and bromine in the case of transition metal-catalysed cross-coupling) and the rising relevance of environmental protection, the cost of such transformations is rising. Particularly in the case of utilization of multistage sequences, an exchange between various solvents is necessary.

A problem which occurs in the electrochemical coupling of different molecules is that the co-reactants generally have different oxidation potentials E_{Ox}. The result of this is that the molecule having the lower oxidation potential has a higher drive to release an electron (e^-) to the anode and a H^+ ion to the solvent, for example, than the molecule having the higher oxidation potential. The oxidation potential E_{Ox} can be calculated via the Nernst equation:

$$E_{Ox} = E° + (0.059/n) * \lg([Ox]/[Red])$$

E_{Ox}: electrode potential for the oxidation reaction (= oxidation potential)
$E°$: standard electrode potential
n: number of electrons transferred
[Ox]: concentration of the oxidized form
[Red]: concentration of the reduced form

If the literature methods cited above were to be applied to two different substrates, the result of this would be to form predominantly radicals of the molecule having a lower oxidation potential, and these would then react with one another. By far the predominant main product obtained would thus be a product which has formed from two identical substrates.
This problem does not occur in the coupling of identical molecules.

The problem addressed by the present invention was that of providing an electrochemical process in which anilines and phenols can be coupled to one another, and multistage syntheses using metallic reagents can be dispensed with.
The problem is solved by a process according to the invention.

Summary

In one embodiment, there is provided an electrochemical process for coupling phenol to aniline, comprising the process steps of:
a') introducing a solvent or solvent mixture and a conductive salt into a reaction vessel,
b') adding a phenol having an oxidation potential $E_{Ox}1$ to the reaction vessel,

c') adding an aniline having an oxidation potential $E_{Ox}2$ to the reaction vessel, where:

$E_{Ox}2 > E_{Ox}1$ and $E_{Ox}2 - E_{Ox}1 = \Delta E$,

the aniline being added in excess relative to the phenol,

and the solvent or solvent mixture being selected such that ΔE is within the range from 10 mV to 450 mV,

d') introducing two electrodes into the reaction solution,

e') applying a voltage to the electrodes,

f') coupling the phenol and the aniline.

In one aspect, there is provided an electrochemical process for coupling phenol to aniline, comprising the process steps of:

a'') introducing a solvent or solvent mixture and a conductive salt into a reaction vessel,

b'') adding an aniline having an oxidation potential $E_{Ox}1$ to the reaction vessel,

c'') adding a phenol having an oxidation potential $E_{Ox}2$ to the reaction vessel, where:

$E_{Ox}2 > E_{Ox}1$ and $E_{Ox}2 - E_{Ox}1 = \Delta E$,

the phenol being added in excess relative to the aniline,

and the solvent or solvent mixture being selected such that ΔE is within the range from 10 mV to 450 mV,

d'') introducing two electrodes into the reaction solution,

e'') applying a voltage to the electrodes,

f'') coupling the phenol and the aniline.

Detailed Description

Electrochemical process for coupling phenol to aniline, comprising the process steps of:

a') introducing a solvent or solvent mixture and a conductive salt into a reaction vessel,

b') adding a phenol having an oxidation potential $E_{Ox}1$ to the reaction vessel,

c') adding an aniline having an oxidation potential $E_{Ox}2$ to the reaction vessel, where:

Claims

1. Electrochemical process for coupling phenol to aniline, comprising the process steps of:

a") introducing a solvent or solvent mixture and a conductive salt into a reaction vessel,

b") adding an aniline having an oxidation potential $E_{Ox}1$ to the reaction vessel,

c") adding a phenol having an oxidation potential $E_{Ox}2$ to the reaction vessel, where:

$E_{Ox}2 > E_{Ox}1$ and $E_{Ox}2 - E_{Ox}1 = \Delta E$,

the phenol being added in excess relative to the aniline,

and the solvent or solvent mixture being selected such that ΔE is within the range from 10 mV to 450 mV,

d") introducing two electrodes into the reaction solution,

e") applying a voltage to the electrodes,

f") coupling the phenol and the aniline.

2. Process according to Claim 1,

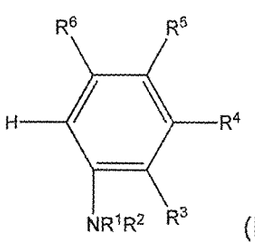
wherein the phenol is used in at least twice the amount relative to the aniline.

3. Process according to either of Claims 1 and 2,
wherein the ratio of aniline to phenol is in the range from 1:2 to 1:4.

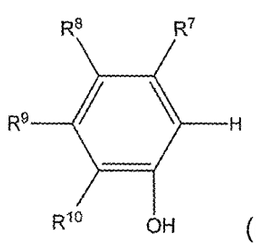
4. Process according to any of Claims 1 to 3,
wherein the solvent or solvent mixture is selected such that ΔE is in the range from 20 mV to 400 mV.

5. Process according to any of Claims 1 to 4,
wherein the reaction solution is free of organic oxidizing agents.

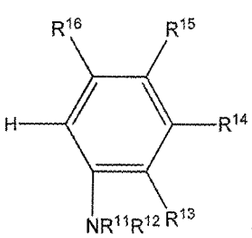
6. Process according to any of Claims 1 to 5,
wherein the phenol and the aniline are selected from: **Ia**, **Ib**, **IIa**, **IIb**, **IIIa**, **IIIb**, **IVa**, **IVb**, **Va**, **Vb**:



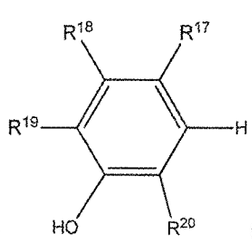
(Ia)



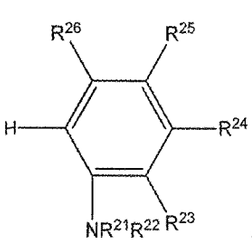
(Ib)



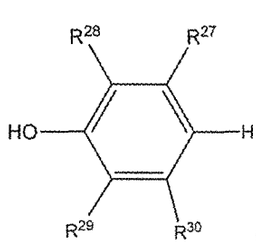
(IIa)



(IIb)



(IIIa)



(IIIb)