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(54) **Superacid Catalyzed
Preparation of Resorcinol From
Meta-diisopropylbenzene**

(57) Resorcinol is prepared in high yield and purity by using as catalyst a superacid (such as perfluorinated alkanesulfonic acids of one to eighteen carbon atoms or polymeric perfluorinated resinsulfonic acids, such as acidified Nafion-H) in the catalyzed cleavage-rearrangement reaction of meta-bis(2-hydroperoxy-2-propyl)-benzene (meta-

diisopropylbenzene dihydroperoxide). Part of the process is the preparation of needed meta-diisopropylbenzene in high purity (98—100%) substantially free of other isomers by treating any mixture of diisopropylbenzenes with an excess of anhydrous hydrogen fluoride or a perfluorinated alkanesulfonic acid of one to six carbon atoms and a Lewis acid fluoride, or by alkylating (transalkylating)cumene with a propyl alkylating agent in the aforementioned superacid systems.

SPECIFICATION

Superacid Catalyzed Preparation of Resorcinol from Meta-diisopropylbenzene

Resorcinol (meta-dihydroxybenzene) is an industrial chemical of substantial utility. Its preparation is usually carried out through the high temperature (about 300°C) alkali fusion of meta-benzenedisulfonic acid. For chemical, energy, as well as environmental reasons, this process is disadvantageous. Efforts were made to apply the Hock reaction for the preparation of phenol from isopropylbenzene, to that of resorcinol from meta-diisopropylbenzene through the dihydroperoxide of meta-diisopropylbenzene (see, for example, U.S. Patent Nos. 2,736,753 and 2,862,857; German Offen. Nos. 2,646,032 and 2,737,302; Japan Kokai Nos. 78 02, 434, 78 02,436, 78 53,626 and 79 03,022; British Patent Nos. 819,450, 857,113, 873,676 and 982,514; and Netherlands Patent No. 6,400,270). However, the presence of two hydroperoxide groups existing simultaneously in the intermediate dihydroperoxide can result, under the usual conditions of the Hock reaction using sulfuric acid or silica-alumina (titania) catalysts in the formation of a significantly increased number of by-products, and, thus, lower yields than in the case of cumene hydroperoxide (see Weissermel and Arpe, "Industrial Organic Chemistry", Verlag Chemie, Weinheim (Germany), New York, 1978, pp. 317—318).

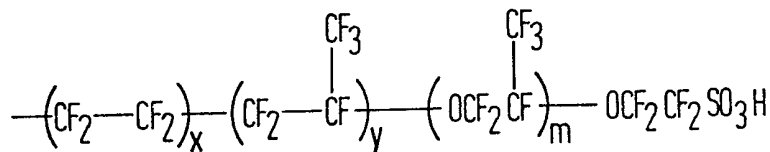
The present invention relates to the improved superacid catalyzed preparation of resorcinol from meta-diisopropylbenzene through its dihydroperoxide, as well as to preparation of the needed meta-diisopropylbenzene in high purity substantially free of other isomers.

According to a first aspect of the present invention there is provided a process of producing resorcinol, selectively and in high yield, which comprises reacting meta-diisopropylbenzene dihydroperoxide with a superacid cleavage-rearrangement catalyst.

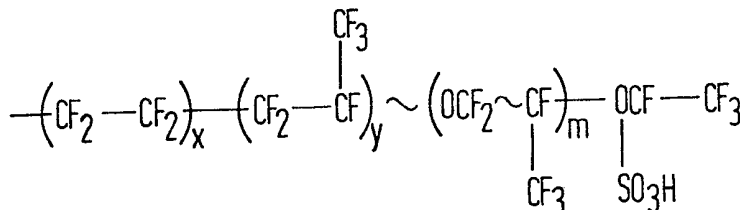
According to a second aspect of the present invention there is provided a process of producing substantially pure meta-diisopropylbenzene which comprises isomerising a mixture of diisopropylbenzene isomers which is not substantially pure meta-diisopropylbenzene with an excess of hydrogen fluoride or a perfluorinated alkanesulfonic acid of one to six carbon atoms and a Lewis acid fluoride catalyst, or alkylating cumene with a propyl alkylating agent in the presence of hydrogen fluoride or a perfluorinated alkanesulfonic acid of one to six carbon atoms and a Lewis acid fluoride catalyst.

We have discovered that meta-diisopropylbenzene dihydroperoxide prepared by known methods, such as the liquid phase oxidation of meta-diisopropylbenzene with oxygen or air in the presence of Cu, Mn or Co salts, HBr or pyridine-HBr (or other tertiary amine-HBr salts) and similar catalysts, can be cleanly converted in high yield (>90%), via its Hock-reaction, to resorcinol, when treated with a superacid catalyst, such as perfluorinated sulfonic acid of one to eighteen carbon atoms or related polymeric perfluorinated resinsulfonic acid, such as acidified Nafion-H. The reaction is generally carried out in solvents, such as benzene, toluene, cumene, meta-diisopropylbenzene, acetone, and sulfolane, or mixtures thereof, at temperatures of from 50° to 150°C, with the superacid catalyst dissolved or dispersed in the solvent system.

The polymeric perfluorinated resinsulfonic acids (Nafion-H) can be prepared from commercially available Nafion-K (DuPont) ion-membrane resin by acidification. This perfluorinated resinsulfonic acid comprises a fluorinated polymer having sulfonic acid groups in the amount of about 0.01 to 5 mequiv/gram catalyst. The polymer catalyst contains a repeating structure, which can be depicted as:



or



where the ratio of x over y varies from about 2 to about 50, and m is 1 or 2. This polymer structure is available commercially under the tradename Nafion resin from DuPont. Polymer catalysts of the above structure can be prepared in various ways. One method, disclosed in Conolly et al. U.S. Patent No. 3,282,875 and Cavanaugh et al. U.S. 3,882,093 comprises polymerizing the corresponding

perfluorinated vinyl compounds. It is also possible to prepare polymer catalyst according to U.S. Patent

No. 4,041,090 by copolymerizing the corresponding perfluorinated vinyl ethers with perfluoroethylene and/or perfluoro- α -olefins. The specific fluorinated repeating structure depicted above is not critical but perfluorinated is preferred. The Nafion ion exchange resins can be acidified in various known manners such as set forth in Example 2 below.

5 The conversion can also be advantageously carried out *in situ* when reacting the corresponding 5
meta-bis(2-hydroxy-2-propyl) benzene with hydrogen peroxide over a perfluorinated sulfonic acid or
perfluorinated resin-sulfonic acid catalyst, while azeotropically distilling off water and acetone formed
from the reaction mixture.

10 Without limiting in any way the scope of the invention or speculating on the effectiveness of 10
superacidic catalysts, it is pointed out that these catalysts are capable of substantially speeding up the
rate of the cleavage-rearrangement reaction of meta-diisopropylbenzene dihydroperoxide, which
otherwise is markedly slower than that of the related reaction of cumene hydroperoxide or para-
diisopropylbenzene dihydroperoxide, resulting in formation of significantly increased amounts of
byproducts, which tend to decrease the yield of conversion.

15 Superacids are those acids having an acidity function below $H_0 = -11$ on the logarithmic 15
Hammett H_0 acidity function scale. For example, 100% sulfuric acid has an H_0 function of -11 while
superacids would have H_0 values of -14 , -20 , etc.

20 It is a significant aspect of the invention to obtain the needed starting material, i.e. *meta*-
diisopropyl benzene in high isomeric purity. Practical methods known for preparation of this compound 20
consist of isopropylation of cumene, giving isomeric mixtures with the ortho and para isomers
predominating. Subsequent acid catalyzed isomerization, using usual Friedel-Crafts conditions or solid
acid catalysts, increase the amount of meta isomer up to about 60% of the mixture, but still
necessitate separation of the isomers which due to their close boiling ranges can generally not be
effected by simple distillation alone and thus separation of the isomers is difficult to achieve and
25 expensive. 25

The thermodynamic mixture of isomeric diisopropylbenzenes contains only about 66% of the
meta-isomer. The aluminum chloride catalyzed Friedel-Crafts isomerization of diisopropylbenzenes was
studied by Olah, Meyer and Overchuck (*J. Org. Chem.*, 29, 2315 (1964)) and was shown to give an
equilibrium composition containing 66% of meta and 34% para isomer, accompanied also by
30 significant disproportionation giving cumene and triisopropylbenzenes. 30

It has now been discovered that when carrying out the isomerization of mixed
diisopropylbenzenes in the presence of an excess of anhydrous hydrogen fluoride, or a perfluorinated
alkanesulfonic acid of one to six carbon atoms and a Lewis acid fluoride, such as boron trifluoride,
phosphorus pentafluoride, antimony pentafluoride, arsenic pentafluoride, tantalum pentafluoride, and
35 niobium pentafluoride, at temperatures from -50 to 200°C , preferentially from 0° to 50°C , results in 35
the formation of practically pure (99 to 100%) meta-diisopropylbenzene. The isomerization is
accompanied by disproportionation to cumene and triisopropylbenzene (mainly, the 1,3,5-isomer). The
latter reaction can be, however, suppressed when adding (recycling) 1,3,5-triisopropylbenzene to
transalkylate cumene. This transalkylation reaction can itself be used to prepare meta-
40 diisopropylbenzene in high purity (99+%) when carrying out the process, for example, in HF-BF_3 at 40
 -20°C to 0°C .

Superacid systems form protonated complexes with aromatics, i.e., arenium ions, in the case of
diisopropylbenzenes, the complex formed from the meta isomer is the most stable. Thus, the superacid
systems tend to selectively extract the meta isomer and allow a selective conversion of all isomers into
45 the *meta* product. Such isomerization shifted beyond the thermodynamic equilibrium of the neutral 45
hydrocarbon isomers was known previously only for methylbenzenes (McCaulay and Lien, *J. Am.*
Chem. Soc., 74, 6246 (1952)), but not for isopropylbenzenes. Methyl-benzenes isomerize
intramolecularly, whereas isopropylbenzenes tend to isomerize by intermolecular process. Thus, no
extrapolation is possible from methyl-benzenes to isopropylbenzenes, which are also expected to
50 significantly disproportionate, nor were any results predictable or expected concerning the treatment of 50
diisopropyl benzenes in superacids.

The alkylation [transalkylation] of cumene with propylene, isopropyl halides or isopropyl alcohol
in anhydrous HF or perfluoroalkanesulfonic acid media in the presence of the aforementioned Lewis
acid fluoride catalysts also results in the exclusive formation of *meta*-diisopropylbenzene.

55 Meta-diisopropylbenzene (in practically 100% purity) can also be obtained by carrying out the 55
isopropylation of cumene by transalkylation with triisopropylbenzene in the same superacid systems.
These conditions also tend to minimize disproportionation of formed meta-diisopropylbenzenes.

The scope of the invention is further described in connection with the following examples, which
are set forth for purposes of illustration only and are not to be construed as limiting the scope of the
60 invention in any manner. 60

Example 1

5g of perfluorinated decanesulfonic acid (PDSA) is dissolved (dispersed) in a mixture of 100 ml
acetone and 100 ml toluene, heated to reflux, and 23 g (0.1 mol) meta-diisopropylbenzene
dihydroperoxide (neat or as a solution in diisopropylbenzene) is then added continuously with good

stirring. After addition is completed, stirring is continued for an hour. Resorcinol is either extracted from the reaction mixture with a suitable solvent, such as diisopropyl ether or is separated by vacuum distillation, giving 9.3 g (85%) of resorcinol in 97% purity.

Example 2

5 Reaction carried out as in Example 1, but using 3 g Nafion-H as a catalyst dispersed in 150 ml 5
sulfolane as solvent, at a temperature of 130° to 150°C. Nafion-H is prepared from commercial
(DuPont) potassium salt of the resin (Nafion-K) by acidification with 20 to 30% nitric acid, stirring at 20
to 50°C for four hours, filtering the resin acid, washing it acid free with water and subsequently drying
it in a vacuum oven at 105—110°C for eight hours. An 87% yield of resorcinol in 96% purity is 10
obtained. 10

Example 3

3 g of trifluoromethanesulfonic acid is dissolved in 100 g of sulfolane. The solution is heated to
around 100°C and about 30% solution of 12 g (0.1 mol) of meta-diisopropylbenzene dihydroperoxide
in meta-diisopropylbenzene is added continuously to the stirred solution, while distilling off formed
acetone from the reaction mixture. Isolation of resorcinol is effected as in Example 1. A 92% yield of 15
resorcinol is obtained with 98% purity. 15

Example 4

19.4 g (0.1 mol) of meta-bis(2-hydroxy-2-propyl) benzene is dissolved in 150 ml of dioxane and
5 g of Nafion-H catalyst (as prepared in Example 2) is added to the stirred mixture and heated to reflux.
20 A solution of 8 g (0.2 mol) 90% hydrogen peroxide in 50 ml dioxane is then slowly added with good 20
stirring during a period of two hours, while stirring is continued. The water and acetone formed is
continuously distilled off during the reaction. Workup and isolation of resorcinol, after filtering off the
solid superacid catalysts, is as in Example 1. Yield 56%, purity 98%.

Example 5

25 A commercial mixture of 16 g (0.1 mol) diisopropylbenzene containing about 60% of the para 25
and 40% of the ortho isomer, is dissolved in 150 ml of anhydrous hydrogen fluoride. The reaction
mixture is cooled to -20 to 0° and saturated, while stirred, with boron trifluoride. After stirring at this
temperature for 30 min. the temperature is raised and HF and BF₃ is distilled off, (which can be
reused). After washing, neutralization and drying, the organic layer is separated, distilled and analyzed
30 by gas liquid chromatography. The diisopropylbenzene fraction consists of 99% meta- 30
diisopropylbenzene and 1% para-diisopropylbenzene. Cumene and 1,3,5-triisopropylbenzene are also
formed, as products of disproportionation, amounting to about 20%.

Example 6

35 12 g (0.1 mol) cumene and 10 g (0.05 mol) triisopropylbenzene are dissolved in 150 ml of 35
anhydrous hydrogen fluoride at a temperature between -20° and 0°. While stirring the reaction
mixture at this temperature, it is saturated with boron trifluoride and stirring is continued for two hours.
After workup, as in Example 5, 36% diisopropylbenzene was obtained, comprised of 99.2% of the meta
and 0.8% of the para isomer.

Example 7

40 12 g (0.1 mol) cumene is dissolved in 150 ml anhydrous hydrogen fluoride and while keeping the 40
stirred solution at -20°C to 0°C, 0.05 mol of propylene is introduced and stirring continued for 15
min. The reaction mixture is then saturated with boron trifluoride and stirring continued for another 15
min. After workup, 41% diisopropylbenzene was obtained, comprised of 99.6% of meta and 0.4% para
isomer, together with about 15% 1,3,5-triisopropylbenzene, which can be recycled under conditions of
45 Example 6 to produce more meta-diisopropylbenzene. 45

Claims

1. A process of producing resorcinol, selectively and in high yield, which comprises reacting
meta-diisopropylbenzene dihydroperoxide with a superacid cleavage-rearrangement catalyst.
2. A process according to Claim 1, in which the super-acid catalyst is a perfluorinated
50 alkanesulfonic acid of one to eighteen carbon atoms or a perfluorinated resin-sulfonic acid. 50
3. A process according to Claim 1 substantially as hereinbefore described in any one of Examples
1 to 3.
4. A process of producing resorcinol, selectively and in high yield, from meta-diisopropylbenzene
dihydroperoxide *in situ*, which process comprises reacting meta-bis-(2-hydroperoxy-2-propyl)-benzene
55 with hydrogen peroxide in the presence of a superacid catalyst which is a perfluorinated alkanesulfonic 55
acid of one to eighteen carbon atoms or a perfluorinated resinsulfonic acid with azeotropic removal of
water and acetone formed during the reaction.
5. A process according to Claim 4, substantially as hereinbefore described in Example 4.

6. Resorcinol whenever prepared by a process as claimed in any one of the preceding claims.

7. A process of producing substantially pure metadiisopropylbenzene which comprises isomerizing a mixture of diisopropylbenzene isomers which is not substantially pure meta-diisopropylbenzene with an excess of hydrogen fluoride or a perfluorinated alkanesulfonic acid of one to six carbon atoms and Lewis acid fluoride catalyst.

5 8. A process according to Claim 7, in which the Lewis acid fluoride catalyst is boron trifluoride, phosphorous pentafluoride, arsenic pentafluoride, antimony pentafluoride, tantalum pentafluoride or niobium pentafluoride. 5

10 9. A process according to Claim 7 or 8, in which the isomerization reaction is performed at a temperature of from -50 to 150°C . 10

10. A process according to Claim 7 substantially as hereinbefore described in Example 5.

11. A process of preparing substantially pure metadiisopropylbenzene which comprises alkylating cumene with a propyl alkylating agent in the presence of hydrogen fluoride or a perfluorinated alkanesulfonic acid of one to six carbon atoms and a Lewis acid fluoride catalyst.

15 12. A process according to Claim 11, in which the propyl alkylating agent is propylene, an isopropyl halide, isopropyl alcohol or triisopropylbenzene. 15

13. A process according to Claim 11 or 12, in which the Lewis acid fluoride catalyst is boron trifluoride, phosphorous pentafluoride, arsenic pentafluoride, antimony pentafluoride, tantalum pentafluoride or niobium pentafluoride.

20 14. A process according to Claim 11 substantially as hereinbefore described in Example 6 or 7. 20

15. Substantially pure meta-diisopropylbenzene whenever prepared by a process as claimed in any one of Claims 7 to 14.