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ELECTROLYTIC REDUCTION OF HYDROPEROXIDES

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8 Claims. (Cl. 204—73)

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This invention relates to the preparation of alcohols, and more particularly to a process of converting organic hydroperoxides to the corresponding alcohols.

It has been known that certain organic hydroperoxides could be converted to the corresponding alcohols through use of various reducing agents, and some of these reducing agents have been found applicable to the reduction of α,α-dialkylarylmethyl hydroperoxides for the preparation of α,α-dialkylarylmethyl alcohols. Electrolytic reduction also has been applied to the preparation of various organic compounds, such as the preparation of aniline from nitrobenzene, but the preparation of alcohols by the electrolytic reduction of hydroperoxides has not been known.

Now in accordance with this invention it has been found that α,α-dialkylarylmethyl alcohols may be simply and economically obtained by reducing the corresponding hydroperoxides by electrolysis between electrodes inert to the hydroperoxides and in the presence of an electrolyte having a pH of at least 7. In carrying out the process in accordance with this invention the well known techniques of electrolytic reduction are utilized. As an example, an electrolytic cell having a platinum cathode and a platinum anode may be charged with α,α-dimethylbenzyl hydroperoxide and an electrolyte such as aqueous potassium hydroxide. An electric current then may be passed through the cell until the hydroperoxide has been substantially converted to the alhocol. Upon completion of the reduction the organic material may be separated from the aqueous electrolyte and treated by well known techniques to recover the α,α-dimethylbenzyl alcohol.

The following examples constitute specific embodiments of the invention:

Example 1

In a glass electrolytic cell fitted with a platinum anode in a porous cup and a rotating platinum cathode was placed 200 parts of a cumene oxidation product containing 47.7% α,α-dimethylbenzyl hydroperoxide, 17.6% α,α-dimethylbenzyl alcohol, 6.7% acetophenone, and 28% unreacted cumene. Also placed in the cell as an electrolyte was 200 parts of aqueous 10% potassium hydroxide. The porous cup surrounding the anode served to isolate the hydroperoxide from the anode. An electric current then was passed through the cell for a period of 26.3 hours at an average current of 1.34 amperes and an average E. M. F. of 6.7 volts. During the reduction samples were removed at periodic intervals for determination of the hydroperoxide content of the organic material. This determination was carried out by adding the sample to an acidified potassium iodide solution and noting the amount of iodine liberated. At the end of 2.3 hours the hydroperoxide content was 35.4% and at the end of 9.2 hours the content was 22.8%. At the end of 11.8 hours 100 parts of aqueous 10% potassium hydroxide was added to the cell and this was repeated at the end of 24.6 hours. At the latter time the hydroperoxide content was 0.16%.

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The weight of the samples removed for determination of hydroperoxide content totaled 20 parts. At the end of the reaction the weight of the organic phase was 127 parts and the weight of the aqueous phase 290 parts. The organic phase then was stripped at a temperature of 94° C. and a pressure of 16 mm. of mercury to remove the unreacted cumene present. There was thus obtained a residue amounting to 107 parts which had a refractive index at 20° C. of 1.5219 and which analyzed for 91.3% α,α-dimethylbenzyl alcohol and 7.5% acetophenone. Calculations based on the percentage of α,α-dimethylbenzyl alcohol in the reaction product and on the amount of alcohol theoretically obtainable from the amount of hydroperoxide originally present, and taking into account the amount of alcohol originally present, showed that the yield of alcohol was 99% of that theoretically obtainable from the amount of hydroperoxide originally present. Calculations also showed that the current efficiency was 96%.

Example 2

The process of Example 1 essentially was duplicated with the exceptions that there were used 200 parts of a cumene oxidation product containing 51.6% α,α-dimethylbenzyl hydroperoxide and 200 parts of aqueous 5% sodium hydroxide, and that a portion of the aqueous sodium hydroxide was added to the porous cup to form the anolyte. During the reduction the current varied from 0.2 to 2.3 amperes and the voltage from 6 volts to 11 volts. At the end of 23 hours the anolyte was dry, consequently the oily and aqueous phases in the catholyte were separated. All of the oil phase and approximately 200 parts of the aqueous phase were returned to the catholyte, and approximately 80 parts of the aqueous phase was charged to the anolyte. The reduction was completed at the end of 45.5 hours. At this time the oily and aqueous phases were separated and

the former was distilled at a temperature of 93° C. and a pressure of 23 mm. to remove cumene. The residual material amounted to 109 parts and analyzed for 83.1% α,α-dimethylbenzyl alcohol, 10% acetophenone and 0.24% α,α-dimethylbenzyl hydroperoxide. The yield of alcohol was 98% of that theoretically obtainable from the amount of hydroperoxide originally present.

Example 3

One hundred parts of a cumene oxidation product containing 51.9% α,α-dimethylbenzyl hydroperoxide and 80 parts of aqueous 5% sodium hydroxide were placed in a glass electrolytic cell fitted with platinum electrodes and a porous clay cup surrounding the anode. In the porous cup there was placed 40 parts of aqueous 5% sodium hydroxide to serve as the anolyte. The reduction was carried out for 25.3 hours and during this time the current varied from 0.6 to 1.5 amperes and the voltage from 3.8 to 6.4 volts. Upon completion of the electrolysis the reduced oils were separated and washed with approximately 200 parts of water, then dried over calcium sulfate. There was thus recovered 53.9 parts of a product which analyzed for 64.8 α,α-dimethylbenzyl alcohol, 12% acetophenone, and 0.36% α,α-dimethylbenzyl hydroperoxide.

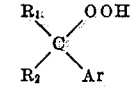
Example 4

In a glass electrolytic cell fitted with a platinum gauze anode in a porous cup and a rotating platinum gauze cathode was placed 50 parts of a p-cymene oxidation product containing 21.1% α,α - dimethyl - p - methylbenzyl hydroperoxide. Also placed in the cell as an electrolyte was 100 parts of aqueous 10% sodium carbonate. Seventy parts of the aqueous sodium carbonate was used to form the catholyte and 30 parts of the aqueous sodium carbonate was added to the porous cup to form the anolyte. An electric current then was passed through the cell for a period of 4.25 hours at an average current of 0.89 ampere and an average E. M. F. of 8.4 volts. At the end of 4.25 hours the hydroperoxide content was 1.65%. The reduction was continued for an additional 1.75 hours and at the end of this time the hydroperoxide content was 0.36%. Analysis also confirmed the presence in the organic phase of 21% α,α-dimethyl-p-methylbenzyl alcohol and 78.6% p-cymene. The yield of α,α-dimethyl-p-methylbenzyl alcohol based on the α,α-dimethyl-p-methylbenzyl hydroperoxide was 80%.

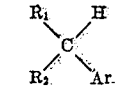
Example 5

Using the apparatus described in Example 4, 50 parts of a p-diisopropylbenzene oxidation product containing 46.5% α,α-dimethyl-p-isopropylbenzyl hydroperoxide and 23.6% α,α-dimethyl-p-isopropylbenzyl alcohol was electrolytically reduced in the presence of 100 parts of 10% aqueous sodium bicarbonate. As in Example 4 the hydroperoxide and 70 parts of the electrolyte were placed in the cathode compartment and the remaining 30 parts of the electrolyte was used as the anolyte. The reduction was carried out for a period of 25.5 hours and during this time the E. M. F. varied from 7.2 to 9.3 volts and the current varied from 0.5 to 1.1 amperes. During the reduction additional amounts of the 10% aqueous sodium bicarbonate were periodically added to the anolyte until at the end of the reduction a total of 100 additional parts had been added. Upon completion of the reduction the oily and aqueous phases were separated and the oily phase was dried over sodium and calcium sulfate. Analysis of the oily phase followed by calculations taking into consideration the percentage of α,α-dimethyl-p-isopropylbenzyl alcohol in the reaction product, the amount of the alcohol theoretically obtainable from the amount of hydroperoxide originally present and the amount of alcohol originally present showed that the yield of alcohol was 100% of that theoretically obtainable from the amount of hydroperoxide originally present.

The process in accordance with this invention has been shown by the examples as applied to the hydroperoxides obtained from the oxidation of cumene, p-cymene and diisopropylbenzene, but the process also is operable in connection with other α,α-dialkylarylmethyl hydroperoxides such as that derived from sec-butylbenzene. These hydroperoxides have the structural formula



and may be prepared by the oxidation of alkyl-substituted aromatic compounds having the structural formula



in both structural formulae R_1 and R_2 representing alkyl groups and Ar representing a substituent selected from the group consisting of aryl and alkaryl groups. The oxidation may be carried out in the liquid phase utilizing air or oxygen as the oxidizing agents. A preferred method of preparing these hydroperoxides involves the liquid phase oxidation of the alkyl-substituted aromatic organic compounds having the above structural formula by passing an oxygen-containing gas through the compounds at a temperature between about 25° C. and about 95° C. in the presence of an aqueous alkali. The concentration of the alkali may be between about 1 and about 35%. Vigorous agitation is desirable during the oxidation reaction.

Illustrative of the alkyl-substituted aromatic organic compounds which may be oxidized are p-cymene, cumene, and p-diisopropylbenzene, these compounds leading to α,α-dimethyl-p-methylbenzyl, α,α-dimethylbenzyl, and α,α-dimethyl-p-isopropylbenzyl hydroperoxides, respectively. Also, in the case of p-diisopropylbenzene, there may be obtained α,α,α',α'-tetramethyl-p-xylylene dihydroperoxide. The aryl and substituted aryl groups need not be derived from benzene as is the case in the aforementioned compounds, for compounds containing aromatic nuclei derived from naphthalene, anthracene, phenanthrene, and the like also are operable when dissolved in a suitable solvent during the oxidation. The aryl group may be substituted with alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, tertiary butyl, and the like to give alkaryl substituents, the same alkyl groups also being representative of R_1 and R_2 in the structural formula. R_1 and R_2 may be either the same or different.

In order to produce the alcohols according to this invention the hydroperoxides may be used either in the pure form or diluted with solvents. When, for example, the hydroperoxides are obtained by oxidation of the alkyl-substituted aro-

matic compounds having the structural formula shown previously, the oxidation usually is interrupted before all of the hydrocarbon has reacted in order to avoid or limit side reactions. In this manner the hydroperoxide is obtained in mixture with smaller or larger amounts of the original hydrocarbon, and the mixture also may contain secondary reaction products such as alcohols, ketones, and the like. It is not necessary to isolate, separate, or even concentrate the hydroperoxide from such a reaction mixture since the reduction can be carried out directly on the reaction mixture. In case it is desirable, the hydroperoxide may be separated from the other constituents of the reaction mixture by, for example, fractional distillation at very low pressures, of the order of 0.01 to 1.0 mm./sq. cm., the hydroperoxides having higher boiling points than the related hydrocarbon, alcohol, and ketone. In some cases the hydroperoxide also may be separated from the oxidation reaction mixture by crystallization, which may be facilitated by first distilling off at least part of the hydrocarbon.

In carrying out the process of this invention, therefore, the hydroperoxides or the oxidation products containing them may be used. The hydroperoxides are added to the solution serving as the electrolyte of the electrolytic cell and are added to the cathode compartment of the cell, since the process desired to be carried out is one of reduction. Preferably the electrolyte is an aqueous alkali. Exemplary is an aqueous solution of an alkali metal hydroxide, such as sodium, potassium, lithium and the like, or of an alkaline earth metal hydroxide, such as calcium or barium. In place of these inorganic bases, strong organic bases such as tetraalkylammonium hydroxides, for example, trimethylbenzylammonium hydroxide may be used. Also operable are inorganic carbonates and bicarbonates, such as sodium carbonate and bicarbonate, and alkali metal salts of weak organic acids. However, neutral salts, such as sodium chloride, also may be used in the form of their aqueous solutions as operable electrolytes in accordance with the process of this invention. The examples have shown the concentration of the aqueous electrolyte as varying between 5% and 10%, but the concentration actually may be varied between about 0.01 and about 50% by weight of the alkali or neutral salt based on the total solution. A preferable concentration on this basis is between about 0.5 and about 20%, and an applicable range is between about 1% and about 10%.

Some of the hydroperoxides utilized in accordance with this invention are somewhat soluble in water, consequently it is not necessary in the case of these hydroperoxides to add a solubilizing agent to the electrolyte, α,α-dimethylbenzyl hydroperoxide and α,α-dimethyl-p-methylbenzyl hydroperoxide, for example, are sufficiently water-soluble that no solubilizing agent need be utilized for efficient electrolytic reduction to take place. In the case of those hydroperoxides, however, which are not at all water-soluble, the reduction may be carried out in an aqueous electrolyte by addition to the electrolyte of a solubilizing agent such as ethanol in order to effect solution of the hydroperoxide in the aqueous electrolyte. Additionally sufficient contact of the hydroperoxide with the electrolyte may be attained by forming an emulsion or suspension of the hydroperoxide in an aqueous electrolyte. Also useful in the case of some of the hydroperoxides is an aqueous electrolyte containing a high concentration of an alkali metal salt of an organic sulfonic acid. The latter not only is soluble in water but also increases the solubility of the hydroperoxide in the water. It is possible, furthermore, to use a nonaqueous electrolyte for those hydroperoxides which are difficultly soluble in water, but this is, of course, somewhat disadvantageous due to the fact that such an electrolyte increases the power consumption during the electrolysis. In any event, the pH of the electrolyte should be at least 7, and preferably should be between about 7.5 and about 10. This is necessary in the electrolytic reduction of the hydroperoxides of this invention since the latter are somewhat sensitive to acid conditions.

The examples have shown the use of platinum electrodes in the process in accordance with this invention, but other electrodes which are inert to the hydroperoxide being reduced also may be used. It is necessary that the electrodes used in the process of this invention be of such characteristics that they will not furnish to the electrolyte metallic ions which would be capable of effecting decomposition of the hydroperoxides. This is particularly true relative to the anode, at which electrode during an electrolytic process there oftentimes is formed metallic ions corresponding to the metal making up the electrode. Such metallic ions, of course, may migrate into the electrolyte solution surrounding the cathode and effect decomposition of the hydroperoxide. This is prevented to a certain extent, however, by use of a porous cup surrounding the anode. In general, it has been found that satisfactory electrodes for use in the process of this invention are those composed of carbon or those composed of metals from groups IB, IIB, IV, and VIII of the periodic table and having an atomic number greater than 27. Exemplary of operable cathodes are carbon, copper, silver, gold, cadmium, mercury, lead, titanium, thorium, nickel, and platinum, and of operable anodes are carbon, platinum, and gold. The electrodes may be used either in the natural state or after having been polished or converted to a spongy mass. In selecting the electrode to be used, consideration should be given, of course, to the nature of the electrolyte to be used in any particular instance, since, as is well known in the art, some electrodes function satisfactorily with certain electrolytes but unsatisfactorily with others.

During the electrolysis the temperature may be maintained at any point below either the boiling point of the electrolyte or the decomposition point of the hydroperoxide. However, for all practical purposes, the electrolysis generally may be carried out at a temperature between about 0° and about 100° C. and preferably at a temperature between about 20° and about 90° C. A temperature between about 20° and about 40° C. usually is satisfactory in the electrolysis of any of the hydroperoxides of this invention. The voltage during the electrolysis may range from about 2 to about 100 volts, preferably from about 6 to about 10 volts, and the amperage may vary from about 0.1 ampere to a maximum limited only by the electrode area and heat-dissipating capacity of the cell. Generally satisfactory is an amperage between about 0.1 and about 3.0 amperes. Similarly, the current density may range from about 0.1 amp./sq. cm. to a maximum limited only by the ability of the cell to dissipate the heat generated. During the electrolysis it also may be desirable to stir the hydroperoxide and electrolyte in order to increase the effective-

ness of contact of the hydroperoxide with the cathode.

Upon completion of the electrolytic reduction the reduced organic material may be separated from the electrolyte and worked up to recover the reaction products. Distillation, for example, preferably under reduced pressure, may be used to fractionate the reaction product into various components, one of which is the α,α-dialkylarylmethyl alcohol formed by the reduction.

The process in accordance with this invention provides one of the simplest and most economical methods for obtaining substantially pure alcohols from the products obtained by the oxidation with molecular oxygen of compounds such as cumene, p-cymene, diisopropylbenzene, and the like. The electrolytic reduction process of this invention is advantageous in that there are no extraneous materials which have to be separated from the reaction product, as is often the case when inorganic reducing agents are utilized. The process is particularly useful in those instances in which the alcohols have been difficultly obtained by other processes. By oxidizing a hydrocarbon and proceeding through the hydroperoxide as an intermediate, it often is possible to obtain, using the process of this invention, the alcohol more easily and more economically than otherwise would be possible. The products obtained according to this invention find various commercial applications. For example, α,α-dimethyl-p-methylbenzyl alcohol is used in the essential oil industry as a perfume base for soaps. This compound also is an efficient frothing agent in the flotation of copper, zinc, and lead sulfide ores. α,α-Dimethylbenzyl alcohol has similar applications. The dihydric alcohols, such as those derived from diisopropylbenzene, also are efficient frothing agents in heavy metal, especially lead sulfide, ore flotations. All of the alcohols are good wetting-out agents.

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

1. The process of preparing an α,α-dialkylarylmethyl alcohol which comprises electrolytically reducing an α,α-dialkylarylmethyl hydroperoxide in admixture with an electrolytic bath having a pH of at least 7 by passing an electric current through the bath between electrodes inert to the hydroperoxide.

2. The process of preparing an α,α-dialkylarylmethyl alcohol which comprises electrolytically reducing an α,α-dialkylarylmethyl hydroperoxide in admixture with an electrolytic bath having a pH between about 7.5 and about 10 by passing an electric current through the bath between electrodes inert to the hydroperoxide.

3. The process of preparing α,α-dimethylbenzyl alcohol which comprises electrolytically reducing α,α-dimethylbenzyl hydroperoxide in admixture with an electrolytic bath having a pH of at least 7 by passing an electric current through the bath between electrodes inert to the hydroperoxide.

4. The process of preparing α,α-dimethyl-p-methylbenzyl alcohol which comprises electrolytically reducing α,α-dimethyl-p-methylbenzyl hydroperoxide in admixture with an electrolytic bath having a pH of at least 7 by passing an electric current through the bath betwen electrodes inert to the hydroperoxide.

5. The process of preparing α,α-dimethyl-p-isopropylbenzyl alcohol which comprises electrolytically reducing α,α-dimethyl-p-isopropylbenzyl hydroperoxide in admixture with an electrolytic bath having a pH of at least 7 by passing an electric current through the bath between electrodes inert to the hydroperoxide.

6. The process of preparing α,α-dimethylbenzyl alcohol which comprises electrolytically reducing α,α-dimethylbenzyl hydroperoxide in admixture with an aqueous potassium hydroxide solution containing about 10% potassium hydroxide by weight by passing an electric current through the solution between platinum electrodes.

7. The process of preparing α,α-dimethyl-p-methylbenzyl alcohol which comprises electrolytically reducing α,α-dimethyl-p-methylbenzyl hydroperoxide in admixture with an aqueous sodium carbonate solution containing about 10% sodium carbonate by weight by passing an electric current through the solution between platinum electrodes.

8. The process of preparing α,α-dimethyl-p-isopropylbenzyl alcohol which comprises electrolytically reducing α,α-dimethyl-p-isopropylbenzyl hydroperoxide in admixture with an aqueous sodium bicarbonate solution containing about 10% sodium bicarbonate by weight by passing an electric current through the solution between platinum electrodes.

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