Patented Dec. 30, 1941

2,267,965

UNITED STATES PATENT OFFICE

2,267,965

HYDROXYALKYL GLYOXALIDINES

Alexander L. Wilson, Sharpsburg, Pa., assignor to Carbide and Carbon Chemicals Corporation, a corporation of New York

No Drawing. Application July 18, 1939, Serial No. 285,081

9 Claims. (Cl. 260—309)

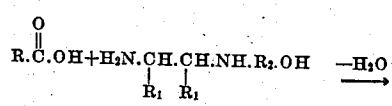
This application is a continuation-in-part of my copending application Serial No. 191,191, filed February 18, 1938.

This invention relates to the production of certain glyoxalidines, or dihydroimidazoles (imidazolines), to wit, those containing alkyl side chains and including at least one hydroxyalkyl side chain. More specifically, the invention comprises the condensation of fatty acid compounds having from 10 to 20 carbon atoms in the molecule, or mixtures of these, with hydroxyalkyl alkylene polyamines to produce substituted glyoxalidines. While it is possible by this process to obtain the tetrasubstituted glyoxalidines, this invention is particularly concerned with the production of the 1,2-disubstituted and the 1,2,4 or 1,2,5-trisubstituted glyoxalidines in which at least one substituent group is a hydroxyalkyl radical.

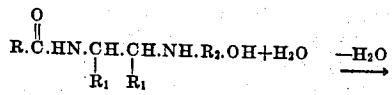
The new compounds are characterized as being either high-boiling viscous liquids, or low-melting, waxy solids and by being highly polar and strongly basic. They are colloidally dispersible in cold water, giving rise to viscous solutions, and they are completely soluble in acids, such as dilute hydrochloric acid. The glyoxalidine compounds of this invention may be used for various purposes, and it has been found that they are especially valuable as emulsifying agents, detergents, wetting, softening and scouring agents, and for other uses where their properties of surface activity can be employed. The new substances, and their salts and soaps, when used as emulsifying agents, are particularly efficacious for producing stable dispersions of mineral oils, or other oleaginous substances and water. The new substances are also valuable as softening and finishing agents for textiles, according to processes set forth in application Serial No. 276,122, filed May 27, 1939, by B. G. Wilkes and A. L. Wilson, and as assistants in dyeing textiles to improve the fastness and other qualities of the dyeing operation.

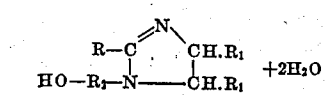
The production of the substituted glyoxalidines of this invention may be accomplished by dehydrating fatty acid amides of various hydroxyalkyl alkylene polyamines and their substitution products, or, more generally stated, by heating, at temperatures between about 120° C. and about 300° C., these amines with free fatty acids, fatty acid esters or amides under such conditions as to effect the splitting out of water in excess of 1.5 mols for each mol of free fatty acid and in excess of 0.5 mol for each mol of combined fatty acid involved. Examples of amines that may be employed in the practice of this invention are hydroxyethyl ethylene diamine, hydroxyisopropyl propylene diamine, hydroxyethyl diethylene triamine hydroxyethyl triethylene tetramine, as well as similar hydroxyalkyl alkylene polyamines. The hydroxyalkyl alkylene polyamines of this invention are of the 1,2 series, that is, at least one amino group and one imino group are attached to adjacent carbon atoms. The term "alkylene polyamine" is also defined as including products containing more than one alkylene group. Fatty acid compounds that may be used in the production of the glyoxalidines may include the fatty acids themselves, such as lauric, oleic, linoleic, ricinoleic, stearic and palmitic acids, as well as their salts and esters. Other fatty acids and their salts and esters naturally occurring in such vegetable oils as olive, cocoanut, linseed and cottonseed oils, which have from 10 to 20 carbon atoms in their molecule, may also be employed.

The substituted glyoxalidines of this invention may be regarded as dehydration products of substituted ethylene diamines and fatty acids, or their salts and esters. The formation of the glyoxalidine or imidazoline ring from these substances may be considered as a two-step reaction involving, first, the formation of an amide and a molecule of water, and, second, the dehydration of this amide to yield a substituted glyoxalidine and a second molecule of water. Thus, when a fatty acid, such as oleic acid, is employed, two molecules of water will be formed per molecule of the starting acid. This reaction is illustrated by the following scheme:



Fatty acid — Hydroxyalkyl alkylene polyamine





Substituted glyoxalidine

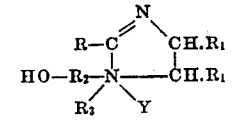
wherein R represents an aliphatic radical containing from 10 to 20 carbon atoms and being the residue of a higher fatty acid; R_1 represents hydrogen or a lower alkyl group; and R_2 represents an alkylene group, a lower alkyl substituted alkylene group, or a radical of the structure $—CHR_1.CHR_1(NH.CHR_1.CHR_1)x—$ where R_1 remains hydrogen or a lower alkyl group and x is an integer.

In comparison with the amino alkyl substituted glyoxalidines, disclosed in my copending application Serial No. 191,191, the hydroxyalkyl substituted glyoxalidines of this application are obtained somewhat more readily and with considerably less tendency towards the formation of polyamides or other high-boiling condensation products. Another point of distinction is that, in preparing the former compounds, it is desirable to use a fairly high molar ratio of alkylene polyamine to fatty acid to insure a high yield of glyoxalidine whereas, in making the latter substances, a satisfactory yield of pure glyoxalidine results when operating with equal molecular quantities of hydroxyalkyl alkylene polyamine and fatty acid.

It is true, nevertheless, that the employment of higher molar ratios of hydroxyalkyl alkylene polyamine to fatty acid will promote a higher yield of the desired hydroxyalkyl substituted glyoxalidine but such practice is not required for the success of the reaction. Other factors which act to increase the yield of the hydroxyalkyl substituted glyoxalidines are higher rates of heating attendant with the use of temperatures in the upper portion of the range indicated to be suitable and an increased rate of removal of the water liberated in the condensation. Such an increase may be effected by distilling the water from the reaction vessel as a constant boiling mixture with a volatile water-immiscible diluent. Examples of such liquids are benzene, xylene, toluene, diisopropyl ether, ethyl acetate, ethylene dichloride, and carbon tetrachloride. If a diluent is used in carrying out the reaction, lower temperatures and lower molar ratios of hydroxyalkyl alkylene polyamine may be used and high yields of the desired glyoxalidine obtained nevertheless. This characteristic is illustrated in Example V.

Since the substituted glyoxalidines contain a reactive hydroxy group, it is possible to form esters of these compounds by the reaction of organic acids with the free alcoholic group. Because the glyoxalidine compounds are basic, it is possible to form salts or soaps of these compounds by their addition with various acidic substances including both mineral and organic acids, such as hydrochloric, sulfuric, acetic, ethyl hexoic, and lauric acids. By the formation of such salts or soaps the solubility of these compounds is enhanced. Quaternary ammonium compounds may also be formed by warming the substituted glyoxalidines with the appropriate reagents, such as diethyl sulfate, dimethyl sulfate, benzyl chloride and the like. These compounds are usually viscous liquids to wax-like bodies, characterized by their nearly neutral reaction and by their ready solubility in water. These quaternary compounds are perhaps less useful as emulsifying agents and as textile finishing agents than the substituted glyoxalidines themselves but they possess exceptional qualities as wetting and flotation agents.

The salts, as well as the quaternary ammonium compounds, are represented by the following general structure:



in which R, R_1, and R_2 are as indicated in the above formula; Y represents an organic or inorganic radical, and R_3 is hydrogen, or an alkyl or aralkyl group. The distinction between the salts and the quaternary ammonium compounds is that, in the former, R_3 is usually hydrogen whereas, in the latter, R_3 is usually an alkyl or aralkyl group and Y is generally an inorganic radical.

The following examples will serve to illustrate the invention:

Example I

One mol of beta-hydroxyethyl ethylene diamine was mixed with 0.5 mol of commercial oleic acid and heated under reflux for 5 hours until a final temperature of about 270° C. was reached. About 2 mols of water per mol of oleic acid were distilled off during this period. Excess hydroxyethyl ethylene diamine was then removed, and the product, 1-hydroxyethyl-2-heptadecenyl glyoxalidine, was purified by vacuum distillation. This substance was found to be a straw-colored, heavy, viscous liquid, with a specific gravity of 0.935 at 20/20° C. and a boiling point from about 230° to 240° C. at an absolute pressure of 1 mm. of mercury. It was miscible with water at 10° C. to yield viscous solutions and it was completely soluble in dilute hydrochloric and acetic acids. This glyoxalidine is particularly useful for dispersing mineral oils in water and in producing water scourable mineral oils for use as textile lubricants.

Example II

One and one-half mols of hydroxyethyl ethylene diamine were mixed with one mol of stearic acid and heated, in the presence of xylene, under reflux for 8 hours at a temperature of from 150° C. to 180° C. About 1.5 mols of water per mol of stearic acid were distilled off as a constant boiling mixture with the xylene during this period. Excess amine and xylene were then removed, and the product, 1-hydroxyethyl-2-heptadecyl glyoxalidine, was purified by vacuum distillation. This substance was a light-colored solid, insoluble in water, melting at 45° to 55° C., and boiling at 240° to 250° C. at an absolute pressure of 1 mm. of mercury. This product is especially valuable as a softening and finishing agent for regenerated cellulose fabrics, cotton, and similar fibrous materials and as an assistant in dyeing textiles to improve the fastness and substantivity. It is also useful where surface active properties are needed, such as in emulsifying, wetting, and flotating agents.

The glyoxalidine was reacted at a temperature of 50° to 60° C. with diethyl sulfate until evolution of heat had ceased. The quaternary compound formed, 1 - hydroxyethyl - 2 - heptadecyl glyoxalidonium ethyl sulfate, was a pasty solid readily soluble in water.

The acetate salt of this glyoxalidine was prepared by reaction with acetic acid. This salt was a water-soluble wax-like solid and is valuable as an emulsifying agent and as a textile finishing

agent. It is also very useful as a detergent being unaffected in its action by hard water, or by dilute salt water or even by acid solutions.

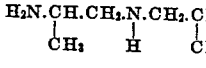
Example III

Two mols of hydroxyethyl ethylene diamine were mixed with one mol of cocoanut fatty acids and heated for 3 hours at a temperature of from 170° C. to 270° C. During this period 1.8 mols of water were distilled off. Excess amine was removed and the product, 1-hydroxyethyl-2-undecyl glyoxalidine, was purified by vacuum distillation. This substance was a straw-colored semi-crystalline solid with a melting point of 35° to 40° C., a specific gravity of 0.950 at 20/20° C. for the super-cooled liquid, and a boiling point of 210 to 220° C. at an absolute pressure of 1 mm. of mercury.

This glyoxalidine was soluble in water at 10° C. to yield a viscous solution but it apparently was not soluble in water at ordinary temperatures. The acetate salt formed by reacting one mol of the glyoxalidine with one mol of acetic acid was a brittle, wax-like solid which is a good wetting agent and possesses high foaming qualities. The ethyl sulfate quaternary ammonium compound also exhibited these properties.

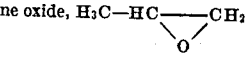
Example IV

One mol of oleic acid was heated with two mols of N-beta-hydroxypropyl propylene diamine, believed to consist of the structure



and its isomers*, for 5 hours at a temperature of from 170° to 273° C. During this period nearly 2 mols of water were removed by distillation. The excess amine was then removed and the product, 1-hydroxyisopropyl - 2 - heptadecenyl-4-methyl glyoxalidine, was purified by vacuum distillation. The pure substance was a light-colored liquid having a specific gravity of 0.920 at 20/20° C. and a boiling point of 225° to 235° C. at an absolute pressure of 1 mm. of mercury. The glyoxalidine was slightly soluble in water and completely soluble in dilute acid solutions. These solutions showed typical surface active properties, such as foaming and emulsifying action.

*This compound may be prepared by reacting propylene diamine, having the structure

with propylene oxide, 

Four isomers are possible depending on the amino group hydroxyalkylated and on whether the propylene oxide adds in its alpha or beta position to the amino group.

Example V

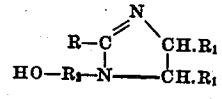
As discussed above, an improved process results if the glyoxalidine reaction is carried out in the presence of a water-immiscible diluent and the water of dehydration continuously distilled off as a constant boiling point mixture with this diluent. Not only is a purer product obtained by the procedure, but also the dehydration may be effected at a lower temperature and without an excess of hydroxylkyl polyamine. The advantages of this procedure is illustrated in the comparative tests below, xylene being used as the water-immiscible diluent in one test and equal molar quantities of the reactants used in each case.

	No. 1 no xylene present	No. 2 xylene present
Hydroxyethyl ethylene diamine parts	104	104
Oleic acid do	282	282
Xylene do	None	91
Time of reaction hours	5	5
Final temperature °C	310	205
Water removed parts	27	28
Appearance of final product	Dark sludge	Light, clear liquid
Solubility in water	Not miscible	Miscible at 12-15° C.
Percent glyoxalidine by distillation at 220° to 280° C. and 2 mm per cent	41	81

From this example, it is apparent that carrying out the reaction in the presence of a water-immiscible liquid diluent is more than a convenient expedient for removal of the water of dehydration. Decidedly superior results have been obtained by this procedure.

I claim:

1. As surface active agents, substituted glyoxalidines of the formula

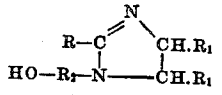


in which R is an aliphatic radical containing from 10 to 20 carbon atoms; R_1 is of the group consisting of hydrogen and lower alkyl; and R_2 is of the group consisting of an alkylene hydrocarbon group, a lower alkyl substituted alkylene hydrocarbon group, and a radical of the structure

$$—CHR_1.CHR_1(NH.CHR_1.CHR_1)_x—$$

where x is an integer.

2. As surface active agents, substituted glyoxalidines of the formula



in which R is an aliphatic radical containing from 10 to 20 carbon atoms; R_1 is of the group consisting of hydrogen and methyl; and R_2 is an alkylene hydrocarbon group, a lower alkyl substituted alkylene hydrocarbon group, or a radical of the structure

$$—CHR_1.CHR_1(NH.CHR_1.CHR_1)_x—$$

where x is an integer.

3. As surface active agents, salts of the glyoxalidines defined in claim 1.

4. As surface active agents, quaternary ammonium compounds of the glyoxalidines defined in claim 1.

5. As a surface active agent, 1-hydroxyethyl-2-heptadecenyl glyoxaldine, being characterized as a viscous liquid, completely soluble in dilute hydrochloric acid, and boiling from about 230° to about 240° C. at an absolute pressure of 1 mm. of mercury.

6. As a surface active agent, 1-hydroxyethyl-2-heptadecyl glyoxalidine, being characterized as a low-melting, waxy solid having a boiling point of about 240° to about 250° C. at an absolute pressure of 1 mm. of mercury.

7. As a surface active agent, 1-hydroxyethyl-2-undecyl glyoxalidine, being characterized as a low-melting solid having a boiling point of about 210° to about 220° C. at an absolute pressure of 1 mm. of mercury.

8. Process for making substituted glyoxalidines which comprises heating a mixture containing a free hydroxyalkyl alkylene polyamine of the 1, 2 series and at least one of group consisting of free fatty acids containing from 10 to 20 carbon atoms, amides of said acids, and esters of said acids, at temperatures between about 120° and about 300° C., and removing water continuously from said mixture during said heating, the temperature and the duration of said heating being so correlated as to cause the splitting out of water in excess of 1.5 mols for each mol of free fatty acid and in excess of 0.5 mol for each mol of combined fatty acid involved.

9. Process for making 1,2-disubstituted glyoxalidines which comprises heating a mixture containing a free hydroxyalkyl alkylene polyamine of the 1, 2 series, a fatty acid containing from 10 to 20 carbon atoms, and a water immiscible diluent at temperatures between about 120° and about 300° C., and removing water continuously from said mixture as a constant boiling mixture with said diluent during said heating, the temperature and the duration of said heating being so correlated as to cause the splitting out of water in excess of 1.5 mols for each mol of fatty acid involved.

ALEXANDER L. WILSON.