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PROCESS FOR PREPARING MONOHYDROXY AROMATIC COMPOUNDS FROM AROMATIC CARBOXYLIC ACIDS

William G. Toland, Jr., San Rafael, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

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This invention relates to the manufacture of monohydroxy aromatic compounds and, more particularly, to a process for converting aromatic monocarboxylic acids to monohydric phenols.

The growing scarcity of benzene renders ever more desirable the discovery of new sources of raw materials suitable for the manufacture of monohydroxy aromatic compounds and, in particular, of monohydroxy benzene, i. e., phenol.

I have found that aromatic monocarboxylic acids such as benzoic acid, tertiary butyl benzoic acids, toluic acids, i. e., meta-, para-, and ortho-methyl benzoic acids, and naphthoic acids can be converted to phenolic esters, e. g., phenyl benzoate, by a liquid phase oxidation at a temperature from about 400 to about 700° F. in the presence of catalytic amounts of copper compounds with oxygen as the oxidizing agent, and that these phenolic esters can be then hydrolyzed to the corresponding phenols or cresols in accordance with the following equations in which Ar designates an aryl radical:

$$(1)\quad 2ArCOOH + \tfrac{1}{2}O_2 \xrightarrow[400\text{–}700^\circ F.]{Cu} ArCOOAr + H_2O + CO_2$$

$$(2)\quad ArCOOAr + H_2O \longrightarrow ArCOOH + ArOH$$

The conversion of aromatic monocarboxylic acids to phenolic esters hydrolyzable to phenols can be also obtained by employing stoichiometric quantities of certain copper compounds in the absence of free oxygen in accordance with the equations in which Ar again designates an aryl radical:

$$(3)\quad 2ArCOOH + CuO \xrightarrow[400\text{–}700^\circ F.]{} ArCOOAr + H_2O + CO_2 + Cu$$

$$(4)\quad ArCOOAr + H_2O \longrightarrow ArCOOH + ArOH$$

In either instance, it may be said that phenolic esters of aromatic monocarboxylic acids convertible to phenols are obtained by heating the aromatic acid in the liquid phase, either in melted state or in solution in a suitable solvent, at a temperature ranging from about 400° F. to about 700° F. in the presence of a copper material associated with oxygen. The copper material can be associated with oxygen by being chemically combined therewith as in a copper oxide, e. g., CuO or Cu_2O, or in an oxygen-containing copper salt capable of decomposing at temperatures from about 400° F. to about 700° F. to yield CuO or Cu_2O. Examples of these salts are: Copper acetate, copper benzoate, copper carbonate, and also others, all equivalent to copper oxides and applied in stoichiometric amounts for converting aromatic monocarboxylic acids to phenolic esters hydrolyzable to phenols in accordance with my invention. When the copper material is employed in catalytic amounts to induce the formation of phenolic esters hydrolyzable to phenols, free oxygen is required to oxidize the aromatic monocarboxylic acid, and the "association" between the copper material and gaseous oxygen is not in the form of a chemical combination but by intimate physical contact. In this case, the copper material need not be necessarily a copper oxide

or a copper salt capable of decomposing at 400 to 700° F. to yield CuO or Cu_2O, but may include other copper salts, e. g., $CuCl_2$ as well as the metallic copper itself. In lieu of pure oxygen, air or any other gas containing free oxygen may be employed.

Where the oxidation of an aromatic monocarboxylic acid is carried out at the expense of oxygen chemically combined with copper, as in a carbonate, an organic oxygen-bearing salt, or an oxide, the quantity of copper material required for the reaction may be varied within wide limits from 1 to 100 mol percent and even higher, based on the aromatic monocarboxylic acid being oxidized, depending on the degree of conversion desired. In most instances amounts from about 5 to about 50 mol percent, based on the acid to be oxidized, are found to be satisfactory. Otherwise, when pure oxygen, air, or any other free oxygen-containing gas is employed to effect oxidation, the copper material, e. g., CuO, in amounts ranging from about 0.1 to about 10% by weight of the acid subjected to oxidation, is found to be sufficient to catalyze the reaction. The use of cupric oxide is usually preferred to that of cuprous oxide, because it secures a much faster oxidation of the aromatic acid and higher yields of phenolic esters convertible to phenols.

The solvents which may be employed to dissolve the aromatic monocarboxylic acids to be converted to phenolic esters in accordance with the invention comprise the very esters to be formed in such a conversion, e. g., phenyl benzoate; various oxidation-stable hydrocarbons, e. g., biphenyl; various perhalo organic compounds, e. g., hexachlorobutadiene. When water is employed as a reaction medium, phenols can be formed directly avoiding a separate hydrolysis step, provided sufficient pressure is applied to reduce vaporization of the reactants at reaction temperatures. When such reaction diluents are used, mole ratios of copper salts to carboxylic acids as high as 1:1 can be employed.

Once the phenolic esters have been formed in the aforementioned step of copper-catalyzed oxidation of aromatic monocarboxylic acids, they can be either split by the method of saponification, as with caustic soda to form a salt which, upon acidification, will yield a phenol and the original acid, or may be subjected to acid hydrolysis and will give a phenol and the original acid which, in either case, can be returned to the oxidation step.

The aromatic monocarboxylic acids, suitable for conversion to phenols by first oxidizing them to yield phenolic esters in the presence of a copper oxide or of an oxygen-containing organic salt equivalent to copper oxide in effecting the formation of phenolic esters, and then hydrolyzing these esters to yield a phenol and the originally-oxidized aromatic monocarboxylic acid, are those aromatic monocarboxylic acids which contain no other nuclear substituents reactive under the conditions of oxidation at temperatures from about 400 to about 700° F. To illustrate: Aromatic monocarboxylic acids containing a phenyl or a naphthyl nucleus as exemplified by tertiary butyl benzoic acid, methyl benzoic acids and naphthoic acids, as well as those containing biphenyl or bibenzyl, or stilbene nuclei can be converted to monohydroxy aromatic compounds in accordance with the process of my invention. Those acids containing alkyl groups or other hydrocarbon substituents attached to the aromatic nucleus give somewhat lower yields than the non-substituted aromatic acids, benzoic acid appearing to furnish the best yield as will be seen from the illustrative examples hereinafter.

A characteristic feature of the oxidation reaction in my process, when employing alkyl-substituted, or other substituted, aromatic monocarboxylic acids which may be considered as being monocarboxy-substituted aromatic compounds in which the only functional group is a single

carboxyl group attached to the aromatic nucleus having no other substituents reactive under the conditions of oxidation at 400 to 700° F., is the concurrent rearrangement of the aromatic acid molecule, so that a carboxyl substituent originally present in the ortho position with respect to the other substituent on the aromatic nucleus of the acid is replaced by a hydroxyl group in the meta position with respect to the other substituent on the aromatic nucleus of the resulting phenol. Meta-substituents with respect to the carboxyl group on the aromatic nucleus of the originally employed acid become para- and ortho-substituents in the nucleus of the resulting phenol, while para-substituents become meta-substituents on the nucleus of the final phenol product. For example, meta-toluic acid, when oxidized in the presence of a copper compound in the absence of free oxygen, under the conditions of my invention, yields a 50 to 50 mixture of ortho- and para-cresol, but fails to yield meta-cresol. Similarly, para-tertiary-butyl benzoic acid produces meta-tertiary-butyl phenol, and ortho-toluic acid yields meta-cresol. Because of this capacity of rearrangement, it becomes feasible, e. g., to employ mixtures of ortho- and para-toluic acids for oxidation to meta-tolyl toluates and subsequent conversion to meta-cresol.

The reaction of oxidation is followed by observing the rate of oxygen absorption by the liquid phase reaction mixture in the case of copper compounds employed as catalysts, or by observing the formation of carbon dioxide and water when no free oxygen is used and copper oxide or an equivalent copper compound is employed in stoichiometrical amounts. Either procedure permits of determining the instant at which the desired degree of conversion is reached. If necessary, the oxidation may be carried out under pressure to increase the rate of reaction.

The following illustrative examples will aid in understanding the operating procedure in preparing monohydroxy aromatic compounds in accordance with my invention and will provide representative data of the many possible conversions of aromatic monocarboxylic acids into phenolic esters and phenols.

Example I

In this case a 200 cc. round-bottomed flask fitted with a water separator, a reflux condenser and a measuring burette for carbon dioxide gas, receives the charge of 61 g. of benzoic acid and 20 g. of cupric oxide as the oxidant, 15 cc. of xylene being added to form an azeotrope with the water of reaction. The flask is electrically heated to 500–565° F. for 5.5 hours. At the end of this heating 4.0 cc. of water and 6640 cc. of carbon dioxide are collected. The final product mixture is cooled and diluted with xylene to facilitate handling. On filtering, 16.1 g. of copper is recovered, and the filtrate is distilled to remove xylene at atmospheric pressure and then further distilled at a pressure of 20 mm. of mercury to give 31 g. of phenyl benzoate which has a saponification equivalent of 183.2 (theoretical value 198.0). After 10 g. of this phenyl benzoate, 8 g. of sodium hydroxide, 72 cc. of water and 25 cc. of 95% ethanol are charged into a stripping still of 150 cc. capacity and refluxed 2 hours, ethanol is stripped off and the product chilled and saturated with CO_2 to liberate phenol which is subsequently steam-stripped. The analysis of the condensate by titration (bromide-bromate) indicates the presence of 3.8 g. of phenol. This amount corresponds to 40.8% by weight yield of phenol (based on the acid consumed), the conversion of benzoic acid to phenyl benzoate being equal to 61.4%.

Example II

This example illustrates the occurrence of rearrangement during the oxidation of alkyl-substituted aromatic monocarboxylic acids.

In Example II, para-tertiary-butyl benzoic acid is oxidized under the conditions and using the equipment of

Example I. The amounts of the acid and of the copper oxide (CuO) are 82.0 g. and 20.0 g. respectively. Temperature of reaction is maintained at 550° F. for 8 hours. The ultimate product, upon hydrolysis of the ester, is found to be meta-tertiary-butyl phenol, the ester being obtained in a yield of 50.5% by weight (based on the acid consumed) which corresponds to a conversion of the acid equal to 75.5 mol per cent.

Example III

In this example 68 g. of meta-toluic acid is oxidized by employing an oxide (CuO) in an amount of 20 g., while heating at a temperature which ranges from 500 to 550° C., for 9 hours, in the equipment and under the conditions of Example I. Upon hydrolysis of the tolyl toluates obtained in a yield of 69.0% by weight, a 50 to 50 mixture of ortho- and para-cresols is recovered.

Example IV

Para-toluic acid in an amount of 68.0 g. is oxidized with a copper oxide (CuO) in an amount of 20 g. for about 16½ hours at a temperature from about 480 to about 560° F. in the same equipment and under the same conditions as in Example I. The meta-tolyl para-toluate is produced with a conversion of 93.0 mol percent of the acid and in a yield of 21.1%, and is subsequently hydrolyzed to meta-cresol.

Example V

A 200 cc. round-bottomed flask fitted with a thermometer, a stirrer, and provided with means for distillation and gas measurements is charged with 61 g. of benzoic acid and 28 g. of copper acetate $Cu(CH_3CO_2)_2.H_2O$. After heating the mixture for about 5.5 hours at about 490° F., the final product mixture is cooled, diluted with xylene and filtered to give 8.9 g. of copper powder. The filtrate is distilled, in the same manner as described in Example I hereinabove, to yield 18.5 g. of phenyl benzoate.

Example VI

A charge of 61 g. of benzoic acid and 27.6 g. of basic copper carbonate is placed into the reaction flask of Example I and heated to about 490° F. for more than 6 hours. The reaction product which remains in the flask is cooled, diluted with xylene and filtered. Powdered copper remains on the filter, and the filtrate, upon distillation as in Examples I and V, gives about 15 g. of phenyl benzoate.

Example VII

The same equipment is employed in this test to convert 86 g. of α-naphthoic acid to β-naphthol with the aid of 20 g. of CuO. The charge of naphthoic acid and copper oxide are heated to 580° F. for 5 hours, to liberate CO_2. The product mixture remaining in the flask is extracted with ether and the extract washed with an aqueous solution of sodium bicarbonate to remove any unreacted naphthoic acid. Upon evaporation of the ether, the residue is hydrolyzed for 2 hours in a sealed tube with the aid of 10% H_2SO_4 at a temperature of 500° F. The hydrolysis product mixture is neutralized with a solution of sodium bicarbonate and steam stripped. The overhead is collected and upon solidfication is found to be β-naphthol in a 27 mol percent yield based on the α-naphthoic acid converted.

The data presented in the aforementioned examples clearly establish the feasibility of preparing phenolic esters and of converting them to phenols and cresols by my process of liquid-phase oxidation of aromatic monocarboxylic acids in the presence of a copper compound from the group consisting of oxides of copper, and oxygen-containing copper salts capable of becoming decomposed at temperatures from 400 to 700° F. to yield CuO or Cu_2O. The exact mechanism of the formation of phenolic esters by this oxidation is not fully understood, although in all probability the presence of copper oxide,

and particularly in stoichiometrical amounts from about 5 to about 50 mol percent, based on the aromatic monocarboxylic acid being oxidized, induces formation of a copper salt of this acid which undergoes decomposition with concurrent liberation of copper or Cu_2O (depending on how far the reaction has been carried out), loss of CO_2 and introduction of oxygen into the phenyl or naphthyl ring of the originally employed acid. This route for converting aromatic monocarboxylic acids to monohydroxy aromatic compounds appears highly attractive for the purposes of chemical industry. In particular, the high yields of phenol secured in the conversion of benzoic acid in accordance with my invention, point to the possibility of employing this new route for the production of phenol, so important as the intermediate material for the manufacture of surface-active agents, additives for lubricating oils, disinfectants, and other valuable products.

The process technique which effects the conversion of aromatic monocarboxylic acids to phenols by heating these acids in the liquid phase at temperatures from about 400 to about 700° F. without employing free oxygen but in the presence of stoichiometric amounts of a copper oxide, and by hydrolyzing the resulting phenolic esters, is likewise applicable for a large number of other conversions. Various homocyclic and heterocyclic aromatic compounds having one carboxyl substituent attached to the aromatic nucleus, which may carry other substituents inert under the conditions of liquid-phase oxidation at 400° to 700° F., can be treated in accordance with my invention in the presence of a copper oxide, or other copper compound equivalent thereto for the purpose of oxidizing these aromatic compounds to hydrolyzable phenolic esters and will furnish valuable hydroxy-aromatic compounds. In order to be capable of such a conversion the aromatic nucleus of the compound to be subjected to the succession of steps of oxidation and hydrolysis must have at least one unsubstituted carbon in the position adjacent (ortho-) to the point of attachment of the carboxyl substituent.

For instance, a phthalic acid half ester (a mono-acid phthalate) $ROOC.C_6H_4.COOH$ can be transformed, by heating it in the liquid phase at 400 to 700° F. in the presence of a copper oxide, or an equivalent copper compound which yields a copper oxide at these temperatures, into an ester $ROOC.C_6H_4.COO.C_6H_4COOR$, which upon hydrolysis forms a hydroxybenzoic acid and the phthalic acid. Thus, isophthalic acid half-ester, heated in the aforedescribed manner, yields salicylic acid upon hydrolysis of the intermediate phenolic ester. Analogously, a phthalic acid half nitrile (a cyanobenzoic acid) is converted to an ester of a cyanobenzoic acid and a cyanophenol, which is then hydrolyzed to a hydroxybenzoic acid. Acetyl benzoic acid can be treated in a similar fashion to give acetyl phenol. Halobenzoic acids, e. g., meta-chlorobenzoic acid or 2,5-dibromobenzoic acid, can be treated to yield halophenyl halobenzoates, which are then converted to halophenols. Likewise nitrobenzoic acids give upon heating nitrophenols; e. g., metanitrobenzoic acid yields a mixture of ortho- and para-nitrophenols. Nicotinic acid (pyridine-3-carboxylic acid) treated in accordance with my invention yields β-pyridone. Salicylic acid and its isomers, para- and meta-hydroxybenzoic acids, can be heated to 400 to 700° F. in the presence of stoichiometrical amounts of a copper oxide and the resulting phenolic esters readily can be hydrolyzed to yield dihydroxybenzenes. Similarly, dihydroxybenzoic acids, in the aromatic nucleus of which there is present at least one unsubstituted carbon atom in the position adjacent to the carboxyl substituent, e. g., protocatechuic acid, are convertible to phenolic esters hydrolyzable to trihydric phenols, e. g., pyrogallol. Alkoxybenzoic acids, e. g., anisic acid, treated in accordance with my invention will also yield phenolic esters which, upon hydrolysis, are converted to dihydric phenols such as

resorcinol. If the phenolic esters produced by oxidation of an alkoxybenzoic acid with a copper oxide are subjected to saponification only, without undergoing hydrolysis, the ether linkage of the initial acid will be retained, so that an alkoxy phenol will be obtained as the ultimate product. Finally, monocarboxy-substituted naphthalenes, which satisfy the requirement for the operativeness of my process, that the aromatic nucleus have at least one unsubstituted carbon atom adjacent to the carboxyl group and that other substituents of the nucleus be inert at oxidation temperatures of 400 to 700° F. in the presence of a copper oxide, are also suitable for conversion to naphthols. Thus α- and β-naphthoic acids can be heated to form naphtholic esters hydrolyzable to naphthols.

The aforementioned conversions of different homocyclic and heterocyclic aromatic compounds having one carboxyl substituent attached to the aromatic nucleus and which may have other substituents inert under the conditions of liquid-phase oxidation at 400° to 700° F. may also be successfully carried out in the presence of catalytic amounts of copper compounds, such as metallic copper, organic and inorganic copper salts (acetate, sulfate, chloride, etc.) and copper oxides, while passing a current of pure oxygen or free oxygen bearing inert gas through the monocarboxy-substituted aromatic compound. Satisfactory conversions to phenolic esters and phenols are obtained, provided the aromatic nucleus of the compound subjected to the successive oxidation and hydrolysis has at least one unsubstituted carbon in the position adjacent (ortho-) to the point of attachment of the carboxyl substituent.

This application is a continuation-in-part of my copending application Serial No. 216,084, filed March 16, 1951.

It is to be understood that my invention is in no way limited by the specific examples given hereinbefore and that many modifications and variations in conformity with the spirit of the invention may be made without departing from the scope of my inventive contribution as defined in the following claims.

I claim:

1. A process, which comprises reacting from about 5 to about 50 mol per cent of a copper oxide, at a temperature from about 400° F. to about 700° F. and in the absence of elemental oxygen, with a meta-monoalkyl substituted aromatic hydrocarbon compound in the liquid phase, said compound having less than 13 nuclear carbon atoms in its molecule, carrying one carboxyl substituent on its aromatic nucleus, and having at least one unsubstituted nuclear carbon atom in the position ortho- to said carboxyl substituent; hydrolyzing the resulting phenolic ester product; and recovering from the hydrolysis product a mixture of ortho- and para-monoalkyl substituted phenol.

2. A process, which comprises reacting from about 5 to about 50 mol percent of a copper oxide, at a temperature from about 400° F. to about 700° F. and in the absence of elemental oxygen, with an ortho-monoalkyl substituted aromatic hydrocarbon compound in the liquid phase, said compound having less than 13 nuclear carbon atoms in its molecule, carrying one carboxyl substituent on its aromatic nucleus, and having at least one unsubstituted nuclear carbon atom in the position ortho- to said carboxyl substituent; hydrolyzing the resulting phenolic ester product; and recovering from the hydrolysis product a meta-monoalkyl substituted phenol.

3. A process, which comprises reacting from about 5 to about 50 mol percent of a copper oxide, at a temperature from about 400° F. to about 700° F. and in the absence of elemental oxygen, with a para-monoalkyl substituted aromatic hydrocarbon compound in the liquid phase, said compound having less than 13 nuclear carbon atoms in its molecule, carrying one carboxyl substituent on its aromatic nucleus, and having at least one unsubsti-

tuted nuclear carbon atom in the position ortho- to said carboxyl substituent; hydrolyzing the resulting phenolic ester product and recovering from the hydrolysis product a meta-monoalkyl substituted phenol.

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