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3,412,140

## POLYFLUORINATED GLUTARATE ESTERS

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11 Claims. (Cl. 260—485)

## ABSTRACT OF THE DISCLOSURE

Bis(polyfluoroalkyl)-3-methyl glutarate esters in which the fluoroalkyl groups have the formula



where  $n$  is an integer of from 0 to 5, preferably 1 to 3, and  $X$  is a member selected from the group consisting of hydrogen and fluorine, and is preferably fluorine, said glutarates having properties of high fire resistance, increased temperature stability, liquidity over a relatively wide temperature range, and improved hydrolytic stability, said glutarates being particularly valuable as functional fluids, e.g., as hydraulic fluids, heat transfer fluids and as lubricants.

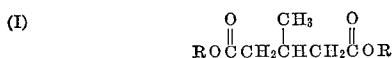
This invention relates to certain polyfluoroalkyl glutarate esters, and is particularly concerned with the provision of novel bis(polyfluoroalkyl)glutarates.

It is an object of the present invention to provide a series of compounds in the form of polyfluorinated glutarate esters having high fire resistance, high temperature stability, and improved hydrolytic stability, and which remain in liquid form over a wide temperature range and are relatively nonvolatile at elevated temperatures, and are substantially noncorrosive to metals employed in the construction of component parts such as steel.

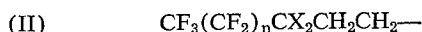
Another object of the invention is the provision of bis(polyfluoroalkyl)-3-methyl glutarate esters having the above-noted properties and other advantages, and having particular utility as hydraulic fluids, heat transfer fluids, and as lubricants, particularly at elevated and at reduced temperatures.

Other objects and advantages will appear hereinafter.

We have discovered that the above-noted objects are achieved according to the invention by the provision of a class of bis(polyfluoroalkyl)-3-methyl glutarates having the formula



where  $R$  has the formula



where  $n$  is an integer of from 0 to 5, preferably 1 to 3, and  $X$  is a member selected from the group consisting of hydrogen and fluorine, and is preferably fluorine.

The combined fluorine content of the bis(polyfluoroalkyl)-3-methyl glutarates of the invention can range from about 31% to about 61%, preferably about 40% to about 57%, by weight. In the compounds noted above, the two alkyl groups of the bis(polyfluoroalkyl)-3-methyl glutarates hereof, defined in Formula II above, can be the same or different.

It has been found that the above-defined bis(polyfluoroalkyl)-3-methyl glutarates are particularly valuable as functional fluids, e.g., as base stocks for hydraulic fluids, and are also useful as heat transfer media and as lubricants due to the advantageous physical properties of such compounds. These properties include high fire

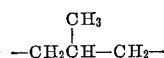
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resistance, increased temperature stability, and liquidity over a relatively wide temperature range. Thus, for example, generally these fluorinated glutarate esters have a thermal stability in the range of about 400° F. to about 550° F., autoignition temperatures up to and in excess of the order of about 700° to about 850° F., and remain liquid down to a temperature of the order of -20° to -40° F. Further the viscosity of such bis(polyfluoroalkyl)-3-methyl glutarates at low temperatures of the order of -20° to -40° F. permit the operative use of such liquids as hydraulic fluids, cooling media and lubricants in these low temperature ranges. Also, certain of the glutarate esters of the invention have relatively low pour points, e.g., in the range of -20° to about -40° F., or lower, which, together with the relatively low viscosity of these materials at low temperatures permits the liquid compounds to be pumped without high expenditure of energy at low temperatures. Moreover, the glutarate esters of the invention have improved hydrolytic stability as compared to prior art bis(polyfluoroalkyl)-3-methyl glutarate esters, and do not adversely affect materials, such as metals, e.g., steel, copper, and the like, with which they may be in contact, and which are often employed in the construction of component parts of hydraulic systems.

The above-noted properties render the glutarate esters hereof particularly useful as hydraulic fluids, lubricants and cooling fluids in aircraft systems, especially modern high-speed aircraft systems.

The bis(polyfluoroalkyl)-3-methyl glutarates of the invention are produced according to one convenient mode of procedure by reacting the corresponding polyfluorinated alcohol with 3-methyl glutaric acid in a proportion of about 2 moles of the alcohol to one mole of the acid in a solvent, e.g., toluene. The mixture is heated at reflux for a period of hours, e.g., about 6 to about 20 hours, while collecting water generated in the esterification reaction. The solvent, e.g., toluene, is removed by distilling at reduced pressure, and the remaining mixture is distilled at still lower pressure to recover the desired bis(polyfluoroalkyl)-3-methyl glutarate compounds.

Specific examples of bis(polyfluoroalkyl)-3-methyl glutarates of the invention are as follows, the symbol  $R'$  in the formula below representing the



portion of the 3-methyl glutarate radical:

- (1)  $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2\text{CF}_2\text{CF}_3$
- (2)  $\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2(\text{CF}_2)_2\text{CF}_3$
- (3)  $\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2\text{CH}_2(\text{CF}_2)_2\text{CF}_3$
- (4)  $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2(\text{CF}_2)_3\text{CF}_3$
- (5)  $\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2(\text{CF}_2)_4\text{CF}_3$
- (6)  $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2\text{CH}_2(\text{CF}_2)_3\text{CF}_3$
- (7)  $\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2\text{CH}_2(\text{CF}_2)_4\text{CF}_3$
- (8)  $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3$
- (9)  $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3$
- (10)  $\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2(\text{CF}_2)_6\text{CF}_3$
- (11)  $\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2\text{CH}_2(\text{CF}_2)_2\text{CF}_3$
- (12)  $\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{OOCR}'\text{COOCH}_2\text{CH}_2\text{CH}_2(\text{CF}_2)_3\text{CF}_3$

The preferred compounds of the invention are Compounds 2 to 6 above.

The following are examples of preparation of compounds of the invention:

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## EXAMPLE 1

Bis(3,3,4,4,5,5,5-heptafluoropentyl)-3-methyl glutarate

To a mixture of 76.2 g. (0.356 mole) of 3,3,4,4,5,5,5-heptafluoropentanol, 24.4 g. (0.167 mole) of 3-methylglutaric acid, and 1 g. of p-toluenesulfonic acid monohydrate, is added 300 cc. of toluene and the mixture is refluxed with an attached Stark-Dean trap to collect the water generated in the esterification.

The toluene layer is shaken twice with saturated sodium bicarbonate solution and dried over anhydrous potassium carbonate, then vacuum stripped at about 4 mm. to remove toluene. The residue is distilled to yield 73.5 g. (75%) of product, B.P. 104.5° C. (0.35 mm. pressure).

The bis(polyfluoropentyl)-3-methyl glutarate ester thus produced, Compound 2 above, has a viscosity at 210° F. of 1.78 centistokes and a viscosity at -30° F. of 2,885 centistokes. The compound has a low pour point, a density of 1.47 g./ml. at 77° F., and a thermal stability of about 473° F. Such glutarate ester has a high autoignition temperature of about 750° F., good hydrolytic stability and high fire resistance. Such compound can be employed as a hydraulic fluid in the hydraulic systems of aircraft, and is essentially non-corrosive to metals such as iron, steel or copper.

The hydrolytic stability of the glutarate ester of Example 1, designated Compound A, is compared with the hydrolytic stability of a related prior art compound

$\text{CHF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OOCCH}_2\overset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{COOCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$  designated Compound B, by shaking each of such compounds with water and titrating according to A.S.T.M. procedure D 974-58T. to obtain the acid number. A comparison of these results for Compounds A and B, together with a comparison of certain other important properties of these compounds, are set forth in the table below. The acid numbers noted in the table below are obtained after exposure of both compounds to water and titrating according to the A.S.T.M. procedure indicated above.

TABLE

|                 | Viscosity (centistokes) |         |         | Acid Number | Density at 77° F., g./ml. |
|-----------------|-------------------------|---------|---------|-------------|---------------------------|
|                 | -30° F.                 | 100° F. | 210° F. |             |                           |
| Compound A..... | 2,885                   | 7.2     | 1.78    | 0.47        | 1.47                      |
| Compound B..... | 7,820                   | 23.2    | 3.49    | 54.50       | 1.55                      |

From the table above it is seen that at temperatures of the order of -30° F. the viscosity of fluid Compound A of the invention is substantially lower than the viscosity of prior art Compound B. Further, Compound A of the invention has a lower density than Compound B, requiring less weight per unit volume of fluid in a hydraulic system of an aircraft than in the case of Compound B, and such reduced density together with the lower viscosity of Compound A at low temperatures, permit pumping of fluid A at low temperatures with a smaller expenditure of pump energy than for fluid B. Of particular significance, it is seen that the acid number representing the extent of hydrolysis of Compound A of the invention is negligible as compared to the high acid number of prior art Compound B, and hence the hydrolytic stability of Compound A is highly superior to that of Compound B. This latter characteristic of resistance to hydrolysis for the compounds of the invention is of particular importance in the operation of hydraulic systems, since the elimination of moisture in such systems is extremely difficult and requires the use of special and complicated equipment and techniques.

## EXAMPLE 2

Bis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-3-methyl glutarate

The procedure of Example 1 is carried out except employing as the fluoroalcohol 3,3,4,4,5,5,6,6,6-nonafluorohexanol in the same molar proportion as the fluoropentanol of Example 1.

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The bis(polyfluoroalkyl)-3-methyl glutarate ester thus produced, Compound 4 above, has a low viscosity at low temperatures, good thermal stability, a high autoignition temperature, good hydrolytic stability and high fire resistance.

The bis(polyfluoroalkyl)-3-methyl glutarate ester of this example has utility as a functional fluid, and is particularly useful as a base stock for hydraulic fluids in an aircraft system operating over a wide temperature range.

## EXAMPLE 3

Bis(4,4,5,5,6,6,6-heptafluorohexyl)-3-methyl glutarate

The procedure of Example 1 is carried out except employing as the fluoroalcohol 4,4,5,5,6,6,6-heptafluoro-1-hexanol in the same molar proportion as the fluoropentanol of Example 1.

The bis(polyfluoroalkyl)-3-methyl glutarate thus produced, Compound 3 above, has a low viscosity at relatively low temperature, high thermal stability, good hydrolytic stability and high fire resistance. Such glutarate ester can serve as a hydraulic fluid of an aircraft system.

## EXAMPLE 4

Compounds 5 and 6 are prepared by procedure similar to that described above in Example 1, except employing in each instance the appropriate corresponding fluorinated alcohol.

The resulting bis(polyfluoroalkyl)-3-methyl glutarate esters thus obtained have properties generally similar to those of Compound 2 of Example 1 above.

From the foregoing, it is seen that the invention provides a novel class of bis(polyfluoroalkyl)-3-methyl glutarates which are designed particularly for use as base stocks of hydraulic fluids in aircraft systems, and which are also useful as lubricants and as heat transfer or cooling media in aircraft systems, without any significant corrosive effect on metals of construction such as iron and steel used in such systems.

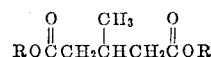
Bis(polyfluoroalkyl)-3-methyl glutarates are known in which the alkyl groups are completely fluorinated except for the carbon atom in 1-position which carries two hydrogen atoms, and the terminal carbon atoms, which carries one hydrogen atom and two fluorine atoms, as illustrated by prior art glutarate Compound B above. As previously noted, the glutarates of the invention such as represented by Compound A above, have certain important advantages over these prior art glutarate compounds, particularly highly improved hydrolytic stability. Further, it has been found that other compounds of the prior art containing such fluorinated alkyl groups as noted above are seriously corrosive to iron, apparently due to liberation of hydrogen fluoride as result of thermal breakdown between the adjacent  $-\text{CH}_2-$  and  $-\text{CF}_2-$  groups in the 1- and 2-positions, respectively, of the fluoroalkyl groups, and also apparently due to liberation of hydrogen fluoride from the terminal carbon atom.

On the other hand, the glutarates of the present invention, which contain  $-\text{CH}_2-$  groups in both the 1- and 2 positions and which carry a fully fluorinated terminal carbon atom, that is, a terminal  $\text{CF}_3$  group, are thermally stable and resist decomposition to form hydrogen fluoride, and accordingly are substantially noncorrosive to metals such as iron and steel at elevated temperatures.

While we have described particular embodiments of our invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention, as set forth in the appended claims.

We claim:

1. A bis(polyfluoroalkyl)-3-methyl glutarate having the formula

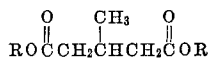


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where R has the formula  $\text{CF}_3(\text{CF}_2)_n\text{CX}_2\text{CH}_2\text{CH}_2-$  where  $n$  is an integer of from 0 to 5, and X is selected from the group consisting of hydrogen and fluorine.

2. A compound as defined in claim 1, wherein  $n$  is an integer of from 1 to 3.

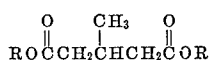
3. A bis(polyfluoroalkyl)-3-methyl glutarate having the formula



where R has the formula  $\text{CF}_3(\text{CF}_2)_n\text{CF}_2\text{CH}_2\text{CH}_2-$  where  $n$  is an integer of from 0 to 5.

4. A compound as defined in claim 3, wherein  $n$  is an integer of from 1 to 3.

5. A bis(polyfluoroalkyl)-3-methyl glutarate having the formula



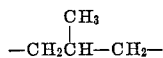
where R has the formula  $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{CH}_2-$  where  $n$  is an integer of from 0 to 5.

6. A compound as defined in claim 5, wherein  $n$  is an integer of from 1 to 3.

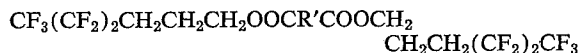
7. The compound having the formula



where R' has the formula

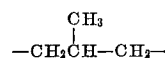


8. The compound having the formula

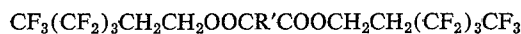


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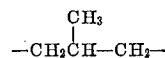
where R' has the formula



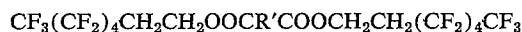
9. The compound having the formula



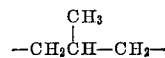
where R' has the formula



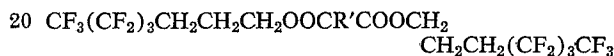
10. The compound having the formula



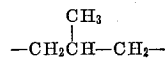
where R' has the formula



11. The compound having the formula



where R' has the formula



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