A process to produce a diene from a lactone

Field

[0001] This application relates to a process to produce a diene from a lactone.

Priority

[0002] This application claims priority from Singaporean patent application no. 201202262-0, the entire contents of which are incorporated herein by cross-reference.

Background

[0003] Concerns for the availability of fossil feedstocks and climate change have led to significant interests in chemicals and polymers derived from biomass. Butadiene is one of the most desired chemicals. It comes mainly as the byproduct of ethylene production from naphtha, Liquefied Petroluem Gas and dehydrogenation of butane. Butadiene is normally used to make styrene butadiene rubber, acrylonitrile-butadiene-styrene, adiponitrile and chloroprene. Among commercial polymers, Nylons and Nylon monomers are exceedingly inefficient in terms of energy and chemical utilization. In this disclosure, we report the invention of a green process for making butadiene and/or adipic acid, a Nylon 66 monomer, from γ-valerolactone. γ-Valerolactone can be derived from hydrogenation of levulinic acid, one of the so-called biobased platform molecules which can be readily obtained from acid-catalyzed decomposition of cellulose or C6 sugars. More generally, the process may be used for production of dienes and/or diacids from lactones.

Summary ~~of Invention~~

[0004] ~~In a first aspect, t~~There is provided a process for preparing an alkyldiene comprising the steps of:

(a) heating a lactone in the presence of a first catalyst system to produce an alkene and carbon dioxide; and

(b) contacting the alkene with a second catalyst system to produce an alkyldiene.

[0004a] In an aspect, there is provided a process for the production of a diene comprising the steps of:

(a) heating a lactone in the presence of a first catalyst system and substantially in the absence of water to produce an alkene and carbon dioxide; and

(b) contacting the alkene with a second catalyst system to produce an alkyldiene.

[0005] Advantageously, step (a) is carried out substantially in the absence of water. This may serve to reduce intermediate purification steps and/or to generate less waste streams for treatment and disposal than if water was required for the process. The lactone and/or other components used in step a) (e.g. the first catalyst system, any carrier used) may be dried prior to use in step a).

[0006] In one embodiment, the heating of the lactone in step (a) is conducted in a flow reactor. Step (a) may comprise passing the lactone through a bed, optionally a heated bed, of the first catalyst system. The bed may be a packed bed. Optionally, the heating of the lactone in step (a) is carried out at a temperature at or above the normal boiling point of the lactone. Preferably, step (a) is carried out at a temperature of between about 200°C and about 400°C or about 220°C to 360°C or about 240°C to 360°C or about 260°C to 340°C or about 280°C to 330°C or about 200°C to 300°C or about 300°C to 400°C or about 250°C to 300°C or about 250°C to 350°C or about 300°C to 350°C, e.g. at about 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390 or 400°C. In some instances even greater temperatures may be used. The flow in the flow reactor (or through the bed) may be from about 0.2 to about 2 h^{-1}, or about 0.5 to 2, 1 to 2, 0.2 to 1, 0.2 to 0.5, 0.5 to 1.5 or 0.5 to $1h^{-1}$, e.g. about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9 or $2h^{-1}$, although other flow rates may be used in particular cases. The unit h^{-1} will be recognised to be a volume independent unit, which may be considered equivalent, for example, to litres reagent per hour per litre of bed volume.

[0007] In one embodiment, step (a) is carried out at a pressure of between about 0.5 bar and about 50 bar, or between about 0.5 and 25, 25 and 50, 10 and 40, 0.5 and 20, 0.5 and 10, 0.5 and 5, 0.5 and 2, 0.5 and 1, 1 and 50, 10 and 50, 20 and 50, 10 and 50, 10 and 20, 5 and 20 or 20 and 30 bar, e.g. about 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45 or

50 bar. In some instances even higher pressures may be used. The pressure may be such that, at the bed temperature, the lactone is a vapour.

[0008] In one embodiment, the first catalyst system comprises an acidic catalyst. The first catalyst system, e.g. the acidic catalyst, may be a heterogeneous solid catalyst. The acidic catalyst may also be a homogeneous catalyst. The acidic catalyst may be selected from a group consisting of alumina, silica, a zeolite, a clay, sulphuric acid, *p*-toluenesulfonic acid and

and low temperatures may be at least about 5 Celsius degrees, or at least about 10, 50, 20, 25, 30, 35, 40, 45 or 50 Celsius degrees.

[00044] In another embodiment, the process further comprises the step of:

(c6) recycling the second portion, comprising the third catalyst system, to step (c).

[00045] In one embodiment, the lactone is γ-valerolactone, the alkene is butene and the alkyldiene is 1,3-butadiene. The lactone may be a bio-based lactone. It may be bio-based γ-valerolactone. The process may comprise the step of preparing the γ-valerolactone. This may for example be by hydrogenation of levulinic acid. The process may further comprise the step of preparing the levulinic acid, e.g. by acid catalysed hydrolysis of cellulose. The process may further comprise the step of preparing the cellulose, e.g. by cracking lignocellulose.

[00046] In one embodiment, the butene comprises 1-butene and 2-butene.

[00047] In one embodiment, the lactone is γ-valerolactone, whereby the alkene is butene, the alkyldiene is 1,3-butadiene, the alkenoic acid is pentenoic acid and the dicarboxylic acid is adipic acid.

[00048] In one embodiment, the pentenoic acid comprises a mixture of at least two of 2-pentenoic acid, 3-pentenoic acid and 4-pentenoic acid.

[00049] In one embodiment, the γ-valerolactone is prepared by hydrogenation of levulinic acid.

[00050] In one embodiment, the levulinic acid is prepared by acid catalysed hydrolysis of cellulose.

[00051] In one embodiment, the cellulose is prepared by cracking lignocellulose.

[00052] In one embodiment~~a second aspect~~, there is provided a process for preparing a dicarboxylic acid comprising the steps of:

(a) heating a lactone in the presence of a first catalyst system to produce an alkenoic acid and carbon dioxide; and

[000148] In ~~third aspect~~one embodiment, there is provided a process to produce an alkyldiene and a dicarboxylic acid, the process comprising the steps of:

(a) heating a lactone in the presence of a first catalyst system to produce an alkene, an alkenoic acid and carbon dioxide; and

(b) contacting the alkene of step (a) with a second catalyst system to produce the alkyldiene,

(c) contacting the alkenoic acid of step (a) with carbon monoxide and water and a third catalyst system to produce the dicarboxylic acid.

[000149] The process may comprise the step of (d) removing the alkyldiene from the carbon monoxide and water before step (c). It should be noted that butadiene may be used a co-feed for step (c). It may slow down the carbonylation reaction or may place different requirements on the Pd catalyst due to pi-allyl formation. Also, small amounts of butene from step (b) may end up in step (c) with the carbon monoxide, however this is unlikely to cause a problem: it is likely that they would be carbonylated to valeric acid, a compound that is formed in small amounts during both step (a) and (c) in any event.

[000150] The process may comprise the step of (e) removing the dicarboxylic acid from the third catalyst system after step (c).

[000151] Advantageously, step (a) is carried out substantially in the absence of water, reducing intermediate purification steps and generating less waste streams for treatment and disposal than if water was required for the process.

[000152] In one embodiment, the heating of the lactone in step (a) is conducted in a flow reactor. Optionally, the heating of the lactone in step (a) is carried out at a temperature at or above the normal boiling point of the lactone. Preferably, step (a) is carried out at a temperature of between 200°C and 400°C or 220°C to 360°C or 240°C to 360°C or 260°C to 340°C or 280°C to 330°C.

[000153] In one embodiment, step (a) is carried out at a pressure of between about 0.5 bar and 50 bar, or 0.5 bar to 25 bar, or 25 bar to 50 bar, or 10 bar to 40 bar.

[000154] In one embodiment, the first catalyst system comprises an acidic catalyst. The acidic catalyst may be a heterogeneous solid catalyst. The acidic catalyst may also be a homogeneous

[000174] In another embodiment, the acid for preparing the palladium catalyst is selected from the group consisting of sulfonic acids, sulphuric acids, phosphorous acids and carboxylic acids.

[000175] In another embodiment, the acid is a C_1-C_{10} aliphatic acid.

[000176] In another embodiment, the acid is selected from the group consisting of methanesulfonic acid, triflic acid, trifluoroacetic acid and *p*-toluenesulfonic acid. Preferably, the acid is methane sulfonic acid.

[000177] In another embodiment, the bidentate diphosphine for the palladium catalyst preparation is 1,2-bis[di(*t*-butyl)phosphinomethyl]benzene.

[000178] In another embodiment, the acid is present in molar excess relative to the palladium compound. Preferably the molar ratio of the acid to the palladium compound is from 2:1 to 10000:1 or from 5:1 to 5000:1 or from 5:1 to 300:1. Most preferably the molar ratio of the acid to the palladium compound is from 5:1 to 300:1.

[000179] In another embodiment, a portion of the lactone is unreacted after step (a), producing a reaction composition comprising unreacted lactone, alkenoic acid and alkene and part or substantially all of the unreacted lactone is present in step (c) producing a reaction composition comprising unreacted lactone and dicarboxylic acid.

[000180] In a ~~fourth aspect~~one embodiment, there is provided an alkyldiene prepared in accordance with the process as defined above.

[000181] In one embodiment, the alkyldiene has a purity of greater than 99%.

[000182] In one embodiment, the alkyldiene is 1,3-butadiene.

[000183] In ~~a fifth aspect~~one embodiment, there is provided use of the 1,3-butadiene produced by the process as defined above in the manufacture of styrene butadiene rubber, acrylonitrile-butadiene-styrene, adiponitrile or chloroprene.

[000184] In ~~a sixth aspect~~one embodiment, there is provided a dicarboxylic acid prepared in accordance with the process as defined above.

[000185] In one embodiment, the dicarboxylic acid has a purity of greater than 99%.

[000186] In one embodiment, the dicarboxylic acid is adipic acid.

Brief Description of Drawings

[000187] Figure 1 shows a scheme of reactions according to the present invention.

Description of Embodiments

[000188] The process provides a cost competitive method of producing butadiene and/or adipic acid from a renewable feedstock. Based on the market need, the ratio of PEA/butene therefore adipic acid/butadiene can be adjusted accordingly.

Process

[000189] The process comprises 3 steps as show in Fig. 1:

[000190] Step 1: Pyrolyze γ-valerolactone (GVL) in a flow reactor to a mixture of pentenoic acid isomers (PEA), butene isomers, and CO_2 in the presence of an acid catalyst. Adjust reaction temperature and residence time to produce the desired ratio of PEA to butene.

[000191] Step 2: Dehydrogenate butene isomers to butadiene.

[000192] Step 3: Convert PEA isomers to adipic acid in the presence of CO, water, and a palladium catalyst. Isolate and purify adipic acid to polymerization grade product by precipitation and recrystallisation. Recycle the filtrate containing catalyst and unreacted pentenoic acid for carbonylation.

[000193] The reaction in step [1] can be carried out in the presence of an acid catalyst. A wide range of acid catalysts can be used. These include homogenous catalysts such as sulfuric acid, p-