation to give 102 grams of perfluoro [N-piperidino) propionic acid] having the structural formula c-$C_5F_{10}NC_2F_4CO_2H$, boiling point 114–116° C. at 30 mm. Hg pressure. Neutral equivalent is found to be 413 while that calculated for cyclic c-$C_5F_{10}NC_2F_4CO_2H$ is 409.

The cyclic amide c-$C_5F_{10}NC_2F_4CO_2NH_2$ is prepared from the above acid fluoride in ethyl ether by the addition of anhydrous ammonia. The ether is removed by evaporation. The crude amide is taken up in ethanol and precipitated by addition of water. Filtration gave the amide, melting point 87–89° C. when recrystallized from chloroform. Analysis gave 23.5 carbon (calculated analysis is 23.52 percent carbon). The over-all acid yield is 34 percent of theoretical based on current, or 33 percent based on organic raw material used.

EXAMPLE 2

Using the procedure of Example 1 (above) 1026 grams of 4-ethyl-1-piperidinopropionyl chloride hydrochloride is electrofluorinated for a period of 108 hours. The cell is operated at 4 to 6 volts direct current, a current density of 20 amperes per square foot, 22° C., and atmospheric pressure. A total of 1357 grams of high boiling fluorocarbon products are obtained from the cell during the operation.

The crude cell products contain perfluorinated propionyl fluorides including perfluoro [(N-4-ethyl-1-piperidino) beta propionic acid fluoride]. This product mixture is admixed with a large excess of aqueous 20 percent sodium hydroxide solution and the resulting mixture is steam distilled to remove inert fluorocarbons. The aqueous residue is acidified with 95 percent sulfuric acid. The resulting mixture is fractionally distilled through an 18 inch glass Helix packed column. There is obtained a fraction boiling at 130° C. under 22 mm. Hg pressure which is the acid, perfluoro [4-ethyl-1-piperidinopropionic acid] having the structural formula c-$C_2F_5C_5F_9NCF_2CF_2COOH$. The calculated neutral equivalent is 509; that experimentally found is 508. The refractive index is 1.3233 at 25° C. This acid represents a 24 percent of theoretical yield based on the amount of current passed or a 21 percent based on the amount of organic raw material used.

EXAMPLE 3

Using the procedure of Example 1 (above), 3-(N,N-diethylamino) propionyl chloride hydrochloride is electrofluorinated at 5.2 volts and a current density of 20 amperes per square foot. During the 66 hour run 332.7 grams of the organic raw material is added to the cell and 60.8 grams of higher boiling fluorocarbon products are obtained from the cell condenser. The high boiling products are fractionated. Material boiling in the range of 90–105° C. is 36.3 grams and is the expected perfluoro [diethyl amino beta propionyl fluoride] having the structural formula $(C_2F_5)_2NCF_2CF_2COF$. A small portion of this material is converted to the amide and analyzed for nitrogen. The nitrogen content is 6.97 weight percent (that calculated for $(C_2F_5)_2NC_2F_4CONH_2$ is 7.07 percent).

An additional portion of the above material is neutralized with an aqueous $Ca(OH)_2$ slurry. The fluorocarbons are removed via steam distillation and the fluorocarbon acid is regenerated by acidification with 95 percent H_2SO_4. Perfluoro (diethylamino beta propionic acid) which has the structural formula $(C_2F_5)_2NC_2F_4CO_2H$ is obtained by distillation from the sulfuric acid. The neutralization equivalent of the resulting acid is calculated to be 397; that actually found is 400.

The yield of this acid (boiling point 97° C. at 22 mm. Hg pressure) based on the best high boiler production rate of 13.1 grams of product for 50 ampere-hours of cell operation is thus found to be 12 percent of theory.

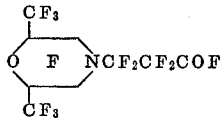
For comparative purposes, data on the electrofluorination of n-octanoyl chloride is obtained. In this case the fluorination and work up procedures were similar to those previously described. In a typical run the recovered acid $C_7F_{15}CO_2H$ represented- 12–13.5 percent of the theoretical amount based on the amount of current passed. The cyclic ether(s) —$C_8F_{16}O$ represented an additional 32 percent of the theroetical amount.

In a like manner hexanoyl chloride is electrofluorinated to yield the corresponding acid $C_5F_{11}CO_2H$ in 18 percent yields, the cyclic ether (c-$C_6F_{12}O$), in 33 percent yields.

EXAMPLE 4

Electrochemical fluorination of the compound N-(β-propionyl chloride)-2,6-dimethylmorpholine hydrochloride, proceeds smoothly at concentrations of 5–15 percent in the electrochemical cell at anode current densities of 20

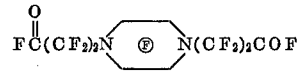
amperes per square foot with an applied voltage of 5.5–6.2 volts. Under these conditions a steady state production rate of high boiling perfluoro compounds of 16 grams per 50 ampere-hours is observed. These compounds consist of two general types. First, 40–50 percent of the fluoro compounds are inert liquids consisting of perfluoroalkyl tertiary amines, boiling point 110–125° C. under 740 mm. Hg pressure. Second, 30–40 percent of the high boiling compounds are a mixture of perfluoroalkyl tertiary amino acid fluorides, mainly having the structure of

(3) 

perfluoro [N-(2,6-dimethyl morpholino) beta propionic acid fluoride], boiling point 125–135° C. under 740 mm. Hg pressure. The mixture of acids obtained from hydrolysis of these acid fluorides boils at 185–205° C. under 740 mm. Hg pressure, though mostly at 200–205° C. The melting point is 50–51° C. This acid perfluoro [N-(2,6-dimethyl morpholino) beta propionic acid] has a neutral equivalent of 501±5.

EXAMPLE 5

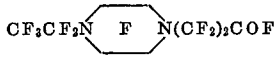
Electrochemical fluorination of N,N'-di(β-propionyl chloride)-piperazine dihydrochloride, proceeds smoothly at concentrations of 3–6 percent in the electrochemical cell at anode current densities of 20 amperes per square foot with an applied voltage of 5.8–6.3 volts. Under these conditions, a steady state production rate of cell drainings of perfluoro compounds totaling 14 grams per 50 ampere-hours is observed. From these high boiling compounds, the compound perfluoro

(4) 

is isolated as follows:

The crude cell drainings are shaken with excess water to hydrolyze the acid fluorides. The dibasic acids are water soluble and may be recovered by separating and concentrating the aqueous phase, acidifying with concentrated H_2SO_4 and isolating the product as crystals. The dibasic acid has a melting point of 183–186° C., and a neutral equivalent of 257.

In addition to Formula 4, the monobasic fluorocarbon acid fluoride perfluoro [N-ethyl-N'-(beta propionic acid fluoride)piperazine] having the Formula 5 is made.

(5) 

The acid perfluoro [N-ethyl-N'-(beta propionic acid) piperazine] is isolated in 40 percent yield based on cell drainings, by hydrolysis, then distillation of the cell products. The acid boils at 86–88° C. at 0.6 mm. Hg pressure, it melts at 56–59° C., and has a neutral equivalent of 496±1. In addition to these fluorocarbon acids which correspond to the acid fluorides of Formulas 4 and 5, inert perfluoro compounds of boiling point 83–80° C. under 740 mm. Hg pressure may be isolated from the fluorocarbon cell products.

EXAMPLE 6

Ethyl imino dipropionyl chloride is prepared as follows: to 45 grams (1 mole) of ethyl amine dissolved in 250 milliliters of absolute ethyl alcohol at 35° C. is added 200 grams (2 moles) of ethyl acrylate in 150 milliliters absolute alcohol. The reaction is allowed to stand for six days at room temperature. Distillation then gave 229 grams $C_2H_5N(C_2H_4CO_2C_2H_5)_2$ which has a boiling point of 95–101° C. at 0.5 mm. Hg pressure.

The ester, 100 grams, is then added slowly to one liter of concentrated hydrochloric acid, keeping the temperature below 30° C. The mixture is brought to reflux and 500 milliliters of distillate collected. The remaining liquid is then removed under reduced pressure and the solid residue vacuum dried at room temperature to give 89 grams of $C_2H_5N(C_2H_4CO_2H)_2 \cdot HCl$ which has a melting point of 185–187° C.

The acid is converted to the acid chloride by addition of 1 part of acid to a slurry of 3 parts PCl_5 in 25 parts benzene. The mixture is stirred at room temperature for 16 hours. The benzene is decanted and the solid product residue washed first with benzene and then CCl_4. Vacuum drying gave 1 part of $C_2H_5N(C_2H_4COCl_2)_2 \cdot HCl$ which has a melting point of 83–88° C. with decomposition.

A total of 365 grams (1.39 moles) of ethyl imino dipropionyl chloride $CH_3CH_2N(CH_2CH_2COCl)_2 \cdot HCl$ is dissolved in liquid hydrogen fluoride to make a 50 percent solution. Electrochemical fluorination of the mixture is carried out by initially maintaining the organic component at 5 to 10 weight percent by adjusting the charging rate during the run. A total of 280 grams of cell drainings are collected during the cell run.

These drainings are washed with liquid hydrogen fluoride to remove dissolved impurities and then they are converted to methyl esters for fractionation as follows:

To 126 grams of cell drainings is added 85 grams of trimethoxy methane. The reaction is allowed to cool and then is distilled at 25 mm. Hg pressure.

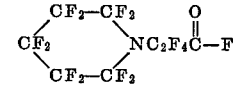
The fraction boiling in the range from 125 to 134° C. has an index of refraction (n_D^{25}) of 1.3475 and is found to be a dibasic ester with a saponification equivalent of 209. Theoretical saponification equivalent for the ester $CF_3CF_2N(CF_2CF_2CO_2CH_3)_2$ is 225. This analysis shows that the compound perfluoro [ethyl amino-N,N-di(beta-propionyl fluoride] having the structural formula

$$CF_3CF_2N(CF_2CF_2CO_2F)_2$$

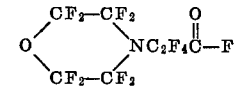
is present in the cell drainings and is isolated in 28 percent yield based on the dibasic acid chloride charged to the cell.

I claim:

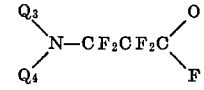
1. Perfluoro (beta diethyl amino propionic acid).
2. A compound having the structure:



3. A compound having the structure:



4. A compound of the formula:

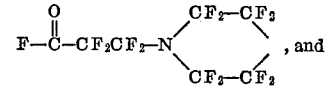


where:

Q_3 is a monovalent radical selected from the group consisting of perfluoroalkyl radicals of less than 9 carbon atoms, cyclo perfluoroalkyl radicals of less than 9 carbon atoms and perfluoroethylene carbonyl fluoride:

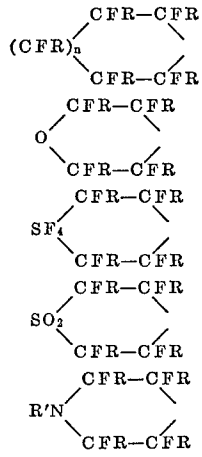
Q_4 is a monovalent radical selected from the group consisting of perfluoroalkyl radicals of less than 19 carbon atoms, perfluorocycloalkyl radicals of less than 9 carbon atoms, and lower perfluoroalkylcycloalkyl radicals of less than 9 carbon atoms; and

Q_3 and Q_4 taken together are a divalent radical selected from the group consisting of:

(a) 

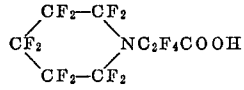
(b) a divalent radical of at least 4 and less than

7 carbon atoms selected from the group consisting of:

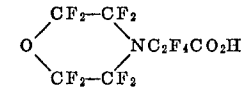


where R is F, CF_3 or C_2F_5, n is 0 or 1, and R' is CF_3 or C_2F_5; and the corresponding acids, alkali metal and ammonium salts.

5. A compound having the structure:



6. A compound having the structure:



7. A perfluoro (di-N-alkyl beta amino propionic acid) wherein one of said alkyl groups has less than 9 carbon atoms and the other has less than 19 carbon atoms.

References Cited

UNITED STATES PATENTS

2,500,388	3/1950	Joseph H. Simons	260—614
2,519,983	8/1950	Joseph H. Simons	204—62
2,567,011	9/1951	Albert R. Diesslin et al.	260—465.7
2,616,927	11/1952	Kauck et al.	260—563
2,950,317	9/1960	Brown et al.	260—543

FOREIGN PATENTS

763,673	12/1956	Great Britain.

ALEX MAZEL, Primary Examiner

J. TOVAR, Assistant Examiner

U.S. Cl. X.R.

204—59; 252—351; 260—75, 243, 247.7, 294, 294.3, 294.7, 482, 501.16, 534, 544

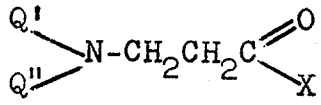
PC-1350
(5/69)

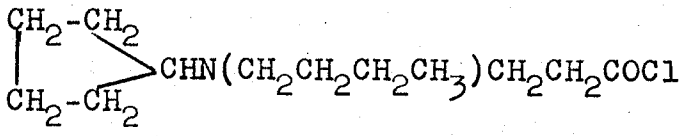
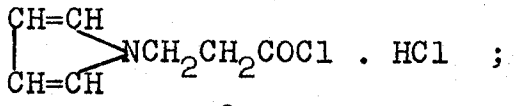
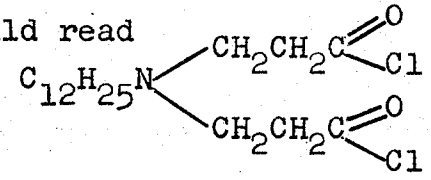
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

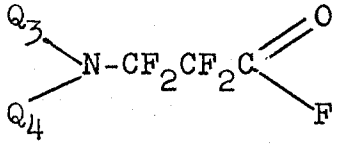
Patent No. 3,471,484 Dated October 7, 1969

Inventor(s) Richard A. Guenthner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, formula (1) should read .

Column 2, line 67, after atoms, insert -- ; --. Column 5, No. 14 should read  ; Column 5, No. 16 should read  ; and Column 5, No. 26 should read  .

Column 9, line 35, after perfluoro, add -- [N,N'-di(betapropionyl fluoride) piperazine] --. Column 10, Claim 4, the formula should read 

SIGNED AND
SEALED
MAY 19 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents

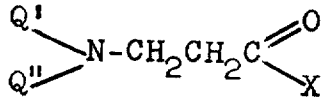
PO-1050
(5/69)

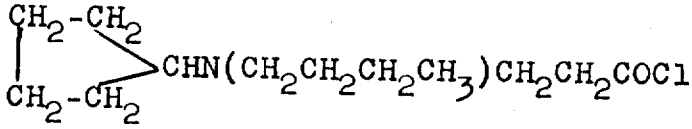
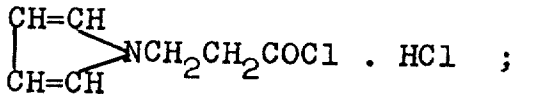
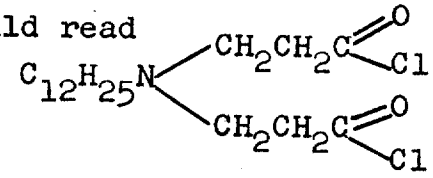
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

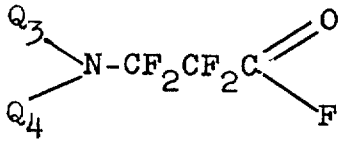
Patent No. 3,471,484 Dated October 7, 1969

Inventor(s) Richard A. Guenthner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, formula (1) should read .

Column 2, line 67, after atoms, insert -- ; --. Column 5, No. 1 should read  ; Column 5, No. 16 should read  ; and Column 5, No. 26 should read  .

Column 9, line 35, after perfluoro, add -- [N,N'-di(betapropionyl fluoride) piperazine] --. Column 10, Claim 4, the formula should read 

SIGNED AND
SEALED
MAY 19 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents