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3,471,555

PROCESS FOR THE OXIDATION OF
ALKYL BENZENES

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9 Claims

ABSTRACT OF THE DISCLOSURE

Benzene carboxylic acids containing 1 to about 4 carboxyl groups can be produced by dissolving acetylsulfuric acid in acetic acid and separately dissolving alkali metal chromate or dichromate in acetic acid so that both mixtures are substantially anhydrous and one or both contain alkyl benzene or partially oxidized alkyl benzene with 1 to about 4 alkyl groups or partially oxidized alkyl groups per molecule. Thereafter the two mixtures thus formed are intermixed at a temperature of about 15 to about 80° C. and the benzene carboxylic acids are recovered.

The present invention relates to new methods for the preparation of benzene carboxylic acids, particularly benzene carboxylic acids which contain from one to about four carboxyl groups.

A wide variety of processes have been taught for the oxidation of the alkyl groups of mono- and poly-alkyl benzenes such as xylenes, toluene, mesitylene, by utilizing strong oxidizing agents such as chromic acid, to produce the corresponding benzene carboxylic acids. In the main, these processes have suffered from either of two disadvantages: they have either failed to completely oxidize the alkyl groups in satisfactory yields or they have excessively oxidized the starting materials causing destruction of the ring.

The present invention embodies the discovery that by the methods taught herein high yields of the desired benzene carboxylic acids may be obtained with little or no attendant ring damage. The invention involves a process which comprises using acetylsulfuric acid in the conjoint presence of acetic solvent and alkali metal chromates or dichromates to oxidize alkyl benzenes. While the present invention is not to be limited to any particular reaction mechanism it appears that the aforesaid acetylsulfuric acid functions as a combination acid catalyst and dehydrating agent. It has been discovered that it is important to the attainment of optimum results with the present invention that the reactions thereof be conducted under substantially anhydrous conditions.

The preferred alkyl benzene starting materials for use with the present invention are 1,2,4,5-tetraalkylbenzene; 1,3,5-trialkylbenzene, 1,2,4-trialkylbenzene, 1,2-dialkyl benzene, 1,3-dialkyl benzene, 1,4-dialkyl benzene and monoalkyl benzene. Particularly preferred are those of the above compounds wherein the alkyl groups are methyl groups. The most preferred starting materials for the practice of the present invention are mesitylene, meta xylene, paraxylene, and toluene.

Partially oxidized alkyl benzenes may be employed as starting materials for the processes of the present invention. For example, aldehydes or alcohol groups may be substituted onto the ring, e.g. parahydroxy-methylbenzaldehyde. In those starting materials which contain alcohol groups, those containing primary alcohol groups are most preferred. Mixtures of starting materials are, of course, permissible.

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The acetylsulfuric acid for use with the present invention may be added directly to the reaction mixture or may be produced in situ by adding approximately stoichiometric quantities of acetic anhydride and sulfuric acid or, alternatively, by adding sulfur trioxide to acetic acid. Preferably from about 4 to about 15, and more preferably, from about 5 to about 7 moles of acetylsulfuric acid should be present for each mole of methyl groups in the alkyl benzenes in the final reaction mixture.

Though still within the above mentioned preferred ranges, a slightly greater amount of acetylsulfuric acid will be used when alkyl and metal chromate is used to compensate for the greater amount of water produced by this reaction as compared to that produced when using the dichromate.

To avoid interaction between the acetylsulfuric acid and the alkali metal chromate or dichromate it is preferable to add the reaction materials in such a manner as to avoid contact between the chromate or dichromate and the acetylsulfuric acid prior to the addition of the alkyl benzene. This can readily be accomplished by preparing a mixture of acetylsulfuric acid dissolved in acetic acid, when preparing a second mixture of alkali metal chromate or dichromate dissolved in acetic acid. Adding the alkyl benzene starting materials to one or both of the aforementioned mixtures and thereafter co-mingling to form a single final reaction mixture. Under some circumstances it will be desirable to add one or the other of the mixtures drop-wise, and in most cases it will be preferable to combine the mixtures slowly in order to avoid excessive evolution of heat of reaction.

The temperature of the final reaction mixture should preferably be from about 15 to about 80 degrees C., and more preferably from 30 to 60 degrees C. The maintaining of this range has been found to be important for obtaining of best results because higher temperatures have been found to cause oxidation of the acetylsulfuric acid and because lower temperatures may cause excessive precipitation of product salts.

While not narrowly critical, pressure for the present invention will preferably be from 0.1 to about 10,000 p.s.i.a. with pressures of from about 0.5 to about 500, and from about 1.0 to about 200 p.s.i.a. being most preferred. The invention may be practiced in conventional apparatus on either a batch or on a continuous basis. Catalysts, while not necessary, may be employed. In the case of continuous practice of the present invention it will, in most cases, be desirable to recycle the acetic acid back after it is separated from the products. In batch embodiments of the invention, the acetic acid will be recovered in most cases and reused in later batches.

Of the alkali metal chromates and dichromates, those most preferred with the present invention, will be the chromates because of their ease of regeneration in cyclic embodiments of the present invention. The preferred cation is sodium because of its ready availability and superior solubility.

Preferably from about 0.2 to 20, more preferably from 0.5 to 5, and most preferably from 1 to about 3 moles of Cr^{+6} in the form of alkali metal dichromate will be present for each mole of alkyl group in the alkyl benzenes present in the final reaction mixture.

The preferred products of the present invention are the benzene carboxylic acids, especially benzoic acid, terephthalic acid, isophthalic acid, trimesic acid, and pyromellitic acid.

The invention will be more fully understood by reference to the following examples which are to be taken as merely illustrative of specific embodiments of the invention. The variety of modifications of the invention will be

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obvious to persons skilled in the art and all such modifications and variations are to be taken as being within the spirit of the claims appended hereto.

EXAMPLE I

A 200 ml. flask fitted with an addition funnel, stirrer, and reflux condenser is charged with 2.00 ml. (16.2 mmoles) of p-xylene, 50 ml. acetic acid, 16.6 g. acetic anhydride and 16.0 g. sulfuric acid (to make 162 moles of acetylsulfuric acid). Cooling is necessary when the acetic anhydride and sulfuric acid are added. A solution of 9.67 g. (32.4 mmoles) of sodium dichromate dihydrate in 35 ml. of acetic acid and 6.62 g. (65 mmoles) acetic anhydride is added drop-wise at a rate such that the temperature does not exceed 45 degrees C. After the addition is complete, the flask is heated at 45 degrees C. for an additional hour while stirring. The terephthalic acid is removed by filtration, washed with additional acetic acid and dried to give 2.12 g., a 79.0% yield. The filtrate is treated with water and extracted with chloroform. Evaporation of the chloroform gives 0.40 g. of p-toluic acid, an 18.2% yield.

EXAMPLE II

A 200 ml. flask fitted with an addition funnel, stirrer, and reflux condenser is charged with 2.72 g. (20.0 mmoles) of p-toluic acid, 50 ml. acetic acid, 0.98 g. sulfuric acid and 10.2 g. acetic anhydride (to make 100 mmoles acetylsulfuric acid). Cooling is necessary when the acetic anhydride and sulfuric acid is mixed. To this is added a solution of 5.96 g. (20 mmoles) of sodium dichromate dihydrate in 35 ml. of acetic acid and 4.1 g. acetic anhydride (to remove the water of hydration) as rapidly as possible without allowing the flask temperature to exceed 45 degrees C. After the addition is complete, the flask is stirred an additional hour at 45 degrees C. Filtration gives 2.95 g. of terephthalic acid, 89.0% yield. Treatment of the filtrate with water and extraction with chloroform gives 0.22 g. unreacted p-toluic acid, 8.3% recovered.

EXAMPLE III

When the procedures of Example I are repeated, substituting stoichiometrically equivalent amount of potassium chromate for the sodium dichromate employed in Example I, the products of Example I are recovered in similar yields.

EXAMPLE IV

When the procedures of Example II are repeated, substituting stoichiometrically equivalent amount of potassium chromate for the sodium dichromate employed in Example II, the products of Example II are recovered in similar yields.

EXAMPLE V

When the procedure of Example I is followed, substituting parahydroxymethylbenzaldehyde (in stoichiometric acid is obtained in good yield.

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EXAMPLE VI

When the process of Example I is repeated, substituting parahydroxymethylbenzaldehyde (in stoichiometric quantity) for the paraxylene of Example I, terephthalic acid is recovered in good yield, illustrating that the starting materials of the present invention may be partially oxidized.

What is claimed is:

1. A method for the production of benzene carboxylic acids containing from 1 to about 4 carboxyl groups per molecule comprising forming a first mixture comprising acetylsulfuric acid dissolved in acetic acid and a second mixture comprising alkali metal chromate or dichromate, dissolved in acetic acid wherein either or both of said solutions contain alkyl benzenes, or partially oxidized alkyl benzenes, containing from 1 to about 4 groups selected from alkyl groups and partially oxidized alkyl groups per molecule and wherein both mixtures are substantially anhydrous, and thereafter intermixing said first and said second mixture at a temperature of from about 15 to about 80 degrees C. and thereafter recovering the benzene carboxylic acids.

2. The process of claim 1 wherein the first mixture is prepared by mixing together approximately stoichiometric quantities of acetic anhydride and sulfuric acid in acetic acid.

3. The process of claim 1 wherein the first mixture is prepared by mixing together sulfur trioxide and acetic acid.

4. The process of claim 1 wherein after the intermingling of the first and second mixtures, the resulting mixture contains from 1 to about 3 equivalents of Cr^{+6} and from 5 to about 10 moles of acetylsulfuric acid for each mole of alkyl groups contained in the alkyl benzene starting material.

5. The process of claim 4 wherein there are present in the mixture, formed by the intermingling of said first and said second mixtures, from 1 to about 100 liters of acetic acid for each liter of alkyl benzene contained in said first and said second mixture.

6. The process of claim 1 wherein the temperature varies from 38 to about 60 degrees C.

7. The process of claim 1 wherein the alkyl benzene contains a major portion of toluene.

8. The process of claim 1 wherein the alkyl benzene contains a major portion of xylenes.

9. The process of claim 1 wherein the alkyl benzenes contain a major portion of paraxylene and wherein the principal product recovered is terephthalic acid.

References Cited

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IN THE UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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James W. Patton, et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the patent, Col. 1, line 46 should read:

-- presence of acetic acid solvent and alkali metal chromates or --

In the patent, Example V should read:

-- When the procedure of Example I is followed, substituting mesitylene for the paraxylene of Example I, trimesic acid is obtained in good yield. --

**SIGNED AND
SEALED
JUN 2 1970**

(SEAL)

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