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PROCESS FOR PRODUCTION OF AROMATIC CARBOXYLIC ACIDS

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This invention relates to a process for converting aromatic alcohols to aromatic carboxylic acids. It also relates to the conversion of aromatic alcohols, which are obtained by some method other than the oxidation of alkylaromatic hydrocarbons, to aromatic carboxylic acids. It especially relates to the conversion of tolyl alcohols to toluic acids and phthalic acids.

In application Serial No. 280,387, filed April 3, 1952, now abandoned, in the name of Ewald Katzschmann, there is described a process for the production of aromatic polycarboxylic acids by the oxidation of alkylaromatic compounds in the liquid phase with elemental oxygen or oxygen-containing gases, under pressure if desired, preferably in the presence of oxidation catalysts, in which process relatively difficultly oxidizable intermediate carboxylic acids are converted into more readily oxidizable functional derivatives, particularly esters, and these derivatives are further oxidized.

It was found that the inventive idea which was the basis of that process, namely: to make the oxidation of intermediate oxidation products easier by conversion into functional derivatives, can also be applied to the oxidation of such materials which, to be sure, are oxidation products of alkylaromatic hydrocarbons when considered chemically, although they are not necessarily formed by oxidation of alkyl aromatics.

Substances which, from the chemical point of view, are conceived to be oxidation products of alkyl aromatics, are, for example, aromatic alcohols, such as, p-tolyl alcohol, m-tolyl alcohol, o-tolyl alcohol and their homologs. These can be oxidized to the corresponding carboxylic or polycarboxylic acids with elemental oxygen or oxygen-containing gases only fairly slowly. It has been shown that their functional derivatives, such as the ethers and esters are relatively very much more rapidly oxidized if they are treated, under the same conditions as the alcohols, with elemental oxygen or oxygen-containing gases.

As relatively readily oxidizable derivatives of aromatic alcohols, the ethers with lower aliphatic alcohols, especially with methanol, and the ethers which are formed from the aromatic alcohols by cleavage of water are considered above all. Of the esters of aromatic alcohols, those are especially suitable which are formed from the lower aliphatic carboxylic acids and especially those formed from the carboxylic acids which correspond to the alcohols.

The source of the aromatic alcohols and their esters and ethers is of no significance for the process of oxidation according to the invention. Commercially, those products are especially significant which can be obtained in known fashion from the products of the chloromethylation of aromatics, alkylated if occasion arises. The aromatic alcohols obtainable from the chloromethylation products or the functional derivatives of these alcohols can be broken down in known fashion into the pure isomers and then oxidized; however, the mixture of isomers can also be processed directly.

Example 1

A mixture of 1380 g. of toluene and 1536 g. of 31.5% formaldehyde solution is saturated with HCl gas (555 g.) between 0 and 12° C. with stirring and then warmed with stirring and with continuous introduction of HCl to 70° C. until no more gas is taken up. The oil which separates is washed free of acid with water and soda solution and, after drying with $CaCl_2$, is fractionated at 12 mm. of Hg (absolute pressure). The fraction which goes over at about 79° C. (about 1550 g.) is chloromethyltoluene.

A 421.5-g. sample of chloromethyltoluene is stirred into a solution of 132 g. of NaOH in 15–18 cc. of methanol at room temperature and, after the reaction which proceeds spontaneously has ceased, is refluxed for one hour with stirring. After cooling, the NaCl which has separated is dissolved with as little water as possible, the methylbenzyl methyl ether is taken up in petroleum ether and, after drying with Na_2SO_4, is distilled at 12 mm. of Hg (absolute pressure) (B. P. 12 mm. 70.5–71.5° C.; yield, about 95%).

A 1000-g. sample of methylbenzyl methyl ether is mixed with 1 g. of a soluble cobalt salt, for example, of the fatty acids with 7–9 carbon atoms obtained by the oxidation of paraffins, and oxidized at 140° C. with 1.5 liters of air per minute. Rapid oxidation occurs, as is evident from the increase of acid and saponification numbers:

After 6 hours acid No. = 58; sapon. No. =148
After 30 hours acid No. =209; sapon. No. =380
After 42 hours acid No. =236; sapon. No. =414

From 945 g. of oxidate, by saponification and the usual processing, 890 g. of toluic acid with a slight content of dicarboxylic acids can be isolated.

If a mixture of o- and p-tolyl alcohol (about 50:50) is treated with air under the same conditions, the oxidation takes place only extremely slowly; after 35 hours, the acid number amounts to only 2, the saponification number, to 18.

Example 2

A 140.5-g. sample of chloromethyltoluene prepared according to Example 1 is refluxed with 1300 cc. of one normal soda solution, the methylbenzyl alcohol taken up in ether, and, after evaporation of the ether, converted into the dixylyl ether by heating for several hours under reflux with separation of the water from the reflux condensate.

A 500-g. sample of a mixture of dixylyl ethers obtained in this way (about 70% p- and 30% o-compounds) is oxidized in the presence of 0.1% of the cobalt salt of Example 1 with 1.5 liters of air per minute at 140° C. as in Example 1:

After 3 hours acid No. = 22; sapon. No. = 44
After 15 hours acid No. = 59; sapon. No. =100
After 30 hours acid No. =151; sapon. No. =214
After 45 hours acid No. =189; sapon. No. =279

After saponification and the usual processing, 240 g. of toluic acids containing dicarboxylic acids are obtained.

If a dixylyl ether mixture which is richer in the o-compounds is analogously oxidized, the oxidation proceeds even more rapidly.

After 3 hours acid No. = 30; sapon. No. = 58
After 15 hours acid No. = 70; sapon. No. =127
After 30 hours acid No. =205; sapon. No. =280
After 45 hours acid No. =226; sapon. No. =353

After saponification and the usual processing, 460 g. of toluic acids containing dicarboxylic acids can be isolated.

Example 3

250 g. of p-tolyl acetate, which were prepared in the known fashion by the esterification of technical p-tolyl alcohol with acetic anhydride, was mixed with 0.2% of the cobalt salt of Example 1 and treated at 125° for 18 hours with ½ liter of air per minute. 253 g. of oxidate were obtained with an acid number of 85 and a saponification number of 422. The acid products, which had been formed, were separated from 226 g. of oxidate with sodium bicarbonate solution, whereupon 145 g. of unchanged p-tolyl acetate was recovered. The acid products produced, after a complete saponification with an excess of KOH and decomposition with HCl, 61½ g. of acids with an acid number of 376, a saponification number of 379, and an OH number of 298. The acids are a mixture of about 1 part p-toluic acid with 4 parts of para-hydroxymethylbenzoic acid.

What I claim and desire to protect by Letters Patent is:

1. The process of preparing a hydroxy methyl benzoic acid which comprises converting a tolyl alcohol into an ester and then oxidizing the ester in liquid phase with a gas containing elemental oxygen at an elevated temperature in the presence of an oxidation catalyst.

2. The process of claim 1, wherein the ester is prepared from a lower aliphatic carboxylic acid.

3. The process of claim 1, wherein the ester is prepared by the use of acetic acid anhydride.

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