

The preparation of carboxylic acids or their esters by carboxylation of olefins

5 Description

The present invention relates to a process for preparing carboxylic acids or their esters by reacting an olefin with carbon monoxide in the presence of water or alcohols and a
10 halogen-free catalyst system, a mixture of nickel or a nickel compound, at least one noble metal or its compound, and a nonmetallic nitrogen, arsenic or phosphorus compound, at from 100 to 270°C under from 30 to 100 bar.

15 Weissermel et al. describe, in Industrielle Organische Chemie, 2nd edition, 1978, Verlag Chemie, page 132 the carboxylation of olefins by the Reppe process, for example the preparation of propionic acid from ethylene, carbon monoxide and water in the presence of catalysts. Nickel propionate is employed as catalyst
20 and is converted into nickel carbonyl under the reaction conditions. High conversion of the ethylene is achieved only under high pressures (200-240 bar). These reaction conditions require great technical elaboration in the construction of suitable reactors and - owing to the corrosivity of the product
25 under the reaction conditions - special and costly materials.

GB-A 1 063 617 discloses the carboxylation of olefins with nickel and cobalt catalysts in the presence of boric acid. High pressures and temperatures are also necessary in this case.

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Carboxylations of olefins can be carried out with noble metal catalysts under about 100 bar. Thus, EP-A 1 495 547 discloses catalysts which consist of a source of palladium and bidentate phosphine ligands. However, catalysts of this type are often
35 inactivated after a short reaction time by deposition of metallic palladium; in particular, the phosphine ligands employed are not thermally stable under the required reaction conditions.

DE-A 4 424 710 describes the carboxylation of olefins with a
40 mixture of nickel or a nickel compound and a noble metal or a noble metal compound as catalyst system. However, the described process is still unsatisfactory in respect of the selectivity and activity for the products to be prepared, especially under pressures below 100 bar.

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It is an object of the present invention to provide a process for the carboxylation of olefins which avoids the abovementioned disadvantages and is improved in respect of selectivity and activity under pressures up to 100 bar.

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We have found that this object is achieved by a novel and improved process for preparing carboxylic acids or their esters from olefins and carbon monoxide in the presence of water or alcohols at from 100 to 270°C under from 30 to 100 bar, preferably
10 from 30 to 80 bar, which comprises employing as catalyst system a mixture of

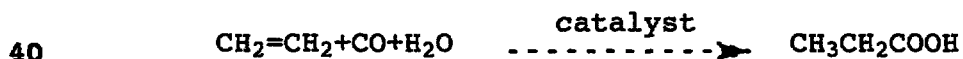
a) nickel or a nickel compound,

15 b) at least one metal from the group of chromium, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold or a compound of these metals and

20 c) at least one nonmetallic compound from the group of tertiary or quaternary nitrogen, phosphorus or arsenic compounds and of nitrogenous heterocyclic compounds.

It was possible by the process according to the invention to
25 improve considerably the activity and the selectivity by comparison with the catalyst system described in DE-A 4 424 710, especially at low pressures of up to 100 bar. In addition, the catalyst system in the process according to the invention is so active, even with low water concentrations of from 0.5 to 5 mol of
30 water per mole of olefin, that it is possible to prepare carboxylic acids which even in the discharge from the reaction have a water content below 1%, which considerably simplifies the workup of the reaction product.

35 The following reaction equation illustrates the process according to the invention for the example of the conversion of ethylene into propionic acid:



Suitable starting materials for the process according to the invention are aliphatic and cycloaliphatic alkenes having, preferably, 2 to 20, particularly preferably 2 to 7, carbon
45 atoms. Examples which may be mentioned are ethylene, propylene,

isobutene, 1-butene, 2-butene and the isomeric pentenes and hexenes, and cyclohexene, of which ethylene is preferred.

These olefins are reacted with water to prepare carboxylic acids
5 or with alcohols to prepare carboxylic esters. These alcohols comprise aliphatic and cycloaliphatic compounds having, preferably, 1 to 20 carbon atoms, particularly preferably having 1 to 6 carbon atoms, such as methanol, ethanol, n-propanol, isopropanol, tert-butanol, stearyl alcohol, diols such as
10 ethylene glycol, 1,2-propanediol and 1,6-hexanediol, and cyclohexanol. If diols are reacted, monoesters and diesters may be obtained, depending on the chosen stoichiometric ratios, with the diol and the olefin being employed in the molar ratio of about 1:2 to prepare diesters, and the diol being employed in
15 excess to prepare the monoesters.

Said starting compounds are reacted with carbon monoxide, which may be employed in pure form or diluted with inert gases such as nitrogen or argon.

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The molar ratios of the olefin and water or alcohol starting compounds may vary within wide limits but, as a rule, at least an equimolar amount of water or alcohol is employed. It is possible in the preparation of carboxylic acids to employ from 0.5 to
25 10 mol of water per mole of olefin, preferably 0.5 to 5 mol.

The molar ratio of olefin to carbon monoxide may also be varied greatly, a preferred molar ratio being from 5:1 to 1:5 mol of olefin per mole of carbon monoxide.

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The halogen-free catalyst system employed in the process according to the invention is a mixture of

a) nickel or a nickel compound,

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b) at least one metal from the group of chromium, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold or a compound of these metals and

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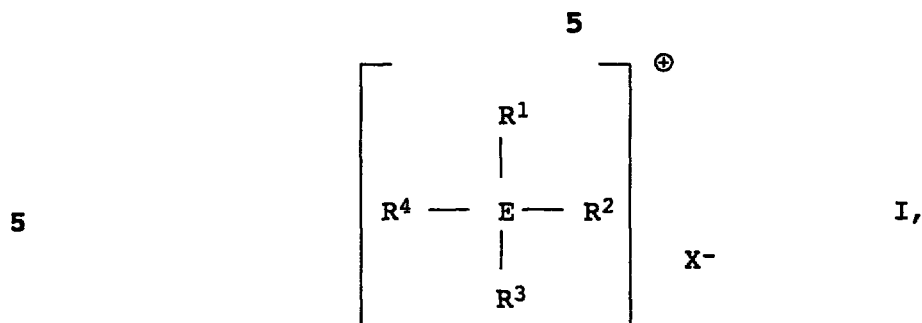
c) at least one nonmetallic compound from the group of tertiary or quaternary nitrogen, phosphorus or arsenic compounds and of nitrogenous heterocyclic compounds.

45 For it to be possible for the active nickel compounds to form, it is expedient to add to the reaction mixture compounds which are soluble therein, such as acetates, propionates, acetylacetonates,

hydroxides and carbonates or mixtures of these compounds. However, it is also possible to introduce $\text{Ni}(\text{CO})_4$ and metallic nickel into the reaction mixture. It is particularly preferred to introduce the nickel component in the form of salts of the
5 carboxylic acids formed in the reaction.

- The second catalyst component used is at least one of the metals or a compound of these metals from the group of chromium, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium,
10 iridium, palladium, platinum, silver and gold, of which rhodium and palladium are preferred, and ruthenium and platinum are particularly preferred. These metals can be introduced, for example as salts as indicated above for nickel, into the reaction solution, ie. as acetates, propionates, acetylacetonates,
15 hydroxides or carbonates. Also suitable are carbonyl compounds, in particular chromium hexacarbonyl, molybdenum hexacarbonyl, tungsten hexacarbonyl, dirhenium decacarbonyl, triruthenium dodecacarbonyl, triosmium dodecacarbonyl and carbonyl compounds which have other ligands, such as rhodium dicarbonyl
20 acetylacetonate or metal compounds stabilized by donor ligands such as phosphines, arsines and nitrogen bases, and olefins. Platinum can also be employed as dibenzalacetoneplatinum. Ruthenium is preferably employed as acetylacetonate. The metals are present either in solution or suspension in the reaction
25 mixture, depending on the relative solubilities. The metals or compounds of these metals in catalyst component b) can also be used on inert organic or inorganic carriers such as active carbon, graphite, alumina, zircon [sic] oxide and silica.
- 30 The third catalyst component used is at least one nonmetallic compound from the group of tertiary or quaternary nitrogen, phosphorus or arsenic compounds and of nitrogenous heterocyclic compounds.
- 35 By quaternary nitrogen, phosphorus or arsenic compounds are meant the quaternary ammonium, arsonium and phosphonium salts.

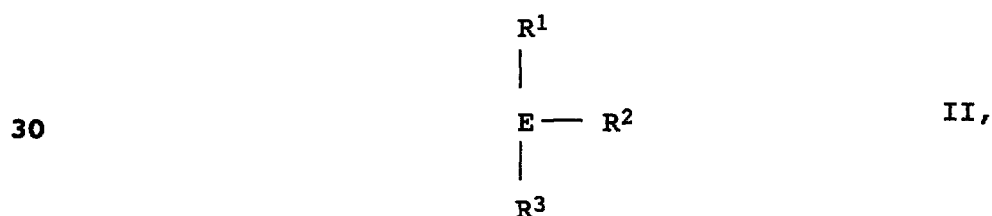
The third catalyst component c) preferably contains as quaternary nitrogen, arsenic or phosphorus compound a compound of the
40 formula (I)



10 where E is nitrogen, phosphorus or arsenic, X⁻ is a halogen-free anion such as a nitrate ion or a hydroxide ion, but particularly preferably an anion of the carboxylic acid formed in the reaction, and R¹, R², R³ and R⁴ are aliphatic radicals such as alkyl groups, which preferably have 1 to 18 carbon atoms and are
15 straight-chain or branched, particularly preferably C₁-C₈-alkyl groups such as methyl, ethyl, n-propyl, n-butyl and octyl.

R¹, R², R³ and R⁴ may also be a cycloaliphatic radical such as cyclopentyl or cyclohexyl, an aromatic radical such as phenyl or
20 an aromatic radical substituted by alkyl groups, such as tolyl or an araliphatic radical such as benzyl.

The third catalyst component c) preferably contains as tertiary nitrogen, phosphorus or arsenic compound a compound of the
25 formula (II)



where E, R¹, R² and R³ have the meanings mentioned above for
35 formula I.

Suitable as nitrogenous heterocyclic compound as third catalyst component c) are pyridine, mono- to tri-C₁-C₄-alkyl-substituted pyridine, quinoline, isoquinoline, pyrimidine, pyridazine,
40 pyrazine, pyrazole, imidazole, thiazole and oxazole, preferably unsubstituted or mono-C₁-C₄-alkyl-substituted pyridine, quinoline, isoquinoline, pyrimidine, pyridazine, pyrazine, pyrazole, imidazole, thiazole and oxazole, and their N-C₁-C₄-alkylated or N,N-C₁-C₄-dialkylated salts with halogen-free anions X⁻, where X⁻
45 has the abovementioned meanings, preferably pyridine,

N-methylpyridinium salts, imidazole and
N,N-dimethylimidazolinium salts.

The molar ratio of the nickel contained in the first component a)
5 of the catalyst system to the second catalyst component b) is
from 1:1 to 100,000:1, preferably 100:1 to 50,000:1. The total
content of the catalytically active metals of components a) and
b) in the reaction solution is from 0.1 to 5% by weight,
calculated as metal. The molar ratio of the nickel in component
10 a) to the third nonmetallic catalyst component c) is generally
from 2:1 to 1:20, preferably 1:1 to 1:10. The content of
nonmetallic catalyst component c) in the reaction solution is
from 1 to 50% by weight.

15 The reaction can be carried out without or with a solvent.
Suitable for this purpose are solvents such as acetone, ether,
dioxane, dimethoxyethane, tetraethylene glycol dimethyl ether,
aprotic polar solvents such as N-methylpyrrolidone [sic] and
aromatic hydrocarbons such as toluene. It is preferred to carry
20 out the reaction to prepare carboxylic acids in the 20-95% by
weight, preferably 50-80% by weight, aqueous carboxylic acid.

Preparation of the carboxylic esters by the process according to
the invention is preferably carried out in the relevant alcohol,
25 which may contain from 1 to 5% by weight of water, as solvent.

The use of aqueous propionic acid as solvent is preferred for
preparing propionic acid.

30 The reaction is usually carried out at from 100 to 270°C,
preferably from 170 to 250°C, under from 30 to 100 bar, preferably
30 to 80 bar, particularly preferably 40 to 60 bar.

The olefin and water starting compounds, and the catalyst system,
35 can be mixed, with or without a solvent, in a reactor before the
reaction. They can then be heated to the reaction temperature,
adjusting the reaction pressure by injecting carbon monoxide or,
when short-chain olefins are used, by injecting a mixture of this
olefin and carbon monoxide.

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The reaction is usually complete after 0.5 to 3 h. It can be
carried out continuously or batchwise in reactors such as tanks,
bubble columns, tubular reactors or circulating reactors.

45 The products of the process are isolated in a preferred
embodiment by decompressing the discharge from the reaction. Then
nickel carbonyl is driven out of the liquid by passing gases such

as air or nitrogen through it. Nickel carbonyl can be separated from the inert gas and worked up to a nickel compound which can then be returned to the reaction. The liquid phase of the discharge from the reaction, which, besides the product, contains soluble or suspended catalyst, is worked up by distillation to isolate the product, where appropriate after precision distillation. The catalyst-containing bottom product from the distillation is returned to the reaction. It is likewise possible to recycle any catalyst constituents removed before the distillation, and volatile catalyst constituents removed as low boilers or as sidestream from a distillation, after appropriate workup.

The process according to the invention allows the products to be prepared with high selectivity and with a high space-time yield.

Examples

Example 1: Batchwise experiments on the preparation of propionic acid

A solution of 2.13 g of basic nickel carbonate and 12 mg of ruthenium acetylacetonate in a mixture of 90 g of propionic acid and 10 g of water was introduced into a 300 ml autoclave with magnetic stirring bar. Then 20 g of a 40% strength aqueous tetrabutylammonium hydroxide solution ($[\text{NBu}_4]\text{OH}$) were added. An initial pressure of 30 bar was then set up with a gas mixture consisting of 50% by volume CO and 50% by volume ethylene, and the reaction solution was heated to 200°C. After the reaction temperature was reached, the final pressure was set at 60 bar, and maintained at this by injecting the CO/ethene gas mixture every quarter hour. After one hour, the mixture was cooled to room temperature and decompressed, and the discharge from the reaction was investigated by titrimetry and gas analysis. The result is shown Table 1.

Example 2

The experiment was carried out as described in Example 1, but 10 g of triethylamine (NEt_3) was employed in place of tetrabutylammonium hydroxide. The result is to be found in Table 1.

Example A

The experiment was carried out as described in Example 1 but without adding a nitrogen compound. The result is shown in Table 1.

Example B

The experiment was carried out as described in Example 1 but without a ruthenium catalyst. The result is shown in Table 1.

Example C

The experiment was carried out as described in Example 1 but without a nickel catalyst. The result is shown in Table 1.

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Table 1

Example	Ni [mmol]	Ru [mmol]	Base [mmol]	STY(PA) [g/l/h]	S(PA) [%]	Ethane [l/h]	S(Ethane) [%]	S(P) [%]	S(DEK) [%]
1	17	0.03	30 [NBu ₄]OH	137	81	0.8	15	1.4	0.5
2	17	0.03	86 NEt ₃	165	83	1.0	16	-	-
A	17	0.03	-	20	40	0.9	30	1.4	0.5
B	17		30 [NBu ₄]OH	-	-	0.2	65	11	24
C		0.03	30 [NBu ₄]OH	2	6	0.8	33	9	14

STY = Space-time yield

S = Selectivity

PA = Propionic acid

P = Propionaldehyde, byproduct

DEK = Diethyl ketone, byproduct

% = percent by weight

It was possible in Examples 1 and 2 according to the invention to obtain distinctly higher space-time yields and selectivities with a catalyst consisting of nickel, ruthenium and tetrabutylammonium hydroxide or triethylamine under 60 bar than in Comparative Experiment A with the two metallic catalyst components alone. Comparative Examples B and C illustrate that addition of tetrabutylammonium hydroxide to one of the two catalyst metals does not result in an active catalyst system. Experiments 1, 2, A and C show that the added nitrogen components in particular speed up the carboxylation reaction, but far less the formation of the byproducts ethane, propionaldehyde and diethyl ketone.

Example 3

A solution of 2.13 g of basic nickel carbonate and 12 mg of ruthenium acetylacetonate in a mixture of 60 g of propionic acid and 40 g of a 40% strength aqueous tetrabutylammonium [sic] hydroxide solution was introduced into a 300 ml autoclave equipped with a gas-introduction stirrer (1000 rpm). An initial pressure of 30 bar was then set up with a gas mixture consisting of 50% by volume CO and 50% by volume ethylene, and the reaction solution was heated to 200°C. After the reaction temperature was reached, the final pressure of 75 bar was set up and kept constant by a continuous injection of the CO/ethene gas mixture. After two hours, the mixture was cooled to room temperature and decompressed, and the discharge from the reaction was investigated by titrimetry and gas analysis. The result is shown in Table 2.

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Example D

A solution of 2.13 g of basic nickel carbonate and 12 mg of ruthenium acetylacetonate in a gas mixture consisting of 50% by volume CO and 50% by volume ethylene in the autoclave described in Example 3 was adjusted to an initial pressure of 30 bar, and the reaction solution was heated to 200°C. After the reaction temperature was reached, the final pressure was adjusted to 75 bar and kept constant by continuous injection of the CO/ethene gas mixture. After two hours, the mixture was cooled to room temperature and decompressed, and the discharge from the reaction was investigated by titrimetry and gas analysis. The result is shown in Table 2.

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Example 4

The experiment was carried out as described in Example 3 but under 55 bar. The result is shown in Table 2.

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Example 5

The experiment was carried out as described in Example 3 but with 60 g of propionic acid, 25 g of a 40% strength aqueous
10 tetrabutylammonium [sic] hydroxide solution and 15 g of water as solvent and under 55 bar. The result is shown in Table 2.

Example E

15 The experiment was carried out as described in Example D but under 55 bar. The result is shown in Table 2.

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Table 2

Exam- ple	p [bar]	Ni [mmol]	Ru [mmol]	Base [mmol]	STY(PA) [g/l/h]	S(PA) [%]	Ethane [l/h]	S(Etha- ne) [%]	S(P) [%]	S(DEK) [%]
3	75	17	0.03	60 [NBu ₄]OH	349	95	0.4	2.4	0.6	0.6
D	75	17	0.03	-	133	91	0.3	5.1	0.8	1.1
4	55	17	0.03	60 [NBu ₄]OH	176	90	0.6	6.8	0.6	0.4
5	55	17	0.03	37 [NBu ₄]OH	208	92	0.5	5.2	0.5	-
E	55	17	0.03	-	86	85	0.3	8.9	0.5	0.4

STY = Space-time yield
 S = Selectivity
 PA = Propionic acid
 P = Propionaldehyde, byproduct
 DEK = Diethyl ketone, byproduct
 % = percent by weight

Example 6

A solution of 2.13 g of basic nickel carbonate and 12 mg of
5 ruthenium acetylacetonate in a mixture of 80 g of propionic acid
and 20 g of a 40% strength aqueous tetrabutylammonium hydroxide
solution ($[H_2O]=12$ g) was introduced into a 300 ml autoclave with
magnetic stirring bar. An initial pressure of 30 bar was then set
up with a gas mixture consisting of 50% by volume CO and 50% by
10 volume ethylene, and the reaction solution was heated to 200°C.
After the reaction temperature was reached, the final pressure
was set at 60 bar, and maintained at this by injecting the
CO/ethene gas mixture every half hour. After two hours, the
mixture was cooled to room temperature and decompressed. 126 g of
15 liquid discharge were obtained from the reaction. Analysis by gas
chromatography and titrimetry revealed the composition shown in
Table 3.

Example 7

20 A solution of 2.13 g of basic nickel carbonate and 12 mg of
ruthenium acetylacetonate in a mixture of 90 g of propionic acid
and 10 g of water and 10 g of triethylamine was introduced into a
300 ml autoclave with magnetic stirring bar. An initial pressure
25 of 30 bar was then set up with a gas mixture consisting of 50% by
volume CO and 50% by volume ethylene, and the reaction solution
was heated to 200°C. After the reaction temperature was reached,
the final pressure was set at 60 bar, and maintained at this by
injecting the CO/ethene gas mixture every half hour. After two
30 hours, the mixture was cooled to room temperature and
decompressed. 134 g of liquid discharge were obtained from the
reaction. Analysis by gas chromatography and titrimetry revealed
the composition shown in Table 3.

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Table 3

Example	P [bac [sic]]	NI [sic] [mmol]	Ru [mmol]	Base [mmol]	STY(PA) [g/l/h]	PA [%]	P [%]	DEK [%]	H ₂ O %
6	100	17	0.03	30 [NBu ₄]OH	152	87.5	0.2	0.2	2.1
7	100	17	0.03	86 NEt ₃	157	90.7	0.1	0.2	<0.1

Examples 6 and 7 illustrate that the catalyst system consisting of a nickel compound, a ruthenium compound and a nitrogenous compound such as triethylamine or tetrabutylammonium hydroxide 5 has a high activity even with a very low water concentration.

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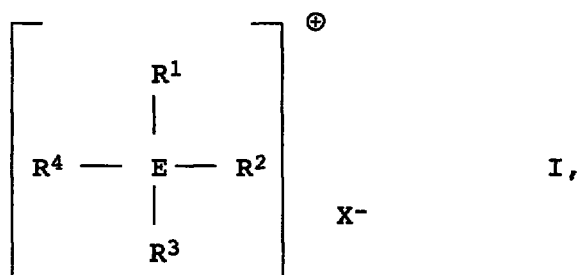
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We claim:

1. A process for preparing carboxylic acids or their esters from olefins and carbon monoxide in the presence of water or alcohols at from 100 to 270°C under from 30 to 100 bar, which comprises employing as halogen-free catalyst system a mixture of
 - a) nickel or a nickel compound,
 - b) at least one metal from the group of chromium, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold or a compound of these metals and
 - c) at least one nonmetallic compound from the group of tertiary or quaternary nitrogen, phosphorus or arsenic compounds and of nitrogenous heterocyclic compounds.
2. A process for preparing carboxylic acids or their esters as claimed in claim 1, wherein the components of the catalyst system are present in an a):b):c) molar ratio of from 1:1:0.5 to 100,000:1:200,000.
3. A process for preparing carboxylic acids or their esters as claimed either of claims 1 and 2, wherein the catalyst system comprises a quaternary compound of the formula (I)



where E is nitrogen, phosphorus or arsenic, R^1 , R^2 , R^3 and R^4 are an aliphatic, cycloaliphatic, araliphatic or aromatic radical and X^- is a halogen-free anion.

4. A process for preparing carboxylic acids or their esters as claimed in any of claims 1 to 3, wherein the catalyst system comprises a tertiary compound of the formula (II)

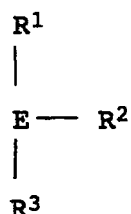
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II,

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where E is nitrogen, phosphorus or arsenic, and R^1 , R^2 and R^3 are an aliphatic, cycloaliphatic, araliphatic or aromatic radical.

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5. A process for preparing carboxylic acids or their esters as claimed in either of claims 1 and 2, wherein the content of nonmetallic compound c) in the reaction solution is from 1 to 50% by weight.

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6. A process for preparing carboxylic acids or their esters as claimed in any of claims 1 to 5, wherein the reaction solution comprises 0.5 - 10 mol of water per mole of olefin.

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7. A process for preparing carboxylic acids or their esters as claimed in any of claims 1 to 6, wherein the reaction is carried out at from 170 to 250°C under from 40 to 60 bar.

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8. A process for preparing carboxylic acids or their esters as claimed in any of claims 1 to 7, wherein carbon monoxide and the olefin are employed in the molar ratio from 5:1 to 1:5.

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9. A process for preparing carboxylic acids or their esters as claimed in any of claims 1 to 7, wherein ethylene is employed as olefin.

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10. A halogen-free catalyst system as defined in at least one of claims 1 to 4, suitable for carrying out processes for preparing carboxylic acids or their esters as defined in at least one of claims 1 to 9.

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11. The use of a catalyst system as defined in at least one of claims 1 to 4 for preparing carboxylic acids or their esters from olefins and carbon monoxide in the presence of water or alcohols.

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