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Metathesis of Rubber Fatty Acid Methyl Esters: A Green Approach for Generating Industrial Platform Chemicals

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Abstract: ***With the increase in environmental concern the demand for renewable sources and modern, greener synthetic routes is growing day by day. In this context, the present study is focused on the use olefin metathesis for the preparation of industrial platform chemicals. Rubber fatty acid methyl esters (6.8 mM), a non- edible, tree-bore oil–based esters were subjected to metathesis employing Grubb's second generation catalyst (0.3m.M) at 45 ºC for 36 h. The organic intermediates generated by olefin metathesis as analysed by GC and GC-MS showed hydrocarbon (9-octadecene (19%) and 6-pentadecene (5%)) as major. A macrocyclic hydrocarbon cyclodecacyclododecene (19%) and cyclopropaneoctanoic acid methyl ester (1.6%) were observed for the first time which can be used as potential synthetic organic intermediates.***

Keywords: Olefin metathesis; Grubb's second generation catalyst; Cyclodecacyclododecene; Rubber fatty acid methyl esters; Platform chemicals.

1. Introduction

With the depletion of fossil fuels and increasing emission of green house gases, the importance of renewable raw materials is increasing day by day. Renewable raw materials significantly contribute to a sustainable development and further utilization can meet the principles of green chemistry such as built-in design for degradation or low toxicity of the resulting products [9]. Unsaturated fatty acids and fatty oils form promising, renewable and cheaper feed stocks for generating a number of oleochemicals to develop a sustainable future [10]. In this context, a number of organic reactions are conducted across the double bonds of vegetable oil fatty acids like oxidations, reductions, polymerizations [2, 17] to prepare a variety of organic intermediates. Olefin metathesis has been a modern versatile tool for the functionalization of plant oil derived chemical intermediates. The approach contributes to a sustainable development and reduction in CO_2 emission as the raw materials employed are safer, and less toxic. Metathesis reactions involve redistribution of fragments of alkenes by scission and regeneration of carbon-carbon double bonds. Metathesis between two similar molecules is termed as self-metathesis. While between two different molecules is termed as cross-metathesis. Self olefin metathesis which involves carbon-carbon bond formation, results in a family of important organic intermediates useful for synthesis [12]

A number of self and cross-metathesis reactions were carried out on oleic acid [11], different vegetable oils [15] to develop a range of organic intermediates useful for lubricants, plasticizers, cosmetics, and grease applications. The researchers employed different homogenous and heterogeneous catalysts like ruthenium based [13, 8], molybdenum based [3] tungsten based [1, 16] for metathesis reactions. Further the researchers also observed that good conversions were obtained using high catalyst loadings. However, modern heterogeneous catalysts namely Grubb's first and second generation catalysts were found to be more efficient in generating platform chemicals which can replace most of the petroleum based chemicals [15].

Grubb's first and second generation catalysts are used in organic synthesis as the first generation catalysts, with higher activity. Recent advances in the development of metathesis catalysts in the Grubb's group resulted in a family of ruthenium carbene catalysts which have significant advantages over the traditional tungsten based catalysts [17]. Grubb's catalysts were shown to be insensitive to the presence of oxygen, and with modifications to the ligand system, these catalysts were actually shown to be active in water [6]. For example the application of Grubb's ruthenium catalyst (Cy3 P)2 Cl2 Ru = CHPh to the acyclic diene metathesis (ADMET) of vegetable oils resulted in a more environmentally friendly, convenient process to produce metathesized vegetable oils [15].

Self-metathesis of a mixture of sunflower fatty acids resulted in cyclo-hexa-1,4-diene, alkenes, mono and dicarboxylic acids [8, 17]. Soybean oil subjected to self-metathesis resulted in polycondensation that lead to branching, with increased molecular weight, thereby the viscosity and drying properties. Heterogeneous catalysts Re_2O_7/SiO_2, Al2O3/SnBu4 catalysts were employed for the metathesis of different fatty acid esters of South African Sunflower which resulted in alkene, mono and diesters of varied chain lengths [4]. Other unsaturated fatty acids namely oleic, ricinoleic, and undecenoic acids were also found to undergo self-metathesis employing Grubb's second generation catalysts to obtain α,ώ-dicarboxylic acids [5, 12], in good conversions. Metathesis of soy, rapeseed, tall and linseed oil fatty acids also resulted in a variety of large number of products [15], for varied applications. However, most of the vegetable oils employed were from edible source or from unusual fatty acids containing non-edible oils [7, 9]. On the other hand india is importing 10.3 million tons, 2012 of edible oil for domestic purpose, hence cannot afford to use edible oils for non-edible applications. In this context, rubber seed which is a non-edible oil seed, available in plenty, about 75,000 tons, annually in India (2013) with oil content about 41% and being cultivated on a commercial scale from past several years, has been exploited in the present study. Rubber trees are found abundantly grown in Amazon valley, Venezuela, Peru, Eucador and Columbia. In India, they are widely grown in Kerala, Tamilnadu, Karnataka and Andaman Islands. It grows in deep, well drained soils, with pH tolerance of the plant from 3.8 to 8.0. It is a small genus plant growing to a height of 60-100 ft. Rubber oil was chosen for the study, as the oil is rich in unsaturation (80.7%), can be subjected to self-metathesis by employing Grubb's second generation catalyst to prepare a variety of platform chemicals. Also, there exists no systematic study on the possible routes involved in the formation of different metathesized products.

2. Materials and Methods

2.1 Materials

Rubber (Hevea brasiliensis) seeds were purchased from M/s Sanjeevani Herbal Health Society, Hyderabad, Ltd. Tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene benzylidene ruthenium (IV) dichloride (Grubb's second generation catalyst) (II), sulfuric acid, dry methanol, dry dichloromethane (99.9%) were purchased from M/s Sigma Aldrich Chemical Co, Hyderabad.

2.2 Methods

2.2.1 Gas Chromatography analysis of rubber fatty acid methyl esters and their self-metathesized products

The fatty acid composition of rubber 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 an FID detector and split/splitless injector. A non-bonded cyano silicone column (DB-225, 30 m x 0.32 i.d., J&W Scientific, USA) was employed for Gas Chromatography analysis. The column temperature was initially maintained at 60 ºC for 2 min, increased to 300 ºC for a hold time of 20 min with a flow rate of 10 ºC/min. The injector and detector temperatures were set at 250 ºC. Chemstation software was used for the data analysis.

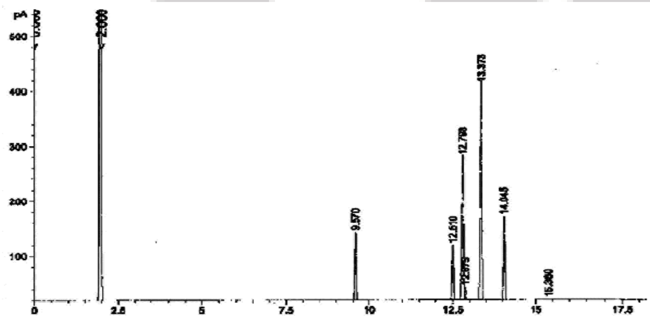


Figure 1: GC analysis of rubber fatty acid methyl esters

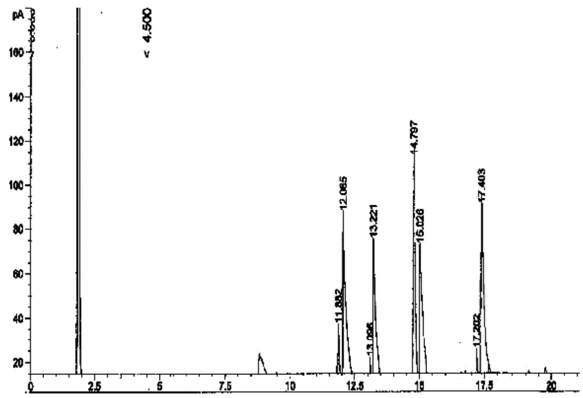


Figure 2: GC analysis of self-metathesized products of rubber fatty acid methyl esters

2.2.2 GC–MS analysis of rubber self-metathesized products

The structure of the products obtained by self-metathesis of rubber methyl ester was analyzed using an Agilent 6890 N (Agilent Technologies, Palo Alto, CA, USA) Series equipped with an DB-225 Column (30 m x 0.25 mm i.d) series Gas Chromatograph connected to an Agilent 5973. Mass Spectrometer operating in the EI mode (70 eV; m/z 50-550; source temperature 230 ºC and a quadruple temperature 150 ºC). The column temperature was initially maintained at 100 ºC for 2 min, increased to 300 ºC at 10 ºC /min with a hold time of 20 min at 300 ºC. The inlet temperature was maintained at 300 ºC 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.

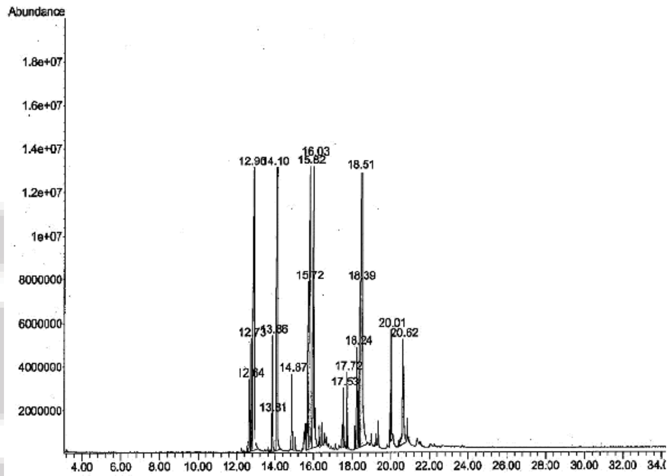


Figure 3: GC-MS of self-metathesized products of rubber fatty acid methyl esters

A. Soxhlet extraction of rubber seed oil

The dried kernels were finely powdered and the powder (500 g) was Soxhlet extracted using hexane (2000 ml) as solvent for 8 h. After 8 h, the solvent was removed using a rotary evaporator and dried under reduced pressure to obtain rubber oil (250 g, 41% yield).

B. Typical procedure for the preparation of rubber fatty acid methyl esters

Fatty acid methyl esters of the rubber oil were prepared by refluxing the oil at 70 ºC for 4 h in 2% sulfuric acid in methanol [4]. The esters were extracted into ethyl acetate, washed until acid free and passed over anhydrous sodium sulphate. The sample was further concentrated using rotary evaporator to obtain fatty acid methyl esters (99%) yield. The converted fatty acid methyl esters were analyzed for its fatty acid composition (wt %) using Gas Chromatography.

C. Typical procedure for self-metathesis of rubber fatty acid methyl esters

Rubber fatty acid methyl esters (2 g, 6.8 mM) dissolved in dry DCM 20 ml was taken into a two necked round bottom flask under N2 atmosphere. Grubb's second generation catalyst (0.3 mM) taken in dry DCM was added to the methyl esters using a 20 ml syringe. The contents were heated at 40-45 ºC for 36 h. The reaction was monitored hourly using 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 (1.6 g, 80% yield). The products were qualitatively and quantitatively identified using GC and GC-MS.

3. Results & Discussion

Self-metathesis of rubber fatty acid methyl esters (80.7%, unsaturation containing palmitic, 10.5%; stearic, 8.3%; oleic, 27.3%; linoleic, 42.1%; linolenic, 11.1%; arachidic, 0.4%; eicosanoic, 0.2%, Fig. 1) was carried out using Grubb's second generation catalyst (Scheme). The method involved a simple, one step process [18], where the heterogeneous catalyst is simply filtered and the metathesized products were analyzed using GC and GC-MS (Fig. 2, 3). However low concentration of the catalyst and lower temperatures resulted in good conversion, unlike the reported methods [15].

Self-metathesis of rubber oil methyl esters using Grubb's second generation catalysts showed the formation of most important hydrocarbon 9-octadecene (Ret.time-12.06 min, 19% GC; m/z 252, GC-MS). This is obtained by the reaction between two 9-octadecenoic acid methyl esters (Fig. 4), a valuable product which can be dimerised and hydrogenated to give (E)-10,11- dioctyleicosane, a lube-oil range hydrocarbon intermediate [10,11]. The hydrocarbon plays an important role in decreasing friction between the moving parts. Most familiar applications is motor oil. In addition to this another hydrocarbon, 6-pentadecene (Ret.time-13.06 min, 5% GC; m/z 210, GC-MS) was obtained in minor amounts by the reaction between 9-octadecenoic acid methyl ester and 9,12-octadecadienoic acid methyl ester as shown in Fig. 4. 6-pentadecene is a type of alarm pheromone found in acarid mite. A cyclic hydrocarbon, cyclodecacyclododecene (Ret.time-17.40 min, 19% GC; m/z 260, GC-MS) was observed in major amounts obtained by the reaction between two 9,12,15-octadecatrienoic acid methyl esters or two 9,12-octadecadienoicacid methyl esters or 9,12,15-octadecatrienoic acid methyl ester and 9,12-octadecadienoic acid methyl esters (Fig. 5). Similar type of reaction was observed in our earlier study on tobacco methyl esters-based metathesis [19]. Another major product monoester 8,11-Eicosadienoic acid methyl ester (Ret.time-14.79 min, 20% GC; m/z 334, GC-MS) with unsaturation at unusual positions was observed for the first time in rubber methyl esters-based metathesis (Fig. 4). This could be due to high unsaturation in rubber seed oil compared to other seed oil based metathesis reported. This is a potential organic intermediate and can be used for a number of synthetic organic reactions. A cyclic monoester cyclopropaneoctanoic acid methyl ester (Ret.time-13.09 min, 1.6% GC; m/z 200, GC-MS) was observed first time in minor amounts (Fig. 4). Further, the diester (E)-dimethyl octadec-9-enedioate formed during the reaction is undergoing metathesis with 9-octadecenoic acid methyl ester to obtain 9-octadecenoic acid methyl ester (Ret.time-15.02 min, 17% GC; m/z 296, GC-MS, Fig. 4) which can be isolated and used for carrying out self and cross-metathesis reactions.

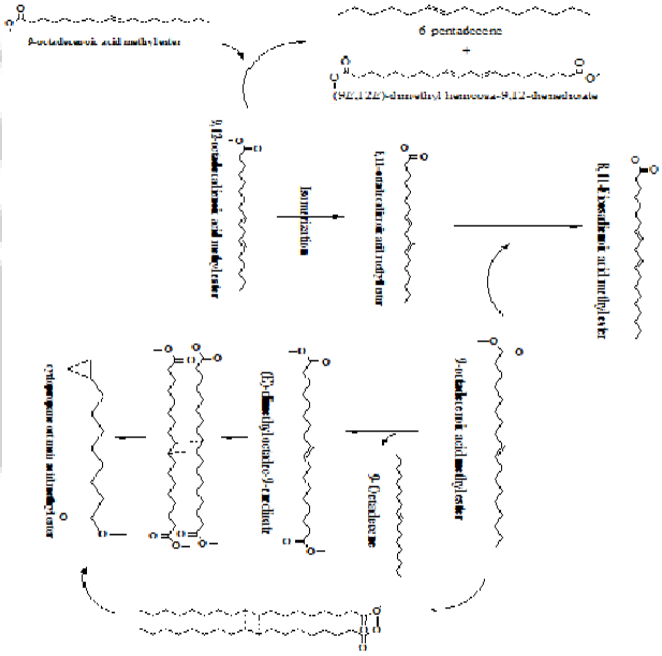
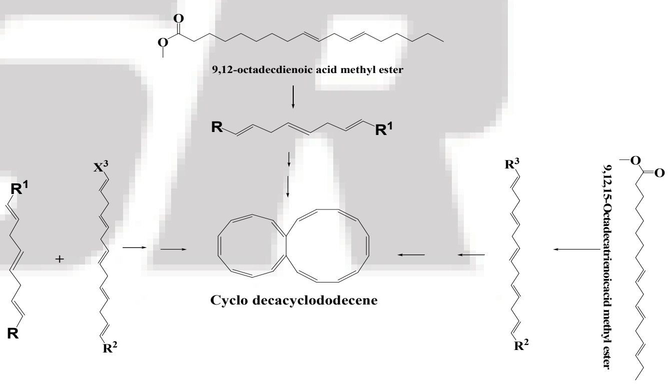


Figure 4: Formation of 9-octadecene, 6-pentadecene, 8,11-eicosenoic acid methyl ester, and 9-octadecenoic acid methyl ester



A) R, $R^1=C_5H_{11}$, B) $R=C_5H_{11}$, $R^1=C_8H_{14}COOMe$, C)R, $R^1=C_8H_{14}COOMe$
A) R^2, $R^3=C_2H_5$, B) $R^2=C_2H_5$, $R^3=C_8H_{14}COOMe$, C) R^2, $R^3=C_8H_{14}COOMe$

Figure 5: Formation of cyclodecacyclododecene.

4. Conclusions

The metathesis of unsaturated rich (80.7%) rubber fatty acid methyl esters was carried out using Grubb's second generation catalyst to develop a number of industrially important platform chemicals. The organic intermediates 9-octadecene, 6-pentadecene, cyclodecacyclododecene, cyclopropaneoctanoic acid methyl ester and 8,11-eicosadienoic acid methyl ester formed during metathesis of rubber fatty acid methyl esters find potential applications as lubricant additives and in synthetic organic reactions which are today petroleum based. 8,11-eicosadienoic acid methyl ester was observed for the first time and can be used as a potential organic intermediate. The method thus involves a simple catalytic route, where a number of industrially important metathesized products are produced. The study also explains the different molecules and possible routes involved in the formation of different metathesized products.

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