

TITLE OF THE INVENTION
PROCESS FOR CARBONYLATION OF AN ALLYLIC BUTENOL
OR BUTENYL ESTER OF A CARBOXYLIC ACID

5 **BACKGROUND OF THE INVENTION**

1. Field of the Invention:

The present invention relates to a process involving the catalytic carbonylation of an allylic butenol or a butenyl ester of a carboxylic acid in a carboxylic acid solvent to produce a beta-gamma unsaturated carboxylic acid anhydride. More specifically but not by way of limitation, the invention relates to the use of a rhodium-containing catalyst promoted by a metal iodide salt under anhydrous conditions for the carbonylation of crotyl acetate, 3-acetoxybutene-1 and mixtures thereof to produce 3-pentenoic acid anhydride.

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 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. However, the use of the hydrogen iodide promoter results in a back reaction producing butadiene and a carboxylic acid. The present invention alleviates this problem and as such is
5 viewed as an improvement relative to this disclosure.

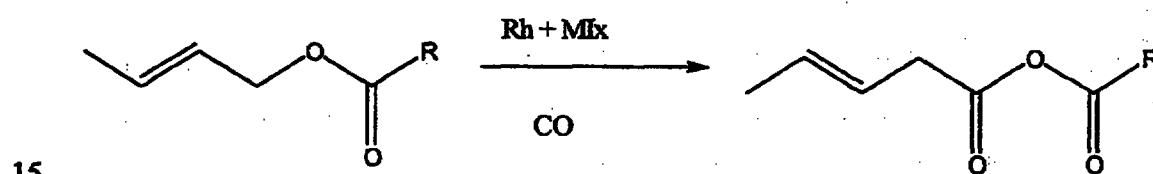
BRIEF SUMMARY OF THE INVENTION

In view of the above, it has now been discovered that the anhydrous carbonylation of crotyl esters to acid anhydrides can be readily achieved with high selectivity and high activity by use of a rhodium-containing
10 catalyst provided a metal iodide or a metal salt which can be converted to an iodide under reaction condition, e.g., a metal acetate with HI, is employed to promote the reaction. It is felt that the metal iodide in an anhydrous carboxylic acid solvent serves mechanistically as a buffered source of iodide which in turn minimizes the undesirable back reaction of the crotyl ester to butadiene and
15 carboxylic acid.

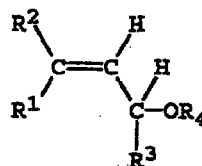
Thus the present invention provides a process for the carbonylation of allylic butenol or butenyl ester of a carboxylic acid and production of beta-gamma unsaturated carboxylic acid anhydride comprising the steps of: (a) reacting an allylic butenyl ester of a carboxylic acid with
20 carbon monoxide in the presence of a rhodium-containing catalyst and a metal iodide promoter in a C₁ to C₂₀ carboxylic acid under anhydrous conditions; and (b) recovering a beta-gamma unsaturated carboxylic acid anhydride. In one particular embodiment of the invention the allylic butenyl ester of a carboxylic acid is selected from the group consisting of crotyl acetate, 3-acetoxybutene-1
25 and mixtures thereof and the beta-gamma unsaturated carboxylic acid anhydride is 3-pentenoic acid anhydride. In another embodiment the metal iodide promoter is selected from the group consisting of as CoI₂, BI₃, AlI₃, GaI₃, GeI₃, SnI₄, LaI₃, TiI₄, ZrI₄, CrI₃, MnI₃, NiI₂, ZnI₂, and HgI₂. Preferably, the metal iodide promoter is cobalt iodide.

DETAILED DESCRIPTION OF INVENTION

The process of the present invention involves a rhodium catalyzed carbonylation of an allylic compound to produce a beta-gamma unsaturated carboxylic acid anhydride wherein the rhodium-containing catalyst is promoted by the use of a metal iodide salt and the carbonylation reaction is performed under anhydrous conditions. The allylic compound being carbonylated is an allylic butenyl ester of a carboxylic acid or the equivalent such as an allylic butenol dissolved in a carboxylic acid. The following representative reaction showing a crotyl ester (i.e., a carboxylic acid ester of 2-buten-1-ol) as the reactant producing a corresponding pentenoic acid anhydride is illustrative of the overall carbonylation.



Suitable allylic compounds 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 selected from the group consisting of H and



wherein R^5 is selected from the group consisting of 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, when the allylic compound is a butenyl alcohol (i.e., when R₄ is H) the presence of the carboxylic acid solvent leads to in-situ ester formation and thus total equivalency relative to the above illustrative carbonylation reaction.

5 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.

10 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
15 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
20 butenyl ester is needed. Typically, an excess of CO is used.

 Suitable solvents for this process are anhydrous carboxylic acids of up to twenty carbon atoms. Such solvents include aliphatic and aromatic carboxylic acid solvents and mixtures thereof. The most preferred solvents are the C₂ to C₁₀ aliphatic monocarboxylic acids and most preferably the solvent is
25 anhydrous acetic acid or 3-pentenoic acid.

 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 , $\text{Rh}(\text{CO})_2\text{I}_3$, $\text{Rh}(\text{CO})\text{I}_3$, $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, $\text{Rh}(\text{acac})_3$, $\text{Rh}(\text{CO})_2(\text{acac})$, $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$, $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Rh}(\text{CO})_2\text{Br}]_2$, $\text{Rh}(\text{COD})(\text{acac})$, $[\text{Rh}(\text{COD})\text{Cl}]_2$, $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, $\text{Rh}_2[\text{O}_2\text{C}(\text{CR}_2)_6\text{CH}_3]_4$, and $\text{Rh}_2(\text{acetate})_4$, where acac is acetylacetonate, COD is 1,5-cyclooctadiene, and Ph is phenyl. Rhodium compounds containing bidentate phosphorus or nitrogen ligands should be avoided. Preferred sources of rhodium catalyst include rhodium(I) compounds such as $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Rh}(\text{COD})\text{Cl}]_2$, $\text{Rh}(\text{COD})(\text{acac})$, and rhodium iodide compounds such as RhI_3 and $\text{Rh}(\text{CO})_2\text{I}_3$.

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 a metal iodide under anhydrous reaction conditions, to achieve a satisfactory rate and selectivity to pentenoic acid anhydrides. Examples of suitable promoters are iodides of Groups IIB, IIIA, IIIB, IVA, IVB, VIB, VII, VIII of the periodic table. Preferred promoters are CoI_2 , BI_3 , AlI_3 , GaI_3 , GeI_3 , SnI_4 , LaI_3 , TiI_4 , ZrI_4 , CrI_3 , MnI_3 , NiI_2 , ZnI_2 , and HgI_2 . Most preferred promoter is cobalt iodide.

The molar ratio of promoter to rhodium can be in the range of about 1:1 to about 30:1. Although high selectivities to the desired 3-pentenoic acid anhydride can be obtained even at low promoter to rhodium ratios, the rate of formation of 3-pentenoic acid anhydride 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 30 to obtain reasonable yields of the unsaturated acid anhydride. Preferably, the molar ratio of promoter to rhodium is between about 2:1 and about 6:1.

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 reactant that is not consumed by chemical reaction (i.e., all isomers). The selectivity to the desired 3-pentenoic acid anhydride is based on and reported as the amount of methyl ester after esterification of the reaction product and as such includes free 3-pentenoic acid inherently produced by anhydride exchange with the carboxylic acid solvent or the like. The comparative examples (Table 2) show that selectivity to methyl-3-pentenoate (M3P) is very low when alkyl iodides are used in place of the metal iodide promoter. When lithium iodide is used, the rate of the reaction is very low.

Example 1

Carbonylation of 3-Acetoxybutene-1 using a Rhodium Catalyst and a Cobalt Iodide Promoter:

A 25 mL glass lined pressure vessel was charged with 5 mL of a solution containing 9.1 grams (80 mmol) of 3-acetoxybutene-1 (3ACB1), 0.258 grams (1.0 mmol) of dicarbonylacetylacetonate rhodium(I), 0.46 grams (1.47 mmol) of cobalt iodide (i.e., CoI_2), and 1.00 grams of o-dichlorobenzene (internal gas chromatograph standard) in 100 mL of acetic acid. 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/H_2 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 to determine unreacted butenyl acetates and butadiene. Pentenoic anhydride and pentenoic acid were determined by esterifying a sample of the solution with excess methanol in the presence of p-toluenesulfonic acid to convert anhydrides and pentenoic acid to their methyl esters. The esterified product was analyzed for methyl esters by gas chromatography (GC) on a 30 M J&W Scientific BD-5 capillary GC column. The results of the analysis follow:

	Before esterification	mmol/100 mL	
	Butadiene	1.1	
20	3-Acetoxybutene-1	9.5	
	Crotyl Acetate (cis & trans isomers)	2.1	
	Conversion = 64.5%		
	After Esterification	mmol/100 mL	selectivity
	Methyl-3-pentenoate	60.9	94.4
25	Methyl-2-pentenoate	3.2	5.0

Examples 2-14

In a manner analogous to the procedure employed in Example 1, an additional thirteen runs were performed using in each example a different

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metal iodide promoter. The resulting data for each of these examples as well as the corresponding data from Example 1 are presented in the following Table 1.

Table 1

Example	Metal Iodide	Conversion	Selectivity to M3P
5	1 CoI_2	64.5	94.4
	2 BI_3	74.7	61.8
	3 AlI_3	74.6	74.8
	4 GaI	71.3	85.4
	5 GeI_3	75.1	87.5
10	6 SnI_4	73.2	72.9
	7 LaI_3	41.6	87.2
	8 TiI_4	74.6	83.4
	9 ZrI_4	75.0	89.0
	10 CrI_3	74.0	91.7
15	11 MnI_3	56.7	93.5
	12 NiI_2	12.8	29.8
	13 ZnI_2	13.2	71.6
	14 HgI_2	12.8	35.6

Comparative Examples 1-4

For comparison the procedure utilizes in Example 1 was repeated except that the metal iodide was replaced with HI, an alkyl iodide (2-iodobutane or 1-iodobutane), or lithium iodide. The results are summarized in Table 2.

9
Table 2

Comparative Example	Additive	Conversion	Selectivity to M3P
1	HI	63.2	7.4
2	2-iodobutane	63.8	1.0
5 3	1-iodobutane	64.3	3.2
4	lithium iodide	2.3	47.7
5	1-iodobutane	16.9	88.2

and lithium iodide

Examples 15-18

10 In a manner analogous to the procedure employed in Example 1, an additional four runs were performed except the 3-acetoxybutene-1 was replaced with crotyl acetate and the promoter was a mixture of HI and a metal acetate or chloride salt. The ratio of HI to Rh was 3 and the ratio of metal to Rh was 1. The resulting data are presented in the following Table 3.

15

Table 3

Example	Metal Promoter	Iodide	Conversion	Selectivity to M3P
15	Al(OAc) ₂ OH ^(a)	57% aq HI	95.0	69.0
16	Aluminum Chloride	anh HI/HOAc ^(b)	90.1	79.8
20 17	Samarium Acetate	anh HI/HOAc	75.6	83.2
18	Cobalt Acetate	anh HI/HOAc	78.4	83.0

(a) monobasic aluminum acetate

(b) a solution of 57% aqueous HI in acetic acid with an amount of acetic acid anhydride equivalent to the water in the aqueous HI

25 The process of the present invention is useful for the preparation of carboxylic acid anhydrides and derivative thereof and in particular the production of 3-pentenoic acid. Such products are useful as difunctional monomers and as 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 butenol or a butenyl ester of a
5 carboxylic acid and production of beta-gamma unsaturated carboxylic acid
anhydride comprising the steps of:
- (a) reacting an allylic butenol or butenyl ester of a carboxylic acid with
carbon monoxide in the presence of a rhodium-containing catalyst and a
metal iodide promoter in a C₁ to C₂₀ carboxylic acid solvent under
10 anhydrous conditions; and
- (b) recovering a beta-gamma unsaturated carboxylic acid anhydride.
2. The process of Claim 1 wherein said allylic butenyl ester of a carboxylic acid
is selected from the group consisting of crotyl acetate, 3-acetoxybutene-1 and
15 mixtures thereof and said beta-gamma unsaturated carboxylic acid anhydride is
3-pentenoic acid anhydride.
3. The process of Claim 2 wherein said metal halide promoter is selected from
the group consisting of as CoI₂, BI₃, AlI₃, GaI₃, GeI₃, SnI₄, LaI₃, TiI₄, ZrI₄,
20 CrI₃, MnI₃, NiI₂, ZnI₂, and HgI₂.
4. The process of Claim 3 wherein said metal halide promoter is cobalt iodide.

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