Patented Sept. 24, 1940

2,215,861

UNITED STATES PATENT OFFICE

2,215,861

MANUFACTURE OF IMIDAZOLINES

Edmund Waldmann, Klosterneuburg, and August Chwala, Vienna, Germany, assignors, by mesne assignments, to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application March 22, 1939, Serial No. 263,393. In Austria April 4, 1936

8 Claims. (Cl. 260—309)

This application is a continuation-in-part of application Serial No. 94,120, filed August 3, 1936.

This invention relates to the manufacture of imidazolines containing aliphatic radicals of high molecular weight as substituents at the 2-carbon atom by heating with a fatty acid or a carboxylic acid of high molecular weight to high temperatures, preferably to temperatures lying between 200 and 300° C., a mixture consisting on the one hand of a base having a primary amino-group and a second primary or secondary amino-group, which are in 1:2-position to each other, the two carbon atoms in 1:2 position being linked by a single bond, and on the other hand a salt of such base formed from a strong acid.

Suitable bases having a primary amino-group and a second primary or secondary amino-group in 1:2-position to each other are ethylenediamine; products such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine; homologues of ethylenediamine such as 1:2-propylenediamine, 2:3-butylenediamine, N-methylethylenediamine.

Suitable strong acids for forming the salts are in particular mineral acids, such as hydrochloric acid, hydrobromic acid, sulfuric acid, and the like.

Suitable fatty acids of high molecular weight are in general aliphatic acids containing more than 8 carbon atoms, for instance caprylic acid, lauric acid, stearic acid, palmitic acid, oleic acid, also mixtures of these acids obtainable by saponifying natural fats like olive oil, tallow, palm oil; also cycloaliphatic acids such as naphthenic acids and the like.

Instead of the fatty acids there may be used suitable derivatives thereof such as esters, amides, anhydrides or halides; according to the selection of the derivative to be used, the simultaneous use of the free base or the salt of the base may, if desired, be omitted, for in the case of halides the suitable mixtures leading to the desired result are formed, due to the mineral acid becoming free, in the course of the acylation.

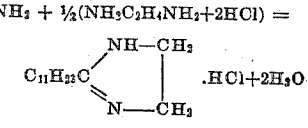
Quite generally, the new process consists in heating with a product selected from the group consisting of fatty acids of high molecular weight and the salts, amides, halides and esters thereof, a mixture consisting on the one hand of a base which is substituted at two carbon atoms adjacent to each other by an amino-group each, of which amino-groups one contains two hydrogen atoms and the other at least one hydrogen atom, and on the other hand of a salt of such base with a strong acid, the heating being carried out at a high temperature.

The procedure may also be such that first of all the salt of the mono-acyl compound is prepared. The process then consists in heating to a high temperature a salt formed from a strong acid and such a diamine mono-acylated with a fatty acid of high molecular weight, in which the two amino groups are bound to two carbon atoms adjacent to each other, one of which amino groups containing two hydrogen atoms and the other at least one hydrogen atom.

In the preferred mode of operating, the mixture made in accordance with the invention is heated to a temperature of 250–290° C. If, for example, there is used a quantity of lauric acid, ethylenediamine and ethylenediaminehydrochloride the hydrochloride which forms a sediment dissolves very quickly in this interval of temperature, even with only gentle stirring, and at the same time causes formation of the undecylimidazolinehydrochloride. This reaction may also be conducted at a temperature lower than 250° C. by heating for a longer period. The use of a vacuum during the second half of the condensation is useful.

When the condensation to the imidazoline derivative starts from a mixture of fatty acid amine and amine-hydrochloride, the three components of the mixture are advantageously selected so that for 1 mole of the fatty acid or its derivative there are at least 1 mole of the diamine and the salt-like bound mineral acid. In using 1 mole of lauric acid therefore, there should be ½ mole ethylenediamine and ½ mole ethylenediaminehydrochloride, corresponding with the equation

$$C_{11}H_{23}CO_2H + \tfrac{1}{2}NH_2C_2H_4NH_2 + \tfrac{1}{2}(NH_2C_2H_4NH_2{+}2HCl) =$$

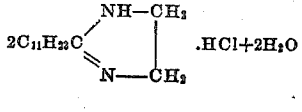


$$.HCl{+}2H_2O$$

and there is obtained the hydrochloride of undecylimidazoline.

If as the lauric acid derivative there is chosen the dilauroylethylenediamine which for one mole of lauric acid already contains ½ mole of ethylenediamine in a bound state, and 1 mole of this diacyl-body is heated with 1 mole of ethylenediaminehydrochloride at about 250–290° C. there is obtained the reaction in the sense of the following equation:

$$C_{11}H_{23}CONHC_2H_4NHCOC_{11}H_{23} + NH_2C_2H_4NH_2.2HCl =$$



$$.HCl{+}2H_2O$$

the product being again undecylimidazolinehydrochloride in approximately quantitative yield.

If, however, the parent material is the monolauroylethylenediaminehydrochloride which already contains in itself per 1 mole fatty acid 1 mole of ethylenediamine and 1 mole of hydrochloric acid, it suffices to heat this hydrochloride by itself to about 250–300° C. in order to obtain an excellent yield of the hydrochloride of undecylimidazoline. This reaction can also be carried out with the other mono-acylderivatives which are obtained from the diamines and the fatty acids of high molecular weight mentioned in paragraphs 2 and 4 of this specification.

Under the effect of the amine salt, particularly the hydrochloride, one finds at comparatively high temperature of reaction evidently an elimination of the acid amide at first formed (as may be seen particularly clearly from the example of dilauroylethylenediamine) and then a combination of the eliminated material directly to the imidazoline hydrochloride. Philipps (Journal of the Chemical Society of London, 1928, page 2393 and following; Chemisches Zentralblatt 1928, vol. 2, page 2466) is of opinion that the formation of benzimidazoles or imidazolines from the acyl-derivatives of the corresponding diamines by boiling with hydrochloric acid occurs of itself in such a manner that the acid amide is first saponified and the eliminated portion united directly to the benzimidazol or imidazoline.

These imidazolines of high molecular weight in the form of their salts are freely soluble in water; solutions foam and have good capillary active properties. They may be used with advantage for improving dyeings on vegetable fibers.

Sulfo-groups may be introduced in their molecules by the methods which have become known from French Specification No. 796,917. These imidazoline-sulfonates of high molecular weight are also valuable as wetting, foaming, washing, emulsifying and dispersing agents. They are valuable as assistants in the textile industry.

The following examples illustrate the invention, the parts being by weight:

Example 1

Into a stirring vessel provided with a thermometer and an inverted condenser there are charged 284 parts of stearic acid, 93 parts of ethylenediaminehydrochloride, 56 parts of ethylenediaminehydrate. The mixture is heated while stirring to 120° C. and the temperature is raised within 90 minutes to 185° C., whereby between 170 and 185° C. a small proportion of a clear liquid distils (ethylenediaminehydrate and water). The mixture is now heated within 30 minutes to 230° C. and then within 15 minutes to 290° C. The mass is kept for a short time at this temperature, which may be raised to 300° C. until a sample of the mass, tested with water, shows that it is soluble in water to a clear solution; the heating is then interrupted and the mass cooled. The brownish mass, which is crystalline when cold, consists almost exclusively of heptadecylimidazolinehydrochloride.

A free base may be separated in known manner by dissolving the hydrochloride with water and liberating the base with an alkali-hydroxide which can then be directly filtered or extracted by means of benzene. For further purification the product may be crystallized from a mixture of 3 parts of methyl alcohol and 1 part of water, whereby 2-heptadecylimidazoline is obtained in crystalline scales melting at 94–95° C.

Example 2

In an apparatus such as is described in Example 1 there is heated a mixture of 130 parts of lauric acid, 40 parts of ethylenediaminehydrate, 60 parts of ethylenediaminehydrochloride in manner described in the same example. As soon as a sample of the mass is clearly soluble in water, the heating is interrupted. On cooling, the mass solidifies in crystalline form; it consists of 2-undecylimidazolinehydrochloride. The base liberated in the usual manner from this salt may be purified by recrystallization from alcohol of 50 per cent. strength, whereby it is obtained in the form of colorless laminae which melt at 82° C.

Example 3

In an apparatus such as is described in Example 1 there is heated to 180° C. a mixture of 140 parts of oleic acid, 15 parts of ethylenediaminehydrate; the mass which at first is somewhat foamy boils finally gently as soon as the water has been distilled. After cooling to 120° C. there are added another 15 parts of ethylenediaminehydrate and heating is renewed to 180° C. 37.5 parts of ethylenediaminehydrochloride are now added, whereupon the temperature of the mass is raised to 280° C. within 15 minutes and kept there for 10 minutes. The mass is then allowed to cool to 120° C., another 10 parts of ethylenediaminehydrate are added, and the mixture is heated within 20 minutes to about 300° C. and kept at this temperature until a sample dissolves clearly in water, whereupon the heating is immediately interrupted.

In this manner there is obtained the 2-heptadecenylimidazolinehydrochloride in the form of a semi-solid brownish mass which dissolves clearly in water with the formation of a strongly foaming solution from which the base may be isolated in the usual manner.

Example 4

10 parts of oleic acid ethylester, 2 parts of ethylenediaminehydrate, 3 parts of ethylenediaminehydrochloride are heated together in the manner described in Example 1, save that the temperature of the mass for the saponification of the ester is allowed to remain for some time (about 5–10 minutes) at 120–130° C. The aqueous solution of the heptadecenylimidazolinehydrochloride is treated with some active carbon and the free base is liberated by means of caustic soda; it is obtained in very good yield.

Example 5

8.5 parts of N-N-di-lauroylethylenediamide are heated with 3.3 parts of ethylenediaminehydrochloride in an open flask, while stirring, in such a manner that after 5–10 minutes the mixture has a temperature of about 270–280° C. The heating is continued for another 10 minutes to 280–290° C., whereby the greater quantity of the hydrochloride passes into solution. A sample then dissolves clearly in water.

Caustic soda solution precipitates from the aqueous solution the undecylimidazoline which is the product of reaction in approximately quantitative yield.

Example 6

10 parts of mono-lauroylethylenediamine-hydrochloride are heated for 5–10 minutes to 260–280° C. and then for a further 5–10 minutes to 285–295° C. The hydrochloride of the

undecylimidazoline is thus formed. A similar result is obtained by substituting the corresponding hydrobromide or sulfate for the mono-lauroylethylene-diamine-hydrochloride or by using instead of the mono-lauroylethylene-diamine-hydrochloride a derivative acylated with another fatty acid of high molecular weight, such as for example the mono-stearoyl-, the mono-oleoyl-, the mono-palmitoyl-, the mono-caprylyl-ethylenediamine-hydrochloride, or finally by using the corresponding 1.2-propylenediamine or 2.3-butylenediamine derivatives.

Example 7

21.4 grams of lauric acid methyl ester in admixture with 5 grams of ethylenediaminehydrate and 7 grams of ethylenediaminedihydrochloride are gradually heated to 180° C. After distilling about 3 grams of water the reaction mass first foaming reacts more calmly. It is further heated to 280° C. until the melt dissolves clearly in water. The heating is then stopped and after cooling to about 150° C. the melt is poured out.

The undecyl-Δ_2-imidazolinehydrochloride is a light brown semi-solid mass which dissolves clearly in water with formation of foam. From an aqueous or alcoholic solution the base may readily be set free by means of alkalies.

We claim:

1. Process for the manufacture of 2-substituted imidazolines which comprises reacting one mol of a product selected from the group consisting of the fatty acid esters and naphthenic acid esters with half a mol of a base which is substituted at two carbon atoms adjacent to each other and linked by a single bond by an amino group each, of which amino groups one contains two hydrogen atoms and the other at least one hydrogen atom, and with half a mol of a salt of such a base with a strong acid, the reaction being carried out at a high temperature.

2. Process for the manufacture of 2-substituted imidazolines which comprises reacting one mol of a product selected from the group consisting of the fatty acid esters and naphthenic acid esters with half a mol of a base which is substituted at two carbon atoms adjacent to each other and linked by a single bond by an amino group each, of which amino groups one contains two hydrogen atoms and the other at least one hydrogen atom, and with half a mol of a salt of such a base with a strong acid, the reaction being carried out at a high temperature while using an excess of the free base.

3. Process for the manufacture of 2-substituted imidazolines which comprises reacting one mol of a product selected from the group consisting of the fatty acid esters and naphthenic acid esters with half a mol of a base which is substituted at two carbon atoms adjacent to each other and linked by a single bond by an amino group each, of which amino groups one contains two hydrogen atoms and the other at least one hydrogen atom, and with half a mol of a salt of such a base with a strong acid, the reaction being carried out at a high temperature while using an excess of the salt of the base with a strong acid.

4. Process for the manufacture of 2-substituted imidazolines which comprises reacting one mol of a product selected from the group consisting of the fatty acid esters and naphthenic acid esters with half a mol of a base which is substituted at two carbon atoms adjacent to each other and linked by a single bond by an amino group each, of which amino groups one contains two hydrogen atoms and the other at least one hydrogen atom, and with half a mol of a salt of such a base with a strong acid, the reaction being carried out at a high temperature while using an excess of the free base and the salt of the base with a strong acid.

5. Process for the manufacture of 2-substituted imidazolines which comprises reacting one mol of a product selected from the group consisting of the fatty acid esters and naphthenic acid esters with half a mol of a base which is substituted at two carbon atoms adjacent to each other and linked by a single bond by an amino group each, of which amino groups one contains two hydrogen atoms and the other at least one hydrogen atom, and with half a mol of a salt of such a base with a strong acid, the reaction being carried out at temperatures lying between 200° C. and 300° C.

6. Process for the manufacture of 2-substituted imidazolines which comprises reacting one mol of a product selected from the group consisting of the esters of fatty acids containing 10 to 18 carbon atoms with half a mol of a base which is substituted at two carbon atoms adjacent to each other and linked by a single bond by an amino group each, of which amino groups one contains two hydrogen atoms and the other at least one hydrogen atom, and with half a mol of a salt of such a base with a strong acid, the reaction being otherwise carried out at a high temperature.

7. Process for the manufacture of 2-substituted imidazolines which comprises reacting one mol of a product selected from the group consisting of the esters of fatty acids containing 10 to 18 carbon atoms with half a mol of ethylene diamine and half a mol of a salt of ethylene diamine with a strong acid, the reaction being carried out at temperatures lying between 200° C. and 300° C.

8. Process for the manufacture of 2-substituted imidazolines which comprises reacting one mol of a produce selected from the group consisting of the esters of fatty acids containing 10 to 18 carbon atoms with half a mol of ethylene diamine and half a mol of ethylene diamine hydrochloride, the reaction being carried out at temperatures lying between 200° C. and 300° C.

EDMUND WALDMANN.
AUGUST CHWALA.