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BENZENE CARBOXYLIC ACIDS ALKYLATED IN THE NUCLEUS AND PROCESS OF PREPARING THEM

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The present invention relates to benzene carboxylic acids alkylated in the nucleus and to a process of preparing them.

Attempts to introduce directly alkyl groups into benzoic acid or a homologue thereof have as yet been unsuccessful.

We have found that benzene carboxylic acids are obtainable in a good yield by oxidizing the corresponding acetophenones or omega-halogenacetophenones, which are substituted in the nucleus by one or several aliphatic or cycloaliphatic hydrocarbon radicals having together at least eight carbon atoms and one of which having at least four carbon atoms, with a hypohalogenite solution, that are solutions of salts of, for instance, hypochlorous or hypobromous acid, to form the corresponding benzene carboxylic acids, the hydrocarbon radicals present as side chains being practically unattacked.

The substituted acetophenones or omega-halogenacetophenones are obtained in known manner by condensing an acetic acid halide or halogen-acetic acid halide with a substituted hydrocarbon of the benzene series. Examples of the latter are the homologous alkyl benzenes obtained by catalytic reduction of the araliphatic ketones which are obtainable from hydrocarbons of the benzene series and higher fatty acid halides; furthermore, condensation products of benzene hydrocarbons with higher aliphatic or cycloaliphatic olefines, alkyl halides and chlorination products obtained from hydrocarbon mixtures containing hydroaromatic hydrocarbons as they are obtained in the hydrogenation of coal and the like.

The oxidation of the substituted acetophonones or omega-halogen-acetophenones is preferably carried out in a dilute solution at temperatures comprising room temperature up to about 100° C., preferably at 70° C. to 80° C., so that at least part of the carboxylic acid salt obtained passes into solution. It is not necessary to start from pure (distilled) acetophenone derivatives or omega-halogen-acetophenone derivatives. When using crude dark condensation products with acetic acid halide or halogen acetic acid halide (if desired, after the elimination of the unchanged starting materials and of by-products having a low boiling point) it is advisable to work with an excess of hypohalogenite solution by which the dark products are bleached and only slightly colored carboxylic acid salts are obtained. The oxidation of the omega-halogen-acetophenones proceeds more rapidly and more smoothly than that of the non-halogenated derivatives. The carboxylic acids are precipitated from the solution of their salts by acidifying with mineral acid or acetic acid, separated from the liquid and, if desired, reconverted into salts by dissolving them in alkalies; by evaporation and drying the salts are obtained in the form of white to light-brown powders.

The benzene carboxylic acids or the salts thereof thus obtained, particularly those containing as substituents hydrocarbon radicals of at least twelve carbon atoms, are soap-like products and may be used instead of soaps or as additions to soaps. The products are likewise valuable intermediate products for the preparation of textile adjuvants and the like.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts being by weight and the ratio of parts by volume and parts by weight is that which exists between the liter and the kilo:

(1) A mixture of 33 parts of acetyl chloride and 100 parts of n-dodecylbenzene, obtained by catalytic reduction of laurophenone are introduced into a suspension of 54 parts of aluminium chloride (anhydrous) in about 200 parts of carbon tetrachloride, while cooling and stirring; after some hours the whole is poured on ice, worked up in the usual manner and distilled under reduced pressure. (Yield 70 to 75 per cent., melting point 48° C).

100 parts of n-dodecylacetophenone are gradually introduced at about 70° C. to 80° C. into 2550 parts by volume of a sodium hypochlorite solution of 3 per cent. strength or the equivalent quantity of potassium hypochlorite solution and stirred at this temperature until a test portion has become soluble in water. An excess of hypochlorite which may be present is decomposed with the aid of bisulfite. The n-dodecylbenzoic acid is separated in the form of a solid product which, as regards its appearance, resembles the fatty acids, by acidifying it with dilute mineral acid or acetic acid. After washing with water the product is dissolved in the calculated amount of hot dilute sodium carbonate solution or caustic soda solution; after evaporation the sodium para-dodecylbenzoate is obtained in the form of a white powder. The yield amounts to 95 per cent. Small amounts of unchanged parent material may be removed with the aid of solvents, for instance, petroleum ether. The sodium salt produces soap-like solutions; the product is, however, sparingly soluble in cold water. The calcium salts and barium salts as well as the heavy metal salts are very sparingly soluble in water.

The free acid is soluble in organic solvents, for instance, in benzene hydrocarbons, halogen hydrocarbons, and alcohols.

(2) To a suspension of 53 parts of aluminium chloride (anhydrous) in about 300 parts of carbon tetrachloride there is added, while stirring below +10° C., a mixture of 44 parts of chloracetyl chloride and 100 parts of alkyl benzene (molecular weight about 260, corresponding to an average chain length of the alkyl substituents of 13 to 14 C-atoms) obtained by condensation of benzene with a chlorination product of a hydrocarbon mixture, containing hydroaromatic compounds and boiling under a pressure of 20 mm. mercury at 50° C. to 125° C., as it is obtained in the hydrogenation of lignite. After a subsequent stirring for 12 hours the whole is poured on ice at room temperature. After washing and drying the condensation product the readily volatile by-products are distilled up to a boiling point of about 130° C. under a mercurial pressure of 6 mm. 112 parts of this crude alkylated omega-chloracetophenone are introduced at about 80° C. into 2500 parts of an industrial sodium hypochlorite solution of 3 per cent. strength and kept at this temperature until the hypochlorite has been consumed. The reaction is promoted by adding a small quantity of sodium salt of the corresponding alkyl benzoic acids to the hypochlorite solution as emulsifying agent. After addition of some animal charcoal the whole is filtered hot from small amounts of resinous by-products and by acidifying the light-brown filtrate there is obtained a mixture of alkylated benzoic acids (average molecular weight about 300, corresponding to an average chain length of the alkyl substituents of 13 to 14 C-atoms) in the form of a mass resembling resinic acid and capable of being pulverized at temperatures below +10° C., but viscous when hot. If desired, this mass is dissolved in dilute alkali and the salts are obtained in the form of a light-brown powder having properties resembling those of resin soaps. (The yield amounts to 105 parts.)

(3) To a mixture containing 100 parts of di-tertiary-butylbenzene, about 200 parts of carbon tetrachloride and 60 parts of chloracetylchloride there are gradually introduced below +10°C., while stirring, 70 parts of anhydrous aluminium chloride; the whole is subsequently stirred for several hours at about 25° C., poured on ice and worked up in the usual manner. 100 parts of a condensation product freed from more easily boiling portions by distillation to a boiling point of about 110° C. under a pressure of 5 mm. are oxidised (as described in Example 1) with 2000 parts of a sodium hypochlorite solution of 3 per cent. strength or the equivalent amount of sodium hyprobromite solution and worked up. The sodium salt of the di-tertiary-butylbenzene-carboxylic acid is obtained in the form of a white powder in a yield of about 70 per cent. of the amount calculated for the di-tertiary-butylbenzene used.

The free acid is prepared from the salts as indicated above. The crude product contains as impurities alkylbenzoic acids which are formed by the alkyl radical in the di-tertiary-butylbenzene being split off by the influence of aluminium chloride; after recrystallization from methanol the di-tertiary-butylbenzoic acid melts at 128° C.

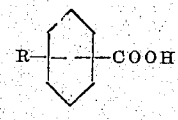
(4) To a mixture from 400 parts of the alkyl benzene mixture, obtained by condensation of diisohexylene and benzene by means of boron fluoride-phosphoric acid and distillation of the easily boiling portions up to a boiling point at 110° C. under a mercurial pressure of 15 mm. (molecular weight 213), about 200 parts of carbon tetrachloride and 100 parts of bromacetylbromide, there are gradually introduced, while stirring, below +10° C. 65 parts of aluminium chloride (anhydrous). The whole is stirred for several hours at about 25° C., poured on ice and worked up in the usual manner.

100 parts of the condensation product freed from the easily boiling portions by distillation up to a boiling point of about 125° C. under a mercurial pressure of 3 mm. are oxidized with 1900 parts of sodium phyochlorite solution of 3 per cent. strength or the equivalent amount of a potassium hypobromite solution (as indicated in Example 1) and worked up. By acidifying with mineral acid or acetic acid a mixture of alkyl benzoic acids having an acid number of about 230 is obtained in the form of a brownish partly solid mass. The alkali or ammonium salts of this acid mixture yield foaming aqueous solutions. The salts of alkaline-earth metals and heavy metals are difficultly soluble in water even in the warmth.

We claim:

1. The n-dodecylbenzoic acid which is soluble in benzene hydrocarbon, halogen hydrocarbons and alcohols and the sodium salt of which being a white powder soluble in water to a soap-like solution, whereas its salts of calcium, barium and of the heavy metals are difficultly soluble in water.

2. The benzoic acid of the formula:



R standing for saturated hydrocarbon radicals of 13 to 14 carbon atoms, being a resinic acid-like product pulverizable at temperatures below +10° C. and of viscous character when hot, the alkali metal salts being light brown powders.

3. The benzoic acids substituted in the nucleus by a hydrocarbon radical of at least 12 carbon atoms selected from the group consisting of aliphatic hydrocarbon radicals and cycloaliphatic hydrocarbon radicals, the alkali metal salts of the acids being soapy products soluble in water and other metal salts being difficultly soluble in water.

4. A mixture of alkyl benzoic acids having an acid number of about 230 and being a brownish partly solid mass.

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