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CARBOCYCLIC MONOCARBOXYLIC ACID SALTS OF GLYOXALIDINES

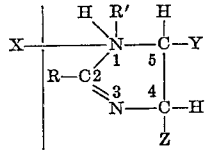
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9 Claims. (Cl. 260—309.6)

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This invention relates to new compounds, more particularly to compounds having the general formula



where X is the negative radical of a carbocyclic monocarboxy acid, R is a higher aliphatic hydrocarbon radical containing at least 11, preferably 17 carbon atoms in an acyclic chain, R' is hydrogen or a lower aliphatic group containing not more than 6 carbon atoms, Y is hydrogen or a lower aliphatic group containing not more than 6 carbon atoms, and Z is hydrogen or a lower alkyl group containing not more than six carbon atoms. These compounds may also be described generally as carbocyclic monocarboxy acid salts of glyoxalidines.

These carbocyclic monocarboxy acid salts of glyoxalidines are viscous liquids or soft greases which are characterized by being soluble or dispersible in water. They are easily prepared by mixing the carbocyclic carboxy acid with the glyoxalidine in equimolecular proportions in the cold or by warming the two together at temperatures up to 100 degrees C. for 5 to 15 minutes.

As examples of carboxy acids that may be used to prepare these salts there may be mentioned: benzoic acid, 4-chlorobenzoic acid, 2,4-dichlorobenzoic acid, salicylic acid, cinnamic acid, 3,5-dinitrobenzoic acid, 2-nitrobenzoic acid, 3-nitrobenzoic acid, ortho cresotinic acid, anthranilic acid, phenylacetic acid, 2-chlorobenzoic acid, 4-chlorobenzoic acid, phenoxyacetic, 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, pentachlorophenoxyacetic acid, naphthenic acids and 2,4-dichlorobenzoic acid.

Examples of glyoxalidines that may be reacted with any of the foregoing acids in preparing these salts are: 1-(2-aminoethyl)-2-heptadecenyl glyoxalidine, 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine, 4-methyl-2-heptadecenyl glyoxalidine, 1-[2-(2-aminoethyl)-aminoethyl]-2-heptadecenyl glyoxalidine, 1-(2-aminoethyl)-2-undecyl glyoxalidine, 1-(2-hydroxyethyl)-2-undecyl glyoxalidine, 4-methyl-2-undecyl glyoxalidine, 1-[2-(2-aminoethyl)-aminoethyl]-2-undecyl glyoxalidine, 1-(2-aminoethyl)-2-tridecyl glyoxalidine, 1-(2-hydroxyethyl)-2-tridecyl glyoxalidine, 4-methyl-2-tridecyl glyoxalidine, 1-[2-(2-aminoethyl)-aminoethyl]-2-tridecyl glyoxalidine, 1-(2-aminoethyl)-2-pentadecyl glyoxalidine, 1-(2-hydroxyethyl)-2-pentadecyl glyoxalidine, 4-methyl-2-pentadecyl glyoxalidine and 1-[2-(2-aminoethyl)-aminoethyl]-2-pentadecyl glyoxalidine.

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The following is a table containing some of the properties of some of the glyoxalidine salts that have been prepared in accordance with the invention.

The naphthenic acid which has been designated "235 XX Socony Vacuum" is a fully refined naphthenic acid having a neutralization equivalent of 235.

The solubility test of the glyoxalidine salt in water was conducted by adding one drop of the salt to 10 ml. of water and agitating and observing the resulting solution.

The solubility of the glyoxalidine salt in oil was determined by adding one drop of the salt to 10 ml. of an aromatic oil such as the catalytically cracked product marketed by Shell Oil Company under the trade name of Shell's medium aromatic oil with a boiling range of 430 degrees F. to 620 degrees F. and a flash point of 225 degrees F. (Cleveland open cup).

These glyoxalidine salts have shown themselves to be very excellent emulsifying agents for aromatic oils in water. Emulsifying tests were conducted as follows: One half gram of the glyoxalidine salt was dissolved in 50 grams of the Shell medium aromatic oil described above. To this 450 ml. of water was added with agitation. The stability of the resulting emulsion was judged by the amount of time required for the oil to start to come out of solution. In some cases no separation of oil occurred, but a cream layer of emulsion rich in oil was noticed to float to the top. The time was noted when this separation could be noticed. The various salts of 2-heptadecenyl-4-methyl glyoxalidine and 1-[2-(2-aminoethyl)-aminoethyl]-2-heptadecenyl glyoxalidine were tested at 2% concentration in the oil. Control tests using aliphatic carboxylic acid salts of glyoxalidines such as the acetic acid and oleic acid salts of 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine were ineffective in forming emulsions of this oil even when used at the concentration of 5% in the aromatic oil.

The salts of this invention are outstanding emulsifying agents. Whereas relatively large amounts (over 5% and up to 25%) of the other emulsifying agents such as, polyoxyalkylene esters and ethers, petroleum sulphonates, alkyl aryl sulphonates, alkyl sulphates are required to emulsify Shell medium aromatic oil in water.

1% or even less of the glyoxalidine salts of this invention are required to give emulsions stable for long periods.

Reactants	Weight ratio	Description	Solubility in water	Solubility in aromatic oil
1 - (2 - hydroxyethyl) - 2 - heptadecenyl glyoxalidine.	3.5	Homogeneous viscous liquid	Cloudy solution; very viscous; foams copiously.	Soluble.
2,4-dichlorophenoxy acetic acid	2.2			
1 - (2 - hydroxyethyl) - 2 - heptadecenyl glyoxalidine.	3.5	do	Slightly cloudy; foams copiously; very viscous.	Do.
Salicylic acid	1.38			
1 - (2 - hydroxyethyl) - 2 - heptadecenyl glyoxalidine.	3.5	do	Clear solution; foams copiously; viscous.	Do.
Benzoic acid	1.22			
2 - heptadecenyl - 4 - methyl glyoxalidine.	3.2	Homogeneous brown viscous liquid	Milky solution; fairly heavy foam.	Do.
2,4-dichlorophenoxy acetic acid	2.2			
2-heptadecenyl-4-methyl glyoxalidine	3.2	Homogeneous yellow viscous liquid	Clear gelatinous solution; fairly heavy foam.	Do.
Salicylic acid	1.38			
1 - [2 - (2 - aminoethyl) - aminoethyl]-2-heptadecenyl-glyoxalidine.	3.93	Homogeneous amber viscous liquid	Clear solution; very heavy foam.	Insoluble.
2,4-dichlorophenoxy acetic acid	2.2			
1 - [2 - (2 - aminoethyl) - aminoethyl]-2-heptadecenyl-glyoxalidine.	3.93	Homogeneous deep yellow viscous liquid.	Clear gelatinous solution; very heavy foam.	Do.
Salicylic acid	1.38			
2-heptadecenyl 4-methyl glyoxalidine	3.2	Clear brown viscous liquid	Disperses in water; some foaming.	Soluble.
Acetic acid	4.4			
2-heptadecenyl 4-methyl glyoxalidine	3.2	Clear amber viscous liquid	Turbid solution; fairly heavy foam.	Insoluble.
Salicylic acid	2.76			
1-[2-(2-aminoethyl)-aminoethyl]-2-heptadecenyl glyoxalidine.	3.93	Cloudy amber taffy-like liquid	Clear solution; very heavy foam.	Do.
2,4-dichloro-phenoxyacetic acid	4.4			
1-[2-aminoethyl)-aminoethyl]-2-heptadecenyl glyoxalidine.	3.93	do	Clear solution; extremely heavy foam.	Do.
Salicylic acid	2.76			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.	3.5	Viscous liquid	Clear solution; some foam	Soluble.
Phenylacetic acid	1.36			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.	3.5	Resinous-like paste	Hazy solution; some foam	Do.
Beta hydroxy naphthoic acid	1.88			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.	3.5	Viscous liquid	Hazy solution; some foam; slightly viscous.	Do.
Ortho cresotinic acid	1.52			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.	3.5	Tan opaque viscous liquid	Hazy solution; some foam	Slightly hazy solution.
2,4,5-trichloro-phenoxyacetic acid	2.55			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.	3.5	Brown clear viscous liquid	Milky solution; fair amount of foam; slightly viscous.	Clear solution.
Pentachlorophenoxy-acetic acid	3.23			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.	3.5	Resinous paste	Clear solution; lots of foam; very viscous.	Soluble.
Anthranilic acid	1.37			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.	3.5	Viscous oil	Clear solution; fair amount of foam; extremely viscous.	Do.
2,4-dichlorobenzoic acid	1.91			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidines.	3.5	Resinous-like paste	Clear solution; some foam	Insoluble.
Para aminophenyl acetic acid	1.51			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.	3.5	Resinous solid	Slightly soluble; lots of foam	Do.
Gallic acid	1.7			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine	3.5	Homogeneous viscous liquid	Clear solution; slightly viscous; lots of foam.	Soluble.
3,5-dinitrobenzoic acid	2.12			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine	3.5	Viscous oil	Hazy solution; quite viscous; lots of foam.	Do.
2,5-dichlorosalicylic acid	2.07			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine	3.5	do	Clear solution; viscous; some foam.	Do.
Ortho chlorobenzoic acid	1.57			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine	3.5	Waxy paste	Hazy solution; viscous; some foam.	Do.
Para chlorobenzoic acid	1.57			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine	3.5	Taffy-like viscous oil	Clear solution; lots of foam	Disperses in oil.
Para-hydroxyphenyl glycine	1.67			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine	3.5	Soft grease	Hazy solution; very viscous; little foam.	Soluble.
Cinnamic acid	1.48			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine	3.5	Wax-like solid	Clear solution; lots of foam	Disperses in oil.
Hippuric acid	1.79			
1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine	3.5	Viscous oil	Hazy solution; quite a bit of foam.	Soluble.
Naphthenic acid (235 XX Socony Vacuum)	2.35			
2-heptadecenyl-4-methyl glyoxalidine	3.2	Light brown viscous liquid	Clear solution; extremely viscous; some foam.	Do.
Cinnamic acid	1.48			

Very stable emulsions of insecticides such as Chlordane, DDT, and Methoxychlor can be made using these glyoxalidine salts.

The emulsifying properties of these new compounds will be further illustrated by the following examples.

Example I

Twenty (20) grams of Methoxychlor dissolved in 79.5 grams of Shell medium aromatic oil containing 0.5 gram of 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine salicylate gave an emulsion which was stable for one hour when mixed with 900 ml. of water. When 5.0 grams of the glyoxalidine stearate salt was used the emulsion broke in 10 minutes. One gram of the 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine cinnamate salt substituted for the salicylate salt gave an emulsion that was stable for 72 minutes. The acetate salt even with up to 5 grams gave an emulsion that was stable for less than 2 minutes.

Example II

Ten grams of Chlordane was dissolved in 89 grams of kerosene and 1 gram of the glyoxalidine

salicylate salt described above was added. When 10 ml. of this mixture was added to 90 ml. of water, the resulting emulsion was stable about 19 minutes. When prepared with 1 gram of the stearate salt of the same glyoxalidine the Chlordane emulsion broke in 5 minutes. Four (4) grams of the stearate salt gave an emulsion that was stable about 11 minutes.

Example III

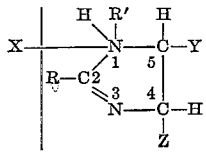
Five (5) grams of DDT was dissolved in 93 grams of Shell medium aromatic oil and 2 grams of the 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine benzoate described above was added. Ten milliliters of the above oil was mixed with 90 ml. of water. The resulting emulsion was stable about fifteen minutes. Under the same conditions 4 grams of the stearate salt of the same glyoxalidine gave an emulsion that was stable about 6 minutes.

In addition to their ability to emulsify oils in water these glyoxalidine salts show other very interesting properties. Dilute (1%) aqueous solutions are extremely viscous such as in the case of the 2,4-dichlorophenoxyacetic acid, salicyclic acid, anthranilic acid, 2,4-dichlorobenzoic acid, orthochlorobenzoic acid, para-chlorobenzoic acid, and cinnamic acid salts of 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine. Where emulsifying agents and thickening agents are needed in the same composition these compounds are very useful. The substituted glyoxalidines themselves have the ability to thicken water solutions but the herein described carbocyclic carboxy acid salts are markedly superior in this respect.

The term "carbocyclic monocarboxy acid" as used herein is intended to cover any monocarboxylic acid containing a carbocyclic ring. The carboxy group may be linked directly to a carbon atom of the carbocyclic ring or may be connected to a side alkyl or alkylene group.

The invention is hereby claimed as follows:

1. A compound having the following general formula



where X is the negative radical of a carbocyclic monocarboxy acid from the group consisting of mono- and di-carbocyclic acids in which the carbocyclic structure is from the group consisting of 5-membered and 6-membered carbon rings, R is a higher aliphatic hydrocarbon radical containing at least 11 carbon atoms, R' and Y are from the group consisting of hydrogen and lower aliphatic groups containing not more than 6 carbon atoms and Z is from the group consisting of hydrogen and lower alkyl groups containing not more than 6 carbon atoms.

2. Carbocyclic monocarboxy acid addition salts of 2-heptadecenyl glyoxalidines from the group consisting of the mono- and dicarbocyclic monocarboxylic acid addition salts of 2-heptadecenyl glyoxalidines wherein the carbocyclic structures consist of 6-membered rings.

3. The 2,4-dichlorophenoxyacetic acid addition salt of 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.

4. The salicyclic acid addition salt of 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.

5. The cinnamic acid salt of 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.

6. The benzoic acid salt of 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.

7. The anthranilic acid salt of 1-(2-hydroxyethyl)-2-heptadecenyl glyoxalidine.

8. The carbocyclic monocarboxy acid addition salts of glyoxalidines substituted in the 2 position with a higher aliphatic acyclic hydrocarbon group containing 11 to 17 carbon atoms wherein the monocarboxy acid salt-forming group is derived from an acid from the group consisting of 2,4-dichlorophenoxyacetic acid, salicylic acid, 2,4-dichlorobenzoic acid, 3,5-dinitrobenzoic acid, 4-chlorobenzoic acid and cinnamic acid.

9. The carbocyclic monocarboxy acid addition salts of 2-heptadecenyl glyoxalidines wherein the monocarboxy salt-forming group is derived from an acid from the group consisting of 2,4-dichlorophenoxyacetic acid, salicylic acid, 2,4-dichlorobenzoic acid, 3,5-dinitrobenzoic acid, 4-chlorobenzoic acid and cinnamic acid.

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