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The Mono- and Di-alkylation of Naphthalene over zeolite catalysts.

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SUMMARY

This thesis is concerned with the alkylation of naphthalene with *sec*-butanol and dimethyl carbonate.

Chapter 1 gives a brief introduction to zeolites. It describes the structure, properties and introduces some zeolites commonly used in industry.

Chapter 2 deals with the alkylation of naphthalene by *sec*-butanol. The experiments investigated the effect of molar ratio, temperature, and time on the yield of 2-*sec*-butylnaphthalene, 2,6-di-*sec*-butylnaphthalene and 2,7-di-*sec*-butylnaphthalene. The optimum conditions for the production of 2,6-di-*sec*-butylnaphthalene over a HM catalyst were a naphthalene: *sec*-butanol molar ratio of 1:4, and a temperature of 180°C for a reaction period of 1 hour and gave a product ratio of 2,6-DsBN: 2,7-DsBN of four.

Chapter 3 details the investigations into the alkylation of naphthalene with dimethyl carbonate. This was again investigated using the same parameters of molar ratio, temperature, and time. Despite the size of the DMC molecule, the results obtained with dimethyl carbonate proved disappointing.

DECLARATION

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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STATEMENT 1

This thesis is the result of my own investigations, except where otherwise stated. Other sources are acknowledged by footnotes giving explicit references. A bibliography is appended.

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Contents

Introduction

Chapter 1 – Zeolites

Chapter 2 – Alkylation of Naphthalene with sec-Butanol

Chapter 3 - Alkylation of Naphthalene with Dimethylcarbonate

Appendix

Introduction

The importance of PEN

In recent years there has been much investigation into the selective alkylation of polyaromatics; in particular, alkylation of naphthalene to produce 2,6-dialkylnaphthalenes has received much attention. These compounds have tremendous value as precursors for high quality polyester fibres and thermotropic liquid crystal polymers. The level of interest shown in these types of molecules, their preparation and synthesis can be seen by the large volume of literature that has been published in recent years.

2,6-Dialkylnaphthalene is a valuable molecule because it is a precursor of poly (ethylene naphthalenedicarboxylate), also known as PEN. The 2,6-dialkylnaphthalene (2,6-DAN) is oxidized to 2,6-naphthalenedicarboxylic acid (2,6-NDCA), which is then esterified to form dimethyl 2,6-naphthalenedicarboxylate (also known as NDC). Dimethyl 2,6-naphthalenedicarboxylate is subsequently transesterified with ethylene glycol to form poly(ethylene naphthalenedicarboxylate) (figure 1).

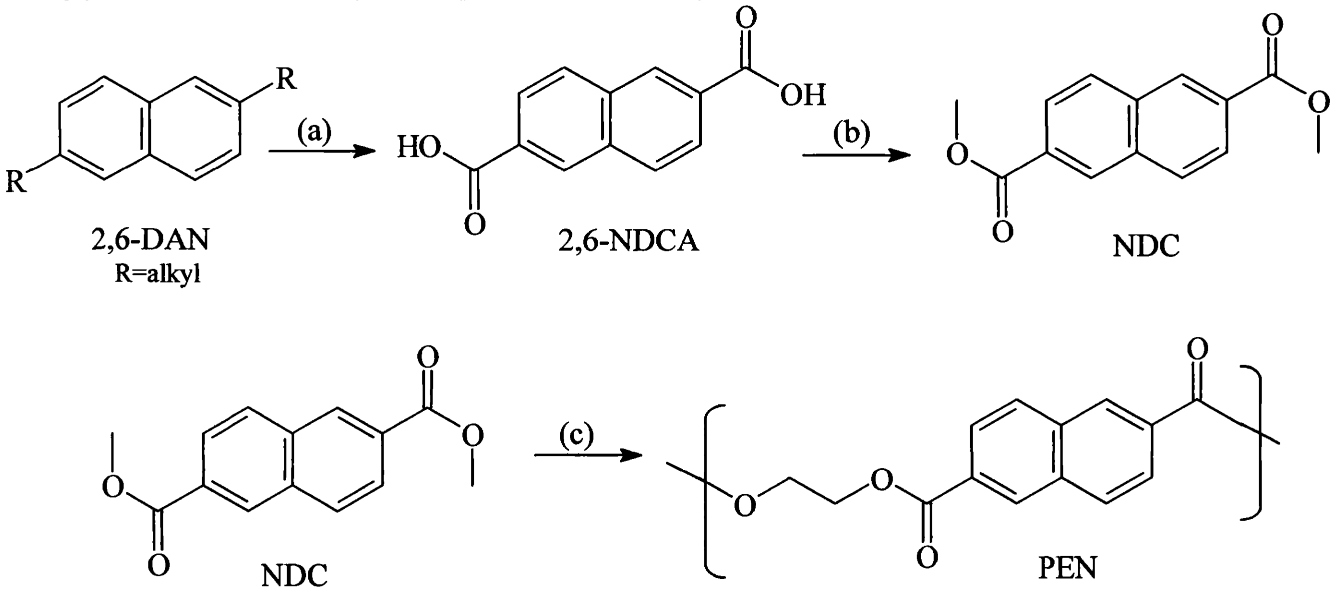

Figure 1: process for production of PEN. (a) 2,6-DAN is oxidized to 2,6-NDCA. (b) 2,6-NDCA is esterified to NDC. (c) Transesterification of NDC with ethylene glycol to produce PEN.

PEN is a versatile polymer, which has a wide range of applications. These applications include adhesives, coatings, films, industrial fibres, inks and packing materials. The cost of NDC production prevents a more comprehensive application of PEN. The potential of this polymer has stimulated a high level of research into more cost effective and less wasteful modes of manufacture of NDC.

The superior mechanical, thermal and chemical resistance properties of PEN mean that potential growth for application of this polymer is great. This potential has led to a large amount of research into a more economical and environmentally friendly route for NDC manufacture. Amoco Chemical has developed one such process. It is a six-step process, which uses the readily available *o*-xylene as the starting material (Figure 2)[1].

The first stage is the side chain alkylation of *o*-xylene with butadiene. This reaction is catalyzed over a fixed bed reactor with a basic catalyst (K on CaO or Na on K_2CO_3) at 140°C. The product, 5-(*o*-tolyl)-2-pentene, undergoes acid catalyzed cyclisation with Cu/Pd doped USY zeolite to give 1,5-dimethyltetralin. The subsequent dehydrogenation of 1,5-dimethyltetralin to 1,5-dimethylnaphthalene (1,5-DMN) is an endothermic reaction, catalyzed by a noble metal catalyst (Pd/Al_2O_3), which takes place at high temperature (220 to 420°C) and pressure (20 atm). The 1,5-DMN is isomerised to 2,6-dimethylnaphthalene (2,6-DMN) over dealuminated zeolite Y or beta at high temperature (240°C to 350°C). The 2,6-isomer is removed from the mixture by either selective adsorption or fractional crystallization. 2,6-DMN is then oxidized by Co- and Mn-acetate with a HBr promoter at high temperature to produce 2,6-naphthalenedicarboxylic acid (2,6-NDCA). The final stage is the esterification of the 2,6-NDCA with methanol in the presence of sulphuric acid to give NDC [1].

Mitsubishi oil are using a similar process but with the starting materials *p*-xylene and butene.

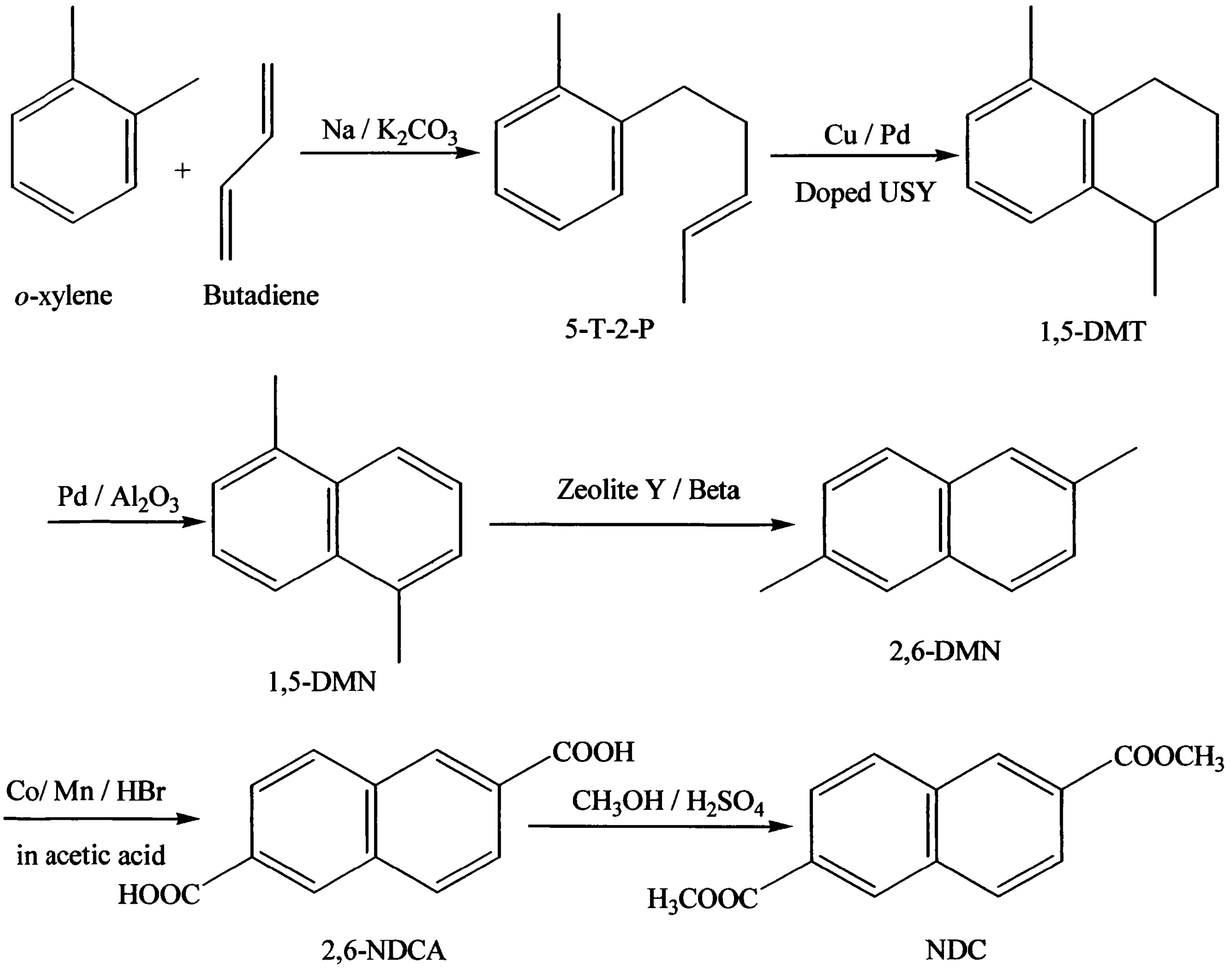

Figure 2: Amoco Chemical commercial process for production of NDC [1].

Naphthalene is a cheap and readily available alternative starting material, derived from coal tar and petroleum. The production of naphthalene in the US, Western Europe and Japan was worth $270-280 million in 2000. In the US 90% of the industrial naphthalene was derived from coal tar as was most of Western Europe's and all of

Japan's naphthalene. By using naphthalene as the starting material in the production of NDC, a number of steps could be eliminated from presently used synthetic routes [2].

At present there are alternative industrial processes for the production of NDC for use in the synthesis of PEN. The company UOP has a semi-commercial plant in Louisiana, USA, where 2,6-DMN is isolated from refinery streams. Mitsubishi Gas Chemical employ a process whereby 2-methylnaphthalene undergoes acetylation using HF-HBr catalyst to form 2-acetyl-6-methylnaphthalene. Finally, NKK and Chiyoda have jointly developed a route whereby naphthalene is alkylated by propylene [1].

Changes in chemical practices [3]

The modification of modern chemical practices has become a goal for both fine and bulk chemical processes. As the public has become more ecologically aware, so the demands for more ecologically friendly industrial processes and products have increased. There is now greater scrutiny over how harmful or toxic the materials used in everyday production are to both people and the environment. Until recently the question of economics dictated the process used for the production of fine chemicals. Today, new legislation to control movement, disposal and storage of chemicals means that industry is moving away from the more hazardous materials.

Friedel-Crafts Reaction

Industry traditionally produced alkylated aromatics by the Friedel-Crafts reaction. In 1877, Charles Friedel and James Craft reported that aromatic benzene could be alkylated by an alkyl chloride, in the presence of a Lewis acid (e.g. aluminum chloride).

This reaction has been the subject of many reviews and encompasses such reactions as cracking, elimination, isomerisation and polymerisation. The alkylating agents used can be alkyl halides, alkenes or alcohols.

Aluminum chloride is the most commonly used catalyst for these reactions, though others are used (e.g. $FeCl_3$ and BF_3). It is reported to be the most active and one of the most widely used metal halide catalysts. Proton acids such as sulphuric acid and hydrogen fluoride have also been employed as catalysts in the past. The use of Friedel-Crafts catalysts is, however, problematic. There is a problem with corrosion of the reaction vessels due to the acidic nature of the catalyst and some reaction by-products. The toxicity of the acidic and metal-containing wastes and the costs incurred because of the equipment corrosion are major disadvantages. There can be a reaction between the acid and the alkylating agent, especially if an alcohol is being used (the conjugate acid does not immediately dissociate from the Lewis acid centre, therefore stoichiometric amounts of Friedel-Crafts catalyst are required). The separation of the reaction products from the homogenous catalyst could prove difficult in some cases. Finally, homogenous catalysts are often very unselective, which leads to a large number of products.

The poor selectivity of the system means that the product mixture can contain mono- di- and poly-alkylated products. Monoalkylation of naphthalene can occur at either the α or β position. Dialkylation could produce 10 isomers: α,α (1,4-, 1,5-, 1,8-), α,β (1,2-, 1,3-, 1,6-, 1,7-), or β,β (2,3-, 2,6- or 2,7-) (Figure 3). The subsequent polyalkylation further complicates the product mixture. Homogeneous catalysts have high specific activities and there is potential for selectivity via ligand variation, which had previously made them the preferred choice. Indeed, Friedel-Crafts catalysts were employed in industry for many years.

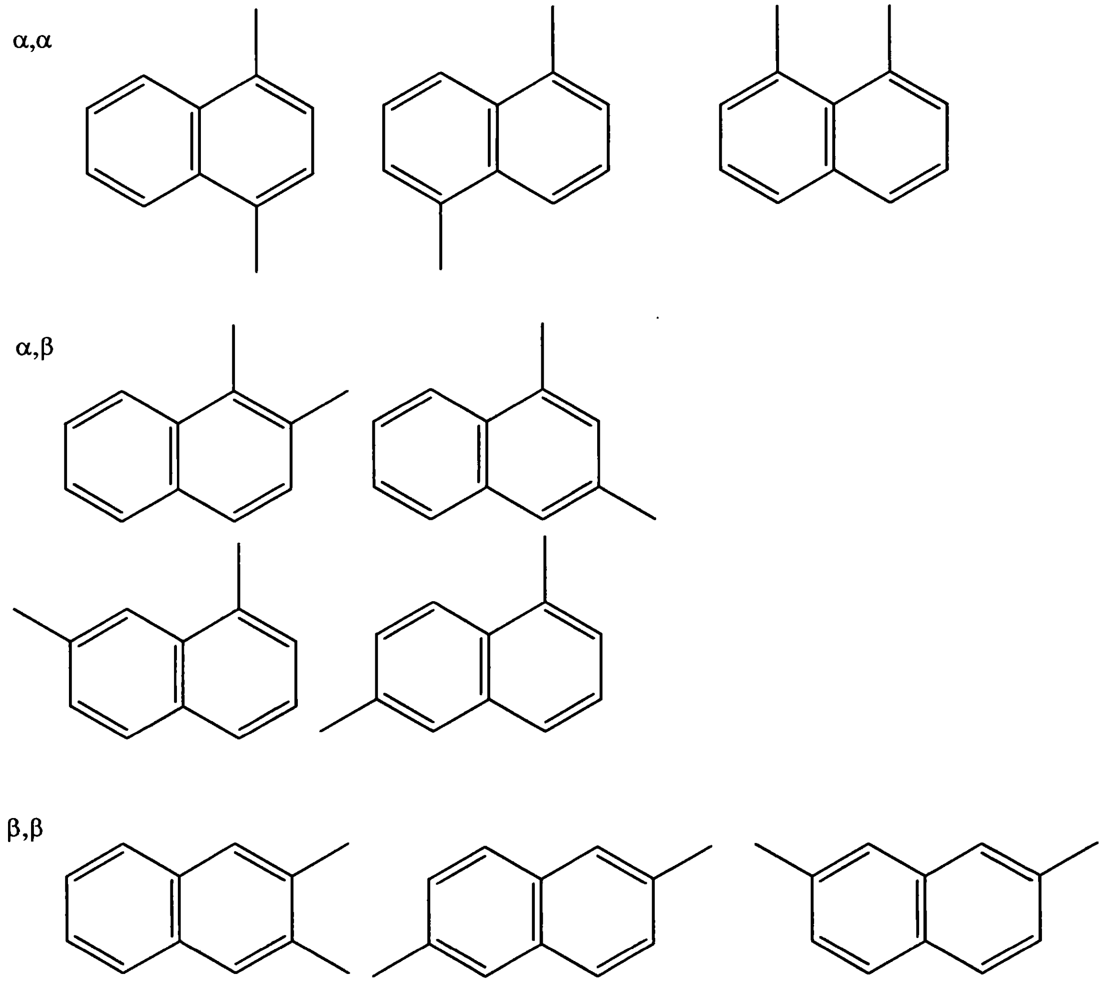

Figure 2: Possible dialkylated isomers of naphthalene. α,α-Isomers 1,4; 1,5 and 1,8. α,β-isomers 1,2; 1,3; 1,6 and 1,7. β,β-isomers 2,3; 2,6 and 2,7.

Due to the many problems associated with aluminum chloride there is now a growing body of research into alternative catalysts [4].

Heterogeneous Catalysts

To overcome the inherent difficulties associated with homogenous Lewis acid catalysts, research has turned to heterogeneous catalysts. Various methods were examined including immobilising Lewis acids on supports [4], pillared clays and alumino-silicates, with various degrees of success. The greatest success has been achieved with zeolites.

Zeolites have a number of advantages over their homogeneous counterparts; principal among these is their potential selectivity for the desired products. This potential is the key to the appeal of zeolites. The first industries to embrace the use of zeolites were the bulk industries such as the petroleum and petrochemical industries. Zeolites were first employed as catalysts on a large scale when the shape-selective property of acidic ZSM-5 was used in the development of the Mobil/Badger process for the synthesis of ethylbenzene. This is now the commercial method for the production of ethylbenzene, which is used to make styrene. The petroleum and petrochemical industries (the so-called bulk industries) still account for the largest use of solid acid catalysts. A recent survey conducted by Tanabe et al.[5] has revealed that more than 40% of the industrial processes using solid acid-base catalysts utilize zeolites.

When looking at the Friedel-Crafts reaction it is easy to compare the two types of catalyst and see the advantages that zeolites offer. Zeolites are non-corrosive in nature; they are heterogeneous and can therefore easily be removed from the reaction products; they are shape selective; and they can be recycled. The advantages of zeolites have the potential to give both economical and environmental benefits to industry-economical in that there is less damage to machinery, less need for effluent clear-up and less waste of starting materials in forming undesirable products; and environmental because of the reduction of toxic or environmentally damaging waste.

The target compounds of fine chemistry are larger, more active and frequently polyfunctional compared with those dealt with in bulk processes of the petrochemical industry. The more dynamic compounds of this industry put a greater demand on the abilities of the catalyst used; they must be more active under milder conditions and have higher chemo-, regio-, stereo- and enantio-selectivity [5]. It is possible to dictate the properties of zeolites themselves or choose a zeolite for a specific characteristic. By varying the Si/Al ratio, the acidity of the framework changes; and the use of zeolites with different pore dimensions allows the passage of only specific isomers to the channel system. By using the selective nature of zeolite catalysts researchers hope to reduce and one day even eliminate the production of waste or by-products; and in some cases to negate the need to use hazardous materials and reduce the number of steps required by a process.

Despite being on a smaller scale, there are more fine chemical processes and these are generally considered to be dirtier in that they produce more waste. This side of industry has been slower to realize the advantages of heterogeneous catalysts. The origins of fine chemistry lie in synthetic organic chemistry, where heterogeneous catalysts are not commonly used. Homogeneous catalysts have high specific activities and potential for selectivity via ligand variation, which previously made them the preferred choice. The fine chemical industry is also on a smaller scale, therefore the cost of developing a catalyst and installing specialized equipment for a specific reaction would take longer to recoup than for the larger bulk industry operations.

Previous research into the alkylation of naphthalene

The number of papers and patents that have been published reflects the interest in this field of study. Initially the interest was based around mononuclear aromatic shape selective reactions. For example, the synthesis of *p*-xylene by alkylation of toluene or isomerisation of other xylene isomers [6]. Interest soon turned to polynuclear, which have the potential to be precursors for a wide range of products. Though naphthalene is the focus for this study there have been comprehensive studies into the alkylations of polynuclear compounds such as biphenyl, anthracene and thianthrene [6] [7] [8].

In the research to find an ideal alkylation for naphthalene a wide range of possible candidates have been studied, including methylation, *iso*-propylation, *tert*-butylation, and cyclohexylation.

Methylation

Many of the initial investigations into the alkylation of naphthalene were using methanol or methane over a series of catalysts. Fraenkel *et al.*[9] investigated the C_{11}-C_{13} gasoline fractions resulting from methylation over the zeolites HZSM-5, HY and H-Mordenite (HM). They found that H-ZSM-5 displayed greater β-selectivity than the other zeolites used in the investigation. The reaction products using H-ZSM-5, were a mixture of methyl- and polymethyl-naphthtalene, while with the larger pore zeolites HY and H-mordenite (HM) the C_{11}-C_{13} fraction contained pentamethylbenzene and hexamethylbenzene. Further investigation into the methylation of 2-methylnaphthalene indicated HZSM-5 to be the most β-directing of the zeolites used. Fraenkel *et al.* attributed the differences seen between these three zeolites to the smaller channel size of H-ZSM-5 having a molecular sieving effect. The larger pore zeolites are unable to impose any constraints upon where the methyl cation can attack; therefore, they produce a larger amount of polymethylated products.

Research by Weitkamp and Neuber [10] concurred with the findings of Fraenkel *et al.* They concluded the selectivity for the β,β-isomers was due to the shape selective effect of the medium pore zeolite.

Isopropylation

Following the successes achieved through methylation research turned to bulkier alkylating agents to improve the yield of the 2,6-isomer. Katayama *et al.* [11] looked at the liquid phase isopropylation with propene and *iso*-propanol. Due to the increased size of the alkylating agents H-ZSM-5 failed to produce the target molecule. It was also reported that HM had a low activity but was selective for the 2,6-isomer (2,6/2,7 ratio of 2). The authors ascribe the result obtained for HM to the shape selective effect. This is imposed by the pore structure and the shape of the 2,6-isomer, which allows the latter to move more easily through the 1-dimensional structure of HM. HY, however, had a high activity and low selectivity for the 2,6-isomer. Success has also been achieved in this area by S.J.Chu *et al.*[12], R. Brzozwski *et al.*[13] and C. He *et al.*[14].

tert-Butylation

Another bulky alkylating agent, which has attracted much attention, is *tert*-butanol. The major advantage of using this agent was that the end product, 2,6-di-*tert*-butylnaphthalene (2,6-DTBN), could be crystallized out of the product mixture. This advantage would eliminate the need for any complex isolation procedure.

A study by Moreau *et al.*[15],[16], using HY and Hβ zeolites of different Si:Al ratios, revealed that a more acidic HY (Si:Al ratio of 20) gave the highest 2,6-/2,7- ratio of 5.9, up to 84% 2,6-DTBN and a β,β'-selectivity (2,6 and 2,7) of 98-99%.

In a recent study by Smith *et al.*[17], a 60% yield of 2,6-di-*tert*-butylnaphthalene (2,6-DTBN) was achieved with a 2,6-/ 2,7- DTBN ratio of 50 over dealuminated HM.

Cyclohexylation

Cyclohexylation using cyclohexene and cyclohexyl bromide was also investigated by Moreau *et al.*[18]. Like tert-butylation, the product compound, 2,6-di-cyclohexyl-naphthalene is able to crystallise. Unsurprisingly the best results were achieved with the large pore zeolite HY. It displayed high naphthalene conversion, a high β,β-selectivity, but unfortunately was not specific for the 2,6-isomer. Moreau *et al.* postulated that because of the presence of supercages within the structure of HY, there is no shape selective effect. Molecular mechanics calculations also revealed that the 2,6- and 2,7-isomers have an almost identical diameter.

Conclusion

There are several inherent problems associated with Friedel-Crafts reactions. These problems include: maintaining selectivity over long reaction times (hours) at low temperatures; use of acid catalysts and organic solvents that cause damage to equipment and environmental problems; and difficulties with separation of catalyst and solvent that subsequently must be either recycled or disposed of[19].

This study will look at the possibility of using sec-butanol and dimethylcarbonate to alkylate naphthalene. Present industrial processes for the production of NDC use a sixstage process; by finding a one-step method of synthesis for 2,6-dialkylnaphthalenes, the process could be shortened, providing economical benefits.

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Chapter 1

Zeolites

1.1 Introduction

Zeolites are a group of aluminosilicate compounds, both man made and naturally occurring, which have in recent years sparked great interest due to their unique and adaptive properties. The word zeolite stems from observations made by Baron Cronstadt in the 18th century, that is their ability to evolve water upon heating (zeo- to boil and lith meaning stone). Zeolites are characterized by their open framework; the uniform assembly of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra into 3-dimensional secondary building units (SBUs) and the subsequent joining of these SBUs to form polyhedral cages provide a series of low density high surface area compounds. The variety of ways in which the $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra can link within a 3-dimensional medium merely mirrors the diversity apparent by the approximately 200 known aluminosilicate framework structures. There are at present 39 known unique naturally occurring zeolites and the number of synthetic zeolites has already reached the hundreds and will continue to grow in number as research into their physical and chemical properties grows. Although the two most common tetrahedra are SiO_4 and AlO_4, others can be incorporated into the framework including PO_4, BeO_4, GeO_4 and ZnO_4.

Large-scale bulk industrial processes have used heterogeneous catalysts in various processes for many years. For example they have been used in the cracking process with the petrochemical industry with much success for a number of years and this process now accounts for 99% of the petrol production from crude oil [1]. The advantages which zeolites can offer also make them highly desirable in the fine chemical industry.

1.2 The History of Zeolites [3]

The naturally occurring members of the zeolite family have been studied by mineralogists for hundreds of years as can be seen by the dates of discovery listed by D.W.Breck in his 1974 publication Zeolite Molecular Sieves (Figure 1.1)[3]. Initially zeolites were determined to be molecular sieves due to their ability to adsorb water and small hydrocarbons but it was their incorporation into industrial processes that illustrated their chemical usefulness.

Zeolite	*Date*	*Zeolite*	*Date*
Stilbite	1756	Mordenite	1864
Natrolite	1758	Clinoptilolite	1890
Chbazite	1772	Offretite	1890
Harmotome	1775	Erionite	1890
Analcime	1784	Kehoeite	1893
Laumontite	1785	Gonnardite	1896
Thomsonite	1801	Dachiardite	1905
Scolecite	1801	Stellerite	1909
Heulandite	1801	Ferrierite	1918
Gmelinite	1807	Viseite	1942
Mesolite	1813	Yugawaralite	1952
Gismondine	1816	Wairakite	1955
Rewsterite	1822	Bikitaite	1957
Epistilbite	1823	Paulingite	1960
Phillipsite	1824	Garronite	1962
Evynite	1825	Mazzite	1972
Herschelite	1825	Barrerite	1974
Edingtonite	1825	Merlinoite	1976
Faujasite	1842		

Figure 1.1 – List of zeolites and the year of their discovery compiled by D.W.Breck & Published in 1974.

1.3 Natural Formation [3]

Zeolites are among the most common naturally occurring minerals on earth. The most abundant source of zeolite deposits is volcano magma flows and volcanic ash deposits. Large deposits coincide closely with the nature of the surrounding rock (zeolites in low silica rock are low in silica), and more than one species of zeolite can occur within a deposit. However, evidence points to a slow conversion rather than co-crystallization. These naturally occurring deposits are generally of little use to industry because of irregularities in morphology and chemical composition. Exceptions are deposits found in salt rich and arid soils. The viability of these zeolites stems from the almost exclusive presence of one zeolite. Natural zeolites have a wide diversity of uses however, from animal feed and fertilizers to cement.

The full picture of zeolite formation is still not fully clear, though it is evident that the zeolite structure, once formed, resists subsequent transformation into other species.

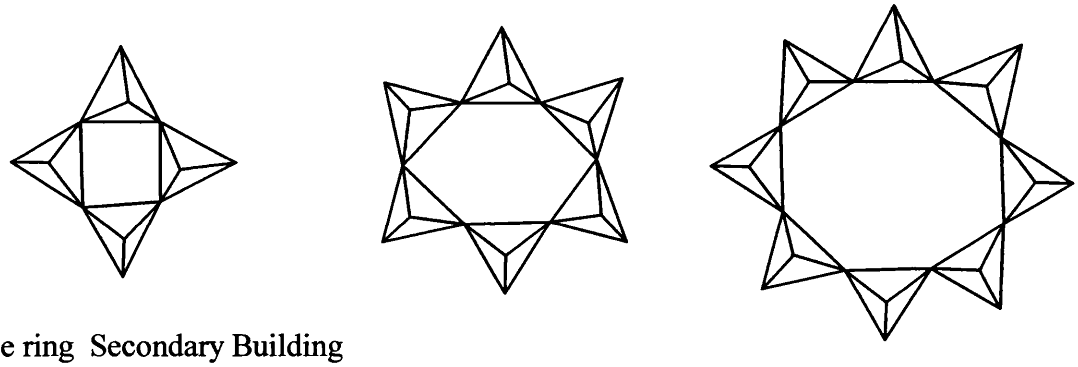
1.4 Nomenclature of Zeolites [2]

There is no strict method of nomenclature for synthetic zeolites. Some are named after minerals of same/similar structure e.g. faujasite, mordenite and sodalite, while others are named according to when and by whom they were discovered e.g. ZSM-5 stands for Zeolite Socony-Mobil Project, fifth product.

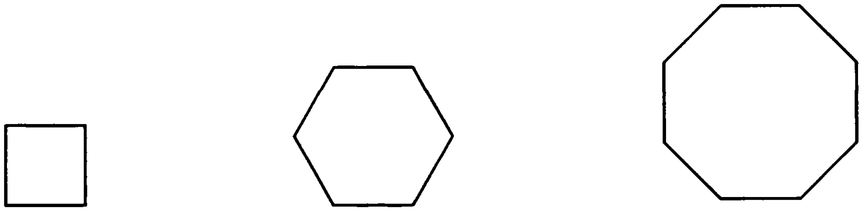
1.5 Structure of Zeolites [2] [4]

As previously mentioned the primary building blocks of zeolites are the tetrahedra $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$, which link by oxygen bridges, i.e. T-O-T (Si and Al are also known as T atoms). When representing a framework structure the O atom is ignored and the tetrahedral centers (T) are simply joined to form the secondary building units (SBUs) which can be single ring, double ring or complex in structure (Fig 1.2).

Tetrahedra join by O-bridges to form Secondary Building Units.

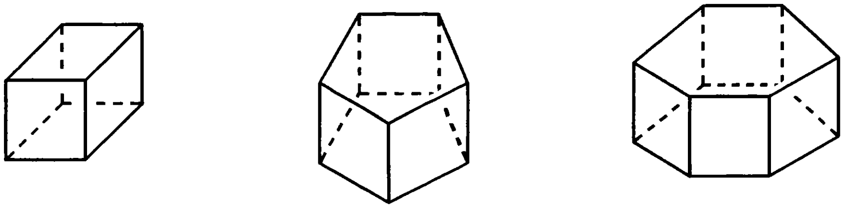


Single ring Secondary Building Units.



4 membered ring 6 membered ring 8 membered ring

Double Ring Secondary Building Units.



Complex ring Secondary Building Units

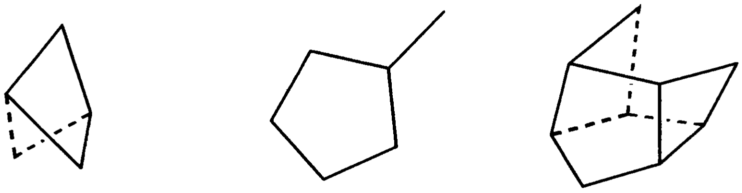
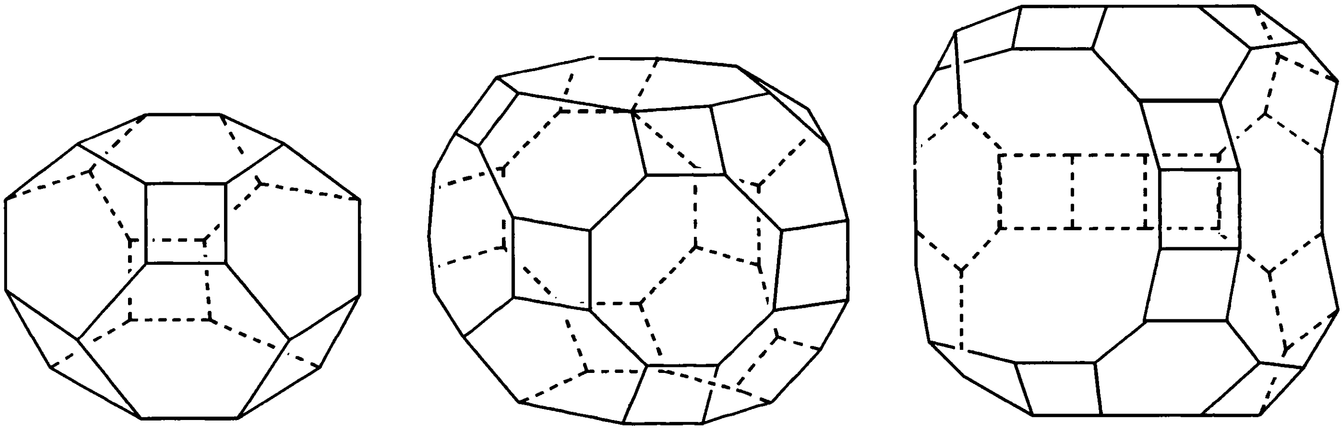


Figure 1.2 – Secondary Building units. The tetrahedra join together through oxygen bridges to form Secondary Building Units (SBUs). These SBUs are depicted, however, as being joined by the T atoms.

The SBUs can be arranged in a variety of orientations to produce 3-dimensional polyhedral cages and channels. These polyhedra subsequently link by face sharing or interconnecting channels to give uniform intracrystalline channel networks. Figure 1.3 gives some examples of polyhedral cages formed by connecting SBUs.



Sodalite cage, 14-hedron I

Alpha cage, 26-hedron I

Supercage 26-hedron II

Figure 1.3 – Polyhedral cages.

The diversity of known zeolite structures comes from the different ways the tetrahedra and SBUs link together. The flexibility of the T-O-T bond angle can range from 120°-180°. The orientation of the polyhedra created by the SBUs dictates the amount of void space in the resulting structure (Figure 1.3). The internal channel system increases the internal surface area available for reactions; the internal surface area can be up to 20 times larger than the external area [1]. This diversity means that the sieving or selective properties of one zeolite can be very different from the properties of another.

Zeolites can contain a wide range of cations, (e.g. Na^+, Ca^+, and K^+) within their channels and cages and these can impose constraints on molecules passing through the channel system [3]. The different sized ions can occupy different volumes of the zeolite channels, thus altering the volume available to molecules entering the channel. In this way changing the size of the ion inside the channel can restrict access to molecules previously able to enter the zeolite. These ions also interact with the electrostatic field set up by the framework ions.

Due to the presence of charged species making up the framework (*i.e.* $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra), small electrostatic fields exist inside the channel system. The field strength is at its greatest when the Si: Al ratio is near 1. The strength of the fields can be altered by changing the composition of the framework *via* dealumination or steaming, and thereby changing such parameters as catalytic activity [1].

1.6 Properties of Zeolites

Zeolites have three properties that make them desirable in industry. The ability to sorb species with a molecular diameter smaller than the diameter of a cavity; ion exchange of charged species within the channels with others in solution, and most importantly in connection with these studies the ability to catalyze reactions.

1.6.1 Sorption Within Zeolites

Zeolites do not contain the same irregularities as other porous species such as silica gels or clays. As discussed previously the regimented morphology of zeolites gives rise to a rigid open framework of channels, cages and even super cages. At room temperature approximately 10% of a typical zeolite's weight is water, which, once removed allows other species to be sorbed. The apertures of the zeolite channels govern the dimensions, both size and shape, of the species sorbed (e.g. straight chain hydrocarbon may be selected over branched).

It was not until the 1940's that the potential of zeolites as molecular sieves was fully realized. The zeolites synthesized at that time were designed for that purpose. Much of this early work led to the discovery that the separations being achieved were quantitative and generally one step.

The bulk industries were quick to take up the new technology, for example for hydrocarbon separation, drying of liquids and gases, removal of sulfur compounds from petroleum and air separation [3]. Zeolites are polar molecules with localized electrostatic fields generated between the anionic nature of the zeolite structure and the cations within the channel network. Species that enter the channels with dipoles or quadrupoles have an increased heat of sorption because of the interactions between the electrostatic fields.

The sieving properties of the zeolite can be dramatically altered by ion exchange. As mentioned earlier, contained within the channels of the zeolite are cations which act as *filters,* allowing the passage of the smaller or "correctly shaped" molecules, but inhibiting the passage of larger or "wrongly shaped" molecules. The cation would be located within a channel normally large enough for the passage of both kinds of molecules, but its presence turns the zeolite into a sieve with preference for one molecule.

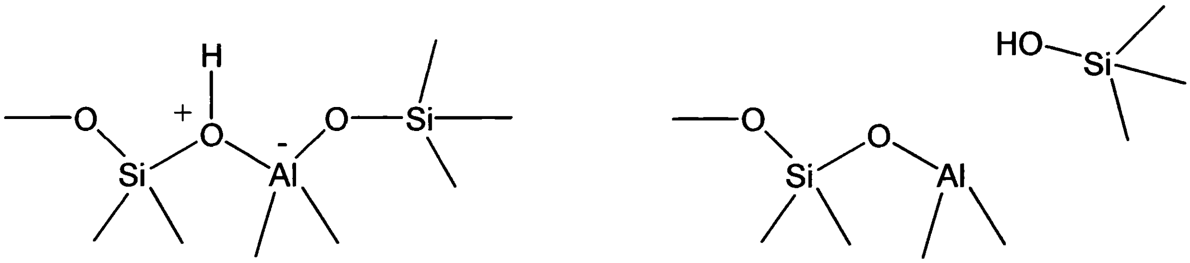
1.6.2 Ion Exchange

As mentioned above, ion exchange can have dramatic effects on the properties of a zeolite, not only on the molecular sieve properties but also on the catalytic properties of the zeolite, that is not only the physical properties but also the chemical properties are changed. The cations within the channel system weakly interact with the anionic framework of the zeolite and promote electroneutrality in the structure. Ion exchange can be used to introduce new active sites into a structure by targeting a specific site within the framework. This process would create a high electrostatic field and thus a new active site. Ion exchange is a reversible process, which is commonly carried out under mild conditions with simple apparatus.

1.6.3 Catalytic Action

Throughout the 1950's and 1960's the areas of selective adsorption and ion exchange grew rapidly. Interest in the catalytic properties began when cracking activity of rare earth and hydrogen forms of some zeolites was found to be greater than that of the silica-alumina catalysts already in use [3]. In 1962, Mobil were the first company to use a zeolite (Y) as a commercial catalyst. Its introduction improved the yield of gasoline by ~25%, as well as reducing coking in the process. The increase in yield and reduction in clean up costs from using silica-alumina catalysts has saved the industry billions of pounds.

Zeolites are widely used in industry as acid catalysts and the most common method for the introduction of acid sites into a structure is by ion exchange with ammonia or polyvalent cations and calcination [4]. Acids are not generally used as they cause leaching of aluminum from the framework, a process known as dealumination. The active acid site of a zeolite can exhibit either BrØnsted or Lewis acidity (Figure 1.4).



A Bronsted Acid Site. A Lewis Acid Site.

Figure 1.4 – Brønsted and Lewis Acidity in Zeolites

The acidity of a zeolite is governed by the amount of aluminum in the framework. As a rule, the higher the Si/Al ratio, the more strongly acidic the zeolite. This ratio can be controlled during synthesis or by chemical alteration of the framework (e.g. dealumination or steaming), to reduce the amount of aluminum present [4].

Zeolites are successful catalysts because they are both active and selective in a reaction. The activity stems from the large surface area of the structure and the acid sites, which are distributed throughout the framework. The selectivity that zeolites display comes from their selective sorption and molecular sieving properties. The selectivity of any reaction can be controlled by the diffusion of the reactant or product or by impinging upon the transition states of a reaction. With reactant selectivity, the zeolite simply sorbs the desired reactants, excluding those of incorrect size, shape or polarity. For example, the linear structure of n-heptane can easily enter the channel system of zeolite ZSM –5, while the branched structure of 2-methylhexane inhibits its entry into the channel (see Figure 1.5).

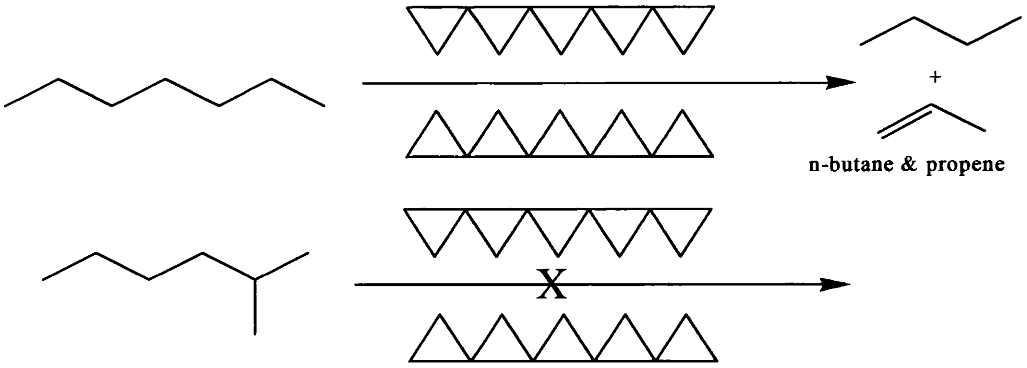


Figure 1.5 – Cleaving of n-heptane.

With product selectivity, only species of the correct size or shape are able to pass out of the channels. Any larger molecules are retained within the framework; for example the methylation of toluene can produce the para-, ortho- and meta- forms of the product xylene. Predominantly the para- isomer is seen over zeolite ZSM-5 because the geometric constraints of the channels hold the ortho- and meta- products in the framework (see Figure 1.6).

The diameters of the channels can impose geometric and steric constraints on both the size and shape of the transition state of a reaction, giving transition state selectivity. An example is in the alkylation of meta-xylene to form 1,2,4-trimethylbenzene over zeolite.

The diameters of the channels impose geometric constraints on the possible transition states, therefore the 1,3,5-isomer is not formed so readily (see figure 1.7).

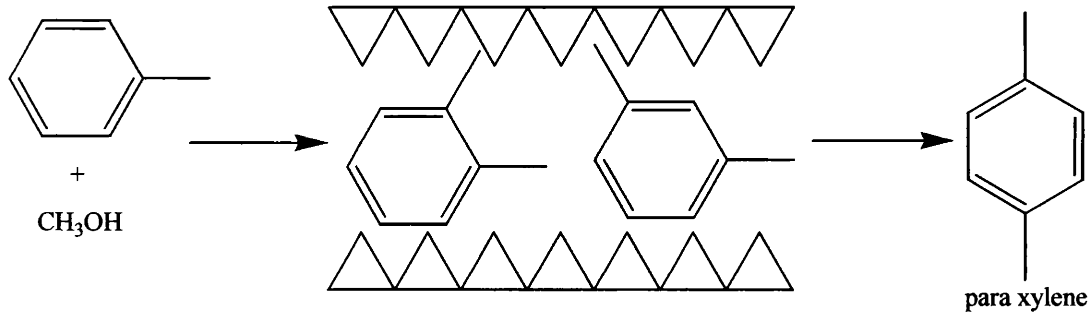


Figure 1.6- Methylation of toluene over ZSM-5

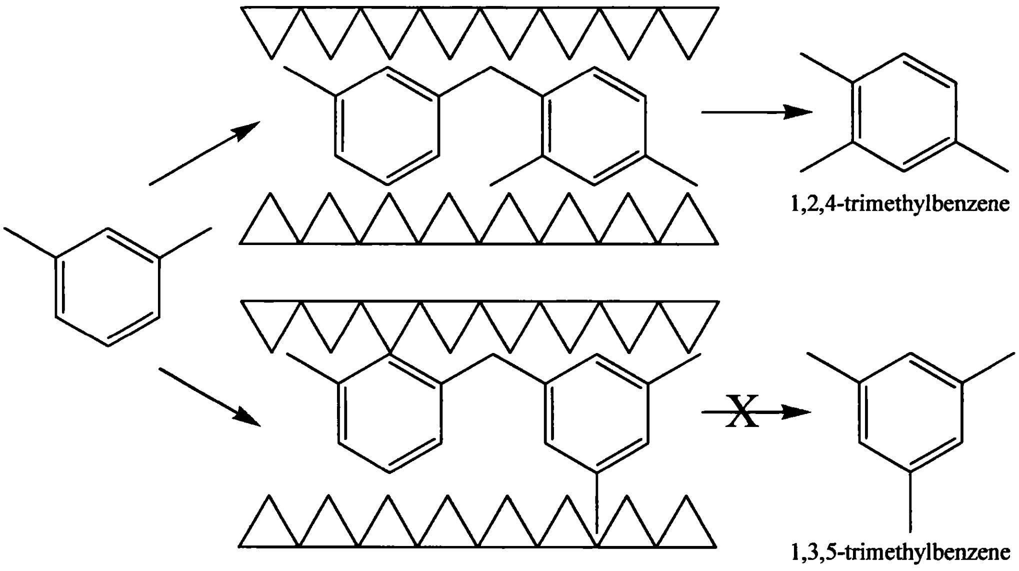


Figure 1.7 – Alkylation of meta-xylene over zeolite.

1.7 Commonly used Zeolites

As previously mentioned, naturally occurring zeolites have many applications, but are considered unsuitable for industrial and commercial processes due to the presence of stacking faults in the structure and impurities. Hereinafter are some common synthetic zeolites regularly used for industrial and commercial applications with a description of their basic structures.

1.7.1 ZSM-5

Zeolite Socony-Mobil Project, 5th Product, is a silicon rich zeolite with no natural equivalent. It has a typical empirical formula of $Na_3Al_3Si_{93}O_{192}.16H_2O$. Industrially ZSM-5 is used in oil refining (e.g. catalytic cracking) and synthesis of petrochemicals.

It is a medium pore zeolite with two types of pore. The first type has straight channels with an almost circular appearance and a dimension of 5.4 x 5.6Å. The second type of pore runs perpendicularly to this in a "zigzag" formation and is elliptical in appearance. It has a dimension of 5.1 x 5.6 Å. ZSM-5 is known as a pentasil zeolite since the repeating unit is made up of 5-membered rings of Si atoms.

1.7.2 Zeolite A

Zeolite A is a very common small pore zeolite with a typical empirical formula $Na_{12}Al_{12}\ Si_{12}O_{48}.27H_2O$. Due to its small pore size it can sorb only small molecules like water and straight chain alkanes Because of this ability to absorb water it is readily used in most laboratories as a drying agent. In industry it is mainly used in separation and purification processes, mainly involving gases because of its limited pore dimensions.

Zeolite A has a 3-dimensional unit cell whose centre is an alpha cage. The unit cell is constructed from both 6-hedra and 14-hedra (I) (also known as a sodalite cage), where the 8 T atom apertures of the unit cell have a diameter of 4.1Å (see figure 1.8).

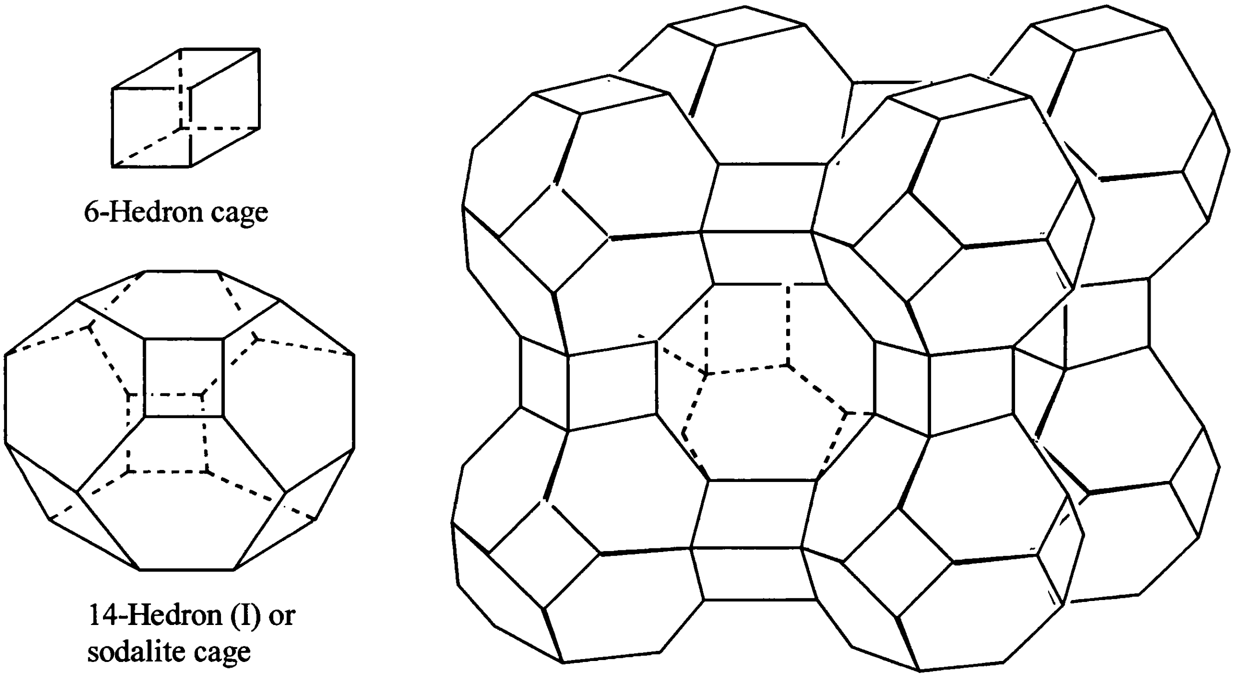


Figure 1.8. The unit cell of zeolite A and the SBUs required to build it – 6-hedron cage and 14-hedron (I) or sodalite cage.

1.7.3 Zeolites X and Y

Zeolites X and Y are synthetic equivalents of a naturally occurring mineral – faujasite. The two forms vary only in their Si/Al ratio which is reflected in their typical empirical formulae: $Na_{86}Al_{86}Si_{106}O_{384}.264H_2O$ for zeolite X and $Na_{56}Al_{56}Si_{136}O_{384}.27H_2O$ for zeolite Y. Zeolite X has been used for the removal of CO_2 from gas streams with great success for many years while zeolite Y is also used in purification of gas flows and for cracking in oil refining.

The unit cell consists of 14-hedron (I) and 8-hedra, which form a 3-dimensional framework (see figure 1.9). This combination creates supercages with 12 T atom apertures of diameter 7.4Å, making both zeolites X and Y large pore zeolites.

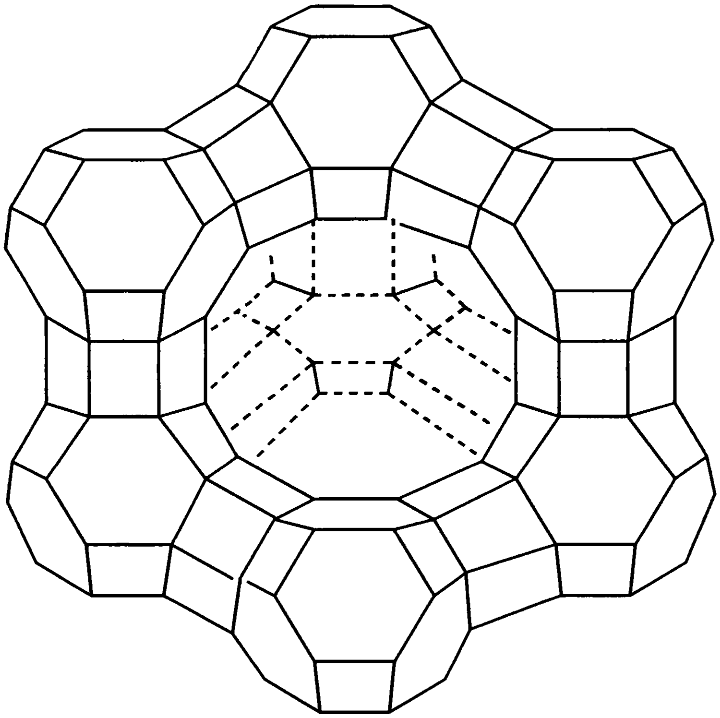


Figure 1.9. The unit cell of zeolite X and Y. The SBUs required for its construction are a 8-hedron cage and a 14-hedron (I) or sodalite cage.

1.7.4 Mordenite

Mordenite is a naturally occurring zeolite, which has many forms such as ferrierite, dachiardite and epistibite. It is also synthetically prepared and was first used as a molecular sieve in the 1940's. Today it is used in oil refining and petrochemical processes. Its typical empirical formula is $Na_4Ca_2Al_8Si_{40}O_{96}.24H_2O$.

Mordenite has a 1-dimensional channel system. There are two sizes of aperture an 8 T atom aperture, and a 12 T atom aperture of dimensions 2.6 x 5.7Å and 6.5 x 7.0Å respectively (see Figure 1.10).

1.8 Conclusion

The possible applications for zeolites in industry are still being researched. The environmental advantages of using a catalyst that reduces waste and can be recycled have the potential to revolutionize many industrial processes.

For this study, however, the focus is principally on H-mordenite and zeolite HY. It has been shown in many studies that mordenite is not the most active zeolite. It is however, frequently the most selective for the β,β'-isomer in the dialkylation reactions of naphthalene. The zeolite HY is used because of its high activity and low selectivity for comparison.

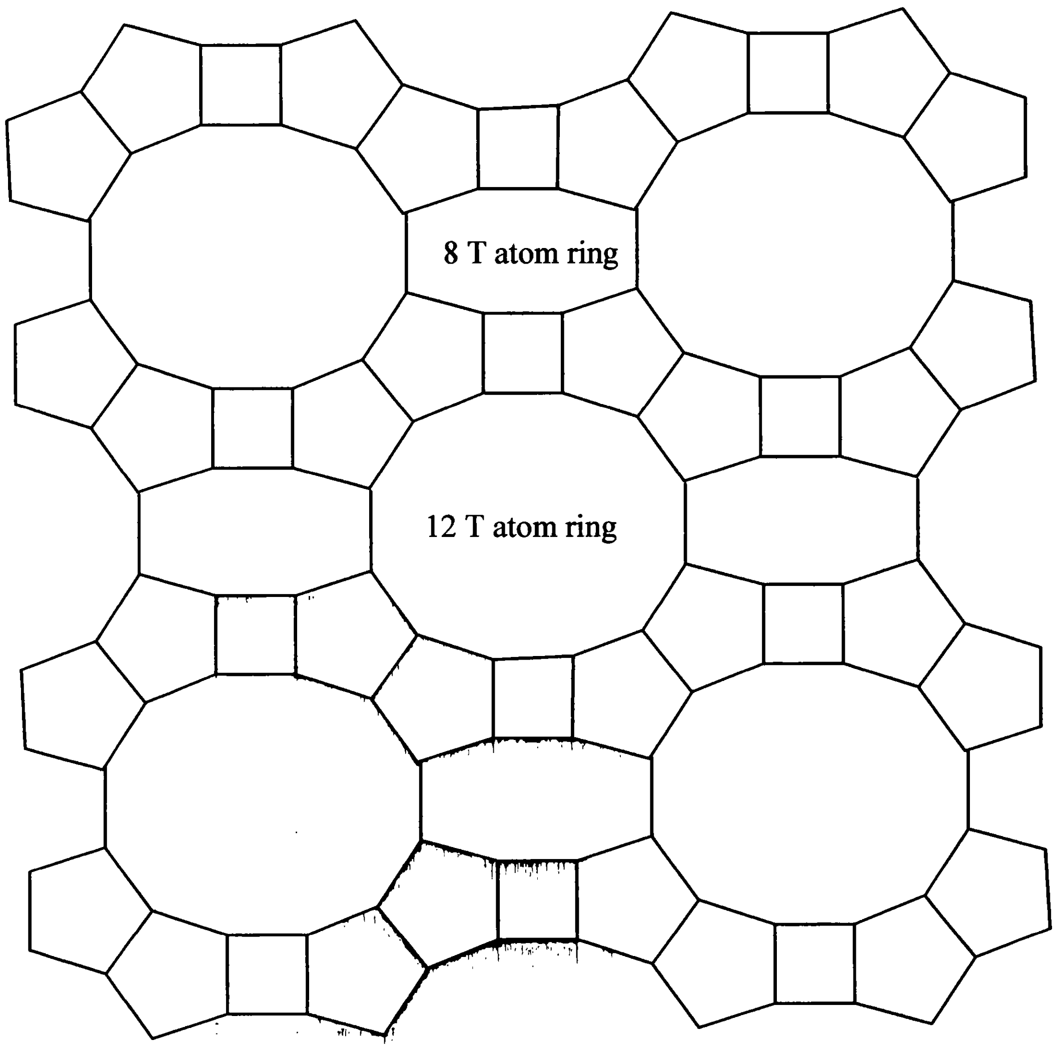


Figure 1.10. Single layer of mordenite. These layers stack to form channels of 12 T atoms and 8 T atoms.

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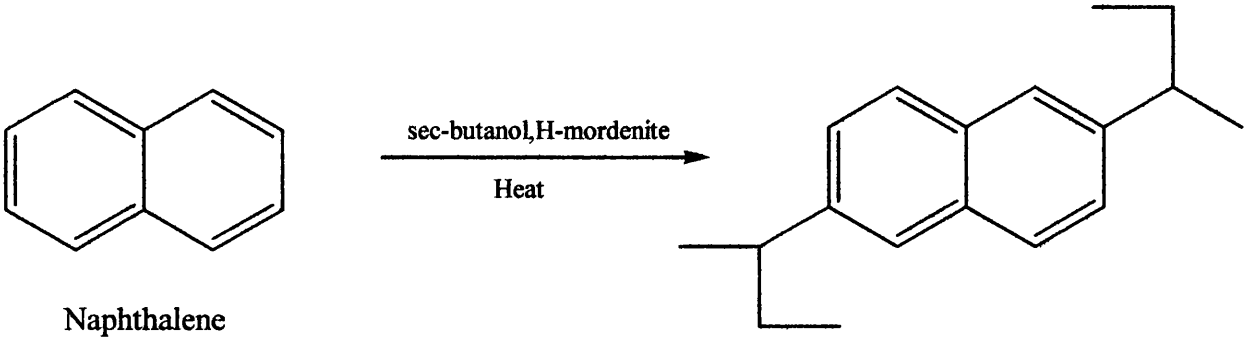
Chapter 2

Alkylation of Naphthalene with *sec*-Butanol

2.1 Introduction

Secondary alcohols are relatively unreactive. Nevertheless, it was proposed to study the reactivity of *sec*-butanol at various temperatures for different lengths of time to find optimum conditions and to investigate whether it is feasible to use *sec*-butanol for dialkylation of naphthalene (figure 2.1).



Naphthalene

2,6-Di-*sec*-butyl-naphthalene

Figure 2.1: Dialkylation of naphthalene by *sec*-butanol.

The reaction may be partially reversible; *i.e.* the product compound may dissociate back into the starting materials on reaction with water. There is also a possibility of secondary reactions, which would compete with the main reaction.

2.1.1 The Reactants

Naphthalene has a fully conjugated cyclic electron system, with p-orbital overlap extending around the ring across the central C-C bridge. The π electrons experience delocalisation and therefore contribute to naphthalene's aromaticity [1]. Disregarding Dewar forms or those with charge separation the main canonical forms of naphthalene are shown in Figure 2.2.

Structure (b) has a double bond across the centre of the molecule, which makes it different from the other two forms, (a) and (c), which are equivalent. If these forms were to contribute equally to the overall structure, the 1,2-bond would have more double bond character than the 2,3-bond, known as "partial bond fixation". This can be seen in evidence from molecular orbital calculations of the bond order and in the actual bond lengths. The bond order of benzene from molecular orbital calculations is 1.667; while for the 1,2- and 2,3-bonds of naphthalene the bond orders are 1.724 and 1.603, respectively. The bond lengths are 1.36 and 1.415, respectively [2]. Because of the symmetry of the molecule naphthalene has three sets of equivalent carbon atoms {C1, C4, C5, C8} and {C2, C3, C6, C7} and {C4a, C8a}.

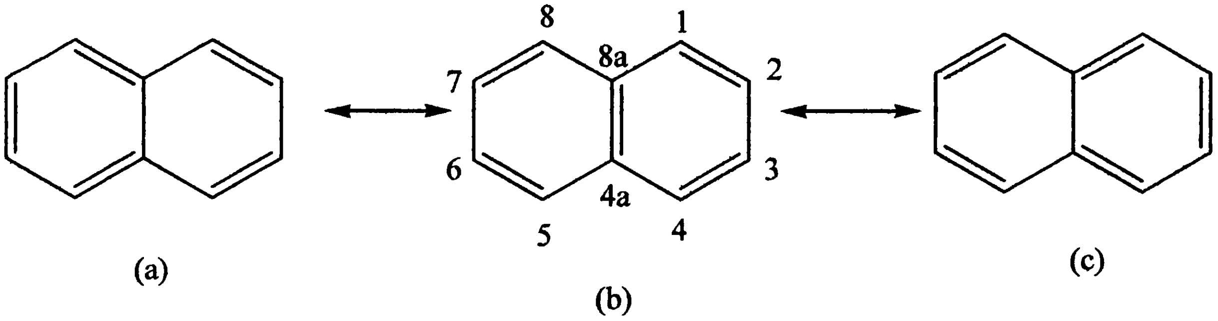


Figure 2.2: Resonance structure of naphthalene.

Alcohols can undergo an array of different reactions including formation of acetals (in the presence of an acid catalyst and carbonyl compound) and ethers (in the presence of a strong base) and reactions with alkyl halides and carboxylic acids. Recent successes with *tert*-butanol in the alkylation of naphthalene have led to interest into the less hindered *sec*-butanol [1]. This alcohol is however not very reactive. Therefore it was decided to investigate the reaction under a variety of conditions in the hope of finding conditions under which a good yield could be obtained.

2.2 Results and Discussion

Three factors were investigated in order to find the optimum conditions for the dialkylation of naphthalene: molar ratio of naphthalene: *sec*-butanol (and thereby the concentration of *sec*-butanol) concentration of starting material, temperature and time.

Beginning with the stoichiometric molar ratio of 1:2 (naphthalene to *sec*-butanol), the ratio was increased up to 1: 8. The temperature range investigated was 160°C to 200°C. The duration of the reaction was also examined to find the optimum reaction time. The results are given in Tables 2.2.1 to 2.2.4

Initially the reaction was carried out under the following conditions. A mixture of naphthalene (1.28g, 0.100mol) and *sec*-butanol (1.482g, 0.200mol) and zeolite HM (2g) in cyclohexane (10ml) was heated in an autoclave at 160 °C for 1 hour. The mixture was then cooled and filtered to remove the zeolite. An aliquot of the concentrated filtrate was subjected to gas chromatography after addition of tetradecane as a standard. (For G.C. profile see figure 2.5)

The GC showed peaks due to solvent, naphthalene, tetradecane and three unknown peaks. These peaks appeared at the following time intervals: naphthalene *ca.* 10.2 minutes, tetradecane *ca.* 14.2 minutes, unknown peak 1 *ca.* 16.6 minutes unknown peak 2 *ca.* 25.8 minutes, and unknown peak 3 *ca.* 26.2 minutes. There were additional minor peaks after the last large unknown peak that appeared after longer lengths of time on the GC, indicating them to have higher boiling points. These could have been due to tri-substituted naphthalene formed on the outer surface of the zeolite. The bulk of the product mixture was therefore, evaporated to remove cyclohexane and subjected to Kugelrohr distillation (full description of apparatus and technique given in experimental, figure 2.6). Seven fractions were collected. Fractions 1, 2 and 3 distilled at a maximum of 80 °C, respectively, and were mainly naphthalene (confirmed by GC). Fraction 4 (distilled at a maximum of 90 °C) was a mixture of naphthalene and one of the unknown products, while fraction five was also a mixture of these two compounds, but richer in the unknown product (about 80% by GC). The mixture was distilled again via Kugelrohr and a recrystallised, to extract a solid product. No solid was obtained. The unknown of fraction five, was shown to correspond to a mono-butyl derivative of naphthalene by ^{1}H-NMR analysis.

^{1}H-NMR of the mixture showed a group of peaks at high field that were in the proportions given below:

^{1}H: δ= 2.8(1H, sextet, J= 7.4 Hz, C$\underline{H}$ (CH$_3$) CH$_2$CH$_3$); 1.7(2H, quartet, J=7.1 Hz, CH (CH$_3$) C$\underline{H_2}$CH$_3$); 1.3(3H, doublet, J= 7.3 Hz, CH (C$\underline{H_3}$) CH$_2$CH$_3$); 0.8(3H, triplet, J=6.3 Hz, CH (CH$_3$) CH$_2$C$\underline{H_3}$).

These peaks clearly showed that the butyl group remained intact as a *sec*-butyl group. The aromatic region of the spectrum showed three major regions, with integral ratios of 4:1:3 at δ 7.4, 7.7 and 7.8, respectively the sum of the main aromatic peaks integrated in a ratio 60.41:109.16 with the aliphatic peaks. This is broadly in line with expectation for mono-*sec*-butylnaphthalene. The aromatic region showed the peak at δ 7.7 to be a singlet, which is consistent with the 2-*sec*-butyl isomer. The evidence indicates this sample to contain a reasonably pure sample of 2-*sec*-butylnaphthalene (see

Appendix, Figure 2). Therefore, this sample could be used to enable calculation of a response factor for 2-*sec*-butylnaphthalene

The response factor (RF) is used in the calculation of the percentage yield. It is worked out using Equation 1:

Equation 1:

$$\mathrm{RF} = \frac{W_R}{A_R} = \frac{\text{Wt Compound}}{\text{Wt Standard}} \times \frac{\text{Area Standard}}{\text{Area Compund}}$$

Where W_R is the weight ratio, *i.e.* the weight of the compound for which the RF is being calculated over the weight of the standard; and A_R is the GC peak area for the compound being investigated over the peak area of the standard.

The RF for every compound is individual and is used to find the percentage yield of the compound using the Equation 2. This calculation is done for each compound detected by GC. As the response factor could vary, it was recalculated every 2-4 weeks to ensure accuracy.

Equation 2:

$$\left(\left(\frac{\text{RF}}{\dfrac{\text{Area of Std}}{\text{Area of Cpd}}}\right) \text{x Wt of Std}\right) \text{x Dilution factor} = \text{Recovered mass}$$

$$\frac{\text{Recovered mass}}{\text{Mr of Cpd}} = \text{Moles of recovered Product}$$

$$\frac{\text{Mass of Nphthalene at start}}{\text{Mr of Naphthalene}} = \text{Moles at start}$$

$$\frac{\text{Moles of recovered Cpd}}{\text{Moles at start}} = \text{\% yield}$$

*Dilution Factor: a weighed aliquot of the product liquor was used for GC analysis. A known weight of standard was added and the sample was dissolved in solvent for injection onto the GC. In order to calculate the mass of any product in the original mixture, the mass calculated from the GC results needed to be corrected for the proportion of the sample used for the GC analysis. The dilution factor is the ratio of the total mass of the sample, divided by the mass of the aliquot taken for GC measurement.

Fractions 6 and 7 from the Kugelrohr distillation were found to be mixtures primarily of the confirmed mono-substituted peak and unknown peaks 2 and 3. GC showed fraction 7 to consist mainly of the unknown peaks 2 and 3. Fraction 7 was re-distilled to separate the unknowns 2 and 3 by Kugelrohr but due to the closeness of the boiling points this proved unsuccessful. The remaining residue was the residue collected from the reaction vessel following Kugelrohr distillation. It was a dark gold liquid. The GC showed minor peaks of a significantly higher retention time than the unknown peaks under investigation. The ^{1}H-NMR spectrum for unknown peaks 2 and 3, in fraction 7, showed spectrum very similar to those for fraction 4, but different in the integrals. The spectrum showed total aromatic protons: total aliphatic protons in a ratio of 29:70, *i.e.* 1:2.4, whereas for di-sec-butylnaphthalene it should be 1:3 and for mono-sec-butyl naphthalene it should be 7:9, i.e. 1:1.3. From the GC, it was clear there was an impurity of a higher boiling point (see Appendix Figure 1). To affect the ratio in this way there must be a higher proportion of aromatic ^{1}H in the impurity suggesting the impurity might have 2 naphthalene rings attached to a single aliphatic residue. The following peaks were recorded:

^{1}H: δ= 7.6 (3H, multiplet); 7.2 (3H, multiplet); 2.8(1H, sextet, J= 7.4 Hz, $C\underline{H}$ (CH_3) CH_2CH_3); 1.7(2H, quartet, J=7.1 Hz, CH (CH_3) $C\underline{H_2}CH_3$); 1.3(3H, doublet, J= 7.3 Hz, CH $(C\underline{H_3})$ CH_2CH_3); 0.8(3H, triplet, J=6.3 Hz, CH (CH_3) $CH_2C\underline{H_3}$).

The residue was subject to redistillation by Kugelrohr and a fraction was obtained that was richer in the di-substituted isomers, 2,6-di-*sec*-butylnaphthalene or 2,7-di-*sec*-butylnaphthalene although the sample contained other products, it was used for the calculation of the RF value. The RF of the di- substituted compounds was calculated by the same means as the mono-substituted one, allowing an approximate yield of di-*sec*-butylnaphthalenes to be calculated. Attempts to further purify the sample by Kugelrohr and crystallisation were unsuccessful. Crystallisation proved unsuccessful because the target molecule is an oil, unlike 2,6-di-*tert*-butylnaphthalene or 2,7-di-*tert*-butylnaphthalene which can be crystallised.

With RF values to hand, it was now possible to conduct experiments in which the reaction parameters were varied and to estimate the yields of the various components in the reaction mixtures. Initially, the effect of reactant proportions was investigated. The results are shown in Table 2.2.1.

The Tables records the percentage of detected components present in the product mixture, using the internal standard tetradecane as a reference. The amount of naphthalene consumed by any reaction is 100 minus the remaining naphthalene.

Table 2.2.1 – Products of reaction according to figure 2.1 at 160°C for 1hr[a].

Molar Ratio Naph:*sec*-Butanol	Remaining Naphthalene %	2-BN [b,c] %	2,7-DsBN [b,c] %	2,6-DsBN [b,c] %	Ratio 2,6-DsBN: 2,7-DsBN[d]
1:2	19	50	2	9	4
1:4	40	46	3	10	4
1:6	18	14	0.4	2	4
1:8	9	24	1	5	4

(a) Naphthalene 1.28g (10mmol); the appropriate quantity of *sec*-butanol (beginning with 1.482g 20mmol), cyclohexane 10ml and zeolite HM 2g.

(b) 2-BN=2-*sec*-butylnaphthalene, 2,7-DsBN 2,7-di-*sec*-butylnaphthalene and 2,6-DsBN=2,6-Di-*sec*-butylnaphthalene.

(c) By GC, to nearest 1%, except for numbers below 1%.

(d) Ratio to nearest whole number, calculated from original GC trace.

Beginning with the stoichiometric ratio of 1:2, the amount of the alcohol was increased in stages up to give a ratio of 1:8. The results that showed the optimum ratio of the starting materials at 160°C was about 1:4 (naphthalene: *sec*-butanol). At this ratio, the yield of dialkylated products was highest and the four compounds estimated, accounted for essentially all of the naphthalene used in the reaction.

In the presence of larger amounts of *sec*-butanol, significant amounts of the starting materials were involved in side reactions as evidenced by the low total mass balances the four compounds estimated. At molar ratios of 1:6 and 1:8 (naphthalene: *sec*-butanol), there was a decline in the amount of the target compound, but no drop in the ratio of the 2,6-DsBN: 2,7-DsBN. A possible explanation for this is that the increased amount of alcohol in the 8T atom apertures of H-mordenite can lead to a higher occurrence of side reactions involving the alcohol, such as oligomerisation. This would prevent a proportion of the alcohol taking part in the main reaction, but might also block the pores, preventing naphthalene compounds from escaping. Despite this drop in the yield of the target molecule with the increased amount of alcohol, the ratio of 2,6-DsBN: 2,7-DsBN remained constant at 4:1.

It was then decided to increase the temperature to 180°C in order to encourage the *sec*-butanol to react more rapidly. A series of reactant proportions from 1:2 to 1:8 was investigated. The results are shown in Table 2.2.2.

The effect of increasing the temperature was to raise the yield of the target products. Generally the patterns concurred with those seen in table 2.2.1. One significant difference seen with these results, however, is the drop in the ratio of 2,6-DsBN: 2,7-DsBN with a starting material ratio of 1:2 (naphthalene: *sec*-butanol). Here the ratio of

2,6-DsBN: 2,7-DsBN dropped to three. The reason for this is not clear. It is to be expected that the reaction would be less selective at higher temperature, but why this should particularly affect the reaction with a lower proportion of *sec*-butanol is not obvious. Perhaps the elevated temperature could cause a higher proportion of the alcohol to be involved in competing reactions, which somehow might affect the proportions of products.

Table 2.2.2 – Products of reaction according to figure 2.1 at 180°C for 1hr[a].

Molar Ratio Naph:*sec*-Butanol	Remaining Naphthalene %	2-BN [b,c] %	2,7-DsBN [b,c] %	2,6-DsBN [b,c] %	Ratio 2,6-DsBN: 2,7-DsBN[d]
1:2	58	31	4	13	3
1:3	60	28	3	10	4
1:4	41	41	4	15	4
1:5	50	35	3	10	4
1:6	37	32	1	5	4
1:8	37	31	2	7	4

(a) Naphthalene 1.28g (10mmol), the appropriate quantity of *sec*-butanol (beginning with 1.482g 20mmol), cyclohexane 10ml and zeolite HM 2g.

(b) 2-BN=2-butylnaphthalene, 2,7-DsBN = 2,7 di-*sec*-butylnaphthalene and 2,6-DsBN=2,6-Di-*sec*-butylnaphthalene.

(c) By GC, to nearest 1%, except for numbers below 1%.

(d) Ratio to nearest whole number, calculated from original GC trace.

The best yields were again achieved with a naphthalene:*sec*-butanol ratio in the region of 1:4, and the mass balances were good for ratios up to 1:5. However, when ratios of 1:6 and 1:8 were used, the mass balances were low, suggesting side reactions were occurring possibly resulting in the blocking of the zeolite pores.

Because of the positive results obtained by raising the temperature, it was again increased, by 20°C, to 200°C (Table 2.2.3). This however, had the effect of decreasing the overall amounts of 2,6-DsBN and 2,7-DsBN. In addition the optimum ratio of starting materials changed; at 160 and 180°C the maximum yield of the dialkylated products had been obtained at the ratio of 1:4 (naphthalene: *sec*-butanol), whereas at 200°C the maximum yield was obtained at the ratio 1:5 (naphthalene: *sec*-butanol), although the yields of dialkylated products were lower than at 180°C. The increase in the temperature apparently results in a greater occurrence of secondary reactions within the system, leading to lower yields and mass balances for ratios 1:2 to 1:4. Thus an increased amount of alcohol introduced into the system is beneficial.

Table 2.2.3 – Products of reaction according to figure 2.1 at 200°C for 1hr[a].

Molar Ratio Naph:*sec*-Butanol	Remaining Naphthalene %	2-BN [b,c] %	2,7-DsBN [b,c] %	2,6-DsBN [b,c] %	Ratio 2,6-DsBN: 2,7-DsBN[d]
1:2	50	35	2	7	4
1:3	56	29	2	6	4
1:4	59	29	2	8	4
1:5	65	35	5	13	3
1:6	60	31	3	11	3

(a) Naphthalene (1.28g 10mmol), the appropriate quantity of *sec*-butanol (beginning with 1.482g 20mmol), cyclohexane 10ml and zeolite HM 2g.

(b) 2-BN=2-butylnaphthalene, 2,7-DsBN =2,7-di-*sec*-butylnaphthalene and 2,6-DsBN =2,6-Di-*sec*-butylnaphthalene.

(c) By GC, to nearest 1%, except for numbers below 1%.

(d) Ratio to nearest whole number, calculated from original GC trace.

For a naphthalene: *sec*-butanol ratio of 1:6, the yields of alkylated products were lower than a 1:5 ratio in the same way that had been seen for ratios of 1:6 and 1:8 at lower temperatures. A similar effect was observed by Liu *et al* [6], during studies into *tert*-butylation of naphthalene. In that case, increasing the temperature resulted in a decrease in 2,6-selectivity. Furthermore the authors suggested that at higher temperatures, secondary reactions occur more readily, driving the reaction mixture to a thermodynamic equilibrium. They schematically represented the possible competing reactions, in which the starting materials and products can be consumed (Figure 2.4).

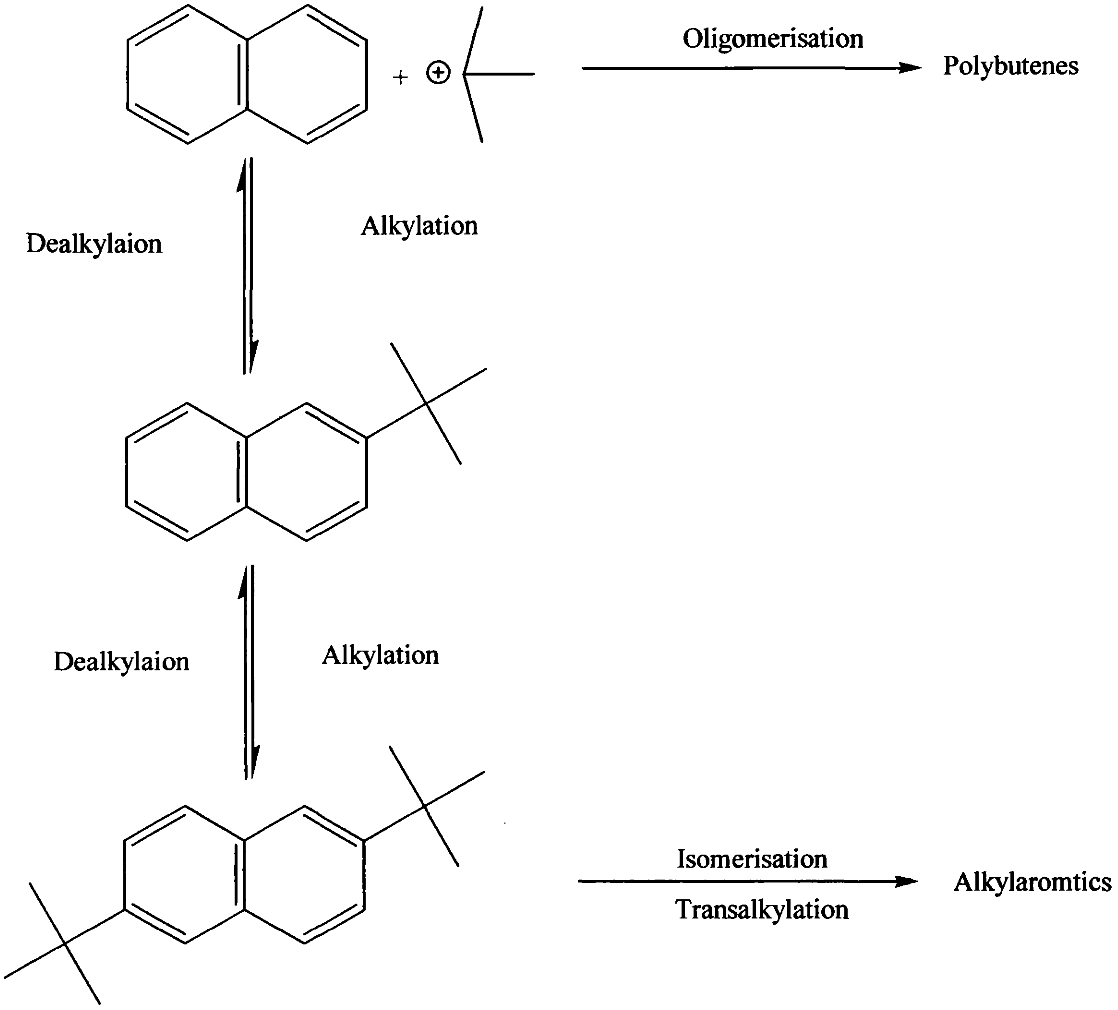


Figure 2.4: Diagrammatic representations of possible competing reactions suggested by Liu *et al.* [6], for the *tert*-butylation of naphthalene.

In the present studies at 200°C, an increase in the recovered naphthalene was observed in the product liquor. This observation could be attributed either to a decrease in the conversion of naphthalene or to dealkylation of the product compounds [6]. In either case it would seem that the alcohol would have to be destroyed, perhaps by oligomerisation in the pores of the zeolite and inhibiting the further activity of the catalyst.

With the higher naphthalene: *sec*-butanol ratios (1:5 and 1:6), at 200°C there is a drop in the 2,7-DsBN: 2,6-DsBN ratio to three. The raised temperature probably caused a higher occurrence of oligomerisation within the smaller H-mordenite apertures, but the reduced selectivity was presumably mainly caused by the higher temperature and some tendency to equilibrium.

From the studies of temperature and reaction proportions reported in Tables 2.2.1 to 2.2.3, it was apparent that the maximum yield of dialkylnaphthalenes was achieved with a naphthalene: *sec*-butanol ratio of 1:4 at 180°C. Therefore the effect of the final factor, time, on the system was investigated under these conditions. Different reactions were run for various lengths of time, between 1 to 24 hours. The results are recorded in Table 2.2.4. The time (stated in the table in hours) does not include the apparatus cooling time of 1.5 hours.

From the table it is clear that no improvements in yield were obtained after 1 hour. Although there was some variability in the results, the reaction mixtures appeared to be broadly static over periods longer than 2 hours. The ratio of 2,6-DsBN: 2,7-DsBN remained constant up to periods of 24 hours, indicating that the duration of the reaction had no effect on the 2,6-DsBN: 2,7-DsBN ratio.

Table 2.2.4 – Products of reaction according to figure 2.1 at 180°C over increasing lengths of time [a].

Time(h)	Remaining Naphthalene %	2-BN [b,c] %	2,7-DsBN [b,c] %	2,6-DsBN [b,c] %	Ratio 2,6-DsBN: 2,7-DsBN[d]
1	41	41	4	15	4
2	51	33	2	8	4
3	49	34	2	8	4
6	60	36	3	10	4
8	58	38	3	11	4
16	36	28	1	4	4
24	50	28	2	8	4

(a) Naphthalene 1.28g (10mmol), *sec*-butanol 2.965g (40mmol), cyclohexane 10ml and zeolite HM 2g.

(b) *(b)* 2-BN=2-butylnaphthalene, 2,7-DsBN =2,7-di-*sec*-butylnaphthalene and 2,6-DsBN=2,6-Di-*sec*-butylnaphthalene.

(c) By GC, to nearest 1%, except for numbers below 1%.

(d) Ratio to nearest whole number, calculated from original GC trace.

During all the reactions studied, the pressure generated by each reaction was noted and the trends are indicated in Table 2.2.5. As indicated in the table the as temperature was increased the self- generated pressure in the reaction vessel increased. This is to be expected on the basis of the effect of temperature on the pressure of a gas at a constant volume. However in general it is also the case the pressure was higher for reactions that contained more *sec*-butanol at the start. This may suggest the build-up of breakdown products such as butenes or may simply be due to the greater volume of total materials in those mixtures. Further studies would be needed to answer such questions.

Table 2.2.5 – Pressure ranges observed at increasing temperatures in the reaction according to figure 2.1

Temperature (°C)	Pressure (Psi)
160	120-140
180	150-170
200	180-200

Mechanism:

The reaction is believed to proceed *via* a carbocation reaction (see figure 2.3). The initial step is protonation of the alcohol. The protonated alcohol then acts as the electrophile, attacking the naphthalene molecule at the C2 position. This would occur within the 12 T atom aperture channels, as the naphthalene molecules cannot enter the 8 T atom apertures. Subsequently, another carbocation will attack the monosubstituted naphthalene molecule at a C6 or C7 position [3].

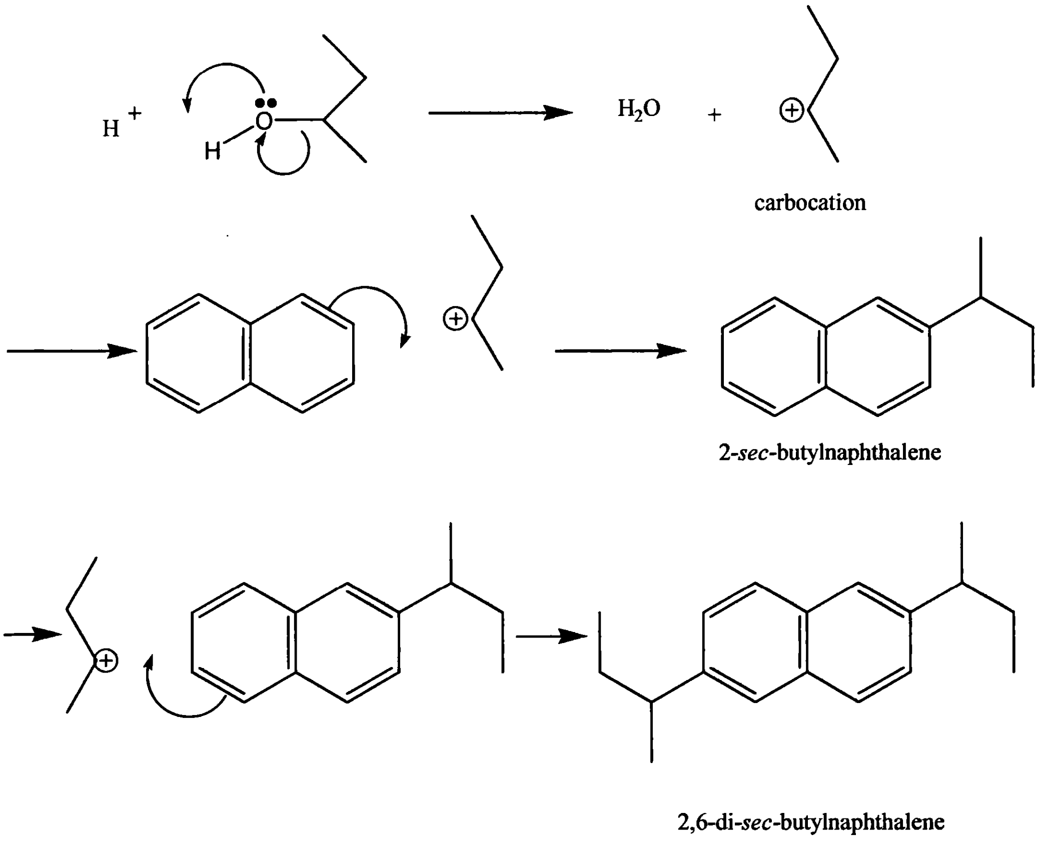


Figure 2.3: Mechanism for the dialkylation of naphthalene by a carbocation, as per figure 2.1

Mordenite achieves its selectivity for the 2,6-isomer by imposing steric constraints upon the reaction species. The α position (or C1) is blocked by the width of the mordenite channels, leaving only the β positions (or C2) accessible to the attacking carbocation. The difficulty of making the target compound, 2,6-di-*sec*-butylnaphthalene, compared to the mono-alkylated product may stem from the restricted diffusion of the mono product through the HM channels. When it comes to alkylation of the second β position, research has shown that the C6 position has a higher electron density in its HOMO (Highest Occupied Molecular Orbital) of a 2-alkylnaphthalene than the C7 position [4].

Despite the narrowness of the zeolite channels preventing the formation of the α product, the isomers 2,6-DsBN and 2,7-DsBN have about the same critical diameter. Nevertheless, it has been argued that 2,6-DsBN is the favoured isomer because of its more linear structure, which permits more rapid diffusion. Investigations into the rates of diffusion by Horsly *et al.* [5] showed 2,6-di-*sec*-butylnaphthalene to have a higher diffusion rate than the 2,7-isomer, thus with a lower barrier to diffusion the 2,6-isomer may be selectively produced.

Competing reactions

The reaction investigated in this study appears to be partially reversible. The temperature of the reaction and the duration of the reaction can affect any partial equilibrium that exists. The loss of starting materials in side reactions, particularly during extended reaction times or at increasing temperatures, would cause the reverse reaction, leading to a drop in the yield of the target compound. Therefore it is interesting to consider possible side reactions of the *sec*-butanol.

Firstly, there is the possibility of oligomerisation of butenes formed by dehydration of the alcohol under the influence of the *sec*-butyl carbocations formed within the channels of the zeolite. If this were to occur within the 8T channels, because of the small size of these channels the naphthalene molecules, would not enter them, therefore leading to a series of branched alkanes obtained solely from the alcohol. If the reaction were to occur in the larger channels, where naphthalene could also penetrate, there could be competition between oligomerisation of the butenes and alkylation of the naphthalene within those channels.

The formation of compounds whose geometry was such that they were unable the leave the channel system of the zeolite, would lead to loss of reagent and products and could lead to lead to the low mass balances sometimes observed. Rearrangement is also a possibility. The most likely rearrangement product of the *sec*-butyl cation would be the *tert*-butyl cation. Therefore, 2-*tert*-butylnaphthalene and 2,6- and 2,7-di-*tert*-butylnaphthalenes would be possible products. These materials were available in the laboratory as a result of the work of Simon Roberts [7], and were monitored under the GC conditions used. Indeed, 2,6- and 2,7-di-*tert*-butylnaphthalenes (and 2,6-DTBN and 2,7-DTBN) appeared to be present as minor components in many reaction mixtures (see Appendix, Figure1 for typical GC trace).

Monoalkylated product

The amount of the monosubstituted product was also monitored during this study and it was found that the main product of the reaction was 2-*sec*-butylnaphthalene. As previously stated in this section, the butyl carbocation ion attacks naphthalene at the β position. The relative inactivity of *sec*-butanol and the reduced mobility of *sec*-butylnaphthalene within the zeolite channels contribute to the monosubstituted form being the major product, rather than the disubstituted products.

Reaction over Zeolite HY

The zeolite HY is a large pore zeolite well known for its high activity. The high activity of HY could encourage/promote the possible occurrence of side reactions and the formation of undesirable isomers. Unlike mordenite, whose catalytic action is governed by the shape selective effect, HY's use of a supercage might prove relatively unselective. Nevertheless, a brief investigation into the use of HY as a reaction catalyst was conducted. The conditions chosen were the same as those found to be optimal with mordenite as a catalyst, i.e. use of the ratio 1:4 (naphthalene:*sec*-butanol), 180°C, 1hr. The results are recorded in Table 2.2.6. The GC of the product liquor revealed several peaks of higher retention time than that of the 2,6- and 2,7-isomers, in greater abundance than seen when using zeolite HM. These peaks could correspond to tri-substituted isomers, which could be formed within the HY framework supercages. The formation of such products could explain the very low mass balance based on the usual four components of the reaction mixtures (see Table 2.2.6). However, since the selectivity was also very low (ratio 2,6-: 2,7-dialkylnaphthalene almost unity), the reaction was not pursued further.

Table 2.2.6: Products of reaction according to figure 2.1, using 2g zeolite HY at 180 °C for 1h[a]

Remaining Naphthalene % [b,c]	2-BN [b,c] %	2,7-DsBN [b,c] %	2,6-DsBN [b,c] %	Ratio 2,6-DsBN: 2,7-DsBN[d]
0	3	11	10	1

(a) Naphthalene 1.28g (10mmol), *sec*-butanol 2.965g (40mmol), cyclohexane 10ml and zeolite HM 2g.
(b) *(b)* 2-BN=2-butylnaphthalene, 2,7-DsBN =2,7-di-*sec*-butylnaphthalene and 2,6-DsBN=2,6-Di-*sec*-butylnaphthalene.
(c) By GC, to nearest 1%, except for numbers below 1%.
(d) Ratio to nearest whole number, calculated from original GC trace.

2.3 Experimental

2.3.1 Materials

Scintillation grade naphthalene (99+%), and sec-butanol (99+%) were obtained from Aldrich and cyclohexane (99+%) was obtained from Fischer Scientific._H-Mordenite, product code- CBV 20A, Si/Al ratio = 10, nominal cation form = NH_4, surface area (m^2/g) =500, was obtained as a gift from Zeolyst International.

2.3.2 Quantification

A Hewlett Packard HP5890 (series II) gas chromatograph, fitted with an RTX-1 (100% dimethylpolysiloxane (30M, 0.32mm ID)) column was used to quantify the samples. The conditions were: 100 °C for 5 min, then ramped to 200 °C at 10 °C/minute and held for 10 minutes, then ramped to 250°C at 5 °C/minute and held for 30 minutes (Figure 2.5).

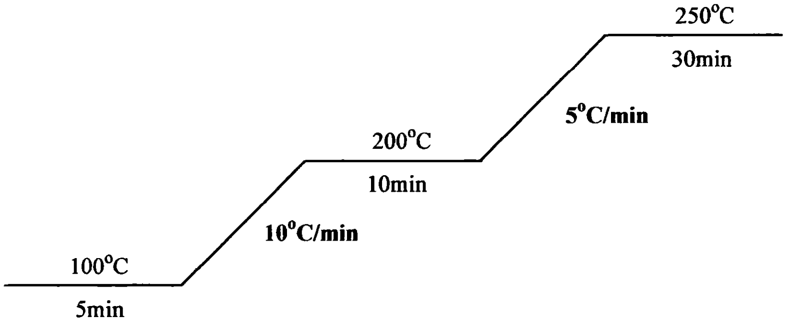


Figure 2.5 – Profile of GC temperature program

Tetradecane was used as the internal standard.

2.3.3 Reaction Procedure

To the glass reaction vessel of the autoclave were added the secondary butanol, naphthalene and cyclohexane and the mixture was stirred until the naphthalene had dissolved (*ca.* 5min).

The zeolite was dried in an oven for at least 24h at 550°C prior to use to ensure all water had been removed from the structure. The catalyst was added to the autoclave vessel, which was sealed into the autoclave and heated for a set time with stirring under a self-generated pressure.

Once the reaction was completed, the autoclave was removed from the heating unit and allowed to cool for approximately 1.5h. The catalyst was separated from the product by filtration and washed with excess solvent. The original solution and washings were combined. The resulting liquor was concentrated *in vacuo*. An aliquot of the product was dissolved in acetone (Analar), mixed with a known standard and subjected to GC.

The 2-*sec*-butylnaphthalene that was the major product and a mixture of the target molecule, 2,6-di-*sec*-butylnaphthalene and its 2,7-isomer were isolated using the kugelrohr apparatus (Figure 2.4) and each subjected to ^{1}H-NMR and mass spectral analysis. Typical NMR traces are shown in the Appendix (Figures 2 and 3 respectively). The mass spectra showed the following characteristic ions (see Appendix, Figure 4). For 2-*sec*-butylnaphthalene a peak at 184, 169 m/z indicates loss of a methyl group and 155 m/z the loss of an ethyl group. For 2,6-/2,7-di-*sec*-butylnaphthalene a peak at 240,and 211 m/z indicates the loss of an ethyl group. Tri-substituted naphthalene also appears to be present, with peaks occurring at 296m/z, for the molecular ion, 281m/z with the loss of a methyl group and 267m/z, with the loss of an ethyl group. The tri-substituted naphthalene would have had a greater retention time on the GC column, so its presence in the mass spectrum would account for the minor peaks eluted after the di-substituted product.

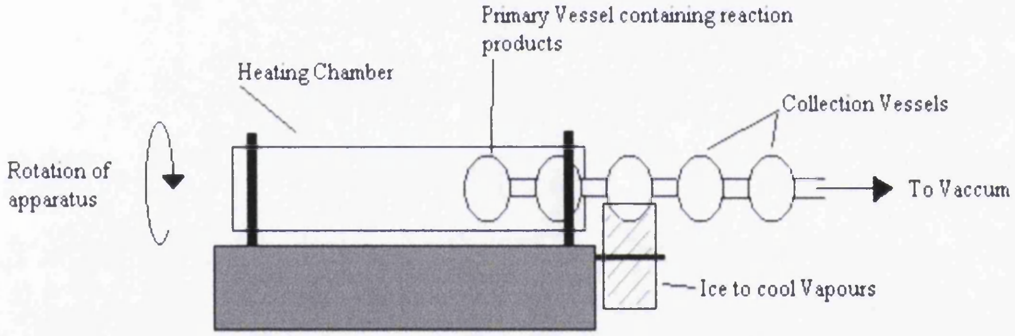


Figure 2.6: Kugelrohr apparatus. The isolated product liquor was placed inside the primary vessel, which was connected to a string of bulbs. The primary bulb (and possibly the second bulb) was pushed inside the heating chamber. The vacuum was initiated and the bulbs were rotated. The first bulb external to the chamber (the collection bulb) was cooled with ice. The temperature in the heating chamber was steadily raised. As each fraction of the product liquor was isolated, the collection bulb was removed from the apparatus and its contents identified by GC.

2.4 Conclusion

The optimum conditions for the production of 2,6-di-*sec*-butylnaphthalene over a HM catalyst were a naphthalene: *sec*-butanol molar ratio of 1:4, and a temperature of 180°C for a reaction period of 1 hour and gave a product ratio of 2,6-DsBN: 2,7-DsBN of four.

The primary zeolite of this study was chosen for its selectivity despite its lower level of activity compared to some other zeolites. Its properties are reflected in the results obtained in the study, *i.e.* a low yield of the desired product was obtained, but there was clear selectivity for the preferred isomer (a 2,6-DsBN: 2,7-DsBN ratio of 4 was obtained).

The three areas investigated in this study all influenced the yield of the target product. Temperature served to provide energy for the reaction to proceed, but when the temperature was too high there were undesirable competing reactions. The same effect applies to the reaction time. It was found that a certain percentage of the starting materials would undergo side reactions and it was necessary for an excess of the alcohol to be present to ensure the optimum amount for the reaction.

When compared to the more active zeolite HY it was found that despite mordenite being less active it was more selective for the desired target compound. The use of zeolite HY produced a ratio of the isomers 2,6-DsBN: 2,7-DsBN of 1. The presence of a more active zeolite did not increase the yield of the target molecule but instead brought about an increase in the products of side reactions or further reactions. This unspecific nature of HY makes it an undesirable catalyst because of both its waste of starting materials and its unspecific nature.

Although some success had been achieved in obtaining 2,6-di-*sec*-butylnaphthalene selectively over HM, the selectivity was not massively better than previously obtained by others using *iso*-propanol, and yields were actually lower. Therefore this approach to selective production of, 2,6-di-*sec*-butylnaphthalene was abandoned. Instead alkylation with dimethyl carbonate was attempted. This is reported in the next chapter.

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Chapter 3

Alkylation of Naphthalene with Dimethyl carbonate

3.1 Introduction

This study was concerned with the dialkylation of naphthalene, over mordenite with dimethyl carbonate (DMC). Previously methylation has been carried out using methanol and methane [1]. Some success has been achieved using these alkylating agents over zeolites. In this study however we are looking at the feasibility of using DMC as the alkylating agent (figure 3.1). It was hoped that the greater bulk of the reagent might allow a greater degree of control over the regioselectivity of the reaction.

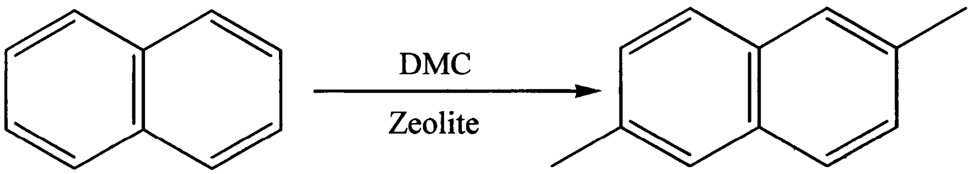

Figure 3.1 – The target reaction, dialkylation of naphthalene with DMC

DMC has been previously used in alkylation of phenol [3] and the selective mono-N- and mono-C- methylation of aniline [4], [5]. For the initial reaction, zeolite HM (mordenite) was chosen as the catalyst.

3.2 Results and Discussion

The conditions chosen for the initial reaction between naphthalene and dimethyl carbonate (DMC) were the same as those used for the first reaction of Chapter 2 (160 °C, 1 hour). A mixture of naphthalene (1.28g, 0.100mol), DMC (1.802g, 0.200mol) and zeolite HM (2g) in cyclohexane (10ml) was heated in an autoclave at 160 °C for 1 hour. The mixture was then cooled and filtered to remove the zeolite. An aliquot of the concentrated filtrate was subjected to gas chromatography after addition of tetradecane as a standard.

The GC revealed peaks for the solvent, naphthalene, tetradecane, 1-methylnaphthalene (1-MN) and 2-methylnaphthalene (2-MN) (see Appendix Figure 5 for GC trace). The Rf values for 1-MN and 2-MN were calculated by the method described in chapter 2, using samples obtained from Aldrich. GC detected no peaks for the di- or poly-substituted compounds. The yield of 1-MN was around 5% and of 2-MN around 3%, with around 70% of the initial naphthalene also still present. It was not clear what had happened to the remaining 22% or so of the initial naphthalene, although there were some small additional peaks in GC trace. However, it was clear that no dimethylnaphthalenes were present.

The absence of any dimethylnaphthalenes and the low yields of the monomethylnaphthalenes were disappointing. However, it was clear that some reaction had taken place, which was an encouraging observation. Furthermore, although 1-MN was predominant over 2-MN, the proportion of 2-MN was not insignificant. It was therefore of interest to see if the reaction temperature would affect the yield and/or selectivity of the reaction. A series of reactions was conducted in which identical reaction mixtures were heated for 1 hour at various temperatures between 120°C and 200°C. The results are reported in Table 3.2.1.

Table 3.2.1- Products of reaction according to figure 3.1; naphthalene:DMC ratio 1:2, over zeolite H-mordenite [a].

Temperature %	Naphthalene %	2-MN [b] %	1-MN [b] %	Ratio 1-MN/2-MN
120	72	2	3	2.0
140	60	3	6	1.6
160	70	3	5	1.5
180	58	5	6	1.3
200	58	4	6	1.4

(a) Naphthalene 1.28g (10mmol), dimethylcarbonate (DMC) 1.802g, cyclohexane 10ml and zeolite HM 2g, heated at the stated temperature for 1hour.
(b) 1-MN = 1-methylnaphthalene, 2-MN = 2-methylnaphthalene
(c) By GC

It is clear from Table 3.2.1 that there was some general increase in the yield of methylation products with increased temperature, at least up to 180°C, although the overall yields remained low and there was still no evidence of dimethylation products. There appeared to be a slight trend towards increasing the proportion of the 2-MN (i.e. lower 1-MN:2-MN ratio) as the temperature was raised, although the changes were sufficiently small that this might be caused by nothing more than errors in the measurement of small peak areas in the GC. It was a concern that up to 30% or so of the initial naphthalene was still not accounted for.

In an attempt to see if the use of a more open zeolite with 3D channels would help to increase the rate of reaction, and thereby, the yield of the products, a similar series of experiments was conducted using zeolite HY instead of HM. The results are shown in Table3.2.2.

Table 3.2.2- Products of reaction according to figure 3.1; naphthalene:DMC ratio 1:2, and zeolite HY.

Temperature %	Naphthalene %	2-MN[b] %	1-MN[b] %	Ratio 1-MN/2-MN
120	74	2	6	2.6
140	58	4	10	2.4
160	41	4	10	2.0
180	24	5	6	1.1

(a) Naphthalene 1.28g (10mmol), dimethylcarbonate (DMC) 1.802g, cyclohexane 10ml and zeolite HY 2g, heated at the stated temperature for 1 hour.
(b) 1-MN = 1-methylnaphthalene, 2-MN = 2-methylnaphthalene.
(c) By GC.

Comparison of the results in Table 3.2.2 with those in Table 3.2.1 revealed that the yields of products at comparable temperatures were generally rather higher with HY than with HM. However, the yields of monomethyl products were still modest, there was still no evidence for dimethylnaphthalenes, the selectivity for 2-MN was worse, and the overall mass balance dropped to 35% at 180°C, suggesting that there were significant alternative pathways for consumption of naphthalene over HY. Therefore, for subsequent experiments, zeolite HM was used.

In order to assess whether the low yields of product resulted from a deficiency of dimethyl carbonate, perhaps because of its reactions by alternative pathways, two series of experiments were conducted, using naphthalene:DMC ratios of 1:4 and 1:8 respectively, over the optimum temperature range of 120°C to 160°C found in the studies described above. The results are shown in Tables 3.2.3 and 3.2.4.

Table 3.2.3- Products of reaction according to figure 3.1; of naphthalene:DMC ratio 1:4, over zeolite H-mordenite[a].

Temperature %	Naphthalene %	2-MN[b] %	1-MN[b] %	Ratio 1-MN/2-MN
120	56	2	6	2.3
140	42	3	5	1.8
160	77	2	2	1.3
180	46	5	11	1.9

(a) Naphthalene 1.28g (10mmol), dimethylcarbonate (DMC) 3.604g, cyclohexane 10ml and zeolite HM 2g, heated at stated temperature for 1 hour.
(b) 1-MN = 1-methylnaphthalene, 2-MN = 2-methylnaphthalene
(c) By GC.

Table 3.2.4- Products of reaction according to figure 3.1; naphthalene:DMC ratio 1:8, over zeolite H-mordenite[a].

Temperature %	Naphthalene %	2-MN[b] %	1-MN[b] %	Ratio 1-MN/2-MN
120	78	2	2	1.3
140	64	3	5	1.8
160	48	4	7	1.6

(a) Naphthalene 1.28g (10mmol), dimethylcarbonate (DMC) 7.208g, cyclohexane 10ml and zeolite HY 2g, heated at stated temperature for 1 hour.
(b) 1-MN = 1-methylnaphthalene, 2-MN = 2-methylnaphthalene
(c) By GC.

Comparison of the results in Tables 3.2.1, 3.2.3 and 3.2.4 revealed that any increases in yield were modest and there was no substantial change in selectivity for reactions conducted with different naphthalene:DMC ratios.

Several general points may be made at this juncture. Due to the small size of the methyl group attack on the naphthalene molecule is possible at both the α and β position.

The α position of naphthalene is more electron rich than the β position and is, therefore, more likely to be attacked in an unconstrained environment. This results in 1-methylnaphthalene being the dominant isomer, as observed here. If time had permitted, it would have been interesting to try the reaction over zeolite HZSM-5, which has smaller pores, to see if this would have given greater selectivity for attack at the β position, as observed with other alkylating agents.

As expected, the activity displayed by zeolite HY was greater than the activity of mordenite. Though both zeolites produced the same approximate amount of 2-MN isomer, the zeolite HY produced more of the 1-MN isomer. This is probably a reflection of the greater space available for reaction within the supercages of HY, leading to an easier reaction pathway and a lower degree of constraint against attack at the α-position.

With both H-mordenite and HY a decrease in the ratio of the 1-MN to 2-MN is observed with increasing temperature. This is probably because, as the temperature increases there is an increase in the thermodynamic product (2-MN), due to some isomerisation of the initially formed kinetic mixture. However, it is also possible that at higher temperatures the kinetic discrimination is less.

It was also observed that an increase in the amount of DMC added to the system had minimal effect on increasing the yield of 2-MN.

3.3 Experimental

3.3.1 Materials

Scintillation grade naphthalene (99+%) and dimethyl carbonate (99+%) were obtained from Aldrich and cyclohexane (99+%) was obtained from Fischer Scientific.

H-Mordenite, product code- CBV 20A, Si/Al ratio = 10, nominal cation form = H following calcination, surface area (m^2/g) =500.and HY, Si/Al ratio = 12, nominal cation form = H following calcination, surface area (m^2/g)= 720, were provided as gifts by zeolite International.

3.3.2 Quantification

A Hewlett Packard HP5890 (series II) gas chromatograph, fitted with a RTX-1 (100% dimethyl polysiloxane (30M, 0.32mm ID)) column was used to quantify the samples. The conditions were:

100 °C for 5 min ramped to 200 °C at 10 °C/minute and held for 10 minutes, then ramped to 250°C at 5 °C/minute and held for 30 minutes (figure 3.2).

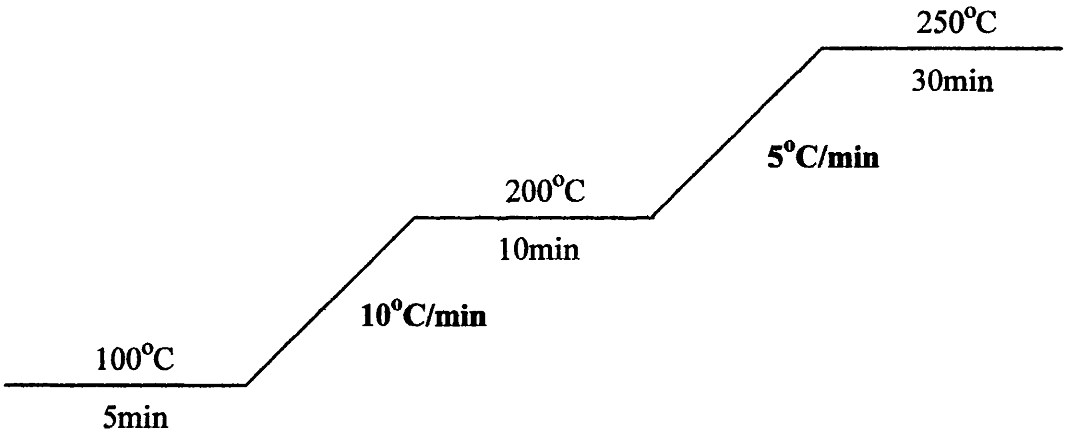

Figure 3.2 – Profile of GC temperature program

Tetradecane was used as the internal standard.

3.3.3 Reaction Procedure

To the glass reaction vessel of the autoclave were added the DMC, naphthalene and cyclohexane and the mixture was stirred until the naphthalene had dissolved (ca. 5min).

The zeolite had been calcined in an oven for at least 24 hrs at 550 °C prior to use to ensure all water had been removed from the structure and any NH_4^+ cations had been decomposed. The catalyst was added to the vessel, which was sealed into the autoclave and heated for a set time with stirring under a self-generated pressure.

Once the reaction was completed, the autoclave was removed from the heating unit and allowed to cool for approximately 1.5 hrs. The catalyst was separated from the product by filtration and washed with excess solvent. The resulting liquor was concentrated in *vacuo.* An aliquot of the product was dissolved in acetone (Analar), mixed with the standard and subjected to GC.

3.4 Conclusion

The results of this study show that large pore zeolites H-mordenite and HY are unsuitable catalysts for this reaction of naphthalene with dimethyl carbonate, despite the size of the DMC molecule. The mono-substitution is not selective for the β position, but instead for the α position, though there is increased β selectivity at increased temperature. The increase in temperature, however, does not cause a drop in 1-MN production. There is also no di-substitution under these conditions. If time had allowed it would have been interesting to see whether HZSM-5, a medium pore zeolite, would have provided greater selectivity and whether conditions could have been found which would have enabled higher yields to be achieved. Such studies must await further projects.

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Appendix

The following inserts are examples of typical spectra obtained during the course of the investigations.

Figure 1: GC trace of products resulting from alkylation of naphthalene with *sec*-butanol.

The components of the product liquor were detected by GC. They eluted in the order: naphthalene, tetradecane, 2-*sec*-butylnaphthalene, 2,7-di-*tert*-butylnaphthalene, 2,6-di-*tert*-butylnaphthalene, 2,7-di-*sec*-butylnaphthalene and 2,6-di-*sec*-butylnaphthalene. Each component was isolated and the RF calculated by the method described in chapter 2.

Figure 2: ^{1}H-NMR of 2-*sec*-butylnaphthalene.

The 2-*sec*-butylnaphthalenewas isolated by kugelrohr distillation and submitted for ^{1}H-NMR. The following peaks were recorded:

δ 0.8	3H	triplet
δ1.3	3H	doublet
δ1.7	2H	quartet
δ2.8	1H	sextet
δ7.4	4H	multiplet
δ7.7	1H	singlet
δ7.8	3H	multiplet

Figure 3: ^{1}H-NMR of 2,7-di-*sec*-butylnaphthalene and 2,6-di-*sec*-butylnaphthalene.

The 2,7-di-*sec*-butylnaphthalene and 2,6-di-*sec*-butylnaphthalene were isolated by kugelrohr distillation from the rest of the product liquor and submitted for ^{1}H-NMR. Unfortunately due to the close boiling points of these two compounds, attempts to separate them by kugelrohr failed. The resulting spectra were a mix of the two. The following peaks were recorded:

δ 0.7	3H	triplet
δ1.2	3H	doublet
δ1.6	2H	quartet
δ2.6	1H	sextet
δ7.2	3H	multiplet
δ7.6	3H	multiplet

Figure 4: The Mass Spectra of 2-*sec*-butylnaphthalene and 2,7-di-*sec*-butylnaphthalene and 2,6-di-*sec*-butylnaphthalene.

Aliquots of 2-*sec*-butylnaphthalene and 2,7-di-*sec*-butylnaphthalene and 2,6-di-*sec*-butylnaphthalene were submitted for analysis using GC-MS.

Figure 5: GC trace of products resulting from alkylation of naphthalene with dimethyl carbonate.

The components of the product liquor were detected by GC. They were eluted in the order: naphthalene, tetradecane, 2-methylnaphthalene, and 1-methylnaphthalene. The RF values were calculated using comparison with samples obtained from Aldrich.

Figure 1: GC trace of products resulting from alkylation of naphthalene with *sec*-butanol.

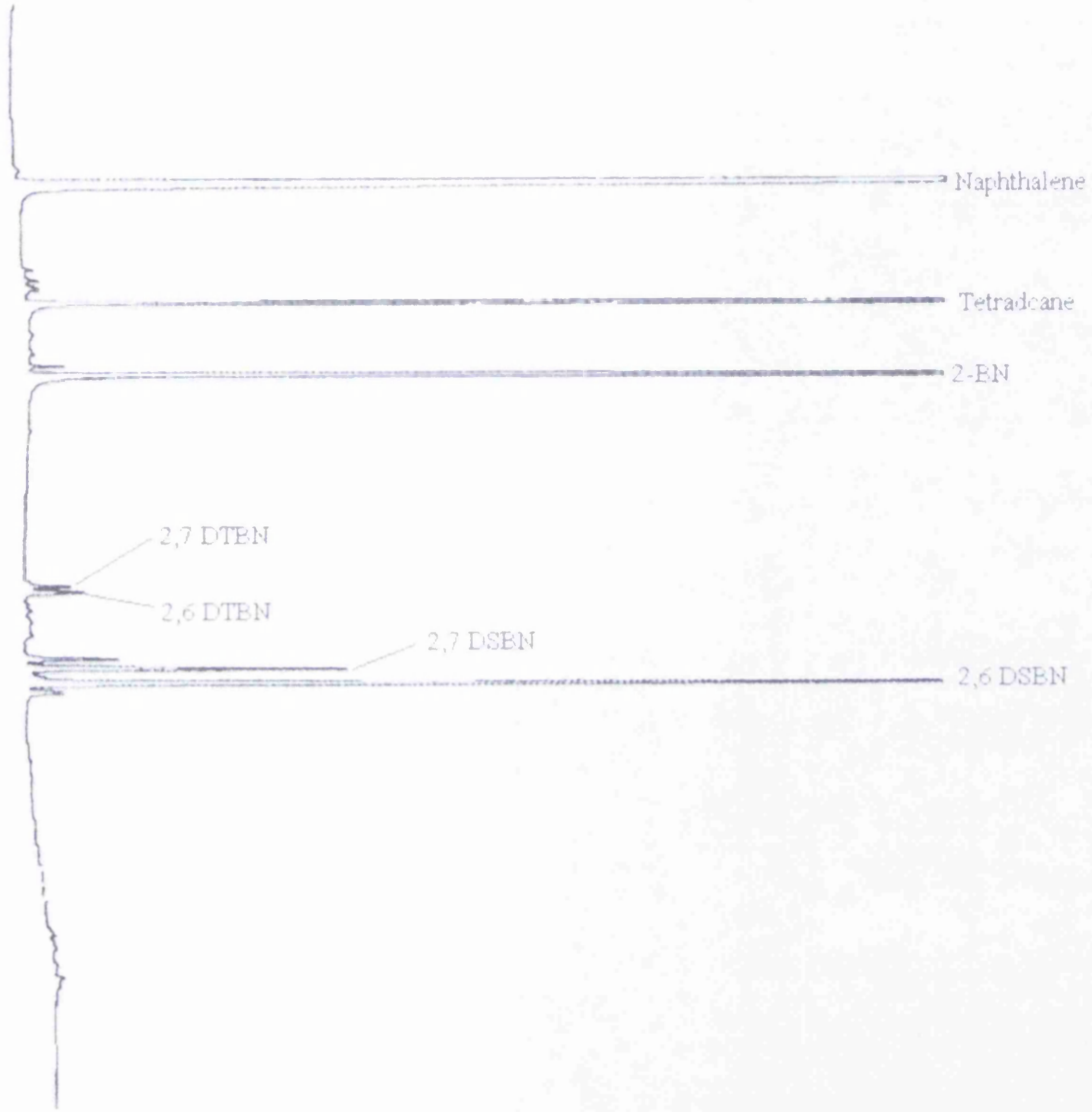

Figure 2: H'NMR of 2-sec-butylnaphthalene

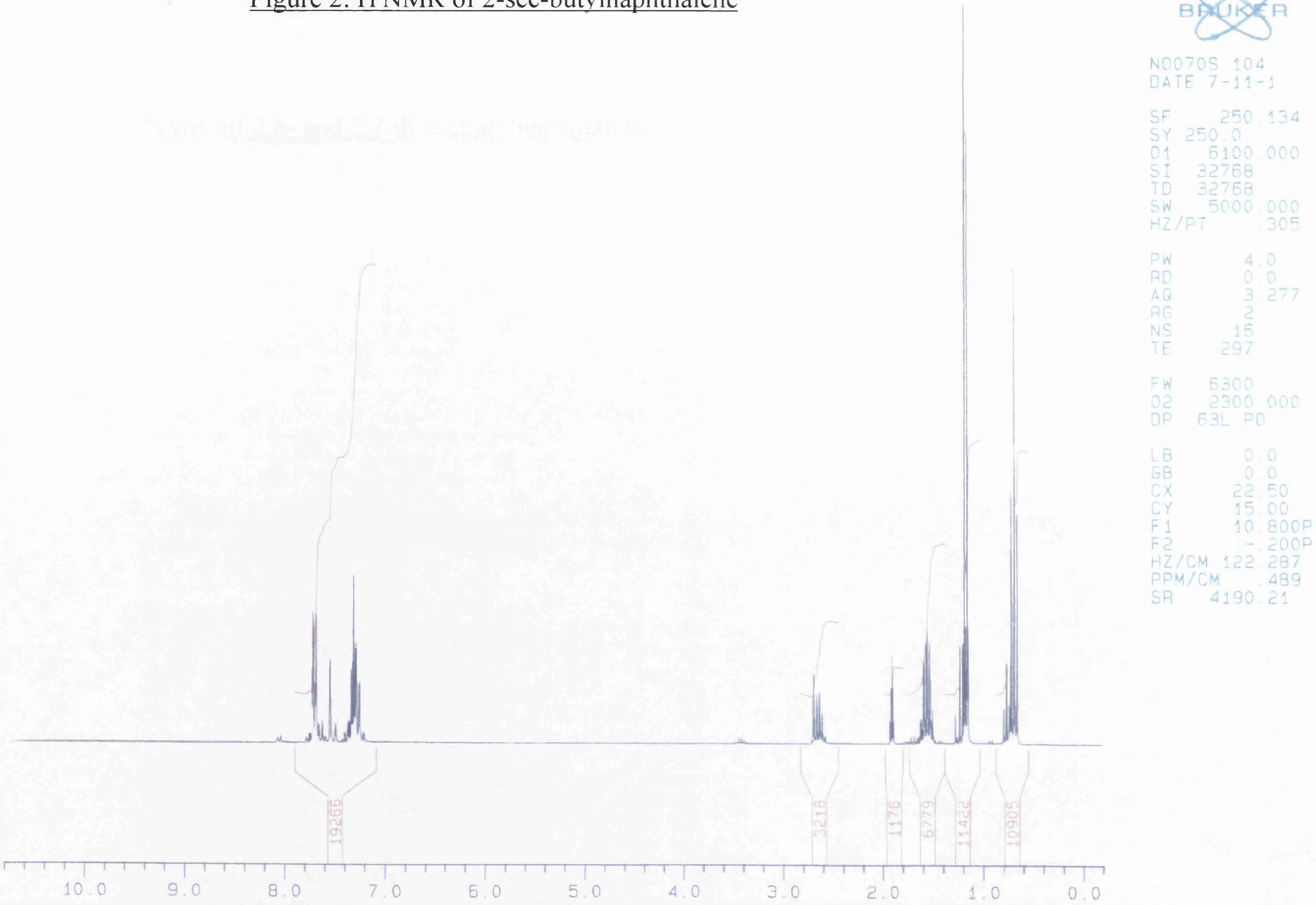

Figure 3: H-NMR of 2,6- and 2,7-di-secbutylnaphthalene

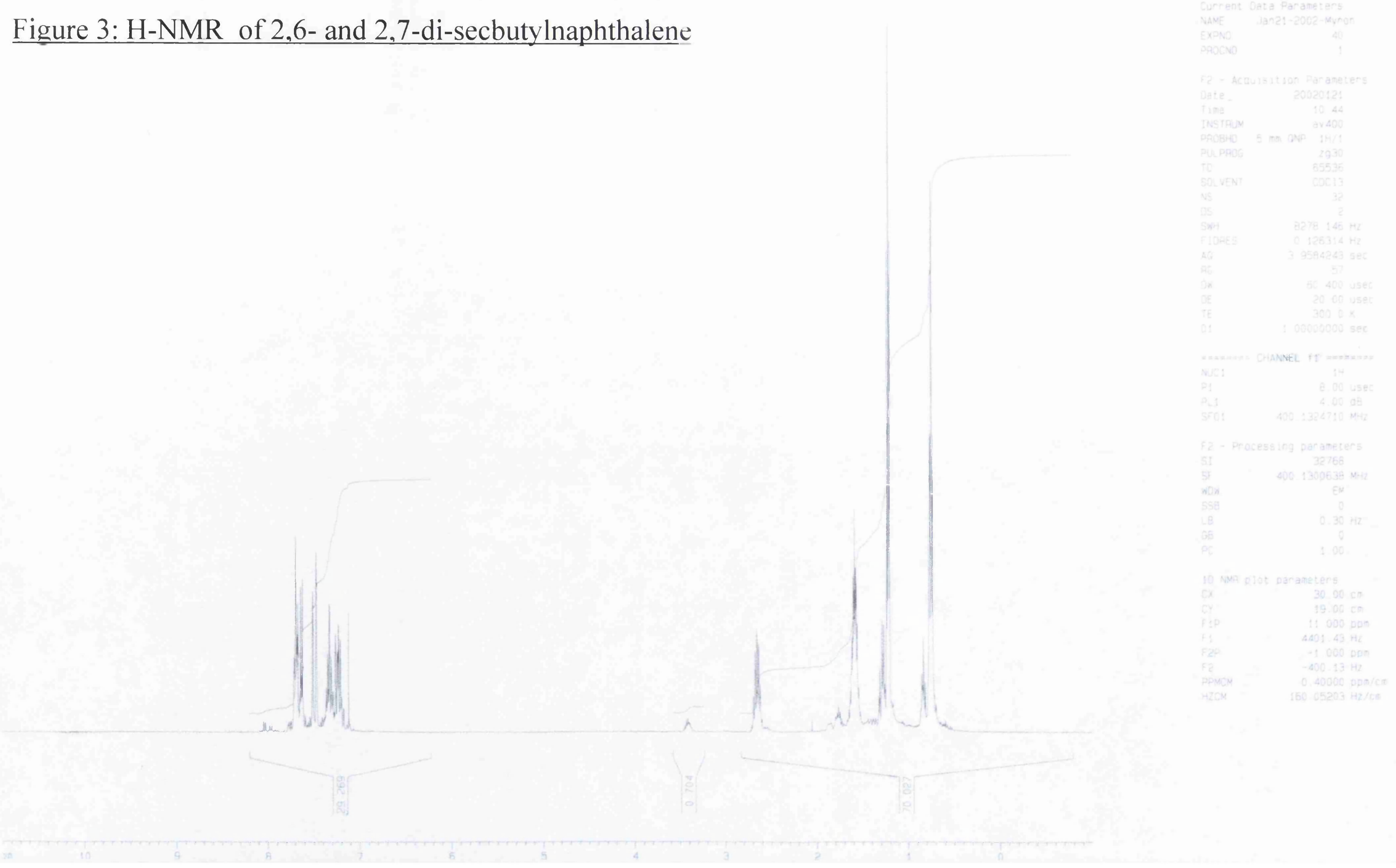

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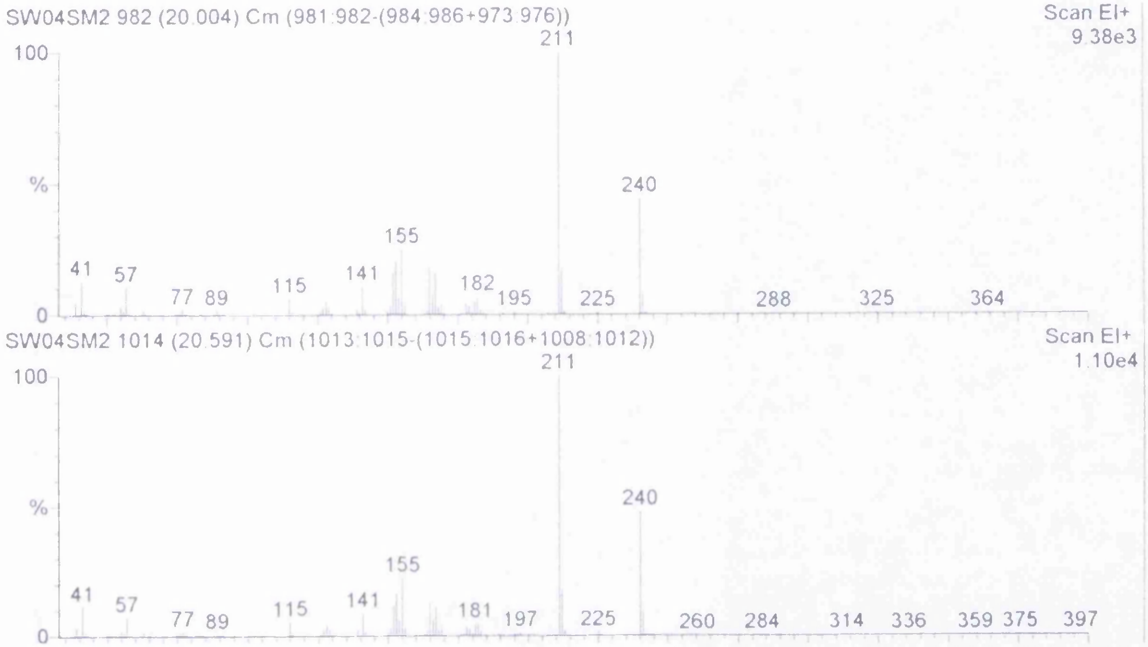
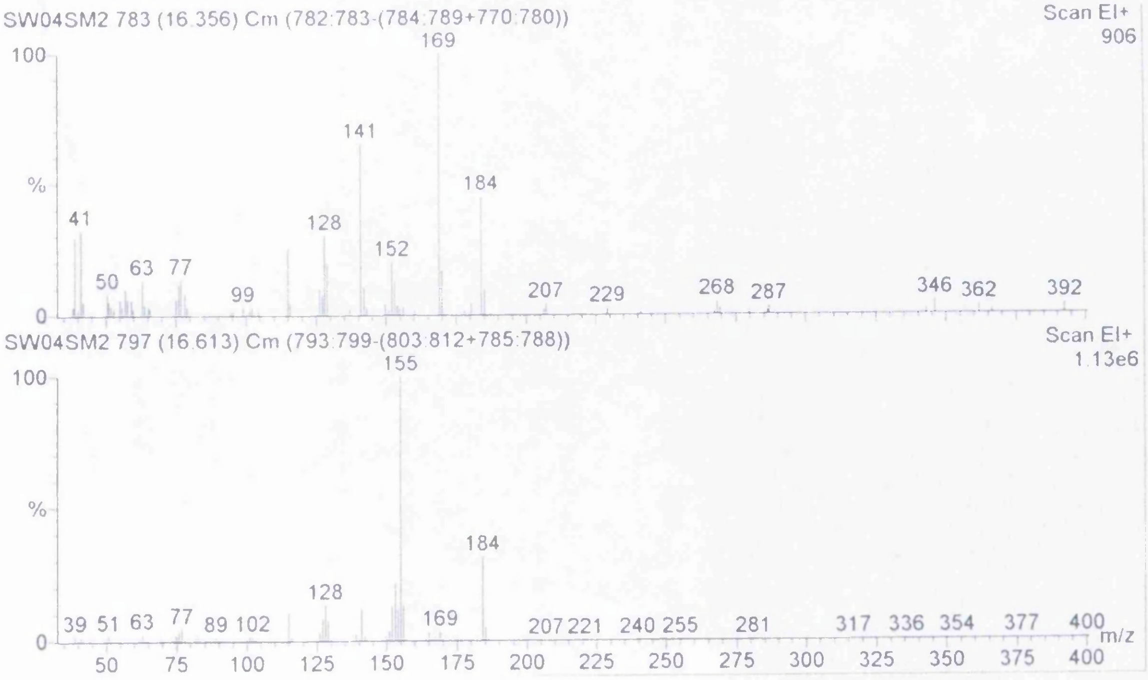
Figure 4: The Mass Spectra of 2-*sec*-butylnaphthalene and 2,7-di-*sec*-butylnaphthalene and 2,6-di-*sec*-butylnaphthalene.

2-*sec*-butylnaphthalene has a peak at 184, 169 m/z indicates loss of a methyl group and 155 m/z the loss of an ethyl group.



2,6- and 2,7-di-*sec*-butylnaphthalene have a peak at 240,and 211 m/z indicates the loss of an ethyl group.



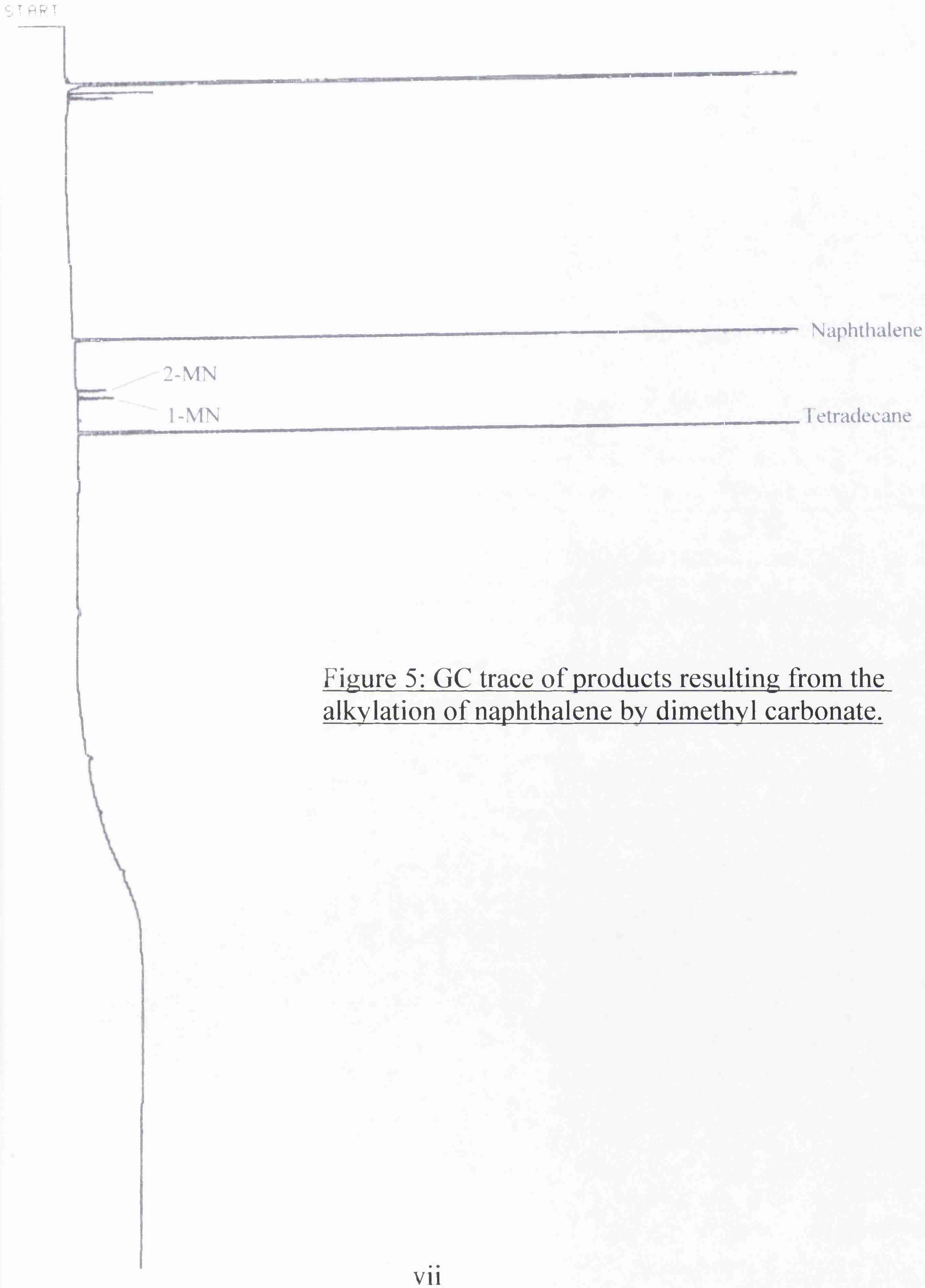


Figure 5: GC trace of products resulting from the alkylation of naphthalene by dimethyl carbonate.