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ALKYLBUTYROLACTONE-α-ACETIC ACIDS

Donald J. Anderson, San Anselmo, and Louis de Vries, Richmond, Calif., assignors to Chevron Research Company, a corporation of Delaware

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2 Claims. (Cl. 252—57)

This application is a continuation-in-part of Donald J. Anderson and Louis de Vries application Serial No. 259,722, filed February 19, 1963 (now abandoned).

This invention pertains to lubricating oil compositions having incorporated therein metal-free detergents.

Present day internal combustion engines operate at high speeds and high compression ratios. When used in the so-called city stop-and-go driving, which includes the greater part of the driving conditions for a large percentage of today's automobiles, the internal combustion engines do not reach the most efficient operating temperature. Under city driving conditions, large amounts of partial oxidation products are formed, and reach the crankcase of the engine by blowing past the piston rings. Most of these partial oxidation products are oil-insoluble, tending to form deposits on the various operating parts of the engine, such as the pistons, piston rings, etc. For the purpose of preventing the deposition of these products on the various engine parts, it is necessary to incorporate detergents in the lubricating oil compositions, thus keeping these polymeric products highly dispersed in a condition unfavorable for deposition on metals.

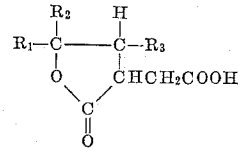
For the most part, the various detergents which are added to crankcase oils to reduce this formation of sludges and varnishes are metal organic compounds, particularly those compounds wherein the metal is linked to an organic group through an oxygen atom. Although these metal-containing organic compounds have some effectiveness as detergents for dispersing the precursors of deposits within the oil itself rather than permitting them to form added deposits on the engine parts, they have the disadvantage of forming ash deposits in the engine. These ash deposits lower engine performance by fouling spark plugs and valves, and contribute to preignition.

It is a particular object of this invention to provide new compounds which are used in the formation of metal-free detergents for lubricating oil compositions.

Therefore, in accordance with this invention, it has been discovered that alkylbutyrolactone-α-acetic acids are new compounds which are useful as intermediates in the formation of amides of alkylbutyrolactone-α-acetic acid. These amides of alkylbutyrolactone-α-acetic acid are effective as detergents in lubricating oil compositions.

The alkylbutyrolactone-α-acetic acids described herein are useful not only as intermediates in the formation of metal-free detergents, but these alkylbutyrolactone-α-acetic acids are useful as rust inhibitors in lubricating oil compositions.

These acids, which are new compounds, are of the formula

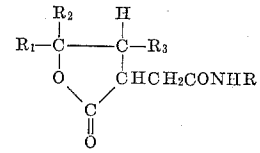


wherein R_1, R_2 and R_3 are hydrogen or alkyl radicals containing a total of from 10 to 300 carbon atoms. The total number of carbon atoms in R_1, R_2 and R_3 is preferably from 10 to 100.

These alkylbutyrolactone-α-acetic acids can be prepared by reacting an olefinic hydrocarbon with dimethyl bromosuccinate to obtain the methyl ester which is then converted to the acid.

The amides of the above-described alkylbutyrolactone-α-acetic acid are those derived from ammonia or amines, including aliphatic, cycloaliphatic and aromatic monoamines, polyamines and heterocyclic amines. In any case, the amino group reacting with the carboxyl groups to form the amide must be a primary or secondary amino group.

The resulting amides include those of the formula



wherein R_1, R_2 and R_3 are the same as defined hereinabove, and R is hydrogen or the residue of an amine radical having from 1 to 20 carbon atoms, preferably from 2 to 12 carbon atoms, and from 0 to 10 nitrogen atoms.

Of particular preference as lubricating oil additives are the gamma alkylbutyrolactone-α-acetic acids wherein the gamma alkyl radical contains from 10 to 300 carbon alkyl radical containing from 10 to 300 carbon atoms, and atoms; that is, wherein R_1 in the above formula is an R_2 and R_3 are hydrogen.

Lubricating oils which can be used as base oils when these alkylbutyrolactone-α-acetic acids are used therein include a wide variety of lubricating oils, such as naphthenic base, paraffin base, and mixed base lubricating oils, other hydrocarbon lubricants, e.g., lubricating oils derived from coal products, and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and mixtures thereof), alkylene oxide-type polymers (e.g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing the alkylene oxide in the presence of water or alcohols, e.g., ethyl alcohol, dicarboxylic acid esters (such as those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkanol succinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc.), liquid esters of acids of phosphorus, alkyl benzenes (e.g., monoalkyl benzene such as dodecyl benzene, tetradecyl benzene, etc.) and dialkyl benzenes (e.g., n-nonyl-2-ethylhexyl benzene), polyphenyls (e.g., biphenyls and terphenyls), alkyl biphenyl ethers, compounds of silicon, e.g., tetraethyl silicate, tetraisopropyl silicate, tetra(4-methyl-2-tetraethyl) silicate, hexyl-(4-methyl-2-pentoxy) disiloxane, poly(methyl) siloxane, poly(methylphenyl) siloxane, etc.

The above base oils may be used individually or in combinations thereof, wherever miscible or wherever made so by the use of mutual solvents.

When used as rust inhibitors the alkylbutyrolactone-α-acetic acids can be used in oils of lubricating viscosity in amounts of 0.1% to 10% by weight, preferably 0.25% to 5% by weight.

The preparation of the alkylbutyrolactone-α-acetic acids described herein is illustrated in the following examples.

EXAMPLE 1.—PREPARATION OF THE METHYL ESTER OF POLYBUTENYLBUTYROLACTONE-α-ACETIC ACID

A mixture of 93.8 g. (0.1 mole) of a polybutene (molecular weight of about 840) in 100 ml. heptane, 225 g. (1 mole) of dimethyl bromosuccinate, and 1.46 g. (0.01 mole) of di-t-butyl peroxide was charged to a rocker bomb, and the vessel purged with nitrogen. The reaction mixture was heated at 130° C. with agitation for 5 hours, then cooled to room temperature, and the methyl bromide vented to the atmosphere. The reaction mixture was vacuum distilled to remove the heptane and the unreacted dimethyl bromosuccinate.

Infrared analysis of the product showed the spectrum characteristics of the lactone (1780 cm.$^{-1}$) and the ester (1735 cm.$^{-1}$).

EXAMPLE 2.—PREPARATION OF THE METHYL ESTER OF DECYLBUTYROLACTONE-α-ACETIC ACID

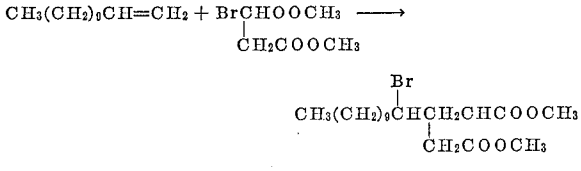
A mixture of 98.5 g. (0.438 mole) of dimethyl bromosuccinate, 14.7 g. (0.0875 mole) 1-dodecene, 1.0 g. (0.00875 mole) of acetyl peroxide in 9 ml. of dimethyl phthalate, and 50 ml. benzene was heated with agitation for 4 hours at 90° C. The benzezne and unreacted dimethyl bromosuccinate were removed by distillation at reduced pressure, followed by heating the residual yellow oil for 10 minutes at 195–205° C. at an absolute pressure of 2 mm. Hg. The final residue was crystallized from an ether-pentane solvent, resulting in a light brown waxy solid having a melting point range at 32–37° C. Infrared analysis of this product showed the spectrum characteristics of a lactone at 1775 cm.$^{-1}$ and the ester at 1735 cm.$^{-1}$.

Further purification resulted in white crystals which had a melting point of 43–45° C. Elemental analysis showed:

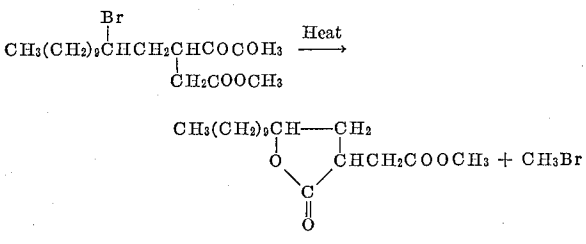
Calculated: 68.40% C., 10.14% H. Found: 68.35% C., 8.19% H.

The following equations exemplify the reactions of Example 2:

(1)



(2)



The methyl ester of decylbutyrolactone-α-acetic acid prepared above was converted to the corresponding acid. A mixture of 2 g. of lactone ester, 50 ml. of 96% sulfuric acid and 50 g. of ice were stirred and warmed to 100° C., at which temperature the stirring was continued for about

3 hours. The mixture was cooled until the lactone acid crystallized on top of the sulfuric acid. The lactone acid was then extracted with diethyl ether using ten separate 50 ml. extractions. The combined ether extracts were chilled in a Dry Ice-acetone bath. The extracts were then filtered to separate the lactone acid in the form of white crystals. Infrared analysis of a melt-smear of the white crystals gave the expected peaks of a lactone acid. Further recrystallization of the white crystals from ether yielded a sample having a melting point of 104° C., the analysis of which showed a percent carbon of 67.73 and percent hydrogen of 9.68 corresponding to theoretical values of 67.61 and 9.86, respectively.

The lactone acids of the invention are useful themselves as rust inhibitors in lubricating oil compositions in the formulations described above. However, another important feature is their utility as intermediates for reaction with various amines to provide effective nitrogen containing ashless detergents for lubricants.

The following example illustrates the use of the alkylbutyrolactone-α-acetic acids as intermediates in the formation of the corresponding amides which are effective as detergents in lubricating oil compositions.

EXAMPLE 3.—PREPARATION OF TETRAETHYLENE PENTAMINE AMIDE OF AN ALKYLBUTYRLACTONE-α-ACETIC ACID DERIVED FROM A BUTYLENE POLYMER

An alkylbutyrolactone-α-acetic acid was prepared from a butylene polymer having a molecular weight of about 850. A 40% solution of this lactone in a hydrocarbon oil was reacted with an ethylene amine condensation product having a molecular weight corresponding to tetraethylene pentamine.

A mixture of 76 g. (0.4 mole) of this tetraethylene pentamine and 1218 g. (0.50 mole) of the the product of the alkylbutyrolactone-α-acetic acid was blended with agitation at 150° C. for one hour, allowed to cool, then stand for 36 hours at room temperature. The mixture was then reheated at 150° C. for 1 hour.

Infrared analysis showed a band at 1650–1700 cm.$^{-1}$ due to the amide carbonyl group, and a band at 1775 cm.$^{-1}$ due to the butyrolactone carbonyl group.

Table I hereinbelow presents data obtained with several illustrative tests of derivatives. Tests B and C are lubricating oil compositions containing 1% by weight of the amide obtained in Example 3 hereinabove in combination with metal dithiophosphates. Tests D and E are lubricating oil compositions containing 1.5% of amides derived from triethylene tetramine and diethylene triamine, respectively. The concentration of the dithiophosphates is expressed in millimoles per kilogram of finished composition (based on the metal), that is, mM./kg.

Dithiophosphate A was a zinc salt of a mixed dialkyl dithiophosphate wherein one of the alkyl radicals contained 4 carbon atoms and the other alkyl radical contained 5 carbon atoms. Dithiophosphate B was a zinc di-(alkylphenyl)dithiophosphate.

The test was made in a Caterpillar L–1 engine according to Supplement I conditions for a period of 120 hours as described in the Coordinating Research Council Handbook, January, 1946.

The "PD Nos." refer to the piston discoloration rating. After the engine test, the three piston lands are examined visually. To a piston skirt which is completely black is assigned a PD number of 800; to one which is completely clean, a PD number of 0; to those intermediate between completely black and completely clean are assigned PD numbers intermediate in proportion to the extent and degree of darkening.

The "GD Nos." refer to the percentage deposits in the piston ring grooves; a 0 evaluation being a clean groove; and a number of 100 being a groove full of deposits.

The base oils were California SAE 30 base oils.

Table I

Additive	A	B	C	D	E
Lactone Amide, weight percent	0.0	1.0	1.0	1.5	1.5
Dithiophosphate:					
(A) mM./kg	0.0	0.0	10	8	8
(B) mM./kg	0.0	0.0	2	0	0
Test Results:					
GD No	[1] 39		2	2	5
PD No	800, 800, 800		35, 1, 2	15, 20, 0	3,3, 0

[1] These test results were obtained in a Caterpillar L-1 test under the MIL-L-2104 conditions. Thus, under the more severe Supplement-1 conditions, these GD Nos. would be considerably higher.

Table II hereinbelow presents data obtained in an FL-2 test, using a 6-cylinder Chevrolet engine operating at 2500 r.p.m. for a period of 36 hours, which test is fully described in a Coordinating Research Council bulletin titled "Research Technique for the Determination of the Effects of Fuels and Lubricants on the Formation of Deposits During Moderate Temperature Operation" (1948).

The piston varnish rating is a visual observation of the amount of varnish on a piston skirt, with "10" being the maximum rating for a perfectly clean piston, and "0" being the rating of a piston fully covered with black varnish. This piston varnish rating correlates with road performance in automobiles.

The total rating is the overall deposit rating of the engine, with the rating values ranging from 0, the poorest value, to 100, the top value. These figures indicate the percentage rating for the engine.

The base oil was an SAE 30 base oil.

The succinimide and the dithiophosphates were the same as those described for Table I hereinabove.

Table II

Additive	F	G	H
Lactone Amide, weight percent	0.0	1.0	1.0
Dithiophosphate:			
(A) mM./kg	0.0	0.0	10
(B) mM./kg	0.0	0.0	2
Test Results:			
Piston Varnish Rating	2.5		6.0
Total Rating			84.3

In an L-38 strip corrosion test, the copper strip weight loss was only 15.5 milligrams when using a petroleum base oil containing 6% by weight of the amide prepared as in Example 3 hereinabove.

Table III hereinbelow presents data obtained in an L-38 engine test, using a 1-cylinder CLR engine. The test period was for 40 hours.

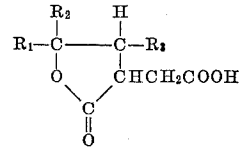
Table III

Additive:	
Amide (Example 3), wt. percent	2.0
Dithiophosphate A, mM./kg.	10
Dithiophosphate B, mM./kg.	2
Test results: Bearing weight loss (mgs.)	55.4

In addition to the dithiophosphate described hereinabove, lubricating oil compositions containing the lactone amides may also contain other detergents, viscosity index improving agents, rust inhibitors, oiliness agents, grease thickening agents, etc.

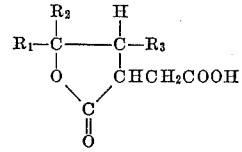
We claim:

1. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.1% to 10% by weight of an alkylbutyrolactone-α-acetic acid of the formula



wherein R_1, R_2 and R_3 are selected from the group consisting of hydrogen and alkyl radicals having a total of from 10 to 300 carbon atoms.

2. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.25% to 5% by weight of an alkylbutyrolactone-α-acetic acid of the formula



wherein R_1, R_2 and R_3 are selected from the group consisting of hydrogen and alkyl radicals having a total of from 10 to 300 carbon atoms.

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DANIEL E. WYMAN, *Primary Examiner.*

W. H. CANNON, *Assistant Examiner.*