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DICARBOXYLATE ESTERS OF ALCOHOL CONTAINING A QUATERNARY CARBON IN THE β-POSITION

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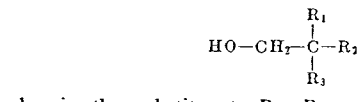
This invention relates to a particular class of novel diesters having outstanding viscosity and thermal stability characteristics which make the esters especially suitable for use as functional fluids—i.e., hydraulic fluids, heat transfer fluids, synthetic lubricants and the like.

Other diesters have previously been utilized as functional fluids, but these prior fluids are not sufficiently stable for some of the modern applications involving high temperature operating conditions. For example, synthetic lubricants for jet engines, hydraulic fluids for supersonic aircraft, coolants for electronic equipment, etc. are often required to withstand extended periods of operation at temperatures as high as 600° or 700° F. At these temperatures the prior art diester functional fluids completely decompose in a relatively short time, whereas the diesters of the present invention are quite stable.

The novel compounds are diesters of certain dibasic acids which have been esterified by monohydric alcohols having only quaternary carbon atoms in the beta-position of said alcohol. The dibasic acids need not be esterified with only one alcohol, but may be esterified with two different alcohols—provided both alcohols satisfy the criteria set forth below.

The acids from which the present diesters are formed are dicarboxylic acids which contain no more than 11 carbon atoms therein, and which preferably contain between about 6 and about 10 carbon atoms. A preferred class of such dicarboxylic acids comprises the aliphatic (including cycloaliphatic) dicarboxylic acids. A further preferred class of acids comprises the saturated aliphatic dicarboxylic acids. Examples of suitable acids for formation of the present diesters are sebacic acid, adipic acid, glutaric acid, methylglutaric acid, pimelic acid, azelaic acid, iso-sebacic acid, α-ethylsuberic acid, α,α'-diethyladipic acid, hexahydrophthalic acid, hexahydroisophthalic acid, hexahydroterephthalic acid, etc.

The critical criterion for the alcohols with which the foregoing dibasic acids are esterified is that such alcohols must have only quaternary carbon atoms in the beta-positions thereof—i.e., the carbon atom adjacent to the —CH_2OH carbinol group must be attached to four other adjacent carbon atoms. A further criterion of such alcohols is that they contain from 5 to 16, inclusive, carbon atoms, and preferably between 7 and 12, inclusive, carbon atoms. Primary alcohols are generally preferred over secondary and/or tertiary alcohols. One particularly preferred class of alcohols comprises compounds having the formula,



wherein the substituents R_1, R_2 and R_3 on the beta-carbon atom are all alkyl groups, and preferably all n-alkyl groups. Another particularly preferred class of alcohols is made up of those compounds in which the beta-carbon atom is a member of a 5- or 6-member saturated aliphatic ring. Examples of suitable alcohols are 2,2,4-trimethylpentyl alcohol, 1-methylcyclohexylmethyl alcohol, 3-cyclopentyl-2,2-dimethyl-1-propanol, 2,2,6,6-tetramethylcyclohexanol, 2,2,5,5-tetramethylcyclopentanol, 2,2-dimethyl-1-butanol, 2,2-dimethyl-1-hexanol, 2,2-dimethyl-1-octanol, etc.

The present compounds can be prepared by usual esterification procedures—e.g., by heating the acid in a slight excess of the alcohol with sulfuric acid as a catalyst, and then azeotroping off the water with toluene. The resulting crude products can be purified by diluting with a solvent, washing free of acid, drying over anhydrous sodium sulfate and vacuum distilling. The following examples are presented as illutrative of this general preparation as applied to particular compounds of the present invention.

EXAMPLE 1

Preparation of bis(2,2,4-trimethylpentyl) sebacate

To a mixture of 70 grams of 2,2,4-trimethyl-1-pentanol and 50.5 grams of sebacic acid, there was added 0.5 cc. of sulfuric acid and sufficient toluene to azeotrope off the water and hold the reflux temperature below 130° C. The water which was removed (9 cc.) was collected in a Dean and Stark trap. Additional benzene was added and the ester was washed free of acid, dryed over anhydrous sodium sulfate and distilled through an 8-inch heated Vigreux column. The product was collected in 92 percent yield (106.5 grams) of bis(2,2,4-trimethyl-1-pentyl) sebacate: boiling 207°–209° C./0.6 mm.; n_D^{25} 1.4471. *Analysis.*—Calculated (as $C_{20}H_{50}O_4$): C, 73.3; H, 11.8. Found: C, 73.27; H, 11.76.

EXAMPLE 2

Preparation of 2,2,4-trimethyl-1-pentanol

This compound was prepared from 2,2,4-trimethyl-1,3-pentanediol by converting the diol to 2,2,4-trimethyl-1,3-diacetoxypentane, selectively pyrolyzing the diacetoxypentane to form 2,2,4-trimethyl-3-penten-1-yl acetate, and then reducing the acetate to the desired 2,2,4-trimethyl-1-pentanol.

The 2,2,4-trimethyl-1,3-diacetoxypentane was prepared by adding (dropwise) 942 grams of acetyl chloride to a vigorously stirred solution of 876 grams of 2,2,4-trimethyl-1,3-pentanediol in 1600 cc. of benzene and 1050 grams of pyridine. The mixture was held below 50° C. during the acetyl chloride addition, then heated at 90° C. for 1½ hours. The reaction mixture was cooled, diluted with 400 cc. of benzene, washed free of pyridine hydrochloride, dried over anhydrous sodium sulfate and topped under water pump vacuum. Fractionation through an 8-inch Vigreux column gave a 90 percent yield (1380 grams) of the diacetate: boiling 115°–116° C./10 mm.; n_D^{25} 1.4308.

One-thousand two hundred and eighty-one grams of the above 2,2,4-trimethyl-1,3-diacetoxypentane was dropped through a vertical pyrolysis tube at 494°–517° C. over a period of 17 hours, and the effluent was collected under a water-cooled reflux condenser. The pyrolysis tube was a pyrex glass tube approximately 25 mm. in diameter and 48 inches long packed with size 3 solid glass beads over a length of 32 inches; it was insulated and electrically heated over approximately 38 inches, with separate heating elements for the top and bottom halves regulated by two powerstats. The temperature was measured by two thermocouples located at distances approximately 8 and 24 inches in the bead bed. During the pyrolysis nitrogen was passed through the tube at a rate of 200 cc. per minute.

The pyrolysis product was fractionated through a 90 x 2.5 cm. column packed with 6 mm. glass helices. By washing the forerun to remove acetic acid and re-

distilling the residue, there was obtained an 83.8 percent yield (644.2 grams) of clear colorless liquid 2,2,4-dimethyl-3-penten-1-yl acetate: boiling 74.5°–75.5° C./12 mm.; n_D^{25} 1.4357. *Analysis.*—Calculated (as $C_{10}H_{18}O_2$): C, 70.5; H, 10.6. Found: C, 70.0; H, 10.46.

The foregoing 2,2,4-trimethyl-3-penten-1-yl acetate was reduced at room temperature in a Parr hydrogenation apparatus using approximately 4 percent catalyst (5 percent palladium on carbon black) and 30 p.s.i.g. of hydrogen. The saturated reduction product was filtered to remove the catalyst, and the filtrate (472 g.) was hydrolyzed by refluxing for 5 hours in a solution of 1200 cc. of absolute ethanol and 100 cc. of water containing 111 grams of sodium hydroxide. The alcohol was removed by distillation, 200 cc. of water was added and the top layer was separated and washed free of caustic with saturated salt solution. The product was then dried over anhydrous sodium sulfate and vacuum distilled through a 30-inch Vigreux column to yield 346 grams (96 percent) of 2,2,4-trimethyl-1-pentanol: boiling 82°–83° C./30 mm.: n_D^{25} 1.4280.

EXAMPLE 3

Preparation of bis(1-methylcyclohexylmethyl) sebacate

A mixture of 108 grams of sebacic acid, 158 grams of 1-methylcyclohexylmethanol, 1 gram of concentrated sulfuric acid and 50 cc. of toluene was heated at reflux under a Dean and Stark trap until 17.5 cc. of water had been collected. The reaction mixture was cooled and dissolved in one liter of ether. The ether solution was washed with four 100 cc. portions of 5 percent sodium hydroxide solution and six 250 cc. portions of water and then dried over sodium sulfate. The solvent and drying agent were removed and the residue was fractionated under vacuum through a 10-inch column packed with 4 mm. glass helices. The product was obtained in 73 percent yield (166 grams) of colorless, oily bis(1-methylcyclohexylmethyl) sebacate: boiling 215°–217° C./0.4 mm.; n_D^{25} 1.4725. *Analysis.*—Calculated (as $C_{26}H_{46}O_4$): C, 73.89; H, 10.97. Found: C, 74.17; H, 11.28.

EXAMPLE 4

Preparation of bis(1-methylcyclohexylmethyl) adipate

A mixture of 87 grams of adipic acid, 158 grams of 1-methylcyclohexylmethanol, 0.4 gram of concentrated sulfuric acid and 60 cc. of toluene was heated at reflux under a Dean and Stark trap until 20.5 cc. of water had been collected. The reaction mixture was purified in the same way as described in the preceding example to give a 73 percent yield (160 grams) of colorless, oily bis(1-methylcyclohexylmethyl) adipate: boiling 186°–188° C./0.7 mm.; n_D^{25} 1.4734. *Analysis.*—Calculated (as $C_{22}H_{38}O_4$): C, 72.09; H, 10.45. Found: C, 72.90; H, 10.01.

EXAMPLE 5

Preparation of bis(1-methylcyclohexylmethyl) hexahydroisophthalate

A mixture of 80 grams of 1-methylcyclohexylmethanol, 60 grams of dimethylhexahydroisophthalate and 0.25 grams of sodium was heated under a Dean and Stark trap for 1½ hours at 165° C., after which time the temperature was raised to 210° C. for ½ hour. During this period 24 cc. of methanol distillate was collected in the trap. The reaction product was dissolved in ether, washed free of caustic, dried over sodium sulfate and twice distilled under vacuum through a 10-inch heated Vigreux column to give a yield of 72 grams of bis(1-methylcyclohexylmethyl) hexahydroisophthalate: boiling 217°–220° C./1.3–1.4 mm.; n_D^{25} 1.4865. *Analysis.*—Calculated (as $C_{24}H_{40}O_4$): C, 73.4; H, 10.19. Found: C, 73.83; H, 9.83.

The above-described esters are particularly useful as functional fluids because of their outstanding properties

with respect to volatility, pour point, viscosity, hydrolytic stability and thermal stability. The particularly outstanding property of thermal stability is illustrated in the following example, showing a comparison of the diesters of the present invention with diesters which do not have quaternary carbon atoms in the beta-position of the alcohol moiety.

EXAMPLE 6

Thermal stability was evaluated by heating samples (10 to 20 grams) of the diesters in glass containers under an atmosphere of nitrogen for 10 hours at 690° F. Since a portion of the decomposition products are volatile, the loss in weight of the sample over the 10 hour period was used as a measure of thermal stability. The change in viscosity of the material was also measured and utilized as an indication of degree of decomposition. The results of typical thermal stability evaluations are shown in the following table:

Compound	Percent loss in weight	Percent loss in 210° viscosity (cs.)
Di(n-octyl) sebacate	62	
Bis(2-ethylhexyl) sebacate	64	
Bis(2,2,4-trimethyl-1-pentyl) sebacate	8.5	10.7
Bis(1-methylcyclohexyl-methyl) sebacate	1.3	12.9
Bis(1-methylcyclohexyl-methyl) hexahydro-isophthalate	1.2	9.5
Bis(1-methylcyclohexyl-methyl) adipate	5.5	7.5

From the foregoing table it can be seen that the diesters of the present invention are as much as 50 times more stable (as measured by percent loss in weight) than the comparable prior art diesters. The change in viscosity of the prior art diesters could not be measured because of a large amount of solid deposits resulting from substantially complete decomposition of the diesters.

When utilized as functional fluids the present diesters, or mixture thereof, will generally comprise a major or predominant portion of the composition. There may, however, be minor proportions of V.I. improvers, dyes, antioxidants, hydrolysis inhibitors, snuffer additives, antiwear additives, diluents and similar commonly used additives incorporated herein in order to impart special properties to the fluids for particular specialty applications.

The present diesters can also be utilized in combination with one or more other functional fluid bases, such as silicates (e.g., tetra(2-ethylhexyl)orthosilicate, tetra(2-ethylbutyl)silicate, tetra(4-methyl-2-pentyl)silicate), hexaalkoxy disiloxanes (e. g., hexa(2-ethylhexyl)disiloxane, hexa(2-ethylbutyl)disiloxane), silicones (e.g., phenylmethyl silicone, methyl silicones), phosphate esters (e.g., tricresyl phosphate, tri-2-ethylhexyl) phosphate, mineral oil functional fluid bases, and similar mixtures, wherein the present diesters comprise either a major or minor proportion of the mixture.

We claim:

1. A diester of (*a*) a saturated aliphatic dicarboxylic acid containing not more than 11 carbon atoms and (*b*) a saturated aliphatic monohydric primary alcohol containing from 7 to 12 carbon atoms, the beta-carbon atom being a quaternary carbon atom and a part of a ring selected from the group consisting of 5- and 6-membered alicyclic rings.

2. The diester of claim 1, wherein the alcohol is 1-methylcyclohexylmethyl alcohol.

3. The diester of claim 2, bis(1-methylcyclohexylmethyl) sebacate.

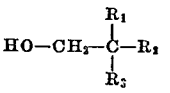
4. The diester of claim 2, bis(1-methylcyclohexylmethyl) adipate.

5. The diester of claim 2, bis(1-methylcyclohexylmethyl) hexahydroisophthalate.

6. A thermally stable functional fluid suitable for use at high temperatures and essentially containing, as substantially the sole dicarboxylate esters therein, diesters

(*a*) saturated aliphatic dicarboxylic acids containing not more than 11 carbon atoms and (*b*) saturated aliphatic monohydric alcohols containing from 7 to 12 carbon atoms and having a quaternary carbon atom in the β-position; and said diesters of (*a*) and (*b*) are present in an amount of at least 50 weight percent of the thermally stable functional fluid composition.

7. A thermally stable functional fluid suitable for use at high temperatures and essentially containing, as substantially the sole dicarboxylate esters therein, diesters of (*a*) saturated aliphatic dicarboxylic acids containing not more than 11 carbon atoms and (*b*) aliphatic monohydric alcohols containing from 7 to 12 carbon atoms and having the formula

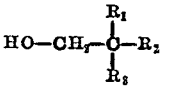


wherein R_1, R_2 and R_3 are saturated aliphatic hydrocarbon radicals; and said diesters of (*a*) and (*b*) are present in an amount of at least 50 weight percent of the thermally stable functional fluid composition.

8. The functional fluid of claim 7, wherein the aliphatic monohydric alcohol is 2,2,4-trimethylpentyl alcohol.

9. The functional fluid of claim 7, wherein the diester is bis(2,2,4-trimethylpentyl) sebacate.

10. A thermally stable functional fluid suitable for use at high temperatures and essentially containing, as substantially the sole dicarboxylate esters therein, diesters of (*a*) saturated aliphatic dicarboxylic acids containing not more than 11 carbon atoms and (*b*) aliphatic monohydric alcohols containing from 7 to 12 carbon atoms and having the formula



wherein R_1, R_2 and R_3 are n-alkyl radicals; and said diesters of (*a*) and (*b*) are present in an amount of at least 50 weight percent of the thermally stable functional fluid composition.

11. A thermally stable functional fluid suitable for use at high temperatures and essentially containing, as substantially the sole dicarboxylate esters therein, diesters of (*a*) saturated aliphatic dicarboxylic acids containing not more than 11 carbon atoms and (*b*) saturated aliphatic monohydric primary alcohols containing from 7 to 12 carbon atoms, the β-carbon atom being a quaternary carbon atom and a part of a ring selected from the group consisting of 5- and 6-membered alicyclic rings; and said diesters of (*a*) and (*b*) are present in an amount of at least 50 weight percent of the thermally stable functional fluid composition.

12. The functional fluid of claim 11, wherein the alcohol is 1-methylcyclohexylmethyl alcohol.

13. The functional fluid of claim 6, wherein the dicarboxylic acid is hexahydrophthalic acid.

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