

Process for the preparation of diaryl carbonates

The present application relates to a process for the preparation of diaryl carbonates (DAC), characterized in that the hydroxyaromatic used as the educt is subsequently
 5 metered in at certain points of time, depending on the reaction procedure.

The preparation of DAC by oxidative direct carbonylation of aromatic hydroxy compounds in the presence of CO, O₂ and a noble metal catalyst is known (see e.g. DE-OS 27 38 437, US-A 4,349,485, US-A 5,231,210, EP-A 667 336, EP-A 858
 10 991, US-A 5,760,272). Palladium is preferably employed as the noble metal. A cocatalyst (e.g. salts of manganese or cobalt), a base, sources of bromide, quaternary salts, various quinones or hydroquinones and drying agents can additionally be employed. The process can be carried out in a solvent.

15 However, the known processes do not give yields which are satisfactory for an industrial reaction and produce relatively large amounts of by-products. It is therefore desirable to provide a process which is optimised in respect of yield and product quality.

20 Since these are processes which are to provide a product on a large industrial scale, small optimizations already mean a great improvement.

A process has now been found which allows a surprising increase in the selectivity of the reaction, i.e. the decrease in by-products with a simultaneously increasing
 25 product yield.

The invention thus provides a process for the preparation of an aromatic carbonate of the formula



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wherein k represents integers of 1 to 2, preferably 1, and n represents integers from 1 to 30, preferably 1 to 10, particularly preferably 1, and R represents an aromatic radical,

5 in which an aromatic hydroxy compound of the formula



wherein R and k are as defined above,

10 CO and O₂ and optionally a solvent and various catalyst components are reacted, characterized in that R-(O-H)_k is subsequently metered into the reaction mixture at least once during the reaction time.

The aromatic hydroxy compounds R-(O-H)_k which can be reacted according to the
15 invention are, for example, monohydroxy compounds (k=1, n=1), such as phenol, o-, m- or p-cresol, o-, m- or p-chlorophenol, o-, m- or p-ethylphenol, o-, m- or p-propylphenol, o-, m- or p-methoxyphenol, 2,6-dimethylphenol, 2,4-dimethylphenol, 3,4-dimethylphenol, 1-naphthol or 2-naphthol, or dihydroxy compounds (k=2, 1 ≤ n ≤ 30, preferably 1 ≤ n ≤ 10, particularly preferably 1 ≤ n ≤ 5), such as resorcinol and
20 hydroquinone, or bisphenols, such as 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A), 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane or 6,6'-dihydroxy-3,3',3'-tetramethyl-1,1'-spiro(bis)-indane, 2,4'-hydroxybiphenyl or 4,4'-hydroxybiphenyl. R-(O-H)_k can have various substituents on the aromatic nucleus
25 R. In the case of substitution of the aromatic hydroxy compound, this is generally by 1 to 3 substituents with the definition of C₁-C₁₈-alkyl, C₆-C₁₈-aryl, C₇-C₁₈-aralkyl, C₁-C₁₈-alkoxy, fluorine, chlorine or bromine, wherein the substituents, in the case of the hydrocarbons, can in their turn be mono- or polysubstituted again by the groups mentioned.

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Mixtures of various R-(O-H)_k can be used, but the use of a single compound R-(O-H)_k is preferred. Bisphenol A is preferably employed. The abovementioned

monohydroxy compounds are furthermore preferably employed, particularly preferably phenol or o-, m- and p-cresol, very particularly preferably phenol.

5 The reaction system of the oxidative direct carbonylation typically comprises several of the following catalyst components:

- a) a metal salt of group VIIIB,
- b) at least one second metal salt,
- c) a source of bromide,
- d) a base and
- 10 e) organic cocatalysts.

The platinum metal catalysts a) which are suitable for the process according to the invention comprise at least one noble metal of group VIII, preferably palladium. It can be added in various forms in the process according to the invention. Palladium
15 can be employed in metallic form, e.g. as palladium black or on a support, such as Pd/C, Pd/Al₂O₃ or Pd/SiO₂, or preferably in the form of palladium compounds of oxidation levels 0 and +2, such as, for example, palladium(II) acetylacetonate, halides, carboxylates of C₂-C₁₈-carboxylic acids, dicarboxylates, such as oxalate, nitrate, sulfate or oxides, or palladium complexes which can comprise, for example,
20 carbon monoxide, olefins, amines, nitriles, phosphorus compounds and halides. Palladium bromide and palladium acetylacetonate are particularly preferred.

The amount of platinum metal catalyst is not limited in the process according to the invention. Preferably, catalyst is added in an amount such that the concentration of
25 the metal in the reaction mixture is 1 to 3,000 ppm, and concentrations of 5 to 500 ppm are particularly preferred.

A metal of groups III A, III B, IV A, IV B, V B, I B, II B, VI B or VII B, of the rare earth metals (atomic numbers 58-71) or of the iron group of the periodic table of the
30 elements (Mendeleev), optionally also mixtures thereof, is used as the second metal salt b) acting as a cocatalyst for the process according to the invention, it being possible for the metal to be employed in various oxidation levels. (See e.g. US-A

5,142,086, US-A 5,231,210, US-A 5,284,964, EP-A 350 697, EP-A 350 700, US-A 5,336,803) Pb, Ti, Mn, Cu, Co, V, Zn, Ce and Mo are preferably employed. Without limiting the process according to the invention, lead(II), manganese(II), manganese(III), copper(I), copper(II), cobalt(II), cobalt(III), vanadium(III) and
5 vanadium(IV) may be mentioned. The metals can be employed, for example, as halides, oxides, carboxylates of C₂-C₁₈-carboxylic acids, diketonates or nitrates and as complex compounds which can comprise, for example, carbon monoxide, olefins, aromatic and aliphatic mono- or polyamines, phosphorus compounds, pyridines, bipyridines, terpyridines, quinolines, isoquinolines, cryptands, Schiff's bases and
10 halides. Mn, Cu, Mo, Pb and Ce are particularly preferably employed. Manganese compounds are very particularly preferably used in the process according to the invention, particularly preferably complexes of manganese(II) and manganese(III), very particularly preferably manganese(II) acetylacetonate or manganese(III) acetylacetonate, and manganese(II) bromide.

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The cocatalyst, which can also be formed in situ, is added in an amount such that its concentration is in the range from 0.0001 to 20 wt.% of the reaction mixture, and the concentration range of 0.001 to 5 wt.% is preferred, particularly preferably 0.005 to 2 wt.%.

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The bromide compounds c) employed in the context of the present invention are, for example, the alkali metal bromides or alkaline earth metal bromides, but preferably the bromide salts of organic cations. The organic cations can be, for example, ammonium, guanidinium, phosphonium or sulfonium salts substituted by organic
25 radicals, and optionally also mixtures thereof. Ammonium, guanidinium, phosphonium and sulfonium salts which contain C₆- to C₁₈-aryl, C₇- to C₁₈-aralkyl and/or C₁- to C₂₀-alkyl radicals as organic radicals are suitable for use in the process according to the invention. Ammonium salts which carry C₆- to C₁₈-aryl, C₇- to C₁₈-aralkyl and/or C₁- to C₂₀-alkyl radicals as organic radicals are preferably employed
30 in the process according to the invention, and tetrabutylammonium bromide, tetraphenylphosphonium bromide and tetrabutylphosphonium bromide are particularly preferred. The amount of such a quaternary salt can be, for example,

0.1 - 20 wt.%, based on the weight of the reaction mixture. This amount is preferably 0.5 - 15 wt.%, particularly preferably 1 - 5 wt.%.

5 Bases which can be employed for the process according to the invention are alkali metal hydroxides, alkali metal salts or quaternary salts of weak acids, such as alkali metal tert-butyldates, or alkali metal salts or quaternary salts of aromatic hydroxy compounds of the formula (II), in which R has the abovementioned meaning. An alkali metal salt or quaternary salt of the aromatic hydroxy compound of the formula (II) which is also to be reacted to give the organic carbonate, for example
10 tetrabutylammonium or potassium phenolate, is very particularly preferably used.

The alkali metal salts can be salts of lithium, sodium, potassium, rubidium or caesium. Lithium, sodium and potassium salts are preferably employed, particularly preferably potassium salts, and very particularly preferably potassium phenolate.

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The quaternary salts can be ammonium, phosphonium, pyridinium, sulfonium or guanidinium salts which have C₆- to C₁₈-aryl, C₇- to C₁₈-aralkyl and/or C₁- to C₂₀-alkyl radicals as organic radicals. The radicals can all be identical or different, and mixtures of several quaternary salts can optionally also be employed. The same
20 cation which is also used as the bromide for component c) is optionally preferably employed here. Tetraphenylphosphonium, tetrabutylammonium and tetrabutylphosphonium are furthermore preferred, and tetrabutylammonium is particularly preferred.

25 Alternatively, trialkylamine bases, such as tributylamine, diisopropylethylamine, DBU or DBN, can also be used.

The base d) is added in an amount independent of the stoichiometry. The ratio of platinum metal, e.g. palladium, to base is preferably chosen such that 0.1 to 5,000, preferably 1 to 1,000, particularly preferably 10 to 300 equivalents of base are
30 employed per mol of platinum metal, e.g. palladium.

Organic cocatalysts e) which can be employed are e.g. various terpyridines, phenanthrolines, quinolines and isoquinolines, semiquinones, hydroquinones and quinones, or the organic cocatalysts mentioned in EP1024132-A1 are employed.

- 5 Concrete examples are 2,2':6',2''-terpyridine, 4'-methylthio-2,2':6'2''-terpyridine, 2,2':6',2''-terpyridine N-oxide, 1,10-phenanthroline, 2,4,7,8-tetramethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, catechol, 1,2-quinone, hydroquinone, p-benzoquinone, anthraquinone, 9,10-dihydroxyanthracene and phenanthrenequinone.

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According to the invention, the hydroxyaromatic $R-(O-H)_k$ is subsequently metered in once or several times in portions. A start concentration, established within the first hour of reaction time, of about 10 to 80 wt.% of the total amount is preferably started with here, and the remaining amount is added at one or more intervals. The start concentration is particularly preferably about 30 to 70 wt.%. The addition is preferably in one to about ten portions. Preferably approximately equidistant intervals of time are chosen. An addition of the last portion at a point in time which is before about 90% of the total reaction time or average residence time is preferred, particularly preferably before about 80%.

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The amount of $R-(O-H)_k$ subsequently metered in can also be passed in continuously, for example by slowly pumping in a solution. A start concentration, established within the first hour of reaction time, of about 10 to 80 wt.% of the total amount is preferably started with, particularly preferably 30 to 70 wt.%, and the remaining amount is then metered in continuously. Various times/concentration metering profiles can be established here, e.g. a larger amount per unit time can be metered in at the start than towards the end of the reaction time or vice versa. An addition of the amount of $R-(O-H)_k$ which is linear with respect to time, in which the amount added per time interval remains approximately constant, is preferred. The addition can be started and interrupted at any desired points in time during the duration of the reaction or the average residence time.

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An ending of the metering at a point in time which is before about 90% of the total reaction time or average residence time is preferred, particularly preferably before about 80%.

- 5 The $R-(O-H)_k$ can be metered in as a solid or as a liquid or solution. $R-(O-H)_k$ can optionally be metered in over heated feed lines. However, the addition as a solution in an inert solvent is preferred.

- 10 The process according to the invention can be carried out here both in a continuous and in a discontinuous manner.

In a discontinuous procedure, $R-(O-H)_k$ is metered in at a point in time after the start of the reaction in the reactor.

- 15 In the case of a continuous procedure, $R-(O-H)_k$ can be metered in, for example, in a cascade of m reaction apparatuses, into at least one of the 2nd to m th reactors during the reaction.

- 20 The process according to the invention for carbonate formation is carried out at a reaction temperature of 30 to 200°C, preferably 50 to 150°C, particularly preferably 60 to 130°C, under a reaction pressure of 1 to 200 bar, preferably 1 to 50 bar, particularly preferably 1 to 10 bar.

- 25 Hydrocarbons, halogenated hydrocarbons and aromatic solvents, such as chlorobenzene, dichlorobenzene, fluorobenzene, benzene, toluene, anisole, cyclohexane, petroleum ether, methylene chloride or 1,2-dichloroethane, dipolar aprotic solvents, such as dimethylacetamide, acetonitrile or N-methylpyrrolidinone, ethers, such as dioxane, tetrahydrofuran, t-butyl methyl ether and etherified glycols, and optionally also mixtures of various solvents can be used as the inert organic
30 solvent. Chlorobenzene is particularly preferably employed. The reaction mixture can comprise the inert solvent in an amount of 1 to 99%, preferably 20 to 98%, particularly preferably 40 to 98%.

The composition of the reaction gases carbon monoxide and oxygen can be varied within wide concentration limits, but a CO:O₂ molar ratio (standardized to CO) of 1:0.001 to 1:1, preferably 1:0.01 to 1:0.5, and particularly preferably 1:0.02 to 1:0.3, is expediently established. The oxygen partial pressure at these molar ratios is high enough to be able to achieve high space/time yields.

All the starting compounds can be contaminated with impurities from their preparation and storage, but in the context of the purity of the end product it is desirable to use chemicals which are as clean as possible. The reaction gases also are not subject to particular purity requirements. Thus, synthesis gas can be used as the source of CO and air as the O₂ carrier, but it is to be ensured that no catalyst poisons, such as e.g. sulfur or compounds thereof, are introduced. The gases can be diluted with one or more other gases, such as nitrogen, argon, carbon dioxide or hydrogen. In a preferred embodiment of the process according to the invention, pure CO and pure oxygen are used.

In another embodiment, instead of the homogeneous catalyst system heterogeneous catalysts in which the platinum metal or the platinum metal and/or the cocatalyst are applied to a heterogeneous support are employed as powders or shaped articles. The other components of the catalyst system, such as the base, the quaternary compound and optionally the cocatalyst, are furthermore dissolved homogeneously in the reaction solution. The proportion of the platinum metal in the total weight of the heterogeneous catalyst is 0.01 to 15 wt.%, preferably 0.05 to 10 wt.%, calculated as platinum metal.

At least one metal compound of the abovementioned type is employed as cocatalysts on the catalyst support.

The proportion of the amount of cocatalyst in the total weight of the heterogeneous catalyst is 0.01 to 15 wt.%, preferably 0.05 to 10 wt.%, calculated as the metal.

Suitable catalyst supports are one or more metal oxides from the group consisting of V, Mn, Ti, Cu, Zr, La and the rare earth metals (atomic numbers 58-71), both in the sense of chemically uniform pure substances and as a mixture, as well as iron and cobalt oxides, nickel, aluminium, silicon and magnesium oxide, zeolites and active
5 charcoals. If the supported catalyst is employed as a powder, for mixing the reaction components the stirred containers to be used are equipped with stirrers which can be used for this, or are designed as a bubble column reactor.

If supported catalyst powders are used as a suspension in stirred vessels or bubble
10 columns, amounts of 0.001 to 50 wt.%, preferably 0.01 to 20 wt.%, particularly preferably 0.1 to 10 wt.% of supported catalyst powder, based on the amount of aromatic hydroxy compound employed, are used.

In preferred embodiments, the heterogeneous supported catalyst is employed in a
15 fixed location in stirred containers, a bubble column, a trickle phase reactor or cascades of these reactors. It is then completely unnecessary to separate off the supported catalyst.

Suitable reactors for the process according to the invention with a homogeneous or
20 heterogeneous catalyst are stirred tanks, autoclaves and bubble columns, it being possible for these to be employed as individual reactors or as a cascade. In a cascade, 2 to 15, preferably 2 to 10, particularly preferably 2 to 5 reactors can be connected in series.

For mixing the reaction components, the stirred containers to be used according to
25 the invention are equipped with stirrers suitable for this. Such stirrers are known to the expert. Examples which may be mentioned are: disc, impeller, propeller, paddle, MIG and intermig stirrers, tubular stirrers and various types of hollow stirrers. Preferred stirrers are those which allow effective mixing of gases and liquids, for
30 example hollow tube gassing stirrers, propeller stirrers etc.

The following types of bubble columns can be employed in the process according to the invention: simple bubble columns, bubble columns with inserts, such as e.g.: bubble columns with parallel chambers, cascade bubble columns with sieve trays or single-hole trays, bubble columns with packing, with static mixers, pulsating sieve
5 tray bubble columns, loop reactors, such as e.g.: mammoth loop reactors, outflow loop reactors, jet loop reactors, free jet reactors, nozzle reactors, bubble columns with liquid immersion jets, outflow-inflow bubble columns and further bubble column reactors known to the expert (Chem. Ing. Tech. 51 (1979) no. 3, p. 208-216; W.-D. Deckwer, Reaktionstechnik in Blasensäulen, Otto Salle Verlag 1985).

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In a preferred embodiment, bubble column reactors and bubble column cascades which allow effective mixing of gas and liquids, such as, for example, cascade bubble columns and loop reactors, are employed. Distributing and redispersing
15 organs can be attached along the longitudinal axis of the bubble column reactors to maintain good thorough mixing of liquid and reaction gas. Single hole trays, perforated trays, sieve trays and further inserts known to the expert are employed as fixed redispersing organs. Conventional devices, such as porous sintered plates, perforated plates, sieve trays, inserted tubes, nozzles, gassing rings and further dispersing devices known to the expert can be employed for the initial dispersing of
20 the reaction gas in the liquid phase during metering in.

The process according to the invention can be carried out in various embodiment variants. One possibility comprises the discontinuous procedure. In this, CO and oxygen are passed into the reaction mixture either through a gassing stirrer, as in the
25 case of a stirred tank, or through other known gas distribution organs. When the optimum conversion is reached, the reaction mixture is removed from the reactor or optionally worked up in the reactor. If pulverulent supported catalysts are used, these can be separated off from the reaction mixture, e.g. by filtration, sedimentation or centrifugation.

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Embodiments which utilize the parameters, compounds, definitions and explanations mentioned as preferred, particularly preferred or very particularly preferred are preferred, particularly preferred or very particularly preferred.

- 5 However, the definitions, parameters, compounds and explanations mentioned above generally or mentioned in preferred ranges can also be combined as desired with one another, that is to say between the particular ranges and preferred ranges.

- 10 Supported catalysts used in discontinuous experiments can be employed repeatedly, optionally without purification, with the same starting substances. In the case of a continuous procedure, the supported catalysts employed can remain in the reactor over a long period of time and can optionally be regenerated.

- 15 A continuous procedure in a single reactor or in a cascade of several reactors is preferably employed. If heterogeneous catalysts of fixed location are used, these can remain in the reactor over a long period of time and can optionally also be regenerated there.

Examples

The reaction components are analysed by gas chromatography, it being possible for the weights of the components to be determined by means of an internal standard.

- 5 The selectivity is calculated by adding together the amount of residual phenol contained in the reaction mixture and phenol converted into DPC and dividing this by the total amount of phenol employed. The phenol not included in this has been converted into by-products.

10 **Example 1**

- 0.03 mmol palladium(II) bromide, 7.5 mmol tetrabutylammonium bromide, 0.7 mmol manganese trisacetylacetonate and 16 g phenol are initially introduced into 50 ml chlorobenzene in an autoclave and the mixture is heated to 80°C while
15 passing through carbon monoxide. 7.5 mmol tetrabutylammonium phenolate in 30 ml chlorobenzene are then added. A gas mixture of carbon monoxide and oxygen (97:3 vol.%) is passed through at 90°C/3 bar. After 15 min an additional 8.2 g phenol in 12.3 g chlorobenzene are pumped in continuously and uniformly in the course of 90 min. After 2 h the reaction is interrupted and the reaction mixture is
20 analysed by means of GC. The results are summarized in Table 1.

Comparison example 1

- 0.03 mmol palladium(II) bromide, 7.5 mmol tetrabutylammonium bromide, 0.7 mmol manganese trisacetylacetonate and 24.2 g phenol are initially introduced into 50 ml chlorobenzene in an autoclave and the mixture is heated to 80°C while
25 passing through carbon monoxide. 7.5 mmol tetrabutylammonium phenolate in 30 ml chlorobenzene are then added. A gas mixture of carbon monoxide and oxygen (97:3 vol.%) is passed through at 90°C/3 bar. After 2 h the reaction is interrupted and the reaction mixture is analysed by means of GC. The results are
30 summarized in Table 1.

Table 1:

	Ex. 1	Comp. 1
Conversion of phenol [%]	36.9	35.9
Selectivity [%]	87.1%	83.8%
Space/time yield [g/l/h]	35.1	33.5
Turn-over number Pd	1,216	1,022

Patent claims:

1. A process for the preparation of an aromatic carbonate of the formula



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wherein k represents integers of 1 to 2 and n represents integers from 1 to 30 and R represents an aromatic radical,

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in which an aromatic hydroxy compound of the formula $R-(O-H)_k$, carbon monoxide and oxygen, and optionally a solvent and various catalyst components are reacted, characterized in that $R-(O-H)_k$ is subsequently metered into the reaction mixture at least once during the reaction time.

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2. Process according to claim 1, in which the amount of $R-(O-H)_k$ metered in during the first half hour of the reaction time is about 10 to 80% of the total amount metered in.

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3. Process according to claim 1, in which the metering of $R-(O-H)_k$ is ended at a point in time which is before about 90% of the total reaction time or average residence time.

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4. Process according to claim 1, in which $(H-O)_{k-1}-R[-O-CO-O-R]_n-(O-H)_{k-1}$ is diphenyl carbonate and $R-(O-H)_k$ is phenol.

5. Process according to claim 1, for the preparation of an oligo- or polycarbonate from bisphenol A.

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6. Process according to claim 1, in which the subsequent metering takes place in portions in one to ten portions.

7. Process according to claim 1, in which the subsequent metering takes place continuously.

8. A process for the continuous preparation of diaryl carbonates, in which a hydroxyaryl, carbon monoxide and oxygen, and optionally a solvent and various catalyst components are reacted, characterized in that, in a cascade of
5 m reaction apparatuses, $R-(O-H)_k$ is metered into at least one of the 2nd to nth reactors during the reaction.