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PROCESS FOR THE PRODUCTION OF AROMATIC DI- AND POLYCARBOXYLIC ACIDS

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This invention relates to the production of aromatic carboxylic acids. The invention more particularly relates to production of aromatic polycarboxylic acids by the rearrangement of carboxyl groups on bivalent metal salts of aromatic carboxylic acids, through heating the salts in an inert atmosphere.

We have previously found that alkali metal salts of aromatic carboxylic acids may be transformed into the salts of other aromatic carboxylic acids by heating to elevated temperatures. In accordance with this process, a number of industrially valuable reaction products such as terephthalic acid, trimesitic acid, naphthalene-2,6-dicarboxylic acid, 4,4'-diphenyldicarboxylic acid and many others may be produced, in many cases from readily accessible starting materials. In addition, the ring systems free from carboxyl groups are in some cases obtained as side products. This process may be carried out at various elevated pressures or at atmospheric pressure, advantageously in an atmosphere of an inert protective gas, and if desired, in the presence of catalytically-active metals or metal compounds.

We have now found that polyvalent metal salts of aromatic mono- or dicarboxylic acids may also be transformed, by heating the same, into the salts of other aromatic carboxylic acids, especially di- and polycarboxylic acids which can be transformed into the free acids or their derivatives in accordance with known methods. In many cases this new process forms other reaction products or other principal products than the transformation of the corresponding alkali metal salts. Often those di- or polycarboxylic acids are formed which contain at least two carboxyl groups in ortho-position with respect to each other. For example, in accordance with the process of the present invention, orthophthalic acid may be obtained from benzoic acid.

It is an object of this invention to produce aromatic polycarboxylic acids by heating bivalent metal salts of other aromatic carboxylic acids in an inert atmosphere to cause rearrangement of the carboxyl groups on the aromatic nucleus.

This and other objects of our invention will become apparent as the description thereof proceeds.

The starting material for the process according to the invention may be a salt of an aromatic mono- or dicarboxylic acid, for example, salts of benzoic acid, α - and β -naphthoic acid, diphenylmonocarboxylic acid, as well as the salts of orthophthalic acid, isophthalic acid, terephthalic acid, naphthalic acid and other naphthalenedicarboxylic acids and also the salts of diphenic acid and other diphenyldicarboxylic acids. Similarly, the salts of mono- or dicarboxylic acids in which the carboxyl groups are attached to another aromatic ring system, for example, to anthracene, terphenyl, diphenylmethane or benzophenone radicals, are suitable as starting materials for the process of this invention. In addition, mixtures of aromatic carboxylic acids may be used, such as those which are obtained by oxidation of raw xylene mixtures or coal in accordance with various known methods.

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In the carboxylic acids which serve as starting materials for the process in accordance with the invention, the aromatic ring may in addition to the carboxyl groups also carry other substituents such as halogen atoms or alkyl radicals, provided that such molecules do not undergo a decomposition at a temperature lower than the reaction temperature.

The carboxylic acids serving as starting materials for our process are used in the form of their polyvalent metal salts. Especially suitable are the alkaline earth metal salts, for example the salts of magnesium, calcium, strontium or barium. In place of these salts, reaction mixtures which produce such salts under the reaction conditions may also be used. Particularly mixtures of carboxylic acid anhydrides and acid-binding metal compounds, for example metal carbonates or metal oxides, are suitable. These mixtures do not need to be present in stoichiometric ratio. One or the other component of the mixture may be used in excess. The salts or salt mixtures are preferably used in as dry a condition as possible.

It has further been found that the reaction according to the invention is favorably influenced by the presence of catalysts. Particular catalysts which may be used are metals such as zinc, cadmium, mercury, lead and iron, as well as compounds of these metals, for example their oxides or their salts formed with inorganic or organic acids. Suitable salts of this type are, among others, the carbonates, bicarbonates, halides, sulfates, phosphates, acetates, formates, oxalates and fatty-acid salts, or also the salts of the above-mentioned metals formed with those acids which are used as starting materials for the reaction according to the invention or which are formed by this reaction, for example benzoates or phthalates. The quantity of the catalyst added to the reaction mixture may vary within wide limits and may range from 0 to 15%, preferably from 0.5 to 5% by weight, based on the weight of reaction mixture. The above-named catalysts may also be employed in conjunction with known carriers, such as kieselguhr.

In addition to these catalysts, the reaction according to the invention may be carried out in the presence of inert liquid or solid additives, for example in the presence of sand, metal powders, metal shavings, kieselguhr, activated charcoal, finely divided aluminum oxide, finely divided silicic acid, or also in the presence of inert salts such as sodium sulfate. In many cases the presence of these additives improves the mechanical properties of the reaction mixture. In place of solid inert substances, inert liquids which do not decompose under the prevailing conditions of the reaction may also be used.

In some cases it is also advantageous to heat the salts of the aromatic mono- or dicarboxylic acids in the presence of acid-binding agents, for example, in the presence of carbonates, bicarbonates or oxalates of the alkali metals, alkaline earth metals or other metals above indicated.

Since the presence of oxygen during the heating step as a rule unfavorably influences the yields, it is advantageous to perform the reaction in the presence of an inert protective gas. For this purpose carbon dioxide is most suitable, but other inert gases, such as nitrogen or methane, may also be used. It is advantageous to carry out the reaction at elevated pressures.

The reaction in accordance with the invention begins in most cases at temperatures between 200 and 300° C. The optimum reaction temperature, however, varies and depends upon the starting material used. While it is possible to operate at temperatures up to about 500° C., it is nevertheless advantageous to use a reaction temperature below 450° C., because at excessively high tempera-

tures undesirable side reactions such as ketonization or carbonization may occur.

In order to avoid local overheating and decomposition brought about thereby, and in order to avoid caking of the reaction mixture in performing the reactions of this invention, the reaction mass should be maintained in motion. This may be accomplished, for example, by working in vessels provided with stirring devices or in rocker or rotary autoclaves. Uniform heating of the reaction mass may, however, also be effected by distributing the reaction mixture in thin layers; in this method the reaction mixture may remain stationary or may be agitated. Good yields are, however, also obtained without these special measures if care is taken that strong local overheating is avoided.

The reaction mixture may be worked up in accordance with well-known methods. For example, the free acids may be obtained by treating the raw reaction product with dilute mineral acids. The acids may then be purified in well-known fashion. Another possibility consists of transforming the raw reaction product into the alkali metal salts of the aromatic di- or polycarboxylic acid formed by the reaction by treatment with an aqueous alkali metal carbonate solution. From the solution of the alkali metal salts the free acids, or also their acid salts, may be precipitated in known fashion by acidification of the solution with an inorganic or organic acid. It is also possible to acidify the solution with the aid of carbon dioxide at atmospheric or elevated pressure. The free acids may be separated by methods based upon their different solubilities or volatilities and thereafter isolated in pure form or, if desired, transformed into their derivatives, such as their halides or esters. The separation and purification of the acids may also be carried out in known fashion by esterifying the acids and distilling or fractionating these esters.

The following examples are illustrative of our invention and will enable persons skilled in the art to understand and practice the invention, but the invention is not intended to be limited to these examples.

Example I

37.9 gm. barium benzoate were placed into an autoclave having a volume of 0.2 liter. The autoclave was evacuated and subsequently 180 gm. carbon dioxide were introduced into the autoclave from a pressure bottle. Thereafter, the contents of the autoclave were heated for 10 hours at 350° C. (In this and the following examples the temperatures were measured with a thermocouple which was located in the center of the pulverulent reaction mixture.) During the heating step a pressure of about 1580 atmospheres developed. After cooling the autoclave and releasing the pressure, the raw reaction product, which weighed 37.5 gm., was boiled together with a solution of 20 gm. potassium carbonate in 500 cc. water. The barium carbonate formed thereby was filtered off and the aqueous solution was acidified with hydrochloric acid. After cooling the solution to room temperature, the acid which had crystallized out was filtered off and the mother liquor was extracted with ether. The crystals obtained by evaporating the ether from the ether extract were combined with the crystals separated by filtration from the aqueous solution and benzoic acid was extracted from this mixture with the aid of chloroform. In this manner 9.65 gm. benzoic acid were recovered. The residue weighing 8.0 gm. consisted of orthophthalic acid.

Example II

A mixture of 37.9 gm. barium benzoate and 2 gm. cadmium fluoride was heated for 10 hours at 350° C. in an autoclave having a volume of 0.2 liter, into which 190 gm. carbon dioxide had been introduced under pressure prior to heating. In the course of the heating step, a pressure of about 2000 atmospheres developed. After cooling the autoclave and releasing the pressure, the raw product

which weighed 32.6 gm. was boiled with a solution of 25 gm. potassium carbonate in 500 cc. water. The barium carbonate formed thereby was filtered off and the aqueous solution was acidified with hydrochloric acid. Upon cooling of the acidified solution, 3 gm. of the acid potassium salt of an aromatic carboxylic acid first crystallized out which was not further identified. 11.75 gm. orthophthalic acid were obtained from the mother liquor by crystallization and extraction with ether.

Example III

33.0 gm. strontium benzoate admixed with 2 gm. mercuric chloride were heated for 10 hours at 330° C. in an autoclave having a volume of 0.2 liter into which 180 gm. carbon dioxide had been introduced under pressure prior to heating. A pressure of about 1850 atmospheres developed during the heating period. After cooling the autoclave and releasing the pressure, the reaction product was boiled with a solution of 20 gm. potassium carbonate in about 400 cc. water. The strontium carbonate formed thereby was filtered off and the aqueous solution was acidified with hydrochloric acid. After allowing the acidified solution to stand at room temperature for some time, the orthophthalic acid which had separated out was filtered off and the mother liquor was extracted with ether. The total amount of orthophthalic acid obtained by this procedure of crystallization and esterification was 14.0 gm.

Example IV

37.9 gm. barium benzoate admixed with 2 gm. mercuric chloride were heated for 10 hours at 330° C. in an autoclave having a volume of 0.2 liter, into which 190 gm. carbon dioxide had been introduced under pressure prior to heating. During the heating period, a pressure of about 2000 atmospheres developed. The reaction product was boiled with a solution of 20 gm. potassium carbonate in about 400 cc. water. The barium carbonate formed thereby was filtered off and hydrochloric acid was added to the hot filtrate until it reacted strongly acid. Terephthalic acid in the amount of 0.6 gm. crystallized out which was filtered off while hot. Subsequently, the solution was cooled to room temperature and, after separating the orthophthalic acid, which crystallized out, was extracted with ether. The total amount of orthophthalic acid obtained thereby was 10.1 gm.

Example V

8 gm. magnesium oxide, 45.2 gm. benzoic acid anhydride and 4 gm. of the double salt $K_2CdF_2Cl_2$ were intimately admixed in a ball mill. The resulting mixture was heated for 10 hours at 300° C. in the presence of 170 gm. carbon dioxide in an autoclave having a volume of 0.2 liter. A pressure of about 2000 atmospheres developed during this period. After cooling the autoclave and releasing the pressure, the reaction product was boiled with a solution of 30 gm. potassium carbonate in 500 cc. water. The basic magnesium carbonate formed thereby was filtered off and the filtrate was acidified with hydrochloric acid while hot. There crystallized out 0.65 gm. of terephthalic acid which was filtered off while hot. By crystallization and extraction with ether in the manner described in Example I 5.3 gm. orthophthalic acid were recovered from the solution. In addition, 16.9 gm. benzoic acid were recovered.

Example VI

37.9 gm. barium benzoate and 2 gm. cadmium fluoride were admixed in a ball mill and the resulting mixture was heated for 5 hours at 350° C. in a rotary autoclave having a volume of 0.2 liter. At the beginning of the run, carbon dioxide was introduced into the autoclave until the internal pressure reached 50 atmospheres. The final pressure at 350° C. was 160 atmospheres.

After cooling the autoclave and releasing the pressure, the reaction product, which weighed 29.7 gm. was boiled

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with a solution of 30 gm. potassium carbonate in 400 cc. water. The barium carbonate formed thereby and the catalyst were filtered off and the filtrate was acidified with hydrochloric acid while hot. There crystallized out 0.95 gm. terephthalic acid which was filtered off while hot. Thereafter, the mother liquor was cooled and by crystallization and extraction with ether in the manner described in Example I, 11.65 gm. of a mixture of organic acids having an acid number of 625 were obtained. By extraction with chloroform, 2.55 gm. benzoic acid were separated from this mixture. The residue weighing 9.1 gm. consisted of a mixture of orthophthalic and isophthalic acid (68.4% orthophthalic acid and 31.6% isophthalic acid).

Example VII

37.9 gm. barium benzoate, 19.75 gm. barium carbonate and 2.5 gm. cadmium fluoride were admixed in a ball mill. The mixture was heated for 5 hours at 350° C. in a rotary autoclave having a volume of 0.2 liter. At the beginning of the run carbon dioxide was introduced under pressure into the autoclave until the internal pressure reached 50 atmospheres. The final pressure at 350° C. was 160 atmospheres.

The reaction product, which weighed 54.8 gm. was boiled with a solution of 50 gm. potassium carbonate in 500 cc. water. After filtering off the barium carbonate formed thereby and the catalyst, the hot solution was acidified with hydrochloric acid and thereafter filtered while still hot. In this manner, 1.95 gm. terephthalic acid were obtained. By crystallization and extraction with ether, a total of 13.6 gm. of a mixture of organic acids (acid number=628) were isolated from the cooled mother liquor. By extraction with chloroform of the organic acid mixture, 2.96 gm. benzoic acid were recovered. The residue which weighed 10.64 gm. consisted of 62.5% orthophthalic acid and 37.5% isophthalic acid.

Example VIII

A mixture of 37.9 gm. barium benzoate and 2 gm. cadmium fluoride was heated for 5 hours at 320° C. in a rotary autoclave having a volume of 0.2 liter. At the beginning of the run carbon dioxide was introduced into the autoclave until the internal pressure reached 5 atmospheres. The final pressure at 320° C. was 20 atmospheres. The reaction product, which weighed 36.6 gm. was boiled with a solution of 40 gm. potassium carbonate in 500 cc. water. The barium carbonate produced thereby was filtered off and the solution was acidified with hydrochloric acid. By crystallization and extraction with ether 20.95 gm. of a mixture of organic acids was obtained which consisted of 75% benzoic acid and 25% orthophthalic acid.

Example IX

A mixture of 42.3 gm. calcium benzoate and 2 gm. of cadmium fluoride was heated for 4 hours at 400° C. in a rotary autoclave having a volume of 0.2 liter. At the beginning of the run, carbon dioxide was introduced into the autoclave until the internal pressure reached 50 atmospheres. The final pressure at 400° C. was 160 atmospheres.

The reaction product, which weighed 31.1 gm., was boiled with a solution of 35 gm. potassium carbonate in 500 cc. water. The calcium carbonate formed thereby was filtered off and the filtrate was acidified with hydrochloric acid while hot. There crystallized out 3.15 gm. terephthalic acid which were filtered off while hot. From the cooled mother liquor 21.1 gm. of a mixture of organic acids was obtained by crystallization and extraction with ether; the mixture contained 13.7 gm. benzoic acid and 6.4 gm. ortho- and isophthalic acid. The ratio between ortho- and isophthalic acid was about 1:3 as determined with the aid of an infra-red spectroscope.

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The total yield of dicarboxylic acids accordingly was 9.55 gm.

Example X

A mixture of 37.9 gm. barium benzoate and 2.0 gm. cadmium fluoride was heated for 3 hours at 340° C. at atmospheric pressure in a stream of carbon dioxide. The reaction product which weighed 31.85 gm. was boiled with a solution of 35 gm. potassium carbonate in 500 cc. water. The barium carbonate formed thereby was filtered off and the filtrate was acidified with hydrochloric acid. By crystallization and extraction with ether, 8.62 gm. benzoic acid and 5.93 gm. orthophthalic acid were isolated. As determined by infra-red analysis, the orthophthalic acid was free from isophthalic acid.

When the above-described run was repeated but the reaction period was extended from 3 hours to 6 hours, 6.32 gm. benzoic acid and 7.48 gm. orthophthalic acid were obtained.

Example XI

A mixture of 38 gm. strontium benzoate and 1.5 gm. cadmium fluoride were heated in an autoclave for 4 hours at 350° C. in an atmosphere of carbon dioxide under a constant pressure of 10 atmospheres.

The reaction product which weighed 32.45 was worked up in the manner above described. 9.72 gm. orthophthalic acid and 6.43 gm. benzoic acid were isolated.

Example XII

A mixture of 400 gm. barium benzoate and 24 gm. of cadmium fluoride were placed into a tube made of sheet steel. The tube was placed into an autoclave having a net volume of 7 liters. The air in the autoclave was displaced by repeated flushings with carbon dioxide. Subsequently, carbon dioxide was introduced into the autoclave until the internal pressure reached 10 atmospheres. The autoclave was then heated to 370° C. for three hours and the internal pressure was kept constant at 10 atmospheres. The excess gas was passed through a cooler and then through two washbottles filled with tetralin and finally through a cooling trap which was cooled to -55° C. with the aid of a suitable cooling mixture.

After completion of the heating step and while the autoclave was still hot, the carbon dioxide and the gases formed by the reaction were carefully bled off and passed through the cooler, the wash-bottles and the cooling trap and the system was flushed with carbon dioxide.

By fractional distillation of the content of the wash-bottles and the cooling trap 39 gm. of pure benzene were obtained. The solid reaction products were worked up in the manner described in the previous examples. We thereby obtained 96.2 gm. orthophthalic acid and 73.2 gm. benzoic acid.

Example XIII

A mixture of 50 gm. barium isophthalate and 3 gm. cadmium fluoride were heated for 4 hours at 440° C. in an atmosphere of carbon dioxide in an autoclave at a constant pressure of 10 atmospheres. The raw reaction product which weighed 46.25 gm. was dissolved in water, the solution was filtered to remove insoluble components and the filtrate was acidified with hydrochloric acid. The organic acids precipitated thereby were filtered off. The mother liquor was extracted from ether. The residue remaining behind after evaporation of the ether from the ether extract was combined with the organic acids previously precipitated and filtered off. By determination of the acid number and through infrared analysis it was determined that the acid mixture isolated in this manner consisted of 13.8 gm. isophthalic acid, 3.9 gm. hemimellitic acid and small amounts of orthophthalic acid.

While we have described particular embodiments of our invention, it will be understood that the invention is

not limited thereto and that various modifications may be made thereof without departing from the spirit of the disclosure and the scope of the following claims.

We claim:

1. A process for the manufacture of salts of benzene polycarboxylic acids having from two to three carboxyl groups attached in adjacent positions on the benzene nucleus by using as starting materials salts of benzene carboxylic acids having from one to two carboxyl groups, said starting material acid having one less carboxyl group than the product acid, said salts being selected from the group consisting of magnesium, calcium, strontium and barium salts which comprises heating said starting salts to a temperature above 300° F. and below the temperature at which said starting materials and said products will substantially decompose, in a substantially oxygen free, inert atmosphere, for a time sufficient to form the corresponding salts of said product acid.

2. A process for the manufacture of salts of benzene polycarboxylic acids having from two to three carboxyl groups attached in adjacent positions on the benzene nucleus by using as starting materials salts of benzene carboxylic acids having from one to two carboxyl groups, said starting material acid having fewer carboxyl groups than the product acid, said salts being selected from the group consisting of magnesium, calcium, strontium and barium salts which comprises heating said starting salts to a temperature above 300° F. and below the temperature at which said starting materials and said products will substantially decompose in a substantially oxygen free, inert atmosphere, in the presence of a catalyst containing a metal selected from the group consisting of zinc, cadmium, mercury, lead and iron, for a time sufficient to form the corresponding salts of said product acid.

3. The process of claim 2 wherein the inert atmosphere is carbon dioxide.

4. The process of claim 2 wherein the reaction is conducted at elevated pressures.

5. A process for the manufacture of salts of benzene polycarboxylic acids having from two to three carboxyl groups attached in adjacent positions on the benzene nucleus, said salts being selected from the group consisting of magnesium, calcium, strontium and barium salts, by using as starting materials the corresponding salts of benzene carboxylic acids having from one to two carboxyl groups, said starting material salts having one less carboxyl group than the product salt, which comprises heating said starting salts to a temperature above 300° F. and below the temperature at which said starting materials and said products will substantially decompose, in a substantially oxygen free, inert atmosphere, in the presence of a catalyst containing a metal selected from the group consisting of zinc, cadmium, mercury, lead and iron, for a time sufficient to form the said corresponding product salts.

6. A process for the manufacture of benzene polycarboxylic acids having from two to three carboxyl groups attached in adjacent positions on the benzene nucleus by using as starting materials benzene carboxylic acids hav-

ing from one to two carboxyl groups, said starting material acids having fewer carboxyl groups than the product acid, comprising the steps of heating salts of said starting materials, said salts being selected from the group consisting of magnesium, calcium, strontium and barium salts to a temperature above 300° F. but below the temperature at which said starting materials and said products will substantially decompose, in a substantially oxygen free, inert atmosphere, for a time sufficient to form the corresponding salts of said product acid, and thereafter liberating the free product acid.

7. The process of claim 6 wherein the inert atmosphere is carbon dioxide.

8. The process of claim 6 wherein the reaction is conducted under elevated pressures.

9. A process for the manufacture of benzene polycarboxylic acids having from two to three carboxyl groups attached in adjacent positions on the benzene nucleus by using as starting materials benzene carboxylic acids having from one to two carboxyl groups, said starting material acids having at least one less carboxyl group than the product acid, comprising the steps of heating salts of said starting materials, said salts being selected from the group consisting of magnesium, calcium, strontium and barium salts to a temperature above 300° F. but below the temperature at which said starting materials and said products will substantially decompose, in a substantially oxygen free, inert atmosphere, in the presence of a catalyst containing a metal selected from the group consisting of zinc, cadmium, mercury, lead and iron, for a time sufficient to form the corresponding salts of said product acid, and thereafter liberating the free acid.

10. A process for the manufacture of orthophthalic acid by heating as a starting material salts of benzoic acid said salts being selected from the group consisting of magnesium, calcium, strontium and barium salts to a temperature above 300° F. but below the temperature at which said starting materials and said products will substantially decompose, in a substantially oxygen free, inert atmosphere, in the presence of a catalyst containing a metal selected from the group consisting of zinc, cadmium, mercury, lead and iron, for a time sufficient to form the corresponding salts of orthophthalic acid and thereafter liberating the free acid.

11. A process for the manufacture of hemimellitic acid by heating as a starting material salts of isophthalic acid said salts being selected from the group consisting of magnesium, calcium, strontium and barium salts to a temperature above 300° F. but below the temperature at which said starting materials and said products will substantially decompose, in a substantially oxygen free, inert atmosphere, in the presence of a catalyst containing a metal selected from the group consisting of zinc, cadmium, mercury, lead and iron, for a time sufficient to form the corresponding salts of hemimellitic acid and thereafter liberating the free acid.

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