OXIDATION OF PINANE MIXTURES TO 2-PINANOL AS A KEY INTERMEDIATE IN THE SYNTHESIS OF LINALOOL

by

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DECLARATION BY CANDIDATE

"I hereby declare that the dissertation submitted for the degree M Tech: Chemistry, at Tshwane University of Technology is my original work and has not previously been submitted to any other institution of higher education. I further declare that all sources cited or quoted are indicated and acknowledged by means of a comprehensive list of references".

TLOU CHOKWE

'If we hope to make positive changes in our lives we have to know what it is that needs changing, and we can't know that until we know ourselves' . . .

Robert T. Kiyosaki

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ABSTRACT

Crude sulphated turpentine (CST) is an industrial waste stream from the Kraft pulp and paper process. CST is a complex mixture of C10 monoterpene hydrocarbons and is composed mainly of α-pinene (60-65%), β-pinene (25-35%) and limonene (5-10%). The main objective of this investigation was to improve the yield of 2-pinanol as an intermediate in the preparation of linalool from a mixture of α- and β-pinene.

Fractional distillation of *cis/trans*-pinane mixtures was not effective in enrichment of *cis*-pinane, but the hydrogenation of a mixture of α- and β-pinene at 80˚C and 15 bar (H_2) using partially poisoned nickel catalyst resulted in high purity pinane (98%) with a *cis*/*trans* ratio of 20:1.

The oxidation of the pinane mixture to pinane hydroperoxide was conducted under various conditions using different oxidants, catalysts and initiators. The most successful reaction was obtained using benzoyl peroxide as an initiator and oxygen gas as the oxidant in the presence of NaOH base. The reaction was conducted at 110˚C under 3 bar oxygen pressure; under those conditions 2-pinanol was obtained directly from a spontaneous decomposition of the hydroperoxide at a selectivity of 96% with a conversion of 31%. The unreacted pinane mixture could be recycled into the oxidation step to increase the overall yield of 2-pinanol.

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GLOSSARY

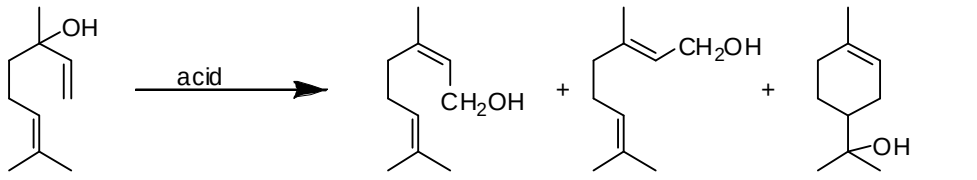
α	alpha
AIBN	azobisisobutyronitrile
β	beta
C10	ten carbon hydrocarbon compound
$Co(OAc)_2$	cobalt acetate
Conv.	conversion
CST	crude sulphated turpentine
CuPcNaY	copper phthalocyanine encaged in sodium form zeolite
DMF	dimethylformamide
DCB	1,2-dicyano benzene
DSP	down stream processing
GC	gas chromatography
GC/MS	gas chromatography coupled with mass spectroscopy
h	hours
ml	millilitre
mmol	millimoles
$Mn(OAc)_2$	manganese acetate
Mord	mordenite form zeolite
MPc	metal phthalocyanine
NaY	zeolite in the sodium form
NH_4Br	ammonium bromide
Pd/ C	palladium on carbon
Psi	pound per square inch
Selec.	selectivity

t-BHP	tertiary butyl hydroperoxide
t-BuOH	tertiary butyl alcohol
Temp	temperature

Chapter 1: Introduction

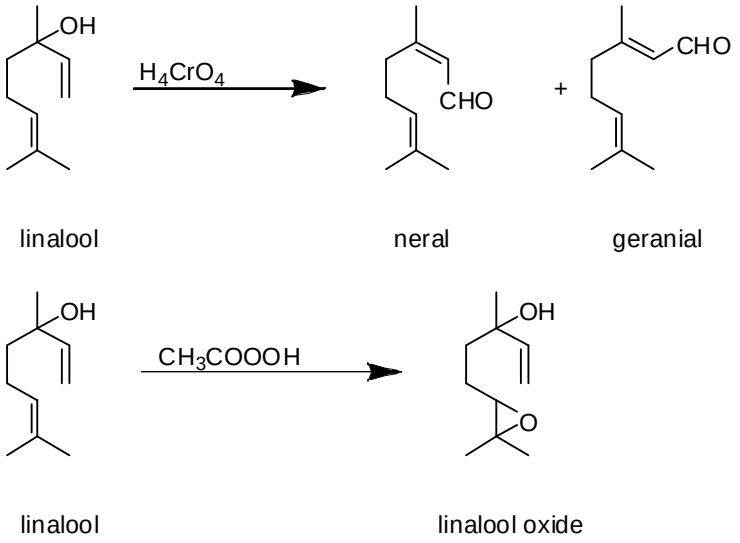
1.1 Background information

In nature terpenes are produced by the isoprene pathway, which is an integral part in normal plant and animal biosynthesis. Linalool and α-terpineol are the two most common terpenoid alcohols, occurring to varying degrees in essentially all plants (Lawrence, 1985). Linalool and α-terpineol are widely dispersed in fruits and vegetables as well as the fermented products prepared from these foods. Principal exposure to these two terpenes arises via consumption of spices, carrots, orange juice, nutmeg, beer, wine and tea (Stofberg and Grundschober, 1987). Linalool accounts for more than 70% of the coriander essential oil. Linalool is a colourless liquid with a flowery-fresh odour, reminiscent of lily of the valley (Ohloff and Klein, 1962). Together with its esters, linalool is one of the most frequently used fragrance substances and is produced industrially in large quantities. Due to its stability in alkali, linalool can also be used in soap and detergents (Bedoukian, 1985; Clark, 1988). In the presence of acids, linalool isomerises readily to geraniol, nerol and α-terpineol (Bauer, Garbe and Surburg, 1990) as shown in Scheme 1.1 below.



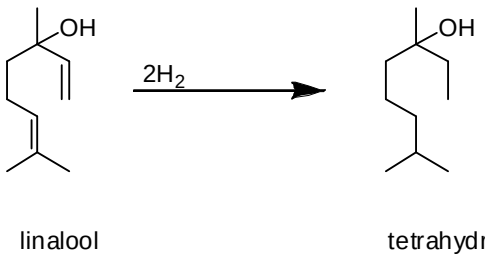
Scheme 1.1: Isomerisation of linalool to nerol, geraniol and α–terpineol

Linalool is oxidised to neral and geranial by chromic acid while oxidation with peracetic acid yields linalool oxide as shown in Scheme 1.2 below. Linalool oxide occurs in small amounts in essential oils and is also used in perfumery.



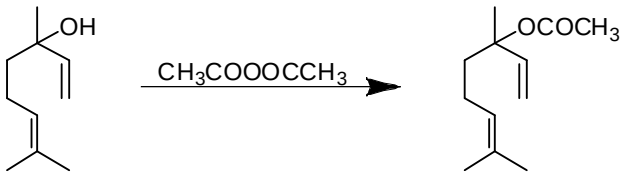
Scheme 1.2: Oxidation of linalool

Hydrogenation of linalool (Scheme 1.3) gives tetrahydrolinalool, a stable fragrant compound whose odour is not as strong as, but is fresher than that of linalool.



Scheme 1.3: Hydrogenation of linalool to tetrahydrolinalool

Linalool can be converted into linalyl acetate (Scheme 1.4) by reaction with ketene or an excess of boiling acetic anhydride (Gradeff and Finer, 1970).

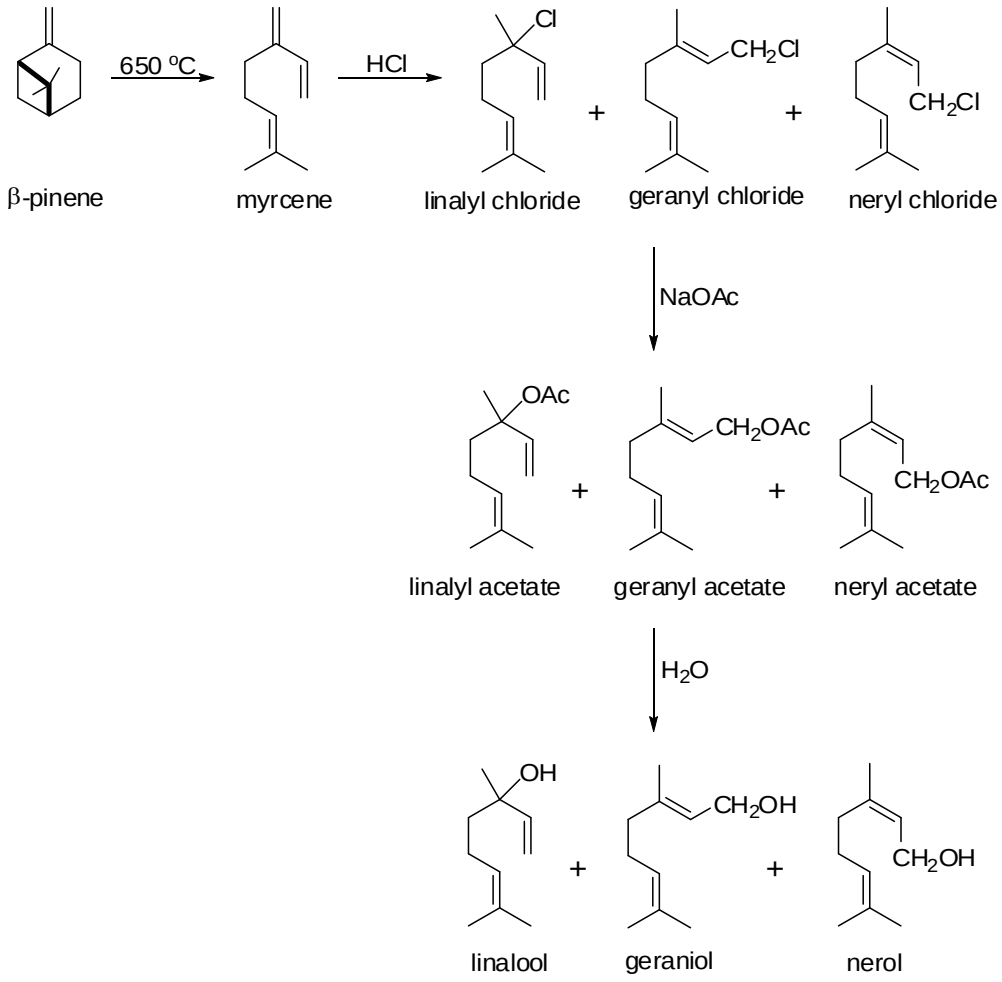


linalool linalyl acetate

Scheme 1.4: Esterification of linalool to linalyl acetate with acetic anhydride

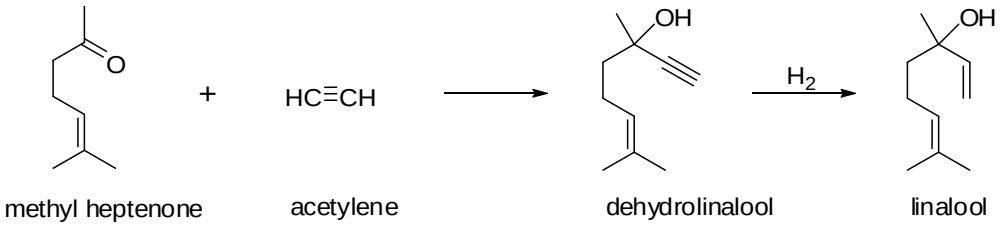
In the 1950s nearly all linalool used in perfumery was isolated from essential oils, particularly from rosewood oil by fractional distillation. Currently this method is used only in countries where plants oils with high linalool content (Brazilian rosewood, coriander oil and Shiu oil) are available and where the importation of linalool is restricted. Most perfumery-grade linalool is synthetic. Since linalool is also an important intermediate in the manufacture of Vitamin E (Mercier and Charbades, 1994), several large scale processes have been developed for its production. The preferred starting materials and/ or intermediate are the pinenes and 6-methyl-6-hepten-2-one (methyl heptenone). The synthesis of linalool from a mixture of α- and β- pinenes (Semikolenov, Ilyna and Simakova, 2001; Webb, 1964) and methyl heptenone (Pommer and Nürrenbach, 1975; Bauer, Garbe and Surburg, 1990) is well documented and provides linalool in reasonable yield, albeit at elevated temperatures (~450˚C). Another synthetic approach to linalool is from the autooxidation of *cis*-pinane (Valente and Vital, 2000; Fisher, Stinson and Goldblatt, 1953) and the main products are *cis*- and *trans*- pinan-2-ol and a *cis*-1-acetyl-3-ethyl-2,2-dimethylcyclobutane (Brose, Pritzkow and Thomas 1992). The pyrolysis of *cis*/*trans* 2-pinanol produces linalool (Ohloff and Klein,

1962). This process is far superior in terms of economics as compared to the β-pinene processes where the β-pinene is converted to myrcene under extreme pyrolysis conditions (>650˚C), followed by treatment with dry HCl to give linalyl chloride and other products. The chloride is then converted to the acetate by treatment with alkali acetate and the hydrolysis of the acetate gives linalool as shown in Scheme 1.5.



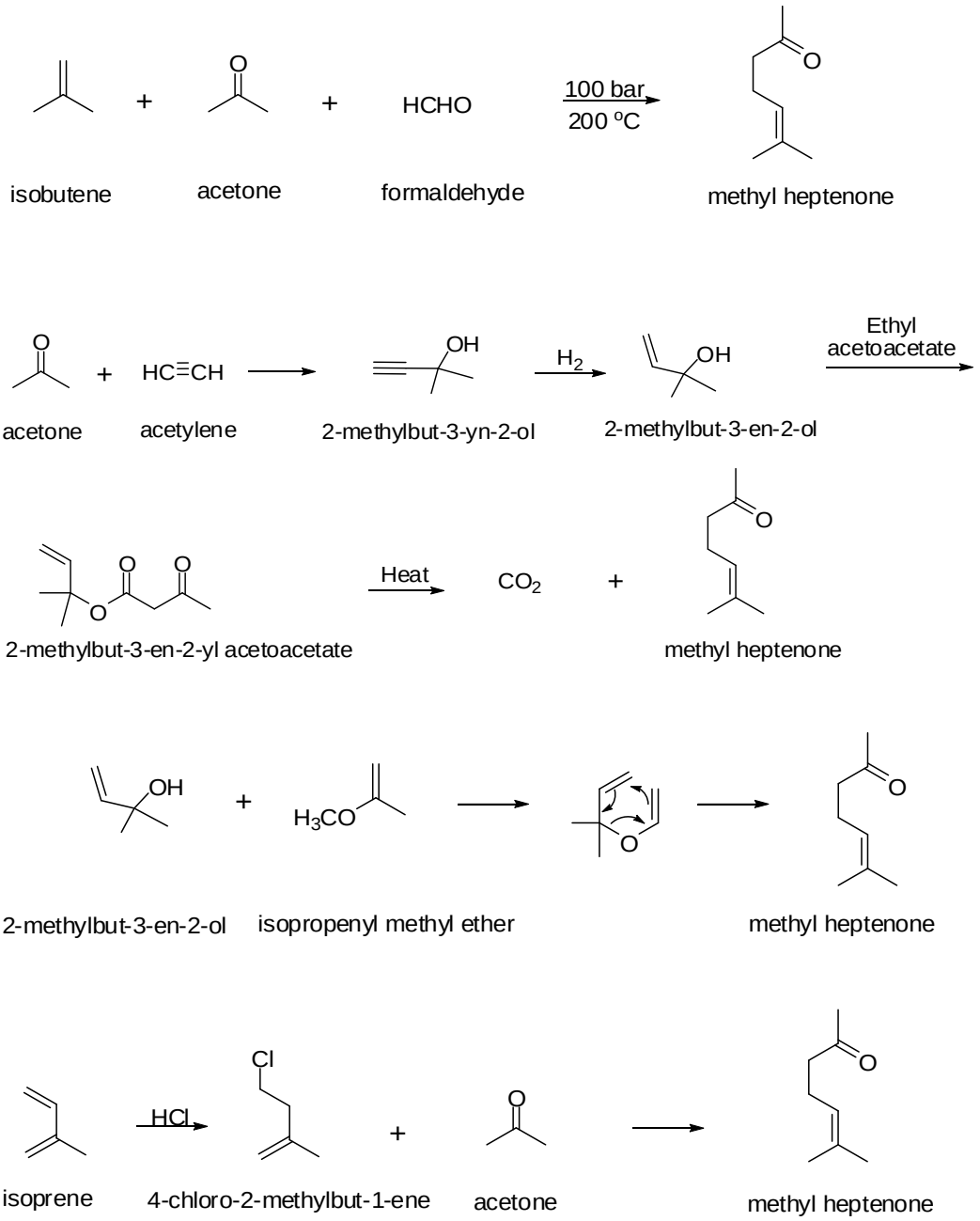
Scheme 1.5: Preparation of linalool from β-pinene

The locally available turpentine streams typically have very low β-pinene content, which requires a nontrivial interconversion of α-pinene to β-pinene using an expensive transition metal catalyst. Therefore, in SA, cheaper alternative methods are needed. One such alternative is the synthesis of linalool from methyl heptenone. Methyl heptenone is converted into linalool in excellent yield by base catalysed ethynylation with acetylene to dehydrolinalool (Bedoukian, 1985). This is followed by selective hydrogenation of the triple bond to a double bond in the presence of a palladium-carbon catalyst as shown in Scheme 1.6.



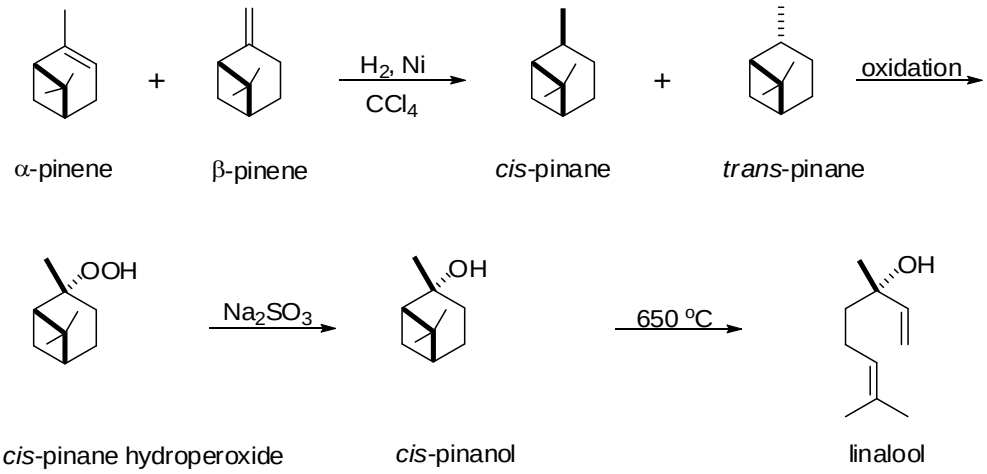
Scheme 1.6: Preparation of linalool from methyl heptenone and acetylene

However, the synthesis of methyl heptenone is non trivial as shown by the many methods that have been used for its preparation as shown in Scheme 1.7 (Bauer, Garbe and Surburg; 1990).



Scheme 1.7: Preparation of methyl heptenone

The oxidation of pinanes to *cis*/*trans*-pinane hydroperoxide mixture (Fisher *et al.,* 1955) and subsequent reduction or hydrogenation to *cis*/*trans*-pinan-2-ol is of industrial interest as an alternative method of linalool synthesis as shown in Scheme 1.8



Scheme 1.8: Schematic route to linalool

1.2 Research Problem

Since the South African crude sulphated turpentine stream is very rich in α-pinene, the oxidation of pinane in Scheme 1.8 represents a viable pathway to linalool synthesis. However, the oxidation of a mixture of pinanes to pinane hydroperoxide is beset by a few challenges:

1. The un-reactivity of the *trans*-pinane in the oxidation step: The *cis*-pinane oxidation occurs at a much faster rate than the *trans*-pinane oxidation (of the order of 10:1). In preliminary reactions we also observed (by GC) that the % area of the *trans*-pinane after the reaction was similar to the % area before the oxidation indicating that *trans*-pinane was not involved in the oxidation. Since the *cis*- and *trans*-pinane are inseparable by fractional distillation the efficiency of the reaction cannot be improved by enriching the *cis*-pinane via distillation.

2. The rate of reaction: The rate of oxidation reaction is reported to be extremely slow (Fisher *et al*, 1951 and 1955; Fisher, Stinson and Goldblatt, 1953) giving only 50% conversion at 95˚C after 20 h. Steric and electronic factors that strengthen the RH bond have a significant effect on the rate of autooxidation. However, bases such as ammonia, hydroxides, carbonates and bicarbonates can be added as oxidation promoters.

1.3 Aims of the study

The aims of the project are:

- To enrich the *cis*/*trans* pinane mixture with the more reactive *cis*-pinane isomer via selective hydrogenation of CST
- To evaluate various radical initiators and oxygen donors (*t*-butylhydroperoxide (*t*-BHP), O_2, H_2O_2, benzoyl peroxide, AIBN) in the oxidation step.
- To assess the effect of various metal catalysts on the oxidation reaction efficiency.
- To identify the key variables of the reaction using statistically designed experiments.
- To identify the optimum reactor configuration and reactor systems that would result in optimum reaction performance.
- To develop an environmentally friendly process for the oxidation of pinane to pinane hydroperoxide.

1.4 Hypothesis

The yield of pinane hydroperoxide from *cis*/*trans* pinane mixtures can be improved by modifying the variables of radical initiator, oxidation donor, metal catalysts and reactor configuration in the oxidation step.

CHAPTER 2: Literature Review

2.1. General

Oxidative transformations of functional groups are basic to organic chemistry, oxidation being extensively used in the laboratory synthesis of fine chemicals as well as in the manufacture of large volume petrochemicals. The majority of the processes employed industrially involve catalysis by metal complexes, and an increasing variety of catalytic processes are being developed for laboratory-scale synthesis (Sheldon and Kochi, 1981). Catalytic processes enjoy the advantage over their non-catalytic counterparts of proceeding efficiently under milder conditions, thus leading to more energy-efficient processes. Furthermore, catalytic processes are generally more selective, and capable of leading to optimal utilisation of raw materials (Bukharkina and Digurov, 2004). Unlike the stoichiometric oxidations with traditional oxidants, such as permanganate and dichromate, the catalytic processes do not produce vast amounts of inorganic effluents which are difficult to dispose of. As a result, a greater emphasis must be placed on the development of new, improved catalytic processes (Sheldon and Kochi, 1981).

2.2 Formation of alkyl hydroperoxide

Hydrocarbon peroxides can be prepared by reaction of a tertiary alkyl sulphate with hydrogen peroxide (Milas and Surgenor, 1946) or by direct

oxidation in the form of vapour (Bell *et al*, 1949) or a homogeneous liquid (Winkler and Hearne, 1961 and Farkas and Stribley, 1947) with air or oxygen. The initial products of autooxidation of alkanes are generally the corresponding hydroperoxides formed by free radical chain mechanism (Sheldon and Kochi, 1981). The reactivity of various C-H bonds decrease in the order tertiary > secondary > primary. Indeed, alkanes containing a tertiary C-H bond can generally be selectively oxidised to the corresponding hydroperoxides with molecular oxygen in the temperature range between 100˚C and 140˚C. The autooxidation is usually carried out without a metal catalyst, but a radical initiator such as *t*-butyl hydroperoxide (*t*BHP) or di-*tert*-butyl peroxide is added. In practice, a compromise is struck between the rate and the selectivity; i.e., in order to achieve a practical and useful rate of oxidation, a certain degree of selectivity is sacrificed. Hydroperoxide selectivity also decreases with hydrocarbon conversion as a result of the increased competition from secondary processes as the alkane is depleted. Thus, hydrocarbon autooxidation are generally carried out to less than 20% conversion (Brose, Pritzkow and Thomas 1992). Autooxidations of hydrocarbon have generally been carried out in neat hydrocarbon as solvent (Sheldon and Kochi, 1981), and a few systematic studies have been made of solvent effects.

2.2.1 Formation of *t*-butyl hydroperoxide

The autooxidation of isobutane to *t*-butyl hydroperoxide has been thoroughly studied (Winkler and Hearne, 1961; Milas and Surgenor, 1946), since the

product is an important initiator for radical polymerisations and an oxidant in metal-catalysed epoxidations.

$$(CH_3)_3CH + O_2 \rightarrow (CH_3)_3COOH$$

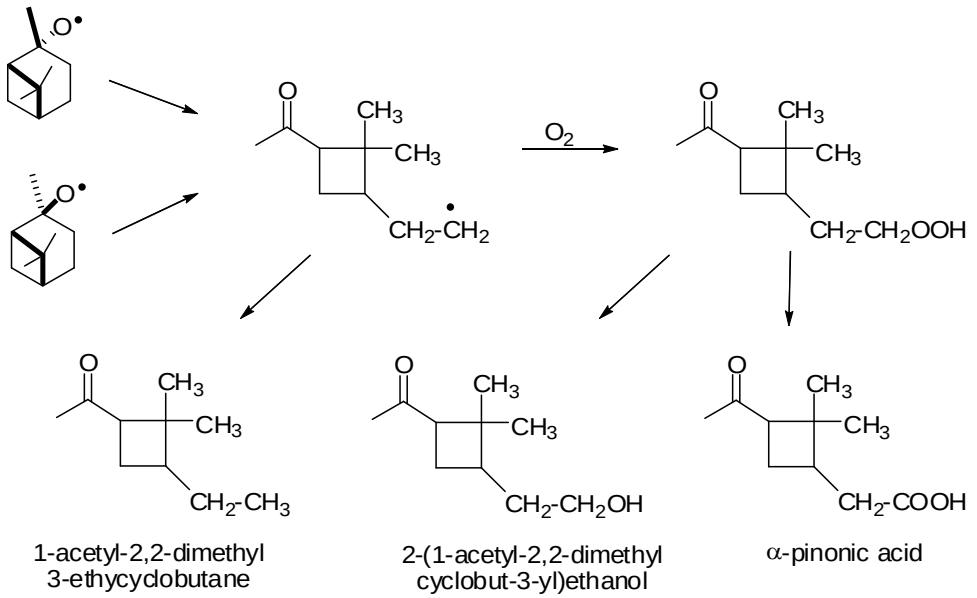
The reaction is carried out in the absence of a catalyst, usually between 100˚ and 140˚C. At low rates of initiation and low conversion, selectivity higher than 90% can be achieved (Mayo, 1968). Other tertiary alkanes such as pinane can be selectively autooxidised in the liquid phase to produce the corresponding hydroperoxide (Ester and Sommer, 1966).

2.2.2 Formation of pinane hydroperoxide

Crude turpentine has been shown to be amenable to peroxidation, and these oxidation products were found to yield rates of polymerisation comparable with those of cumene hydroperoxide (Fisher *et al*, 1951). The work was also used as a preliminary investigation to find out which of those hydrocarbons derivable from turpentine were most promising with regard to ease of preparation of peroxides in high concentrations and effectiveness of the peroxides as replacement for cumene hydroperoxide. Technical grades of pinane hydroperoxide having purities of up 90% can readily be prepared using gum turpentine or its constituents, α-pinene and β-pinene (Fisher *et al*, 1955), as starting materials and pinane as an intermediate. Four steps are involved: hydrogenation of pinene to pinane, distillation of the pinane, oxidation of pinane to pinane hydroperoxide and removal of unoxidised pinane. Even without the last step, oxidates containing 50% pinane hydroperoxide can be obtained. The peroxide content of the various oxidates were determined by a

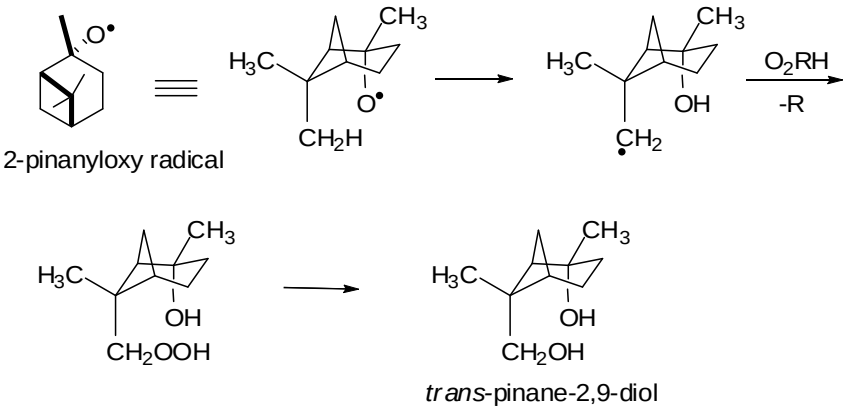
slight modification of the iodometric methods (Wagner, Smith and Peters; 1947). To obtain high quality products, it is important that the pinane be free from unsaturated impurities. Temperatures in the range of 120˚ to 130˚C are helpful in accelerating the oxidation in the initial stages, but the reaction temperature should be lowered to about 105˚ to 110˚C as the reaction progresses. Iron appears to be harmless but cobalt, copper and similar heavy metals and their salts must be vigorously excluded. It is also essential to maintain vigorous agitation and strong flow of oxygen during the oxidation step. Failure to provide adequate contact between the oxygen and pinane slows the rate of oxidation and lowers the yield per pass that can be obtained without excessive production of by-products.

Since the pyrolysis of *cis*/*trans*-2-pinanol delivers linalool (Coxon, Garland and Hartshorn, 1972), the oxidation of the pinanes to *cis*/*trans*-2-pinane hydroperoxide and subsequent reduction or hydrogenation of the hydroperoxide mixture to *cis*/*trans*-pinanols is of industrial interest. It has been reported that pinane is oxidised with pure oxygen at temperatures between 70 and 130˚C and the reaction stopped after 15% weight of pinane hydroperoxide was formed (Brose, Pritzkow and Thomas, 1992). The oxidation at position 2 of the pinanes delivers not only the *cis*/*trans*-hydroperoxide but also, as short-lived intermediates, the corresponding 2-pinanyloxy radicals. These radicals fragment forming carbon radicals with cyclobutyl structures whose oxidation products are shown in Scheme 2.1 below.



Scheme 2.1: Formation of cyclobutane derivatives from the 2-pinanyloxy radicals

Besides fragmentation of the 2-pinanyloxy radical an intramolecular H-transfer from the methyl group in 9-position to the oxygen of the *trans* 2-pinanyloxy radical also takes place leading to 9-hydroperoxy *trans*-pinane 2-ol as shown in Scheme 2.2 below



Scheme 2.2: Intramolecular H-transfer in the *trans*-2-pinanyloxy radical to form *trans*-2,9-pinane-diol.

The oxidation of pinane to pinane hydroperoxide is one step of the so-called "α-pinene route" for linalool that has been used as a feedstock for the manufacture of vitamin E and flowery-fresh-based fragrances such as nerol and geraniol (Osadchii and Tolstikov, 1997). The influence of the oxygen donor (*t*-butyl hydroperoxide, oxygen and hydrogen peroxide) and the central metal (Cu, Co, Fe and Mn) on the activity and selectivity of metallophthalocyanines when free or encaged in zeolite in the sodium form (NaY), for the oxidation of *cis*-pinane was reported (Valente and Vital; 2000). The effect of encapsulation enhances catalyst stability and influences its activity and selectivity. Encaged complexes yield mainly 2-pinane hydroperoxide and insignificant amounts of 2-pinanol (Valente and Vital, 1997), while with their homogeneous counterpart, selectivity to 2-pinanol are higher. The ratio of 2-pinane hydroperoxide/ 2-pinanol depends on the amount of the complex, indicating that 2-pinane hydroperoxide is also in the last case, the primary oxidation product.

2.3. Formation of alcohols

t-Alkyl hydroperoxides formed in the autooxidation of tertiary alkanes can be selectively reduced to the corresponding alcohol by aqueous sodium sulfite (Brose, Pritzkow and Thomas, 1992) or by catalytic hydrogenation (Semikolenov, Ilyana and Simakova, 2001). *t*-Alkyl hydroperoxides also decompose thermally to give the corresponding alcohol and dioxygen (Lempers *et al,* 1998).

$$2ROOH \rightarrow 2ROH + O_2$$

However, the thermal decomposition of *t*-BHP either neat at 100˚C (Milas and Surgenor, 1946) or in chlorobenzene at 140˚C yields *t*-BuOH and oxygen in almost quantitative amounts. The chain decomposition of alkyl hydroperoxides can also be initiated by metal catalysts (Valente and Vital, 1997). The decomposition of hydroperoxides to alcohols is also catalysed by boron compounds (Wolf, McKeon and Cannell, 1975). The conversion of alkanes to alcohols should be accomplished in one step, in principle, by carrying out the autooxidation under conditions in which the hydroperoxide is simultaneously decomposed (i.e. high temperatures and metal catalysts). However, this method often leads to substantial amounts of ketone via β-scission of the intermediate alkoxy radicals, e.g.:

$$(CH_3)_3CO^{\cdot} \rightarrow (CH_3)_2C{=}O + CH_3^{\cdot}$$

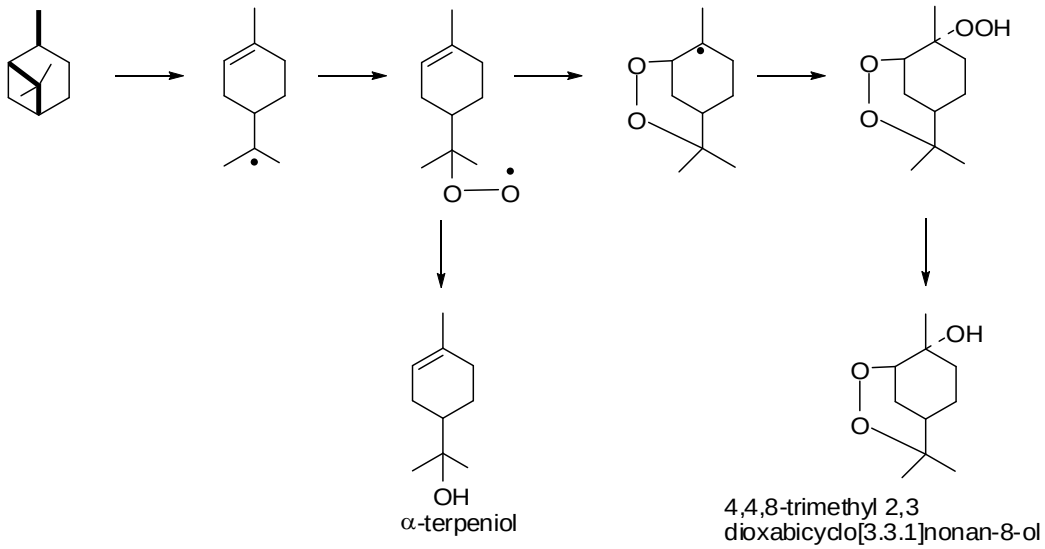
2.3.1 Formation of 2-pinanol from pinane hydroperoxide intermediate

The 2-pinanol may be obtained during the oxidation of pinane to pinane hydroperoxide in one step by using homogeneous catalyst (Valente and Vital, 1997). These happen when the centre metal is not encaged with NaY zeolite. It is known that metal catalyst do decompose alkyl peroxides (Sheldon and Kochi, 1981). If oxidation is carried out without encaged metal, the hydroperoxide formed can decompose on the surface of the metal (Valente and Vital, 2000).

2-Pinanol can also be obtained from the pinane hydroperoxide by hydrogenation under Pd/C catalyst (Semikolenov, Ilyana and Simakova, 2001). The hydrogenolysis of O-O peroxide bond does not change the pinanyl framework configuration and pinanol isomers distribution is determined by the pinane hydroperoxide isomers ratio in the pinane hydroperoxide used. 2-Pinanol can also be formed from pinane hydroperoxide by reduction with sodium sulfite solution (Brose, Pritzkow and Thomas, 1992).

The thermal decomposition of pinane hydroperoxide was studied (Schmidt and Fisher, 1954 and 1959) and ketone $C_{10}H_{18}O$ was obtained in yields of 20% by weight of the hydroperoxide used; it was reported that the ketone formed via the pinanol intermediate. Further studies of the decomposition of pinane hydroperoxide have revealed that the yield of 2-pinanol can be as high as 50% by carrying out the reduction in the presence of both pinane and base (Schmidt and Fisher, 1959). Evidence also was obtained for attack at the secondary carbon atoms of pinane during oxidation and for isomerisation of pinane to monocyclic hydrocarbons during decomposition. Decomposition was carried out in the presence of sodium methoxide base to remove acids as they formed and the decomposition mixture washed before distillation. The mixture of decomposition products was complex, but careful distillation gave adequate separation for identification of major products 2-pinanol (11%), isopinanol (38%), α-terpeniol (12%) and other impurities. The formation of isopinanol was not expected as it was not detected in the reduction products of the hydroperoxide (Fisher, Stinson and Goldblatt, 1953). Moreover, with increasing temperature, more and more products with *p*-menthane skeleton

are obtained. These compounds must be formed via a fragmentation of the pinanyl radical as shown in Scheme 2.3 below,



Scheme 2.3: Formation of the *p*-menthane skeleton from a pinanyl radical

This fragmentation becomes more important with increasing temperature because of two reasons: firstly, the activation energy of the fragmentation is higher than that of the competitive reaction of the pinanyl radical with oxygen; and secondly, the steady state concentration of oxygen in the reaction mixture decreases with increasing temperature (Brose, Pritzkow and Thomas, 1992).

2.3.2 Direct formation of 2-pinanol from pinane

Autooxidation of the pinanes were performed with or without solvent, using the catalytic system $Co(OAc)_2/Mn(OAc)_2/NH_4Br$ in a 9:1:5 molar ratio, and dioxygen as the oxidant (Sercheli *et al,* 1997). The best selectivity for the pinanols was 71% (*cis/trans* ratio, 3:1) with 17% conversion when

chlorobenzene was the solvent. As the catalytic oxidation eliminates the reduction step of the hydroperoxide and does not require reagents in stoichiometric amounts, it suggests an interesting alternative for the industrial production of linalool.

2-Pinanol is obtained upon oxidation of pinane in the presence of a base, such as sodium hydroxide, and free radical initiator, such as azobisisobutyronitrile (Filliatre and Lalande, 1968). Oxygen was introduced into the mixture (anhydrous or aqueous) of pinane, base and initiator until the desired yield of pinanol was obtained. The 2-pinanol was recovered by extraction and distillation (Risco and Seymour, 1970). In the absence of the base, the oxidation yields a mixture of products, suggesting that the base directs the reaction preferentially to give 2-pinanol. These results were obtained when *cis*-pinane was used as a starting reagent. When *trans*-pinane was used, the reaction was less selective because of the formation of camphene and verbenols as by-products.

Chapter 3: Theoretical Considerations

3.1 Fundamentals of radical chain reactions

The liquid-phase autooxidation of hydrocarbons has been studied extensively and is a subject of several monographs and reviews (Mayo, 1968; Sheldon and Kochi, 1981). Autooxidation proceeds via a free radical mechanism described by the following general elementary reaction steps:

(i) ***Initiation***

$$In_2 \rightarrow 2In^{\cdot}$$

$$In^{\cdot} + RH \rightarrow InH + R^{\cdot}$$

These reactions are endothermic and quite slow (Suresh, Sharma and Sridhar, 2000). Therefore, induction periods are often observed in oxidations without added initiators (Sheldon and Kochi, 1981). Indeed initiation from the hydrocarbon is kinetically and thermodynamically unfavourable and that initiation in the absence of added initiators is due to the decomposition of adventitious peroxidic impurities. Direct attack can be favoured when it involves compounds in which hydrogen is bonded to elements other than carbon, as illustrated by the facile air oxidation of thiols, phosphines, and a variety of organometallic compounds (Brilkina and Shushunov, 1966). Use of initiators is preferred in fundamental studies where it circumvents problems such as poor reproducibility of induction periods in batch reactors. When used, these initiators are usually peroxides or hydroperoxides with reasonable rates of decomposition in the temperature range 50-150˚C (Suresh, Sharma and Sridhar, 2000).

(ii) *Propagation*

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$$

$$RO_2^{\cdot} + RH \rightarrow RO_2H + R^{\cdot}$$

At oxygen partial pressure greater than about 0.133 bar, the first reaction is usually faster than the second reaction so that the alkyl radicals ($R^{\cdot}$) are effectively scavenged, and overall reaction shows zero-order behaviour in oxygen (Sheldon and Kochi, 1981). Each occurrence of the second reaction represents the formation of a link in the chain reaction, and the chains are said to be long when the number of occurrences of the second reaction per initiation event is large. A kinetic chain length, which represents average number of links per chain, can be calculated as the ratio of the rate of propagation reaction to the rate of initiation reaction (assuming that each initiation event starts one chain). When chains are long, hydrocarbon consumption occurs essentially via the second reaction. The kinetic chain length can be related to the efficiency of hydroperoxide formation. The rate of the second reaction depends on the nature of the hydrocarbon as well as on the nature of the radical. The peroxy radicals are relatively stable, and abstract preferentially only the most weakly bound hydrogen atom. Thus, the facility of hydroperoxide formation decreases in the order tertiary C > secondary C > primary C. Thus for example, in the oxidation of cumene, attack always occurs on the tertiary C in the isopropyl group, with negligible attack on the ring or methyl carbons. On the other hand, the reactivity of the alkylperoxy radical strongly depends on its structure, steric as well as polar effects; in general increasing as the electron-withdrawing capacity of the α-substituent increases (Suresh, Sharma and Sridhar, 2000). Thus

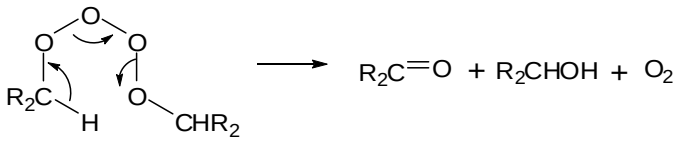
autooxidation rates depend not only on the nature of the hydrocarbon itself, but also on the structure of the peroxy radical derived from it (Howard, 1972).

(iii) *Termination*

$$R^{\cdot} + RO_2^{\cdot} \rightarrow RO_2R$$

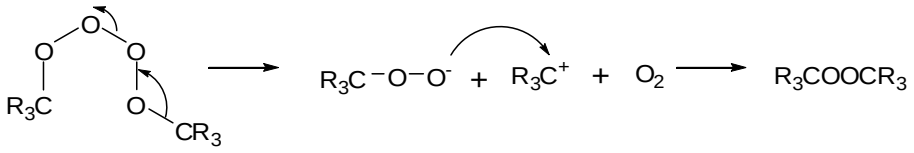
$$2RO_2^{\cdot} \rightarrow RO_4R \rightarrow \text{nonradical products} + O_2$$

It is possible that mutual termination between different types of radicals becomes important under conditions of extremely low oxygen pressures, when other types of radicals other than peroxy radicals can also accumulate in solution. The tetroxide that forms in the reaction, shown above, undergoes decomposition in a manner that depends on its structure. Thus, tetroxides derived from secondary and primary alkylperoxy radical decompose by disproportionation to the corresponding alcohol and carbonyl compoundas shown in Scheme 3.1.



Scheme 3.1: Alkoxy radical dispropotionation to alcohol and carbonyl compounds

Such a pathway is unavailable to tetroxide derived from *tert*-alkylperoxy radicals, which undergo decomposition to dialkyl peroxides and molecular oxygen as shown in Scheme 3.2.



Scheme 3.2: Formation of dialkyl peroxide and oxygen from *tert*-alkyl tetroxide

However, when chains are long, most of the observed concentration of alcohols and ketones in the reaction mixture comes from the decomposition of the hydroperoxide. In general, the rate constant for the termination of primary alkylperoxy radical is higher than those of secondary radicals, which are themselves much higher than those of tertiary alkylperoxy radicals (Suresh, Sharma and Sridhar, 2000).

The above elementary steps become considerably more complicated at high conversion of the substrate owing to the accumulation of secondary products, such as the easily oxidised aldehydes and ketones, formed by the thermal decomposition of the alkyl hydroperoxide. Autooxidative syntheses are thus usually carried out at lower conversions (<20%) and the excess unreacted substrate is re-cycled (Sheldon and Kochi, 1981). It has been observed that in the oxidation of pinane, *cis*-2-pinanol is predominant with a ratio 80:20 *cis*/*trans*-pinanol. This observation suggests that the conformation of tertiary carbon C-2 and the pinanyl radical is planar or very slightly pyramidal (Filliatre and Lalande, 1968). The hybridisation of the bond should be sp^2 with the remaining p-orbitals containing the single electron. The fixation of oxygen by a free radical is usually very rapid. Thus the intermediate pinanyl radical is immediately transformed into a pinanyl peroxy radical. However, this fixation/

trapping of oxygen may be influenced by steric effects. In the case of the pinanyl radical, the methyl groups of the cyclobutyl bridges may lead to the entry of oxygen from the opposite side and would lead preferentially to the *trans*-isomer. In this way the observed stereospecificity in the attack of oxygen on C-2 and the identity of *cis*/*trans* ratio of 2-pinanol obtained may be explained by intermediate of free radical close to planarity and the preferred entry/ attack of oxygen due to steric effects. The reactivity of different conformations of pinane must be determined by steric and electronic effects. Therefore, an important steric effect may explain the difficulty in oxidation of *trans*-pinane where the C-H bond is being protected by the *gem*- dimethyl group (Coates *et al*, 1987) and its homolysis is thus more difficult. It was noted that the oxidation of C-3 and C-4 is greater and that complicated the results rendering the reaction less selective than *cis*-isomer (Brose, Pritzkow and Thomas, 1992).

According to the observation by Parton and co-workers (1990; 1991 and 1992) on the cyclohexane oxidation, pinane oxidation with *t*-BHP using encapsulated MPc (metal phthalocyanine) complexes should lead to direct formation of pinanol but is not the case with encaged MPc complexes. However, with free MPc complexes, 2-pinanol was formed and even as the main product in the case of free iron phthalocyanine (FePc). When the amount of free FePc was reduced by a factor of 10, selectivity to pinane hydroperoxide increases from 0% to 30% (Valente and Vital, 2000). These results suggested that the oxygen rebound mechanism (Parton *et al*, 1996) for cyclohexane oxidation is not valid for pinane oxidation in the presence of free

or encaged MPc complexes. Instead, pinane hydroperoxide is, in both cases, the primary oxidation product. In homogeneous phase, pinane hydroperoxide easily reaches the central metal of the complex and is reduced to 2-pinanol accounting for the highest selectivity of alcohol in those conditions. The initial catalytic activity for pinane oxidation of free and encapsulated complexes exhibits opposite behaviour. While with encapsulated complexes the catalyst activity increases in order Mn(II)< Fe(II)< Co(II)< Cu(II), with the free complexes, the catalyst activity decrease in the same order Mn(II)> Fe(II)> Co(II)> Cu(II). This dependence of activity on the central metal is a strong indication that metal complexes play an important role in the reaction mechanism. Since pinane hydroperoxide is the primary product in the presence of free or encaged MPc complexes, the role of the metal complexes is most probably the metal-catalysed-homolytic decomposition of *t*-BHP. The decomposition proceeds via a reaction-generating chain initiating radicals for which relative reaction rates have been roughly correlated with redox potential of the $M^{(n+1)}$/ $M^{(n+)}$ couple (Sheldon and Kochi, 1981). However, it is reported that the redox potential of MPc complexes in organic solvent are unknown (Valente and Vital, 2000). It seems somehow unjustified to relate the activity of these complexes to known standard redox potentials of the corresponding metal ions (determined in aqueous solution) since the ligand and solvent significantly influence the electrochemical behaviour of the complexes (Bottcher *et al*, 1996). Moreover, the superstructure of the molecular sieve can modify the redox potential of the metal complex by imposing unusual high energy geometry at the central metal ion (Sheldon, 1998).

The observed differences in the activity order for pinane oxidation between free and encaged complexes have more to do with the protection given to the complex molecule by the zeolite structure than any other factors. In fact, although CoPc and CuPc show the lowest activities towards pinane conversion, a rapid change in colour of the respective reaction mixtures is observed, clearly indicating destruction of the complexes. The following conclusions for the pinane oxidation in the presence of free or encaged MPc complexes can thus be made:

- The primary product of pinane oxidation by *t*-BHP in the presence of free or encaged metal phthalocyanine is pinane hydroperoxide.

- The role played by the MPc complexes consists the metal-catalysed homolytic decomposition of *t*-BHP, via reactions generating chain initiating radicals.

- Due to steric hindrances, pinane molecules cannot approach the metal active site of the encaged complex, that is, they only react with the generated radicals in supercages in the vicinity of that occupied by metallophthalocyanines.

- In homogeneous phase, with free complexes, 2-pinane hydroperoxide is also decomposed, leading to 2-pinanol. This decomposition occurs more or less extensively, depending on the amount of complex present.

- In heterogeneous phase, with encaged complexes, and also due to steric hindrances, 2-pinane hydroperoxide molecules cannot approach the metal centre, which explains the high selectivity obtained.

Based on the above conclusions, the following mechanism can be proposed where the main role of the metal phthalocyanine is the decomposition of the *t*-BHP. This in agreement with what has been proposed for the metal-catalysed decomposition of alkyl peroxide (Sheldon and Kochi 1981):

$$t\text{-BuOOH} + M^{n+} \rightarrow t\text{-BuO}^{\cdot} + M^{(n+1)} + OH^{-}$$

$$t\text{BuOOH} + M^{(n+1)} \rightarrow t\text{-BuOO}^{\cdot} + M^{n+} + H^{+}$$

These reactions can be followed by the radical chain decomposition of the hydroperoxide according to the following steps (Sheldon and Kochi, 1981):

$$2t\text{-BuO}_2^{\cdot} \rightarrow 2t\text{-BuO}^{\cdot} + O_2$$

$$t\text{-BuO}^{\cdot} + t\text{-BuOOH} \rightarrow 2t\text{-BuO}_2^{\cdot} + t\text{-BuOH}$$

It is assumed that the termination step occurs exclusively by the self-reaction of two alkoxy radicals according to reaction:

$$2t\text{-BuO}^{\cdot} \rightarrow (t\text{-Bu})_2OO$$

Similar to what has been proposed by previous models for the autooxidation of saturated hydrocarbons; we consider the following reactions for pinane autooxidation chain reaction, assuming fast reaction of hydrocarbon radicals with molecular oxygen (Minisci *et al*, 1995)

$$2t\text{-BuO}^{\cdot} + PH \rightarrow t\text{-BuOH} + P^{\cdot} \rightarrow PO_2^{\cdot}$$

$$PO_2^{\cdot} + PH \rightarrow POOH + P^{\cdot} \rightarrow PO_2^{\cdot}$$

$$PO_2^{\cdot} \rightarrow S + O_2$$

Where PH and POOH stand for pinane and pinane hydroperoxide, respectively, and S lumps together several minor products resulting from the cyclohexyl ring opening. Assuming this mechanistic proposal, a kinetic model was built for the reaction carried out in heterogeneous phase, under semi-batch conditions. The following simplifying assumptions were made:

- All reactions take place inside the zeolite supercages; and
- Since the zeolite surface has a hydrophilic character, mass transfer limitations are assumed only for pinane.

During the course of the reaction, the nature of the reaction mixture changes, not only due to the continuous addition of *t*-BHP and water, but also due to the formation of the pinane hydroperoxide. Due to the hydrophilic character of the zeolite surface, it is expected that the reaction mixture inside the zeolite supercages becomes increasingly richer in the more polar components, namely hydroperoxides and water. This means that the transport of pinane into the zeolite become more and more difficult. Therefore, it is reasonable to assume that the value of pinane diffusivity decreases exponentially with the amount of *t*-BHP solution added as well as the amount of the pinane hydroperoxide formed.

Chapter 4: Methods and Materials

4.1 Chemicals used in the study

Table 4.1: Chemicals used in the oxidation reactions

Compound	Chemical Formula	Source	Grade
Acetone	$(CH_3)_2CO$	Crest Chemicals	98%
Azobisisobutyronitrile	$C_8H_{12}N_4$	Saarchem	99%
Benzoyl peroxide	$(PhCO_2)_2$	Sigma- Aldrich	75%
t- Butanol	$(CH_3)_3COH$	Sigma-Aldrich	95%
t- Butyl hydroperoxide	$(CH_3)_3COOH$	Sigma- Aldrich	70%
Carbon tetrachloride	CCl_4	Saarchem	>99.8%
Chlorobenzene	C_6H_5Cl	Saarchem	>95%
Cobalt II acetate	$Co(OAc)_2$	Sigma-Aldrich	99%
Copper phthalocyanine	$CuC_{32}H_{16}N_8$	Sigma- Aldrich	>98%
1, 2 dicyanobenzene	$C_6H_4(CN)_2$	Sigma- Aldrich	>98%
Dimethylformamide	C_3H_7NO	Sigma-Aldrich	96%
Ferrocene	$(C_5H_5)_2Fe$	Sigma- Aldrich	>97%
Iron phthalocyanine	$FeC_{32}H_{16}N_8$	Sigma- Aldrich	>95%
Manganese II acetate	$Mn(OAc)_2$	Sigma-Aldrich	99%
Modernite zeolite	$FeC_{32}H_{16}N_8$	Zeolyst International	396 m^2/g
Ni 96B	Ni	Sud Chem	16% Ni on C
Oxygen	O_2	Air Products	99.5%
α/β-Pinene	$C_{10}H_{16}$	Clive Teubes pty	85:15 α: β
Sodium bromide	NaBr	Saarchem	99+
Sodium hydroxide	NaOH	Saarchem	>98%
Sodium sulfite	Na_2SO_3	Crest Chemicals	>95%
Zeolite NaY	NaY	Zeolyst International	598 m^2/g

4.2 Apparatus and Equipment used in Oxidation Reactions

4.2.1 Glass reactor

The oxidation reactions were carried out in a 3-neck round bottom flask equipped with a condenser, a thermometer and a magnetic stirrer as shown in Figure 4.1. The reaction temperature was controlled by immersing the flask in a thermostatically controlled oil bath. The reaction mixture was stirred at 750-1000 rpm. Oxygen was introduced into the reactor either through a gas sparger (porosity 1) or through a bent tip Pasteur pipette. The oxygen flow was controlled using a needle valve.

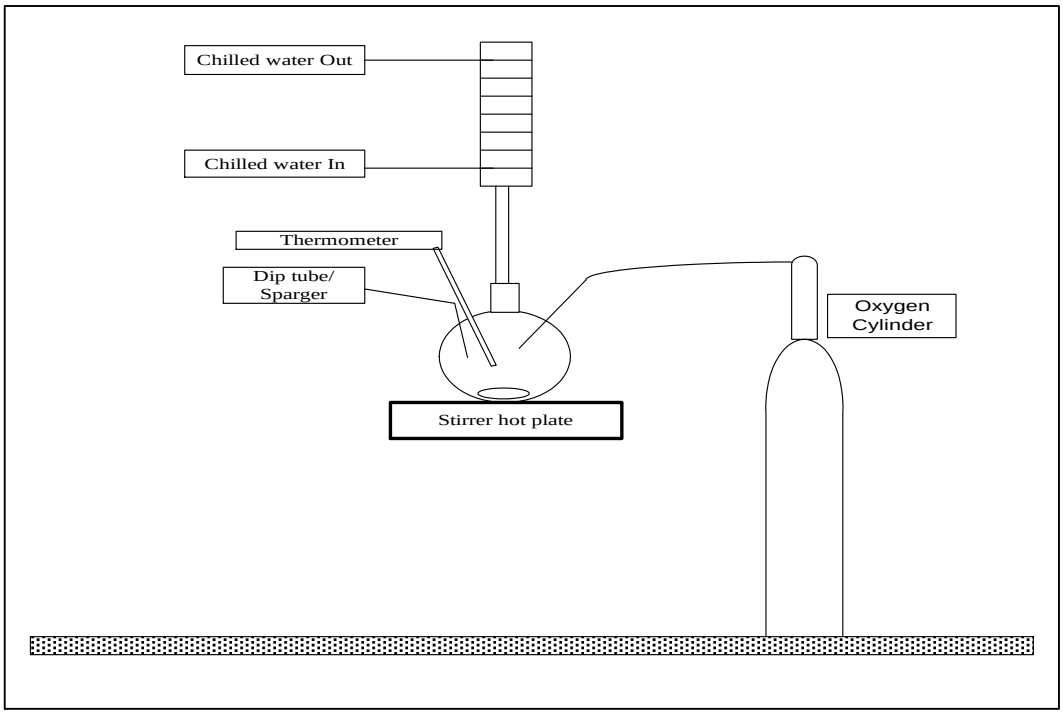


Figure 4.1: Schematic drawing of a glass reactor

4.2.2 Baffled reactor

A glass flange jacketed reactor equipped with a thermometer and a condenser was also used. The reactor was heated and temperature controlled using an external heater. The oxygen flow was controlled using a needle valve and introduced via a pipette ~ 1 cm above the stirrer. The reaction mixture was stirred using an overhead stirrer at 750 rpm. The reaction mixture was stirred using a 4 blade 45°C pitch.

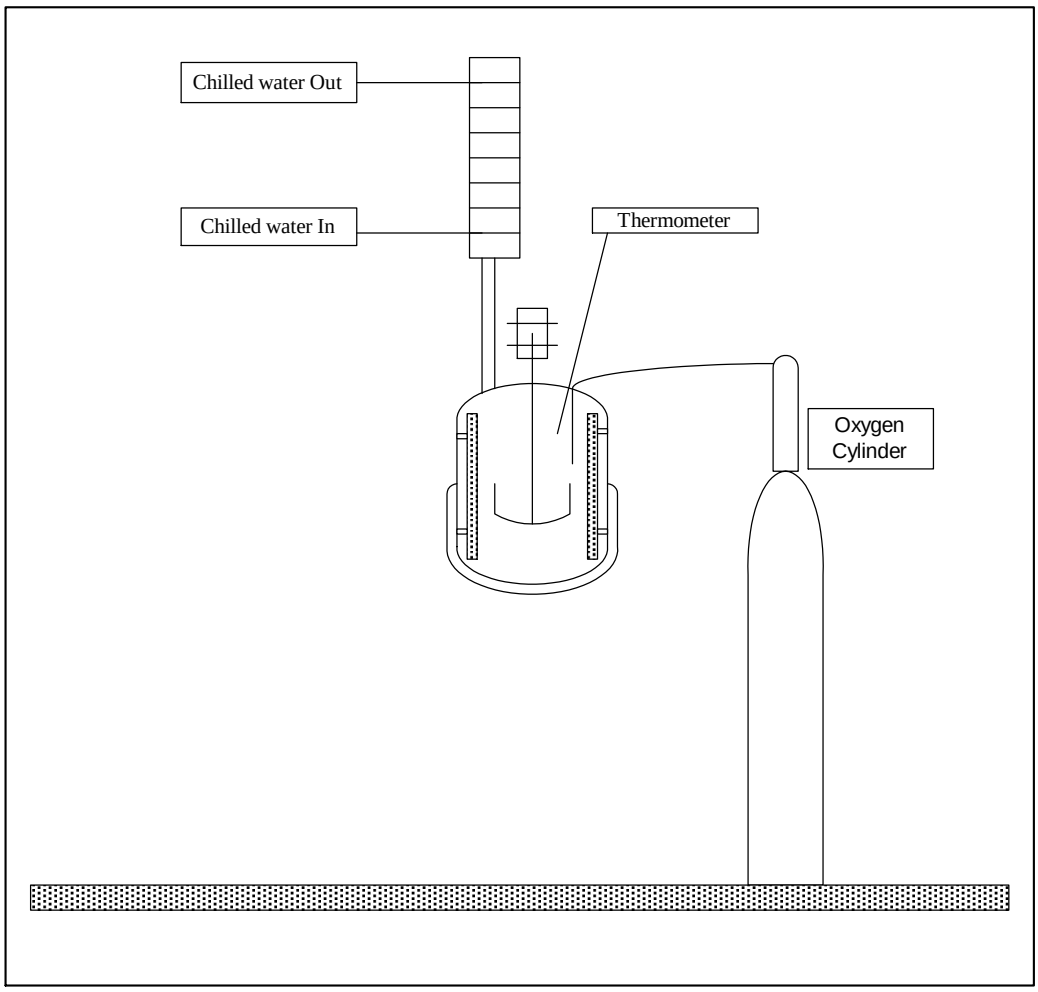


Figure 4.2: Schematic drawing of a baffled reactor

4.2.3 Parr reactor

Reactions that were carried out under pressure were conducted in 300 ml or 600 ml stainless steel Parr pressure reactors as shown in Figure 4.3. These reactors were equipped with mechanical overhead stirrers with pitched blade agitators, internal cooling coils and a thermocouple. The reactor was heated by a surrounding mantle and the stirring speed was 740 rpm. Pressure was monitored by a needle-type gauge.

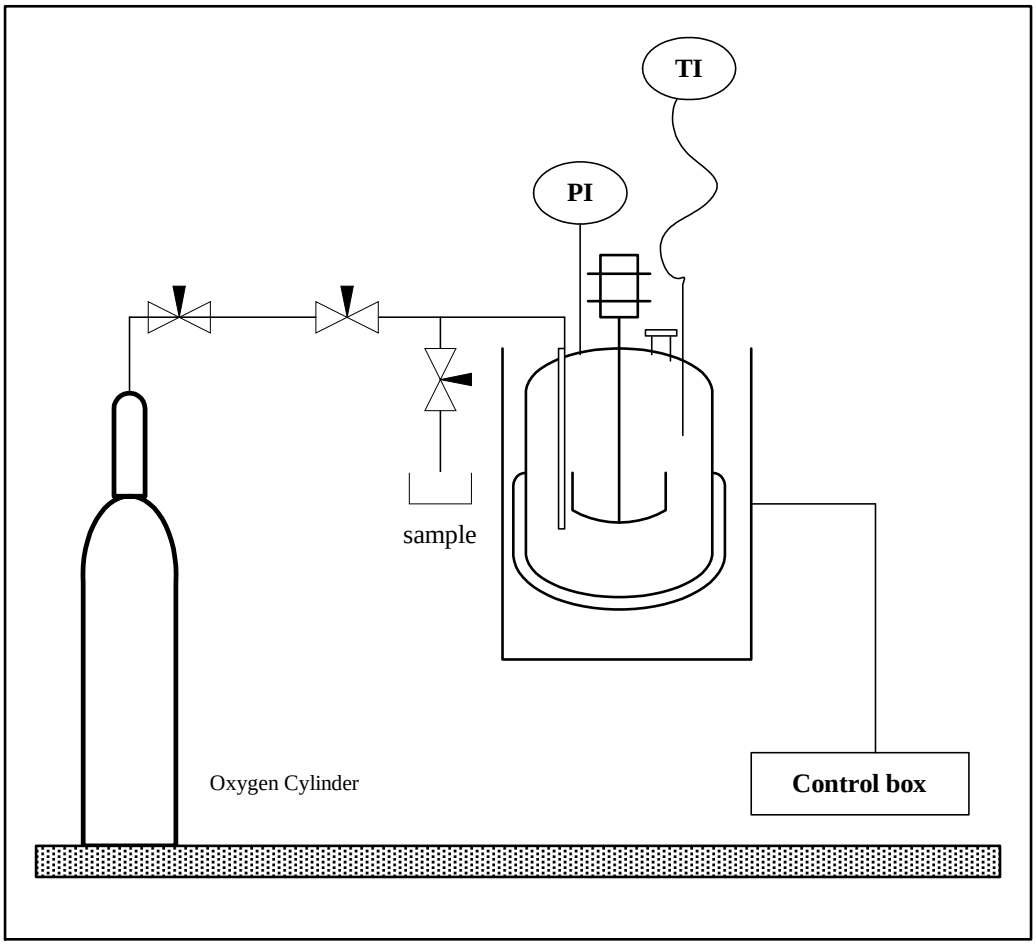


Figure 4.3: Schematic drawing of a Parr reactor

4.2.4 1L Labmax glass pressure reactor

This glass pressure reactor can be operated up to a pressure of 10 bar and is very useful for observing reactions under pressure. The reactor is equipped with a mechanical overhead stirrer (Rushton type), a thermocouple and a pressure transducer for the monitoring and logging of pressure as shown in Figure 4.4. The reactor is jacketed and is heated by an oil system, which is controlled by a computer programme for very precise temperature control. The reactor system is therefore excellent for investigating the reproducibility and robustness of experimental protocols.

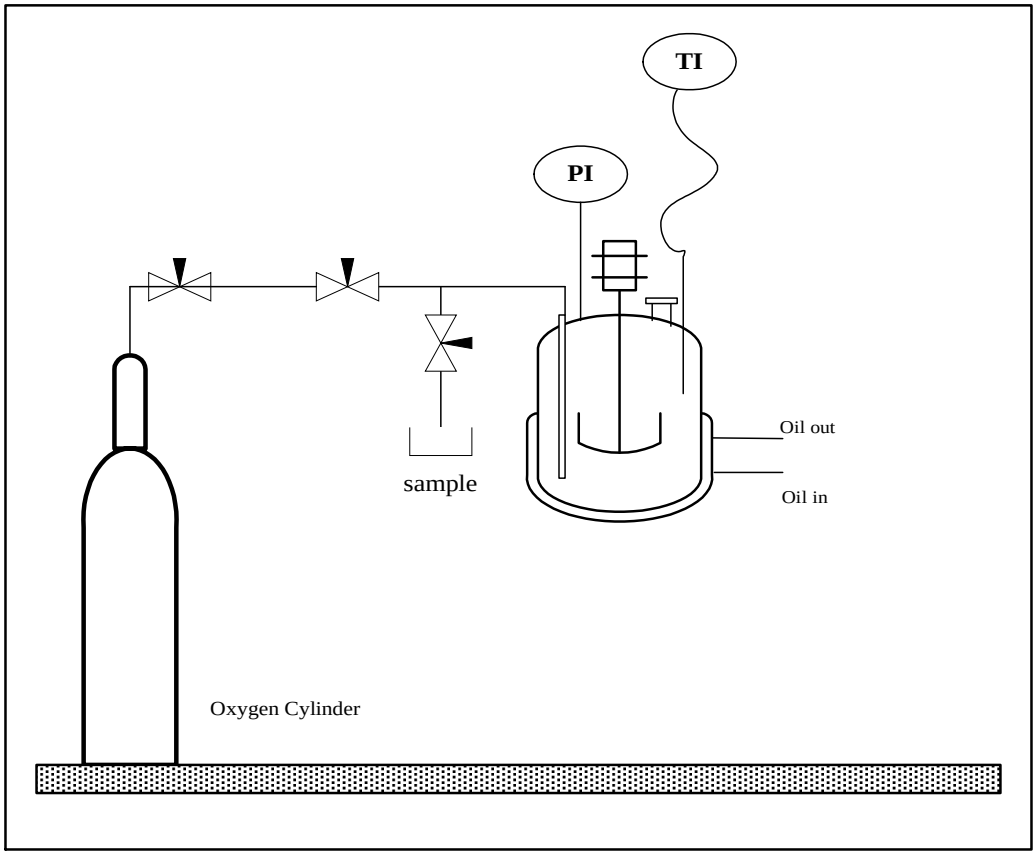


Figure 4.4: Schematic drawing of 1L Labmax pressure reactor

4.2.5 Falling film micro reactor (FFMR)

The falling film micro reactor with viewing window made of glass was developed for investigating mass and heat transport phenomena found in gas-liquid systems. The FFMR has been designed for operation under atmospheric pressure up to 10 bar at a maximum temperature of 180˚C. The cooling- heating passage should only be loaded with maximum pressure of 5 bar if there is no backpressure in the gas chamber.

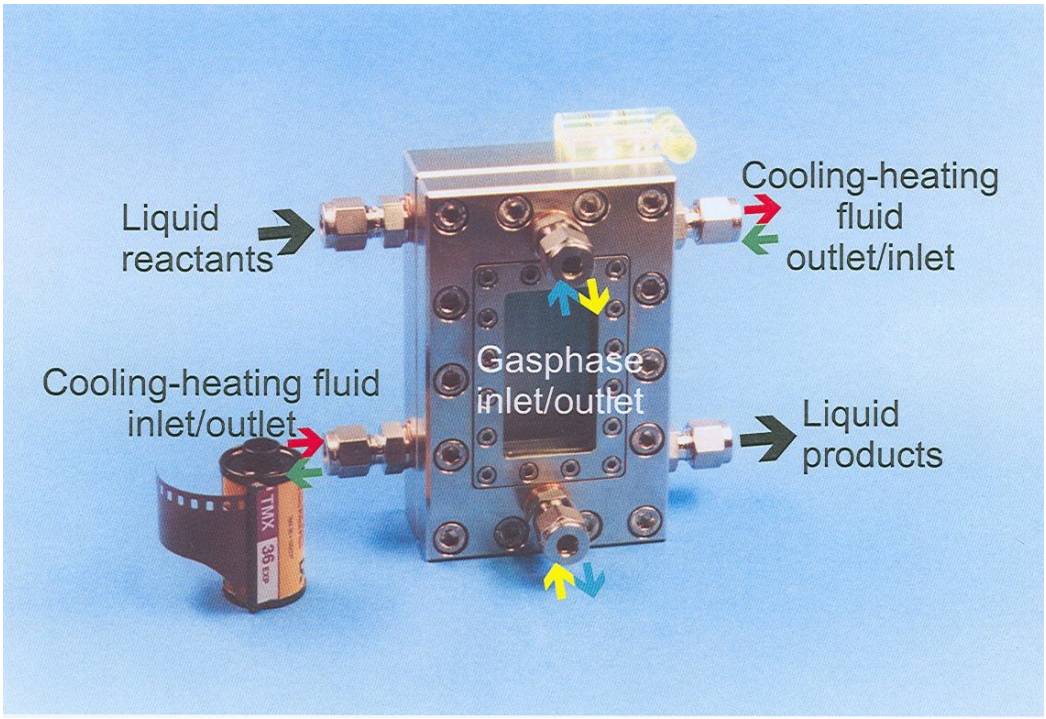


Figure 4.5: Picture of a falling film micro reactor

4.2.6 High vacuum distillation apparatus

The distillations were carried out in a 3-neck round bottom flask equipped with a condenser, a thermometer, a stopper and a magnetic stirrer as shown in Figure 4.6. The distillation temperature was controlled by immersing the flask in a thermostatically controlled oil bath. The reaction mixture was stirred at 750-1000 rpm. Water at 60˚C was circulated through the condenser to prevent any solidification in the condenser.

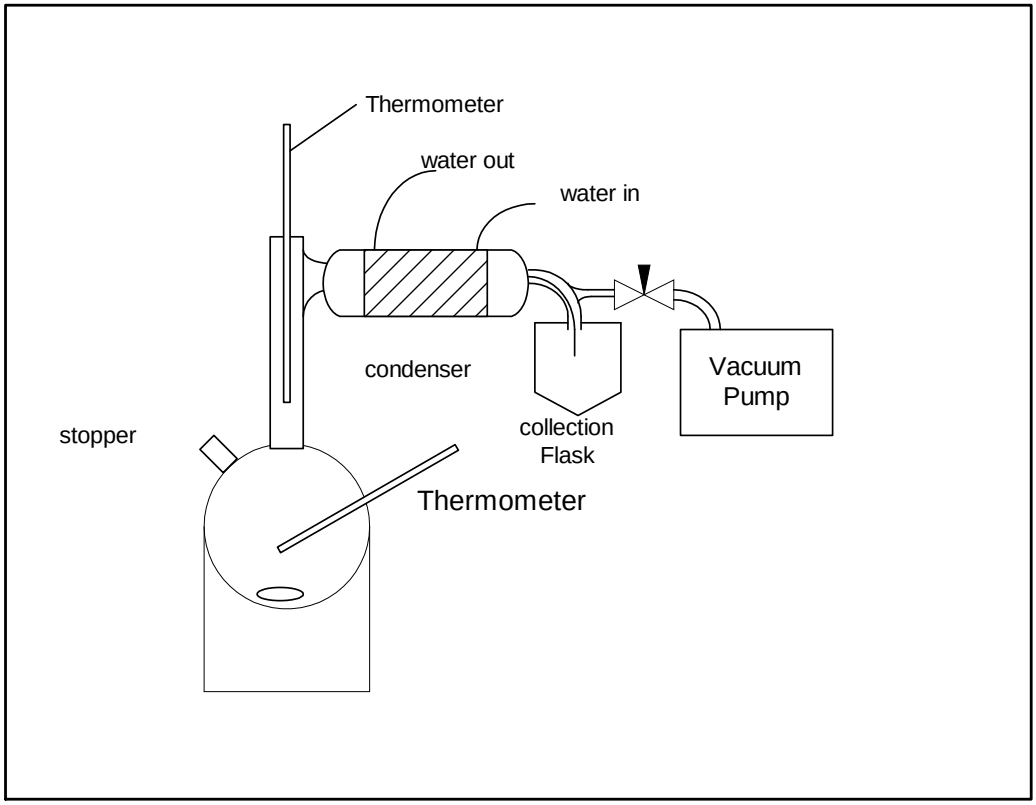


Figure 4.6: Schematic drawing for a high vacuum distillation

4.3 General procedures

4.3.1 General procedure for the α/β -pinene hydrogenation

A mixture of α,β-pinenes (300 g, 2.174 mol), Ni 96B catalyst (30 g, 10% by mass of pinenes) and carbon tetrachloride (CCl_4) (0.2681 g, 1.763 mmol) were charged in a 600 ml Parr reactor. The contents were flushed with hydrogen gas three times before being heated to 80˚C. At 80˚C, the contents were pressurized to 15 bar with hydrogen. The reaction was monitored by gas chromatography by sampling every hour until the reaction was complete. The reaction was deemed complete when 98% of pinenes were consumed. The catalyst was removed by filtration and the filtrate was distilled using a rotary evaporator at 80˚C and 20 mbar before the oxidation reaction.

In the 8L parr reactor, pinenes (4.321 kg, 31.31 mol), Ni 96B (430 g, 10% by mass to pinenes) and CCl_4 (3.63 g, 23.88 mmol) were used. The pinane was also distilled using rotary evaporator at 80˚C and 20 mbar before the oxidation reaction was performed.

4.3.2 General procedure for preparation of encaged catalyst

CuPc (1 g), DCB (1.8 g) and NaY zeolite (3.3 g) were charged in a round bottom flask and heated to ~300˚C using a heating mantle. The contents were heated for ~20 h. After that, the contents were cooled to room temperature.

The product was purified by refluxing with acetone, then DMF and acetone with extended soxhlet extraction.

4.3.3 General procedure for oxidation reactions in an open system

A mixture of *cis*/*trans*-pinane (50.0 g, 0.362 mol), benzoyl peroxide (0.110 g, 0.454 mmol), sodium hydroxide (1.02 g, 0.255 mol) and CuPcNaY (0.0578 g, 0.1% by mass to pinanes) were charged in a three neck round bottom flask fitted with a thermometer, condenser, magnetic stirrer and oxygen gas line sparger or pipette. The contents were then heated to 90˚C and oxygen bubbled through the reaction either with a sparger or pipette. The reaction was monitored by gas chromatography.

4.3.4 General procedure for oxidation reactions under pressure

In a 300 ml Parr reactor, pinanes (120 g, 0.870 mol), benzoyl peroxide (0.280 g, 1.157 mmol) and 50% NaOH (aq.) (17.4 g) were used. The Parr reactor was sealed and evacuated and the content heated to 110˚C. The reactor was then pressurized to 3 bar with oxygen. The reaction was monitored by gas chromatography. Samples were taken hourly to check the progress. The reaction was stopped when ~25% of pinanes was converted. This was done to prevent the formation of by-products by further decomposition of the product. After this, the reactor contents were cooled to room temperature and drained.

4.3.5 General procedure for oxidation using falling film micro reactor

To a pre-heated micro reactor at 110˚C and oxygen flow of 3 bar, a pre-mixed mixture of pinanes (20 g, 0.145 mol), sodium hydroxide (1.45 g, 0.0363 mol), azoisobutyronitrile (0.035 g, 0.214 mmol) and water (1.5 ml) were pumped at 0.1 ml/min.

4.3.6 General procedure for hydroperoxide reduction

In a 2 L round bottom flask, Na_2SO_3 (350 g) was dissolved in water (1400 ml) and then heated to 60˚C. At 60˚C, the post-oxidized mixture (350 g) was added slowly with vigorous stirring. The reaction was run for 4 h at 60˚C. The contents were transferred to a separating funnel and phases separated. The organic phase was washed three times with 200 ml of warm (~60˚C) water. The excess pinane was distilled at 80˚C, 20 mbar of vacuum using a rotary evaporator.

4.3.7 General procedure for high vacuum distillation

The pinanol residue was placed in a round bottom flask fitted with thermometer, magnetic stirrer and still head connected to receiver flask. The contents were heated to 60˚C under 0.2 mbar vacuum pressure. Pinane started distilling at ~T_v =35-50˚C. After collecting the pinane the vacuum was broken and the receiver flask changed and pinanol distilled at T_v = 60-75˚C.

4.4 Statistical design of pinane oxidation reaction

A statistical design was applied to the pinane oxidation reaction in order to improve pinane conversion and selectivity to 2-pinanol. The variables are shown in Table 4.2, the sodium hydroxide equivalents were kept constant at 0.25 and were added as 50% m/m in water.

The response studied were conversion of pinane and selectivity of 2-pinanol.

The variables and responses were studied in a full factorial design.

The experiments that were generated by computer design expert programme are shown in Table 4.3.

Table 4.2: Temperature, Initiator loading and pressure at high and low levels

Factor	Name	Units	Type	Low Actual	High Actual
A	Temperature	deg. C	Numeric	100	120
B	Pressure	bar	Numeric	2	4
C	Initiator loading	mol%	Numeric	0.04	0.15

Table 4.3: Statistically designed experiments

Run	Temperature, ˚C	Pressure, bar	Initiator loading, mol%
1	120	4	0.04
2	120	2	015
3	100	2	015
4	120	2	0.04
5	100	4	0.04
6	100	2	0.04
7	110	3	0.10
8	120	4	0.15
9	110	3	0.10
10	100	4	0.15

4.5 Gas chromatography (GC) analysis conditions

Instrument: HP 5890

Column: DB 5 capillary column (30 m long * 0.25 mm internal diameter)

Detector temperature: 300˚C; Injector temperature: 250˚C

Initial temperature: 50˚C; Initial time: 5 minutes

Rate: 30˚C/ minutes

Final temperature: 220˚C

Final time: 2 minutes

Total run time: 12.66 minutes

Column head pressure: 10 psi

Chapter 5: Results and Discussions

5.1 Enrichment of *cis*/ *trans*-pinanes mixture with more reactive *cis*-pinane

Higher concentration of *trans*-pinane in the *cis*/ *trans*-pinanes mixture results in slower oxidation reaction (Fisher, Stinson and Goldblatt; 1953). Therefore, there was a need to obtain the *cis*/*trans*-pinane mixture with high levels of the more reactive *cis*-pinane.

5.1.1 Distillation

The mixture of *cis*/*trans*-pinanes was placed in a round bottom flask fitted with stillhead, thermometer, condenser, magnetic stirrer and collecting vessel. To the apparatus was connected a vacuum of 45 mbar. At a vapour temperature of between 45-48˚C the *cis*- and *trans*- pinanes co-distilled. The stillhead was replaced by a Vigreux column. This column differs from the stillhead in that it is packed with glass beads and is longer (15 cm) while the stillhead is a short (8 cm), hollow tube. At a vapour temperature of 68-71˚C the distillate showed both the *cis*- and *trans*- pinane indicating that no separation had occurred. Another distillation set up consisted of a round bottom flask, a 1 m long column with 0.025 m internal diameter packed with glass beads, condenser and the receiver. At a vapour temperature of 67˚C and 10 mbar vacuum pressure both the *cis*- and *trans*- pinanes co-distilled. The distillation methods failed to separate the two compounds due to the closeness of the boiling point. *Cis*-pinane boils at 165˚-166˚C while the *trans*-pinane boils at 169˚-

171˚C. The number of theoretical plates on the 1 inch column was calculated to be approximately 36 while in the literature the column that was used had 100 theoretical plates (Fisher, Stinson and Goldblatt, 1953). The distilled mixture consists of 85% *cis*- and 15% *trans*-pinanes.

5.1.2 Selective hydrogenation of CST

When the hydrogenation of α/β-pinenes is done under partially poisoned Ni catalyst (Canova, 1977), the selectivity of the more reactive *cis*- pinane is increased. The nickel catalyst can have a substantial portion of its reactive surface deactivated by employing catalyst modifiers that are non-toxic to the catalyst; toxicity is the effect which results in substantial reduction in reaction rate and / or yield. The modifying agent should not be one which is reactive with the *cis*-pinane. Carbon tetrachloride was used as the modifier in the hydrogenation reaction step. Since carrying out the hydrogenation in presence of a modifier increases the ratio of the more reactive *cis*-pinane, the oxidation reaction should thus lead to a higher yield of the desired *cis*-pinane hydroperoxide.

Table 5.1: Hydrogenation results in Parr reactor

Entry	Feed	CCl_4	Temp/ ˚C	Pres/ bar	% pinene	% Conv	% *cis* pinane	% *trans* pinane	% Selec.
1	A	No	50	15	57	43	35.4	2.7	93
2	A	No	80	15	3	97	86.5	6.8	93
3	A	No	80	10	5	95	82.6	7.0	92
4	B	No	80	15	2	98	76.8	15.8	83
5	B	Yes	80	15	13	87	82.0	2.7	97
6	B	Yes	80	15	69	31	28.6	0.7	98
7	B*	Yes	80	15	1	99	96.0	4.0	96
8	B*	Yes	80	15	1	99	97.0	3.0	97
9	B*	Yes	80	15	0.4	99.6	97.0	3.0	97

Feed A: Contained 96% α-pinene and 4% β-pinene, no modifier was used because the feed had a higher concentration of α-pinene
Feed B: Contained 85% α-pinene and 15% β-pinene
* Reactions done in 8 L Parr reactor

Initially, pinenes were hydrogenated at 50˚C and 15 bar. The results showed that under those conditions (Entry 1) the hydrogenation was slow (43% pinene was converted) and the selectivity of the more reactive *cis*-pinane obtained was high (35.4%: 2.7% *trans*-pinane). This gave *cis*-pinane selectivity of 93% after 4 h. In Entry 2, the temperature was raised to 80˚C and the pressure to 15 bar. The results obtained after 5 h showed that 97% of the pinenes were converted with 93% selectivity of the more reactive *cis*-pinane. In Entry 3, the pressure was dropped to 10 bar and the temperature kept at 80˚C to see the effect of reaction pressure on the hydrogenation. The results obtained showed that 95% of the pinenes were converted with a 92% selectivity of the more reactive *cis*-pinane. However, in Entry 4, a new batch of the CST containing 85% α-pinene and 15% β-pinene was provided and the hydrogenation did not work as expected as the selectivity of the more reactive *cis*-pinane dropped to 83% after 98% pinenes were converted. The reason for the sudden drop is

not known but it could be due to the composition of the starting material. The 85% of α–pinene which could have converted to *cis*-pinane and the remaining β-pinene could have converted to *trans*-pinane.

In Entry 5, the hydrogenation was done under partially poisoned catalyst, the reaction gave a conversion of 87.5% with the selectivity of *cis*-pinane of 97% after 6 h. In Entry 6, the catalyst from Entry 5 was used again under the hydrogenation conditions to see if it will be recyclable and to test if Ni was still active. The results showed the catalyst was not as active as before and showed 31% conversion, after 20 h, with 28.55% of *cis*-pinane. However, the selectivity for *cis*-pinane was still high at 97%; the reaction was slower but the selectivity was not compromised.

Three runs were performed in the 8L pressure reactor (Entry 7 to Entry 9) under the same conditions to produce more material as well as to check if the reaction was reproducible. In all the experiments, the results showed 99% conversion of the pinenes with >95% selectivity of the more reactive *cis*-pinane. The results showed that the reaction was reproducible at the 8L reactor scale. The recovery of the pinane mixture was 86% after distillation. This was done by distilling the filtrate (after filtration of the catalyst) on the rotary evaporator at 80˚C under 20 mbar vacuum. This was to eliminate any high boiling compounds from the pinanes before oxidation and also to remove any residual Ni catalyst. The following figures show a typical *cis*/*trans*-pinane gas chromatograph as well as the ^{1}H and ^{13}C NMR spectra.

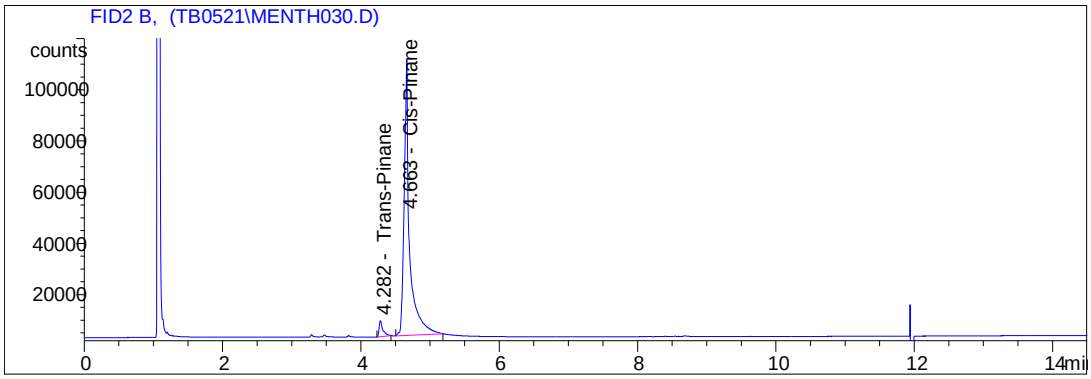


Figure 5.1: Gas chromatogram of *cis/trans*-pinane

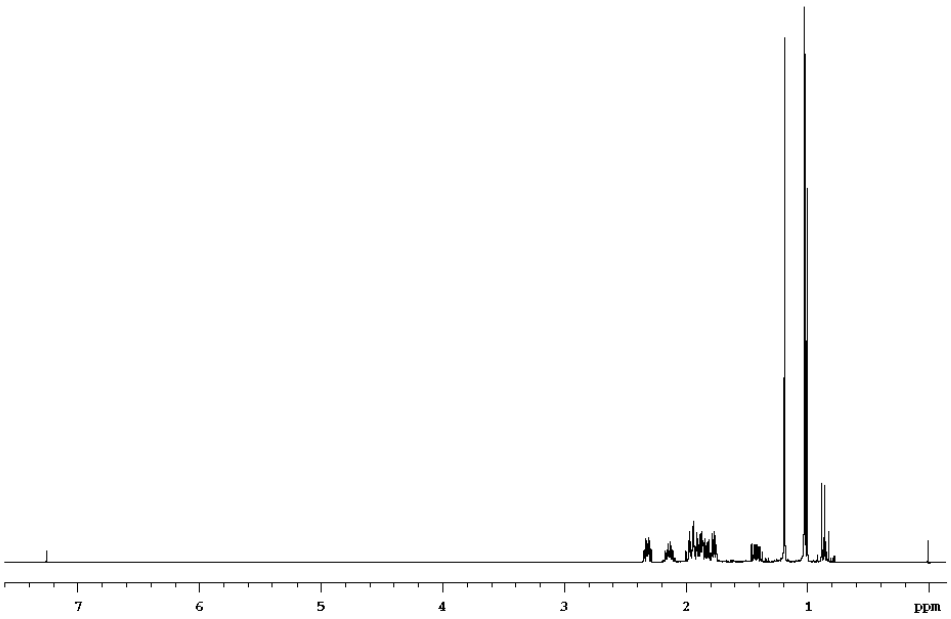


Figure 5.2: ^{1}H NMR spectrum of *cis/trans*-pinane

From the ^{1}H NMR spectrum (Figure 5.2), the alkene signal between 4.5 – 6.0 ppm had disappeared indicating that the hydrogenation was successful. The ^{13}C NMR spectrum (Figure 5.3) also confirmed disappearance of any alkene carbon (105-145 ppm).

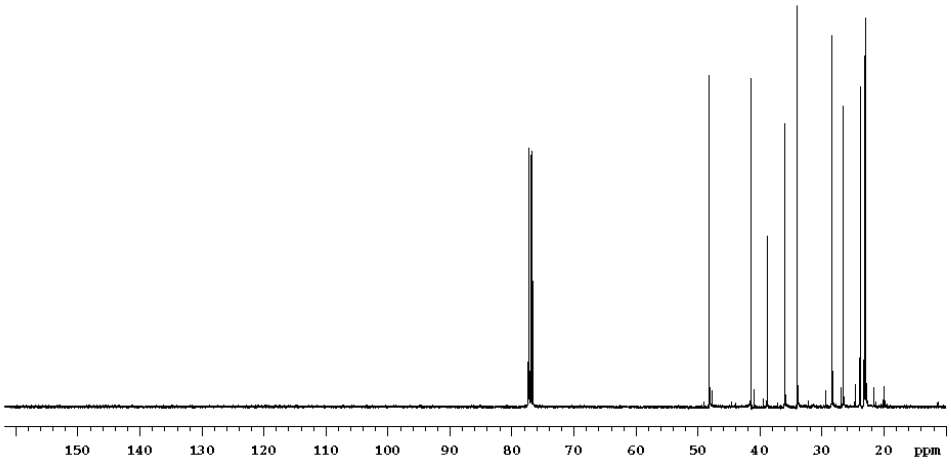


Figure 5.3: ^{13}C NMR spectrum of *cis*/*trans*-pinane

5.2 Oxidation of enriched pinane

It was reported that *cis*-pinane autooxidises a lot more rapidly than *trans*-pinane which absorbs very little oxygen (Fisher, Stinson and Goldblatt, 1953). Oxidation of the enriched pinane was done in four different types of reactors (i.e. round bottom flask, baffled glass reactor, Parr reactor and falling film micro reactor). During the analysis, it was suggested that the sample be reduced with sodium sulfite before injecting into the gas chromatography instrument so as to get clear composition of the product. Earlier literature used peroxide titration as a method for determining the pinane hydroperoxide (Wagner, Smith and Peters, 1947), but this method was found to be time consuming and tedious. The reduction of the hydroperoxide to alcohol group was reported to occur without a change in the positional and steric configuration of the alcohol molecule (Il'ina, Simakova and Semikolenov, 2000). The oxidation reaction had to be stopped at a conversion lower than

35% since at higher conversion, the selectivity of 2-pinanol decreased as the pinane hydroperoxide started forming by-products.

5.2.1 Oxidation of enriched pinane in round bottom flask reactor

Table 5.2: Results of oxidation in a round bottom flask

Entry	Initiator	Catalyst	Temp/ ˚C	O_2 purge	% pinane	% Conv	% 2-pinanol	% Selec.
1	H_2O_2	H_2SO_4	20	No	97	3	0	0
2	*t*-BHP	No	95	No	75	25	2	8
3	*t*-BHP	No	95	Yes	10	90	10	11
4	No	Co/ Mn	80	Yes	83	17	12	71
5	*t*-BHP	FePcMod	20	Yes	6	94	17	18
6	*t*-BHP	FePcNaY	20	Yes	24	76	16	21
7	*t*-BHP	CuPcNaY	20	Yes	82	18	4	22
8	*t*-BHP	CuPcNaY	95	Yes	48	52	10	19
9	$(BzO)_2$	No	95	Yes	84	16	5	31
10	$(BzO)_2$	CuPcNaY	95	Yes	0	100	49	49
11	AIBN	No	95	Yes	88	12	3	25
12	AIBN	CuPcNaY	95	Yes	65	36	12	33

When H_2O_2 was used as an initiator and source of oxygen and sulphuric acid as catalyst (Entry 1, Table 5.2), the reaction gave 3% conversion of pinane but no 2-pinanol formation. In Entry 2, hydrogen peroxide and sulphuric acid was substituted by *t*-BHP and the reaction ran at 95˚C for 20 h. The conversion of pinane as shown by GC chromatograph was 25% with lots of other unidentified peaks. In this reaction the *t*-BHP acted both as initiator and oxygen source. In Entry 3, the reaction was done with oxygen purging with *t*-BHP added as catalyst. The conversion of pinane was 90% but the selectivity of 2-pinanol was 10% with numerous unidentified products.

In Entry 4, 2-pinanol was prepared using the $Co(OAc)_2$, $Mn(OAc)_2$ in chlorobenzene as solvent over 20 h. The conversion of pinane was 17% with selectivity of 2-pinanol of 71%. The reaction was stopped to prevent further decomposition of the product as have been observed by Sercheli *et al* (1997). Since the procedure replaced the oxidation and reduction steps as 2-pinanol was formed directly from the reaction, it suggested an interesting alternative for the industrial production of linalool. If the conversion as well as selectivity for the procedure could be improved, the procedure would be a cheap and industrially viable method. However, after numerous reactions were done, the above results (Entry 4) were the best obtained.

In Entry 5, FePcMod was used as a catalyst with *t*-BHP as initiator. The results showed pinane conversion of 94% with the 2-pinanol selectivity of 18%. The reaction was done at 20˚C as it was reported that oxidation reaction can happen at temperature lower than 30˚C when done with encaged catalysts (Valente and Vital, 2000). 2-Pinanol was obtained even before the reduction step indicating that during oxidation the catalyst gave a free FePc. The free phthalocyanines are reported to decompose the hydroperoxides and hence the formation of 2-pinanol (Valente and Vital, 1997 and Valente *et al*, 2000). In Entry 6, FePcMod was replaced by FePcNaY. The conversion was lower compared to results in Entry 5 but the selectivity was almost the same. The 2-pinanol was obtained only after the reduction step. This indicated that the zeolite was a better encaging compound than the mordenite. In Entry 7, the CuPcNaY was used as the catalyst. The conversion as shown by gas chromatograph was 18% with selectivity of 2-pinanol, after the reduction step,

of 22%. These reactions were unsuccessful in our hands and the reasons for poor results are not known. In Entry 8, the temperature was increased to 95˚C. The conversion of pinane was 52% but the selectivity of 2-pinanol, after the reduction step, was only 19%. The results obtained when *t*-BHP was used as the initiator, under different conditions showed a poor selectivity of 2-pinanol as selectivity of less than 30% was obtained.

In Entry 9, benzoyl peroxide was used as an initiator and the reaction was done first at 20˚C, but since the reaction showed no conversion of pinane, the temperature of the reaction was increased to 95˚C. At 95˚C, the conversion of pinane as shown by gas chromatograph was 16% with a selectivity, after reduction, of 31%. Though the conversion was unsatisfactory, it was better than conversion obtained when *t*-BHP was used as an initiator. The selectivity was also better (i.e. 31%). In Entry 10, CuPcNaY was used as a catalyst and a 100% conversion of pinane was obtained but the selectivity of 2-pinanol was 49%, after reduction step. These results indicated that the oxidation took place to a large extent in the supercages as 2-pinanol was obtained after the reduction step (Valente and Vital, 1997).

In Entry 11, AIBN was used as an initiator. The reaction gave a conversion of 12% with 2-pinanol selectivity of 25%, after reduction. In Entry 12, CuPcNaY was used as a catalyst. The conversion of pinane improved to 36% but the selectivity of 2-pinanol, after reduction, was marginally improved to 33%. These results were also poor when compared to results obtained when benzoyl peroxide was used as initiator.

5.2.2 Oxidation of enriched pinane in a baffled reactor

The baffled reactor differs from the round bottom flask in that its mixing is turbulent while in round bottom flask the mixing is vortex.

Table 5.3: Results of oxidation in a baffled reactor

Entry	Initiator	Catalyst	Temp/ ˚C	O_2 purge	% pinane	% Conv	% 2-pinanol	% Selec.
1	*t*-BHP	No	95	Yes	56	46	18	39
2	*t*-BHP	CuPcNaY	95	Yes	24	76	35	46
3	No	Co/ Mn	80	Yes	69	31	14	45
4	$(BzO)_2$	No	95	Yes	88	12	2	17
5	$(BzO)_2$	CuPcNaY	95	Yes	12	88	38	43
6	$(BzO)_2$	CuPcNaY	90	Yes	24	76	51	67
7	AIBN	No	90	Yes	91	9	1	11
8	AIBN	CuPcNaY	95	Yes	65	35	16	46

In Entry 1, when *t*-BHP was used as an initiator without the catalyst, pinane conversion was 46% with selectivity of 2-pinanol, after reduction step, of 39%. When a catalyst was added during the reaction as in Entry 2, pinane conversion was 76% but the selectivity of 2-pinanol after reduction step was 46%. There was an improvement in terms of pinane conversion but the selectivity of 2-pinanol was not satisfactory. The results were better than the results obtained when using a round bottom flask in terms of selectivity of 2-pinanol (Table 5.2, Entry 8).

In Entry 3, $Co(OAc)_2$, $Mn(OAc)_2$ catalyst were used without the presence of initiator; as earlier mentioned, this protocol would be cheaper and industrially viable as it produces 2-pinanol directly during the reaction. However, the

results obtained suggested that the baffled reactor was not suitable type of reactor as the results obtained were lower in the baffle reactor as compared to the results obtained when using round bottom flask (Table 5.2, Entry 4). Though conversion of pinane was higher at 35%, the selectivity of 2-pinanol decreased to 45%.

In Entry 4, when benzoyl peroxide was used, the reaction gave pinane conversion of 12% with a selectivity to 2-pinanol of 17% after 20 h. In Entry 5, a catalyst was added all at once and the results showed an improvement in terms of conversion and selectivity; the conversion increased to 88% while the selectivity increased to 43%. In Entry 6, the catalyst was added in two portions. One portion was added and the reaction ran for 8 h then the other portion was added and the reaction was allowed to continue for further 12 h, making the total reaction time of 20 h. Pinane conversion was 76% with 2-pinanol selectivity, after reduction step, of 67%. Though the conversion was lower, in terms of selectivity when catalyst was added in two portions, it gave better results. However, the 2-pinanol was isolated with 50% recovery as during the distillation, the 2-pinanol started to decompose to other un-wanted products. This meant that for better isolation, high selectivity of 2-pinanol was required so as to minimise formation of other un-wanted products during distillation.

In Entry 7, when AIBN was used as an initiator, the results showed pinane conversion of 9% with 2-pinanol selectivity of 11% after 20 h. After the addition of the catalyst, as in Entry 8, pinane conversion increased to 35%

while the 2-pinanol selectivity increased to 46% after 20 h. When compared to results obtained using round bottom flask, when no catalyst was added, the round bottom flask gave better results (Table 5.2, Entry 11) in terms of selectivity of 2-pinanol (11 vs 25). When the catalyst was added, the baffled reactor gave better selectivity (33 vs 46)

5.2.3 Oxidation of enriched pinane in Parr reactor

The liquid-phase oxidation of pinane to 2-pinane hydroperoxide by oxygen was studied at 80˚C- 120˚C and under oxygen pressure of 3 to 4 bar as previously done by Il'ina, Simakova and Semikolenov (2000).

Table 5.4: Results of oxidation in a Parr reactor

Entry	Initiator	Cat.	Temp/˚C	Pres/ bar	% pinane	% Conv	% 2-pinanol	% Selec.
1	H_2O_2	No	95	4	12	88	19	22
2	t-BHP	No	95	4	36	64	40	63
3	t-BHP	CuPcNaY	110	3	75	25	8	32
4	$(BzO)_2$	No	95	3	54	46	19	41
5	$(BzO)_2$	No	110	3	65	35	33	95
6	$(BzO)_2$	CuPcNaY	110	3	58	42	34	81
7	AIBN	No	110	3	71	29	23	79
8	AIBN	CuPcNaY	110	3	81	19	16	84
9	AIBN	No	110	3	63	37	28	76

In Entry 1, the results showed a conversion of pinane of 88% with a selectivity of 2-pinanol of 22% after 20 h reaction time at 4 bar. All the results using hydrogen peroxide (Table 5.2, 5.4) gave high conversion of pinane but the selectivity of 2-pinanol in all reactions was low. In Entry 2, hydrogen peroxide was replaced by *t*-BHP. The reaction gave a conversion of pinane of 64% with the selectivity of 2-pinanol, after reduction, of 63% after 20 h. In Entry 3,

CuPcNaY was added as the catalyst. As observed in earlier experiments it does not improve the selectivity of 2-pinanol as the selectivity dropped to 32%. The reaction temperature of the reaction was increased to 110˚C. The results gave a conversion of 25% with a selectivity of 2-pinanol, after reduction step, of 32%. The reason for lower selectivity is not yet known; maybe under these conditions there is catalyst leaching and the hydroperoxide decomposed. The reaction was run for 4 h; the increase in temperature improved the conversion within shorter reaction times.

In Entry 4, benzoyl peroxide was used as an initiator at 95˚C. After 2.5 h, the results showed a conversion of pinane of 46% but the selectivity of 2-pinanol, after reduction, was 41%. However, after the temperature was increased to 110˚C as in Entry 5, the conversion of pinane decreased to 35% but the interesting thing was that the selectivity of 2-pinanol increased to 95%. The 2-pinanol started forming with a ratio 2:1 to the hydroperoxide after 2.5 h. These results were the best obtained thus far in that the isolation of 2-pinanol involved only evaporating the unreacted pinane, leaving the 2-pinanol product as residue. In Entry 6, CuPcNaY was added as the catalyst in order to improve the reaction conversion and the selectivity of 2-pinanol. However, the reaction conversion obtained a slight increase to 42% but the selectivity unexpectedly dropped to 81%. When reaction was run longer without the catalyst, the conversion was steady at 40% but the selectivity of 2-pinanol did show some decline. This showed that the catalyst just speeded up the conversion without increasing the selectivity.

In Entry 7, AIBN was used as an initiator without addition of a catalyst. The reaction gave pinane conversion of 29% with 2-pinanol selectivity, after reduction step, of 79%. The results were obtained after 4 h. When CuPcNaY was added as catalyst, as in Entry 8, the conversion of pinane decreased to 19% while the selectivity increased to 84%. In these reactions 2-pinanol started forming even before the reduction step. In Entry 9, the reaction was run with chlorobenzene as solvent. The results gave pinane conversion of 37% with 2-pinanol selectivity of 76%, in this reaction the 2-pinanol also started forming even before the reduction step.

5.2.4 Oxidation of enriched pinane with micro reactors

The micro reactor was used in order to improve the yield of 2-pinanol compared to other reactors (Parr, round bottom flask and baffled reactors) that gave low yields due to formation of by-products. With the micro reactor the reaction was continuous in that the pinane was fed into the reactor at certain flow rate and fixed temperatures and pressures.

In all experiments in which *t*-BHP was used as an initiator, the results showed poor oxidation of pinane. After mixing the reactants, the contents formed two layers due to the presence of 30% water in the *t*-BHP and 50% water in the NaOH solution. The solution was stirred and pumped into the pre-heated (110˚C) and pre-pressurised (3 bar) reactor as a stirred solution. At 0.5 ml/min flow rate, the reaction gave no conversion. The flow rate was decreased to 0.01 ml/min but still the results also showed no oxidation of pinane. The

temperature was increased to 130˚C and the stirred solution pumped but again the results showed no conversion of pinane.

The benzoyl peroxide was not all soluble in the pinane even at 60˚C. The mixture contained some solid and due to the presence of solids, the mixture was not pumped through to the reactor to avoid blockage of the Teflon tubes.

At room temperature the AIBN was not completely soluble in the pinane. But after increasing the temperature to 60˚C, all the AIBN dissolved. The mixture was pumped as a stirred solution through the reactor. With batch feed type, where the solution was pumped into the reactor and collected into a different flask, the results showed no conversion of pinane even after running the reaction at 130˚C and 0.01 ml/min flow rate. Then the reaction mixture was circulated through the reactor by connecting the feed and the collection line in the same flask with feed line. The progress of the reaction was monitored by sampling hourly. After 6 h, the results showed pinane conversion of 2% with selectivity of 2-pinanol at 85%.

From the results obtained, it showed that the Parr reactor was the best reactor system that can be used in the oxidation reaction with benzoyl peroxide as initiator at 3 bar and 110˚C with NaOH as base. The use of novel zeolite catalysts did not help in our case as the reaction still needed higher temperatures to obtain reasonable conversion.

5.3 Statistically designed oxidation reaction

Statistically designed experiments were done using benzoyl peroxide as an initiator as it gave the best results compared to other initiators tested in the study. The aim was to see how pressure, temperature and initiator loading would affect the oxidation reaction.

Table 5.5: Results of statistically designed experiments

Run	Temp/ ˚C	Pressure/ bar	Initiator loading/ %mol	% Conv.	% Selec.
1	120	4	0.05	55.1	68.2
2	120	2	0.15	24.0	84.3
3	100	2	0.15	30.3	78.9
4	120	2	0.05	24.7	78.2
5	100	4	0.05	36.4	76.5
6	100	2	0.05	20.9	88.4
7	110	3	0.10	32.2	93.7
8	120	4	0.15	36.1	82.8
9	110	3	0.10	33.3	94.8
10	100	4	0.15	34.0	93.3

5.3.1 Results of conversion as a response

The effect list in Table 5.6 shows the contribution that each significant variable makes to the chosen response factor, i.e. conversion. As indicated in the table the most significant factor, by far, was pressure (Prob > t = 0.0295).

Table 5.6: Effects list for conversion

Term	Coefficient	Effect	Sum of quares	% contribution	Prob> t
Intercept	33.83				
Pressure	6.57	13.15	345.84	51.42	0.0295
Temperature and Pressure		8.05	129.61	19.27	0.1123

The contribution to conversion was 51.42%. The effect indicates whether the variable makes a negative or positive contribution. In the case of pressure, increasing the pressure results in an increase in the conversion. The conversion was not high at lower pressure (2 bar). It can be assumed that at 2 bar the contact between the pinane and oxygen is not as much as oxygen pressure of 4 bar and reaction was limited by mass transfer characteristics.

Table 5.7: Analysis of Variance for conversion

Source	Sum of Squares	DF	Mean Squares	F Value	Prob> F
Model	345.84	1	345.84	7.45	0.0294
Curvature	1.85	1	1.85	0.04	0.8475
Residual	324.90	7	46.41		
Lack of fit	324.29	6	54.05	89.34	0.0808
Pure error	0.30	1	0.60		
Predicted R-Squared		0.1392			

The ANOVA for conversion of pinane (Table 5.7) indicated that the selected model was significant since the Probability > F was less than 0.05 (i.e. 0.0294).

5.3.2 Results with selectivity as a response

Table 5.8: Effect list for selectivity

Term	Coefficient	Effect	Sum of Squares	% Contribution	Prob> t
Intercept	83.91				
Pressure	-1.13	-2.25	10.13	1.48	0.7181
Initiator loading	3.50	7.00	98.0	14.34	0.2836
Pressure and initiator loading	4.35	8.7	151.38	22.15	0.1937

The results in Table 5.8 showed how each variable contribute to the response factor, i.e. selectivity. From the results, it showed how difficult it is to make any conclusion as all the variables gave a Probability > t of above 0.050. The only variable closest to give the Probability > t of 0.05 was the combination of pressure and initiator loading. This to some extent was expected as temperature had negative response to selectivity as high temperature decomposes the product. The variable pressure and initiator loading made a contribution of 22.15% and were lower than expected.

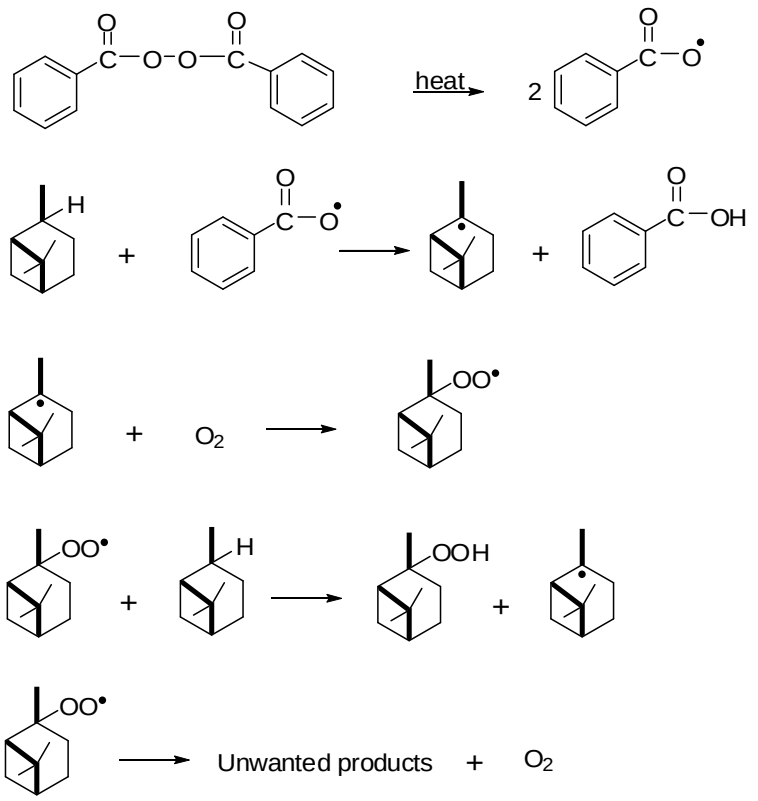
Table 5.9: Analysis of variance table

Source	Sum of Squares	DF	Mean Squares	F Value	Prob> F
Model	259.50	3	86.50	1.22	0.3796
Curvature					
Residual	424.06	6	70.68		
Lack of fit	423.46	5	84.69	139.99	0.0641
Pure error	0.60	1	0.6		

The ANOVA model for selectivity to 2-pinanol showed the model was not significant as the Probability > F was greater than 0.050 (i.e. 0.3796)

5.4 Optimisation on oxidation of enriched pinane

Optimisation was done with benzoyl peroxide as an initiator in the Parr reactor. Initial results showed better selectivity of 2-pinanol. The following reaction sequence was proposed for the oxidation of *cis*-pinane to *cis*-pinane hydroperoxide:



Scheme 5.1: Reaction sequence for the oxidation of pinane

5.4.1 Effect of reaction temperature

Oxidation was performed at 100˚C and 120˚C to see what effect the temperature was going to have on both the conversion of pinane and the selectivity to 2-pinanol.

Table 5.10: Results of effect of temperature on oxidation

Time (min)	Oxidation at 100˚C			Oxidation at 120˚C		
	%Conv.	% 2-pinanol	%Selec	%Conv.	% 2-pinanol	%Selec.
30	5.9	5.7	96.6	14.4	12.5	86.8
60	11.7	9.9	84.6	16.2	13.4	82.7
90	13.4	11.1	82.8	21.0	16.3	77.6
120	15.5	12.4	80.0	24.2	17.4	71.9
150	16.8	13.2	78.6	27.4	17.9	65.3

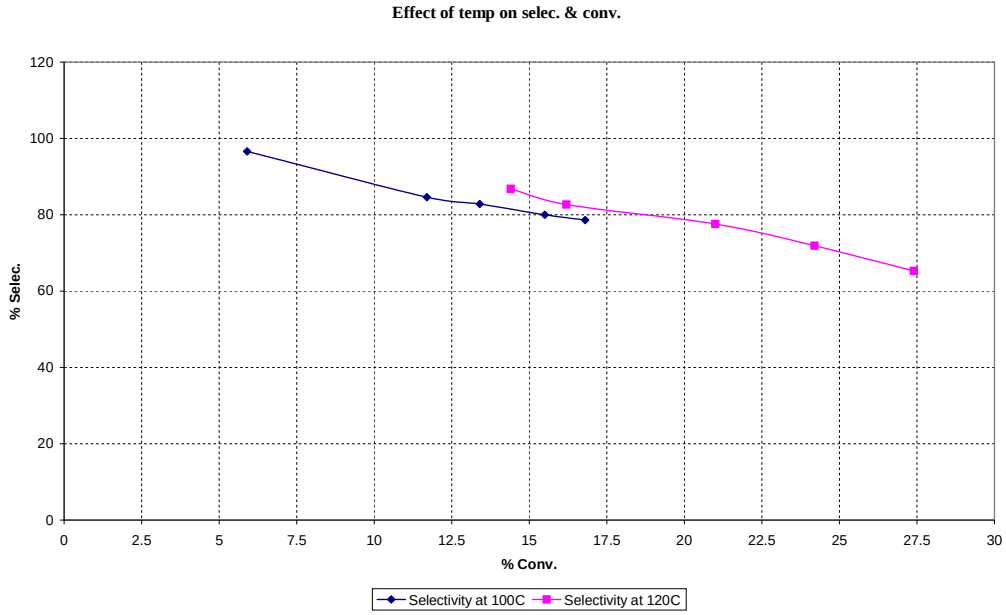


Figure 5.4: Effect of temperature on conversion and selectivity

The results indicated that at high temperature, high conversion of pinane was obtained but the selectivity of 2-pinanol was lower. The highest conversion of pinane was 27.5% with a selectivity to 2-pinanol of 65.3%. At 100˚C, the conversion after 2.5 h of reaction time was 78.6%. The best selectivity 96.6% was obtained at 100˚C with a conversion of 5.9%. At this time most of the pinane that was converted formed 2-pinanol. The graph showed that at conversion higher than 10%, the selectivity of 2-pinanol was compromised as it fell to below 90% at the temperatures used (100 and 120˚C). The effect of

temperature from the statistical design experiment showed a negative contribution towards the selectivity of 2-pinanol.

5.4.2 Effect of pressure

The oxidation was performed at 2 and 4 bar to see the effect pressure will have on the conversion of pinane and selectivity to 2-pinanol. Temperature and reaction time were kept constant at 110˚C and 2.5 h respectively.

Table 5.11: Results of effect of pressure on oxidation

Time (min)	Oxidation at 2 bar			Oxidation at 4 bar		
	%Conv.	% 2-pinanol	%Selec.	%Conv.	% 2-pinanol	%Selec.
30	4.4	3.6	81.8	11.5	11.6	100.9
60	9.5	7.9	83.2	20.7	17.1	82.6
90	12.6	10.8	85.7	26.2	23.6	89.7
120	14.9	12.7	85.2	28.5	26.9	94.2
150	18.2	16.2	89.0	33.8	31.3	92.6

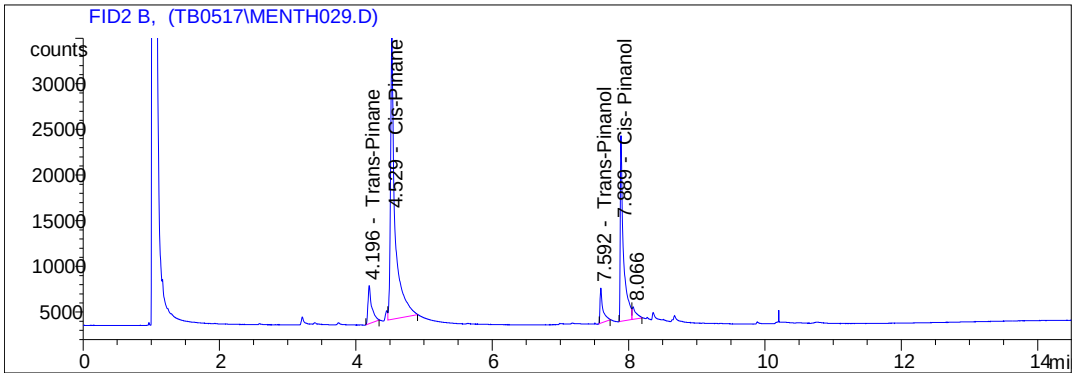


Figure 5.5: Gas chromatogram of post-reduced oxidates

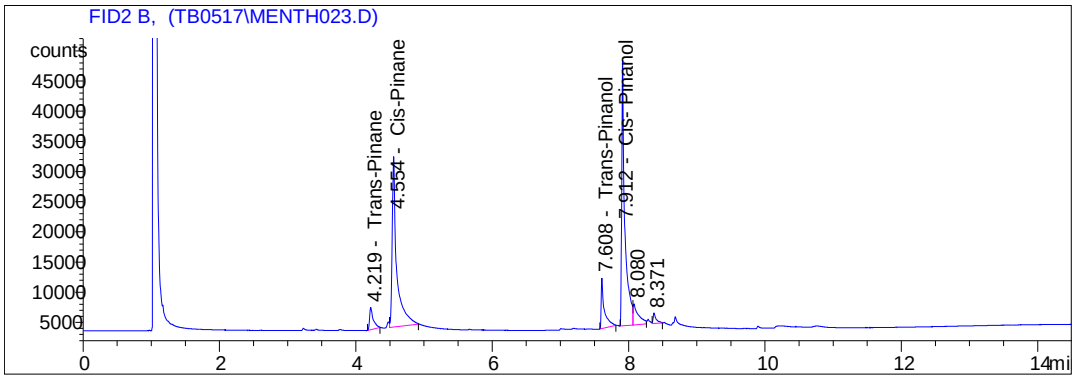


Figure 5.6: Gas chromatogram of residue after pinane distillation

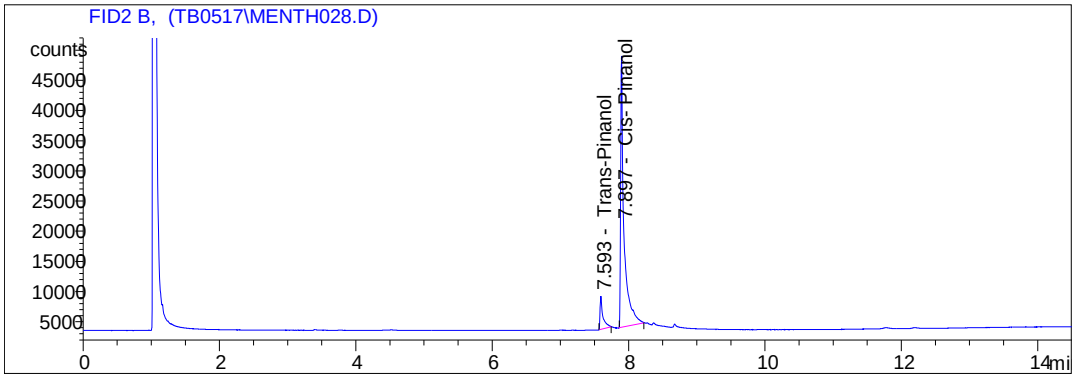


Figure 5.7: Gas chromatogram of distilled 2-pinanol

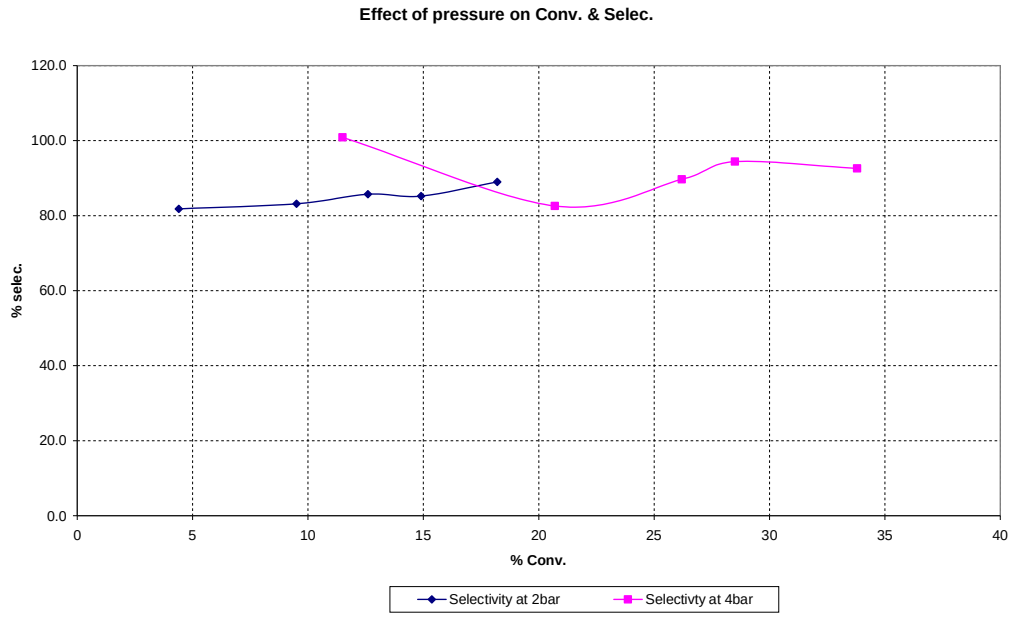


Figure 5.8: Effect of pressure on conversion and selectivity

The results showed that pressure had positive influence in the conversion of pinane to 2-pinanol as at lower pressure (2 bar) low conversion of pinane was obtained. However, the selectivity of 2-pinanol was almost the same except for when 4 bar was used as after 0.5 h the selectivity was 100.9%. When it comes to selectivity of 2-pinanol, the reaction has a zero order with respect to oxygen pressure (Il'ina, Simakova and Semikolenov, 2000). The results showed that at high pressure, high conversion can be obtained as 33.8% conversion was obtained after 2.5 h at 4 bar with a selectivity of 92.6%. At 2 bar under the same condition, 18.2% conversion was obtained at 89% selectivity of 2-pinanol.

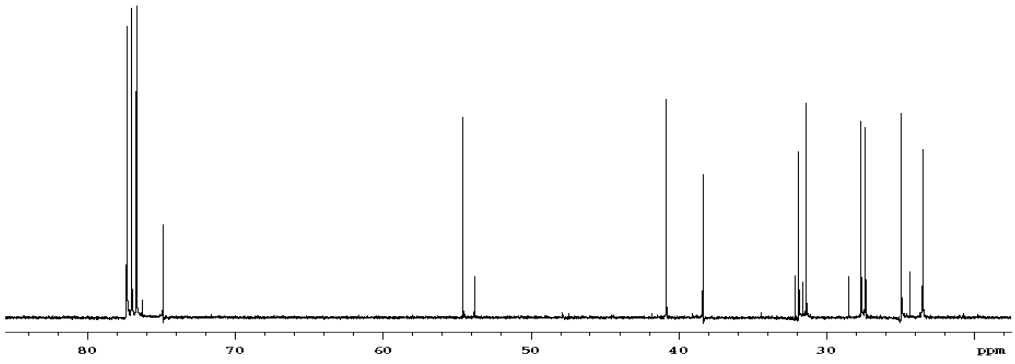


Figure 5.9: ^{13}C NMR spectrum for 2-pinanol

^{13}C NMR confirmed the product as an alcohol with carbon shift at 75 ppm as that indicated the presence of C-O in the compound. The mass spectrum confirmed the alcohol as 2-pinanol as it matched the library. No conclusive results can be confirmed from the proton NMR spectra as the O-H signal at between 3- 4 ppm was not observed.

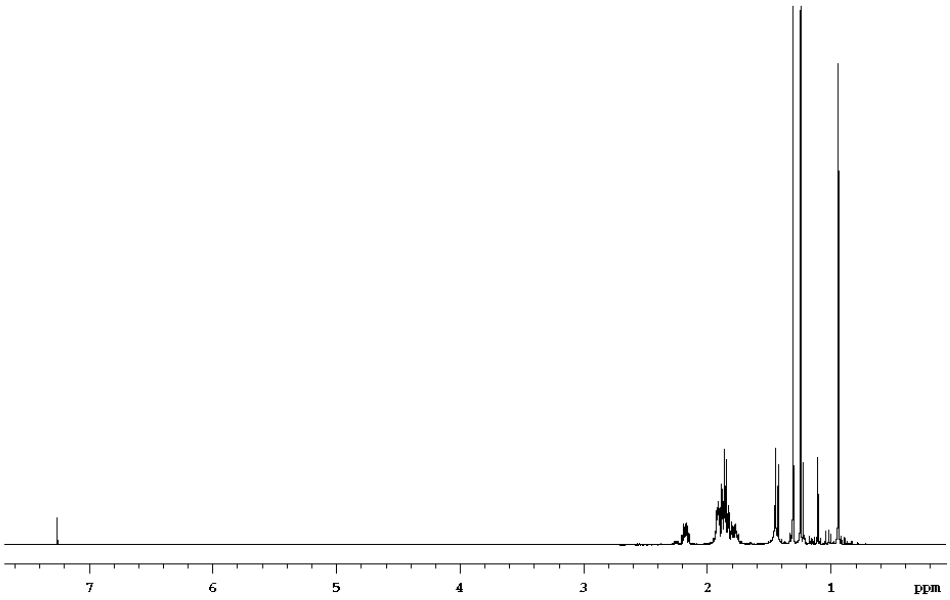


Figure 5.10: ^{1}H NMR spectrum for 2-pinanol

5.4.3 Effect of initiator loading

Oxidation was performed at 0.05 and 0.2% initiator loading to see what effect that will have on the conversion of pinane and selectivity of 2-pinanol.

Table 5.12: Results of effect of initiator loading on oxidation

Time (min)	Oxidation at 0.05 mol% loading			Oxidation at 0.2 mol% loading		
	%Conv.	% 2-pinanol	%Selec.	%Conv.	% 2-pinanol	%Selec.
30	8.3	6.6	79.5	9.6	7.6	79.2
60	16	12.7	79.4	16.9	14	82.8
90	21.4	17.5	81.8	20.7	16.9	81.6
120	24.3	20.1	82.7	23.9	18.4	77
150	25.7	20.8	80.9	27.4	21.1	77.1

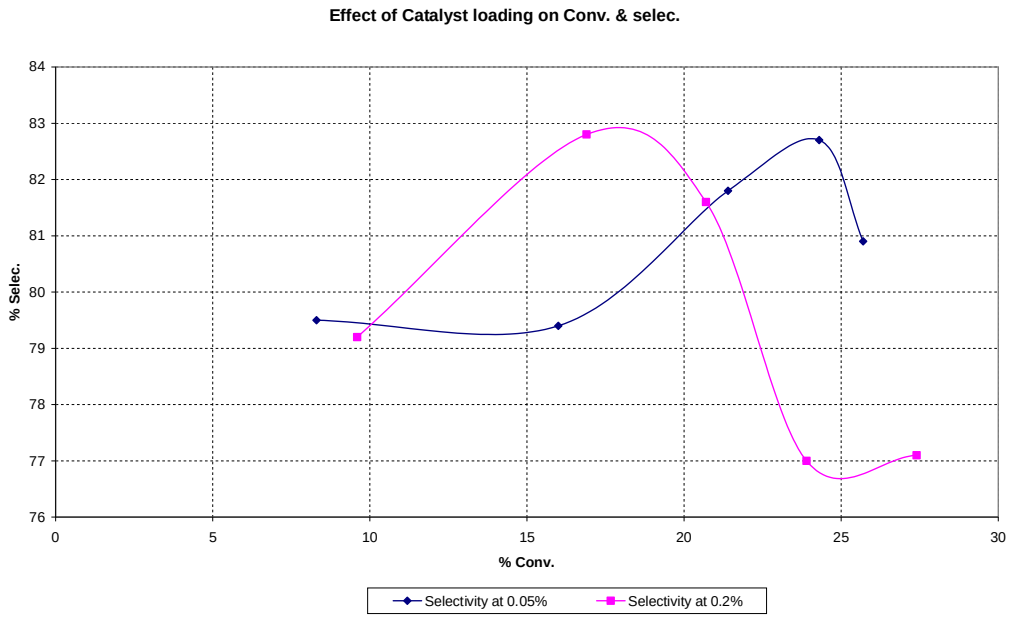


Figure 5.11: Effect of initiator loading on conversion and selectivity

The results showed a similar trend with regard to pinane conversion. In both cases the conversion after 2.5 h was 25.7 and 27.4% at 0.05 and 0.2% respectively. There was not a big difference in selectivity in both instances. At 0.2% mol initiator loading, the selectivity was higher (82.8%) after only 60 minutes while the same selectivity with 0.05% mol initiator loading was obtained after 120 min. The graph (Fig.5.11) shows that after the results reached a selectivity of 83%, the product started to decompose leading to selectivity drop. It will be advisable to stop the reaction after 82% selectivity to avoid forming more by-products so as to make the down stream processing (DSP) to be easy.

5.4.4 Effect of time

The reaction was run for a longer period of time to see what effect time has on the conversion of pinane and the selectivity of 2-pinanol. As reported (Kucher and Opeida, 1985), the oxygen-containing products, pinane hydroperoxide/ pinanol, can react further under the reaction conditions giving rise to low selectivity.

Table 5.13: Results of effect of time on oxidation

Time (min)	%Conv.	% 2-pinanol	%Selec.
0	0	0	
30	8.2	7.5	91.5
60	14.0	13.1	93.6
90	20.0	19.4	97.0
120	23.6	22.2	94.1
150	31.5	30.1	95.6
180	32.1	27.1	84.4
210	34.1	27.2	79.8
240	35.1	26.3	74.9
270	35.9	27.1	75.5
300	38.9	30.1	77.4
330	40.2	29.7	73.9

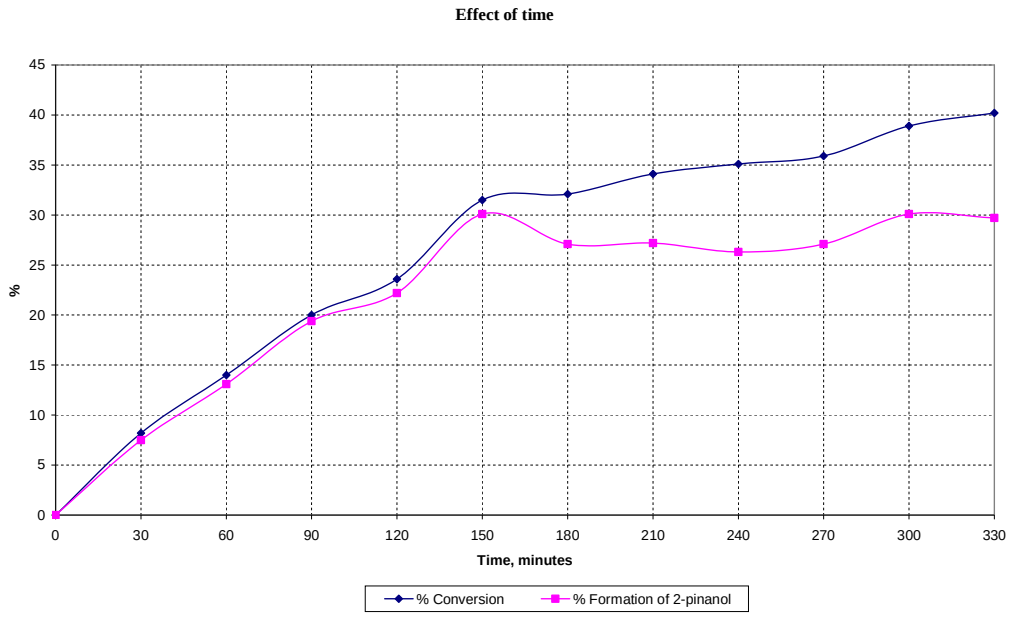


Figure 5.12: Effect of time on reaction profile

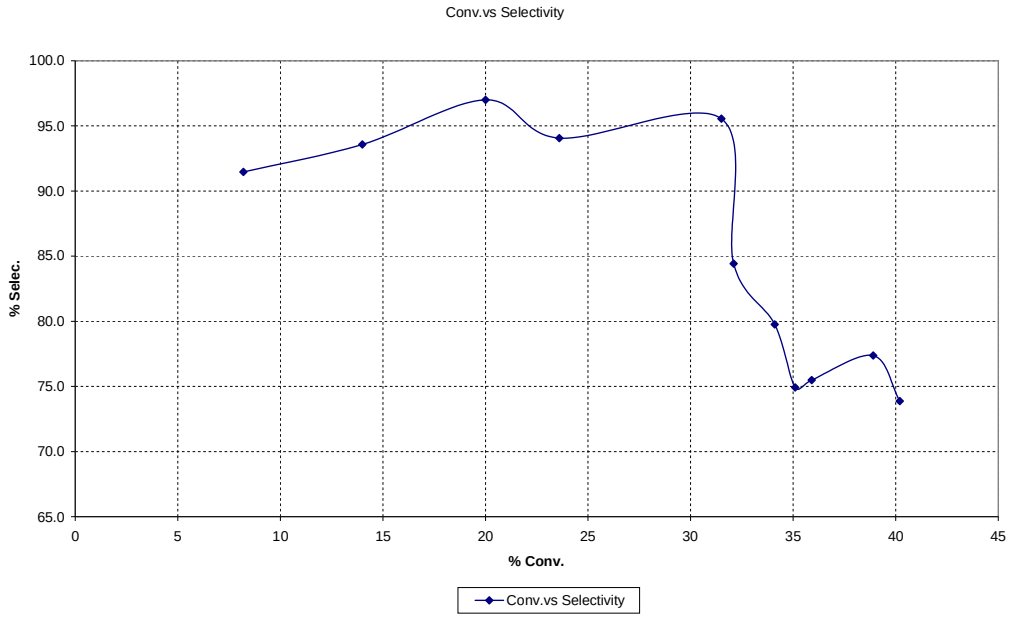


Figure 5.13: Effect of time on conversion and selectivity

The results show that at shorter reaction time, the oxidation was selective as higher selectivity (97.0%) was obtained after 90 min with a conversion of 20%. The reaction was allowed to run and after 150 min, a conversion of 31% with

selectivity of 95.6% was obtained. The results were still reasonable at this stage. However, as the reaction proceeds, the selectivity started to drop. The drop in selectivity was not accompanied by huge increase in conversion of pinane indicating that the pinane hydroperoxide/ pinanol started to react forming other by-product faster than the conversion of pinane to pinane hydroperoxide/ pinanol. The total reaction time was 330 min. After 150 min of reaction time, the selectivity started dropping to below 90% indicating the decomposition of the products to other impurities. When the reaction was stopped (after 330 min), the conversion was 40.2% with a selectivity of 73.9%.

CHAPTER 6: Conclusions

6.1 Conclusions

6.1.1 Enrichment of *cis*/*trans*-pinane mixture with more reactive *cis*-pinane

The hydrogenation of a mixture of $\alpha-$ and β-pinenes at 80˚C and 15 bar using a partially poisoned nickel catalyst resulted in the preparation of high purity *cis*-pinane with a *cis/trans* ratio of 20:1. The reaction was successfully reproduced in the 8L Parr reactor where kilogram quantities of *cis*-pinane were produced.

6.1.2 Oxidation of enriched *cis*-pinane

The oxidation of *cis*-pinane was conducted under various conditions using different oxidants (*t*-butyl hydroperoxide, oxygen and hydrogen peroxide), catalyst ($Co(OAc)_2$, $Mn(OAc)_2$, CuPcNaY, FePcNaY and FePcMORD), initiators (azoisobutyronitrile AIBN, *t*-butyl hydroperoxide and benzoyl peroxide) and reactor types (round bottom flask, baffled reactor, pressure reactors and falling film micro reactors).

Benzoyl peroxide proved to be the best initiator in our studies as it gave reasonable results in terms of both the conversion as well as the selectivity of 2-pinanol in all the reactors except when the falling film micro reactor was

used; benzoyl peroxide was insoluble in the mixture and the reaction could not be carried out in the falling film micro reactor.

The use of novel zeolite catalyst did not help as the reactions still needed higher temperatures to obtain reasonable conversion. However, the selectivity of 2-pinanol could not be improved.

The most successful reaction was obtained using benzoyl peroxide as an initiator and oxygen as oxidant in the presence of NaOH base. The reaction was conducted at 110˚C under 3 bar oxygen pressure and 2-pinanol was obtained at a selectivity of 96% and a conversion of 31%. The unreacted pinane could easily be distilled off and undergoes further oxidation to improve the overall yield of 2-pinanol per pass of pinane. The oxidation reaction had to be stopped after 31% conversion because the 2-pinanol started to decompose forming other unwanted products. The following compounds were identified by mass spectroscopy as major impurities in the oxidation reaction (iso-pinocampheol or 3-pinanol; pinane -2.9-diol, 1-acetyl-2,2dimethyl-3-ethylcyclobutane and 2-(1-acetyl-2,2-dimethyl-cyclobut-3-yl)ethanol. All these impurities have also been observed previously (Brose, Pritzkow and Thomas, 1992).

From the statistical experiments, temperature showed a negative contribution towards the selectivity of 2-pinanol. This was also confirmed during the optimisation reaction as the selectivity of 2-pinanol dropped to below 90% when higher temperature (120˚C) was used. Pressure showed no effect on

selectivity. Both low and high pressure had similar selectivity profiles on the reaction. The initiator loading showed a negative contribution to the selectivity of 2-pinanol since higher loading led to poorer selectivity.

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ANNEXURE A: GC / MS spectra of residues

```
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Operator   : Clement Stander
Acquired   : 22 May 2007  10:28     using AcqMethod LINALOOL
Instrument :   GC/MS Ins
Sample Name: TBC-4 Bar-Res
Misc Info  : Chokwe
Vial Number: 1
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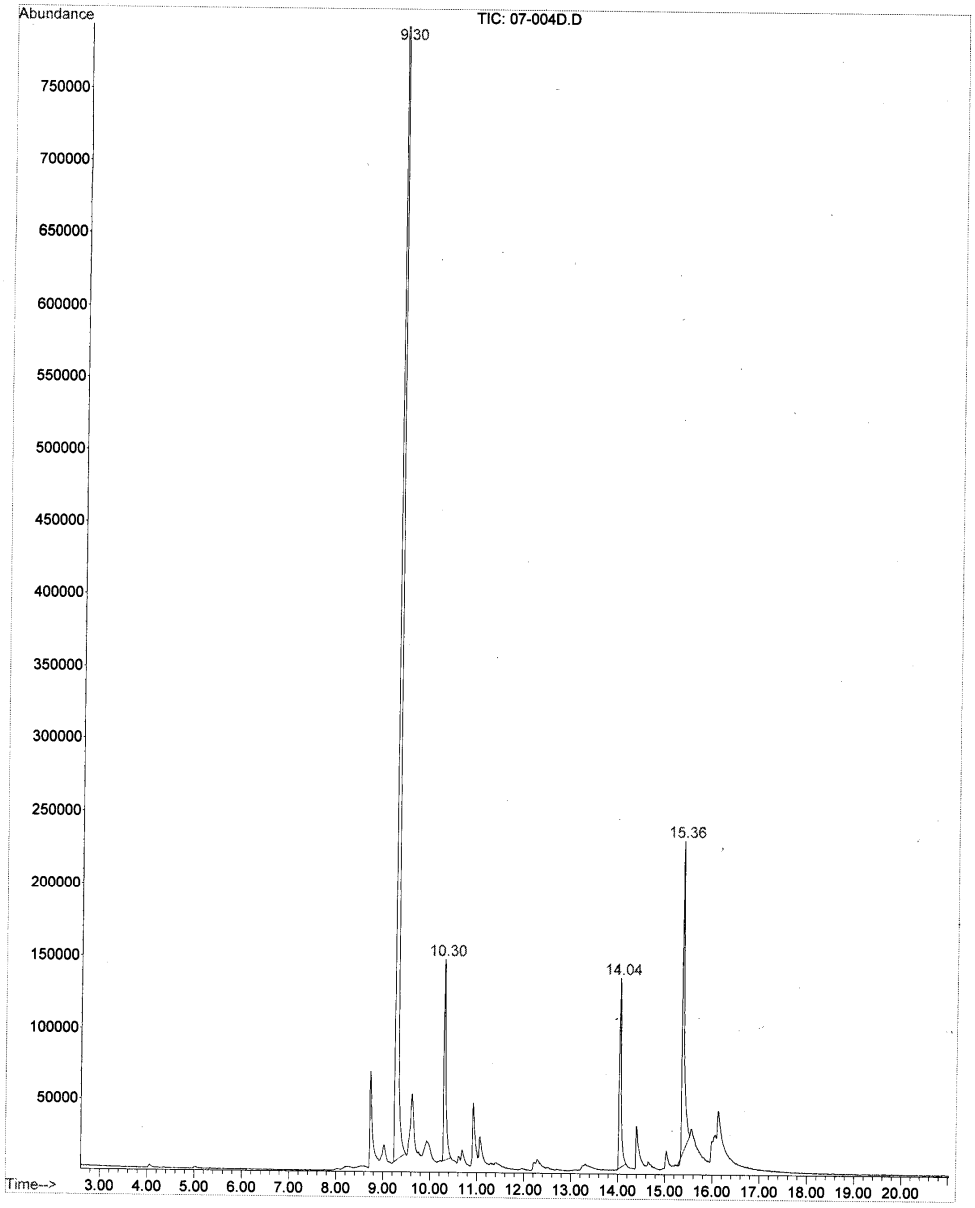

Figure 8.1: GC/MS spectrum of the 2-pinanol distillation residue

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Misc Info : Chokwe
Vial Number: 1

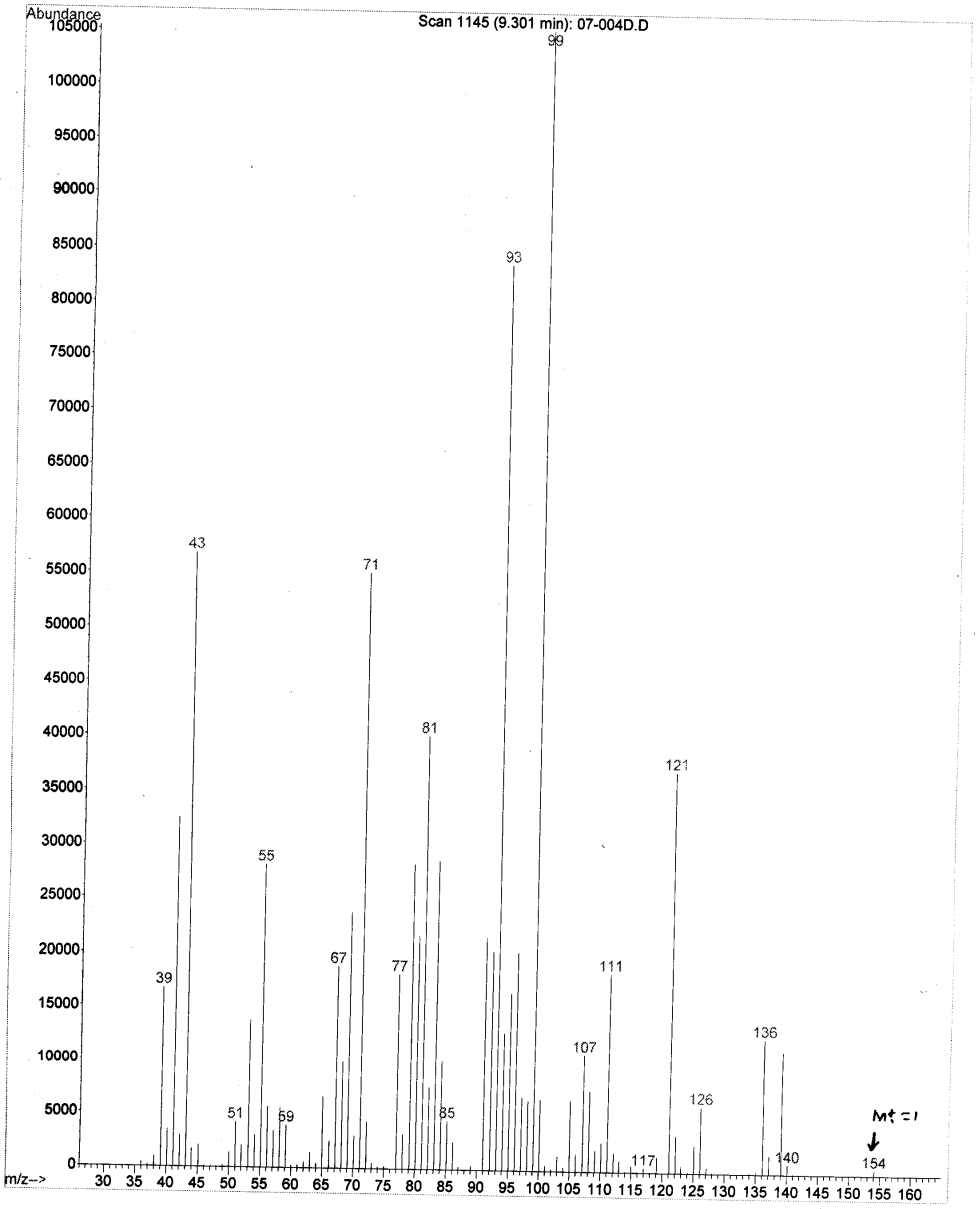

Figure 8.2: Mass spectrum for 2-pinanol (9301 min)

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Sample Name: TBC-4 Bar-Res
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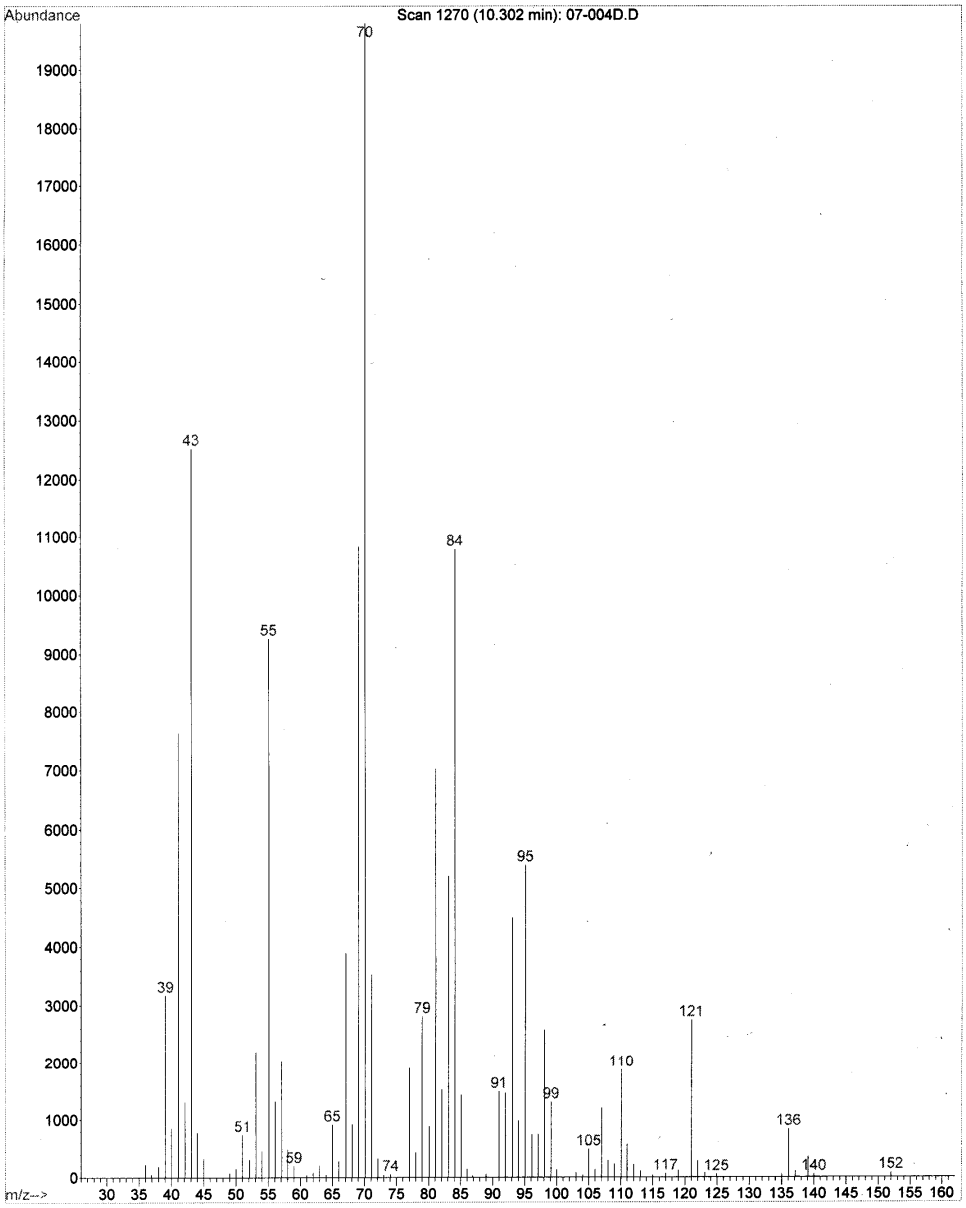

Figure 8.3: Mass spectrum of by-product 3-pinanol (10.302 min)

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Vial Number: 1
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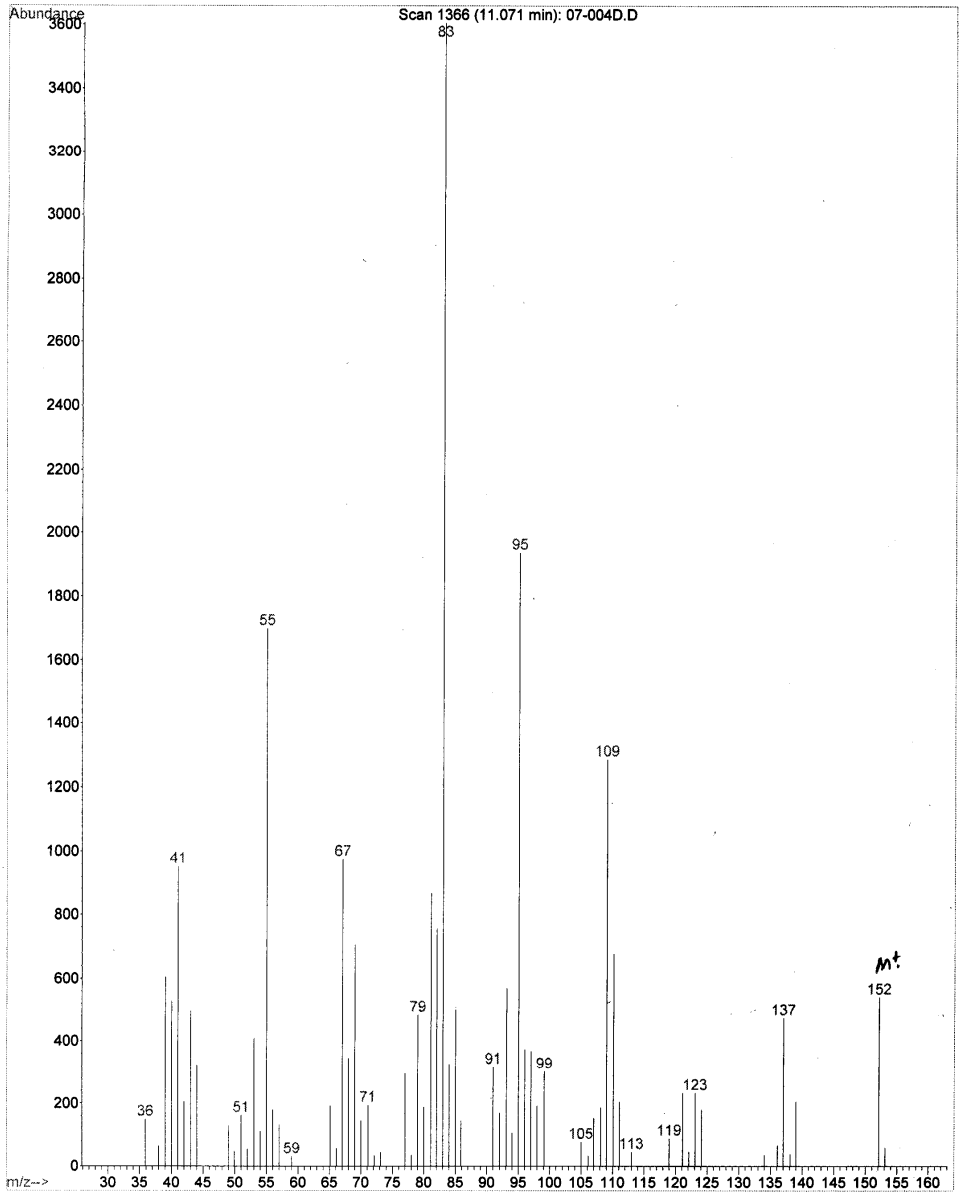

Figure 8.4: Mass spectrum of by-product 1-acetyl-3-ethyl-2,2-dimethyl cyclobutane (11.071 min)

```
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Instrument :   GC/MS Ins
Sample Name: TBC-4 Bar-Res
Misc Info  : Chokwe
Vial Number: 1
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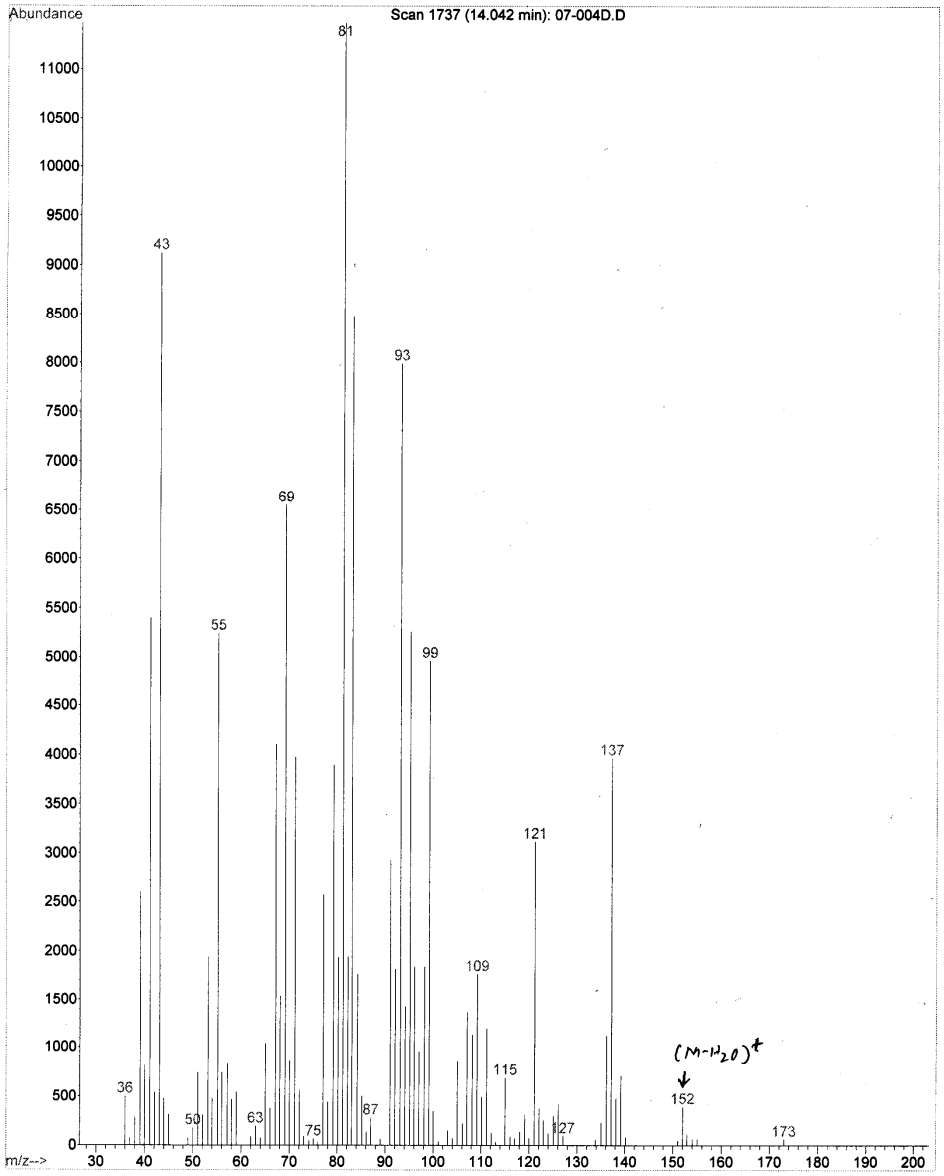

Figure 8.5: Mass spectrum of by-product 2-(1-acetyl-2,2-dimethyl-cyclobut-3-yl)ethanol (14.042 min)

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Acquired   : 22 May 2007  10:28     using AcqMethod LINALOOL
Instrument :   GC/MS Ins
Sample Name: TBC-4 Bar-Res
Misc Info  : Chokwe
Vial Number: 1
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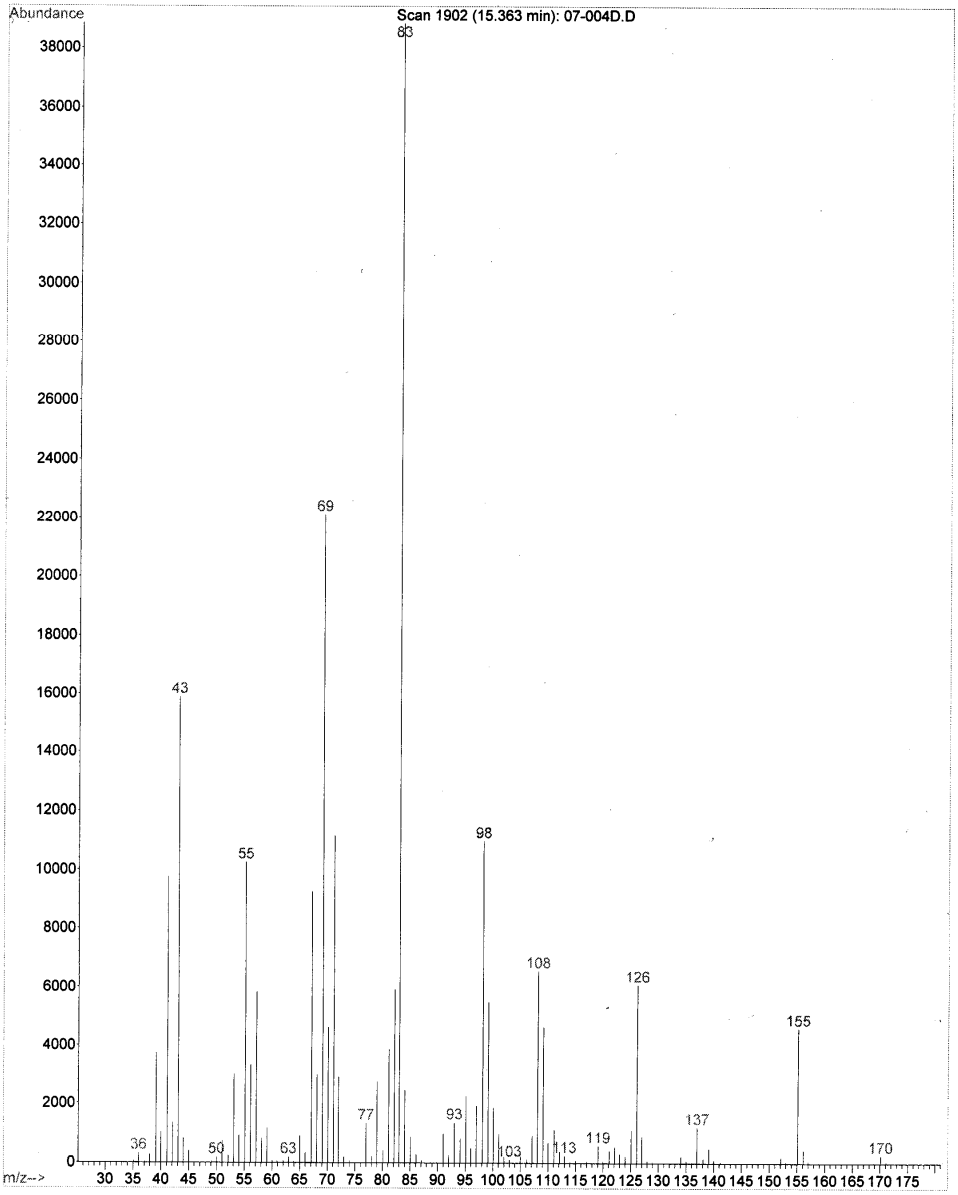

Figure 8.6: Mass spectrum of by product *trans*–pinane 2,9-diol (15.363 min)