

Cross-metathesis of unsaturated natural oils with 2-butene. High conversion and productive catalyst turnovers

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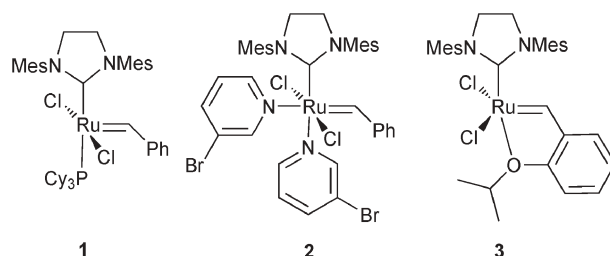
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The cross-metathesis of synthetic and natural triglycerides containing unsaturated fatty acids with 2-butene can be achieved with high conversion and excellent productive turnovers. These reactions are catalysed by second-generation ruthenium-based olefin metathesis catalysts and can be conducted at $-5\text{ }^{\circ}\text{C}$ in liquid 2-butene.

The recognition that sustainability will become increasingly important for the chemical industry has led to a growing interest in the use of renewable resources.¹ Natural oils represent one of the renewable organic feedstocks that are currently produced on a large scale, and the conversion of these oils into useful feedstocks for commercial applications is an issue that has received considerable attention.² One approach to this issue, which has been actively pursued for several decades, is the cross-metathesis of low molecular weight simple alkenes with either natural oils containing unsaturated fatty acids or fatty acid esters derived from these oils.^{3–5} Of the simple alkenes explored in these cross-metathesis reactions, ethene has received the most attention. Ethenolysis is particularly attractive due to the low cost and abundant supply of ethylene. However, to date, all publications employing ethenolysis have reported limited catalyst turnovers and/or low conversion.^{6–8} These problems may be associated with the generation of a relatively unstable methylidene intermediate in the catalytic cycle, and the production of terminal olefins. The latter can compete with the internal olefins in the starting material in binding to the catalyst.⁸ The combination of these factors has a detrimental effect on the reaction time, conversion and turnovers for the catalyst. In this communication we demonstrate that 2-butene can be used in cross-metathesis reactions with natural oils (butenolysis) avoiding many of the problems associated with ethenolysis.

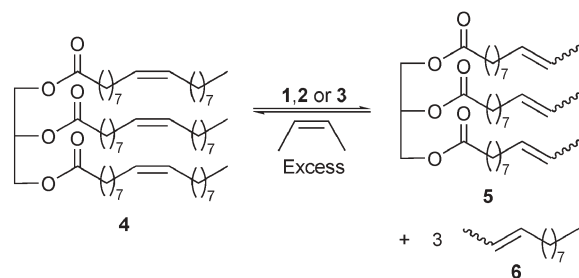
Second-generation ruthenium-based metathesis catalysts (1–3)^{9–11} were chosen for this study due to their functional group tolerance¹² and their ability to catalyse metathesis reactions involving internal double bonds.⁵ Experiments were initially conducted using the synthetic triglyceride of oleic acid, triolein (4, Scheme 1).

The addition of catalysts 1–3 to solutions of triolein (4) in liquid *cis*-2-butene (2-butene : triolein = 30 : 1) at $-5\text{ }^{\circ}\text{C}$ resulted in conversion to the cross-metathesis products 5 and 2-undecene (6).¹³ Catalyst 3 was found to be the most active reaching maximum conversion of oleate chains to 9-undecenoate chains (>95%) in less than 4 minutes with a 0.6 mol% loading of



catalyst. With the same loading, catalyst 2 required >200 minutes to approach similar conversion, while catalyst 1 gave only a trace of butenolysis products.¹⁴ With a lower loading of 3 (3×10^{-3} mol%) a conversion of 93% was reached within 256 minutes (Fig. 1). This conversion equates to productive catalyst turnovers of 93×10^3 which to the best of our knowledge is the highest productive turnovers reported to date for the cross-metathesis of a simple alkene with an unsaturated fatty-acid ester.

The selectivity for and conversion to butenolysis products in this reaction is determined by the molar ratio of 2-butene : fatty acid



Scheme 1 Cross-metathesis of triolein with 2-butene catalysed by second-generation ruthenium-based metathesis catalysts 1–3.

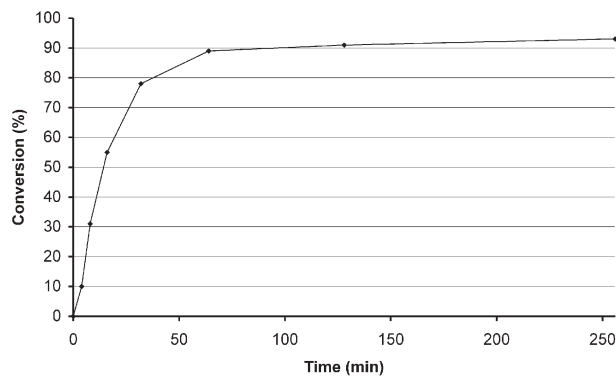
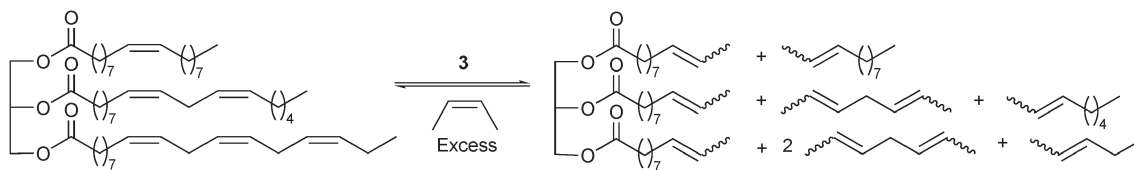


Fig. 1 Butenolysis of triolein with 3×10^{-3} mol% of catalyst 3. Conversion of oleate chains to 9-undecenoate chains.

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Scheme 2 Products from the cross-metathesis of 2-butene with a model unsaturated natural oil containing oleic, linoleic and linolenic acid.

Table 1 Butenolysis of natural oils with catalyst **3**

Oil	Fatty acid composition in the oil (%) ¹⁷				TON ^a
	C18 : 1	C18 : 2	C18 : 3	Saturated	
Triolein ^c	100	0	0	0	93 × 10 ³
Sunflower ^{b,d}	81	10	0	9	38 × 10 ³
Canola ^d	63	18	11	8	37 × 10 ³
Soya ^e	22	54	7	17	24 × 10 ³
Linseed ^e	22	13	53	12	23 × 10 ³

^a Reaction time = 18 h. ^b High oleic. **3** : C=C = ^c 1 : 100 × 10³.
^d 1 : 40 × 10³. ^e 1 : 25 × 10³.

double bonds (C=C). Hence the 2-butene : C=C ratio of 10 : 1 used in the butenolysis of triolein gave a selectivity of >96% and conversion of >95%.

The olefinic cross-metathesis products **5** and **6** were found to be mixtures of *cis* and *trans* isomers, the ratio of which changed during the course of the reaction. At low conversion no selectivity for either isomer was observed while at high conversion the *trans* isomer was found to predominate.¹⁵

Distillation of the final reaction mixture at 5 °C gave a *cis* and *trans*-2-butene mixture which could be reused without further purification.

A selection of four vegetable oils was also subjected to butenolysis with **3** in the same manner as described for triolein, with a ratio of 2-butene : C=C of 10 : 1.¹⁶ Each of the oils examined were composed of differing proportions of oleic acid (C18 : 1), linoleic acid (C18 : 2) and linolenic acid (C18 : 3), and thus in addition to **5**, a range of linear alkenes and dienes was produced from the cross-metathesis with 2-butene (Scheme 2).

Each of the natural oils gave excellent conversion to butenolysis products, and high catalyst turnovers (Table 1). Higher turnovers were obtained for the oils containing predominantly oleic acid compared to those with higher proportions of polyunsaturated fatty acids.

High purity 2-butene was found to be critical for high turnovers in this reaction. When the reaction was conducted with commercially available *cis+trans*-2-butene only traces of butenolysis products were detected, even with catalyst loadings as high as 1 mol%. GC analysis of the isomeric mixture showed that it was contaminated with 2.6% of butadiene while none was found in the commercially available *cis*-2-butene. The addition of butadiene (2%) to *cis*-2-butene gave a mixture that did not give cross-metathesis products with triolein while a *cis+trans*-2-butene mixture (30 : 70)¹⁸ free of butadiene was found to give the same activity in butenolysis reactions as pure *cis*-2-butene. These results suggested that the butadiene was acting as a poison in reactions employing commercial grade *cis+trans*-2-butene.¹⁹

The impressive conversions and turnovers obtained in the butenolysis reactions described herein (compared to those reported

for similar ethenolysis reactions) support recent observations that the presence of terminal olefinic products and methylidene intermediates are detrimental in ethenolysis reactions.⁸ These results are also consistent with recent reports that demonstrate that ruthenium–ethylidene complexes are significantly more stable than methylidene analogues.^{20,21} The butenolysis products, possessing internal double bonds, are therefore ideal substrates for further metathesis driven transformations.

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- A Schlenk tube under an argon atmosphere was equipped with a magnetic stirrer bar and placed in a cold-bath set at –5 °C. The tube was charged with triolein or natural oil and *cis*-2-butene. The reaction was started by the addition of a freshly prepared solution of catalyst in dichloromethane (~20 µL). The reaction mixture was monitored by removal of 50 µL samples using a pre-cooled gas-tight syringe. Each sample was quenched by addition to a solution of ethyl vinyl ether (100 µL) in dichloromethane (1 mL), transesterified with methanol by conventional means and analysed by GC.
- High conversion and selectivity were achieved with **1** when the reaction was conducted in an autoclave at 50 °C.
- At maximum conversion the *trans/cis* ratios for 2-undecene and 9-undecenoate chains were found to be 4.66 and 4.54 respectively.
- Each of the oils was degassed and purified by passage through activated alumina prior to use.
- Determined by ¹H NMR, see: G. Knothe and J. A. Kenar, *Eur. J. Lipid Sci. Technol.*, 2004, **106**, 88–96.
- The *cis+trans*-2-butene mixture (30 : 70) free of butadiene was obtained by isomerisation of *cis*-2-butene with **2** at –5 °C.
- The reaction of butadiene with the first-generation Grubbs catalyst has been shown to produce a vinyl alkylidene which is inactive for acyclic metathesis reactions, see: P. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 100–110.
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