



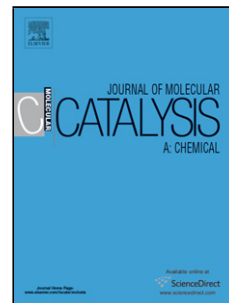
Unsaturated Fatty Acid Esters Metathesis Catalyzed by Silica Supported WMe5

Item Type	Article
Authors	Riache, Nassima;Callens, Emmanuel;Talbi, Karima;Basset, Jean-Marie
Citation	Unsaturated Fatty Acid Esters Metathesis Catalyzed by Silica Supported WMe5 2015 Journal of Molecular Catalysis A: Chemical
Eprint version	Post-print
DOI	10.1016/j.molcata.2015.11.003
Publisher	Elsevier BV
Journal	Journal of Molecular Catalysis A: Chemical
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Download date	2024-04-12 10:29:51
Link to Item	http://hdl.handle.net/10754/582471

Accepted Manuscript

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Author: Nassima Riache Emmanuel Callens Karima Talbi
Jean-Marie Basset



PII: S1381-1169(15)30143-6
DOI: <http://dx.doi.org/doi:10.1016/j.molcata.2015.11.003>
Reference: MOLCAA 9683

To appear in: *Journal of Molecular Catalysis A: Chemical*

Received date: 30-6-2015
Revised date: 29-10-2015
Accepted date: 9-11-2015

Please cite this article as: Nassima Riache, Emmanuel Callens, Karima Talbi, Jean-Marie Basset, Unsaturated Fatty Acid Esters Metathesis Catalyzed by Silica Supported WMe_5 , Journal of Molecular Catalysis A: Chemical <http://dx.doi.org/10.1016/j.molcata.2015.11.003>

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Unsaturated Fatty Acid Esters Metathesis Catalyzed by Silica Supported WMe₅

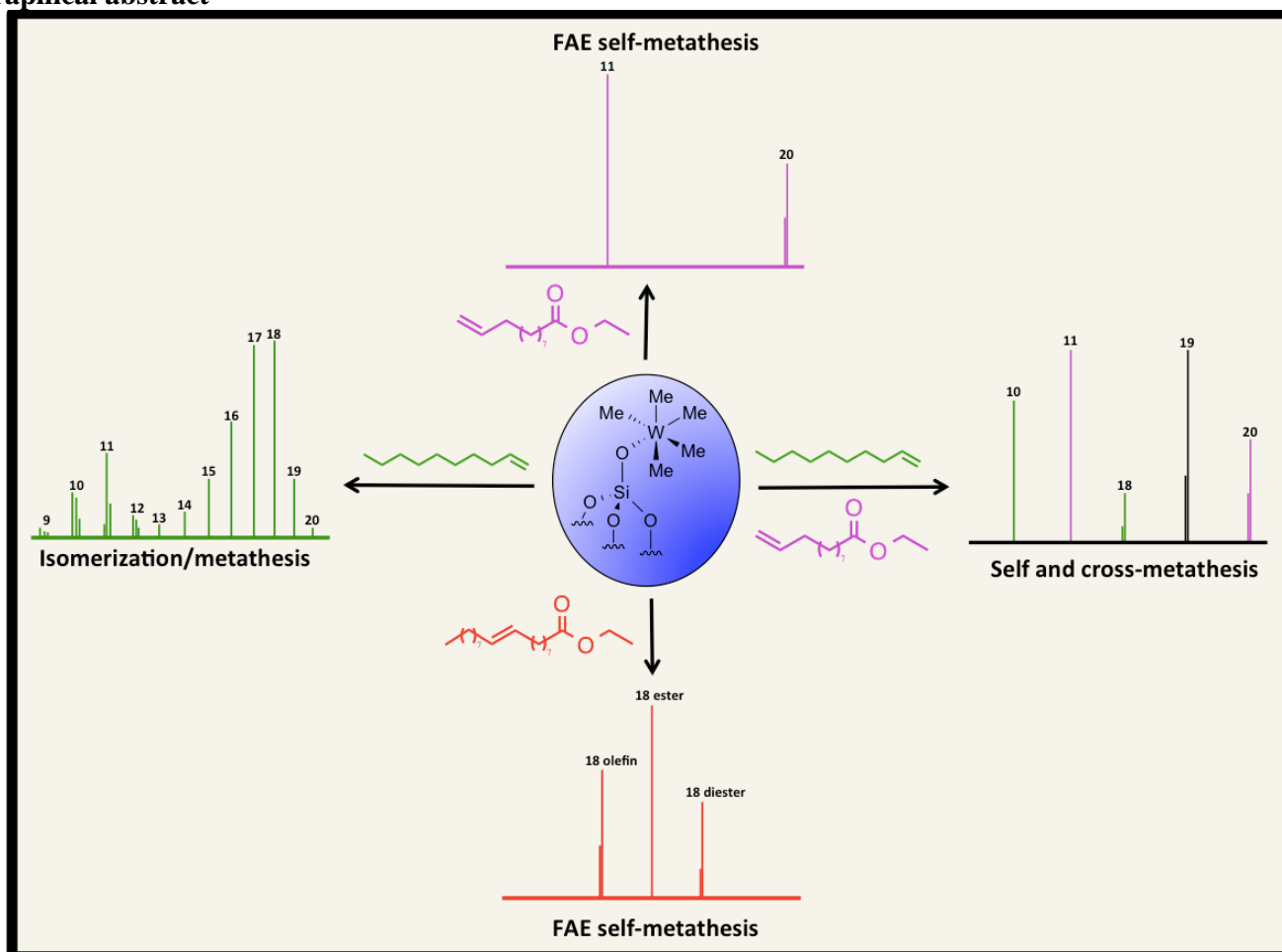
Nassima Riache, Emmanuel Callens,* Karima Talbi and Jean-Marie Basset^{a,*}

^a KAUST Catalysis Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

* Corresponding authors. Tel.: +0-966(2)808-02995; emmanuel.callens@kaust.edu.sa, jeanmarie.basset@kaust.edu.sa

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Graphical abstract



Highlights

Metathesis of unsaturated fatty acid esters (FAEs) by W-based single catalytic system resulted only on the primary self-metathesis products (diesters).

The selectivity of this transformation *via* multifunctional catalyst, which previously found to be active in isomerization and metathesis (ISOMET) of unfunctionalized α -olefins is studied.

ABSTRACT

Metathesis of unsaturated fatty acid esters (FAEs) by silica supported multifunctional W-based catalyst is disclosed. This transformation represents a novel route towards unsaturated di-esters. Especially, the self-metathesis of ethyl undecylenate results almost exclusively on the homo-coupling product whereas with such catalyst, 1-decene gives ISOMET (isomerization and metathesis olefin) products. The olefin metathesis in the presence of esters is very selective without any secondary cross-metathesis products demonstrating that a high selective olefin metathesis could operate at 150 °C. Additionally, a cross-metathesis of unsaturated FAEs and α -olefins allowed the synthesis of the corresponding ester with longer hydrocarbon skeleton without isomerisation.

Keywords:

Unsaturated Fatty Esters

Silica Supported WMe₅ Catalyst

Metathesis

Surface Organometallic chemistry

1. Introduction

With the decrease of fossil organic feedstock, renewable resources in particular unsaturated fatty acid esters (FAEs) have been widely studied as starting materials in the chemical industry.^{1,2} These chemicals are interesting building blocks possessing two modifiable functional groups, the ester and the olefin. The reactivity of the alkene moiety has been illustrated in particular *via* the metathesis of unsaturated FAEs toward the synthesis of unsaturated diesters of fatty acids. In fact, metathesis reactions of unsaturated FAEs are a convenient approach to long chain diesters, useful intermediates towards macromolecules and polyesters synthesis.³ Pioneer in this field, Boelhouwer and co-workers discovered that homogeneous WCl_6/Me_4Sn system catalyzed the metathesis of methyl oleate.^{4,5,6} This provides an approach towards the preparation of mono- and diesters of fatty acids and their corresponding fatty acid esters. Following this work, numerous homogeneous and heterogeneous catalysts using transition metals, W, Mo, Re have been reported.^{7-9,1} In particular, Ru Grubbs catalysts with an alkylidene moiety were found to be the most effective catalysts. Recently, we reported the synthesis of the homoleptic WMe_6 grafted on silica, $[(=Si-O)WMe_5]$ (**1**).¹⁰ This precursor catalyzes the metathesis of alkanes into lower and higher homologues: cyclooctane is transformed into macrocyclic alkanes¹¹ and linear alkanes are converted into higher and lower linear alkanes.¹² As during this alkane metathesis process olefins are formed in minute amount,¹³ we also examined the reactivity of terminal olefins with W-based catalysts supported on silica.¹² For instance, 1-decene is transformed into a distribution of linear terminal and internal olefins (up to C_{30} olefins) through successive reactions of isomerization and metathesis (ISOMET).¹² Thus, we envisaged employing solely this multifunctional full supported methylated catalyst for the metathesis of unsaturated FAEs. Herein, we report the unprecedented catalytic activity of $[(=Si-O)WMe_5]$ (**1**) towards readily available monounsaturated FAEs.

2. Results and Discussion

2.1. Ethyl undecylenate metathesis catalyzed by silica supported W-based catalyst $[(=Si-O)WMe_5]$ (**1**).

In the present work, we evaluate the catalytic activity of (**1**) in ethyl undecylenate (C_{11}) metathesis in a sealed glass tube. At the end of the catalytic run, an aliquot of the reaction mixture was analyzed by gas chromatography and GC-MS spectroscopies. At room temperature, only traces of the diesters products from self-metathesis were detected. However when conducting the catalytic run at 150 °C for 3 h, we exclusively observed the expected diesters, corresponding to non-degenerative metathesis process associated with the concomitant release of ethylene (**Scheme 1**) (see also Figure S2). The regiochemistry of the diester alkene consists of a mixture of E/Z internal olefins with the formation of trans ester thermodynamically favored (molar ratio, 7:3).

The conversion of ethyl undecylenate *versus* time was carried out at 150 °C. The plots of TONs and conversion *versus* time are given in **Figure 1**. A final conversion of 12% is reached with 26 TONs. A plateau is observed after 3 h which would correspond to a thermodynamic equilibrium. The reaction is very fast reaching 8% conversion and 17 TONs at $t=15$ min. The observable equilibrium must result from the degenerative metathesis process and to the accumulation of ethylene in this closed system. The reaction conversion could further be optimized by varying the concentration of the precatalyst. The study on the concentration of the substrate is illustrated in Figure S3. Varying the W/substrate ratio (from 2.3% to 9.3%) gave a higher conversion of 19% with TONs of 33 (see Figure S3).

Despite the need of heating, the level of temperature of the reaction was found to have a minor impact on the efficiency of the catalyst. Indeed, for a given period of 18 h at 80 °C, 150 °C or 200 °C, the maximum unsaturated FAE conversion based on diester products reached respectively 14%, 12% and 11%. At 200 °C, traces amount of isomerized ethyl undecylenate were detected by GC-MS. Employing Ru based catalyst, Grubbs first generation complex, under similar reaction conditions, afforded self-metathesis products and two newly formed isomers of ethyl undecylenate with 28% conversion towards expected diesters after 24 h reaction time (See Figure S4). Yet, our turnovers are comparable with the ones obtained with the supported catalytic system WCl_6/Me_4Sn .⁶ This suggests that with the latter system, the *in situ* alkylation of WCl_6 should initially occur to form the desired propagative W carbene species. To account for the low activity for this silica supported W system, we assume that the geometry of the W metallacyclobutanes plays an important role. Indeed, extensive DFT studies on metallacyclobutanes with 5-coordinated W metal center have shown that a square pyramidal (SP) geometry is likely to be responsible for the deactivation of the catalyst.^{14, 15} While in the case for the Grubbs Ru catalyst, calculations have shown that the trigonal bipyramidal metallacyclobutane, (required for the cycloreversion metathesis step) is generally much more stable than SP metallacyclobutanes. Following the same catalytic procedure described for ethyl undecylenate, we found that (**1**) catalyzes also FAEs with internal double bond. For instance, ethyl oleate was converted to the corresponding primary metathesis products: the symmetrical unsaturated diesters and 9-octadecene (mixture of substituted symmetrical olefins, ratio of Z/E, 34:66) at 150 °C for 3 h (See Figure S5).

Surprisingly, this reaction catalyzed by silica-supported precursor (**1**) is highly selective leading only to the primary self-metathesis products of ethyl undecylenate or ethyl oleate without apparent isomerization of the starting unsaturated FAE. These observations strongly suggest that the ester group plays a role in the inhibition of the isomerization process. In fact as mentioned earlier under the same reaction conditions, using solely 1-decene as a substrate gave a distribution of terminal and internal olefins corresponding to the self-metathesis and secondary cross-metathesis products (ISOMET) (see Figure S6).

We previously proposed a mechanism involving in the metathesis of α -olefins by **1**, in which the isomerization steps take place through the *in situ* formation of a W-H species (insertion of the olefin followed by β -elimination of the possible metal alkyls). These elementary steps are important to account for the ISOMET reaction. Moreover, a dual tandem Ru/W catalysts has been recently in which the Ru catalyst serves only as the isomerization catalyst in an ISOMET reaction.¹⁶ As silica supported tungsten species (**1**) acts as

a multifunctional catalyst, we initially thought that (**1**) would be ideal to produce a distribution of unsaturated diesters of fatty acids with variable chain length from a functionalized olefin (monounsaturated FAEs in our case), together with a distribution of resulting olefins and monoesters. Indeed, it is known that unsaturated fatty acid methyl esters (FAMES) in presence of both isomerizing and metathesis catalysts represent an elegant access to a mixture of unsaturated diesters of fatty acids. Grubbs *et al.* disclosed one of the first tandem isomerization/metathesis processes of unsaturated FAMES by employing a dual catalytic Ir/Ag system.¹⁷ Later on, Gooßen and co-workers employed a Pd/Ru system for this transformation.¹⁸ Starting from an unsaturated FAME, with an internal double bond, they observed the formation of a distribution of olefins, unsaturated diesters and unsaturated monoesters (resulting from both primary and secondary self-metathesis and isomerization/cross metathesis reactions) (**Scheme 2**).

With silica supported [(=Si-O)WMe₅] (**1**) such diesters distribution could not be observed. Interestingly, we also found that the reaction of saturated FAE (as the ethyl undecylate) with **1** did not produce alkane metathesis products at 150°C for 3 days period. This result can be rationalized by considering the possible coordination of a W-methylidene hydride, propagative species in alkane metathesis,¹² into the functional ester group. And, this would prevent two crucial steps in the alkane metathesis: the C-H alkane activation required for the olefin intermediate and the release of catalytic amount of hydrogen. These observations are consistent with the absence of isomerization using unsaturated FAEs as substrates, pointing out a detrimental effect from the ester group by preventing the isomerization step in the olefin metathesis process.

2.2. Cross metathesis study between α -olefin and an unsaturated fatty acid ester.

As species (**1**) is active in α -olefins ISOMET reaction but led only to the self-metathesis products with unsaturated FAEs, we investigated the reactivity of (**1**) in presence of both unsaturated FAE and α -olefins. We examined the cross reaction of 1-decene and ethyl undecylenate. The cross-metathesis involving a functionalized and an unfunctionalized olefin gave only three types of primary products: i) self-metathesis product of 1-decene metathesis, ii) self-metathesis product of ethyl undecylenate metathesis and iii) cross metathesis products (with ethylene formation in each metathesis reaction) as shown in **Scheme 3**. The reaction of 1-decene (C₁₀) with ethyl undecylenate (C₁₁) (molar ratio of 1:1) catalyzed by (**1**) produced the internal olefins, 9-octadecene (C₁₈), the higher molecular weight FAE (C₁₉) and the symmetrical diester of fatty acid (C₂₀). By comparison with the linear α -olefins metathesis, the conversions observed for the unsaturated FAE metathesis or for the metathesis with a 1:1 molar ratio of α -olefin/unsaturated FAE metathesis were found to be low. Metathesis of 1-decene and ethyl undecylenate was also studied at different molar ratios of ethyl undecylenate / 1-decene; the results are depicted in **Figure 2** (See Figure S7 for chromatogram, and Figure S8 for molar fraction selectivity). Regardless the molar unsaturated FAE/olefin ratio, only the expected primary products of self-metathesis and cross-metathesis were observed. Besides, varying the molar ratio did not affect the conversion toward self-metathesis of ethyl undecylenate under these reaction conditions. A selective formation of longer chain unsaturated fatty acid monoester was constantly obtained. Interestingly, for all these catalytic runs, no secondary metathesis products from ISOMET reaction were observed suggesting that no isomerization occurred in neither for 1-decene nor ethyl undecylenate substrates. These results corroborate with our previous observations in regards to the inhibition of the double bond isomerization in the presence of a functionalized ester olefins. Even if 1-decene is introduced in large excess compared to ethyl undecylenate (molar ratio 4:1), secondary metathesis products are not observed despite traces of detectable 1-decene isomers. This functional group appears also to be unfavorable regarding the efficiency of the metathesis reaction. Indeed, the conversion based on products reaches only 5 % for the internal olefin, 6% for the fatty acid monoester and 9% for the diester of fatty acid. Similar results have been obtained while substituting 1-decene by 1-hexene or 1-octene (See Figure S9).

Finally, we also studied if the ISOMET transformation could occur in the presence of terminal alkyne with a ratio of substrate per catalyst of 446-469 under similar reaction conditions (150 °C, 3 h). In principle, the alkyne group should also react with the supported W-H intermediate. We recently discovered that (**1**) converts terminal alkynes into substituted benzene derivatives *via* cyclotrimerization mechanism under solvent free conditions.¹⁹ Following the same line of thought, **1** being active for olefins (ISOMET) (**Figure 3a**) and alkynes (cyclotrimerization) (**Figure 3c**), catalytic experiments with a molar mixture of 1-decene/1-decyne were carried out (**Figure 3b**). **Figure 3c** displays the GC chromatogram corresponding to the total conversion of 1-decyne, showing only cyclotrimerization products.²⁰ No secondary metathesis products from ISOMET reactions were observed and no enyne metathesis products were detected. These results strongly suggest that alkyne functions are playing apparently the same role of the ester function by preventing the olefin isomerization process to occur.

3. Conclusion

Within this study, we have demonstrated that silica-supported precatalyst $[(\equiv\text{Si-O})\text{WMe}_5]$ (**1**) catalyzes the metathesis transformation of monounsaturated FAE highlighting the importance of the methylation of $\text{WCl}_6/\text{Me}_4\text{Sn}$. Additionally, the cross-metathesis of olefins with unsaturated fatty esters was also possible representing a powerful tool towards the formation of mono and diesters of fatty acids with variable chain length. Although in our previous work, (**1**) was found to act as a multifunctional pre-catalyst promoting ISOMET reaction of α -olefins and alkane metathesis reaction, in the presence of unsaturated FAEs, the W catalytic intermediate is only participating to the olefin metathesis transformation. We believe that these results will enable us to have a better understanding on the metathesis of the challenging functionalized saturated alkanes.

Acknowledgments

This work was supported by the King Abdullah University of Science and Technology.

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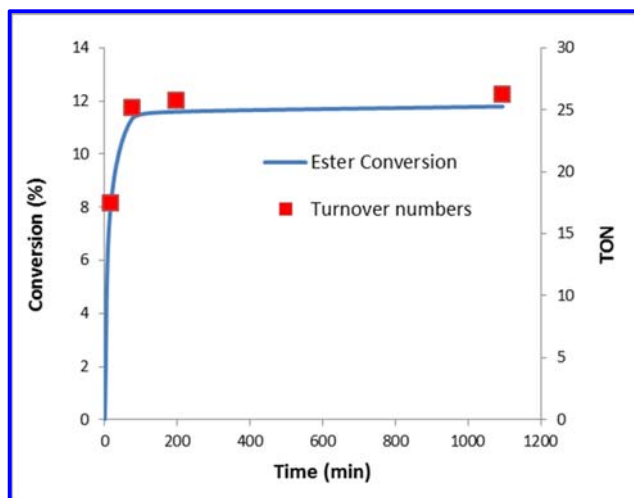
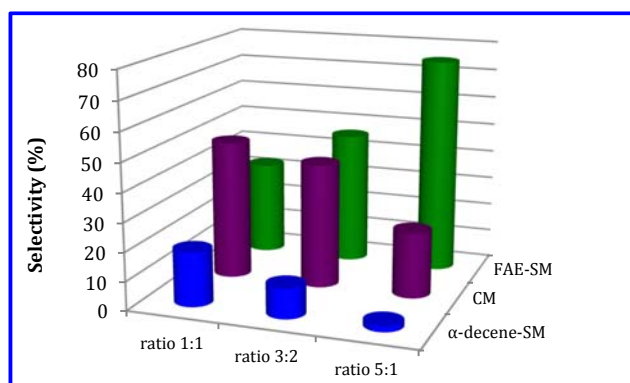
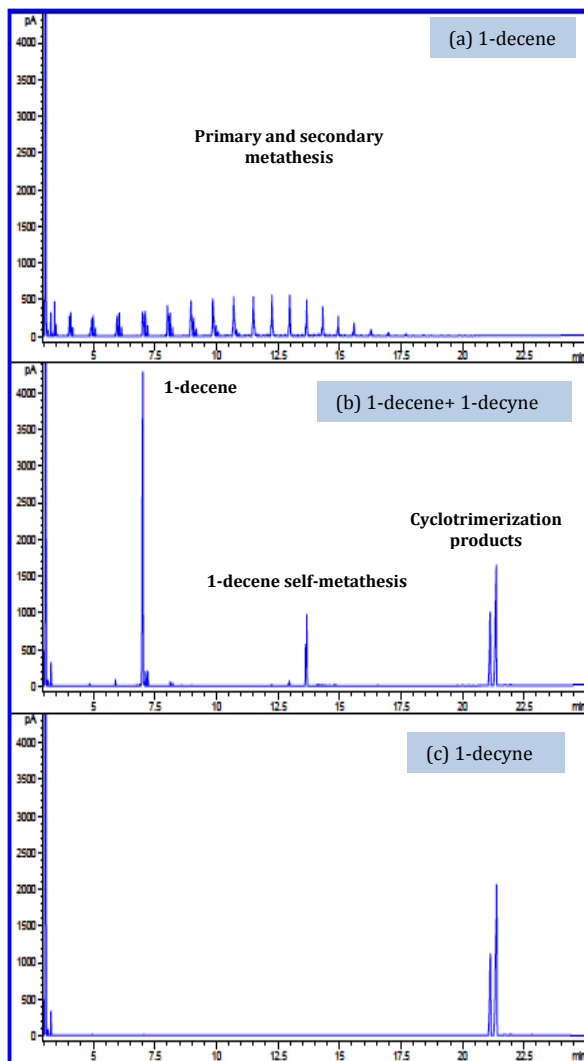
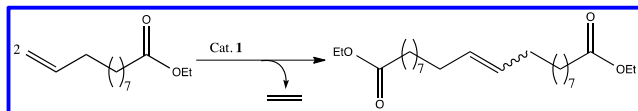
Figure 1: Ethyl undecylenate metathesis catalytic performance**Figure 2:** Ethyl undecylenate and 1-decene cross metathesis catalyzed by **1** at variable molar ratio 1:1; 3:2 and 5:1 (ethyl undecylenate/ 1-decene). Self-metathesis product of 1-decene, in blue, cross metathesis products, in purple and self-metathesis products of ethyl undecylenate, in green. Reaction conditions: batch reactor, **1** (50 mg, 9.3 μ mol, W loading: 3.44%wt), 500 rpm, 150 $^{\circ}$ C.

Figure 3: Reaction conditions: batch reactor, precursor (**1**) (50 mg, 5.92 μmol , W loading: 2.19 %wt): (a) 1-decene (0.5 mL, 2.64 mmol), (b) mixture of 1-decene and 1-decyne (0.25 mL, 1.32 mmol and 0.25 mL, 1.39 mmol) and (c) 1-decyne (0.5 mL, 2.78 mmol), 150°C, 500 rpm, 3 h.

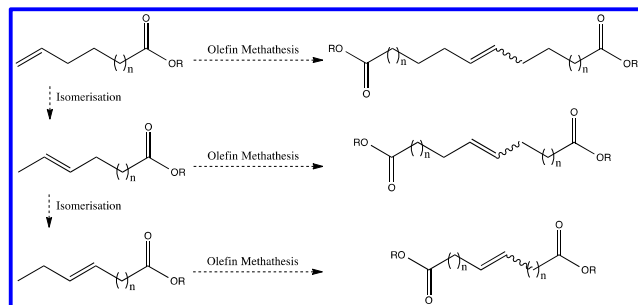


Scheme 1: Self-metathesis (SM) of ethyl undecylenate catalyzed by silica supported W-based catalyst



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Scheme 2: Primary and secondary metathesis of unsaturated fatty acid ester catalyzed by Ir/Ag or Pd/Ru catalytic systems.



Scheme 3: Metathesis of a mixture of 1-decene and ethyl undecylenate catalyzed by (1) leading to the self-metathesis (SM) of 1-decene, SM of ethyl undecylenate and cross metathesis of both substrates.

