United States Patent Office 2,773,089 Patented Dec. 4, 1956

2,773,089

FLUORINATED OLEFINIC NITRILES

John Lynde Anderson, Northwood, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application October 29, 1954, Serial No. 465,748

11 Claims. (Cl. 260—465.7)

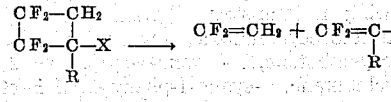
This invention relates to unsaturated organic compounds containing fluorine and to a method for their preparation.

Polyfluorocyclobutanes have been subjected to elevated temperatures in order to convert them to other fluorine-containing products. In such pyrolysis reactions, the nature of the products obtained is quite unpredictable and varies with the particular substituents on the polyfluorocyclobutane nucleus.

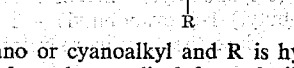
This invention has as an object the provision of a process for the preparation of fluorinated olefinic nitriles. Other objects will appear hereinafter.

These objects are accomplished by the present invention of difluoroolefins of up to ten carbons having but the one non aromatic carbon-carbon unsaturation, having the two fluorines on one doubly bonded carbon and having the other doubly bonded carbon attached to a cyano, —CN, group through a $-C_nH_{2n}-$ group, n being a cardinal number, i. e., either zero or a positive integer, the remaining valence of the second doubly bonded carbon, when not satisfied by hydrogen, being satisfied by a monovalent hydrocarbon radical free from non aromatic unsaturation.

The invention also includes the process for the preparation of these fluorinated olefinic nitriles wherein a tetrafluorocyclobutane of not more than twelve carbons having the fluorines on adjacent annular carbons, having an annular CH_2 group, and having the remaining annular carbon bonded to a cyano group through a $-C_nH_{2n}-$ radical, n being a cardinal number, any remaining valence of said annular carbon not bonded to hydrogen being bonded to a monovalent hydrocarbon radical free from non aromatic unsaturation, is pyrolyzed by exposure to a temperature in the range 600–1000° C. The course of this reaction is illustrated by the following equation:



or



wherein X is cyano or cyanoalkyl and R is hydrogen or a monovalent hydrocarbon radical free of aliphatic unsaturation, e. g., alkyl, cycloalkyl, or aryl, the total carbons in X and R being no more than eight. As the above equation indicates, the cyclobutane ring can be cleaved in either of two ways. Under some conditions, cleavage takes place predominantly in but one of these ways with minor amounts of cleavage in the other way, while under other conditions both types of cleavage take place in not widely differing amounts. However, olefinic nitriles having but two fluorines and these on a terminal carbon are always produced. The particular substituents on the annular carbon atoms of the cyclobutane ring influence the type of cleavage taking place.

The products of this invention are obtained when the tetrafluorocyclobutanes having cyano or cyanoalkyl substituents are pyrolyzed at temperatures ranging from 600–1000° C. However, it is preferable to pass the tetrafluorocyclobutane through a reaction zone heated to a temperature between 750° and 900° C. since this narrower range of pyrolysis temperature gives better conversions to the desired 1,1-difluoro-2-cyano-(or cyanoalkyl-) olefins.

The pressure at which the pyrolysis of the cyano- or cyanoalkyl-substituted tetrafluorocyclobutanes is carried out is not critical, pressures ranging from a few microns of mercury to atmospheric or even superatmospheric being operable. In general, it is preferred to use the lower pressures, i. e., pressures of less than 50 mm. of mercury, in order to remove the reaction products from the reaction zone as rapidly as possible so that formation of undesirable by-products is minimized. In general, it is also desirable to use the lower pyrolysis temperatures in the above-specified range when operating at the higher pressures.

The rate at which the cyano-substituted tetrafluorocyclobutane is passed through the reaction zone is not critical, although for economical reasons it is preferred to use as high a rate as possible. It is only necessary to heat the reactant to the reaction temperature for a short time to obtain the desired cleavage of the cyclobutane ring. Since the rate of gas flow through the reactor is greater at the lower pressures, the shortest contact times of the reactant in the reaction zone are obtained with the lowest operating pressures.

The reactor can be constructed of any inert, heat-resistant material. For example, the reactor can be made of quartz, heat-resistant glass, stainless steel or other inert metal. The reactor can, if desired, be packed with inert materials, e. g., granular quartz, to provide better heat transfer in the reaction zone. Metals or other materials which react with the cyano-substituted tetrafluorocyclobutane under the operating conditions to give undesirable by-products should not be used. Inert metals such as nickel and platinum can be used. The reaction zone can be heated by conventional means. Electric heaters are very satisfactory for this purpose.

The tetrafluorocyclobutanes having a cyano or cyanoalkyl group attached to one of the annular carbons used as starting materials in the process of this invention can be prepared by reacting tetrafluoroethylene with an appropriate terminally unsaturated ethylenic compound. This general process is described in U. S. Patents 2,462,345 and 2,462,346 issued to P. L. Barrick.

In the large scale preparation of the cyano-substituted difluoroolefins of this invention, it is very convenient to carry out the process, including preparation of the cyano-substituted tetrafluorocyclobutane starting materials, by a continuous vapor phase method at atmospheric pressure. In this embodiment, the cyano-substituted terminally unsaturated ethylenic compound, e. g., acrylonitrile, and tetrafluoroethylene in equal volumes or with an excess of the former, with or without nitrogen as a diluent, are metered into a reaction tube heated by an electric furnace. The reaction tube is conveniently made of the heat-resistant glass known commercially as "Vycor" and is packed with quartz chips to provide better heat transfer. When the reaction tube is maintained at about 580° C., the conversion of tetrafluoroethylene and acrylonitrile to 1-cyano-2,2,3,3-tetrafluorocyclobutane is about 10%, and about 1% of β,β-difluoroacrylonitrile is obtained. However, when the reaction tube is heated at 680°–730° C., the conversion to the cyclobutane derivative is about the same, 10–14%, but 19–26% of β,β-difluoroacrylonitrile is isolated. Presumably at these higher temperatures the cyanotetrafluorocyclobutane first formed cleaves to the

difluoroacrylonitrile. Under the range of operating conditions just described there is also formed 17–19% of tetrafluoroethylene dimer. The formation of tetrafluoroethylene dimer can be reduced and formation of desired products increased by using an excess, e. g., 100% excess, of the cyano-substituted ethylenic compound.

The invention is further illustrated by the following examples in which the proportions of ingredients are expressed in parts by weight unless otherwise specified.

In these examples the reactor consists of a vertical cylindrical reaction tube approximately one inch in diameter and twelve inches long made of quartz or of a heat-resistant glass, e. g., the type of glass known commercially as "Vycor." The reaction tube is packed with 6-mm. sections of quartz tubing six millimeters in diameter and is heated externally by means of a cylindrical electric furnace. The temperature of the reaction zone is recorded by a thermocouple placed in the center of the reaction tube. A high capacity vacuum pump maintains the reaction system at the desired reduced pressure. Pressures down to a few microns of mercury are obtained by the use of a mercury diffusion pump. The pressures are measured between the mercury pump and the cold trap in which the reaction products are isolated. This cold trap is conveniently cooled by liquid nitrogen. The cyano-substituted tetrafluorocyclobutante reactant is introduced into the reaction zone gradually by conventional means, e. g., by means of a dropping funnel, or by distillation.

Example I

Fifty parts of 1-cyano-1-methyl-2,2,3,3-tetrafluorocyclobutane is passed through a reaction tube of the type described in the preceding paragraph. The reaction tube is maintained at 800° C. and 4 mm. mercury pressure. The pyrolysis products are rapidly cooled in a trap surrounded by liquid nitrogen. After the addition has been completed, the trap is removed from the reaction system and the gaseous products are allowed to evaporate at room temperature. This reaction sequence is repeated on fifty parts of 1-cyano-1-methyl-2,2,3,3-tetrafluorocyclobutane. The liquid residues are combined, 17.2 parts of xylene is added, and the mixture is distilled through an efficient fractionating column. There is isolated approximately 10 parts of β,β-difluoro-α-methyl-acrylonitrile, B. P. 80–83° C., and refractive index, $n_D^{25.5}$, 1.3583.

Analysis.—Calculated for $C_4H_3F_2N$: C, 46.60%; H, 2.93%; N, 13.59%. Found: C, 46.63%; H, 3.48%; N, 12.20%, 12.42%.

The infrared absorption spectrum also confirms the structure of this compound.

Example II

One hundred and twelve parts of 1-cyano-2,2,3,3-tetrafluorocyclobutane is pyrolyzed at 800° C. and 4 mm. mercury pressure by the procedure used in Example I. The liquid reaction product isolated in the cold trap is rapidly distilled and the fraction boiling below 80° C. is collected. This reaction sequence is repeated on two 100-part samples of 1-cyano-2,2,3,3-tetrafluorocyclobutane. The three fractions boiling below 80° C. are combined and the composite product amounts to 94 parts, containing about 45% β,β-difluoroacrylonitrile, with the remainder of the product being acrylonitrile.

The β,β-difluoroacrylonitrile is isolated from its mixture with acrylonitrile by a polymerization process which polymerizes the acrylonitrile but not the 1,1-difluoroacrylonitrile. The composite sample of products boiling below 80° C. is subjected to solution polymerization at 100° C. for 8 hours in the presence of 0.5 part of 1,1'-azodicyclohexanecarbonitrile and approximately 43 parts of xylene. Monomeric material is removed from the polymerization product by distillation and the portion boiling below 70° C. is again subjected to polymerization in the presence of 1,1'-azodicyclohexanecarbonitrile at 100° C. for 15 hours. The polymerization product is added to diethyl phthalate and the mixture is distilled. There is obtained material boiling at 66–69° C. and having a refractive index, n_D^{25}, of 1.3482. This product is principally β,β-difluoroacrylonitrile slightly contaminated with acrylonitrile. Essentially pure β,β-difluoroacrylonitrile is obtained by another polymerization treatment, followed by distillation. The monomer has a refractive index, n_D^{25}, of 1.3465 and a boiling point of 67–68° C.

Analysis.—Calculated for C_3HF_2N: C, 40.6%; H, 1.14%; F, 42.67%. Found: C, 41.15%; H, 1.63%; F, 42.1%.

The infrared absorption spectrum of the β,β-difluoroacrylonitrile also confirms its structure.

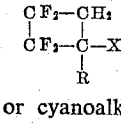
Example III

Forty-seven parts of 1-cyanomethyl-2,2,3,3-tetrafluorocyclobutane is pyrolyzed at 850° C. and 1–2 mm. mercury pressure in the manner described in the preceding examples. The liquid nitrogen coolant is removed from the trap in which the reaction products are collected and the lower boiling products are allowed to distill into a second trap cooled by liquid nitrogen. There are obtained approximately 5 parts of a product boiling at 122–125° C., consisting of an approximately equal mixture of allyl cyanide and 1,1-difluoro-3-cyano-1-propene.

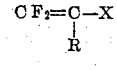
Example IV

Five parts of 1-cyano-2,2,3,3-tetrafluorocyclobutane is passed through a quartz reaction tube at 825° C. and at 10–20 microns mercury pressure by a procedure similar to that used in Example I. The products isolated in the cold trap cooled by liquid nitrogen comprise vinylidene fluoride, tetrafluoroethylene, acrylonitrile, and β,β-difluoroacrylonitrile.

The examples above have illustrated the preparation of certain difluoroolefinic nitriles by the pyrolysis of certain tetrafluorocyclobutanes having cyano or cyanoalkyl substituents. However, the invention is generic to difluoroolefinic nitriles of not more than ten carbons wherein the two fluorines are on one carbon of the sole aliphatic carbon-carbon unsaturation of the compound, the cyano group is bonded to the other doubly bonded carbon through a $-C_nH_{2n}-$ group wherein n is a cardinal number and any remaining valence of the second doubly bonded carbon, not satisfied by hydrogen, is satisfied by a monovalent hydrocarbon radical including, not only those described above but also β,β-difluoro-α-ethylacrylonitrile, β,β-difluoro-α-n-butylacrylonitrile, β,β - difluoro-α-cyclohexylacrylonitrile, β,β-difluoro-α-phenylacrylonitrile, 1,1-difluoro-2-(β-cyanoethyl)ethylene, 1,1 - difluoro-2-(δ-cyanobutyl)ethylene, and 1,1-difluoro-2-(δ-cyanobutyl)-1-butene. These specific products are made by pyrolysis of the following tetrafluorocyclobutanes: 1-cyano-1-ethyl-2,2,3,3-tetrafluorocyclobutane, 1-cyano-1-n-butyl - 2,2,3,3-tetrafluorocyclobutane, 1 - cyano-1-cyclohexyl-2,2,3,3-tetrafluorocyclobutane, 1-cyano-1-phenyl-2,2,3,3-tetrafluorocyclobutane, 1-(β-cyanoethyl) - 2,2,3,3-tetrafluorocyclobutane, 1-(δ-cyanobutyl) - 2,2,3,3-tetrafluorocyclobutane, and 1-(n-butyl)-1-(δ-cyanobutyl) - 2,2,3,3-tetrafluorocyclobutane. Since the tetrafluorocyclobutanes of the formula

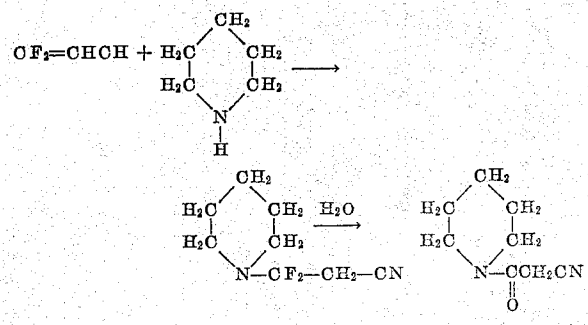


wherein X is cyano or cyanoalkyl, the alkyl group of which has up to four carbon atoms, and R is hydrogen or monovalent hydrocarbon radical of up to four carbon atoms and free of aliphatic unsaturation, and the total number of carbon atoms in X and R is not more than eight, are most readily available, the preferred products of this invention have the formula



wherein X and R have the same significance as in the definition of the preferred reactants above.

The 1,1-difluoro-2-cyano (or cyanoalkyl) olefins of this invention are useful as chemical intermediates. For example, 1,1-difluoroacrylonitrile readily adds one mole of piperidine and the adduct hydrolyzes spontaneously in accordance with the following equation:



The products of this invention are also useful as insecticides and as algicides. Thus β,β-difluoroacrylonitrile is useful as an algicide; it kills algae (*Chlorella pyrenoidosa*) at a concentration of 20 micro moles per liter.

In the preparation of this application U. S. 2,437,998, U. S. 2,439,505, U. S. 2,617,836 were considered.

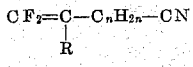
The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described for obvious modifications will occur to those skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. β,β-Difluoroacrylonitrile.

2. β,β-Difluoromethacrylonitrile.

3. A difluoronitrile of up to ten carbons and of the formula



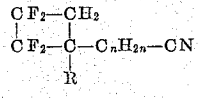
wherein n is a cardinal number up to six and R is a member of the class consisting of hydrogen and monovalent hydrocarbon radicals free of aliphatic unsaturation, R and $C_nH_{2n}CN$ totaling up to eight carbons.

4. A difluoronitrile of up to ten carbons having but one carbon to carbon unsaturation and that a double bond, having two fluorines on one of the doubly bonded carbons, having a cyano group bonded to the other doubly bonded carbon through a divalent —C_nH_{2n}— group wherein n is a cardinal number and having any remaining valence of said other doubly bonded carbon not bonded to hydrogen bonded to a monovalent hydrocarbon radical free from aliphatic unsaturation.

5. A process for preparing difluoro olefinic nitriles which comprises exposing to a pyrolysis temperature, in the range 600–1000° C., a tetrafluorocyclobutane of up to twelve carbons having the four fluorines on two adjacent annular carbons, having two hydrogens on one annular carbon, having the remaining annular carbon bonded to a cyano, —CN, group through a saturated divalent —C_nH_{2n}— radical wherein n is a cardinal number and having any remaining valence of said remaining annular carbon not satisfied by hydrogen satisfied by a monovalent hydrocarbon radical free from aliphatic unsaturation.

6. Process of claim 5 wherein the pyrolysis is carried out at 750°–900° C.

7. Process for preparing difluoro olefinic nitriles which comprises exposing to a pyrolysis temperature, in the range 750–900° C., a compound of up to twelve carbons and of the formula



wherein n is a cardinal number up to six and R is selected from the group consisting of hydrogen and monovalent hydrocarbon radicals of no more than six carbons and free from aliphatic unsaturation.

8. Process for preparing β,β-difluoroacrylonitrile which comprises exposing to a pyrolysis temperature, in the range 750–900° C., 1-cyano-2,2,3,3-tetrafluorocyclobutane.

9. Process for preparing β,β-difluoromethacrylonitrile which comprises exposing to a pyrolysis temperature, in the range 750–900° C., 1-cyano-1-methyl-2,2,3,3-tetrafluorocyclobutane.

10. Process for preparing 1,1-difluoro-3-cyano-1-propene which comprises exposing to a pyrolysis temperature, in the range 750–900° C., 1-cyanomethyl-2,2,3,3-tetrafluorocyclobutane.

11. 1,1-difluoro-3-cyano-1-propene.

References Cited in the file of this patent

UNITED STATES PATENTS

2,406,153	Lewis	Aug. 20, 1946
2,437,998	Clifford et al.	Mar. 16, 1948
2,439,505	Chaney	Apr. 13, 1948
2,541,466	Dickey	Feb. 13, 1951
2,617,836	Pearlson	Nov. 11, 1952
2,674,631	Miller et al.	Apr. 6, 1954