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FACULDADE DE CIÊNCIAS E TECNOLOGIA

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Employment of the side product of biodiesel production in the formation of surfactant like molecules

Por
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Resumo

Uma nova reacção que emprega o produto secundário da produção de biodiesel e os seus derivados com 1,3-dieno foi testada usando um método convencional e em CO_2 supercrítico. Neste tipo de reacção designada telomerização, 1,3-dieno como β-myrcene (7-Metil-3-metilen-1,6-octadieno) foi usado com o objectivo de formar moléculas importantes na preparação de surfactantes. Telomerização foi realizada a 90 bare 120 bar de CO_2 usando catalisador heterogéneo de paládio. Glicerol, etileno glicol e glicerol protegido (rac-1,2-O-ciclohexilidenglicerol) foram usados para aumentar a eficiência da reacção.

Abstract

A novel reaction which employs side product from production of biodiesel and its derivatives with 1,3-diene was tested using a conventional method and in supercritical CO_2 conditions. In this type of reaction called telomerisation, 1,3-diene such as β-myrcene (7-Methyl-3-methylene-1,6-octadiene) was used in order to form building blocks important in formation of surfactants. Telomerisation was performed at 90 bar and 120 bar of CO_2 using Pd heterogeneous catalyst. Glycerol, ethylene glycol and protected glycerol (*rac*-1,2-*O*-cyclohexylideneglycerol), were used to increase efficiency of the reaction.

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1. Introduction

1.1. Telomerisation

Telomerisation reaction is dimerisation of two molecules of 1,3-diene in presence of an appropriate nucleophile, e.g. diols[1], water[2], amines[3] which leads to important applicable products Figure 1.1.

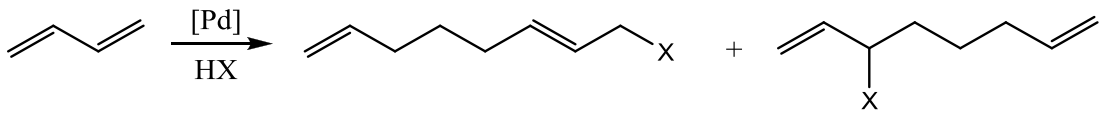

Figure 1.1 - General reaction scheme for telomerisation with nucleophile HX over Pd catalyst[4]

This synthetic methodology was independently discovered in 1967 by Smutny.[5] In telomerisation non-ionic surfactant can be produced in a 100% atom economical reaction.[4] Preparation of molecules with different surfactant properties is among many potential applications coming from the telomerisation. Different dienes and nucleophiles can be used as reactants in telomerisation, and therefore numerous reaction products for countless application might be obtained. Some of them, such as telomers formed in reaction of 1,3-butadiene with water or methanol, are produced on an industrial scale leading to intermediates for synthesis of plasticizers (1-octanol) or copolymers (1-octene).[6] Other telomers, for example, products of conversion of 1,3-butadiene with amines or polyols, are interesting amphiphilic compounds which found use as surfactants or emulsifiers. Moreover, required chemicals being of interest for fragrances or intermediates for production of pharmaceuticals, can be obtained by the proper choose of a suitable diene/nucleophile combination.

A surfactant industry is dominated by several types: alkylbenzene sulfonates, alcohol ethoxylates, sulfates and ethersulfates. They are major components of laundry detergents, household, and personal care products and account for over half of all use of surfactants.[7] Application of surfactants in industry area is quite diverse and has a great practical importance. Surfactants might be applied to improve production and processing of food, agrochemicals, pharmaceuticals, petroleum, fuel additives and lubricants, paints, coatings and adhesives, and photographic films.

Surfactants have characteristic molecular structure consisting of hydrophobic group and hydrophilic group. This is known as an amphiphilic structure. Nature of the polar head group is used to divide surfactants into different categories. A non-ionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic.

One of the most investigated 1,3-dienes in telomerisation is 1,3-butadiene. Telomerisation of 1,3-butadiene with pentose[8] can be carried out in an aqueous medium using $Pd(acac)_2$-TPPTS as a catalytic precursor and tertiary amine as a promoter. A simple variation of the experimental conditions allows preparing two classes of surfactant molecules having a different hydrophilic–lipophilic balance.

Bessmertnykh et al.[9] reported palladium catalysed telomerisation of 1,3-butadiene with sugars. Hydrogenation of mono- and dioctadienyl ethers into saturated non-ionic surfactants has been investigated, using the residual telomerisation catalyst or a commercial palladium heterogeneous catalyst.

An important issue in telomerisation with polyols is selectivity for target products. Weckhuysen and co-workers[10] reported telomerisation of 1,3-butadiene with glycerol. Mono- and especially diethers presented ideal target molecules as subsequent hydrogenation followed by sulfonation produced molecules with potential detergent properties (Figure 1.2).

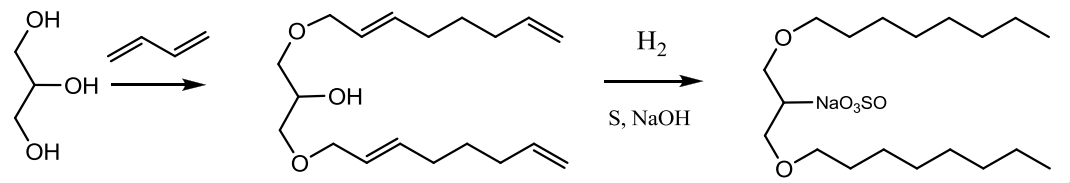

Figure 1.2 - Telomerisation of 1,3-butadiene with glycerol and subsequently hydrogenation and sulfonation[10]

Telomerisation has also been investigated in presence of surfactants. The effect of phosphines and surfactants combinations was studied on activity and selectivity. Monflier et al. reported the efficient use of surfactants for 1,3-butadiene telomerisation with water to improve mass transfers in an

aqueous media.[11] Recently telomerisation of 1,3-butadiene with starch in presence of surfactants using exclusively water as solvent was reported.[12]

1.1.2. Telomerisation with 1-butanol

Telomerisation of 1,3-butadiene with higher, primary alcohols generally proceeds easily to give high yields of telomeric products. Telomerisation with secondary and tertiary alcohols is less efficient and gives small amounts of telomers. Length of the alcohol chain seems to affect reactivity of a nucleophile. Homogeneous telomerisation of 1,3-butadiene with 1-butanol has been investigated Figure 1.3. The major product was cis- and trans-1-alkoxy-2,7-octadiene with selectivity of a 70% after 18 hours with the conversion of a 100%.[13]

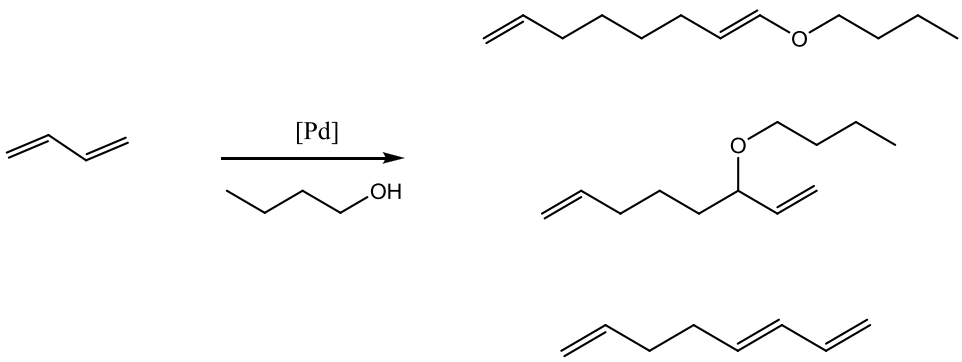

Figure 1.3 – Telomerisation of 1,3-butadiene with 1-butanol over Pd catalyst[13]

1.1.3. Telomerisation with glycerol

Glycerol is considered a potential renewable building block for the synthesis of existed as well as new chemicals. A promising route is telomerisation of 1,3-butadiene with glycerol leads to C8 chain ethers of glycerol. Such building block molecule has an application in surfactant chemistry. Products such as, octa-2,7-dienyl ethers are obtained with 100% atom efficiency when unwanted parallel reactions in particular dimerisation of 1,3-butadiene without addition of a nucleophile is omitted. Glycerol has three hydroxyl groups and therefore its telomerisation can give mono-, di- or tri-ethers (see Figure 1.4). Reaction can lead to linear or branched telomers and mixed linear and branched octadienyl telomers which can find many applications.[10]

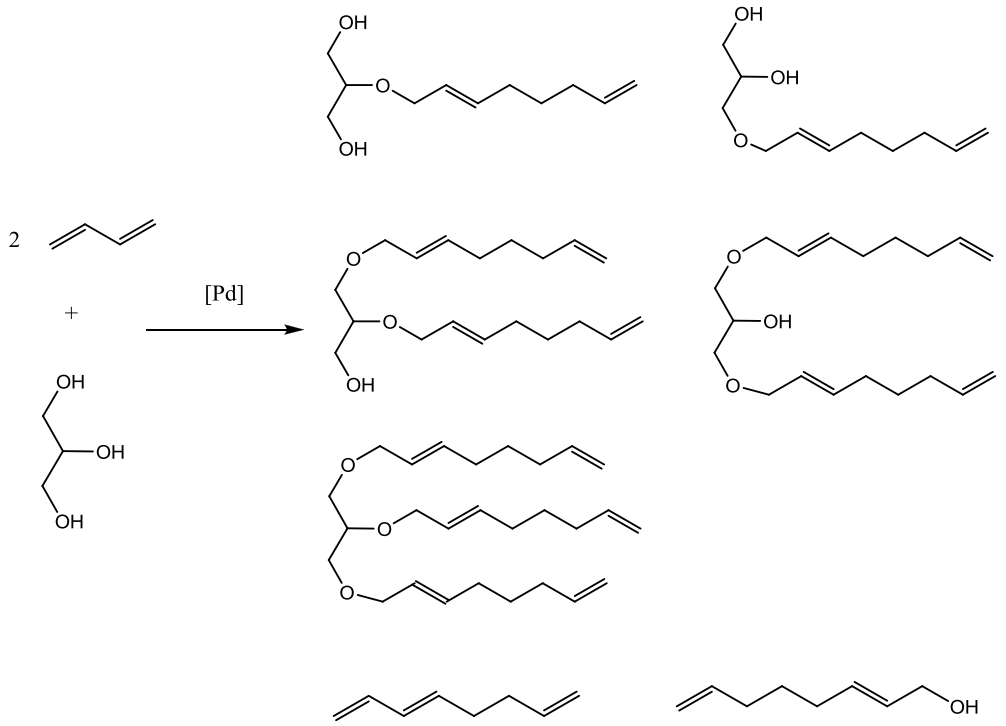

Figure 1.4 - Telomerisation of 1,3-butadiene with glycerol over Pd catalyst[10]

Polar groups are advantageous because they improve solubility of homogeneous catalyst system in glycerol.[10] However the formation of di- and triethers of glycerol is very demanding of the catalyst system and requires a high acceptance of a sterically demanding substrate.

1.1.4. Telomerisation with ethylene glycol

Behr et al.[14] reported telomerisation of 1,3-butadiene with ethylene glycol. Reaction of 1,3-butadiene with ethylene glycol yielded complex mixtures of monotelomers, ditelomers and butadiene dimers when was performed in single liquid phase systems (Figure 1.5).

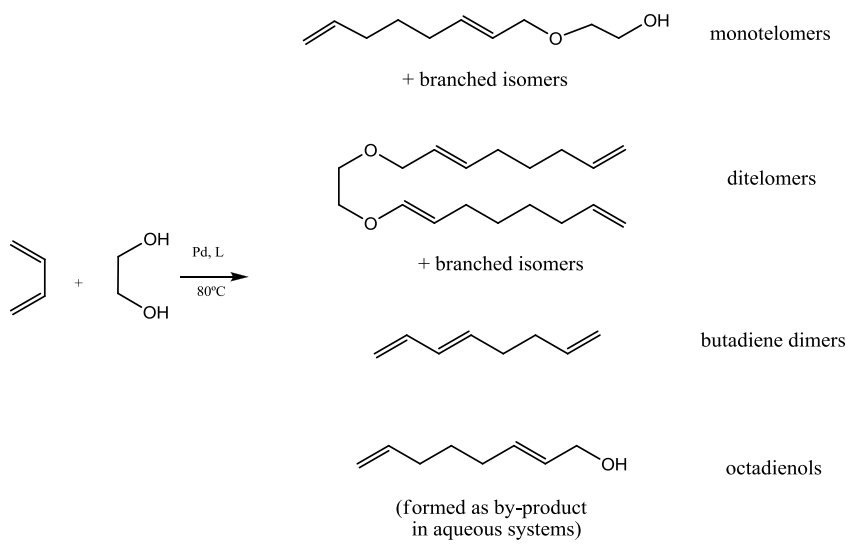

Figure 1.5 - Telomerisation of 1,3-butadiene with ethylene glycol[14]

All monotelomer products were synthesized with very good selectivity (95%) whereas butadiene dimers, octadienols and the corresponding ditelomers were only produced as by-products in yields of about 1-2% each. [14]

1.2. Supercritical fluids and their applications

1.2.1. Supercritical fluids

A fluid is considered as "supercritical" when its temperature and pressure exceed the critical temperature and pressure. Above critical point, there is no superficial tension and no separation of liquid and vapour phases in equilibrium, which gives one supercritical phase with intermediate properties from both states. In vicinity of the critical point, in the biphasic area, difference between densities of the liquid and gas decreases and is equal to zero at the critical temperature.[15]

One of the main differences between supercritical fluids and conventional solvents is their compressibility. Conventional solvents in the liquid phase require very large pressures to change density. Considering supercritical fluids, significant changes in density and thus solvating properties can be achieved with small change of pressure and/or temperature, particularly around the critical point. In general supercritical fluids are less dense than conventional solvents which mean they are less viscous. This leads to greater diffusivity resulting in significantly faster reaction rates.

Use of supercritical fluid reaction medium is advantageous because allows to increase selectivity of a reaction, keep high conversion, dissolve reactants and catalyst in a single fluid phase (reaction occurs homogeneously), and improve or greatly facilitate separation of product species from reactants, catalyst, and unwanted by-products.

1.2.1. Carbon dioxide as supercritical fluid

Supercritical carbon dioxide ($scCO_2$) is by far the most widely used fluid because it is freely available, inexpensive and chemically inert (critical temperature, 31^{o}C; critical pressure, 73.8 bar). $scCO_2$ is an environmentally acceptable replacement solvent for a wide range of potentially toxic organic solvents.

A crucial aspect of carrying out reactions in $scCO_2$ is solubility. Supercritical carbon dioxide is a relatively non-polar solvent, but other compounds (e.g. MeOH) can be added to improve solubility of polar molecules. Alternatively, when reactions involve more than one reagent, less polar reagent can enhance solubility of more polar reagents avoiding additional co-solvents.[16]

1.3. Glycerol as major by-product of biodiesel production

In short term biodiesel is one of the best choices of alternative fuels to reduce dependence on petroleum which can be used in conventional diesel engines with a little impact in the engine performance. Biodiesel production is a relatively simple process that uses accessible chemical reactants. It occurs at moderate temperatures and pressures and can utilize a variety of oil feedstocks.[17] Now biodiesel is comparable in cost with petroleum diesel due to high cost of crude oil. At present, availability of glycerol is increasing due to the expanding manufacture of the biodiesel

fuel obtained by methanol transesterification of seed oils, a process which generates about 10% weight of glycerol as a side-product.[18] As a result, the price of glycerol has fallen significantly and biodiesel refiners are faced with limited options for managing the glycerol by-product. Technologies for the direct conversion of crude glycerol have the potential to facilitate the entrance of glycerol as an important feedstock into the chemical market.[19]

1.3.1. Glycerol telomers

Behr et al.[20] showed that an atom-economic way to get unsaturated ethers of glycerol is transition-metal catalysed telomerisation of 1,3-butadiene with glycerol (Figure 1.6), due to their amphiphilic nature after hydrogenation of the remaining double bonds ethers of glycerol. These compounds have potential applications in surfactant chemistry and as chemical building blocks.[20] The telomerisation of 1,3-butadiene with glycerol was catalysed homogeneously at 80˚C by metal complexes of palladium containing suitable ligands, such as phosphines, leading to the telomer selectivities higher than 95%.

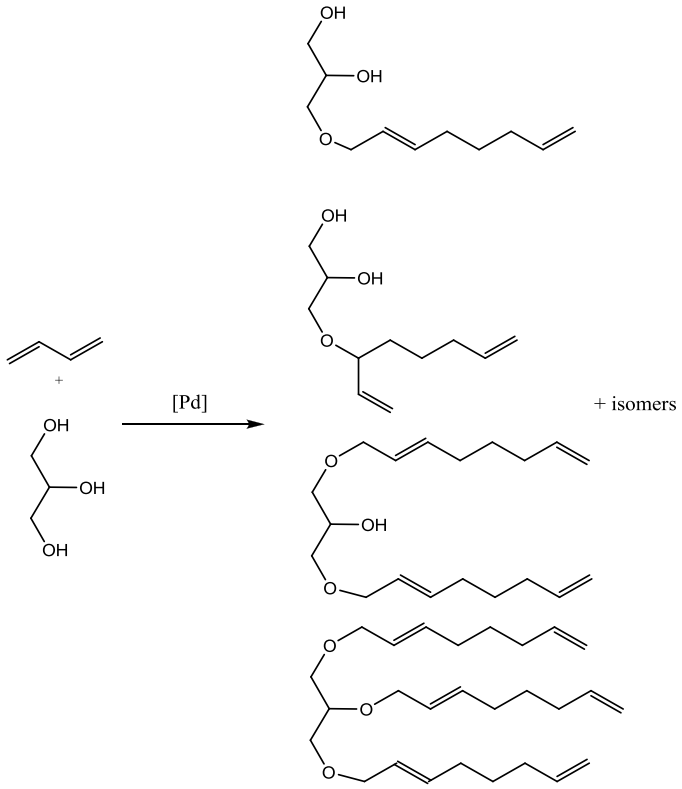

Figure 1.6 - Telomerisation of 1,3-butadiene with glycerol over Pd catalyst[20]

Recently, a report on development of new highly efficient homogeneous catalytic systems for the telomerisation of isoprene[21] with polyols such as glycerol (Figure 1.7) has been published. Pd-carbene complexes were shown to be highly active and selective giving a 99% of linear monotelomer products. Since isoprene and glycerol are immiscible at practical concentrations, a monophasic reaction medium was achieved by adding various co-solvents

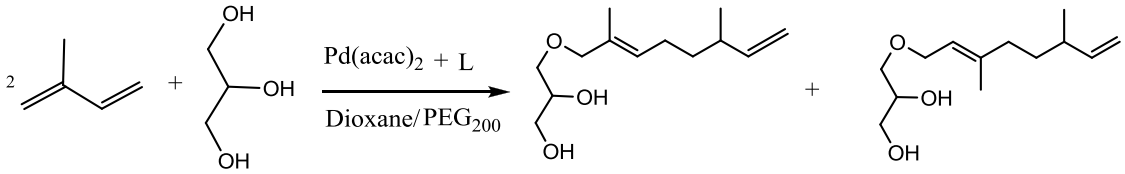

Figure 1.7 - Homogeneous catalysed telomerisation of isoprene with glycerol[21]

1.3.2. Glycerol ketals

Glycerol can undergo a large number of chemical transformations to products of commercial value using various catalysts. Acetals or ketals can be formed in reaction of glycerol with various aldehydes or ketones.[20] Glycerol is a triol and its ketalisation leads to a mixture of two products and water (Figure 1.8).[22]

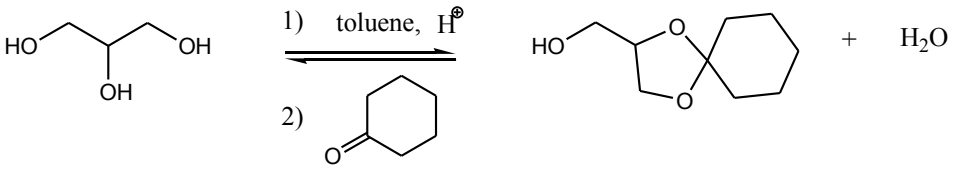

Figure 1.8 - Glycerol ketalisation with cyclohexanone[22]

Protected glycerol named *rac*-1,2-*O*-cyclohexylideneglycerol can be prepared by a simple reaction of glycerol and cyclohexanone using acid catalyst.[23] These acids are not reusable, and are destroyed after reaction. Therefore, for industrial use, application of heterogeneous or recyclable catalyst would be more promising.

In the case of acetalization reaction, strong acid catalysts at high temperatures could induce undesirable reactions, for example, they can induce dehydration of glycerol[24] and the product. Recently, ketalisation of glycerol with various ketones in presence of phosphomolybdic acid towards 1,3-Dioxalane-4-methanol derivatives was reported.[22] *Rac*-1,2-*O*-cyclohexylideneglycerol was prepared in 95% using environmentally friendly process. The catalyst was reused several times without loss of activity or regiospecificity, and all unconsumed reagents were easily recovered and recycled.

1.4. Effect of palladium precursor

1.4.1. Pd/Al_2O_3

Although homogeneous palladium catalysts afford very high selectivities under moderate conditions, the separation of these catalysts hampers their significant use on a large industrial scale. Use of a heterogeneous catalyst has some advantages: 1) easy separation from the reaction products, 2) recycling and anchored metal catalysts may assure a greater stability.[2] For this reasons heterogeneous catalysts are more attractive from the industrial point of view. However, heterogeneous catalysts employed for the liquid phase reaction show leaching of palladium into the reaction medium and a reduced activity compared to the homogeneous catalysts. [2]

Lee et al.[2] investigated telomerisation of 1,3-butadiene with water using different heterogeneous catalysts. One of the catalysts studied was Pd supported on alumina. Compared to the homogeneous catalysts, 5% Pd/Al_2O_3 provided lower activity. This could be explained by dissolution of palladium metal into the reaction medium, but in all cases, palladium in solution was less than 1% of total Pd in catalysts. The problem of deactivation of the catalyst by high-molecular-weight carbon product appeared.

Reducing the catalyst does not enhance activity because an oxidized palladium is more active than Pd(0) in this reaction system.[2]

Behr et al.[25] has investigated telomerisation and hydrogenation of 1,3-butadiene as shown in Figure 1.9.

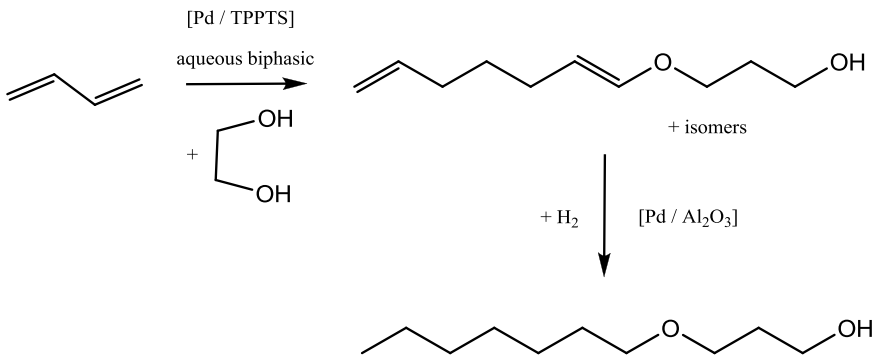

Figure 1.9 - Telomerisation and hydrogenation of 1,3-butadiene[25]

Monotelomers molecules are hydrogenated to increase stability against oxidation and unwanted decomposition reactions. 1% Pd/Al_2O_3 was used for hydrogenation with a 100% selectivity. Mixtures of linear and branched telomers can be hydrogenated as well. [25]

Palladium supported on alumina was successfully applied in hydrogenation of monotelomers from 1,3-butadiene and ethylene glycol. Nevertheless it should be emphasised that generally the conversion of glycerol using heterogeneous catalysts is by far lower than using homogeneous catalysts.

1.5 Telomerisation of terpene

1.5.1 β-myrcene (7-Methyl-3-methylene-1,6-octadiene)

Telomerisation of common petrochemical 1,3-dienes, such as 1,3-butadiene and isoprene (2-methyl-1,3-butadiene) has been studied with different nucleophiles. Acyclic monoterpene, β-myrcene (7-Mehtyl-3-methylene-1,6-octadiene), a 1,3-diene, is a renewable compound suitable for sustainable chemistry in area of fine chemicals. The structure of β-myrcene is presented in Figure 1.10. It is colourless oil with a characteristic odour of geranium, low oral and dermal toxicity. β-Myrcene is already used in industrial processes yielding products for different applications: polymers, pharmaceuticals, insect repellents, flavours and fragrances, vitamins, and biodegradable surfactants.[26] Terpenes are dimmers of isoprene and β-myrcene is one of the most important β-isomers naturally occurred.

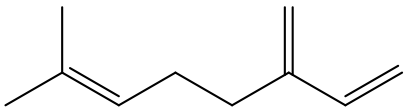

Figure 1.10 - Structure of β-myrcene

At room temperature β-myrcene is nearly insoluble in water and polymerizes spontaneously resulting in a higher viscosity. Hydrogenation of β-myrcene was investigated in supercritical carbon dioxide. Noble metal catalysts, such as (Pd, Ru, Rh) supported on alumina were employed.[27,28] Reactions were carried out in biphasic conditions (liquid +gas), at lower CO_2 pressure and compared with the outcome of the hydrogenation reactions executed in one, supercritical phase. Palladium (0.5 wt%) catalyst was the most active metal which led to high conversion and good selectivity. A fully hydrogenated product was obtained with 95% yield.[27] However, reaction performed in the one-phase region was slightly slower than in biphasic conditions. The pressure of CO_2 strongly affects the reactions conditions. The systems containing a terpene and CO_2 usually exhibit relatively low critical pressures, which allow an easy change from CO_2 expanded to supercritical conditions, with small pressure changes.[28] The pressure tuning changes not only the number of phases, but also controls the concentration of the reagents.

Behr et al.[29] reported hydroamination of β-myrcene with morpholine catalysed by palladium complexes with bidentate ligands. Besides hydroamination of β-myrcene under single phase conditions, side reaction routes were observed, especially telomerisation, isomerisation and dimerisation. If the pathway was telomerisation, the tail-to-tail telomer could be mainly generated. Other telomers occurred only as minor compounds (Figure 1.11).

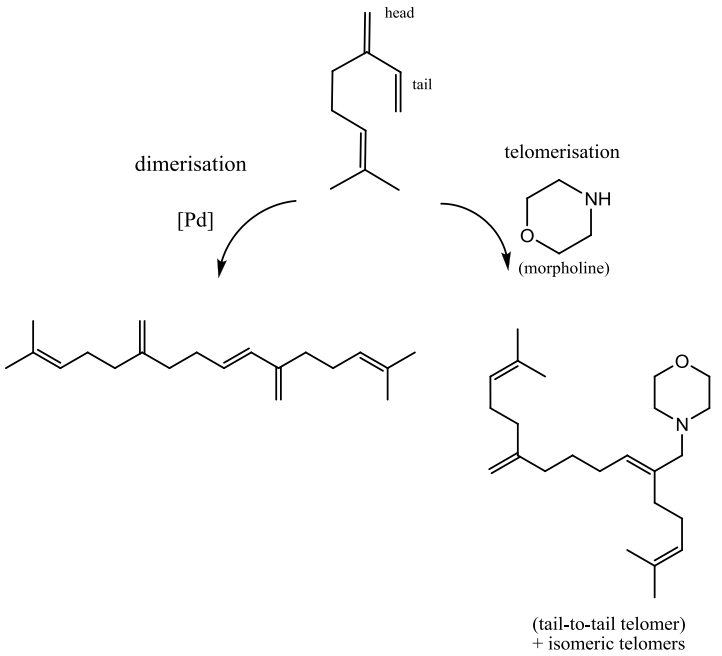

Figure 1.11 - Dimerisation and telomerisation of β-myrcene with morpholine[29]

For the hydroamination reaction (0.2 mol%), more catalyst is necessary than for telomerisation (0.05 mol%). A significant excess of β-myrcene to palladium should favour the coordination of two molecules to the catalytic active species, thereby lead to the telomerisation pathway.

Recently, a first telomerisation of β-myrcene has been reported.[3] Reaction of β-myrcene with diethylamine provided an atom-economical way of generating C_{20} amines in a single step (Figure 1.12). Several Pd (0.05 %mol) precursors were used. A tail-to tail telomer was mainly generated with selectivity up to 93%. A second product of telomerisation was the tail-to-head telomer with selectivity up to a 28 %.

Theoretically, 12 different isomers can be formed in β-myrcene telomerisation. There are four different linkages of two β-myrcene molecules and the nucleophile can attack the chain of these molecules at positions 1 and 3, resulting in eight telomers.

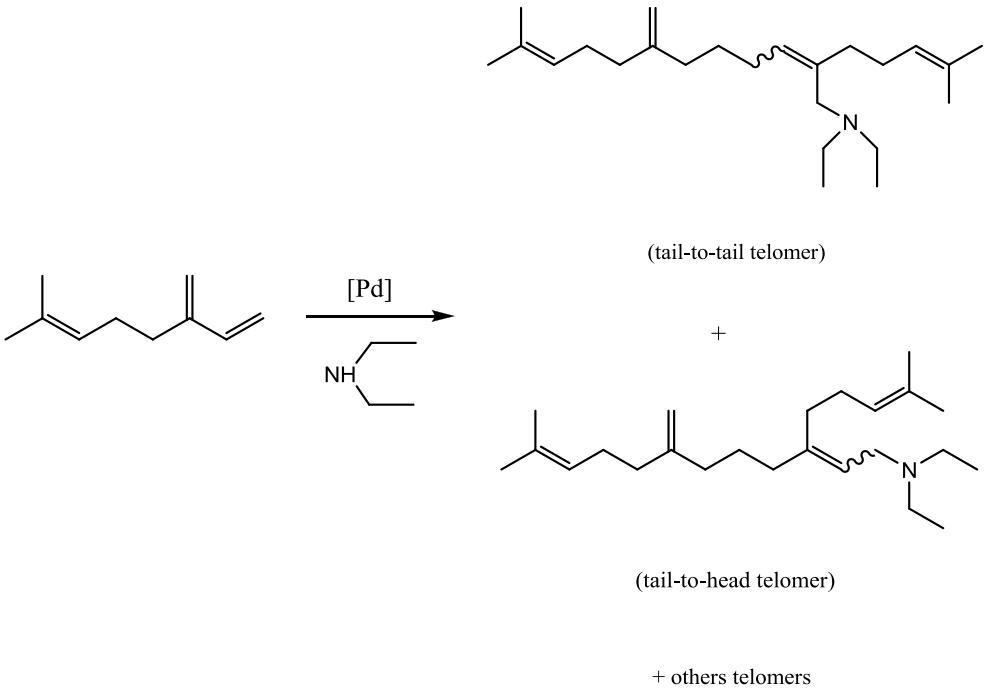

Figure 1.12 - Telomerisation of β-myrcene with diethylamine[3]

2. Objective

The aim of this work is to study telomerisation of β-myrcene using conventional solvents and $scCO_2$ as reaction medium for heterogeneously catalysed reactions. Telomerisation of 1,5-hexadiene was also tested with conventional solvent. Palladium supported on alumina showed to be most successful in hydrogenation of β-myrcene[27] in supercritical carbon dioxide. Driven by this, Pd/Al_2O_3 was employed. 1-butanol is the nucleophile chosen to test telomerisation with β-myrcene and Pd catalyst. This alcohol was used several times in telomerisation with 1,3-diene and as was reported[13] gave high selectivity and conversion. Subsequently glycerol is planned to be tested as the significant increase in crude glycerol has made a need to quick convert large quantities of glycerol into useful products. Glycerol telomerisation together with β-myrcene can be a new way of preparing amphiphilic molecules from priceless product such as glycerol. As was already reported,[14] ethylene glycol is more reactivate than glycerol in telomerisation reaction. Therefore glycerol, and ethylene glycol were employed in telomerisation reaction proceeded conventionally or in supercritical CO_2. Finally the protected glycerol (*rac*-1,2-*O*-cyclohexylideneglycerol) was employed as well to observe

the effect of blocking of side hydroxyl group on the telomerisation and formation potentially interesting product containing either non-polar aliphatic skeleton and after deprotection two strong hydrophobic groups. Preparation of 2,2-diphenyl-1,3-dioxalane-4-methanol with potential use in telomerisation was tested, as other dienes: 1,3-hexadiene, 2-ethyl-1,3-butadiene, 5,5-dimethylhexa-1,3-diene.

3. Experimental part

3.1. Reagents and solvents

Chemical	Supplier	Purity
Argon	Air Liquid	99.9%
Acetonitrile	Sigma Aldrich	99.8%
Allylbromide	Sigma Aldrich	99%
Barium oxide	Sigma Aldrich	90%
Benzophenone	Sigma Aldrich	99%
tert-Butanol	Sigma Aldrich	≥99%
1-Butanol	Merck	min 99.5%
Carbon dioxide	Air Liquid	99.9%
Cyclohexane	Sigma Aldrich	≥99%
Cyclohexanone	Fluka	≥99.5%
Deuterated chloroform	Cambridge Isotope Laboratories	99.8%
Dimethylacetamide	Fluka	99.8%
Dimethylformamide	Sigma Aldrich	99.8%
Dichloromethane	Sigma Aldrich	≥99.9%
Dimethylsulfone	Sigma Aldrich	≥98%
Dimethylsulfoxide	Merck	99.7%
Ethanol	Panreac	99.5%
Ethylene glycol	Sigma Aldrich	99.8%
Glycerol	Sigma Aldrich	≥99.5%
1,5-Hexadiene	TCI Europe nv	≥97%
Methanesulfonic acid	Sigma Aldrich	≥99.5%
4-Methoxybenzaldehyde	Sigma Aldrich	98%
β-Myrcene	Fluka	90%
Oxalyl chloride	Fluka	96%
Pentane	Riedel-de Haën	≥99%
3-Pentanone	Sigma Aldrich	98%
Pd/Al_2O_3 (0,5wt%Pd) pellets	Sigma Aldrich	-
Pd/Al_2O_3 (5wt%Pd) powder	Sigma Aldrich	-
Potassium carbonate	Panreac	99%
Potassium tert-butoxide	Merck	95%
Propionaldehyde	SAFC	≥97%
Sodium chloride	Merck	99.5%
Sodium hydroxide	Sigma Aldrich	≥98%
Sodium methoxide	Merck	97%
Sodium sulphate	Panreac	99.5%
Triethylamine	Merck	≥99%
Triethylphosphine	Fluka	≥99.5%
Tridecane	Sigma Aldrich	≥99%
Trimethylacetaldehyde	Aldrich	96%
Toluene	Sigma Aldrich	≥99.5%
Tungstophosphoric acid	Merck	99%
Tungstosilic acid	Sigma Aldrich	99%

Table 3.1 – Reagents and solvents used in the experiments with the corresponding supplier and purity

3.2. Apparatus used for telomerisation under high pressure

The core of the apparatus used in this work was a 3.5 cm^3 cell with a sapphire window. The cell has one entrance and two exits: one to the manometer and one to extraction tube. The feed tube was connected to a back line connected to another monometer. The back line was connected to the cell by a middle valve. Filters were placed in the entrance and in both exits to avoid flow of the catalyst out of the catalyst bed. The CO_2 depressurization extraction was controlled by two valves. Two glass traps with a solvent were assembled to collect extracts from reaction. The scheme of apparatus is presented in Figure 3.1.

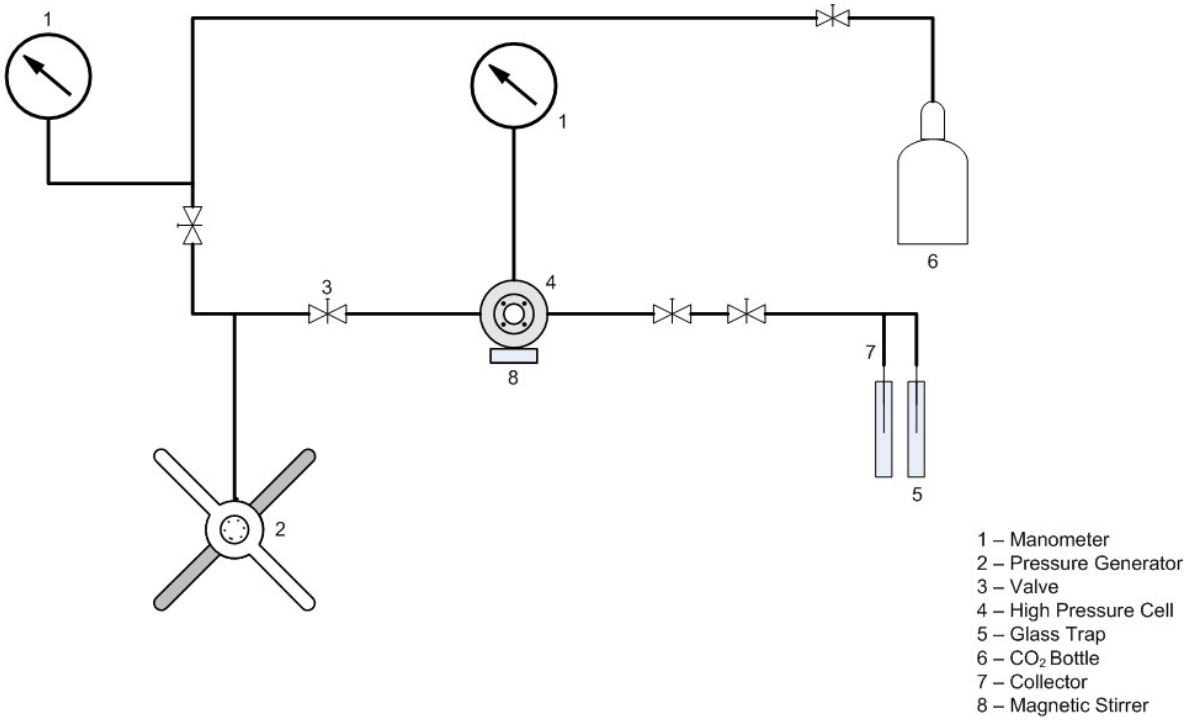

Figure 3.1 – Scheme of the apparatus used in telomerisation with CO_2

3.3. Sample analysis

3.3.1. Gas Chromatography

Products, intermediate compounds and by-products were analysed by Gas Chromatography (GC). This technique is based on the passage of the compounds through a capillary column by the flow of inert gas which consists in the mobile phase. A DB-Wax column (30 m; 0.32 I.D.; 0.25 µm film) was used in the following conditions: carrier flow 0.5 mL/min; injector temperature 240˚C; split ratio 1/30; attenuation 5. Temperature program: start temperature 40˚C hold for one minute, rate 1: 4˚C/min to 120˚C, rate 2: 20˚C/min to 220˚C hold for 5 minutes. Using these chromatographic conditions was possible to determine retention time of all compounds except glycerol. This alcohol has a high boiling point (290˚C).[30] One of the weaknesses of the GC is the requirement of volatile compounds, but its major problem is the lack of definitive proof of the nature of the detected compounds as they are separated.

3.3.2. Gas Chromatography-Mass Spectroscopy

Gas Chromatography-Mass Spectroscopy (GC-MS) is a method that combines gas chromatography for separation and mass spectroscopy for detection and identification of the components of a mixture of compounds. This method is extensively used for the analysis of compounds such as esters, fatty acids, alcohols, aldehydes, terpenes and other groups of compounds. The analysis conditions were the following: Mass Spectrometer: Gas Chromatography-Time of Flight (GC-TOF); Model: GCT from Micromass; Ionization method: Electronic Impact (EI); Column: DB-Wax (30 m; 0.32 I.D.; 0.25 µm film); Temperature program: 40°C (0min), 4°C/min (1min) to 220°C (5min); Injector: 240˚C; Split: 1/40. The DB - Wax column has a polyethylene glycol stationary phase ideal for the separation of glycols. Tailing effects however were obtained in the case of glycerol.

3.4. Methods

3.4.1. Telomerisation of 1,5-hexadiene

3.4.1.1. Reaction with tert-butanol

Method I

To check a solubility of substrates, 1,5-hexadiene (0.5 mL) and tert-butanol (0.8 mL) were placed and mixed in a 5 mL flask at room temperature. After the positive solubility test, in a 50 mL flask 1,5-hexadiene (8.4 mL, 69 mmol) and tert-butanol (13.2 mL, 139 mmol) were mixed for 24h at 70˚C being in contact with 0.5wt% Pd/Al_2O_3 pellets (1.5 g, 14 mmol) catalyst. The catalyst and liquid were separated through decantation. The reaction mixture was analyzed by Gas Chromatography (GC) and Gas Chromatography with Mass Spectroscopy (GC-MS).

Method II

In a 50 mL flask 1,5-hexadiene (8.4 mL, 69 mmol) and tert-butanol (12.7 mL, 134 mmol) were mixted for 24h at 85˚C being with contact with 5wt% Pd/Al_2O_3 powder (1.0 g, 9 mmol) catalyst. The reaction mixture was stirred. The catalyst and liquid were separated through decantation. The reaction mixture was analyzed by GC and GC-MS.

3.4.1.2. Reaction with 1-butanol

Method I

The solubility of 1,5-hexadiene (0.4 mL) and 1-butanol (0.6 mL) at room temperature was checked. In a 50 mL flask 1,5-hexadiene (8.4 mL, 69 mmol) and 1-butanol (12.7 mL, 139 mmol) were mixed for 96h at 85˚C being in contact with 5wt% Pd/Al_2O_3 (1 g, 9 mmol) powder catalyst. The catalyst and reaction mixture were separated through decantation. Products were analysed by GC and GC-MS.

3.4.2. Telomerisation of β-myrcene

3.4.2.1. Reaction with 1-butanol

Method I

The solubility of β-myrcene (7-Methyl-3-methylene-1,6-octadiene) (1.7 mL) and 1-butanol (0.9 mL) in acetonitrile (0.5 mL) was checked at room temperature to reach a complete miscibility. Then in a 50 mL flask assembled with a condenser β-myrcene (17.2 mL, 100 mmol), 1-butanol (9.2 mL, 100 mmol) and acetonitrile (5.2 mL, 100 mmol) were placed together with 5wt% Pd/Al_2O_3 (1.0 g, 9 mmol) powder catalyst. The mixture was heated at temperature of solvent reflux (82˚C) and stirred for 72h. The catalyst and reaction liquid were separated through decantation. During the reaction, mixture was sampled and analysed by GC. Final product was analysed by GC and GC-MS.

Method II

β-Myrcene (1.20 mL, 7 mmol) and 1-butanol (0.64 mL, 7 mmol) were placed in a 3.5 mL high-pressure cell together with 5wt% Pd/Al_2O_3 catalyst (0.07 g, 1 mmol) powder catalyst. To this mixture 90 bar CO_2 was added. Reaction mixture was stirred for 6h at 80˚C. The reaction mixture was centrifuged to settle the catalyst. Products were analysed by GC and by GC-MS.

Method III

β-Myrcene (1.20 mL, 7 mmol) and 1-butanol (0.64 mL, 7 mmol) were placed in a 3.5 mL high-pressure cell 5wt% Pd/Al_2O_3 catalyst (0.07 g, 1 mmol) powder catalyst was introduced. To this mixture 120 bar CO_2 was added. Reaction mixture was stirred for 6h at 80˚C. The reaction mixture was centrifuged to settle the catalyst. Products were analysed by GC and GC-MS.

3.4.2.2. Reaction with glycerol

Method I

A solubility of β-myrcene (1.7 mL), glycerol (0.7 mL) in dichloromethane (0.6 mL) at room temperature was checked giving a complete miscibility. In a 50 mL flask assembled with a condenser and a magnetic stirrer β-myrcene (17.2 mL, 100 mmol), glycerol (7.3 mL, 100 mmol) and dichloromethane (6.4 mL, 100 mmol) were placed and 5wt% Pd/Al_2O_3 (1.0 g, 9 mmol) powder catalyst was added. The reaction mixture was stirred for 48h. The reaction mixture was analysed by GC and GC-MS.

Method II

β-myrcene (1.20 mL, 7 mmol) and glycerol (0.64 mL, 7 mmol) were placed in a 3.5 mL high-pressure cell. 5wt% Pd/Al_2O_3 catalyst (0.07 g, 1 mmol) powder catalyst was introduced. Reaction mixture after introducing of 90 bar $CO_2$was stirred for 6h at 80˚C. Products were analysed by GC and by GC-MS.

Method III

The experimental procedure was the same as previous; however the CO_2 pressure was changed to 120 bar.

3.4.2.3. Reaction with ethylene glycol

Method I

A solubility of β-myrcene (1.7 mL), and ethylene glycol (0.6 mL) in dichloromethane (0.6 mL) at room temperature was checked resulting in their complete solubility. In a 50 mL flask assembled with a condenser and a magnetic stirrer β-myrcene (17.20 mL, 100 mmol), ethylene glycol (5.60 mL, 100 mmol), dichloromethane (6.40 mL, 100 mmol) and 5wt% Pd/Al_2O_3 (1.01 g, 10 mmol) powder were added. The reaction mixture was refluxed with stirring for 120h. The catalyst and liquid were separated through decantation. During reaction, the mixture was sampled and analysed by GC. Final products were analysed by GC-MS.

Method II

β-myrcene (1.20 mL, 7 mmol) and glycerol (0.40 mL, 7 mmol) were placed in a 3.5 mL high-pressure cell. 5wt% Pd/Al_2O_3 powder catalyst (0.07 g, 1 mmol) was introduced. To this mixture 90 bar CO_2 was added. Reaction mixture was stirred for 6h at 80˚C. Products were analysed by GC and by GC-MS.

Method III

Experimental procedure is the same as the previous except this that the CO_2 pressure changed to 120 bar.

3.4.2.4. Reaction with protected glycerol (rac-1,2-O-cyclohexylideneglycerol)

Method I

A solubility test of β-myrcene (1.7 mL), and protected glycerol (1.6 mL) in dimethylformamide (0.8 mL) at room temperature performed in a 5 mL flask showed their complete solubility. In a 50 mL flask assembled with a condenser and a magnetic stirrer β-myrcene (17.2 mL, 100 mmol), protected glycerol (15.7 mL, 100 mmol), dimethylformamide (7.7 mL, 100 mmol) and 5wt% Pd/Al_2O_3 (1.0 g, 10 mmol) powder catalyst were added. Reaction mixture was stirred for 72h. The catalyst and liquid were separated through decantation. During reaction, the mixture was sampled and analysed by GC. Final products were analysed by GC-MS.

Method II

β-myrcene (1.20 mL, 7 mmol) and glycerol (1.10 mL, 7 mmol) were placed in a 3.5 mL high-pressure cell. 5wt% Pd/Al_2O_3 powder catalyst (0.07 g, 1 mmol) was introduced. To this mixture 90 bar CO_2 was added. Reaction mixture was stirred for 6h at 80˚C. Products were analysed by GC and GC-MS.

Method III

Experimental procedure is the same as the previous but the CO_2 pressure was changed to 120 bar.

3.4.3. Experiment for preparation of 1,3-dienes

3.4.3.1. 1,3-hexadiene

Method I

Synthesis of allyl-triethylphosphonium bromide: Into a 50 mL flask triethylphosphine (1.0 mL, 6.8 mmol), dry dichloromethane (6.8 mL) and allylbromide (0.6 mL, 6.8 mmol) were added under Ar at 0˚C. Solution was heated to room temperature and stirred for 50 min. Solvent was evaporated under vacuum and a white solid was obtained. NMR spectral data of allyl-triethylphosphine bromide: ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.24-1.32 (dt, 9H); δ=2.46-2.55 (m, 6H); δ=3.47-3.53 (dd, 2H); δ=5.38-5.78 (m, 3H).

Synthesis of 1,3-hexadiene: Into a sealed tube the allyl-triethylphosphonium bromide (1.73 g, 7.27 mmol) was added to distilled water (2.9 mL). NaOH (1.163 g, 29.08 mmol) was added slowly and mixture was stirred for 15 min at room temperature. After 2 minutes propionaldehyde (0.524 mL, 7.27 mmol) was added slowly. Reaction mixture was stirred at 70˚C for 1 h. A yellow liquid was obtained. The flask was heated to room temperature. Saturated solution of NaCl was added. Sodium sulfate was added to eliminate water. The ^{1}H and ^{13}C NMR (Nuclear Magnetic Resonance) and DEPT (Distortionless Enhancement by Polarization Transfer) ($CDCl_3$) analyses were performed. A pure product was not obtained.

Method II

Synthesis of allyl-triethylphosphonium bromide: Into a 100 mL flask triethylphosphine (6.2 mL, 42.3 mmol), dry dichloromethane (25 mL) and allylbromide (3.6 mL, 42.3 mmol) were added under Ar at 0ºC. Solution was heated to room temperature and stirred for 50 min. Solvent was evaporated under vacuum and a white solid was obtained. The product was analyzed by ^{1}H NMR. A pure product was not produced.

Synthesis of 1,3-hexadiene: Into a flask the allyl-triethylphosphonium bromide (9.453 g, 39.7 mmol) and distilled water (15.8 mL) were added. NaOH (6.352 g, 158.8 mmol) was added slowly. Mixture was stirred for 15 min at room temperature. After 2 min propionaldehyde (2.8 mL, 39.7 mmol) was added slowly. Reaction mixture was stirred at room temperature for 1 h. The flask was heated to room temperature. Saturated solution of NaCl was added. Sodium sulfate was added to eliminate water. Pentane was distilled from reaction mixture.

Method III

Synthesis of allyl-triethylphosphonium bromide: experimental procedure is the same as Method II for preparation of 1,3-hexadiene.

Synthesis of 1,3-hexadiene: Into a flask the allyl-triethylphosphonium bromide (9.8767 g, 41.5 mmol) and distilled water (16.6 mL) were added. NaOH (6.640 g, 166 mmol) was added slowly and stirred for 15 min at room temperature. After 2 min propionaldehyde (3 mL, 41.5 mmol) dissolved in pentane (5 mL) was added slowly to the reaction flask. Reaction mixture was stirred at 0˚C for 1 h. Saturated solution of NaCl was added at 0˚C. Sodium sulfate was added to eliminate water. The reaction mixture obtained was an emulsion.

Method IV

Synthesis of allyl-triethylphosphonium bromide: experimental procedure is the same as Method II for preparation of 1,3-hexadiene.

Synthesis of 1,3-hexadiene: Into a flask the allyl-triethylphosphonium bromide (9.293 g, 39 mmol) and distilled water (15.6 mL) were added. After 20 min the NaOH (6.244 g, 156 mmol) was added slowly to the contents of the flask and stirred for 15 min at 0˚C. After 2 min propionaldehyde (2.8 mL, 39 mmol) was added slowly. Reaction mixture was stirred at 0˚C for 2 h. Saturated solution of NaCl was added to the reaction mixture to separate in two phases. Sodium sulphate was added to dry the

organic phase. The product was purified over a silica gel column (hexane : ethyl acetate = 85:15) and analyzed by ^{1}H NMR. A pure product was not produced.

3.4.3.2. 5,5-dimethylhexa-1,3-diene

Method I

Synthesis of allyl-triethylphosphonium bromide: experimental procedure is the same as Method II for preparation of 1,3-hexadiene.

Synthesis of 5,5-dimethylhexa-1,3-diene: Into a sealed tube the allyl-triethylphosphonium bromide (9.09 g, 38.23 mmol) and distilled water (15.30 mL) were added. NaOH (6.12 g, 152.92 mmol) was added to the contents of the flask and stirred for 15 min at room temperature. After 2 min trimethylacetaldehyde (4.15 mL, 38.23 mmol) was added slowly. The reaction mixture was stirred at 70˚C for 2 h. In the mean time the mixture was stirred manually every 5 minutes because stirring was not efficient. Saturated solution of NaCl was added to the reaction mixture and pentane as well to separate in two phases. Sodium sulphate was added to dry the organic phase. Pentane was removed from mixture using the rotary evaporator and distilled. Mixture was analysed by ^{1}H NMR ($CDCl_3$) before and after distillation. A pure product was not produced.

Method II

Synthesis of allyl-triethylphosphonium bromide: experimental procedure is the same as Method II for preparation of 1,3-hexadiene.

Synthesis of 5,5-dimethylhexa-1,3-diene: In a Schlenk tube distilled water was added under Ar for 30 min. This procedure was necessary to free water from O_2. In a 250 mL flask NaOH (6.75 g, 169 mmol) was added. Then slowly allyl-phosphonium bromide (10.01 g, 42 mmol) was added and stirred for 15 min at room temperature. After 2 min trimethylacetaldehyde (4.6 mL) was added and mixture was stirred for 1h at 70˚C. After finishing reaction was added NaCl saturated solution and pentane to

separate in two phases. After 3 times extraction with pentane sodium sulphate was added to the organic phase and solvent was evaporated using the rotary evaporator. To isolate the product it was necessary to do distillation with vacuum. A product sample was analysed by ^{1}H NMR. A pure product was not produced.

3.4.3.3. 1-[(1E,3E)-buta-1,3-dienyl]-4-methoxybenzene

Method I

Synthesis of allyl-triethylphosphonium bromide: experimental procedure is the same as Method I for preparation of 1,3-hexadiene.

Synthesis of 1-[(1E,3E)-buta-1,3-dienyl]-4-methoxybenzene: In a flask allyl-phosphonium bromide (1.615 g, 6.80 mmol) and distilled water (2.7 mL) were added. To this mixture NaOH (1.088 g, 27.19 mmol) was added. Then after 2 min 4-methoxybenzylaldehyde (0.925 g, 38.45 mmol) was added and stirred for 1h at 70˚C. Sodium chloride saturated solution was added and dichloromethane was used for extraction. Sodium sulphate was added to dry mixture. Then solvent was evaporated using the rotary evaporator. Reaction mixture was purified over a short silica gel column (35% ethyl acetate in hexane). Sample was analysed by ^{1}H NMR. The NMR spectral data of 1-[(1E,3E)-buta-1,3-dienyl]-4-methoxybenzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.85-7.83 (d, 2H); δ=6.53-6.32 (d, 2H); δ=5.63 (dt, 1H) corresponds well to the reported in the literature. [31]

3.4.3.4. 2-ethyl-1,3-butadiene

Method I

BaO was added to dimethylacetamide (500 mL) and refluxed for 1h under Ar. Then dimethylacetamide was distilled at 72-75˚C (40mmHg). A 250 mL three neck round bottom flask with a stirrer, thermometer and a condenser was charged with dimethylacetamide (62.5 mL, 674 mmol), 3-pentanone (8.8 mL, 84 mmol), dimethylsulfone (21.6 g, 230 mmol), and potassium tert-butoxide (26.8 g, 240 mmol). Product was distilled within 1h at 74˚C. In extraction flask reaction mixture was washed with ice and water. Then saturated solution of NaCl and pentane was added. Next, pentane

was distilled from a reaction mixture. A sample of product was analysed by ^{1}H NMR. A pure product was not obtained.

Method II

A 250 mL three neck round bottom flask with a stirrer, thermometer and a condenser was charged with dimethylacetamide (62.5 mL, 674 mmol), 3-pentanone (8.8 mL, 84 mmol), dimethylsulfone (21.6 g, 230 mmol), and sodium methoxide (13.0 g, 240 mmol). Reaction did not occur.

Method III

Method III was carried out by analogy to method II but instead of sodium methoxide potassium tert-butoxide (26.8 g, 240 mmol) was employed. A product was distilled within 1h at 74˚C, and yielding a 8% of reaction mixture composed by 2-ethyl-1,3-butadiene and tert-butanol. An extraction flask reaction mixture was washed with ice and water. Then saturated solution of NaCl and pentane were added. Pentane was distilled from reaction mixture.

3.4.4. Experiment for preparation of protected glycerol

Method I

In a 500 mL flask glycerol (7.9 mL, 108.58 mmol) and cyclohexanone (11.5 mL, 108.58 mmol) were added. To this mixture methanesulfonic acid (0.1 mL, 1.75 mmol) and toluene (50 mL) were added. Mixture was refluxed with a removal of water by Dean-Stark trap for 2h. After 2h the mixture was cooled and washed with water. Then to the organic phase saturated solution of sodium chloride and potassium carbonate were added. Mixture was filtered and solvent was evaporated. After distillation (bp 110˚C at 20 mmHg) a sample of alcohol was given for analysis by ^{1}H NMR.

Method II

In a 2000 mL flask glycerol (160.5 mL, 2.2 mol) and cyclohexanone (227.7 mL, 2.2 mol), methanesulfonic acid (2.3 mL, 35.4 mmol) and toluene (610 mL) were added. Mixture was refluxed

with a removal of water by Dean-Stark trap and stirred for 5h. Mixture was cooled and washed with water and saturated solution of sodium chloride. Next it was dried with potassium carbonate and sodium sulphate for two days. The liquid obtained was slightly yellow. First the mixture was filtered using vacuum and transferred to the flask prepared for distillation. Then the solvent (toluene) was evaporated using the rotary evaporator. Then ethanol was added and evaporated. An alcohol was distilled at 80˚C (2 mmHg). A sample was analysed by ^{1}H NMR analysis.

Method III

In a two neck round bottom flask assembled with a Dean-Stark, glycerol (7.3 mL, 103 mmol) and tungstophosphoric acid (1.4 g, 0.5 mmol) were placed and the mixture was stirred. Toluene (100 mL) was added and mixture was refluxed with stirring for 2h. After cooled to room temperature, cyclohexanone (10.4 mL, 100 mmol,) was added to the reaction mixture. Reaction time equalled to 3h. After cooled down to room temperature toluene was decanted and the mixture filtered. Catalyst was not recovered from the flask. The solvent was evaporated. Mixture was filtered with celicate dried in vacuum pump and a sample was analysed by ^{1}H NMR. NMR spectral data of *rac*-1,2-*O*-cyclohexylideneglycerol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.23-4.20 (m, 1H); δ=4.03-3.99 (m, 1H); δ=3.78-3.68 (m, 2H); δ=3.59-3.53 (m, 1H); δ=2.10 (br s, 1H); δ=1.61-1.37 (m, 10H).

3.4.5. Experiment for preparation of cyclohexylideneglyceraldehyde

Method I

In a flask under Ar a 2M solution of oxalyl chloride (2.7 mL, 31 mmol) in CH_2Cl_2 (18 mL) was added to a solution of dimethyl sulfoxide DMSO (3.7 mL, 52 mmol) in CH_2Cl_2 (80 mL) at -60˚C and stirred for 20 min. Then protected glycerol (4.1 mL, 26 mmol) in CH_2Cl_2 (20 mL) was added and stirred for 10 min. Triethylamine (18 mL) was added to the reaction mixture that was heated to room temperature and stirred for 30 minutes. Reaction mixture was washed with water and extracted with CH_2Cl_2. The solvent was evaporated. A product sample was analysed by ^{1}H NMR.

Method II

In a flask under Ar a 2M solution of oxalyl chloride (3.1 mL, 36 mmol) in CH_2Cl_2 (18 mL) was added to a solution of DMSO (4.2 mL, 59 mmol) in CH_2Cl_2 (80 mL) at -60˚C and stirred for 20 min. Then protected glycerol (4.1 mL, 26 mmol) in CH_2Cl_2 (20 mL) was added and stirred for 10 min. Triethylamine (20.7 mL) was added to reaction mixture that was heated to room temperature and stirred for 30 min. Reaction mixture was washed with water and extracted with CH_2Cl_2. The solvent was evaporated. A product sample was analysed by ^{1}H NMR. A pure product was not obtained.

3.4.6. Experiment for preparation of 2,2-diphenyl-1,3-dioxalane-4-methanol

Method I

Tungstophosphoric acid (1.4g 0.5 mmol) was added to a two-neck round flask fitted with a magnetic stirrer and Dean-Stark assembly. Toluene (100 mL) was added and mixture was refluxed and stirred. Then glycerol (7.8 mL 100 mmol) was added and water present in the glycerol was removed within 1h. Next benzophenone (18.2g 100 mmol) was then added and reaction mixture was stirred for 18h. Reaction mixture was cooled to room temperature and analysed by Thin Layer Chromatograph, TLC. Toluene was decanted and evaporated. Then dichloromethane was added and evaporated. This procedure was repeated with ethanol and with dichloromethane. At the end flask was connected to the vacuum pump. Toluene was evaporated and sample of mixture was analysed by ^{1}H NMR and GC-MS.

Method II

The experimental procedure is the same as the previous except the reaction time which changed to 48h. ^{1}H NMR analysis was performed.

Method III

Tungstosilic acid (1.4g 0.5 mmol) was added to a two-neck round flask fitted with a magnetic stirrer and Dean-Stark assembly. Toluene (100 mL) was added and mixture was refluxed with stirring. Then

glycerol (7.8 mL 100 mmol) was added and water present in the glycerol was removed within 1h. Benzophenone (18.2g 100 mmol) was then added to the reaction mixture. A sample was analysed by TLC every two hours. Mixture was stirred for 18h. Reaction mixture was heated to room temperature and toluene was decanted. Solvent was evaporated. This procedure was repeated with ethanol and with dichloromethane. A sample of a product was analysed by ^{1}H NMR.

Method IV

The experimental procedure was the same except the reaction time which changed to 48h.

Method V

Cyclohexane was added (102 mL) to a flask assembled with a condenser and a Dean-Stark. Then tungstosilic acid (1.4g) and glycerol (7.8 mL) were placed. Solvent was refluxed for 1h. Benzophenone was added (18.3g) to mixture which was stirred for 48h. After 18h was added more cyclohexane (102 mL). Reaction mixture was analysed by TLC after 18h and after 48h.

In all methods used NMR spectral data, GCMS, and TLC analyses of the reaction mixture showed a product and unconsumed benzophenone. A pure product was not obtained.

4. Results

4.1. Preparation of monoalcohols

4.1.1. Preparation of *rac*-1,2-*O*-cyclohexylideneglycerol (protected glycerol)

Methanesulfonic acid (MSA) and tungstophosphoric acid (TPA) were used as catalysts to prepare *rac*-1,2-*O*-cyclohexylideneglycerol (protected glycerol) - Figure 4.1.

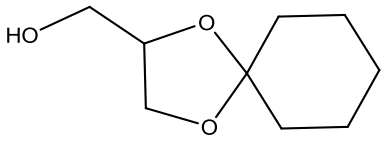

Figure 4.1 – Structure of protected glycerol (*rac*-1,2-*O*-cyclohexylideneglycerol)

The literature reveals that toluenesulphonic acid (TSA) and phosphomolybdic acid (PMA),[22,23] catalysts were broadly used, however in this work MSA and TPA were used respectively. The yields of product are presented in Table 4.1.

Catalyst	Reaction time	Yield
MSA	2h	49%
MSA	5h	72%
TPA	3h	89%

Table 4.1 - Acid catalyzed preparation of *rac*-1,2-*O*-cyclohexylideneglycerol

When alcohol was produced in small scale with MSA gave a higher yield after a 2h reaction. Time of reaction was longer because the catalyst used was less soluble in toluene. Reaction can be controlled by observing the amount of water released during reaction into the Dean-Stark. On larger scale it was possible to observe water released and finish reaction after 5h with the higher yield of 72%. *Rac*-1,2-*O*-cyclohexylideneglycerol was prepared in a 89% yield in reaction of glycerol with cyclohexanone in presence of the tungstophosphoric acid (TPA). This catalyst allowed reducing reaction time to 3h.

Reaction was also tested with tungstosilic acid but unfortunately secondary reactions started to occur after 1h. Tungstosilic acid is a very strong acid. During reaction protonates acetal group from alcohol did not let the reaction to be finished.

4.1.1.1. Oxidation of protected glycerol (Swern reaction)

A preparation of 1,3-diene entirely from glycerol seems to be an interesting idea since many ways of employing of glycerol are welcomed. A process to obtain 1,3-diene is oxidation of rac-1,2-*O*-cyclohexylideneglycerol (protected glycerol) to *rac*-2,3-cyclohexylideneglyceraldehyde, and apply in a Wittig reaction to produce a diene which could be used in telomerisation reaction. Swern oxidation[32] allows preparation of aldehydes from primary and secondary alcohols using oxalyl chloride $(COCl)_2$, dimethyl sulfoxide (DMSO), and quenching with Et_3N. Dimethyl sulphide is a by-product of that reaction. Figure 4.2 shows a proposal for synthesis of *rac*-2,3-cyclohexylideneglyceraldehyde via protected glycerol oxidation basing on the general mechanism for Swern oxidation.[33]

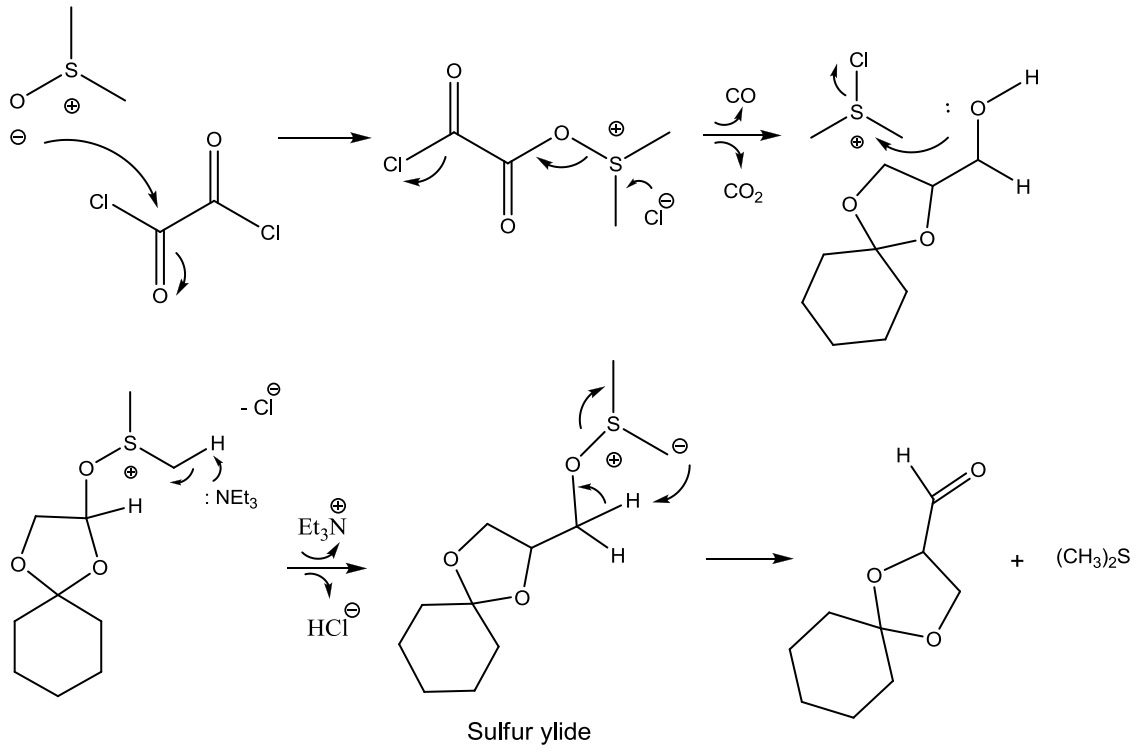

Figure 4.2 - Swern oxidation mechanism of protected glycerol

Unfortunately the performed reaction did not give *rac*-2,3-cyclohexylideneglyceroaldehyde. Presence of acid in the reaction hydrolysed acetals from alcohol and aldehyde. Acetal from aldehyde is very

unstable in solution. A final mixture was composed of those two species. Proper equipment such as Kugelrohr to distil aldehyde from alcohol is required. Therefore this aldehyde is not suitable to be used in Wittig reaction which uses water as solvent.

4.1.2. Preparation of 2,2-diphenyl-1,3-Dioxalane-4-methanol

Driven by results coming from synthesis of protected glycerol, the next reaction, ketalisation of glycerol with benzophenone was performed. A stable monoalcohol was planned to be obtained and use in telomerisation. The reaction of glycerol ketalisation (Figure 4.3) was tested with tungstophosphoric acid (TPA) and tungstosilic acid as catalysts. Low yields were obtained due to unconsumed benzophenone.

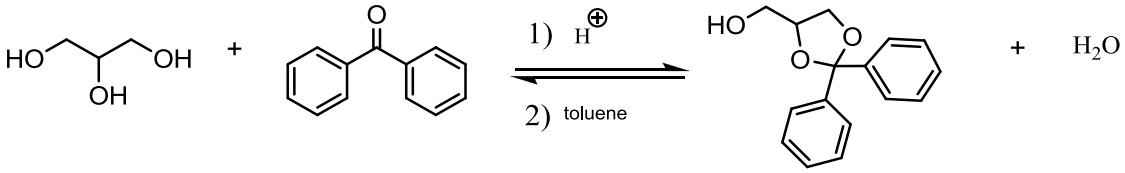

Figure 4.3 – General scheme of glycerol ketalisation with benzophenone[22]

As it was reported[22] good yields were obtained using phosphomolybdic acid (PMA) after 18h of reaction. Following the same procedure, reaction with benzophenone, was studied using TPA. After 18h the reaction was not completed and only a 63% of pure alcohol was produced. After 48h reaction was also not completed yet. Then reaction was also tested with the same conditions using tungstosilic acid. After a 6h reaction the analysis by Thin Layer Chromatography (TLC) revealed unconsumed benzophenone. After 8h, the reaction started to produce a secondary product from acetal hydrolysis. To prevent hydrolysis water was removed from Dean-Stark after 6h of reaction and molecular sieves were added. Unfortunately the reaction was not completed after 18h and the catalyst changed its form. It was formed brownish tar. A possible explanation might be given: acid used as the catalyst seems to be a strong acid as it is not tested on a support but it is pure TSA. When

the concentration of glycerol and water in solution diminished at the end of the reaction, only species that could be protonated by strong acid were acetal product of the reaction (Figure 4.4) and unreacted benzophenone (Figure 4.5). Therefore the strong acid could protonate and open acetal ring or protonate benzophenone and form carbocation of the opened acetal ring or protonated benzophenone. This carbocation could enter self-condensation with other aromatic groups (other molecules of benzophenone or acetal) because the acid is strong and there is no other nucleophile to react with carbocation. A final product of this condensation is tar-like brownish product.

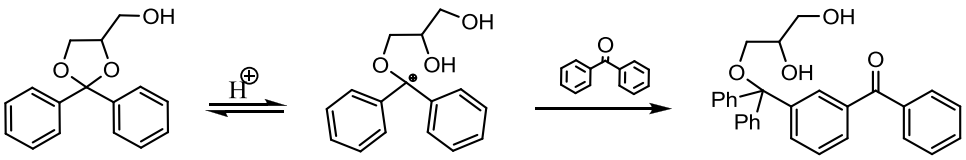

Figure 4.4 - Carbocation of opened acetal ring condensation[34]

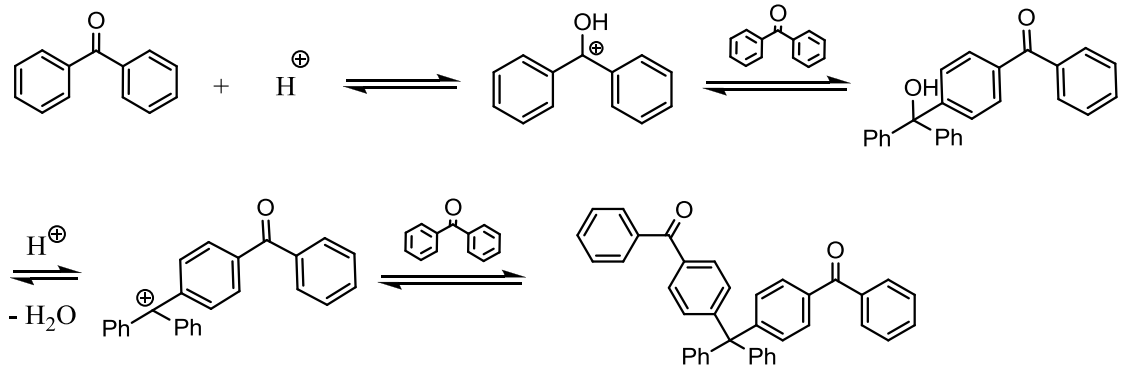

Figure 4.5 - Benzophenone condensation[34]

4.2. Preparation of 1,3-dienes

4.2.1. Test for preparation of 1,3-hexadiene (Wittig reaction)

Wittig reaction is used in conversion of aldehydes and ketones into olefins. In a typical Wittig reaction (Figure 4.6) a phosphonium salt, is treated with a base to generate the ylide, which is

subsequently reacted with a ketone or aldehyde to produce an alkene. [34]

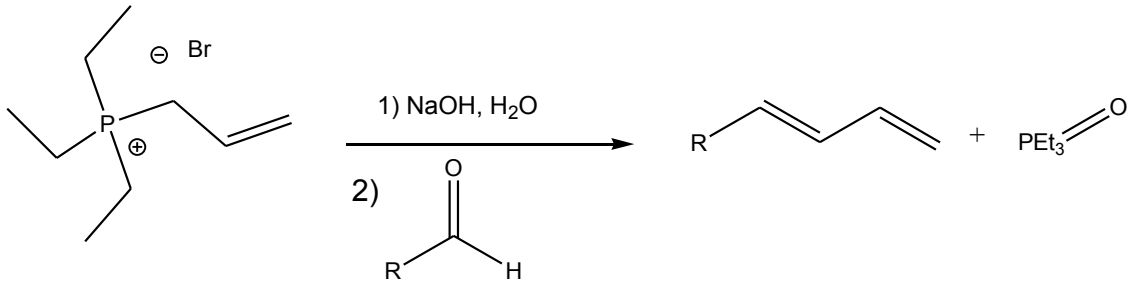

Figure 4.6 – General mechanism of Wittig reaction[34]

Aqueous Wittig reaction was recently applied[31] in synthesis of phenyl- and aryl- substituted 1,3-butadienes as also some higher aliphatic 1,3-diene. Using water as solvent synthesis of 1,3-diene is environmentally benign which is interested for green development. Easy separation of the water soluble triethylphosphine oxide from the organic product is an advantage of this process. All Wittig reactions start with synthesis of allyl-triethylphosphonium bromide reacting triethylphosphine and allyl bromide at room temperature. The reaction of trialkylphosphines with alkyl halides is particularly useful, since the resultant phosphonium salts are easily converted to the phosphonium ylide on treatment with a suitable base.[34] In this experiment allyl-triethylphosphonium bromide was produced with yield of a 92% (Figure 4.7).

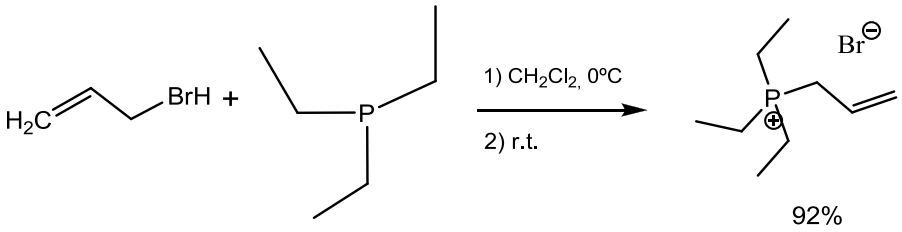

Figure 4.7 - Preparation of allyltriehtylphosphonium bromide[31]

Aqueous Wittig reaction was tested with propionaldehyde (Figure 4.8) at 70°C, at room temperature and at 0°C. In all cases it was obtained a mixture of 1,3-hexadiene with high weight compound since distillation of the diene was not possible. The required product was not separated and was not possible to identify it by nuclear magnetic resonance (NMR).

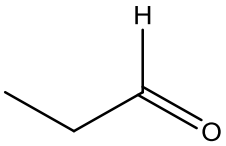

Figure 4.8 – Structure of propionaldehyde

The probable explanation is that molecules of propionaldehyde are very small and remained in water. In aqueous solution aldehydes molecules are deprotonated and aldol condensation (Figure 4.9) might occur.

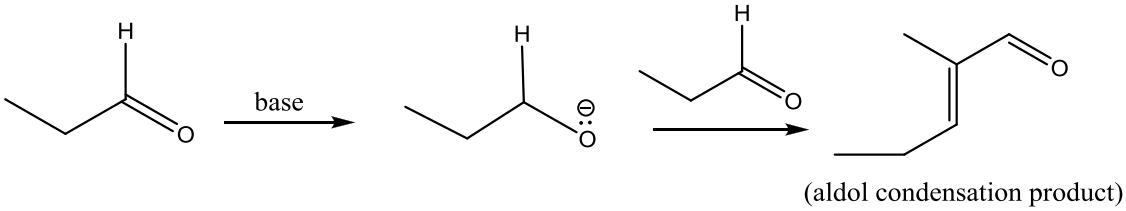

Figure 4.9 - Aldol Condensation with propionaldehyde[34]

Base eliminates hydroxyl group from aldol products producing enones. When hydrocarbon substitution of the enones become sufficiently large they enter ylide micelles, react with ylide and produce molecules of high molecular weight (Figure 4.10) which are not possible to isolate from reaction mixture by distillation.

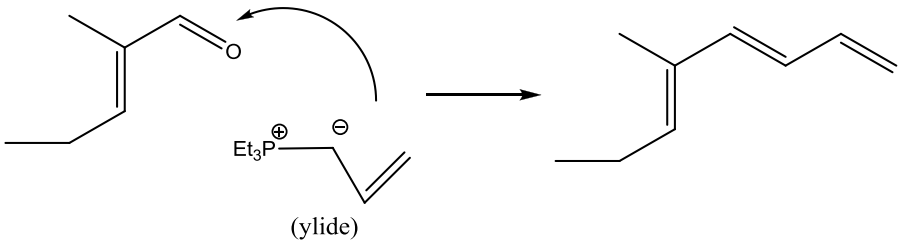

Figure 4.10 - Wittig reaction with aldol condensation product[34]

Reaction was also tested with trimethylacetaldehyde (Pivaldehyde) in order to produce 5,5-dimethyhexa-1,3-diene (Figure 4.11).

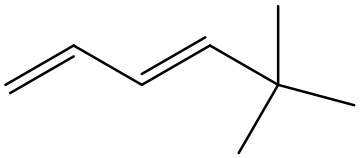

Figure 4.11 – Structure of 5,5-dimethylhexa-1,3-diene

The size of the aldehyde was interesting. Pivaldehyde is a small molecule lacking hydrogen in the alpha position and therefore cannot enter aldol condensation under applied conditions. However, from nucleophilic addition of hydroxide anion to the carbonyl carbon of the aldehyde results in a reactive species that serve as a hydride donor to another molecule of aldehyde resulting a carboxylate anion and an alcohol (Cannizzaro reaction).

5,5-dimethylhexa-1,3-diene was not identified in reaction mixture because of small size of aldehyde molecules which leads to autodegradation of aldehydes by Cannizarro reaction as shown in Figure 4.12. The ylide decomposes most probably by self-alkylation (Figure 4.13).

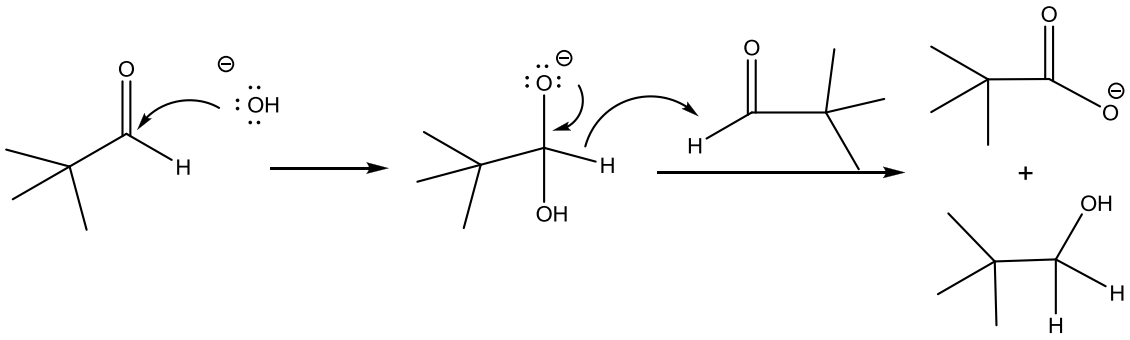

Figure 4.12 - Decomposition of Pivaldehyde by Cannizzaro reaction[34]

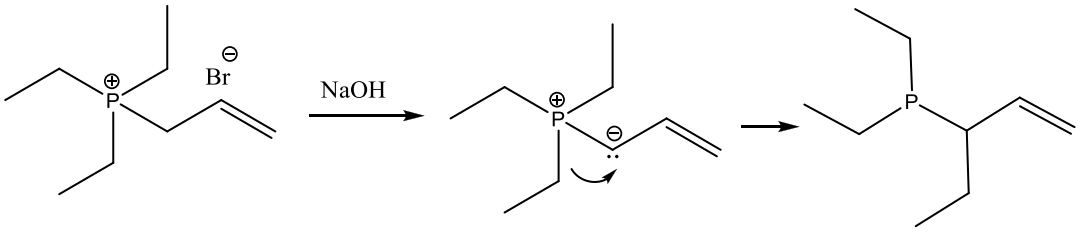

Figure 4.13 - Self-alkylation of ylide[34]

To confirm the reagent and solvent purity and liability of the thesis that only reaction of the small aldehyde molecules is problematic reaction with 4-methoxybenzaldehyde (anisaldehyde).

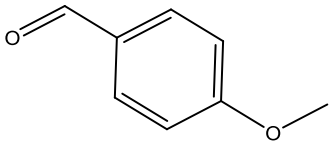

Figure 4.14 – Structure of anisaldehyde

The reaction mixture was purified over a short silica gel column providing 1-[(1E,3E)-buta-1,3-dienyl]-4-methoxybenzene with a high purity of 92% (Figure 4.15).

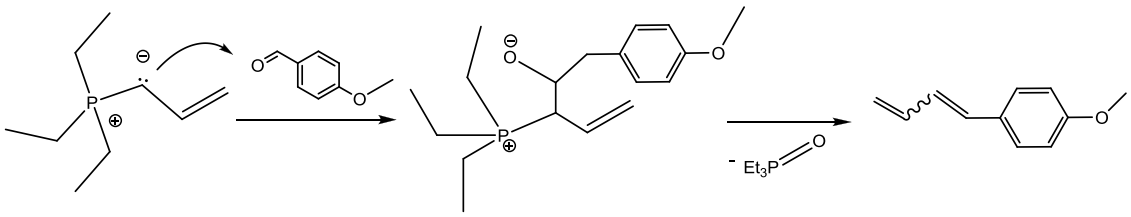

Figure 4.15 - Synthesis of 1-[(1E,3E)-buta-1,3-dienyl]-4-methoxybenzene[31]

Therefore it was confirmed that aqueous Wittig reaction works with bigger molecules in this case with aromatic aldehydes, but not with smaller aldehydes.

4.2.2. Test for preparation of 2-ethyl-1,3-butadiene

1,3-Dienes can be prepared by condensation of ketones with sulfones. Garst and co-workers[35] prepared 2-methyl-1,3-butadiene in 26% and 2,3-dimethyl-1,3-butadiene in 36%. Based on this procedure 2-ethyl-1,3-butadiene was prepared by condensation of dimethylsulfone with 3-pentanone in 14%. A possible mechanism of this reaction is shown in Figure 4.16.

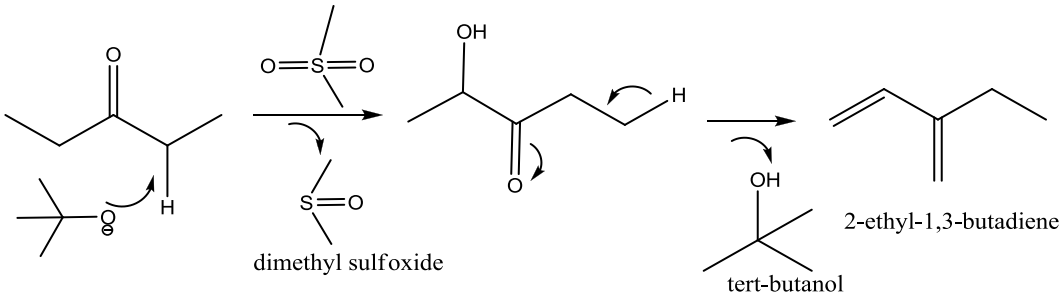

Figure 4.16 - Synthesis of 2-ethyl-1,3-butadiene[35]

The NMR analysis revealed that 3-pentanone was not totally consumed and there were traces of tert-butanol in final mixture even though water was used in extraction. A pure product was not obtained.

In order to remove completely 3-pentanone from the mixture, 1 hour of reflux was used before distillation. This procedure provided purer product although the yield of diene product dropped to 8%. In fact there were no traces of ketone in final mixture but due to an extraction with excess of pentane together with an inefficient distillation the yield obtained was very low. In order to use a cheaper base than potassium tert-butoxide, reaction was also tested with sodium methoxyde as base. Unfortunately no reaction occurred.

4.3. Telomerisation

The telomerisation of dienes was studied with 1,5-hexadiene using 0.5wt% Pd/Al_2O_3 pellets and 5wt% Pd/Al_2O_3 powder catalyst. Two different alcohols were tested: tert-butanol and 1-butanol. Since these two substrates showed to be soluble at room temperature in 1,5-hexadiene there was no need of solvent to perform reaction conventionally. Unfortunately no products were obtained. Consequently 1,5-hexadiene was not tested with $scCO_2$. The reactions did not run.

4.3.1. Telomerisation of β-myrcene with 1-butanol

The telomerisation of β-myrcene with 1-butanol is presented in Figure 4.17.

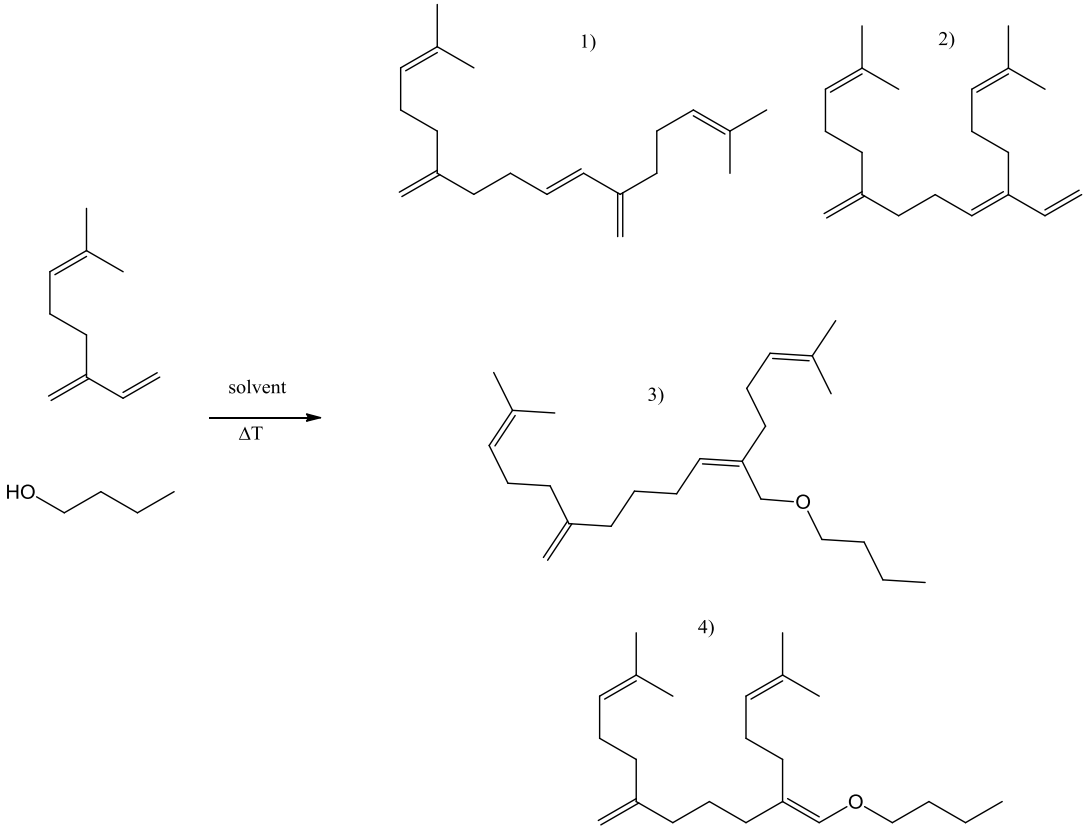

Figure 4.17 - Products of telomerisation of β-myrcene and 1-butanol: 1) - (E)-2,15-dimethyl-6,11-dimethylenehexadeca-2,7,14-triene; 2) - (E)-2,14-dimethyl-10-methylene-6-vinylpentadeca-2,6,13-triene; 3) - (Z)-6-(butoxymethyl)-2,15-dimethyl-11-methylenehexadeca-2,6,14-triene; 4) - (Z)-6-(butoxymethylene)-2,14-dimethyl-10-methylenepentadeca-2,13-diene

The conversion of β-myrcene after 48 hours was 9% and allowed to obtain one of the potential dimmers of β-myrcene namely 1) (tail to tail) and 2) (tail to head) with the overall yield of 31.4%. The telomerisation products such as: 3) (tail to tail) and 4) (tail to head) were obtained with the yield of 32.6% and 36.0% respectively. The obtained results reaction carried out for 54 hours showed that reaction proceeds and after 3 days the conversion of β-myrcene was 19.8%. Dimmers of β-myrcene were detected only up to 48 hours of the reaction and later the product fraction contains only the products of telomerisation. Tail to head telomer is formed with the yield of 34.6% while tail to tail

with the twice higher yield (65.4%). The composition of the product fraction remains constant at 72 hours.

It is known that CO_2 is a good solvent for hydrocarbons (i.e. β-myrcene[36]) and aliphatic alcohols are relatively well soluble in CO_2 as well.[37] These information leads to employment of CO_2 as acetonitrile substitute that makes the reaction more sustainable. To validate this possibility the literature search for vapour-liquid equilibrium data for systems CO_2 + butanol and CO_2 + β-myrcene were performed. VLE for system CO_2 + butanol was studied extensively.[37,38,39,40] The vapour-liquid equilibrium data for system containing CO_2 and 1-butanol at 80˚C are presented in Figure 4.18 and shows that CO_2 fraction in 1-butanol phase is as high as 0.4[39] or 0.43[40] depending on the literature data.

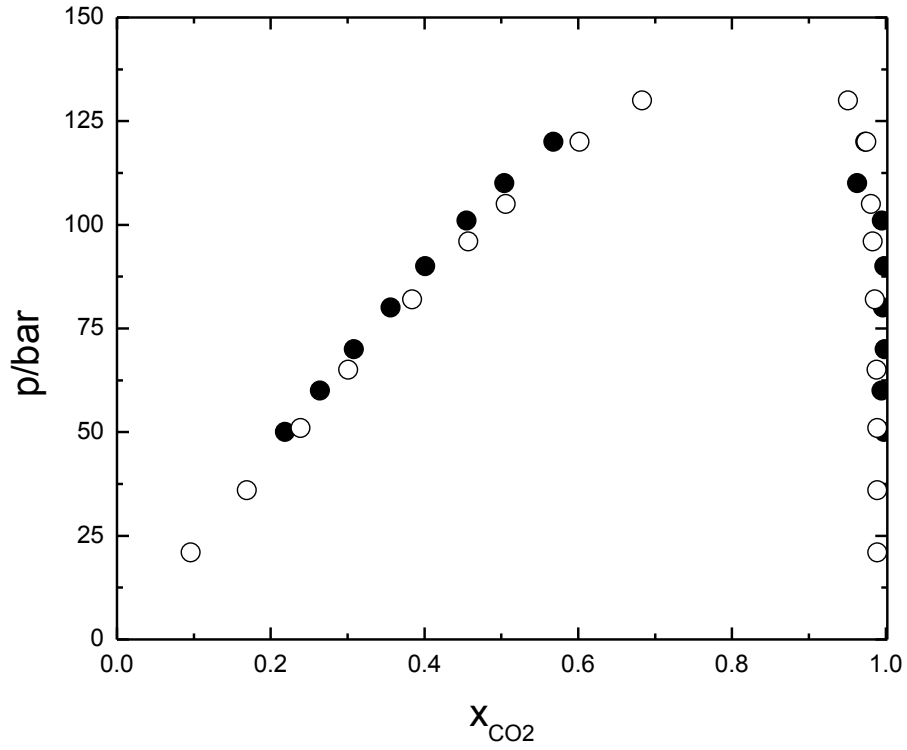

Figure 4.18 - VLE data for system containing CO_2 + 1-butanol. ● data from Chen et al.[39], ○ data from Elizalde-Solis et al.[40]

The literature data for system consisting of β-myrcene and CO_2 at 80˚C does not exist, however the only available literature data[1] allows to predict the phase envelope for the mentioned system at the

telomerisation reaction temperature. The phase envelope was predicted by PE Software[41] using Peng-Robinson EOS[42] and Mathias-Klotz-Prausnitz mixing rule[43] using the methods described elsewhere.[36] The phase envelope for CO_2 + β-myrcene at 80˚C is presented in Figure 4.19 and obtained results showed that at 90 bar the CO_2 expanded liquid phase contains up to 0.92 mole fraction of CO_2.

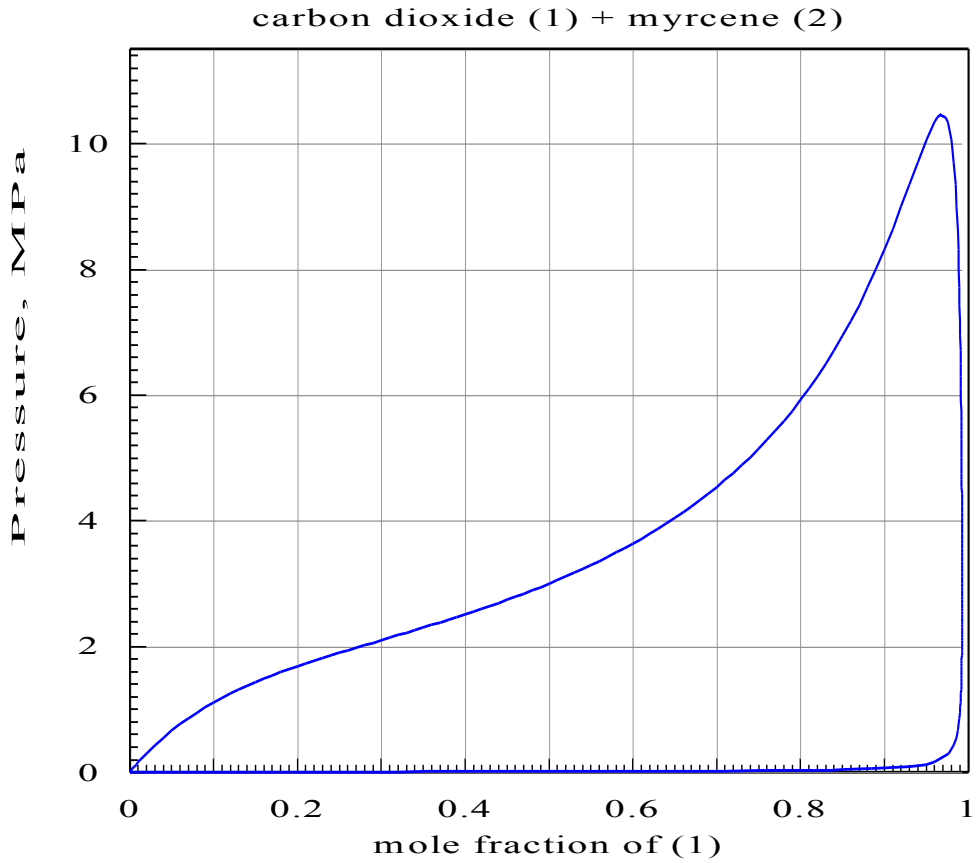

Figure 4.19 - The predicted VLE phase envelope for CO_2 + β-myrcene at 80˚C using the literature data[1]

Additionally at 120 bar the CO_2-1-butanol expanded phase contains even 0.56[39]- 0.60[40] mole fraction of CO_2 while CO_2 and β-myrcene mixture forms a single gas phase.

This information showed that theoretically CO_2 is good solvent for both reagents and might substitute acetonitrile making reaction more sustainable. Surprisingly the reaction carried out for 6 hours at 80˚C and in the presence of CO_2 as solvent showed that reactions neither at 90 nor at 120 bar of CO_2 pressures do not occur.

4.3.2. Telomerisation of β-myrcene with glycerol

The telomerisation of β-myrcene with glycerol is presented in Figure 4.20.

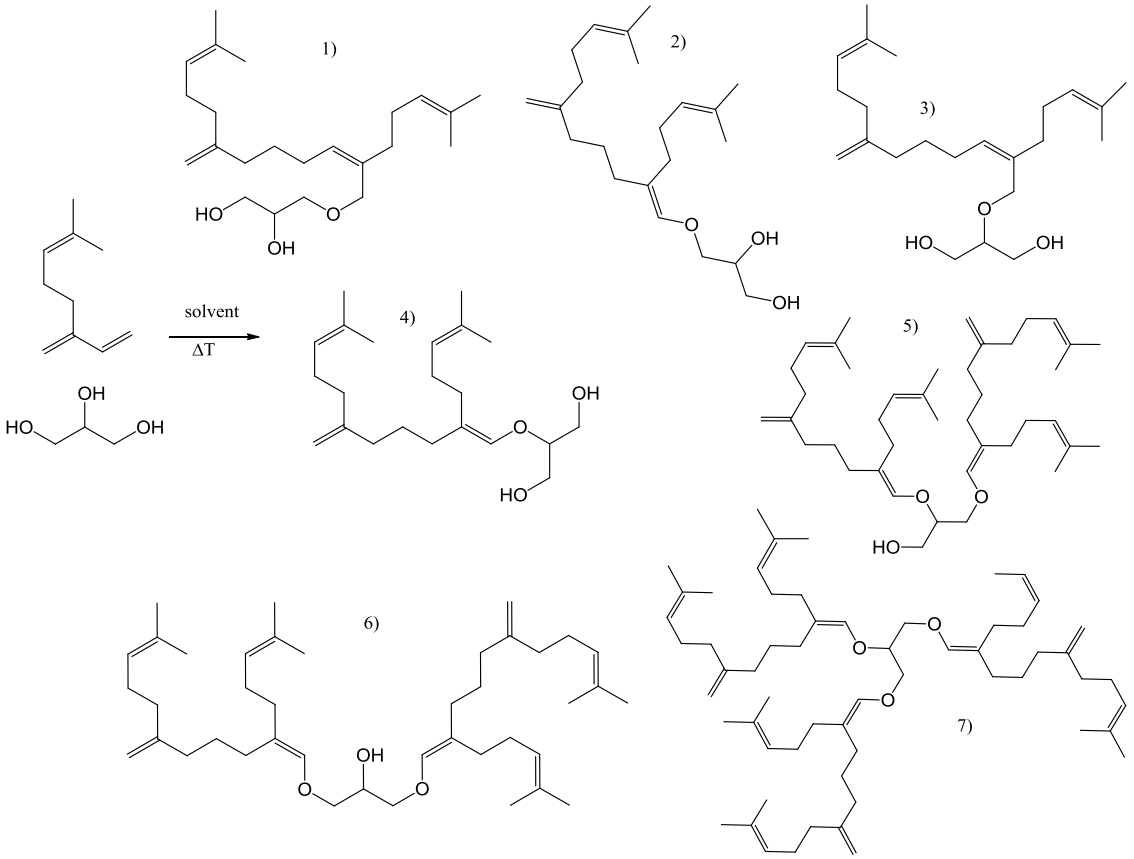

Figure 4.20 - Products of telomerisation of β-myrcene and glycerol: 1) - ((Z)-3-((11-methyl-7-methylene-2-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-yl)oxy)propane-1,2-diol; 2) - (Z)-3-((10-methyl-6-methylene-2-(4-methylpent-3-en-1-yl)undeca-1,9-dien-1-yl)oxy)propane-1,2-diol; 3) - ((Z)-2-((11-methyl-7-methylene-2-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-yl)oxy)propane-1,3-diol; 4) - (Z)-2-((10-methyl-6-methylene-2-(4-methylpent-3-en-1-yl)undeca-1,9-dien-1-yl)oxy)propane-1,3-diol); 5) - 2,3-bis(((Z)-10-methyl-6-methylene-2-(4-methylpent-3-en-1-yl)undeca-1,9-dien-1-yl)oxy)propan-1-ol; 6) - 1-(((E)-10-methyl-6-methylene-2-(4-methylpent-3-en-1-yl)undeca-1,9-dien-1-yl)oxy)-3-(((Z)-10-methyl-6-methylene-2-(4-methylpent-3-en-1-yl)undeca-1,9-dien-1-yl)oxy)propan-2-ol; 7) - ((Z)-6-((2,3-bis(((E)-10-methyl-6-methylene-2-(4-methylpent-3-en-1-yl)undeca-1,9-dien-1-yl)oxy)propoxy)methylene)-2,14-dimethyl-10-methylenepentadeca-2,13-diene

The conversion of β-myrcene in reaction carried out in dichloromethane after 48 hours was 18.4% and the product fraction contained the mixture of products that the major were telomers formed by β-myrcene dimmers and glycerol connected via edge hydroxyl group of glycerol. These telomers 1) and 2) were formed with the overall yield of 57.3%. The telomers 3) and 4) formed by the bonding β-myrcene dimmers and glycerol via internal hydroxylgroup were produced with the twice lower yield of 28.8%. Furthermore the groups of telomers created by double (position 1,2 and 1,3) or triple bonding (1,2,3) of glycerol were formed. The 1,2 bonding i.e. 5) and 6) telomers were formed with the yield of 3.5% and 7.0%. Additionally triple substituted glycerol 7) was obtained as well with the yield of 1.3%.

The reaction in CO_2 was performed to verify CO_2 affinity to work as solvent in the telomerisation of β-myrcene with glycerol. Additionally the aim of this study was to disclose the observed lack of reaction in case of 1-butanol. The results showed that conversion of β-myrcene was low (9.8%) and mixture of monosubstituted glycerol 1) and 2) were formed with the overall yield of 67.7% and 67.4% at 90 and 120 bar respectively. Other monosubstituted telomers 3) and 4) were obtained as well with the overall yield of 32.3% and 32.6% at 90 and 120 bar of CO_2 respectively.

4.3.3. Telomerisation of β-myrcene with ethylene glycol

The telomerisation of β-myrcene with ethylene glycol is presented in Figure 4.21.

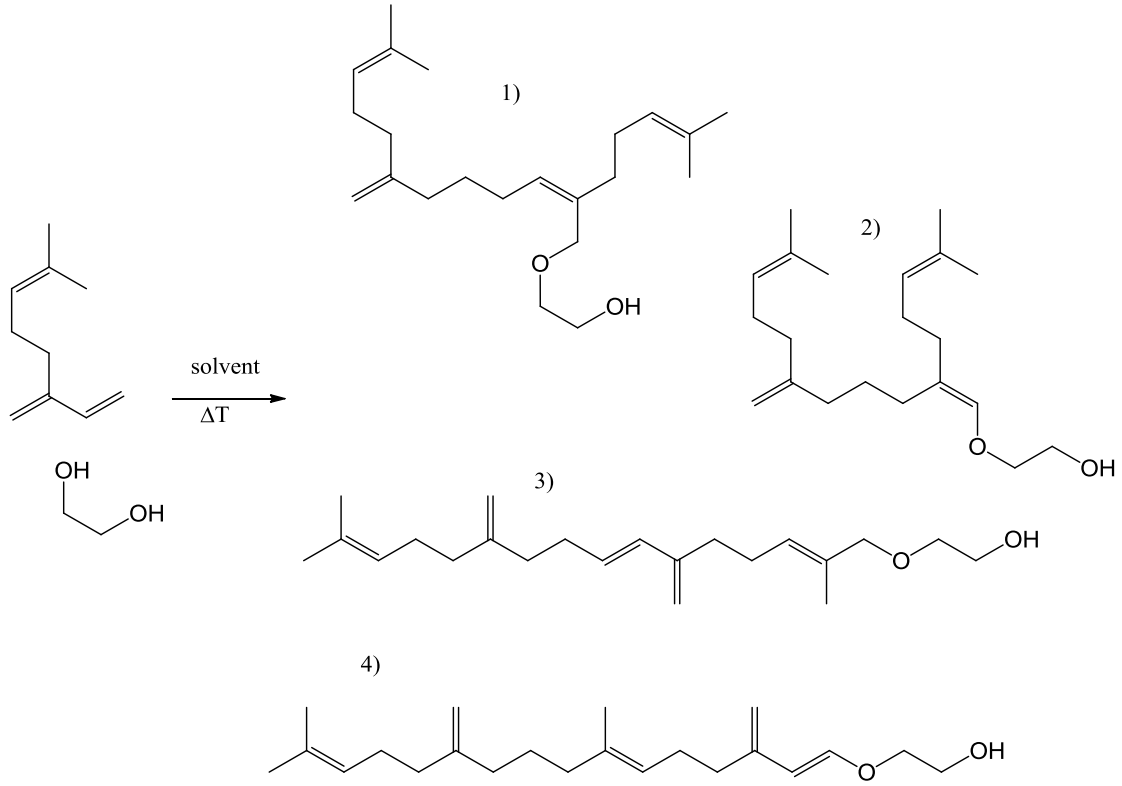

Figure 4.21 - Products of telomerisation of β-myrcene and ethylene glycol: 1) - (Z)-2-((11-methyl-7-methylene-2-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-yl)oxy)ethanol; 2) - (E)-2-((10-methyl-6-methylene-2-(4-methylpent-3-en-1-yl)undeca-1,9-dien-1-yl)oxy)ethanol; 3) - 2-(((2E,7E)-2,15-dimethyl-6,11-dimethylenehexadeca-2,7,14-trien-1-yl)oxy)ethanol; 4) - 2-(((1E,6E)-7,15-dimethyl-3,11-dimethylenehexadeca-1,6,14-trien-1-yl)oxy)ethanol

The conversion of β-myrcene in the reaction carried out for 120 hours at 80˚C was 21.4% and allowed to obtained the mixture of products among which the dominant were following telomers: 1) and 2) with the equal yield of 43.4%. Among other minor products the following two: 3) and 4) were formed in the significant amount (6.6% each).

To verify the influence of CO_2 as solvent on the reaction the analogous reactions were performed in CO_2 at 90 and 120 bar of CO_2 pressure. The VLE data for CO_2 and ethylene glycol were reported in

literature. One of the example[44] shows that even at very high pressure the amount of CO_2 is ethylene glycol phase is moderate and at the working pressure range is around 0.1 mole fraction as presented in Figure 4.22.

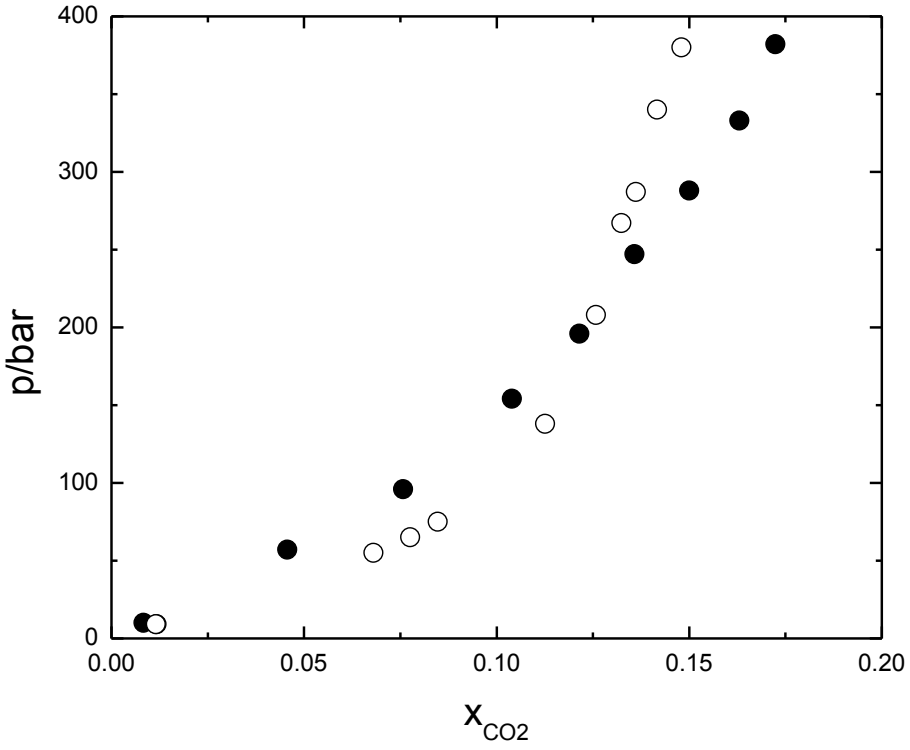

Figure 4.22 - VLE data for system containing CO_2+ethylene glycol[44] data for 90˚C, data for 50˚C

The conversion of β-myrcene was 11.2% and the obtained results showed that either at 90 and 120 bar of CO_2 the only products are 1) and 2) with the equal yield of 50%.

4.3.4. Telomerisation of β-myrcene with rac-1,2-O-cyclohexylideneglycerol

The telomerisation of β-myrcene with *rac*-1,2-*O*-cyclohexylideneglycerol is presented in Figure 4.23.

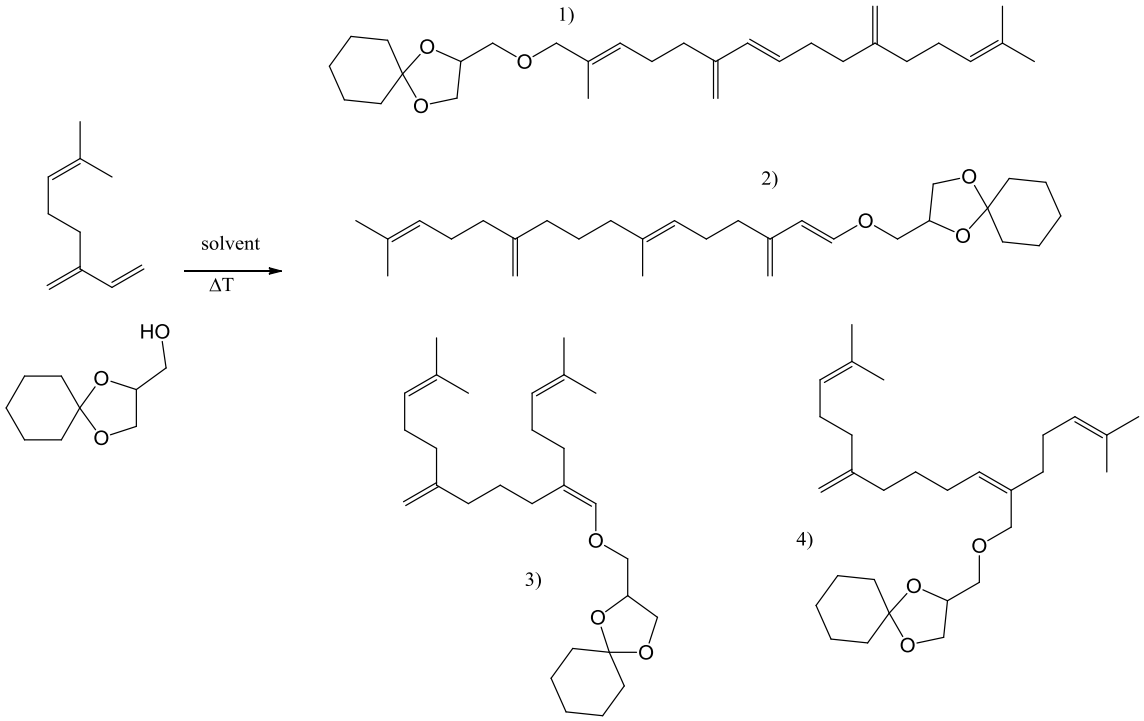

Figure 4.23 - Products of telomerisation of β-myrcene and *rac*-1,2-*O*-cyclohexylideneglycerol: 1) - 2-((((2E,7E)-2,15-dimethyl-6,11-dimethylenehexadeca-2,7,14-trien-1-yl)oxy)methyl)-1,4-dioxaspiro[4.5]decane; 2) 2-((((1E,6E)-7,15-dimethyl-3,11-dimethylenehexadeca-1,6,14-trien-1-yl)oxy)methyl)-1,4-dioxaspiro[4.5]decane; 3) - (E)-2-(((10-methyl-6-methylene-2-(4-methylpent-3-en-1-yl)undeca-1,9-dien-1-yl)oxy)methyl)-1,4-dioxaspiro[4.5]decane; 4) - (Z)-2-(((11-methyl-7-methylene-2-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-yl)oxy)methyl)-1,4-dioxaspiro[4.5]decane

The conversion of β-myrcene was 15.8%. Reaction between protected glycerol and β-myrcene give the mixture of products among which the major were 1) and 2) obtained with the yield of 45.6% each. Other products such as 3) and 4) were produced with the yield of 4.4% each. The VLE data for system consisting of protected glycerol (*rac*-1,2-*O*-cyclohexylideneglycerol) and CO_2 are unknown, however to verify the impact of CO_2 on the reaction, the reaction in CO_2 atmosphere at analogous conditions to previous reactions were performed. The results of the reactions performed at 90 and 120 bar showed that conversion was 11.2% and products were 1) and 2) obtained with the equimolar quantities (50%).

5. Discussion

5.1. Synthesis of monoalcohols and dienes

Glycerol, a by-product from biodiesel production, was employed in the development of an adding value product. The methanesulfonic and tungstophosphoric acids were used as efficient regioselective catalysts for the preparation of protected glycerol with yields of 72% and 89% respectively. The tungstosilic acid catalyst in the synthesis of protected glycerol did not allow obtaining the required product. Benzophenone was also tested in glycerol ketalisation and a mixture of product and unconsumed ketone were obtained. Protection of glycerol was followed by Swern oxidation of ketal but unfortunately the crude aldehyde was unstable.

Synthesis of 1,3-dienes was tested in a environmentally benign solvent such as water. Aqueous Wittig reaction of ylide derived from allyltriethylphosphonium bromide produced in a yield of 92% has been tested unsuccessfully with different aldehydes. Propionaldehyde was tested the synthesis of 1,3-hexadiene. Trimethylacetaldehyde was used to synthesise 5,5- dimethylhexa-1,3-diene. The reactions were observed to be chemeoselective to Aldol condensation and Cannizaro disproportionation reactions instead of olefination. However, 4- methoxybenzaldehyde was used to test the procedure yielding 1-[(1E, 3E)-buta-1,3-dienyl]-4- methoxybenzene in 92%.

Condensation of 3-pentanone with dimethylsulfone was performed to provide 2-ethyl-1,3-butadiene, but 3-pentanone was not totally converted.

5.2. Telomerisation reactions

The reaction performed in organic solvent showed that generally conversion of reaction is moderate. One of the major reasons of this fact is the heterogeneous catalyst employed in the reaction. To the best of our knowledge this is the first time when heterogeneous catalyst was used in telomerisation of β-myrcene. Nevertheless obtained conversion of β-myrcene was in some cases only slightly lower (21.4% to 35% for reaction carried out in [Pd(MeCN)4](BF4)2 (0.05 mol%), PPh3, Pd/P=1:8, solvent mixture (30 mL), nβ-myrcene=75 mmol, β-myrcene/diethylamine=2:1, t=4 h, T=100°C, 800 rpm, 0.5 MPa argon, 70 mL reactor[3]) than presented in literature with homogenous catalyst.[3] Furthermore

obtained results reveals that generally the CO_2 pressure (90 or 120 bar) does not influence on the reaction products. Telomerisation of β-myrcene with 1-butanol produces chiefly telomers (Z)-6-(butoxymethyl)- 2,15-dimethyl-11-methylenehexadeca-2,6,14-triene and (Z)-6-(butoxymethylene)-2,14- dimethyl-10-methylenepentadeca-2,13-diene in the twice higher yield than the corresponding dimmers ((E)-2,15-dimethyl-6,11-dimethylenehexadeca-2,7,14-triene and (E)-2,14-dimethyl- 10-methylene-6-vinylpentadeca-2,6,13-triene). Contrary to the classical solvent, the reaction performed in CO_2 as solvent at 90 bar of pressure does not occur. One of reasons might be short time of the reaction (6 hours); however other more probably obstacle might be related to the inhibition or deactivation of the catalyst by CO_2. It might be caused by the fact that terpene in the presence of high pressure of CO_2 forms CO_2-expanded liquid. Due to this the real concentration of terpene is lower that also significantly reduces probability of formation of dimmers which are first products synthesized in the classical organic process.

Similarly to the telomerisation of β-myrcene with 1-butanol the reactions with glycerol in classical organic and CO_2 solvents were performed. Reaction performed in organic solvents allowed to obtain higher conversion of β-myrcene compared to telomerisation in CO_2 (18.4% vs. 9.8%). It can be explained by the fact that solubility of CO_2 in glycerol is very low that limits the mutual solubility of reagents (glycerol and β-myrcene) guiding to significant reduction of β- myrcene conversion. The VLE data for CO_2+glycerol system are scarce and the mentioned system was investigated occasionally. For example Francis[45] presented only one pair of data for LLE for system consisting of CO_2 and glycerol (for 25°C and 65 bar), while Sovova gave the solubility of glycerol in CO_2 without information about the composition of the liquid phase for pressures in the range of 99 – 283 bar and temperatures between 23.05°C and 60.05°C.[46] Lack of systematic VLE data for system CO_2 + glycerol limits its applicability in many reactions including presented here. On the other hand the benefit of low conversion in the presence of CO_2 is high selectivity of the reaction. Contrary to the organic solvents, CO_2 allows to obtain monosubstituted telomers exclusively. This reported high selectivity is a typical behavior that was already observed in case of other processes with high pressure CO_2.[47] This effect is

explained by the limited solubility of reagents in CO_2 while in organic solvents solubility is not a driving factor that leads to the formation of mono-, di- or three substituted telomers of glycerol.

The reaction with ethylene glycol was characterized by higher conversion either in organic solvent or CO_2 than with glycerol. Similarly to glycerol conversion of ethylene glycol in organic solvent was higher than in CO_2 and was 21.4% and 11.2% respectively. The reaction in organic solvent was less selective and in the final mixture four products were obtained while in case of CO_2 only tail to tail telomers and tail to head telomers were formed in the equimolar quantity.

Analysing the influence of CO_2 on the example of ethylene glycol and glycerol reactions it can be stated that even higher solubility of ethylene glycol (than glycerol) in CO_2 allows maintaining relatively high selectivity towards monosubstituted ethylene glycols.

The reaction with home-made protected glycerol allowed obtaining moderate conversion of β-myrcene (15.8% and 11.2% in organic and CO_2 solvents respectively). Analogously to other studied reactions, the conversion in organic solvents was higher than in CO_2. Reaction in organic solvent leads to the formation of product mixture while CO_2 assisted process is more selective and at both studied CO_2 pressures two major products 1) and 2) were produced exclusively.

6. Conclusions

Telomerisation is one of the most interesting reactions as it allows obtaining potentially important chemicals in various fields of chemistry. The studies presented in this work demonstrate the potential employment of chemicals of natural origin like β-myrcene and side-product of 2nd generation biofuels production which is glycerol. Obtained results allow concluding that telomerisation of β-myrcene could be a green process in formation of surfactant-like. Glycerol and ethylene glycol were used in telomerisation to increase efficiency. The protected glycerol (*rac*-1,2-*O*-cyclohexylideneglycerol) was produced and used in telomerisation to increase selectivity of products. Telomers from protected glycerol would be advantageous because the alcohol is produced from glycerol which is a side product of biodiesel production. Furthermore the research performed to accomplish this work demonstartes that although conversion of the process is moderate, however the reaction with CO_2 as solvent are extremely selective and allows to limit produced telomers. The obtained results illustrate that solvent is important factor of the reaction that governs the reaction by the limiting the solubility of reactants in catalyst vicinity.

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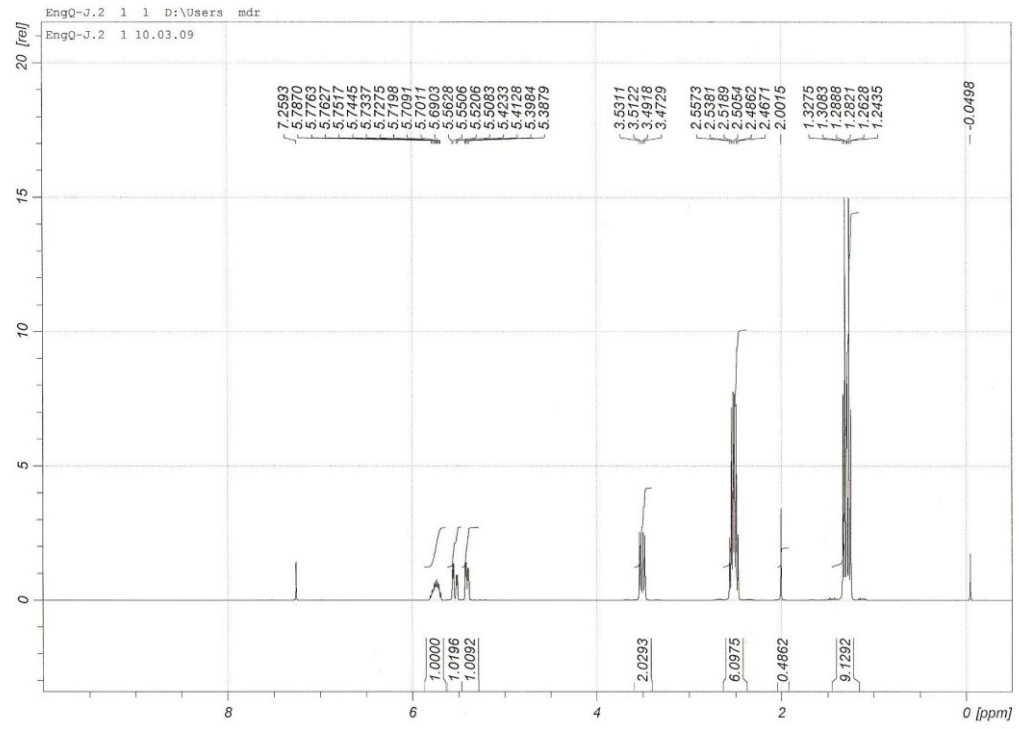
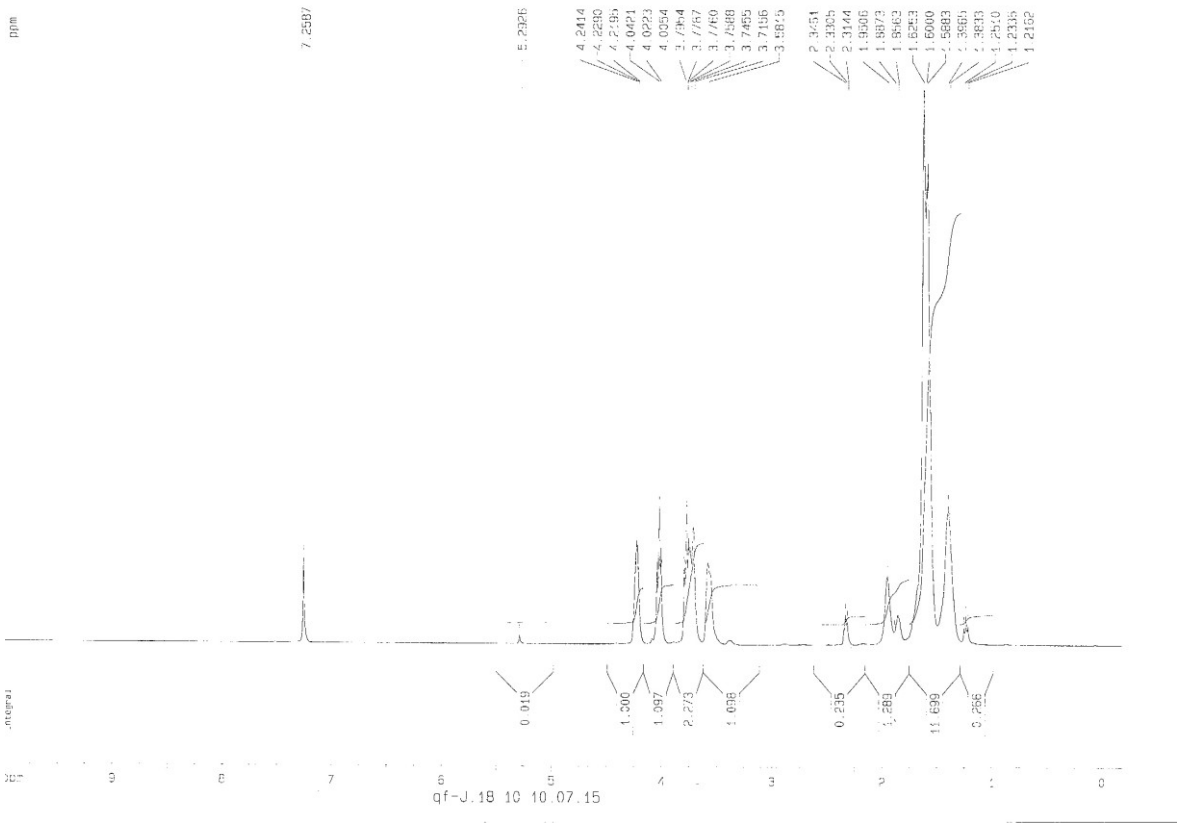
Appendix

^{1}H NMR



Spectrum 1. NMR spectral data of allyl-triethylphosphine bromide



Spectrum 2. NMR spectral data of 1,2-*rac*-*O*-Cyclohexylideneglycerol