

RESERVE COPY.

AMENDED SPECIFICATION

Reprinted as amended in accordance with the Decision of the Superintending Examiner acting for the Comptroller General dated the twenty-fifth day of September, 1963, under Section 29, and under Section 15 of the Patents Act, 1949.

PATENT SPECIFICATION

NO DRAWINGS

905,994

905,994



Date of Application and filing Complete Specification: Aug. 2, 1960.

No. 26776'60.

Application made in Germany (No. F29202) on Aug. 18, 1959.

Complete Specification Published: Sept. 19, 1962.

Index at acceptance:—Class 2(3), C3A13B2(A4:H).

International Classification:—C07c.

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act 1949 are DR. HEINRICH KRIMM, of Bodelschwinghstrasse 16, Krefeld-Bockum, Germany, and DR. HERMANN SCHELL, of Am Oberfeld 39, Krefeld-Uerdingen, Germany, both of German nationality.

COMPLETE SPECIFICATION

Process for the production of α -Alkenyl, α -Cycloalkenyl and α -Aralkenyl Phenols

35

ERRATA

40

AMENDED SPECIFICATION

No. 905,994

Page 1, heading, for "HERMANN SCHELL"
read "HERMANN SCHNELL"

45

Page 1, line 61, for "aralkanyl" read "aral-
kenyl"

Page 1, line 62, for "with" read "without"

50

THE PATENT OFFICE
25th March 1964

55

25 particularly in the case of the commonly used important 2,2 - (4,4' - dihydroxy - diphenyl)-propane (bisphenol A), which is produced in large quantities, the previously known splitting processes have proved to be completely unsatisfactory. The *p*-isopropenyl phenol which is to be expected from the decomposition of this dihydroxy - diaryl - alkane has hitherto not been producible, only isopropyl phenol being formed together with large amounts of useless resinous residues.

30 We have now found a process for the production of α -alkenyl, α -cycloalkenyl and α -

According to this process, it is possible to decompose dihydroxy-diphenyl alkanes, cycloalkanes and aralkanes by a particularly smooth reaction, into corresponding α -alkenyl, α -cycloalkenyl and α -aralkanyl phenols and phenol with appreciable amounts of non-distillable residues being formed. By re-distillation, possibly with the further addition of alkaline-acting materials, alkenyl phenols of high purity are obtained in good yields.

60 65 Disproportionate reactions which are usual in the purely thermal splitting and which lead

AMENDED SPECIFICATION

Reprinted as amended in accordance with the Decision of the Superintending Examiner acting for the Comptroller General dated the twenty-fifth day of September, 1963, under Section 29, and under Section 15 of the Patents Act, 1949.

PATENT SPECIFICATION

905,994



NO DRAWINGS

905,994

Date of Application and filing Complete Specification: Aug. 2, 1960.

No. 26776'60.

Application made in Germany (No. F29202) on Aug. 18, 1959.

Complete Specification Published: Sept. 19, 1962.

Index at acceptance:—Class 2(3), C3A13B2(A4:H).

International Classification:—C07c.

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act 1949 are DR. HEINRICH KRIMM, of Bodelschwinghstrasse 16, Krefeld-Bockum, Germany, and DR. HERMANN SCHELL, of Am Oberfeld 39, Krefeld-Uerdingen, Germany, both of German nationality.

COMPLETE SPECIFICATION

Process for the production of α -Alkenyl, α -Cycloalkenyl and α -Aralkenyl Phenols

5 We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of Germany, of (22c) Leverkusen-Bayerwerk, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is performed, to be particularly described in and by the following statement:—

10 The present invention is concerned with a process for the production of α -alkenyl, α -cycloalkenyl and α -aralkenyl phenyl phenols.

15 It is known to split dihydroxy-diaryl-alkanes by heating to temperatures over 300°C., possibly in the presence of acidic catalysts, phenols and the corresponding alkyl phenols being obtained as main reaction products. In some cases, the formation of small amounts of alkenyl phenols is also observed but, nevertheless, considerable amounts of non-distillable resinous residues also result. Particularly in the case of the technically very important 2,2 - (4,4¹ - dihydroxy - diphenyl)-propane (bisphenol A), which is produced in large quantities, the previously known splitting processes have proved to be completely unsatisfactory. The *p*-isopropenyl phenol which is to be expected from the decomposition of this dihydroxy - diaryl - alkane has hitherto not been producible, only isopropyl phenol being formed together with large amounts of useless resinous residues.

aralkenyl phenols by heating dihydroxy-diphenyl-alkanes, cycloalkanes and aralkanes in which both hydroxy-phenyl groups are attached to the same carbon atom of the alkane, cycloalkane or aralkane residue, said residue having at least one —CH< group attached directly to said carbon atom, in the presence of an alkaline-acting catalyst, characterised in that the process is carried out (a) by heating the dihydroxy-diphenyl compound with an alkali metal compound at a temperature between 150 and 250°C. under reduced pressure, or (b) by heating the dihydroxy-diphenyl compound at a temperature between 220 and 300°C. under normal pressure, with an alkaline-acting catalyst other than an alkali metal compound, or (c) by passing the vapour of the dihydroxy-diphenyl compound over a solid alkaline-acting catalyst at a temperature between 300 and 600°C., the reaction product being rapidly cooled, if desired, to a temperature below its melting point.

According to this process, it is possible to decompose dihydroxy-diphenyl alkanes, cycloalkanes and aralkanes by a particularly smooth reaction, into corresponding α -alkenyl, α -cycloalkenyl and α -aralkenyl phenols and phenol with appreciable amounts of non-distillable residues being formed. By re-distillation, possibly with the further addition of alkaline-acting materials, alkenyl phenols of high purity are obtained in good yields.

Disproportionate reactions which are usual in the purely thermal splitting and which lead

We have now found a process for the production of α -alkenyl, α -cycloalkenyl and α -

to the formation of alkyl phenols, are not observed in this case. It is particularly surprising that, according to the process of the invention, it is possible, for the first time, to produce pure *p*-isopropenyl phenol in good yields and in crystalline form because it was hitherto supposed that this compound is so unstable that it polymerises or resinifies at the moment of its formation.

Thus, for example, according to the process of the present invention the following α -alkenyl, α -cycloalkenyl and α -aralkenyl phenols can be obtained:—(*p*-hydroxyphenyl)ethane from 1,1-(4,4¹-dihydroxydiphenyl)ethane, 1-(*p*-hydroxyphenyl)prop-1-ene from 1,1(4,4¹-dihydroxydiphenyl)-propane, *p*-isopropenyl-phenol from 2,2-(4,4¹-dihydroxy-diphenyl)-propane, 1-(*p*-hydroxy-phenyl)-but-1-ene from 1,1-(4,4¹-dihydroxy-diphenyl)-butane, 2-(*p*-hydroxyphenyl)-but-2-ene from 2,2-(4,4¹-dihydroxydiphenyl)-butane, 2-(*p*-hydroxyphenyl)-3-methyl-but-2-ene from 2,2(4,4¹-dihydroxy-diphenyl)-3-methyl-butane, 1-(*p*-hydroxy-phenyl)-isobut-1-ene from 1,1(4,4¹-dihydroxy-diphenyl)-2-methyl-propane, 2-(*p*-hydroxyphenyl)-pent-2-ene from 2,2-(4,4¹-dihydroxydiphenyl)-pentane, 3-(*p*-hydroxyphenyl)-pent-3-ene from 3,3-(4,4¹-dihydroxydiphenyl)-pentane, 2-(*p*-hydroxyphenyl)-4-methyl-pent-2-ene from 2,2(4,4¹-dihydroxy-diphenyl)-4-methyl-pentane, 4-(*p*-hydroxyphenyl)-hept-4-ene from 4,4(4,4¹-dihydroxy-diphenyl)-heptane, *o*-isopropenyl-phenol from 2,2-(2,2¹-dihydroxy-diphenyl)-propane, 1-(4-hydroxyphenyl)-cyclohex-1-ene from 1,1-(4,4¹-dihydroxy-diphenyl)-cyclohexane, 1,1(*p*-hydroxydiphenyl)-ethene from 1,1,1-(4,4¹-dihydroxy-triphenyl)ethane, *p*-isopropenyl-*o*-cresol from 2,2-(4,4¹-dihydroxy-3,3¹-dimethyl-diphenyl)-propane and *o*-isopropenyl-*p*-tert-butyl phenol from 2,2-(2,2¹-dihydroxy-4,4-di-tert-butyl-diphenyl)-propane.

Even the non-crystalline residues obtained in the production of dihydroxy-diphenyl alkanes by the condensation of aldehydes or ketones with phenols, are suitable starting materials for the process.

Suitable basic catalysts are, for example, alkali metals or alkaline earth metals or the oxides, hydroxides, alcoholates, phenolates, alkyl-carboxylates, carbonates, amides and hydrides thereof, as well as aluminium, zinc, cadmium and lead or the above-mentioned compounds of these metals.

For carrying out the splitting, it is preferably to add between 0.01% and 10% of the catalyst, referred to the amount of dihydroxy-diphenyl alkane used. in the case of using alkali metal compounds, the reaction temperatures are particularly low, being be-

tween about 150 and 250°C. When using other catalysts, temperatures of 220—300°C. are necessary. According to these reaction temperatures, the splitting can be carried out either in the presence of very effective catalysts with the use of reduced pressure or in the presence of less effective catalysts under normal pressure, the reaction components being heated together in a simple distillation apparatus. In the case of carrying out the reaction in a continuous manner, it can be expedient to pass the dihydroxy-diphenyl-alkane in the form of vapour at temperatures of 300—600°C. over a solid catalyst and subsequently to quench the split products to temperatures below the melting point.

The separation of the split products, alkenyl phenol and phenol, takes place either by recrystallisation from suitable solvents or by a second distillation, if desired again in the presence of alkaline-acting materials.

The alkenyl phenols obtained according to the process are, for example, intermediate products and adjuvants for the production of plastics, pesticides, stabilizers and dye-stuffs.

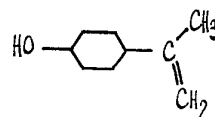
The following Examples are given for the purpose of illustrating the present invention:—

EXAMPLE 1.

300 g. 2,2-(4,4¹-dihydroxy-diphenyl)-propane are heated in a distillation apparatus with stirring and at a pressure of 18 mm Hg. after the addition of 3 g. sodium hydroxide, the split products being collected in an ice cooled receiver. As soon as the internal temperature has reached 180°C., the distillation of the split products commences. The distillation velocity is so controlled that the distillation temperature does not exceed 150°C. Toward the end of the distillation, the distillation vessel reaches a temperature of 260°C. 270 g. of a distillate are obtained which, for the greater part, solidifies. A sample recrystallised from cyclohexane gives yellowish leaflets of *p*-isopropenyl phenol with a melting point of 85°C.

Analysis

$C_9H_{10}O$ molecular weight 134.17



Calculated: C=80.56%; H=7.51%
Found: C=80.35%; H=7.63%

The distillate, which consists of phenol and *p*-isopropenyl-phenol is subjected to a second distillation with the addition of 0.5 g. sodium hydroxide. At 85—110°C./18 mm Hg. 120 g. Phenol distil over and at 110—130°C./18

mm Hg. 145 g. *p* isopropenyl phenol distil over which solidify to a yellowish crystalline mass.

The total yield amounts to 82% of theory.

5

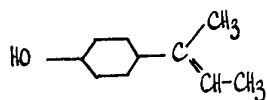
EXAMPLE 2.

After the addition of 0.5 g. potassium hydroxide, 100 g. 2,2 - (4,4¹ - dihydroxydiphenyl) - butane are distilled at a pressure of 20 mm Hg. in such a manner that the distillation temperature does not exceed 150°C. The amount of crystalline solid distillate, consisting of phenol and 2-(*p*-hydroxyphenyl) - but - 2 - ene, amounts to 94 g. The 2 - (*p* - hydroxyphenyl) - but - 2 - ene can be obtained in pure form by recrystallisation from cyclohexane or by re-distillation.

53 g., corresponding to yield of 86% theory, of 2 - (*p* - hydroxy phenyl) - but - 2 - ene with a melting point of 83—84°C. are obtained.

20

Analysis

C₁₀H₁₂O molecular weight 148.2

25

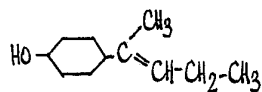
Calculated: C = 81.04%; H = 8.16%
Found: C = 80.78%; H = 8.17%

EXAMPLE 3.

After the addition of 2 g. of the sodium salt of 2,2 - (4,4¹ - dihydroxy - diphenyl) - pentane, 100 g. 2,2 - (4,4¹ - dihydroxydiphenyl) - pentane are heated at a pressure of 20 mm Hg. in such a manner that the distillation temperature does not exceed 150°C. The liquid distillate (98 g.) consisting of phenol and 2 - (*p* - hydroxyphenyl) - pent-2-ene is redistilled. 56 g., corresponding to 89% of theory, of 2 - (*p* - hydroxyphenyl) - pent - 2 - ene are obtained as a liquid. The boiling point is 85—87°C./0.1 mm Hg.

40

Analysis

C₁₁H₁₄O molecular weight 162.2

45

EXAMPLE 4.

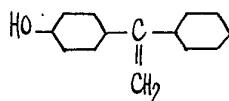
After the addition of 1 g sodium methylate, 100 g. 1,1,1 - (4,4¹ - dihydroxy - triphenyl) - ethane are heated at a pressure of 20 mm Hg. in such a manner that the distillation temperature does not exceed 180°C. From the reaction product (95 g.) there is obtained by redistillation at 149—151°C./0.1 mm Hg.

50

the gradually solidifying 1,1 - (*p* - hydroxydiphenyl)-ethene in a yield of 69 g. corresponding to 97% of theory.

55

Analysis

C₁₄H₁₂O molecular weight 196.2

Calculated: C = 85.68%; H = 6.16%

Found: C = 85.45%; H = 6.31%

60

After recrystallisation from cyclohexane pure 1,1 (*p* - hydroxy - diphenyl) - ethene is obtained with a melting point of 59—60°C.

EXAMPLE 5.

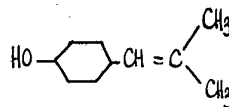
After the addition of 0.5 g. sodium hydroxide, 100 g. 1,1 - (4,4¹ - dihydroxydiphenyl) - 2 - methyl - propane are heated at a pressure of 20 mm Hg. in such a manner that the distillation temperature does not exceed 150°C. The reaction product (84 g.) is redistilled. The boiling point of the 1-(*p* - hydroxy - phenyl) - isobut - 1 - ene is 80—92°C./0.1 mm Hg. and the melting point, after recrystallisation from light petroleum ether, is 57—58°C. The yield amounts to 90% of theory.

65

70

75

Analysis

C₁₀H₁₂O molecular weight 148.2

Calculated: C = 81.04%; H = 8.16%

Found: C = 80.69%; H = 8.12%

80

EXAMPLE 6.

After the addition of 1 g. lead oxide, 100 g. 2,2 - (4,4¹ - dihydroxy - diphenyl) - propane are heated at normal pressure in such a manner that the distillation temperature of the split products does not exceed 220°C. The reaction product (90 g.) is redistilled. At 70—85°C./0.25 mm Hg. 40 g. phenol distil over and at 90—110°C./0.25 mm Hg 41 g. *p*-isopropenyl phenol distil over.

85

90

EXAMPLE 7.

Molten 2,2 - (4,4¹ - dihydroxy - diphenyl) - propane are placed on a film evaporator by means of a heated dropping funnel and evaporated at a pressure of 18 mm Hg. and an internal wall temperature of 260°C. The vapour is passed, without cooling, through a 25 mm. thick and 400 mm. long horizontal tube which is half filled with a soda-lime catalyst. The tube is contained in a muffle furnace heated to 500°C. The reaction products are collected in a receiver cooled with

95

100

ice water. The distillate partially solidifies in the receiver to fine yellowish crystals. It consists of phenol and *p*-isopropenyl phenol. The components are expediently separated by a second distillation in the manner described in Example 1.

WHAT WE CLAIM IS:—

1. Process for the production of α -alkenyl-, α -cycloalkenyl- and α -aralkenyl-phenols by heating dihydroxy-diphenyl alkanes, -cycloalkanes or -aralkanes, in which both hydroxyphenyl groups are attached to the same carbon atom of the alkane, cycloalkane or aralkane residue, said residue having at least one —CH< group attached directly to said carbon atom, in the presence of an alkaline-acting catalyst, characterised in that the process is carried out (a) by heating the dihydroxy-diphenyl compound with an alkali metal compound at a temperature between 150 and 250°C. under reduced pressure, or (b) by heating the dihydroxy-diphenyl compound with an alkaline-acting catalyst other than an alkali metal compound at a temperature between 220 and 300°C. under normal pressure, or (c) by passing the vapour of the dihydroxy-diphenyl compound over a solid alkaline-acting catalyst at a temperature between 300 and 600°C.
2. Process according to claim 1, wherein the products are rapidly cooled to a temperature below their melting point.

3. Process according to claim 1 or 2, wherein the products are purified by redistillation.

4. Process according to claim 3, wherein the redistillation is carried out in the presence of an alkaline-acting material.

5. Process according to any of the preceding claims, wherein the catalyst is an alkali metal or alkaline earth metal or an oxide, hydroxide, alcoholate, phenolate, alkyl-carboxylate, carbonate, amide or hydride thereof or aluminium, zinc, cadmium or lead or the above-mentioned compounds of these metals.

6. Process according to any of the preceding claims, wherein the catalyst is used in an amount of 0.01 to 10%, referred to the amount of dihydroxy-diaryl-alkane used.

7. Process for the production of α -alkenyl, α -cycloalkenyl and α -aralkenyl phenols according to claim 1, substantially as hereinbefore described and with reference to any of the specific Examples.

8. α -alkenyl, α -cycloalkenyl and α -aralkenyl phenols, whenever prepared by the process according to any of claims 1—7.

9. 2-(*p*-hydroxyphenyl)-pent-2-ene.

For the Applicants,
 CARPMAELS & RANSFORD,
 Chartered Patent Agents,
 24, Southampton Buildings, Chancery Lane,
 London, W.C.2.