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METHOD FOR THE MANUFACTURE OF BASIC SUBSTITUTED CARBOXYLIC ACID AMIDES

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It has been found that valuable basic carboxylic acid amides can be obtained by the reaction of carboxylic acids which contain in the molecule basic nitrogen atoms unbound with hydrogen atoms, or their inner molecular salts or their salts formed with acids or bases, upon organic compounds containing primary or secondary amino-groups in the presence of any water-binding media. The conversion is advantageously accomplished in the presence of an inert diluting agent.

The nitrogen atoms of the aforementioned carboxylic acids may be in the form of tertiary amines or of quaternary ammonium compounds. In both cases the nitrogen atom may also be a component-part of a heterocyclic ring-system. As examples of the former may be mentioned: dimethyl-amino-acetic acid, N-piperidino-acetic acid, the three dimethyl-amino-benzoic acids, the three pyridine-mono-carboxylic acids, the various pyridine-di-carboxylic acids, quinoline-carboxylic acids and others. In the second place the group comprises such compounds as: betaine and its homologues, trimethyl-m- or -p-benz-betaine, as well as the addition products of alkyl- or of aralkyl–halides or of dialkyl-sulfates or aryl-sulfonic acid-alkyl esters on dimethyl-amino-acetic acid and on the other aforesaid carboxylic acids containing a tertiary nitrogen atom.

The amino-compounds suitable for the present method may be of quite varied constitution. All primary and secondary amines of the aliphatic, aromatic, mixed aliphatic-aromatic and heterocyclic series are applicable. The amines may also contain any substituents whatever, provided they do not react or interfere with the conversion in question. In applying amino-compounds, whose mineral acid salts do not hydrolyze or hydrolyze only slightly in water, i. e., such as salts of alkyl-amines or aniline and its homologues, it has proved desirable to accomplish the condensation in the presence of tertiary amines, such as tri-ethyl-amine, dimethyl-aniline or pyridine. The aforesaid tertiary amines may also serve as diluting agents. With particularly low-basic amines, e. g., with diphenyl-amine, p-nitraniline or with the amino-anthraquinones, one can do without such addition.

As dehydrating agents the phosphor-halides and phosphor-oxyhalides as well as thionyl-chloride are primarily to be considered. Though the process of condensing carboxylic acids with amines by means of dehydrating agents is already known, it is, however, new and quite surprising, that carboxylic acids which contain a basic and nitrogen-bearing residue are likewise operable in a condensation process, as indeed it was rather to be expected that by the basic residue the reactivity of the carboxylic acids would be considerably reduced. This applies particularly to betaine and other compounds belonging to the same class and being of a betaine-like structure, which compounds represent "inner salts". The latter as well as their mineral acid-addition products such as betaine-hydrochloride, are practically insoluble in the usual inert diluting agents such as hydrocarbons and halogen-hydrocarbons, nitrobenzene and the like. It is for this reason too that the course of the new condensation-reaction could not be expected.

The technical progress of the present method is evident when in one single operation, starting from the carboxylic acids with either a tertiary or quaternary nitrogen atom, which in many cases are readily obtainable, one directly attains the substituted basic carboxylic acid-amides which are useful in many commercial operations, and which according to the hitherto-known methods could only be obtained by a sequence of various operations.

It is known that betaine is found in considerable amounts in the spent wash of molasses and in the manufacture of beet. Hence sugar the present method is also of a great economic importance due to the fact that in this way the betaine can, for the first time, be utilized in the form of derivatives of high value.

Example 1

185 parts by weight of n-dodecyl-amine are dissolved in 300 parts of pyridine. This solution is added to 3000 parts of toluol, whereupon 117 parts of finely pulverized dry betaine are suspended therein. 125 parts of phosphor-trichloride are then slowly added and the mixture is gradually heated to 110° C. under permanent and vigorous stirring. At this temperature one continues stirring for 3 to 4 hours, then the mixture is cooled down to room-temperature and the crystalline precipitate is sucked off. The latter consists of the N-dodecyl-acetamide-ω-trimethyl-ammonium chloride, which is readily soluble, in water, gives copious lather and cannot be salted out by common salt from this solution, while with potassium-iodide it can be separated in the form of iodide (melting point 176–177° C.) and is readily easily soluble in hot water and with some difficulty in cold water.

The above described compound may advantageously be used for all purposes for which one

hitherto has used quaternary ammonium compounds containing high molecular alkyl-residues, e. g., to render dye on a textile fibre fast to water, or in using it as an auxiliary agent in the reductive drawing off of vat dyeings from the fibre, or as a dispersion agent for greases, oils and waxes in aqueous liquids, or as a flotation-expedient and the like.

Example 2

138 parts by weight of m-nitraniline and 153.5 parts by weight of betaine-hydrochloride are both finely pulverized and suspended in 1500 parts by volume of toluol. To this mixture one adds first 250 parts by weight of pyridine and then gradually 140 parts of phosphor-oxy-chloride. Now the mixture is warmed up to 100–110° C. and at this temperature it is stirred for 4 hours. After cooling down the mixture to 60° C. one adds 1500 parts of water and continues stirring until the separated mass has become flocculent, whereupon one cools the mixture down to room-temperature and filters it. From the aqueous stratum of the filtrate a small part of the reaction-product can be separated by saturating with common salt, but the main part of it is left in the filtering-residue which is dissolved in 2000 parts of hot water. The hot solution is then rendered slightly ammoniacal, filtered from insoluble matters, whereupon the filtrate is cooled down to 0°. The abundantly formed yellowish white separated mass is then filtered off and dried. By saturating this mass with common salt one may obtain an additional amount of the reaction-product from the filtrate. The total yield of acetyl-m-nitraniline-ω-trimethyl-ammonium-chloride (melting point 218° C.) is approximately 80% of the theoretical amount.

In reducing the nitro-group to the amino-group in the well-known way, one obtains a useful intermediate product for the preparation of basic azo-dyestuffs and it is applicable either as a diazo- or as an azo-component. The azo-dyestuffs resulting in the latter case allow a further diazotizing and coupling with azo-components.

Example 3

For the m-nitraniline mentioned in the preceding example one substitutes the same amount of p-nitraniline and continues the process as indicated in Example 2. In the process one obtains a similarly good yield of acetyl-p-nitraniline-ω-trimethyl-ammonium-chloride in the form of brown crystals having a melting point between 214–216° C.

This product also represents a valuable intermediate product for the preparation of basic azo-dyestuffs.

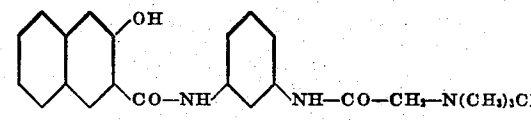
Example 4

223 parts by weight of α-amino-anthraquinone and 170 parts of betaine-hydrochloride in a finely pulverized state are suspended in 3000 parts by volume of nitrobenzene and then 180 parts by weight of thionylchloride are added. The mixture is heated while being stirred whereby, beginning at about 90° C., a reaction will be observed which at 100° C. occurs with a vivid developing of hydrogen chloride and sulfur-dioxide. The thickish mixture changes gradually with the exception of an unimportant suspension into a clear brown solution, which is continuously stirred for 3½ hours at 110–115° C. Then one cools the mixture, neutralizes it with a soda solution, blows off the nitrobenzene by means of water-vapour, whereupon the remaining aqueous solution is filtered while warm and the filtrate is cooled down to 0°. The thus formed acetyl-α-amino anthraquinone-ω-trimethyl-ammonium-chloride (melting point 208–209° C.) is almost entirely precipitated as a yellow microcrystalline powder, which is filtered and dried. The yield amounts to 82–85% of the theoretical amount.

This compound has but little dyestuff-properties. However, if the α-amino-anthraquinone mentioned in the preceding example is substituted by arylized or amino-arylized derivatives of the 1,4 or of the 1,5 diamino-anthraquinone, e. g., by the 1-amino-4-phenylamino-anthraquinone or by the 1,4-di-(4',4''-aminophenyl-) amino-anthraquinone, one obtains very good basic dyestuffs which are fast to light. In these cases it is advisable to add to the reaction-mixture a tertiary base as indicated in the preceding examples.

Example 5

278 parts by weight of 2,3-hydroxy-naphthoic acid-3'-amino-anilide and 153.5 parts of betaine-hydrochloride are suspended in 3000 parts of toluol. Now one adds 125 parts of phosphortrichloride and then gradually 250 parts of pyridine. While stirring one slowly heats the mixture until the toluol begins to boil and allows the mixture to boil for 2 hours under reflux. Then one cools the mixture down to 60° C., whereupon one adds 3000 parts of water. When the mixture has reached room-temperature, it is finally filtered. The residue is digested at 90–100° C. with 4000 parts of water for quite a period of time simultaneously with an addition of just enough soda to cause the disappearing of the Congo-acid reaction, and then the hot brownish solution is poured off from the parts left undissolved. By cooling in ice the condensation product separates itself amorphously. It is filtered and dried at 80° C. According to its way of formation and to its properties the constitution-formula of the thus obtained product is as follows:

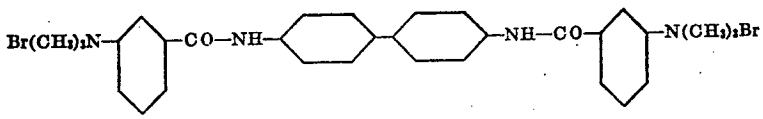


This condensation product may serve as an azo-component in the preparation of basic azo-dyestuffs according to the method of the French Patent 768,263 or as a developer for direct dyeings diazotized on the fibre according to the method of the French Patent 778,608. Finally the cellulose fibre may also be treated with a solution of this product and one is in a position to obtain development-dyeings by an after-treatment of the thus treated fibre, with diazonium-compounds which, according to the French Patent 778,608, may also contain sulfo- or carboxyl groups.

Example 6

92 parts by weight of benzidine and 213.5 parts of trimethyl-m-benzbetaine-hydrochloride (trimethyl-(m-carboxyphenyl-) ammonium-chloride) are suspended in 2000 parts of xylol. Then 180 parts of phosphor-tribromide are stirred in and then one adds gradually 300 parts of triethylamine, whereupon the mixture is slowly heated up to 100° C. while continuously stirring. The temperature is kept at this point for 4 hours; then the mass is cooled down, mixed with 3000 parts of water and filtered. The residue is treated with a large amount of boiling water; the solution is filtered while hot and the filtrate is

cooled down, whereby the condensation-product is almost completely separated off in the form of the bromide. Its constitution formula is most probably as follows:



The reaction-product has a pronounced affinity to the cellulose fibre and may serve as a textile assistant in producing water- and washing-fast fixation of acid substantive dyestuffs on the cellulose fibre according to the French Patent 758,199, i. e., in treating it with the aqueous solution of the above compound by the double bath-process, either before or after the dyeing with the acid substantive dyestuff.

Example 7

165 parts by weight of N-piperidino-acetic acid sodium in a finely pulverized form are introduced into 1500 parts by volume of monochlorobenzene; then one adds 93 parts by weight of aniline, 250 of pyridine, and then finally stirs in 125 parts of phosphor-trichloride gradually. Now one heats the mixture to 110° C. and at this temperature continues stirring for 3 hours, whereupon the mixture is cooled. It is then diluted with 1000 parts of water and rendered litmus-neutral, whereupon any volatile matters are blown off by water-vapour. When the product has grown cold it is filtered off and the residue is dissolved in 2500 parts of boiling water after an addition of just enough hydrochloric acid to attain a slight Congo-acid reaction of the liquid. Now the mixture is filtered from the insoluble resinous residue and the filtrate is cooled in ice after an addition of 700 parts of common salt, whereby the reaction-product (which will be of the formula of a ω-piperidino-acetanilide) is separated as chlorohydrate in the form of small colourless leaves. The precipitate is filtered and dried, its melting point being 180 to 181° C.

Example 8

123 parts by weight of picolinic acid and 138 parts of p-nitraniline are finely pulverized and suspended in 1500 parts by volume of nitrobenzene, whereupon 175 weight-parts of thionyl-chloride are stirred in. Now the mixture is heated for about 4 hours, while being stirred up to 105 to 110° C. until the development of gas, which begins at about 80° C., is finished. When the reaction mass has grown cold the light powdery residue is filtered off, the sticky nitrobenzene is washed out with cold alcohol and then it is dried at 90–100° C. The yield of raw picoloyl-p-nitraniline (picolinic acid-p-nitranilide) is 92% of the theoretical amount. The product can be purified by re-crystallizing from a large amount of boiling pyridine. By heating it carbonizes at approximately 300° C. without melting.

By the reduction of the nitro-group to the amino-group one comes to the picoloyl-p-phenylene-diamine (picolinic acid-p-amino-anilide) which forms a valuable diazo-component for the preparation of substantive azo-dyestuffs.

I claim:

1. Method for the manufacture of basic substituted carboxylic acid amides comprising the condensation of carboxylic acids containing basic nitrogen atoms unbound with hydrogen atoms with amines containing at least one hydrogen atom on the nitrogen atom in the presence of water-binding agents.

2. Method for the manufacture of basic substituted carboxylic acid amides comprising the condensation of carboxylic acids containing basic groups selected from the group consisting of tertiary amino groups and quaternary ammonium groups and amines containing at least one hydrogen atom on the nitrogen atom in the presence of water-binding agents.

3. Method for the manufacture of basic substituted carboxylic acid amides comprising the condensation of carboxylic acids containing basic nitrogen atoms unbound with hydrogen atoms with organic amino compounds of the group consisting of primary and secondary amines of the aliphatic, aromatic, aliphatic-aromatic and heterocyclic series in the presence of water-binding agents.

4. Method for the manufacture of basic substituted carboxylic acid amides comprising the condensation of carboxylic acids containing basic nitrogen atoms unbound with hydrogen atoms with substituted organic amino compounds of the group consisting of primary and secondary amines of the aliphatic, aromatic, aliphatic-aromatic and heterocyclic series in the presence of water-binding agents.

5. Method for the manufacture of basic substituted carboxylic acid amides comprising the condensation of carboxylic acids containing tertiary amino groups of the group consisting of dialkyl-amino-acetic acids, N-piperidino-acetic acid, the three dimethyl-amino-benzoic acids, the three pyridine-mono-carbonic acids, the pyridine-dicarboxylic acids, the quinoline-carboxylic acids with amines containing at least one hydrogen atom on the nitrogen atom in the presence of water-binding agents.

6. Method for the manufacture of basic substituted carboxylic acid amides comprising the condensation of carboxylic acids containing quaternary ammonium groups of the group consisting of betaine and its homologues, trimethyl-m-benzbetaine, trimethyl-p-benzbetaine, addition products of alkyl-halides, aralkyl-halides, dialkyl-sulfates, aryl-sulfonic acid-alkyl-esters on di-alkyl-amino-acetic acids with amines containing at least one hydrogen atom on the nitrogen atom in the presence of water-binding agents.

7. Method for the manufacture of basic substituted carboxylic acid amides comprising the condensation of carboxylic acids containing basic nitrogen atoms unbound with hydrogen atoms and amines containing at least one hydrogen atom on the nitrogen atom in the presence of water-binding agents and in the presence of tertiary amines.

8. Method for the manufacture of basic substituted carboxylic acid amides comprising the condensation of salts of the carboxylic acids containing basic nitrogen atoms unbound with hydrogen atoms of the group consisting of salts formed with acids, salts formed with bases and inner molecular salts with amines containing at least one hydrogen atom on the nitrogen atom in the presence of water-binding agents.

9. Condensation products of carboxylic acids containing basic nitrogen atoms unbound with

hydrogen atoms, and amines containing at least one hydrogen atom and a hydrocarbon radical of at least 6 carbon atoms on the nitrogen atom.

10. Condensation products of carboxylic acids containing basic groups of the class consisting of tertiary amino groups and quaternary ammonium groups, and amines containing at least one hydrogen atom and a hydrocarbon radical of at least 6 carbon atoms on the nitrogen atom.

11. Condensation products of carboxylic acids containing basic nitrogen atoms unbound with hydrogen atoms, and organic amino compounds of the group consisting of primary and secondary amines of the aliphatic, aromatic, aliphatic-aromatic and heterocyclic series having a radical attached to the amine nitrogen atom containing at least 6 carbon atoms.

12. Condensation products of carboxylic acids containing basic nitrogen atoms unbound with hydrogen atoms, and substituted organic amino compounds of the group consisting of primary and secondary amines of the aliphatic, aromatic, aliphatic-aromatic and heterocyclic series having a radical attached to the amine nitrogen atom containing at least 6 carbon atoms.

13. A new compound, N-dodecyl-acetamide-ω-trimethyl-ammonium chloride.

14. A new compound, acetyl-p-nitraniline-ω-trimethyl-ammonium chloride.

15. Acetyl-α-amino-anthraquinone-ω-trimethyl-ammonium chloride.

16. The process of producing basic substituted carboxylic acid amides comprising the step of condensing carboxylic acids containing basic nitrogen atoms unbound with hydrogen atoms with amines containing at least one hydrogen atom and a hydrocarbon radical of at least 6 carbon atoms, in the presence of a water-binding agent.

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CERTIFICATE OF CORRECTION.

Patent No. 2,186,769. January 9, 1940.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 28, strike out the word "sugar" and insert the same after "beet" and before the period in same line; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of March, A. D. 1940.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)