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CYCLOALKENE-1-MERCAPTOALKANOIC ACIDS, ALKYL ESTERS AND METAL SALTS

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13 Claims. (Cl. 260—468)

The present invention relates to the preparation of unsaturated sulfur containing carboxylic acids and to the preparation of salts and esters of such acids.

The preparation of heterocyclic compounds by the reaction of perhaloketones with thioacetic acid or thiopropionic acid is disclosed in Simmons Patent 2,911,414.

It is an object of the present invention to prepare sulfur containing unsaturated acids and esters and salts thereof which are devoid of a heterocyclic ring.

Another object is to prepare novel alkene and cycloalkene thio esters of mercaptoalkanoic acids and the esters and salts thereof.

A further object is to improve the heat and light stability of halogen-containing resins.

An additional object is to provide novel stabilized vinyl resin compositions.

Yet another object is to provide novel synergistic stabilizers of halogen-containing resins.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiment of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

The novel compounds of the present invention have the formula $R_1S(CH_2)_n—COOR_2$ where R_1 is alkenyl, aralkenyl or cycloalkenyl in which the aliphatic or cycloaliphatic double bond is attached to the carbon atom directly attached to the sulfur atom and R_2 is hydrogen, alkyl, ammonium or a metal, e.g. sodium or potassium and n is an integer up to 10, preferably 1 or 2.

Examples of compounds within the invention are

cyclohexene-1-mercaptopropionic acid,
cyclohexene-1-mercaptoacetic acid,
buytl cyclohexene-1-mercaptopropionate,
hexyl cyclohexene-1-mercaptopropionate,
methyl cyclohexene-1-mercaptoacetate,
methyl cyclohexene-1-mercaptopropionate,
octadecyl cyclohexene-1-mercaptopropionate,
octadecyl cyclohexene-1-mercaptoacetate,
cyclohexene-1-mercaptobutyric acid,
cyclohexene-1-mercaptodecanoic acid,
sodium cyclohexene-1-mercaptoacetate,
sodium cyclohexene-1-mercaptopropionate,
ammonium cyclohexene-1-mercaptopropionate,
potassium cyclohexene-1-mercaptoacetate,
cyclopentene-1-mercaptopropionic acid,
cyclopentene-1-mercaptoacetic acid,
butyl cyclopentene-1-mercaptoacetate,
butyl cyclopentene-1-mercaptopropionate,
hexyl cyclopentene-1-mercaptobutyrate,
octyl cyclopentene-1-mercaptopropionate,
ethene-1-mercaptopropionic acid,
ethene-1-mercaptoacetic acid,
amyl ethene-1-mercaptopropionate,
propene-1-mercaptoacetic acid,
propene-1-mercaptopropionic acid,
hexyl propene-1-mercaptopropionate,

isodecene-1-mercaptopropionic acid,
butyl S-2-heptene mercaptoacetate,
S-2-heptene mercaptopropionic acid,
2-thia-3-decenoic acid,
3-thia-5-ethyl-4-heptenoic acid,
2-thia-4-ethyl-3-hexenoic acid,
3-thia-4-undecenoic acid,
butyl 3-thia-4-undecenoate,
3-thia-4-eicosenoic acid,
methyl 3-thia-4-eicosenoate,
propene-2-mercaptoacetic acid,
propene-2-mercaptopropionic acid,
heptyl propene-2-mercaptoacetate,
S-2-butene mercaptopropionic acid,
S-3-pentene mercaptoacetic acid,
butyl S-3-pentene mercaptopropionate,
4-phenyl-2-thia-3-butenoic acid,
3-methyl cyclohexene-1-mercaptopropionic acid,
1-phenylethene-1-mercaptopropionic acid.

The compounds of the present invention can be prepared by heating 1 mole of a mercaptoalkanoic acid with 1 mole, or preferably a slight excess of 1 mole, of the appropriate aldehyde or ketone and removing 1 mole of water. The reaction is carried out in the presence of a water entrainer such as a hydrocarbon solvent, e.g. toluene, benzene, xylene or naphtha in the presence or absence of an acid catalyst such as hydrochloric acid, hydrobromic acid, p-toluenesulfonic acid, benzenesulfonic acid or sulfuric acid.

When mercaptoacetic acid is employed as a reactant there are found substituted oxathiolanes as by-products. The desired alkene-1-mercaptoacetic acid (or cycloalkene-1-mercaptoacetic acid) can be separated from the 1-oxathiolane by adding dilute aqueous alkali such as sodium bicarbonate, potassium bicarbonate or ammonium hydroxide. The alkene-1-mercaptoacetic acid goes into the aqueous layer while the oxathiolane remain in the organic layer. The aqueous layer can be separated and then evaporated to recover the salt of the alkene-1-mercaptoacetic acid or cycloalkene-1-mercaptoacetic acid. Alternatively the separated aqueous layer can be acidified, e.g. with hydrochloric acid to precipitate the alkene-1-mercaptoacetic acid or cycloalkene-1-mercaptoacetic acid.

Since mercaptopropionic acid does not form cyclic compounds with the aldehydes and ketones there is no need to add aqueous alkali to the reaction product for separation purposes. However, aqueous alkali can be added to form the salt of alkene or cycloalkene-1-mercaptopropionic acid. The salts thus are useful for forming the free alkene and cycloalkene-1-mercaptoalkanoic acids.

The alkene and cycloalkene mercaptopropionic acid compounds can be recovered by distillation as can the alkylesters of alkene or cycloalkene mercaptopropionic (or mercaptoacetic) acids.

Distillation can also be employed to further purify the alkene or cycloalkene mercaptoacetic acids.

As starting aldehydes or ketones, there can be used acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, isovaleraldehyde, caprylaldehyde, 2-ethyl-butyraldehyde, stearaldehyde, phenylpropionaldehyde, acetone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, methyl isobutyl ketone, stearanone, diethyl ketone, dipropyl ketone, ethyl propyl ketone, acetophenone, propiophenone, cyclopentanone, cyclohexanone, 2-methyl cyclohexanone, methyl amyl ketone, and isodecaldehyde.

The compounds of the present invention, especially the free acids and the alkyl esters are useful as stabilizers for halogen containing minerals particularly when used with

tin compounds such as dialkyltin oxide and dialkyltin acylates.

The stabilizers of the present invention can be used with halogen containing vinyl and vinylidene resins in which the halogen is attached directly to the carbon atoms. Preferably, the resin is a vinyl halide resin, specifically, a vinyl chloride resin. Usually, the vinyl chloride resin is made from monomers consisting of vinyl chloride alone or a mixture of monomers comprising at least 70% vinyl chloride by weight. When vinyl chloride copolymers are stabilized, preferably the copolymer of vinyl chloride with an ethylenically unsaturated compound copolymerizable therewith contains at least 10% of polymerized vinyl chloride.

As the chlorinated resin there can be employed chlorinated polyethylene having 14 to 75%, e.g., 27%, chlorine by weight. Polyvinyl chlorine, polyvinylidene chloride, polyvinyl bromide, polyvinyl fluoride, copolymers of vinyl chloride with 1 to 90%, preferably 1 to 30%, of a copolymerizable ethylenically unsaturated material such as vinyl acetate, vinyl butyrate, vinyl benzoate, vinylidene chloride, diethyl fumarate, diethyl maleate, other alkyl fumarates and maleates, vinyl propionate, methyl acrylate, 2-ethylhexyl acrylate, butyl acrylate and other alkyl acrylates, methyl methacrylate, ethyl methacrylate, butyl methcrylate and other alkyl methacrylates, methyl alpha chloroacrylate, styrene, trichloroethylene, vinyl ethers such as vinyl ethyl ether, vinyl chloroethyl ether and vinyl phenyl ether, vinyl ketones such as vinyl methyl ketone and vinyl phenyl ketone, 1-fluoro-1-chloroethylene, acrylonitrile, chloroacrylonitrile, allylidene diacetate and chloroallylidene diacetate. Typical copolymers include vinyl chloride-vinyl acetate (96:4 sold commercially as VYNW), vinyl chloride-vinylacetate (87:13), vinyl chloride-vinyl acetate-maleic anhydride (86:13:1), vinyl chloride-vinylidene chloride (95:5), vinyl chloride-diethyl fumarate (95:5), vinyl chloride trichloroethylene (95:5), vinyl chloride-2-ethylhexyl acrylate (80:20).

The stabilizers of the present invention can be incorporated with the resin by admixing in an appropriate mill or mixer or by any of the other well-known methods which provide for uniform distribution throughout the resin compositions. Thus, mixing can be accomplished by milling on rolls at 100–160° C.

In addition to the novel stabilizers there can also be incorporated with the resin conventional additives such as plasticizers, pigments, fillers, dyes, ultraviolet light absorbing agents, densifying agents and the like.

If a plasticizer is employed, it is used in conventional amount, e.g., 30 to 150 parts per 100 parts of resin. Typical plasticizers are di-2-ethyl-hexyl phthalate, dibutyl sebacate, dioctyl sebacate, tricresyl phosphate.

Examples of suitable tin compounds for use as stabilizers with the compounds of the present invention are dibutyltin oxide, dibutyltin dilaurate, dioctyltin oxide, dioctyltin dilaurate.

The compounds of the present invention are normally used in an amount of 0.01 to 10% by weight of the resin.

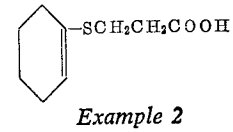
The tin compounds are also normally used in an amount of 0.01 to 10% by weight of the resin. More preferably 0.2 to 5% of the tin compound and 0.2 to 5% of the alkene or cycloalkene mercaptoalkanoic acid (or alkyl ester thereof) of the present invention are used based on the weight of the resin.

Unless otherwise indicated all parts and percentages are by weight.

The alkene and cycloalkene group containing compounds of the present invention can also be prepared by forming a thioacetal or thioketal from 2 moles of mercaptoacetic acid or mercaptopropionic acid or an alkyl ester thereof and 1 mole of the appropriate aldehyde or ketone and then heating to remove 1 mole of mercaptoacetic acid.

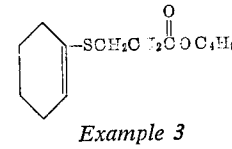
Example 1

1 mole of mercaptopropionic acid and 1.1 mole of cyclohexanone were refluxed in toluene with removal of water (the reactants together equalled 80% by weight of the total mixture) until 18 grams of water were obtained. The product was then distilled and cyclohexene-1-mercaptopropionic acid was recovered as a yellow liquid having an n_D^{23}1.5319 and a B.P. of 142–145° C. at 0.5 mm. Hg. The product had the formula



Example 2

The procedure of Example 1 was repeated replacing the mercaptopropionic acid by 1 mole of butyl mercaptopropionate. The product was butyl cyclohexene-1-mercaptopropionate, a colorless liquid having an n_D^{20}1.4983, having a B.P. of 133° C. at 0.5 mm. Hg and having the formula

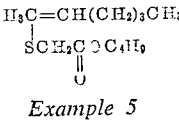


Example 3

The procedure of Example 1 was repeated replacing the mercaptopropionic acid by 1 mole of butyl mercaptoacetate. The product was butyl cyclohexene-1-mercaptoacetate, a colorless liquid having an n_D^{20} of 1.5022 and having a B.P. of 133–140° C. at 1.9 mm. Hg.

Example 4

The procedure of Example 1 was repeated but the reactants employed were 1 mole of butyl mercaptoacetate and 1.1 mole of methyl amyl ketone. The product was butyl S-2-heptene mercaptoacetate, a colorless liquid having an n_D^{18} 1.4739, a B.P of 117–126° C., at 0.3 mm. and having the formula

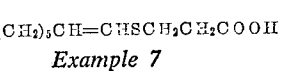


Example 5

To a mixture of 1 mole of mercaptopropionic acid and 1.1 mole of cyclopentanone in toluene there was added 3 grams of p-toluenesulfonic acid as a catalyst. The reactants equalled 80% by weight of the toluene. The mixture was refluxed with removal of water until 18 grams thereof were obtained. The product was then washed with dilute aqueous sodium bicarbonate, the toluene removed by distillation and cyclopentene-1-mercaptopropionic acid recovered as a yellow solid M.P. 33–35° C.

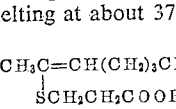
Example 6

The procedure of Example 1 was repeated replacing the cyclohexanone by 1.1 mole of isodecaldehyde. The product was isodecene-1-mercaptopropionic acid, a colorless liquid having an n_D^{20} 1.4878, a B.P. of 163–173° C., at 0.4 mm. Hg and having the formula



Example 7

The procedure of Example 5 was repeated replacing the cyclopentanone by 1.1 mole of methyl amyl ketone. The product was S-2-heptene mercaptopropionic acid, a light brown solid melting at about 37° C. and having the formula



Example 8

1 mole of mercaptoacetic acid and 1.1 mole of caprylaldehyde were refluxed in toluene with removal of water

until 18 grams of water were obtained. The reactants together equalled 80% by weight of the total mixture. The product was then treated with an equal weight of dilute (10%) aqueous sodium bicarbonate and the water layer containing the sodium salt of 2-thia-3-decenoic acid separated from the organic layer. The water layer was then neutralized with hydrochloric acid to separate the free 2-thia-3-decenoic acid, from the water. After removal of the aqueous layer the 2-thia-3-decenoic acid having the formula $CH_3(CH_2)_5CH{=}CHSCH_2COOH$ was recovered as a colorless liquid having an n_D^{20} 1.4919 and a boiling point of 130–138° C. at 0.5 mm. Hg.

Example 9

The procedure of Example 1 was repeated replacing the cyclohexanone by 1.1 mole of 2-ethylbutyraldehyde. The product was 3-thia-5-ethyl-4-heptenoic acid, a deep yellow liquid having an n_D^{21} 1.5015, a B.P. of 132–138° C. at 0.3 mm. and the formula

$$CH_3CH_2\underset{\displaystyle C_2H_5}{\overset{|}{C}}{=}CHSCH_2CH_2COOH$$

Example 10

The procedure of Example 1 was repeated using as the reactants 1 mole of mercaptoacetic acid and 1.1 mole of 2-ethylbutyraldehyde. The product was 2-thia-4-ethyl-3-hexenoic acid, a colorles liquid having an n_D^{20} 1.5008 and a B.P. of 130–140° C. at 2 mm. Hg.

Example 11

The procedure of Example 5 was followed replacing the cyclopentanone by 1.1 mole of caprylaldehyde. The product was 3-thia-4-undecenoic acid, a yellow liquid having n_D^{20} 1.4898 and a B.P. of 147–150° C. at 0.3 mm. Hg.

Example 12

The procedure of Example 1 was followed employing as the reactants 1 mole of butyl mercaptopropionate and 1.1 mole of caprylaldehyde. The product was butyl 3-thia-4-undecenoate, a pale yellow liquid having an n_D^{22} 1.4731 and a B.P. of 136–146 ° C. at 1 mm. Hg.

Example 13

100 parts of Geon 101EP (vinyl chloride homopolymer) was mixed with 0.37 part dibutyltin oxide and 0.30 part of cyclohexane-1-mercaptopropionic acid to form a heat stable product.

Example 14

Example 13 was repeated but 50 parts of dioctyl phthalate was included in the composition. The product was heat stable.

What is claimed is:

1. A compound having the formula $R_1S(CH_2)_nCOOR_2$ where R_1 is cycloalkenyl in which the double bond is on the carbon atom adjacent to the sulfur atom, R_2 is selected from the group consisting of hydrogen, alkyl and a metal and n is an integer of at least 1.

2. A compound according to claim 1 wherein R_2 is lower alkyl.

3. Cycloalkene-1-mercaptoalkanoic acids wherein the cycloalkene group has 5 to 6 carbon atoms and the mercaptoalkanoic group has 2 to 3 carbon atoms.

4. Cyclohexene-1-mercaptoalkanoic acids wherein the mercaptoalkanoic group has 2 to 3 carbon atoms.

5. Cyclohexene-1-mercaptoacetic acid.

6. Cyclohexene-1-mercaptopropionic acid.

7. Cyclopentene-1-mercaptoalkanoic acids wherein the mercaptoalkanoic group has 2 to 3 carbon atoms.

8. Alkyl esters of cycloalkene-1-mercaptoalkanoic acids wherein the cycloalkene group has 5 to 6 carbon atoms and the mercaptoalkanoic group has 2 to 3 carbon atoms wherein the alkyl group has 1 to 18 carbon atoms.

9. A compound according to claim 8 where the alkyl is lower alkyl.

10. Alkyl esters of cyclohexene-1-mercaptoalkanoic acids wherein the mercaptoalkanoic group has 2 to 3 carbon atoms wherein the alkyl group has 1 to 18 carbon atoms.

11. A compound according to claim 10 where the alkyl is lower alkyl.

12. Alkyl esters of cyclohexene-1-mercaptopropionic acid wherein the alkyl group has 1 to 18 carbon atoms.

13. A compound according to claim 12 where the alkyl is lower alkyl.

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