Alpha Olefins from Fatty Acids

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Introduction

Bio-Based internally unsaturated long chain hydrocarbons, obtained from unsaturated fatty acids, can serve as feedstock for the production of linear alpha olefins (LAO's) via ethenolysis. Currently, LAO's are produced petrochemically, and serve as starting materials for e.g. detergents and plastics (LLDPE).
Since the decarboxylation-products of unsaturated fatty acids are not commercially available, we have previously prepared these materials by means of stoichiometric oxidative decarboxylation [1]. Here we report our preliminary results on ethenolysis using a series of commercially available metathesis catalysts. Both high conversions and high selectivities towards the desired LAO's were obtained.

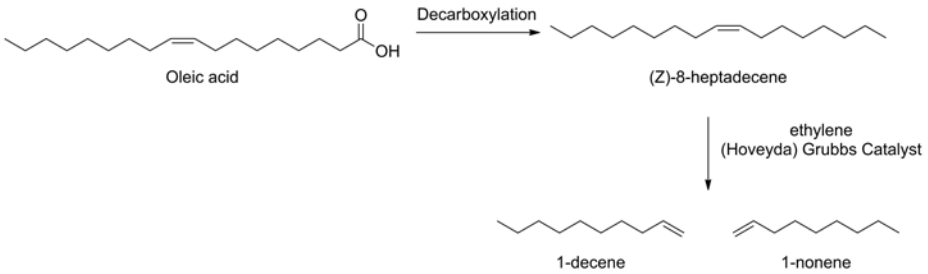

Figure 1. Two step process for the production of Linear Alpha Olefins from oleic acid.

Experimental

Reactions were carried out using a 6x75mL Parr MRS5000 parallel reactor. Catalysts (Sigma Aldrich) were introduced in the reactors under N_2 atmosphere. Then a solution of (*Z*)-8-heptadecene (1 mmol) in 10 mL distilled solvent was added and the reactors were closed. After applying the desired ethylene pressure, stirring was started (500 rpm) and the reaction mixtures were heated to the desired temperature. After reaction the solutions were filtered over silica to remove the catalyst. Product composition was determined with GC-MS and, after removal of the solvent, by $^{1}H/^{13}C$ NMR.

Results/Discussion

We initially investigated the ethenolysis of (*Z*)-8-heptadecene in dichloromethane at 40°C for 20h. Ethylene pressure was varied (1-10 bar) and three types of catalysts were screened: 1st Generation Grubbs (G1) and 1st and 2nd Generation Hoveyda-Grubbs (HG1 & HG2). Although all catalysts gave the desired C9 and C10 LAO's, highest activity and selectivity were obtained using 3.5 mol% HG2 catalyst at 5 bar ethylene pressure.

In order to replace dichloromethane by a more environmentally benign solvent, a solvent screening was performed (Table 1).

Table 1. Product composition after reaction according to GC-MS. Conditions: (*Z*)-8-heptadecene (1 mmol), HG2 catalyst (3.5 mol%), solvent (10 mL), ethylene (5 bar), 40°C, 20h.

Solvent	C9 & C10 LAO (%) (Ethenolysis products)	C16-C18 internal alkenes (Self metathesis products)
Dichloromethane	85	15
Methanol	0	100
Ethyl acetate	5	95
Acetic acid	40	60
Dimethyl carbonate	Degradation products	
Toluene	70	30
Hexane	85-90	10-15

Non-polar solvents like toluene and hexane show highest yields in LAO's. Hexane performed even better then dichloromethane. Further optimisation showed that reaction time and catalyst loading can be decreased, using hexane as solvent.

Decarboxylated unsaturated fatty acids are excellent starting materials for the production of renewable Linear Alpha Olefins. High conversions and selectivity's towards the desired LAO's were obtained.

References

1. F. van der Klis, M.H. van den Hoorn, R. Blaauw, J. van Haveren, D.S. van Es, *Eur J Lipid Sci Technol.* (2011)