Patented Mar. 27, 1945 2,372,358

UNITED STATES PATENT OFFICE

2,372,358

ACYL PHENYL DITHIOPHOSPHORIC ACIDS AND THEIR PREPARATION

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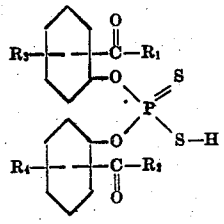
No Drawing. Application December 10, 1942, Serial No. 468,552

4 Claims. (Cl. 260—461)

This invention relates to new chemical compounds and their preparation; more particularly to new compounds which may be broadly designated as di-(acyl phenyl)-dithiophosphoric acids and salts thereof.

The di-(acyl phenyl)-dithiophosphoric acids of the present invention may be represented by the general formula



in which R_1 and R_2 are alkyl, cycloalkyl or aryl radicals and R_3 and R_4 are hydrogen or alkyl, cycloalkyl or aryl radicals. The salts of these compounds are also included within the scope of our invention as set forth in the appended claims.

The di-(acyl phenyl)-dithiophosphoric acids and their salts are, in general, yellowish-brown viscous liquids or soft solids. Most of the compounds of this new class are water insoluble but easily soluble in most organic solvents and in lubricating oils. The compounds, particularly the alkaline earth metal salts, have both detergent and corrosion inhibiting properties and when dissolved in hydrocarbon lubricating oils are extremely valuable in the prevention of bearing corrosion, sludge and varnish formation, ring sticking and other undesirable conditions which develop when ordinary lubricating oils are subjected to heavy duty service. The carbonyl groups of our new compounds also tend to increase the oiliness characteristics of the oil in which they are dissolved. Because of their sulfur and phosphorous content they may be advantageously added to hypoid gear greases and other extreme pressure lubricants. Being water-insoluble and polar in character they are valuable in the preparation of slushing oils. Most of the compounds of this new class have pour point depressing properties and are useful in controlling the viscosity of lubricating and other oils. Because of their surface active properties some of the compounds of the group are useful in the flotation of ores. Still others may be employed as insecticides and fungicides. Since these new compounds have good heat stability those which are liquid are valuable as plasticizers for synthetic rubber.

The di-(acyl phenyl)-dithiophosphoric acids of the present invention are prepared by reacting an acylated phenol with P_2S_5 as described hereinafter. The acylated phenols which may be employed in our reaction to prepare new and useful compounds are those obtained by acylating phenol or an alkyl, cycloalkyl or aryl substituted phenol with alkyl, cycloalkyl or aryl acyl halides. Suitable acylating agents for this latter reaction include acyl halides such as acetyl chloride, butyryl chloride, caproyl chloride, lauroyl chloride, myristoyl chloride, stearoyl chloride, naphthenoyl chloride, benzoyl chloride, amyl benzoyl chloride, octyl benzoyl chloride, phenyl stearoyl chloride, and others. Particularly useful as acylating agents are those mixed acyl halides derived from mixed fatty acids obtained upon hydrolysis of animal, fish and vegtable oils. These products contain varying proportions of different long chain fatty acid halides in admixture. The naphthenoyl chloride mentioned above is composed of a mixture of various cycloaliphatic acyl halides such as are prepared from naphthenic acid, a product of the petroleum industry.

The alkyl, cycloalkyl and aryl substituted phenols which may be employed by us are easily obtained products of commerce such as, cresol, isobutyl phenol, amyl phenol, tertiary amyl phenol, ethylhexyl phenol, n-octyl phenol, dodecyl phenol, tetradecyl phenol, octadecyl phenol, cyclopentyl phenol, cyclohexyl phenol, p-hydroxybiphenyl and the like. Although the preparation of acylated phenols has been previously described some of the acylated phenols employed by us are new compounds, and accordingly, preparation of some of the typical ones are given in the specific examples which follow. In general, however, the acyl phenols are prepared by treating phenol or an alkyl, cycloalkyl or aryl substituted

phenol with an acyl halide of the type disclosed above in the presence of anhydrous aluminum chloride followed by decomposition of the resulting aluminum complex with dilute hydrochloric acid and washing.

As will be seen from the above, R_1 and R_2 in the general formula are aliphatic, aromatic, or cycloaliphatic radicals such as methyl, ethyl, butyl, isobutyl, amyl, heptyl, nonyl, undecyl, tridecyl, pentadecyl, heptadecyl, cyclopentyl, cyclohexyl, methyl cyclohexyl, dimethyl cyclohexyl, phenyl, and the like. R_1, R_2, R_3 and R_4 may be the same, or different, radicals.

Since the principal use of our new compounds is expected to be in lubricating oils it is desirable that the compounds be easily soluble in hydrocarbon oils. For this reason R_3 and R_4 in the general formula above are preferably straight or branched chain, primary, secondary or teritary alkyl radicals such as methyl, ethyl, butyl, isobutyl, amyl, tertiary amyl, ethylhexyl, n-octyl, decyl, dodecyl, tetradecyl, octadecyl and the like or cycloalkyl radicals such as cyclopentyl, cyclohexyl, methylcyclohexyl, and other alkyl substituted cyclohexyl radicals, such as the ethyl, propyl, butyl, and amyl mono-, di- and tri-substituted cyclohexyl radicals. Radicals of these types in the compounds promote oil solubility. R_3 and R_4 may also be hydrogen or aryl radicals particularly when R_1 and R_2 are alkyl or cycloalkyl radicals and when the compounds are intended to be used for purposes not requiring their solution in mineral oils.

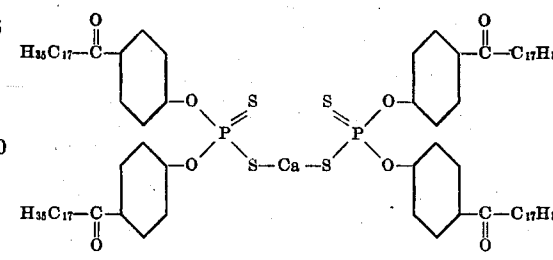
Our new compounds may be prepared by mixing and heating approximately 4 mols of an acylated phenol or substituted acylated phenol as named above with one mol of P_2S_5 at temperatures between 80–140° C. until most of the P_2S_5 has dissolved and the evolution of H_2S has subsided. This usually requires 2–4 hours at these temperatures. If desired, an inert solvent such as toluene may be added to the reaction mixture, either before or after the reaction, to facilitate handling. The crude product may be decanted or filtered from unreacted P_2S_5 and employed as such for certain purposes or it may be further purified by extraction or made into salts.

Salts of the di-(acyl phenyl)-dithiophosphoric acids may be prepared from the acids by simple neutralization of the above reaction product with a suitable salt-forming base or by double decomposition. A wide variety of salt-forming radicals including those of Ni, Al, Pb, Hg, Cd, Sn, Zn, Mg, Na, NH_4, Ca, Sr, Ba and others may be introduced by neutralization of the acid with a corresponding oxide, hydroxide or carbonate or in some cases sulfide. Some of these salts are more easily prepared by double decomposition of the sodium salt of the di-(acyl phenyl)-dithiophosphoric acid with a desired metal salt; as for example, zinc chloride or the like.

Preparation of our new compounds will now be described in greater detail by means of the following examples in which the preparation of representative (di-(acyl phenyl)-dithiophosphoric acids and some of their salts are described. All parts are by weight unless otherwise stated. It will be understood that our invention is not limited to the preparation of these particular compounds since the examples are given primarily for purposes of illustration and our invention is to be construed as broadly as the appended claims permit.

Example 1

Preparation of di-(stearoyl phenyl)-dithiophosphoric acid and its calcium salt

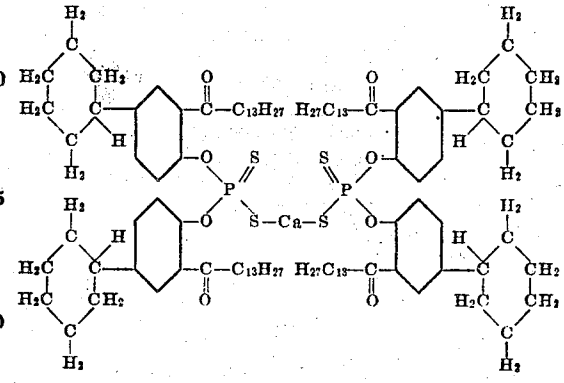


A mixture of 230 parts by weight of stearoyl chloride and 71 parts by weight of dry phenol was stirred at 95° C. for one-half hour, cooled and diluted with 100 parts of octane. When 33.6 parts by weight of anhydrous aluminum chloride had been added, the solution was heated with steam for two hours. After it had cooled, the product was stirred with warm dilute hydrochloric acid and the aqueous layer discarded. The upper layer was washed with warm dilute hydrochloric acid again, hot water three times, dilute sodium carbonate, and finally with sodium sulfate solution. Before it was washed with sodium carbonate, the solution was mixed with butanol to decrease emulsification. The stearoylphenol was isolated by distilling the solvents from it in vacuo. The product, a viscous yellow colored liquid, solidified on standing and cooling.

A mixture of 248 parts by weight of stearoylphenol and 42 parts by weight of P_2S_5 was stirred for three hours at a temperature of 85–95° C. and the resulting di-(stearoylphenyl)-dithiophosphoric acid decanted from the excess P_2S_5. The acid was diluted with 43 parts of 95% ethanol, 43 parts of absolute ethanol, and 172 parts of toluene and then 15 parts of calcium hydroxide was added slowly, followed by 3 parts of calcium hydroxide and 172 parts more of toluene. The solution of calcium di-(stearoylphenyl)-dithiophosphate was treated with activated carbon, filtered and the solvents removed by vacuum distillation. The product was a viscous reddish-brown liquid that became semi-solid on standing. It was readily soluble in lubricating oil.

Example 2

Preparation of di-(o-myristoyl-p-cyclohexylphenyl)-dithiophosphoric acid and its calcium salt



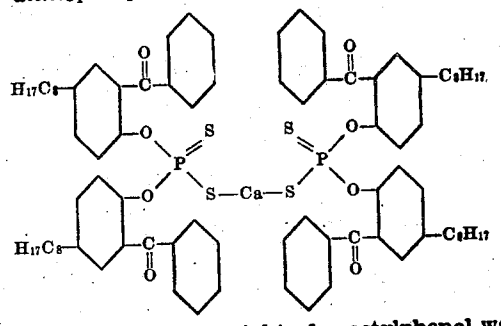
A mixture of 114 parts by weight of myristoyl chloride and 81 parts by weight of p-cyclohexylphenol was stirred on a steam bath for one-half

hour, cooled and diluted with 50 parts of octane. When 21 parts of anhydrous aluminum chloride had been added, the mixture was stirred on a steam bath for two hours and after it had been cooled and diluted with 250 parts of toluene, the aluminum complexes were decomposed with warm dilute hydrochloric acid. The upper layer was washed successively with hot dilute hydrochloric acid, hot water twice, a warm solution of sodium carbonate with butanol to prevent emulsification, and finally with warm water. The toluene, octane, butanol, and water were removed by vacuum distillation leaving 165 parts by weight of o-myristoyl-p-cyclohexylphenol, a yellowish-brown liquid.

A mixture of 35 parts by weight of o-myristoyl-p-cyclohexylphenol and 5.6 parts by weight of P_2S_5 was stirred at 95–110° C. for three hours and the resulting di-(o-myristoyl-p-cyclohexylphenyl)-dithiophosphoric acid was decanted from a slight residue of unreacted P_2S_5. The product was cooled, diluted with 26 parts of toluene, 6.5 parts of 95% ethanol, and 6.5 parts of absolute ethanol, and then reacted with 1.9 parts by weight of calcium hydroxide. The solution was treated with activated carbon, filtered, and vacuum distilled to remove the solvents from the calcium di-(o-myristoyl-p-cyclohexylphenyl)-dithiophosphate. The product, a brownish-yellow liquid was easily soluble in lubricating oil.

Example 3

Preparation of di-(o-benzoyl-p-octylphenyl)-dithiophosphoric acid and its calcium salt

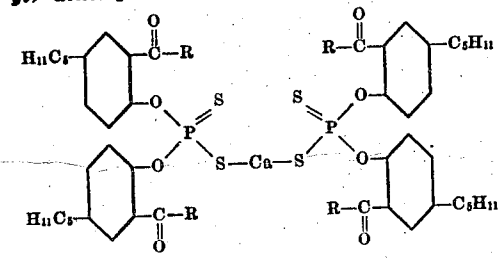


With 100 parts by weight of p-octylphenol was mixed 69 parts of benzoyl chloride and the solution was stirred at 95° C. for a half hour. When the liquid had cooled, 50 parts of octane and 21.7 parts of anhydrous aluminum chloride were slowly introduced. The mixture was stirred for two hours on a steam bath and then, after the products were at room temperature, 250 parts of toluene and an excess of warm dilute hydrochloric acid were added. The upper layer was washed again with warm dilute hydrochloric acid and then twice with hot water, once with warm aqueous sodium carbonate, and finally with warm water again. The solvents and water were removed by vacuum distillation, leaving 139 parts by weight of o-benzoyl-p-octylphenol, a viscous yellowish-brown liquid.

A mixture of 38 parts by weight of o-benzoyl-p-octylphenol and 7.4 parts of P_2S_5 was stirred at 95–110° C. for 2.5 hours, and then decanted from excess P_2S_5. The di-(o-benzoyl-p-octylphenyl)-dithiophosphoric acid was diluted with 28 parts of toluene, 7 parts of absolute ethanol, and 7 parts of 95% ethanol and then reacted slowly with 2.4 parts by weight of calcium hydroxide. Finally 28 parts of toluene and 0.5 part of calcium hydroxide more were added, the mixture treated with activated carbon, and filtered. The solvents were removed by vacuum distillation leaving the calcium di-(o-benzoyl-p-octylphenyl)-dithiophosphate as a semi-solid product that was only slightly soluble in oil.

Example 4

Preparation of di-(o-naphthenoyl-p-amylphenyl)-dithiophosphoric acid and its calcium salt



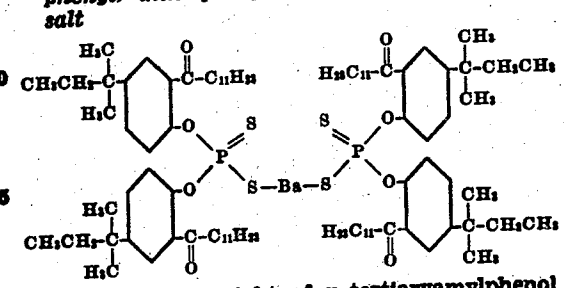
where R is a naphthenyl radical.

64 parts p-tertiarylamylphenol was dissolved in 40 parts warm octane and 100 parts naphthenoyl chloride added gradually with stirring. The solution was heated on the steam bath for 30 minutes, then cooled down to room temperature and 17 parts anhydrous aluminum chloride added with stirring. The mixture was gradually warmed up on the steam bath and heating continued for 2 hours. After cooling, the mixture was diluted with 150 cc. toluene and extracted with warm dilute hydrochloric acid three times, followed by warm dilute sodium carbonate solution and finally with water. The solvents were evaporated under reduced pressure leaving o-naphthenoyl-p-tertiarylamylphenol as a fluorescent yellowish-green liquid.

69 parts by weight of o-naphthenoyl-p-amylphenol was reacted with 13.2 parts by weight of P_2S_5 at 105–110° C. for three hours. The resulting di-(o-naphthenoyl-p-amylphenyl)-dithiophosphoric acid was decanted from the slight amount of P_2S_5 residue and, after dilution with 52 parts of toluene, 13 parts of 95% ethanol, and 13 parts absolute ethanol, it was reacted with 4.4 parts of calcium hydroxide. Finally, 0.8 part more of calcium hydroxide was added with 52 parts of Solvesso and the mixture was warmed to 60° C. for a half hour. Activated carbon was stirred in, the liquid filtered, and the solvents removed by vacuum distillation, leaving the calcium di-(o-naphthenoyl-p-amylphenyl)-dithiophosphate. The product was yellowish-brown and was easily soluble in oil.

Example 5

Preparation of di-(o-lauroyl-p-tertiaryamylphenyl)-dithiophosphoric acid and its barium salt



164 parts by weight of p-tertiaryamylphenol was warmed with 219 parts lauroyl chloride on the steam bath for 30 minutes. After cooling, 80 parts octane was added, followed by 45 parts anhydrous aluminum chloride. The mixture was stirred and slowly warmed up on the steam bath. Heating was continued for 2 hours. 200 parts of

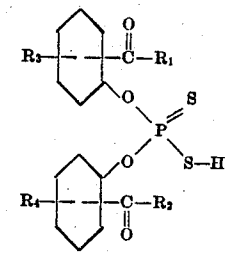
toluene was added and after cooling down was extracted and washed three times with dilute hydrochloric acid, followed with dilute sodium carbonate solution and finally with water. A quantity of butanol, about 50 parts by weight was added to prevent emulsification during the washing. After washing the solvents were removed by evaporation under reduced pressure. o-Lauroyl-p-tertiaryamylphenol remained as a brownish-yellow liquid.

346 parts o-lauroyl-p-tertiaryamylphenol was stirred and warmed with 61 parts finely ground P_2S_5 at 125–135° C. for 2.5 hours. At the end of this time practically all of the P_2S_5 had disappeared and the evolution of H_2S had practically ceased. The crude di-(lauroyl-p-tertiaryamylphenyl)-dithiophosphoric acid was decanted from a small amount of unreacted P_2S_5. It was a brownish-yellow liquid.

78 parts di-(o-lauroyl-p-tertiaryamylphenyl)-dithiophosphoric acid was dissolved in a mixture of 40 parts toluene and 20 parts 97.5% alcohol. With stirring and cooling below 40° C. 10 parts finely ground barium oxide was added. As soon as neutral, which required about 10 minutes 40 parts toluene was added and the solution filtered from traces of inorganic barium salts. The solvent was removed by evaporation in vacuo. The barium di-(o-lauroyl - p - tertiaryamylphenyl)-dithiophosphate was a yellowish-brown thick viscous liquid.

We claim:

1. Chemical compounds having the general formula



in which R_1, R_2, R_3 and R_4 are alkyl radicals, and the salts of such compounds.

2. Di-(o-lauroyl - p - tertiaryamylphenyl)-dithiophosphoric acid and the salts of such compounds.

3. Di-(stearoylphenyl)-dithiophosphoric acid and the salts of such compounds.

4. Di-(o - naphthenoyl-p-tertiaryamylphenyl)-dithiophosphoric acid and the salts of such compounds.

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