Synthesis of Polyols for the preparation of biodegradable polyurethanes

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Synthesis of Polyols for the Preparation of Biodegradable Polyurethanes

Submitted by

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Abbreviations

CDI	Cyclohexane diisocyanate
CTAB	Cetyltrimethylammonium bromide
CTAP	Cetyltrimethylammonium permanganate
DCM	Dichloromethane
DTAB	Dodecyltrimethylammonium bromide
DTAP	Dodecyltrimethylammonium permanganate
FT-IR	Fourier transform infrared
HMDI	Hexamethylene-1,6-diisocyanate
m-CPBA	meta-Cchloroperbenzoic acid
MDI	Methylene diphenyl diisocyanate
NMR	Nuclear magnetic resonance
UMIST	The University of Manchester Institute of Science and Technology
RIM	Reaction injection molding
Rpm	Rotations per minute
TDI	Toluenediisocyanate
TDTAB	Tetradecyltrimethylammonium bromide
TDTAP	Tetradecyltrimethylammonium permanganate
br	Broad
s	Singlet
d	Doublet
m	Multiplet

Abstract

Natural oils such as rapeseed oil do not contain the necessary chemical functionality (hydroxyl groups) required for the synthesis of the target biodegradable polyurethane. The main aim of this work was to find an appropriate dihydroxylation reaction route to convert natural oils containing double bonds into polyols that can be used to produce biodegradable polyurethanes. We were particularly aiming for a low-cost process which could also be scaled up. Initial experiments were performed on model substrates containing double bonds (hexene and decatriene) to allow complete characterization of the compounds and consequently gain a more thorough understanding of the chemistry taking place. Several methods were investigated to find a suitable process to dihydroxylate alkenes and also to convert the unsaturated oils into polyols suitable for the preparation of polyurethanes. The permanganate and water system was suitable for the model compounds, but requiring a stoichiometric amount of catalyst was a disadvantage for scale-up. The results of hydroxylation reaction of alkenes using hydrogen peroxide and formic acid were not encouraging. The results of hydroxylation reactions using phosphoric acid and hydrogen peroxide were quite encouraging. The reactions using natural oils were quite successful producing polyols with the hydroxide numbers of 187 and 164 for soyabean and rapeseed samples respectively. The method using organic peroxide, meta-chloro perbenzoic acid (*m*-CPBA) was also encouraging. The ^{1}H NMR analysis of the reaction of *m*-CPBA with the decatriene model compound revealed that *m*-CPBA selectively hydroxylates the internal double bonds. However, when natural oils, water and *m*-CPBA powder were mixed and stirred the reaction mixtures became dough-like and were therefore difficult to manipulate.

CONTENTS

CHAPTER 1

INTRODUCTION

1.1. Polyurethanes

Polyurethanes are polymers that include materials which combine the carbamate functional group as well as other functional groups, such as ester, amide and urea. The name polyurethane was derived from ethyl carbamate, known as urethane. These polymers were discovered by Otto Bayer and co-workers[1-3] in 1937. The usual production method for polyurethanes is the reaction of a polyfunctional isocyanate with a polyol or other reactant containing two or more antagonist groups, most often hydroxyls. A wide variety of branched or cross-linked polymers can be formed as the functionality of the hydroxyl-containing reactant or the isocyanate can be adjusted. The hydroxyl-containing groups cover a wide range of molecular weights and types, including polyester and polyether polyols. The polyfunctional isocyanates can be aromatic, aliphatic, cycloaliphatic, or polycyclic in structure and can be used directly as produced or modified. This flexibility in the selection of the reactants leads to the wide range of physical properties that allows polyurethanes to play an important role in the world market for quality products.

Polyurethanes have commercially been developed in Germany from the time of the early reports in 1930s, through World War II, to the present day. In addition there was also early interest in polyurethane chemistry at DuPont and other U.S companies, at ICI in the UK, and in other locations. The rapid growth of the polyurethane industry in the United States awaited the transfer in 1950s of the Bayer technology achievements that have allowed the manufacture of a broad spectrum of foams, both flexible and rigid, elastomers, coatings, adhesives and binders.

The recent growth in the commercial importance of polyurethane products formed by reaction injection molding (RIM) has provided the impetus for the basic studies of relationships between molecular structure and bulk properties. For example, RIM technology enables the conversion of polyurethane elastomers into automotive components such as bumpers, fascia, and other exterior parts was well as non-automotive products, including business-machine housings and parts for heavy-duty industrial equipment. The ability to select RIM formulations for applications covering such a range of required physical properties is being facilitated by the understanding of the segmented structures of such polyurethanes and how the chemical nature and length of these segments control the morphology.

Briefly, polyurethane elastomers can be considered as block copolymers consisting of alternating polyurethane and polyol segments. The polyurethane and the polyol segments are designed as hard and soft segments, respectively, since they are below and above their softening temperatures at the normal use temperatures. The elastomeric properties of these block copolymers are generally attributed to the phase separation of the polyurethane and the polyol segments, whereby the hard polyurethane domains serve as cross-links and filler particles in the matrix of the polyol soft segment. Studies by both physical and chemical methods have shown that bulk properties depend on the nature and extent of phase separation.

1.1.1. Preparation of Polyurethanes

As stated previously, polyurethanes result from the irreversible reactions between diols with isocyanates. Unlike most other polycondensation reactions, urethane formation does not involve release of small molecules such as H_2O, HCl, CH_3OH, etc. The general reaction is shown in Scheme 1.

$$\mathrm{nOCN(CH_2)_6NCO + nHO(CH_2)_6OH \longrightarrow \left((CH_2)_6{-}NH{-}CO{-}O(CH_2)_6{-}OCONH \right)_n}$$

Scheme 1. Formation of polyurethanes

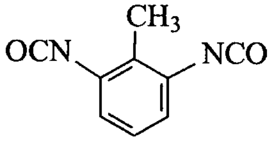
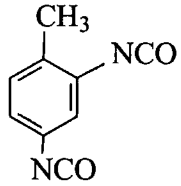
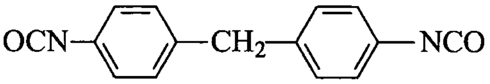
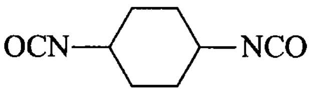
Although the reaction can be performed in the absence of catalysts, tertiary amines and metal salts, namely dibutyl dilaurate are known to accelarate the reaction rate by a factor of 10^3.[4-7]

1.1.1.2. Components of Polyurethanes

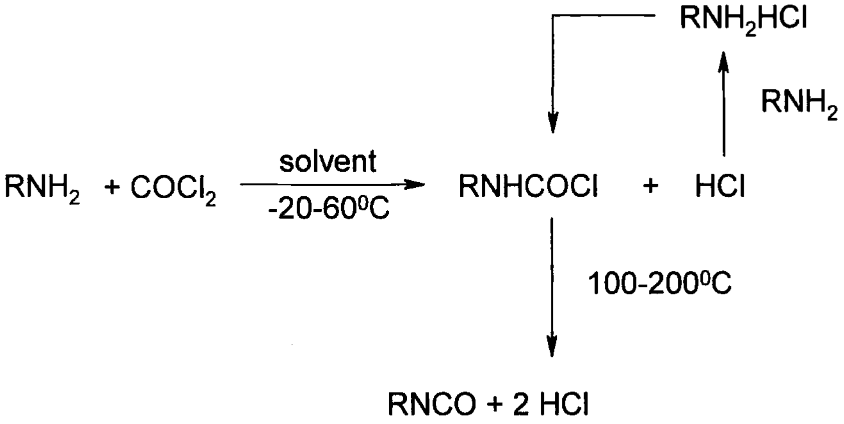
1.1.1.2.1. Isocyanates

Among the isocyanates that are commonly used in polyurethane synthesis, those quoted in Table 1 should be noted. Toluene diisocyanate (TDI) is usually a mixture of toluene-2,6-toluene-2,4-diisocyanate in the ratio of 80:20. With TDI, the two isocyanate functions exhibit markedly different reactivities, and the rate expressions have to be considered. However, the distribution of chain length is not significantly affected by this difference in reactivity, if the reagents are in stoichiometric proportions.

Table 1. Structure of the isocyanates used in polyurethane synthesis

Diisocynate	Structure	Abbrevation
Toluene-2,6-diisocyanate		TDI
Toluene-2,4-diisocyanate		TDI
Methylene diphenyldiisocyanate		MDI
Cyclohexane diisocyanate		CDI
Hexamethylene-1,6-diisocyanate	$OCN—(CH_2)_6—NCO$	HMDI

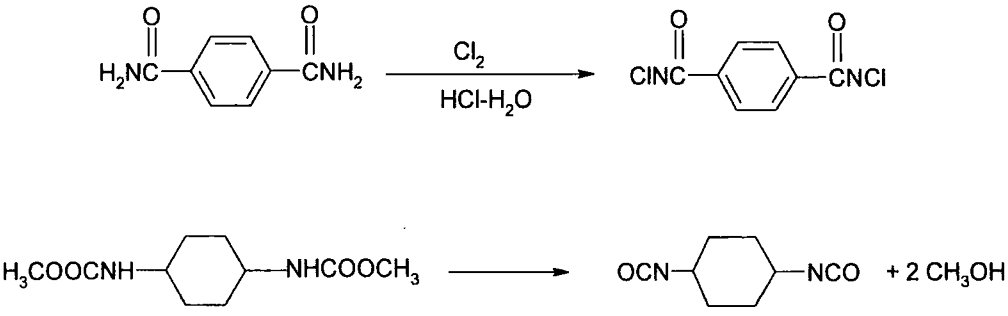
These series of multifunctional aromatic or aliphatic isocyanates are used as crosslinkers in polyurethane foams especially. More detailed information concerning synthesis, reactions and manufacture of isocyanates can be found in the literature.[4-12] Polyurethane isocyanates are usually produced commercially by the phosgenation of amines (Scheme 2):



Scheme 2. Production of polyurethane isocyanates

Solutions of the amine and excess phosgene are vigorously mixed to form a slurry of carbamic chloride and amine hydrochloride. Upon gradual heating, the amine salt reacts preferentially with excess phosgene. The resulting carbamic chloride releases HCl to form the isocyanate. Unreacted phosgene, HCl and solvent are recovered and the product is usually distilled.

The classical Curtius,[13,14] Hofmann[15-17] and Lossen[18] rearrangements are useful laboratory procedures for isocyanate synthesis, but are not commercially significant. However, a Hofmann-type reaction has recently been applied to the manufacture of benzene-1,4-diisocyanate and trans-cyclohexane 1,4-diisocyanate (Scheme 3).



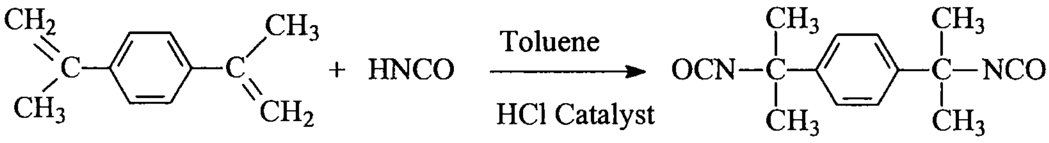
Scheme 3. The synthesis of benzene 1,4-diisocyanate and trans-cyclohexane-1,4-diisocyanate

Alkyl isocyanates can be synthesized from salts of cyanic acid and alkyl halides or sulfates: the most important is methoxymethyl isocyanate (Scheme 4).

$$\mathrm{KCNO} + \mathrm{CH_3OCH_2Cl} \longrightarrow \mathrm{CH_3OCH_2NCO} + \mathrm{KCl}$$

Scheme 4. Synthesis of methoxymethyl isocyanate

The reaction of olefins with isocyanic acid gives isocyanates. Unless a stable carbenium ion can be formed at the site of NCO addition, the yields are poor; therefore, this method is used only for tertiary isocyanates (Scheme 5).



Scheme 5. Synthesis of tertiary isocyanate

1.1.1.2.2. Polyols

By convention, two component polyurethane systems consist of a compound or mixture of compounds containing functional groups which react with isocyanates. The functional groups usually contain active hydrogen atoms. In general, this active hydrogen is connected to an oxygen, nitrogen or sulphur. Most often the reactant is a polyfunctional alcohol or polyol whose reaction product with the isocyanate yields the carbamate or urethane linkage. The second most frequent components are polyfunctional primary or secondary amines. A blend of polyamine and polyol can also be used.

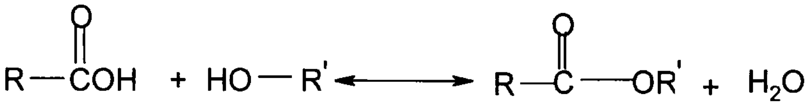
The simplest polyols are glycols, such as ethylene glycol, 1,4-butanediol, and 1,6-hexanediol. These low molecular weight reactants result in polymer segments that are hard and stiff because of the high concentration of urethane groups formed in the polymer chain. Current polyurethane elastomers are formulated with low molecular weight glycols or diamines in combination with longer chain polyols.

Higher molecular weight polyols produce polymer chains with fewer urethane groups and more flexible alkyl chains. These soft segments are more flexible than those produced from low molecular weight polyols. Most high molecular weight polyols are produced by polymerization processes. Castor oil, a trihydroxy fatty triglyceride, is an example of a naturally occurring polyol.

High molecular weight polyols form polyethers and polyesters. Both are low molecular weight polymers terminated by hydroxyl groups. Manufacturing processes allow a wide variety of materials differing in molecular weight, chain structure, functionality, and reactivity to be prepared. Long-chain polyols (1000-6000 mol wt) with low hydroxyl functionality give a more rigid and cross-linked product.

Polyether-based polyols obtained by propoxylation or ethoxylation by a variety of starting materials are much more widely used than polyester or polyether based polyols because polyurethane production is heavily weighted toward flexible and rigid foams. They are low density materials that expose a large surface area to the atmosphere and whose applications, therefore, require the more hydrolytically stable polyether backbone. Finally polyether-based flexible foams are softer and more resilient. Compared with polyethers, polyesters provide a more polar bond structure and a more basic oxygen with which stronger dipolar and hydrogen-bonding interactions can occur with the urethane segments. Thus a polymer with better chemical properties is formed.

Polyester polyols[19] are prepared by condensation or step-growth polymerization. The reaction for the production of a polyester involves an equilibrium (Scheme 6). Formation of polyester chains is a random process and leads to a broad distribution of molecular weights. Linear polymers are formed from bi-functional monomers. The main diacids for polyester polyols are adipic acid and the three isomeric phthalic acids. Adipic acid is used for applications requiring flexibility (flexible foams, cast elastomers), whereas phthalic anhydride is used for those requiring rigidity. Typical diols include ethylene glycol, 1,4-butanediol, and 1,6-hexanediol.



$$R-\overset{O}{\overset{\|}{C}}OH + HO-R' \rightleftarrows R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

Scheme 6. The esterification reaction.

Polyurethanes made from polyester polyols are low molecular weight (<3500g) hydroxyl-terminated polymers, produced by using an excess of hydroxyl equivalents. Typically, hydroxyl:carboxyl ratios range from 2:1 to 15:14. The nearer to unity the ratio is the higher the molecular weight. The extent of conversion of carboxylic acid is typically 99.9%. This high degree of conversion is required because in many applications, the residual acidity of carboxylic groups from even a 99 % complete reaction could retard the final cure of polyurethane system.

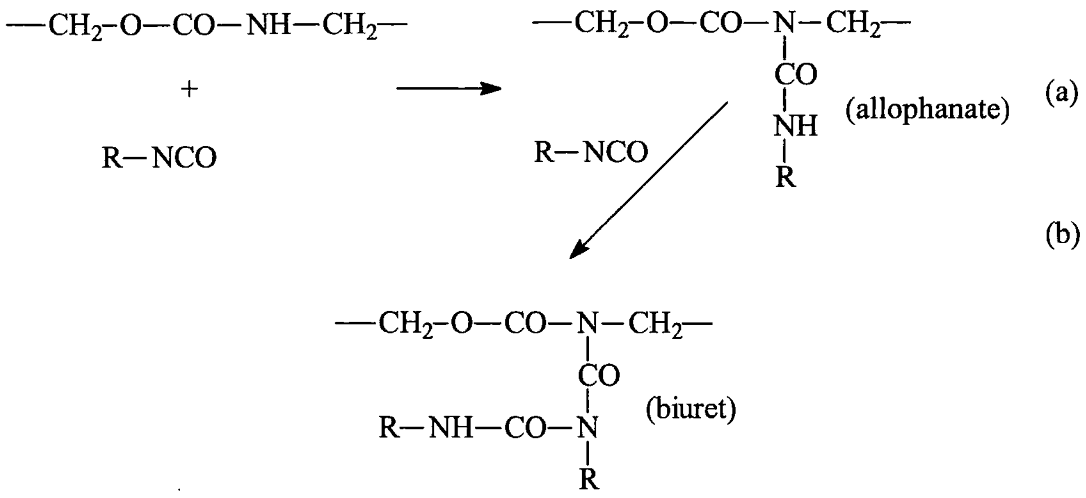
Polyether polyols[20] are prepared by an anionic, ring-opening, addition polymerization of epoxides. The polymerization has the characteristics of a chain reaction, whose chemistry may be represented by initiation, propagation and termination steps.

Ethylene oxide (EO) and propylene oxide (PO), two large volume and low priced epoxides produced by the oxidation of ethylene and propylene, respectively, are the raw materials on which these polyols are based.

Filled polyethers are important ingredients of flexible and semi-flexible foams. These polyols contain finely divided solids in the form of a dispersed phase in the base polyol which give polyurethanes with exceptional properties like increasing the resilience and load–bearing properties of flexible foams.

1.1.2. Side Reaction in Polyurethane Synthesis

There are two known reactions that can occur during polyurethane formation (Scheme 7). Formation of allophanate (reaction a) and of biuret linkages (reaction b) occurs from an isocyanate function and an already existing urethane link. They not only affect stoichiometry, but they also introduce branching, yielding crosslinked species as depicted in Scheme 7.



Scheme 7. Side reaction in polyurethane formation

1.1.3. Polyurethane Foams

The polyurethanes, originally intended as fibers competitive with nylon, found greatest commercial success as foams.[12, 21-24] Use of both types and numerous specialized foams has grown steadily since the original technology was developed over 30 years ago. Acceptance can be attributed to excellent properties at reasonable cost and simple, easily controlled production processes. Foam products are made from liquid materials and are available in a wide range of types and forms designed for specific applications.

1.1.3.1. Reactants

Polyurethane foams, or urethane foams as they are often called, are prepared, except for a few specialities, from aromatic isocyanates and mainly aliphatic polyols. Toluene diisocyanate (TDI) usually the commercial blend of 80% 2,4- and %20 2,6-isomers, is chosen for most flexible foams.

The traditional flexible urethane foam polyol is a 3000-6000 molecular weight polyether triol prepared by the addition of propylene oxide to glycerol. Linear diols of similar equivalent weight are sometimes added to minimize branching.

Highly branched polyether polyols with functionalities as high as 8 are suitable to prepare rigid urethane foams. The increased branching and shorter aliphatic chains contribute to more rigid molecules. Because of the lower hydroxyl equivalent weight of the polyol, a higher concentration of aromatic polyisocyanates is needed to obtain the same equivalent ratio. This in turn increases the aromatic structure and therefore molecular rigidity.

If the polyol is too highly branched, it becomes weak and difficult to process. Urethane foam formulations usually contain isocyanate and hydroxyl groups in approximately equivalent concentrations.

Flexible urethane foams are formed by a process of simultaneous polymerization and expansion. The gas responsible for expansion is primarily carbon dioxide produced by the reaction of isocyanate and water (Scheme 8).

$$\mathrm{R{-}NCO} + \mathrm{H_2O} \longrightarrow \mathrm{R{-}NH_2} + \mathrm{CO_2}$$

$$\mathrm{R{-}NH_2} + \mathrm{OCN{-}R} \longrightarrow \mathrm{R{-}NH{-}CO{-}NH{-}R}$$

Scheme 8. The reaction of isocyanates with water

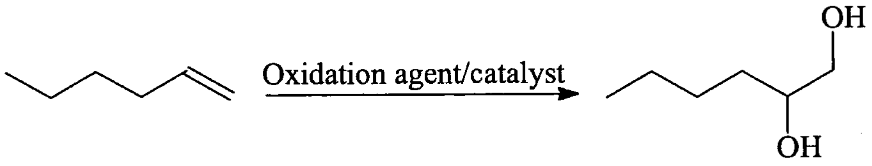
The isocyanate concentration is calculated at 90-120 % of the theoretical amount required to react with both hydroxyl groups and water. This percentage is known as the isocyanate index. The reaction with water also produces substituted urea cross-links, which stabilize the expanding foam. Carbon dioxide is an effective blowing agent but diffuses out of completely formed and closed cells more rapidly than it can be replaced by nitrogen and oxygen from the air, to prevent serious foam shrinkage, the cells must be open to allow the air to penetrate.

Much of the commercial acceptance of urethane foams can be attributed to catalysts that precisely control the polymerization and blowing process. This control is essential for flexible urethane foams. Imbalance between polymerization and foam expansion can lead to a foam collapse and serious imperfections.

Polyether-urethane foams constitute a large fraction of commercial production. The polyester urethane foams that were originally produced are still available for special applications. Flexible foams are based on hydroxyl-functional polyesters prepared from adipic acid, simple glycols, and glycerol. The technology of polyester-urethane foam production is similar to that of polyether-urethane foams. Standard organic surfactants can be used instead of the silicone copolymers and, because most polymers terminate in primary hydroxyl groups, milder organic bases can be used as catalysts. The viscosity of polyesters is usually higher than that of polyethers, requiring some changes in processing.

1.2. Dihydroxylation of Alkenes

In the literature a number of routes utilizing various oxidation agents and catalyst systems for the dihydroxylation of alkenes as illustrated generally in Scheme 9 have been reported. Each route has been briefly explained in the following section.



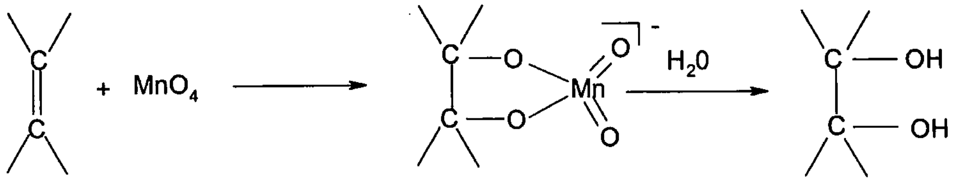
Scheme 9. Potential routes for dihydroxylation of alkenes

Dihydroxylation of the double bond of unsaturated fatty acids has been accomplished through the use of a number of oxidizing agents. The configuration of a specific vicinal dihyroxy acid is dependent upon the geometrical configuration of the unsaturated fatty acid from which it is derived (cis or trans) and the reagent employed to introduce the hydroxyl groups.

1.2.1. Oxidation strategies

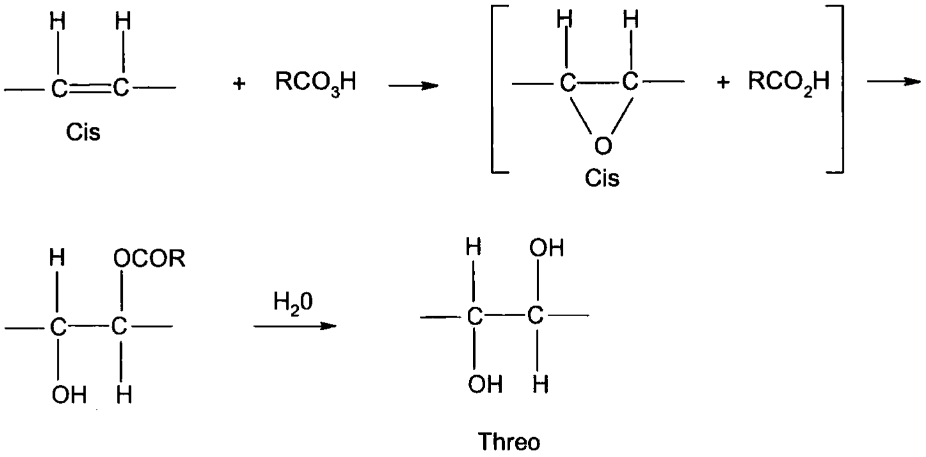
1.2.1.1. The Use of Permanganate as Dihydroxylation Agent

Cis hydroxylation by MnO_4^- or OsO_4 is attributed to the formation of a cyclic diester which hydrolyzes without inversion. Through the use of potassium permanganate[25-27] it has been demonstrated that hydroxyl groups originate from the permanganate (Scheme 10).



Scheme 10. Dihydroxylation by MnO_4^-

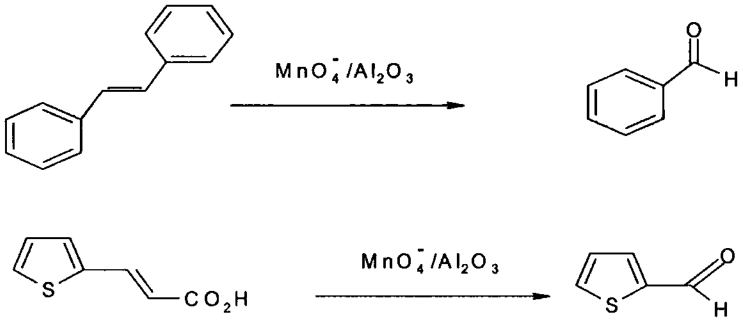
Dihydroxylation by means of peroxy acids is believed to proceed through the epoxide, which reacts with acid to open the ring and then form the acyloxy-hydroxy compound. Hydrolysis of the latter leads to the dihydroxy compound (Scheme 11).



Scheme 11. Dihydroxylation by peroxy acids

Permanganate has been the most popular oxidant whose reactions are studied in general organic chemistry textbooks, and its chemistry has a long and extensive story. Permanganate is frequently proposed as the prototypical stoichiometric oxidant giving metal ion or oxide products for which green chemistry is searching replacement using catalytic oxidations. The main problem of the use of permanganate arises from the need of stoichiometric amounts and the production of large amounts of metal by-products, rather than from its toxicity. Indeed, recycling of manganese dioxide, by reducing the product in basic media can help to circumvent the problem of waste making the use of permanganate more environmentally attractive for industrial applications. Permanganate is a strong oxidant that has been used for the degradation of industrial pollutants and metal ions in effluent. Thus, it is particularly suitable to oxidize phenols that are organic pollutants. Phenols are found in high concentration in industrial waste waters from the petrochemical industry and paint stripping.

The wide interest in permanganate has promoted a series of studies to find effective ways of insolubilizing the oxidant allowing separation and reuse. In this way, it has been found that the activity and selectivity of permanganate can be modulated by adsorption on various solid supports. In contrast to the products obtained when an inert support such as bentonite is used, permanganate adsorbed on moist alumina cleaves C-C bonds with the formation of aldehydes in good yields (70-95%) under mild conditions. Apparently, the Lewis acidity[28] of alumina participates in the proton-transfer step that accompanies the oxidation reactions (Scheme 12). Systematic studies on the specific reactivity of supported permanganate have, however, not been undertaken. Supported permanganate may be an interesting oxidant, provided that a recycling/reoxidation procedure is devised making its re-use possible.[29]

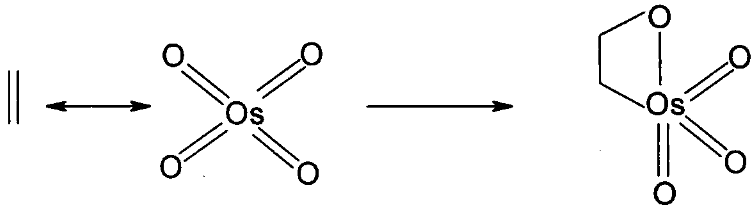


Scheme 12. Cleavage of double bonds by alumina

1.2.1.2. The Use of Osmium Tetroxide as Dihydroxylation Agent

Osmium tetroxide[30-33] (OsO_4) is the most reliable reagent available for the cis hydroxylation of alkenes to give the corresponding cis-diols. The cis hydroxylation of alkenes by osmium tetraoxide is well established to take place via the formation of an osmium(VI) intermediate which on reductive or oxidative hydrolysis yields the corresponding cis-diol.

The oxidation of alkenes by osmium tetraoxide is thought to proceed via direct oxygen attack at the unsaturated center (Scheme 13). The six electron transition state thus formed will lead to the cis addition of osmium tetraoxide to the alkene,

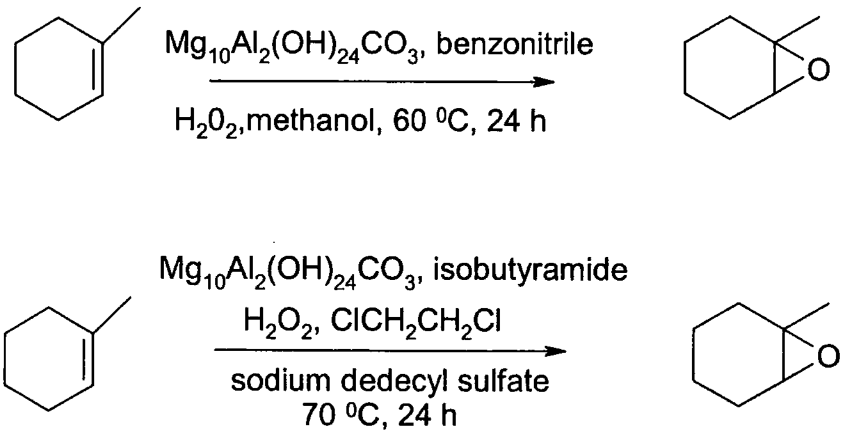


Scheme 13. Attack of osmium tetraoxide to double bond

Although stoichiometric oxidations of alkenes by osmium tetraoxide usually give better yields of diol products and are particularly applicable for the small-scale oxidation of precious materials, it is more usual, for reasons of cost and convenience, to use osmium tetraoxide catalytically in the presence of reagents like hydrogen peroxide, metal chlorates, *tert*-butyl hyroperoxide, *N*-methylmorpholine *N*-oxide, sodium periodate, sodium hypochlorite or with oxygen. Various methods are used for hydroxylation of alkenes with these reagents.

1.2.2. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide

Considering the environmental and economic conditions hydrogen peroxide is probably the best terminal oxidant after dioxygen.[34-37] Indeed, in certain circumstances, it is better than oxygen so far as O_2/ organic mixtures can sometimes spontaneously ignite. As a result, epoxidation systems that use hydrogen peroxide in conjunction with catalytic amounts of cheap, relatively non-toxic metals are potentially viable for large-scale production of inexpensive products, and for specialized applications in development, process, and research. Typical hydrotalcite epoxidations using 30 % hydrogen peroxide with two different peroxide carriers namely, benzonitrile and *iso*-butyronitrile are demonstrated in reactions in scheme 14 respectively.



Scheme 14. Hydrotalcite epoxidation

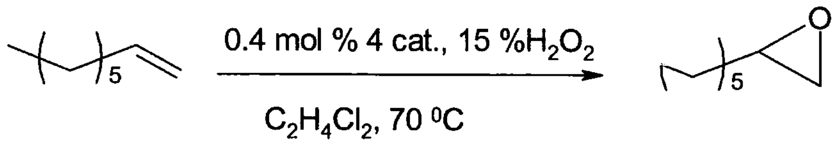
1.2.2.1. Soluble Metal Oxides

1.2.1.1.1. Polyoxometalates

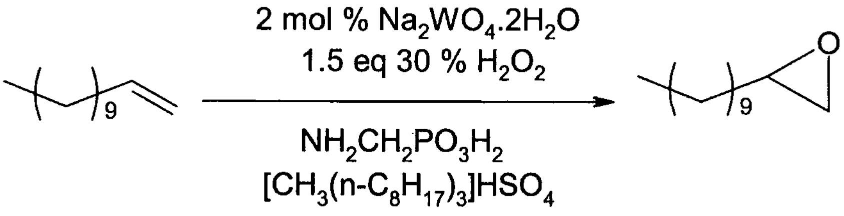
Polyoxometalates are salts composed of complex anions incorporated with two or more metal cations. They act as homogeneous epoxidation catalysts, but the conversions obtained, the selectivities for epoxide products, and the range of solvents that can be used for the reaction are mostly inferior compared to other methods. For example, $(R_4N)_6SiW_{10}Fe(OH_2)_2O_{38}$ (where R = alkyl) salts epoxidize aliphatic alkenes slowly at 32 °C in acetonitrile but also mediate C-H activation of alkanes, causing lack of selectivity. Better selectivities were obtained for some substrates using systems with $(R_4N)_9Ni(OH_2)H_2F_6NaW_{17}O_{55}$ but at 60 °C in biphasic systems that include halogenated solvents.

1.2.1.1.2. Peroxotungstates

Systems derived from tungstic acid (H_2WO_4), phosphate, and ammonium or phosphonium counter ions that act as phase transfer agents are prominent among simple, soluble metal oxide salts for catalytic epoxidation with H_2O_2. They are nearly always formed *in situ*, but catalytically active complexes such as $(R_4N)_3\{PO_4(W(O)(O_2)_2)_4\}$ have been isolated and characterized crystallographically by Venturello and co-workers.[38-40] Tungsten catalysts of this type use H_2O_2 and give more efficient reactions (Scheme 15) than many other epoxidation catalysts.



Scheme 15. Epoxidation using Venturello catalyst, $(R_4N)_3\{PO_4(W(O)(O_2)_2)_4\}$



Scheme 16. Epoxidation using Noyori's solvent-free catalyst

On the other hand Noyori[41-42] proved that (Scheme 16) terminal aliphatic alkenes could be epoxidized at 90 °C without organic solvents by means of rapid-stirring. However, only simple aliphatic alkenes are usually cited as substrates; slightly acid-sensitive epoxides such as phenyl oxiranes are not stable to such reactions conditions, resulting in low yields. This is common for systems with Lewis-acidic catalysts that use aqueous H_2O_2 at high temperatures. Due to the above limitations, such tungsten catalysts may only be used to produce relatively stable epoxides, particularly terminal aliphatic ones, despite their high conversions and selectivities.

1.2.1.1.3. Peroxomolybdates

Molybdenum catalysts (e.g.,$[NMe_4]_2[(PhPO_3)\{MoO(O_2)_2\}_2.\{MoO(O_2)_2(H_2O)\}]$, $[(NH_4)_6Mo_7O_{24}.4H_2O]$, etc., similar to peroxotungstates), have been prepared and investigated for the epoxidation of alkenes with H_2O_2. They give low turnovers and selectivities for the desired products, and their reactions are performed under harsh conditions. Soluble molybdenum oxide complexes are often used in stoichiometric quantities in which an active oxidant is generated from 30 % H_2O_2 and commercially available ammonium molybdate.

1.2.1.1.4. Methyltrioxorhenium

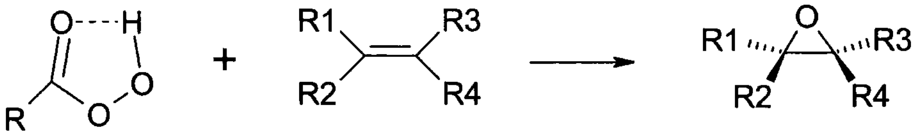
The discovery of methyltrioxorhenium, $MeReO_3$ or MTO, epoxidations by Herrmann and co-workers[43] is a milestone in this area. A variety of alkenes were epoxidized with anhydrous H_2O_2 in t-BuOH or THF at room temperature or below using 0.1-1.0 mol % of this catalyst in *tert*-butyl alcohol or THF.

In conclusion, a good epoxidation catalyst should activate H_2O_2 without radical production. Most homogeneous epoxidation systems are greatly enhanced by adding some additives to the reaction mixture. These additives are often tertiary heterocyclic amines (i.e., pyridines, pyrazoles, and imidazoles) or carboxylates (i.e., acetates, benzoates or glyoxylates). Useful additives favourably change catalytic efficiencies, selectivities, and reactivities and do not complicate isolation of the epoxide products.

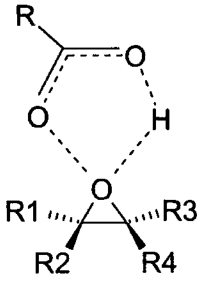
There is no single method for epoxidation using hydrogen peroxide that is uniformly better than the rest. The best method available depends on the nature of desired substrate and reaction scale. Zeolites can be superior for large-scale production of small, stable epoxides; these catalysts are cheap, robust, and easily removed from the products. Methyltrioxorhenium or manganese sulfate systems allow convenient production of racemic, acid-sensitive epoxides using commercially available reagents. Phosphate/tungstic acid systems are more Lewis acidic and require elevated temperatures.

1.2.3. Epoxidations with Organic Peroxy Acids

A large number of organic peroxycarboxylic acids readily epoxidize alkenes (Scheme 17).[44-46] The stereochemistry of the alkene is retained in the epoxide. The reaction is believed to take place *via* the transition state (Scheme 18) and involves the nucleophilic attack on the O-O bond by the π-electrons of the double bond. The reaction rate increases when the groups R^1 R^2 R^3 and R^4 are electron releasing and also when R is an electron-withdrawing group. In the case of polyunsaturated hydrocarbons, if the double bonds differ in their degree of substitution the regioselectivity can be easily predicted; the more substituted double bond is more reactive. The peroxy acid has a relatively low steric requirement. For example, epoxidation is the only addition reaction which has been carried out on the sterically hindered alkene.



Scheme 17. Epoxidations of alkenes using peroxycarboxylic acids



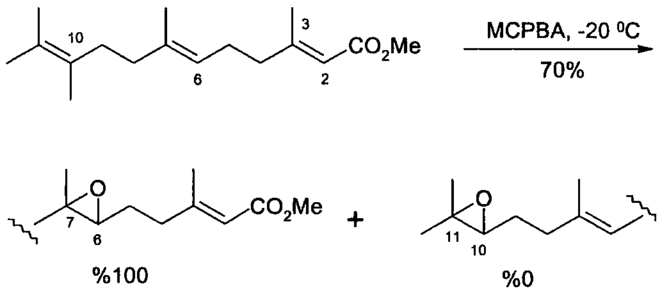
Scheme 18. The transition state occurring during epoxidation of alkenes

It is believed that the epoxidation of alkenes with peroxycarbocylic acids take place via the transition state shown in Scheme 18.

1.2.3.1. Epoxidation with *m*-Chloroperbenzoic acid (*m*-CPBA)

m-CPBA is a relatively stable solid which is soluble in many common organic solvents. It is the reagent of choice for laboratory scale experiments and is commercially available. The reactions are carried out normally at 0-25 ^{0}C in CH_2Cl_2 or in $CHCl_3$. The experimental conditions for the reaction and the subsequent work-up depend on the stability of the epoxides.[44-46] In the case of acid sensitive epoxides, the pH should be controlled.

The reactivity of an alkene depends on the degree of substitution; the least reactive are the monosubstituted (terminal) alkenes. Scheme 19 illustrates typical epoxidation reactions[45] of a triene namely, 3,7,10,11-tetramethyl-dodeca-2,6,10-trienoic acid methyl ester, containing monosubstituted alkenes in the structure by *m*-CPBA. The preparation of allylic epoxides from conjugated dienes requires careful control of pH, since allylic epoxides undergo ring opening by nucleophiles at acidic pH.



Scheme 19. Epoxidation of 3,7,10,11-tetramethyl-dodeca-2,6,10-trienoic acid methyl ester using *m*-CPBA

1.3 Biodegradation

The use of synthetic polymers has accelerated to the extent that the disposal of the polymer products currently in use, most of them bioresistant, has become increasingly difficult. One of the important current incentives for the study of biodegradable polymers is their easier disposal. Moreover, biodegradable polymers are useful for applications such as sutures, surgical implants, controlled-release formulations of drugs and agricultural chemicals, etc, and interest in them continues to increase.[47-50]

Biodegradation of polymers is studied by using the polymers as the carbon and nitrogen sources for the growth of microorganisms. The degree of biodegradation of the polymer samples is determined by observing the evidence of the colony growth[51], the increase in cell count or cell mass[52], the production of the carbon dioxide[53] , oxygen consumption[52], product formation analysis and the changes in polymer[52].

CHAPTER 2

EXPERIMANTAL

2.1. Materials

1-Hexene (97 %), dodecyltrimethylammonium bromide (DTAB) (99%), trimethyl tetradecyl ammonium bromide (TDTAB) (99%), cetyltrimethylammonium bromide (CTAB) (99 %), Adogen ® 464, potassium permanganate (97%), formic acid (96% A.C.S reagent), phosphoric acid (crystals 98+ %), tungsten (monocrystalline powder, 0.6-1 micron, 99.9+ % A.C.S reagent), hydrogen peroxide (30 wt. % solution in water A.C.S reagent) sodium sulfite (98+ % A.C.S reagent), 3-chloroperoxy benzoic acid (77 % max), phenolphthalein (0.5 wt. % solution in 50 wt. % ethyl alcohol), potassium hydrogen phthalate (99.95-100.05 %, A.C.S acidimetric standard), pyridine (anhydrous 99.8%), acetic anhydride (99+ %) and chloroform-d (99.9 D) were all obtained from Aldrich Chemicals and used as received. 1,5,9–Decatriene (cis + trans 97 %) was purchased from Avocado Chemicals and used without further purification. The natural oils (Soybean, Sunflower, Rapeseed and Fish) used in this study were commercially available products and used as received.

2.2. Analytical Measurements

Both ^{1}H- and ^{13}C-NMR measurements were carried out using a Bruker-400 MHz spectrometer, with resonances quoted relative to TMS. FT-IR spectra were taken by using a Perkin Elmer FT-IR 1600 series. For elemental analysis; carbon, hydrogen and nitrogen were determined using a CE-440 Elementel Analyzer.

2.3. Permanganate System

2.3.1. Synthesis of Phase Transfer Agent, Cetyltrimethylammonium Permanganate (CTAP)

To a stirred solution of potassium permanganate (3.168 g, 20 mmol) in water (100 ml) , a solution of Cetyltrimethylammonium bromide, CTAB, (8.02 g, 22 mmol) in water (100 ml) was added dropwise over 20 min at 20^0C. A fine violet precipitate was formed immediately. The mixture was stirred for 30 min. The precipitate was isolated by filtration, washed thoroughly with water, and was dried under reduced pressure at room temperature. The product obtained as a fluffy violet solid; yield 6.5 g (80%). The product was stored in a brown bottle in the refrigerator.

Elemental analysis for $C_{19}H_{42}MnNO_4$, Calculated (Found) %: C, 56.54 (56.93); H 10.51 (10.05); N 3.47 (3.6).

2.3.2. Dihydroxylation of 1-Hexene using CTAP

A solution of CTAP (2.02 g, 5 mmol) in dichloromethane (30 ml) was added dropwise to a stirred solution of the 1-hexene (0.42 g, 5 mmol) in dichloromethane (15 ml) at 20 ^{0}C. Stirring was continued for 5 h and the mixture was concentrated to half of its volume under reduced pressure. The residual solution was diluted with ether (50 ml) and was filtered through a bed of Celite and then anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography or recrystallization form ethyl acetate/petroleum ether to obtain 1,2-hexanediol; yield 0.18 g, 32 %.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 ppm (t, J=7.1 Hz, 3H, CH_3); 1.12-1.39 ppm (m, H, CH_2); 3.27 ppm (m, H, CH); 3.43 ppm (m, 2H, CH_2); 3.65 ppm (br, 2H, OH). **^{13}C NMR (100 MHz, $CDCl_3$):** 13.9 (s, CH_3); 22.18, 26.91, 32.01 (3 x s, CH_2); 70.62 (s, CH_2OH); 71.38 (s, CHOH)

2.3.3. Synthesis of Phase Transfer Agent, Trimethyl Tetradecyl Ammonium Permanganate (TDTAP)

To a stirred solution of potassium permanganate (7.9 g, 50 mmol) in water (250 ml) a solution of tetradecyltrimethyl ammonium bromide (TDTAB) (17.5 g, 52 mmol) in water (250 ml) was added dropwise over 20 min at 20^{0}C. A fine violet precipitate was formed immediately. The mixture was stirred for 30 min, the precipitate was isolated by filtration, washed thoroughly with water, and was dried under reduced pressure at room temperature. Yield: 18.3 g, 85 %.

2.3.4. Dihydroxylation of Alkenes Using TDTAP and Two-phase Three-component Solvent System

2.3.4.1. 1-Hexene as Substrate

To a magnetically stirred solution of 1-hexene (0.082 g, 1 mmol) in *t*-BuOH (10 ml) and CH_2Cl_2 (2 ml) at 30 ^{0}C was added a solution of KOH (0.006 g 0,1 mmol) in water (0.5 ml) followed by TDTAP (0.420 g, 1.12 mmol) in small portions during five minutes. The reaction mixture was stirred at this temperature for 1h and then quenched with a saturated aqueous solution of sodium bisulphite solution (10 ml). The mixture was stirred for another 30 min. The solvent was evaporated under reduced pressure and the residue was extracted with ethyl acetate (3 x 25 ml). The combined extracts was washed with water first and then with saturated brine. The solution was dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography to obtain 1,2-hexanediol; yield 0.075g, 64 %.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 ppm (t, J=6.4 Hz, 3H, CH_3); 1.14-1.33 ppm(m, 6H, CH_2); 3.22 ppm (m, H, CH); 3.42 ppm (m, 2H,CH_2); 3.61 ppm (br, 2H, OH), **^{13}C NMR (100 MHz, $CDCl_3$):** 14.3 (s, CH_3); 22.81, 27.23, 32.36 (3 x s, CH_2); 69.62 (s, CH_2OH); 73.83 (s, CHOH)

2.3.4.2. 1,5,9-Decatriene as Substrate

The same experimental procedure described in section 2.3.4.1 was followed for 1,5,9-decatriene. In this case, the following amounts were used: 1,5,9- decatriene (0.1361 g, 1 mmol), *t*-BuOH (10 ml), CH_2Cl_2 (2 ml), KOH (0.006 g 0.1 mmol) in water (0.5 ml), TDTAP (0.420 g, 1.12 mmol) and sodium bisulphite solution (10 ml). The product was contaminated with large amount of TDTAP and proved difficult to purify.

FT-IR (KBr disc), (cm^{-1}): 3352 (br, s, H-bonded O-H stretch), 3109 (s, C-H); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 1.2 ppm (t, CH_2); 2.03 ppm (m,CH_2); 3.30 ppm (br, OH); 3,38 ppm (s, CH); 4.82-4.92 ppm (m,CH_2); 5.71 ppm (m, CH); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.39 ppm (2.x s CH) (C1,9); 130.31 ppm (C5); 114.62 ppm (C10); 66.64 ppm (C1); 33.78 ppm (C3); 27.07 ppm (C4,7)

2.3.5. Dihydroxylation of Alkene Using Dodecyltrimethyl Ammonium Permanganate (DTAP) and Two-phase Three-component Solvent System

The phase transfer catalyst DTAP was prepared with the same procedure as described in section 2.3.3 for the preparation of TDTAP. The reactants with following amounts were used: DTAB (16.7 g, 52 mmol) in water (250 ml) and potassium permanganate (7.9 g 50 mmol) in water (250 ml).

2.3.5.1. 1-Hexene as Substrate

To a magnetically stirred solution of 1-hexene (0.658 g, 8.04 mmol) in *t*-BuOH (90ml) and CH_2Cl_2 (18 ml) at 30 ^{0}C was added a solution of KOH (0.06g, 1 mmol) in water (5 ml) followed by the addition of DTAP (3.129 g, 9 mmol) in small portions during five minutes. The reaction mixture was stirred at this temperature for 1h and then quenched with saturated aqueous solution of sodium bisulphite solution (90 ml). The mixture was stirred for another 30 min. The solvent was evaporated under reduced pressure and the residue was extracted with ethyl acetate (3 x 40 ml). The combined extracts were washed with water followed with saturated brine. The solution was dried over Na_2SO_4 and was filtered. The solvent was removed under reduced pressure to obtain 1,2-hexanediol; yield 0.48g, 50%.

FT-IR (KBr disc), (cm^{-1}): 3375 (br, s, H-bonded O-H stretch), 2930 (s, C-H);

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82 ppm, (CH_3); 1.10-1.26 ppm (CH_2); 3.39 ppm (m,CH); 4.07 ppm (br, OH); **^{13}C NMR (100 MHz, $CDCl_3$):** 14.9 (CH_3); 22.07, 27.65, 32.72 (CH_2); 68.61 (CH_2OH); 72.03 (CHOH).

2.3.5.2. 1,5,9-Decatriene as Substrate

The same experimental procedure described in section 2.2.5.1 was also followed for 1,5,9-decatriene. The reactants with the following amounts were used: 1,5,9-decatriene (1.08 g, 8 mmol), *t*-BuOH (90ml), CH_2Cl_2 (18 ml), KOH (0.06g 1 mmol) in water (5 ml), DTAP (3.129 g, 9 mmol) and sodium bisulphite solution (10ml).

The reaction was not successful as confirmed by ^{1}H-NMR analysis. In the spectrum of the product, apart from the several signals in the region of 0.8-2.02 ppm, the vinyl groups of starting material remained unchanged.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81-2.02 ppm (m, CH_2); 3,28-3.56 ppm (s, CH); 4.87-4.90 ppm (m, CH_2); 5.71 (m, CH).

2.3.6. Dihydroxylation of Alkenes Using CTAP and Two-phase Three-component Solvent System

The transfer catalyst CTAP was prepared with the same procedure as described in section 2.3.3. The reactants with the following amounts were used: CTAB (19.6 g, 52 mmol) in water (250 ml) and potassium permanganate (7.9 g, 50 mmol) in water (250 ml).

2.2.6.1. 1-Hexene as Substrate

To a magnetically stirred solution of 1-hexene (0.658 g, 8.035 mmol) in *t*-BuOH (90ml) and CH_2Cl_2 (18 ml) at 30 ^{0}C was added a solution of KOH (0,06 g, 1 mmol) in water (5ml) followed by CTAP (3.64 g, 9 mmol) in small portions during five minutes. The reaction mixture was stirred at this temperature for 1h and then quenched with saturated aqueous solution of sodium bisulphite solution (90ml). The mixture was stirred for another 30 min. The solvent was removed by rotary evaporator and the residue was extracted with ethyl acetate (3 x 45 ml). The combined extracts were washed with water followed with saturated brine, dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure to obtain 1,2-hexanediol; yield .37 g, 40 %.

FT-IR (KBr disc), (cm^{-1}): 3410 (br, s, H-bonded O-H stretch), 2915 (s, C-H); **^{1}H-NMR (400 MHz,$CDCl_3$):** δ 0.83 ppm, (CH_3); 1.10-1.35 ppm (CH_2); 3.30 ppm (m, CH); 3.42 ppm; 3.76(br, OH); **^{13}C-NMR (100 MHz, $CDCl_3$):** 14.4 (CH_3); 21.96, 27.06, 30.53 (CH_2); 67.54 (CH_2OH); 76.41 (CHOH).

2.3.6.2. 1,5,9-Decatriene as Substrate

The same experimental procedure as described in section 2.2.6.1. was followed for 1,5,9-decatriene. The reactants with the following amounts were used: 1,5,9-decatriene (1.08 g, 8 mmol) using *t*-BuOH (90 ml), CH_2Cl_2 (18 ml), KOH (0.06g, 1 mmol) in water (5 ml), DTAP (3.129 g, 9 mmol) and sodium bisulphite solution (10 ml). The reaction yield was low and the isolation of the pure product was difficult.

2.4. Dihydroxilation of Alkenes Using Hydrogen Peroxide and Formic Acid

2.4.1. 1-Hexene as Substrate

To a well-stirred solution of 2-hexene (0.02 g, 0.23 mmol) in formic acid (16.92 ml) at 25 ^{0}C, in a 250 ml round bottomed flask equipped with a reflux condenser, hydrogen peroxide (2.76 g, 25.3 % aqueous solution) was added in one portion. The reaction became vigorously exothermic after about five minutes. The temperature was maintained at 40 ^{0}C with a cold water bath at the beginning and with warm water bath toward the end of the reaction. The reaction mixture became homogenous in about twenty minutes. One gram samples were withdrawn at half-hour intervals for determination of the peroxide content. After approximately 3 h reaction time, excess formic acid and water were removed by distillation under reduced pressure and the residue was analyzed.

Although the NMR spectrum indicated the presence of signals attributed to hexane-diol, some impurities were noted.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 ppm (CH_3); 1.1-1.14 ppm (CH_2); 3.22 ppm (m, CH); 3.43 ppm (m, CH_2); 3.68 ppm (br, OH); **^{13}C NMR (100 MHz, $CDCl_3$):** 13.1 (s,CH_3); 18.47, 28.76, 33.12 (3 x s, CH_2); 69.43 (s, CH_2OH); 76.28. (s, CHOH).

2.4.2. 1,5,9-Decatriene as Substrate

1,5,9-Decatriene (3.4 g, 25 mmol), formic acid (21 ml) and hydrogen peroxide (3.46 g) were placed in a 250 ml round bottomed flask equipped with a stir bar and a reflux condenser. The reaction appeared to be slightly exothermic at the beginning. After about 30 min, the temperature was kept at about 40 ^{0}C using a water bath. The progress of reaction was monitored by TLC. When a satisfactory conversion was not attained, the reaction was further continued overnight. The reaction was then cooled and water was added. The product was then extracted with diethyl ether (4 x 30 ml). The ether solution was washed with water and was dried over $MgSO_4$. The solvent was removed under reduced pressure to give the crude epoxide compound. The epoxide was placed in a 250 ml round bottomed flask and sodium hydroxide (25 ml, 3N) was added. The temperature was raised to 100 ^{0}C and the reaction was monitored by TLC. The reaction did not appear to have gone to completion after 24 h. So it was left over the weekend and a further

NaOH (25 ml) was added. The reaction was then allowed to cool, extracted with diethyl ether and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was analyzed. The yield of the expected alkanediol was very low.

FT-IR (KBr disc), (cm^{-1}): 3363 (br, s, H-bonded O-H stretch), 3085 (s, C-H)

^1H NMR (400 MHz, $CDCl_3$): δ 1.49 ppm (t, 2H, CH_2); 2,11 ppm (m, 4H, CH_2); 2.2 ppm (br, 2H, OH); 3,48 ppm (m, 2H, CH); 4.97-5.03 ppm (m, 4H, CH_2); 5.71 ppm (m, 2H, CH).

2.5. Dihydroxylation of Alkenes Using Hydrogen Peroxide and Phosphoric Acid

2.5.1. One-Pot, Three-Step Method

Tungsten powder (0.025 g, 0.135 mmol) was added to a round bottomed flask equipped with a magnetic stirrer bar and a reflux condenser. First water (2 ml) and then hydrogen peroxide (0.2 ml) were added. After stirring for 30 minutes at 50 °C, phosphoric acid (0.015 g, 0.153 mmol) in water (0.2 ml) was added along with 1-hexene (0.5 g), hydrogen peroxide (2.5 ml), water (7.5 ml) and Adogen 464 (0.04 g). The reaction was maintained at 50°C for 3 h. Phosphoric acid (50% by weight with respect to alkene) in water (2 ml) was added to the reaction and the temperature was raised to 100°C and the reaction was left overnight. The reaction was cooled and the aqueous phase was saturated with sodium chloride. The reaction mixture was extracted with THF. The organic layer was dried over magnesium sulfate, filtered and the solvent was removed under reduced pressure to obtain 1,2-hexanediol; yield 0.105 g, 15%.

^1H NMR (400 MHz, $CDCl_3$): δ 0.84 ppm (t, J=6.3 Hz, 3H, CH_3); 1.11-1.34 ppm (m, 6H, CH_2); 3.41 ppm (m, H, CH); 3.56-3.69 ppm (m, 2H, CH_2); 3.81 ppm (br, 2H, OH),

^{13}C NMR (100 MHz, CDCl$_3$): 16.23 (s, CH$_3$); 22.92, 27.29, 32.95 (3 x s, CH$_2$); 67.97 (s, CH$_2$OH); 70.56 (s, CHOH).

2.5.2. One-Pot, One-Step Method

2.5.2.1. 1-Hexene as Substrate

Tungsten powder (0.125 g, 0.135 mmol), 1-hexene (2.579 g, 30 mmol), phosphoric acid (1.33 g, 13 mmol), hydrogen peroxide (13.5 mL), Adogen 464 (0.215g) and water (35 mL) were all placed in a round bottomed flask equipped with a magnetic stirrer bar and a reflux condenser. The reaction was then heated to 50°C and was left stirring overnight. The aqueous phase was saturated with sodium chloride and then extracted with THF. The organic layer dried over magnesium sulphate and the solvent was removed under reduced pressure to obtain 1,2-hexanediol; yield 0.028g, 0.78 %.

^{1}H NMR (400 MHz, CDCl$_3$): δ 0.90 ppm (t, 3H, CH$_3$); 1.20-1.23 ppm (m, 6H, CH$_2$); 3.48 ppm (m, H, CH); 3.61-3.76 ppm (m, 2H,CH$_2$); 4.3 ppm (br, 2H, OH); **^{13}C NMR (100 MHz, CDCl$_3$):** 14.33 (s, CH$_3$); 22.52, 27.68, 33.24 (3 x s, CH$_2$); 67.96 (s, CH$_2$OH); 72.30 (s, CHOH).

2.5.2.2. 1,5,9-Decatriene as Substrate

The same experimental procedure as described for 1-hexene in section 2.5.2.1 was followed for 1,5,9-decatriene. The reactants with the following amounts were used: 1,5,9-decatriene (2.505 g), tungsten powder (0.125 g), hydrogen peroxide (13.5 ml), Adogen 464 (0.215 g) and 35 ml of water.

The hydroxylation reaction was unsuccessful as confirmed by ^{1}H-NMR analysis and the reason for the failure is not clear.

2.5.3. Dihydroxylation of Soybean Oil, Sunflower Oil, Rapeseed Oil and Fish Oil with Hydrogen Peroxide and Phosphoric Acid Using a One-pot, three-step Method

Tungsten (0.25 g, 1.35 mmol), water (1ml) and hydrogen peroxide (2 ml) were placed in a flange flask equipped with a mechanical stirrer and reflux condenser. The mixture was stirred at 50°C for 30 min. Phosphoric acid (0.15 g, 1.5 mmol), water (75 ml), hydrogen peroxide (25 ml), Adogen 464 (0.35 g) and rapeseed oil (50 g) were added to the mixture and the reaction was left stirring for 3 h. Phosphoric acid (25 g, 0.25 mol, 50% by weight with respect to oil) in water (10 ml) was added and the reaction temperature was increased to 100°C and was left stirring overnight. The reaction was then cooled and the resulting emulsion was transferred to a separating funnel and left for 90 min to allow phase separation. The aqueous layer was removed. The oil layer was distilled (150°C, 50 mbar) to remove any remaining water to yield an orange/brown waxy solid. Almost quantitative yield was obtained (56 g polyol was recovered). The product was found to be difficult to characterise by NMR spectroscopy but was characterised by measuring its hydroxyl value.

The same procedure was used for dihydroxylation of Soyabean, Sunflower and Fish oils.

2.6. Dihydroxylation of Alkenes with meta-Chloroperbenzoic Acid (*m*-CPBA)

2.6.1. 1-Hexene as Substrate

1-Hexene (2.5 g, 30 mmol) and water (100 ml) were placed in a round bottomed flask equipped with a magnetic stirrer and placed in an ice bath. To this dispersion the required amount of *m*-CPBA (2.453 g, 15 mmol) was added in small portions over approximately 10 min. The flask was allowed to reach the room temperature and was left stirring overnight. Sulphuric acid (10 %, 5 ml) was added to the mixture and again was left overnight. Solid NaOH was added until the solution became clear. The aqueous solution was saturated with sodium chloride and was extracted with ethyl acetate (3 x 50 ml). The organic layer was washed with saturated sodium sulfite (4 x 50 ml) and subsequently with saturated sodium hydrogen carbonate (4 x 50 ml). The organic layer was dried over magnesium sulphate. The solution was filtered and the solvent was removed under reduced pressure to obtain 1,2-hexanediol; yield 2.28 g, 65%.

^{1}H NMR (400 MHz,$CDCl_3$): δ 0.91 ppm (t, J=6.7 Hz, 3H, CH_3); 1.24-1.44 ppm (m, 6H, CH_2); 3.21 ppm (m, H, CH); 3.59-3.73 ppm (m, 2H, CH_2); 3.82 ppm (br, 2H, OH)

2.6.2. 1,5,9-Decatriene as Substrate

The same synthetic and recovery procedures as described in section 2.6.1 were followed for 1,5,9-decatriene. The reactants with the following amounts were used: 1,5,9-decatriene (2.54 g), *m*-CPBA (4.77 g), sulphuric acid (5 ml, 10%), ethyl acetate (3 x 50 ml), sodium sulfite (4 x 50 ml) and sodium hydrogen carbonate (4 x 50 ml). The product obtained hydroxyl groups; yield 1.017 g, 32%.

^{1}H NMR (400 MHz,$CDCl_3$): δ 1.53 ppm (t, 4H, CH_2); 2,11 ppm (m, 4H, CH_2); 3.65 ppm (br, 2H, OH); 3,41 ppm (m, 2H, CH); 4.95-5.06 ppm (m, 4H, CH_2); 5.71 ppm (m, 2H, CH);

^{13}C NMR (100 MHz, $CDCl_3$) 138.71 ppm (C1,9); 130.7 ppm (C5); 115.15 ppm (C10); 70.91ppm(C1); 33.67 ppm (C3); 27.1ppm (C4,7)

2.7. Calculation of Hydroxyl Value

In our experiments we have used the direct method[54] for the calculation of hydroxyl value. This method requires the use of the following reagents.

Pyridine: It was purified by heating at refluxing with powdered barium oxide and then distilled.

Acetic anhydride; Butan-1-ol; Phenolphthalein indicator.

Aceylating reagent: One volume of acetic anhydride was mixed with seven volumes of pyridine.

Sodium hydroxide solution: Sufficient amount of sodium hydroxide (600 g/L) was mixed with ethanol (94-97 % (v/v)) to make a 0.30 N to 0.35 N solution. The precipitated carbonate was removed by filtration.

An example for the calculations is given below for the titration of rapeseed oil (O5) sample.

Prodecure: The test sample (O5) (1.89 g) was weighed into the round bottommed flask fitted with a condenser. The acetylating agent (5.00 ml) was transferred into the flask. The sample and acetylating agent was mixed by shaking the flask well. The contents were boiled gently for 60 min. The flask was then cooled to about 50 °C and water (5 ml) was added. The mixture was again shaken and then boiled gently for 5 to 10 min. After cooling, the condenser was washed with sufficient amount of butan-1-ol which was eventually completed to total 100 ml. The same procedure was followed with the acetylating reagent (5.00 ml) alone, and also with the same amount of oil with pyridine (5.00 ml) to determine the free fatty acids present. Hydroxyl value was calculated according to the following formula:

Hydroxide Value = [(A + B – C) N x 56.1] / W

For the sample O5 (see Table 4):

NaOH solution required:

For titration of the sample plus pyridine alone in ml **(A)**: 1.5

For titration of acetic anhydride plus pyridine blank in ml **(B)**: 8.7

For titration of sample plus pyridine plus acetic anhydride in ml **(C):** 7.3

The normality of NaOH **(N):** 0.318

The weight of the sample in g **(W)**

Hydroxyl value = [(1.5 + 8.7 – 7.3) x 0.318 x 56.1] / 1.89 = 27.3

The samples A, B and C are prepared as 100 ml and 20 ml intervals are taken and titrated, hence we multiply the result by 5.

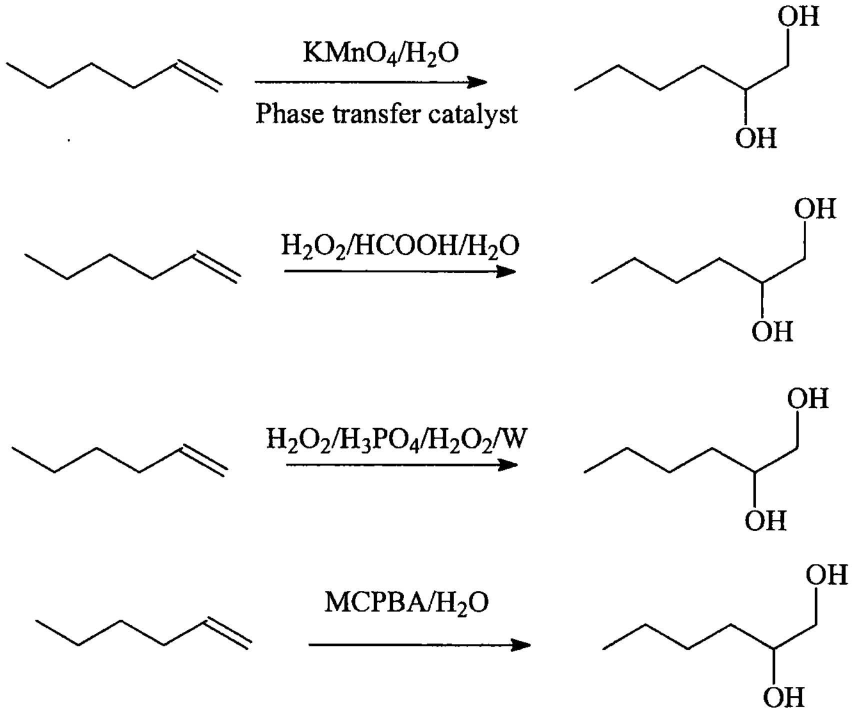
Hydroxyl value for the rapeseed oil sample is: 27.3 x 5 = 135

CHAPTER 3

RESULTS AND DİSCUSSION

3. 1. Dihydroxylation of Alkenes

In the work described here we employed the following four major routes (Scheme 20) for the dihydroxylation of double bonds in natural oil to synthesize polyols suitable for the production of polyurethanes.[27, 28, 55-58]



Scheme 20. The dihydroxylation routes followed in this study.

It was decided that each of these methods should be tried initially, on smaller model substrates containing double bonds (simple alkenes), to allow complete characterization of the compounds and therefore gaining a more thorough understanding of the chemistry taking place. Then, the most promising systems would be used for the reactions with different oils on an approximately 50 g scale before moving on to the 1 kg scale.

3.1.1. Permanganate System

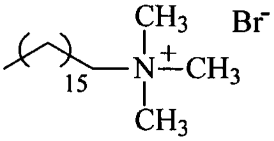
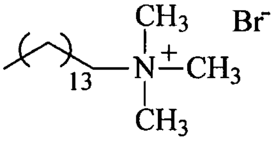
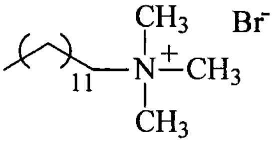
There are several methods in the literature to convert alkenes to diols using an aqueous permanganate system. A phase transfer catalyst is required in order to allow the aqueous permanganate and the double bond, which is soluble in organic solvents, to react.

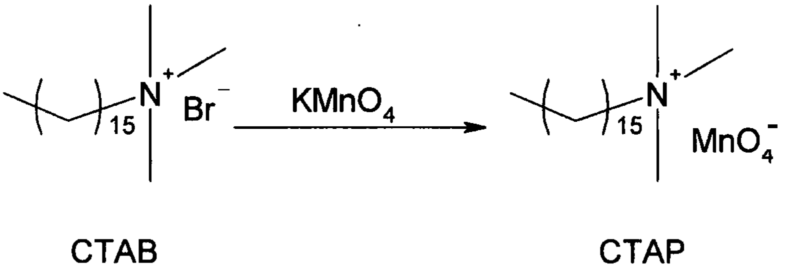
In this work, different procedures and transfer catalysts were investigated. In order to find the most efficient system for the hydroxylation of the model compounds, 1-hexene and 1,5,9-decatriene three different phase transfer agents, namely cetyl trimethylammonium bromide (CTAB), tetradecyltrimethyl ammonium bromide (TDTAB) and dodecyltrimethyl ammonium bromide (DTAB) were used to prepare phase transfer catalysts. The structures of the phase transfer agents are given in Table 2.

The permanganate salt of each phase transfer agent was synthesized by a counter anion exchange reaction and isolated prior to use. This method gave phase transfer catalysts, CTAP, TDTAP and DTAP which were used for hydroxylation reactions of alkenes. A typical counter anion exchange reaction is depicted in Scheme 21 for the reaction of CTAB resulting in the formation of cetyl trimethylammonium permanganate CTAP.

The first method we investigated comprised CTAP as the phase transfer catalyst and dichloromethane as the solvent. Characterization by ^{1}H and ^{13}C NMR spectroscopy showed that hexene was converted to the corresponding diol successfully although yields were low. This could be partially due to unconverted hexene being removed along with the solvent prior to NMR characterization.

Table 2. The structure and abbreviation of the phase transfer agents used

Catalyst	Structure	Abbreviation
Cetyl trimethylammonium bromide		CTAB
tetradecyltrimethyl ammonium bromide		TDTAB
Dodecyltrimethyl ammonium bromide		DTAB



Scheme 21. Counter anion exchange reaction

As a different method, a three-component, two-phase system based on *tert*-butanol (*t*-BuOH) and dichloromethane (DCM) was chosen. Reaction was conducted in a two phase solvent system of *t*-BuOH, DCM and water in the ratio of 50: 10: 1.25 in the presence of catalytic amounts of potassium hydroxide. This was the most efficient method with regard to the yield. The crude product was subjected to column chromatography to remove tertiary butanol (*t*-BuOH) and TDTAP. The purification was essential because the resonences in ^{1}H NMR for *t*-BuOH and TDTAP were interfering with those from the diol product.

The ^{1}H NMR spectrum of the 1,2-hexanediol product obtained is shown in Figure 1. For comparison, the ^{1}H NMR spectrum of 1,2-hexanediol supplied from Aldrich is presented in Figure 2. As can be seen from Figure 1, the disappearance of the signals centered at 4.9 and 5.8 ppm originating from the olefinic protons of the starting compound clearly confirms the successful reaction. In addition, new signals emerged at 3.2-3.6 ppm range which establish the formation of diol groups. Moreover, the spectrum of the reaction product matches well with that of an authentive sample obtained from Aldrich . All these results indicate that the hydroxylation has been successfully achieved.

A similar procedure was then extended to the use of 1,5,9-decatriene as a model compound. Characterization by ^{1}H-NMR spectroscopy showed the presence of hydroxyl groups. However, the presence of some remaining vinylic protons indicated that complete conversion has not been achieved.

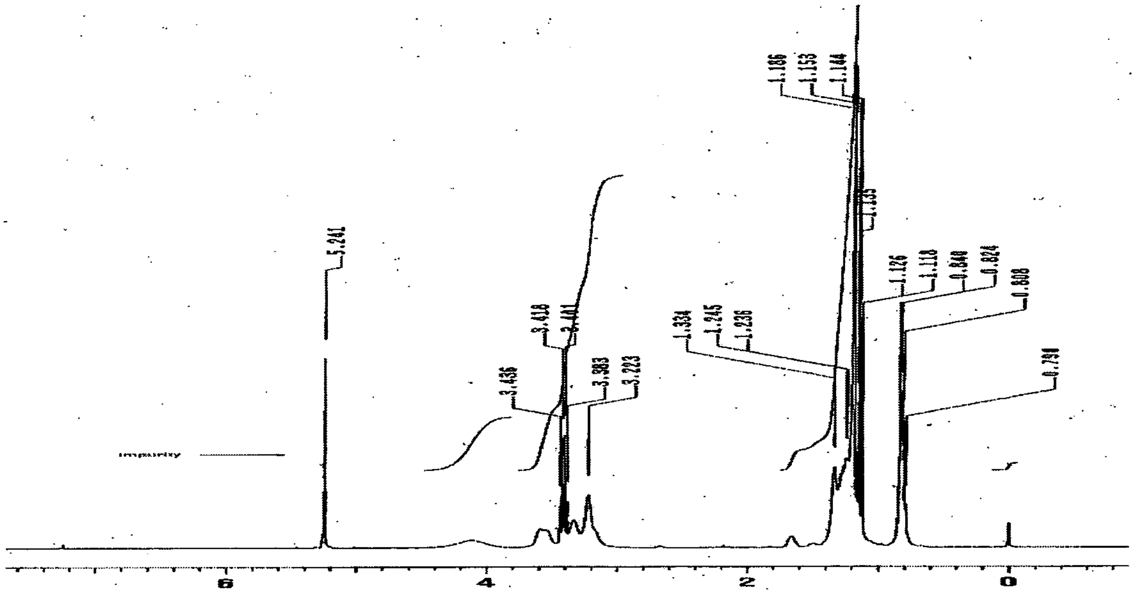


Figure 1. ^{1}H-NMR ($CDCl_3$) spectrum of 1,2-hexanediol obtained through the reaction of 1-hexene with TDTAP catalyst.

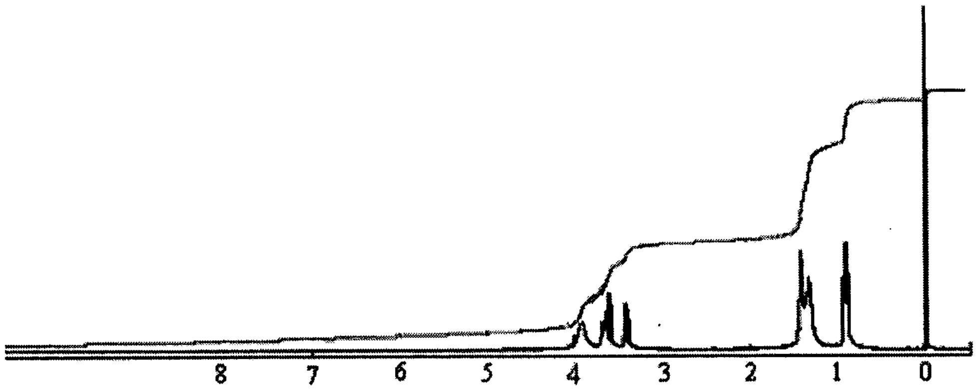


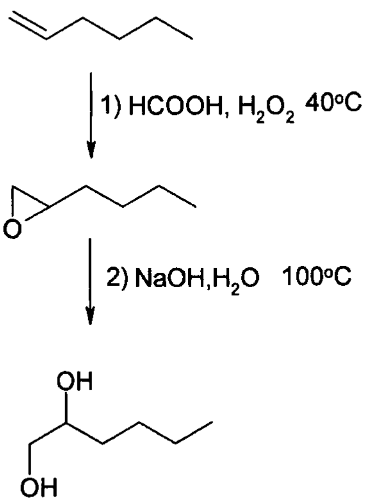
Figure 2. ^{1}H-NMR spectrum of 1,2-hexanediol (Aldrich sample) in $CDCl_3$

After observing the success of the three-component, two-phase solvent system using tertiary butanol (*t*-BuOH) and dichloromethane (DCM), the hydroxylation reactions of 1-hexene and 1,5,9-decatriene with all three phase transfer catalysts CTAP, TDTAP and DTAP were further investigated. Although the ^{1}H and ^{13}CNMR results and conversions were similar for all phase transfer catalysts, it was found that the highest conversion was achieved with TDTAP.

The pre-reacting of the permanganate and the phase transfer catalyst creates some problems. Firstly, it requires a large quantity of the phase transfer catalyst to be used, essentially a stoichiometric amount, rather than a catalytic amount. It also introduces an additional step into the reaction which may hinder scale up once work is commenced on the oils.

3.1.2. Hydrogen Peroxide and Formic Acid System

This method involves epoxidation of the double bond using formic acid (HCOOH) and hydrogen peroxide prior to ring opening using sodium hydroxide to (NaOH) give dihydroxylation of the double bond. The sequences of the overall process are given in Scheme 22.



Scheme 22. Epoxidation of the double bond using formic acid (HCOOH)and hydrogen peroxide

This reaction was tried varying the starting material, reaction time, one step/ two steps, and both acidic and basic conditions for opening epoxide (see Table 3) and all appeared to be unsuccessful. All the reactions with decatriene resulted in a mixture of products with the starting material believed to be the major component. However, it was believed that if this procedure could be made to work, it would be very appealing when scaling up the reaction for industrial production. The procedure was relatively simple, the starting materials were cheap and a one pot, two-stage process may have been possible. This method also used a smaller volume of water than the permanganate systems, reducing the amount of drying required. A further literature search was undertaken and an alternative experimental procedure was found (see experimental section for details). This involved careful monitoring of the reaction temperature. The unreacted formic acid and hydrogen peroxide were simply removed from the system by distillation, which is again an acceptable industrial technique.

For the hydroxylation reaction of 1-hexene, the ^{1}H-NMR spectroscopy analysis showed a mixture of products but no vinylic protons could be seen, although any unreacted hexene could probably have been removed during the distillation to remove formic acid and hydrogen peroxide. However, some of the peaks present in the ^{1}H NMR spectrum correspond to peaks seen in the ^{1}H-NMR spectrum of hexandiol obtained from Aldrich. More investigation is required on this system before its success can be confirmed.

Table 3. Reactions of alkenes with formic acid and hydrogen peroxide

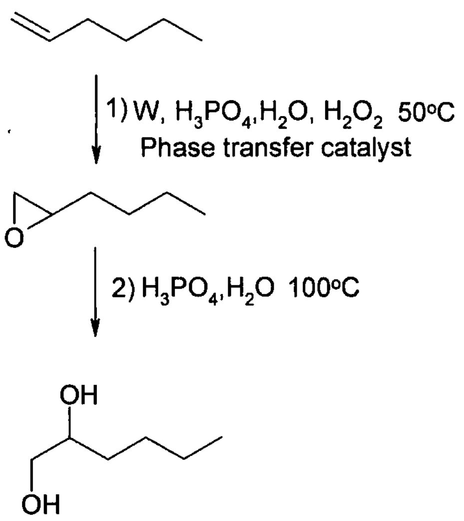
Alkene	Formic acid (%)*	H_2O_2 (%)*	Reaction Temp.	Time	Comments
Hexene	1000	166	Room temp then 40°C	3 h	Epoxide isolated before opening, basic conditions, but not characterized
Decatriene	617	100	Room temp then 40°C	24 h	Epoxide isolated before opening, basic conditions, but not characterized
Decatriene	617	100	Room temp then 40°C	3 days	Epoxide not isolated before opening, basic conditions
Decatriene	617	100	Room temp then 40° C	6 h	Epoxide not isolated before opening, acidic conditions
Hexene	950	200	5°C then room temp	24 h	Different experimental procedure, epoxide isolated, (not characterized) then opened, basic conditions

*Percentages given above are the ratios to the alkene by weight in the reaction.

3.1.3. Hydrogen Peroxide and Phosphoric Acid System

This method uses tungsten powder (W) and phosphoric acid (H_3PO_4) to generate Venturello's catalyst $Q_3PO_4[W(O)(O_2)]_4$, where Q is a phase transfer agent (Adogen 464).

The catalyst then allows epoxidation of the double bond by hydrogen peroxide, followed by ring opening of the epoxide using phosphoric acid and water (Scheme 23).[55,58]



Scheme 23. Epoxidation and hydroxylation using hydrogen peroxide and phosphoric acid system

3.1.3.1. 1-Hexene as Initial Substrate

The results of the reactions are shown in Table 4. The reaction with 1-hexene as was quite successful but the yield was rather low (A1, A2 and A3). The ^{1}H NMR analysis indicated the absence of the vinyl protons. This could be due to the evaporation of unreacted 1-hexene (which is relatively volatile) during the removal of the solvent prior to performing the NMR measurement.

According the literature procedure, the reaction requires sequential addition of reactants after various times and at various temperatures which may not be ideal for industrial production. Therefore, the reaction was attempted as a one-pot reaction, which we envisaged would allow easier scale-up when using oils. This gave similar results to the multi-stage reaction indicating that a one pot synthesis may be possible. See Table 4, and also experimental section (see 2.5) for the reaction conditions.

Table 4. Conditions for the reaction of alkenes with phosphoric acid and hydrogen peroxide

Code	**Alkene**	**Water %***	**H_2O_2 %***	**H_3PO_4 %***	**Reaction Time Hours**	**Yield %***
A1	Hexene	1900	540	50	6	-
A2	Hexene	1000	540	80	6	9.55
A3	Hexene	1357	540	53	18	0.78
A4	Decatriene	1400	540	54	48	1
A5	Decatriene	1400	540	56	18	4
A6	Decatriene	1400	540	56	18	2

*The percentages given in the table are relative to alkene (A) by weight in the experiment

3.1.3.2. 1,5,9-Decatriene

The results of the reactions are shown in Table 4. The hydroxylation of a more complex alkene, 1,5,9-decatriene, was investigated using a one pot method, before moving to the hydroxylation of the oils. The results were disappointing as the ^1H NMR spectra were rather complex, which was probably due to the presence a mixture of several different products. In order to try and resolve this, the reaction was repeated on a slightly larger scale to obtain enough material to isolate each component by column chromatography. The TLC of the reaction mixture revealed the presence of 4 compounds, but we were unable to separate them using column chromatography.

3.1.3.3. Natural Oils

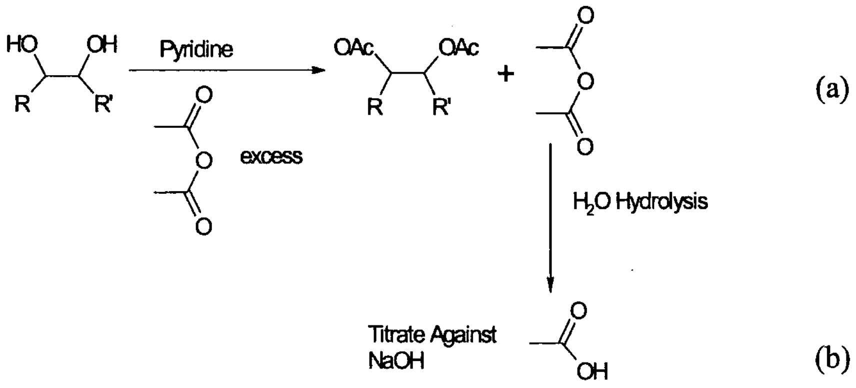
Initially three hydroxylation reactions were carried out with rapeseed, soybean and sunflower oils (samples O1, O7 and O10). The results are presented in Table 5.

Table 5. Results from reaction of natural oils with phosphoric acid and hydrogen peroxide

Code	Natural Oil	Water %*	H_2O_2 %*	H_3PO_4 %*	OH number mg KOH/g	Comments	Reaction Times (Hours)	Polyol yield from 50g Oil (g)
O1	Rapeseed	160	60	52	80	Magnetic stirring	17	23
O2	Rapeseed	160	60	52	164	Dried over molecular sieves	17	26
O3	Rapeseed	80	60	52	169	Dried by distillation	17	52
O4	Rapeseed	160	60	52	241	Dried by distillation	17	56
O5	Rapeseed	160	30	52	135	Dried by distillation	17	48
O6	Soyabean	160	60	52	187	Dried by distillation	17	47
O10	Soyabean	160	60	52	37	Magnetic stirring	17	25
O7	Sunflower	160	60	52	-	Magnetic stirring	17	48
O8	Fish	160	60	52	37	Dried by Distillation	17	43
O9	Fish	160	60	52	45	Dried by Distillation	17	47

*The percentages given in the table are rational to oil (O) by weight in the experiment

The experimental conditions used were a two stage, one pot method (see experimental 2.5.3), using magnetic stirrer bars to agitate the reaction mixtures. During the reaction the phases did not appear to mix very well and on isolating the oil the Adogen phase transfer agent was left as a lump in the bottom of the reaction vessel suggesting that it had not taken part in the reaction. Therefore, all subsequent reactions were carried out in reaction vessels equipped with mechanical stirrers at 300 rpm (samples O1, O3, O4, O5). Some problems were encountered with removing water from the reaction mixtures after the completion of the reactions as the mechanical stirring resulted in the formation of emulsions. Initially the emulsion was left to separate for several days and the water phase was removed. The polyol product was then left over molecular sieves to remove the remaining water (sample O2). This method was very time consuming and did not remove water from the product efficiently. A more successful method was to let the reaction separate, remove the majority of water, followed by distillation under reduced pressure (Samples O2, O4, O5, O8 and O9). The initial phase separation is required to remove the bulk of the phosphoric acid which is soluble in the aqueous phase. The polyol products recovered were soft waxy solids which were soluble in chloroform. The polyols were characterized by titration to calculate the number of OH groups present in the system. Briefly, the titration[54] method involves the reaction of the polyol with a mixture of pyridine and excess acetic anhydride (Scheme 24-a). The acetic anhydride acetylates the hydroxyl functionality in the polyols.



Scheme 24. Titration reactions for the calculation hydroxyl groups

The remaining acetic anhydride is hydrolysed by water which results in production of the free acid (Scheme 24-b). This acid can then be titrated against NaOH. If the initial addition of acetic anhydride is known then the amount which has reacted with the OH groups can be calculated according to the following equation:

$$\text{Hydroxyl value} = [(A + B - C)\,N \times 56.1] / W$$

where A is NaOH solution required for titration of the sample plus pyridine alone in ml, B is NaOH solution required for titration of acetic anhydride plus pyridine blanc in ml, C is NaOH solution required for titration of sample plus pyridine plus acetic anhydride in ml, N is the normality of NaOH solution and W is the weight of the polyol sample in g.

A sample which is only reacted with pyridine under the same conditions is also titrated to correct the acidity due to the presence of the terminal COOH groups in the polyols. The results obtained from these titrations are shown in Table 5. An example for the calculation of hydroxyl value is given for the titration of rapeseed oil in the experimental section (see Section 2.7).

The results suggest that the reaction did not proceed efficiently when the stirrer bar used for mixing producing polyols with the low hydroxyl numbers of 37 for the soyabean sample (O10) and 80 for the rapeseed sample (O1).

In the systems with mechanical stirring, the reactions were quite successful producing polyol samples with the hydroxyl numbers of 187 for soybean sample (O6) and 164 for rapeseed sample (O2). The hydroxyl values obtained for the polyols are comparable with those for NOWA polyol, produced by Enviromental Technology

International Limited, which is already being used for the synthesis of polyurethane foams at UMIST.

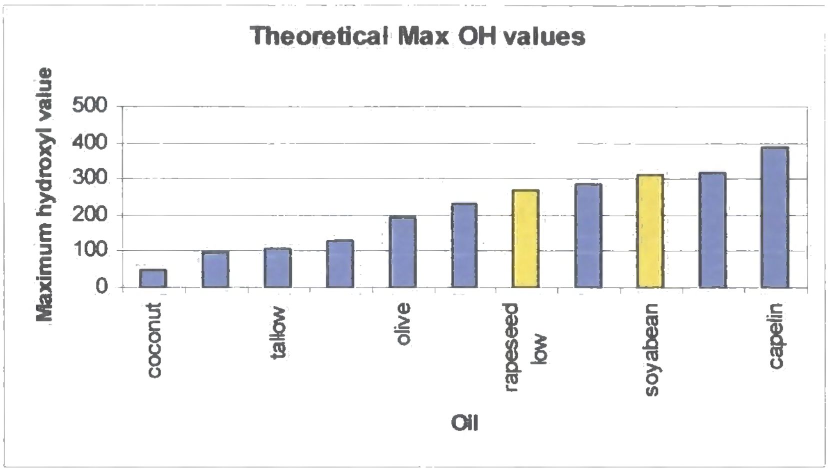


Chart 1. Theoretical maximum hydroxyl values for different oils

The exact experimental conditions, not surprisingly, affected the hydroxyl number. Reduction of the water in the system, appears to reduce the hydroxyl value (O3 vs. 04); water probably increases the solubility and decreases the viscosity and hence more dihydroxylation. Reduction of the amount of hydrogen peroxide (O5 vs. O4) reduces the hydroxyl number; reduction of the oxidizing agent expectedly results in less epoxidation and hence less dihydroxylation. Changing the oil from rapeseed to soyabean oil also affected the hydroxyl number (O6 vs O4), again this is expected as changing the oil will affect the number of double bonds available for the dihydroxylation reaction. In fact the hydroxyl value of the oils depends on the nature of the oil, i.e. the number of olefinic bonds and isomers (cis/trans). The theoretical hydroxyl value for the different oils can be estimated by taking structural characteristics into account and these values are represented in Chart 1. As it can be seen that the hydroxyl value may vary from 40 to 400 mg KOH/mg, depending on the type of the oil used. Obviously, the experimental conditions and the solubility of the reactants and the nature of oil may bring about additional differences. Samples (~48g) of O2-O5 were sent to UMIST for initial formulation studies and the preliminary results were quite encouraging. The reactions of the polyols produced here with diisocyanates were slower than the NOWA Polyol which was believed to be due high viscosity probably as the result of the hydrogen bonding. The polyols produced here are the result of dihydroxylation reaction of double bonds in natural oils forming two OH groups per double bond. All the polyols were obtained as high by viscous oils.

3.1.3.3.1. Scaling Up

The hydroxylation of rapeseed oil was scaled up in a Buchi reactor, shown in Figure 3. The same experimental conditions as described for sample O4 was used and 1 kg of rapeseed-based polyols was prepared. The titration of the resulting polyol gave the same hydroxyl number as that for the same polyol on 50g scale. The 1 kg sample was sent to UMIST for the polyurethane foam production.

Figure 3. Buchi reactor.

3.1.4 Organic Peroxide System

The hydroxylation of alkenes to form diols was also investigated using meta-chloro perbenzoic acid (*m*-CPBA), an organic peroxide.[48] The reaction was tried on both hexene and 1,5,9-decatriene, using a range of 0.8 to 3 equivalents of *m*-CPBA. The reaction with 1-hexene was unsuccessfull but some interesting results were obtained for the reaction with 1,5,9-decatriene. The ^{1}H-NMR spectrum of 1,5,9-decatriene, Figure 5 shows resonances at 5.5 ppm and 5.7ppm due to protons of the internal olefinic group.

After reaction with *m*-CPBA, the ^{1}H NMR spectrum shows the intensity of the resonances at 5.5ppm is greatly reduced in conparison with the resonances at 5ppm and 5.7 ppm, see Figure 6. Moreover, the integral ratio of the protons at 5.5 ppm to those at 5.7 ppm is reduced from unity to 0.3 after treatment with *m*-CPBA. This result implies that a 70 % conversion is achieved.

Increasing the *m*-CPBA ratio with respect to the alkene, had no affect on the results. It appears that *m*-CPBA selectively hydroxylates the internal double bonds. However, this system requires further investigation. This finding is interesting when natural oils investigated in this project contain mainly internal double bonds. The hydroxylation of oils was therefore carried out using *m*-CPBA. However when oils water and the *m*-CPBA powder were mixed and stirred the reaction became dough-like and difficult to manipulate.

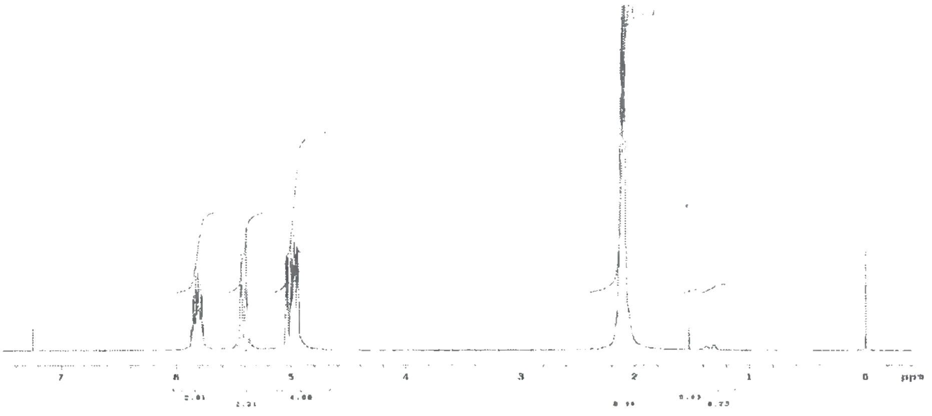


Figure 5. ^{1}H NMR spectrum of 1,5,9-decatriene in $CDCl_3$.

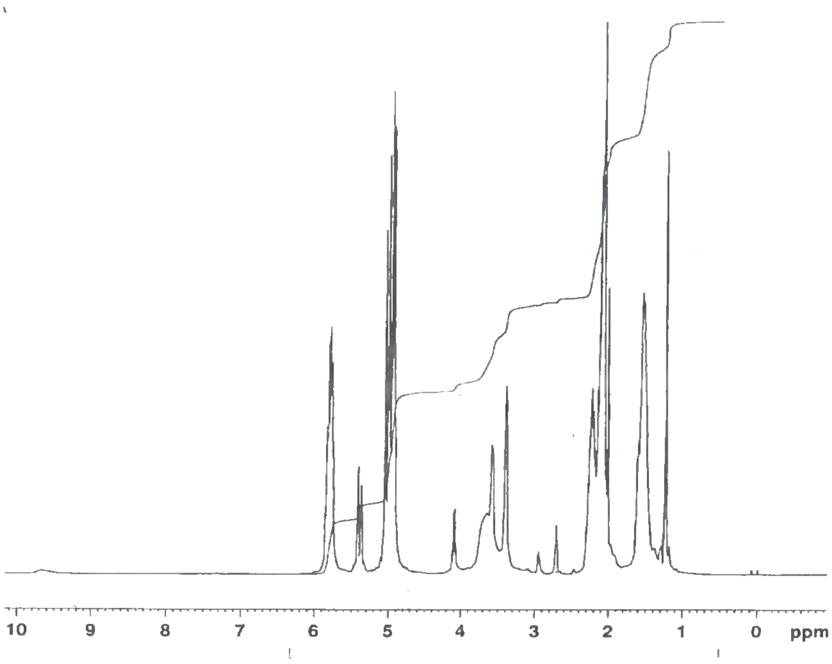


Figure 6. ^{1}H NMR spectrum of the reaction product of 1,5,9-decatriene with *m*-CPBA in $CDCl_3$.

Addition of the sodium hydroxide at the end of the reaction (see experimental for the details) reduced this but the reaction mixture did not become clear. Despite trying several solvents and methods we were unable to extract the oil from the mixture. The hydroxylation of oils using *m*-CPBA requires further refinement to achieve optimum results.

CHAPTER 4

CONCLUSIONS AND FUTURE WORK

4.1. Conclusion

Several methods were investigated to find a suitable process to convert unsaturated oils into hydroxylated materials suitable for the preparation of polyurethanes. The permanganate and water system was suitable for small hydrocarbons like alkenes but requiring stoichiometric amounts of catalyst was a disadvantage for scale-up. The trial of hydrogen peroxide and formic acid method did not give encouraging results with alkenes. However if it is optimized to work, it could easily be used for scale-up reactions due to the inexpensive and fairly clean and practical reaction conditions.

The results of hydroxylation reactions using phosphoric acid and hydrogen peroxide method were quite encouraging. The reactions using natural oils were quite successful producing polyols with the hydroxide numbers of 187 and 164 for soyabean and rapeseed samples respectively. The hydroxyl numbers obtained here for the polyols ara comparable with those for NOWA polyol, produced by Enviromental Technology International Limited, which is already being used for the synthesis of polyurethane foams at UMIST.

The production of diols from alkenes using an organic peroxide, meta-chloro perbenzoic acid (*m*-CPBA), were also encouraging. It appears that *m*-CPBA selectively hydroxylates the internal double bonds. This finding is very interesting since natural oils investigated in this project contain mainly internal double bonds. However, when the oils, water, and the *m*-CPBA powder were mixed and stirred the reaction became dough-like and difficult to manipulate. The hydroxylation of oils using *m*-CPBA requires further refinement to achieve optimum results.

4.2. Future Work

Several methods were tried for the dihydroxylation reactions of model compounds and the natural oils containing double bonds to produce polyols. The hydrogen peroxide-formic acid system was unsuccessful using a literature procedure despite varying the starting material, reaction time, and being under both acidic and basic conditions. However, the procedure would be very appealing when scaling up the reaction for industrial production. The hydrogen peroxide-formic acid system is relatively simple, the starting materials are cheap and a one pot, two-stage process may easily be applied. A further literature search and alternative experimental procedures are required to get the system to work.

A wide range of natural oils are available with varying amounts of unsaturation (double bonds). Further work is required to establish which natural oils are more suitable for the preparation of polyols and hence for the production of polyurethanes

Another future task that must be considered is testing the biodegradability of the polyurethane samples produced using natural oil-based polyols. The test for biodegradability of polyurethanes involves disintegrating the polymer under controlled composting conditions and calculating the amount of degradation based on the analysis of the evolved carbon dioxide.[59-61]

REFERENCES

1. O. Bayer, *Angew. Chem.,* 59, 275 (1947).

2. O. Bayer, W. Siefkin, L. Orthner, H. Shild, *Ger. Pat.,* 728, 981 (1942).

3. O. Bayer, E. Muller, S. Petersen, H.F. Pienbrink, E. Windemuth, *Angew.Chem.*, 62, 57 (1959).

4. G. Oertel, *Polyurethane Handbook: Chemistry-Raw Material-Processing-Application-Properties*, Hanser Publishers, New York, 1985.

5. J.H Saunders, K.C. Frish, *Polyurethanes: Chemistry and Technology*, Vol. XVI of High Polymers, John Wiley & Son, Inc., New York, 1962, Part 1.

6. R. Richter, H. Ulrich in, The *Chemistry of Cyanates and Their Thio Derivatives (Ed.* S. Patai) John Wiley & Son, Inc., New York , 1977, Vol. 2,

7. Urethane Chemicals Bulletin 85-89, Akzo America Inc. Enka, N.C., 1985

8. J.T. Chapin, K.B. Onder, W.J Farrissey, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem., 21(2).*

9. W. Siefken, Justus Liebigs *Ann. Chem* 562, 205 (1949)

10. Z. W. Wicks, *Prog. Org. Coat.* 9, 3 (1981)

11. R. Vieweg, Hoechtlen, *Polyurethane, Band VII of Kunststoff-Handbuch,* Carl Hanser Verlag, Munich, 1966

12. 1985 Urethane Market Summary, Mobay Corp., Pittsburgh, Pa., Apr. 1986.

13. T. Curtius, *Ber.,* 23, 3023 (1890).

14. T. Curtius, *J. Prakt. Chem.*, 50, 275 (1894).

15. A.W. Hofmann, *Ber.,*14, 2725 (1881).

16. E.S.Wallis, J.F. Lane, *Org. React.,* 3, 267 (1949).

17. T. Shioiri, *Comp. Org. Syn.,* 6, 800 (1991).

18. W. Lossen, *Ann.* 161, 347 (1872) and 175, 271, 313 (1874).

19. I. Goodman in *Encyclopedia of Polymer Science and Technology,* (N. Bikales,

Ed.) 1st ed. Vol.11, Wiley-Interscience, New York, 1969, pp 62-128.

20. N.G. Gaylord, *Polyethers,* Vol. *XIII of High Polymers*, John Wiley & Sons, Inc., New York, 1963, Pt. 1.

21. P. Remp, E.W. Merill, "*Polymer Synthesis*", Huthig & Wepf, 2nd Ed., Basel, 1991, p.52.

22. A.H. Landrock, *Polyurethane Foams: Technology, Properties, and Applications*, NTIS AD-688132 (Plastic Report 37), *Plastics Technical Evaluation Center*, Picatinny Arsenal, Dover, NJ, Jan. 1969.

23. E.N. Doyle, *The Development and Use of Polyurethane Products*, McGraw-Hill, Inc., New York, 1971.

24. H.J. Harwood, *Chem. Rev.* 62, 99 (1962).

25. V. Bhushan, R. Rathore, S. Chandrasekaran, *Syn. Stuttgart.* 5; 431 (1984)

26. B.J. Hazra, M.D.Chordia, B.B. Bahule, V.S.Pore, S.Basu, *J. Chem. Soc. Perkin Trans.1*; 13; 1667 (1994).

27. B.J. Hazra, M.D.Chordia, B.B. Bahule, V.S.Pore, S.Basu *J. Chem. Res.* (S), 500 (2001).

28. B. Wang, R.G. Burau, *Environ. Sci. Technol. 29*, 1504 (1995).

29. S. Miyahara, T. Kamiguchi, M. Hashimukai, K. Nitsuta, 1987, *Jpn. Kokai Tokkyo Koho*, J P62262727.

30. F.D Gimstone, *Adv. Org Chem.,* 1, 110 (1960).

31. P.N. Rylander, Engelhard Ind., *Tech. Bull.*, 9, 90 (1968).

32. L.G. Marzilli, *Prog. Inorg.Chem.,* 23, 255 (1977).

33. H.O. House, " *Modern Synthetic Reactions",* 2nd ed., Benjamin, San Francisco, CA, 1972, p 277.

34. C.W. Jones, *Applications of Hydrogen Peroxide and Derivatives*; MPG Books Ltd.: Cornwall, U.K., 1999.

35. K.A. Jorgensen, *Chem. Rev., 89*, 431 (1989).

36. W. Adam, *Peroxide Chemistry Mechanistic and Preparative Aspects of Oxygen Transfer*; Wiley-VCH: Darmstadt, 2000.

37. R.A.; Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

38. C. Venturello, E. Alneri, M. Ricci, *J. Org. Chem., 48*, 3831 (1983).

39. C. Venturello, R. D'Aloisio, *J. Org. Chem., 53*, 1553 (1988).

40. C. Venturello, R. D'Aloisio, J.C.J. Bart, M. Ricci, *J. Mol. Catal., 32*, 107 (1985).

41. K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, *J. Org. Chem., 61*, 831 (1996).

42. K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D.Panyella, R. Noyori, *Bull. Chem. Soc. Jpn., 70*, 905 (1997).

43. W.A. Herrmann; *J. Organomet. Chem.*, 1995, 500, 149.

44. Y.S. Angelis, M. Orfanopoulos, *J. Org. Chem.*, 62, 6083 (1997).

45. A.S. Rao, *Addition Reactions with Formation of Carbon-Oxygen Bonds, (I) General Methods of Epoxidation*, in *Comprehensive Organic Synthesis*, (Ed. B.M. Trost, I. Fleming) Pergamon Press, New York, 1991, vol. 7 (Vol. Ed. S. V. Ley), Ch. 3.1.

46. L.F. Fieser, M. Fieser, *Reagents for Organic Synthesis*,Wiley, New York, 1967, vol. 1, p. 135.

47. S.J. Huang, J.P. Bell, J.R. Knox, H. Atwood, eds., *Proceedings of the 3rd International Biodegradation Symposium*, Applied Science Publishers, New York,1976, pp 731-741.

48. J.E Potts in M. Grayson, ed., *Kirk-Othmer Encyclopedia of Chemical Technology,* Suppl. Vol,. Wiley-Interscience, New York, 1984, pp 626-668.

49. R.D. Fields, F. Rodriquez, and R.K. Finn, *J. Appl. Polym. Sci.,* 18, 3571(1974).

50. J. Kopecek and K. Ulbrich, *Prog. Polm. Sci.,* 9, 1 (1983).

51. ASTM D G 21-70, *Annual Book Of Standarts, American Society for Testing and Materials, Philadelphia,* Pa., 1976, pp. 781-785.

52. Y. Tokiwa and T. Suzuki, *J. Ferment. Technol.*, 52, 393 (1974).

53. N.B. Nykvist, *Proceedings of the Comferance on Degradation of Polymer Plastics,* Vol. 1, 1973.

54. British Standard, BS 684: Section 2.9 (1977).

55. D. Swern, G.N. Billen, T.W. Findley, J.T. Scanlan, *J. Am. Chem.Soc.,* 67; 1786 (1945).

56. F. Fringuelli, R. Germani, F. Pizzo, G. Savelli., *Synth Commun.*, 19,1939 (1989).

57. Author unknown, *Org. Synth. Coll.*, 5, 467 (1973).

58. J.A. Sherringham, A.J. Clark, B.R.T. Keene, *Lipid Technology*; 12, 129, R 38 (2000).

59. British Standard, BS ISO 14855:1999.

60. A. Ohtaki, N. Sato, K. Nakasaki, *Polym. Degrad. & Stabl.,* 61, 499 (1998).

61. E. Chiellini, A. Corti, R. Solaro, *Polym. Degrad. & Stabl.,* 64, 305 (1999).