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PROCESS OF PREPARING CYCLIC CARBOXYLIC ACIDS SUBSTITUTED IN THE NUCLEUS

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The present invention relates to a process of preparing cyclic carboxylic acids substituted in the nucleus.

We have found that cyclic carboxylic acids substituted in the nucleus are obtainable by causing aliphatic or cycloaliphatic olefines, alcohols or halogenated hydrocarbon compounds to act, in the presence of condensing agents, upon carboxylic acids of the following general formula: A—X—R_1—COOH wherein A represents a mono- or a polynuclear aromatic hydrocarbon radical which may also be substituted, X stands for oxygen or sulfur and R_1 stands for an aliphatic hydrocarbon radical the carbon chain of which may be interrupted once or several times by oxygen.

Carboxylic acids of the above-indicated formula are, for instance: phenoxy-acetic acid, phenoxyethoxy-acetic acid and their homologues having the following constitution:

$$C_6H_5O(CH_2CH_2O)_nCH_2COOH$$

n being 2 or a whole number greater than 2, or analogous carboxylic acids from other aromatic hydroxy compounds, for instance, from naphthols, hydroxy-anthracenes, hydroxy-phenanthrenes; there may, furthermore, be used cresoxy-acetic acid, xylenoxy-acetic acid, beta-phenoxy-propionic acid, alpha-phenoxy-butyric acid, alpha-phenoxylauric acid, alpha- and beta-naphthoxy-acetic acid and the like. Olefines suitable for use in the present process are, for instance: the olefines of the aliphatic or cycloaliphatic series, be it with straight or branched carbon chains, especially those where the double bond is present in a tertiary bound carbon atom, such as, for instance, propylene, butylenes, amylenes, hexylenes, heptylenes, octylenes, nonylenes, decylenes, dodecylenes, octodecylenes etc. and mixtures of these compounds. Furthermore there are suitable olefines of high molecular weight formed by polymerization of olefines of low-molecular weight and such as are obtained by different technical processes, for instance, by the cracking of paraffines or of products of the distillation of mineral oils or of hydrogenation products of coal or carbon oxide, furthermore olefines formed, for instance, by dehydrating alcohols or alcohol mixtures obtained by reduction of natural fatty, resinic and ceric acids. There may also be used the dehydration products of the alcohols obtained by oxidizing paraffine.

As alcohols which may be caused to react with the aromatic carboxylic acids mentioned, there may be named the following: the aliphatic primary, secondary and tertiary alcohols, such as isopropyl-alcohol, isobutyl-alcohol, tertiary butyl-alcohol, undecyldimethylcarbinol, the alcohols or alcohol mixtures obtainable by reduction of natural fatty, ceric and resinic acids; naphthene-alcohols, hydrogenated aromatic hydroxy compounds, for instance, cyclohexanol, the methyl-cyclohexanols, and the alcohols obtained by hydrogenating carbon monooxide.

As halogen compounds there are suitable the primary, secondary, tertiary aliphatic or cycloaliphatic chlorides, bromides, iodides. It is of special advantage to use halogen compounds obtained by halogenating natural or synthetic hydrocarbon mixtures; it is not necessary that these products be pure mono-halogenated hydrocarbons, but there may also be used products containing less halogen, and containing, therefore, hydrocarbons in addition to halogen compounds. The non-halogenated hydrocarbons may be separated after complete condensation, be halogenated and be used again.

The condensing agents appropriate for being used in the present process are, for instance: boron trifluoride or its addition compounds with other molecules, aluminium chloride, zinc chloride, perchloric acid, phosphoric acid, sulfuric acid, furthermore bivalent metals, for instance, zinc, magnesium, copper, iron, their alloys, amalgams or mixtures of the said substances. The kind of the condensing agents to be used depends on the nature of the substances entering into reaction. In the case of olefines, there are best used as condensing agents BF_3, its compounds with other molecules, or $ZnCl_2$. In the condensation of alcohols, $ZnCl_2$ is the most suitable condensing agent. In the case of halogenated hydrocarbons, there are best used as catalysts zinc or zinc amalgams.

The process may be performed in the following manner: If olefines are caused to react with carboxylic acids of the above-indicated formula, the olefine is preferably mixed with the carboxylic acid, if desired with use of an indifferent solvent, for instance, carbon tetrachloride, dichlorethylene, aliphatic hydrocarbons, and the condensing agent is then introduced into the mixture. It is, however, also possible to add the condensing agent to the carboxylic acid used, in which case an indifferent solvent may also be used, and to introduce the olefine into the mixture. When using alcohols as reaction component, one proceeds in a completely analogous manner. When using halogen compounds of aliphatic or cycloaliphatic nature, the process

is, for instance, performed by mixing the halogen compound, if desired while heating, with the carboxylic acid, and adding the condensing agent, for instance a bivalent metal to the mixture, the whole being further heated for some time. The condensing agent may likewise be added to the mixture in portions, if necessary, in the course of a long period of time. There may also be used indifferent solvents. When using partially halogenated hydrocarbons, the non-halogenated portions may serve as solvent. The condensing agent, for instance a bivalent metal, may also be dissolved in the molten acid by heating it, for a prolonged time before adding the halogen compound. When 1 mol of metal is used for 1 mol of the acid and an amount of hydrocarbon containing 1 mol of halogen, very light-colored products are obtained, but good yields may also be obtained with a considerably smaller amount of metal. This applies especially to amalgams.

When the reaction is completed, the condensing agents used are washed out, by means of a dilute acid or with water, and the products formed are freed from water by heating, if desired under reduced pressure. If an indifferent solvent has been used in the reaction, the same may be expelled by distillation, after removal of the condensing agents. The new alkylated carboxylic acids obtained according to the above-described method of working, may further be purified by distillation under reduced pressure, by distillation with steam under reduced pressure or by distillation with superheated steam or by recrystallization.

The determination of the constants of the carboxylic acids obtained, for instance, of the acid or saponification number, shows that an almost exclusively nuclear alkylation of the aromatic carboxylic acid used has taken place, even in cases in which substituents were already present in the aromatic nucleus.

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

(1) 1960 grams of di-isoheptylene ($C_{14}H_{28}$) are added to 1520 parts of phenoxy-acetic acid, and the mixture is heated to 125° C. 100 parts of boron fluoride are introduced at this temperature and the whole is further heated for one hour. After cooling, the reaction product is washed with water, carbon tetrachloride, xylene or benzene being preferably added as diluents. After removing the boron fluoride, the di-isoheptyl-phenoxy-acetic acid formed is dried; it may be purified by distillation under reduced pressure.

The tetradecyl-phenoxy-acetic acid is a light-yellow, viscous substance which distills, under a pressure of 3 mm., at 180° C.–240° C. The acid and the saponification numbers of the substance obtained are practically the same and differ but very little from the calculated value.

(2) 152 parts of phenoxy-acetic acid are dissolved, at 60° C., in 500 parts by volume of carbon tetrachloride and 8 parts of boron fluoride are introduced therein. 112 parts of di-isobutylene, boiling at 101° C. to 104° C., are added thereto and the whole is further stirred for 8 hours at 60° C.–70° C. The boron fluoride is removed by washing with water and the carbon tetrachloride is evaporated. The octyl-phenoxy-acetic acid frequently obtained in a crystalline form after evaporation of the carbon tetrachloride may be purified by distillation under reduced pressure.

The octyl-phenoxy-acetic acid purified by recrystallizing it from benzine (boiling point 60° C.–100° C.) separates in the form of fine, white needles melting at 106° C.–108° C. When mixed with octyl-phenoxy-acetic acid, prepared from para-octylphenol and Cl—CH_2—COOH, the melting point is not depressed. The acid number found is 214.2, the calculated value: 212.1.

(3) 760 parts of phenoxy-acetic acid are heated to 130° C. together with 925 parts of an olefine (middle molecular weight 185 and boiling point situated between 130° C. and 260° C.) prepared by dehydrating and dimerizing an olefine fraction containing for the main part iso-hexylene and isoheptylene and obtained by dehydrating the corresponding alcohols formed in the catalytic reduction of carbon mono-oxide. 50 parts of boron fluoride are introduced at the same temperature, and the whole is further heated for one hour. The reaction product is washed, while adding carbon tetrachloride, and dried. By distillation under reduced pressure, a light-yellow, viscous substance is obtained which distills, under a pressure of 3 mm., at 180° C.–250° C. The acid and the saponification numbers are practically the same.

(4) 152 parts of phenoxy-acetic acid are heated with 196 parts of di-isoheptylene to 140° C. 200 parts of zinc chloride are introduced, at this temperature, into the clear solution, the temperature rising to 150° C. After a quarter of an hour, the whole is allowed to cool and the reaction product is well washed with hot water. The tetradecylphenoxy-acetic acid formed is identical with the product prepared according to the process of Example 1. The acid and saponification numbers correspond to the calculated value and are practically the same.

(5) 152 parts of phenoxy-acetic acid are heated to 150° C. together with 150 parts of iso-butanol and 225 parts of zinc chloride. After a further stirring for one hour at the above-indicated temperature, the whole is allowed to cool and the reaction product is washed with hot water. The mono-iso-butylphenoxy-acetic acid may be obtained from the mixture of the acids partly substituted several times by distillation under reduced pressure and recrystallization from benzine (boiling point: 60° C.–100° C.). After repeated recrystallization, it melts at 94° C. and separates in the form of fine, white needles which dissolve in sodium carbonate solution to a clear solution. The acid number found is: 266.7, the acid number calculated is 269. The percentage contents of carbon and hydrogen found by analysis are:

C:69.60
H:8.17

The calculated values are:

C:69.25
H:7.83

(6) 202 parts of alpha-naphthoxy-acetic acid are heated to 140° C. together with 196 parts of tetradecylene (dimerized isoheptylene). 35 parts of boron fluoride are then introduced into the melt and the mixture is stirred, for 1½–2 hours, at a temperature of 140° C. The boron fluoride is removed by boiling with water. After dehydrating, a mixture of isomeric tetradecyl-naphthoxy-acetic acids is obtained in the form of a viscous brown oil.

(7) 168 parts of phenyl-thio-acetic acid $C_6H_5.S.CH_2.COOH$ are heated to 140° C. together

with 279 parts of dodecyl-alcohol, and 200 parts of zinc chloride are added at that temperature. After stirring, for one hour, at the same temperature, the reaction product is boiled with water and the water is removed. A brown sirupy mass is obtained which yields with sodium carbonate a difficultly soluble sodium salt.

(8) 166 parts of cresoxy-acetic acid are heated to 110° C. together with 196 parts of diisoheptylene. 25 parts of boron fluoride are then introduced into the mixture in such a manner that the temperature rises to 135° C.–140° C. The whole is stirred, for half an hour, at this temperature, water is added to the reaction product and the boron fluoride is removed by washing. After drying, the reaction product is distilled; a mixture of isomeric tetradecyl-cresoxy-acetic acids passes over, under a pressure of 10 mm., at a temperature of 200° C.–260° C. The product is a light-yellow, viscous oil which is soluble in sodium carbonate. Its acid and saponification numbers show that an almost exclusively nuclear substitution has taken place and that, to a certain extent, more than one tetradecyl radical has entered the nucleus, under the conditions selected.

(9) 152 parts of phenoxy-acetic acid are heated to 105° C. together with 148 parts of isooctyl-chloride or with 193 parts of isooctyl bromide or 240 parts of isooctyl iodide, in such a manner that the phenoxy-acetic acid is melted and dissolved in the alkyl halide. 50 parts of zinc are then added and the whole is further stirred, for 5 hours, at a temperature of 120° C. After 2 hours, an additional 15 grams of zinc are added. When the reaction is finished, the product is then well boiled out with 2N-hydrochloric acid, washed with water and dried. The isooctylphenoxy-acetic acid is purified by recrystallizing it from benzine; it is obtained in the form of white needles melting at 106° C.–108° C.

(10) 32.5 parts of zinc dust are dissolved, at a temperature of 110° C., in 152 parts of phenoxy-acetic acid. 148 parts of octyl chloride are introduced into the melt at 120° C., and the whole is further stirred, for 5 hours, at this temperature. The product is worked up as indicated in Example 9; an octylphenoxy-acetic acid is obtained which is nearly completely free from esters.

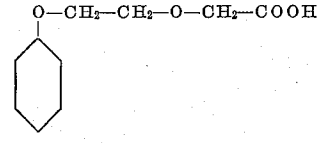
(11) 166 parts of cresoxy-acetic acid are dissolved by heating at 120° C., in 500 parts of an alkyl halide obtained by introduction of 13.6 per cent by weight of chlorine into a fraction, boiling at 130° C.–270° C., of a middle oil obtained by hydrogenating coal, this middle oil containing, both aliphatic hydrocarbons and naphthenic hydrocarbons having an average molecular weight of 170. 50 parts of zinc, amalgamated with 100 parts of a mercuric chloride solution of 2.5 per cent. strength, are then introduced and the mixture is heated, for 8 hours, to a temperature of 145° C. The reaction product is worked up as described in Example 9. It is distilled under a pressure of 5 mm., and there is obtained, after expelling some first runnings of unaltered hydrocarbon, a light-yellow, viscous oil passing over at a temperature of 180° C. to 245° C. and dissolving in a 2N-solution of sodium carbonate to a clear solution. The crude product which remains after expelling the unaltered hydrocarbon is likewise soluble in a dilute sodium carbonate solution.

(12) 152 parts of phenoxy-acetic acid are heated for 12 hours to 150° C. together with 500 parts of a natural petroleum fraction containing about 13% of chlorine and having a middle molecular weight of hydrocarbons of 168, in the presence of either 100 grams of copper or 100 grams of iron. 25 grams of zinc are added, after 8 hours, in order to clarify the product and to complete the reaction. The alkyl-phenoxy-acetic acid formed boils, under a pressure of 5 mm., at a temperature situated at 185° C.–245° C. and is a light-yellow viscous substance, the acid and saponification numbers of which are nearly the same. Its sodium salt is soluble in water.

(13) 202 parts of alpha-naphthoxy-acetic acid are heated to 125° C. together with 232 parts of tetradecyl chloride and 50 grams of magnesium are slowly added thereto. The mixture is then further heated, for 5 hours, at a temperature of 140° C. and 2N-hydrochloric acid is added to the reaction product which is worked up as indicated in the foregoing examples. After dehydrating, a mixture of isomeric tetradecyl-naphthoxy-acetic acids is obtained in the form of a viscous brown oil.

(14) 168 parts of phenyl-thio-acetic acid ($C_6H_5.S.CH_2$–COOH) are heated, for 3 hours, to 125° C. together with 500 parts of the alkyl halide described in Example 11 and 65 grams of zinc. Hydrochloric acid is added to the reaction product which is then washed with water and dried. A brown sirupy mass is obtained which yields a difficultly soluble sodium salt.

(15) 196 parts of phenoxyethoxy-acetic acid:



are heated, for 5 hours, to 125° C., with 500 grams of the alkyl halide described in Example 12 and 65 grams of zinc. After decomposing the reaction product by means of hydrochloric acid and washing with water, a brown substance is obtained which yields a soluble sodium salt. Its acid and saponification numbers are almost the same.

(16) 181 parts of phenoxy-butyric acid are heated with 196 parts of di-isoheptylene to a temperature of 110° C., and 18 parts of boron trifluoride are introduced into this mixture. After further stirring for one hour at 100° C., water is added to the reaction mixture, the whole is well washed and dried. The tetradecyl-phenoxy-butyric acid being obtained in the form of a brown viscous oil is best purified by steam-distillation under reduced pressure.

We claim:

1. The process which comprises causing compounds of the general formula A.X.R.COOH wherein A is an aromatic radical, X stands for a member of the group consisting of O and S, R stands for a member of the group consisting of hydrocarbon radicals and aliphatic radicals the carbon chain of which is at least once interrupted by O to react with olefines in the presence of a member of the group consisting of $ZnCl_2$ and BF_3.

2. The process which comprises causing compounds of the general formula A.O.CH_2.COOH wherein A is an aromatic radical the nucleus of which consists of 6 carbon atoms to react with olefines in the presence of a member of the group consisting of $ZnCl_2$ and BF_3.

3. The process which comprises causing phenoxyacetic acid to react with olefines in the presence of BF_3.

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