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CONDENSATION PRODUCTS AND A PROCESS OF PREPARING THEM

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The present invention relates to condensation products and to a process of preparing them and it especially relates to sulfonic acid derivatives.

We have found that valuable condensation products may be obtained by reacting products containing sulfur, oxygen and chlorine, formed by the simultaneous action of chlorine and sulfur dioxide on saturated aliphatic hydrocarbons, with hydroxy-amines eontaining at least one reactive hydrogen atom at the nitrogen atom. The new condensation products have the general formula

$$R—SO_2—X$$

wherein $R—SO_2$ means the radical of a sulfochloride obtained by the simultaneous action of chlorine and sulfur dioxide on saturated aliphatic hydrocarbons and X stands for the radical of a hydroxy amine having at least one hydrogen atom bound to nitrogen.

By the simultaneous action of chlorine and sulfur dioxide on saturated aliphatic hydrocarbons, particularly with the simultaneous action of active rays of light and, if required, while applying catalysts, compounds are produced having the character of sulfonic acid halides.

As hydroxy amines containing at least one reactive hydrogen atom at the nitrogen atom, such products may be named as contain one or several hydroxy groups besides a primary or secondary amino group, or such products as contain several amino groups and one or several hydroxy groups in the molecule, e. g. ethanolamine, diethanolamine, the reaction products of glycide on primary amines, propanolamine-1.2, methylethanolamine, phenylethanolamine, cyclohexylethanolamine, naphthyl-ethanolamine, benzylethanolamine, dodecylethanolamine, furthermore aminodihydroxypropane, aminotrimethylolmethane prepared from nitromethane and 3 mols of formaldehyde and reduction of the nitro-trimethylolmethane produced; furthermore glucamine, methylglucamine, ethanol-glucamine, phenylglucamine or 1.3-methylaminopropanol.

According to the conditions applied in the reaction compounds constituted in an acid-amide-like and/or an ester-like manner may be obtained. The reaction may, for instance, be effected by stirring together the anhydrous starting materials; for binding the hydrogen chloride formed the hydroxyamine itself or another acid-binding agent may be used. If the hydroxyamine is applied in excess chiefly amide-like compounds are formed, whereas mainly basic, ester-like products are obtained if molecular proportions of the hydroxyamine and another acid-binding agent are used.

The ester-like products are readily saponifiable and, insofar as they contain free amino-groups, they are readily transformed on heating into the ammonium salts of the corresponding sulfonic acids.

As acid-binding agents there may, for instance, be used tertiary bases, such as pyridine, triethylamine, dimethylaniline; furthermore alkali hydroxides or alkali carbonates; in that case, however, a partial saponification of the sulfochloride sets in, owing to the formation of water. The reaction is best performed in the cold or at a slightly raised temperature; it may also be carried out in an indifferent solvent, such as benzine, benzene, carbon-tetrachioride, dioxane, or the like.

The products obtained according to the process herein described are more or less viscous oils or solid, sometimes crystalline bodies. They are suitable for instance as softening agents for plastic masses and for finishing textile materials, furthermore as intermediate products for the manufacture of adjuvants for the textile industry.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts being by weight:

(1) A solution of 71 parts of propane sulfochloride (obtained by the action of sulfur dioxide and chlorine on a solution of propane in carbontetrachloride with the simultaneous action of short-wave light) in 80 parts of dioxane is added at a temperature of 5° C–10° C in the course of about two hours; while well stirring, to 91 parts of anhydrous monocthanolamine. After stirring has been continued for two hours at 20° C the mixture is neutralized with alcoholic hydrochloric acid. From the consumption of hydrochloric acid there is calculated that 1.95 to 1.99 mols of base have been consumed per 1 mol of sulfochloride, i. e. that sulfonic acid ethanolamide is obtained in a yield of 95 to 99 per cent of the theoretical yield. After the distillation of the solvent, suitably under a reduced pressure, the product is mixed with 150 parts of acetonitrile, the ethanolamine-hydrochloride is filtered with suction and subsequently washed with a small quantity of acetonitrile. After the solvent has been distilled under reduced pressure, the propane-sulfonic acid ethanol amide is obtained from the filtrate in the form of a light brown, viscous oil which very readily dissolves in water, alcohols and esters and sparingly dissolves in hydrocarbons, chlorinated hydrocarbons and ether.

If only 61 parts of ethanolamine are used instead of 91 parts and if otherwise the process is effected as described above; about 18 per cent of an esterlike condensation product are obtained besides about 82 per cent of an amide-like condensation product.

(2) 71 parts of propane sulfochloride are added in the course of two hours, at a temperature between 5° C and 10° C, while well stirring, to an

anhydrous mixture of 31 parts of ethanolamine and 48 parts of dimethylaniline. After about two hours the content of non-consumed base is ascertained by titration in a test portion. Per 1 mol of sulfochloride a consumption of 1 mol of base is found, i. e. sulfonic acid ester has been substantially completely been formed. After a dilution with benzene and a filtration with suction the hydrochloride of the ethanolaminopropanol-sulfonic acid ester is obtained in the form of hygroscopic crystals.

(3) 71 parts of propane-sulfochloride are caused to run in the course of two hours, while well stirring and cooling with ice, into 112 parts of anhydrous methylethanolamine. The yield of propane-sulfonic acid methylethanol amide, calculated as described in example 1, amounts to 94 per cent of the theoretical yield. The propane-sulfanic acid methylethanolamide mixed with the hydrochloride of the methylethanolamine is obtained in the form of a honey-like oil which is very readily soluble in water, alcohol and acetonitrile and is substantially insoluble in hydrocarbons, chlorinated hydrocarbons, ether and dioxane.

If 160 parts of diethanolamine are used instead of 112 parts of methylethanolamine, the propane-sulfonic acid diethanolamide is obtained in a yield of 90 per cent of the theoretical yield.

(4) 100 parts of a product containing 11.76 per cent of a hydrolysable chlorine are caused to run in the course of 2–3 hours, at a temperature between 5° C and 10° C, while well stirring, into 80 parts of anhydrous ethanolamine. The product named was obtained by the action of sulfur dioxide and chlorine, with the simultaneous action of short-wave light, on a mixture of hydrocarbons boiling between 240° C and 340° C formed by hydrogenation of carbon monoxide without application of pressure, and separation of the unaltered portion of hydrocarbons by means of sulfur dioxide. After the whole has been stirred for about 3 hours at room temperature, the consumption of base is ascertained as described in example 1. It is proved that sulfonic acid ethanolamide has substantially completely been formed.

The mixture of reaction may be worked up as follows: By the introduction of gaseous hydrochloric acid the ethanolamine is completely transformed into the hydrochloride and, suitably after the addition of benzene, it may substantially completely be separated by filtration and may be washed with benzene. The benzene is removed from the filtrate by distillation. Otherwise there may also be added to the mixture a quantity of concentrated alkali lye equivalent to that of hydrolyzable chlorine and the ethanolamine together with small portions of hydrocarbons may be driven off suitably under reduced pressure. The alkali chloride may be readily separated by filtration. By both methods the sulfonic acid ethanol amide is obtained in the form of a viscous, light-brown oil which is soluble in about 2N-caustic soda solution and most organic solvents to form a clear solution. It is readily emulsifiable in water.

(5) 324 parts of a product containing chlorine, oxygen and sulfur in an approximately molecular proportion of 1:2:1, obtained by the action of chlorine and sulfur dioxide on hexadecane, while simultaneous subjecting the reaction mixture to the action of ultraviolet rays, the dissolved in 400 parts of benzene and the solution is caused to run at room temperature, while stirring, into 135 parts of ethanol amine. The mixture is then heated for 2 hours to 60° C–70° C. After cooling the solution is washed with a solution of sodium sulfate of 5 per cent strength. The benzene solution is dried with sodium sulfate, filtered and the benzene is removed by distillation. There are obtained 250 parts of a clear, feebly yellow oil. The product chiefly consists of sulfamide-like condensation products and is soluble in 2N-caustic soda solution.

(6) 310 parts of a product containing chlorine, oxygen and sulfur in an approximately molecular proportion of 1:2:1, obtained by the action of chlorine and sulfur dioxide on a saturated hydrocarbon fraction boiling between 240° C and 340° C and obtained by the reduction of carbon monoxide without application of pressure, are mixed at about 20° C—30° C, while cooling, with 320 parts of diethanolamine. The mixture is further stirred for 2 hours at 20° C—30° C. The product is freed by washing it with a sodium sulfate solution of 20 per cent strength from the diethanolamine hydrochloride which has precipitated. After drying a feebly brownish, viscous oil is obtained which chiefly consists of sulfonamides.

(7) 349 parts of a product containing chlorine, oxygen and sulfur and obtained by the action of chlorine and sulfur dioxide on paraffine having a molecular weight of 251, are dissolved in 500 parts of carbon tetrachloride. The solution is caused to run into 140 parts of phenyl-ethanolamine saturated with ammonia, the ammonia being passed through the mixture. When the reaction is complete the mixture is separated by filtration from the ammonium chloride which has precipitated and the solvent is removed by distillation. There is obtained a brown, viscous mass which chiefly consists of the basic sulfonic acid ester.

(8) 27 parts of N-dodecansulfochloride obtained by the action of sulfur dioxide and chloride on n-dodecane while simultaneously subjecting the product to the action of ultraviolet rays, are slowly introduced, at room temperature, into a solution of 23 parts of methyl-glucamine in 1000 parts by volume of pyridine. The whole is subsequently stirred for about 1 hour at 40° C.–45° C. When a test portion dissolves in water to a clear solution, the pyridine is distilled, suitably under reduced pressure. The residue is taken up with a small quantity of hot water, mixed with 6 parts of calcined sodium carbonate and evaporated. The residual pyridine escapes during said operation and the condensation product is obtained in the form of a viscous solid mass, still containing sodium chloride. The condensation product may be purified by extraction from the crude product with an organic solvent, such as benzene, acetone or methylene chloride. The condensation product dissolves in water to form clear, strongly foaming solutions. The crude product consists of a mixture of sulfonic acid esters and sulfonic acid amides and may also contain methylglucamine-dodecane-sulfonate.

If, instead of 27 parts of n-dodecane-sulfochloride, 35 parts of octadecane-sulfochloride are used, obtained from n-octadekane by means of chlorine and sulfur dioxide, and if the process is otherwise carried through as described above, a condensation product of quite similar properties is obtained.

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