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PHENOL PRODUCTION

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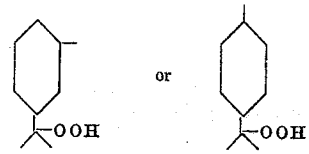
9 Claims. (Cl. 260—621)

This invention relates to the cleavage of alkaryl hydroperoxides to phenolic materials. More particularly, it relates to the cleavage of cymene hydroperoxides to cresols.

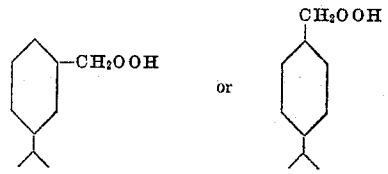
This application is a continuation-in-part of applications, Serial Nos. 249,621 and 249,622, filed October 3, 1951, which in turn are divisions of application, Serial No. 31,385, filed June 5, 1948, and now abandoned.

In these earlier filed applications the process of subjecting α,α-dialkylarylmethyl hydroperoxides to phenolic cleavage in substantially anhydrous solution in an inert organic solvent in the presence of an acidic condensation catalyst is described. The present invention relates specifically to the cleavage of cymene hydroperoxide in solution in a low molecular weight alcohol.

In the oxidation of m- or p-cymene to hydroperoxide the product is chiefly an 8-hydroperoxycymene,



However, there is usually from 5–20% of a 7-hydroperoxycymene



present as an impurity. When the cymene oxidation product containing these two hydroperoxides is subjected to phenolic cleavage according to known methods for cleaving hydroperoxides to phenols, the 8-hydroperoxycymene breaks down into a cresol and acetone, and the 7-hydroperoxycymene breaks down into an isopropylphenol and formaldehyde. The formaldehyde formed in the latter reaction then combines under the acidic conditions of the cleavage reaction with the cresol formed in the cleavage of the 8-hydroperoxycymene with the formation of a resin. As a result, the yield of cresol is reduced from the theoretical yield by an amount proportional to the amount of 7-hydroperoxycymene in the oxidized cymene. To prevent loss due to this side reaction, it has, heretofore, been

necessary to remove the 7-hydroperoxycymene before subjecting the 8-hydroperoxycymene to cleavage.

Now in accordance with the present invention, it has been found that an improved yield of a cresol is obtained from an oxidized cymene containing a 7-hydroperoxycymene by cleaving said oxidized cymene at a temperature in the range of about 0° C. to about 100° C. in a homogeneous solution of a low molecular weight alcohol in the presence of a catalytic amount of an acidic condensation catalyst.

The process of this invention does not depend upon a cymene hydroperoxide produced by any particular method of air oxidizing cymene to the hydroperoxide. The cymene hydroperoxide is suitably prepared by oxidation of the cymene in liquid phase by passing an oxygen-containing gas through the cymene at a temperature in the range of about 25° C. to about 95° C. in the presence of a 1–35% aqueous alkali solution. Such methods are well known in the art. The crude cymene oxidation mixture may contain from about 5% to about 90% cymene hydroperoxide and the excess cymene can be stripped off by distillation to increase the cymene hydroperoxide concentration, if desired. The cleavage process of the present invention may be carried out on either the crude unstripped oxidate or on the stripped oxidate.

The oxidized cymene treated in accordance with the process of this invention contains a major amount of 8-hydroperoxycymene and a minor amount of 7-hydroperoxycymene. However, the process is operable with mixtures over a wide range of ratios, and the improvement in yield of the desired cresol is greatest where the amount of primary hydroperoxide is greatest. Thus, the process is applicable not only to oxidized cymene which may contain from 5% to 20% 7-hydroperoxycymene based on the total hydroperoxide content, but is applicable also to mixtures containing even larger amounts of 7-hydroperoxycymene. The process of the present invention apparently prevents resin formation caused by reaction between the formaldehyde with the phenol, thereby increasing the isolable yield of cresol. The process of this invention yields p-cresol from oxidized p-cymene, and m-cresol from oxidized m-cymene. The term "oxidized cymene" refers in this specification and claims to the mixture of primary and tertiary hydroperoxides obtained by oxidizing m- or p-cymene, as the case may be, without reference to unoxidized cymene and oxidation by-products which may be present but not included in any weights, percentages or ratios set forth or used in making calculations.

In carrying out the process of this invention, the catalyst is, for example, dissolved in the alcohol and the oxidized cymene is added gradually to the alcohol solution of the catalyst while maintaining the cleavage temperature, suitably at about the boiling point of the solvent in the case of the low boiling alcohols. In the table are shown data for Examples 1–8 carried out in this manner. All parts, percentages and ratios in this specification are by weight. These examples show the effect of using various alcohols, and the use of other solvents along with them. For comparison, there are also given blank runs to show the improvement in the use of alcohols over a non-alcoholic solvent, acetone. Substantially similar results were found when the oxidized cymene was oxidized m-cymene and the components were 8-hydroperoxy-m-cymene and 7-hydroperoxy-m-cymene.

Table

Example	1	2	Blank	3	4	5	6	7	8	Blank
8-Hydroperoxy-p-cymene (parts)	146.6	146.6	146.6	137.5	137.5	137.5	137.5	137.5	137.5	137.5
7-Hydroperoxy-p-cymene (parts)	9.5	9.5	9.5	18.8	18.8	18.8	18.8	18.8	18.8	18.8
Unreacted cymene and oxidation by-products (parts)	21.9	21.9	21.9	17.7	17.7	17.7	17.7	17.7	17.7	17.7
Hexane (parts)							77.0			
Benzene (parts)					1.0	7.0				
Acetone (parts)		52.0	52.0					52.0	52.0	52.0
Glycerol (parts)								23.0		
Ethylene glycol (parts)									25.0	
Methanol (parts)	52.0	13.0								
Isopropyl alcohol (parts)				52.0			23.0			
Ethyl alcohol (parts)					51.0	343.0				
Catalyst (98% H_2SO_4)	0.76	0.3	0.3	0.3	0.5	0.5	1.5	0.5	0.5	0.3
Cleavage temperature, ° C.	56–72	58–67	57–75	74–86	79–83	79	63–65	65–68	66–80	58–77
Cresol (percent of theory)	89.6	91.9	85.0	81.5	83.1	87.5	80.5	90.0	83.0	74.7

The process of this invention is carried out in solution in any of the low molecular weight normally liquid alcohols having not more than 4 carbon atoms. This includes methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, and the butyl alcohols, and the polyhydric alcohols, glycerol, ethylene glycol, and propylene glycol. Methyl alcohol is the best solvent from the standpoint of yield of cresol. Ethyl and n-propyl alcohol are more practical from the standpoint of recovery from the by-product acetone. The primary alcohols are superior to the secondary and tertiary alcohols on the basis of yields of cresol. Mixtures of alcohols and mixtures of alcohols with other solvents may also be used to advantage. Moreover, a methanol-acetone azeotrope is particularly satisfactory.

The alcohol used is preferably anhydrous and may contain at the most about 5% but not more than 10% water. Thus, 95% ethanol is satisfactory but it is improved by azeotropic removal of most of the water by means of benzene or toluene. A small amount of residual benzene or toluene does not detract from the utility of the alcohol. In the case of polyhydric alcohols, there should be no water present unless an additional solvent such as a monohydric alcohol or acetone is used to improve solubility and thus aid in forming a completely miscible solution.

The cleavage reaction is carried out in homogeneous nonaqueous solution and the amount of alcohol used as the solvent is selected so as to accomplish this end. In a completely anhydrous system a minimum of about 5% alcohol based on the weight of the oxidized cymene shows some improvement in the case of methanol. It is preferred to use at least 10% alcohol based on the weight of oxidized cymene. There is no critical upper limit on the amount of alcohol that can be used. For practical reasons the upper limit is about 10 times the weight of the oxidized cymene, i. e., the total cymene hydroperoxide content. If other solvents than the alcohol (e. g., acetone, benzene, toluene, etc.) are present, the total solvent should not exceed about 10 times the weight of the total cymene hydroperoxide content.

The catalyst required for the cleavage is any acidic condensation catalyst. Examples are: anhydrous ferric chloride, boron trifluoride, boron trifluoride-etherate, an acid-treated bentonite, montmorillonite, kaolinite (Peerless clay), vermiculite, silica gel, kaolin, fuller's earth, illite, attapulgite, diatomaceous earth, halloysite, trichloroacetic acid, picric acid, dichloroacetic acid and chloroacetic acid; sulfonic acids and acid sulfate such as benzenesulfonic acid, p-toluenesulfonic acid, and sulfonated phenol-formaldehyde, sulfonated styrenedivinylbenzene polymers and acid sulfates of lower molecular weight alcohols; phosphorus halides, for example, phosphorus trichloride, phosphorus pentachloride and phosphorus oxychloride; Friedel-Crafts catalysts such as aluminum chloride, ferric chloride, boron trifluoride, zinc chloride, stannic chloride and magnesium chloride, all of which may be supported on a carrier, which itself may have catalytic activity; inorganic acids, for example, sulfuric acid, hydrogen chloride, phosphoric acid, and phosphoric acid supported on alumina, fuller's earth or silica; chloroacetic acids, for example, trichloroacetic acid, dichloroacetic acid, and monochloroacetic acid; and acidic surface active clay catalysts, for example, the acid-treated clays as well as other acidic surface active silicates, hydrosilicates, kieselguhr and bauxite. Silica gel likewise may be used.

The catalyst is used in an amount sufficient to catalyze cleavage of the oxidized cymene but generally not in excess of about 5% based on the cleavage mixture. In the case of catalysts completely soluble in the reaction mixture, an amount of catalyst in the range of 0.1 to 0.5% of the reaction mixture has been found to be particularly satisfactory. Since the cleavage process is carried out in substantially anhydrous homogeneous solution, water in the catalyst must be considered and must be kept sufficiently low to avoid increasing the water in the system above about 5%. When sulfuric acid is used as the catalyst, the acid is probably in the form of a partial ester such as the acid sulfate. Sulfuric acid or the partial ester of sulfuric acid and the alcohol used in the process is the preferred catalyst.

The reaction temperature is any temperature in the range of about 0° C. to about 100° C. The reaction is slow at 0° C. and is preferably carried out at about 65° C. to about 85° C. The cleavage is generally carried out at the boiling point of the solvent used but not above about 100° C.

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

1. The process of producing a cresol which comprises cleaving an oxidized cymene of the group consisting of m- and p-cymene containing a major amount of the corresponding 8-hydroperoxycymene and a minor amount of the corresponding 7-hydroperoxycymene at a temperature in the range of about 0° C. to about 100° C. in a substantially anhydrous homogeneous solution with a low molecular weight alcohol having 1–4 carbon atoms and 1–3 hydroxyl groups in the presence of a catalytic amount of sulfuric acid.

2. The process of producing p-cresol which comprises cleaving oxidized p-cymene containing a major amount of 8-hydroperoxy-p-cymene and a minor amount of 7-hydroperoxy-p-cymene at a temperature in the range of about 0° C. to about 100° C. in a substantially anhydrous solution with a low molecular weight alcohol having 1–4 carbon atoms and 1–3 hydroxyl groups in the presence of a catalytic amount of sulfuric acid.

3. The process of producing m-cresol which comprises cleaving oxidized m-cymene containing a major amount of 8-hydroperoxy-m-cymene and a minor amount of 7-hydroperoxy-m-cymene at a temperature in the range of about 0° C. to about 100° C. in a substantially anhydrous solution with a low molecular weight alcohol having 1–4 carbon atoms and 1–3 hydroxyl groups in the presence of a catalytic amount of sulfuric acid.

4. The process of producing m-cresol which comprises cleaving oxidized m-cymene containing a major amount of 8-hydroperoxy-m-cymene and a minor amount of 7-

hydroperoxy-m-cymene at a temperature in the range of about 0° C. to about 100° C. in a substantially anhydrous solution with methanol in the presence of a catalytic amount of sulfuric acid.

5. The process of producing p-cresol which comprises cleaving oxidized p-cymene containing a major amount of 8-hydroperoxy-p-cymene and a minor amount of 7-hydroperoxy-p-cymene at a temperature in the range of about 0° C. to about 100° C. in a substantially anhydrous solution with methanol in the presence of a catalytic amount of sulfuric acid.

6. The process of producing m-cresol which comprises cleaving oxidized m-cymene containing a major amount of 8-hydroperoxy-m-cymene and a minor amount of 7-hydroperoxy-m-cymene at a temperature in the range of about 0° C. to about 100° C. in a substantially anhydrous solution with a methanol-acetone azeotrope in the presence of a catalytic amount of sulfuric acid.

7. The process of producing p-cresol which comprises cleaving oxidized p-cymene containing a major amount of 8-hydroperoxy-p-cymene and a minor amount of 7-hydroperoxy-p-cymene at a temperature in the range of about 0° C. to about 100° C. in a substantially anhydrous solution with a methanol-acetone azeotrope in the presence of a catalytic amount of sulfuric acid.

8. The process of producing a cresol which comprises

cleaving an oxidized cymene of the group consisting of m- and p-cymene containing a major amount of the corresponding 8-hydroperoxycymene and a minor amount of the corresponding 7-hydroperoxycymene at a temperature in the range of about 0° C. to about 100° C. in a substantially anhydrous homogeneous solution with ethylene glycol in the presence of a catalytic amount of sulfuric acid.

9. The process of producing a cresol which comprises cleaving oxidized cymene of the group consisting of m- and p-cymene containing a major amount of the corresponding 8-hydroperoxycymene and a minor amount of the corresponding 7-hydroperoxycymene at a temperature in the range of about 0° C. to about 100° C. in a substantially anhydrous solution with glycerol in the presence of a catalytic amount of sulfuric acid.

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