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2,211,771

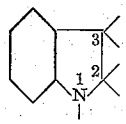
QUATERNARY INDOLE DERIVATIVES AND THEIR MANUFACTURE

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3 Claims. (Cl. 260—319)

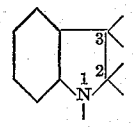
In the specifications Ser. No. 142,284 of May 12, 1937, and Ser. No. 201,423 of April 11, 1938, there is described a method of converting derivatives of the indole series into water-soluble bodies by treating with sulphonating agents, under suitable conditions, compounds of the following general structure:



which contain an aliphatic or alicyclic substituent with more than 5 carbon atoms in position 1 or 2, and which may be substituted in the free positions of the benzene nucleus in any desired manner and in the remaining free positions 1, 2 and 3 by alkyl-, aralkyl- or aryl- groups and may also contain double linkage in the heterocyclic nucleus. These novel sulphonic acids and their salts are used as wetting, dispersing, emulsifying and impregnating agents and as detergents, and in particular may be used as lime soap emulsifying agents.

As a result of further study in this field of indole and hydroindole derivatives it has now been found that new and valuable indoles and hydroindoles are obtained if the water solubility is produced, not by the introduction of sulphonic acid groups, but by means of quaternary N-atoms.

As in the case of the specifications Ser. No. 142,284 of May 12, 1937, and Ser. No. 201,423 of April 11, 1938, the invention starts from the assumption that in the indole body of the general structure



there is an aliphatic or alicyclic substituent containing more than 5 carbon atoms, in the positions 1 or 2. The remaining positions can be substituted in the manner set forth in the specifications Ser. No. 142,284 and Ser. No. 201,423.

As a consequence of the special composition of the new compounds, the method of preparation can be carried out in a large number of ways. The aliphatic or alicyclic radical with more than 5 carbon atoms in position 1 or 2 may be present in the starting material that is converted into the quaternary nitrogen compound, or can be introduced by exhaustive alkylating. Finally, there is the third possibility that both methods be combined, whereby a further, high molecular aliphatic or alicyclic residue containing more than 5 carbon atoms be introduced, during the alkylation, into the positions 1 or 2 of the indole or dihydro-indole body with a radical having more than 5 carbon atoms.

The products obtained in this way may be used as valuable assistants in the textile industry or in other branches of industry in which such assistants are used. A particular property of the new compounds, which may be mentioned by way of example, is that these compounds for the most part form insoluble precipitates with dyes containing acid groups, so that they are suitable for rendering dyeings fast to water. Finally, it is worth while pointing out that a number of the novel products may also be used as plasticizers, as carbonizing, bactericidal and fungicidal agents.

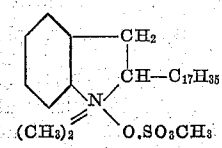
As in the specifications Ser. No. 142,284 and Ser. No. 201,423, indoles or hydroindoles can quite generally be employed as the raw material for the present process, and these can be readily obtained by known methods, inter alia by splitting off water from suitable acylated o-alkyl- or -aralkyl- substituted aniline derivatives with sodium alcoholate (according to Madelung, Ber. d. deutschen chem. Ges. 45, p. 1128), or by means of sodium amide (per Verley, Bull. de la Soc. Chim. vol. 35, pp. 1039–40 (1924) and vol. 37, pp. 189–91 (1925) and German Patent Specification No. 479,283). Other methods of preparing indoles and their substitution products may equally well be employed however.

By catalytic hydrogenation of the indoles, products are obtained which may be regarded as equivalent starting materials to the indoles themselves. Any other known method of producing hydrogenised indoles can, however, be used with equal success.

Example 1

34 gms. of 2-heptadecyl-2:3-dihydroindole, obtained in known manner from 2-heptadecylindole, are dissolved in 100 ccs. of chlorobenzene and 17 gms. of anhydrous sodium carbonate are added. 20 gms. of dimethylsulphate are dropped in at 100° C. and the whole is stirred for 12 hours. Thereupon a further 20 gms. of dimethylsulphate are run in in drops and the whole is kept a further 6 hours at 120° C. Thereafter the soluble portion is filtered off from the undissolved inorganic salts, the chlorobenzene is distilled off by means of steam and the aqueous solution evaporated under a vacuum. A wax-like semi-solid mass is obtained which forms a colourless solution in water.

The product of the reaction between 2-heptadecyl-2:3-dihydroindole and dimethylsulphate corresponds to the following formula



Example 2

34 gms. of 2-heptadecyl-2:3-dihydroindole are dissolved in chlorobenzene and anhydrous sodium carbonate added as in Example 1. 20 gms. of dimethylsulphate are dropped in and the whole stirred for 12 hours. 20 gms. of benzylchloride or also 27 gms. of the bromide of technical dodecyl alcohol are then added in drops and heated to 140° C. for 6 hours. After the salts have been filtered off, the chlorobenzene and excess benzylchloride are removed by steam. The aqueous solution obtained may be etherised and evaporated to the dry state under a vacuum. A final product having similar properties to the product of Example 1 is obtained, and aqueous solutions of the product likewise have a high foaming capacity.

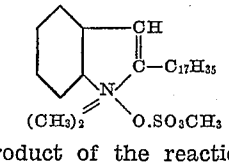
Example 3

34 gms. of 2-heptadecyl-2:3-dihydroindole are dissolved in 100 ccs. chlorobenzene, 17 gms. of anhydrous sodium carbonate added, 20 gms. of dimethylsulphate added in drops at 100° C. and the whole is stirred for 12 hours. 15 gms. of chloracetic ethyl ester are then added gradually and the mixture heated to 140° C. for 6 hours. After the salts separating out have been filtered off, the chlorobenzene is distilled off by means of steam and, where required, the aqueous solution obtained is etherised and evaporated to dryness under a vacuum. A waxy mass, readily soluble in water, is obtained.

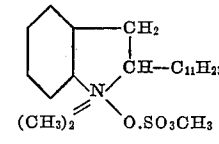
Example 4

34 gms. of 2-heptadecyl-2:3-dihydroindole are, as described in the above example, first treated with 20 gms. of dimethylsulphate at 100° C. for 12 hours, and then 12 gms. of glycerin α-chlorohydrin is added drop by drop and the whole heated 6 hours to 120° C. After the salts have been filtered off, the chlorobenzene is distilled off with steam and, if desired, the aqueous solution is separated from insoluble impurities by filtration. The final product, which is obtained as set forth above, is a viscous oil of good capillary properties.

2-heptadecenyl- or 2-undecyl-2:3-dihydroindole or the numerous other starting materials set out in the specifications Ser. No. 142,284 and Ser. No. 201,423 may be used in place of the heptadecyldihydroindole employed in the above examples. Thus, the product of the reaction between 2-heptadecylindole and dimethylsulphate corresponds to the formula:



while the product of the reaction between 2-undecyldihydroindole and dimethylsulphate corresponds to the formula:



There may be named: The indoles derived from the o-toluidides of stearic, palmitic, oleic acid, hydrogenized codliver oil fatty acid, hydrogenized soya bean fatty acid, palm nut oil fatty acid, coconut fatty acid, naphthenic acid, resin acid, campholic acid, fencholic acid, cyclohexane-carboxylic acid and so on; the corresponding dihydroindoles are obtainable therefrom by known methods of hydrogenation.

Other indoles are obtained by fusion of formyl- or acetyl-N-dodecyl-ortho-toluidines. Instead of the dodecyl radical may be present in the starting materials the residues of olein-alcohol, naphthene-alcohol, terpene-alcohol, cyclo-hexanol and so on. If instead of a formyl- or acetyl-residue there is introduced a phenylacetyl-, phenoxyacetyl- or benzoyl-residue, there will be present in 2-position after the indole ring closure a benzyl-, phenoxymethyl- or phenyl-group. Instead of ortho-toluidine there may be used as parent material ortho-aminoethylbenzene, meta- or paraxylidine, mesidine or other homologues of the ortho-methyl-aminobenzene.

Example 5

44 gms. of ethylene oxide are reacted on 28 gms. of 2-undecyl-2:3-dihydroindole in a closed vessel at 100–120° C. 20 gms. of this reaction product are dissolved in 20 ccs. of toluene and 17 gms. of anhydrous sodium carbonate are added. 20 gms. of dimethyl-sulphate are added in drops at 100° C. and the whole stirred for 12 hours. Thereupon, a further 20 gms. of dimethylsulphate are added in drops and the whole heated at 120° C. for 6 hours. After filtering off the salts the toluene is removed by steam distillation and the aqueous solution obtained is evaporated to dryness under a vacuum. A semi-solid, waxy mass is obtained.

Example 6

34 gms. of 2-heptadecyl-2:3-dihydroindole are chloracetylated by cooking with 15 gms. of chloracetylchloride in benzene, and the acid amide obtained is isolated in known manner.

50 gms. of 2-heptadecyl-2:3-dihydro-N-chloracetoindole is added drop by drop to 150 gms. of a 20.4% aqueous solution of dimethylamine. There is scarcely any increase in temperature of the reaction mixture at first, and this only occurs when the whole of the indole has been added. The reaction mixture is stirred for 24 hours at 60–70° C., and the oil separating out is then removed, for example by etherising.

46 gms. of the 2-heptadecyl-2:3-dihydro-N-dimethyl-amino-acetic acid-indole so obtained are dissolved in 100 ccs. of chlorobenzene and 15 gms. of dimethylsulphate are added to the solution in drops. The whole is then stirred for 12 hours at 100° C. After the chlorobenzene has been distilled off with steam, the aqueous solution obtained may be etherised and evaporated to dryness under a vacuum. A final product having similar properties to the compounds hereinbefore described is obtained.

If, in the above example, an equimolecular quantity of the bromide of technical dodecyl alcohol is used in place of dimethylsulphate, after the same procedure has been followed, a quaternary compound with 2 high molecular aliphatic residues in the molecule is obtained, such compound also having very marked capillary properties.

Example 7

40 gms. of 2-undecyl-2:3-dihydro-N-dimethyl-aminoacetic acid indole are dissolved in 100 ccs. of chlorobenzene and 15 gms. of chloracetic ester added in drops. The whole is stirred for 12 hours at 100° C. The aqueous solution obtained after the chlorobenzene has been distilled off with

steam may be etherised and evaporated to dryness under a vacuum.

Example 8

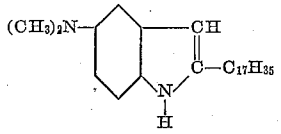
Molecular quantities of 2-dimethyl-aminomethylene-indole (see Annalen d. Chemie 520, pp. 6 et seq.) and the bromide of technical dodecyl alcohol are heated on a water bath until water-soluble. The new quaternary compound is obtained as a semi-solid, waxy mass, solutions of which have good capillary properties.

If instead of the indole mentioned above the corresponding 2:3-dihydroindole (which can easily be obtained by known reducing methods, for instance with tin and hydro-chloric acid) is employed, the process described in the above example will produce a quaternary compound with similar properties.

By using the numerous possible variations of these processes similar compounds can be obtained in an equivalent manner. By way of example, there may be mentioned the compound obtained by reacting 1:2-dimethyl-dihydroindole with the bromide of technical dodecyl alcohol.

Example 9

38 gms. of 5-dimethylamino-2-heptadecylindole



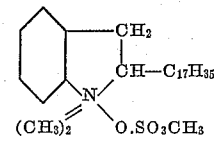
(obtained by fusion of 5-dimethylamino-2-stearoyl-amino-1-methyl-benzene with sodium alcoholate at 280–310° C.) are heated on the water bath with 12.6 gms. of dimethylsulphate until water solubility is reached.

A slightly colored wax-like mass is obtained which is soluble colorless in water, being a softening agent for regenerated cellulose.

The analogous compound containing instead of the heptadecyl radical the residue of palm nut fatty acid, is a very good agent for stripping dyeings.

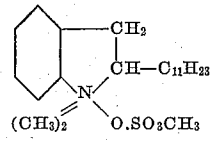
What we claim is:

1. The quaternary dihydro-indole of the following formula



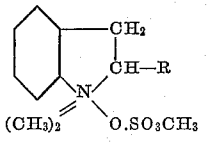
being a wax-like semi-solid mass forming colorless aqueous solutions of high capillary activity.

2. The quaternary dihydro-indole of the following formula



being a wax-like semi-solid mass forming colorless aqueous solutions of high capillary activity.

3. The quaternary indoles selected from the class consisting of the compounds corresponding to the formula



wherein R represents an alkyl group containing more than 5 carbon atoms.

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