

TITLE OF THE INVENTION
PROCESS FOR THE PREPARATION OF
BETA-GAMMA UNSATURATED ESTERS

5 BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a process for the preparation of beta-gamma unsaturated carboxylic acid esters by catalytic carbonylation starting with either an allylic butenyl ether or mixture of butadiene and an alcohol. More specifically but not by way of limitation, the invention relates to the use of a rhodium-containing catalyst in combination with an iodide promoter for the carbonylation of methyl crotyl ether, 3-methoxybutene-1 and mixtures thereof to produce methyl-3-pentenoate.

1. Description of Related Art

15 The use of rhodium-containing catalyst with various types of co-catalysts and promoters for the carbonylation of a variety of saturated and unsaturated organic compounds is generally known. For example, U.S. Pat. No. 4,603,020 claims a process for the carbonylation of O-acetyl compounds, such as acetic anhydride, at 130 to 250 °C using a rhodium catalyst and an
20 aluminum accelerator. U.S. Pat. No. 4,625,058 teaches a similar process but uses boron, bismuth or tertiary amide compounds as accelerators. U.S. Pat. No. 4,642,370 discloses a process for the carbonylation of hydrocarbyl halides which uses a boron, silicon, aluminum, or zirconium accelerator. U.S. Pat. No. 4,563,309 claims a process for the production of carboxylic acid anhydride of
25 the formula $RC(O)O(O)CCH_3$ by reaction of a methyl carboxylate ester of formula $RC(O)OCH_3$ with carbon monoxide in the presence of a rhodium catalyst and a phosphorous-containing ligand.

European patent application 0 428 979 A2 discloses the carbonylation of allylic butenols and butenol esters using a rhodium catalysts

and a hydrogen bromide or hydrogen iodide promoter under anhydrous conditions for the production of 3-pentenoic acid.

BRIEF SUMMARY OF THE INVENTION

In view of the above prior art, it has now been discovered that the
5 an allylic butenyl ether such as an alkyl crotyl ether or a corresponding mixture of butadiene and an alkanol will readily undergo carbonylation directly to a beta-gamma unsaturated carboxylic acid ester, such as alkyl-3-pentenoate, at high selectivity and high activity by use of a rhodium-containing catalyst in the presence of an iodide-containing promoter.

10 Thus the present invention provides a process for the carbonylation of allylic butenyl ether or mixture of butadiene and an alcohol and the production of beta-gamma unsaturated carboxylic acid ester comprising the steps of:

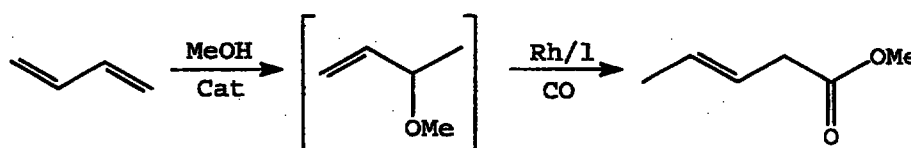
- 15 (a) reacting an allylic butenyl ether or mixture of butadiene and an alcohol with carbon monoxide in the presence of a rhodium-containing catalyst and an iodide-containing promoter; and
- (b) recovering a beta-gamma unsaturated carboxylic acid ester.

In one embodiment of the invention the allylic butenyl ether is selected from the group consisting of methyl crotyl ether, 3-methoxybutene-1 and mixtures
20 thereof and the beta-gamma unsaturated carboxylic acid ester is methyl-3-pentenoate. In another embodiment, the carbonylation involves reacting butadiene and methanol and the beta-gamma unsaturated carboxylic acid ester is again methyl-3-pentenoate. Preferably, the iodide-containing promoter is selected from the group consisting of HI, AlI₃, SnI₄, TiI₄, CrI₃, and
25 CoI₂ and the rhodium-containing catalyst is dicarbonylacetylacetonate rhodium(I).

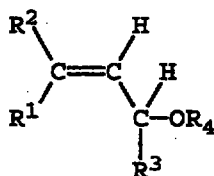
DETAILED DESCRIPTION OF INVENTION

The process of the present invention involves a rhodium catalyzed carbonylation of an allylic butenyl ether to produce a beta-gamma unsaturated

carboxylic acid ester wherein the rhodium-containing catalyst is promoted by the use of HI, HBr or a metal halide salt. The allylic butenyl ether being carbonylated is either an alkyl crotyl ether, a positional isomer thereof such as 3-alkoxybutene-1 or mixtures of the same. For purposes of the present invention, mixtures that produce the allylic butenyl ether or equivalent in-situ are equivalent starting materials and such butadiene in the presence of an alkanol is to be considered an alternate starting material. The following representative reaction showing a butadiene in the presence of methanol under catalytic reaction conditions producing the 3-methoxybutene-1 intermediate (a positional isomer of methyl crotyl ether) which is then combines with carbon monoxide to produce methyl pentenoate is illustrative of the overall carbonylation.



Suitable allylic butenyl ethers are of the form



where one of the groups R^1 , R^2 , and R^3 is methyl and the other two groups are H and wherein R_4 is a C_1 to C_{10} alkyl. It should be appreciated that acceptable allylic compounds includes both cis and trans isomers, other positional isomers such as that illustrated by 3-alkoxybutene-1 and crotyl ester as well as mixtures of various allylic compounds. Also, for purposes of the present invention, butadiene in combination with a C_1 to C_{10} alkyl alcohol leads to in-situ ether formation and thus total equivalency relative to the use of allylic butenyl ether as starting material for the carbonylation reaction.

The reaction can be performed at a temperature in the range of 40 °C to about 200 °C. Below 40 °C the reaction becomes too slow to be commercially feasible, and above 200 °C the formation of undesirable products leads to significant yield losses. Preferably the reaction temperature is between 90 °C and 150 °C and most preferably between 90 °C and 150 °C.

Suitable total pressures for the reaction are in the range 25 to 3,000 psig. Preferably the pressure is between 100 and 2,000 psig with 200 to 1,000 psig being most preferred.

The source of the carbon monoxide (CO) reactant for the present invention is not crucial. Commercially available grades of carbon monoxide are acceptable. As such, the carbon monoxide can contain inert impurities such as carbon dioxide, methane, nitrogen, noble gasses, and other hydrocarbon having up to four carbon atoms. Preferably the carbon monoxide also contains hydrogen typically at about a ten mole percent concentration relative to the carbon monoxide. At least 1 molar equivalent of carbon monoxide to allylic butenyl ether or butadiene is needed. Typically, an excess of CO is used.

Suitable solvents for this process are those which are compatible with the reactants and the catalyst system under the reaction conditions. Such solvents include aromatic hydrocarbon solvents, saturated halocarbon solvents, and mixtures thereof. Carboxylic acid esters and lactones, such as methyl-3-pentenoate, valerolactone and the like, are also acceptable solvents. Suitable aromatic hydrocarbon solvents include benzene, toluene, 1,2,4-trichlorobenzene and other C₂ to C₄ alkyl substituted benzenes. Suitable saturated halocarbon solvents include chlorinated and fluorinated hydrocarbons such as methylene chloride, dichloroethane and chloroform as well as the so-called HCFC's including in particular HCFC-113 (FCCl₂CF₂Cl) and HCFC-123 (CHCl₂CF₃) or the like. The most preferred solvents are toluene, HCFC-113 and HCFC-123. Alternatively, the process of this invention where the starting material is a methoxybutene may be run in the absence of solvent.



The rhodium catalyst can be provided from any source or by any material which will produce rhodium ions under the carbonylation reaction conditions. Among the materials which can be employed as the source of the rhodium catalyst are rhodium metal, rhodium salts, rhodium oxides, rhodium carbonyl compounds, organorhodium compounds, coordination compounds of rhodium, and mixtures thereof. Specific examples of such compounds include, but are not limited to, RhCl_3 , RhI_3 , $\text{Rh}(\text{CO})_2\text{I}_3$, $\text{Rh}(\text{CO})\text{I}_3$, $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, $\text{Rh}(\text{acac})_3$, $\text{Rh}(\text{CO})_2(\text{acac})$, $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$, $[\text{Rh}(\text{C}_2\text{H}_4)\text{Cl}]_2$, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Rh}(\text{CO})_2\text{Br}]_2$, $\text{Rh}(\text{COD})(\text{acac})$, $[\text{Rh}(\text{COD})\text{Cl}]_2$, $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, $\text{Rh}_2[\text{O}_2\text{C}(\text{CR}_2)_6\text{CH}_3]_4$, and $\text{Rh}_2(\text{acetate})_4$, where acac is acetylacetonate, COD is 1,5-cyclooctadiene, and Ph is phenyl. Rhodium compounds containing bidentate phosphorous or nitrogen ligands should be avoided. Preferred sources of rhodium catalyst include rhodium(I) compounds such as $\text{Rh}(\text{CO})_2(\text{acac})$, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Rh}(\text{COD})\text{Cl}]_2$, $\text{Rh}(\text{COD})(\text{acac})$, and rhodium iodide compounds such as RhI_3 and $\text{Rh}(\text{CO})_2\text{I}_3$. Most preferably the rhodium-containing compound is $\text{Rh}(\text{CO})_2(\text{acac})$.

Suitable concentrations of rhodium in the reaction are in the range of 0.005 to 0.50 % by weight of rhodium metal based on the reaction medium. Preferably the concentration of rhodium is in the range of 0.02 to 0.20 wt%. Although high reaction rates on a per Rh basis can be obtained even at low concentrations of Rh, it is generally more economical to operate at Rh concentrations above 0.01 wt%. Similarly, Rh concentrations below 2.0 wt% are preferred to minimize the formation of unwanted by-products.

The rhodium, which may be pre-formed or generated in situ, must be promoted by HI, HBr or a metal halide, preferably by HI or a metal iodide, to achieve a satisfactory rate and selectivity to pentenoate ester. Examples of suitable promoters are the acid halides as well as halides of Groups IIB, IIIA, IIIB, IVA, IVB, VIB, VII, VIII of the periodic table. Preferred promoters are

those where the halide is iodide, such as but not limited to HI, AlI_3 , SnI_4 , TiI_4 , CrI_3 , and CoI_2 .

The molar ratio of promoter to rhodium can be in the range of about 1:1 to about 50:1. Although high selectivities to the desired methyl-3-pentenoate can be obtained even at low promoter to rhodium ratios, the rate of formation of methyl-3-pentenoate on a per Rh basis decreases significantly when the molar ratio of promoter to rhodium is less than 1. This decrease in reaction rates, coupled with the high cost of rhodium makes it more economical to use promoter to rhodium ratios greater than 1:1. Similarly, the molar ratio of promoter to rhodium must be less than about 50 to obtain reasonable yields of the unsaturated ester. Preferably, the molar ratio of promoter to rhodium is between about 10 and about 30.

Reaction times can be varied and depend on choice of reactants, solvent, catalyst and promoter as well as their respective concentration and reaction conditions such as temperature and pressure. Residence times of the order of about 1 minute to about 20 hours are acceptable.

The reaction of the present invention may be carried out in a batch or continuous mode. The products can be isolated and recovered by any of the techniques generally known in the art including by example but not limited thereto, extraction, distillation or the like.

The following examples are present to further illustrate specific features and advantages of the present invention and as such are not intended to limit the scope of the invention. The conversion data reported is based on quantitative measurement of the relative amount of the primary or limiting reactant (e.g., 3-methoxybutene-1 or alternatively butadiene) that is not consumed by chemical reaction. The selectivity to the desired methyl-3-pentenoate (M3P) is based on and reported as the amount of methyl ester produced relative to the amount of the primary reactant consumed by the reaction.

Example 1

3-Methoxybutene-1 Carbonylation to M3P

with Rh Catalyst Promoted by Aluminum Iodide:

A 120 mL mechanically stirred Hastelloy-C autoclave was
5 charged with 0.258 grams (0.1 mmole) of dicarbonylacetylacetonate
rhodium(I), 1.63 grams (4.0 mmole) of anhydrous aluminum iodide and 72.1
grams (83.4 mL) toluene. The reaction vessel was pressurized to 400 psig with
a 90/10 mixture of CO and hydrogen. The solution was heated to a temperature
of 120 °C and the carbonylation reaction was initiated by injecting a solution of
10 8.6 grams (100 mmole) of 3-methoxybutene-1 and 1.0 grams of ortho-
dichlorobenzene (ODCB, internal GC standard) in 5 grams of toluene. The
total pressure was then adjusted to 700 psig with the 90/10 CO/H₂. Carbon
monoxide and H₂ (90/10 ratio) were continuously fed to the autoclave from a
reservoir so as to maintain the total pressure constant at 700 psig. Samples
15 were removed at intervals for GC analysis on a DBFFAP 30 M J&W Scientific
capillary GC column. The analysis showed that 62.5% of the methoxybutene
charged was converted in the first hour and the selectivity to methyl-3-
pentenoate (M3P; cis and trans isomers) was 93.9%. After 4 hours the
conversion was 98% and the selectivity to M3P was 93%. The only significant
20 by-products were mixed butenes and butadiene (not separated, 5.2%),
valerolactone (1.5%) and 3-pentenoic acid (0.3%). The first order rate constant
for the formation of M3P was 1.02 hr⁻¹, corresponding to a space-time yield
(STY) of 734 mmole M3P per liter per hour.

Example 2

25 Methoxybutene Carbonylation to M3P With Rh Catalyst Promoted by
Aluminum Iodide (Higher Iodide/Rh ratio and Higher Temperature):

The experiment in Example 1 was repeated except that the
3-methoxybutene-1 was replaced with a 70/30 mixture of 1-methoxybutene-2
(methyl crotyl ether) and 3-methoxybutene-1, the iodide to rhodium ratio was



increased from 12/1 to 18/1 and the temperature was increased to 130°C. The GC analysis showed a methoxybutene conversion of 85.8% after 30 minutes and a selectivity to M3P of 82%. After 60 minutes the conversion was 97% and the selectivity to M3P was 84.6%. The first order rate constant for the formation of M3P was 2.96 hr⁻¹, corresponding to a space-time yield (STY) of 2,135 mmole M3P per liter per hour.

Example 3

Carbonylation of 3-Methoxybutene-1 using
a Rhodium Catalyst and aqueous HI Promoter:

10 A 25 mL glass lined pressure vessel was charged with 5 mL of a solution containing 5.9 grams (69 mmol) of 3-methoxybutene-1 (3MB1), 0.258 grams (1.0 mmol) of dicarbonylacetylacetonate rhodium(I), 1.34 grams (6.0 mmol) of 57% aqueous HI solution, and 1.00 grams of o-dichlorobenzene (internal gas chromatograph standard) in 100 mL of toluene. The pressure vessel was freed from air by purging first with nitrogen (twice) and then with carbon monoxide containing 10 mol% hydrogen (twice). The vessel was then pressurized to 500 psig of 90/10 CO/H₂ and heated to 120 °C with agitation for 3 hours. The heat was shut off, the pressure vessel was allowed to cool to room temperature and the excess gases were vented. The product was analyzed by gas chromatography on a DBFFAP 30 M J&W Scientific capillary GC column. The results of the analysis are summarized below:

Before esterification		mmol/100 mL
25	Butadiene	13.3
	Methoxybutenes	0.9
	3-Pentnoic acid	9.0
	Methyl-3-pentenoate	54.9

Methoxybutene conversion was 94.0%, selectivity to methyl-3-pentenoate (M3P) was 84.8% and selectivity to 3-pentenoic acid was 13.9%. Product accounting was 99%.

Example 4

In a manner analogous to the procedure employed in Example 3, an additional run was performed except that 0.064 grams of methanol (MeOH) per 100 grams of methoxybutene (2 equivalents per 100 equivalents) was added. The resulting data for this example as well as the corresponding data from Example 1 are presented in Table 1.

Example 5

The procedure employed in Example 4 was repeated except that 0.19 grams of methanol per 100 grams of methoxybutene (6 equivalents per 100 equivalents) was added. The resulting data are presented in Table 1.

Example 4

The procedure employed in Example 1 was repeated except that the toluene solvent was replaced with the halocarbon HCFC-123 (CHCl_2CF_3). The resulting data are presented in Table 1.

Example 7

The procedure employed in Example 5 was repeated except that the aqueous HI promoter was replaced with an equivalent amount of AlI_3 (2 equivalents of AlI_3 per g-atom of Rh). The resulting data are presented in Table 1.

Example 8

The procedure employed in Example 3 was repeated except that the toluene solvent was replaced with the halocarbon HCFC-113 ($\text{FCCl}_2\text{CF}_2\text{Cl}$). The resulting data are presented in Table 1.

Example 9

The procedure employed in Example 3 was repeated except that the toluene solvent was replaced with the halocarbon HCFC-113 ($\text{FCCl}_2\text{CF}_2\text{Cl}$) and the aqueous HI promoter was replaced with an equivalent amount of TiI_4 (2 equivalents of TiI_4 per g-atom of Rh). The resulting data are presented in Table 1.

10
Table 1

	Example	Solvent	Iodide Promoter (6I/Rh)	MeOH per 100 meq substrate	Conversion	Selectivity to M3P
5	3	Toluene	aq HI	0	94.0	84.8
	4	Toluene	aq HI	2	93.7	87.0
	5	Toluene	aq HI	6	94.0	83.5
	6	HCFC-113	aq HI	0	95.8	94.8
	7	Toluene	AlI ₃	6	80.8	97.2
10	8	HCFC-113	aq HI	0	95.4	91.2
	9	HCFC-113	TiI ₄	2	17.8	67.6

Examples 10-15

The procedure employed in Example 3 was repeated for a series of six additional runs except that the iodide promoter was varied and the resulting product was esterified with methanol to determine total carbonylation selectivity including dibasic esters (DBE's; esters of adipic acid, 2-methylglutaric and ethylsuccinic acids). The results are summarized in Table 2.

Table 2

	Example	Iodide Promoter	I/Rh	Conversion	Selectivity to M3P	Selectivity to M2P	Selectivity DBE's
20	10	anh*, HI	3	33.2	95.9	0	1.9
	11	aq HI	3	22.1	94.9	1.3	1.4
	12	aq HI	3	7.2	100	0	0
	13	aq HI	3	22.0	94.0	0	1.6
	25	14	AlI ₃	3	97.2	10.1	53.3
	15	aq HI	3	31.2	96.4	0	1.4

* anhydrous HI in Acetic acid

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Example 16

Carbonylation of butadiene in the presence of methanol using
a Rhodium Catalyst and aqueous HI Promoter:

A 25 mL glass lined pressure vessel was charges with 5 mL of a
5 solution containing 5.4 grams (100 mmol) of butadiene, 1.34 grams (6.0 mmol)
of 57% aqueous HI, 3.2 grams methanol (100 mmole), 0.258 grams (1.0 mmol)
of dicarbonylacetylacetonate rhodium(I), and 1.00 grams of o-dichlorobenzene
(internal gas chromatograph standard) in 100 mL of toluene. The pressure
vessel was freed from air by purging first with nitrogen (twice) and then with
10 carbon monoxide containing 10 mol% hydrogen (twice). The vessel was then
pressurized to 500 psig of 90/10 CO/H₂ and heated to 120 °C with agitation for
3 hours. The heat was shut off, the pressure vessel was allowed to cool to room
temperature and the excess gases were vented. The product solution was
analyzed directly by gas chromatography on a DBFFAP 30 M J&W Scientific
15 capillary GC column. The results of the analysis are summarized below in
Table 3.

Examples 17-27

The procedure employed in Example 16 was repeated for a series
of eleven additional runs except that the iodide promoter, the temperature, and
20 the solvent were varied. The results are summarized in Table 3.

Table 3

Example	Temp. (°C)	Solvent	Iodide Promoter	I/Rh	Conversion	Selectivity to M3P
25 16	120	Toluene	aq HI	6	59.6	22.0
17	120	Toluene	AlI ₃	6	74.2	46.6
18	120	HCFC-123	aq HI	6	60.6	44.5
19	120	HCFC-123	AlI ₃	6	83.0	32.7
20	140	Toluene	AlI ₃	6	85.7	58.1

This Sheet Has Been Replaced



Table 3(continued)

Example	Temp.	Solvent	Iodide	I/Rh	Conversion	Selectivity
21	140	HCFC-123	AlI_3	6	87.5	47.7
22	120	Toluene	anh HI	3	62.9	28.0
5 23	120	Toluene	AlI_3	3	69.2	39.8
24	120	Toluene	SnI_4	6	52.6	19.3
25	120	Toluene	CrI_3	3	53.7	33.0
26	120	Toluene	TiI_4	3	63.6	41.8
27	120	Toluene	aq HI	3	60.5	29.8

10 The process of the present invention is useful for the preparation of beta-gamma unsaturated carboxylic acid esters and in particular the production of methyl-3-pentenoate by the carbonylation of methyl crotyl ether, 3-methoxybutene-1 and their mixtures or directly from a mixture of butadiene and methanol. Such products are useful as difunctional monomers and as
15 intermediates in the synthesis of adipic acid.

Having thus described and exemplified the invention with a certain degree of particularity, it should be appreciated that the following claims are not to be so limited but are to be afforded a scope commensurate with the wording of each element of the claim and equivalents thereof.

CLAIM OR CLAIMS

I claim:

1. A process for the carbonylation of allylic butenyl ether or mixture of
5 butadiene and an alcohol and the production of beta-gamma unsaturated
carboxylic acid ester comprising the steps of:
- (a) reacting an allylic butenyl ether or mixture of butadiene and an
alcohol with carbon monoxide in the presence of a rhodium-containing
catalyst and an iodide-containing promoter; and
 - 10 (b) recovering a beta-gamma unsaturated carboxylic acid ester.
2. The process of Claim 1 wherein said allylic butenyl ether is selected from the
group consisting of methyl crotyl ether, 3-methoxybutene-1 and mixtures
thereof and said beta-gamma unsaturated carboxylic acid ester is
15 methyl-3-pentenoate.
3. The process of Claim 1 wherein said carbonylation involves reacting
butadiene and methanol and said beta-gamma unsaturated carboxylic acid ester
is methyl-3-pentenoate.
- 20 4. The process of Claim 2 or 3 wherein said iodide-containing promoter is
selected from the group consisting of HI, AlI_3 , SnI_4 , TiI_4 , CrI_3 , and CoI_2 and
said rhodium-containing catalyst is dicarbonylacetylacetonate rhodium(I).

