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Rapko et al.

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[54] **CARBOXYMETHYL DIOXOLANE POLYCARBOXYLATES**

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[52] **U.S. Cl.**..... **260/340.9,** 252/341, 252/546, 252/548, 252/523, 252/527

[51] **Int. Cl.**..... **C04d 13/04**

[58] **Field of Search**..... 260/340.9

[56] **References Cited**

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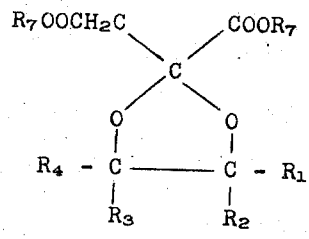
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[57] **ABSTRACT**

Compounds represented by the formula



wherein R_1 is $-COOR_7$ or $-CH_2COOR_7$; R_2, R_3 and R_4 are $-COOR_7$, $-CH_2COOR_7$, hydrogen or methyl; and R_7 is alkali metal or ammonium are useful sequestrants and detergency builders. The lower alkyl ester and acid forms of such compounds are useful intermediates for their production.

3 Claims, No Drawings

CARBOXYMETHYL DIOXOLANE POLYCARBOXYLATES

BACKGROUND OF THE INVENTION

This invention relates to novel compounds and precursors thereof useful as sequestrants and detergency builders, to methods of making such compounds, and to detergent formulations containing such compounds.

Numerous materials are known which, by virtue of sequestering characteristics and/or capability to enhance the cleansing ability of detergent formulations in combination with various surfactants are useful in water treating applications, or as adjuvants, reenforcers, supplements, augmentors, potentiators and/or benefactors in detergent formulations wherein such materials are usually referred to as detergency builders.

Many materials of the foregoing type are characterized by high phosphorus content such as the alkali metal tripolyphosphates widely employed as detergency builders. It has recently been suggested by some researchers that such compounds may contribute to the acceleration of eutrophication processes and, particularly in the detergent builder field, extensive efforts have been exerted to provide alternate functional compounds free of phosphorus. In view of this, the provision of compounds containing little or no phosphorus which exhibit sequestration and/or builder function is recognized as an advance in the art.

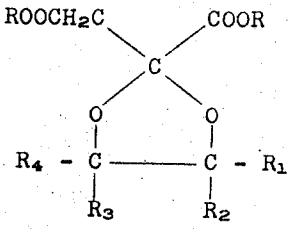
SUMMARY OF THE INVENTION

It is an object of this invention to provide novel compounds and intermediates useful for the production of such compounds which are useful as sequestrants and as detergency builders, and to provide methods of manufacture of such compounds. A further object of the invention is to provide novel detergent formulations containing such compounds as detergency builders.

The novel compounds of this invention and their manufacture and utility will be understood from the following description of the preferred embodiments.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The novel compounds of this invention are represented by the formula

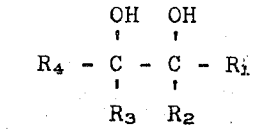


wherein R_1 is —COOR or $—CH_2COOR$; R_2, R_3 and R_4 are —COOR, $—CH_2COOR$, hydrogen or methyl; and R is methyl, ethyl, propyl, butyl, hydrogen, alkali metal or ammonium. For convenience in more specifically describing the ester and salt forms encompassed by the above formula and precursors thereof, the following additional representations will be employed. R_5 will be used to represent methyl, ethyl, propyl or butyl groups (ester form). R_6 will be used to represent alkali metal or ammonium (salt form).

The ester forms of the compounds of the present invention are prepared by reacting well known acetylene dicarboxylic acid esters (preferably methyl esters) represented by the formula

$$R_5OOC\text{-}C \equiv C\text{-}COOR_5$$

with vicinal dihydroxy acid esters represented by the formula



wherein R in the substituents R_1, R_2, R_3 and R_4 is the ester form, R_5.

Many of the diol acid esters are commercially available materials such as dimethyl tartrate, diethyl tartrate and ethyl glycerate to mention a few. Others not commercially available may be prepared by esterification of the appropriate diol acid using standard esterification techniques. For example, diol acids of this type can be prepared via hydrolysis of the corresponding epoxy acids. The latter may be prepared by oxidation of the appropriate olefin acid with H_2O_2 using the method of Payne and Williams [*J. Org. Chem.*, 24, 51 (1959)], or by oxidation with other oxidizing agents such as perbenzoic acid, peracetic acid and pertrufluoro acetic acid. The appropriate olefinic acid may be prepared by bromination of the appropriate alkane acid followed by elimination of HBr to form the desired olefinic linkage.

A catalyst is required to promote the reaction yielding the ester forms of the compounds of this invention. Acids or bases may be employed with base catalysts being preferred. Such bases include metallic sodium, sodium methoxide, sodium amide, potassium t-butoxide, tertiary amines such as triethyl amine and pyridine and other alkali metal hydroxides, alkoxides and amides.

The reaction may be carried out either in the absence or presence of a solvent over a temperature range from −20° to +200°C with the range 25 to 150°C being preferred. Many solvents may serve as the reaction medium. Included among these are diethyl ether, tetrahydrofuran, dioxane, dimethoxymethane, 1,2-dimethoxyethane, benzene, toluene, xylene, bis(2-methoxy)-ethyl ether to name just a few. Preferably, the reaction is carried out at atmospheric pressure but lower or higher pressures may be employed if desired.

The esters of the carboxylated-2-carboxymethyl-1,3-dioxolanes may be converted to salts by saponification with an appropriate base (e.g. sodium hydroxide or ammonium hydroxide).

Acidification of the salts produces the corresponding acids.

Both the acid and salt forms of the compounds of this invention are useful as metal ion sequestrants and as detergency builders, the use of the salt form being preferred.

The detergent formulations utilizing the compounds of this invention will contain from 1 to 75% by weight, preferably from 5 to 50% by weight of the salt, preferably sodium salt forms of the compounds of this invention. Such compounds can be utilized as the sole detergency builder in the compositions or in combination

with other known detergency builders such as water soluble inorganic builder salts, for example, alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates or organic builders such as salts of phytic acid, sodium citrate, water soluble polymeric polycarboxylates as described in U.S. Pat. No. 3,308,067 and the like.

The detergent formulations will additionally contain at least 8% by weight of a surfactant. Any of the numerous well-known anionic, nonionic, zwitterionic or ampholytic surfactants can be employed.

Examples of suitable anionic surfactants include alkyl ethyl sulfonates, alkyl sulfates, acyl sarcosinates; acyl esters of isocyanates, acyl N-methyl taurides, and alkyl aryl sulfonates. The foregoing materials are used in the form of their water-soluble sodium, potassium, ammonium and alkyl ammonium salts. Specific examples include sodium laryl sulfate; sodium N-methyl aluryll tauride; sodium dodecyl benzene sulfonate; and triethanol amine undecanol benzene sulfonate.

Examples of suitable nonionic detergents include alkyl phenol and alcohol alkoxylates including condensates of 1-decanol or 1-undecanol with from 3 to 5 molecular proportions of ethylene oxide such as described in U.S. patent application Ser. No. 707,480 filed Feb. 23, 1968 and now abandoned; condensates of monohydroxy or polyhydroxy alcohols such as oleyl alcohol or 1-tridecanol with from 9 to 15 molecular proportions of ethylene oxides; alkyl internal vicinal dialkoxy or hydroxy alkoxy compounds as described in U.S. patent application Ser. No. 852,898 filed Aug. 25, 1969 and now abandoned; and condensates of alkylene oxides with organo amines, for example, ethylene diamine and amides such as N-octadecyl diethanol amide.

Examples of cationic surfactants include octadecyl ammonium chloride; straight chain fatty amines having 8 to 18 carbon atoms; and quaternary ammonium compounds such as octadeyl trimethyl ammonium chloride.

Suitable ampholitic surfactants include the amido alkene sulfonates such as sodium C-pentadecyl, N-methyl amido ethyl sulfonate potassium C-octyl N-naphthalene amido propyl sulfonate; ammonium C-decyl, N-cyclo propyl amido butyl sulfonate, and aliphatic amine derivatives in which the aliphatic substituent contains an anionic water-solubilizing substituent such as a carboxy, sulfo, phosphato, or phosphino group, for example, sodium-3-dodecyl amino propionate and sodium-3-dodecyl amino propane sulfonate.

Examples of zwitterionic surfactants include derivatives of quaternary ammonium phosphonium and sulfonium compounds such as 3-(N,N-dimethyl-N-hexadecyl ammonio) propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecyl ammonio-2-hydroxy propane-1-sulfonate).

It will be understood that the above examples of supplementary surfactants are by no means comprehensive. Numerous other surfactants are known to those skilled in the art and are set forth in such familiar references as *Surface Active Agents* by A. M. Schwartz and James W. Perry. It will be further understood that the use of such surfactants will be in accordance with conventional, well-understood practices of detergent formulation. For example, cationic and anionic detergents will not normally be employed in combination due to recognized problems of precipitation of insoluble products.

In accordance with general practice, the ratio of the detergency building components to the surfactant components will be in the range of from 1:2 to about 12:1 by weight.

In addition to surfactant and builder components, the detergent formulations may contain fillers such as sodium sulfate and minor amounts of bleaches, dyes, optical brighteners, soil anti-redeposition agents, perfumes and similar conventional detergent formulation additives.

In the interest of conciseness, the invention will be exemplified by the preparation of dimethyl diethyl-2-carboxy-methyl-1,3-dioxolane-2-trans-4,5-tricarboxylate and the salt and acid forms thereof and the properties of this material and compositions containing the same. It will be understood that analogous procedures can be employed for production of other compounds of this invention which are characterized by similar properties. In the examples, all parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A 1000 ml 4 neck round bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer and drying tube is charged with 75.1 gms diethyl d-tartrate in 350 ml 1,2-dimethoxyethane solvent. To this mixture is added 51.7 gms dimethyl acetylene dicarboxylate and 3.0 gms sodium methoxide. The solution is heated to 50°C and maintained at this temperature for 40 hrs. After cooling, the reaction mixture is filtered and the filtrate evaporated to remove the solvent. The residue is dissolved in 250 ml $CHCl_3$, washed with 100 ml saturated NaCl solution and dried over $MgSO_4$. The solvent is removed by evaporation and the residue is fractionally distilled under vaccum. Dimethyl diethyl 2-carboxymethyl-1,3-dixoxlane-2-trans-4,5-tricarboxylate is obtained (27.0g) as a viscous liquid in the range of 150–170°C at 0.1 mm Hg. Further purification is achieved by redistilling the product, bp 155–162°C at 0.1 mmHg.

Analysis confirms that the product is diethyl dimethyl 2-carboxymethyl-1,3-dioxolane-2-trans-4,5-tricarboxylate.

A 500 ml 3 neck round bottom blask equipped with a mechanical stirrer is charged with 26.7g of the dimethyl diethyl 2-carboxymethyl-1,3-dioxolane-2-trans-4,5-tricarboxylate and 200 ml water. To this is added, dropwise, 12.3 g of NaOH in 200 ml H_2O. Stirring is continued until the solution becomes homogenous (8 hrs). The water and alcohol are removed by evaporation and the remaining solid is dried for 24 hrs in vaccuo at 60°C to yield 28.0 g of solid tetrasodium salt.

Acidification with H_2SO_4 converts the salt to the corresponding acid.

EXAMPLE II

The salt and acid produced according to Example I are tested for sequestration characteristics and are found to effectively sequester Ca^{++} ions.

EXAMPLE III

Detergent formulations containing 12% linear alkylbenzene sulfonate having an average alkyl chain length of about 12 carbon atoms; from 5% to 75% of the salt product of Example I; 12% sodium silicate having an SiO_2 to Na_2O ratio of about 2:4; and a quantity of sodium sulfate sufficient to equal 100% are found, in con-

ventional laundry operations, to clean soiled fabric samples substantially better than otherwise identical formulations containing no builder salt. These tests demonstrate that this compound is an effective detergency builder.

EXAMPLE IV

The tests of Example III above are repeated using a detergent formulation in which Neodole 45-11 (a nonionic surfactant which is an aduct of a modified oxo type C_{14}–C_{15} alcohol with an average of 11 moles of ethylene oxide is substituted for the alkylbenzene sulfonate. Comparable results are obtained.

EXAMPLE V

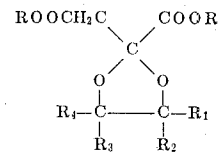
The tests of Example III are repeated with a detergent formulation wherein sodium hydroxyalkyl (C_{14}–C_{16} alkyl chain length) N-methyl taurate, an ampholytic surfactant, is substituted for the alkylbenzene sulfonate. Comparable results are obtained.

EXAMPLE VI

The tests of Example III are repeated with a detergent formulation wherein cocodimethylsulfopropylbetaine, a zwitterionic surfactant is substituted for the alkylbenzene sulfonate. Comparable results are obtained.

What is claimed is:

1. A compound represented by the formula



wherein R_1 is selected from the group consisting of —COOR and —CH_2COOR; R_2, R_3 and R_4 are selected from the group consisting of —COOR, —CH_2COOR, hydrogen and methyl; and R is selected from the group consisting of methyl, ethyl, propyl, butyl, hydrogen, alkali metal and ammonium.

2. The compound of claim **1** wherein R is methyl.

3. The compound of claim **1** wherein R is sodium.

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