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ALKYLATION OF p-ALKOXYPHENOLS

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This invention relates to the alkylation of p-alkoxyphenols and more particularly to a novel method for producing high yields of 2-tert.-alkyl-4-alkoxyphenol and low yields of 3-tert.-alkyl-4-alkoxyphenol.

In the alkylation of p-alkoxyphenol with a tertiary alcohol, the product consists of a major proportion of 2-tert.-alkyl-4-alkoxyphenol, a lesser proportion of 3-tert.-alkyl-4-alkoxyphenol, as well as varying amounts of 2,5-di-tert.-alkyl-4-alkoxyphenol. For certain uses the 2-tert.-alkyl-4-alkoxyphenol is very desirable, while the 3-tert.-alkyl-4-alkoxyphneol is undesirable. For example, in the preparation of an inhibitor to retard oxidative deterioration of food products, 2-tert.-butyl-4-methoxyphenol is considerably more potent than the 3-isomer. Therefore, it is important to produce increased yields of the 2-isomer with decreased yields of the 3-isomer. Also, the 2,5-di-tert.-butyl-4-methoxyphenol is not as satisfactory as is the 2-tert.-butyl-4-methoxyphenol and it is likewise desirable to reduce the yields of the dialkyl compound to a minimum. The present invention offers a novel method for accomplishing these results.

In one embodiment the present invention relates to a method for producing high yields of 2-tert.-alkyl-4-alkoxyphenol and low yields of 3-tert.-alkyl-4-alkoxyphenol which comprises reacting p-alkoxyphenol with a tertiary-alcohol in a ratio of at least 2 mols of p-alkoxyphenol per mol of tertiary-alcohol at a temperature of not more than about 175° C.

In a specific embodiment the present invention relates to a method for producing high yields of 2-tert.-butyl-4-methoxyphenol and low yields of 3-tert.-butyl-4-methoxyphenol and 2,5-di-tert.-butyl-4-methoxyphenol, which comprises reacting p-methoxyphenol with tert.-butyl-alcohol in a ratio of from about 2 to about 10 mols of p-methoxyphenol per mol of tert.-butyl-alcohol at a temperature of from about 125° to about 175° C. in the presence of a silica-metal oxide catalyst.

As hereinbefore set forth, the present invention is directed to a novel method for producing high yields of desired 2-tert.-alkyl-4-alkoxyphenols and low yields of the undesired 3-tert.-alkyl-4-alkoxyphenols and 2,5-di-tert.-alkyl-4-alkoxyphenols. These improved results are obtained by the use of selected concentrations of reactants and at selected operating conditions.

As an essential feature of the present invention, the ratio of p-alkoxyphenol to tertiary-alcohol should be within the range of from about

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2 to 10 mols of p-alkoxyphenol per mol of tertiary-alcohol. It has been found that these selected concentrations, in conjunction with the use of selected temperature conditions, result in the production of a higher yield of the desired 2-isomer with lower yields of the undesired 3-isomer and dialkylated product.

Another essential feature of the present invention is the use of a temperature of not more than about 175° C. and, when using the preferred catalyst, the temperature is within the range of from about 125° to about 175° C. It has been found that the use of this temperature range, in conjunction with the selected molar concentrations of reactants, results in higher yields of the desired 2-isomer and lower yields of the undesired 3-isomer and dialkylated product.

A preferred final product comprises 2-tert.-butyl-4-methoxyphenol and, for its preparation, p-methoxyphenol is reacted with tert.-butyl-alcohol under the conditions hereinbefore set forth. When other tert.-alkyl-alkoxyphenols are desired, the reactants will be selected to produce the desired compounds. Thus, in place of 4-methoxyphenol, 4-ethoxyphenol, 4-propoxyphenol, 4-butoxyphenol, 4-pentoxyphenol, etc .may be employed. Similarly, in place of tert.-butyl-alcohol, tert.-amyl-alcohol, tert.-heptyl-alcohol, tert.-octyl-alcohol, etc. may be utilized.

The reaction of p-alkoxyphenol with tertiary-alcohol is readily effected in the presence of a suitable catalyst. A preferred catalyst comprises silica-metal oxide, either synthetically prepared or naturally occurring. A particularly preferred catalyst comprises silica-alumina which may be synthetically prepared or may comprise naturally occurring aluminum-silicates such as Filtrol, Tonsil, etc. Other suitable metal oxide catalysts include silica composited with one or more of the oxides of magnesium, zirconium, thorium, titanium, molybdenum, tungsten, manganese, etc. It is understood that the various catalysts are not necessarily equivalent and also that other suitable catalysts, particularly acids such as phosphoric acid, sulfuric acid, etc., either in liquid state or composited with a suitable supporting component, may be utilized but not necessarily with equivalent results. In general, the last mentioned catalysts are utilized at a lower temperature which may be within the range of 50° to 100° C. or more.

The preferred silica-alumina catalyst is synthetically prepared and may be manufactured by separate, successive or co-precipitation methods. In one method a suitable acid, such as sulfuric

acid, is reacted with a sodium silicate solution, such as water glass, to form silica gel. When spherical catalysts are desired, the mixture of acid and water glass are dropped through a suitable orifice onto a rotating disk and therefrom into a suitable suspending medium, such as mineral seal oil, Nujol, etc. and maintained therein until the silica gel sets into firm spheres. Usually the spheres are transferred from the forming zone by means of a layer of water disposed beneath the oil layer, and the spheres are washed to remove alkali metal ions. The spheres are then composited with alumina by suspending the same in a suitable aluminum salt solution such as that of aluminum chloride, aluminum nitrate, aluminum sulfate, etc., aluminum hydroxide being precipitated by the addition of a suitable basic reagent, after which the composite is dried at a temperature of from about 200° to about 500° F. and calcined at a temperature of from about 800° to about 1200° F. The amount of alumina in the catalyst will range from about 5 to about 20% by weight and generally is within the range of from about 8 to about 12% by weight, the remainder being composed substantially of silica.

The alkylation reaction may be effected in either a batch or a continuous flow process. In a batch type operation, the reactants and catalyst are introduced into a reaction zone equipped with stirring or other suitable means for effecting intimate contact of the catalyst and reactants. The desired heating may be applied to the reactants and/or reaction zone by well known means. In a continuous type operation, when employing a solid catalyst, the catalyst is disposed in the reaction zone and the reactants, at the desired temperature, are passed into contact with the catalyst, in either upward or downward flow. When using a liquid catalyst and continuous flow operation, a reaction zone equipped with stirring or other suitable means is employed. Another type of operation is the suspensoid type of operation in which the catalyst is carried into the reaction zone by means of one or more of the reactants or by means of an inert carrying medium. Another type of operation includes the fluidized type process in which the reactants and catalyst are maintained in a state of turbulence under hindered settling conditions in the reaction zone. The pressure to be employed will depend upon the type of operation to be utilized and will vary from atmospheric to 1000 pounds or more per square inch.

The products from the above reaction may be treated in any suitable manner such as by fractionation, solvent extraction, etc. to separate unreacted alkoxyphenol which preferably is recycled to the reaction zone for further conversion therein and the desired 2-tert.-alkyl-alkoxy-phenol from the reduced amounts of 3-tert-alkyl-4-alkoxy-phenol and 2,5-di-tert-alkyl-4-alkoxyphenol. As hereinbefore set forth, when operating under the selected conditions of the present invention, the yields of the desired 2-isomer will be high and the yields of the unsired 3-isomer and 2,5-dialkylated product will be lower than heretofore obtainable.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

EXAMPLE I

p-Methoxyphenol was reacted with tert-butyl-alcohol in a continuous type flow operation utilizing a silica-alumina catalyst at a temperature of 150° C. and a pressure of 250 pounds per square inch. The mol ratio of methoxyphenol to tert-butyl-alcohol was varied as shown in the following table. The table indicates the weight per cent of the 2- and 3-isomers in the monobutyl fraction.

Table 1

Run No.	Molar ratio p-methoxyphenol : tert-butyl-alcohol	Wt. Percent of 2-isomer	Wt. Percent of 3-isomer
1	1.1:1	69	31
2	1.55:1	78.5	21.5
3	2:1	88	12

The results reported in the above table are the averages of at least two different run periods.

From the above data it is apparent that, at a temperature of 150° C., the use of a molar ratio of p-methoxyphenol to tert.-butyl-alcohol of 2 gives a considerably greater yield of the desired 2-isomer than does the use of a lower molar ratio of the reactants.

EXAMPLE II

In another operation utilizing the silica-alumina catalyst, at a temperature of 170° C. and a pressure of 300 pounds per square inch, the results obtained when using different molar ratios of 4-methoxyphenol to tert.-butyl-alcohol are shown in the following table. These results are based on analyses of a heart cut separated from the product of the reaction and show the composition of the 2-isomer, 3-isomer and dibutyl compounds.

Table 2

Run No.	Molar ratio p-methoxyphenol : tert-butyl-alcohol	Wt. Percent of 2-isomer	Wt. Percent of 3-isomer	Wt. Percent of dibutyl
4	2:1	86	12	2
5	5:1	82	15	0

The results reported in the above table are the averages of at least two different run periods.

From these data it is apparent that the use of a temperature of 170° C. and a molar ratio of 2 and above results in high yields of the desired 2-isomer, low yields of the undesired 3-isomer and very small amounts of the undesired dibutyl compounds.

EXAMPLE III

In contrast to the above, runs made in the same manner as described in Example I but utilizing a temperature of 200° C. gave lower yields of the desired 2-isomer as indicated in the data in the following table.

Table 3

Run No.	Molar ratio p-methoxyphenol : tert-butyl-alcohol	Wt. Percent of 2-isomer	Wt. Percent of 3-isomer
6	.67:1	75	25
7	1.1:1	75	25
8	1.5:1	74	26
9	2:1	74	26

From the above data it is seen that a temperature of 200° C. is undesired in that it produces

only 75% of the desired 2-isomer even when utilizing a molar ratio of 2:1 of p-methoxyphenol to tert.-butyl-alcohol.

The examples in the above data clearly show that the use of a temperature below 175° C. and a molar ratio of p-methoxyphenol to tert.-butyl-alcohol of above 2 is critical in the production of high yields of the desired 2-tert.-butyl-4-methoxyphenol and low yields of undesired 3-tert.-butyl-4-methoxyphenol and undesired 2,5-di-tert.-butyl-4-methoxyphenol.

I claim as my invention:

1. A method for producing high yields of 2-tert.-alkyl-4-alkoxyphenol and low yields of 3-tert.-alkyl-4-alkoxyphenol which comprises reacting p-alkoxyphenol with a tertiary-alcohol in a ratio of at least 2 mols of p-alkoxyphenol per mol of tertiary-alcohol at an alkylating temperature of not more than about 175° C.

2. A method for producing high yields of 2-tert.-alkyl-4-alkoxyphenol and low yields of 3-tert.-alkyl-4-alkoxyphenol which comprises reacting p-alkoxyphenol with a tertiary-alcohol in a ratio of at least 2 mols of p-alkoxyphenol per mol of tertiary-alcohol at an alkylating temperature of not more than about 175° C. in the presence of a silica-metal oxide catalyst.

3. A method for producing high yields of 2-tert.-alkyl-4-alkoxyphenol and low yields of 3-tert.-alkyl-4-alkoxyphenol which comprises reacting p-alkoxyphenol with a tertiary-alcohol at an alkylating temperature of not more than about 175° C. in the presence of a silica-alumina catalyst.

4. A method for producing high yields of 2-tert.-butyl-4-methoxyphenol and low yields of 3-tert.-butyl-4-methoxyphenol which comprises reacting p-methoxyphenol with tert.-butyl-alcohol in a ratio of at least two mols of p-alkoxyphenol per mol of tert.-butyl-alcohol at an alkylating temperature of not more than about 175° C.

5. A method for producing high yields of 2-tert.-butyl-4-methoxyphenol and low yields of 3-tert.-butyl-4-methoxyphenol which comprises reacting p-methoxyphenol with tert.-butyl-alcohol in a ratio of at least two mols of p-alkoxyphenol per mol of tert.-butyl-alcohol at an alkylating temperature of not more than about 175° C. in the presence of a silica-metal oxide catalyst.

6. A method for producing high yields of 2-tert.-butyl-4-methoxyphenol and low yields of 3-tert.-butyl-4-methoxyphenol which comprises reacting p-methoxyphenol with tert.-butyl-alcohol in a ratio of at least two mols of p-alkoxyphenol per mol of tert.-butyl-alcohol at an alkylating temperature of not more than about 175° C. in the presence of silica-alumina catalyst.

7. A method for producing high yields of 2-tert.-butyl-4-methoxyphenol and low yields of 3-tert.-butyl-4-methoxyphenol and 2,5-di-tert.-butyl-4-methoxyphenol, which comprises reacting p-methoxyphenol with tert.-butyl-alcohol in a ratio of from about 2 to about 10 mols of p-methoxyphenol per mol of tert.-butyl-alcohol at a temperature of from about 125° to about 175° C. in the presence of a silica-metal oxide catalyst.

8. A method for producing high yields of 2-tert.-butyl-4-methoxyphenol and low yields of 3-tert.-butyl-4-methoxyphenol and 2,5-di-tert.-butyl-4-methoxyphenol, which comprises reacting p-methoxyphenol with tert.-butyl-alcohol in a ratio of from about 2 to about 10 mols of p-methoxyphenol per mol of tert.-butyl-alcohol at a temperature of from about 125° to about 175° C. in the presence of silica-alumina catalyst.

9. A method for producing high yields of 2-tert.-alkyl-4-alkoxyphenol and low yields of 3-tert.-alkyl-4-alkoxyphenol which comprises reacting p-alkoxyphenol with a tertiary-alcohol at an alkylating temperature of not more than about 175° C. in the presence of a silica-magnesia catalyst.

10. A method for producing high yields of 2-tert.-alkyl-4-alkoxyphenol and low yields of 3-tert.-alkyl-4-alkoxyphenol which comprises reacting p-alkoxyphenol with a tertiary-alcohol at an alkylating temperature of not more than about 175° C. in the presence of a silica-zirconia catalyst.

11. A method for producing high yields of 2-tert.-alkyl-4-alkoxyphenol and low yields of 3-tert.-alkyl-4-alkoxyphenol which comprises reacting p-alkoxyphenol with a tertiary-alcohol at an alkylating temperature of not more than about 175° C. in the presence of a silica-thorium oxide catalyst.

12. A method for producing high yields of 2-tert.-alkyl-4-alkoxyphenol and low yields of 3-tert.-alkyl-4-alkoxyphenol which comprises reacting p-alkoxyphenol with a tertiary-alcohol at an alkylating temperature of not more than about 175° C. in the presence of a silica-molybdenum oxide catalyst.

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