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PAPER

Polyamide precursors from renewable 10-undecenenitrile and methyl acrylate *via* olefin cross-metathesis†

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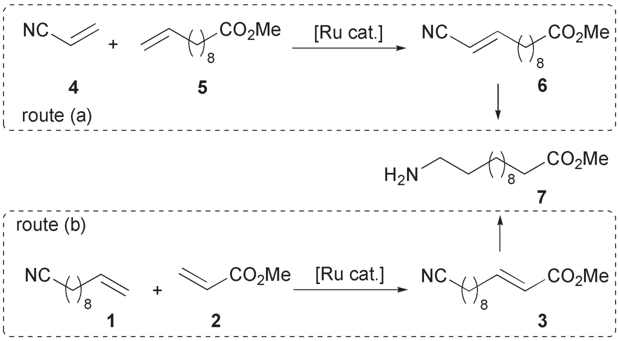
The ruthenium-catalyzed cross-metathesis of the unsaturated fatty acid derivative 10-undecenenitrile **1** arising from castor oil with methyl acrylate produces a C12 nitrile ester with high turnover number. This product has potential as a new bio-sourced intermediate for the production of polyamides. This route competes favourably with the reverse cross-metathesis of methyl 10-undecenoate with acrylonitrile leading to the same C12 α,ω-amino ester **7** after hydrogenation of the carbon–carbon double bond and the nitrile functionality.

Introduction

In the context of petrochemical resources shortage,[1] among renewable carbon sources, fats and oils present a strong potential for a variety of applications depending on the control of selective catalytic transformation reactions and have already received much attention.[2,3]

10-Undecylenic acid derivatives constitute valuable feedstock readily available from castor oil.[4] These renewable compounds have already been used for the industrial production of C11-polyamide (PA11) in the Rilsan® process.[5] They have also a huge potential for the generation of C12-amino esters, the precursors of C12-polyamide, upon cross-metathesis with functional olefins. Catalytic olefin metathesis is a powerful tool in organic chemistry[6] and polymer synthesis.[7] In particular, the cross-metathesis reaction has opened up efficient routes for the formation of new C=C bonds under mild conditions to readily give higher value to simple synthetic intermediates,[8] or to introduce a desired functionality into complex architectures.[9] The introduction of a polar functionality into unsaturated fatty acid derivatives, by cross-metathesis with alkynes[10] or electron poor olefins, such as acrylates,[11] or even allyl chloride,[12] leading to end-functionalized long chain alkenes, is now possible thanks to the development of very active and functional group tolerant catalysts.[13]

Acrylonitrile is not a very reactive partner in olefin metathesis reactions,[14] however the cross-metathesis of methyl 10-undecenoate with acrylonitrile offers sustainable catalytic access to the precursor of C12-polyamide **7** (Scheme 1, route (a)).[15,16]



Scheme 1 Syntheses of methyl 12-aminododecanoate **7**.

We now report that the linear C12 α,ω-amino ester **7**, the same polyamide precursor, can be prepared *via* cross-metathesis of methyl acrylate with the bio-sourced 10-undecenenitrile **1** in the presence of ruthenium-alkylidene catalysts (Scheme 1, route (b)).[17]

We show that the second generation Hoveyda type catalysts are the most efficient for these transformations. The reactions are drastically improved by slow addition of the catalyst to reach high TON in linear nitrile esters.

Results and discussion

Cross-metathesis reaction

Cross-metathesis of acrylates with fatty ester derivatives was first investigated with methyl oleate as partner.[12] Meier showed that 99% conversion of the oleate into the cross-metathesis products was obtained with second generation Grubbs (**I**) and Hoveyda–Grubbs (**II**) catalysts. The metathesis with catalyst **II** could be performed with an excess of acrylate and no additional solvent, indicating that the catalyst was not inhibited by the acrylate.[11] Cross-metathesis of methyl acrylate was extended to methyl

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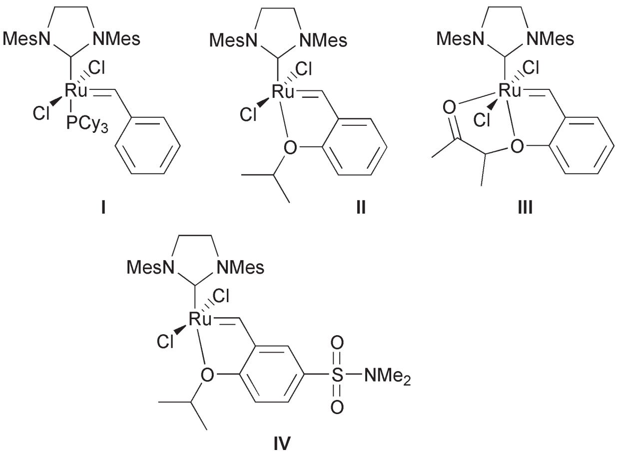
ricinoleate,[11d,15a] methyl erucate and methyl petroselinate,[11b] and also to oleyl alcohol and acetate in solvent free conditions.[11a]

Methyl undecenoate is obtained by thermal cleavage of methyl ricinoleate at high temperature. 10-Undecenoic acid arises from hydrolysis of the ester and provides a variety of 10-undecylenic acid derivatives, including the corresponding nitrile. Cross-metathesis of methyl acrylate and other electron deficient olefins with methyl 10-undecenoate[15a,18] and 10-undecylenic aldehyde[19] has been efficiently achieved with catalyst **II** in order to produce α,ω-bifunctional derivatives. The advantage of using 10-undecenenitrile, another biosourced substrate obtained upon ammoxidation[20] of 10-undecenoic acid, as a potential source of amine has never been evaluated. The cross-metathesis with methyl acrylate was thus investigated with the objective of producing compound **3** and then the amino ester **7**, under optimized conditions.

Based on our previous studies on cross-metathesis transformations of fatty derivatives, the second generation ruthenium complexes **I–IV**[21] were investigated (Scheme 2).

Our first attempts were carried out with 2 equivalents of acrylate in toluene in the presence of 0.5 mol% of catalyst (Scheme 1, route (b)). Catalyst **I** appeared to be less efficient as the conversion was not completed after 19 h at 50 °C (Table 1, entry 1). The catalysts **II**, **III** and **IV** bearing a chelating benzylidene ligand were very efficient at temperatures as low as 50 °C (Table 1, entries 2, 4, 6) and even at room temperature (Table 1, entries 3, 5, 7), leading to complete conversion and high yield of the desired product **3**. The cross-metathesis reaction took place with high stereoselectivity in favour of the *E* isomer.



Scheme 2 Ruthenium-based olefin metathesis catalysts.

Table 1 Cross-metathesis of 10-undecenenitrile with methyl acrylate[a]

Entry	Cat.	*T* (°C)	*t* (h)	Conv.[b] (%)	Yield[b] (%)	*E*/*Z* ratio[b]
1	**I**	50	19	64	51	9.4
2	**II**	50	1	99	99[c]	13.3
3	**II**	25	2	99	99	12.8
4	**III**	50	2	99	98	12.7
5	**III**	25	2	97	95	14.2
6	**IV**	50	1	99	99	8.9
7	**IV**	25	1	99	96	9.7

[a] **1** (0.5 mmol), [**1**] = 0.05 M, **2** (1 mmol), catalyst (0.0025 mmol, 0.5 mol%), toluene (10 ml). [b] Determined by GC using dodecane as an internal standard. [c] Isolated yield = 98%.

As it was previously shown that cross-metathesis of acrylate could be carried out without a solvent, cross-metathesis of 10-undecenenitrile in neat methyl acrylate as the solvent was tested. The metathesis reaction took place using 1 mol% of catalyst **II** and 2 equivalents of acrylate and led to 64% conversion of **1** and 41% isolated yield of **3** – due to the competitive self-metathesis reaction of **1** – after 22 h of reaction at 50 °C (Table 2, entry 1). When the temperature was increased to 100 °C, the reaction efficiency was enhanced (85% conversion, 74% isolated yield of **3** – Table 2, entry 4).

Increasing the amount of methyl acrylate under otherwise identical conditions improved the efficiency and allowed the reaction to reach 85% conversion of **1** with 78% yield of **3** in the presence of 20 equivalents of acrylate (Table 2, entry 5). Lower catalyst loadings resulted in lower conversions. For comparison, the reaction of methyl 10-undecenoate with methyl acrylate (10 equivalents – bulk conditions) in the presence of 0.1 mol% of catalyst **II** gave 99% of the expected unsaturated C12-diester at 50 °C after 3 h reaction time. This result compared with the data of Table 2, entry 4 reveals that the nitrile functionality has a negative effect on the metathesis reaction as compared to the ester.

To improve the TON values while maintaining high conversion, we investigated the slow addition of the catalyst into the reaction mixture. This technique can drastically improve the efficiency of catalytic reactions when the lifetime of the catalytic species is short, and was successfully used in the cross-metathesis with acrylonitrile[15a] (Scheme 1 – route (a)). The results are gathered in Table 3. Catalyst **II** was dissolved in toluene and slowly injected with a syringe pump apparatus (dropwise addition) in order to ensure a reliable continuous addition of the catalyst into the reaction mixture. The catalyst solution was added within 2 h 40 min and the reaction mixture was maintained at the desired temperature until a total time of 5 h. With a catalyst loading of 0.05 mol%, the temperature could be decreased down to 50 °C to ensure a TON close to 2000 with almost complete conversion (Table 3, entries 1–2). At 25 °C, the reaction was too slow and a conversion of only 42% could be obtained (Table 3, entry 3). With lower catalyst loadings, a higher temperature of 100 °C had to be applied to reach satisfactory conversion. With 0.01 mol% catalyst loading, 92% conversion of **1** leading to **3** with high selectivity toward the cross-

Table 2 Cross-metathesis of 10-undecenenitrile with methyl acrylate in bulk conditions[a]

Entry	**2** (equiv.)	*T* (°C)	*t* (h)	Conv.[b] (%)	Yield[b] (%)	*E*/*Z*[b]
1	2	50	22	64	41	12.7
2	5	50	19	72	63	7.3
3	10	50	23	79	73	9.5
4	10	100	23	85	74	10.3
5	20	50	20	85	78	11.7

[a] **1** (3 mmol), catalyst **II** (1 mol%), open system. [b] Determined by GC using dodecane as an internal standard.

Table 3 Cross-metathesis of **1** with methyl acrylate using slow addition of catalyst[a]

Entry	Cat. (mol%)	*T* (°C)	Conv.[b] (%)	Yield[b] (%)	*E*/*Z*[b]	TON[c]	STON[c]
1	0.05	100	98	98[e]	8.3	1960	1960
2	0.05	50	96	96	13.4	1920	1920
3	0.05	25	42	36	11.2	840	720
4	0.025	100	98	98	9.5	3920	3920
5	0.01	100	92	92[f]	8.1	9200	9200
6	0.0075	100	80	66	7.1	10 667	8800
7[d]	0.0075	100	91	80	8.2	12 133	10 667
8	0.005	100	73	61	6.6	14 600	12 200
9[d]	0.005	100	86	63	7.9	17 200	12 600

[a] **1** (2 mmol), **2** (8 mmol), toluene (38 ml), [**1**] = 0.05 M, catalyst **II** was dissolved in toluene (2 ml), added in 2 h 40 min, then the reaction mixture was maintained at the desired temperature until a reaction time of 5 h. [b] Determined by GC using dodecane as an internal standard. [c] TON: conv. of **1**/cat. loading; selective TON (STON): GC yield of **3**/cat. loading. [d] [**1**] = 0.5 M. [e] Isolated yield: 97%. [f] Isolated yield: 90%.

metathesis product (92% yield) provided a TON of 9200 (Table 3, entry 5).

When the catalyst loading was decreased below 0.01 mol%, 10-undecenenitrile was not completely consumed within 5 h and the lower the catalyst loading the lower the conversion (Table 3, entries 6, 8). However, the conversions were improved when the concentration of the substrate was increased from 0.05 M to 0.5 M (entries 6–9). It is noteworthy that below 0.01 mol% catalyst loading, the selective TONs (STONs), indicators of the conversion into the desired product **3**, were significantly lower than the TONs based on the conversion of **1**, which revealed the presence of byproducts. Finally, the best STON (12 600) was obtained at 100 °C in the presence of 0.005 mol% of catalyst **II** with the slow addition technique. The *E* isomer was still formed as the major product.

In order to understand this evolution of the reaction and identify the byproducts, the reaction profile of the metathesis reaction was monitored under the reaction conditions depicted in Table 3 entry 7 (Fig. 1 – [**1**] = 0.5 M; **II**: 0.0075 mol%, 100 °C) and entry 9 (Fig. 2 – [**1**] = 0.5 M; **II**: 0.005 mol%, 100 °C).

In both cases, a short induction period of about 15 min was detected before the reaction started. As soon as the cross-metathesis with methyl acrylate was initiated, the self-metathesis of 10-undecenenitrile **1** giving the corresponding symmetrical unsaturated C20-dinitrile **8** (Scheme 3) started at a comparable rate.

With low catalyst loading (0.005 mol%) the self-metathesis product **8** can reach up to 34% after 110 min, whereas a maximum of 22% is obtained after 75 min with 0.0075 mol% catalyst loading. It can be noted that the maximum values for the formation of **8** are obtained when the same amounts of catalyst (0.007 mmol) are added and the consumption of 10-undecenenitrile is around 75%. Then, part of the self-metathesis product **8** is consumed by cross-metathesis with methyl acrylate, but not completely and the evolution of the metathesis transformations is stabilized around 200 min, after complete injection of the catalyst at 160 min. Consequently, the yield of **3** is higher starting from 0.0075 (80%) than from 0.005 mol% (63%) catalyst loading. Higher concentration of the catalyst is necessary to ensure high selectivity that is cross-metathesis rather than self-metathesis. This is illustrated in Table 3 where the GC yields are close to the conversions when the amount of catalyst is higher than 0.01 mol% and then the gap between these 2 numbers increases when the catalyst loading decreases. For comparison, compound **6**, another precursor of the amino ester **7** (Scheme 1, route (a)), was obtained with a highest TON of 1900 using 0.05 mol% of catalyst **II**,[15a] thus demonstrating (i) the superiority of the herein reported pathway for the synthesis of **7** (Scheme 1, route (b) > route (a)) and (ii) the inhibiting character of acrylonitrile in cross-metathesis transformations.

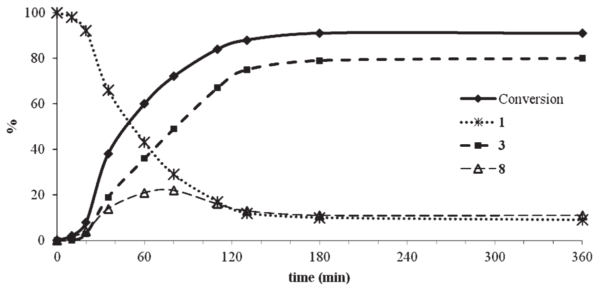


Fig. 1 Cross-metathesis of **1** with methyl acrylate. [**1**] = 0.5 M; **II**: 0.0075 mol%, 100 °C. Conversion *vs.* internal standard. **1**/**3**/**8**: GC ratio.

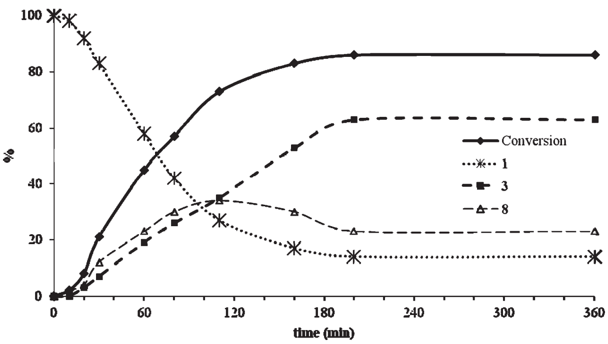
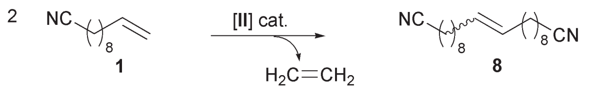


Fig. 2 Cross-metathesis of **1** with methyl acrylate. [**1**] = 0.5 M; **II**: 0.005 mol%, 100 °C. Conversion *vs.* internal standard. **1**/**3**/**8**: GC ratio.



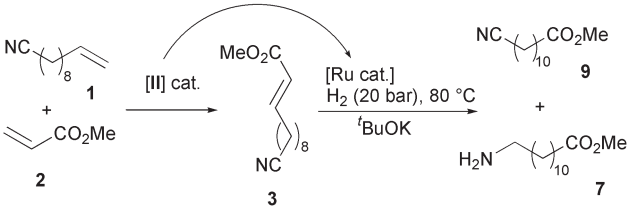
Scheme 3 Self metathesis of 10-undecenenitrile.

Tandem cross-metathesis/C=C and CN hydrogenation

The ruthenium residues arising from olefin metathesis are known to catalyze hydrogenation of carbon–carbon double bonds resulting from olefin ring closing and cross-metathesis.[22]

We have also shown that the tandem cross-metathesis/hydrogenation sequence could be adapted to the hydrogenation of unsaturated fatty derivatives.[19] For example, under 10 bar of hydrogen pressure at 50 °C for 24 h, **6** obtained upon cross-metathesis of **4** and **5** in the presence of 0.5 mol% of catalyst **II** (Scheme 1, route (a)) quantitatively led to the saturated C12 nitrile ester, which was isolated in 91% yield.

In order to produce the desired amino ester from **1** and **2**, we directly investigated the tandem cross-metathesis/hydrogenation in the presence of ^{t}BuOK (Scheme 4), which has recently been shown to generate efficient nitrile reduction catalytic systems in the presence of olefin metathesis residue.[23,24] The results shown in Table 4 indicate that both the amount of base and catalyst loading are important parameters. The nitrile hydrogenation could not be achieved with the very low 0.05 mol% catalyst loading used for the cross-metathesis reaction. When the metathesis reaction was performed at 100 °C the conversion into **3** was completed within 1 h and the same efficiency was obtained at room temperature with catalyst loadings of 1 and 3 mol%. Whatever the metathesis temperature applied during the first step, at 1 mol% catalyst loading, hydrogenation under 20 bar of hydrogen at 80 °C led to complete conversion into the saturated nitrile ester **9** (Table 4, entries 1 and 4). It is also noteworthy that full conversion into the saturated amino ester **7** was obtained only in the presence of a high amount of ^{t}BuOK and 3 mol% of catalyst loading in the metathesis step (Table 4, entries 3, 5, 6). When the metathesis step was carried out at 100 °C, 30 mol% of ^{t}BuOK were necessary to reach 96% yield of **7**, whereas with 15 mol% of base a mixture of **7** and **9** was obtained (Table 4, entry 2). On the other hand, when the metathesis reaction took place at room temperature, 95% yield of **7** was obtained with only 20 mol% of base (Table 4, entry 5) and the yield reached 97% with 30 mol% of ^{t}BuOK. In the latter case the amino ester **7** was isolated in 90% yield and no trace of secondary amine could be detected, thus demonstrating the high selectivity of the catalytic system.[25]



Scheme 4 Sequential cross metathesis/hydrogenation.

Table 4 Tandem cross-metathesis/hydrogenation from **1** and **2**[a]

Entry	Cat. (mol%)	T^b (°C)	^{t}BuOK (mol%)	t (h)	9^c (%)	7^c (%)
1	1	100	30	40	97	—
2	3	100	15	40	43	50
3	3	100	30	40	—	96
4	1	r.t.	30	40	96	—
5	3	r.t.	20	40	—	95
6	3	r.t.	30	40	—	97

[a] **1** (0.5 mmol), **2** (1 mmol), toluene (10 ml), metathesis reaction: 1 h, complete conversion into **3**, hydrogenation reaction under 20 bar of hydrogen at 80 °C for 40 h. [b] Temperature of the metathesis step. [c] GC yield.

Conclusion

We have shown that the cross-metathesis of 10-undecenenitrile with methyl acrylate takes place very efficiently with the Grubbs–Hoveyda second generation catalyst. The best productivity is obtained using continuous injection of the catalyst into the reaction mixture at 100 °C. Under these conditions a turnover number of 17 200 at 86% conversion of the fatty nitrile is obtained. Hydrogenation of the carbon–carbon double bond and the nitrile functionality in the presence of the ruthenium catalyst residue gives access to the C12 amino ester, the precursor of polyamide. This reaction takes place in the presence of ^{t}BuOK as a base under 20 bar of hydrogen at 80 °C. This procedure (Scheme 1, route (b)) is more favorable than the one starting from methyl 10-undecenoate and acrylonitrile, which allows one to obtain a maximum turnover number of 1900 at 95% conversion of the fatty ester during the metathesis step.[15a] This overall tandem procedure provides a sustainable route to linear amino esters, useful polyamide precursors, as a single catalyst is introduced from the outset of the process to perform 3 catalytic transformations (cross-metathesis, carbon–carbon double bond hydrogenation and nitrile reduction) from methyl acrylate and undecenenitrile, 2 biosourced substrates.

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