Patented Sept. 20, 1938 2,130,989

# UNITED STATES PATENT OFFICE

2,130,989

## CARBOXYLIC ACIDS OF CAPILLARY ACTION CONTAINING ISOCYCLIC RING-SYSTEMS AND A PROCESS OF PREPARING THEM

Kurt Schimmelschmidt, Frankfort-on-the-Main-Hochst, Germany, assignor to I. G. Farbenindustrie Aktiengesellschaft, Frankfort-on-the-Main, Germany

No Drawing. Application December 4, 1935, Serial No. 52,929. In Germany December 7, 1934

4 Claims. (Cl. 260—514)

The present invention relates to carboxylic acids, of capillary action, containing isocyclic ring-systems and to a process of preparing them.

I have found that compounds of the general formula $R_1—A—R_2—COOH$

wherein

$R_1$ means an alkyl or cyclo-alkyl radical,

$R_2$ an alkylene radical and

A an aromatic or hydroaromatic ring-system,

are obtainable by introducing fatty acid radicals into alkylated or cycloalkylated aromatic hydrocarbons by condensing alkylated or cycloalkylated aromatic hydrocarbons with aliphatic dicarboxylic acids including their anhydrides, acid chlorides or ester-acid chlorides and reducing the ketocarboxylic acids thus formed to the corresponding carboxylic acids. In order to obtain the hydroaromatic compounds corresponding to the above formula, these alkyl- or cycloalkyl-aryl-substituted fatty acids or the esters thereof are subjected to a catalytic hydrogenation and, if necessary, the hydrogenated esters are saponified.

The alkyl-aryl-fatty acids of the formula

$$R_1—A—R_2—COOH$$

wherein

$R_1$ means alkyl,

A means an aromatic ring-system and

$R_2$ means $CH_2CH_2CH_2$, or $CH_2CH_2CH_2CH_2$,

are, for instance, obtained by condensation of the alkylated aromatic hydrocarbons with lactones or functional derivatives of the succinic acid, the glutaric acid or the adipic acid series, such as their anhydrides, chlorides and ester-acid chlorides. The keto-carboxylic acids obtained by using the acid anhydrides, the acid chlorides or the ester-acid chlorides, are reduced to the corresponding fatty acids in an alkaline solution in the presence of zinc dust or catalytically activated hydrogen.

The alkyl- or cycloalkyl-aryl fatty acids obtainable according to these methods may be hydrogenated, if necessary, with formation of hydroaromatic compounds which are completely saturated with hydrogen. The hydrogenation is carried out in a particularly smooth manner by treating with hydrogen the esters of these acids with monohydric or polyhydric alcohols in the liquid phase at a temperature between 130° C. and 200° C. in the presence of a nickel catalyst and with application of pressure. The esters of the hydrogenated alkylaryl-fatty acids thus obtained are saponified to form the free acids.

As examples of the new compounds, there may be mentioned: 4-methylphenyl-delta-valeric acid, 4-ethylphenyl-gamma-butyric acid, 4-ethylphenyl-epsilon-caproic acid, 4-propylphenyl-beta-propionic acid, 4-propyl-cinnamic acid, butylphenylacetic acid, 4-butylphenyl-gamma-butyric acid, 4-butylcyclohexyl-gamma-butyric acid, 4-sec.butyl-phenyl-gamma-butyric acid, sec.butylphenyl-beta-butyric acid, 4-cyclohexyl-phenyl-gamma-butyric acid, beta-decahydronaphthylphenyl-gamma-butyric acid, octylphenyl-gamma-butyric acid, dodecylphenyl-gamma-butyric acid, 4'-butyldiphenyl-4-gamma-butyric acid, 2-butylnaphthyl-6-gamma-butyric acid, alkyl-phenanthrene fatty acids, 4-isobutyl-cyclohexyl-gamma-butyric acid, 4-cyclohexyl-cyclohexyl-gamma-butyric acid, dicyclohexyl-methane-4-gamma-butyric acid etc.

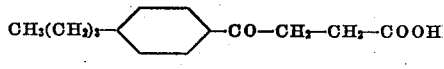
As alkylated aromatic hydrocarbons there may be mentioned besides toluene, ethyl-, propyl-, butyl-benzenes, methylnaphthalene, cyclohexyl-benzene or the like, the products which are, for instance, obtained by reaction of benzene, naphthalene or phenanthrene with commercial mixtures of alcohols, as, for instance, isobutyl oil (a by-product which is obtained in the methanol-synthesis) or with the mixtures of alcohols obtained from commercial fatty acids by hydrogenation, or with mixtures of the alcohols obtainable by the oxidation of paraffin; furthermore, the condensation products from benzene, naphthalene or phenanthrene with olefines or the polymerization products thereof as, for instance, di-isobutylene, or with the unsaturated constitu-

ents of the compounds obtained in the cracking process or with oil of turpentine.

Whereas the alkali salts of aryl-fatty acids as, for instance, phenylacetic acid, phenyl-gamma-butyric acid and so on, do not froth in aqueous solution, the alkali salts of alkylaryl-fatty acids and the hydrogenation products thereof show a very good foaming power. Their wetting action surpasses that of the alkali salts of the corresponding natural fatty acids. The alkali salts of the perhydrogenated alkylaryl-fatty acids show in spite of the completely saturated character of the carboxylic acids from which they are prepared, an excellent solubility in water. It is easily possible to prepare a cold parent solution of 20% strength and even of a higher percentage this being impossible when the saturated aliphatic carboxylic acids corresponding to them in the length of the chain are used. Furthermore, they show a very good washing action by which they surpass, for instance, on removal of the fat from wool, the alkali salts of saturated natural fatty acids, for instance, lauric acid. The perhydrogenated alkylaryl-fatty acids are, on account of their saturated character, entirely stable. They are suitable, so far as they are liquid at room temperature, on account of their good lubricating power as gliding agents for different purposes, for instance, greasing of wool, and show certain advantages over the oleic acid hitherto used for this purpose.

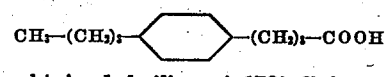
The following examples serve to illustrate the invention, but they are not intended to limit it thereto; the parts are by weight:

(1) 134 parts of n-butylbenzene (1-phenylbutane) are mixed with 100 parts of succinic acid anhydride and 500 parts of tetra-chlorethane and at 20° C.–30° C. 270 parts of anhydrous aluminium chloride are slowly introduced. After about 12 hours the mixture is heated to 50° C. until the reaction is finished; then it is poured on ice and after the addition of hydrochloric acid the whole is subjected to a steam distillation. The condensation product remains in the distillation vessel, after the complete elimination of the tetrachlorethane, in the form of a solid, granular mass and is separated from the aqueous solution of aluminium salts by filtration with suction. The crude product may be purified by recrystallization from chloro-benzene and there is thus obtained the 4-butylphenyl-gamma-oxo - gamma - butyric acid of the following formula:



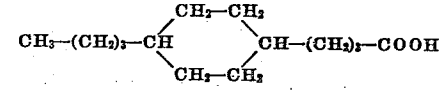
in the form of pearly leaflets melting at 115° C. to 116° C.

200 parts of 4-butylphenyl-gamma-oxo-gamma-butyric acid are introduced into a suitable hydrogenation autoclave together with 200 parts of water and the calculated quantity of caustic soda solution and the mixture is treated with hydrogen, after the addition of a nickel catalyst, at a temperature between 70° C. to 200° C. under a pressure of 20 to 100 atmospheres. When the absorption of hydrogen is finished the content of the autoclave is freed from the catalyst by filtration with suction and the reaction product is isolated from the alkaline solution by acidification. The 4-butyl-phenyl-gamma-butyric acid of the following formula:



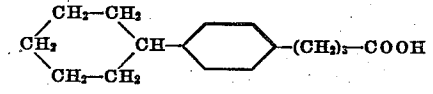
is thus obtained, boiling at 170° C. in a vacuum of 3 mm. and solidifying at 53° C. in the form of a white solid mass which on crushing falls into fatty flaky leaflets. It is insoluble in water and very easily soluble in most of the organic solvents. In dilute caustic alkali solutions it is very easily soluble and yields strongly foaming solutions. The solution of 20% strength of the sodium salt thereof in water is a completely clear liquid even when cold. The aqueous solution of the sodium salt may be used as a wetting agent.

(2) The 4-butyl-phenyl-gamma-butyric acid obtainable according to Example 1 is esterified with methanol and sulfuric acid. The 4-butyl-phenyl-gamma-butyric acid-methylester is obtained as a colorless liquid boiling at 124° C. in a vacuum of 3 mm. and at 162° C. in a vacuum of 12 mm. The ester is introduced into a hydrogenation autoclave together with a nickel catalyst and treated at 130° C. to 200° C. with hydrogen under a pressure of 50 to 150 atmospheres until the absorbtion of hydrogen is finished. The contents of the autoclave are filtered from the catalyst and subjected to distillation. The 4-butyl-cyclohexyl-gamma-butyric acid-methylester is obtained in the form of a colorless liquid boiling at 125° C. in a vacuum of 3 mm. By saponifying the ester the 4-butyl-cyclohexyl-gamma-butyric acid of the following formula:



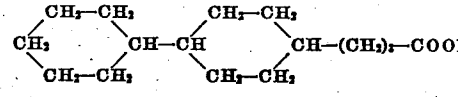
is obtained, constituting at room temperature a colorless semi-solid mass and boiling at 150° C. in a vacuum of 3 mm. It is practically insoluble in water, but very easily soluble in most of the organic solvents. It is easily soluble in dilute caustic alkali solutions and forms even in a solution of 20% strength of the sodium salt thereof in water a clear liquid in the cold. The aqueous solutions of the sodium salt are suitable as wetting agents, emulsifying agents and washing agents.

(3) By replacing in Example 1 the butylbenzene by 160 parts of cyclohexylbenzene, there is obtained by way of the 4-cyclohexyl-phenyl-gamma-oxo-gamma butyric acid melting at 132° C. to 133° C., the 4-cyclohexyl-phenyl-gamma-butyric acid of the following formula

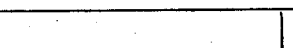
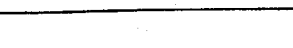


in the form of a colorless fatty mass having the structure of leaflets and solidifying at 56° C. The dilute aqueous solutions of its sodium salt have a very good foaming action and are suitable as wetting agents. From concentrated aqueous solutions the sodium salt crystallizes in the form of pearly leaflets.

(4) By replacing in Example 2 the 4-butyl-phenyl-gamma-butyric acid by the 4-cyclohexyl-phenyl-gamma-butyric acid obtainable according to Example 3, there is obtained by way of the 4-cyclohexyl-phenyl-gamma-butyric acid-methyl ester and the 4-cyclohexyl-cyclohexyl-gamma-butyric acid-methyl ester, both representing colorless liquids boiling under a pressure of 3 mm. at 140° to 145° C., the 4-cyclohexyl-cyclohexyl-gamma-butyric acid of the following formula



forming a white crystaline mass solidifying at 83° C. and boiling under a pressure of 3 mm. at 170° C.

| R= |  |  |  |
|---|---|---|---|
| $CH_3-CH_2-CH_2-$ | Melting at 118°-120° C | Methyl ester boiling under a pressure of 3 mm. at 134° C. | Boiling under a pressure of 3 mm. at 150° C. liquid. |
|  | Melting at 93° C | Boiling under a pressure of 3 mm. at 155° C.<br>Methyl ester boiling under a pressure of 3 mm. at 133° C. | Boiling under a pressure of 3 mm. at 150° C. liquid. |
|  | Melting at 97° C. to 99° C. | Melting at 44° C. to 45° C., boiling under a pressure of 2 mm. at 153° C. | Solidifying at 65° C., boiling under a pressure of 2 mm. at 160° C. |
| $CH_3-(CH_2)_8-$ | Melting at 95° C | Melting at 56° C. to 57° C. | Boiling under a pressure of 2 mm. at 170° C. |
| $CH_3-(CH_2)_7-$ | Melting at 103°-104° C | Solidifying at 62° C., boiling under a pressure of 3 mm. at 205° C. | Boiling under a pressure of 2 mm. at 180° C. |
| $CH_3-(CH_2)_{11}-$ | Melting at 91°-92° C | Solidifying at 71° C. | |

It is practically insoluble in water and easily soluble in most of the organic solvents. By recrystallization from cyclohexane it may be separated into two stereoisomeric forms. The sodium salt of 4-cyclohexyl-cyclohexyl-gamma-butyric acid is easily soluble in water and yields strongly foaming solutions which in a concentration of 20% strength form clear liquids even in the cold. They show very good wetting, emulsifying and washing action.

The same product may be obtained by condensing diphenyl with succinic acid anhydride to form diphenyl-4-gamma-oxo-gamma-butyric acid, melting at 187° C. to 188° C. and transforming it by way of diphenyl-4-gamma-butyric acid melting at 120° C. to 121° C. into the 4-cyclohexyl-cyclohexyl-gamma-butyric acid.

(5) In analogous manner there may be obtained the products indicated in the following table, forming colorless or white compounds some of which are liquid, some solid, and having also the other properties mentioned, dissolving in dilute caustic alkali solutions to strongly foaming liquids.

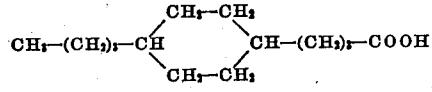
I claim:

1. The products of the following formula:

$$R_1A(CH_2)_3COOH$$

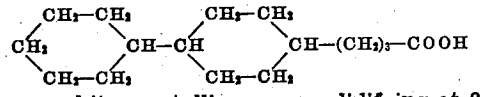
wherein $R_1$ means a member of the group consisting of alkyl and cycloalkyl radicals containing at least 3 carbon atoms and A means a hexahydrogenated benzene radical being colorless, liquid to solid bodies dissolving in dilute caustic alkali solutions to strongly foaming liquids.

2. The 4-butyl-cyclohexyl-gamma-butyric acid of the formula



being a colorless semi-solid mass boiling at 150° C. under a pressure of 3 mm. and being easily soluble in dilute caustic alkali solutions.

3. The 4-cyclohexyl-cyclohexyl-gamma-butyric acid of the formula



being a white crystalline mass, solidifying at 83° C. and boiling under a pressure of 3 mm. at 170° C. and being easily soluble in dilute caustic alkali solution.

4. The process which comprises condensing compounds of the formula $R_1C_6H_5$ wherein $R_1$ means a member of the group consisting of alkyl and cycloalkyl radicals containing at least 3 carbon atoms, with succinic acid anhydride, reducing the keto-carboxylic acids thus obtained to the corresponding substituted butyric acids, treating the acids thus obtained, in the form of their esters, in the liquid phase with hydrogen under pressure at a temperature between 130° C. and 200° C. in the presence of a nickel catalyst and finally saponifying the reaction product.

KURT SCHIMMELSCHMIDT.