## PATENT SPECIFICATION 1 574 096 (11)

(22) Filed 27 Jul. 1977 (21) Application No. 31620/77 (19)Convention Application Nos. 25782 (32) Filed 28 Jul. 1976 (31)7 Apr. 1977 in 22223 (33)Italy (IT) (44) Complete Specification Published 3 Sep. 1980 C07C 69/02 (51) INT. CL.<sup>3</sup> (52)Index at Acceptance C2C 20Y 30Y 366 368 37X 408 43X 491 628 AB CE FB (72) Inventors: GIUSEPPE BRACA GLAUCO SBRANA GUGLIELMO GREGORIO (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 of esters by carbonylation of ethers or esters of lower homologous alcohols. Esters are employed as solvents in several application fields. 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. 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 methanol catalyzed by cobalt (German Patent No. 921,938) or by rhodium (Italian Patent No. 836,365). 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. 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: RCOOCH<sub>2</sub>R' or R'COOCH<sub>2</sub>R in which R and R' may be the same or different and each represents a linear or branched alkyl 30 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: ROR' or esters of the formula: 35 RCOOR' or R'COOR 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 hydroiôdic 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: RCOOR' and R'COOR

in which carbon monoxide and hydrogen are reacted, at a temperature in the range 150 to

350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:

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in which R and R' are defined above,

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ROR'

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:

ROR' + CO +  $H_2 \rightarrow RCOOCH_2R' + R'COOCH_2R$  (1) R'COOR' + CO +  $H_2 \rightarrow RCOOCH_2R'$  (2) R'COOR + CO +  $H_2 \rightarrow R'COOCH_2R$  (3)

When the process starting from the ethers according to the reaction 1 is followed it is 15 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:

 $R'OR' + CO \rightarrow R COOR' + R' COOR$  (4)

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 30 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 byproduct 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.  $Ru_3(CO)_{12}$ ,  $Ru(CO)_4I_2$ ,  $RuCl(A - \dot{C}_3H_5)(CO)_3$  and  $[Ru(CO)_3Br_2]_2$  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++ iodides, of the tetraalkylammonium iodides or any

combination thereof. The iodide/ruthenium atom ratio that is particularly suited fro 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  $H_2 + CO$  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

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.

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5	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 $H_2$ and CO atmosphere. The autoclave is heated to the reaction temperature and the desired pressure maintained by feeding a $H_2$ +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	5
0	reaction.  The process according to this invention offers several advantages. The main advantage is that it is possible to utilize the by-products of otherprocessing 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.	10
5	The invention will now be illustrated with reference to the Examples.	15
0	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 $100 \text{cm}^3$ 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 $200^{\circ}\text{C}$ maintaining a pressure of 240 atmospheres by feeding the H <sub>2</sub> + CO instaure in a 2:1 ratio.	20
5	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:	25
	$CH_4$ 12.8%	
	Alcohols (Me, Et, Pr) 13.0%	
	Higher ethers 4.5%	
	Methyl acetate 42.3%	

CH₄	12.0%
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	

Examples 2 to 8
A number of carbonylation reactions were conducted at a temperature of about 200°C at a catalyst concentration of  $1.5 \cdot 10^{-2}$  gram atoms/litre. The other reaction conditions and products are reported in the following Table.

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	<b>8</b>	21.6 2.3 3.2 20.7 19.3	20.8 20.8 2.9 31.7 18.4 3.6 17.8	7.8 1.3 3.2 50.1 18.4 3.3	10.8 2.6 2.1 42.3
TS	: H				
REACTION PRODUCTS	YIELDS* Product (moles)	CTII, Alcohols (Mc. iit. Pr) Higher ethers Methyl acetate Ethyl acetate Other esters Aeids	CH, Alcohols (Me, Et, Pr) Higher ethers Methyl acetate Ethyl acetate Methylpropionate Acids	CH4 Alcohols (Mc, Et, Pr) Higher ethers Methyl acetate Ethyl acetate Methyl propionate Acids	CH, Alcohols (Me, Et) Higher ethers Methyl acctate Ethyl acctate Acctic acid (0.343) Propionic acid (0.006)
	Conv.	84.8 CO <sub>2</sub> % 8.4	86 CO2% 3.0	92 CO2% 1.1	>95" 21 <sup>h</sup> CO <sub>2</sub> % 2.0
	H <sub>2</sub> /CO		<b>-</b>	-	. · · · · · · · · · · · · · · · · · · ·
	Time requi- red bours	23. 8.	28.5	28.5	26.5
	P/in hot con- ditions atm	245 265 265	235 	240 	250 
ONS	H <sub>2</sub> /CO initial (final)	0.5	0.5	(0.92)	0.22 (0.49)
REACTION CONDITIONS	initial H2pres atm	90	50	2.5	30
REACTION	initial CO pres. atm	001	100	12.5	135
<b>X</b>	REAGENT and SOLVENT (moles)	dimethyl- ether (0.125) toluene (25 ml)	dimethylether ether (0.123) toluene (25 ml)	dimethyl- ether (0.124) toluene (25 ml)	dimethyl- ether(0.1) acetic acid (0.430)
CATALYST SYSTLM	I/Ru ratio	9	01	10	01
	TYPE	Ru(CO),4,/CH,1	Ru(Acac),¹/CH₁l	Ru(Acac), 'CH,I	Ru(Acac),/CH,I
	Examples	7	m,	4	v

	6	,9	21.8 8.7 86.7 46.7 5.3	12.9 9.4 29.4 46.7	4.2	10.8	32.2 44.6
RODUCTS	1 <b>*</b>		s nate nate			;	
REACTION PRODUCTS	YIELDS	roduct	C <sub>2</sub> H <sub>6</sub> Alcohols Higher ethers Ethyl Propionate Propylpropionate Acids	CH, Alcohols Acids Ethyl acetate Propylacetate		CH, Alcohol Ethers + acetal Acids Ethyl acetate	
	Conv.	54.3		33.2	CO <sub>2</sub> %	99.8* 30.4°	CO <sub>2</sub> %
	H <sub>2</sub> /CO	2		7		0.5	
	Time requi- red hours	15		16		28	
: 2	r/ III hot condit- ions atm.	238	262	240   260		235	0/7
S	H <sub>2</sub> /CO initial (final)	0.5	(0.69)	0.76		0.2	(0.02)
REACTION CONDITIONS	initial H <sub>2</sub> pres atm.	50		29		25	
ACTION	initial CO press. atm.	100		88		125	
RE	REAGENT and SOLVENT (moles)	diethyl- ether	(0.20) toluene (25 ml)	methyl acetate (0.364)		dimethyl- ether	methyl acetate (0.312)
_	I/Ru ratio	7		<b>∞</b>		01	
CATALYST SYSTEM	TYPE	Rut I(#-C3H3)(CO)3	_	RuC1(π-C <sub>3</sub> H <sub>3</sub> )(CO) <sub>3</sub> · CH <sub>3</sub> l		Ru(Acae), CH,I	
CATA	LXAMPLES	o RuCl	OID.	7 RuC		o Ru(A	

• calculated in respect to the disappeared reagent
•• calculated on the reacted dimethylether
a) dimethylether conversion
b) acette acid conversion
c) methyl acettae conversion
l) ruthenium acetylacetonate

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	Example 9  This example was performed to prove that if no free HI is present in the reacting medium as in the provious examples the provious example.	
	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	
5	of Ru(CO) <sub>4</sub> I <sub>2</sub> (the I/Ru ratio = 2) and 0.061 moles of dimethylether were charged into 100	_
_	cm <sup>3</sup> autoclave. Successively, 25 atm. of $H_2$ and 125 atm. of $H_2$ arm of $H_2$ and 125 atm. of $H_2$ arm	5
	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 pratically	
10	neutral.	10
	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 cm <sup>3</sup> . The catalystic system consisting of	
1 =	Ruthenium trisacetylacetonate (0.4 m. moles) and sodium iodide (4 m. moles) corresponding	
15	to a I/Ru = 10 was fed in to the autoclave with the solvent.	15
	The autoclave was then pressurized with a $H_2 + CO$ mixture in a ratio $H_2:CO = 0.5$ 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.	
20	The conversion of the starting ether was 70% and the yields were:	20
	and the yields were.	20
	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%	
30	Example 11  The catalytic system used in Example 10 was recovered by the distillation of the reaction	
50	products and of part of the acetic acid and was mixed dimethylether and acetic acid in such	30
	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:	
35		35
	Methane traces	33
	Methyl alcohol 0.6 %	
	Ethyl ether 0.2 %	
40	Methylether 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 catalystic system, consisting of	
45	$Ru(CO)_4I_2$ (0.4 m.moles) and of NaI (4 m.moles) equal to a I/Ru ratio of 10, was fed into a	45
	Hastelloy C autoclave of 100 cc holding capacity together with the solvent.	43
	The autoclave was pressurized with an $H_2 + CO$ mixture having a ratio $H_2:CO = 1$ , at 150	
	atm., the temperature raised up to 200°C and the pressure maintained at 250 atm., for 18	
	hours.	
50	When the reaction was completed, the products were discharged and then analyzed by gas	50
	chromatography.	
	A conversion of 70% was obtained and the following yields:	
	Methane 4 %	
55	Ethyl alcohol 0.36 %	55
	Propionic acid 3 %	33
	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	
65	moles of methyl acetate, was reacted for 25 hours under the same conditions as those	C.E
05	as those	65

	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% Ethyl alcohol 0.5% Acetic acid 10.5% Ethyl acetate 60.6%	5
0	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.	10
5	A conversion of the kimethylether of 54.8% was obtained and the following yields  Methylethyl ether 0.2%	15
)	Ethyl ether 0.9% Methylacetate 34.3% Ethylacetate 8.9%	20
5	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 $CH_3I$ equal to a $I/Ru=10$ were introduced into a Hastelloy C autoclave of 100 cc holding capacity together with the solvent.  The autoclave was pressurized with a $H_2+CO$ mixture in a ratio $H_2:CO=0.5$ at 150 atm. and the temperature raised to 200°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% Methyl alcohol 1.2% Propyl alcohol 2.3% Ethyl ether 1.0%	30
5	Methyl acetate 38.4% Ethyl acetate 38.0% 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	35
0	Example 15.  The autoclave was then pressurized with a $H_2 + CO$ mixture in a ratio $H_2:CO = 1$ at 150 atm., the temperature raised up to 200°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% Methyl alcohol 5.5% Ethyl alcohol 1.55% Acetic acid 1% Propionic acid 1.2%	45
0	Methylether 2.3% Ethylether 0.7% Ethylacetate 73% Methyl propionate 0.5% Ethyl propionate 0.13%	50
5	Example 17 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 $CH_3I$ and 1 m.mole of $NiI_2.6H_2O$ corresponding to a $I/Ru = 10$ .  A conversion of 76.2 % was obtained with the following yields:	55
)	Methane 9.66% Methyl alcohol 4.65% Ethyl alcohol 1.95%	60
5	Acetic acid 0.95% Methyl formiate 0.22%	65

A mixture of U.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 catalystic 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 1/Ru = 10.  10 A conversion of 35% of dimethylether was obtained with the following yields:    Methyl alcohol	<u> </u>	1,57 1,050	8
Ethyl ether Ethyl excetate 79.2% Methyl propionate 2.26%  Example 18  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 catalystic 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.  A conversion of 35% of dimethylether was obtained with the following yields:  Methyl alcohol 10.2% Ethyl alcohol 2.1% Methyl formate 1.3% Ethyl ether 10.1% Ethyl ether 10.1% Ethyl ether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula: RCOOCH <sub>3</sub> R' or RCOOCH <sub>3</sub> R  in which R and R' may be the same or different and each 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:  RCOOR' OR R'COOR  in which R and R' are as defined above, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor bydroiodic 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, 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 minorganic 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, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promoter hydroiodic acid, a carboxylic acid solution of a inorganic bromide or iodide, a carboxyl	-	Methylethylether 0.750	
Ethyl acetate 79.2% Methyl propionate 2.26%  Methyl propionate 2.26%  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 330 atm. The catalystic 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.  A conversion of 35% of dimethylether was obtained with the following yields:  Methane 5%  Methyl alcohol 10.2%  Ethyl alcohol 10.2%  Ethyl alcohol 2.1%  Methyl formiate 1.3%  Ethyl ether 10.1%  Ethyl acetate 68%  Methylether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula:  RCOOCH <sub>3</sub> R  in which R and R' may be the same or different and each 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:  RCOOR R'COOR 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 tetralkylammonium bromide or iodide, a carboxylic acid solution of tetralkylammonium bromide or iodide or any combination thereof.  2. A process for preparing esters having the general formula:RCOOR 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 tetralkylammonium bromide or iodide or any combination thereof.  2. A process for preparing esters having the general formula:RCOOR in which R and R' are as defined in Claim 1, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor hydroiodic acid, a carboxylic acid solution of an inorganic oriodic or any combination or in tetralkylammonium bromide or 350°C, at a pressure in the ra		THE A STATE OF THE	
Methyl propionate Example 18  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 catalystic 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.  A conversion of 35% of dimethylether was obtained with the following yields:  Methyl alcohol 10.2% Ethyl alcohol 2.1% Methyl formiate 1.3% Ethyl ether 10.1% Ethyl ether 10.1% Ethyl ether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS: 1. A process for preparing esters having the general formula: RCOOCH <sub>3</sub> R in which R and R' may be the same or different and each 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 other of the formula: RCOOR OR R'COOR in which R and R' are as defined above, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor bydroiodic acid, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of tetraalkylammonium bromide or iodide or any combination thereof.  A process for preparing esters having the general formula: RCOOR in which R and R' are as defined in Claim 1, in which hearbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR  35 Or Containing 1 to 16 carbon atoms.  ROR  350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR  360°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR  37 A process as claimed in Claim 1, in the presence of a catalyst system comprising a ruthenium carbonyla and as a promoter hydroiodic acid, a carboxylic acid solution			
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 catalystic 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.  A conversion of 35% of dimethylether was obtained with the following yields:  Methane  Methyl alcohol  Ethyl alcohol  2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula:  RCOCH <sub>2</sub> R' or R'COOCH <sub>2</sub> R  in which R and R' may be the same or different and each 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:  RCOR' OR R'COOR  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 a ninorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, and R'COOR in which R and R' are as defined in Claim 1, 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 an inorganic bromide or iodide			
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 catalystic 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.  A conversion of 35% of dimethylether was obtained with the following yields:  Methyl alcohol 10.2% Methyl formiate 1.3% 10.2% Ethyl alcohol 2.1% Methyl formiate 1.3% 11. A process for preparing esters having the general formula: RCOOCH <sub>2</sub> R or RCOOCH <sub>2</sub> R 1. Methylethylether 2.7% 11. Methylethylethylether 2.7% 11. Methylethylethylethylethylether 2.7% 11. Methylethylethylethylethylethylethylethyl	_		
A mixture of 0.2 moles of dimethylether, 0.15 moles of acetic acid and 0.13 moles of methylectate was reacted for 5 hours at 200°C and a pressure of 350 atm. The catalystic 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.  Methyl aloohol 10.2% Ethyl alcohol 2.1% Methyl alcohol 10.2% Ethyl alcohol 2.1% Methyl formiate 1.3% Ethyl alcohol 2.1% Methyl formiate 1.3% Ethyl acetate 68% Methylethylether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  In which R and R' may be the same or different and each 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:  RCOOR' OR R'COOR 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 tartalkylammonium bromide or iodide or any combination thereof.  A process for preparing esters having the general formula: RCOOR 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 an inorganic bromide or iodide. A carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide. A carboxylic acid solution of an inorganic bromide or iodide. A carboxylic acid solution of an inorganic bromide or iodide. A carboxylic acid solution of an inorganic ordide and in the range 50 to 1000 atmospheres, with an ether of formula: RCOOR in which R and R' are as defined in Claim 1, 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.	5	Example 18	5
methylacetate was reacted for 5 hours at 200°C and a pressure of 350 atm. The catalystic 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.  A conversion of 35% of dimethylether was obtained with the following yields:  Methyl alcohol 10.2% Ethyl alcohol 2.1% Methyl formiate 1.3% Ethyl alcohol 2.1% Methyl formiate 1.3% Ethyl ether 10.1% Ethyl acetate 68% Methylethylether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula: RCOOCH <sub>2</sub> R in which R and R' may be the same or different and each 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: ROR' or esters of the formula: RCOOC OR in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor hydroicdic acid, a carboxylic acid solution of etraalkylammonium 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, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor hydroicdic acid, a carboxylic acid solution of etraalkylammonium bromide or iodide or any combination thereof.  3. A process for preparing esters having the general formula: RCOOR and R'COOR in which R and R' are as defined in Claim 1, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor hydroicdic acid, a carboxylic acid solution of a traalkylammonium bromide or iodide, a carboxylic acid solution of a catalyst system comprising a ruthenium carbonyl and as a promotor hydroicdic acid, a carboxylic acid solution of an inorganic bromide or iodide, a magnetic properation of the promotor is solution of a catalyst system comprising a rutheni		A mixture of 0.2 moles of dimethylether, 0.15 moles of acetic acid and 0.13 moles of	
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.  Methane		methylacetate was reacted for 5 hours at 200°C and a pressure of 350 atm. The catalystic	
m.moles of Nat corresponding to a J/Ru = 10.  A conversion of 35% of dimethylether was obtained with the following yields:  Methyl alcohol 10.2% Ethyl alcohol 2.1% Methyl formiate 1.3% Ethyl alcohol 2.1% Methyl formiate 1.3% Ethyl acetate 68% Methylether 10.1% Ethyl acetate 68% Methylether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula: RCOOCH <sub>2</sub> R or R'COOCH <sub>2</sub> R in which R and R' may be the same or different and each 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: RCOOR OR R'COOR in which R and R' are as defined above, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor bydroiodic 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 in which R and R' are as defined in Claim 1, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor bydroiodic acid, a carboxylic acid solution of a tertaalkylammonium bromide or iodide or any combination thereof.  3. A process ac claimed in Claim 1, 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 retraalkylammonium bromide or iodide or any combination thereof.  3. A process ac claimed in Claim 1 or Claim 2 in which the ruthenium carbonyl is formed in situ" from subdivided metallic ruthenium, ruthenium carbonylic acid solution of a retraalkylammonium iodide or bromide or any combination thereof.  4. A process as claimed in any preceding claim in which the inorganic iodide or bromide is an alkalin metal		system consisted of 0.66 moles of ruthenium tris-acetylacetonate, 2 m.moles of CH <sub>2</sub> I and 4	
Methyl alcohol 10.2% Ethyl alcohol 11.2% Ethyl alcohol 12.1% Ethyl alcohol 12.1% Ethyl alcohol 13.3% 14 Ethyl alcohol 15.4% Ethyl alcohol 16.4% Ethyl alcohol 17.4% Ethyl alcohol 18.4% Ethyl alcohol 19.2% Et		m.moles of NaI corresponding to a $J/Ru = 10$ .	
Methyl alcohol Ethyl alcohol Ethyl alcohol Ethyl acher Bethyl acher Ethyl acher Ethyl acher Ethyl acetate 68% Methylethylether 10.1% Ethyl acetate 68% Methylethylether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS: 1. A process for preparing esters having the general formula: RCOOCH <sub>2</sub> R' or R'COOCH <sub>2</sub> R  in which R and R' may be the same or different and each 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 30° C and at a pressure in the range 50 to 1000 atmospheres, with an ether of the formula: RCOOR' OR R'COOR in which R and R' are as defined above, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor hydroicdic acid, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of tetraalkylammonium bromide or iodide or any combination which R and R' are as defined in Claim 1, in which R and R' are as defined in Claim 1, in which R and R' are as defined in Claim 1, in which R and R' are as defined in Claim 1, in which R and R' are as defined in Claim 1, in which R and R' are as defined in Claim 1, in which a row such a	10	A conversion of 35% of dimethylether was obtained with the following yields:	10
Methyl alcohol Ethyl alcohol Ethyl achor Ethyl achor Ethyl achor Ethyl achor Ethyl achor Ethyl acetate Methyl formiate Ethyl acetate Sethyl acetate Methylethylether 10.1% Ethyl acetate Methylethylether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS: 1. A process for preparing esters having the general formula: RCOOCH <sub>2</sub> R' or R'COOCH <sub>2</sub> R  in which R and R' may be the same or different and each 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: RCOOR' OR R'COOR in which R and R' are as defined above, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor hydroicdic acid, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of tetraalkylanmonium 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, 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 an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide or bromide is an alkali metal or alkaline-earth metal iodide or bromide.  5.	,	Methane 50%	
Ethyl alcohol 2.1% Methyl formiate 1.3% Ethyl acetate 68% Methylethylether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula:  RCOOCH <sub>2</sub> R' or R'COOCH <sub>2</sub> R  in which R and R' may be the same or different and each 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:  RCOOR' OR R'COOR 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 tertaalkylammonium 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, 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 an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide or any combination thereof.  350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR' in which R and R' are as defined in Claim 1, 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 any combination thereof.  3 A process as claimed in Claim 1 or Claim 2 in which the ruthenium carbonyl is formed in studylided metallic ruthenium, ruthenium acetylacetonate, ruthenium salts of carboxylic acid, sodium hexachlororuthenate, ruthenium acetylacetonate, ruthenium salts of carboxylic acid, sodium hexachlororuthenate, ruthenium acetylacetonate, ruthenium acetylacetonate, ruthenium monium iodide or bromide or any combination t	-		
1.3% Ethyl acetate Ethyl acet			
Ethyl acetate 68% Methylethylether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula:  RCOOCH <sub>2</sub> R' or R'COOCH <sub>2</sub> R in which R and R' may be the same or different and each 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:  RCOOR' OR R'COOR 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 internal plants of the strategy of the strateg	5		
Ethýl acetate Methylethylether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula:  RCOOCH <sub>2</sub> R' or R'COOCH <sub>2</sub> R  in which R and R' may be the same or different and each 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:  RCOOR' OR R'COOR  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 tetraalkylammonium bromide or iodide or any combination thereof.  2. A process for preparing esters having the general formula: RCOOR' in which R and R' are as defined in Claim 1, 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 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 an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide or any combination thereof.  350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:  ROR'  in which R and R' are as defined in Claim 1, 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 an inorganic bromide or iodide, a carboxylic acid solution of a tetraalkylammonium bromide or ionorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution	3		15
Methylether 2.7%  The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula:  RCOOCH <sub>2</sub> R' or R'COOCH <sub>2</sub> R  in which R and R' may be the same or different and each 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:  ROR'  or esters of the formula:  RCOOR' OR R'COOR  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 tertaalkylammonium bromide or iodide or any combination thereof.  2. A process for preparing esters having the general formula: RCOOR' in which R and R' are as defined in Claim 1, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor which a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of a nanorganic bromide or iodide, a carboxylic acid solution of a nanorganic bromide or iodide, a carboxylic acid solution of a nanorganic bromide or iodide, a carboxylic acid solution of a tetraalkylammonium bromide or iodide, a carboxylic acid solution of a tetraalkylammonium bromide or iodide, a carboxylic acid solution of a tetraalkylammonium iodide or any combination thereof.  3. 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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexaciolororuthenate or ruthenium tribromide.  5. A process as claimed in Claim			
The word "Hastelloy" is a registered Trade Mark.  WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula:  RCOOCH <sub>2</sub> R' or R'COOCH <sub>2</sub> R  in which R and R' may be the same or different and each 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:  RCOOR R'COOR  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 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, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:  ROR'  in which R and R' are as defined in Claim 1, 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.  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>3</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 mitrioidde, ammoniumhexachlororuthenate or ruthenium tribromide.  5. A process as claimed in Claim 1 or Claim 2 in which the promoter is a carboxylic acid solution of an inorganic iodide or bromide is an alkali metal or alkaline-earth metal iodide or bromide.  5. A process as claimed in Claim 5 in which the inorganic iodide or bromide is			
<ul> <li>WHAT WE CLAIM IS: <ol> <li>A process for preparing esters having the general formula:</li> <li>RCOOCH<sub>2</sub>R' or R'COOCH<sub>3</sub>R</li> <li>in which R and R' may be the same or different and each 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:</li> <li>RCOOR' OR R'COOR</li> <li>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 tetraalkylammonium bromide or iodide or any combination thereof.</li> <li>A process for preparing esters having the general formula: RCOOR in which R and R' are as defined in Claim 1, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 100 atmospheres, with an ether of formula: ROR'</li> <li>in which R and R' are as defined in Claim 1, 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.</li> <li>A process as claimed in Claim 1 or Claim 2 in which the ruthenium carbonyl is Ru<sub>2</sub>(CO)<sub>1</sub>. Ru<sub>2</sub>(CO)<sub>3</sub>Er<sub>3</sub> <sub>2</sub>Ru<sub>2</sub>(CO)<sub>4</sub>I<sub>3</sub> or RuCl (π -C<sub>3</sub>H<sub>3</sub>)(CO)<sub>3</sub>.</li> <li>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 carboxylic acid, sodium hexachlororuthenate, ruthenium acetylacetonate, ruthenium salts of carboxylic acid, sodium hexachlororuthenate, ruthenium acetylacetonate, ruthenium actylacetonate, or activation of a nalkali metal or alkaline-earth metal iodide or bromide.</li> <li>A process as claimed in Claim 5 in which the inorganic iod</li></ol></li></ul>		Methylethylether 2.7%	
WHAT WE CLAIM IS:  1. A process for preparing esters having the general formula:  RCOOCH <sub>2</sub> R' or R'COOCH <sub>2</sub> R  in which R and R' may be the same or different and each 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:  RCOOR' OR R'COOR  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 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, in the presence of a catalyst system comprising a ruthenium carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR'  in which R and R' are as defined in Claim 1, 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.  3. A process as claimed in Claim 1 or Claim 2 in which the ruthenium carbonyl is formed insitu" from subdivided metallic ruthenium, ruthenium acetylacetonate, ruthenium salts of carboxylic acid, solution of an inorganic iodide or bromide.  5. A process as claimed in Claim 1 or Claim 2 in which the promoter is a carboxylic acid solution of an inorganic iodide or bromide or or any combination thereof.  6. A process as claimed in Claim 5 in which the inorganic iodide or bromide is 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 an alkali metal or	)	The word "Hastelloy" is a registered Trade Mark.	20
<ol> <li>A process for preparing esters having the general formula:         RCOOCH<sub>2</sub>R' or R'COOCH<sub>3</sub>R         in which R and R' may be the same or different and each 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:</li></ol>		·	
RCOOCH <sub>2</sub> R' or R'COOCH <sub>2</sub> R  in which R and R' may be the same or different and each 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:  RCOOR'  or esters of the formula:  RCOOR OR R'COOR  in which R and R' are as defined above, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor bydroiodic acid, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic acid solution of tetraalkylammonium bromide or iodide or any combination thereof.  A process for preparing esters having the general formula: RCOOR' and R'COOR in which R and R' are as defined in Claim 1, 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 near the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:  ROR' in which R and R' are as defined in Claim 1, 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.  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>3</sub> )(CO) <sub>3</sub> .  4. A process as claimed in Claim 1 or Claim 2 in which the promoter is a carboxylic acid solution of an inorganic iodide or bromide or any combination thereof.  5. A process as claimed in Claim 5 in which the inorganic iodide or bromide is 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 an alkali metal or alkaline-earth metal iodide or bromide.  7. A pr			
s in which R and R' may be the same or different and each 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:  RCOOR' OR R'COOR 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 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, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR' in which R and R' are as defined in Claim 1, 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.  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> l <sub>2</sub> , Ru (CO) <sub>4</sub> l <sub>2</sub> or RuCl (π -C <sub>3</sub> H <sub>3</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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammonium hodide or bromide or any combination thereof.  5. A process as claimed in any preceding claim in which the promoter is a carboxylic acid solution of an inorganic iodide or any combination thereof.  6. A process as claimed in any preceding claim in which the promoter is a carboxylic acid solution of an inorganic iodide or any combination thereof.  7. A process as claimed in lam in th		1. A process for preparing esters having the general formula:	
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:  RCOOR' OR R'COOR 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 tetraalkylammonium bromide or iodide or any combination thereof.  A process for preparing esters having the general formula: RCOOR in which R and R' are as defined in Claim 1, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR' in which R and R' are as defined in Claim 1, 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.  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>3</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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammonium hexachlororuthenate 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 is an alkali metal or alkaline-earth metal iodide or bromide.  A process as claimed in Claim 5 in which the inorganic iodide or bromide is an alkali metal or alkaline-earth metal iodide or bromide is hydroiodic acid or is formed "in situ" under the reaction conditions from element	_	in which D and D' may be the same an interest of the large of the same and the same	
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:  ROR'  or esters of the formula:  RCOOR' OR R'COOR  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 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, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR' in which R and R' are as defined in Claim 1, 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.  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> F <sub>12</sub> , Ru (CO) <sub>4</sub> F <sub>2</sub> or RuCl (π -C <sub>3</sub> H <sub>3</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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate or ruthenium ribromide.  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 tetraalkylammonium iodide or bromide or any combination thereof.  6. A process as claimed in any preceding claim in which the promoter is hydroiodic acid or isformed "in situ" under the reaction conditions from elementary iodine or organic io	)	which A and K may be the same or different and each	25
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:  RCOOR' OR R'COOR  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 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, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR' in which R and R' are as defined in Claim 1, 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.  3. A process as claimed in Claim 1 or Claim 2 in which the ruthenium carbonyl is Rus(CO) <sub>12</sub> , Ruc(CO) <sub>13</sub> E <sub>12</sub> , Ru (CO) <sub>14</sub> E <sub>2</sub> or RuC( (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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 is 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 an alkali metal or alkaline-earth metal iodide or bromide.  8. A process as claimed in lamy of claims 1 to 4 in which the promoter is hydroiodic acid or is formed "in situ" from iodime compounds capable			
or esters of the formula:  RCOOR' OR R'COOR  in which R and R' are as defined above, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor bydroiodic 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, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:  ROR' in which R and R' are as defined in Claim 1, 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.  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 actylacetonate, ruthenium salts of carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexach- 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.  6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is 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 an alkali metal or alkaline-earth metal iodide or bromide.  8. A process as claimed in Claim 5 in which the promoter is hydroiodic acid or is formed "in si		containing 1 to 16 carbon atoms,	
or esters of the formula:  RCOOR' OR R'COOR  in which R and R' are as defined above, in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor bydroiodic 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, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:  ROR'  in which R and R' are as defined in Claim 1, 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.  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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 is an alkali metal or alkaline-earth metal iodide or bromide.  6. A process as claimed in Claim 5 in which the inorganic iodide or bromide is an alkali metal or alkaline-earth metal iodide or bromide.  7. A process as claimed in Claim 5 in which the promoter is hydroiodic acid or is formed "in situ" from iodine compounds capable of forming HI in the reaction conditions.  9. A process as claimed in Claim 9 in which the organic iodides are alkyl or alkylaryl iodides having 1 to 20 carbon		in which carbon monoxide and hydrogen are reacted, at a temperature in the range 150 to	
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 tetraalkylammonium bromide or iodide or any combination thereof.  2. A process for preparing esters having the general formula: RCOOR in which R and R' are as defined in Claim 1, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:  ROR'  in which R and R' are as defined in Claim 1, 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.  3. A process as claimed in Claim 1 or Claim 2 in which the ruthenium carbonyl is Rus(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>3</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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 is 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 an alkali metal or alkaline-earth metal iodide or bromide.  8. A process as claimed in Claim 8 in which the hydroiodic acid 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 are alkyl or alkylaryl iodides hav		350°C and at a pressure in the range 50 to 1000 atmospheres, with an ether of the formula:	
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 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, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR' in which R and R' are as defined in Claim 1, 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.  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 ( $\pi$ -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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 is 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 an alkali metal or alkaline-earth metal iodide or bromide.  8. A process as claimed in Claim 8 in which the hydroiodic acid 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 cl	)	ROR'	30
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 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, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR' in which R and R' are as defined in Claim 1, 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.  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 ( $\pi$ -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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 tetraalkylammonium iodide or bromide or any combination thereof.  6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is an alkali metal or alkaline-earth metal iodide or bromide.  7. A process as claimed in any preceding claim in which the promoter is hydroiodic acid or is formed "in situ" 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 o			- <b>-</b>
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 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, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:  ROR' in which R and R' are as defined in Claim 1, 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.  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>3</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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 tetraalkylammonium iodide or bromide or any combination thereof.  6. A process as claimed in Claim 5 in which the inorganic iodide or bromide is 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** iodide.  8. A process as claimed in Claim 5 in which the hydroiodic acid is formed "in situ" under the reaction conditions.  9. A process as claimed in Claim 9 in which the or		RCOOR' OR R'COOR	
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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 in which R and R' are as defined in Claim 1, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR' in which R and R' are as defined in Claim 1, 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.  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> L <sub>2</sub> or RuCl (π -C <sub>3</sub> H <sub>3</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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 tetraalkylammonium iodide or bromide or any combination thereof.  6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is 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.  8. 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		in the presence of a catalyst system comprising a ruthenium carbonyl and as a promotor	
<ul> <li>acid solution of tetraalkylammonium bromide or iodide or any combination thereof.</li> <li>2. A process for preparing esters having the general formula: RCOOR in which R and R' are as defined in Claim 1, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR' in which R and R' are as defined in Claim 1, 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.</li> <li>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>.</li> <li>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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate or ruthenium tribromide.</li> <li>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 tetraalkylammonium iodide or bromide or any combination thereof.</li> <li>6. A process as claimed in Claim 5 in which the inorganic iodide or bromide is an alkali metal or alkaline-earth metal iodide or bromide.</li> <li>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.</li> <li>8. 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.</li> <li>9. A process as claimed in Claim 8 in which the organic iodides are alkyl or alkylaryl iodides having 1 to 20 carbon atoms.<!--</td--><td>i</td><td>hydroiodic acid, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic</td><td>35</td></li></ul>	i	hydroiodic acid, a carboxylic acid solution of an inorganic bromide or iodide, a carboxylic	35
<ol> <li>A process for preparing esters having the general formula: RCOOR in which R and R' are as defined in Claim 1, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR' in which R and R' are as defined in Claim 1, 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.</li> <li>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>3</sub>)(CO)<sub>3</sub>.</li> <li>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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate or ruthenium tribromide.</li> <li>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 tetraalkylammonium iodide or bromide or any combination thereof.</li> <li>A process as claimed in Claim 5 in which the inorganic iodide or bromide is an alkali metal or alkaline-earth metal iodide or bromide.</li> <li>A process as claimed in Claim 5 in which the inorganic iodide or bromide is solution of an insitu" from iodine compounds capable of forming HI in the reaction conditions.</li> <li>A process as claimed in Claim 8 in which the organic iodides are alkyl or alkylaryl iodides having 1 to 20 carbon atoms.</li> <li>A process as claimed in nay preceding claim in which the carboxylic acid is acetic acid</li> </ol>		acid solution of tetraalkylammonium bromide or iodide or any combination thereof.	
in which R and R' are as defined in Claim 1, in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to 350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:  ROR' in which R and R' are as defined in Claim 1, 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.  3. A process as claimed in Claim 1 or Claim 2 in which the ruthenium carbonyl is Ru₃(CO)₁2, [Ru(CO)₃Br₂]2, Ru (CO)₄I₂ or RuCl (π -C₃H₂)(CO)₃.  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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 tetraalkylammonium iodide or bromide or any combination thereof.  6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is 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 an alkali metal or alkaline-earth metal iodide or bromide.  8. A process as claimed in nany of claims 1 to 4 in which the promoter is hydroiodic acid or is formed "in situ" under the reaction conditions from elementary iodine or organic iodides.  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.		2. A process for preparing esters having the general formula: RCOOR and R'COOR	
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<ul> <li>350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula: ROR* in which R and R' are as defined in Claim 1, 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.  3. A process as claimed in Claim 1 or Claim 2 in which the ruthenium carbonyl is Ru₃(CO)₁₂, [Ru(CO)₃Br₂]₂, Ru (CO)₄I₂ or RuCl (π -C₃H₅)(CO)₃.  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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 tetraalkylammonium iodide or bromide or any combination thereof.  6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is 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 an alkali metal or alkaline-earth metal iodide or bromide.  8. 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*+ iodide.  8. 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.  11. A process as claimed in any preceding claim in which the carboxylic acid is acetic acid.  12. A process as claimed in any preceding claim in which the carboxylic acid is acetic acid.  13. A process as claimed in a</li></ul>		in which carbon monoxide and hydrogen are reacted at a temperature in the range 150 to	
in which R and R' are as defined in Claim 1, 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.  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 ( $\pi$ -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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 tetraalkylammonium iodide or bromide or any combination thereof.  6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is 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** iodide.  8. 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.  11. A process as claimed in any preceding claim in which the carboxylic acid is acetic acid	)	350°C, at a pressure in the range 50 to 1000 atmospheres, with an ether of formula:	40
in which R and R' are as defined in Claim 1, 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.  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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 tetraalkylammonium iodide or bromide or any combination thereof.  6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is 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.  8. A process as claimed in any of claims 1 to 4 in which the promoter is hydroiodic acid or 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.  11. A process as claimed in any preceding claim in which the carboxylic acid is acetic acid			+∪
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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 tetraalkylammonium iodide or bromide or any combination thereof.  6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is 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.  8. A process as claimed in any of claims 1 to 4 in which the promoter is hydroiodic acid or 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.  11. A process as claimed in any preceding claim in which the carboxylic acid is acetic acid			
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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate 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 tetraalkylammonium iodide or bromide or any combination thereof.  6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is 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.  8. A process as claimed in any of claims 1 to 4 in which the promoter is hydroiodic acid or 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.  11. A process as claimed in any preceding claim in which the carboxylic acid is acetic acid		ruthenium carbonyl and as a promoter hydroiodic acid a carbonylic acid solution of an	
<ul> <li>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>.</li> <li>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 carboxylic acid, sodium hexachlororuthenate, ruthenium triiodide, ammoniumhexachlororuthenate or ruthenium tribromide.</li> <li>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 tetraalkylammonium iodide or bromide or any combination thereof.</li> <li>6. A process as claimed in any preceding claim in which the inorganic iodide or bromide is an alkali metal or alkaline-earth metal iodide or bromide.</li> <li>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.</li> <li>8. A process as claimed in any of claims 1 to 4 in which the promoter is hydroiodic acid or is formed "in situ" from iodine compounds capable of forming HI in the reaction conditions.</li> <li>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.</li> <li>10. A process as claimed in Claim 9 in which the organic iodides are alkyl or alkylaryl iodides having 1 to 20 carbon atoms.</li> <li>11. A process as claimed in any preceding claim in which the carboxylic acid is acetic acid</li> </ul>		inorganic bromide or iodide, a garbovylic acid colution of a tetroalization manion beautiful or	
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or propionic acid.			65
* *		or propionic acid.	03
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	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 calim 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	5
	presence of a solvent.	
	15. A process as claimed in Claim 14 in which the solvent is a carboxylic acid of the	
	formula R''COOH in which R'' 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	10
	reaction mixture is in the range 0.1.1 to 2:1.	
	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.	
	18. A process for the preparation of esters substantially as herein described with refer-	
15		15
	19. An ester when prepared by a process as claimed in any preceding claim.	
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