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REACTION PRODUCTS OF POLYFLUOROETHYLENES AND TERMINALLY UNSATURATED COMPOUNDS

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20 Claims. (Cl. 260—85)

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This invention relates to a new class of polymerizable fluorine-containing organic compounds, and more particularly to new cyclic fluorine-containing organic compounds and their polymers.

This application is a continuation-in-part of application Serial No. 484,239, filed April 23, 1943, and of application Serial No. 501,146, filed September 3, 1943, now abandoned.

The usual methods of preparing organic fluorine compounds have been to replace chlorine or bromine with fluorine by means of various inorganic fluorinating reagents such as antimony fluorides, silver fluoride, mercuric fluoride, and hydrogen fluoride. These methods are disadvantageous in that they are hazardous and expensive, give mixtures of products, and are adapted only to certain types of halogenated hydrocarbons. The unsaturated fluorine-containing organic compounds which have heretofore been prepared comprise, for the most part, the fluoroethylenes.

It is an object of the present invention to prepare new, unsaturated, fluorine-containing organic compounds and their polymers. A further object is the production of compounds containing a fluorine-substituted ring and an unsaturated side chain. A further object is the preparation of polymerizable compounds having low flammability and thermally stable ring structures. A still further object is the preparation of polymeric materials useful in the coating, plastics, and electrical insulation arts. Other objects appear hereinafter.

These objects are accomplished by reacting a monomeric polyfluoroethylene, wherein any substituents besides fluorine atoms are other halogen atoms, with a terminally unsaturated diene or enyne of the kind more fully described hereinafter, and, when polymers are desired, by subjecting the resulting unsaturated fluorocyclic compound, alone or in the presence of other polymerizable unsaturated compounds, to conditions generally known for effecting polymerization of vinyl and vinylidene compounds. The monomeric compounds of the invention are characterized by a polyfluorocyclobutane or -cyclobutene ring having a terminally unsaturated side chain, and the polymeric products by repeating structural units which are analogous thereto except for the disappearance of the terminal unsaturation.

More specifically, the polyfluoroethylenes employed in the practice of the invention have the formula $CX_2=CX_2$, wherein at least two X's are fluorine and any X's which are not fluorine are hydrogen or other halogen. Dienes and enynes suitable for the practice of the invention are characterized generically as compounds having two terminal carbon-to-carbon multiple bonds,

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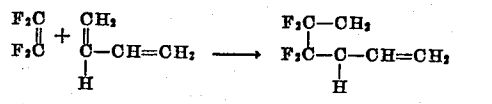
one of the unsaturated terminal carbons being that of a methylene group and the other being that of a methylene or methinyl group; i. e., the additional valences of the terminal unsaturated carbons are satisfied only by hydrogen. By a "terminal carbon" is meant the carbon at the end of a carbon chain; it will be acyclic and joined to only one other carbon. By "terminal unsaturation" is meant a carbon-to-carbon multiple bond between a terminal carbon and the carbon adjacent thereto.

As an illustration of the above mentioned reactants and of the structure of the resulting products, reaction of tetrafluoroethylene at elevated temperatures with 1,3-butadiene yields 1-vinyl-2,2,3,3-tetrafluorocyclobutane, according to the equation:



This is an unusual result since the normal expectation would be either extensive polymerization of some kind or a Diels-Alder type condensation.

The tetrafluoroethylene can be replaced by other monomeric polyfluoroethylenes provided the atoms other than fluorine which are attached to the ethylenic carbons are hydrogen and/or other halogen atoms, as has been indicated above. The atoms, fluorine or otherwise, which are joined to the ethylenic carbons will be found attached to the corresponding pair of carbon atoms in the resulting ring compound, these carbons constituting ring positions 2 and 3 when the carbon having the terminally unsaturated side chain is regarded as constituting ring position 1. One of the remaining pair of carbons in the ring, viz., that constituting ring position 4, will be unsubstituted since it is one of the unsubstituted terminal unsaturated carbons in the diene or enyne. The nature of the atoms or radicals attached to the carbon atom which is adjacent to the methylene or methinyl carbon just mentioned (and which in the product becomes the remaining ring carbon, viz., that constituting ring position 1) has not been found on extended investigation to affect the course of the reaction in the formation of the four-carbon ring compound described herein and in my previously mentioned applications. In the invention claimed in the present application, the second terminally unsaturated linkage present in the companion reactant to the polyfluoroethylene, while in some instances forming a second ring if the polyfluoroethylene is employed in excess, is generally unaffected in the primary ring-forming reaction and is present in the product at the outer end of a side chain attached at ring position 1. This unaffected terminal un-

saturated linkage in such side chain constitutes the element of structure by means of which this polyfluorocyclic compound can be polymerized.

It will be seen from the foregoing that the monomeric compounds of this invention have a ring of four atoms consisting of carbon atoms which comprise a pair of adjacent saturated carbon atoms (ring positions 2 and 3) having as the sole substituents thereon from two to four halogen atoms of which at least two are fluorine atoms, that one of the two other ring carbon atoms is unsubstituted (ring position 4), and that the remaining ring carbon atom (ring position 1) has attached thereto a substituent having a terminal unsaturated carbon joined only to carbon and hydrogen. When the reactant used in forming the four-carbon-ring compounds is an enyne instead of a diene and reaction takes place at the triple bond, ring carbon atoms 1 and 4 are joined by a double bond and the compound is a cyclobutene rather than a cyclobutane as illustrated in the foregoing formula.

The monomeric compounds of this invention are best prepared by heating the polyfluoroethylene and an excess of the diene or enyne to reaction temperature, which will usually be in the range of about 50 to 250° C., in a closed stainless steel or glass-lined vessel for periods of time on the order of 2 to 18 hours, precise times and temperatures depending on the reactivity of the particular materials chosen. In instances in which the chosen reactants tend to polymerize individually or with each other at temperatures required for the cyclization reaction, or in which the desired product itself tends to polymerize under the reaction conditions, it is advisable to employ oxygen-free materials and/or to include polymerization inhibitors such as hydroquinone in small amounts, e. g., 0.2% to 2.0% based on the weight of the reactants; in other instances, these measures are unnecessary, the reactants appearing to have a mutual inhibitory action on each other. The crude reaction product is separated from any polymer present by steam distillation, then washed, dried, and redistilled under appropriate conditions, e. g., in vacuo if the product is of such high molecular weight it cannot be distilled at atmospheric pressure, or through a suitable fractionating column if the reactants are such that the formation of isomers is possible.

The fluorine-substituted four-carbon-ring compounds described herein yield valuable polymeric products when these compounds are polymerized, alone or with other polymerizable compounds having at least one ethylenic double bond. Such polymerizations may be effected by means generally suitable for polymerization of vinyl and vinylidene compounds, preferably by heating to polymerizing temperatures in an aqueous emulsion, and in the presence of a peroxy catalyst.

Specific typical embodiments of the invention are illustrated by the following examples, in which parts are by weight.

Example I

Monomeric 1-vinyl-2,2,3,3-tetrafluorocyclobutane

A silver-lined reaction vessel was evacuated and charged with 54 parts of butadiene and 100 parts of tetrafluoroethylene. The vessel was then closed and heated at 100° C. for 12 hours. The reactor was cooled, bled of excess gas, opened and the product discharged. There was obtained 123 parts of colorless organic liquid which on distillation yielded 102 parts of 1-vinyl-2,2,3,3-tetrafluorocyclobutane boiling at 83–85° C. and having the following refractivity and density: n_D^{25}, 1.3489; d_4^{25}, 1.1866. The structure of the product was substantiated by oxidation with 50% nitric acid to obtain tetrafluorocyclobutanemonocarboxylic acid which distilled at 101° C./25 mm., and by hydrogenation with nickel catalyst to yield 1-ethyl-2,2,3,3-tetrafluorocyclobutane boiling at 90–91° C.; n_D^{25}, 1.3370; d_4^{25}, 1,1506.

Example II

Polymeric 1-vinyl-2,2,3,3-tetrafluorocyclobutane

A stainless-steel autoclave was charged with 150 parts of 1-vinyl-2,2,3,3-tetrafluorocyclobutane (obtained as in Example I) and 1.5 parts of benzoyl peroxide. The autoclave was closed and heated for 7 hours at 100° C. After removing unchanged monomeric vinyltetrafluorocyclobutane, 32 parts of polymeric material remained which set to a hard resin on cooling to room temperature. This polymer was soluble in acetone, dioxane, benzene, and butyl acetate. Analysis showed 47.88% fluorine. The percentage of fluorine calculated for polymeric vinyltetrafluorocyclobutane $(C_8F_4H_6)n$ is 49.3%.

Example III

1 - vinyl - 2,2,3,3 - tetrafluorocyclobutane/methyl methacrylate copolymer

A mixture of 35 parts of 1-vinyl-2,2,3,3-tetrafluorocyclobutane (obtained as in Example I) and 665 parts of methyl methacrylate were placed in a stainless steel autoclave with 1400 parts water, 1.75 parts benzoyl peroxide, 14 parts disodium phosphate, and 1.2 parts of the sodium salt of polymethacrylic acid. The autoclave was sealed and the mixture heated with stirring at 125° C. for one hour, the resulting autogenous pressure being about 60 lb./sq. in. The autoclave was then cooled and opened, additional water added, and the suspended granular polymer filtered off, washed and dried. This polymer is suited for injection molding into bars, rods, and the like. Such bars had a softening temperature of 88° C. as compared to 71° C. for a similarly prepared and molded unmodified methyl methacrylate polymer (determined as described in Example I of Howk and Johnston Serial No. 479,894, filed March 20, 1943 now U. S. Patent No. 2,450,000). Similar results are obtained if the amount of 1-vinyl-2,2,3,3-tetrafluorocyclobutane is reduced to 14 parts, i. e., from 5% to 2%, except that the softening temperature is 80° C. These results show that the softening point of methyl methacrylate polymer is considerably raised by copolymerization with only very small proportions of 1-vinyl-2,2,3,3-tetrafluorocyclobutane, a result which could not be predicted on the basis of the properties of the homopolymers.

Example IV

Monomeric 1-methyl-1-methallyloxymethyl-2,2,3,3-tetrafluorocyclobutane

One hundred and twenty (120) parts of dimethallyl ether and 1.5 parts of benzoyl peroxide were charged into a silver-lined autoclave. After cooling, evacuating, and adding 50 parts of tetrafluoroethylene, the autoclave was closed and heated 8.25 hours at 110° C. with agitation. After cooling to room temperature, the pressure was released and the product discharged. The reaction mixture was steam-distilled and the steam-volatile, water-insoluble organic layer was sepa-

rated, dried, and fractionated through an efficient packed column. After removing the unreacted dimethallyl ether, 1-methyl-1-methallyloxymethyl-2,2,3,3-tetrafluorocyclobutane was obtained, boiling at 70–72° C./19 mm. and having a refractivity, n_D^{25}, of 1.3918.

Analysis

	Percent F	Percent C	Percent H	Iodine Number
Found	32.72	54.47	6.71	120.2, 121.6.
Calcd. for $C_{10}F_4H_{14}O$	33.6	53.2	6.18	112.3 (for one ethylenic bond).

A small amount (4.4 parts) of a soft, sticky, fluorine-containing polymer, not steam-volatile, was also obtained.

EXAMPLE V

Monomeric 1-vinyl-1-chloro-2,2,3,3-tetrafluorocyclobutane and 1-(α-chlorovinyl)-2,2,3,3-tetrafluorocyclobutane

A silver-lined reaction vessel was charged with 88.5 parts of chloroprene, 100 parts of water, and one part of hydroquinone. The vessel was closed, cooled, and evacuated. It was then further charged with 100 parts of tetrafluoroethylene. The temperature of the reaction vessel was maintained at about 100° C. for 9.75 hours. At the end of this time the reactor was cooled to room temperature and the product discharged. The reaction mixture, consisting of a water layer and an organic liquid layer heavier than water, was steam-distilled and the organic layer separated. The resulting 115 parts of colorless liquid product was dried over calcium chloride and was then carefully fractionated through a packed column, whereby a principal fraction boiling at about 108° C., and a small amount of a second fraction boiling at about 122–124° C., were obtained. The fluorine and chlorine analyses of both products corresponded to those for $C_6F_4C1H_5$. The principal product was 1-vinyl-1-chloro-2,2,3,3-tetrafluorocyclobutane, while the smaller fraction was 1-(α-chlorovinyl)-2,2,3,3-tetrafluorocyclobutane.

Fraction	Boiling Point	n_D^{25}	d_4^{25}	Structure
	° C.			
I	108	1.3838	1.3483	$CF_2(CH_2)CF_2C(Cl)CH=CH_2$
II	122-124	1.3864	1.3654	$CF_2(CH_2)CF_2CH(Cl)C=CH_2$

EXAMPLE VI

Monomeric 1 vinyl - 1,2,2,3,3 - pentafluorocyclobutane and 1-(α-fluorovinyl)-2,2,3,3-tetrafluorocyclobutane

A stainless-steel autoclave was flushed with nitrogen, evacuated, and charged with 128 parts of fluoro-2-butadiene-1,3 and 100 parts of tetrafluoroethylene containing less than 20 P. P. M. of oxygen. The autoclave was closed and heated for about 8 hours at 125° C. It was then cooled to room temperature and the product discharged. The reaction mixture was steam-distilled, 142 parts of steam-volatile, colorless liquid products being thereby separated from a small amount of a residual, non-volatile, rubbery polymer. The liquid products were dried and carefully fractionated through a packed column. Two principal products, boiling at about 84–86° C. and 93–95.5° C., were obtained in about equal amounts. These products were identified as 1-vinyl-1,2,2,3,3-pentafluorocyclobutane and 1-(α-fluorovinyl)-2,2,3,3-tetrafluorocyclobutane.

Fraction	Boiling Point	Per Cent F[1]	n_D^{25}	d_4^{25}	Structure
	° C.				
I	85	55.63	1.3405	1.2941	$CF_2(CH_2)CF_2C(F)CH=CH_2$
II	95	56.36	1.3458	1.3193	$CF_2(CH_2)CF(F)CH=CH_2$

[1] Calcd. for $C_6F_5H_5$: 55.2%.

EXAMPLE VII

Monomeric 1-ethinyl-2,2,3,3-tetrafluorocyclobutane and 1-vinyl-2,2,3,3-tetrafluorocyclobutene

A stainless-steel reactor was flushed with nitrogen, evacuated, and charged with 50 parts of monovinylacetylene and 50 parts of tetrafluoroethylene (containing less than 20 P. P. M. of oxygen). The autoclave was heated at 100° C. with agitation for 16.5 hours and then cooled to room temperature and opened. Eighty-two (82) parts of a light yellow liquid reaction mixture was obtained. When this liquid was steam-distilled, about 60 parts of steam-volatile, colorless liquid heavier than water passed over, leaving about 20 parts of a non-volatile, light yellow polymer containing about 26% fluorine. Fractional distillation of the steam-volatile material through a precision still yielded two products as follows:

Fraction	Boiling Point	Analysis[1]			n_D^{25}	d_4^{25}	Structure
		Per Cent F	Per Cent C	Per Cent H			
	° C.						
I	82-84	50.51	51.65	3.63	1.3589	1.2498	$CF_2(CH_2)CF_2CH(C\equiv CH)$
II	96-99	51.13	46.66	2.81	1.3800	1.2588	$CF_2(CH)CF_2C(=CH_2)CH$

[1] Calcd. for $C_6H_4F_4$: F, 50.0%; C, 47.37%; H, 2.63%.

Fractions I reacts with aqueous silver nitrate in the manner typical of acetylenic compounds, and its infra red absorption spectrum shows the presence of a carbon-to-carbon triple bond. Upon hydrogenation, both fractions I and II give 1-ethyl-2,2,3,3-tetrafluorocyclobutane having the same properties as and being indistinguishable from the 1-ethyl-2,2,3,3-tetrafluorocyclobutane obtained by hydrogenating the product of Example I. Based on their analyses, reactions, and physical properties, fraction I is 1-ethinyl-2,2,3,3-tetrafluorocyclobutane and fraction II is 1-vinyl-2,2,3,3,-tetrafluorocyclobutene, the structural formulae being as shown above. On standing at room temperature, fraction II polymerizes to a clear, transparent polymer.

Example VIII

Polymeric 1-vinyl-2,2,3,3-tetrafluorocyclobutene

A glass pressure vessel was flushed with nitrogen and charged with 0.21 part sodium hydroxide, 28 parts of distilled water, 0.8 part of oleic acid, 0.2 part of a condensation product of formaldehyde and sodium naphtalene sulfonate (prepared as described in U. S. Patent 1,336,759), 0.2 part of potassium persulfate, and 20 parts of 1 - vinyl-2,2,3,3 - tetrafluorocyclobutene obtained as in Example VII. The vessel was closed and shaken in a constant-temperature water bath at 37° C. for 48 hours. The latex thereby formed was treated with a few drops of dilute acetic acid, and the resulting polymer was separated, washed with water, and dried in an oven at 65° C., 17.2 parts being thus obtained. This polymeric vinyltetrafluorocyclobutene was readily moldable, was soluble in butyl acetate, and was found on analysis to have a fluorine content of 49.21%.

Example IX

1-vinyl-2,2,3,3-tetrafluorocyclobutene/methyl methacrylate copolymer

A glass pressure vessel was flushed with nitrogen and charged with .05 part of sodium hydroxide, 7 parts of water, 0.2 part of oleic acid, 0.05 part of a condensation product of formaldehyde and sodium naphthalene sulfonate, 0.05 part of potassium persulfate, 3 parts of methyl methacrylate, and 2 parts of 1-vinyl-2,2,3,3-tetrafluorocyclobutene, obtained as in Example VII. The reactor was closed, and the mixture was emulsified by shaking. It was then heated at 37° C. with agitation in a constant-temperature water bath for 48 hours. The resultant latex was acidified with dilute acetic acid and coagulated with brine, the coagulated product washed thoroughly with water and alcohol, and the polymeric material dried in an oven at 65° C. An 82% yield (4.1 parts) of a colorless methyl methacrylate/vinyltetrafluorocyclobutene copolymer was thus obtained. This copolymer was soluble in dioxane, butyl acetate, and chloroform, and was insoluble in alcohol. It was found on analysis to have 24.39% fluorine, which indicates a methyl metacrylate/vinyltetrafluorocyclobutene mole ratio of 1.6:1 in the copolymer.

Example X

1-vinyl-2,2,3,3-tetrafluorocyclobutene/styrene copolymer

The copolymerization of 3 parts of 1-vinyl-2,2,3,3-tetrafluorocyclobutene with 2 parts of styrene according to the procedure described in Example IX for methyl methacrylate yielded 4.4 parts of a colorless copolymer which was soluble in alcohol, dioxane, butyl acetate, and chloroform. It had a fluorine content of 30.84%, indicating a styrene/vinyltetrafluorocyclobutene mole ratio of 0.91:1 in the copolymer.

Example XI

1-vinyl-2,2,3,3-tetrafluorocyclobutene/acrylonitrile copolymer

The copolymerization of 3 parts of 1-vinyl-2,2,3,3-tetrafluorocyclobutene with 2 parts of acrylonitrile according to the procedure described in Example IX for methyl methacrylate yielded 3.5 parts of polymer which was insoluble in alcohol, toluene, and chloroform but was swelled by warm butyl acetate. It had a fluorine content of 35.79%, indicating an acrylonitrile/vinyltetrafluorocyclobutene mole ratio in the copolymer of 1.14:1.

Example XII

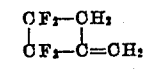
1-vinyl-2,2,3,3-tetrafluorocyclobutene/butadiene copolymer

A pressure vessel was charged with 56 parts of water, 0.4 part of potassium persulfate, 0.4 part of condensation product of sodium naphthalene sulfonate and formaldehyde, 0.42 part of sodium hydroxide, and 1.6 g. of oleic acid. After these ingredients had dissolved, the vessel was cooled and 4 parts of a 1% solution of potassium ferricyanide, 0.24 part of n-dodecanethiol, 32 parts of butadiene, and 8 parts of 1-vinyl-2,2,3,3-tetrafluorocyclobutene were added. The vessel was closed and heated at 40° C. for 39 hours with agitation. A small portion of the latex was coagulated by means of alcohol and brine and the coagulum washed and dried. It had a fluorine content of 14.81%, which indicates that the copolymer contains 29.6% polymerized 1-vinyl-2,2,3,3-tetrafluorocyclobutene. To the remainder of the latex was added 4 parts of a 50% aqueous dispersion of a mixture consisting of 55% phenyl-beta-naphthylamine and 45% of diphenylamine as an antioxidant. This emulsion was acidified with acidic acid, then treated with a saturated sodium chloride solution, an elastomer being thereby obtained which after washing and drying amounted to 36.4 parts. Thirty (30) parts of this washed and dried elastomer was compounded with 15 parts of carbon black, 1.5 parts of zinc oxide, 0.6 part of stearic acid, 0.6 part of sulfur, and 0.375 part of 2-mercaptothiazoline, and this composition was then cured by heating for 30 minutes at 153° C. The resulting vulcanizate had a tensile strength of 1250 lbs./sq. in. at 210% elongation, good hardness, and fair resilience.

Example XIII

1-methylene-2,2,3,3-tetrafluorocyclobutane

Thirty parts of allene and 75 parts of tetrafluoroethylene were heated in a silver-lined pressure reaction vessel at 150° C. for 14 hours. The reaction vessel was cooled, bled of excess gas, opened and the product discharged. There was obtained 18 parts of a liquid product which on distillation through a packed column yielded 1-methylene-2,2,3,3-tetrafluorocyclobutane,

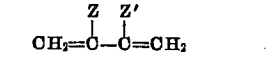


boiling at 64–66° C., having a refractivity, n_D^{25}, of 1.3318, and a density, d_4^{25}, of 1.2288.

	Per Cent C	Per Cent H	Per Cent F
Analysis:			
Calc'd for $C_4H_4F_4$	42.87	2.88	54.25
Found	42.98	3.72	52.9

The invention has been illustrated in the examples with tetrafluoroethylene since it is commercially available and will normally be employed for that and other reasons. However, the invention may be practiced with any polyfluoroethylene of the hereinbefore mentioned type, with formation therefrom of other polyfluorocyclobutanes and -butenes having a terminally unsaturated side chain, e. g., a vinyl, vinylidene, or ethinyl radical, all of which products are embraced by the invention. Other polyfluoroethylenes which may be used are trifluorochloroethylene, 1,1-difluoro-2,2-dichloroethylene, 1,2-difluoro-1,2-dichloroethylene, 1,2-difluoro-1,2-dichloroethylene, trifluoroiodoethylene, 1,1-difluoro-2-chloroethylene, trifluorobromoethylene, 1,1-difluoroethylene, and trifluoroethylene. The tetrahalogenoethylenes, especially those having at least three fluorine atoms, and, in particular, tetrafluoroethylene, are preferred because of their greater reactivity.

With respect to the companion reactant, any compound having two terminal carbon-to-carbon multiple bonds, one of which is the carbon of a methylene or methinyl group, may be employed in the practice of this invention. The remainder of the molecule is immaterial, the reaction proceeding irrespective of molecular size, chain length, configuration, or other atoms or groups. While, as shown in Example IV, the unsaturation in such compounds may be unconjugated, the preferred compounds contain conjugated unsaturation, and of these the most useful may be expressed by the general formula



wherein Z and Z' are hydrogen, halogen, cyano, alkyl, aryl, or alkoxy.

Other examples of particular di-, tri-, or tetrafluoro four-carbon ring compounds which can be obtained by the practice of this invention comprise: 1-methyl-1-(alphamethylvinyl)-2,3,3-trifluorocyclobutane and 1-methyl-1-(alphamethylvinyl)-2,2,3-trifluorocyclobutane, obtained from trifluoroethylene and 2,3-dimethylbutadiene-1,3; 1-vinyl-2-chloro-3,3-difluorocyclobutane and 1-vinyl-2,2-difluoro-3-chlorocyclobutane, obtained from 1-chloro-2,2-difluoroethylene and butadiene-1,3; 1-vinyl-2,2-dichloro-3,3-difluorocyclobutane and 1-vinyl-2,2-difluoro-3,3-dichlorocyclobutane, obtained from 1,1-dichloro-2,2-difluoroethylene and butadiene-1,3; and 1-vinyl-1,2-dichloro-2,3,3-trifluorocyclobutane and other structural isomers, obtained from chloroprene and chlorotrifluoroethylene.

The following additional polyfluorocyclobutanes and -butenes are obtained from tetrafluoroethylene and the diene or enyne reactant indicated:

Fluorocyclic Compound	Diene or Enyne
1-Phenyl-1-vinyl-2,2,3,3-tetrafluorocyclobutane	2-Phenylbutadiene-1,3.
1-Methyl-1-vinyl-2,2,3,3-tetrafluorocyclobutane	2-Methylbutadiene-1,3.
1-Cyano-1-vinyl-2,2,3,3-tetrafluorocyclobutane	2-Cyanobutadiene-1,3.
1-Methyl-1-(α-methylvinyl)-2,2,3,3-tetrafluorocyclobutane	2,3-Dimethylbutadiene-1,3.
1-Allyl-2,2,3,3-tetrafluorocyclobutene	Allylacetylene.
1-Bromo-1-vinyl-2,2,3,3-tetrafluorocyclobutane	2-Bromobutadiene-1,3.
1-Ethoxy-1-vinyl-2,2,3,3-tetrafluorocyclobutane	2-Ethoxybutadiene-1,3.
1-Allyl-2,2,3,3-tetrafluorocyclobutane	Pentadiene-1,4.
1-Vinyloxy-2,2,3,3-tetrafluorocyclobutane	Divinyl ether.
1-Allyloxymethyl-2,2,3,3-tetrafluorocyclobutane	Diallyl ether.
1-(p-vinylphenyl)-2,2,3,3-tetrafluorocyclobutane	Divinylbenzene.
1-Methylene-2,2,3,3-tetrafluorocyclobutane	Allene.
1-Vinylethinyl-2,2,3,3-tetrafluorocyclobutane	Divinylacetylene.
1-Carbovinyloxy-2,2,3,3-tetrafluorocyclobutane and	Vinyl acrylate.
1-Acrylyloxy-2,2,3,3-tetrafluorocyclobutane	
1-Chloro-1-carboallyloxy-2,2,3,3-tetrafluorocyclobutane	Allyl alpha-chloroacrylate.
1-Methyl-1-carbomethallyloxy-2,2,3,3-tetrafluorocyclobutane	Methallyl methacrylate.
1-Methyl-1-carbomethacrylyloxy-2,2,3,3-tetrafluorocyclobutane	Methacrylic anhydride.

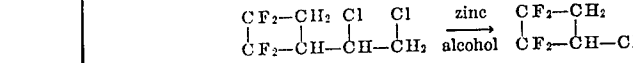
The enynes and many dienes of the kind employed in this invention are "unsymmetrical" in that different residual molecular configurations are attached to the two terminal unsaturated carbons. With such compounds, two structural isomers are formally possible, and they are generally obtained through reaction of the polyfluoroethylene with part of the diene or enyne at one of its multiple bonds, and with the remainder of the diene or enyne at its other multiple bond, as is shown in Examples V, VI, and VII. Many of the reactants in the foregoing table are also "unsymmetrical," and they give like results although all the isomeric products are not shown. Normally predominating is the isomer obtained by reaction at the unsaturated carbons having activating atoms or groups (e. g., halogen, phenyl, cyano, alkoxy, carbonyl) attached thereto, and these are preferentially shown in the table. Isomeric products may likewise be obtained when the polyfluoroethylene is "unsymmetrical," as is shown in the paragraph preceding the table.

From the formulae in the above table and in the examples, and from other explanation hereinbefore given, it will be seen that these monomeric cyclic compounds have a ring of four atoms (all of them carbon) which include a pair of adjacent saturated carbons having as the sole substituents thereon from two to four halogen atoms of which at least two are fluorine, a carbon which is unsubstituted, and another carbon which has attached thereto the "residue" of the diene or enyne after ring formation, i. e., the part of the molecule remaining after removal of one of the terminal carbons and all atoms directly attached thereto. One of the valances of the last-mentioned ring carbon thus must be satisfied by a radical having a terminal unsaturated carbon joined only to carbon and hydrogen.

The practice of this invention is not necessarily confined to methods given in the examples and the paragraphs immediately preceding them. Thus, in the cyclization reaction, it is often advantageous to include an inert solvent such as benzene or toluene, and/or an inert liquid medium such as water, particularly when the reaction tends to become exothermic after having

been initiated. While the reaction normally proceeds satisfactorily at the autogenous pressure generated by the reactants at reaction temperature, externally applied pressures up to as high as 1000 atm. are possible and may assist the reaction in some instances. On the other hand, the reaction can on occasion be carried out in an open system by mixing the vapors of the reactants and passing them through a hot tube. With some of the more highly reactive combinations, reaction may begin at temperatures below 50° C., and there is no absolute upper limit for the more sluggish reactants except that at which they or the desired products decompose.

The monomeric products of this invention can be prepared by other procedures such as by dehalogenation, dehydrohalogenation, deactylation, and dehydration, etc., of selected substituted fluorocyclobutanes and fluorocyclobutenes, as illustrated by the following equation:



When the reactants are not themselves particularly sensitive to polymerization, the monomeric compounds of this invention may be prepared and polymerized to at least some degree in one operation by inclusion of polymerization catalysts. However, such procedure is likely to give a complex polymeric mixture and is not recommended, it being preferable as illustrated in the examples to effect the cyclization reaction under conditions which prevent or minimize polymer formation, the cyclic monomer then being separated and polymerized under controlled conditions. Any polymer which might still be formed along with the cyclic monomer in the primary reaction does not affect the utility of the latter compound, which may readily be separated by steam distillation.

The examples illustrate emulsion polymerization, which is generally the best method. These polymerizations may, however, also be effected in "bulk" or in solution in an organic solvent. Whatever the medium or method, they are promoted by ultraviolet light and by the usual catalysts, e. g., oxygen, peroxy compounds generally, amine oxides, hydrazines, active halogen compounds, and the newly discovered azo compounds, in the usual amounts of about 0.01% to 5.0%. These polymerizations may advantageously be carried out in aqueous emulsion by the so-called "activated persulfate" and "activation-reduction" methods, involving, respectively, a combination of a persulfate catalyst with a long-chain hydrocarbon sulfate or sulfonate, and a combination of a peroxy catalyst with a salt of sulfurous acid, e. g., sodium bisulfite. Temperatures may be varied as necessary, e. g., from as low as 0° C. in the more active systems to up to 150° C. in others. Closed systems, and therewith autogenous pressures, will be employed if the polymerization temperature is above the atmospheric boiling point of the monomer or monomers used. Acidic, neutral, and alkaline aqueous media are contemplated. Dispersing agents chosen will vary according to the nature of the aqueous medium: in neutral media, polyvinyl alcohol, agar, gelatin, methylstarch, sodium polymethacrylate, and modified polyethylene oxides may be used; in alkaline media, the alkali metal or amine salts of longchain fatty acids, e. g., sodium oleate, potassium laurate, or triethanolamine stearate, are suitable; and in acid media, salts of long-chain alkyl sulfates and sulfonates, e. g., sodium cetyl sulfate, the sodium salt of sulfonated paraffin white oil, or the sodium salt of sulfonated oleyl acetate, may be employed.

As has been indicated, one phase of the invention includes copolymers of the unsaturated polyfluorocyclic compounds with other unsaturated, readily polymerizable compounds, among them the following: vinyl esters, such as vinyl acetate, vinyl chloride, and vinyl fluoride; acrylic and methacrylic acids and their esters, anhydrides, amides, and nitriles; hydrocarbons having olefinic unsaturation, such as ethylene, propylene, isobutylene, styrene, butadiene, and isoprene; haloprenes, such as chloro-2-butadiene-1,3 and fluoro-2-butadiene-1,3; vinylidene halides, such as vinylidene chloride; fumaric and maleic esters, such as diethyl fumarate; unsaturated ketones, such as methyl vinyl ketone; and (vinylalkynyl) carbinols, such as dimethyl(vinylethinyl) carbinol. The unsaturation in the co-monomer is preferably terminal. As will be seen from Example III, the effect of the fluorocyclic component of these copolymers is apparent even when the amount is quite small, and the invention therefore comprehends polymers in which the fluorocyclic compound is present in amounts of 5–100%. Preferably, however, the amount exceeds 50%.

The products of this invention contain a high percentage of fluorine and are particularly advantageous in view of their superior stability and decreased flammability. The monomers are useful as chemical intermediates and solvents. The polymeric products are useful in making plastics, coatings, films, foils, fibers, electrical insulation, and adhesives. For any of these purposes, the polymer may be combined with or prepared in the presence of plasticizers, stabilizers, fillers, pigments, dyes, softeners, natural resins, or other synthetic resins.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for preparing organic fluorine compounds containing a four-carbon ring, said process comprising heating to reaction temperature within the range of about 50° C. to 250° C. reactants consisting of (1) a monoethylenic compound of two and only two carbon atoms having attached thereto from two to four halogen atoms of which at least two are fluorine, and (2) a compound having two terminal carbon-to-carbon multiple bonds of which at least one is ethylenic, the remaining valences of the terminal unsaturated carbons of said last-mentioned compound being satisfied by hydrogen.

2. A process for preparing organic fluorine compounds containing a four-carbon ring, said process comprising heating to reaction temperature within the range of about 50° C. to 250° C. and under superatmospheric pressure reactants consisting of (1) a tetrahalogenoethylene containing at least two fluorine atoms and (2) a compound having two conjugated terminal carbon-to-carbon multiple bonds of which at least one is ethylenic, the remaining valences of the terminal unsaturated carbons of said last-mentioned compound being satisfied by hydrogen.

3. A compound having a ring of four atoms consisting of carbon atoms, said atoms comprising a pair of adjacent saturated carbon atoms hav-

ing as the sole substituents thereon from two to four halogen atoms of which at least two are fluorine atoms, the carbon atom in one of the two remaining positions in said ring being unsubstituted, and the carbon atom in the other of the two remaining ring positions having attached thereto a substituent having a terminal unsaturated carbon joined only to carbon and hydrogen.

4. A compound having a ring of four atoms consisting of carbon atoms, said atoms comprising a pair of adjacent saturated carbon atoms having as the sole substituents thereon from two to four halogen atoms of which at least two are fluorine atoms, the carbon atom in one of the two remaining positions in said ring being unsubstituted, and the carbon atom in the other of the two remaining ring positions having attached thereto a substituent having a terminal methylene group.

5. A compound having a ring of four atoms consisting of carbon atoms, said atoms comprising a pair of adjacent saturated carbon atoms having attached thereto four halogen atoms of which at least two are fluorine, the carbon atom in one of the two remaining positions in said ring being unsubstituted, and the carbon atom in the other of the two remaining ring positions having attached thereto a substituent having a terminal unsaturated carbon joined only to carbon and hydrogen and separated from the ring by a single chain carbon.

6. The compound defined in claim 3 in which four fluorine atoms are attached to said first mentioned pair of adjacent carbon atoms.

7. The compound defined in claim 4 in which four fluorine atoms are attached to said first mentioned pair of adjacent carbon atoms.

8. The compound defined in claim 5 in which four fluorine atoms are attached to said first mentioned pair of adjacent carbon atoms.

9. The compound defined in claim 5 in which said substituent is the vinyl radical.

10. The compound defined in claim 5 in which said substituent is the vinyl radical, and in which four fluorine atoms are attached to said first mentioned pair of adjacent carbon atoms.

11. A fluorocyclobutane consisting of the compound defined in claim 3.

12. 1-vinyl-2,2,3,3-tetrafluorocyclobutane.

13. A polymer of the compound defined in claim 3.

14. A polymer of the compound defined in claim 4.

15. A polymer of the compound defined in claim 5.

16. A polymer of the compound defined in claim 6.

17. Polymeric 1-vinyl-2,2,3,3-tetrafluorocyclobutane.

18. A process for preparing monomeric organic fluorine compounds containing a four-carbon ring, said process comprising heating, in contact with a polymerization inhibitor, to reaction temperature within the range of about 50° C. to 250° C., reactants consisting of (1) a monoethylenic compound of two and only two carbon atoms having attached thereto from two to four halogen atoms of which at least two are fluorine, and (2) a compound having two terminal carbon-to-carbon multiple bonds of which at least one is ethylenic, the remaining valences of the terminal unsaturated carbons of said last-mentioned compound being satisfied by hydrogen.

19. 1-vinyl-1-chloro - 2,2,3,3 - tetrafluorocyclobutane.

20. 1-vinyl-2,2,3,3-tetrafluorocyclobutene.

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No references cited.