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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C07D 317/42 — A2

(11) International Publication Number: WO 91/03472

(43) International Publication Date: 21 March 1991 (21.03.91)

(21) International Application Number: PCT/US90/04505

(22) International Filing Date: 16 August 1990 (16.08.90)

(30) Priority data:
399,100 28 August 1989 (28.08.89) US

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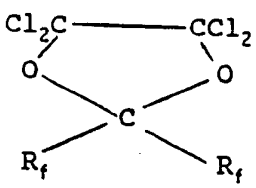
(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: PROCESS FOR THE PREPARATION OF HALOGENATED 2,2-BIS(TRIFLUOROMETHYL)-1,3-DIOXOLANES



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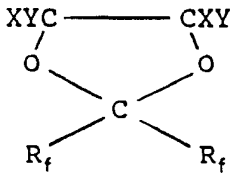

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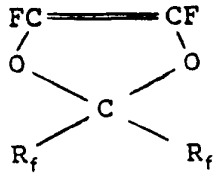

(III)

(57) Abstract

A process for the production of a halogenated 2,2-bis(trihaloalkyl)-1,3-dioxolane of formula (I), wherein R_f is perhaloalkyl comprising a 2,2-bis(trihaloalkyl)-1,3-dioxolane in the presence of at least one of La, Ni, Sn, Zn, Fe, Co or Cu is disclosed. A process for the production of a halogenated 2,2-bis(trihaloalkyl)-1,3-dioxolane of formula (II), wherein X is Cl and each Y is independently Cl or F and wherein at least one Y is F, comprising fluorinating a halogenated 2,2-bis(trifluoromethyl)-4,4,5,5-tetrachloro-1,3-dioxolane in the presence of a catalyst which is preferably Cr_2O_3 is disclosed. A process for the production of a 2,2-bis(trihaloalkyl)-1,3-dioxole of formula (III), comprising dehalogenating substantially only a corresponding trans-2,2-bis(perhaloalkyl)-4,5-difluoro-4,5-dichloro-1,3-dioxolane is disclosed.

* See back of page

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PROCESS FOR THE PREPARATION OF HALOGENATED 2,2-BIS(TRIFLUOROMETHYL)-1,3-DIOXOLANES

Background of the Invention

The invention concerns a catalytic process for the preparation of halogenated 2,2-bis(trifluoromethyl)-1,3-dioxolanes.

2,2-Bis(trifluoromethyl)-1,3-dioxolane is a known compound which may be halogenated according to a number of known methods to produce various halo-isomers at the 4,5 or 4 and 5 positions. For example, U.S. Patent No. 2,925,424 describes a batch photochemical chlorination of 2,2-bis(trifluoromethyl)-1,3-dioxolane. The reaction was conducted at 50°C for 2.5 hours. A 68% yield of 2,2-bis(trifluoromethyl)-4,4,5,5-tetrachloro-1,3-dioxolane was obtained upon fractionation of crude product. See Example 9.

U.S. Patent No. 4,535,175 discloses a batch photochemical chlorination of 2,2-bis(trifluoromethyl)-1,3-dioxolane to yield a mixture of di-, tri- and tetra-chloro derivatives. The reaction proceeds rather slowly. Example 1 of the patent details the production of 2,2-bis(trifluoromethyl)-4,4,5-trichloro-5-fluoro-1,3-dioxolane by reacting 2,2-bis(trifluoromethyl)-4,4,5,5,-tetrachloro-1,3-dioxolane, HF and antimony chloride at 70°C for 5 hours.

U.S. Patent No. 3,794,791 discloses a batch photochlorination of 2,2-bis(trifluoromethyl)-1,3-dioxolane at -15°C. Example 1 describes the synthesis of 2,2-bis(trifluoromethyl)-4-chloro-1,3-dioxolane. Example

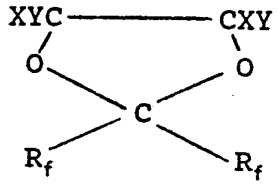
2 of the patent describes the synthesis of 2,2-bis(trifluoromethyl)-4,5-dichloro-1,3-dioxolane.

G.B. 1,361,346 discloses the preparation of 2,2-bis(trifluoromethyl)-4,5-dichloro-4,5-difluoro-1,3-dioxolane by fluorinating 2,2-bis(trifluoromethyl)-4,4,5,5,-tetrachloro-1,3-dioxolane with $SbF_3/SbCl_5$ at 120°C.

Summary of the Invention

The invention provides a process for the preparation of 2,2-bis(perhaloalkyl)-4,4,5,5-tetrachloro-1,3-dioxolane by chlorinating 2,2-bis(perhaloalkyl)-1,3-dioxolane with a source of chlorine in the presence of a catalyst which contains at least one of La, Ni, Sn, Zn Co, Fe, or Cu.

The invention also provides a process for the preparation of fluorinated 2,2-bis(perhaloalkyl)-1,3-dioxolanes of the formula



wherein X is Cl, each Y is independently Cl or F and at least one Y is F, and each R_f is independently perhaloalkyl in which the alpha carbon is substituted by at least one fluorine atom.

The process comprises fluorinating 2,2-bis(perhaloalkyl)-4,4,5,5-tetrachloro-1,3-dioxolane with a source of fluorine under fluorination conditions, so as to effect fluorine-chlorine exchange, in the presence of a catalyst which is a catalyst as noted above in the chlorination reaction or is chromium (III) oxide, i.e., Cr_2O_3 or one or more of a metal supported on carbon wherein the metals are chosen from Cr, Co, La, Fe, Ni, Cu, Sn, or Zn.

Detailed Description

Preferably, R_f is trifluoromethyl. The 2,2-bis(perhaloalkyl)-1,3-dioxolane starting material for the chlorination is a known compound which may be readily prepared by reacting perfluoroacetone and ethylene chlorohydrin under basic conditions as described in U.S. Patent No. 2,925,424.

The chlorination is preferably conducted in the vapor phase, and is preferably conducted continuously. However, the reaction may be conducted in the liquid phase using the reactants as solvents, at the same temperatures noted for the vapor phase, under autogenous pressure. Preferred temperatures for the reaction are 250° - 300°C. The molar ratio of chlorine to 2,2-bis(perhaloalkyl)-1,3-dioxolane is preferably about 4:1 to 10:1, more preferably about 4:1 to 5:1. The reaction time is generally about 1 to 120 seconds, and is preferably about 30 to 60 seconds. The reaction pressure is preferably about 1 to 20 atmospheres, more preferably about 10 to 20 atmospheres. The preferred source of chlorine is chlorine gas. The catalyst metal may be in the form of any soluble compound of the metal such as the oxide, oxyhalide, halide, pseudohalide, nitrate, sulfate, or organic salt such as acetate and propionate. The halides include chlorides, fluorides and bromides. The pseudohalides include cyanides, cyanates and thiocyanates. The form of the catalyst is not critical and may be pellets, powders or granules. Preferably, the catalysts are used in a fixed bed; however, fluidized bed reactors may also be used. Preferably, the catalysts are in the form of their chlorides, and preferably are supported on carbon. The preferred catalyst for the chlorination is $CuCl_2/C$.

General Procedure for Preparing Catalysts MCl_x/C

The desired amount of metal chloride was dissolved in water (35 to 75 mL) and the entire solution poured

over 40 g of commercial carbon granules (Girdler 411, 0.32 cm pellets). The resulting mixture was allowed to stand at room temperature for one hour and was then placed in a vacuum oven at 110°C for 16 to 24 hours to remove the water. The catalyst was then pretreated by heating in an atmosphere of nitrogen gas at 400°C followed by heating in HF at 400°C prior to its use as a fluorination catalyst. For chlorination reactions, the catalyst was heated in an atmosphere of nitrogen gas at 400°C followed by adjusting the temperature to the desired value and treatment with chlorine gas. Preferably, 0.1 - 30% b.w. based on the support of active metal is incorporated in the catalyst.

Catalyst Preparation

The following catalysts were prepared by the general procedure for MCl_x/C:

$CoCl_2/C$	35 g $CoCl_2.6H_2O$/35 mL H_2O
$FeCl_3/C$	39.7 g $FeCl_3.6H_2O$/35 mL H_2O
$ZnCl_2/C$	20.44 g $ZnCl_2$/75 mL H_2O
$NiCl_2/C$	34.94 g $NiCl_2$2.$6H_2O$/35 mL H_2O
$LaCl_3/C$	62.43 g LaCl3.$7H_2I$/75 mL H_2O
$CrCl_3/C$	39.17 g $CrCl_3.6H_2O$/60 mL H_2O
$SnCl_2/C$	38.36 g $SnCl_2.2H_2O$/70 mL H_2O
$CuCl_2/C$	25.06 g $CuCl_2.2H_2O$/70 mL H_2O

Cr_2O_3 is commercially available and was treated with HF as described above prior to its use as a fluorination catalyst.

The catalysts having differing anions are prepared analogously.

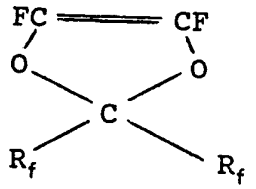
The fluorination is preferably conducted in the vapor phase, and is preferably conducted continuously. The reaction may be conducted in the liquid phase as indicated for the chlorination. The reaction temperature is preferably 150° to 350°C, more preferably 150° to

200°C. The preferred source of fluorine is HF. The molar ratio of HF to 2,2-bis(perhaloalkyl)-4,4,5,5-tetrachloro-1,3-dioxolane is preferably about 2:1 to 10:1, more preferably about 2:1 to 5:1. Preferred reaction time is about 1 to 120 seconds, more preferably about 30 to 60 seconds. The preferred catalyst for the fluorination is Cr, more preferably unsupported Cr_2O_3.

The production of the fluoro-compounds may be conducted in two steps, with, e.g., isolation of a 2,2-bis(perhaloalkyl)-4,4,5,5-tetrachloro-1,3-dioxolane intermediate, or may be conducted in one enclosure with the addition of the fluorine source preferably after substantial completion of the first reaction.

The catalysts of the invention are extremely active and selective. In the fluorination, where Cr_2O_3 is the catalyst, the ratio of trans to cis isomers is desirably high.

The products of the process of the invention are useful as intermediates in the production of perhalodioxoles of the formula



by dehalogenation of the appropriate precursor according to conventional processes, for example, as disclosed in U.S. Patent Nos. 4,535,175, 3,865,845, and 3,978,030.

Preferably, trans-2,2-bis(perhaloalkyl)-4,5-difluoro-4,5-dichloro-1,3-dioxolane is used to produce the dioxole. A multi-plate distillation column may be used to separate the cis and trans isomers. Preferably, the cis isomer as well as 2,2-bis(perhaloalkyl)-4,4,5,5-tetrachloro-1,3-dioxolane and -4-fluoro-4,5,5-trichloro-1,3-dioxolane are recycled to the fluorination step.

The dioxole in turn may be used to prepare homopolymers and copolymers which possess advantageous properties such as chemical inertness to hydrogen fluoride, optical clarity and film-forming ability.

For example, the dioxoles may be copolymerized under standard polymerization conditions with tetrafluoroethylene to form crystalline copolymers suitable for use as a dielectric in electronic equipment. Preferably, in these applications the dioxole is employed in an amount of about 12 mole % or less.

Polymers having more than about 12% dioxole are more generally amorphous, and are soluble in various organic liquids, e.g., 1,1,2-trichloro-1,2,2-trifluoroethane. These polymers are useful in the production of chemically inert, stain and weather resistant coatings and finishes.

Further, the dioxoles may be reacted with vinylidene fluoride or tetrafluoroethylene to produce plastic and/or elastomeric terpolymers useful in the production of corrosion-resistant seals, gaskets or linings.

Finally, the dioxoles may be homopolymerized to produce amorphous resins suitable for use as transparent glazing materials and sight glasses in apparatuses employed in handling chemically corrosive materials.

In particular, the amorphous polymers are useful in the production of optical fiber cladding materials, e.g., in accordance with U.S. Patent Nos. 4,530,569 and 4,754,009.

Various fluoropolymers have been proposed from time to time for this purpose, mainly because of their good performance under a variety of temperature and atmospheric conditions and resistance to many chemicals. A good polymeric cladding material for optical fibers should be completely amorphous because crystallites present in polymers would cause light scattering. Further, it should have a high glass transition temperature, Tg, especially if intended for use at high temperatures because above its Tg, it would lose some of

its desirable physical properties; and, in particular, it would be unable to maintain good bonding to the fiber core. A desirable Tg would be above 85°C, preferably above 120°C.

As the amount of dioxole in the copolymer increases, the Tg also increases, although not necessarily in a linear fraction.

A homopolymer of dioxole appears to be amorphous and has a high Tg. However, dioxole is a much more expensive monomer than tetrafluoroethylene so that use of dioxole homopolymers, rather than of dioxole/tetrafluoroethylene copolymers, is economically much less attractive. Furthermore, the copolymers are easier to fabricate. The dipolymers have low refractive indices, which is a particularly desirable feature for optical fiber cladding. Furthermore, films of these copolymers are clear and transparent, compared with hazy or translucent films of crystalline polymers. For this reason, the amorphous copolymers of the present invention are suitable for such applications as, for example, windows for chemical reactors, especially for processes using or manufacturing hydrogen fluoride.

Amorphous terpolymers can be made by copolymerizing certain ethylenically unsaturated monomers with perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene. These include selected olefins, vinyl compounds, and perfluoromonomers. Typical olefins are, for example, ethylene, propylene, 1-butene, isobutylene, trifluoropropene, and trifluoroethylene. Vinyl monomers can be, for example, vinyl fluoride, vinylidene fluoride, and chlorotrifluoroethylene. Perfluoromonomers may be of different chemical types, for example, perfluoropropene, perfluoro(1,3-dioxole), perfluoro(alkyl vinyl ethers), methyl 3-[1-[difluoro(trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-2,2,3,3-tetrafluoropropanoate

$$CF_2=CFOCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FOCF_2CF_2COOCH_3,$$

and 2-[1-[difluoro[(trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluorooethoxy]-1,1,2,2-tetrafluoroethanesulfonyl fluoride

$$CF_2=CFOCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FOCF_2CF_2SO_2F.$$

The proportion of dioxole in the amorphous terpolymers of this invention should preferably be at least 12 mole percent of the tetrafluoroethylene content, while the mole percent content of the third monomer should be the smallest of all three monomers. Outside these limits, either an amorphous terpolymer may not be obtained; or, if made, its maximum tensile modulus and strength may not be realized.

Copolymerization is carried out in the presence of a free radical generator, preferably at a slightly elevated temperature, for example, 55°-65°C. Well-agitated pressure equipment should be used.

In addition to tetrafluoroethylene, amorphous copolymers may be fabricated from the dioxole and chlorotrifluoroethylene; vinylidene fluoride; hexafluoropropylene; trifluoroethylene; perfluoro(alkyl vinyl ethers) of the formula $CF_2=CFOR_F$, where R_F is a normal perfluoroalkyl radical having 1-3 carbon atoms; fluorovinyl ethers of the formula $CF_2=CFOQZ$, where Q is a perfluorinated alkylene radical containing 0-5 ether oxygen atoms, wherein the sum of the C and O atoms in Q is 2 to 10, and Z is a group selected from the class consisting of -CN, -COF, and $-OCH_3$, where R is a C_{1-C4} alkyl; vinyl fluoride; and (perfluoroalkyl)ethylene, $R_fCH=CH_2$, where R_f is a C_{1-C8} normal perfluoroalkyl radical.

The maximum preferred mole percentage of the comonomer in the copolymers are as follows:

for tetrafluoroethylene, 35;
for chlorotrifluoroethylene, 30
for vinylidene fluoride, 20;
for hexafluoropropylene, 5;
for trifluoroethylene, 30;
for $CF_2=CFOR_f$, 30;
for $CF_2=CFOQZ$, 20;
for vinyl fluoride, 25; and
for $R_fCH=CH_2$, 10.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.

In the preceding text and the following examples, all temperatures are set forth uncorrected in degrees Celsius and all parts and percentages are by weight, unless otherwise indicated. Amounts of compounds listed in the Tables are given in area %. C.T. represents contact time.

In the following examples, the numbers identifying the compounds in the tables are as follows:

D456 - 2,2-Bis(trifluoromethyl)-1,3-dioxolane

D436 - 2,2-Bis(trifluoromethyl)-4,5-dichloro-1,3-dioxolane

D436a - 2,2-Bis(trifluoromethyl)-4,4-dichloro-1,3-dioxolane

D426 - 2,2-Bis(trifluoromethyl)-4,4,5-trichloro-1,3-dioxolane

D416 - 2,2-Bis(trifluoromethyl)-4,4,5,5-tetrachloro-1,3-dioxolane

D417 - 2,2-Bis(trifluoromethyl)-4-fluoro-4,5,5-trichloro-1,3-dioxolane

D418a - 2,2-Bis(trifluoromethyl)-4,4-difluoro-5,5-dichloro-1,3-dioxolane

D418 - 2,2-Bis(trifluoromethyl)-4,5-dichloro-4,5-dichloro-1,3-dioxolane

D419 - 2,2-Bis(trifluoromethyl)-4,4,5-trifluoro-5-chloro-1,3-dioxolane.

EXAMPLES

General Procedure for Chlorination

The reactor (0.5 inch ID Inconel\/nickel alloy pipe) was charged with the designated amount of catalyst, sealed and placed into a sand bath. The bath was heated to 400°C, at which time nitrogen gas at a flow rate of 50 ml/minute was passed through the reactor to remove all traces of water. Chlorine gas at a flow rate of 25.7 cc/min was passed through the reactor and the temperature adjusted to the desired value. The flow of nitrogen gas was turned off and the flow of D456 started. The flow of chlorine and D456 were adjusted to give the desired molar ratio.

The reactor effluent was scrubbed with aqueous potassium hydroxide to remove Cl_2, HCl and HF and sampled on line by a HP 5890 gas chromatograph using a 5 foot Krytox\ perfluorinated polyether column. Conditions were 70°C for 3 minutes followed by temperature programming to 180°C at a rate of 6°C/minute. Helium flow was 35 cc/minute.

General Procedure for Fluorination

The reactor (0.5 inch ID Inconel\ nickel alloy pipe) was charged with the designated amount of catalyst, sealed and placed into a sand bath. The bath was heated to 400°C, at which time nitrogen gas at a flow rate of 50 ml/minute was passed through the reactor to remove all traces of water. The temperature was lowered to 200°C, and HF and nitrogen gas (1:4 molar ratio) was passed through the reactor, and the nitrogen flow was decreased with time until neat HF was being passed through the reactor. At this point, the temperature is raised to 350°C and maintained there for 15 to 30 minutes. The temperature is then decreased to the desired temperature, and the D416 flow is started. The flow of HF and D416 were adjusted to give the desired molar ratio.

The reactor effluent was scrubbed with aqueous potassium hydroxide to remove Cl_2, HCl and HF and sampled on line by a HP 5890 gas chromatograph using a 5 foot Krytox\ perfluorinated polyether column. Conditions were 70°C for 3 minutes followed by temperature programming to 180°C at a rate of 6°C/minute. Helium flow was 35 cc/minute.

EXAMPLES 1 - 16

Chlorination of 2,2-Bis(trifluoromethyl)-1,3-Dioxolane (D456)

$CuCl_2$/C 19.7 grams (30 cc)

Exp	Temp	Cl_2/D456	C.T.	D436	D426	D416	Unk
1	225	6/1	30	14	40	43	3
2	235	6/1	30	5	29	62	3
3	245	6/1	30	3	21	74	2
4	255	6/1	30	1	9	88	2
5	265	6/1	30	0	5	93	2
6	195	6/1	60	43	33	16	8
7	205	6/1	60	25	44	24	5
8	215	6/1	60	10	44	42	4
9	225	6/1	60	5	34	57	3
10	235	6/1	60	1	18	80	1
11	245	6/1	60	0	7	90	3
12	255	6/1	60	0	2	95	3
13	265	6/1	60	0	0	97	3
14	275	6/1	60	0	0	96	4
15	285	6/1	60	0	0	95	5
16	285	4/1	60	0	1	95	4

The conversion of D456 to products was 100%, as shown in the Table.

EXAMPLES 17-23

Chlorination of 2,2-Bis(trifluoromethyl)-1,3-Dioxolane (D456)

$CuCl_2$/C 19.7 grams (30 cc)

Exp	Temp	Cl_2/D456	C.T.	D426	D416	D417	Unk
17	265	6/1	60	1	97	0	2
18	265	6/1	60	1	97	0	1
19	265	6/1	60	1	97	0	3
20	265	5/1	75	1	97	1	0
21	265	4/1	75	3	95	0	2
22	265	5/1	60	2	95	0	3
23	275	5/1	60	0	97	0	2

The conversion of D456 to products was 100%, as shown in the Table.

EXAMPLES 24-28

Chlorination of 2,2-Bis(trifluoromethyl)-1,3-Dioxolane (D456)

$LaCl_3$/C 4.25 grams (5 cc)

Exp	Temp	Cl_2/D456	C.T.	D456	D436	D426	D416	D417	Unk
24	200	6/1	10	3	74	12	10	0	1
25	225	6/1	10	4	64	11	18	0	3
26	250	6/1	10	1	43	9	43	1	2
27	275	6/1	10	0	22	6	67	1	4
28	300	6/1	10	0	9	3	72	3	13

EXAMPLES 29-32

Chlorination of 2,2-Bis(trifluoromethyl)-1,3-Dioxolane (D456)

$SnCl_2$/C 4.0 grams (5 cc)

Exp	Temp	Cl_2/D456	C.T.	D436	D426	D416	D427	D417	Unk
29	225	6/1	10	36	37	23	1	0	2
30	250	6/1	10	13	29	53	1	1	3
31	275	6/1	10	2	8	74	1	2	8
32	275	5/1	10	2	9	70	0	2	12

The conversion of D456 to products was 100%, as shown in the Table.

EXAMPLES 33-37

Chlorination of 2,2-Bis(trifluoromethyl)-1,3-Dioxolane (D456)

$FeCl_3$/C 3.4 grams (5 cc)

Exp	Temp	Cl_2/D456	C.T.	D456	D436	D426	D416	D427	D417	Unk
33	200	6/1	10	11	36	2	8	4	0	39
34	150	6/1	10	36	51	1	0	3	0	9
35	200	6/1	1	67	21	1	1	2	1	7
36	250	6/1	1	37	25	1	6	3	0	28
37	250	4/1	1	42	19	1	5	2	0	31

EXAMPLES 38-41

Chlorination of 2,2-Bis(trifluoromethyl)-1,3-Dioxolane (D456)

$ZnCl_2$/C 3.8 grams (5 cc)

Exp	Temp	Cl_2/D456	C.T.	D456	D436	D426	D416	D417	Unk
38	200	6/1	10	27	62	5	4	0	2
39	225	6/1	10	15	70	10	4	0	1
40	250	6/1	10	7	66	15	11	0	1
41	275	6/1	10	1	28	13	50	2	6

EXAMPLES 42-51

Fluorination of
2,2-Bis(trifluoromethyl)-4,4,5,5-tetrachloro-1,3-Dioxolane

Cr_2O_3 28.9 g (30 cc) -12 + 20 mesh

Exp	Temp	HF/D416/HCl	C.T.	D419	tD418	cD418	D418a	D417	D416	Unk
42	175	2/1/0	60	2	74	18	0	4	0	1
43	200	2/1/0	60	37	10	3	36	10	1	0
44	165	2/1/0	60	19	37	9	13	20	1	1
45	175	2/1/0	60	15	62	16	2	5	0	0
46	175	3/1/0	45	3	77	19	0	0	0	1
47	175	3/1/4	45	13	66	18	1	2	0	0
48	175	4/1/4	40	4	75	20	0	2	0	0
49	175	5/1/4	35	3	75	20	0	1	0	1
50	175	5/1/4	40	3	75	20	0	1	0	1
51	175	5/1/4	40	4	74	20	0	1	0	1

t = trans

c = cis

EXAMPLES 52-54

Fluorination of
2,2-Bis-trifluoromethyl)-4,4,5,5-
tetrachloro-1,3-Dioxalane

$CoCl_2$/C 12.3 g (30 cc)

Exp	Temp	HF/D416	C.T.	tD418	cD418	D417	Unk
52	200	10/1/0	30	44	35	8	7
53	200	5/1/0	60	39	33	16	6
54	165	10/1/0	30	47	37	8	3

EXAMPLES 55-59

Fluorination of
2,2-Bis(trifluoromethyl)-4,4,5,5-
tetrachloro-1,3-Dioxolane

Cr_2O_3 14.4 g (15 cc) -12 + 20 mesh

Exp	Temp	HF/D416	C.T.	D419	tD418	cD418	D417	Unk
55	200	3/1/0	30	1	72	22	0	5
56	200	3/1/0	30	0	71	26	0	3
57	210	3/1/0	30	1	73	24	0	2
58	220	3/1/0	30	1	72	24	0	3
59	230	3/1/0	30	1	73	23	1	2

COMPARATIVE EXAMPLES 60-68

Fluorination of
2,2-Bis(trifluoromethyl)-4,4,5,5,-tetrachloro-1,3-Dioxolane

$LaCl_3$/C 4.25 g (5 cc)

Exp	Temp	HF/D416	C.T.	tD418	cD418	D417	D416	Unk
60	225	2/1/0	10	2	4	85	3	6
61	250	2/1/0	10	14	13	67	0	5
62	275	2/1/0	10	26	27	0	0	4
63	300	2/1/0	10	34	33	26	0	7
64	300	2/1/0	20	43	35	11	0	10
65	300	2/1/0	20	44	36	9	0	11
66	250	2/1/0	40	41	38	14	0	7
67	250	2/1/0	40	38	35	20	0	7
68	300	2/1/0	40	46	31	4	0	11

EXAMPLES 69-72

Fluorination of
2,2-Bis(trifluoromethyl)-4,4,5,5-
tetrachloro-1,3-Dioxolane

$FeCl_3$/C 3.4 g (5 cc)

Exp	Temp	HF/D416	C.T.	tD418	cD418	D417	D416	Unk
69	200	2/1/0	5	0	0	24	71	5
70	225	2/1/0	5	0	0	42	54	8
71	275	2/1/0	10	7	8	76	1	8
72	275	3/1/0	10	9	10	70	0	11

EXAMPLES 73-79

Fluorination of
2,2-Bis(trifluoromethyl)-4,4,5,5-
tetrachloro-1,3-Dioxolane

$NiCl_2$/C 1.66 g (3 cc)
1/8-inch Pellets

Exp	Temp	HF/D416	C.T.	tD418	cD418	D417	D416	Unk
73	200	2/1/0	5	0	0	5	91	4
74	220	2/1/0	5	0	0	7	88	5
75	240	2/1/0	5	0	0	13	80	7
76	260	2/1/0	5	0	0	31	61	6
77	280	2/1/0	5	1	2	45	39	10
78	280	4/1/0	5	5	4	66	10	13
79	325	4/1/0	5	8	7	34	2	48

EXAMPLES 80-83

Fluorination of
2,2-Bis(trifluoromethyl)-4,4,5,5-tetrachloro-1,3-Dioxolane

$CuCl_2$/C 19.7 g (30 cc)

Exp	Temp	HF/D416	C.T.	tD418	cD418	D417	D416	Unk
80	200	3/1/0	30	2	2	66	13	16
81	200	3/1/0	30	6	5	73	3	13
82	250	3/1/0	30	4	4	85	0	5
83	250	3/1/0	30	4	4	85	0	6

EXAMPLES 84-85

Fluorination of
2,2-Bis(trifluoromethyl)-4,4,5,5-
tetrachloro-1,3-Dioxolane

$SnCl_2$/C 4.0 g (5 cc)

Exp	Temp	HF/D416	C.T.	tD418	cD418	D417	D416	Unk
84	275	2/1/0	10	9	10	74	2	5
85	275	2/1/0	20	19	17	60	0	4

EXAMPLES 86-87

Fluorination of
2,2-Bis(trifluoromethyl)-4,4,5,5-
tetrachloro-1,3-Dioxolane

$ZnCl_2$/C 3.8 g (5 cc)

Exp	Temp	HF/D416	C.T.	tD418	cD418	D417	D416	Unk
86	300	2/1/0	10	6	7	73	10	4
87	250	2/1/0	10	1	2	53	44	1

EXAMPLE 88

Examples Describing the Rearrangement of Cis-D418 to Trans-D418

A mixture of 150 g D-418 (65.5% trans isomer), 6.0 g antimony pentachloride, and 20 g anhydrous hydrogen fluoride was heated at 100° for one hour and 135° for five hours. The reaction mixture was added to ice/ice water and the lower layer washed with 400 ml ice water to give 139.3 g of product. Analysis showed this product to contain 1.3 g D-419 and 138.0 g D-418 (79.8% trans isomer). Thus the amount of trans D-418 rose from 98.3 g to 110.1 g, while the amount of cis isomer fell from 51.7 to 27.9 g.

A mixture of 40.5 g D-418 (53.5% trans isomer), 4.0 g antimony pentachloride, and 20 g anhydrous hydrogen fluoride was heated at 100° for one hour and 135° for four hours. The reaction mixture was added to ice/ice water and the lower layer separated to give 35.4 g of product containing 26.7 g trans D-418 and 8.5 g cis D-418 (78.4% trans isomer). Thus the amount of trans D-418 rose from 21.7 g to 26.7 g, while the amount of cis D-418 declined from 18.8 g to 8.5. g.

EXAMPLE 89

Variation in Yield of Perfluoro-2,2-bis-trifluoromethyl-1,3-dioxole (PDD) with cis/trans bis-2,2-trifluoromethyl-4,5-dichloro-4,5-difluoro-1,3-dioxolane (D418)

A mixture of 24.9 g magnesium turnings and 395 ml tetrahydrofuran was heated 60°. After addition of 2.75 ml, 1,2-dibromoethane approximately 4.5 g bis-2,2-trifluoromethyl-4,5-dichloro-4,5-difluoro-1,3-dioxolane (D418) was added. The reaction mixture was cooled to 35-40° and a total of 133 g cis/trans D418 added. After stirring for 15 minutes, the mixture was distilled until the pot temperature reached 70°. The distillate boiling to 45° was washed with 100 ml of ice water. Gas chromatographic analysis of the lower layer showed it to be greater than 99% PDD.

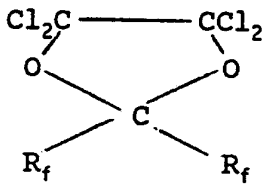
Percent Trans Isomer in Starting D418	Yield of PDD Percent
97.7	60.7
83.6	51.7
64.7	40.2

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

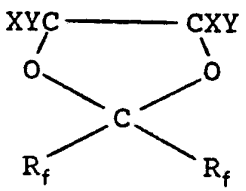
WHAT IS CLAIMED IS:

1. A process for the production of a halogenated 2,2-bis(perhaloalkyl)-1,3-dioxolane of the formula



wherein each R_f independently is perhaloalkyl in which the alpha carbon atom is substituted by at least one fluorine atom, comprising reacting under chlorination conditions a 2,2-bis(perhaloalkyl)-1,3-dioxolane and a source of chlorine in the presence of a catalyst which is at least one of La, Ni, Sn, Zn, Fe, Co or Cu.

2. A process for the production of a halogenated 2,2-bis(perhaloalkyl)-1,3-dioxolane of the formula

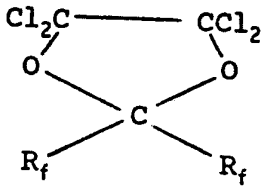


wherein X is Cl and each Y is independently Cl or F and at least one Y is F, and wherein each R_f independently is perhaloalkyl in which the alpha carbon atom is substituted by at least one fluorine atom, comprising reacting,

under fluorination conditions, 2,2-bis(perhaloalkyl)-4,4,5,5-tetrachloro-1,3-dioxolane and a source of fluorine in the presence of a catalyst which is at least one of Cr, La, Ni, Sn, Zn, Fe, Co or Cu.

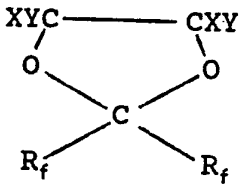
3. In a process for the production of a halogenated 2,2-bis(perhaloalkyl)-1,3-dioxolane comprising

(a) chlorinating 2,2-bis(perhaloalkyl)-1,3-dioxolane to produce a compound of the formula



and

(b) fluorinating the product compound of (a) to produce a compound of the formula



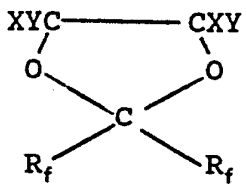
wherein X is Cl and Y is Cl or F, at least one Y being F, and wherein each R_f independently is perhaloalkyl in which the alpha carbon atom is substituted by at least one fluorine atom,

the improvement comprising conducting the chlorination in (a) in the presence of a catalyst which is at least one of La, Ni, Sn, Zn, Fe, Co or Cu.

4. In a process for the production of a halogenated 2,2-bis(perhaloalkyl)-1,3-dioxolane comprising

(a) chlorinating 2,2-bis(perhaloalkyl)-1,3-dioxolane, and

(b) fluorinating the product compound of (a) to produce a compound of the formula



wherein X is Cl and Y is Cl or F, at least one Y being F, and wherein each R_f independently is perhaloalkyl in which the alpha carbon atom is substituted by at least one fluorine atom,

the improvement comprising conducing the fluorination in (b) in the presence of a catalyst which is at least one of Cr, La, Ni, Sn, Zn, Fe, Co or Cu.

5. A process according to claim 1, wherein the catalyst is in the form of a supported metal chloride.

6. A process according to claim 5, wherein the catalyst is in the form of metal chloride supported on carbon.

7. A process according to claim 2, wherein the catalyst is in the form of a supported metal chloride.

8. A process according to claim 2, wherein the catalyst is Cr_2O_3.

9. A process according to claim 3, wherein the catalyst in (b) is Cr_2O_3.

10. A process according to claim 1, wherein the catalyst is $CuCl_2/C$.

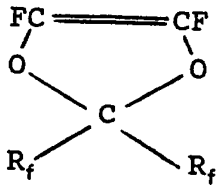
11. A process according to claim 1, wherein the temperature is about 250-300°C, the ratio of chlorine to 2,2-bis(perhaloalkyl)-1,3-dioxolane is about 4:1-10:1,

the reaction time is about 1-120 sec, and the reaction pressure is about 1-20 atm.

12. A process according to claim 1, wherein R_f is CF_3.

13. A process according to claim 2, wherein R_f is CF_3.

14. In a process for the production of 2,2-bis(perhaloalkyl)-1,3-dioxole of the formula



wherein each R_f independently is perhaloalkyl in which the alpha carbon atom is substituted by at least one fluorine atom, comprising chlorinating a corresponding 2,2-bis(perhaloalkyl)-1,3-dioxolane, fluorinating the product and subsequently dehalogenating to form the 1,3-dioxole,

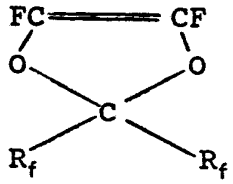
the improvement comprising conducting the chlorination in the presence of a catalyst which is at least one of La, Ni, Sn, Zn Fe, Co or Cu.

15. A process according to claim 14, wherein the improvement further comprises conducting the fluorination in the presence of a catalyst which is at least one of Cr, La, Ni, Sn, Zn, Fe, Co or Cu.

16. A process according to claim 14, wherein the improvement further comprises, prior to dehalogenating, separating trans-2,2-bis(perhaloalkyl)-4,5-difluoro-4,5-dichloro-1,3-dioxolane and dehalogenating substantially only said isomer.

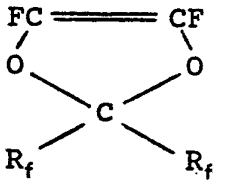
17. A process according to claim 15, wherein the improvement further comprises, prior to dehalogenating, separating trans-2,2-bis(perhaloalkyl)-4,5-difluoro-4,5-dichloro-1,3-dioxolane and dehalogenating substantially only said isomer.

18. A process for the production of a 2,2-bis(perhaloalkyl)-1,3-dioxole of the formula



wherein each R_f independently is perhaloalkyl in which the alpha carbon atom is substituted by at least one fluorine atom, comprising dehalogenating a corresponding trans-2,2-bis(perhaloalkyl)-4,5-difluoro-4,5-dichloro-1,3-dioxolane which has been separated from a mixture of said trans isomer and other isomers.

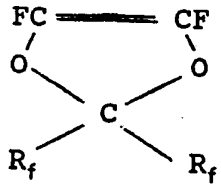
19. In a process for the production of 2,2,-bis(perhaloalkyl)-1,3-dioxole of the formula



wherein each R_f independently is perhaloalkyl in which the alpha carbon atom is substituted by at least one fluorine atom, comprising chlorinating a corresponding 2,2-bis(perhaloalkyl)-1,3-dioxolane, fluorinating the product and subsequently dehalogenating to form the 1,3-dioxole,

the improvement comprises conducting the fluorination in the presence of a catalyst which is at least one of Cr, La, Ni, Sn, Zn, Fe, Co or Cu.

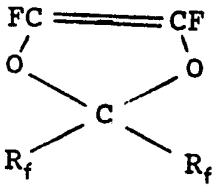
20. In a process for the preparation of a polymer formed from monomers which comprise 2,2-bis(perhaloalkyl)-1,3-dioxoles of the formula



wherein each R_f independently is perhaloalkyl in which the alpha carbon atom is substituted by at least one fluorine atom, the improvement comprising preparing the dioxoles by dehalogenating corresponding trans-2,2-bis(perhaloalkyl)-4,5-difluoro-4,5-dichloro-1,3-dioxolanes separated from a mixture of cis and trans isomers.

21. A process according to claim 20, wherein the polymer is produced by homopolymerization of the dioxole, copolymerization of the dioxole with tetrafluoroethylene or copolymerization of the dioxole with vinylidene fluoride.

22. In a process for the preparation of a polymer formed from monomers which comprise 2,2-bis(perhaloalkyl)-1,3-dioxoles of the formula



wherein each R_f independently is perhaloalkyl in which the alpha carbon atom is substituted by at least one fluorine atom, the improvement comprising preparing the dioxoles by dehalogenating corresponding trans-2,2-bis(perhaloalkyl)-4,5-difluoro-4,5-dichloro-1,3-dioxolanes produced by enhancing the amount of trans-isomer in a mixture of

cis- and trans-isomers by rearranging cis- to trans-isomers.