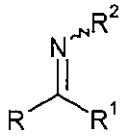
Claims

1. Process for preparing azomethines of the general formula (V)



(V),

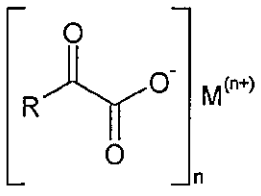
where

R is an optionally substituted carbocyclic aromatic radical having 6 to 24 carbon atoms or an optionally substituted alkyl radical or an optionally substituted heteroaromatic radical having 5 to 24 carbon atoms, and

R^1 is an optionally substituted carbocyclic aromatic radical having 6 to 24 carbon atoms or an optionally substituted heteroaromatic radical having 5 to 24 carbon atoms,

R^2 is hydrogen or an optionally substituted carbocyclic aromatic radical having 6 to 24 carbon atoms or an optionally substituted alkyl radical or an optionally substituted cycloalkyl radical or an optionally substituted heteroaromatic radical having 5 to 24 carbon atoms

by reacting alpha-oxocarboxylates of the general formula (I)



(I),

where

n is a number in the range from 1 to 6,

$M^{(n+)}$ is a cation, and

R has the meaning indicated for formula (V),

with aryl bromides of the general formula (IV)

$$R^1\text{-Br} \qquad \text{(IV)}$$

where

R^1 has the meaning indicated for formula (V),

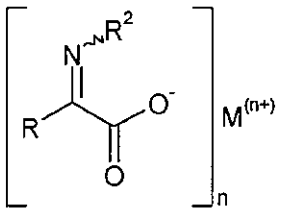
and amines of the general formula (II)

$$R^2\text{-}NH_2 \qquad \text{(II)}$$

where

R^2 has the meaning indicated for formula (V)

via the alpha-iminocarboxylate intermediate of the general formula (III),



(III),

where

n is a number in the range from 1 to 6,

$M^{(n+)}$ is a cation, and

R has the meaning indicated for formula (V),

R^2 has the meaning indicated for formula (V),

in the presence of two transition metals or compounds thereof as catalyst.

2. Process according to Claim 1, where the catalyst comprises two different transition metals and/or transition metal compounds, characterized in that one transition metal or one transition metal compound is selected from those able to assume oxidation states differing from one another by one unit, and the other transition metal or the other transition metal compound is selected from those able to assume oxidation states differing from one another by two units.

3. Process according to either of Claims 1 or 2, where the one transition metal or the transition metal compound is selected from the series of metals Ag, Cu, Mn, Fe, Co, Ni, Mo, Ru and compounds thereof and the other transition metal or the other transition metal compound is selected from the series of metals Pd, Ni, Fe, Au, Rh, Pt, Ru, Ir and compounds thereof.

4. Process according to any of Claims 1-3, where at least one of the transition metals is stabilized by ligands from the series of amines, N-heterocyclic carbenes, nitriles, olefins or phosphines.

5. Process according to Claim 4, characterized in that the ligand is a chelating amine from the series phenanthroline, bipyridine, terpyridine and/or a trialkylphosphine.

6. Process according to Claim 1, characterized in that a combination of copper(I) bromide with 1,10-phenanthroline as ligand and bis(1,1,1,5,5,5-hexafluoroacetylacetonato)-palladium with 1,1'-bis(diphenylphosphino)ferrocene (dppf) as ligand is employed as

catalyst.

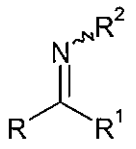
7. Process according to any of Claims 1 to 5, where the amounts of the two catalysts employed independently of one another are from 0.001 mol% to 50 mol% based on the compound of the formula (IV).

8. Process according to any of Claims 1 to 7, characterized in that the process is carried out at temperatures from 60°C to 140°C.

9. Process for the synthesis of aryl ketones characterized in that an azomethine prepared according to any of Claims 1 to 8 is hydrolyzed.

Claims

1. Process for preparing azomethines of the general formula (V)



(V),

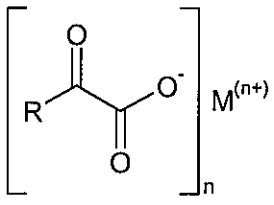
where

R is an unsubstituted or substituted carbocyclic aromatic radical having 6 to 24 carbon atoms or an unsubstituted or substituted alkyl radical or an unsubstituted or substituted heteroaromatic radical having 5 to 24 carbon atoms, and

R^1 is an unsubstituted or substituted carbocyclic aromatic radical having 6 to 24 carbon atoms or an unsubstituted or substituted heteroaromatic radical having 5 to 24 carbon atoms,

R^2 is hydrogen or an unsubstituted or substituted carbocyclic aromatic radical having 6 to 24 carbon atoms or an unsubstituted or substituted alkyl radical or an unsubstituted or substituted cycloalkyl radical or an unsubstituted or substituted heteroaromatic radical having 5 to 24 carbon atoms

by reacting alpha-oxocarboxylates of the general formula (I)



(I),

where

n is a number in the range from 1 to 6,

$M^{(n+)}$ is a cation, and

R has the meaning indicated for formula (V),

with aryl bromides of the general formula (IV)

$$R^1\text{-Br} \qquad \text{(IV)}$$

where

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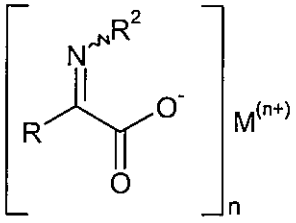
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where

R^2 has the meaning indicated for formula (V)

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(III),

where

n is a number in the range from 1 to 6,

$M^{(n+)}$ is a cation, and

R has the meaning indicated for formula (V),

R^2 has the meaning indicated for formula (V),

in the presence of two transition metals or compounds thereof as catalyst and wherein the process is carried out at temperatures from 60 to 140°C.

2. Process according to Claim 1, where the catalyst comprises two different transition metals and/or transition metal compounds, characterized in that one transition metal or one transition metal compound is selected from those able to assume oxidation states differing from one another by one unit, and the other transition metal or the other transition metal compound is selected from those able to assume oxidation states differing from one another by two units.

3. Process according to either of Claims 1 or 2, where the one transition metal or the transition metal compound is selected from the series of metals Ag, Cu, Mn, Fe, Co, Ni, Mo, Ru and compounds thereof and the other transition metal or the other transition metal compound is selected from the series of metals Pd, Ni, Fe, Au, Rh, Pt, Ru, Ir and compounds thereof.

4. Process according to any of Claims 1-3, where at least one of the transition metals is stabilized by ligands from the series of amines, N-heterocyclic carbenes, nitriles, olefins or phosphines.

5. Process according to Claim 4, characterized in that the ligand is a chelating amine from the series phenanthroline, bipyridine, terpyridine and/or a trialkylphosphine.

6. Process according to Claim 1, characterized in that a combination of copper(I) bromide with 1,10-phenanthroline as ligand and bis(1,1,1,5,5,5-hexafluoroacetylacetonato)-palladium with 1,1'-bis(diphenylphosphino)ferrocene (dppf) as ligand is employed as catalyst.

7. Process according to any of Claims 1 to 5, where the amounts of the two catalysts employed independently of one another are from 0.001 mol% to 50 mol% based on the compound of the formula (IV).

8. Process according to any of Claims 1 to 7, characterized in that the process is carried out at temperatures from 80°C to 120°C.

9. Process for the synthesis of aryl ketones characterized in that an azomethine prepared according to any of Claims 1 to 8 is hydrolyzed.