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PREPARATION OF PERFLUORODIENES

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9 Claims. (Cl. 260—653.3)

This invention is concerned with polyfluorinated organic compounds; more particularly, but not exclusively, this invention is concerned with conjugated and unconjugated perfluorodienes and certain derivatives of such compounds.

U. S. specification No. 2,668,864 discloses the preparation of terminally unsaturated aliphatic perfluoro monoolefins by a dry reaction which is conveniently carried out at atmospheric pressure and which involves the pyrolytic decarboxylation and defluorination of an anhydrous alkali metal salt of a perfluoro-alkyl monocarboxylic acid. It is stated in this U. S. specification that the obtaining of high yields of fluorocarbon olefins from this reaction is peculiar to the salts of monocarboxylic acids and that salts of polycarboxylic acids do not produce perfluoro olefins in good yield.

In accordance with a first aspect of this invention, it has been discovered that the above pyrolysis reaction can, in fact, be applied to the dialkali metal salts of perfluoroalkyl dicarboxylic acids to produce satisfactory yields of dienes, either conjugated or unconjugated, provided the pyrolysis reaction is carried out at subatmospheric pressure.

That this pyrolysis reaction can be satisfactorily applied to the production of dienes from salts of dicarboxylic acids is surprising, for it was to have been expected that the product theoretically obtainable by the pyrolysis reaction would, by reason of the two double bonds therein, be too reactive and unstable to permit of satisfactory yields. This is particularly the case where the product theoretically obtainable from the pyrolysis reaction is a conjugated diene, since a compound of this type is far more reactive than, and exhibits properties markedly different from, a non-conjugated diene and might thus have been expected to undergo side reactions and/or complete breakdown; thus, for example, the compound hexafluorobutadiene-1,3, the theoretical product of the pyrolysis of a dialkali metal salt of octafluoroadipic acid, is extremely reactive and yields dimers and trimers when subjected to elevated temperatures at atmospheric pressure. The pyrolysis reaction is therefore of particular interest in its application to the preparation of conjugated dienes, notably the useful diene hexafluorobutadiene-1,3.

More specifically, this first aspect of the invention may be stated to reside in subjecting to pyrolysis, at a subatmospheric pressure, an anhydrous compound having the formula:

$$MO_2C(CF_2)_nCO_2M$$

in which M is an alkali metal, preferably sodium, and n is an integer of at least 4, preferably an integer from 4 to 20 or 24 or so. The diene recovered from the pyrolysis has two carbon atoms less than its precursor and has the formula:

$$F_2C{=}CF(CF_2)_mCF{=}CF_2$$

in which $m{=}n{-}4$, so that, when $n{=}4$ to 20, m is zero or an integer from 1 to 16.

In the pyrolysis of the dialkali metal salts, the salts must be anhydrous and are desirably spread in a thin layer upon an inert supporting material such as platinum foil, for example, and placed in a furnace tube constructed of some inert material, such as nickel. An inert reaction vessel is necessary in order to prevent reaction thereof with gaseous products at the high temperatures of pyrolysis. The furnace is in general evacuated to a pressure of below 300 mm. and preferably 10^{-3} to 20 mm., of mercury absolute and is heated rapidly to a temperature in the range of 100 to 450° C. Preferably the temperature is raised rapidly to that at which reaction begins. The time of reaction may be between 0.1 and 10 hours depending upon the reaction temperature.

The volatile products of the reaction are collected in traps cooled to a low temperature by a medium such as liquid oxygen, for example, and are then transferred to a distillation system where they are separated into fractions. Exemplary of the dialkali metal salts of perfluoro dicarboxylic acids which may be pyrolyzed according to the process of the invention are $NaO_2C(CF_2)_4CO_2Na$, $NaO_2C(CF_2)_5CO_2Na$, $NaO_2C(CF_2)_8CO_2Na$, $NaO_2C(CF_2)_{20}CO_2Na$, $KO_2C(CF_2)_4CO_2K$, and $LiO_2C(CF_2)_{12}CO_2Li$.

Particularly when the above-described pyrolysis of dialkali metal salts of perfluoro-alkyl dicarboxylic acids is carried out under relatively mild conditions, there may be formed, as a by-product, the acyl fluoride of a perfluoroalkly monocarboxylic acid having a terminal olefinic bond produced by decarboxylation (and concomitant defluorination) of only one of the carboxylic acid groups present in the starting material subjected to pyrolysis. This acyl fluroide on hydrolysis yields the corresponding terminally unsaturated monocarboxylic acid, the alkali metal salt of which may likewise be subjected to pyrolysis at subatmospheric pressures to produce satisfactory yields of dienes which again may be either conjugated or unconjugated. This reaction, which constitutes a second aspect of this invention, is also surprising in view of the greater reactivity of the mono-olefinic starting material as compared with a corresponding fully saturated material as employed in the U. S. specification cited above, and also of course for reasons similar to those advanced above in connection with the pyrolysis of the dicarboxylic acid salts.

In accordance therefore with this second aspect of the invention, there is subjected to pyrolysis, at sub-atmospheric pressures, an anhydrous compound having the formula:

$$F_2C{=}CF(CF_2)_nCO_2M$$

in which M is an alkali metal, preferably sodium, and n is an integer of at least 2, preferably an integer from 2 to 18. The dienes recovered as products of this process possess one less carbon atom than their precursors and have the formula:

$$F_2C{=}CF(CF_2)_mCF{=}CF_2$$

in which $m{=}n{-}2$, so that m has a value from zero to 16 when $n{=}2$ to 18. When in the above formulae $n{=}2$ and $m{=}0$, the invention provides a novel route to the useful conjugated diene perfluorobutadiene-1,3.

In the pyrolysis of the alkali metal salts of unsaturated perfluoro monocarboxylic acids, the salt is powdered, thoroughly dried and pyrolyzed on a platinum or other inert support placed in an evacuated nickel furnace tube in a manner similar to that described above in connection with the pyrolysis of dialkali metal salts of saturated perfluoro dicarboxylic acids. The pyrolysis may be effected at a temperature in the range of 100 to 450° C. during a period of 0.1 to 10 hours depending upon the

reaction temperature. The volatile products are separated by distillation. Exemplary of the salts of unsaturated perfluoro monocarboxylic acids which may be treated in accordance with this process are the following:

$F_2C=CF(OF_2)_4CO_2Na$, $F_2C=CF(CF_2)_5CO_2Na$
$F_2C=CF(CF_2)_{10}CO_2Na$, $F_2C=CF(CF_2)_{20}CO_2Na$
$F_2C=CF(OF_2)_2CO_2K$, and $F_2C=CF(CF_2)_7CO_2Li$

Although unsaturated perfluoro monocarboxylic acids may be produced, as mentioned above, from the by-products of the pyrolysis of dialkali metal salts of saturated perfluoro dicarbooxylic acids, it is to be understood that these compounds can be prepared in other ways for use in the invention.

In both the above reactions involving alkali metal salts of perfluoro carboxylic acids, the sodium salts are preferred for reasons of cheapness, but it is to be understood that lithium, potassium, rubidium and cesium salts are also usable.

The alkali metal salts of unsaturated perfluoro monocarboxylic acids used in the pyrolysis reaction just described, or the free acids themselves, may be converted to the corresponding silver salts which on reaction with iodine, bromine or chlorine undergo decarboxylation to yield a polyfluoro halogenoalkene and/or a polyfluorohalogenoalkane. These reactions which, it may be noted, are quite generally applicable to silver salts of the formula $CF_2=CF(CF_2)_nCOOAg$ where n is an integer of 1 or more, may be represented as follows:

(1)

$$F_2C=CF(CF_2)_nCO_2M \xrightarrow[\text{Silver Salt}]{\text{Inorganic}} F_2C=CF(CF_2)_nCO_2Ag$$

where M is an alkali metal or hydrogen, and n is an integer of 1 or more, preferably not more than 20.

(2)

(a) $$F_2C=CF(CF_2)_nCO_2Ag \xrightarrow{X_2} F_2C=CF(CF_2)_nX$$

when $X=I$

(b) $$F_2C=CF(CF_2)_nCO_2Ag \xrightarrow{X_2} F_2C=CF(CF_2)_nX$$

and/or

$$CF_2=XCFX(CF_2)_nX$$

when X=Cl or Br.

Although it is known (vide, Haszeldine, J. Chem. Soc. 4259, 1952) that the silver salts of perfluoroalkyl monocarboxylic acids undergo decarboxylation with halogens to form the corresponding halides, it was surprising to find that the reaction also proceeds and gives high yields with the silver salts of unsaturated perfluoro monocarboxylic acids.

As an example of the silver salt reaction with halogen, silver perfluoro-4-pentenoate (prepared by treating perfluoro-4-pentenoic acid with an inorganic silver salt) may be caused to react with iodine to form 4-iodo-perfluorobutene-1, which latter compound may in turn be caused to react with chlorine or bromine to form 1,2,4-trichloro- or -bromo-heptafluorobutane.

Reactions (1) and (2) indicated above are of particular interest in that they yield new classes of compounds. Reaction (1) yields new compounds of the formula $F_2C=CF(CF_2)_nCO_2Ag$, where n is an integer preferably from 1 to 20; and reaction (2) yields new iodo compounds of the formula $F_2C=CF(CF_2)_nI$ where n is an integer of at least 2, preferably 2 to 20, and also new compounds of the formula $CF_2XCFX(CF_2)_nX$ where n is an integer of at least 2, preferably 2 to 10, and X is chlorine or bromine.

Although the silver salt/halogen reaction is set forth above as applying to unsaturated silver salts of the formula $F_2C=CF(CF_2)_nCO_2Ag$, where n is an integer of 1 or more, it is to be noted that the reaction also surprisingly proceeds between iodine and the compound $F_2C=CFCO_2Ag$ to produce the compound $CF_2=CFI$.

The invention will be further illustrated by reference to the following specific examples in which all parts are by weight:

Example 1

Octafluoroadipic acid was prepared by one of the routes reported in the literature, namely by the oxidation of perfluorocyclohexene (Haszeldine, Nature 168, 1028, 1951), and was converted into the disodium salt by neutralization with aqueous sodium hydroxide. The salt, isolated by evaporation of the aqueous solution to dryness in vacuo, was ground in a mortar and thoroughly dried at a temperature of 120° C. in vacuo.

Five parts of the anhydrous disodium octafluoroadipate were spread in a thin layer in a horizontal open cylinder of platinum foil, which was then inserted into a horizontal nickel furnace tube having an internal diameter of one inch. The furnace tube was sealed at one end and evacuated to a pressure of 10^{-2} mm. Two glass traps cooled by liquid oxygen were connected in series between the furnace tubes and the vacuum pump. The furnace was then heated stepwise to a temperature of 450° C. during a period of 2.5 hours, the traps being periodically examined during the heating. No reaction was detected at a furnace temperature up to and including 200° C., but appreciable reaction occurred when a temperature of 300° C. was attained, and there was little sign of further reaction at temperatures above 370° C. The combined volatile products were transferred to a vacuum system where they were separated into fractions boiling above or below a temperature of 10° C.

Infra-red spectroscopic examination of the more volatile fraction showed it to contain hexafluorobutadiene-1,3, contaminated by carbon dioxide and by material (probably acyl fluorides) which showed carbonyl absorption at 5.3μ. This fraction was then washed with 2 N aqueous sodium hydroxide and distilled to yield 0.73 part of hexafluorobutadiene-1,3, a yield of 30 percent, boiling point 5.7° C. (Found: C, 29.7; M, 162. Calculated for C_4F_6; C, 29.6; M, 162.) The boiling point and infra-red spectrum of the purified material were identical with those reported earlier (Haszeldine, J. Chem. Soc. 4423, 1952). Repetitions of this experiment produced yields of hexafluorobutadiene of 32, 37 and 25 percent by weight.

Infra-red spectroscopic examination of the less volatile fraction (M, 240) showed it to contain the $-CF_2COF$ group (C=O absorption at 5.31μ; cf. CF_3COF 5.25μ; C_2F_5COF 5.29μ; cf. $CF_3CF=CF_2$ 5.56μ; $C_2F_5CF=CF_2$ 5.56μ; see J. Chem. Soc. 4423, 4259, 1952). The fraction was shaken with 5 parts of water in a sealed tube and the primary portion of the fraction dissolved, leaving 0.05 part of an unidentified fraction, boiling point 150° C. (isoteniscope) (M, 275). The aqueous solution, which gave a positive test for fluoride, was extracted ten times with a total of 21 parts of ether. The ethereal solution was dried over sodium sulfate and, after removal of the ether, the residual liquid was distilled from a small amount of phosphoric anhydride through a short column and 0.69 part of perfluoro-4-pentenoic acid was recovered, equivalent to a yield of 21 percent by weight, boiling point 75 to 76° C./59 mm. Hg absolute. (Found: C, 26.4; H, 0.5; equivalent 226. $C_5HO_2F_7$ requires C, 26.6; H, 0.4; equivalent 226.) The infra-red spectrum of the acid showed a band at 5.62μ revealing the presence of a carboxyl group; the C=C stretching absorption is combined with this band.

Examination of the solid residue from the pyrolysis of sodium octafluoroadipate showed it to contain sodium fluoride, carbon and carbonaceous material.

Example 2

1.02 parts of perfluoro-4-pentenoic acid were neutralized with 5 N aqueous sodium hydroxide and the anhydrous sodium salt was obtained by evaporation of the aqueous solution in vacuo. The salt was powdered, re-

dried at a temperature of 120° C. and a pressure of 10^{-2} mm. Hg absolute, and then placed in the platinum cylinder and furnace described in Example 1 above. The pyrolysis of the salt was accomplished by raising the temperature of the furnace from 160 to 450° C. over a period of 2.5 hours. The residual sodium fluoride contained only a small amount of carbon. The volatile products were shaken in a sealed tube with 2 N aqueous sodium hydroxide and then distilled to yield 61 percent by weight of hexafluorobutadiene-1,3 identified by comparison of its infra-red spectrum with that recorded in J. Chem. Soc. 4423, 1952. When mixed with a slight excess of chlorine and exposed to ultra-violet light, two molecules of chlorine were absorbed to give 1,2,3,4-tetrachlorohexafluorobutane identical with the compound described in J. Chem. Soc. 4423, 1952.

Example 3

1.2 parts of perfluoro-4-pentenoic acid were dissolved in water and treated with a slight excess of freshly prepared silver carbonate and a 97 percent yield of silver perfluoro-4-pentenoate was obtained. (Found: Ag, 32.3. $C_5O_2F_7Ag$ requires Ag, 32.4.) The product was isolated as a white crystalline solid by evaporation of the aqueous solution to dryness in vacuo.

Example 4

1.5 parts of silver perfluoro-4-pentenoate were mixed with a 300 percent excess of dry, finely powdered iodine in a silica flask connected to two traps cooled by liquid oxygen. The pressure in the apparatus was maintained at 300 mm. Hg absolute and the solid mixture was heated by means of a small flame. A smooth reaction occurred, and, after pumping the evolved gases into the traps, the combined volatile material was washed in a sealed tube with aqueous sodium hydroxide. The residual organic material was purified by distillation in vacuo to provide a 72 percent by weight yield of 4-iodoperfluorobutene-1, boiling point (isoteniscope) 20° C./65 mm. Hg absolute, ca. 70° C./760 mm. Hg absolute (micro). (Found: C, 15.4; M, 309. C_4IF_7 requires C, 15.6; M, 308.) The compound shows a band at 5.58μ in the infra-red.

Example 5

0.7 part of 4-iodoperfluorobutene-1 was treated with an excess of chlorine in a sealed silica tube exposed to ultra-violet light for two days to produce an 83 percent by weight yield of 1,2,4-trichloroheptafluorobutane, boiling point 96 to 97° C. (micro). (Found: C, 16.8; M, 285. $C_4Cl_3F_7$ requires C, 16.7; M, 287.5.)

The same compound was obtained by reaction of an excess of dry chlorine with a silver heptafluoropentenoate in a sealed tube at a temperature of 100° C.

The new silver salts provided by this invention are useful for the preparation of esters and anhydrides as illustrated by the following reactions:

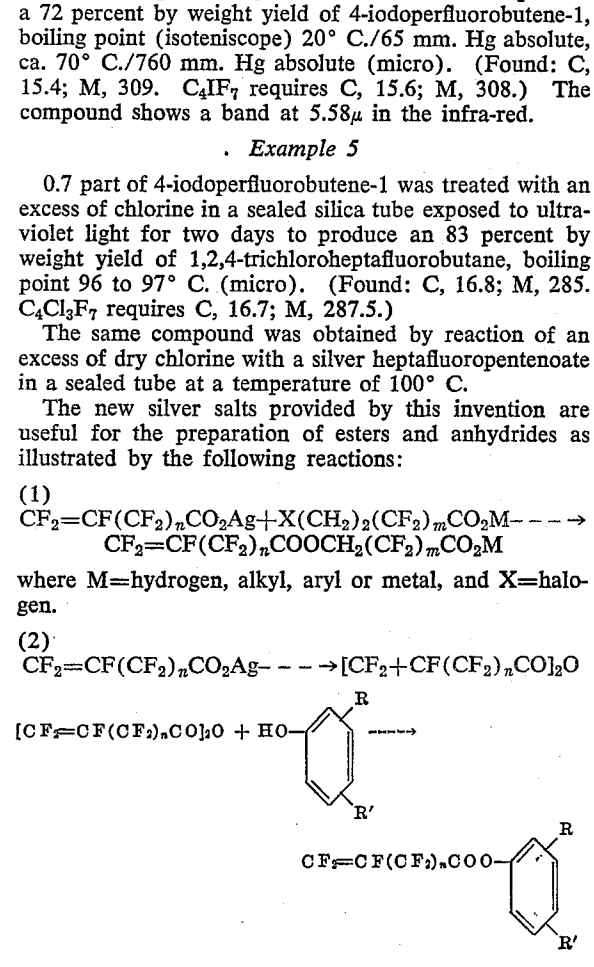
(1)

$$CF_2{=}CF(CF_2)_nCO_2Ag + X(CH_2)_2(CF_2)_mCO_2M \dashrightarrow CF_2{=}CF(CF_2)_nCOOCH_2(CF_2)_mCO_2M$$

where M=hydrogen, alkyl, aryl or metal, and X=halogen.

(2)

$$CF_2{=}CF(CF_2)_nCO_2Ag \dashrightarrow [CF_2{+}CF(CF_2)_nCO]_2O$$



where R and R' are alkyl, substituted alkyl, aryl, substituted aryl, halogen or a suitable functional group.

The new silver salts may also be used for the preparation of fire extinguishing media, as illustrated by reaction (3) below, and for the preparation of unsaturated compounds which are in turn useful in the preparation of plasticisers and polymers as illustrated by reaction (4) below:

(3)

$$CF_2{=}CFCO_2Ag \xrightarrow{Br_2} CF_2BrCFBr_2$$

(4)

$$CF_2{=}CFCO_2Ag \longrightarrow CF_2ClCFCl_2 \xrightarrow[\text{dechlorination}]{} CF_2{=}CFCl \longrightarrow \text{polymer}$$

The new iodo compounds provided by this invention are useful for the preparation of dienes as illustrated by reaction (1) below and are also particularly useful for the preparation of coupled products as described in my copending application No. 377,716, filed August 31, 1953, and as illustrated by reaction (2) below.

(1)

$$CF_2{=}CF(CF_2)_2I + CH_2{=}CHF \longrightarrow CF_2{=}CF(CF_2)_2CHFI$$

$$CF{=}CF(CF_2)_2CH_2CHFI \xrightarrow[\text{iodination}]{\text{dehydro-}} CF_2{=}CF(CF_2)_2CH{=}CHF$$

(2)

$$CF_2{=}CF(CF_2)_2I \xrightarrow[h\nu]{Hg} CF_2{=}CF(CF_2)_4CF{=}CF_2$$

I claim:

1. A process for the preparation of a perfluorodiene which comprises subjecting to pyrolysis, at a pressure below about 300 mm. of mercury absolute, an anhydrous compound having the formula

$$MO_2C(CF_2)_nCO_2M$$

in which M represents an alkali metal and *n* is an integer from 4 to 20, thereby producing a perfluorodiene having two less carbon atoms than its precursor and having the formula

$$F_2C{=}CF(CF_2)_mCF{=}CF_2$$

in which *m* has a value from zero to sixteen.

2. A process according to claim 1, wherein the pyrolysis is carried out at a pressure in the range from 10^{-3} to 20 mm. of mercury absolute.

3. A process according to claim 1, in which M in the formula of the starting material represents sodium.

4. A process according to claim 1, in which M in the formula of the starting material represents potassium.

5. A process for the production of hexafluorobutadiene which comprises subjecting an alkali metal octafluoroadipate to pyrolysis under anhydrous conditions and at a pressure below about 300 mm. of mercury absolute.

6. A process according to claim 1, wherein the pyrolysis is carried out under relatively mild conditions whereby there is formed as by-product a compound of the formula:

$$F_2C{=}CF(CF_2)_nCO_2M$$

where M represents an alkali metal and *n* an integer from 2 to 18.

7. A process for the preparation of a perfluorodiene which comprises subjecting to pyrolysis, at a pressure below about 300 mm. of mercury absolute, an anhydrous compound having the formula:

$$F_2C{=}CF(CF_2)_nCO_2M$$

in which M is an alkali metal radical and *n* is an integer from 2 to 18, thereby producing a perfluorodiene having one less carbon atom than its precursor and having the formula:

$$F_2C{=}CF(CF_2)_mCF{=}CF_2$$

in which *m* has a value from zero to sixteen.

8. A process according to claim 7, in which M in the formula of the starting material represents sodium.

9. A process for the preparation of a perfluorodiene which comprises subjecting to pyrolysis at a pressure below about 300 mm. of mercury absolute, an anhydrous compound having the formula

$$MO_2C(CF_2)_nCO_2M$$

in which M represents an alkali metal and n is an integer from 4 to 20, to form a compound having the formula

$$F_2C{=}CF(CF_2)_{n-2}CO_2M$$

and then further heating the last identified compound at a pressure below about 300 mm. of mercury absolute and at a temperature between about 100° C. and about 450° C. to produce a diene having the formula

$$F_2C{=}CF(CF_2)_{n-4}CF{=}CF_2$$

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UNITED STATES PATENT OFFICE

Certificate of Correction

Patent No. 2,833,831 May 6, 1958

Robert Neville Haszeldine

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, lines 5 and 7, for that portion of the formula reading "(OF_2)", each occurrence, read $-(CF_2)-$; line 12, for "dicarbooxylic" read —dicarboxylic—; line 39, for "when X=1" read —when X=I—; line 43, the formula should appear as shown below instead of as in the patent:

$$CF_2XCFX(CF_2)_nX$$

column 5, line 64, Formula 2, the right-hand portion should appear as shown below instead of as in the patent:

$$[CF_2=CF(CF_2)_nCO]_2O$$

column 6, line 27, for that portion of the first formula reading

$CF=CF(CF_2)_2CH_2CHFI$ read $CF_2=CF(CF_2)_2CH_2CHFI$

Signed and sealed this 19th day of August 1958.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.