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(54) **PROCESS FOR THE PRODUCTION OF ALKENYL AND
CYCLOALKENYL PHENOLS**

(57) **Abstract:**

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The present invention is concerned with a process for the production of alkenyl and cycloalkenyl phenols.

5 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
10 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-(4,4'-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
15 hitherto not been producible, only isopropyl phenol being formed together with large amounts of useless resinous residues.

We have now found a process for the production of alkenyl and cycloalkenyl phenols by the thermal splitting of dihydroxy-diaryl alkanes and cycloalkanes which is characterized by carrying out the splitting by heating with the addition of alkaline-
20 acting materials and the reaction product cooled, if desired, quickly, to temperatures below its melting point.

According to this process, it is possible to decompose dihydroxy-^{diphenyl}~~diphenyl~~ alkanes and cycloalkanes by a particularly
25 smooth reaction into corresponding alkenyl and cycloalkenyl phenols and phenol without 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 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 alkenyl and cycloalkenyl phenols can be obtained: 1-(p-hydroxy-phenyl)-ethene from 1,1-(4,4'-dihydroxy-diphenyl)-ethane, 1-(p-hydroxy-phenyl)-prop-1-ene from 1,1-(4,4'-dihydroxy-diphenyl)-propane, p-isopropenyl-phenol from 2,2-(4,4'-dihydroxy-diphenyl)-propane, 1-(p-hydroxy-phenyl)-but-1-ene from 1,1-(4,4'-dihydroxy-diphenyl)-butane, 2-(p-hydroxy-phenyl)-but-2-ene from 2,2-(4,4'-dihydroxy-diphenyl)-butane, 2-(p-hydroxy-phenyl)-3-methyl-but-2-ene from 2,2-(4,4'-dihydroxy-diphenyl)-3-methyl-butane, 1-(p-hydroxy-phenyl)-isobut-1-ene from 1,1-(4,4'-dihydroxy-diphenyl)-2-methyl-propane, 2-(p-hydroxy-phenyl)-pent-2-ene from 2,2-(4,4'-dihydroxy-diphenyl)-pentane, 3-(p-hydroxy-phenyl)-pent-3-ene from 3,3-(4,4'-dihydroxy-diphenyl)-pentane, 2-(p-hydroxy-phenyl)-4-methyl-pent-2-ene from 2,2-(4,4'-dihydroxy-diphenyl)-4-methyl-pentane, 4-(p-hydroxy-phenyl)-hept-4-ene from 4,4-(4,4'-dihydroxy-diphenyl)-heptane, o-isopropenyl-phenol from 2,2-(2,2'-dihydroxy-diphenyl)-propane, 1-(4-hydroxy-phenyl)-cyclohex-1-ene from 1,1-(4,4'-dihydroxy-diphenyl)-cyclohexane, 1,1-(p-hydroxy-diphenyl)-ethene from 1,1,1-(4,4'-dihydroxy-triphenyl)-ethane, p-isopropenyl-o-cresol from 2,2-(4,4'-dihydroxy-3,3'-dimethyl-diphenyl)-propane and o-iso-

propenyl-p-tert.butyl-phenol from 2,2-(2,2'-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 metal or alkaline earth metal oxides, hydroxides, alcoholates, phenolates, alkyl-carboxylates, carbonates, amides and hydrides, 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 per cent and 10 per cent 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 between 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 dyestuffs.

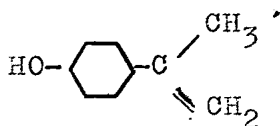
The following Examples are given for the purpose of illustrating the present invention:

Example 1

300 grams 2,2-(4,4'-dihydroxy-diphenyl)-propane are heated in a distillation apparatus with stirring and at a pressure of 18 mms mercury gauge after the addition of 3 grams 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 transition temperature does not exceed 150°C. Toward the end of the distillation, the distillation vessel reaches a temperature of 260°C. 270 grams of a distillate are obtained which, for the greater part, solidifies. A sample recrystallized 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



25 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 grams sodium hydroxide. At 85-110°C./18 mms mercury gauge 120 grams phenol distil over and at 110-130°C./18 mms mercury gauge 145 grams *p*-isopropenyl phenol distil over which solidify to a yellowish crystalline mass.

The total yield amounts to 82 per cent of theory.

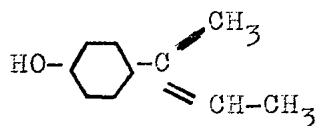
Example 2

After the addition of 0.5 grams potassium hydroxide, 100 grams 2,2-(4,4'-dihydroxy-diphenyl)-butane are distilled at a pressure of 20 mms mercury gauge in such a manner that the transition temperature does not exceed 150°C. The amount of crystalline solid distillate, consisting of phenol and 2-(*p*-hydroxy-phenyl)-but-2-ene, amounts to 94 grams. The 2-(*p*-hydroxy-phenyl)-but-2-ene can be obtained in pure form by re-crystallisation from cyclohexane or by re-distillation.

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

20 Analysis:

$C_{10}H_{12}O$ molecular weight 148.2



Calculated: C = 81.04 %; H = 8.16 %

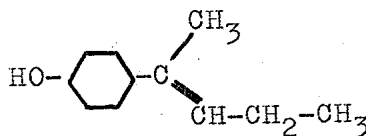
25 Found: C = 80.78% ; H = 8.17 %

Example 3

After the addition of 2 grams of the sodium salt of 2,2-(4,4'-dihydroxy-diphenyl)-pentane, 100 grams 2,2-(4,4'-dihydroxy-diphenyl)-pentane are heated at a pressure of 20 mms mercury gauge in such a manner that the transition temperature does not exceed 150°C. The liquid distillate (98 grams) consisting of phenol and 2-(p-hydroxy-phenyl)-pent-2-ene is redistilled. 56 grams corresponding to 89 per cent of theory, of 2-(p-hydroxy-phenyl)-pent-2-ene are obtained as a liquid. The boiling point is 85-87°C./0.1 mms mercury gauge.

Analysis

$C_{11}H_{14}O$ molecular weight 162.2



Calculated: C = 81.44 % ; H = 8.70 %

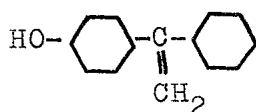
Found: C = 81.72 % ; H = 8.79 %

Example 4

After the addition of 1 gram sodium methylate, 100 grams 1,1,1-(4,4'-dihydroxy-triphenyl)-ethane are heated at a pressure of 20 mms mercury gauge in such a manner that the distillation temperature does not ~~exceed~~ ^{exceed} 180°C. From the reaction product (95 grams) there is obtained by redistillation at 149-151°C./0.1 mms mercury gauge, the gradually solidifying 1,1-(p-hydroxy-diphenyl)-ethene in a yield of 69 grams corresponding to 97 per cent of theory.

Analysis:

$C_{14}H_{12}O$ molecular weight 196.2



Calculated: C = 85.68 % ; H = 6.16 %

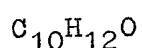
Found: C = 85.45 % ; H = 6.31 %

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

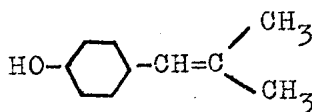
Example 5

10 After the addition of 0.5 grams sodium hydroxide, 100 grams 1,1-(4,4'-dihydroxy-diphenyl)-2-methyl-propane are heated at a pressure of 20 mms mercury gauge in such a manner that the transition temperature does not exceed 150°C. The reaction product (84 grams) is redistilled. The boiling point of the 1-(p-hydroxy-phenyl)-isobut-1-ene is 80-92°C./0.1 mms mercury gauge and the melting point, after recrystallisation from light
15 petroleum ether, is 57-58°C. The yield amounts to 90 per cent of theory.

Analysis:



molecular weight 148.2



20 Calculated: C = 81.04 % ; H = 8.16 %

Found: C = 80.69 % ; H = 8.12 %

Example 6

25 After the addition of 1 gram lead oxide, 100 grams 2,2-(4,4'-dihydroxy-diphenyl)-propane are heated at normal pressure in such a manner that the transition temperature of

the split products does not exceed 220°C. The reaction product (90 grams) is redistilled. At 70-85°C./0.25 mms mercury gauge 40 grams phenol distil over and at 90-110°C./0.25 mms mercury gauge 41 grams p-isopropenyl phenol distil over.

5 Example 7

Molten 2,2-(4,4'-dihydroxy-diphenyl)-propane are placed on a film evaporator by means of a heated dropping funnel and evaporated at a pressure of 18 mms mercury gauge and an internal wall temperature of 260°C. The vapour is passed, without
10 cooling, through a 25 mms thick and 400 mms 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 ice water. The
15 distillate partially solidifies in the receiver to fine yellowish crystals. It consists of phenol and p-isopropenyl phenol. The components are expeditiously separated by a second distillation in the manner described in Example 1.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Process for the production of alkenyl and cycloalkenyl phenols by thermal splitting of dihydroxy-diphenyl alkanes in the presence of catalysts, characterized in that the splitting is carried out in the presence of alkaline-acting materials.
2. Process according to claim 1, wherein the split products are rapidly cooled to temperature below their melting point.
3. Process according to claim 1, wherein the split 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 claim 1, wherein the catalyst is an alkali metal or alkaline earth metal oxide, hydroxide, alcoholate, phenolate, alkyl-carboxylate, carbonate, amide or hydride, aluminium, zinc, cadmium or lead or the above-mentioned compounds of these metals.
6. Process according to claim 1, wherein the catalyst is used in an amount of 0.01 to 10 per cent based on the amount of dihydroxy-diaryl-alkane used.



SUBSTITUTE

REPLACEMENT

SECTION is not Present

Cette Section est Absente