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3,555,057

AROMATIC ESTERS OF DIMER ACID

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9 Claims

ABSTRACT OF THE DISCLOSURE

Benzyl esters of dimerized linoleic acid and hydrogenated dimerized linoleic acid were prepared by reacting the dimer acid with the appropriate alcohol in the presence of an acid catalyst. The esters were evaluated and found to have viscosity characteristics, lubricating properties and thermal stabilities desired in lubricants, lubricant additives and hydraulic fluids.

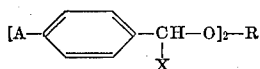
A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sub-licenses for such purposes, is hereby granted to the Government of the United States of America.

This application is a division of Ser. No. 433,524, filed Feb. 17, 1965, now U.S. Pat. No. 3,393,214.

This invention relates to benzyl and substituted benzyl esters of dimer (dilinoleic) acid and has among its objects the preparation of fluids of high thermal stability for use as lubricants, lubricant additives and hydraulic fluids.

Modern industry has an increasing need for superior lubricants for use in equipment designed to operate over a great temperature differential. There are many lubricant problems which cannot be solved by the use of mineral hydrocarbon lubricating oils. Synthetic materials previously prepared and used as specialty lubricants include the compounds bis(2-ethylhexyl) sebacate and dibenzyl sebacate employed as controls for evaluating the compounds of the present invention. These sebacate esters have many desirable properties, but compounds of greater thermal stability are needed.

The compounds of the present invention may be represented by the formula



wherein R is a diacyl radical derived from dimerized linoleic acid or the hydrogenated product thereof and, when X is hydrogen, A may be hydrogen, a short carbon chain alkoxy group, a straight or branched chain low molecular weight alkyl group, or the nitro group. When X is a phenyl group, A is hydrogen.

Representative compounds were prepared, characterized, and evaluated for usefulness. In general, the compounds of the present invention have favorable viscosity characteristics and are equal to or better than the sebacate ester controls in regard to lubricating properties as indicated by the wear scar test. Most of the present compounds have excellent thermal stability; onset of decomposition for several being in the range of about 370–390° C. as compared to about 290–300° C. for the controls.

Among the preferred compounds are those in which A is hydrogen or an alkyl group. The highest thermal stabilities were exhibited by bis(benzyl)-dilinoleate and the corresponding ester of the hydrogenated dimer, called

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hydrogenated bis(benzyl)-dilinoleate. An alkyl group at A is typified with the isopropyl radical, the compound being designated bis(p-isopropylbenzyl)-dilinoleate, but it is readily apparent that other alkyl groups such as methyl, ethyl, propyl, butyl and isobutyl provide esters of high thermal stability. A compound in which A is an alkoxy group, as in the methoxy derivative, bis(anisyl)-dilinoleate, has high thermal stability and is both a viscosity-temperature improver and wear improver for base oils. The alkoxy group may also be ethoxy, propoxy or isopropoxy. The presence of a nitro group at A is exemplified with bis(p-nitrobenzyl)-dilinoleate. An aryl group at X is demonstrated with a phenyl group in bis(benzhydryl)-dilinoleate.

In a typical procedure for preparation of the esters a ratio of two moles alcohol to one mole dimer acid and a small amount of an acid catalyst were dissolved in an inert organic solvent such as benzene and refluxed until the reaction was complete, as indicated by amount of water collected. The benzene solution was washed until free of acid, dried over calcium sulfate, the benzene removed, and the crude product purified by molecular distillation. We have found that the dilinoleate esters of the present invention are liquids, even though total molecular weight of a compound is as high as about 900.

The dimer acid employed in the preparation of the esters contained 95% dilinoleic acid, 4% trimer acid and 1% monobasic acid and had characteristics of acid number, 191.2; neutralization equivalent, 293.4; and molecular weight, 565. The hydrogenated dimer acid had an acid number of 192.8; neutralization equivalent, 288.0; and iodine number 29.0. The alcohols were commercial products and only the anisyl alcohol was redistilled before use. Best results were obtained with use of naphthalene-2-sulfonic acid as the catalyst. Naphthalene-1-sulfonic acid, methane sulfonic acid and sulfuric acid gave poorer results than naphthalene-2-sulfonic acid.

Preparation of the esters of the invention is illustrated by the following examples:

EXAMPLE 1

Dimer acid, 149 g.; benzyl alcohol, 58 g.; and 3 g. naphthalene-2-sulfonic acid were combined with 200 ml. benzene in a one-liter 3-neck flask. The flask was equipped with a thermometer, a magnetic stirrer, and a Dean and Stark tube with a water cooled condenser. The mixture was heated at 90° C. reflux temperature until the calculated amount of water (9.5 ml.) was separated; reaction time 3 hours. After cooling the reaction mixture was washed until acid-free. The benzene solution was dried over calcium sulfate, filtered, and the benzene evaporated under vacuum. The crude product, an amber fluid, weighed 189 g., a yield of 95%. The product has an acid No. of zero, and infrared spectra indicated absence of acid and presence of ester carbonyl. The crude product was purified by molecular distillation, the main fraction being collected between 280–300° C. at 9 to 15 microns pressure. This fraction weighed 156.2 g. and had a molecular weight of 750.

EXAMPLE 2

The process of Example 1 was repeated except that 151 g. of hydrogenated dimer acid was used in place of the dimer and the mixture was refluxed 4 hours. Yield of crude ester was 90.4%.

EXAMPLE 3

Following the typical procedure, 282.5 g. dimer acid, 150.2 g. p-isopropylbenzyl alcohol and 5.65 g. naphthalene-2-sulfonic acid were refluxed for 5 hours and the crude bis(p-isopropylbenzyl)-dilinoleate was separated

from the reaction mixture in 99% yield. The product was purified by molecular distillation.

EXAMPLE 4

In a procedure similar to previous examples, dimer acid, 28.3 g.; benzhydryl alcohol (α -phenylbenzyl alcohol) 18.3 g.; and 0.65 g. catalyst were refluxed 8 hours, the crude ester separated from the reaction mixture in 90% yield and the bis(benzhydryl)-dilinoate purified by molecular distillation.

EXAMPLE 5

Dimer acid, 45.6 g.; p-nitrobenzyl alcohol, 25.0 g.; and 1.82 g. of naphthalene-2-sulfonic acid were combined in benzene solution and refluxed 8 hours, the crude ester separated from the reaction mixture (90% yield) and the bis(p-nitrobenzyl)-dilinoate purified by molecular distillation.

EXAMPLE 6

Dimer acid, 10.2 g.; anisyl alcohol, 5.0 g.; and 0.4 g. catalyst were combined in benzene and refluxed 6 hours, the crude ester separated as described in Example 1 and bis(anisyl)-dilinoate purified by molecular distillation. Yield was 80%.

EXAMPLE 7

As a control material, dibenzyl sebacate was prepared from sebacic acid and benzyl alcohol. The typical procedure for preparation of esters was followed.

Physical and chemical data pertaining to the compounds of the examples were determined. Some of the data are presented in Table I.

Among the evaluations for usefulness of the compounds of the present invention were properties of thermal stability, viscosity characteristics and lubrication as indicated by wear scar test. In these evaluations bis(2-ethylhexyl)-sebacate, dibenzyl-sebacate and paraffin oil having a viscosity of 100 Saybolt seconds at 100° F. were included as reference materials. The data are summarized in Table II.

Thermal stability was determined by thermogravimetry, heating the compound in a specially designed sample holder suspended from a weighing mechanism.

TABLE I.—CHARACTERISTICS OF DILINOATE ESTERS AND SEBACATE CONTROL

Example No.	Compounds	B.P. ¹		N _D ³⁰	Carbon, percent		Hydrogen, percent		Saponification number		Saponification equivalent	
		° C.	Microns		Calculated	Found ²	Calculated	Found	Calculated	Found	Calculated	Found
1.....	Bis(benzyl)-dilinoate.....	280	9	1.5028	81.03	81.11	10.35	10.54	151.4	146.4	270.6	383.2
2.....	Hydrogenated bis(benzyl)-dilinoate.....	275	10	1.5013	80.59	80.68	10.52	10.56	150.6	147.0	371.8	381.5
3.....	Bis(p-isopropylbenzyl)-dilinoate.....	300	10	1.5020	81.50	80.95	10.74	10.84	136.0	138.3	412.7	406.0
4.....	Bis(benzhydryl)-dilinoate.....	(³)		1.5295	83.36	82.72	9.48	9.53	125.6	126.2	446.8	444.6
5.....	Bis(p-nitrobenzyl)-dilinoate. ⁴	>200	10	1.5177	72.25	72.33	8.98	9.32	135.0	139.5	415.6	403.0
6.....	Bis(anisyl)-dilinoate.....	>225	6	1.5230	77.95	77.80	10.06	9.60	140.1	143.5	400.6	391.0
7.....	Dibenzyl sebacate ⁵	180	7	1.5162	75.36	75.49	7.91	8.03				

¹ Molecularly distilled.

² Based on calcd. molecular weight of dilinoic acid (M.W. 561), not on molecular weight derived from commercial dimer acid (M.W. 565).

³ Alcohol insol. fraction.

⁴ Nitrogen, % calcd. 3.37; found, 3.12.

⁵ Control sample.

⁶ Solid at room temperature.

TABLE II.—THERMAL STABILITY, VISCOSITY, AND LUBRICATING PROPERTIES OF DILINOATE ESTERS AND CONTROLS

Sample	Onset of decomposition temperature ° C. ¹	Viscosity index	Wear scar diameter mm.	
Example No.:				
1.....	Bis(benzyl).....	384	124.3	0.653
2.....	Hydrogenated bis(benzyl).....	392	126.0	0.748
3.....	Bis(p-isopropylbenzyl).....	368	110.2	0.843
4.....	Bis(benzhydryl).....	306	78.4	0.829
5.....	Bis(p-nitrobenzyl).....	273	95.4	0.863
6.....	Bis(anisyl).....	345		0.473
	Bis(2-ethylhexyl)sebacate.....	289	148.8	0.830
7.....	Dibenzyl sebacate.....	300		0.950
	100 paraffin oil.....		112.7	0.803

¹ Temperatures determined on average of 3 runs. Accuracy, $\pm 4^\circ$.

The sample holder was made from 4 mm. Pyrex glass tubing, 24 cm. long. A small bulb (capacity-approximately 0.5 ml., 1.0 cm. diameter was formed at one end of the tube and a flared lip was formed at the other. The size of the bulb may be varied for the weight of the sample being used. The bulb, with the above dimensions, will accommodate a sample weighing 100 mg. The sample was placed in the holder with a long, thin dropper, being careful not to deposit liquid on the wall of the tube. The holder was then attached to the eyelet of the weighting mechanism (support rod) with a hook made from 22 gauge Nichrome wire. Using this arrangement, the sample holder tube extends approximately 7.5 cm. above the top of the furnace while the bulb is located approximately 6 mm. above the sample thermocouple well. This distance can be adjusted by the wire hook.

The samples were heated to 525–575° C. at a heating rate of 3° C. per minute in a dry air atmosphere which flowed at a rate of 10 ml. per minute at atmospheric pressure. Decomposition took place at a maximum of one-third of the distance up the sample holder tube as evidenced by observation of carbonaceous matter. Onset of decomposition is defined as the point where (a) the material shows the first detectable weight loss as determined by a deviation from a blank run and/or (b) the slope, dw/dT shows a radical change from some minimum value.

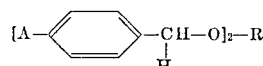
The viscosity index was determined according to the procedure given in ASTM D567–53, using semi-micro viscometers.

Lubricating property was evaluated using the four ball wear test as described by Peale et al., Lubrication Eng. Trans. 3, 48 (1960).

In the wear test, the smaller value denotes the best lubricating property. Several of the compounds were noticeably superior to the controls and the remainder compared favorably.

We claim:

1. An ester of the formula



wherein R is selected from the group consisting of the diacyl radical of dimerized linoleic acid and the diacyl

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radical of hydrogenated dimerized linoleic acid and A is selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, nitro, and a short carbon chain alkoxy group.

2. An ester of claim 1 in which R is the diacyl radical of dimerized linoleic acid. 5
3. The ester of claim 2 in which A is hydrogen.
4. The ester of claim 2 in which A is isopropyl.
5. The ester of claim 2 in which A is nitro.
6. An ester of claim 2 in which A is a short carbon chain alkoxy group. 10
7. The ester of claim 6 in which A is methoxy.

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8. An ester of claim 1 in which R is the diacyl radical of hydrogenated dimerized linoleic acid.
9. The ester of claim 8 in which A is hydrogen.

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