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SULPHO ESTERS OF CIS-ENDOMETHYLENE-3,6-Δ⁴-TETRAHYDROPHTHALIC ACID

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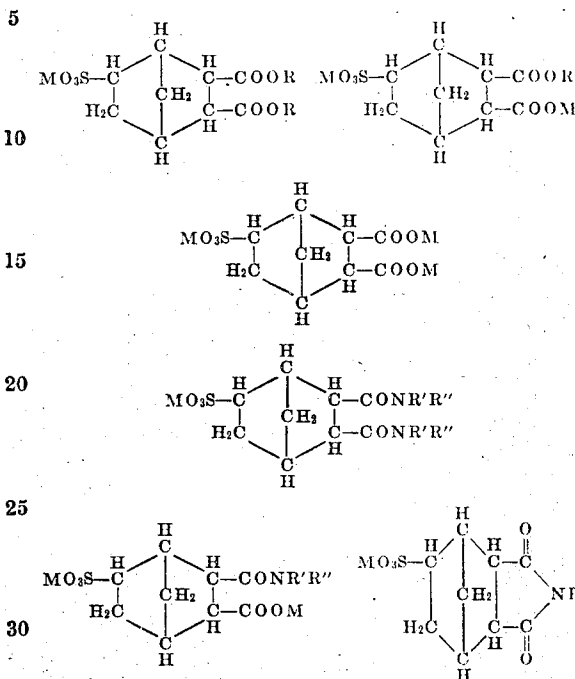
This invention relates to a new class of esters of cis-endomethylene-3,6-sulpho-hexahydrophthalic acid which have been found to possess wetting, emulsifying and detergent properties and to methods of making the same.

We have found that it is possible to sulphonate the mono-, di- and mixed esters of cis-endomethylene-3,6-Δ⁴-tetrahydrophthalic acid and its anhydride at the double bond position in the ring, although there are no adjacent activating groups, by means of sulphites and bisulphites under appropriate conditions which will be described hereinafter.

The sulphonated esters of cis-endomethylene-3,6-Δ⁴-tetrahydrophthalic acid are particularly valuable principally on account of their wetting and detergent properties. As stated above the mono-, di- or mixed esters may be sulphonated. Those esters prepared from alcohols of 3 to 8 carbon atoms when sulphonated possess marked wetting properties, the wetting power generally increasing with the length of the alcohol chain. The sulphonated esters prepared from longer chain alcohols, such as lauryl, have more pronounced detergent and foaming qualities. The monobutyl, mono-octyl, monolauryl, monocetyl, dibutyl, diamyl, dioctyl and dilauryl esters may be sulphonated according to the procedure described below and are representative of the entire class of wetting and detergent compounds of the invention.

Our invention enables us to prepare all alkyl, aryl or alkyl-aryl diesters of sulphonated cis-endomethylene-3,6-Δ⁴-tetrahydrophthalic acid and its metallic, ammonium or organic salts; the diesters of partially esterified polyhydric alcohols of the sulphonated acid and its salts; alkyl or aryl monoesters of the sulphonated acid and its salts; and half-esters of partially esterified (alkyl or aryl) polyhydric alcohols of the sulphonated acid and its salts. In addition to the preparation of esters, this invention also permits us to prepare the alkyl, aryl or mixed (alkyl-aryl) diamides of the sulphonated acid and their metallic, ammonium or organic base salts; alkyl or aryl monoamides of the sulphonated acid and metallic, ammonium or organic base salts; alkyl or aryl substituted imides and the metallic, ammonium or organic base salts thereof; mixed amides (alkyl,

aryl or alkyl-aryl) and esters (alkyl or aryl) of the sulphonated acid. These various compounds are illustrated by the following general structural formulas:



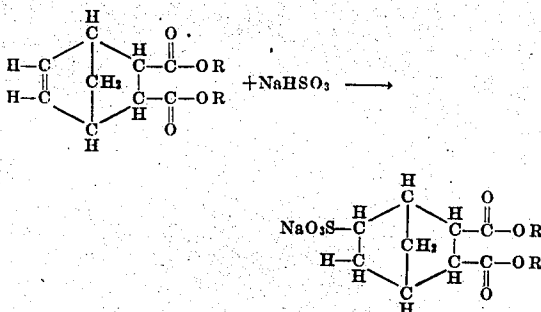
in which R represents an alkyl or aryl radical, R' represents an H, alkyl, aryl or alkyl-aryl radical, R'' represents an alkyl, aryl or alkyl-aryl radical and M represents a salt-forming radical such as H, NH₄ or a metal or organic base radical.

The compounds prepared in this manner have wetting and detergent properties which make them useful in wetting, detergent, dispersing, emulsifying and foaming processes; in processing and in improving textiles; in the preparation of sizing compositions; in dye assistants; in the leather industry for wetting agents in soaking, deliming, bating, tanning and dyeing; in textiles for delustering, cleaning, scouring and fulling and filling assistants; in waxes and polishes; shampoos; dentifrices; in the paper industry as penetrants for cooking pulp and the like; in latex sta-

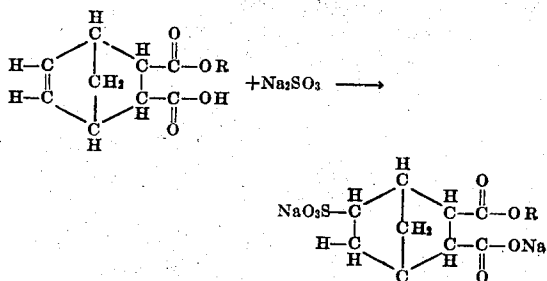
bilization; for prevention of pelling in electroplating; in pigment dispersion for grinding; in cosmetic creams; insecticide and fungicide sprays; and for the breaking of petroleum emulsions of the water-in-oil type.

We prefer to prepare our new class of sulphonated compounds by sulphonating the esters, amides or imides of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid. In carrying out the sulphonation we prefer to use sulphites when sulphonating the monoesters or mono-amides and bisulphites when sulphonating the diesters, diamides or imides. Ordinarily we use the sulphites or bisulphites in the form of their sodium, potassium or ammonium salts. A mixture of the ester, amide or imide to be sulphonated, a solvent such as ethyl alcohol and water or water alone, and the desired sulphite or bisulphite, are heated in a vessel fitted with a reflux condenser until the sulphonation is complete. In some cases it may be more practical to charge the vessel with the ester, amide or imide and an aqueous or alcoholic solution of an alkali and add SO_2 to the mixture as the reaction proceeds.

The sulphonation of the diester of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid may be illustrated with the following reaction equation:



The sulphonation of the monoesters with sodium sulphite is believed to be as follows:

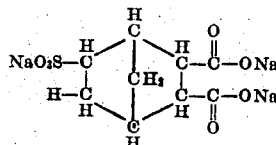


It is not definitely known whether the NaSO_3 -group takes the 4 or 5 position in the ring or whether a mixture is obtained. It is probable that in most cases a mixture of 4-sulpho and 5-sulpho acids is obtained but we wish it understood, however, that we intend to cover both possibilities in the appended claims.

The sulphonates prepared according to the above equations may if desired be hydrolyzed with dilute acids to yield the corresponding sulphonic acids.

An alternative method of preparing our new class of compounds is to react cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid or its anhydride with a solution of caustic soda to obtain the disodium salt. This may be sulphonated by reacting with sodium bisulphite to yield a com-

pound having the following structural formula



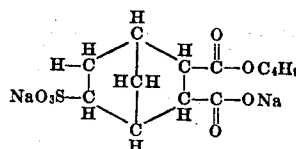
which may be hydrolyzed with dilute acids and then esterified with a desired alcohol to yield the sulphonic acid ester of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid.

Specific examples will now be given to illustrate in greater detail the preparation of esters and half-esters of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid and the subsequent sulphonation procedures using both sulphites and bisulphites. It should be understood that the invention is not limited to these particular examples which are given by way of illustration and not of limitation.

Example 1

16.4 parts of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic anhydride and 81 parts of n-butyl alcohol were heated under a reflux condenser for 4 hours and the unreacted butanol then distilled off. The solid half-ester from this process when washed with n-hexane was found to have an acid number very nearly that of the calculated value.

5.7 parts of the half-ester prepared above was sulphonated by refluxing for 20 hours in 30 parts of water and 47 parts of ethyl alcohol containing 3.1 parts of sodium sulphite. The excess sodium sulphite was filtered off and the solution evaporated to dryness. A white, water-soluble powder was obtained which was believed to be disodium n-butyl cis-endomethylene-3,6-sulpho-4-hydrophthalate with the probable structural formula

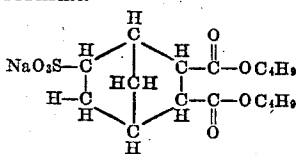


Example 2

33 parts of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic anhydride, 162 parts of n-butyl alcohol and 1 part of toluene sulphonic acid as catalyst were heated in a vessel equipped with a reflux condenser and water collector. When the acid number of the reaction mixture had dropped to a very low value the unreacted butanol was removed by distillation under reduced pressure. The ester was then distilled off. A 95% yield of a pale yellow liquid boiling at 170-175° C. at 5 mm. was obtained. The index of refraction of the liquid was 1.4702 and an analysis showed 68.59% carbon and 8.90% hydrogen.

29.4 parts of the di-n-butyl ester of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic anhydride thus obtained was refluxed for 4 days with 16.5 parts of sodium bisulphite in 30 parts water and 47 parts ethyl alcohol. A clear solution was obtained. This solution upon drying gave a yellow resinous material which was ground to a white, hygroscopic powder analyzing 48.35% carbon, 6.93% hydrogen, and 7.91% sulphur which corresponds closely to the expected values calculated from di-n-butyl-sodium sulpho-4-cis-endometh-

ylene-3,6-hexahydrophthalate of the probable structural formula



Example 3

17.2 parts cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic anhydride, 106 parts active amyl alcohol and 0.25 part H_2SO_4 were heated at about 130–135° C. for 4½ hours, under a reflux condenser fitted with a water collector. At the end of this time the reaction was practically complete as indicated by the acid number of the reaction mixture and the amount of water collected in the water collector. The crude ester-alcohol mixture was washed with dilute Na_2CO_3 followed by water until no longer alkaline and then the water and alcohol were removed by distilling under reduced pressure. An 82% yield of the diamyl ester of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic anhydride was obtained.

11.0 parts of the diamyl ester thus prepared were sulphonated by adding to it 3.3 parts sodium bisulphite in 47 parts ethyl alcohol and 30 parts water and refluxing for 48 hours. A sticky yellowish product of good wetting properties was obtained. On analysis it was found to contain 51.07% carbon, 7.33% hydrogen and 7.14% sulphur which corresponds closely to the expected value calculated from diamyl cis-endomethylene-3,6-sodium sulpho-4-hexahydrophthalate.

Example 4

16.4 parts cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic anhydride and 13 parts 2-ethyl hexyl alcohol were heated together at 130° C. for 2 hours. The reaction mixture was allowed to cool and unreacted anhydride was filtered off. The 2-ethyl hexyl half-ester of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic anhydride was obtained as a yellow oily liquid.

13 parts of the octyl half-ester thus prepared were sulphonated with 7.6 parts sodium bisulphite dissolved in 47 parts ethyl alcohol and 30 parts water by refluxing for 30 hours. Upon removal of the solvent by evaporation disodium mono-octyl cis-endomethylene-3,6-sulpho-4-hexahydrophthalate was obtained.

What we claim is:

1. An ester of sulphonated cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid.
2. An alkyl ester of sulphonated cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid.
3. A dialkyl ester of sulphonated cis-endo-

methylene-3,6- Δ^4 -tetrahydrophthalic acid in which the esterifying alkyl groups contain at least 3 carbon atoms.

4. A monoalkyl ester of sulphonated cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid in which the esterifying alkyl group contains at least 3 carbon atoms.

5. Disodium mono-octyl cis-endomethylene-3,6-sulpho-4-hexahydrophthalate.

- 10 6. Disodium mono-n-butyl cis-endomethylene-3,6-sulpho-4-hexahydrophthalate.

7. Diamyl cis-endomethylene-3,6-sodium sulpho-4-hexahydrophthalate.

8. A process for the production of sulphonated esters of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid which comprises heating esters of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid with a member of the group consisting of water-soluble sulphite and bisulphite salts.

- 20 9. A process for the production of sulphonated alkyl esters of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid which comprises heating alkyl esters of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid with a member of the group consisting of water-soluble sulphite and bisulphite salts.

10. A process for the production of sulphonated dialkyl esters of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid which comprises heating dialkyl esters of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid with a water-soluble bisulphite.

- 30 11. A process for the production of sulphonated monoalkyl esters of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid which comprises heating monoalkyl esters of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid with a water-soluble sulphite.

- 40 12. A process for the production of disodium mono-octyl cis-endomethylene-3,6-sulpho-4-hexahydrophthalate which comprises heating the mono-octyl ester of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid with a water-soluble sodium sulphite.

- 45 13. A process for the production of disodium mono-n-butyl-cis-endomethylene-3,6-sulpho-4-hexahydrophthalate which comprises heating the mono-n-butyl ester of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid with a water-soluble sodium sulphite.

- 50 14. A process for the production of diamyl-cis-endomethylene-3,6-sodium-sulpho-4-hexahydrophthalate which comprises heating the diamyl ester of cis-endomethylene-3,6- Δ^4 -tetrahydrophthalic acid with a water-soluble sodium bisulphite.

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