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(54) PROCESS FOR PREPARING ESTERS FROM LOWER HOMOLOGOUS ETHERS OR ESTERS

(71) We, MONTEDISON S.p.A, an Italian body corporate of 31 Foro Buonoparte, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

5 This invention relates to a process for preparing esters and in particular to the preparation 5 of esters by carbonylation of ethers or esters of lower homologous alcohols.

Esters are employed as solvents in several application fields.

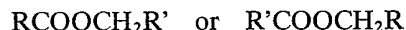
10 Esters of aliphatic carboxylic acids may be prepared starting from alcohols having one carbon atom less than the acid or from the ethers derived from such alcohols, by reaction with 10 carbon monoxide and hydrogen at high temperatures and pressures, with catalysts consisting of cobalt or nickel as disclosed in United States Patent Specification No. 2,457,204 and Y. Y. Aliev et al. Dokl. Akad. Nauk Uzbek SSR 1960 (9) 37.

15 Esters are also obtained as by-products of the synthesis of carboxylic acids from alcohols: for example, methyl acetate is obtained as a by-product of the synthesis of acetic acid from 15 methanol catalyzed by cobalt (German Patent No. 921,938) or by rhodium (Italian Patent No. 836,365).

20 Considering the esters as compounds derived from the reaction between an acid and an alcohol by elimination of a water molecule, the processes described above yield esters of the starting alcohol or, in the case when starting from an ether, esters of the alcohol, of which the 20 ether may be considered a derivative. Only the acid radicle has in its chain a carbon atom more than the starting compounds.

25 United States Patent Specification No. 3,285,948 discloses the reaction conditions for the additional carbon monoxide and hydrogen to an alcohol in order to obtain the higher homologous alcohol. Such processes, however require critical conditions and do not yield 25 corresponding esters.

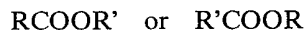
According to the present invention there is provided a process for preparing esters having the general formula:



30 in which R and R' may be the same or different and each represents a linear or branched alkyl 30 group containing 1 to 16 carbon atoms, in which carbon monoxide and hydrogen are reacted, at a temperature in the range 150 to 350°C and at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:

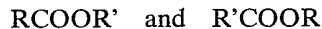


35 or esters of the formula:



35 in which R and R' are as defined above, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor hydroiodic acid, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of a tetraalkylammonium bromide or iodide or any combination thereof. 40

40 Also according to the invention there is provided a process for preparing esters having the general formula:



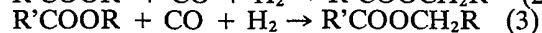
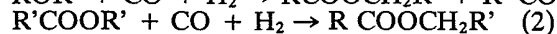
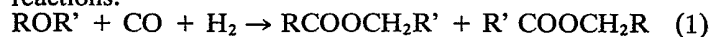
45 in which R and R' are defined above, in which carbon monoxide and hydrogen are reacted, at a temperature in the range 150 to 45 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:

## R O R'

in which R and R' are as defined above, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promoter hydroiodic acid, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of a tetraalkylammonium bromide or iodide or any combination thereof.

The invention provides a process by which it is possible to attain good yields of esters of higher homologous alcohols with respect to those from which the starting compounds may be considered as derived from.

The process according to the invention may be represented by one of the following reactions:



When the process starting from the ethers according to the reaction 1 is followed it is assumed that, as an intermediate reaction, the esters constituting the starting compounds of reactions (2) and (3) may form. This intermediate reaction (which, however, has been already indicated as possible under different conditions and with other catalyst systems) may be represented as follows:



Thus, for example, by reacting carbon monoxide and hydrogen with dimethylether, a mixture of products is obtained, that prevailingly consists of methyl acetate and ethyl acetate in ratios varying according to the reaction conditions.

Since a side reaction to the reaction which gives place to the formation of the desired products, that is of the homologous higher esters R'COOCH<sub>2</sub>R' and R'COOCH<sub>2</sub>R, starting from ROR' ether, may be represented by the attach of a carboxylic acid, used as a solvent, on the starting ether, carboxylic acids of formula R''COOH in which R'' represents an alkyl or cycloalkyl radical having up to 8 carbon atoms and may be the same or different to R and R', prove to be useful as solvents in the process of the invention.

Preferred carboxylic acids are those whose radical R'' is equal to R or R' since in such a case the esters that are formed are intermediates of the synthesis of the end product. Those acids may moreover, be present in their turn as by-products of the reaction according to the process under examination.

For example, in the carbonylation reaction of the dimethylether to ethyl acetate, a particular suitable solvent is acetic acid. Operating with such a solvent results in the formation of methyl acetate which may be considered an intermediate product of the main synthesis, without accumulating in the reaction mixtures. Moreover, the acetic acid forms as a by-product of the carbonylation reaction, and under suitable conditions, the quantity produced corresponds to the amount consumed.

Ruthenium compounds suitable for use in the process on the invention are ruthenium carbonyls e.g. Ru<sub>3</sub>(CO)<sub>12</sub>, Ru(CO)<sub>4</sub>I<sub>2</sub>, RuCl(A-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>3</sub> and [Ru(CO)<sub>3</sub>Br<sub>2</sub>]<sub>2</sub> or the compounds that, under reaction conditions, form ruthenium carbonyls "in situ" e.g. subdivided metallic ruthenium, ruthenium acetylacetonate, ruthenium salts of carboxylic acids, sodium hexachloro-ruthenate, ammonium hexachloro-ruthenate, ruthenium triiodide and ruthenium tribromide.

Compounds suitable for use as a promoter in the catalyst system are hydroiodic acid or its precursors such as elementary iodine or its organic compounds which, as is known from M. Busch, H. Stove-Berichte vol. 49, 1063 - 1916, in the presence of hydrogen at high temperatures yield HI, and carboxylic acid solution of inorganic iodides or bromides or iodides or bromides of tetraalkylammonium. Preferred organic iodides are the alkyl or alkyaryl iodides having 1 to 20 carbon atoms. Preferred carboxylic acid solutions are acetic and propionic solutions of the alkali metal iodides and bromides, of alkaline-earth metal iodides and bromides, of Fe, Co, Ni, Zn, Cd, Sn<sup>++</sup> iodides, of the tetraalkylammonium iodides or any combination thereof.

The iodide/ruthenium atom ratio that is particularly suited for use in the process according to the invention are in the range 2:1 to 10:1. The reaction is conducted at a temperature in the range 150 to 350°C, preferably in the range 180 to 250°C.

The H<sub>2</sub> + CO partial pressure shall be at least 50 atmospheres, the total pressure having to be such, as to ensure that at least a part of the reagents may be in the liquid phase. The H<sub>2</sub>/CO ratio in the reaction mixture may range from 0.1:1 to 2:1 higher hydrogen concentrations do not badly affect the reaction trend, but may limit its selectivity, thus favouring the forming of methane.

The best suited reaction medium consists in the reagents themselves or in the reaction by-products, in which the catalyst is dissolved. It is possible to use solvents such as aromatic hydrocarbons, for example toluene or a carboxylic acid as described above in addition to when it is not present in the catalytic system.

A reaction mixture particularly suitable to the process of invention comprises an ether RCOR' with the ester, or a mixture of esters, RCOOR' + R'COOR, that are generally less volatile than the ether itself. The catalytic system as described above, the solvent and the ether or the ester, or mixtures thereof, are fed to an autoclave in a H<sub>2</sub> and CO atmosphere. The autoclave is heated to the reaction temperature and the desired pressure maintained by feeding a H<sub>2</sub> + CO mixture. At the conclusion of the reaction the desired products can be easily separated from the resulting mixture by fractionated distillation. The by-products, non-homologous esters and non-esterified carboxylic acids may be employed in a further reaction.

The process according to this invention offers several advantages. The main advantage is that it is possible to utilize the by-products of other processing e.g. dimethylether, a by-product of the methanol synthesis, and methyl acetate, a by-product of the acetic acid synthesis for the preparation of higher homologous esters. Another advantage is that the reaction may be carried out in a single step.

The invention will now be illustrated with reference to the Examples.

*Example 1*

25 ml of toluene, 0.38 m.moles of RuCl( $\pi$ -C<sub>3</sub>H<sub>5</sub>) (CO)<sub>3</sub> (prepared according to the method described by G. Sbrana, G. Braca, F. Piacenti and P. Pino, J. Organometal. Chem., 13, 240 (1968) and 1.52 m.moles of CH<sub>3</sub>I corresponding to a I/Ru ratio = 4, were introduced into 100cm<sup>3</sup> autoclave made of Hastelloy C. 0.195 m.moles of gaseous dimethylether were condensed in the autoclave cooled under vacuum, and 50 atm. of H<sub>2</sub> and 100 atm. of CO were fed into the autoclave. The autoclave was then heated to 200°C maintaining a pressure of 240 atmospheres by feeding the H<sub>2</sub> + CO mixture in a 2:1 ratio.

After 18.5 hours the autoclave was cooled to yield a solution which was markedly acid and the products were subjected to a gas chromatographic analysis.

The conversion of the starting ether was of 42.5%, the yields (referred to the converted product) were:

CH <sub>4</sub>	12.8%
Alcohols (Me, Et, Pr)	13.0%
Higher ethers	4.5%
Methyl acetate	42.3%
Ethyl acetate	16.0%
Acids (acetic, propionic)	6.0%

*Examples 2 to 8*

A number of carbonylation reactions were conducted at a temperature of about 200°C at a catalyst concentration of 1.5 · 10<sup>-2</sup> gram atoms/litre. The other reaction conditions and products are reported in the following Table.

Examples	CATALYST SYSTEM		REACTION CONDITIONS					REACTION PRODUCTS				
	TYPE	I/Ru ratio	REAGENT and SOLVENT (moles)	initial CO prcs. atm	initial H <sub>2</sub> prcs atm	H <sub>2</sub> /CO initial (final)	P/in hot conditions atm	Time required hours	H <sub>2</sub> /CO fed	Conv. %	YIELDS* Product (moles)	%
2	Ru(CO) <sub>2</sub> /CH <sub>3</sub> I	10	dimethyl-ether (0.125) toluene (25 ml)	100	50	0.5 (1.1)	242	28.5	2	84.8	CH <sub>4</sub>	21.6
							265				Alcohols (Me, Et, Pr)	2.3
											Higher ethers	3.2
3	Ru(Acac) <sub>3</sub> /CH <sub>3</sub> I	10	dimethyl-ether (0.123) toluene (25 ml)	100	50	0.5 (0.77)	235	28.5	1	86	Methyl acetate	20.7
							280				Ethyl acetate	19.3
											Other esters	4.3
											Acids	18.8
											CH <sub>4</sub>	20.8
4	Ru(Acac) <sub>3</sub> /CH <sub>3</sub> I	10	dimethyl-ether (0.124) toluene (25 ml)	125	25	0.2 (0.92)	240	28.5	1	92	Alcohols (Me, Et, Pr)	7.8
							270				Higher ethers	1.3
											Methyl acetate	3.2
											Ethyl acetate	50.1
											Methyl propionate	18.4
5	Ru(Acac) <sub>3</sub> /CH <sub>3</sub> I	10	dimethyl-ether(0.1) acetic acid (0.430)	135	30	0.22 (0.49)	250	26.5	0.5	>95 <sup>n</sup>	**	15.0
							270				CH <sub>4</sub>	10.8
											Alcohols (Me, Et)	2.6
											Higher ethers	2.1
											Methyl acetate	42.3
	Ethyl acetate	Acetic acid (0.343)	42.2									
		Propionic acid (0.006)										
			2.0									

CATALYST SYSTEM			REACTION CONDITIONS					REACTION PRODUCTS				
EX-AMPLI-FS	TYPE	I/Ru ratio	REAGENT and SOLVENT (moles)	initial CO press. atm.	initial H <sub>2</sub> pres atm.	H <sub>2</sub> /CO initial (final)	P/ in hot conditions atm.	Time required hours	H <sub>2</sub> /CO fed	Conv. %	YIELDS Product	%
6	RuCl( $\pi$ -C <sub>3</sub> H <sub>5</sub> )(CO) <sub>2</sub> CH <sub>2</sub> I	4	diethyl-ether (0.20) toluene (2.5 ml)	100	50	0.5 (0.69)	238 262	15	2	54.3	C <sub>3</sub> H <sub>6</sub> Alcohols Higher ethers Ethyl Propionate Propylpropionate Acids	21.8 8.7 3.6 46.7 2.7 5.3
7	RuCl( $\pi$ -C <sub>3</sub> H <sub>5</sub> )(CO) <sub>2</sub> CH <sub>2</sub> I	8	methyl acetate (0.364)	88	67	0.76 (1.0)	240 260	16	2	33.2	CH <sub>4</sub> Alcohols Acids Ethyl acetate Propylacetate	12.9 9.4 29.4 46.7 2.4
8	Ru(AcAc) <sub>2</sub> CH <sub>2</sub> I	10	dimethyl-ether (0.123) methyl acetate (0.312)	125	25	0.2 (0.62)	235 270	28	0.5	99.8* 30.4* CO <sub>2</sub> % 1.0	CH <sub>4</sub> Alcohol Ethers + acetal Acids Ethyl acetate	10.8 2.9 1.5 32.2 44.6

\* calculated in respect to the disappeared reagent

\*\* calculated on the reacted dimethyl/ether

a) dimethyl/ether conversion

b) acetic acid conversion

c) methyl acetate conversion

l) ruthenium acetylacetonate

*Example 9*

This example was performed to prove that if no free HI is present in the reacting medium as in the previous examples, the reaction does not proceed.

The procedure of Example 1 was adopted and 0.15 moles of methyl acetate, 0.38 m. moles of  $\text{Ru}(\text{CO})_4\text{I}_2$  (the I/Ru ratio = 2) and 0.061 moles of dimethylether were charged into 100  $\text{cm}^3$  autoclave. Successively, 25 atm. of  $\text{H}_2$  and 125 atm. of CO in a  $\text{H}_2/\text{CO}$  ratio = 0.2 were fed into the autoclave and the autoclave was then heated to 200°C, maintaining a pressure of 260 atmospheres. After 8 hours virtually no reaction had taken place; negligible amounts of alcohols, methane and acetic acid were obtained. The discharged solution was practically neutral.

*Example 10*

0.1 moles of dimethylether and 0.43 moles of acetic acid were introduced into a Hastelloy C autoclave having a holding capacity of 100  $\text{cm}^3$ . The catalytic system, consisting of Ruthenium trisacetylacetonate (0.4 m. moles) and sodium iodide (4 m. moles) corresponding to a I/Ru = 10 was fed in to the autoclave with the solvent.

The autoclave was then pressurized with a  $\text{H}_2 + \text{CO}$  mixture in a ratio  $\text{H}_2:\text{CO} = 0.5$  at 150 atm., and the temperature was raised to 200°C, maintaining a pressure of 250 atm. for 28 hours. When the reaction was complete, the products were discharged and then analyzed by gas chromatography.

The conversion of the starting ether was 70% and the yields were:

	Methane	4.4%	
	Methyl alcohol	2.1%	
	Propyl alcohol	0.3%	
25	Propionic acid	0.6%	25
	Ethyl ether	1.1%	
	Methyl acetate	12%	
	Ethyl acetate	79%	

*Example 11*

The catalytic system used in Example 10 was recovered by the distillation of the reaction products and of part of the acetic acid and was mixed dimethylether and acetic acid in such amounts was to get respectively 0.1 moles and 0.43 moles.

Operating under the same conditions as those described in Example 10 for a period of 8 hours, resulted in a conversion of 70% and the following yields:

	Methane	traces	35
	Methyl alcohol	0.6 %	
	Ethyl ether	0.2 %	
	Methylethylether	0.4 %	
40	Methyl acetate	38.7 %	40
	Ethyl acetate	54.6 %	

*Example 12*

Adopting the same procedure as Example 10 there were introduced 0.1 moles of dimethylether and 0.43 moles of propionic acid, and a catalytic system, consisting of  $\text{Ru}(\text{CO})_4\text{I}_2$  (0.4 m. moles) and of NaI (4 m. moles) equal to a I/Ru ratio of 10, was fed into a Hastelloy C autoclave of 100 cc holding capacity together with the solvent.

The autoclave was pressurized with an  $\text{H}_2 + \text{CO}$  mixture having a ratio  $\text{H}_2:\text{CO} = 1$ , at 150 atm., the temperature raised up to 200°C and the pressure maintained at 250 atm., for 18 hours.

When the reaction was completed, the products were discharged and then analyzed by gas chromatography.

A conversion of 70% was obtained and the following yields:

	Methane	4 %	
55	Ethyl alcohol	0.36 %	55
	Propionic acid	3 %	
	Methylethylether	0.284 %	
	Methyl acetate	2.5 %	
	Ethyl acetate	56.8 %	
60	Methyl propionate	15.15 %	60
	Ethyl propionate	11 %	
	Propyl propionate	9.6 %	

*Example 13*

A mixture consisting of 0.1 moles of dimethylether, 0.23 moles of acetic acid and 0.19 moles of methyl acetate, was reacted for 25 hours under the same conditions as those

described in Example 10 using the same catalytic system.

A conversion of the starting ether amounting to 54.3% was obtained and the following yields:

5	Methane	9.2%	5
	Ethyl alcohol	0.5%	
	Acetic acid	10.5%	
	Ethyl acetate	60.6%	
	Propyl acetate	1%	

*Example 14*

A mixture of 0.1 moles of dimethylether and 0.43 moles of acetic acid were reacted operating under the same conditions as those described in Example 10 in the presence of a catalytic system consisting of 0.4 m. moles of ruthenium trisacetylacetonate and 4 m. moles of NaBr, for a period of 28 hours.

5 A conversion of the kimethylether of 54.8% was obtained and the following yields 15

	Methylethyl ether	0.2%	
	Ethyl ether	0.9%	
	Methylacetate	34.3%	
0	Ethylacetate	8.9%	20

*Example 15*

Adopting the same procedure as in Example 10 0.1 moles of dimethylether 0.43 moles of acetic acid and a catalytic system consisting of 0.4 m. moles of ruthenium trisacetylacetonate and 4 m. moles of  $\text{CH}_3\text{I}$  equal to a  $\text{I/Ru} = 10$  were introduced into a Hastelloy C autoclave of 100 cc holding capacity together with the solvent.

5 The autoclave was pressurized with a  $\text{H}_2 + \text{CO}$  mixture in a ratio  $\text{H}_2:\text{CO} = 0.5$  at 150 atm. and the temperature raised to  $200^\circ\text{C}$ , and a pressure of 250 atm. maintained for 28 hours. A conversion of the starting ether of 95% was obtained with the following yields 25

0	Methane	5%	30
	Methyl alcohol	1.2%	
	Propyl alcohol	2.3%	
	Ethyl ether	1.0%	
	Methyl acetate	38.4%	
5	Ethyl acetate	38.0%	35

*Example 16*

A mixture consisting of 0.1 moles of dimethylether, 0.23 moles of acetic acid and 0.19 moles of methyl acetate was introduced into the autoclave with the same catalytic system of Example 15.

0 The autoclave was then pressurized with a  $\text{H}_2 + \text{CO}$  mixture in a ratio  $\text{H}_2:\text{CO} = 1$  at 150 atm., the temperature raised up to  $200^\circ\text{C}$  and a pressure of 250 atm. maintained for 14 hours. A conversion of the starting ether of 58.4% was obtained with the following yields 40

5	Methane	8.6%	45
	Methyl alcohol	5.5%	
	Ethyl alcohol	1.55%	
	Acetic acid	1%	
	Propionic acid	1.2%	
	Methylethylether	2.3%	
0	Ethylether	0.7%	50
	Ethylacetate	73%	
	Methyl propionate	0.5%	
	Ethyl propionate	0.13%	

*Example 17*

5 A mixture of 0.1 moles of dimethylether, 0.23 moles of acetic acid and 0.19 moles of methylacetate was reacted for 15.5 hours under the same conditions as described in Example 16, the catalytic system consisted of 0.4 m. moles of ruthenium tris-acetylacetonate and 2 m. moles of  $\text{CH}_3\text{I}$  and 1 m. mole of  $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$  corresponding to a  $\text{I/Ru} = 10$ . 55

A conversion of 76.2 % was obtained with the following yields: 60

0	Methane	9.66%	60
	Methyl alcohol	4.65%	
	Ethyl alcohol	1.95%	
	Acetic acid	0.95%	
5	Methyl formiate	0.22%	65

Methylethylether	0.75%
Ethyl ether	traces
Ethyl acetate	79.2%
Methyl propionate	2.26%

5 *Example 18* 5

A mixture of 0.2 moles of dimethylether, 0.15 moles of acetic acid and 0.13 moles of methylacetate was reacted for 5 hours at 200°C and a pressure of 350 atm. The catalytic system consisted of 0.66 moles of ruthenium tris-acetylacetonate, 2 m.moles of CH<sub>3</sub>I and 4 m.moles of NaI corresponding to a J/Ru = 10.

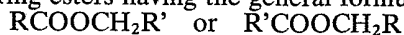
10 A conversion of 35% of dimethylether was obtained with the following yields: 10

Methane	5%
Methyl alcohol	10.2%
Ethyl alcohol	2.1%
Methyl formiate	1.3%
Ethyl ether	10.1%
Ethyl acetate	68%
Methylethylether	2.7%

15 20 The word "Hastelloy" is a registered Trade Mark. 20

#### WHAT WE CLAIM IS:

1. A process for preparing esters having the general formula:



25 in which R and R' may be the same or different and each 25  
represents a linear or branched alkyl group  
containing 1 to 16 carbon atoms,

in which carbon monoxide and hydrogen are reacted, at a temperature in the range 150 to 350°C and at a pressure in the range 50 to 1000 atmospheres, with an ether of the formula:



30 or esters of the formula: 30



in which R and R' are as defined above,

35 in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor 35  
hydroiodic acid, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic  
acid solution of tetraalkylammonium bromide or iodide or any combination thereof.

2. A process for preparing esters having the general formula: RCOOR' and R'COOR

in which R and R' are as defined in Claim 1,

40 in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 40  
350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:



45 in which R and R' are as defined in Claim 1, in the presence of a catalyst system comprising a 45  
ruthenium carbonyl and as a promoter hydroiodic acid, a carboxylic acid solution of an  
inorganic bromide or iodide, a carboxylic acid solution of a tetraalkylammonium bromide or  
iodide or any combination thereof.

3. A process as claimed in Claim 1 or Claim 2 in which the ruthenium carbonyl is  
Ru<sub>3</sub>(CO)<sub>12</sub>, [Ru(CO)<sub>3</sub>Br<sub>2</sub>]<sub>2</sub>, Ru(CO)<sub>4</sub>I<sub>2</sub> or RuCl(π-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>3</sub>.

4. A process as claimed in Claim 1 or Claim 2 in which the ruthenium carbonyl is formed  
"in situ" from subdivided metallic ruthenium, ruthenium acetylacetonate, ruthenium salts of  
50 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexach- 50  
lororuthenate or ruthenium tribromide.

5. A process as claimed in any preceding claim in which the promoter is a carboxylic acid  
solution of an inorganic iodide or bromide salt; a carboxylic acid solution of a tetraalkylam-  
monium iodide or bromide or any combination thereof.

55 6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is 55  
an alkali metal or alkaline-earth metal iodide or bromide.

7. A process as claimed in Claim 5 in which the inorganic iodide or bromide is selected  
from Na and K iodides, Na and K bromides, Fe, Co, Ni, Zn, Cd and Sn<sup>++</sup> iodide.

60 8. A process as claimed in any of claims 1 to 4 in which the promoter is hydroiodic acid or 60  
is formed "in situ" from iodine compounds capable of forming HI in the reaction conditions.

9. A process as claimed in Claim 8 in which the hydroiodic acid is formed "in situ" under  
the reaction conditions from elementary iodine or organic iodides.

10. A process as claimed in Claim 9 in which the organic iodides are alkyl or alkylaryl  
iodides having 1 to 20 carbon atoms.

65 11. A process as claimed in any preceding claim in which the carboxylic acid is acetic acid 65  
or propionic acid.



12. A process as claimed in any preceding claim in which the reaction is conducted at a temperature in the range 180 to 250°C.

13. A process as claimed in any preceding claim in which the reaction is conducted under pressure in the range 100 to 400 atmospheres.

5 14. A process as claimed in any preceding claim in which the reaction is conducted in the presence of a solvent. 5

15. A process as claimed in Claim 14 in which the solvent is a carboxylic acid of the formula R<sup>n</sup>COOH in which R<sup>n</sup> represents an alkyl or cycloalkyl group having 8 carbon atoms, an ester thereof, an aromatic hydrocarbon or any combination thereof.

10 16. A process as claimed in any preceding claim in which the H<sub>2</sub>/CO mole ratio in the reaction mixture is in the range 0.1:1 to 2:1. 10

17. A process as claimed in any preceding claim in which the iodide/ruthenium atom ratio in the reaction mixture is in the range 2:1 to 10:1.

15 18. A process for the preparation of esters substantially as herein described with reference to any of Examples 1 to 8 and 10 to 18. 15

19. An ester when prepared by a process as claimed in any preceding claim.

For the Applicants:  
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