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METHOD FOR PREPARING 3,3'-5,5'-TETRA-ALKYL-4,4'-DIPHENOQUINONES

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6 Claims. (Cl. 260—396)

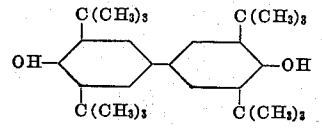
This invention relates to improved methods for preparing gasoline stabilizers of the 4,4'-dihydroxy diphenyl type, wherein all four positions ortho to the hydroxy groups are substituted with alkyl groups. In particular the invention concerns an improved method for preparing 3,3'-5,5'-tetra-alkyl-4,4'-diphenoquinones, which may be susequently reduced to the corresponding diphenols.

It is an object of this invention to provide inhibitors for gasolines which are highly effective in very small proportions.

A further object is to provide convenient and economical methods for preparing such inhibitors.

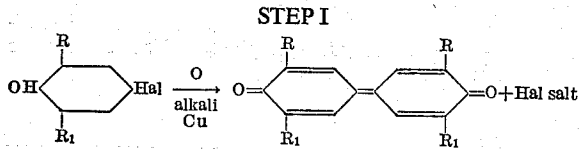
Other objects will appear from the more detailed description which follows.

U. S. Patent No. 2,479,948 discloses a class of inhibitors which may be designated as 3,5,3',5'-tetra-alkyl-4,4'-dihydroxy diphenyls wherein not more than two of the alkyl groups are tertiary alkyl groups. The compound 3,3'-5,5'-tetra-tert-amyl-4,4'-dihydroxydiphenyl is disclosed therein as being relatively ineffective as an inhibitor, being less active than the reference standard, cresylic acids. The other compounds disclosed, which contain primary and/or secondary alkyl groups, while stated to be relatively active as inhibitors, are more or less soluble in alkaline solutions. It has now been found that the specific compound 3,3'-5,5'-tetra-tert-butyl-4,4'-dihydroxy diphenyl:

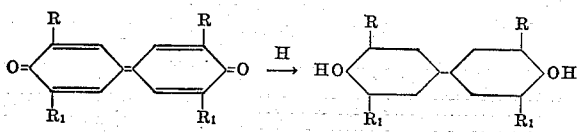


is highly active as an inhibitor and is also very insoluble in alkaline solutions. The invention embraces a novel and advantageous method for the preparation of this and other such compounds. The method consists broadly in treating an appropriate 4-halo-phenol, preferably a 4-halo-2,6-dialkyl phenol, under mild alkaline oxidizing conditions in the presence of a copper catalyst to produce a corresponding p-diphenoquinone, and then hydrogenating the diphenoquinone under mild hydrogenating conditions to produce the corresponding dihydroxy diphenyl. These reactions may be summarized as follows:

STEP I



STEP II



wherein R and R1 may be any inert substituents, but are preferably tertiary alkyl groups.

The prior art methods for preparing these compounds have generally involved an oxidation of a non-halogenated phenol with strong acidic oxidizing agents such as chromic acid, followed by hydrogenation of the resulting diphenoquinone. The present process is carried out under mild alkaline oxidizing conditions at low temperatures, resulting in a minimum of undesired side reactions and decomposition. The process is also easily controlled, and avoids the use of dangerous or corrosive reagents.

Examples of phenols which may be employed in Step I of my process include 2,6-di-tert-butyl-4-chlorophenol; 2,6 - di - isopropyl - 4 - chlorophenol; 2,6 - diethyl - 4-chlorophenol; 2,6 - dihexyl - 4 - chlorophenol; 2 - tert-butyl - 6 - ethyl - 4 - chlorophenol; 2 - tert - amyl - 6-tert - butyl - 4 - chlorophenol; 2 - tert - butyl - 6 - cyclohexyl - 4 - chlorophenol; 2 - methyl - 4 - chlorophenol, or any of the bromo or iodo analogs of the above compounds.

The oxidizing conditions employed in Step I above generally involve air or other oxygen containing gas as the oxidizing agent. Finely divided reduced copper powder is the preferred catalyst, although other metal powders may be employed. The alkaline material acts as a halogen acceptor, and may be any alkaline acting material such as ammonia, calcium hydroxide, sodium hydroxide, primary, secondary or tertiary amines, sodium carbonate etc. The reaction may be carried out at any desired temperature and pressure. Normal atmospheric pressures and room temperatures are ordinarily preferred. A solvent such as ethanol may be employed if desired. It is preferred that some water should be present in the reaction mixture, since this appears to accelerate the reaction. If refluxing is employed it is preferred to employ either water or some relatively low boiling solvent in the reaction mixture in order to maintain a reflux temperature below about 150° C., thereby avoiding thermal decomposition of the reactants or products. Air may be bubbled slowly through the mixture throughout the reaction period or a suitable solid or liquid oxidizing material may be present in the mixture.

After completion of the oxidation, the solid diphenoquinone, which ordinarily separates as bright red crystals, is filtered from the mixture and washed with water to remove excess alkaline materials and salts.

The diphenoquinone is then reduced with hydrogen under mild hydrogenation conditions, as for example with zinc and acetic acid, or tin and hydrochloric acid. Care must be exercised to insure that the hydrogenation conditions are not sufficiently drastic to cause the benzene rings to also become partially or wholly hydrogenated. Only two atoms of hydrogen are required to reduce the diphenoquinone to the corresponding dihydroxy diphenyl. The above hydrogenating materials will ordinarily add the desired hydrogen selectively at normal temperatures and pressures. With higher temperatures and/or pressures, or with other more drastic hydrogenation catalysts, as for example Raney nickel, the reaction time must be closely controlled in order to avoid undesired types of hydrogenation, or scission of the bicyclic structure.

After hydrogenation is completed, as may be evidenced by the disappearance of color from the reaction mixture, the dihydroxy diphenyl compound may be recovered by filtration, washed with water, and if desired recrystallized from solvents such as alcohol, acetone, benzene, etc.

In order to illustrate the method of preparing these compounds, the following examples are cited, which should be considered as illustrative only and not limitative:

Example I–A

20 gms. of 2,6-di-tert-butyl-4-chrophenol was intro-

duced into a flask and treated at room temperature with a mixture of 70 ml. mono-n-butylamine, 20 ml. of water, and 0.2 gm. of copper powder. Air was bubbled slowly through the mixture at atmospheric pressure for about eight hours. During the reaction the mixture was observed to become red in color. Upon cooling, bright red needles of 3,3'-5,5'-tetra-tert-butyl-diphenoquinone, precipitated out, and were separated by filtration. Upon washing with water and recrystallization from benzene, the crystals were found to have the following characteristics:

Melting Point, 229° C.
Analysis:
Found ..... H, 9.32%; C, 82.6%
Calculated 9.86%; 82.3%
Mol. Wt.:
Found 398
Calculated 408.6

The phosphomolybdic acid test for hindered phenols was negative.

Example I–B

15 gms. of the 3,3'-5,5'-tetra-tert-butyl diphenoquinone was mixed in a flask with about 3.0 gms. of zinc dust. Dilute acetic acid was admitted periodically over a period of about 3 hours at room temperature. At the end of this period, the red color of the quinone was observed to completely disappear. The light colored crystals obtained on cooling were removed by filtration and washed with water. Upon recrystallization from benzene, pure 3,3'-5,5'-tetra-tert-butyl-4,4'-dihydroxy diphenyl was obtained in almost quantitative yield. The material had the following characteristics:

Melting Point, 184° C.
Analysis:
Found ..... C, 81.1%; H, 10.2%
Calculated ..... C, 81.9%; H, 10.3%
Mol. Wt.:
Found 420
Calculated 411

The ultra violet spectra showed the typical characteristics of phenolic OH groups when compared in ethanol and iso-octane solution.

Example II

3 gms. of 2,6-di-tert-butyl-4-chlorophenol was dissolved in 30 ml. of 95% ethanol and 0.1 gm. of copper powder was added. Air was slowly bubbled through the mixture while 12 ml. of concentrated ammonium hydroxide solution was gradually added. The reaction was continued at room temperature for about 2 hours. At the end of the reaction period excess ammonia and alcohol was removed by distillation. The remaining solid was water washed, then redissolved in benzene, filtered and recrystallized. 3,3'-5,5'-tetra-tert-butyl diphenoquinone was obtained in about 80% yield, which gave upon hydrogenation the corresponding dihydroxy diphenyl as in Example I–B.

Example III

Example II was repeated using a 10% sodium hydroxide solution in place of the ammonium hydroxide. After 10 hours treatment with air at reflux temperature, a somewhat smaller yield of 3,3'-5,5'-tetra-tert-butyl diphenoquinone was recovered by the purification procedure of Example II.

Example IV

The procedure of Example I is repeated using as the starting material 2,6-di-isopropyl-4-bromo phenol. A good yield of 3,3'-5,5'-tetra-isopropyl diphenoquinone is obtained, which gives 3,3'-5,5'-tetra-isopropyl-4,4'-dihydroxy diphenyl upon mild hydrogenation with tin and hydrochloric acid.

The procedures outlined in the above examples may be employed for preparing substantially any substituted 4,4'-dihydroxy diphenyl by employing as the starting material the appropriate substituted 4-halophenol in place of the halophenols employed in the examples. The slight modifications of procedure which may be necessary to accommodate the slight differences in solubility and reactivity of the various starting materials will be obvious to those skilled in the art. The above procedures are particularly valuable for preparing sterically hindered dihydroxy diphenyls, wherein the reactivity of the phenol groups is hindered by the presence of a tertiary alkyl group in each of the positions ortho to the hydroxy groups.

The compound prepared in Example I–B, namely 3,3'-5,5'-tetra-tert-butyl-4,4'-dihydroxy diphenyl is found to be particularly valuable as an inhibitor for petroleum products. It is active in small proportions, ranging from about 0.0001% to 0.2%, and is very insoluble in aqueous alkaline solutions, such as the alkaline solutions employed in sweetening gasoline stocks. While this material is particularly suitable for use in cracked gasolines, it is also satisfactory for use as a stabilizer in other oxidizable organic compounds such as aviation gasoline, turbine oils, lubricating oils, unsaturated hydrocarbon polymers, resins, turpentine, corn oil, cottonseed oil, fish oils, animal oils, fats, oils, soaps, terpenes, essential oils, cellulose esters and ethers etc. The proportion of inhibitor to be used in these materials is within the same range as mentioned above in connection with petroleum products. With cracked gasolines, about 10 pounds of the inhibitor per 1,000 barrels of gasoline may suitably be used, which corresponds to about 0.0035% by weight.

Cracked gasolines containing from 0.001% to 0.1% of 3,3'-5,5'-tetra-tert-butyl-4,4'-dihydroxy diphenyl are found to exhibit substantially increased induction periods when tested according to the standard oxygen absorption test. In this test oxygen is bubbled through the sample of gasoline at 150° C., and the time required for a given amount of oxygen absorption is measured. This test, while being a standard method, does not necessarily correlate accurately in all gasoline stocks with the overall stability in actual use of the particular gasoline. For gasolines derived from western crudes, a more reliable index of stability is usually obtainable by a determination of their peroxide content. High peroxide numbers indicate low stability and low peroxide numbers indicate high stability. These peroxide numbers are determined by titrating a sample of the gasoline with a reducing solution consisting essentially of 0.01 N titanous chloride. This method is more particularly described in U. O. P. Laboratory Test Methods for Petroleum and its Products, Universal Oil Company (1940).

Example V

In order to test the stabilizing activity of the inhibitor produced in Example I–B, peroxide numbers were determined for three samples, A, B, and C, of a light cracked gasoline boiling between about 100–300° F. and derived from a California crude. Sample A contained no inhibitor; sample B contained 0.0035% of 2,6-di-tert-butyl-p-cresol; and sample C contained 0.0035% of 3,3'-5,5'-tetra-tert-butyl-4,4'-dihydroxy diphenyl. The results were as follows:

Sample	Peroxide No.		
	after 24 hours' exposure to air	after 72 hours' exposure to air	after 17 days' exposure to air
A	0.9	4.3	----------
B	0.03	0.05	0.13
C	0.03	0.03	0.08

This data shows that 3,3'-5,5'-tetra-tert-butyl-4,4' - di-

hydroxy diphenyl is effective in extremely small amounts in preventing the formation of peroxides in cracked gasolines, and that it retains its activity for a longer period of time than its monocyclic analog, 2,6-di-tert-butyl p-cresol. Inasmuch as these peroxides are considered to be precursors or essential factors in the formation of gums in gasolines, it is clear that the above compound is a highly effective stabilizer.

The foregoing disclosure of this invention is not to be considered as limiting since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. A method for preparing a 3,3'-5,5'-tetra-alkyl-4,4'-diphenoquinone which comprises oxidizing a 2,6 dialkyl 4-halophenol with a mild oxidizing agent in the presence of an alkaline-acting material and a metallic copper catalyst.

2. A method as defined in claim 1 wherein said oxidizing agent is an oxygen-containing gas.

3. A method for preparing a 3,3'-5,5'-tetra-tert-alkyl-4,4'-diphenoquinone which comprises oxidizing a 2,6-di-tert-alkyl-4-halophenol with a mild oxidizing agent in the presence of an alkaline-acting material and a metallic copper catalyst.

4. A process according to claim 3 wherein said oxidizing agent is an oxygen-containing gas.

5. A method as defined in claim 1 wherein said alkaline-acting material is a basic nitrogen compound.

6. A method as defined in claim 3 wherein said 2,6-di-tert-alkyl-4-halophenol is a 2,6-di-tert-butyl-4-halophenol.

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