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3,531,519 OXIDATION PROCESS

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8 Claims

ABSTRACT OF THE DISCLOSURE

The α -positions of alkyl-substituted aromatic compounds can be oxidised using hydrogen peroxide using a 15 ferric, titanic, chromic or cupric ion as catalyst.

Many reagents have been proposed for the oxidation of aromatic hydrocarbons. Oxidations which give products other than aromatic carboxylic acids or their derivatives are usually difficult to control to obtain the desired product in a good yield and in a form which purification is possible. With most reagents, several products are formed, which cannot be separated on an economic scale. 25

It is an object of the present invention to provide a process for the oxidation of the α position in alkyl substituted aromatic compounds in good yield.

It is a further object of the present invention to provide a process for the oxidation of α positions in alkylsubstituted aromatic compounds with relatively little hydroxylation of the aromatic ring concurrently occurring.

It is a further object of the present invention to provide a process for the oxidation of methyl-benzenes which results in the production of the corresponding aldehydes 35 with, if desired, only a small amount of the corresponding carboxylic acid being concurrently formed.

Other or further objects of the present invention will be understood by those skilled in the art from the following description.

This invention relates to the oxidation of alkyl-substituted aromatic compounds.

Many reagents have been proposed for the oxidation of aromatic hydrocarbons. It is usually difficult to control oxidations which give products other than aromatic carboxylic acids of their derivatives if the desired product is to be obtained in a good yield and in a form of which purification is possible. With most reagents several products are formed, which cannot be separated on an economic scale.

Fenton's reagent, which is an aqueous solution of ferrous ions and hydrogen peroxide, can be used as a source of hydroxyl radicals in order to hydroxylate benzene. The use of Fenton's reagent to oxidise alkylbenzenes, however, results in the production of the corresponding phenols, with little or no oxidation of the alkyl group.

The present invention provides a process for the oxidation of alkyl-substituted aromatic compounds in which the α carbon atom has two or three hydrogen atoms bonded to it wherein the alkyl-substituted aromatic compound is reacted with hydrogen peroxide at a pH below 6.0 in an aqueous medium in the presence of a catalyst containing cations of trivalent iron, tetravalent titanium, trivalent chromium and/or divalent copper. Preferably a catalyst containing trivalent iron is used. The invention 65 includes the use of suitable mixtures of these ions.

A considerable variety of compounds can be oxidised in this way. For example, derivatives of benzene, naphthalene, and other aromatic compounds can be oxidised. The alkyl group can be any alkyl group that has at least two hydrogen atoms bonded to the α carbon atom, such as the methyl, ethyl, n-propyl, n-butyl, isobutyl, n-pentyl,

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isopentyl, n-hexyl, n-octyl, n-decyl, n-dodecyl and other groups. The compound may contain one or more such alkyl groups and one or more of the groups can be oxidised. The compound may contain, in addition to the alkyl group or groups, other substituents on the aromatic ring, such as chloro, nitro, hydroxy, alkoxy, or carboxylic or sulphonic acid or ester groups. It may contain aldehydic or ketonic groups, particularly those derived from oxidation processes according to the present invention, although aldehydic groups may be oxidised further in the process.

For the avoidance of doubt by the expression " α position," as used herein, we mean that carbon atom of the alkyl group which is adjacent to the aromatic ring.

The following compounds are particular examples of compounds that can be oxidised: Toluene, ethylbenzene, n-butylbenzene, n-hexylbenzene, n-decylbenzene, n-dodecylbenzene, p-xylene, m-xylene, o-xylene, the methylnaphthalenes, the ethylnaphthalenes, the three toluenealdehydes, the three toluic acids and their esters, the three toluene sulphonic acids and their esters, and the chlorotoluenes.

A particularly important extension of the invention concerns the xylenes, and this is illustrated with reference to o-xylene although it is perfectly valid for the other xylenes. Scheme 1 illustrates the various reactions possible, and the routes by which the various products can be obtained. Reactions A, B and C are desirably performed by the process of the present invention whereas reactions D, E. and F can be performed by any other suitable oxidation method, which could include the use of hydrogen peroxide, although a process analogous to the present invention may, if desired, be employed.

While, in general, the main product of the reaction according to the invention is the α -oxo-derivative, side reactions still occur, particularly hydroxylation of the aromatic ring. Preferably the reaction is carried out at an elevated temperature, which minimises any side reactions. A further advantage of the use of elevated temperatures is the increased solubility of the aromatic compound in the aqueous phase. Conveniently the temperature range within which the reaction is conducted is from 0° C. to 200° C., desirably from 50° C. to 110° C., preferably from 80° C to 90° C.

The pressure at which the reaction takes place is preferably at least sufficient to maintain reagents and products in the liquid phase at the temperature of the reaction. Subject to this condition the reaction pressure may, if desired, be above or below atmospheric pressure.

Any acid may in principle be used to acidify the solution. Particularly suitable are those mineral acids which do not readily coordinate with metal cations, for example, sulphuric acid and nitric acid.

Excess of the aromatic reagent is conveniently used, desirably sufficient excess is used to saturate the aqueous phase throughout the whole reaction, and suitably at least sufficient to form a permanent non-aqueous phase. Preferably the reaction is carried out with a considerable excess of the aromatic reagent, and it is particularly convenient to operate the reaction when the ratio of the two phases, by volume, in the vessel in which the reaction is being carried out, is from 5:1 to 1:5. As the result of this, the organic product of the reaction is often preferentially extracted, and this has the advantage of diminishing the extent of which hydrogen peroxide reacts with the reaction product.

The aromatic compound may, however, be added to the aqeous reaction phase in solution in a suitable solvent. Preferably the solvent should be inert. Desirably it should not be miscible with water. The distribution ratios of the aromatic compound and the product between aqueous phase and the solvent, if the latter is im-