

PROCESS FOR THE CARBONYLATION OF ACETYLENICALLY
UNSATURATED COMPOUNDS

The invention relates to a process for the carbonylation of acetylenically unsaturated compounds in the presence of a nucleophilic compound having at least one removable hydrogen atom.

The invention is of particular interest for the preparation of esters of unsaturated carboxylic acids such as acrylic acid and methacrylic acid. The alkyl esters of these acids, in particular the methyl and butyl esters, are of established commercial interest.

The preparation of esters of unsaturated acids by carbonylation of acetylenically unsaturated compounds is known. In EP-186228 a process for the carbonylation of acetylenically unsaturated compounds is described, in which use is made of a catalyst system comprising a palladium compound, a phosphine and a protonic acid. The examples illustrate the use of, optionally substituted, hydrocarbylphosphines such as (substituted) tri-phenylphosphine. The said phosphines are used in relatively large amounts, i.e. 5 to 500 moles per gramatom of palladium.

Another process for the carbonylation of acetylenically or olefinically unsaturated compounds is disclosed in EP 441.446. In this process esters of unsaturated acids are prepared using a catalyst system which comprises a source of a Group VIII metal, a phosphine having an aromatic substituent which contains an imino nitrogen atom, a protonic acid and a tertiary amine. All examples relate to the use of catalyst systems containing palladium and a pyridylphosphine ligand.

It has been investigated whether the preparation of

esters by carbonylation of unsaturated compounds is restricted to the use of palladium containing catalysts, or that satisfactory conversions and yields can be obtained, if the catalyst is based on a Group VIII metal, other than palladium.

In GB 2202165 a process is described in which ethene, acrylic acid, or an acrylate ester is reacted with carbon monoxide in the presence of hydrogen, using a catalyst system formed by combining a platinum (II) compound, an organic ligand containing at least two phosphorus atoms coordinating with the platinum atom and a protonic acid having a pKa below 3. As unsaturated starting materials only ethene, acrylic acid and acrylic esters are mentioned.

Moreover, although conversion of the starting materials is excellent, in this process the predominant reaction product is not an ester, but a ketone.

Surprisingly, it has now been found that by selecting an acetylenically unsaturated compound as starting material, platinum containing catalysts can also be advantageously used for preparing esters of unsaturated carboxylic acids. Furthermore, it has been observed that, often in good yield, diolefinic by-products are formed, which, owing to the presence of two double bonds, are suitable intermediates for the preparation of various interesting products.

The invention may be defined as relating to a process for the carbonylation of acetylenically unsaturated compounds in the presence of a nucleophilic compound having one or more removable hydrogen atoms and a catalyst system based on

- (a) a source of platinum
- (b) a bisphosphine of the general formula



wherein each of R^1, R^2, R^3 and R^4 independently

represents a hydrocarbaryl group, which may be unsubstituted or substituted with one or more substituents selected from the group consisting of halogen atoms, cyano, alkoxy, acyl, alkylamino and dialkylamino groups, and R represents a bivalent bridging group containing 2 to 5 atoms in the bridge, and

- (c) a source of anions being the conjugated base of an acid having a pKa of less than 4.

The catalyst systems of the invention, as regards (a), are based on a source of platinum. As source of platinum, any compound of platinum can be used, which is capable of complexing with the two phosphorus atoms of the bisphosphine of formula (I)

Suitable compounds include platinum (II) salts, such as potassium tetracyanoplatinate, sodium tetracyanoplatinate, potassium trichloro(ethylene) platinate (II), platinum -bis(cyanobenzene)disulphate, potassium tetrachloroplatinate (II), platinum bis(triphenylphosphine)disulphate and potassium trichloro(ethylene) platinate (II). Salts of platinum with carboxylic acids, in particular with carboxylic acids having up to 12 carbon atoms, e.g. acetic acid, are also suitable.

Preferred sources of platinum are organic platinum (II) complexes, in particular platinum (II) acetyl-acetate.

In the bisphosphines of formula (I), constituting component (b) of the catalyst systems of the invention, preferably each of R^1, R^2, R^3 , and R^4 independently represents an aryl group which may be unsubstituted, or may be substituted with one of more substituents selected from the group consisting of halogen atoms and alkoxy groups containing from 1 to 4 carbon atoms.

Suitable aryl groups represented by R^1, R^2, R^3 and R^4 ,

include substituted and non substituted naphthyl-, and phenyl- groups. Examples are phenyl-, p-tolyl-, p-methoxyphenyl- and p-chlorophenyl groups. R^1, R^2, R^3 and R^4 may represent different groups, but preferably are the same.

The bivalent bridging group in the bisphosphines of formula (I), represented by R, preferably contains from 2 to 4 atoms in the bridge, in particular 3 atoms. The bridging atoms are preferably all carbon atoms, but bridging groups containing a carbon chain, interrupted by a hetero atom, such as an oxygen atom, are also suitable.

Examples of suitable bisphosphines are 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylphosphino)ethene, 1,3-bis(diphenylphosphino)propane, 1,3-bis(diethylphosphino)propane, 1,4-bis(diphenylphosphino)butane, 1,3-bis(di-isopropylphosphino)propane and 1,3-bis(di-p-methoxyphenylphosphino)propane. 1,3-bis(diphenylphosphino)propane is in particular preferred.

As anion source, constituting component (c) of the catalyst system of the invention, any compound generating these anions, is considered suitable. Preferably the anion is a non-coordinating or substantially non-coordinating anion. In the context of the present specification this means that little or no co-valent interaction occurs between the anion and the platinum in the catalyst.

Preferred anion sources are the acids, of which the anions are the conjugated base. The acids have a pKa of less than 4 (measured in aqueous solution at 18 °C) and preferably less than 2.

Other suitable anion sources are salts of these acids. Conveniently metal salts may be used, containing a non-noble transition metal, such as zirconium, vanadium, chromium, manganese, cobalt, nickel and iron (II).

Typical examples of suitable anions in the catalyst system of the invention, are anions of phosphoric acid, phosphonic acid, sulphuric acid, sulphononic acids and trihaloacetic acid.

Sulphonic acids are preferred anion sources, for example: methanesulphonic acid, trifluoromethanesulphonic acid and p-toluenesulphonic acid.

Alkylsulphonic acids are most preferred, in particular tert.butylsulphonic acid.

In the process according to the invention the molar amount of bisphosphine versus the amount of noble metal of Group VIII of the Periodic Table, is relatively small. This is in contrast to the process known from EP-186228. Nonetheless, a molar excess of bisphosphine is usually advantageous.

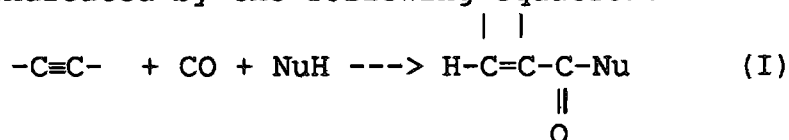
Preferably the bisphosphine of formula (I) is applied in an amount of 0.5 to 10 moles per gramatom of platinum, amounts in the range of 0.7 to 3 moles per gramatom of platinum being in particular preferred.

The amount of platinum (II) is not critical. Usually catalytic amounts of platinum compounds are applied, whereby the quantity of platinum is preferably in the range of 10^{-6} to 10^{-1} gramatom of platinum per mole of acetylenically unsaturated compound.

The acetylenically unsaturated compound is usually a linear alkyne having from 2 to 20 carbon atoms. If desired, the compound may be substituted with one or more inert substituents such as halogen atoms or hydroxy groups. The acetylenically unsaturated bond is as a rule the only carbon-carbon unsaturation in the molecule and is preferably located at a terminal position. Examples of suitable acetylenically unsaturated compounds are acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, phenylacetylene, 3-chlorobutyne, 4-hydroxypentyne and 1-nonyne.

Acetylene and propyne are in particular preferred as starting material.

Without wishing to be bound by any specific reaction mechanism, it is believed that in the carbonylation process of the invention, the overall reaction can best be indicated by the following equation:



wherein Nu represents the nucleophilic moiety of the nucleophilic co-reactant after removal of a hydrogen atom.

As evident from the equation (I), the obtained reaction product largely depends on the nature of the nucleophilic compound, represented by NuH. Thus, if NuH represents a carboxylic acid, the resulting product will contain an anhydride moiety, if NuH represents water the product will be an acid and if NuH represents an alcohol, an ester will be formed.

The carbonylation reaction of the invention is preferably carried out with an alcohol as nucleophilic compound. Suitable alcohols include mono alcohols having from 1 to 12 carbon atoms, in particular from 1 to 6 carbon atoms and dihydric alcohols having from 2 to 8 carbon atoms. It will be appreciated that in a reaction in which a nucleophilic compound participates, from which two hydrogen atoms can be removed, other reaction products can be formed such as glycolesters.

Examples of suitable alcohols are methanol, ethanol, n-propanol, iso-propanol, butanol-1, butanediol-1,4, cyclohexanol, and ethyleneglycol.

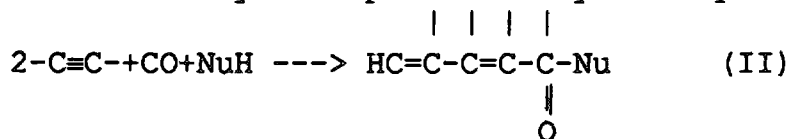
Lower monohydric alcohols having from 1 to 4 carbon atoms are preferred, in particular methanol and 1-butanol.

The reaction may be carried out in the presence of a

separate diluent, if so desired. Preferred diluents are aprotic liquids such as ketones and ethers. In particular with the dimethylether of ethylene glycol (diglyme) attractive results have been obtained.

Because of the reactivity of acetylenically unsaturated compounds, in addition to the carbonylation reaction, indicated by the equation (I) a reaction between two molecules of the acetylenically unsaturated compound, carbon monoxide and the nucleophilic co-reactant may take place to form a diolefinic reaction product.

This reaction may be represented by the equation:



The formation of the diolefinic compound may be enhanced or suppressed by modifying the reaction conditions such as temperature, mole ratio acetylenically unsaturated compound over carbon monoxide, pressure and acidity of the reaction medium.

Suitable reaction temperatures are usually in the range of 30 to 250 °C, preferably in the range of 50 to 200 °C and more preferably in the range of 70 to 140 °C.

The reaction pressure is preferably in the range of 20 to 80 bar. Higher pressures are generally not recommended, because of the requirements the reactor then has to fulfil.

The invention is further illustrated with the following examples.

Examples I - X

A solution of 0.2 mmol of platinum (II) acetylacetonate in 40 mL of diglyme (2,5,8-trioxanonane), also containing bisphosphine, anion source and nucleophilic co-reactant in the amounts, as specified below, were introduced into a 250 mL „Hastelloy C"

(Trade Mark) autoclave, provided with a magnetic stirrer.

The reactor was closed and the gaseous acetylenically unsaturated compound and subsequently carbon monoxide (20 bar) was added. (In Examples VIII and IX phenylacetylene was introduced in the reactor together with the catalyst solution.)

The contents of the autoclave were then heated under stirring to the desired reaction temperature, indicated in the Table and maintained at that temperature during the reaction period (1-5 hour). After completion of the reaction, the reaction mixture was cooled to room temperature. The product was analysed by means of high performance liquid chromatography.

The analytical results, viz. the average rate in moles of product per gramatom of platinum and per hour, the selectivity with respect to the desired ester and the co-formed byproducts, are shown in the Table.

The abbreviations used in the Table, have the following meanings:

PA	= platinum (II) acetylacetonate
BDPP	= 1,3 - bis(diphenylphosphino)propane
BDPB	= 1,4 - bis(diphenylphosphino)butane
BEPP	= 1,3 - bis(diethylphosphino)propane
BCPP	= 1,3 - bis(di-2-cyanoethylphosphino)propane
BIPP	= 1,3 - bis(di-isopropylphosphino)propane
TBSA	= tertiary-butylsulphonic acid
TFA	= trifluoroacetic acid
BA	= butylacrylate
AA	= acrylic acid
1-BPA	= butylester of 1-phenylacrylic acid
2-BPA	= butylester of 2-phenylacrylic acid
MMA	= methylmethacrylate
MCA	= methylcrotonate
BPD	= butylpentadienoate
MDPPD	= methylester of 2,4-diphenylpentadienoic acid

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MDPD = methylester of 2,4-dimethylpentadienoic acid

DBA = dibutylacetal

PDA = pentadienoic acid.

Table

Ex. No	Catalyst Components (mmol)			Acetylenically unsat. compound (bar) or mL*	Nucleophilic Co-reactant (mL)	Temp. (°C)	Average rate mol/gat Pt.h	Products (sel%)	
	Pt source	bi-phosphine	anion source					(1)	(2)
I	0.20 PA	0.22 BDPP	0.4 TBSA	1,4 Ethyne	15 butanol	100	125	BA 92	BPD
II	0.20 PA	0.22 BDPP	0.4 TBSA	1,4 Ethyne	30 butanol	125	200	BA 91	BPD
III	0.20 PA	0.22 BDPB	0.4 TBSA	1,4 Ethyne	30 butanol	100	50	BA 90	BPD
IV	0.20 PA	0.22 BEPP	0.5 TFA	1,4 Ethyne	30 butanol	100	50	BA 60	BPD + BDA
V	0.20 PA	0.20 BCPP	0.4 TBSA	1,4 Ethyne	30 butanol	100	20	BA 60	BCD + BDA
VI	0.20 PA	0.20 BCPP	0.4 TBSA	1,4 Ethyne	30 butanol	100	120	BA 70	BPD 25

Table (Cont'd)

Ex. No	Catalyst Components (mmol)			Acetylenically unsat. compound (bar) or (mL*)	Nucleophilic Co-reactant (mL)	Temp. (°C)	Average rate mol/gat Pt.h	Products (sel%)	
	Pt source	bis-phosphine	anion source					(1)	(2)
VII	0.20 PA	0.20 BCPP	0.4 TBSA	1,4 Ethyne	2 water	100	150	BA 91	PDA
VIII	0.20 PA	0.20 BCPP	0.4 TBSA	15 Phenyl-ethyne*	30 butanol	125	120	(95) 1-BPA ⁹⁵ (5) 2-BPA ⁹⁵	MDPPD
IX	0.20.P A	0.20 BIPP	0.4 TBSA	15 Phenyl-ethyne*	10 methanol	125	30	(90) 1-BPA ⁹⁰ (10) 2-BPA ⁹⁰	MDPPD
X	0.20.P A	0.20 BDPP	0.4 TBSA	15 Propyne*	10 methanol	125	120	(94) MMA ⁹⁵ (6) MCA	MDPD

(1) Mono unsaturated ester

(2) Di-unsaturated ester, acetal

Comparison of the results of Examples I and III supports the preference for bisphosphines in which the phosphorus atoms are separated by a trimethylene group instead of a tetramethylene group.

Similarly, the preference for bis-diarylphosphines over bis-dialkylphosphine is supported by comparing the results of Examples IV and V with those of Example I and by comparing the results of Example IX with those of Example VIII.

C L A I M S

1. A process for the carbonylation of acetylenically unsaturated compounds in the presence of a nucleophilic compound having one or more removable hydrogen atoms and a catalyst system based on
 - (a) a source of platinum
 - (b) a bisphosphine of the general formula
$$R^1R^2PRPR^3R^4 \quad (I)$$
wherein each of R^1, R^2, R^3 and R^4 independently represents a hydrocarbyl group, which may be unsubstituted or substituted with one or more substituents selected from the group consisting of halogen atoms, cyano, alkoxy, acyl, alkylamino and dialkylamino groups, and R represents a bivalent bridging group containing 2 to 5 atoms in the bridge, and
 - (c) a source of anions being the conjugated base of an acid having a pKa of less than 4.
2. A process as claimed in claim 1, characterized in that a catalyst system is used which, as regards (a), is based on an organic platinum complex.
3. A process as claimed in claim 1 or 2, characterized in that the catalyst system, as regards (a), is based on platinum (II) acetylacetonate.
4. A process as claimed in any of claims 1-3, characterized in that a catalyst system is used which, as regards (b), is based on a bisphosphine of formula (I), wherein each of R^1, R^2, R^3 and R^4 independently represents an aryl group, which may be unsubstituted or substituted with one or more substituents selected from the group consisting of halogen atoms and alkoxy groups containing from 1 to 4 carbon atoms, and R represents a bivalent

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bridging group containing 3 carbon atoms in the bridge.

5. A process as claimed in claim 4, characterized in that the catalyst system, as regards (b), is based on 1,3-bis(diphenylphosphino)propane.

6. A process as claimed in any of claims 1-5, characterized in that a catalyst system is used which, as regards (c), is based on a sulphonic acid.

7. A process as claimed in claim 6, characterized in that the sulphonic acid is an alkylsulphonic acid.

8. A process as claimed in claim 6 or 7, characterized in that the sulphonic acid is tertiary-butylsulphonic acid.

9. A process as claimed in any of claims 1-8, characterized in that the bisphosphine of formula (I) is applied in an amount of 0.5 to 10 moles per gramatom of platinum.

10. A process as claimed in claim 9, characterized in that the amount of bisphosphine of formula (I) is in the range of 0.7 to 3 moles per gramatom of platinum.

11. A process as claimed in any of claims 1-10, characterized in that the catalyst is applied in an amount such that per mole of acetylenically unsaturated compound 10^{-6} to 10^{-1} gramatom of platinum is present.

12. A process as claimed in any of claims 1-11, characterized in that as acetylenically unsaturated compound acetylene or propyne is used.

13. A process as claimed in any of claims 1-12, characterized in that as nucleophilic compound having one of more removable hydrogen atoms an alcohol having from 1 to 6 carbon atoms is used.

14. A process as claimed in claim 13, characterized in that as nucleophilic compound butanol-1 is used.

15. A process as claimed in any of claims 1-14, characterized in that the reaction is carried out at a temperature in the range of 50 to 200 °C.

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16. A process as claimed in claim 15, characterized in that the reaction temperature is in the range of 70 to 140 °C.
17. A process as claimed in any of claims 1-16, characterized in that the reaction is carried out at a pressure in the range of 2 to 80 bar.
18. a process as claimed in any of claims 1-17, characterized in that the reaction is carried out in the additional presence of an aprotic solvent.
19. A process as claimed in claim 18, characterized in that as solvent an ether is used, in particular the dimethyl ether of diethylene glycol.
20. A process for the preparation of unsaturated esters, as claimed in claim 1, substantially as described hereinbefore, with reference to the examples.
21. Unsaturated esters, whenever prepared according to any of claims 1-20.

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PROCESS FOR THE CARBONYLATION OF ACETYLENICALLY
UNSATURATED COMPOUNDS

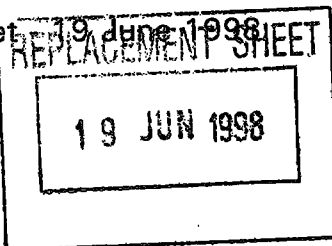
A process for the carbonylation of acetylenically unsaturated compounds in the presence of a nucleophilic compound having one or more removable hydrogen atoms and a catalyst system based on

- (a) a source of platinum
- (b) a bisphosphine of the general formula



wherein each of R^1, R^2, R^3 and R^4 independently represents a hydrocarbyl group, which may be unsubstituted or substituted with one or more substituents selected from the group consisting of halogen atoms, cyano, alkoxy, acyl, alkylamino and dialkylamino groups, and R represents a bivalent bridging group containing 2 to 5 atoms in the bridge, and

- (c) a source of anions being the conjugated base of an acid having a pK_a of less than 4.



C L A I M S

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5 a catalyst system based on
 - (a) a source of platinum
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 $R^1R^2PRPR^3R^4$ (I)
wherein each of R^1, R^2, R^3 and R^4 independently
10 represents a hydrocarbyl group, which may be unsubstituted or substituted with one or more substituents selected from the group consisting of halogen atoms, cyano, alkoxy, acyl, alkylamino and dialkylamino groups, and R represents a
15 bivalent bridging group containing 2 to 5 atoms in the bridge, and
 - (c) a source of anions being the conjugated base of an acid having a pKa of less than 4.
2. A process as claimed in claim 1, characterized in
20 that a catalyst system is used which, as regards (a), is based on an organic platinum complex.
3. A process as claimed in claim 1 or 2, characterized in that the catalyst system, as regards (a), is based on platinum (II) acetylacetonate.
254. A process as claimed in any one of claims 1-3, characterized in that a catalyst system is used which, as regards (b), is based on a bisphosphine of formula (I), wherein each of R^1, R^2, R^3 and R^4 independently represents an aryl group, which may be unsubstituted or substituted
30 with one or more substituents selected from the group consisting of halogen atoms and alkoxy groups containing from 1 to 4 carbon atoms, and R represents a bivalent



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- bridging group containing 3 carbon atoms in the bridge.
5. A process as claimed in claim 4, characterized in that the catalyst system, as regards (b), is based on 1,3-bis(diphenylphosphino)propane.
 - 5 6. A process as claimed in any one of claims 1-5, characterized in that a catalyst system is used which, as regards (c), is based on a sulphonic acid.
 7. A process as claimed in claim 6, characterized in that the sulphonic acid is an alkylsulphonic acid.
 - 10 8. A process as claimed in claim 6 or 7, characterized in that the sulphonic acid is tertiary-butylsulphonic acid.
 9. A process as claimed in any one of claims 1-8, characterized in that the bisphosphine of formula (I) is applied in an amount of 0.5 to 10 moles per gramatom of platinum.
 - 15 10. A process as claimed in claim 9, characterized in that the amount of bisphosphine of formula (I) is in the range of 0.7 to 3 moles per gramatom of platinum.
 - 20 11. A process as claimed in any one of claims 1-10, characterized in that the catalyst is applied in an amount such that per mole of acetylenically unsaturated compound 10^{-6} to 10^{-1} gramatom of platinum is present.
 - 25 12. A process as claimed in any one of claims 1-11, characterized in that as acetylenically unsaturated compound acetylene or propyne is used.
 - 30 13. A process as claimed in any one of claims 1-12, characterized in that as nucleophilic compound having one of more removable hydrogen atoms an alcohol having from 1 to 6 carbon atoms is used.
 14. A process as claimed in claim 13, characterized in that as nucleophilic compound butanol-1 is used.
 15. A process as claimed in any one of claims 1-14, characterized in that the reaction is carried out at a temperature in the range of 50 to 200 °C.



* C L H S *

16. A process as claimed in claim 15, characterized in that the reaction temperature is in the range of 70 to 140 °C.
17. A process as claimed in any one claims 1-16, characterized in that the reaction is carried out at a pressure in the range of 2 to 80 bar.
18. A process as claimed in any one of claims 1-17, characterized in that the reaction is carried out in the additional presence of an aprotic solvent.
19. A process as claimed in claim 18, characterized in that as solvent an ether is used, in particular the dimethyl ether of diethylene glycol.
20. A process for the preparation of unsaturated esters, as claimed in claim 1, substantially as described hereinbefore, with reference to the examples.
21. Unsaturated esters, whenever prepared according to any one of claims 1-20.

