SYNTHESIS OF DIACIDS

Technical Field

The present invention relates to processes for synthesising dicarboxylic acids.

Related Application

This application claims priority from United States Provisional Patent Application No. 61/468,494, which is incorporated herein in its entirety by cross-reference.

Background of the Invention

Any discussion of the background art throughout the specification should in no way be considered as an admission that such background art is prior art, nor that such background art is widely known or forms part of the common general knowledge in the field.

Dicarboxylic acids may be used as monomer units in the preparation of polymers. For example, adipic acid is used as a monomer unit in the preparation of Nylon 6-6.

Existing processes for producing many diacids rely on fossil feedstocks. Among commercial polymers, processes for preparing Nylons and Nylon monomers require a high use of energy and chemicals. Concerns for the future availability of fossil feedstocks and environmental factors have led to significant interest in chemicals and polymers derived from renewable sources, such as biomass.

Accordingly, there is a need to provide processes for preparing diacids, such as adipic acid, from renewable feedstock.

~~*Summary of Invention*~~

~~According to a first aspect of the present invention t~~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

(b) contacting the alkenoic acid with carbon monoxide, water and a second catalyst system to produce a reaction composition comprising the second catalyst system and the dicarboxylic acid.

In a first aspect, there is provided a process for preparing a dicarboxylic acid comprising the steps: (a) heating a lactone in the presence of a first catalyst system to produce an alkenoic acid; and (b) contacting the alkenoic acid with carbon monoxide, water and a second catalyst system to produce a reaction composition comprising the second catalyst system and the dicarboxylic acid, said second catalyst system comprising a palladium catalyst.

The following options may be used in combination with the first aspect, either individually or in any suitable combination.

Step (a) may be carried out substantially in the absence of water. The process according to the first aspect above may further comprise a step of removing water from the lactone and/or from the first catalyst system prior to step (a).

In another embodiment there is provided a process for preparing adipic acid comprising the steps:

(a) heating γ-valerolactone to a temperature in the range 200 to 350°C, at a pressure of between about 1 to 40 bar, in the presence of a first catalyst system to produce pentenoic acid, the first catalyst system comprising a mixture of alumina and silica; and

(b) contacting the pentenoic acid with carbon monoxide, water and a second catalyst system, the second catalyst system comprising a palladium catalyst, at a temperature in the range 80 to 120°C and a pressure in the range 1 to 80 bar, to produce a reaction composition comprising the second catalyst system and the adipic acid,

wherein step (a) is carried out substantially in the absence of water and the heating of the γ-valerolactone in step (a) comprises reactive distillation, thereby providing a distillate comprising the pentenoic acid, and

wherein the palladium catalyst is prepared by combining palladium acetate, 1,2-bis[di(*t*-butyl)phosphinomethyl]benzene, and methane sulfonic acid.

In another embodiment there is provided a process for preparing adipic acid comprising the steps:

(a) refluxing γ-valerolactone in the presence of a mixture of alumina and silica as a first catalyst system at a temperature in the range 200 to 350°C and at a pressure of about 1 bar for 1 to 3 hours, substantially in the absence of water, to produce a composition comprising pentenoic acid;

(a') distilling the composition from step (a) to produce a distillate comprising pentenoic acid;

(b) degassing the distillate and combining the degassed distillate with degassed deionised water and a degassed solvent (e.g., diglyme);

(b') combining palladium acetate, 1,2-bis[di(*t*-butyl)phosphinomethyl]benzene and methane sulfonic acid to form a second catalyst system;

(b") adding the second catalyst system to the combined distillate, water and solvent under a stream of argon gas and flushing with carbon monoxide;

(b"') heating at a temperature in the range 80 to 120°C and a pressure in the range 1 to 80 bar of carbon monoxide for 2 to 10 hours, to produce a reaction composition comprising the second catalyst system and the adipic acid,

According to one embodiment~~a second aspect~~ of the present disclosure~~invention~~ there is provided a dicarboxylic acid prepared in accordance with the process of the first aspect above. The

dicarboxylic acid may have a purity of greater than about 99%. The dicarboxylic acid may be adipic acid.

According to one embodiment~~a third aspect~~ of the present disclosure~~invention~~ there is provided a method of preparing Nylon 6-6 comprising the step of copolymerising adipic acid prepared in accordance with the embodiment described~~third aspect~~ above with hexamethylenediamine, thereby forming the Nylon 6-6.

In a second aspect, there is provided a method of preparing Nylon 6-6 comprising the steps: (a) heating γ-valerolactone in the presence of a first catalyst system to produce pentenoic acid; (b) contacting the pentenoic acid with carbon monoxide, water and a second catalyst system to produce a reaction composition comprising the second catalyst system and adipic acid, said second catalyst system comprising a palladium catalyst, and (c) copolymerising the adipic acid with hexamethylenediamine, thereby forming the Nylon 6-6.

Brief Description of the Drawings

Embodiments of the present invention will now be described, by way of an example only, with reference to the accompanying drawings wherein:

Figure 1 is a schematic diagram of an embodiment of the process for preparing a diacid according to the present invention.

Detailed Description of the Preferred Embodiments

Disclosed herein is a process for making a dicarboxylic acid from a lactone. The process for preparing a dicarboxylic acid according to the present invention generally comprises a step (a) of heating a lactone in the presence of a first catalyst system to produce an alkenoic acid. In a subsequent step (b), the alkenoic acid is contacted with carbon monoxide, water and a second catalyst system to produce a reaction composition comprising the second catalyst system and the dicarboxylic acid.

In embodiments, the present invention includes a process for preparing adipic acid, a Nylon 6-6 monomer, from γ-valerolactone. γ-Valerolactone can be derived from hydrogenation of levulinic acid, a so-called bio-based platform molecule. In turn, levulinic acid can be readily obtained from acid-catalysed decomposition of cellulose or C_6 sugars. Thus, the process according to the present invention provides a method of producing adipic acid from a renewable feedstock.

The term "substantially", as used herein in relation to an amount, such as in "substantially in the absence" or similar phrases, means that the amount referred to is sufficiently low that it does not significantly affect operation of the invention.

The phrase "substantially in the absence of water", as used herein, may mean that the concentration of water is sufficiently low that any reduction of this concentration would not increase the yield of alkenoic acid by more than about 10% or more than about 1%. Such concentrations may be less than about 0.1, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02 or 0.01 moles of water per mole of lactone. This phrase may additionally or alternatively indicate the absence of any added water.

The phrase "substantially in the absence of oxygen", as used herein, may mean that the concentration of oxygen is less than about 0.1 moles of oxygen per mole of