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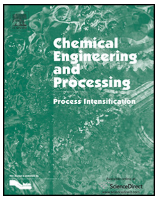

Hydroesterification of methyl 10-undecenoate in thermomorphic multicomponent solvent systems—Process development for the synthesis of sustainable polymer precursors

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ABSTRACT

In this paper, we present a process concept for the atom economic hydroesterification of renewable methyl 10-undecenoate in thermomorphic multicomponent solvent (TMS) systems. Resulting dimethyl dodecanedioate is a polymer building block used e.g. in Nylon 6,12. As a suitable recycling technique a thermomorphic multicomponent solvent system consisting of methanol and dodecane is employed to recycle the palladium/1,2-bis(di-*tert*-butylphosphino)methyl)benzene/methanesulfonic acid catalyst. Product yields up to 79% and a high regioselectivtiy of 94% to the linear product are obtained. Low leaching of the catalyst into the product phase with 1% in respect of palladium and phosphorous is observed. Robustness and stability of the catalyst is shown in eight recycling runs without any loss of selectivity in the reaction.

1. Introduction

In times of increasing scarcity of fossil fuels and climatic change the usage of renewable feedstocks in industrial chemistry gets more and more attractive from ecological point of view. For their implementation it would be a great advantage if existing production lines may continue to be used with intermediates gained from renewables [1]. In this paper, we describe an alternative process concept for the synthesis of dimethyl dodecanedioate (**2**) based on renewable starting materials.

Main application of dodecanedioic acid is in polyester and polyamide synthesis [2]. Polyamide 6,12 for example, which is synthesised by condensation of dodecanedioic acid with hexamethylenediamine, provides a high melting point (212 °C), high mechanical strength and dimensional stability, high robustness against chemicals and low water absorption [3].

Industrial synthesis of dodecanedioic acid usually starts from butadiene which is trimerised to 1,5,9-cyclododecatriene (CDT). CDT can be converted into dodecanedioic acid either in a three or a two stage reaction sequence. In case of three reaction steps CDT is initially hydrogenated to cyclododecane. Subsequent oxidation with air or oxygen is carried out yielding in a mixture of cyclododecanol and cyclododecanone. The third reaction step is the oxidation with nitric acid to dodecanedioic acid. The second route consists of a partial hydrogenation of CDT to cyclododecene. Subsequent oxidative ozonolytic cleavage results in desired 1,12-dodecanedioic acid [2]. A possible direct synthesis route based on renewable resources starts from 10-undecenoic acid, which can easily be obtained by pyrolytic cleavage of ricinoleic acid [4]. Andrade and co-workers describe a reaction sequence consisting of hydroformylation of 10-undecenoic acid and subsequent oxidation to the corresponding dicarboxylic acid [5]. Another approach is hydroesterification of methyl 10-undecenoate (**1**) leading to the corresponding linear diester dimethyl dodecanedioate (**2**) [6], which is used instead of the free acid as substrate in condensation reactions to form polyesters or polyamides.

The hydroesterification is a transition metal catalysed atom-economical direct transformation of unsaturated substrates,

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Abbreviations: [$Pd_2(dba)_3$], tris(dibenzylideneacetone)dipalladium; 1,2-DTBPMB, 1,2-bis((di-tert-butylphosphino)methyl)benzene; CDT, 1,5,9-cyclododecatriene; DPEphos, (oxybis(2,1-phenylene))bis(diphenylphosphine); DPPB, 1,4-bis(diphenylphosphino)butane; DPPE, 1,2-bis(diphenylphosphino) ethane; DPPH, 1,6-bis(diphenylphosphino)hexane; ICP-OES, inductive coupled plasma optical emission spectrometry; MSA, methanesulfonic acid; NiXANTphos, 4,6-bis(diphenylphosphino)-10H-phenoxazine; $Pd(acac)_2$, palladiumacetylactonate; $Pd(hfacac)_2$, palladiumhexaflouroacetylactonate; t-Bu-XANTphos, (9,9-dimethyl-9H-xanthene-4,5-diyl) bis(di-*tert*-butylphosphine); TMS, thermomorphic multicomponent solvent; XANTphos, (9,9-dimethyl-9H-xanthene-4,5-diyl) bis (diphenylphosphine).

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carbon monoxide (CO) and an alcohol to form a new ester moiety. In this reaction discovered by Walter Reppe in 1953 [7], a wide range of substrates can be applied [8]. In the early 2000s hydroesterification has gained industrial importance since 100,000 tons of methyl propionate per year are synthesised by hydroesterification from ethene [9–15].

Efficient catalysts for the hydroesterification with high regioselectivity towards the linear product were already described in literature. Cole-Hamilton et al. applied a catalyst consisting of tris (dibenzylideneacetone) dipalladium [$Pd_2(dba)_3$] as precursor, 1,2-bis(di-*tert*-butylphosphinomethyl)benzene (1,2-DTBPMB, Fig. 3) and methanesulfonic acid (MSA) in hydroesterification of several terminal and internal olefins. This catalyst system is highly selective towards linear products. Even if internal olefins are used as starting materials, linear hydroesterification products are formed via isomerisation/hydroesterification tandem reaction (>93% linearity) [16]. Since then, this catalyst system was utilised to transform numerous substrates into linear esters. Especially unsaturated esters are interesting starting materials because the corresponding linear diesters are of high interest in polymer synthesis [17–20]. Those linear diesters can be obtained from unsaturated fatty acid methyl esters [6,21], fatty acids [6], triglycerides [22–26] and terpenes [27] with high selectivities. In consequence several studies on catalyst activity [28–32] and mechanistic elucidations on isomerising hydroesterification were conducted [33–35].

A particular challenge in homogeneous palladium-catalysed hydroesterification reactions is the recovery of the valuable noble-metal catalyst. García-Suárez et al. reported about palladium/1,2-DTBPMB catalyst immobilisation using ionic liquids in the hydroesterification of ethene [36]. While this system is well suited for simple, short chained olefins, catalyst recycling with more complex substrates is still an issue due to their high boiling points and polar properties.

A promising recycling technique for separating homogeneous catalysts from middle to non-polar products is the application of thermomorphic multicomponent solvent (TMS) systems. These solvent systems take advantage of the temperature dependend miscibility gap of a polar and a non-polar solvent mixture. Heating the solvent system to reaction temperature leads to the formation of one single homogeneous reaction mixture overcoming mass transfer limitations during the reaction. Cooling after reaction initiates phase separation and the polar, catalyst containing phase can be separated from the non-polar product phase via simple decantation (Fig. 1) [37,38].

TMS systems were already successfully applied as catalyst recycling concept in several reactions such as cooligomerisations [39,40], hydrosilylations [41], hydroaminomethylations [42–44] and hydroformylations [45–50]. The hydroformylation of 1-dodecene was also conducted into miniplant scale enabling a continuous and stable process control [51].

The first application of TMS systems in hydroesterification were reported by Behr et al. in the year 2013 in the hydroesterification of methyl oleate [52] and oleyl alcohol [43] using a palladium precursor and XANTphos as ligand (Fig. 3). Within these reaction systems, the unsaturated C18 compounds were predominately transformed into branched hydroesterification products.

However, application of TMS systems in carbonylation reactions of shorter-chained fatty acid derivates is more challenging due to the higher polarity of substrates and products. Ternel et al. investigated the applicability of TMS systems in hydroformylation of 10-undecenenitrile. The relatively high polarity of the resulting bifunctional product leads to an accumulation (99%) in the polar, catalyst containing phase which made an efficient separation of the catalyst impossible [53].

Herein, we describe a process concept for the linear hydroesterification of methyl 10-undecenoate (**1**) towards dimethyl dodecanedioate (**2**) using TMS systems as recycling technique.

2. Materials and methods

All experiments were conducted under argon atmosphere using Schlenk technique. All chemicals are commercial available. The ligand 1,2-DTBPMB was provided by Digital Speciality Chemicals Ltd., in a 28 w% solution in methyl propionate. Methyl propionate was removed under reduced pressure before use. Further chemicals were degased and stored under argon. Carbon monoxide was purchased by Messer Industriegase GmbH in 98% purity.

2.1. Hydroesterification of methyl 10-undecenoate

In a typical hydroesterification experiment the palladium precursor and the ligand were weighted into a 20 mL stainless steel autoclave [54]. Afterwards the reactor was evacuated and flushed with argon three times. Then methanol was introduced under inert atmosphere by syringe and the mixture was allowed to stir at 600 rpm for three hours at room temperature under argon atmosphere. Afterwards, dodecane, methyl 10-undecenoate and methanesulfonic acid in methanol were introduced into the reactor inertly. The reactor was pressurised with 30 bar CO and heated to 90 °C. After two hours, the reactor was placed in an ice bath to quench the reaction and was vented. The reaction mixture was introduced into a separating funnel for 20 min until phases were separated. Analysis of the composition of phases was conducted by gas chromatography (Hewlett-Packard, HP 6890 Series). The gas chromatograph was equipped with a capillary column (HP-INNOWAX 30 m × 0.25 mm × 0.25 μm) and a flame ionisation detector. 1-Hexanol was used as internal standard. Concentrations of palladium and phosphorous were determined via inductive coupled plasma optical emission spectrometry (ICP-OES). For sample preparation for ICP-OES measurement 0.230 g of

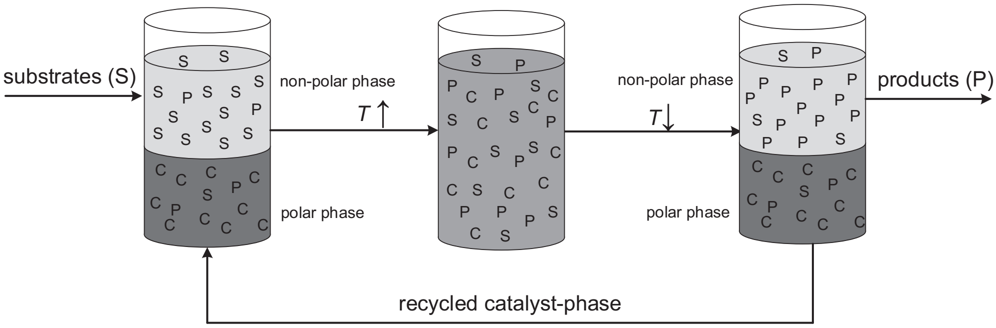

Fig. 1. [a] Principle of a TMS system [49].
[a] C = catalyst, P = products, S = substrates, T = temperature.