United States Patent Office

3,467,674

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2,2,5,5-TETRAPERHALOALKYL-4,4-DIALKOXY SUBSTITUTED-1,3-DIOXOLANE

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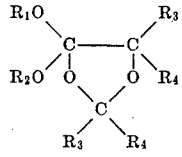
No Drawing. Continuation-in-part of application Ser. No. 439,452, Mar. 12, 1965, which is a continuation-in-part of application Ser. No. 325,468, Nov. 21, 1963. This application May 24, 1967, Ser. No. 640,802

Int. Cl. C07d *13/04, 15/04, 17/04*

U.S. Cl. 260—340.9 4 Claims

ABSTRACT OF THE DISCLOSURE

Compounds having the formula



R_1 and R_2 can be alkyl or substituted alkyl, alkenyl, cycloalkyl, phenyl or substituted phenyl,

R_1 and R_2 can be bridged by various divalent radicals,

R_3 can be a perfluoroalkyl or monochloroperfluoroalkyl, and

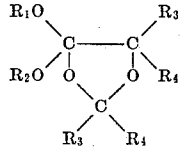
R_4 can be perfluoroalkyl.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 439,452, filed Mar. 12, 1965, which in turn is a continuation-in-part of application Ser. No. 325,468, filed Nov. 21, 1963 both now abandoned.

SUMMARY OF THE INVENTION

This invention relates to fluoro-substituted dioxolanes. It is more particularly directed to compounds represented by the structural formula

(1) 

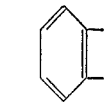
where

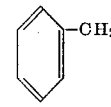
R_1 and R_2 can be alkyl of 1 through 18 carbon atoms; alkyl of 1 through 18 carbon atoms substituted with chlorine or fluorine; alkenyl of 2 through 6 carbon atoms; cycloalkyl of 3 through 7 carbon atoms; phenyl; phenyl substituted with chlorine, bromine, fluorine,

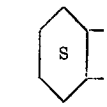
$-OCH_3$, alkyl of 1 through 5 carbon atoms or $-NO_2$;

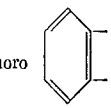
R_1 and R_2 can be connected by

$-CH_2-CH=CH-CH_2-$

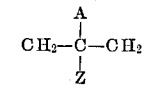








perchloro— or perfluoro



where A can be hydrogen or alkyl of 1 through 5 carbon atoms, and Z can be alkyl of 1 through 17 carbon atoms or $-CH_2-O-CH_2-CH=CH_2$

$-(CH_2)_{2-5}-$ or $-\left(\overset{|}{C}H\right)_{2-5}-X$

where X can be —Cl, —Br, —F, —CN, $-COOR_5$ (R_5 can be an alkyl radical of 1 through 5 carbon atoms), —OH, $-O-CH_2-CH=CH_2$, —SH, —SCN, or



where R_6 and R_7 can be alkyl of 1 through 5 carbon atoms, halo-substituted alkyl of 1 through 5 carbon atoms or phenyl, and can be connected by a

$-(CH_2)_{2-6}-$

radical;

R_3 can be perfluoroalkyl or monochloroperfluoroalkyl containing 1 through 5 carbon atoms; and

R_4 can be perfluoroalkyl of 1 through 5 carbon atoms.

Illustrative of the perhaloalkyl radicals which can be in the R_3 and R_4 positions are $-CF_3$, $-CF_2Cl$, $-C_2F_5$, $-C_3F_7$, $-C_4H_9$, and $-CF_2CF_2Cl$.

Utility

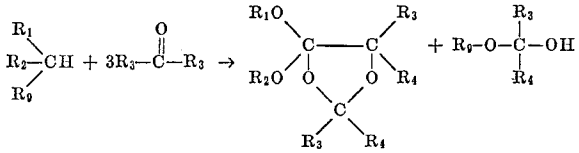
The compounds of the invention are unusually stable, even in the presence of strong acids and bases. This is unexpected because the compounds are ortho esters and such compounds are generally considered unstable compounds, especially in the presence of acids and bases. The compounds leave metals, plastics and rubbers largely unaffected and are non-flammable. A large number of them are liquids having wide ranges between their atmospheric freezing and boiling points.

These properties make the compounds of the invention useful as dielectric, heat transfer and hydraulic fluids, and as buoyancy and damping fluids in measuring and recording instruments. Those compounds which are viscous liquids or low melting solids are also useful as extreme temperature bearing lubricants.

The compounds of the invention which bear polymerizable vinyl groups can be polymerized using conventional vinyl polymerization techniques. The resulting polymers, because of their high fluorine content, are useful as soil and water repelling agents and as film forming components in coating compositions which given highly durable finishes.

Preparation of the compounds

The compounds of the invention can be prepared according to the following general equation:



where R_1, R_2, R_3 and R_4 are as described in Formula 1, R_8 is lower alkyl and R_1 and R_2 can be joined by an alkylene bridge of 2 through 5 carbon atoms.

Stoichiometric quantities of the ortho ester and ketone reactant are placed in a sealed container, which is then heated to a temperature of from 50 to 175° C., for from 2 to 10 hours, preferably 125 to 150° C. for from 6 to 8 hours. Generally speaking, one must use the lowest possible temperature to avoid rupturing the ring of the cyclic acetal product. In most cases, reaction temperatures up to about 150° C. will give high yields, but in some instances higher temperatures can be used.

The reaction mixture is then cooled to room temperature. The hemiketal by-product is removed under vacuum and can be collected in a vacuum trap for recovery of the ketone reactant. The compounds of the invention are left behind as residue.

If a high purity product is desired, it can be obtained by fractional distillation, using conventional techniques.

Ordinarily no solvent is required in the reaction, but if the orthoformate reactant is solid at room temperature, the reaction can be run in a solvent such as benzene or hexane.

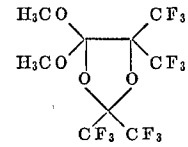
The ketone reactants are commercially available. Those orthoformate reactants which are not commercially available can be made by the trans(ortho esterification) reaction described in J. Am. Chem. Soc., 77, 3801 (1955) and Chem. Ber., 91, 650 (1958).

DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention will be more easily practiced by referring to the following illustrative examples:

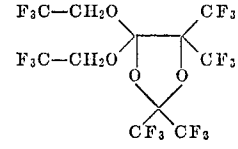
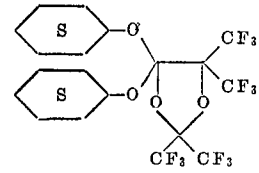
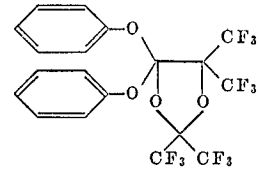
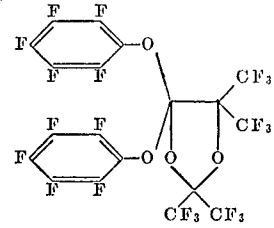
Example 1

A mixture of 15.9 parts of trimethyl orthoformate and 74.8 parts of hexafluoroacetone was heated at 150° C. for six hours in a bomb. The resulting liquid product was fractionated to give 2,2,4,4-tetrakis-trifluoromethyl-5,5-dimethoxy-1,3-dioxolane, having a boiling point of 160–161°/760 mm., a freezing point of 0° C. and the structural formula



The product did not burn or support combustion. It was unreactive with the following at 25° C. and 100° C.: concentrated sulfuric acid, concentrated nitric acid, 50% sodium hydroxide, boron trifluoride gas and 50% hydrochloric acid.

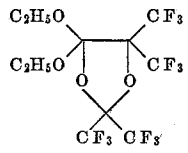
The orthoformates in the following list can be substituted, in the listed amounts, for the trimethylorthoformate used in Example 1 to give the corresponding compounds of the invention:

Orthoformate	Amount, parts	Product
Tri(2,2,2-trifluoroethyl) orthoformate	46.5	
Tri-cyclohexyl orthoformate	46.5	
Diphenyl methyl orthoformate	34.6	
Di(perfluorophenyl) methyl orthoformate	61.5	

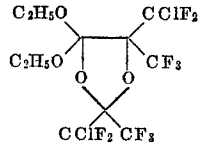
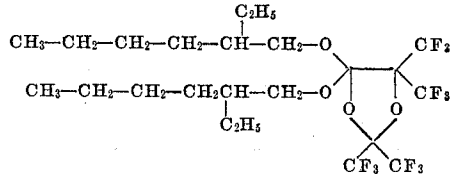
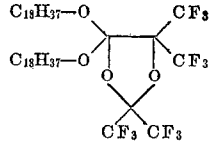
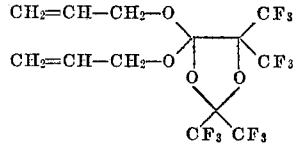
Example 2

A mixture of 22.2 grams of triethyl orthoformate and 67.5 grams of hexafluoroacetone was heated at 150° C. for six hours in a bomb at autogenous pressure. The resulting liquid was fractionated at 45 mm. of pressure.

The 2,2,4,4-tetrakis - trifluoromethyl - 5,5 - diethoxy-1,3-dioxolane product recovered was a colorless liquid having a boiling point of 177° C. at 760 mm. of pressure and a freezing point of −12° C. Its structural formula is

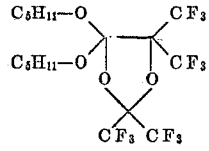


The reactants in the following list can be substituted, in the listed proportions, for the hexafluoroacetone or triethyl orthoformate used in Example 2, to produce the corresponding dioxolane products:

Reactant	Amount, parts	Product
Chloropentafluoroacetone	81	
Tri-2-ethylhexyl orthoformate	60	
Tristearyl orthoformate	123	
Triallyl orthoformate	26.4	

Example 3

A mixture of 25 parts of tri-n-amyl orthoformate and 45.5 parts of hexafluoroacetone was heated at 150° C. for eight hours in a bomb. The residue was fractionated to give 25.9 parts of 2,2,4,4-tetrakis-trifluoromethyl-5,5-di-n-amyl-oxy-1,3-dioxolane having a boiling point of 231° C. at 760 mm. of pressure, a freezing point of less than −50° C. and the structural formula

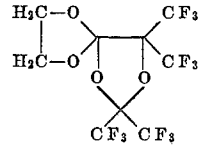


This dioxolane was stable in air at 231° C.

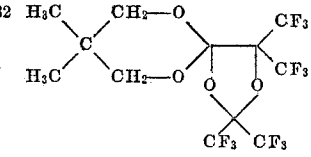
Example 4

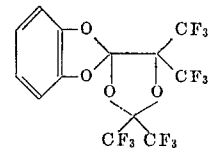
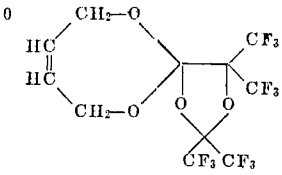
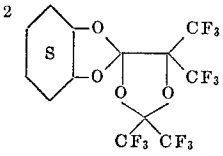
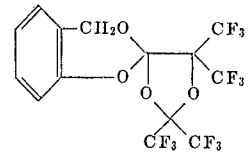
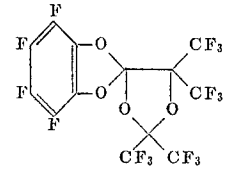
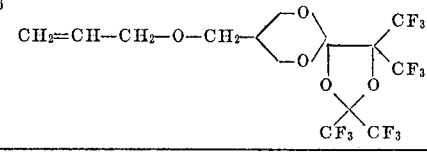
A mixture of 66.5 grams of hexafluoroacetone and 2-methoxy-1,3-dioxolane was heated in a stainless steel bomb at 150° C. for six hours.

The residue was fractionated to give a colorless, odorless oil having a boiling point of 176° C. at 760 mm. and a freezing point of 24° C. This product had the structure



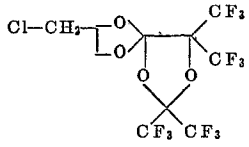
The cyclic ortho ethers in the following list can be used, in the listed proportions, in place of the 1,3-dioxolane in Example 4, to give the corresponding compounds of the invention:

Cyclic Ortho Ether	Amount, parts	Product
2-methoxy-5,5-dimethyl-1,3-dioxane	32	

Cyclic Ortho Ether	Amount, parts	Product
2'methoxy-1,2-methylene dioxybenzene	30.4	
2-methoxybutenediolformal	26.0	
2-ethoxy-4,5-tetramethylene 1,3-dioxolane	31.2	
2-methoxy-4,5-benzo-1,3-dioxane	33.2	
2'-methoxy-3,4,5,6-tetrafluoro-1,2-methylene dioxybenzene	44.8	
2-methoxy-5,5-bis(allyloxymethyl) 1,3-dioxane	51.6	

Example 5

A mixture of 100 parts of 2-ethoxy-4-chloromethyl-1,3-dioxolane and 100 parts of hexafluoroacetone was heated in a bomb at 150° C. for six hours. The crude product was fractionated to give a chloromethylspiro-dioxolane having the structure



This compound had a boiling point of 197° C. at 760 mm. of pressure and a freezing point of less than −50° C.

Example 6

Other compounds of the invention can be prepared from the products of Example 5 by simple reactions, using customary procedures.

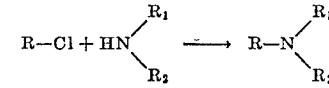
For brevity, the product of Example 5 will be designated R—Cl. Using this compound as a starting material, the reactions illustrated by the following equations can be run to produce the corresponding compounds of the invention.

(1) $$R{-}Cl + KCN \longrightarrow R{-}CN$$

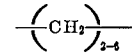
(2) $$R{-}Cl + OH^{\ominus}\ (base) + H_2O \longrightarrow R{-}OH$$

(3) $$R{-}OH + H^{+} + CH_2{=}C(CH_3){-}COOCH_3 \longrightarrow H_2C{=}C(CH_3){-}C(=O){-}O{-}R$$

This methacrylate monomer can be used to prepare polymeric film-forming components for use in coating compositions and for soil and water repellant textile treatments by polymerizing it according to conventional techniques, in solution or emulsion, using free radical catalysts.

(4) 

where R and R_1 are hydrogen or alkyl of 1 to 5 carbon atoms or phenyl, or where R and R_1 are connected by a



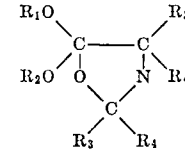
radical.

(5) $$R{-}Cl + NH_4SCN \rightarrow RSCN$$

Reactions of this type are discussed in greater detail in J. Gen. Chem., 32, 3189 (1962).

I claim:

1. A compound having the formula



where

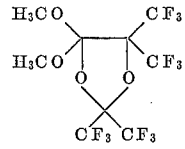
R_1 and R_2 are alkyl of 1 through 18 carbon atoms;

alkyl of 1 through 18 carbon atoms substituted with chlorine or fluorine; alkenyl of 2 through 6 carbon atoms; cycloalkyl of 3 through 7 carbon atoms; phenyl; phenyl substituted with chlorine, bromine, fluorine, —OCH_3, alkyl of 1 through 5 carbon atoms or —NO_2;

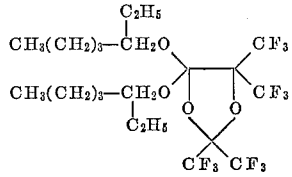
R_3 is perfluoroalkyl or monochloroperfluoroalkyl, both containing 1 through 5 carbon atoms; and

R_4 is perfluoroalkyl of 1 through 5 carbon atoms.

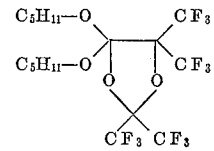
2. A compound having the formula



3. A compound having the formula



4. A compound having the formula



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ALEX MAZEL, Primary Examiner

JAMES H. TURNIPSEED, Assistant Examiner

U.S. Cl. X.R.

260—239, 294.7, 326.16, 338, 340.5