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(54) **PROCESS FOR THE PRODUCTION OF DI- AND
POLYHYDROXY-DIARYL-ALKANES**

(57) **Abstract:**

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The present invention is concerned with a process for the production of di- and polyhydroxy-diarylalkanes.

It is known that dihydroxy-diaryl-alkanes can be produced by the condensation of aldehydes or ketones with monobasic phenols in the presence of alkaline and, preferably, of acidic catalysts. Considerable technical difficulties are bound up with the use of acidic catalysts since the acids used either as aqueous solutions or the aqueous acidic solutions formed from anhydrous acids by the water produced during the condensation attack the materials usually employed in the technology. This danger is considerable because, due to the reduced catalytic effect by dilution with reaction water, it is necessary to introduce considerable quantities of acids.

According to the present invention, there is provided a new process for the production of di- and polyhydroxy-diaryl-alkanes, wherein a phenol is added to a p-vinylphenol in the presence of a catalytic amount of an anhydrous acidic or alkaline compound. Some of the products of the new process are also new.

This new process shows considerable advantages over the known processes. Thus, an important advantage consists in that the new process is based not on a condensation reaction with the formation of water but on an addition reaction. Therefore, the reaction can be carried out under anhydrous conditions and with the use of only catalytic amounts of anhydrous acids or of alkaline catalysts. Even ionic exchangers with strongly acidic groups, such as sulphonated polystyrenes, are able to catalyse the addition of the components. Under working conditions of this type there is little danger of corrosion damage.



In comparison with the known processes, the new process is further characterized by a broader field of application. Thus, it is possible, for the first time, to produce in one working step and in a definite manner assymmetrical dihydroxy-
5 diaryl-alkanes with different hydroxyaryl residues by selecting appropriate components as starting materials for the addition process. Polybasic phenols can also be successfully added to the p-vinylphenols, whereby tri- and higher functional phenols are easily obtainable.

10 The following p-vinylphenols are examples of starting materials which may be used for the new process: p-vinylphenol, p-(2-methyl-vinyl)-phenol, p-(2-ethylvinyl)-phenol, p-(2-ethyl-
vinyl)-phenol, p-(2,2-dimethylvinyl)-phenol, p-(2-propylvinyl)-phenol, p-(2-isopropyl-vinyl)-phenol, p-(2-butylvinyl)-phenol,
15 p-(2-methyl-2-propylvinyl)-phenol, p-(2-methyl-2-isopropyl-vinyl)-phenol, p-(2,2-diethylvinyl)-phenol, p-(2-ethyl-2-isopropylvinyl)-phenol, p-(1-methylvinyl)-phenol (p-isopropenylphenol), p-(1-
methyl-2-methylvinyl)-phenol, (p-isobutenylphenol), p-(1-methyl-2-ethylvinyl)-phenol, p-(1-methyl-2-propylvinyl)-phenol, p-(1-
20 methyl-2-isopropylvinyl)-phenol, p-(1-methyl-2-methyl-2-ethylvinyl)-phenol, p-(1-ethylvinyl)-phenol, p-(1-ethyl-2-methylvinyl)-phenol, p-(1-ethyl-2-ethylvinyl)-phenol, p-(1-ethyl-2-propyl-
vinyl)-phenol, p-(1-ethyl-2-isopropylvinyl)-phenol, p-(1-propyl-
vinyl)-phenol, p-(1-propyl-2-methylvinyl)-phenol, p-(1-propyl-
25 2-ethylvinyl)-phenol, p-(1-isopropylvinyl)-phenol, p-(1,2-tetra-
methylenevinyl)-phenol, p-(1-phenylvinyl)-phenol and p-(1-methyl-
vinyl)-o-cresol.

The p-vinylphenols, particularly the especially valuable p-isopropenylphenol, are, for example, obtainable by catalytic fission of the corresponding dihydroxy-diaryl-alkanes, particularly with the use of alkaline materials as fission catalysts
5 by the process according to the Canadian Application 803,902 of Krimm and Schnell, filed July 25, 1960.

Phenols capable of addition are, for example, phenol, o-m- and p-cresol, o-, m- and p-ethylphenol, o-, m- and p-propylphenol, o-, m- and p-isopropylphenol, o-, m- and p-butylphenol,
10 o-, m- and p-isobutylphenol, o-, m- and p-tert.-butylphenol, o-, m- and p-octylphenol, o-, m- and p-dodecylphenol, 2,4-dimethylphenol, 3,4-dimethylphenol, 3,5-dimethylphenol, 2,5-dimethylphenol, 2,6-diethylphenol, o-,m- and p-cyclohexylphenol, o-, m- and p-chlorophenol, o-, m- and p-bromophenol, 2,6-dichlorophenol,
15 α -naphthol, β -naphthol, hydroquinone, resorcinol, pyrocatechol, hydroquinone-monomethyl ether, guaiacol, phloroglucinol and pyrogallol.

As acidic catalysts there can be used, for example, hydrogen fluoride, hydrogen bromide and hydrogen iodide, sulphur trioxide, benzene sulphonic acid, p-toluene sulphonic acid and the
20 so-called Lewis acids, such as magnesium chloride, zinc chloride, boron trifluoride, boron tri-fluoride etherate, boron tri-fluoride acetic acid, aluminium chloride, ferric chloride and tin tetrachloride. Furthermore, cationic exchanger resins of the
25 sulphonated polystyrene type may also be used as catalysts.

Examples of alkaline catalysts which may be used are alkali and alkaline earth metals and the oxides, hydroxides, alcoholates, phenolates, alkyl carboxylates, carbonates, amides and hydrides thereof.

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The following general instructions can be given for the carrying out of the reaction: the phenols are preferably used in excess, i.e. about 2-5 mol to 1 mol p-vinylphenol. Lower substituted phenols react more easily than higher substituted phenols and monobasic phenols easier than polybasic phenols. p-positioned hydrogen atoms are more reactive than o-, and m-positioned hydrogen atoms.

The amount of the catalyst depends upon the reactivity of the components, particularly of the phenols, and can easily be determined by tests. It amounts, in the case of acidic catalysts to about 0.001 to about 20 per cent and, in the case of alkaline catalysts, to about 0.01 to about 20 per cent of the total weight of the components.

In the case of using acidic catalysts, the reaction temperature should, in general, not substantially exceed room temperature. The most favourable temperature range lies between about 0° and about 40°C. The addition admittedly still takes place at temperatures of up to 100°C., but then many side reactions and resin formation are observed.

In the case of the use of alkaline catalysts, the reaction temperatures expediently lie between about 50 - 200°C., preferably between about 100° and 160°C.

If desired, inert solvents, such as aromatic hydrocarbons, chlorinated hydrocarbons, ethers or alcohols, can also be used.

In general, the working up takes place by neutralization, distilling off of the solvent and of the excess phenol and re-crystallization or distillation of the reaction product.

The products of the new process are valuable intermediates for the production of plasticizers, pharmaceuticals and pesticidal agents.

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

Example 1

134 grams (1 mol) *p*-isopropenylphenol and 188 grams
5 (2 mol) phenol are dissolved in 500 cc. toluene, the solution cooled to 0°C. and mixed dropwise with 10 cc. of a 10 per cent solution of *p*-toluene sulphonic acid in methanol. The solution immediately becomes coloured red-brown and warms up. Within
10 two hours, crystals have separated out together with decolourisation. After 24 hours, the crystals are brought into solution by the addition of ether. The solution is shaken up several times with water until a pH of 5-6 is reached. After distilling off the solvent and unreacted phenol, 220 grams of crystalline residue remain behind which consists of 2,2-(4,4'-dihydroxy-
15 diphenyl)-propane. After recrystallization from toluene, the yield amounts to 203 grams (89 per cent of the theory).

Example 2

60 grams sulphonated polystyrene are introduced portions-
wise into a solution of 134 grams (1 mol) *p*-isopropenylphenol
20 and 188 grams (2 mol) phenol in 500 cc. toluene. The temperature of the reaction mixture is maintained at 30°C. by stirring and cooling. After 3 days, the separated crystals are brought into solution by briefly heating to 60°C. The catalyst is filtered off with suction and washed with toluene. The
25 toluene solution is then distilled. After evaporation of the solvent and phenol, 195 grams of a crystalline residue remain behind . After re-crystallization from toluene the melting point amounts to 155-156°C. Yield: 81 per cent of the theory.

Example 3

10 drops of ether saturated with hydrogen chloride are added at 5°C. to a solution of 13.4 grams (0.1 mol) p-isopropenyl phenol and 21.6 grams (0.2 mol) o-cresol in 50 cc. toluene, 5 whereupon the solution becomes deep red-brown coloured and warms up to 30°C. The reaction mixture is held overnight at room temperature and adjusted to a pH of 5-6 with a few drops of sodium carbonate solution. After distilling off the solvent and the excess o-cresol, 22 grams of a crystalline residue of 10 2,2-(4,4'-dihydroxy-3-methyl-diphenyl)-propane are obtained. M.p. (from toluene) 118-119°C. Yield: 18.6 grams (77 per cent of the theory).

Example 4

1 gram p-toluene-sulphonic acid dissolved in 2 cc. methanol 15 is added at 10°C. to a solution of 67 grams (0.5 mol) p-isopropenylphenol and 162 grams (1.5 mol) m-cresol in 150 cc. toluene. The reaction mixture is cooled so that the temperature of the red-brown solution does not exceed 30°C. After 24 hours, the acid is shaken out with water and the solution dried over an- 20 hydrous sodium sulphate. After distilling off the solvent and excess m-cresol, the 2,2-(4,4'-dihydroxy-2-methyl-diphenyl)-propane distills over at 165°C./0.03 mm.Hg. as a non-crystallizing, viscous , colourless oil. Yield: 91 grams (75 per cent of the theory).

25 Example 5

1 gram p-toluene-sulphonic acid dissolved in 2 cc. methanol is added at 20°C. to a solution of 67 grams (0.5 mol) p-isopropenylphenol and 162 grams (1.5 mol) p-cresol in 300 cc. toluene.

The temperature of the red-brown solution is maintained below 30°C. by cooling. After 3 days, the acid is shaken out with water and the solution dried over anhydrous sodium sulphate. By distillation, there are obtained 2,2-(2,4'-dihydroxy-5-methyl-diphenyl)-propane of b.p. 175°C./0.1 mm.Hg. Yield: 63 grams (52 per cent of the theory). M.p.(from cyclohexane) 126-127°C.

Example 6

1.5 grams p-toluene-sulphonic acid dissolved in 5 cc. methanol are added at 20°C. to a solution of 67 grams (0.5 mol) p-isopropenylphenol and 193 grams (1.5 mol) o-chlorophenol in 300 cc.toluene. The temperature increases to 30°C. After 10 days, the acid is shaken out with water and the solution worked up by distillation. The 2,2-(4,4'-dihydroxy-3-chlorodiphenyl)-propane obtained boils at 165°C./0.05 mm.Hg. Yield: 45 grams (34 per cent of the theory).

Example 7

A solution of 1 gram p-toluene-sulphonic acid in 10 cc. methanol is added at 20°C. to a solution of 26.8 grams (0.2 mol) p-isopropenylphenol and 105.6 grams (0.6 mol) o-cyclohexylphenol and 50 cc. methanol. The temperature increases to 40°C. and is maintained for two hours. After 5 days, the reaction mixture is dissolved in methylene chloride and shaken up with water until a pH of 5-6 is obtained.

After distilling off the solvent and unreacted o-cyclohexylphenol, 56 grams 2,2-(4,4'-dihydroxy-3-cyclohexyldiphenyl)-propane distil over ^{at} 195-200°C./0.15 mm Hg. Yield: 90 per cent of the theory. M.p. (from carbon tetrachloride/toluene) 145-146°C.

Example 8

A solution of 1 gram p-toluene-sulphonic acid in 10 cc. methanol is added at 20°C. to a solution of 26.8 grams (0.2 mol) p-isopropenylphenol and 90 grams (0.6 mol) 2,6-diethylphenol in 50 cc. methanol. The temperature rises to 30°C. After two days, the reaction mixture is dissolved in methylene chloride and washed with water until a pH of 5-6 is obtained. After distilling off the excess diethylphenol, 2,2-(4,4'-dihydroxy-3,5-diethyl-diphenyl)-propane distills over at 165-167°C./0.5 mm.Hg. Yield: 45 grams (79 per cent of the theory). M.p. (from cyclohexane) 105-106°C.

Example 9

1 cc. ether saturated with hydrogen chloride is added to a mixture of 26.8 grams (0.2 mol) p-isopropenylphenol, 44 grams (0.4 mol) resorcinol and 100 cc. toluene. The temperature of the red-brown mixture increases to 40°C. After the addition of 50 cc. methanol, the solution is left to stand 3 days. The solvents are then distilled off under water pump vacuum. The residue is shaken up with twice the amount of water and the reaction product, which crystallises out, is filtered off with suction. The yield of 2,2-(2,4,4'-trihydroxy-diphenyl)-propane is 40 grams (82 per cent of the theory). M.p. (from toluene/ethanol) 181-182°C.

Example 10

14.8 grams (0.1 mol) p-isobutenylphenol are added portionswise to a solution of 1 gram p-toluene sulphonic acid in 32.5 grams (0.3 mol) o-cresol. in such a manner that the temperature of the red-brown mixture does not exceed 30°C. After 3 days, the reaction mixture is dissolved in methylene chloride

and shaken up with water until a pH of 5-6 is obtained. The solution is then worked up by distillation. 22 grams 2,2-(4,4'-dihydroxy-3-methyl-diphenyl)-butane of b.p. 168°C./0.5 mm.Hg. are obtained. Yield: 85 per cent of the theory.

5 Example 11

19.6 grams (0.1 mol) *p*-(1-phenylvinyl)-phenol are added portionwise to a solution of 1 gram *p*-toluene sulphonic acid in 32.5 grams (0.3 mol) *o*-cresol in such a manner that the temperature of 30°C. is not exceeded. After two days, the reaction mixture is diluted with methylene chloride and shaken up with water until a pH of 5-6 is obtained. After distilling off the solvent and unreacted *p*-(1-phenylvinyl)-phenol, the residue is treated with toluene, whereupon it crystallizes. The yield of 1,1,1-(4,4'-dihydroxy-3-methyl-triphenyl)-ethane is 24 grams (79 per cent of the theory). M.p. 166-167°C.

15 Example 12

A mixture of 134 grams (1 mol) *p*-isopropenylphenol, 257 grams (2 mol) *o*-chlorophenyl and 15 grams (0.1 mol) sodium 2-chlorophenolate is heated for 1 hour at 150°C. The reaction product is then dissolved in methylene chloride and shaken up with water until a pH of 5-6 is obtained. After distilling off the solvent and excess *o*-chlorophenol, 212.5 grams 2,2-(4,4'-dihydroxy-3-chlorodiphenyl)-propane distill over at 165°C./0.05 mm.Hg. M.p.(from carbon tetrachloride) 101-102°C.

25 Yield: 81 per cent of the theory.

Example 13

A mixture of 26.8 grams (0.2 mol) *p*-isopropenylphenol, 128.5 grams (1 mol) *o*-chlorophenol and 6.16 grams sodium hydroxide (0.004 mol) are heated for 4 hours at 150°C. The

reaction product is worked up as in Example 1.

Yield: 45 grams (86 per cent of the theory).

Example 14

5 A mixture of 26.8 grams (0.2 mol) p-isopropenylphenol,
108 grams (1 mol) p-cresol and 2.76 grams (0.02 mol) potassium
carbonate is heated for 8 1/2 hours at 150°C. The reaction
mixture is then dissolved in methylene chloride, the solution
shaken up with water until a pH of 5-6 is obtained and the sol-
vent and excess p-cresol distilled off. The residue, which con-
10 sists of 2,2-(2,4'-dihydroxy-5-methyl-diphenyl)-propane, is tri-
tuated with carbon tetrachloride. Yield: 43 grams (89 per
cent of the theory). M.p. from cyclohexane 127-128°C.

Example 15

15 A mixture of 26.8 grams (0.2 mol) p-isopropenylphenol,
131 grams (0.8 mol) 2,6-dichlorophenol and 1.12 grams (0.02 mol)
potassium hydroxide is heated for 7 hours at 150°C. The react-
ion mixture is then dissolved in methylene chloride and worked
up as described in Example 3. Yield: 50 grams (84 percent of
the theory). M.p. of the 2,2-(4,4'-3,5-dichlorodiphenyl)-pro-
20 pane (from cyclohexane) 100-101°C.

Example 16

25 A mixture of 26.8 grams (0.2 mol) p-isopropenylphenol,
176 grams (1 mol) o-cyclohexylphenol and 0.46 grams (0.02 mol)
sodium is heated for 4 hours at 150°C. The reaction mixture is
taken up with methylene chloride, shaken up with dilute acetic
acid and water until a pH of 5-6 is reached and the solvent and
excess o-cyclohexylphenol distilled off. The 2,2-(4,4'-dihy-
droxy-3-cyclohexyl-diphenyl)-propane distills at 198-200°C./0.1
30 mm.Hg. as a viscous oil. Yield: 54 grams (87 per cent of the
theory).

Example 17

A mixture of 26.8 grams (0.2 mol) p-isopropenylphenol, 144 grams (1 mol) α -naphthol and 0.8 grams sodium hydroxide is heated for 4 hours at 150°C. The reaction mixture is worked up
5 as in Example 5. 46 grams 2,2-(4,4'-dihydroxyphenyl-naphthyl)-propane distil over at 200-204°C./0.1 mm.Hg. Yield: 83 per cent of the theory.

Example 18

A mixture of 29.6 grams (0.2 mol) p-isobutenylphenol, 108
10 grams (1 mol) o-cresol and 0.8 grams (0.02 mol) sodium hydroxide is heated for 4 hours at 150°C. The reaction mixture is worked up as in Example 5. The 2,2-(4,4'-dihydroxy-3-methyl-diphenyl)-butane obtained boils at 178-180°C./0.05 mm.Hg. Yield: 39 grams (76 per cent of the theory).

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

1. Process for the production of di- and polyhydroxy-diaryl-alkanes, wherein a phenol is added to a p-vinylphenol in the presence of a catalytic amount of an anhydrous acidic or alkaline compound.
2. Process according to claim 1, wherein 2 to 5 mol equivalents of phenol are used per mol of p-vinylphenol.
3. Process according to claim 1 wherein the reaction is carried out under anhydrous conditions.
4. Process according to claim 1, 2 or 3 wherein the catalyst is an anhydrous acid, a Lewis acid or an ion exchanger containing strong acid groups.
5. Process according to claim 1, 2 or 3 wherein the catalyst is an alkali metal or alkaline earth metal or an oxide, hydroxide, alcoholate, phenolate, amide, hydride, alkylcarboxylate or carbonate thereof.
6. Process according to claim 1, 2 or 3 wherein the acid catalyst is used in an amount of about 0.001 to about 20 per cent, based on the total weight of the components, or wherein the alkaline catalyst is used in an amount of about 0.01 to about 20 per cent, based on the total weight of the components.
7. Process according to claim 1, 2 or 3 wherein an acidic catalyst is used and the reaction is carried out at a temperature of about 0 to about 100°C.
8. Process according to claim 1, wherein an alkaline catalyst is used and the reaction is carried out at a temperature of about 50 to about 200°C.
9. Process according to claim 8, wherein the reaction is carried out at a temperature of about 100 to about 160°C.

10. Process according to claim 1, 2 or 3 wherein a polybasic phenol is used.
11. Process according to claim 1, 2 or 3 wherein the aromatic nucleus of the phenol is different from or is substituted in a different manner to the aromatic nucleus of the p-vinylphenol.
12. Process according to claim 1, 2 or 3 wherein the reaction is carried out in an inert solvent.



SUBSTITUTE

REPLACEMENT

SECTION is not Present

Cette Section est Absente