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ALKENYL DICARBOXYLIC ACID LACTONES, THEIR METHOD OF PREPARATION AND UTILITY

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5 Claims. (Cl. 44—63)

The present invention concerns alkenyl aliphatic dicarboxylic acid lactones, the method of preparing these lactones, and the utility of these lactones as rust inhibitors. In particular, the invention relates to monoalkenyl succinic acid lactones and their utility in hydrocarbon fuel compositions and in inhibiting corrosion of metallic fuel exhaust systems.

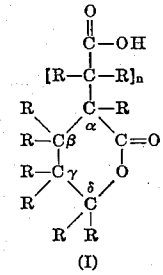
A problem which has long existed in the handling, transportation, storage and use of petroleum products and other organic liquids is the tendency of these products to contain trace amounts of water, which promotes the oxidation or rusting of ferrous and other metals subject to corrosion and oxidation. Rusting frequently occurs in pipelines, storage tanks, exhaust systems of internal combustion engines, and other areas where the moisture-containing petroleum products come into direct or indirect, liquid or vapor contact with metals such as iron and zinc. Moisture is inevitably present in petroleum distillates; and while water is not appreciably dissolved in hydrocarbon oils, trace amounts of moisture are in fact dissolved in these products. Either dissolved moisture as obtained, for example, from absorption of atmospheric moisture, or the presence of water in a separate layer as obtained, for example, from sea water present in the bilges of tanker vessels promotes the rusting tendencies of the products. To overcome corrosion due to moisture carried by petroleum products, certain rust inhibitor additives have been employed. Frequently, these additives are not wholly satisfactory since the water soluble additive agents are unduly extracted by water contact, and thus lost when the water is separated from the oil during handling, and thereafter provides little or no subsequent rust inhibition for the residual water traces left in the oil product. Also, many hydrocarbon soluble additives are unsatisfactory, since they fail to provide adequate rust protection except at high or uneconomical concentration levels. A further disadvantage of many oil soluble rust inhibitors, such as some of the fatty acid amines, is their inability to survive the combustion cycle in an internal combustion engine; and thus they fail to contribute to inhibiting the rusting of the metallic fuel exhaust system, particularly the muffler, by the unburned mixture of fuel gases and moisture. Other oil soluble products degrade the consumer acceptance characteristics or the desirable properties of the oil products in which they are incorporated, such as the decreasing octane number or promoting the formation of haze or water emulsions and the like.

It is, therefore, an object of this invention to disclose novel alkenyl aliphatic dicarboxylic acid lactones and the method of preparing these lactones. An additional object is to provide petroleum products containing very small quantities of the inventive lactones to inhibit the formation of rust. A further object is to provide improved hydrocarbon fuel compositions which provide enhanced protection from corrosion of the exhaust system of the engine in which the fuel is combusted. Another object is to provide improved gasoline compositions which significantly reduce the corrosiveness of the exhaust gases on the ferrous components of the exhaust system at surprisingly low concentration levels.

The alkenyl aliphatic dicarboxylic acid lactones of the invention are those prepared by the hydration of one, two

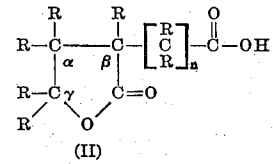
or more of the ethylenically unsaturated linkage of the alkenyl radical and the subsequent intramolecular condensation or esterification of one of the carboxylic acid radicals with the hydrated hydroxy radical. In particular, the inventive lactones are those monoalkenyl C_4 and C_5 aliphatic dicarboxylic acid lactones prepared by heating the acid, preferably in an organic solvent, to a temperature, e.g. not more than 212° F., sufficient to effect conversion to the lactone, but insufficient to form the acid anhydride. The preferred method of preparing these lactones is the heating of the acid in the presence of an acid catalyst, e.g. a strong mineral acid.

The acid lactones of the invention are those stable, oil soluble, five- (gamma) membered and six- (delta) membered lactones or mixtures thereof represented by the Formulae I and II.



(I)

and



(II)

wherein R is selected from the group consisting of hydrocarbon radicals such as aliphatic radicals like hydrogen and alkyl or alkylene radicals, preferably hydrogen, and alkyl radicals such as C_1 to C_{30} alkyl radicals or any combination thereof, and n is a number from 0 to 6, preferably from 1 to 3. The alkyl radical on the delta carbon atom of Formula I and the gamma carbon atom of Formula II is the residual alkyl portion of the alkenyl radical and is preferably an oil solubilizing radical and may have from 1 to 50 or even 100 carbon atoms, e.g. 6 to 30, a molecular weight of from 300 to 3000, e.g. 500 to 2000, and is normally derived from the polymerization of a C_2 to C_6 mono- or polyolefin, but preferably contains from 1 to 30 carbon atoms.

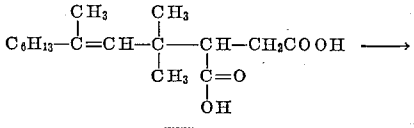
As a nonlimiting example of the formation of lactones within the scope of the instant invention is the formation of tetrapropenyl succinic acid lactones having a free carboxylic acid radical. Formation of the lactones of the instant invention requires that at least one of the ethylenically unsaturated linkages of the alkenyl radical be on the beta, gamma or delta carbon atom of one of the carboxylic acid groups, with the delta position preferred. Alkenyl succinic acids are normally prepared by the reaction of an olefin or polyolefin having terminal unsaturation with maleic anhydride to form the alkenyl succinic acid anhydride. The lactones of the invention require the acid function with the anhydride form being wholly unsuitable for the purposes of this invention due to the absence of the COOH group.

Suitable nonlimiting examples of alkenyl succinic acids are those wherein the alkenyl radical is octenyl, diisobutenyl, 2-methylheptenyl, 4-ethylhexenyl, nonenyl, decenyl, undecenyl, dodecenyl, triisobutenyl, tetrapropenyl, tetradecenyl, hexadecenyl, octadecenyl, heptadecenyl, polyisobutenyl, tricosenyl, mixed C_{16} to C_{18} alkenyl, and the like.

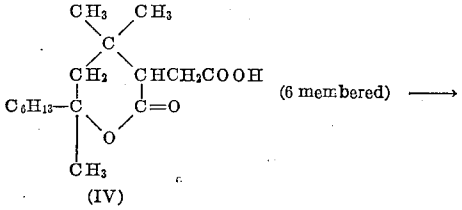
For example, the reaction of the tetramer of propylene with maleic anhydride forms the tetrapropenyl succinic acid anhydride, which on hydration becomes the acid. The heating of this compound by itself or preferably in a nonpolar solvent, such as a petroleum naphtha boiling between 100° and 325° F., kerosene, benzene, toluene, xylene, to reduce the tendency to polymerize or reform the anhydride or resinify, yields the inventive lactones. The temperatures employed should be those sufficient to form the lactone, but insufficient to resinate or dehydrate the acid, i.e. less than about 212° F., e.g. between 100° and 200° F.

The preferred method of preparation is the heating of the acid in the presence of acid catalysts such as strong hydrating mineral acids like boiling 50% sulfuric acid, dilute hydrochloric acid, dilute sulfuric acid, dilute phosphoric acid, and the like, at temperatures between 100° F. and 212° F., e.g. 150° F. and 200° F.

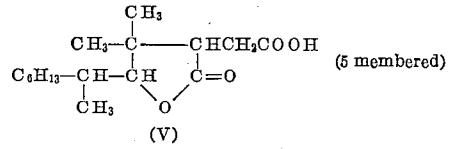
Depending upon the isomeric nature of the alkenyl radical, lactones of the Formulae IV and V are prepared from tetrapropenyl succinic acid, III.



(III)



(IV)



(V)

The oil soluble lactones of the invention are effective rust inhibitors for petroleum products and other organic nonpolar products. These lactones may be employed in minor amounts with solid and liquid hydrocarbons and petroleum products, but are particularly effective in hydrocarbon oils, especially fuels, boiling in the range between 75° and 900° F., e.g. 75° and 750° F. Suitable products in which the lactones may be profitably employed either in small quantities or in a concentrate form include, but are not limited to, waxes, greases, asphalts, lubricating oils, such as those having an SUS viscosity of between 50 and 1000 SUS at 100° F., e.g. 75 to 500; and solvent oils both mineral, such as Coastal and Mid-Continent distillate oils, and synthetic oils, such as diester oils, polyalkylene glycols, silicones, phosphate esters, polypropylenes, polybutylenes, and the like, or combinations thereof; heating oils such as Bunker C oil, jet fuels, gasoline, diesel fuels, transformer oils, turbine oils, and the like.

The lactones are particularly effective in very low concentrations in hydrocarbon motor fuels to prevent corrosion of the exhaust system. The fuels in which the lactones are employed include those fuels used to operate internal combustion engines having spark ignition, compression ignition, and glow plug ignition or combinations thereof, such as dual fuel engines for automotive, stationary diesel, marine, railroad, aviation or other use. The motor fuels are those conventional petroleum distillate fuels and usually comprise a mixture of hydrocarbons including aromatics, olefins, paraffins, isoparaffins, naphthenic and occasionally diolefins and includes those petroleum products derived from petroleum crude oil by

refining processes such as fractional distillation, thermal and catalytic cracking, hydroforming, alkylation, isomerization, polymerization and solvent extraction. Suitable products include liquefied gaseous fuels such as butane, propane and the like; gasolines having a boiling range of between about 75° F. and 450° F., such as described in ASTM Specification D–439–58T in types A, B and C; aviation gasolines having a boiling point range between about 100° F. and 330° F. and described in ASTM specifications D–910–57T; aviation turbojet fuels as described in ASTM specifications D–1655–59T; diesel fuels described in ASTM specifications D–975–53T; heating oils as described in ASTM specifications D–396–48T, particularly grades 1 and 2 thereof.

The lactones are generally employed in hydrocarbon products as described above in minor amounts sufficient to inhibit rusting or in small quantities such as in concentrations of from 0.001 to 0.50 wt. percent, e.g. 0.005 to 0.10 wt. percent, while concentrations of from 0.01 to 0.05 wt. percent are especially effective in gasoline. The lactones may be employed as additives or in concentrate form alone or together with other additives such as detergents, antiknock agents, halohydrocarbon scavengers, solvent oils, dyes, rust inhibitors, metal deactivators, antioxidants, dispersants, and the like.

The lactones may be dissolved, dispersed or emulsified in a carrier medium and be brushed, sprayed, dipped, painted, or otherwise placed in contact with the surfaces or materials to be protected from rusting. For example, the lactone may be placed in a volatile solvent in concentrate form and sprayed on the exterior and interior of an automotive muffler, while the lactone is additionally added to the fuel on which the motor operates to provide further protection.

The following nonlimiting examples are for the purposes of illustration and demonstrating the effectiveness of the instant invention.

EXAMPLE 1

The viscous liquid, tetrapropenyl succinic acid, was heated with 50% aqueous sulfuric acid until the water began to boil. The mixture was then cooled and the organic material extracted with ether, washed with a sodium bicarbonate solution and distilled water, dried over a magnesium sulfate desiccant, and the ether evaporated on a steam bath. The material recovered was identified as a lactone by the characteristic strong carbonyl infrared absorption at 5.83 of the free carboxylic acid radical and the additional lactone absorption peak at 5.68.

EXAMPLE 2

A polybutene succinic acid lactone mixture as described is prepared by heating to about 200° F. with a 50% aqueous sulfuric acid catalyst, a polybutene succinic acid, in a 50% kerosene solution wherein the polybutene radical has an average molecular weight of between 1000 and 2000. The five- and six-membered lactone mixture having a free carboxylic acid group is recovered as in Example 1 to yield about 50 wt. percent mixture of lactones in kerosene.

EXAMPLE 3

An acid lactone mixture is prepared by dissolving the 4-ethylhexenyl succinic acid in 50% by weight of toluene and heating the resulting mixture to a temperature of about 200° F. for about 6 hours and then recovering the lactone mixture as in Example 1 to yield a 50% mixture of lactone in toluene.

EXAMPLE 4

The remarkable rust preventive properties of the lactones prepared as in Example 1 are demonstrated by the results achieved in a galvanic cell experiment. The galvanic cell comprises electrically coupled, dissimilar metals, in this case, zinc and steel strips, which are commonly contacted by hydrocarbons, immersed in a fuel such as

gasoline containing the designated additive and simulated tank bottoms or synthetic sea water contaminants. For the following experiment, a premium gasoline motor fuel was employed together with one half cubic centimeter of methanol and an equal amount of synthetic sea water to accelerate corrosion. The effectiveness of each additive as a rust inhibitor is then estimated from the appearance of the metal strips after a fixed period of time, e.g. in this case 24 hours, and the results reported as percent reduction in corrosion as compared with the additive free fuel.

Table I

ALKENYL SUCCINIC ACID LACTONES AS RUST INHIBITORS

Additive	Percent reduction in corrosion							
	1 [1]		5 [1]		10 [1]		40 [1]	
	Zn	Fe	Zn	Fe	Zn	Fe	Zn	Fe
Tetrapropenyl succinic acid anhydride	0	0	0	0	0	0	0	0
Tetrapropenyl succinic acid lactone	95	100	95	100	95	100	95	100

[1] Concentration expressed in pounds of additive per 1,000 barrels of fuel or approximately 100 p.p.m. per 25#/M B.

The foregoing demonstrates the superior effectiveness of the lactones as rust inhibitors in hydrocarbon products. In a direct comparison test, the lactone was surprisingly more effective than its corresponding acid anhydride form. Of additional importance is the prevention of rusting achieved at the remarkably low concentration level of only about 1 pound per thousand barrels with the use of the instant lactones, while the anhydride provided no rust protection.

EXAMPLE 5

Another outstanding characteristic of the lactones of the invention is the ability to prolong the life of the automotive exhaust systems such as the intake manifold, the muffler and tailpipe, by significantly and unexpectedly reducing corrosion in these areas. This characteristic of the lactones is believed to be due to the unique ability to survive the combustion process and still function effectively as a rust inhibitor.

To demonstrate the effectiveness of the lactones as muffler corrosion inhibitors in comparison with other prior art oil soluble rust inhibitors, a premium gasoline having the following characteristics described in Table II was used to operate a six-cylinder 1961 Ford engine at 2000 r.p.m. and 25 p.s.i. vacuum, collecting the exhaust gas condensate at 120 to 125° F.

Table II

BASE GASOLINE INSPECTIONS

ASTM distillation, Method D–86:	
Initial boiling point, ° F.	102
10% boiling point, ° F.	-----
50% boiling point, °F.	214
90% boiling point, ° F.	-----
Final boiling point, ° F.	369
Reid vapor pressure, p.s.i.	12
General Motors gum, mg./100 ml.	0.1
ASTM breakdown time, min.	960+
FIA analysis:	
Vol. percent saturates	63.8
Vol. percent olefins	14.2
Vol. percent aromatics	22.0
Tetraethyl lead, cc./gal.	3.0
Research octane No. (RON)	104.1
Motor octane No. (MON)	94.4

The gasoline employed contained various additive agents or no additives as designated. The exhaust condensate of the combusted gases was collected and tested by periodically immersing, for 24 hours, steel panels in the liquid condensate, and then withdrawing these panels to dry in the atmosphere at 175° F. The condensate from the same gasoline without corrosion inhibitor additives was employed and used as a base case. This procedure then closely simulated the actual wet and dry corrosive cyclic exposure of a metallic automobile muffler to exhaust gases. The results were obtained by the weight loss of the steel panels, and are expressed as the percent reduction in corrosion as compared with the additive-free fuel.

Table III

ALKENYL SUCCINIC ACID LACTONES AS MUFFLER COR ROSION INHIBITORS

Additive	Concentration wt. percent	Percent reduction in corrosion
Lactone as prepared in Example 1	0.02	95.5
2-ethylhexylamine	0.4	10.0
Product A [1]	0.1	11.5
Product B [2]	0.1	3.9
Product C [2]	0.1	[3] 3.9
Product D [4]	0.1	[3] 4.5
Product E [4]	0.1	[3] 13.9
Product F [5]	0.1	[3] 73.5
Product G [5]	0.1	[3] 139.0

[1] A commercial high molecular weight aliphatic C_8–C_{18} alkyl amine derived from coconut oil.
[2] A commercial C_8–C_{18} alkyl trimethyl or dialkyl C_8–C_{18} dimethyl quarternary ammonium chloride.
[3] Increase.
[4] A polyethoxylated quarternary ammonium salt.
[5] A polyethoxylated amine.

The above data demonstrate the surprising effectiveness of the tetrapropenyl succinic acid lactones in protecting the exhaust system from excessive corrosion. Thus, the lactones of the instant invention at a concentration level of only 0.02 wt. percent gave 95% protection, while other well known rust inhibitor amine type additives required much higher concentration levels, and provided significantly reduced protection or even, in some cases, increased corrosion.

For example, the additive 2-ethylhexylamine gave almost complete protection when 0.4 wt. percent was added directly to the exhaust condensate, but when incorporated in the fuel on which an engine is operated, only 10% reduction in exhaust system corrosion was found indicating its inability to provide rust protection through the combustion cycle. The inventive lactones thus provide excellent rust inhibition both in the liquid fuels and in the exhaust combustion gases of the fuel.

EXAMPLE 6

A superior turbojet engine fuel boiling between about 275° F. and 490° F. is enhanced in rust inhibition characteristics in storage and during operation of the engine by the addition of about 0.01 wt. percent of an oil soluble gamma allyl beta methyl succinic acid-gamma lactone.

EXAMPLE 7

A significant improvement in the prevention of corrosion of the exhaust system of a spark ignition internal combustion engine operating on the Otto cycle is provided by the addition of about 0.02 wt. percent of delta polyisobutenyl succinic acid-delta lactone to a regular gasoline fuel on which the engine operates, which gasoline has an amount of an alkyl lead antiknock agent sufficient to reduce knock, with from 0.5 to 3.0 theories of a halohydrocarbon scavenger agent and a 50% ASTM distillation point of less than 310° F.

EXAMPLE 8

A mineral paraffinic lubricating oil having an SUS viscosity of between 90 to 500 at 100° F. and containing about 0.01 wt. percent of a mixture of a tetrapropenyl glutaric acid-delta lactone has a reduced tendency to promote the rusting of ferrous metals.

EXAMPLE 9

A heating oil boiling in the range between 324° F. and 643° F. and containing more than about 10% by volume of catalytically cracked stock and about 0.01 wt. percent of delta tricosenyl gamma methyl succinic acid-delta lactone has enhanced rust inhibition characteristics.

EXAMPLE 10

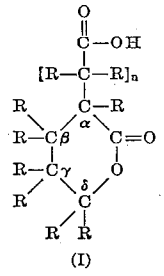
An improved solvent oil for use in lubricating the upper cylinder areas of internal combustion engines and having improved rust inhibition properties to the internal engine areas and the exhaust system is provided by incorporating about 0.01 wt. percent of a delta polyisobutenyl gamma dimethyl beta propyl succinic acid-delta lactone into a silica gel extracted, deasphalted, solvent extracted bright stock solvent oil having less than 5% aromatics and a pour point of less than +30° F.

It is, of course, within the scope of this invention that the inventive lactones may be injected singly or in combination with other additives directly into the carburetors, fuel lines, intake manifold, muffler, cylinders, or other engine areas to provide corrosion protection.

Additionally, the free carboxylic acid group of the lactones may be further reacted with alkyl and aromatic amines such as polyamines, like diethylene triamine, ammonia, diamines, tertiary alkyl primary amines, hydroxyl amines like ethanol amine, quaternary ammonium hydroxides, alcohols such as C_1 to C_{30} alkanols like C_8 oxo alcohols, glycols like 1,6-hexanediol, ether alcohols like diethylene glycol monobutyl ether, epoxides such as ethylene oxide, epichlorohydrin and the like, or combinations thereof, to modify or improve the properties of the inventive lactones, enhancing their value as hydrocarbon additives.

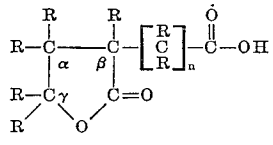
What is claimed is:

1. A hydrocarbon oil boiling in the range between about 75 and 900° F. and containing an amount sufficient to inhibit the corrosion of metals of an additive selected from the group consisting of



(I)

and



(II)

where R is selected from the group consisting of hydrogen and alkyl radicals and *n* is a number from 0 to 6.

2. A hydrocarbon oil as defined by claim **1** wherein said hydrocarbon oil is in a motor fuel boiling within the gasoline boiling range.

3. A hydrocarbon oil as defined by claim **1** wherein said alkyl radical is a C_1 to C_{30} alkyl radical and *n* is from 1 to 3.

4. An oil according to claim **1** wherein said hydrocarbon oil is gasoline and said small amount is between 0.001 and 0.1 wt. percent.

5. A hydrocarbon oil according to claim **1** wherein said metal is selected from the group consisting of ferrous metal and zinc.

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KARL J. ALBRECHT, *Primary Examiner.*