United States Patent Office 2,790,815 Patented Apr. 30, 1957

2,790,815

PROCESS OF MAKING FLUORINATED ACYL FLUORIDES

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No Drawing. Application September 1, 1954, Serial No. 453,679

3 Claims. (Cl. 260—408)

This invention relates to our discovery of a new and useful process of making certain fluorinated acyl fluoride compounds.

More particularly, in the product compounds of our herein claimed process, the carbonyl fluoride group (—COF) is bonded to a perfluoroalkyl chain, or to a chloroperfluoroalkyl chain, containing 3 to 11 carbon atoms, there being 4 to 12 carbon atoms in the complete molecule.

The term "perfluoroalkyl" signifies a saturated fluorocarbon group consisting solely of fluorine and carbon, having the formula C_nF_{2n+1}—, which may be regarded as a fully fluorinated alkyl group (all hydrogen atoms having been replaced by fluorine atoms). The term "chloroperfluoroalkyl" signifies a saturated group consisting solely of chlorine, fluorine, and carbon, in which there are fewer chlorine atoms than fluorine atoms and each carbon atom is bonded to at least one fluorine atom, constituting a stable and inert structure having modified fluorocarbon characteristics. These chloroperfluoroalkyl chains, as well as the fully fluorinated (perfluoroalkyl) chains, are sufficiently inert and stable so that a good yield can be obtained by our process from a corresponding starting compound that contains the same chain.

The starting compounds used in our process correspond to the product compounds except that they contain a terminal difluoromethyl group (—CF_2H), which is converted by the process to a carbonyl fluoride group (—COF). The acyl fluoride product compounds can be readily converted to desirable derivatives, such as the corresponding carboxylic acids and salts.

Thus our starting compounds can be generically defined as being compounds of the class consisting of perfluoroalkyldifluoromethyl and chloroperfluoroalkyldifluoromethyl compounds, containing 4 to 12 carbon atoms in the molecule.

We have found that these starting compounds can be converted to the corresponding acyl fluoride product compounds in good yields by a simple procedure involving the thermal reaction in vapor phase of the fluorinated starting compound with a mixture of nitrogen dioxide (or nitric oxide) and chlorine (or bromine).

Using the symbol "R" to generically represent the inert fluorinated alkyl group (i. e., the perfluoroalkyl group or chloroperfluoroalkyl group as defined above), which contains 3 to 11 carbon atoms, the reaction can be represented by the following equation:

$$RCF_2H \xrightarrow[Cl_2 \text{ or } Br_2]{NO_2 \text{ or } NO} RCOF$$

The present availability of starting compounds makes the process of particular value:

(A) For converting perfluoroalkyldifluoromethyl starting compounds to the corresponding perfluoroalkanoyl fluorides:

$$F(CF_2)_nCF_2H \rightarrow F(CF_2)_nCOF$$

These starting compounds are obtained as by-products in the operation of the Simons electrochemical fluorination process (cf., U. S. Patents Nos. 2,519,983 and 2,567,011).

(B) For converting omega-monochloroperfluoroalkyldifluoromethyl starting compounds to the corresponding omega-monochloroperfluoroalkanolyl fluorides:

$$Cl(CF_2)_nCF_2H \rightarrow Cl(CF_2)_nCOF$$

These starting compounds are described in U. S. Patent No. 2,551,573 and in the paper of J. D. Park et al., published in Industrial and Engineering Chemistry, vol. 39, p. 354 (March 1947).

In the two above equations n (the number of carbon atoms in the inert fluorinated alkyl chain) has an integer value of 3 to 11; the product compounds having a total of 4 to 12 carbon atoms in the molecule.

These two equations can be represented generically by the equation:

$$X(CF_2)_nCF_2H \rightarrow X(CF_2)_nCOF$$

where "X" stands for F or Cl.

The perfluoroalkanoyl fluoride products of the process, and corresponding carbonyl derivatives such as the acids and salts, are described in the Diesslin, Kauck and Simons Patent No. 2,567,011 (September 4, 1951) and in a paper by Kauck and Diesslin published in Industrial and Engineering Chemistry, vol. 43, pp. 2332–2334 (October 1951). The present process provides a new route to their preparation.

The omega-monochloroperfluoroalkanoyl fluoride products of the process, containing 4 to 12 carbon atoms in the molecule, and corresponding carbonyl derivatives, such as the acids, $Cl(CF_2)_nCOOH$, and salts,

$$Cl(CF_2)_nCOOM$$

are believed to be novel compounds. So far as we are aware, the present process is the only practical route to their preparation thus far discovered. These novel compounds have value as surface active agents and as starting compounds for making surface active agents.

A feature of our process is its simplicity. Good results can be obtained by merely passing a gaseous mixture of the fluorinated starting compound, NO_2 (or NO), and Cl_2 (or Br_2), through an empty tube which is maintained at a temperature of the order of 500 to 650° C. Tubes of nickel, nickel alloys, stainless steel, mild steel, and platinum can be employed. A reaction contact time of less than 30 seconds has been found sufficient to produce a substantially complete conversion and a useful yield. The minimum amount of reactants theoretically needed is one mole of NO_2 or NO and one-half mole of Cl_2 or Br_2 per mole of the fluorinated starting compound. However it is preferred that ratios somewhat in excess of this be used. A charging mixture of NO_2 and NO can be used in place of either alone. It may be noted that when NO_2 is used, dissociation results in a mixture of NO_2 and NO in the reaction zone. The gas mixture feed stock can be diluted with an inert gas if desired. Reactants can be supplied by using compounds that decompose in the reaction zone, or in advance thereof, to form them in situ. The nitrosyl and nitryl halides, NOCl, NOBr, NO_2Cl and NO_2Br, should be useful since they decompose to give Cl_2 or Br_2 and NO or NO_2, for instance. The preferred reactants are nitrogen dioxide and chlorine. Good results have been obtained with mole ratios of about 1:3:2 for the fluorinated starting compound, nitrogen dioxide, and chlorine, respectively. Although the reaction can be satisfactorily performed in an empty tube and without the use of a catalyst, the use of packed tubes and of catalysts is not precluded.

The combination of the above-mentioned NO_2 or NO and Cl_2 or Br_2 reactants has a peculiar utility in our process. The NO_2 or NO is ineffective in the absence of

chlorine or bromine, and iodine does not work. If chlorine or bromine were used alone, the product would be a chlorinated or brominated compound resulting from replacement of the hydrogen atom with a chlorine or bromine atom (see U. S. Patent No. 2,658,928). Nor is the result obtained merely on account of the NO_2 (or NO) being an oxygen-containing oxidizing agent, since air, oxygen, nitrous oxide, sulfur dioxide and sulfur trioxide are not useful substitutes. So far as we are aware, our process is the only one thus far discovered by which our starting compounds can be converted to the corresponding acyl fluorides in good yields.

The reaction product mixture, after leaving the reaction tube, can be condensed and the fluorinated acyl fluoride product recovered by fractional distillation. However, it is not necessary to recover this product as such, especially as it will ordinarily be employed in making a derivative. It can be usefully recovered by treating a reaction product mixture so as to convert it to a derivative that is recovered, as by hydrolyzing with a base to form the corresponding carboxylate salt, or by hydrolyzing with water to form the corresponding carboxylic acid, which is recovered.

The following experiments are illustrative of our process.

Example 1

In this experiment $C_7F_{15}H$ was converted by our process to $C_6F_{13}COF$, which was recovered as the acid, $C_6F_{13}COOH$, employing NO_2 and Cl_2 as reactants. The thermal reaction can be written as follows:

$$F(CF_2)_6CF_2H \xrightarrow[Cl_2]{NO_2} F(CF_2)_6COF$$

The reactor was an empty nickel pipe 1 inch in diameter and 21 inches long, mounted in an inclined position in a 13 inch electric furnace. The temperature was measured with a thermocouple embedded midway in the wall of the pipe. The NO_2 and Cl_2 were metered at controlled rates through flowmeters, and the $C_7F_{15}H$ in liquid form was continuously mixed into the gas stream from a calibrated burette and vaporized to provide the gaseous mixture charging stock, which was fed in through a tube connected to the upper end of the reactor pipe. The exit (lower end) of the reactor pipe was connected to a trap cooled with ice, and the volatile products passing from the latter were condensed in a liquid air trap. The experiment was conducted at atmospheric pressure.

The reactor tube was maintained at a center wall temperature of approximately 600° C. The charging stock was passed through it during a period of 15 minutes and consisted of 24.7 grams of $C_7F_{15}H$, 6.6 grams of NO_2, and 5.2 grams of Cl_2. The liquid product collected in the ice-cooled trap weighed 17.8 grams, and contained the $C_6F_{13}COF$ reaction product (perfluoroheptanoyl fluoride), and a minor proportion of $C_5F_{11}COF$ by-product, together with small amounts of other materials. This fraction was hydrolyzed by being poured into 100 ml. of cold water contained in a separatory funnel, and the mixture was acidified with 25 grams of concentrated sulfuric acid to cause separation of a lower phase containing the fluorinated acid. To ensure that no fluorinated acid remained in the upper water phase, addition was made of 125 ml. of c-$C_6F_{12}O$, a water-insoluble inert cyclic fluorocarbon ether (cf., U. S. Patent No. 2,644,823) in which fluorocarbon acids are soluble, which settled to the bottom carrying with it any acid extracted from the water. The lower layer of fluorocarbon ether and acids was removed and the fluorocarbon ether was evaporated off by gentle heating under vacuum.

The crude acid was subjected to fractional distillation, resulting in a fraction having a boiling range of 170–175° (at 740 mm.), weighing 11.1 grams, identified as relatively pure perfluoroheptanoic acid, $C_6F_{13}COOH$.

Example 2

This experiment illustrates the use of bromine.

Using the same apparatus, with the center wall temperature maintained at approximately 600° C., a charging stock containing 10.1 grams of $C_7F_{15}H$, 3.7 grams of NO_2 and 7.0 grams of Br_2, was passed through the tube during a period of 8 minutes. The liquid collected in the ice-cooled trap weighed 8.3 grams. The excess NO_2 and Br_2 contained in the liquid was removed by adding mercury and the precipitate was separated by filtration. The liquid was subjected to hydrolysis and the product was found to consist mainly of $C_6F_{13}COOH$.

Example 3

This example illustrates the conversion of chloroperfluoroalkyldifluoromethyl compounds. Specifically, it illustrates the conversion of $Cl(CF_2)_6H$ to $Cl(CF_2)_5COF$, and the hydrolysis of the latter to $Cl(CF_2)_5COOH$. The thermal reaction can be written as follows:

$$Cl(CF_2)_6CF_2H \xrightarrow[Cl_2]{NO_2} Cl(CF_2)_6COF$$

Using the same apparatus, with the center wall temperature maintained at approximately 550° C., a charging stock containing 25.2 grams of $Cl(CF_2)_6H$, 10.4 grams of NO_2 and 7.9 grams of Cl_2, was passed through the tube during a period of 23 minutes. The liquid collected in the ice-cooled trap weighed 21.0 grams, and contained the desired $Cl(CF_2)_5COF$, omega-chloroperfluorohexanoyl fluoride, in a yield of 72%. Fractional distillation resulted in recovery of this compound in relatively pure form (B. P. of 81° C. at 740 mm.) together with a fraction identified as the corresponding acid (B. P. of 180–183° C. at 740 mm.), namely,

$$Cl(CF_2)_5COOH,$$

omega-chloroperfluorohexanoic acid, which had been formed as the result of moisture from the atmosphere, or water present as a by-product of the hot tube process, hydrolyzing some of the acyl fluoride.

This acid had a refractive index at 25° C. of 1.3280, and a neutral equivalent value of 326 (calc. 330). Analysis showed 11.2% Cl (calc. 10.8%). The terminal chlorine atom elevates the boiling point by about 25° C., since the boiling point of the corresponding fully fluorinated acid, $F(CF_2)_5COOH$, is 156° C. The surface activity of this omega-chloro acid is indicated by the fact that it reduces the surface tension of water at 25° C. from 72 dynes/cm. to a value of 40 dynes/cm. at a concentration of 1% by weight. It is a strong stable acid and carbonyl derivatives, such as acid anhydrides, acid chlorides, metal and ammonium salts, esters and amides, can be prepared by methods used in making the derivatives of the corresponding fully fluorinated acids (see U. S. Patent No. 2,567,011). The higher members of the series have even stronger surface active properties owing to the greater length of the chloroperfluoroalkyl chain which is both hydrophobic and oleophobic. These acids can be employed instead of fully fluorinated acids in making chromium coordination complexes, as by employing the procedure described in U. S. Patent No. 2,662,835 (December 15, 1953), to obtain complexes useful for treating papers, textile products, glass and metals, to provide surface coatings that are both water-repellent and oil-repellent.

Example 4

This example illustrates the preparation of a higher member of the omega-chloroperfluoroalkanoyl fluoride series and the corresponding acid.

Using the same apparatus, with the center wall maintained at a temperature of approximately 550° C., a run was made employing a mixture of $Cl(CF_2)_8H$, NO_2 and Cl_2 in a mole ratio of 1.0:6.7:3.4. The liquid condensate was found to contain the desired $Cl(CF_2)_7COF$,

omega-chloroperfluorooctanoyl fluoride, in a yield of about 40%. It was hydrolyzed to form the corresponding omega-chloroperfluorooctanoic acid,

$$Cl(CF_2)_7COOH$$

The latter is only slightly water-soluble and is a solid material having a melting point of about 50° C. The neutral equivalent value was found to be 428 (calc. 430.5). Analysis showed 8.4% Cl (calc. 8.2%). This 8-carbon acid has a markedly higher surface activity than does the 6-carbon acid of the preceding example.

We claim:

1. A process of making fluorinated acyl fluoride compounds which comprises thermally reacting in vapor phase a starting compound of the class consisting of perfluoroalkyldifluoromethyl and chloroperfluoroalkyldifluoromethyl compounds containing 4 to 12 carbon atoms in the molecule, with a mixture of a reactant of the class consisting of nitrogen dioxide and nitric oxide and a reactant of the class consisting of chlorine and bromine.

2. A process of making a perfluoroalkanoyl fluoride compound having the formula:

$$F(CF_2)_nCOF$$

from a corresponding perfluoroalkyldifluoromethyl starting compound having the formula:

$$F(CF_2)_nCF_2H$$

where n has an integer value of 3 to 11, which comprises passing a gaseous mixture of said starting compound with at least one mole of NO_2 and one-half mole of Cl_2 per mole of said starting compound, through a heated reactor tube maintained at a temperature of about 500 to 650° C.

3. A process of making an omega-chloroperfluoroalkanoyl fluoride compound having the formula:

$$Cl(CF_2)_nCOF$$

from a corresponding omega-chloroperfluoroalkyldifluoromethyl starting compound having the formula:

$$Cl(CF_2)_nCF_2H$$

where n has an integer value of 3 to 11, which comprises passing a gaseous mixture of said starting compound with at least one mole of NO_2 and one-half mole of Cl_2 per mole of said starting compound, through a heated reactor tube maintained at a temperature of about 500 to 650° C.

References Cited in the file of this patent

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OTHER REFERENCES

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