Metathesis of 9-octadecenoic acid methyl ester: diversity and mechanism of product formation at various Grubbs’ catalyst concentrations

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ARTICLE INFORMATION

ABSTRACT

Self-metathesis of 9-octadecenoic acid methyl ester was carried out with varying the concentration of Grubbs’ second generation catalyst from 0.03 mmol to 0.18 mmol at 40-45 °C for 36 h. Only two products (9-octadecene 30%, and dimethyl-9-octadecene-dienoate 23%) resulted when 0.06 mmol of catalyst was employed, while at other concentrations four metathesized products were observed. 9-Octadecene generated at 0.03, 0.06 and 0.12 mmol completely disappeared and dimethyl-9-octadecene-dienoate (64%) was observed in major amounts at 0.18 mmol concentration.

1. Introduction

Depletion of fossil resources and increasing interest in renewable feed stock transformations is constantly growing day by day [1-6]. Natural oils and fats are potential sources of unsaturated fatty acids where a number of chemical modifications across the double bonds [7,8] result in a variety of organic intermediates. Owing to their long carbon chains, fatty acid methyl esters offer interesting perspectives for surfactant and polymer applications. The development of oleochemistry towards fine chemicals with the aid of homogeneous and heterogeneous catalysts is more recent, but has limitations [9-12].

However, more efficient and catalytic processes that can transform carbon-carbon double bond are in more demand. In this context, metathesis of unsaturated fatty acid methyl esters provides a convenient route to synthesize organic intermediates useful for the production of polymers, biolubricants and biosurfactants. Self-metathesis of unsaturated fatty acids with double bonds at different positions as found in alkenes, cyclodienes, monocyclic and bicyclic esters [13] result in a number of important oleochemicals for a variety of polymer applications [14]. Self-metathesis of long chain fatty acids namely oleic, 11-eicosenoic, erucic, 10-undecenoic, ricinoleic and linoleic acids was carried out to synthesize symmetrical long chain unsaturated α,ω-dicarboxylic acids (C18-C26) in high conversions by Ngo et al. [15,16]. They observed 39-82% isolated yields of diesters/acid. Bosma et al. [9] studied the self-metathesis of esters of various unsaturated carboxylic acids. They observed that all active esters underwent co-metathesis with trans-3-hexene resulting in α-methyl, α,ω-unsaturated esters. Metathesis of unsaturated esters derived from sunflower oil (viz. alkyl oleates and linoleates) resulted in intermediates for the synthesis of products with medical, cosmetic, polymer and other applications [17].

A variety of homogenous and heterogeneous catalysts like WCs/ SnMe4 and Re:O3/Al2O3 are generally employed for metathesis of unsaturated fatty acid methyl esters. Most of the reactions involved relatively large quantities of the catalyst. Further the catalysts were also found to be moisture sensitive [18-20]. Ngo et al. [15] carried out self-metathesis of long chain unsaturated fatty acids, C18-C26 to prepare α,ω-dicarboxylic acids and hydrocarbons with 80% conversion employing 0.315 mmol of Grubbs’ second generation catalyst. Two types of ruthenium carbene catalysts were employed to carry out self-metathesis of oleate-type fatty acids containing ester, hydroxyl epoxy type of functional groups [13] to obtain a variety of intermediates for polymer, pharmaceutical and
petrochemical industries. Marvey observed that the functional group had a significant effect on the catalyst activity Marvey et al. carried out self-metathesis of sunflower-based biodiesel (ethyl ester) using a homogenous WCl6/SnMe4 catalyst [21].

They have also employed 3% ReO3/SiO2-Al2O3 heterogenous catalyst for the metathesis of sunflower bio-diesel [13]. Both catalysts resulted in high conversion of olefins, mono and diesters from biodiesel. Self-metathesis of 9-octadecenoic acid methyl ester and methyl ricinoleate were carried out to obtain hydrocarbons and diesters employing ruthenium alkylidene catalyst in different ionic liquids [11]. Effect of temperature on metathesis activity was studied and better conversions were observed at higher temperatures. They observed that the catalyst could be recycled for three consecutive runs without loss in activity.

On the other hand, Grubbs’ first and second generation catalysts are most stable, less sensitive to oxygen and found active particularly in aqueous medium. Further Grubbs’ second generation catalyst involves more environmentally friendly, convenient processes to produce platform chemicals from a number of vegetable oils [21,22]. However, the catalyst being expensive, it is important to optimize the catalyst concentration for maximum conversions.

2. Experimental

2.1. Materials

Cis-oleic acid methyl ester (99%), and tricyclohexyl phosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene ruthenium (IV) dichloride (Grubbs’ second generation catalyst) (II), sulfuric acid, dry methanol, dry dichloromethane (99.9%) were purchased from Sigma Aldrich Chemical Co, Hyderabad and used as received.

2.2. Methods

2.2.1. Typical procedure for self-metathesis of oleic acid methyl ester

Cis-oleic acid methyl ester (2.00 g, 6.7 mmol) was dissolved in 20 mL dry DCM taken into a two necked round bottom flask under N2 atmosphere. Grubbs’ second generation catalyst (0.026 g, 0.03 mmol) taken in dry DCM was added to the methyl ester using a 20 mL syringe. The contents were heated at 40-45 °C for 15 h. The reaction was monitored by TLC eluted with hexane: ethyl acetate (90:10, v/v). The contents were washed with ethyl acetate and passed over anhydrous sodium sulphate. The solvent was removed using rotary evaporator and dried under reduced pressure (2-5 mm Hg) to obtain metathesized products (0.160 g, 80% yield). The products were qualitatively and quantitatively identified using GC and GC-MS (Scheme 1).

Similar procedure was followed for metathesis of oleic acid methyl ester by increasing the concentration of Grubbs’ second generation catalyst to 0.06 mmol (0.510 g), 0.12 mmol (0.102 g) and 0.18 mmol (0.152 g). The reactions were also carried out by the subsequent addition of 0.03, 0.06, 0.12 and 0.18 mmol catalyst in a single pot by increasing the concentration for every 36 h under the above reaction conditions. All the reactions were repeated twice and found similar results. The formation of the above products was also confirmed using GC and GC-MS analysis.

2.3. Instrumentation

2.3.1. Gas chromatography analysis

The fatty acid methyl esters and the products obtained after self-metathesis were analyzed using an Agilent 6890 Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) fitted with a FID detector and split/splitless injector. A non-bonded cyanosilicone column (DB-225, 30 m × 0.32 mm i.d., J&W Scientific, USA) was employed for gas chromatography analysis. The column temperature was initially maintained at 60 °C for 2 min, increased to 300 °C for a hold time of 20 min with a flow rate of 10 °C/min. The injector and detector temperatures were set at 250 °C. Chemstation software was used for the data analysis.

2.3.2. GC-MS analysis

The structure of the products obtained by self-metathesis of fatty acid methyl ester was analyzed using an Agilent 6890 N (Agilent Technologies, Palo Alto, CA, USA) Series equipped with a DB-225 Column (30 m × 0.25 mm id) series Gas Chromatograph connected to an Agilent 5973. Mass Spectrometer operating in the EI mode (70 eV; m/z 50-550; source temperature 230 °C and a quadrupole temperature 150 °C). The column temperature was initially maintained at 100 °C for 2 min, increased to 300 °C at 10 °C/min with a hold time of 20 min at 300 °C. The inlet temperature was maintained at 300 °C and split ratio of 50:1. Structural assignments were based on interpretation of mass spectrometric fragmentation and confirmed by comparison of retention times as well as fragmentation pattern of authentic compounds and the spectral data obtained from the Wiley and NIST libraries.

Scheme 1
Table 1. Self-metathesis of 9-octadecenoic acid methyl ester.

<table>
<thead>
<tr>
<th>Metathesized product</th>
<th>Fatty acid composition (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.03 mM</td>
</tr>
<tr>
<td></td>
<td>1 hr</td>
</tr>
<tr>
<td>9-Octadecene</td>
<td>13</td>
</tr>
<tr>
<td>Cyclopropene octanoic acid methyl ester</td>
<td>46</td>
</tr>
<tr>
<td>11-Eicosenoic acid methyl ester</td>
<td>11</td>
</tr>
<tr>
<td>Dimethyl-9-octadecene-dienoate</td>
<td>22</td>
</tr>
<tr>
<td>9-Octadecenoic acid methyl ester</td>
<td>-</td>
</tr>
</tbody>
</table>

*Self-metathesis was carried out in DCM at 45 °C.

3. Results and discussion

Though there exist several reports on self-metathesis of fatty acid methyl esters, there is no systematic data available on the metathesized products formed when different unsaturated fatty acids are involved. Also literature reports show self-metathesis reaction on various fatty acid methyl esters at single catalyst concentration, 0.15 mmol and formation of only two products [18,20]. There exist no literatures on the catalyst behaviour at different concentrations on self-metathesis. In this context, we have taken pure cis-9-octadecenoic acid methyl ester and carried out self-metathesis at four different catalyst concentrations. The reactions were carried out independently and also in a single pot increasing the concentration for every 36 h. The products formed after self-metathesis were characterized using GC and GC-MS which are shown by taking the chromatograms of the reactions with 0.03 and 0.06 mmol catalyst concentrations (Figure 1, 2 and 3). The work also explains the possible routes involved in the formation of different metathesized products.

Formation of 11-eicosenoic acid methyl esters was observed for the first time and this may be used as a synthetic intermediate in organic synthesis reactions. Figure 4 gives a detailed mechanism of formation of these products. At 0.06 mmol catalyst concentration only two products namely 9-octadecene (m/z = 252, 20%) and dimethyl-9-octadecene-dienoate (m/z = 325, 23%) were observed along with the regeneration of 9-octadecenoic acid methyl ester (m/z = 296, 49%, Table 1). However, the hydrocarbons and eicosenoic acid methyl ester as observed at 0.03 mmol of Grubbs’ second generation catalyst, completely disappeared with increase in catalyst concentration. The possible mechanism involved in the formation of the products from the cyclic and eicosenoic acid methyl esters is shown in Figure 4. At 0.12 and 0.18 mmol, 9-octadecenoic acid methyl ester generated at 0.06 mmol further underwent metathesis and completely disappeared (Table 1).

4. Conclusion

The study explains the influence of Grubbs’ second generation catalyst on self-metathesis reaction at various concentrations. Self-metathesis of 9-octadecenoic acid methyl ester (oleic methyl ester, 99%) was carried out at four different catalyst concentrations 0.03, 0.06, 0.12 and 0.18 mmol. Self-metathesis of 9-octadecenoic acid methyl ester with 0.03, 0.12, 0.18 mmol concentrations resulted in four products. While at 0.06 mmol only two products resulted, 9-octadecene, 9-octadecenoic acid methyl ester and dimethyl-9-octadecene-dienoate. The study explains the possible routes followed by the molecules to obtain the above products.
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References