

NEW PERSPECTIVES OF EUROPEAN OLEOCHEMISTRY
LES NOUVELLES PERSPECTIVES DE L'OLÉOCHIMIE EUROPÉENNE

Ultrasound-assisted self-metathesis reactions of monounsaturated fatty acids

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Abstract – An efficient protocol for the self-metathesis of oleic acid, using ruthenium catalysts is described. The self-metathesis reaction under ultrasonic activation allows the conversion of monoenic fatty acids such as oleic acid, elaidic acid and erucic acid into diacids and olefins with very short reaction times in the presence of Grubbs ruthenium catalysts. These yields and selectivity towards the desired products are influenced by the nature of solvents. This study demonstrated that metathesis reaction carried out in DCM or 1-butanol showed promising results, since it produced a variety of products, like n-alkenes and diacids with good yields (45–75%) and high selectivities (75–95%).

Keywords: Self-metathesis / long-chain diacids / oleic acid / 1,18-octadec-9-enedioic acid / 1,26-hexacos-13-enedioic acid

Résumé – **Métathèse activée par les ultrasons : homocouplage d'acides gras monoinsaturés.** Un nouveau protocole efficace pour l'homocouplage de l'acide oléique par réaction métathèse utilisant des catalyseurs de ruthénium est décrit dans cet article. La réaction d'homocouplage activée par ultrasons permet d'obtenir avec des temps de réaction très faibles, la conversion d'acides gras insaturés tels que l'acide oléique, l'acide élaïdique et l'acide érucique en diacides et oléfines en présence de catalyseurs au ruthénium de Grubbs. Les rendements et la sélectivité des produits obtenus sont influencés par la nature du solvant utilisé. Cette étude a démontré que la réaction de métathèse réalisée dans du dichlorométhane ou du 1-butanol donne des résultats prometteurs : elle permet d'obtenir une grande variété d'alcènes et des diacides à longues chaînes avec de bons rendements (45–75 %) et des sélectivités élevées (75–95 %).

Mots clés : Homocouplage / métathèse / diacides à longue chaîne / acide oléique / acide 1,18-octadéc-9-enedioïque / acide 1,26-hexacos-13-enedioïque

1 Introduction

Vegetable oils high in monounsaturated fatty acids have attained the status of technical oils. Indeed, sunflower cultivation has shifted from traditional food varieties containing 24% oleic acid (OA) to higholeic acid varieties with an OA content of 86 to 87% (Dufaure *et al.*, 1999), with one recently developed variety having an OA content as high as 90 to 92% (Kab, 2000; OLEOVISION; Godard *et al.*, 2013a, 2013b). The crucifer *Crambe abyssinica* also appears to be a good source of technical oil as its oil naturally contains 55 to 60% erucic acid, whereas rapeseed oil contains only 40 to 45% erucic acid (Nieschalg and Wolff, 1971). These commercial monounsaturated vegetable oils are now used extensively in chemical processes for manufacturing chemical feedstocks, lubricants,

detergents, plastics and polyamides, for example (Van Dyne and Blase, 1990).

Very-high OA oil is considered a pure substance with well-defined chemical and physical characteristics. Its oxidative stability is high due to its very low linoleic acid content (3–10%), and linolenic acid is entirely absent. Its temperature characteristics are also very good, due to its very low saturated fatty acid content (palmitic acid C16: 0.4%, stearic acid C18: 0.2%).

These plants conform well to the concept of oil crop platforms producing technical oils (Carlsson, 2009) but this notion should be extended to monounsaturated fatty acids. In organic synthesis oleic acid (C18:1) and erucic acid (C22:1) are pure chemical substances characterized by exact defined functional groups such as a double bond and a terminal methyl group. They are good candidates for the production of new chemicals, including dibasic acids. For example, the ozonolysis reaction, an oxidative cleavage, converts oleic acid into azelaic

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acid or erucic acid into brassylic acid with pelargonic acid as a co-product. We recently described an improved oxidative cleavage process, based on the use of catalytic amounts of a peroxo-tungsten complex in the presence of hydrogen peroxide as an oxidant. With OA from a very higholeic acid sunflower oil (VHOSO, 86–87% OA) and commercial erucic acid, these mild and efficient catalytic conditions generated very interesting C9 mono/dibasic acids and dibasic azelaic acid, with excellent yields (Godard *et al.*, 2013a, 2013b).

We describe here the continuation of our research into the synthesis of new platform chemicals, and a new process for obtaining long-chain dibasic acids such as 1,18-octadec-9-enedioic acid and 1,26-hexacos-13-enedioic acid from oleic, elaidic and erucic acid. The availability of these new unsaturated dibasic acids opens up real possibilities for novel uses in the future. For example, octadec-9-enedioic acid has potential applications in cosmetics due to its inhibition of melanin synthesis, resulting in skin-lightening effects (Wiechers *et al.*, 2005; Bernard and Mahe, 2007; Hansenne and Sore, 2005). Long-chain dibasic acids are also used in numerous industrial applications including the production of synthetic resins, polyesters, polyamides and anticorrosion products (Kroha, 2004).

For academic and industrial purposes, C18 dibasic acid synthesis is based on biopathways involving the ω -oxidation of the terminal methyl group of fatty acids through microbial fermentation (Yang *et al.*, 2011). However, the chemical process is also of potential interest. It does not rely on an oxidative process, but is instead based on redistribution of the olefinic bonds of unsaturated fatty acids *via* a self-metathesis reaction (Behr *et al.*, 2014; Chikkali and Mecking, 2012; Jenkins *et al.*, 2015; Levin *et al.*, 2015; Meier, 2000; Montero de Espinosa and Meier, 2012; More *et al.*, 2013; Ngo and Foglia, 2009; Nicolaou *et al.*, 2005; Ohlmann *et al.*, 2012; Ozturk *et al.*, 2015; Le Ravalec *et al.*, 2010; Tomasek and Schatz, 2013; Vilela *et al.*, 2012; Vyshnavi *et al.*, 2013; Wels *et al.*, 2013; Winkler and Meier, 2014). For example, Foglia has shown that 1,18-octadec-9-enedioic acid (**2**) can be obtained with a yield of 71% from oleic acid (**1**) if it is stirred mechanically at 45 °C for three days in the presence of catalytic amounts of a second-generation Grubbs catalyst **C1** (Ngo *et al.*, 2006). Octadec-9-ene (**3**) (Scheme 1) was also obtained as a co-product but its yield and use were not discussed in the article.

The main objective of this study was the achievement of self-metathesis reactions for monounsaturated C18:1 and C22:1 fatty acids, in new conditions, such as sonochemical activation in conventional organic solvents or bio-based solvents, to improve the existing processes.

2 Experimental section

Oleic acid (90%) and erucic acid (90%) were purchased from Sigma-Aldrich. Elaidic acid (96%) was purchased from Alfa Aesar. Grubbs ruthenium catalysts **C1–C3** and **C4–C6** (Scheme 2) were purchased from Sigma-Aldrich and Omega Cat System, respectively. They were stored under N₂ before use. All solvents were obtained from Sigma-Aldrich and used without further purification. The reactions were performed in air.

Product characterization. ¹H NMR and ¹³C NMR were carried out on a Bruker Fourier300 spectrometer (300 MHz for ¹H NMR and 75 MHz ¹³C NMR), using CDCl₃ or CD₃OD as the solvent and tetramethylsilane (TMS) as an internal standard. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer (KBr discs). Melting points were determined with a Fisher-Johns melting point apparatus. GC analyses were performed after the methylation of fatty acids with trimethylsulfonium hydroxide (TMSH) dissolved in methyl tert-butyl ether (MTBE). Pentadecanoic acid was used as an internal standard. Chromatograms were obtained with a Varian 3900 GC instrument equipped with a fused silica capillary column (50 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID). The injector temperature was set at 250 °C. The oven temperature profile was: initial temperature 100 °C, held for 2 min, ramp of 8 °C/min to 180 °C, held for 10 min, ramp of 10 °C/min to 250 °C, held for 5 min. Measurements were performed in the splitless and split-split modes (ratio 1:100) using helium as the carrier gas (flow rate 1.2 ml/min).

General procedure for ultrasound-assisted self-metathesis reactions. A 15 ml vial equipped with a magnetic stirrer was charged with a 20 mmol solution of the chosen fatty acid, the ruthenium catalyst (0.02 mmol, 0.1 mol%) and the appropriate solvent. The reaction mixture was exposed to ultrasonic irradiation delivered by a microtip probe connected to a 500 W Sonics Vibracell Ultrasonic machine (W75042) from Fisher Bioblock Scientific operating at 20 kHz at 20% of the maximum power output. The resulting mixture was filtered through a silica gel pad, and washed with solvent. The solvent was removed under reduced pressure, yielding the crude product, which was characterized by GC and purified by chromatography on a silica gel column (cyclohexane/ethyl acetate: 10/0 to 7/3 v/v).

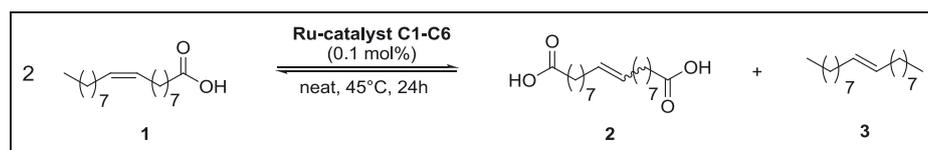
Octadec-9-enedioic acid (**2**): m.p. 98 °C; ¹H NMR (300 MHz, CD₃OD, 25 °C, TMS): δ = 5.40–5.36 (m, 2H), 2.26 (t, J = 7.4 Hz, 4H), 1.99–1.95 (m, 4H), 1.66–1.48 (m, 4H), 1.32–1.27 (m, 16H); ¹³C NMR (75 MHz, CD₃OD, 25 °C, TMS): δ = 178.1, 131.8, 35.3, 33.9, 31.0, 30.6, 30.5, 30.3, 26.4; IR (KBr): ν = 2925, 2850 (OH), 1699 (C=O), 975 (C=C *trans*) (Ngo *et al.*, 2006).

Octadec-9-ene (**3**): ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 5.42–5.38 (m, 2H), 2.12–1.85 (m, 4H), 1.49–1.11 (m, 24H), 0.98–0.95 (m, 6H); ¹³C NMR (75 MHz, CD₃OD, 25 °C, TMS): δ = 130.3, 32.6, 31.9, 29.6, 29.5, 29.3, 29.1, 22.7, 14.1; IR (KBr): ν = 2924, 2854, 1466, 966 (C=C *trans*) (Oikawa *et al.*, 2004).

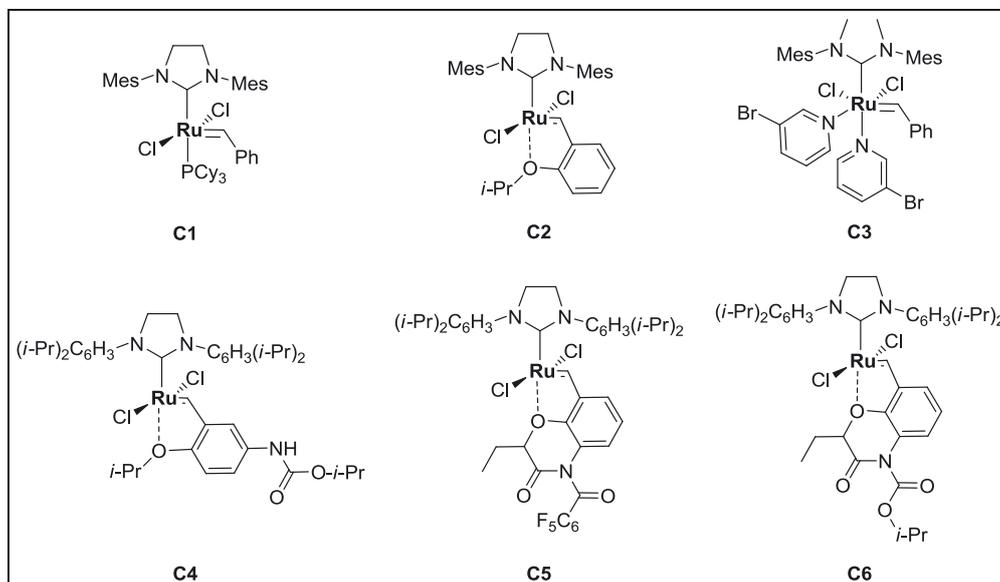
Hexacos-13-enedioic acid (**6**): m.p. 105 °C; ¹H NMR (300 MHz, CD₃OD, 25 °C, TMS): δ = 5.42–5.36 (m, 2H), 2.27 (t, J = 7.4 Hz, 4H), 2.06–1.89 (m, 4H), 1.61–1.56 (m, 4H), 1.33–1.27 (m, 32H); ¹³C NMR (75 MHz, CD₃OD, 25 °C, TMS): δ = 177.8, 131.6, 35.1, 33.6, 30.8, 30.7, 30.6, 30.5, 30.4, 30.3, 30.2, 30.1, 26.2; IR (KBr): ν = 2918, 2850 (OH), 1702 (C=O), 962 (C=C *trans*) (Ngo *et al.*, 2006).

3 Results and discussion

Based on the work published by Foglia, we first carried out a self-metathesis reaction on oleic acid (**1**) in the presence of catalytic amounts of a second-generation Grubbs catalyst **C1**



Scheme 1. Self-metathesis of oleic acid (**1**).



Scheme 2. Catalysts used (**C1-C6**) for the self-metathesis reactions.

Table 1. Results of catalyst-screening for self-metathesis reactions of oleic acid (**1**)^[a].

Entry	Catalyst	Conv. (%) ^[b]	2 (%), E/Z ^[c]	3 (%) ^[c]
1	C1	86	82, 20/1	75
2	C2	96	73, 25/1	76
3	C3	91	67, 7/1	63
4	C4	94	66, 11/1	58
5	C5	95	69, 13/1	61
6	C6	96	78, 20/1	63

[a] Reaction conditions: **1** (20 mmol), **C1-C6** (0.1 mol%), neat, magnetic stirring, 45 °C, 24 h. [b] Substrate conversion was determined by GC, with pentadecanoic acid as the internal reference. [c] Yields were determined after purification by flash chromatography on silica gel.

(0.1 mol%, Scheme 1) (Scholl *et al.*, 1999) at 45 °C without solvent. The desired compounds, octadec-9-enedioic acid (**2**) and octadec-9-ene (**3**), were obtained with yields of 82% and 75%, respectively, after 24 h of reaction (Tab. 1, entry 1).

Various commercially available metathesis catalysts (Scheme 2) were then tested in the same reaction conditions (Tab. 1).

Higher conversion rates were obtained with a second-generation Hoveyda-Grubbs catalyst **C2** (Tab. 1, entry 2) (Garber *et al.*, 2001; Gessler *et al.*, 2000; Kingsbury *et al.*, 1999; Van Veldhuizen *et al.*, 2002), a third-generation Grubbs catalyst **C3** (Tab. 1, entry 3) (Love *et al.*, 2002) and Omega Cat System catalysts **C4-C6** (Tab. 1, **C4-C6**) (Caijo *et al.*, 2013). However, the use of these catalysts resulted in slightly lower yields of (**2**) and (**3**). The E/Z ratio of (**2**) depended strongly

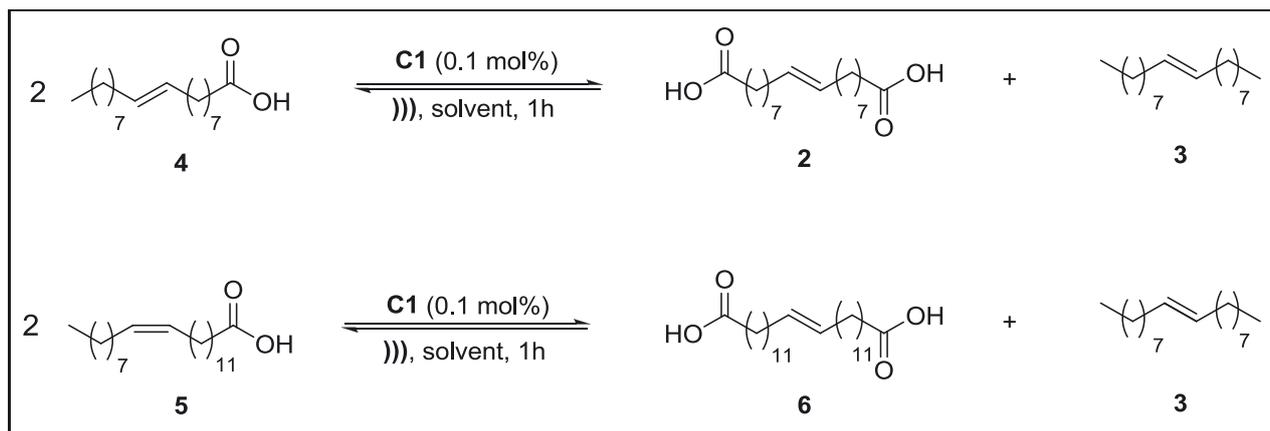
Table 2. Results of the self-metathesis of oleic acid (**1**) in sonication conditions^[a].

Entry	Solvent	Catalyst	Conv. (%) ^[c]	2 (%), E/Z ^[d]	3 (%) ^[d]
1	–	C1	91	53, 4/1	51
2	–	C2	90	51, 4/1	53
3	–	C3	84	43, 3/1	41
4	Toluene	C1	92	56, 4/1	59
5	DMC ^[b]	C1	91	57, 4/1	58

[a] Reaction conditions: **1** (20 mmol), **C1-C3** (0.1 mol%), ultrasound, 5 h. [b] DMC: dimethyl carbonate. [c] Substrate conversion was determined by GC, with pentadecanoic acid as the internal reference. [d] Yields were determined after purification by flash chromatography on silica gel.

on the nature of the catalyst: catalysts **C1**, **C2** and **C6** yielded (**2**) excellent ratios of 20/1 to 25/1. A lower ratio was obtained with catalysts **C3-C5**.

A viscous precipitate formed during these reactions. We assumed that this was due to molecular interactions between the ruthenium-based carbene complex and oleic acid, and concluded that some catalyst may have stuck to the wall of the reaction vial, thus limiting reaction yields. An ultrasound probe was used to ensure effective mixing (Gulajski *et al.*, 2008; Jakobs and Sijbesma, 2012; Piermattei *et al.*, 2009; Sacco *et al.*, 2015; Sari *et al.*, 2013). With sonication and in the absence of solvent, higher rates of oleic acid conversion were observed after only 5 h of reaction (Tab. 1, entry 1 vs. Tab. 2, entry 1). However the yields of compounds (**2**) and (**3**)



Scheme 3. Self-metathesis reactions of elaidic acid (4) and erucic acid (5).

Table 3. Solvent-screening results for self-metathesis reactions of oleic acid (1)^[a].

Entry	Solvent	Conv. (%) ^[d]	2 (%) ^[e]	2, E/Z ^[e]	3 (%) ^[e]
1	DMC ^[b]	91	57	4/1	58
2	Ethanol	68	24	3/1	23
3	1-Propanol	74	48	3/1	47
4	1-Butanol	91	67	4/1	59
5	2-Butanol	90	66	4/1	65
6	Iso-butanol	90	60	4/1	63
7	Iso-hexane	89	61	4/1	61
8	Chloroform	90	50	4/1	57
9	DCM ^[c]	94	75	11/1	65

[a] Reaction conditions: 1 (20 mmol), C1 (0.1 mol%), solvent, ultrasound, 1 h. [b] DMC: dimethyl carbonate. Reaction time: 5 h. [c] DCM: dichloromethane. [d] Substrate conversion was determined by GC, with pentadecanoic acid as the internal reference. [e] Yields were determined after purification by flash chromatography on silica gel.

were moderate (Tab. 2, entries 1–3). We added toluene to the reaction mixture, to overcome the problem of viscosity, which might influence reaction yields. This classical solvent for metathesis reactions gave yields of 56% and 59% for (2) and (3), respectively (Tab. 2, entry 4). Toluene was successfully replaced with dimethyl carbonate (DMC) (Miao *et al.*, 2008) a more environmentally friendly alternative, resulting in the production of (2) and (3) with similar conversion rates and yields (Tab. 2, entry 5).

A kinetic study was then conducted to optimize the reaction time. The OA consumption and the appearance of (2) and (3) were monitored by GC. Maximal conversion was achieved in one hour, so subsequent assays were carried out with this reaction time.

Different solvents were then screened. Alcohols with various chain lengths were tested (Tab. 3, entries 2–6). A general trend was found towards alcohols with longer chains giving the best conversion rates and yields. This was probably due to the higher solubility of oleic acid in less polar solvents (Hoerr

and Harwood, 1952). The use of *iso*-hexane resulted in similar yields of the desired compounds (Tab. 3, entries 7). We also tested chlorinated solvents. The use of chloroform and dichloromethane (Tab. 3, entries 8–9) did not significantly improve the results, indicating that the self-metathesis of oleic acid can be achieved in green solvents, such as 1-butanol, with the same reactivity as in conventional metathesis solvents.

We broadened the scope of the reaction, by considering the self-metathesis reactions of elaidic (4) and erucic (5) acids (Scheme 3). In the presence of 0.1 mol% catalyst, these fatty acids gave rise to the desired alkenes and diacids after one hour of sonication in 1-butanol or dichloromethane. The same products, (2) and (3) were obtained whether we started from elaidic acid or oleic acid (Tab. 4, entries 1–4). However, elaidic acid gave a lower conversion rate and yield, because the *cis* double bond of oleic acid was more reactive than the *trans* isomer of elaidic acid in metathesis conditions (Chatterjee *et al.*, 2003). In particular, a diacid with a 26-carbon chain was obtained with a yield of 58% yield, through the self-metathesis of erucic acid (Tab. 4, entries 5–6), demonstrating the great potential of this process for generating verylong chain alkenes and diacids from renewable resources.

4 Conclusion

In summary, we describe here a new process for the self-metathesis of fatty acids, based on the use of sonication to activate this ruthenium-catalyzed reaction, which can be performed with very short reaction times in a green solvent. These mild, efficient and greener reaction conditions give good yields of the desired long-chain diacids, along with long-chain olefins. These interesting alkenes should be considered not only as by-products, but also as new biosourced platform molecules with potential uses in lubricant applications, for example.

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Table 4. Results of self-metathesis reactions of elaidic acid (4) and erucic acid (5)^[a].

Entry	Starting material	Solvent	Conv (%) ^[c]	Diacid (%) ^[d]	Alkene (%) ^[d]
1	Oleic acid (1)	DCM ^[b]	94	1,18-Octadec-9-enedioic acid (2, 75)	Octadec-9-ene (3, 65)
2	Oleic acid (1)	1-Butanol	90	1,18-Octadec-9-enedioic acid (2, 67)	Octadec-9-ene (3, 59)
3	Elaidic acid (4)	DCM	60	1,18-Octadec-9-enedioic acid (2, 48)	Octadec-9-ene (3, 58)
4	Elaidic acid (4)	1-Butanol	55	1,18-Octadec-9-enedioic acid (2, 45)	Octadec-9-ene (3, 53)
5	Erucic acid (5)	DCM	94	1,26-Hexacos-13-enedioic acid (6, 72)	Octadec-9-ene (3, 55)
6	Erucic acid (5)	1-Butanol	93	1,26-Hexacos-13-enedioic acid (6, 58)	Octadec-9-ene (3, 58)

[a] Reaction conditions: Fatty acid (20 mmol), C1 (0.1 mol%), solvent, ultrasound, 1 h. [b] DCM: dichloromethane. [c] Substrate conversion was determined by GC, with pentadecanoic acid as the internal reference. [d] Yields were determined after purification by flash chromatography on silica gel.

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