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PREPARATION OF C-ALKYL HYDROQUINONES AND C-ALKYL p-AMINOPHENOLS

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13 Claims. (Cl. 260—580)

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This invention relates to a process for reducing p-nitroalkylbenzenes, and to the products obtained by such a process.

In my copending application Serial No. 547,296, filed July 29, 1944, now Patent Number 2,446,519, I have shown that treatment of nitrobenzenes in which there is no substituent in the position para to the nitro group, with aluminium and an aqueous solution of a mineral acid, e. g. sulfuric acid, yields, not aniline nor phenylhydroxylamine, but rather p-aminophenol. I have now found that p-nitroalkylbenzenes when treated in the same manner yield C-alkylhydroquinones and C-alkyl-p-aminophenols even though the para position of the starting nitro compound is occupied by an alkyl group.

It is, accordingly, an object of my invention to provide a process for reducing p-nitroalkylbenzenes. A further object is to provide a process for preparing C-alkylhydroquinones and C-alkyl-p-aminophenols. Still further objects will become apparent hereinafter.

In accordance with my invention, I reduce a nitrophenyl compound containing in the position para to the nitro group a primary alkyl group containing from 1 to 4 carbon atoms, simultaneously with aluminium and an aqueous solution of an acid. The aluminium which I employ is preferably used in finely divided form; for example, as flakes or a powder. The aqueous solution of the acid advantageously contains not more than 50 per cent by weight of acid, and I have found that aqueous solutions containing not more than from 10 to 15 per cent by weight of acid are especially useful in practicing the process of my invention. The quantity of acid used, as well as the concentration, should be sufficient to maintain an acid medium until the reduction is substantially complete. Especially advantageous results have been obtained when sulfuric acid was used, although other mineral acids, such as phosphoric acid or hydrochloric acid, can be used. Organic acids have also been found to be useful in practicing the process of my invention, and those acids having a dissolution constant in water at 25° C. not smaller than that of oxalic acid (first hydrogen) have been found to be especially useful. Acids which react with any of the intermediate or final products formed in my process under the conditions employed are to be avoided. For example, formic acid is to be avoided due to its reactivity with the amine derivatives formed. Typical organic acids include oxalic acid, an alkane sulfonic acid containing from 1 to 4 carbon atoms (e. g.

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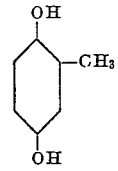
methanesulfonic, ethanesulfonic, propane-1-sulfonic, propane-2-sulfonic, n-butane-1-sulfonic, isobutane-1-sulfonic, sulfoacetic, β-hydroxyethanesulfonic, etc. acids, a sulfonic acid of the benzene series (e. g. benzenesulfonic, p-toluenesulfonic, o-toluenesulfonic, m-benzenedisulfonic, 1,3,5-benzenetrisulfonic, etc. acids) and a sulfonic acid of the naphthalene series (e. g. naphthalene-α-sulfonic acid, naphthalene-β-sulfonic acid, 1,5-naphthalenedisulfonic, 2,6-naphthalenedisulfonic, etc.). The reduction of the nitrophenyl compound containing in the position para to the nitro group an alkyl group containing from 1 to 4 carbon atoms with the aluminium and aqueous solution of the acid is advantageously effected at temperatures varying from 50° C. to 100° C. Although the temperature is apparently not critical, especially efficacious results have been obtained at temperatures between 80° C. and 100° C. In the case of the higher melting aromatic nitro compounds containing an alkyl group in the para position, a water miscible solvent, such as ethyl alcohol, or a water immiscible solvent, such as a hydrocarbon, can be added to the reaction mixture to promote dispersion in the aqueous acid.

When I reduce my nitrophenyl compounds, containing in the position para to the nitro group a primary alkyl group containing from 1 to 4 carbon atoms, in the presence of aluminum and an aqueous solution of an acid, a C-alkylhydroquinone whose alkyl group is correspondingly a primary alkyl group containing from 1 to 4 carbon atoms is always obtained in substantial proportion. A minor or very small proportion of the corresponding p-alkylaniline is usually obtained in addition to the C-alkylhydroquinone. When the primary alkyl group in the position para to the nitro group of my nitrophenyl compounds contains from 2 to 4 carbon atoms, there are obtained varying amounts of a C-alkyl-p-aminophenol, the amounts depending upon the conditions of reaction and the type of compound being reduced. That is to say, that upon reduction of p-nitrotoluene in the presence of aluminium and an aqueous solution of an acid, such as sulfuric acid, for example, no 2-hydroxy-p-toluidine (4-amino-o-cresol) can be detected. I have found further that when nitrophenyl compounds, containing in the position para to the nitro group an alkyl group which is not a primary alkyl group, are reduced in the presence of aluminium and an aqueous solution of an acid, the reaction proceeds in a manner contrary to that set forth above.

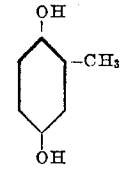
Example I.—Toluhydroquinone



17.5 g. of p-nitrotoluene, 37.5 cc. of sulfuric acid (sp. g. 1.84) and 500 cc. water were heated to about 95° C. and maintained at that temperature while 7.5 g. of aluminium flakes were slowly added to the mixture over a period of 1.5 to 2 hours. The reaction mixture turned orange to reddish in color and finally became light yellow as the aluminium was added. The reaction mixture was stirred for about one hour after the aluminium has been added. The small amount of excess aluminium was then filtered off and the filtrate was subjected to steam distillation. A small amount of p,p'-dimethyldiphenylamine came over (M. P. 78° to 79° C.). No cresol could be detected. The reaction mixture was cooled and extracted with 500 cc. of diethyl ether. Upon evaporting the ether extract, 4.5 g. of toluhydroquinone were obtained. On recrystallization from benzene and then from petroleum ether, it melted at 125° C. When a portion of the product toluhydroquinone was mixed with an authentic sample of toluhydroquinone, no depression in melting point of the sample was observed. the mixture melting at 124° C. to 125° C. It acted as a photographic developer and on oxidation the product toluhydroquinone gave toluquinone melting at 69° C.

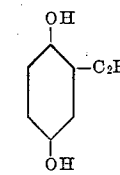
The reaction mixture remaining after the extraction with petroleum ether was made alkaline to brilliant yellow paper by the addition of sodium sulfite and sodium carbonate. The mixture was then filtered, and the filtrate extracted with diethyl ether while the precipitate was washed with alcohol. After evaporation of alcohol washings and ether extract, 0.65 g. of p-toluidine melting at 44° C. was obtained. When it was mixed with an aqueous solution of sodium hydroxide, and the mixture extracted with diethyl ether, no p-aminophenol could be detected when the alkalinity of the aqueous alkali layer was reduced until it was only faintly alkaline by the addition of sodium bisulfite.

Example II.—Toluhydroquinone



35 g. of p-nitrotoluene, 75 cc. of sulfuric acid (sp. g. 1.84) and 1000 cc. of water were heated to about 95° C. and maintained at that temperature while 12 g. of aluminium flakes were added to the mixture over a period of 1.5 to 2 hours. The reaction mixture turned orange-red in color and finally became light yellow as the aluminium was added. At this point a noticeable odor of cresol was present. The reaction mixture was stirred for about one hour after the aluminium was added and the small amount of excess aluminium was filtered off. On subjecting the filtrate to steam distillation, 2.5 to 3 cc. of p-cresol came over. On further steam distillation a small amount of p,p'-dimethyldiphenylamine came over (M. P. 78° C. to 79° C.). The reaction mixture was allowed to cool down to room temperature and was extracted with diethyl ether. Upon evaporating the ether extract 17 gm. of toluhydroquinone were obtained. When recrystallized first from benzene and then petroleum ether, it melted at 125° C. It acted as a photographic developer when added to an aqueous solution of sodium sulfite and sodium carbonate. The p-toluidine present in the aqueous acid solution after extraction was not recovered.

Example III.—Ethylhydroquinone

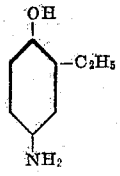


A mixture of 15 g. of p-nitroethylbenzene, 35 cc. of sulfuric acid (sp. g. 1.84) and 300 cc. of water was heated to 95° C. and maintained at that temperature while 5 g. of aluminium flakes were added with vigorous stirring over a period of 1.5 to 2 hours. The reaction mixture turned orange to reddish in color and finally became light yellow as the aluminium was added. The reaction mixture was then stirred for an additional hour after all of the aluminium had been added, and the small amount of undissolved aluminium was filtered off. The filtrate was extracted with diethyl ether, and upon evaporation of the ether extract, 3.6 g. of ethylhydroquinone were obtained. When this product was subjected to steam distillation a very small amount of a sweet smelling oil, the odor of which resembled acetophenone, came over. When the product ethylhydroquinone remaining in the distilling flask was recrystallized from water and then from a mixture of benzene and petroleum ether, it gave a melting point of 114° to 115° C. It also acted as a photographic developer. It was found to contain 69.46 per cent carbon and 7.13 per cent hydrogen (calculated for carbon 69.52 per cent and for hydrogen 7.3 per cent). Its identity was further established by oxidation to a quinone having a melting point of 37.5° C., which is the recorded melting point of ethylquinone.

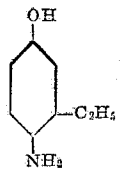
The reaction mixture remaining after extraction with the diethyl ether was made alkaline to brilliant yellow paper by the addition of sodium sulfite and sodium carbonate and filtered hot. The filter cake was thoroughly washed with ethyl alcohol while the filtrate was extracted with ethyl acetate. The washings were combined with the extraction liquid and the mixture evaporated to dryness to give 6.9 g. of an oily solid. When 50 cc. of a 15 per cent solution of sodium hydroxide to which a small amount of sodium hyposulfite had been added was added to the oily solid, part of it dissolved in the liquid while the remainder formed a second liquid layer lighter than the alkaline solution. When this top liquid layer was extracted with diethyl ether and the ether evaporated off, p-ethylaniline was obtained as an oil having the odor of aniline. When purified by steam distillation, it was obtained as a clear, practically colorless liquid. Its sulfate was prepared by dissolving the p-ethylaniline in dilute sulfuric acid. The sulfate was found to have a carbon content of 56.71 per cent, a hydrogen content of 6.87 per cent and a nitrogen content of 8.02 per cent (carbon calculated as 56.42 per cent, hydrogen as 7.11 per cent and nitrogen as 8.22

per cent). Acetylation of the p-ethylaniline with acetic anhydride in dilute aqueous acetic acid gave p-ethylacetanilide melting at 91° C. It was found to have a carbon content of 73.5 per cent, a hydrogen content of 8.2 per cent and a nitrogen content of 8.3 per cent (calculated for carbon 73.57 per cent, for hydrogen 8.58 per cent and for nitrogen 8.03 per cent).

To the lower aqueous layer remaining after the ether extraction sodium bisulfite was added until it was only slightly alkaline to brilliant yellow paper. A precipitate of 2-ethyl-p-aminophenol having the formula:



was obtained in the form of light colored crystals. On drying 4 g. of crude product remained. It was recrystallized from benzene to give a solid melting at 168° to 168.5° C. with decomposition and discoloration. Typical of the behavior of aminophenols, it dissolved in cold aqueous sodium hydroxide, was insoluble in cold aqueous sodium carbonate, but was dissolved by cold dilute mineral acids. Its alkaline solution darkened rapidly due to aerial oxidation, and it was found to act as a photographic developer when dissolved in aqueous sodium carbonate-sodium sulfite solution. The 2-ethyl-p-aminophenol was proved to be a p-aminophenol by diazotizing a portion of the product obtained above with cold dilute sulfuric acid and sodium nitrite, and decomposing the diazo compound formed by boiling in a hot solution of about 10 per cent aqueous sulfuric acid. The dihydroxybenzene compound so obtained did not form a precipitate when treated with a 20% lead acetate solution and had a melting point of 114° to 115° C. These data indicated the dihydroxybenzene compound was not derived from an o-aminophenol, and it gave the same melting point as ethylhydroquinone. When a small quantity of the 2-ethyl-p-aminophenol was oxidized with dichromic acid (sulfuric acid plus potassium dichromate), ethyl-p-quinone melting at 37.5° C. was obtained. An o-aminophenol would have been oxidized completely and no quinone could have been isolated. The 2-ethyl-p-aminophenol gave a hydrochloride which was found to contain 54.89 per cent carbon, 6.63 per cent hydrogen and 8.30 per cent nitrogen (calculated for carbon 55.04 per cent, for hydrogen 6.93 per cent and for nitrogen 8.02 per cent). Since the reduction of p-nitroethylbenzene could have given 3-ethyl-p-aminophenol instead of 2-ethyl-p-aminophenol, the aminophenol of the above example (designated Sample A in the table below) was compared with 3-ethyl-p-aminophenol:



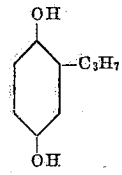
(designated Sample B in the table below) prepared from 3-ethylphenol by nitrosation and reduction of the nitroso derivative to the aminophenol and another specimen of 3-ethyl-p-aminophenol prepared from o-nitroethylbenzene (designated Sample C in the table below) by reduction with aluminium and aqueous sulfuric acid (Bean application Serial No. 547,296, filed July 29, 1944). The results are given in the table below:

Sample	Melting Pt.	Analysis [1]	Melting Pt., Acetyl Deriv.	Analysis,[2] Acetyl Deriv.
A	168°–168.5° C.	[3]	141°–142° C.	C 67.0%. H 7.2%. N 7.6%.
B	166°–167° C.	C 69.7%. H 8.0%. N 10.4%.	171° C.	C 67.1%. H 7.5%. N 7.8%.
C	167°–168° C.	C 70.1%. H 8.1%. N 10.4%.	171° C.	C 66.7%. H 7.2%. N 7.7%.

[1] Calculated: C—70.02%; H—8.08%; N—10.21%.
[2] Calculated: C—67.00%; H—7.31%; N—7.81%.
[3] Analysis for hydrochloride given above.

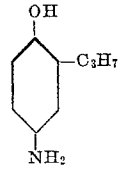
From the above table it can be seen that the aminophenol resulting from the reduction of p-nitroethylbenzene contains its ethyl group in the 2-position, since only two isomers are possible, and the derivatives of Samples B and C (both 3-ethyl compounds) show that this aminophenol (Sample A) is not a 3-ethyl compound.

Example IV.—n-Propylhydroquinone



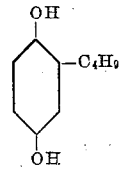
8.25 g. of p-nitro-propylbenzene, 15 cc. of sulfuric acid (sp. g. 1.84) and 200 cc. of water were heated at 95° C. and maintained at that temperature while 3 g. of aluminium flakes were added over a period of 1.5 to 2 hours with vigorous stirring. The reaction mixture turned orange to reddish in color and finally became light yellow as all of the aluminium was added. The reaction mixture was stirred for an additional hour after all of aluminium was added, and the small amount of excess aluminium was filtered off. The filtrate was cooled and then extracted with diethyl ether. After evaporation of the ether from the extract, there remained 1.5 g. of n-propylhydroquinone. It was recrystallized from a mixture of benzene and petroleum ether to give a pure product melting at 89° to 90° C. On oxidation with dilute aqueous potassium dichromate, it gave a yellow oil having a pungent odor resembling that of a quinone. The n-propylhydroquinone was soluble in ether and its aqueous solution with sodium sulfite and sodium carbonate acted as developers for exposed photographic paper and film. It had a carbon content of 71.7 per cent and a hydrogen content of 7.8 per cent (calculated for carbon 71.00 per cent and for hydrogen 7.88 per cent). The reaction mixture which remained after extraction with the diethyl ether was made alkaline with sodium sulfite and sodium carbonate and then filtered. The filter cake was washed with alcohol and the filtrate was extracted with diethyl ether. The washings were combined with the extract, and the mixture was made acid and evaporated to dryness. The dried residue was taken up in 50 cc. of water and an excess of 40% sodium hydroxide to which some sodium sulfite and sodium hyposulfite had been added was stirred into the aqueous solution. An oily layer formed on top the aqueous lower layer and this was removed

in a separatory funnel. This oil, p-n-propylaniline, was insoluble in sodium hydroxide, had a strong odor resembling that of aniline, and it acted as a photographic developer in sodium sulfite-sodium carbonate solutions. It was converted to its hydrochloride for analysis. The hydrochloride contained 62.8 per cent carbon, 8.1% hydrogen and 8.4 per cent nitrogen (calculated for carbon 62.89, for hydrogen 8.22 per cent and for nitrogen 8.10 per cent). The alkalinity of the lower aqueous alkaline layer remaining after removal of the oily layer was reduced by the addition of sodium bisulfite until it was only slightly alkaline to brilliant yellow paper. A precipitate of 2-n-propyl-p-aminophenol separated which was recrystallized from a mixture of benzene and petroleum ether to give a product melting at 91° C. and having the formula:



It was soluble in sodium hydroxide and also dilute acids. Its aqueous solutions with sodium sulfite and sodium carbonate acted as strong developers for exposed photographic paper or film. On oxidation with dichromic acid (sulfuric acid plus potassium dichromate), it gave n-propyl-p-quinone as a yellow oil which was liquid at room temperature. On reduction, the n-propyl-p-quinone gave n-propyl-p-hydroquinone having a melting point of 89° to 90° C. The 2-n-propyl-p-aminophenol had a carbon content of 71.52 per cent, a hydrogen content of 8.64 per cent and a nitrogen content of 9.38 per cent (calculated for carbon 71.47 per cent, for hydrogen 8.60 per cent and for nitrogen 9.26 per cent). The propyl group in the aminophenol prepared by the reduction of p-nitro-n-propyl-benzene was proved to be in the 2-position by preparing 3-n-propyl-p-aminophenol and comparing the properties of the two compounds. The 3-n-propyl-p-aminophenol was prepared by the reduction of o-nitro-n-propylbenzene according to the process described in Bean application 547,296, filed July 29, 1944, and after purification by recrystallization from a mixture of benzene and petroleum ether, it gave a pure product melting at 119° to 120° C. It analyzed 71.10 per cent carbon, 8.40 per cent hydrogen and 9.30 per cent nitrogen (calculated for carbon 71.47 per cent, for hydrogen 8.60 per cent and for nitrogen 9.26 per cent). Since the 3-n-propyl-p-aminophenol had a melting point far removed from that of the aminophenol obtained by the reduction of p-nitro-n-propylbenzene and there are only two possible isomers for a n-propyl-p-aminophenol, the aminophenol obtained by the reduction of p-nitro-n-propylbenzene had a n-propyl group in the 2-position.

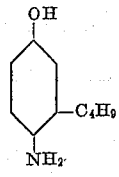
Example V.—n-Butylhydroquinone



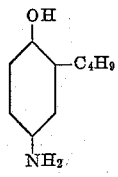
8.95 g. of p-nitro-n-butylbenzene, 15 cc. of sulfuric acid (sp. g. 1.84) and 250 cc. of water were heated to 95° C. and maintained at that temperature while 2 g. of aluminium flakes were added over a period of 3 to 4 hours with vigorous stirring. The reaction mixture turned from yellow to red in color and finally changed to brownish yellow as the last of the aluminium was added. Since the reaction proceeded quite slowly toward the end of the four-hour period of heating, the reaction mixture was stirred at 95° C. for an additional 1.5 hours after all of the aluminium had been added. The reaction mixture was then diluted to 750 cc. with water, and a small amount of gummy material and undissolved aluminium were filtered off while the mixture was still hot. After allowing the filtrate to cool, it was extracted with diethyl ether. The ether was evaporated off from the extract to give 1.3 g. of n-butylhydroquinone. After recrystallization from a mixture of benzene and petroleum ether, the n-butylhydroquinone melted at 86.5° to 87° C. On analysis, it was found to contain 72.08 per cent carbon and 8.53 per cent hydrogen (calculated for carbon 72.24 per cent and for hydrogen 8.49 per cent). On oxidation with potassium dichromate in dilute aqueous sulfuric acid, it gave n-butyl-p-quinone as a light yellow product having a noticeable quinone odor and a melting point of 31.5° C. The n-butylhydroquinone was soluble in aqueous caustic alkalis and diethyl ether, but was insoluble in dilute mineral acids. It acted as a photographic developer and could be employed as an antioxidant for gasoline, oils, rubber, etc.

The reaction mixture remaining after the extraction with diethyl ether was cooled to 0° C. and 3.85 g. of precipitate separated out. On evaporating the mixture to 250 cc. and cooling to 0° C. again, another 0.47 g. of precipitate was obtained. The mother liquor was made alkaline to brilliant yellow paper by the addition of sodium sulfite and sodium carbonate and filtered hot. The filter cake was washed with hot ethyl alcohol and the filtrate was extracted with diethyl ether. The washings were combined with the ether extract and the mixture made acid to Congo red with dilute sulfuric acid, and then evaporated to dryness. The 2.5 g. of dried product so obtained were combined with the 3.85 g. and 0.47 g. of precipitate obtained above by cooling the reaction mixture. The mixture of solids was mixed with water and made strongly alkaline with excess sodium hydroxide. An oily layer formed on top of the alkaline aqueous layer and was extracted with diethyl ether. The ether was evaporated from the extract to give 2.7 g. of p-n-butylaniline having a strong aromatic amine odor. It was converted to the sulfate which gave a melting point of 210° to 215° C. with discoloration. The sulfate on analysis was found to contain 60.64 per cent carbon, 8.18 per cent hydrogen and 7.06 per cent nitrogen (calculated for carbon 60.6 per cent, for hydrogen 8.1 per cent and for nitrogen 7.02 per cent). The sulfate was soluble in alkali and dilute aqueous acids. The alkalinity of the lower aqueous alkaline layer remaining after extraction with diethyl ether was reduced by the addition of sodium bisulfite and a small amount of dilute hydrochloric acid until it was only slightly alkaline to brilliant yellow paper. A precipitate separated out at once, and the aqueous layer was cooled and then filtered. There were thus obtained 1.26 g. of n-butyl-p-aminophenol. After recrystallization from a mixture of benzene and petroleum ether, it melted at 81° to 82° C. On analysis it

contained 73.06 per cent carbon, 8.84 per cent hydrogen and 8.63 per cent nitrogen (calculated for carbon 72.67 per cent, for hydrogen 9.15 per cent and for nitrogen 8.47 per cent). It was soluble in aqueous caustic alkali and dilute aqueous acids, and it also acted as a photographic developer. On oxidation with dichromic acid (potassium dichromate plus sulfuric acid) it gave n-butyl-p-quinone as a yellow solid (an o-aminophenol would have been completely oxidized). On reduction of the quinone with aqueous sodium hyposulfite it gave n-butylhydroquinone as a solid melting at 86° to 87° C. To prove that the n-butyl group in the p-aminophenol obtained by the reduction of p-nitro-n-butylbenzene was in the 2-position, its properties were compared with those of 3-n-butyl-p-aminophenol prepared by the reduction of o-nitro-n-butyl-benzene prepared according to the process described in Bean application Serial No. 547,296. The 3-n-butyl-p-aminophenol so prepared had the formula:



and after recrystallization from a mixture of benzene and petroleum ether it melted at 80° to 81° C. On microanalysis, it contained 72.6 per cent carbon, 9.0 per cent hydrogen and 8.2 per cent nitrogen (calculated for carbon 72.67 per cent, for hydrogen 9.15 per cent and for nitrogen 8.47 per cent). It was soluble in aqueous sodium hydroxide and dilute aqueous acids. On oxidation with dichromic acid (potassium dichromate plus aqueous sulfuric acid) the 3-n-butyl-p-aminophenol gave n-butyl-p-quinone melting at 31.5° C. Since the melting point of the n-butyl-p-aminophenol prepared by the reduction of p-nitro-n-butylbenzene was too close to the melting point of the 3-n-butyl-p-aminophenol to serve as a means of differentiation, a mixed melting point determination was made. A mixed melting point of 60° C. to 70° C. was obtained which showed that the two compounds were not identical. Since there are only two possible n-butyl-p-aminophenols and the n-butyl-p-aminophenol obtained by the reduction of p-nitro-n-butylbenzene was not identical to the 3-n-butyl-p-aminophenol obtained by the reduction of o-nitro-n-butylbenzene, the former compound must contain its n-butyl group in the 2-position, thus:



Instead of adding the aluminium flakes to the the mixture of the p-nitroalkylbenzene, water and sulfuric acid as is done in the above examples, a sulfuric acid solution in water can be added to a hot, stirred suspension of aluminium in water and the nitroalkylbenzene. Other acids can be advantageously employed in place of the sulfuric acid in the above examples, such as oxalic acid, phosphoric acid, hydrochloric acid, the alkane-sulfonic acids (e. g. methanesulfonic acid, ethanesulfonic acid, etc.) and the aromatic sulfonic acids (e. g. those of the benzene and naphthalene series, such as p-toluenesulfonic acid, β-naphthalene-sulfonic acid, etc.).

Example VI

A mixture of 15 g. of p-nitroethylbenzene, 40 g. of oxalic acid and 200 g. of water was heated at 95°–100° C., and maintained at that temperature while 5 g. of aluminum flakes were added with vigorous stirring over a period of 1½ to 2 hours. The reaction mixture was stirred an additional 1½ to 2 hours after all of the aluminum had been added. The undissolved aluminum was filtered off and the reaction mixture was subjected to steam distillation. A very small amount of sweet smelling oil came over. Its odor resembled acetophenone.

The cooled reaction mixture was extracted with diethyl ether. Upon evaporation of the ether about 4 g. of ethyl hydroquinone were obtained.

The reaction mixture, after ether extraction, was made hot and then made alkaline to brilliant yellow paper with sodium sulfite and sodium carbonate. Some p-aminoethylbenzene came out of solution at this point and was separated off. On cooling the alkaline solution, 2-ethyl-p-aminophenol precipitated with some p-aminoethylbenzene. These organic bases were filtered off and then treated with a small amount of sodium hyposulfite and an excess of sodium hydroxide solution causing the 2-ethyl-p-aminophenol to dissolve and the p-aminoethylbenzene to separate as an oil. The oil was extracted with a small amount of ether. On evaporation it was converted to the hydrochloride with hydrochloric acid and 2 g. of product were obtained.

The 2-ethyl-p-aminophenol contained in solution wtih the sodium hydroxide was precipitated by adding sodium bisulfite. 3 g. of product were obtained.

Operating in a similar manner, other acids and nitrobenzenes containing a primary alkyl group in the para position can advantageously be utilized in the process of my invention.

What I claim and desire secured by Letters Patent of the United States is:

1. A process for preparing an alkyl substituted hydroquinone comprising reducing a nitrophenyl compound containing in the para position a primary alkyl group having from 1 to 4 carbon atoms, simultaneously with finely divided aluminium and an aqueous solution of an acid selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, oxalic acid, an alkane sulfonic acid containing from 1 to 4 carbon atoms, a sulfonic acid of the benzene series and a sulfonic acid of the naphthalene series, said solution containing not more than 50% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete, and separating the alkyl-substituted hydroquinone from the reaction mixture.

2. A process for preparing an alkyl substituted hydroquinone comprising reducing a nitrophenyl compound containing in the para position a primary alkyl group having from 1 to 4 carbon atoms simultaneously with finely divided aluminium and an aqueous solution of sulfuric acid, said solution containing not more than 50% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the re-

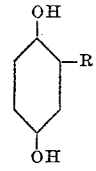
duction is substantially complete, and separating the alkyl-substituted hydroquinone from the reaction mixture.

3. A process for preparing an alkyl substituted hydroquinone comprising reducing a nitrophenyl compound containing in the para position a primary alkyl group having from 1 to 4 carbon atoms, simultaneously with finely divided aluminium and an aqueous solution of an acid selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, oxalic acid, an alkane sulfonic acid containing from 1 to 4 carbon atoms, a sulfonic acid of the benzene series and a sulfonic acid of the naphthalene series, said solution containing not more than 10% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete, and separating the alkyl-substituted hydroquinone from the reaction mixture.

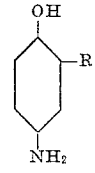
4. A process for preparing an alkyl substituted hydroquinone comprising reducing a nitrophenyl compound containing in the para position a primary alkyl group having from 1 to 4 carbon atoms simultaneously with finely divided aluminium and an aqueous solution of sulfuric acid, said solution containing not more than 10% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete, and separating the alkyl-substituted hydroquinone from the reaction mixture.

5. A process for preparing an alkyl substituted hydroquinone comprising reducing, at a temperature of from 50° C. to 100° C., a nitrophenyl compound containing in the para position a primary alkyl group having from 1 to 4 carbons atoms, simultaneously with finely divided aluminium and an aqueous solution of an acid selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, oxalic acid, an alkane sulfonic acid containing from 1 to 4 carbon atoms, a sulfonic acid of the benzene series and a sulfonic acid of the naphthalene series, said solution containing not more than 50% by weight of said acid the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete, and separating the alkyl-substituted hydroquinone from the reaction mixture.

6. A process for preparing a mixture of an alkyl hydroquinone selected from those represented by the general formula:

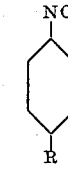


wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, and an alkyl p-aminophenol selected from those represented by the general formula:



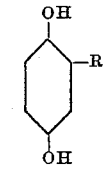
wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, comprising reducing

a compound selected from those represented by the general formula:

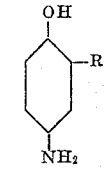


wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, with finely divided aluminium and an aqueous solution of an acid selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, oxalic acid, an alkane sulfonic acid containing from 1 to 4 carbon atoms, a sulfonic acid of the benzene series and a sulfonic acid of the naphthalene series, said solution containing not more than 50% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete.

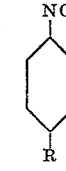
7. A process for preparing a mixture of an alkyl hydroquinone selected from those represented by the general formula:



wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, and an alkyl p-aminophenol selected from those represented by the general formula:

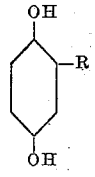


wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, comprising reducing, at a temperature of from 50° C. to 100° C., a compound selected from those represented by the general formula:

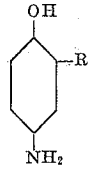


wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, with finely divided aluminium and an aqueous solution of an acid selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, oxalic acid, an alkane sulfonic acid containing from 1 to 4 carbon atoms, a sulfonic acid of the benzene series and a sulfonic acid of the naphthalene series, said solution containing not more than 50% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete.

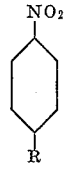
8. A process for preparing a mixture of an alkyl hydroquinone selected from those represented by the general formula:



wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, and an alkyl p-aminophenol selected from those represented by the general formula:

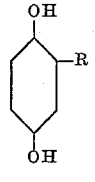


wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, comprising reducing, at a temperature of from 50° C. to 100° C., a compound selected from those represented by the general formula:

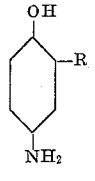


wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, with finely divided aluminium and an aqueous solution of an acid selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, oxalic acid, an alkane sulfonic acid containing from 1 to 4 carbon atoms, a sulfonic acid of the benzene series and a sulfonic acid of the naphthalene series, said solution containing not more than 10% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete.

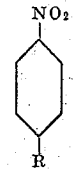
9. A process for preparing a mixture of an alkyl hydroquinone selected from those represented by the general formula:



wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, and an alkyl p-aminophenol selected from those represented by the general formula:

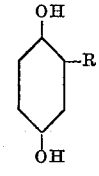


wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, comprising reducing a compound selected from those represented by the general formula:

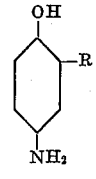


wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, with finely divided aluminium and an aqueous solution of sulfuric acid, said solution containing not more than 50% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete.

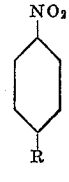
10. A process for preparing a mixture of an alkyl hydroquinone selected from those represented by the general formula:



wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, and an alkyl p-aminophenol selected from those represented by the general formula:



wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, comprising reducing, at a temperature of from 50° C. to 100° C., a compound selected from those represented by the general formula:



wherein R represents a primary alkyl group having from 2 to 4 carbon atoms, with finely divided aluminium and an aqueous solution of sulfuric acid, said solution containing not more than 10% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete.

11. A process for preparing a mixture of ethylhydroquinone and 2-ethyl-p-aminophenol comprising reducing, at a temperature of from 80 C. to 100° C., p-ethylnitrobenzene simultaneously with finely divided aluminium and an aqueous solution of sulfuric acid, said solution containing not more than 10% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete.

12. A process for preparing a mixture of n-propylhydroquinone and 2-n-propyl-p-aminophenol

comprising reducing, at a temperature of from 80° C. to 100° C., p-nitropropylbenzene simultaneously with finely divided aluminium and an aqueous solution of sulfuric acid, said solution containing not more than 10% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete.

13. A process for preparing a mixture of n-butylhydroquinone and 2-n-butyl-p-aminophenol comprising reducing, at a temperature of from 80° C. to 100° C., n–butylnitrobenzene simultaneously with finely divided aluminium and an aqueous solution of sulfuric acid, said solution containing not more than 10% by weight of said acid, the quantity of said acid present being sufficient to maintain an acid medium until the reduction is substantially complete.

FREDERIC R. BEAN.

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