1. DESIGN AND SYNTHESIS OF NEW CHIRAL UNITS FOR POTENTIALLY

FERROELECTRIC LIQUID CRYSTALS: LIQUID CRYSTALS CONTAINING A

THIIRAN UNIT. 2. HETEROGENEOUS CATALYSIS OF THE RACEMIZATION OF

1,1'-BINAPHTHYL BY TITANIUM DIOXIDE POWDER.

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XIN WANG

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Department of _____ Chemistry _____

The University of British Columbia
1956 Main Mall
Vancouver, Canada
V6T 1Y3

Date _____ Dec _____ 1987 _____

Abstract

Supervisors: Dr. R.E. Pincock and Dr. G.S. Bates

New liquid crystals have been synthesized and their transition phases have been studied. It was found that a family of (−)-2-methyl 2R,3S-epithio-4'-alkoxybiphenyl pentanoates are liquid crystals but a similar system of (+)-2-methyl 2S,3R-epoxy-4'-alkoxybiphenyl pentanoates are not. Of the liquid crystals, MEAOBP-S-7 exhibits smectic A and B phases; MEAOBP-S-8 and MEAOBP-S-9 show only the smectic B phases; MEAOBP-S-10 shows a monotropic chiral smectic C phase. This distinction is in agreement with the argument that the internal dipolar interaction of the molecule plays an important role in determining liquid crystalline behaviour of this ester system.

The reaction rate of the racemization of optically active binaphthyl can be moderately increased in the presence of finely divided titanium dioxide (anatase) powder. This first order catalyzed reaction has a proportional relationship with the concentrations of both the catalyst and the binaphthyl.

The catalyzed reaction can be poisoned permanently by the addition of polynuclear aromatic compounds and the poisoning efficiency is dependent of the number of the aromatic rings the poison posesses. By comparison with the catalyzed racemizations of binaphthyl by platinum, nickel and carbon and from the kinetic and mechanistic studies on the titanium dioxide catalyzed racemization, we conclude that (1) this catalytic phenomenon is common among heterogeneous inorganic solids and can be extended to other simple reactions, and that (2) the mechanism of the catalysis probably involves a radical anion intermediate.

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CHAPTER 1 DESIGN AND SYNTHESIS OF NEW CHIRAL UNITS FOR POTENTIALLY FERROELECTRIC LIQUID CRYSTALS: LIQUID CRYSTALS CONTAINING A THIIRAN UNIT

1. INTRODUCTION

The advent of a bistable, fast-switching, electrooptic light-valve based on the properties of ferroelectric smectic liquid crystals[1] has aroused considerable interest in the synthesis and engineering of new smectogens suitable for applications of this nature. The first part of this thesis will deal with the synthesis of novel organic compounds, which potentially can exhibit the properties of liquid crystals and hopefully also be ferroelectric.

1.1 TRANSITION PHASES OF LIQUID CRYSTALS

The science of liquid crystals began in 1888, with the research of Friedrich Reinitzer, an Austrian botanist who prepared cholesteryl benzoate and found it to have two interesting properties. When heated, its crystal lattice collapses at 145°C to form a turbid liquid. At 179°C, the turbid liquid disappears and an isotropic liquid is formed. Since then, about one of every two hundred organic compounds has been found to exhibit liquid crystal phase(s).

For centuries, scientists have considered only three states of matter —————— solids, liquids, and gases. In solids, atoms or molecules are bound and ordered; in liquids, they are bound and disordered; in gases, they are only very weakly bound and also are disordered. Liquid crystals are materials in which order is progressively relaxed as one proceeds from a true solid to a true liquid.

Liquid crystals occupy a grey area between true solids and true liquids. Although liquid crystals exhibit certain aspects of both the solid and liquid states, they also possess properties that are not found in either liquids or solids. Their ordering properties, for example, can be controlled by ordinary magnetic and/or electric fields.

The liquid crystals commonly referred in the literature are thermotropic liquid crystals, i.e. their properties are temperature dependent. The other major branch of liquid crystals, called lyotropic liquid crystals, are often two-component systems composed of water and amphiphilic compounds, and will not be described. (See references 2-3 for reviews on this subject)

Thermotropic liquid crystals, which form naturally over a specific temperature range, are further classified as either nematic or smectic. "Nematic" comes from the Greek word for thread; nematic crystals have a thread-like pattern when viewed through a microscope equipped with crossed polarizers. "Smectic" from the Greek for soap, decribes these crystals' greasy or soapy properties.

Isotropic structure (unordered, nonliquid crystalline)

Ordinary nematic structure

Cholesteric structure

Smectic A structure

Smectic C structure

(Reproduced from reference 2)

A general description of many of the various types of liquid crystal phases are given below (page 4). In a typical nematic liquid crystal, the only structural restriction is that the long axes of the molecules maintain a

Thermotropic liquid crystals have either nematic or smectic structures

Class	Optical properties	Textures	Structure	Examples
NEMATICS				
Ordinary nematic	Uniaxially positive	Schlieren; threaded; marbled; pseudo-isotropic; homogeneous	Parallelism of long molecular axes	p-Azoxyanisole; p-methoxybenzylidene; p-(n-butyl)aniline
Cholesteric-nematic	Uniaxially negative or isotropic; optically active	Focal conic with Grandjean steps; homogeneous; isotropic	Nematic packing in planes; superimposed twist in direction perpendicular to long axes of molecules	Cholesteryl nonanoate
Blue phase	Isotropic; optically active	Platelet with Grandjean steps	Cubic	Cholesteryl nonanoate
STRUCTURED SMECTICS				
Smectic B	Uniaxially positive	Mosaic; stepped drops; pseudo-isotropic; homogeneous	Layer structure; molecular axes orthogonal to the layers; hexagonal arrangement within the layers	Ethylethoxybenzylidene-aminocinnamate; terephthal-bis-butylani-line
Smectic E	Biaxially positive	Mosaic; pseudo-isotropic	Layer structure; molecular axes orthogonal to the layers; ordered arrangement within the layers	Di-n-propylterphenyl-dicarboxylate
Smectic G	Biaxially positive	Mosaic	Layer structure with ordered arrangement within the layers	2-(4-n-Pentylphenyl)-5-(4-n-pentyloxyphenyl)pyrimidine
Smectic H	Biaxially positive	Fan	Tilted analogue of smectic F	
Smectic I	Biaxially positive	Mosaic; fan-shaped texture with stripes across the fans	Hexagonal correlation in-the-plane and the tilt direction is uniform toward neighboring molecules	4-n-Pentylbenzenethio-4'-n-octyloxybenzoate
UNSTRUCTURED SMECTICS				
Smectic A	Uniaxially positive	Focal conic (fan-shaped or polygon); stepped drops; homogeneous; pseudo-isotropic	Layer structure; molecular axes orthogonal to the layers; random arrange-ment within the layers	Diethylazoxybenzoate
Smectic C	Biaxially positive	Broken focal conic; schlieren; homogeneous	Layer structure; molec-ular axes tilted to the layers; random arrange-ment within the layers	Dodecyloxyazoxybenzene
Smectic D	Isotropic	Isotropic; mosaic	Cubic structure	4'-Octadecyloxy-3'-nitrodi-phenyl-4-carboxylic acid
Smectic F	Biaxially positive	Schlieren; broken focal conic	Layer structure	2-(4-n-Pentylphenyl)-5-(4-n-pentyloxyphenyl)-pyrimidine

Source: "Liquid Crystals and Biological Systems" by J. J. Wolken and G. H. Brown

(Reproduced from reference 2)

parallel or nearly parallel arrangement over macroscopic distances. The nematic phase always changes on heating to an isotropic liquid.

Cholesteric liquid crystals, first observed with cholesteryl esters, are formed by some optically active organic compounds, or mixtures of such compounds. They are miscible with ordinary nematic liquid crystals and have local nematic packing of the molecules.

There are basically two types of smectic phases, of which orthogonal smectics include the smectic A, B, and E phases; and tilted smectics[4] include smectics C, F, G, H, I, J, and K.

Smectic A liquid crystals are the least ordered of the orthogonal smectic phases. In the smectic A phase, the molecules are arranged with their molecular long axes perpendicular to the phases of the layers. The lateral distribution of the molecules within each layer is random, and the molecules are able to rotate freely about their long axes. In the smectic B phase, the molecules are arranged in layers with the molecular centers positioned in a hexagonal close-packed array. The molecules are also rotating quite rapidly about their long axes. The smectic E phase has in-plane packing which is rectangular, with long-range positional correlations.

The smectic C phase is one in which the molecules are randomly close packed in layers; in a given domain the molecules are tilted in particular direction with respect to the layer planes. Like smectics A and B, the molecules in smectic C phase rotate about their long axes with no associated processional rotation.

In smectics I and F[5-6], the molecules are tilted in their layers. In the plane, at right angles to the tilt direction, the molecules are hexagonally close packed. In the I phase the molecules are tilted towards the apex,

while in the F phase they are tilted towards one side of the hexagon.

In smectics J and G[5,7], the molecules again are tilted within the layers. In the plane at right angles to the tilt direction they are hexagonally close packed. Smectics J and G are distinguished by their tilt directions, J is tilted towards the apex while G towards the side of the hexagonal net.

Smectic H and K phases are similar to J and G except the molecules are packed in a rectangular base centered net which has smaller dimerisons than the hexagonal net of J and G.

While liquid crystals have been known for a century or more, ferroelectric liquid crystals were first recognized by Meyer[9] in 1975.

A ferroelectric liquid crystal (FLC) is a compound or a mixture possessing at least one chiral smectic phase which exhibits the ferroelectric property, i.e. shows spontaneous polarization. The material constants[10], with which ferroelectric liquid crystals may be characterized, are (1) the transition temperature; (2) the tilt angle; (3) the helical pitch; (4) the refractive index; (5) the spontaneous polarization; (6) the critical field to unwind the helix; (7) the elastic constant and (8) the viscosity coefficient. It is beyond the scope of this thesis to describe all of the elements concerning a ferroelectric liquid crystal. From the applicative point of view, a chemist's greatest interest is the transition temperature, i.e., the temperature range where ferroelectric smectic phases are retained.

There are seven smectic modifications which have the symmetry elements required to exhibit ferroelectric behaviour. Of these, three are fluid smectic liquid crystal phases (Sm* C, Sm* I, and Sm* F, here * denotes a chiral smectic phase), and another four (Sm* J, G, H, and K) are orientationally disordered crystal phases. Chiral smectogens possessing those

smectic phases may exhibit ferroelectic properties. The Sm* C phase is the least ordered phase of the seven known chiral smectic phases and is thus the most important one in so far as the application is concerned.

For the purpose of applications, FLC materials are required to exhibit a high spontaneous polarization, to have a wide liquid crystalline temperature range, and to be stable, to exhibit a smectic A phase on cooling from the isotropic liquid required for alignment purposes. It is common practice to broaden the temperature range of desired phases by formulating eutectic mixtures. Indeed, many commercial liquid crystal materials are multi-component mixtures in some cases containing seven or eight individual compounds. In given liquid crystal phases (e.g. the SmA and Sm*C phases) different compounds are in general miscible, and there is no depression observed in, for example, the SmA to Sm*C transition upon mixing. For pure compounds with monotropic phases, it is generally possible to obtain thermodynamically stable liquid crystal phases by such formulation.

1.2 STRUCTURE OF FERROELECTRIC LIQUID CRYSTALS

Ferroelectric smectic liquid crystals show potential for becoming increasingly important in electrooptic display device applications. However, the numbers of materials available for these applications are limited, particularly those which exhibit a ferroelectric, chiral smectic C phase.

A number of typical ferroelectric liquid crystals are listed in Table 1. They have been classified into two types: type A in which the chiral unit is connected to the core unit by means of etherification (-Ph-O-R*, R*=chiral unit), and type B in which the chiral unit is joined to the core unit by esterification (-Ph-COO-R* or -Ph-OCO-R*).

Table 1. Selected structures of ferroelectric liquid crystals

Type A

RO-Ph-OCO-Ph-O-CH$_2$C*H(CH$_3$)C$_2$H$_5$

RO-Ph-COO-Ph-O-CH$_2$C*H(CH$_3$)OCH$_3$

RO-Ph-N=CH-Ph-O-CH$_2$C*H(CH$_3$)C$_2$H$_5$

RO-Ph-CH=CH-COO-Ph-O-CH$_2$C*H(CH$_3$)C$_2$H$_5$

RO-Ph-OCO-Ph-OCO-PH-O-CH$_2$C*H(CH$_3$)C$_2$H$_5$

RO-Ph-Ph-OCO-Ph-CH$_2$C*H(CH$_3$)C$_2$H$_5$

Type B

RO-Ph-Ph-COO-CH$_2$C*H(CH$_3$)C$_2$H$_5$

RO-Ph-Ph-OCO-C*H(Cl)C$_2$H$_5$

RO-Ph-COO-Ph-COO-CH$_2$C*H(CH$_3$)C$_2$H$_5$

RO-Ph-COO-Ph-CH=CX-COOCH$_2$C*H(CH$_3$)C$_2$H$_5$, X=CN, Cl. H.

RO-Ph-CH=N-Ph-CH=CH-COO-C*H(CH$_3$)C$_2$H$_5$

RO-Ph-CH=CH-COO-Ph-COO-CH$_2$C*H(CH$_1$)C$_2$H$_5$

Where R = CnH2n+1;

     Ph = 1,4-substituted phenyl group;

     * = chiral center;

     (The same notation also is applied in subsequent sections)

Examination of the structures of materials which typically exhibit ferroelectric smectic phases shows that the optical center (hereafter simply referred to as the chiral unit) is normally at one end of the molecule. In this position, it is relatively free to rotate independently of the rest of the molecule (hereafter simply referred to as the core unit) which is also rotating, and in particular to the highly sensitive polarizable central core which contains the delocalized π electrons[11]. In this situation, the contribution by the core to the dipole associated with the chiral center will be reduced because the lateral dipole of the core will be rotating independently of the asymmetric center and therefore will not contribute greatly to the net resultant dipole[11].

Spontaneous polarization is the second most important physical property of a FLC, next to the transition temperature. Tilted chiral smectic phases possess a spontaneous ferroelectric polarization or macroscopic dipole moment, derived from dissymmetry in the orientation of the molecular dipoles in the liquid crystal phase. The strength of the spontaneous polarization can be increased considerably by restricting the freedom of rotation of the chiral center in relation to the molecule as a whole. Moving the chiral unit closer to the core creats a direct interaction between the the chiral unit and the core unit via dipolar coupling and restricted rotation thus also strengthening the spontaneous polarization.

Table 2 Ferroelectric liquid crystals[12-14] with large spontaneous polarizations

FLC	Ps(nc/cm^2)
$C_{11}H_{15}$-Ph-OCO-Ph-Ph-O-C*H(CH$_3$)C$_6$H$_{13}$	60
C_8H_{17}-O-Ph-OCH$_2$-Ph-COO-C*H(CH$_3$)C$_3$H$_7$	99
C_6H_{17}-O-Ph-Ph-OCH$_2$-Ph-COO-C*H(CH$_3$)C$_3$H$_7$	99
$C_{16}H_{33}$-O-Ph-Ph-OCH$_2$-Ph-COO-C*H(CH$_3$)C$_6$H$_{13}$	145
C_7H_{15}-O-Ph-Ph-OCO-C*HClC*H(CH$_3$)C$_2$H$_5$	220

Type B FLC's generally possess higher spontaneous polarization than type A systems. For instance, $C_7H_{15}OPhPhOCOC^*HClC^*H(CH_3)C_2H_5$ exhibits the highest spontaneous polarization known to date to the best of our knowledge. It is then concluded that the greater the dipolar interaction between the chiral unit and the adjacent carbonyl group of the core unit and the less internal rotation of the chiral unit with respect to the core unit the greater will be the spontaneous polarization in type B FLC's.

Unfortunately, it seems that the dipolar interaction between the chiral and the core unit can have detrimental effects on the stability of the ferroelectric phase. This is especially the type of Sm* C phase which is often lost from the phase diagram as the chiral center is positioned adjacent to the core[11]. It may be possible to design the "ideal" FLC's by placing the chiral units, especially those with the strong polar groups attached, into the "right" location in the structure of the type B FLC's, thereby producing a FLC series not only showing a wide range of chiral smectic C phase around room temperature but also exhibiting extremely high spontaneous polarization.

1.3 DESIGN AND SYNTHESIS OF POTENTIALLY FERROELECTRIC LIQUID CRYSTALS

The first requirement in the synthesis of materials which possess ferroelectric phases is to produce materials which exhibit tilted smectic phases. Many studies of numerous ferroelectric liquid crystals have already provided guidelines for this initial operation[11]. Three fundemental criteria[11] are in general considered essential: (a) an alkyl-aryl-alkyl system; (b) strong terminal lateral dipoles; and (d) a chiral center which produces the asymmetry of the phase, and produces the ferroelectric properties. In

simpler terms, the design of a new potentially FLC is to develop the appropriate chiral and core units and then properly connect them together.

The core units found in most known ferroelectric liquid crystals have been well established in the past decade. The greater difficulty in synthesizing new ferroelectric liquid crystals now lies in the preparation of the appropriate chiral units and their fusion with central core units in a way that the resulting molecules possess the necessary liquid crystalline properties.

Relatively little investigation of new chiral units has occurred. So far, readily available optically active commercial compounds and their derivatives have been successfully incorporated into almost all of the well-established core units.

For example one of the main precusors is commercially available S(-)-2-methylbutanol which has been modified to suitable derivatives as shown below.[11]

These derivatives have been used in almost all of the known FLC structures. However, a disadvantage of those compounds is the fact that

the chiral center is not polar enough to induce very high spontaneous polarizations.

There are a number of commerically available optically active amino acids and several have been modified for incorporation into liquid crystals. L-Isoleucine, for instance, was converted to optically active 3-methyl 2-chloropentanoic acid, which could further be reduced to the corresponding optically active alcohol[16]. Optically active 3-methyl 2-chloropentanoic acid and optically active 3-methyl 2-chloropentanol have been reported extremely useful since ferroelectric liquid crystals derived from them possess two chiral centers showing unusual ferroelectric properties[16].

Similarly, 2-chloro-2-methyl butanoic acid also prepared from the corresponding amino acid has been successfully used in synthesizing many new ferroelectric liquid crystals[17].

The advantage for those chlorine containing materials over the alkyl series above is the fact that these chiral units are more polarizable.

1.4 THE PREVIOUS WORK CONCERNING RO-PH-PH-OCO-R*

Studying the system of RO-Ph-Ph-OCO-R* (R* = chiral unit) is of great interest to us not only because of the potential for exploring and utilizing new chiral units but also because of its great relationship to general problems involving a wide variety of FLC systems.

Table 3 illustrates how in general some chiral units are used in this system. The use of the group $-C^*HClC^*(CH_3)C_2H_5$ was reported by Yoshino et al.[16] and the rest of the chiral units in the table was used by Goodby and Lesile[17]. The insertion of a new chiral center $-C^*H(CH_3)-$ into the chiral unit $-C^*ClHC_2H_5$ not only changes the phase diagram completely but also lowers the transition temperature considerably. A chiral smectic C phase

emerges as three other less important smectic phases are lost and the phase temperature is decreased to near room temperature.

Talbe 3. Phase transition of liquid cyrsatls #[1] $C_8H_{17}-O-Ph-Ph-OCO-R^*$

R*	Phase transition (°C)
C*HClC*H(CH₃)C₂H₅	Iso—66→SmA→53→Sm*C→30→Cryst.
C*HClC₂H₅	Iso—115→SmA→96→Sm*F—93→Sm*G—71→Sm*H
CH₃C*H(CH₃)C₂H₅	Iso——→Sm*G
CH₃CH₂C*H(CH₃)C₂H₅	Iso—93→SmA—92.5→Sm*G

As for the non-chlorine containing esters in this table, there are no chiral smectic C phase observed. The smectic A phase is squeezed out of the phase diagram as the chain of the chiral unit is lengthened. It is worth noting that similar esters[17] such as $C_8H_{17}-O-Ph-Ph-\underline{COO}-(CH_2)nC^*H(CH_3)C_2H_5$ (n=1, 2, 3) exhibit Sm*C (n=1, 2) and Sm*G (n=3) in addition to the SmA phase. It then illustrates that the direction of the carbonyl group in relation to the chiral unit is of less importance in type B FLC's.

1.5 THE PRESENT WORK

The original idea of the present study was to incorporate some polar chiral units such as the epoxide unit into the system of RO-Ph-Ph-OR*. The use of an epoxide unit[15] in a series of type A FLC's was reported shortly after our project started.

The proposed chiral units are the acetal unit, the diol unit, the epoxide unit, the thiiran unit and the Mosher unit derived from the so

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#[1] Since there is a limited information available for a complete series of the listed esters, only the octyloxy homologue of those liquid crystal esters is given in this table.

$$Et \quad Et$$
$$O \quad O$$
$$Et \qquad COO-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-O-CnH2n+1$$
$$H \qquad Me$$

$$OH \quad OH$$
$$Et \qquad COO-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-O-CnH2n+1$$
$$H \qquad Me$$

$$H \qquad O$$
$$\qquad COO-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-O-CnH2n+1$$
$$Et \qquad Me$$

$$Et \qquad S \qquad Me$$
$$H \qquad COO-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-O-CnH2n+1$$

$$CF_3$$
$$Ph-C^*-COO-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-O-CnH2n+1$$
$$OCH_3$$

called Mosher acid#[2]. There are a number of reasons for proposing these new chiral units.

All of them have a polarizable group be rigidly associated with a tetrahedral stereocenter of a chiral unit. In comparison with the chiral unit $-C^*HClC^*H(CH_3)C_2H_5$, each of the chiral centers of the proposed chiral units is more polarizable. Especially in the acetal unit, the epoxide unit and the thiiran unit, the cancellation of the two dipole moments due to internal rotation, which occurs in the 2-chloro-3-methylpentyl group and probably also in the diol unit, is eliminated by the bond linkage between the two chiral centers. As a result, the polar contribution by the two chiral centers to the the whole chiral unit is maximized.

In addition, the length of those new chiral units is the same as that of the 2-chloro-3-methylpentyl group. This is important because the length of the chiral unit has a detrimental factor on the properties of the FLC's.

Furthermore, there are some points with regard to the acetal and the diol units. It is known that the introduction of the hydroxy group into the aromatic rings of some FLC's enlarge the temperature range of ferroelectricity. It is then interesting to see if such effect can be applied in the case of the introduction of the hydroxy group into the chiral units. The existence of a large bulky molecular component of the acetal unit near the molecular dipole like C-O may suppress the free rotation and relative intramolecular motion in favour of the increase of the spontaneous polarization. However, it has been known that such a bulky group is not desired in terms of the introducment of liquid crystalline phases. .

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[2]This acid, usually served as a reagent to determine the enantiomeric excess of optically active alcohols, also was used mainly because there was no evidence that it has been used in the synthesis of any FLC's.

Finally, those systems are conveniently available synthetically or commercially from two simple starting materials in optically pure form ------ 2S,3S-dihydroxy-2-methylpentanoic acid[11] and the Mosher acid (S(-)-(α)-methyoxy-(α)-trifluoromethyl acetic acid).

By analogy with similar molecules, those target compounds are expected to have chiral smectic phases and also hoped to exhibit even higher spontaneous polarization.

2. RESULTS AND DISCUSSION

2.1 SYNTHESIS OF NEW COMPOUNDS

The synthesis of the target compounds started with the resolution of the two enantiomers, (+)2R,3R-dihydroxy-2-methylpentanoic acid and (-)2S,3S-dihydroxy-2-methylpentanoic acid (hereafter simply referred to as the diol acid) and the preparation of 4'-alkoxybiphenol from the starting material 4,4'-biphenol.

The reaction of resolving agent D-(-)-threo-2-amino-(4-nitrophenyl)-1,3-propandiol[18] and racemic diol acids (previously prepared in our laboratory) gave a solid [(-)amine-(-)acid] salt which precipitated from the reaction solution and an oily [(-)amine-(+)acid] salt which left in the solution. A simple filtration followed by decomposition of those two salts by ammonia solution yielded the (-) diol acid and the (+) diol acid in good yields. The optical purity was examined by the measurement of optical rotation of the two enantiomers. The (-) diol acid had a value of $[\alpha] = -14.0^\circ$ (ca. 95% ee) and the (+) diol acid at $[\alpha] = +11.3^\circ$ (ca. 77% ee). Because of the optical purity requirement of ferroelectric liquid crystals, only the (-) diol acid was used in the synthesis of the designed materials

The conventional Williamson synthesis was employed in preparation of 4'-alkoxybiphenol. In practice, it was found that the key in applying this method to the preparation of the desired phenolic monoether was to choose the appropriate base for the conversion of the biphenol to the corresponding alkoxide, which then reacts with an alkyl bromide or iodide to give 4'-alkoxybiphenol. In this case, sodium methoxide in methanol solution was far superior to sodium hydroxide in aqueous solution or sodium hydride in anhydrous tetrafuran solution. The isolated yields are in

Synthetic Route

R = -O-⟨benzene⟩-⟨benzene⟩-O-CnH2n+1

n = 7, 8, 9, 10, 12.

a. 3-pentanone, HOTs, benzene, reflux 3hr;

b. ROH, DCC, DMAP, 18hr;

c. 6N HCl, dioxane-H₂O, reflux 1hr;

d. TsCl, pyridine, 2 days;

e. (Et)₃N, 2 days;

f. CF₃COOH, 3-methylbenzothiazole-2-thione, reflux 18 hr.

a range of 50-60% for the preparation of 4'-heptyloxybiphenol to 4'-dodecyloxybiphenol #[3].

The DCC (N,N-dicyclohexyldiimide) esterification reactions of the above 4'-alkoxybiphenols and the Mosher acid yielded a new series of low melting point esters (hereafter simply referred to as the Mosher esters) in good yields.

The two hydroxy groups of (-)-diol acid [1] were protected by etherification with 3-pentanone in acidic solution to afford the acetal [2] in good yield. This protection reaction did not succeed when acetel formation with acetone was attempted.

The esterification of [2] and 4'-alkoxybiphenol was successfully carried out by a conventional DCC coupling reaction in the presence of DMAP (4-dimethylaminopyridine) as a catalyst, to produce compound [3] in high yields.

The hydrolysis of [3] in a dioxane dilute aqueous HCl solution yielded compound [4] which could also be prepared via direct DCC coupling of the diol acid [1] and 4'-alkoxybiphenol. A high yield for the direct coupling should not be unreasonable. Because the Ka value of phenol is 10^5 higher than that for alcohol, the -OH group of 4'-alkoxybiphenol is more nucleophilic and thus more reactive to the intermediate acylpyridinium species, the phenol should be able to compete with the alcohols in [1]. Unfortunately, the direct coupling could only be achieved in inconsistent yields of 20-50%.

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[3]The lower yields for 4'-propyloxybiphenol to 4'-hexyloxybiphenol were due to a less efficient work up procedure.

(Reproduced from reference 19)

The three step procedure (protection, esterification and deprotection, overall yield 45%) was generally preferred to the direct esterification.

The dehydration of the diol ester 4 was accomplished by the reaction of 4 and p-toluenesulphonyl chloride in a methylene chloride, DMAP and pyridine solution, with subsequent treatment with triethylamine to yield the desired compound 5 in 50% yield. The optical purity of 5 should be the same as that of the starting material 1, since there are no steps capable of causing the racemization in the above procedure.

The next task was to replace the oxygen atom of the epoxide in 5 with the sulfur atom and to prepare the final target compound 6. The procedure[20] chosen involved the use of 2-methylbenzothiazole 2-thione and trifluoroacetic acid. The reaction should again retain the optical purity of the target compound 6. It is interesting to note that the configuration of both stereocenters attached to the former epoxide are cleanly inverted. The

double inversion can be explained by the following mechanism[20].

(Reproduced from reference 20)

In a model study, racemic 2R,3R-epoxy 2-methyl methylpentanoate was converted to its thiiran counterpartner at room temperature in 75% yield. The conversion of 5 (50% yield) however required slightly more rigorous condition (refluxing).

During the course of the above experiments, it was found that the ^{1}H nmr chemical shift of the single hydrogen of compounds 1 to 6 provide a unique fingerprint to identify each compound concerned.

The use of ^{1}H nmr spectra for the determination of constitution has depended largely on the relationships between chemical shifts and structural environment[21]. The chemical shift of the tertiary proton in these esters is higher for the thiiran ester than for the epoxide ester, as seen in Table 4. The magnitude of chemical shift of the tertiary proton also depends on the type of groups attached to the carbonyl groups. By replacing the methyl group with the 4-alkoxybiphenyl group, the value of the chemical shift of the tertiary proton increases by up to 0.31 ppm in the epoxide esters. This is apparently attributed to the long-distance deshielding effect by the

Table 3 ^{1}H nmr chemical shift of the tertiary proton in the thiiran ester
and its precursors

COMPOUND	CHEMICAL SHIFT (ppm)	SIGNAL SHAPE
	3.92	double doublet
	3.45	dd
	3.36	triplet
	3.70	dd
	3.53	triplet
	3.05	triplet
	3.56	dd

[a]. Excerpted from G.S. Bates' Ph.D thesis, University of Alberta (1976).

Figure 1 Partial ¹H nmr spectra of (-)-2-methyl 2R,3S-epithio-4'-heptyloxy-biphenyl pentanoate (400MHz, CDCl₃): (1) normal spectrum; (2) spectrum with irradiation at 3.70 ppm; (3) spectrum with irradiation at 1.21 ppm

4'-alkoxybiphenyl group.

Another interesting aspect of ^{1}H nmr spectrum of the thiiran ester is that the methylene adjacent to the only tertiary proton gave two multiple signals confirming that those protons are not chemically equivalent, which was verified by the decoupling experiments (see figure 1). If the irradiations are respectively applied at the chemical shifts 3.70 ppm and 1.21 ppm of the two adjacent protons the methylene protons are coupled with, the two multiple peaks of the two protons (at 1.65-1.74 and 1.96-2.07 ppm, respectively) will collapse into less multiple peaks accordingly.

It is expected that the shielding effect by the ethylene sulphide ring is different on these two protons. As seen in the following conformation, Ha is shielded by the thiiran ring resulting in the chemical shift for Hb being 0.32 ppm higher than for Ha.

In the case of the epoxide ester, the corresponding two protons could not be distinguished.

2.2 IDENTIFICATION OF NEW LIQUID CRYSTALS

By using a polarizing microscope coupled with a heating stage, the compounds described in the proceeding section were studied in an attempt to identify which are the liquid crystals and whether they possess phases which are capable of being ferroelectric.

Unfortunately, it was observed that none of the Mosher esters was the liquid crystal, although the melting points are generally around room temperature.

It was disappointing to observe that the n-heptyloxy, the n-decyloxy, the dodecyloxy homologues of the acetal esters, the diol esters and the epoxide esters did not exhibit any liquid crystal phases at all. However, it was pleasing to note that all five compounds of the thiiran esters prepared (MEAOBP-S-7, 8, 9, 10, 12#*, MEAOBP is the abbreviation of 2-methyl 2,3-epithio 4'-alkoxybiphenylpentanoate) were indeed liquid crystal materials.

Identification of the phase types was made by microscopic observations of the textures exhibited by four of the thiiran esters

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#*The n-dodecyloxy homologue also was prepared and preliminarily measured of the phase temperature, showing similar phase sequence to the decyloxy.

(1)

(2)

Figure 2 Liquid crystal phases of (-)-2-methyl 2R,3S-epithio-4'-heptyloxy-biphenyl pentanoate: (1) smectic A; (2) smectic B (X100)

Figure 3 Chiral smectic C phase of (-)-2-methyl 2R,3S-epithio 4'-decyloxy-
biphenyl pentanoate (X200)

(MEAOBP-S-7, 8, 9 10). Typically for the n-heptyloxy homologue the A phase appears from the isotropic liquid on cooling. The n-heptyloxy to n-nonyloxy members inclusive exhibit B phases on cooling from either the A phase or the isotropic liquid. But the decyloxy member shows the desired chiral smectic C phase on cooling directly from the isotropic liquid.

Liquid Crystals	Transition Temperatures (°C)
MEAOBP-S-7	I —64→ SmA —60→ SmB —57→ C
MEAOBP-S-8	I —62.6→ SmB —49→ C
MEAOBP-S-9	I —62.0→ SmB —55→ C
MEAOBP-S-10	I —62→ SmC* —47→ C

Of these liquid crystal materials, MEAOBP-S-8 and MEAOBP-S-9 only show a crystal like liquid crystal phase and MEAOBP-S-7 shows smectics A and B. Since they do not possess any chiral smectic phases, they will not be FLC materials.

MEAOBP-S-10 is a potentially monotropic ferroelectric liquid crystal ("monotropic" means that this phase is only shown on cooling). A measurement of the spontaneous polarization is required to finally determine the ferroelectric property of this compound.

It is rare that a compound shows the chiral smectic C phase directly cooling from the isotropic liquid. Virtually, all of the FLC's exhibit either smectic A or cholesteric phase prior to smectic C phase. However, it was recently reported that the compound[22]
$C_{16}H_{33}-O-Ph-COO-Ph-COO-(CH_2)_2C^*H(CH_3)(CH_2)_3C^*H(CH_3)CH_3$ also exhibits the same phase sequence (isotropic liquid to smectic C).

Like many liquid crystal families, this family of liquid crystals exhibit a variety of different phases dependent of the length of the long

chain attached to the core aromatic rings.

By comparing the liquid crystal thiiran esters to the other three non-liquid epoxide esters, it has been seen how difficult in practice to discover new liquid crystal materials. It was surprising that the epoxide esters are not the liquid crystal materials. The only essential difference between the epoxide esters and the thiiran esters is the slight difference of polarizability of the two three membered rings. The stabilization of smectic liquid crystal phases in the thiiran esters is ascribed to the presence of the more polarizable thiiran unit.

In comparison with the FLC's in Table 3, especially the esters derived from the 2-chloro-3-methylpentyl group, no chiral smectic C phase is observed by rising the temperature, but the temperature range of the n-decyloxy thiiran ester is quite large (15 degree range) and the transition temperature also is not far above room temperature. As mentioned previously, thermodynamically stable smectic A and chiral C phases may be obtained by formulating for instance MEAOBP-S-7 and MEAOBP-S-10 compounds.

2.3 CONCLUSION

A new family of potentially ferroelectric liquid crystal materials has been prepared by utilizing a novel chiral unit containing a thiiran unit. Replacing the thiiran unit with an epoxide unit, i.e., substituting an oxygen atom for the sulfur atom of the new liquid crystals above, eliminated any liquid crystalline phases.

3. EXPERIMENTAL

3.1 GENERAL

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Dichloromethane and pyridine were distilled from calcium hydride under nitrogen when used as reaction solvents. Sodium hydride was obtained in 50% dispersions in mineral oil from Alfa. All other reagents were obtained from Aldrich and used without further purification. All extraction solvents were distilled before use.

Initial melting points were taken on a Gallenkamp melting point apparatus and were uncorrected. Identification of liquid crystals was obtained using a Nikon Optiphot Pol Mircoscope coated with a lab-made heating system accurate to $0.1°C$. The phase photos were taken using Nikon FA camera and using Fuji ISO 1600 or Kodak ISO 1000 color films. The whole measurements were made by Barbara Frisken (Physics, UBC) at Kent State University.

Proton magnetic resonance spectra were obtained using WH-400 400MHz spectrometer. Spectra were run in deuterochloroform solution with tetramethylsilane as an internal reference. Chemical shift was reported on the ppm scale. Infrared spectra were recorded either as a liquid film or in chloroform solution using a Perkin-Elmer model 1710 Fourier Transform spectrophotometer. Both Low resolution and high resolution mass measurements were obtained using a Kratos MS-50 mass spectrometer. Specific rotations were determined using a Perkin-Elmer 241 MC polarimeter at the sodium d-line at room temperature. Elemental analyses were performed at the Microanalytic Laboratory, Department of Chemistry,

University of British Columbia.

Merck Pre-Coated TLC sheets silica Gel 60F-254 were used for analytical thin layer chromatorgraphy, while BDH silica Gel 60-120 mesh were used for column chromatography.

The following abbrieviations are used in the description of the multiplicity of each signal in the ^{1}H nmr spectrum: s = signal, d = double, t = triplet, m = multiplet, dd = doublet of doublets.

3.2 4'-ALKOXY-BIPHENOL: GENERAL PROCEDURE

4,4'-Biphenol (9.3g, 50mmol) was dissolved in a solution of MeONa/MeOH (0.50M, 100ml). After the solution was refluxed for 10min, Alkylbromide (50mmol) and (n-Bu)$_4$NI (0.90g) were added into the refluxing solution in one portion. The reaction solution was then refluxed for 3 hr, cooled to room temperature, and next poured into aqueous HCl solution (1N, 100ml). Ether was used to extract the organic compounds (3x100ml). The combined organic solution was washed with saturated NaHCO$_3$ solution (3x30ml), saturated NaCl solution (1x50ml) and water (1x50ml). This solution was dried over MgSO$_4$ and then evaporated to dryness to afford the crude mixture containing dialkoxy, monoalkoxy derivatives and unreacted biphenol. The three compounds can be separated by using column chromatography on silica gel, eluting with dichloromethane. (See Table 5)

Table 5: 4'-Alkoxybiphenols by alkylation of 4,4'-biphenol

R	Yield(%)	m.p.(°C)	^{1}H nmr (ppm)
C_3H_7	21	176-177	7.44(t, 4H), 6.96(d, 2H), 6.88(d, 2H), 3.96(t, 2H), 1.83(m=6, 2H), 1.06(t, 3H)
C_4H_9	24	171-172	7.44(d, 2H), 7.38(d, 2H), 6.93(d, 2H), 6.90(d, 2H), 3.99(t, 2H), 1.78(m=5, 2H), 1.51(m=6, 2H), 1.00(t, 3H)
C_5H_{11}	38	157-158	7.44(t, 4H), 6.95(d, 2H), 6.88(d, 2H), 3.97(t, 2H), 1.79(m=5, 2H), 1.34-1.53(m, 4H), 0.93(t, 3H)
C_6H_{13}	43	169-170	7.44(d, 2H), 7.38(d, 2H), 6.93(d, 2H), 6.90(d, 2H), 3.98(t, 2H), 1.80(m=5, 2H), 1.44-1.53(m, 2H), 1.32-1.40(m, 4H), 0.92(t, 3H)
C_7H_{15}	55	148-149	7.43(t, 4H), 6.94(d, 2H), 6.88(d, 2H), 3.98(t, 2H), 1.80(m=5, 2H), 1.41-1.51(m, 2H), 1.26-1.40(m, 6H), 0.89(t, 3H)
C_8H_{17}	51	160-161	7.45(d, 2H), 7.40(d, 2H), 6.93(t, 4H), 3.99(t, 2H), 1.80(m=5, 2H), 1.43-1.52(m, 2H), 1.25-1.42(m, 8H), 0.90(t, 3H)
C_9H_{19}	49	143-144	7.45(d, 2H), 7.40(d, 2H), 6.96(d, 2H), 6.93(d, 2H), 3.98(t, 2H), 1.80(m=5, 2H), 1.40-1.50(m, 2H), 1.24-1.40(m, 10H), 0.89(t, 3H)
$C_{10}H_{21}$	56	139-140	7.45(d, 2H), 7.40(d, 2H), 6.95(d, 2H), 6.93(d, 2H), 3.99(t, 2H), 1.80(m=5, 2H), 1.41-1.51(m, 2H), 1.24-1.40(m, 12), 0.88(t, 3H)
$C_{12}H_{25}$	60	160-161	7.44(d, 2H), 7.40(d, 2H), 6.96(d, 2H), 6.93(d,2H), 3.98(t, 2H), 1.80(m=5, 2H), 1.40-1.51(m, 2H), 1.24-1.40(m, 16H), 0.88(t, 3H)

3.3 (-)2S,3S-DIHYDROXY-2-METHYLPENTANOIC ACID

The procedure used was analogous to that of Bergl'son[11]. Finely ground racemic acid (3.24g, 21.2mmol) and D-(-)-threo-2-amino 1-(4-nitrophenyl)- 1,3-propanediol (4.5g, 21.2mmol) were mixtured in ethanol (15ml). The solid dissolved on heating. The solution was then left to stand at room temperature for 18 hr, and the precipitated salt was collected and recrystallizad from ethanol to give 3.4g of the [(-)base-(-)acid] salt. The salt was then decomposited by using aqueous 10% ammonium hydroxide (40ml). The mixture was filtered to recover 1.4g of optically active (-)amine. The filtrate was acidified to pH 1 with aqueous 2N HCl and continuously extracted with ether for 24 hr to give 1.2 g (70.5%) of crude (-)diol acid. Recrystallization from ethyl acetate gave 1.15 g of the pure product.

m.p.($^\circ$C): 150-151.

$[\alpha]^{23} = -14.0^\circ$ (c 3.53, H_2O, 95% ee).

1H nmr ($CDCl_3$) in ppm: 0.97 (t, 3H); 1.39 (s, 3H); 1.50 (m=5, 2H); 3.25 (dd, 1H).

In addition, the (+)-diol acid ($[\alpha] = +11.3^\circ$, c 4.43, H_2O, 77% ee) was also obtained from the mother solution via the same procedure in 68% yield and 1.5 g of optically active (-)amine was recovered.

3.4 3-PENTANONE ACETAL OF (-)-2S,3S-DIHYDROXY-2-METHYLPENTANOIC ACID

(-)-2R,3R-Dihydroxy-2-methylpentanoic acid (1.47g, 10mmol) and p-tolunesulphonic acid (0.147g) were dissolved into a mixed solvent of pentanone-benzene (1:1, 60ml). The mixture was then heated in a water-extraction apparatus until the solution turned yellow. The reaction solution was cooled to room temperature, and next evaporated to give a yellow oily mixture, which was purified by column chromotography on silica gel, eluting with a solvent of ethyl acetate-petrolum ether (1:4) to afford a yellowish oil 1.61g (yield 75%). The structure was confirmed by ^{1}H nmr spectrum.

^{1}H nmr (CDCl$_3$) in ppm: 9.65 (s, 1H); 3.88 (dd, 1H); 1.69-1.87 (m, 6H); 1.56 (s, 3H); 1.06 (t, 3H); 0.99 (t, 3H); 0.92 (t, 3H).

ir (CHCl$_3$): 1747 cm^{-1}.

3.5 3-PENTANONE ACETAL OF (-)-2-METHYL 2S,3S-DIHYDROXY-4'-HEPTYLOXYBIPHENYLPENTANOATE

3-Pentanone acetal of (-)-2S,3S-dihydroxy-2-methylpentanoic acid

(2.16g, 10mmol), 4'-heptyloxybiphenol (3.13g, 11.0mmol),

N,N'-dicyclohexylcarbodiimide (2.25g, 11.0mmol) and 4-dimethylaminopyridine

(1.0mmol) were mixed in CH_2Cl_2 (20ml). The mixture solution was stirred at

room temperature for 18 hr. The precipitated N,N'-dicyclohexyl urea was

filtered and the filtrate washed with water (1x50ml), 5% acetic acid solution

(2x50ml), and again with water (2x50ml), dried over anhydrous $MgSO_4$ and

the solvent evaporated to produce the crude ester. The crude product was

further purified by column chromatography on silica gel, eluting with

dichloromethane to give a yellowish solid. Recrystallization from petroleum

ether gave pure solid 3.60g (yield 80%).

m.p.($^\circ$C): 71-72.

^{1}H nmr ($CDCl_3$) in ppm: 7.53 (d, 2H), 7.47 (d, 2H), 7.14 (d, 2H), 6.96 (d, 2H),

3.99 (t, 2H), 3.92 (dd, 1H), 1.92 (m=5, 2H), 1.80 (m=5, 2H), 1.68-1.80 (m, 4H),

1.67 (s, 3H), 1.28-1.50 (m, 8H), 1.13 (t, 3H), 0.92-1.13 (m, 6H), 0.90 (t, 3H).

ir ($CHCl_3$): 1748 cm^{-1}.

exact mass for $C_{30}H_{42}O_5$: cacld 482.3021, found 482.3023

3.6 (-)2-METHYL 2S,3S-DIHYDROXY-4'-HEPTYLOXYBIPHENYLPENTANOATE

This ester can be prepared by two methods.

Method A: 3-Pentanone acetal of (-)2-methyl 2S,3S-dihydroxy

4'-heptyloxybiphenyl pentanoate (1.2g, 2.5mmol) was dissolved in a mixed

solvent of H_2O-dioxane (1:5) (60ml) and a solution fo 2N HCl (2ml) was

added in one portion. After the mixture solution was refluxed for 1 hr, the solution was cooled to room temperature and diethyl ether used to extract the solution (3x50ml). The combined organic layer was dried over anhydrous Mg_2SO_4 and evaporated to dryness to produce the crude ester, which was purified by column chromatography on silica gel eluting with dichloromethane, followed by recrystallization from ethyl acetate to give pure ester 0.73g (yield 70%).

Method B: (-)2S,3S-dihydroxy-2-methylpentanoic acid (73.5mg, 0.5mmol), n-heptyloxybiphenol (156mg, 0.6mmol), N,N-dicyclohexylidimide (112mg, 0.6mmol), and 4-dimethylaminopyridine (0.1mmol) were mixed in dichloromethane (5ml). The mixture solution was stirred at room temperature for 18 hr. The precipitated N,N-dicyclohexyl urea was removed and the filtrate washed with water (2x5ml), 5% acetic acid solution (1x5ml), and again with water (2x5ml), dried over $MgSO_4$ and evaporated to dryness to give the crude product. The purification was the same as Method A. (yield 20-50%).

^1H nmr ($CDCl_3$) in ppm: 7.56 (d, 2H), 7.47 (d, 2H), 7.14 (d, 2H), 6.96 (d, 2H), 3.99 (t, 2H), 3.68 (dd, 1H), 1.80 (m=5, 2H), 1.84 (s, 3H), 1.50-1.65 (m, 2H), 1.40-1.50 (m, 2H), 1.28-1.40 (m, 6H), 0.89 (t, 3H).

m.p.($^\circ$C): 113-114.

ir ($CHCl_3$): 1747 cm^{-1}.

$[\alpha]$ = -0.5° (c 2.10, $CHCl_3$)..

exact mass for $C_{25}H_{34}O_5$: cacld 414.2397, found 414.2394.

microanalysis for $C_{25}H_{34}O_5$: calcd C: 72.42, H: 8.27; found C: 72.50, H: 8.33.

(-)2-Methyl 2S,3S-dihydroxy-4'-decyloxybiphenyl pentanoate

m.p.($^\circ$C): 121-122.

¹H nmr: 7.56 (d, 2H), 7.47 (d, 2H), 7.14 (d, 2H), 6.96 (d, 2H), 3.99 (t, 2H), 3.68 (dd, 1H), 1.80 (m=5, 2H), 1.84 (s, 3H), 1.50-1.65 (m, 2H), 1.40-1.50 (m, 2H), 1.28-1.40 (m, 12H), 0.89 (t, 3H).

ir (CHCl₃): 1747 cm⁻¹.

[α] = -0.5° (c 2.88, CHCl₃).

exact mass for $C_{28}H_{40}O_5$: cacld 456.2865, found 456.2866.

microanalysis for $C_{28}H_{40}O_5$: calcd C: 73.65, H: 8.83; found C: 73.68, H: 8.91.

(-)2-Methyl 2S,3S-dihydroxy-4'-dodecyloxybiphenyl pentanoate

m.p.(°C): 118-119.

¹H nmr: 7.56 (d, 2H), 7.47 (d, 2H), 7.14 (d, 2H), 6.96 (d, 2H), 3.99 (t, 2H), 3.68 (dd, 1H), 1.80 (m=5, 2H), 1.84 (s, 3H), 1.50-165 (m, 2H), 1.40-1.50 (m, 2H), 1.28-1.40 (m, 14H), 0.89 (t, 3H).

ir (CHCl₃): 1747 cm⁻¹.

[α] = -0.5° (c, 3.01, CHCl₃).

exact mass for $C_{30}H_{44}O_5$: cacld 484.3177, found 484.3175.

microanalysis for $C_{30}H_{44}O_5$: calcd C: 74.33, H: 9.16; found C: 74.26, H: 9.27

3.7 (+)2S-METHYL 2S,3R-EPOXY-4'-HEPTYLOXYBIPHENYLPENTANOATE

4-Toluenesulphonyl chloride (318mg, 0.15mmol) and 4-dimethylaminopyridine (50mg) were added into a solution of (-)diol ester (414mg, 0.1mmol) in anhydrous pyridine-dichloromethane (1:1 4ml) at 0°C. The reaction mixture was stirred at room temperature for 48 hr.

Distilled triethylamine (2ml) was then added into the reaction solution, which immediately turned a red color. The reaction was stirred at room temperature for an additional 48 hr. The reaction was quenched by adding cold 6N HCl solution extremely slowly until the pH value became seven. The solution was then extracted with dichloromethane and the combined organic solvent was washed with brine (1x20ml), and water (3x10ml), dried over $MgSO_4$. The solvent was removed to afford a mixture, which was then purified by column chromatography on silica gel with dichloromethane as eluent, followed by recrystallization from petroleum ether to give 158mg pure product (yield 50%).

$[\alpha]$ = +1.3° (c 2.46, $CHCl_3$).

m.p.(°C): 89-90.

¹H nmr ($CDCl_3$) in ppm: 7.46 (d, 2H), 7.48 (d, 2H), 7.14 (d, 2H), 6.96 (d, 2H), 3.99 (t, 2H), 3.36 (t, 1H), 1.80 (m=5, 2H), 1.70 (m=5, 2H), 1.67 (s, 3H), 1.40-1.50 (m, 2H), 1.24-1.38 (m, 6H), 1.15 (t, 3H), 0.89 (t, 3H).

ir ($CHCl_3$): 1753 cm⁻¹.

exact mass for $C_{25}H_{32}O_4$: cacld 396.2292, found 396.2293.

microanalysis for $C_{25}H_{32}O_4$: cacld C: cacld C: 75.73, H: 8.13, found C: 75.60, H: 8.28.

(+)2-Methyl 2S,3R-epoxy-4'-decyloxybiphenyl-pentanoate

$[\alpha]$ = +1.3° (c 3.39, $CHCl_3$).
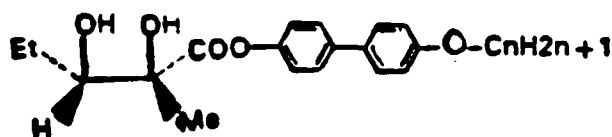
m.p.(°C): 85-86.

¹H nmr in ppm: 7.45 (d, 2H), 7.48 (d, 2H), 7.14 (d, 2H), 6.96 (d, 2H), 3.99 (t, 2H), 3.36 (t, 1H), 1.80 (m=5, 2H), 1.70 (m=5, 2H), 1.67 (s, 3H), 1.40-1.50 (m, 2H), 1.24-1.38 (m, 12H), 1.15 (t, 3H), 0.89 (t, 3H).

ir ($CHCl_3$): 1753 cm⁻¹.

exact mass for $C_{28}H_{38}O_4$: cacld 438.2760, found 438.2765.

microanalysis for $C_{28}H_{38}O_4$: cacld C: 76.68, H: 8.73; found C: 76.55, H: 8.80.

.

(+)2-Methyl 2S,3R-epoxy-4'-dodecyloxybiphenyl-pentanoate

$[\alpha] = +1.3°$ (c 1.98, $CHCl_3$).

m.p.(°C): 88–89.

^{1}H nmr in ppm: 7.45 (d, 2H), 7.48 (d, 2H), 7.14 (d, 2H), 6.96 (d, 2H), 3.99 (t, 2H), 3.36 (t, 1H), 1.80 (m=5, 2H), 1.70 (m=5, 2H), 1.67 (s, 3H), 1.40–1.50 (m, 2H), 1.24–1.38 (m, 16H), 1.15 (t, 3H), 0.89 (t, 3H).

ir ($CHCl_3$): 1753 cm^{-1}.

exact mass for $C_{30}H_{42}O_4$: cacld 466.3072, found 466.3071.

microanalysis for $C_{30}H_{42}O_4$: calcd C: 77.21, H: 9.07, found C: 77.10, H: 9.11.

3.8 2-METHYL 2S,3R-EPITHIO-METHYLPENTANOATE

To a solution of racemic 2-methyl 2R,3S-epoxy methylpentanoate (144mg, 1mmol) and N-methylbenzothiazole-2-thione (220mg, 1.2mmol) in 2 ml dichloromethane was dropwise added a solution of trifluoroacetic acid (140mg, 1.2mol) in dichloromethane (3 ml) at 0°C. The mixture was further stirred at room temperature for 18 hr. The solution was then evaporated to dryness. The product was purified twice by column chromatography, on silica gel, eluting with dichloromethane and a mixed solvent of dichloromethane-petroleum ether (3:7), respectively, to afford neat liquid

171mg (yield 70%).

¹H nmr (CHCl₃) in ppm: 3.77 (s, 3H); 3.56 (dd, 1H); 1.87-2.02 (m, 1H); 1.76 (s, 3H); 1.58-1.72 (m, 1H); 1.18 (t, 3H).

ir (CHCl₃): 1724 cm⁻¹.

<u>exact mass</u> for C₇H₁₂O₂S: cacld 160.0555, found 160.0554.

3.9 (-)2-METHYL 2R,3S-EPITHIO-4'-HEPTYLOXYBIPHENYLPENTANOATE (MEAOBP-S-7)

To a solution of (+)2-methyl 2S,3R-epoxy-4'-heptyloxybiphenyl-pentanoate (100mg, 0.25mmol) and N-methylbenzothiazole-2-thione(55mg, 0.3mmol) in 2ml dichloromethane was dropwise added a solution of trifluoroacetic acid (35mg, 0.3mmol) in 3ml dichloromethane at room temperature. The reaction solution was next refluxed for 18 hr. Evaporation of the solvent gave the crude product, which was purified twice by column chromatography, on silica gel, eluting with dichloromethane and a mixed solvent of dichloromethane-petroleum ether (3:7), respectively. Recrystallization from petroleum ether-ethyl acetate (20:1) gave 53mg pure product (yield 51%)

m.p.(°C): 67-68.

[α] = -1.2° (c 1.80, CHCl₃).

¹H nmr (CHCl₃) in ppm: 7.25 (d, 2H), 7.47 (d, 2H), 7.12 (d, 2H), 6.95 (d, 2H), 3.99 (t, 2H), 3.70 (dd, 1H), 1.96-2.07 (m, 1H), 1.89 (s, 3H), 1.80 (m=5, 2H), 1.65-1.74 (m, 1H), 1.41-1.51 (m, 2H), 1.28-1.32 (m, 6H), 1.21 (t, 3H), 0.90 (t,

3H).

ir (CHCl₃): 1725 cm⁻¹.

exact mass for C₂₅H₃₂O₃S: calcd 412.2064, found 412.2066.

microanalysis for C₂₅H₃₂O₃S: calcd C: 72.96, H: 7.59, S: 7.79; found C: 72.91, H: 7.43, S: 7.88.

(-)2-Methyl 2R,3S-epithio-4'-octyloxybiphenylpentanoate (MEAOBP-S-8).

m.p.(°C): 63-64.

[α] = -1.2° (c 2.32, CHCl₃).

ir (CHCl₃): 1725 cm⁻¹.

exact mass for C₂₆H₃₄O₃S: calcd 426.2220, found 426.2215.

¹H nmr in ppm: 7.53 (d, 2H), 7.47 (d, 2H), 7.12 (d, 2H), 6.95 (d, 2H), 3.99 (t, 2H), 3.70 (dd, 1H), 1.96-2.07 (m, 1H), 1.89 (s, 3H), 1.80 (m=5, 2H), 1.65-1.74 (m, 1H), 1.41-1.51 (m, 2H), 1.28-1.32 (m, 8H), 1.21 (t, 3H), 0.90 (t, 3H).

microanalysis for C₂₆H₃₄O₃S: calcd C: 73.22, H: 8.04, S: 7.50; found C: 73.11, H: 7.90, S: 7.30.

(-)2-Methyl 2R,3S-epithio-4'-nonyloxybiphenylpentanoate (MEAOBP-S-9)

m.p.(°C): 62.5-63.5.

[α] = -1.2° (c 3.07, CHCl₃).

ir (CHCl₃): 1725 cm⁻¹.

exact mass for C₂₇H₃₆O₃S: calcd 440.2376, found 440.2377.

microanalysis for C₂₇H₃₆O₃S: calcd C: 73.59, H: 8.24, S: 7.28; found C: 73.43, H: 8.13, S: 7.12.

¹H nmr in ppm: 7.52 (d, 2H), 7.47 (d, 2H), 7.12 (d, 2H), 6.95 (d, 2H), 3.99 (t, 2H), 3.70 (dd, 1H), 1.96-2.07 (m, 1H), 1.89 (s, 3H), 1.80 (m=5, 2H), 1.65-1.74 (m, 1H), 1.41-1.51 (m, 2H), 1.28-1.32 (m, 10H), 1.21 (t, 3H), 0.90 (t, 3H).

(-)2-Methyl 2R,3S-epithio-4'-decyloxybiphenyl-pentanoate (MEAOBP-S-10).

m.p.(°C): 75-76.

$[\alpha]$ = -1.2° (c 2.11, CHCl$_3$).

^{1}H nmr in ppm: 7.52 (d, 2H), 7.47 (d, 2H), 7.12 (d, 2H), 6.95 (d, 2H), 3.99 (t, 2H), 3.70 (dd, 1H), 1.96-2.07 (m, 1H), 1.89 (s, 3H), 1.80 (m=5, 2H), 1.65-1.74 (m, 1H), 1.41-1.51 (m, 2H), 1.28-1.32 (m, 12H), 1.21 (t, 3H), 0.90 (t, 3H).

ir (CHCl$_3$): 1725 cm^{-1}.

exact mass for C$_{28}$H$_{38}$O$_3$S: cacld 454.2532, found 454.2530.

microanalysis for C$_{28}$H$_{38}$O$_3$S: calcd C: 73.98, H: 8.43, S: 7.03; found C: 73.87, H: 8.59, S: 7.16.

(-)2-Methyl 2R,3S-epithio-4'-dodecyloxybiphenylpentanoate (MEAOBP-S-12).

m.p.(°C): 64-65.

$[\alpha]$ = -1.2° (c 2.38 CHCl$_3$).

^{1}H nmr in ppm: 7.52 (d, 2H), 7.47 (d, 2H), 7.12 (d, 2H), 6.95 (d, 2H), 3.99 (t, 2H), 3.70 (dd, 1H), 1.96-2.07 (m, 1H), 1.89 (s, 3H), 1.80 (m=5, 2H), 1.65-1.74 (m, 1H), 1.41-1.51 (m, 2H), 1.28-1.32 (m, 16H), 1.21 (t, 3H), 0.90 (t, 3H).

ir (CHCl$_3$): 1725 cm^{-1}.

exact mass for C$_{30}$H$_{42}$O$_3$S: cacld 482.2844, found 482.2843.

microanalysis for C$_{30}$H$_{42}$O$_3$S: calcd C: 74.66, H: 8.77, S: 6.62; found C: 74.61, H: 8.86, S: 6.79.

3.10 S(-)-(α)METHOXY-(α)TRIFLUOROMETHYLPHENYL 4'-ALKOXYBIPHENYL ACETATES

A solution of S(-)-(α)-methoxy-(α)trifluoromethylphenylacetic acid (0.855mmol, 200mg), N,N-dicyclohexylcarbodiimide (1.03mmol), 4'-alkoxybiphenol (1.03mmol), and 4-dimethylaminopyridine (0.09mmol) in dichloromethane (5ml) was stirred at room temperature for 18 hr. The N,N-dicyclohexyl urea was removed by filtration and the filtrate washed with water (3x5ml), 5% acetic acid solution (3x5ml) and again with water (1x5ml), dried over MgSO₄ and the solvent evaporated to give the crude ester, which was purified by column chromatography on silica gel, eluting with dichloromethane. The ester was further purified either by recrystallization from petroleum ether or by sublimation. The yield was typically 80% or higher.

ir (CHCl₃): 1766 cm⁻¹ (on all samples).

The m.p.(°C), ¹H nmr (ppm) data, exact mass, and element analysis data are listed in this order as follows.

C₃H₇-: 80-81; 7.64-7.71 (m, 2H), 7.57 (d, 2H), 7.45-7.53 (m, 5H), 7.18 (d, 2H), 6.96 (d, 2H), 4.00 (t, 2H), 3.71 (s, 3H), 1.84 (m=6, 2H), 1.06 (t, 3H); cacld 444.1508, found 444.1520; calcd C: 67.71, H: 5.23, found C: 67.67, H: 5.14.

C₄H₉-: 55-56; 7.64-7.71 (m, 2H), 7.57 (d, 2H), 4.00 (t, 2H), 3.71 (s, 3H), 1.80 (m=5, 1H), 1.45-1.55 (m, 2H), 1.00 (t, 3H); calcd 458.1664, found 458.1667; calcd C: 68.26, H: 5.51, found C: 68.21, H: 5.42.

C₅H₁₁-: 20-21; 7.64-7.71 (m, 2H), 7.57 (d, 2H), 7.45-7.53 (m, 5H), 7.18 (d, 2H), 6.96 (d, 2H), 4.00 (t, 2H), 3.71 (s, 3H), 1.80 (m=5, 2H), 1.40-1.52 (m, 2H), 1.25-1.40 (m, 2H), 0.90 (m, 3H); calcd 472.1820, found 472.1817; calcd C: 68.78, H: 5.77; found C: 68.79, H: 5.66.

$C_6H_{13}-$: 31–32; 7.64–7.71 (m, 2H), 7.57 (d, 2H), 7.45–7.53 (m, 5H), 7.18 (d, 2H), 6.96 (d, 2H), 4.00 (t, 2H), 3.71 (s, 3H), 1.80 (m=5, 2H), 1.40–1.52 (m, 2H), 1.25–1.40 (m, 4H), 0.89 (m, 3H); calcd 486.1976, found 486.1977; calcd C: 69.27, H: 6.02; found C: 69.21, H: 5.94.

$C_7H_{15}-$: 16–17; 7.64–7.71 (m, 2H), 7.57 (d, 2H), 7.45–7.53 (m, 5H), 7.18 (d, 2H), 6.96 (d, 2H), 4.00 (t, 2H), 3.71 (s, 3H), 1.80 (m=5, 2H), 1.40–1.52 (m, 2H), 1.25–1.40 (m, 6H), 0.88 (m, 3H); calcd 500.2132, found 500.2132; calcd C: 69.73, H: 6.26, found: C: 69.66, H: 6.23.

$C_8H_{17}-$: 41–42; 7.64–7.71 (m, 2H), 7.57 (d, 2H), 7.45–7.53 (m, 5H), 7.18 (d, 2H), 6.96 (d, 2H), 4.00 (t, 2H), 3.71 (s, 3H), 1.80 (m=5, 2H), 1.40–1.52 (m, 2H), 1.25–1.40 (m, 8H), 0.89 (m, 3H); calcd 514.2288, found 514.2286; calcd C: 70.16, H: 6.48, found C: 70.10, H: 6.41.

$C_9H_{19}-$: 43–44; 7.64–7.71 (m, 2H), 7.57 (d, 2H), 7.45–7.53 (m, 5H), 7.18 (d, 2H), 6.96 (d, 2H), 4.00 (t, 2H), 3.71 (s, 3H), 1.80 (m=5, 2H), 1.40–1.52 (m, 2H), 1.25–1.40 (m, 8H), 0.89 (t, 3H); calcd 528.2444, found 528.2443; calcd C: 70.57, H: 6.69, found C: 70.55, H: 6.63.

$C_{10}H_{21}-$: 34–35; 746–7.71 (m, 2H), 7.57 (d, 2H) 7.45–7.53 (m, 5H), 7.18 (d, 2H), 6.96 (d, 2H), 4.00 (t, 2H), 3.71 (s, 3H), 1.80 (m=5, 2H), 1.40–1.52 (m, 2H), 1.25–1.40 (m, 12H), 0.89 (t, 3H); calcd 542.2600, found 542.2603; calcd C: 70.96, H: 6.89, found C: 70.93, H: 6.77.

$C_{12}H_{25}-$: 47–48; 7.64–1.71 (m, 2H), 7.57 (d, 2H), 7.45–7.53 (m, 5H), 7.18 (d, 2H), 6.96 (d, 2H), 4.00 (t, 2H), 3.71 (s, 3H), 1.80 (m=5, 2H), 1.40–1.52 (m, 2H),

1.25–1.40 (m, 14H), 0.88 (t, 3H); calcd 570.2912, found 570.2910; calcd C: 71.68, H: 7.25, found C: 71.60, H: 7.34.

CHAPTER 2 HETEROGENEOUS CATALYSIS OF THE RACEMIZATION OF OPTICALLY ACTIVE 1,1'-BINAPHTHYL BY TITANIUM DIOXIDE POWDER

4. INTRODUCTION

Heterogeneous catalysis is crucial in the production of many industrial chemicals and therefore has become a focus of intense efforts in both industry and academia. The second part of this thesis deals with the surface catalysis of the racemization of optically active 1,1'-binaphthyl.

4.1 HETEROGENEOUS CATALYSIS

Heterogeneous catalysts are solids which increase the rates of chemical reactions by virtue of the specific properties of their surfaces, and which increase the rates at which chemical systems attain equilibrium without themselves undergoing chemical change.

A heterogeneous catalytic system is a process in which catalyst and substrate are to be found in two different phases. The reaction naturally takes place, at least in so far as it is catalytic, only at the phase boundary, at the two dimensional surface bounding the two three dimensional phases. The important distinction of heterogeneous catalysis as compared with homogeneous catalysis lies in the fact that topchemical problems, such as the structure of the surface and the distribution of its active areas, the modification and change of the surface by the reaction occurring, must be considered.

Reactions proceeding at the surfaces of solids differ from those proceeding homogeneously in several ways. First, in the former case, the reactants and intermediates are confined to a thin layer over the surface, the volume of which is relatively small. Second, the kinetics of surface reactions are less accessible than those of homogeneous reactions in that the rates of the former are determined by the concentrations of the reactants in the reactive layer. Third, the kinetics of surface reactions are

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less reproducible than those of homogeneous reactions since the nature of the surface and its method of prepartion have profound effects.

The progress of a heterogeneous catalytic reaction consists of five steps[23]: (1) the diffusion of the reactants to the catalyst, (2) the formation of the adsorption–compound, catalyst–reactant, (3) the chemical change at the surface, (4) the decomposition of the compound, the catalyst–product, and finally (5) the diffusion of the reaction products away from the catalyst. Unless they all accidentally possess the same velocity, it is the slowest of these five processes which determines the overall velocity since they all follow each other (consecutive reactions).

Completely understanding how a catalyst carries out a particular reaction would involve knowing the extent and importance of each of the several steps for all reactants and products during the course of the reaction. Needless to say, this formidable task has yet to be achieved. Nevertheless, a great deal of information has been collected for a variety of heterogeneous catalyzed reactions. Exactly what type of information is obtained is determined to a large extent by the method used to study the reaction.

Kinetic methods are useful in determining the number of steps in given reaction and also in determing which step or steps in the catalytical process may be rate–determing. To determine how the reaction rate or product(s) change with the structure and electric character of the catalyst should be one of many mechanistic approaches towards studying heterogeneous catalyzed reactions. In addition, the stereochemistry of the product(s) and the variation of product(s) with reactant stereochemistry could also provide valuable information for analyzing catalyzed reactions. Furthermore, well–developed isotopic tracer method has been applied

successfully to studying the nature of adsorbed species, identifying rate-determing steps, and studying stereochemical changes during the course of a reaction.

A great deal of insight into the mechanism of heterogeneous catalysis has been gained by studying the nature of the molecule or molecules adsorbed on the surface. There are roughly two types of adsorption which might occur. The first type involves formation of chemical compounds on the surface, with a heat of adsorption usually in the order of 10 kcal/mole or higher, and is termed chemisorption. The second type of adsorption involves forces of attraction which are similar to those occurring during condensation and heats of adsorption are correspondingly less than those in chemisorption, usually less than 10 kcal/mole. This adsorption is called physisorption. However, in a specific heterogeneous catalyzed reaction, either of two adsorptions may not be precisely classified.

Despite the fact that there are a wide variety of methods available for studying heterogeneous catalysis, each approach has certain limitations as applied to specific catalyzed reactions. Mechanisms of many heterogeneous catalyzed reactions still remain mysterious and disputed due to the lack of precise mechanistic methods.

Kinetic studies have traditionally been hampered by problems of reproducibilty, which, in many cases, could cause a thorough kinetic study impossible. Even when a good kinetic analysis is possible, the interpretation of the results may not be straightforward. Therefore, the best understanding of heterogeneous catalysis comes only when the problem are approached from as many points of view as possible.

Heterogeneous catalysts may be classified according to the functions they perform, and of great significance is the correlation between these and their electrical and thermal conductivity[24].

Table 6. A Classification of Heterogeneous Catalysts According to their Principal Functions

Class	Metals	Metal oxides and sulphides	Salts and acids
Conductivity type	conductors	semi-conductors or insulators	------
Functions	hydrogenation dehydrogenation Hydogenolysis	oxidation-reduction dehydrogenation isomerization	polymerization isomerization cracking

----

A key aspect of heterogeneous catalysis is the presence of active sites in the solid for which there are no equivalents in the reference reaction run in the absence of a support, thus a finely divided solid is often optimal[25].

The exploration and utilization of new catalysts is fundamantally a matter of trial and error efforts, intuitive assessments, and above all, a great deal of luck.

4.2 CATALYST TITANIUM OXIDE

There are numerous literature references dealing with the chemistry and technology of oxide and sulfide semiconductors, of which TiO_2 is the most extensively studied over years. Its applications cover a variety of areas such as catalysis, adsorption, supports, and TiO_2 also is one of the most common pigments. The use of titanium dioxide as a catalyst has

received more and more attention since the first report on the sustained oxidation of water on illuminated TiO_2 in a photoelectric chemical cell in 1972[26].

Titanium dioxide can be formed in the three crystalline modifications, anatase, rutile and brookite, all of which can be prepared synthetically and can occur naturally. Small amounts of impurities Fe, Nb, Ta, Sn, Cr, and V are normally present in the three forms to render TiO_2 a n-type semiconductor[27]. Brookite is less important because of the nature of its inert chemical activity[27]. Rutile has 6:3 co-ordination and is isomorphous with cassiterite, SnO_2, while linear molecules of TiO_2 are present in anatase.

A number of selected properties of the different forms of the titanium dioxide are summarized in Table 2.

Table 7. Properties of the Different Forms of Titanium Dioxide

Property	Anatase	Rutile	Brookite
m.p.(°C)[a]	change to rutile	1855	change to rutile
Density(g/l)[b]	3.90	4.27	4.13
Dielectric Constant[a]	48(powder)	110-117(powder)	78(natural crystal)
Hardness[a] (mohs' scale)	5.5-6.0	7.0-7.5	5.5-6.0

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[a]. JANAF Thermochemical Tables, Air Force Contract AFO 4(611)- 7554, midland, Michigan, Aug. 1965. [b]. P. Pascal, Nouveau Traite de Chemie Minerale, Masson, Paris(1963).

Stoichiometric titanium dioxide is an insulator with a resistivity of about 10^{35} ohm cm at room temperature; this can be lowered to 0.1 ohm cm by controlled introduction of oxygen vancancies[28].

There has been limited reports in studying thermal catalytic activity of titanium dioxide. However, it is known that titanium dioxide could facilitate a number of isomerization of alkenes.

Thermal isomerization of α-pinene over TiO_2 catalyst gave different isomers selectively depending on heat treatment on the activity of TiO_2 catalyst[29]. It was explained by Liu[30] that, the difference in catalytical activities of SiO_2, Al_2O_3 and TiO_2 in converting α camphene are due to their differences in chemical structure and the nature of bonding electrons, and their surface properties are of secondary importance in so far as the activity of isomerizations is concerned. In the case of the isomerization of propylene oxide over TiO_2 to Me_2CO or EtCHO, Fukui[31] suggested that an adsorbed substrate was bound to the Ti atom through the O atom in order to covert its isomers.

One of the well-established examples is the isomerization of butenes over titanium dioxide. It is concluded by Guisnet[32], after extensive mechanistic studies, that the isomerization of butenes on TiO_2 (anatase prepared from $TiCl_4$) proceeds through three different mechanisms, involving respectively, protonic sites, Lewis acid sites, and basic sites, depending on the pretreatment temperature of the TiO_2 catalyst.

In other words, as has been observed on alumina, those catalytic reactions can take place on Bronsted acid sites of the catalyst. Double bond migration takes place on the basic sites[33] of TiO_2, through allylic carbanions as on MgO,[34] while cis-trans isomerization occurs through σ-bonded carbocations as in the case of Webb's carbonium ion (A)[35], where L is a Lewis acid site.

A
$$C-\underset{\underset{L}{|}}{C}-\overset{+}{C}-C$$

Such an intermediate (A), which allows only geometrical isomerization, can be formed without any C-H bond-breaking[32]. Indeed, titanium dioxide has been proven to be able to provide electron (negative charge) and positive charge (hole) to adsorbed molecules on the surface of catalyst due to its semiconductor structure, even under thermal conditions.

However, most of organic reactions catalyzed by TiO_2 can not occur unless the catalyst is being irradiated by photons. It is the photocatalytical activity of TiO_2 that comprises the special importance of this catalyst.

A pioneering approach concerning the production of hydrogen gas by catalytic splitting of water, by Fujishma and Honda[26], has stimulated a worldwide effort at discovering new, alternate catalyzed routes for photoredox reactions occurring on illuminated semiconductors. Studying sensitized organic phototransformations by semiconductors is important not only because of its potential for uncovering new techniques for functional group modiification but also because of its relationship to general problems involving heterogeneous photocatalysis and radical ion intermediates.

In irradiated heterogeneous systems, either the solid or the contacting liquid may be initially excited. Semiconductor sensitized redox reactions involve the absorption of light and the induction of electron transfer across the semiconductor/liquid interface. Specifically, for reactions occurring at the semicoductor/liquid interface, either the semiconductor itself or the adsorbent may function as the chromophore. In the former case, net chemical change results through direct production of an excited state, whereas in the latter case, sensitization through either electron or energy transfer initiates reactions.

The energetics for the critcal interfacial electron transfer can be derived from the working model proposed originally by Gerisher[36]. As

shown below, a semiconductor is characterized by a band structure, i.e., a filled valence band (VB) separated by an energy gap from a vacant conduction band (CB).

Band structure in a semiconductor: (a) before contact with an electolyte; (b) after contact with an electrolyte (Reproduced from reference 37)

After a semiconductor is immersed in a liquid electrolyte solution containing a redox couple, charge transfer occurs across the interface to equilibrate the potentials of the two phases, an electric field is thus formed at the surface of the semiconductor, and the bands bend from the bulk of the semiconductor towards the interface.

Photon exciting the semiconductor promotes an electron from the filled valence band to the vacant conduction band, leaving an electron deficiency or positive hole in the valence band. In a n-type semiconductor, for example, doping with effective electron donors renders the semiconductor electron rich and band bending provides a method for electron-hole pair separation, i.e., for inhibition of the collapse of the photogenerated hole. Thus when this pair forms in the space charge region of the semiconductor by virture of absorption of a photon, the electron will move away from the interface to the bulk of the semiconductor as the positive charge hole migrates towards the interface where oxidation can

occur. As the oxidation of the adsorbate occurs, sufficient charge can build up in the bulk of semiconductor to render the particle electrophoretically mobile.[38] Ultimately, such a charged aggregate can act as a reducing center and effect solution-phase reductions. In the same principle, reduction-oxidation reactions could be also carried out over p-type semiconductors.

Numerous photocatalytic organic reactions on semiconductors have been studied, some of which are summarized as follows.

Fox[39] demonstrated, for instance, that the cyclooctatetraene dianion, a participant in a reversible organic redox couple, could be generated by photocatalytic TiO_2 in ammonia solution,[40] and in addition, closed-shell monoanions could be similarly photogenerated.

Fox[36] also showed that a net endothermic oxidative coupling could be driven by light absorption either by the tetraphenylcyclopentdienide anion adsorbed on a single crystalline TiO_2 electrode or by the semiconductor itself.

One of the first reported oxidative cleavages of an organic molecule induced by long-wavelength ultraviolet irradiation of a semiconductor involves the photodecarboxylation of acetic acid.[41]

$$CH_3COOH \xrightarrow{hv, TiO_2} CH_3CH_3 \text{ or } CH_4 + CO_2$$

Ethane and methane are the different main products formed by using crystalline TiO_2 and powdered TiO_2 respectively. It was confirmed by Bard that a methyl radical $CH_3\cdot$ is the intermediate of the reaction[41].

The most successful organic reaction catalyzed by irradiated TiO_2, in so far as the synthetic application is concerned, is the oxidative cleavage of arylated olefins, which sometimes experiences virtually quantitative conversion[42].

$$(Ph)_2C=CH_2 \xrightarrow{\text{hv, } TiO_2} (Ph)_2C=O$$

One of the most exciting examples in the irradiation of semiconductor suspensions containing organic molecules is the synthesis of amino acids. The products of glycine, alanine, serine, aspartic acid, and glutamic acids can be simply generated by irradiation of platinized TiO_2 suspensions in aqueous ammoniacal methane, although in poor conversion and with no selectivity at all[43].

Most of the examples mentioned above, however, mainly deal with oxidation reactions by valence band holes and/or hydrogen production by conduction band electrons. Recently, Gratzal[44] reported that pyruvate could be efficiently reduced to lactate under illumination of aqueous suspensions of titanium dioxide powder.

In addition to pure TiO_2, modified TiO_2 catalyst systems such as plantized TiO_2 and titanium-silicon oxides, are also effective catalysts in a variety of organic reactions. The choice of a specific catalyst in order to obtain the most efficient reaction is not predictable, but totally depends on the type of reaction concerned.

4.3 RACEMIZATION OF BINAPHTHYL

Because of hindered rotation about the 1,1' bond, 1,1'-binaphthyl exists in two enantiomeric forms. The racemization reaction consists in the conversion of a solution with an excess of one enantiomer into an equimolar mixture of both enantiomers.

(R)-(-)-1,1'-binaphthyl   (S)-(+)-1,1'-binaphthyl

This is definitely one of the simplest reactions in organic chemistry. Furthermore, this simple system has been proven to be appropriate for studying the catalytic activity of a variety of heterogeneous catalysts[45-52] and used successfully for the study of photoracemization[53-56]. A brief review of all kinds of racemizations of binaphthyl, spontaneous, homogeneously catalytic, heterogeneously catalytic, and photocatalytic, will be presented.

4.3.1 UNCATALYZED RACEMIZATION OF BINAPHTHYL

The conversion of enantiomers of 1,1'-binaphthyl has been studied by Cooke and Harris[57], and later on by Carter and Liljefors[58]. As pointed out by those researchers, hindered rotation about the 1,1'-bond prevents the two naphthalene units from achieving coplanarity. It has been considered that interference of groups in the 1 and 8 positions in each naphthalene moiety prevents coplanarity from being achieved in either one of the two ring systems. Each naphthalene unit consequently exists in one of two forms,

called d or l.

(d)   (1)

d and l forms of substituted naphthalenes

Either enantiomer of binaphthyl can then exist in one of three forms

(a) a racemoid, l-l, (b) a racemoid, d-d, (c) a mesoid, l-d, form.

l   l   d   l

Racemoid   Mesoid

**Racemoid and mesoid conformations of
S-(+)-1,1'-binaphthyl**

Mathematically, there are totally six different conformational configurations

for binaphthyl: R(d-d), R(d-l), R(l-l), S(d-d), S(d-l) and S(l-l). Because of

rapid d = l conversion at ambient temperatures, the conformation of the

ground state molecule would be simply referred to as R or S. Nevertheless,

it is believed that in the crowded transition state leading to the conversion

of R to S or vice versa, there is a considerable difference between a

conversion involving, say, R(d-l) = S(d-l) and R(l-l) = S(l-l).[53-54] In the

latter case there are two simultaneous hydrogen-hydrogen contact points

between the ring systems in the transition state. In the former case there

is no point along the conversion path where two hydrogens interact

simultanously with two other hydrogens. Rather, there are two successive

hydrogen-hydrogen interactions as the enantiomers convert. The pathway

involving successive interactions is energetically much more favorable than the simultanous route[51]. It is thus concluded that it is through the mesoid forms the R and S 1,1'-binaphthyl convert. The activation energy of the reaction was measured 22.5 kcal/mole[57].

4.3.2 PHOTOCATALYTIC RACEMIZATION OF BINAPHTHYL

The work dealing with photoracemization of 1,1'-binaphthyl was nicely done by Irie and his co-workers[53-55]. The mechanism for this photoracemization has been studied from the effect of additives (photo sensitizers or quenchers) as well as by a laser photolysis. The effect of additives revealed that photoracemization occurs in the triplet excited state. The conversion to its enantiomer 1,1'-binaphthyl has to overcome the barrier at the angle of $0°$ due to steric hindrance of hydrogens at the 2 and 8 positions in the coplanar conformation. Compared to the higher barrier in the ground state (22 kcal/mol)[57], the barrier in the triplet state is only 1.9 kcal/mol. In other words, the photoracemization occurs much faster than the thermal racemization.

It is also noted that since the higher bond order in the excited state causes a smaller bond distance and gives rise to a large steric hindrance, the low barrier observed in the triplet state suggests that the electronic stablization energy gained as a result of the interaction of the two naphthyl groups is superior to steric hindrance.

The same researchers[56] further observed that γ-ray radiation induced racemization of 1,1'-binaphthyl occurs mainly in a radical anion state of 1,1'-binaphthyl in tetrahydrofuran, while the reaction occurs mainly in the triplet excited state in toluene. The low activation energies of the reaction in both solvents, 1.1 kcal/mol in THF and 1.9 kcal/mol in toluene, as

compared to thermal racemization, indicates that the introduction of an electron to the lowest vacant molecular orbital causes an electronic structural change favorable to rotation along the intraannular C–C bond.

4.3.3 CATALYZED RACEMIZATION OF BINAPHTHYL BY C, NI, AND PT

The catalyzed conversion of enantiomers of 1,1'-binaphthyl over carbons, Raney nickel and platinum was extensively investigated by Pincock et al[45-52]. Since they reported the first case of the surface catalysis of this simple reaction[52], there have been much work about if and how this type of catalysis actually occurs. The conculsions obtained in these studies have contributed a variety of ideas and evidences towards the understanding of the general heterogeneous catalysis, especially in areas of those three different solids.

Since our work is closely related to and, in some aspects, similar to the previous work, it is therefore appropriate to review some features of heterogeneous catalysis by carbons[49-52], nickel[45-51]and platinum[47-52] as it applies to this simple reaction.

4.3.3.1 The carbon catalyzed racemization

The racemization of binaphthyl on various carbon surfaces probably proceeds by a mechanism in which electron density is donated to the binaphthyl by the carbon surface.

The catalytical sites for binaphthyl racemization are located on the basal planes and not on the disorganized areas or the edge atoms, because the catalytic rate is unaffected by oxidations and reductions which occur at the disorganized areas of the surface.

Racemization of binaphthyl in the presence of the carbon may involve the formation of a binaphthyl radical anion on the surface.

The idea was supported by the fact that intercalating potassium into graphite enhances the catalytic activity of the graphite. Since intercalating potassium-graphite is well known to catalyze reactions by one electron transfer, it could appear that a radical anion mechanism for this particular catalytic reaction is reasonable.

4.3.3.2 Platinum catalyzed racemization

The platinum catalyzed reaction follows simple first order kinetics. There is no detectable adsorption or interferring reduction during the reaction.

The aspect of the reaction that is difficult to explain is that the catalysis shows a peculiar kinetic effect in that the reaction rate is independent of the concentration of platinum.

Oxygen present in the reaction solution poisoned the reaction, apparently because of competing adsorption and its reduction to water. Cyclohexane and cyclohexene which is reduced to cyclohexane, however, show a permanent inhibitory effect which increases with the concentration of the compound. It is therefore concluded that the reduction and racemization sites were the same in platinum catalyzed racemization.

Variations in activity and the complete loss of the activity probably due to uncontrollable poisoning were pointed out.

4.3.3.3 The Interaction of binaphthyl with Raney nickel

Raney nickel catalyzes both the racemization process and the reduction of binaphthyl to 4,5,6,7-octahydro-binaphthyl. There was also a greater adsorption process of binaphthyl than with platinum.

The racemization follows first order kinetics after an initial non-first order period, which is probably caused by the concurrent adsorption. The relative effects of added poisons, e.g. sulphur or 1-decylmercaptan, suggested that there were three different catalytic sites, each responsible for a separate type of interaction with binaphthyl.

4.4 THE OBJECT OF THE PRESENT STUDY

The aim of the present study is to discover the possible catalytic effect (activity) of highly dispersed titanium oxide on the racemization of optically active binaphthyl and, if so, to experimently examine the kinetics of the catalysis, and thus, hopefully, to formulate a reaction scheme that is consistent with experimental findings.

The following sections describe various kinetic results for the titanium dioxide (anatase from Aldrich) catalyzed racemization of binaphthyl.

5. RESULTS AND DISCUSSION

5.1 PRELIMINARY KINETIC STUDIES AND REPRODUCIBILITY

It was found that small amounts of highly divided TiO_2 (anatase, Aldrich) in acetone (ca. 10.0mg/ml) would catalyze the racemization of optically active 1,1'-binaphthyl without concurrent side reaction or detectable adsorption.

As in the case the other catalyzed racemizations studied by Pincock and his coworkers[45-52], the TiO_2 catalyzed reaction shows good first order kinetics, as seen in Figure 4 for several runs.

It was also found that TiO_2 would show catalytic activity only when commercially available TiO_2 is further divided into colloidal particles in acetone solvent by the means of stirring. Finely divided TiO_2 can be simply obtained by intensively stirring powder TiO_2 over a period of 24 hr in a flask. With a catalytically active batch of finely divided TiO_2 in acetone it was observed that the colloidal particles of TiO_2 would not precipitate for a period of 4 hr after the completion of the stirring. A good reproducibility was observed (see Figure 5 for several identical runs), and this reproducibility allowed some quantitative kinetic studies to be done in the subsequent section.

The interesting fact is that the titanium dioxide catalyzed racemization was independent of the stirring rate. Although the stirring speeds were varied with a variable speed magnetic stirrer, the rate of a kinetic run was never changed by increasing or decreasing the stirring speed during a run. This is, of course, consistent with a reaction which is not affected by diffusion control factors. Because increasing the area of liquid-gas (or liquid-solid) interface will increase the rate of reactions

Figure 4 First order kinetic catalyzed racemization of optically active
1,1'-binaphthyl by highly dispersed titanium dioxide

Figure 5 Several identical kinetic runs of catalyzed racemization of optically active binaphthyl by highly dispersed titanium dioxide

whose rate determining step is diffusion across this interface.

There are two characteristic features in these plots in comparison with platinum, nickel and carbon catalyzed racemization of optically active 1,1'-binaphthyl.

Like platinum catalyzed racemization of binaphthyl, no initial rapid decrease or increase in optical rotation of binaphthyl was observed when titanium dioxide was used as a catalyst in this simple organic reaction. Another important aspect is that the first order plots were simply straightforward throughout the kinetic runs (up to halftime) in the titanium dioxide catalyzed racemization of binaphthyl, which also was an important discovery in the previous metal or carbon catalyzed reaction. The nonexistence of curvature in the plots might indicate that the catalyst titanium dioxide was not undergoing any progressive deactivation, which many heterogeneous catalysts often experience during the catalysis. The nickel and the carbon, for instance, exhibit the maximum catalytic activity at the very beginning of the catalyzing racemization of binaphthyl[49].

At this point, it was initially decided to determine how the catalytical activity of TiO_2 might be influenced by the concentrations of binaphthyl and TiO_2 in order to draw a further comparison with the other catalyzed racemizations by C, Ni, and Pt.

5.2 THE EFFECT OF CONCENTRATIONS OF CATALYST, BINAPHTHYL AND ADDITIVES ON CATALYTIC ACTIVITY

Kinetics were studied by adding optically active binaphthyl (0.00435g) into a finely divided titanium dioxide acetone solvent (25.0ml). All reactions were carried out at a low temperature (10°C) in order that the rate of the uncatalyzed, spontaneous racemization was minimized. The binaphthyl concentration was low (6.82×10^{-4} mole/l) and the measurement of the rotations of the samples was carried out at the mercury line (456nm) rather the more usual sodium line (589nm) where the absolute rotation is much less. The rate constants were determined from the slope and are plotted against the weight of catalyst in Figure 5. The results clearly showed that the observed rate constant (Kobs) is directly proportional to the concentration of the titanium dioxide used. Unlike the plantium catalyzed racemization, but like carbon catalyzed racemization, as the concentration of catalyst TiO_2 is increased and the concentration of binaphthyl is kept constant, the reaction rate constant (Kobs) increases due to the availability of more catalytical sites in the solution.

The dependence of Kobs on the concentration binaphthyl is the same as that found for carbon or platinum catalyzed reaction. As the concentration of binaphthyl is increased and the concentration of the catalyst TiO_2 remains the same, a large number of both R and S binaphthyl molecules compete for a limited number of racemization sites and the predominant mode of racemization is the uncatalyzed reaction. Table 8 shows the kinetic data in which the kinetic rate constant was decreased as the concentration of binaphthyl was gradually increased.

Figure 6 Dependence of the concentration of titanium dioxide on the observed kinetic rate constants of catalyzed racemization of optically active 1,1'-binaphthyl by highly dispersed titanium dioxide

Table 8 The dependence of Kobs of Aldrich anatase catalyzed racemization of binaphthyl on the concentration of binaphthyl

Concentration of binaphthyl (mole/l)	Kobs $\times 10^4 (min^{-1})$
6.82×10^{-4}	6.8
5.70×10^{-4}	6.8
6.11×10^{-4}	7.4
7.64×10^{-4}	6.6
13.3×10^{-4}	6.0
14.7×10^{-4}	5.3
20.5×10^{-4}	3.1
20.5×10^{-4}	4.0

$[TiO_2] = 10.0$ mg/ml.

Following the kinetic work above, it was then decided to pursue an investigation to determine whether the catalysis was sensitive to organic molecules which are planar simple aromatic compounds.

Figure 6 to figure 10 illustrate how the course of the catalyzed reaction was effected by the addition of aromatic compounds, benzene, naphthalene, anthracene, and pyrene. As shown in these figures, the presence of very small amounts of additives permanently poisoned the catalyzed racemization. The more aromatic rings the added compound possesses, the more effective does it stop the reaction (benzene < naphthalene < anthrance < pyrene).

The result was probably due to chemisorption which involves adsorption of the poison on the surface. The decrease of catalyst activity was caused by coverting the active sites into inactive surface compound or

Figure 7 Dependence of the concentration of the additive benzene on the observed kinetic rate constant of catalyzed racemization of optically active 1,1'-binaphthyl by highly dispersed titanium dioxide

Figure 8 Dependence of the concentration of the additive naphthalene on the observed kinetic rate constant of catalyzed racemization of optically active 1,1'-binaphthyl by highly dispersed titanium dioxide

Figure 9 Dependence of the concentration of the additive anthrance on the observed kinetic rate constant of catalyzed racemization of optically active 1,1'-binaphthyl by highly dispersed titanium dioxide
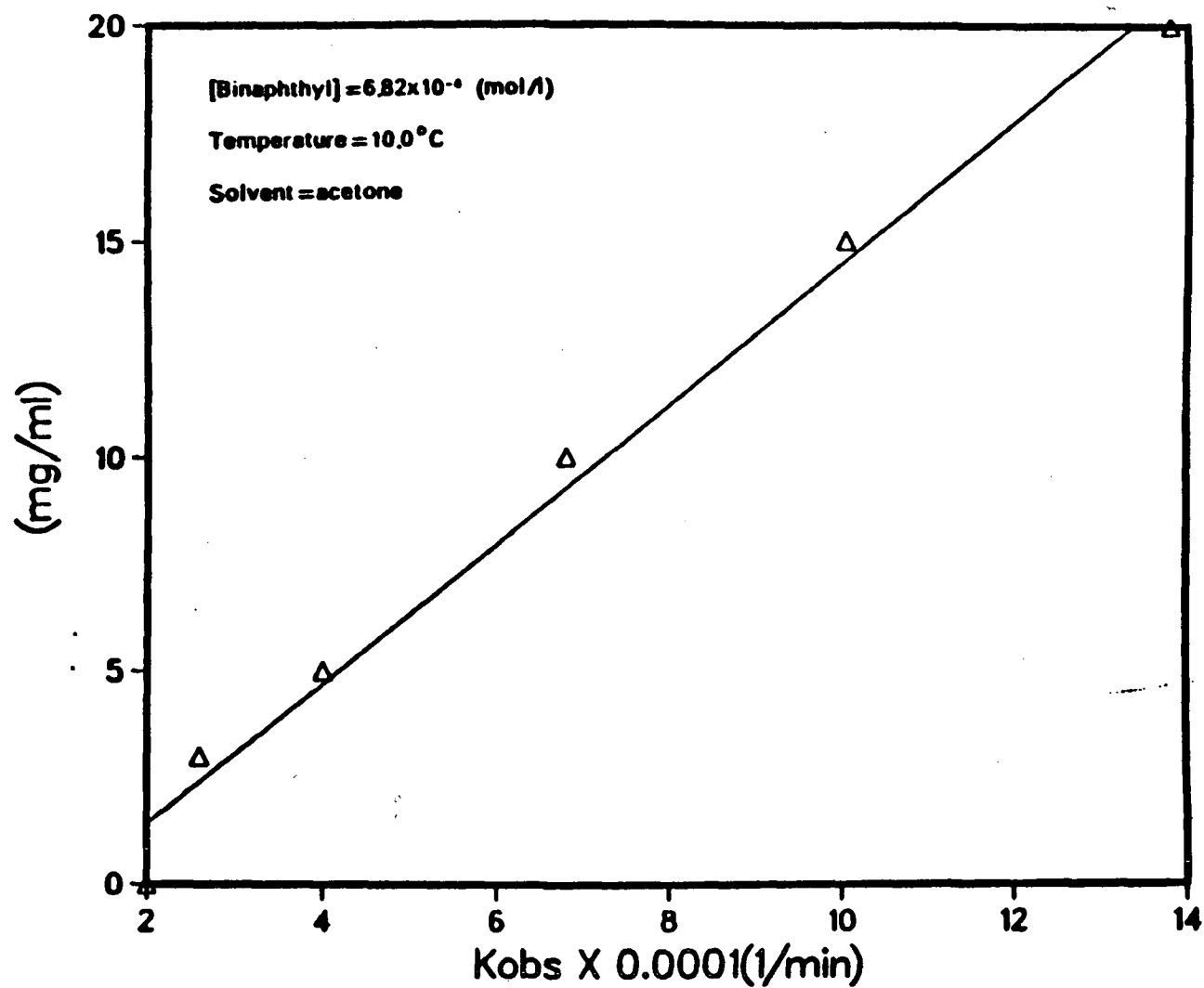
Figure 10 Dependence of the concentration of the additive pyrene on the observed kinetic rate constant of catalyzed racemization of optically active 1,1'-binaphthyl by highly dispersed titanium dioxide

by adversely affecting the number of free electrons, unpaired electrons or "holes" on the surface of the solid catalysts.

The mechanism fits the other assumption that the active surface is substantially uniform and that activity decline is proportional to the fraction converted to inactive surface compound or that certain favored spots responsible for the activity are preferentially covered by the poisons[59]. In our case, the poisoning is perhaps best attributed to the competition for adsorption of those additives on the catalytical sites. It is worth noting that a similar case has been observed in this lab for the carbon catalyzed reaction[52].

5.3 CATALYTIC ACTIVITY OF MODIFIED TITANIUM DIOXIDE

In this section are described some experiments involving the kinetic studies on a variety of titanium dioxide modifications. These experiments grew out of attempts to obtain highly efficient, reproducible titanium dioxide towards the racemization of binaphthyl. The kinetic procedure was identical to the previous kinetic studies except for that otherwise mentioned.

5.3.1 PREHEATING TITANIUM DIOXIDE

It has been reported that the heat treatment of TiO_2 can change the catalytical activity[32-33]. Since preheat-treatment is one of the simplest methods to modify the catalytic effect of titanium dioxide, at the early stage of this project, anatase (Aldrich) was heated in a furnace at the temperature ranging from 500-700°C for one to eighteen hours. The treatment was carried out while a small stream of nitrogen gas passed over the catalyst to maintain a low partial pressure of the evolved vapors.

However, preheating of TiO_2 neither improved nor destroyed the catalytic property. It clearly indicated that the racemization catalytic sites remained the same under heat-treatment. In other words, the catalytical activity of titanium dioxide is independent of the heat treatment, which has modified the catalysis of isomerization of butenes by anatase powders[33-34]. Apparently, the nature of this catalyzed racemization is different from that for the catalyzed isomerization of alkenes on the same semiconductor catalysts. Also it meant that this calcination treatment could not activate more catalytic sites in addition to those that existed.

Table 9 Catalytic activity of modified titanium dioxide towards the
racemization, part 1

Entry	[TiO₂] (mg/ml)	Kobs x10⁴(min⁻¹)
Aldrich anatase, 2 hr heat treatment (500°C)	10.0	7.1
Aldrich anatase, 8 hr heat treatment (700°C)	10.0	6.8
Aldrich anatase, 18 hr heat treatment (700°C)	10.0	6.9
Aldrich anatase, acid washed	10.0	no catalytic effect

1. Solvent distilled actone.

2. Concentration of binaphthyl is kept precisely at 6.82×10^{-4} (mole/ml).

5.3.2 ACID-WASHING TITANIUM DIOXIDE

The object of the washing step is primarily to remove impurities from the catalysts[60], that is to "polish" the surface of the catalysts. That titanium dioxide is chemically inert to strong acids led us to apply this simple technique.

Accordingly, Aldrich anatase powder was immersed in the concentrated HCl or H_2SO_4 solution for about 20 mintues. The TiO_2 was used after filtering, rinsing with a lot of water and with acetone, and drying at 120°C overnight. The procedure probably represents the simplest possible washing method.

Under the identical kinetic procedure used above, the acid-treated, previously active anatase powder lost their catalytic ability completely. The deactiviation was obviously caused by the destruction of the catalytic sites. This is one of the cases in which a straightforward interpretation is impossible. We only can say that somehow the interaction between the acids and the surface of the catalysts resulted in the deactivation of the catalysts.

5.3.3 ILLUMINATING TITANIUM DIOXIDE

As mentioned previously, the exploration of new titanium dioxide photocatalytic reactions is of great interest to chemists. We did some preliminary studies on possible TiO_2 photocatalytic racemization of binaphthyl (procedure see experimental section)

In some irradiated catalytic reactions[61], catalytic effectiveness can be considerably enhanced by substituting pure titanium dioxide with modified titanum dioxide catalyst systems, such as, platnized titanium dioxides. Accordingly, platnized TiO_2 prepared by Bard's method[62] was also tried in

this type of experiment.

Because the photoracemization occurs via a triplet state intermediate and because oxygen is the best quencher to the photoracemization[54-54], some of attempted heterogeneous photocatalytic reactions were carried out in the presence of oxygen gas, which was bubbled through the reaction solution for 30min before the beginning of the kinetic run. This operation was based on the fact that the triplet state of binaphthyl is not likely the intermediate of TiO_2 photocatalysis.

Nevertheless, there was no apparent catalytic activity drawn from the kinetic plots. Namely, the kinetic rate constants of TiO_2 added solutions were lower than that of the corresponding TiO_2 free solutions without exception. The TiO_2 photocatalytic effect (if any) could be outbalanced by much more powerful photoracemization. The kinetic rate constant of the photoracemization was increased as the concentration of binaphthyl was decreased. It was found that the halftime of the photoracemization was as low as 5 seconds in the absence of oxygen at the concentration of binaphthyl (6.82×10^{-4} mole/l, the usual concentration in the kinetic studies). In the experiment, the removal of oxygen was carried out by bubbling a small stream of nitrogen or argon for 30 min before use.

5.3.4 REDUCING TITANIUM DIOXIDE

The reduction of an oxide semiconductor is one of the methods to further dope the semiconductor thus increasing the catalytic activity[63]. This process is analogous to the removal of oxygen from the TiO_2 lattice by evacuation at high temperatures[63]. Loss of oxygen is associated with the generation of surface Ti(III) sites[63]. We, at this point, simply wanted to test the doping effect on the catalysis.

Table 10 Catalytic activity of modified titanium dioxide towards the racemization, part 2

Entry	$[TiO_2]$ (mg/ml)	Kobs $x10^4(min^{-1})$
Irradiating Aldrich anatase	10.0	300
Irradiating Aldrich anatase	1.0	730
Irradiating	0.0	833
Irradiating Aldrich anatase, in the presnece of O_2	0.1	217
Irradiating platinized Aldrich anatase, in the presence of O_2	0.5	53
Irradiating, in the presence of O_2	0.0	263
Irradiating Aldrich anatase, in the absence of O_2	0.1	58,000
Irradiating, in the absence of O_2	0.0	114,000
Reduced Aldrich anatase by H_2 (1hr)	10.0	6.5
ibid (4hr)	10.0	10.3
ibid (4hr)	10.0	7.2
ibid (4hr)	10.0	7.5
ibid (4hr), new batch	10.0	6.9
ibid (4hr), another batch	10.0	7.6
ibid (8hr)	10.0	7.8
ibid (18hr)	10.0	3.9

1. Solvent distilled actone.

2. Concentration of binaphthyl is kept precisely at 6.82×10^{-4} (mole/ml).

It has long been known that there exists a correlation between the catalytic activity and electrical conductivity[64]. Many experimental works[65] in which such correlation has been observed were reported. These two properties of the semiconductor vary in the same or in opposite directions from one sample to another depending on the type of the reaction. The procedure of this reduction is described in the experimental section.

The results obtained from the reduced anatase catalyzed racemization (Table 10) seemed to be in agreement with the above theory. The kinetic rate constant was slightly higher than that for the unreduced Aldrich anatase. This could be interpreted that the reduction created more Ti(III) thus increasing the electric conductivity which helped the racemization.

In the case of the platinum catalyzed reaction, Pincock and Hutchins[49] reported that in order to obtain highly active platinum by the hydrogen reduction of platinum oxide, at least a period of 120 minutes was required. Since pure PtO_2 is not catalytically active in the racemization of binaphthyl, it therefore indicated that the above theory also is applied to the Pt catalyzed racemization. That is, in the case of platinum catalyzed racemization, the catalytic sites are generated as the Pt is produced and as the electric conductivity of the surface is increased. This important finding is later used in an arguement to clarify the catalytic mechanism (see subsection 5.4).

5.3.5 OTHER SOURCES OF TITANIUM DIOXIDE

5.3.5.1 Titanium dioxide from titanium tetrachloride

In many cases of catalytic studies, the modification of titanium dioxide used was not obtained directly from commercially available materials, but prepared by the hydrolysis[66-67] of titanium tetrachloride.

Table 11 Catalytic activity of modified titanium dioxide towards the racemization. part 3

Entry	[TiO₂] (mg/ml)	Kobs ×10⁴(min⁻¹)
TiO₂ freshly prepared from TiCl₄	10.0	7.1
ibid	10.0	6.7
ibid	10.0	6.6
Colloidal Aldrich anatase after one filtration	5.0	5.0
ibid	4.8	5.4
ibid	5.3	4.9

1. Solvent distilled actone.

2. Concentration of binaphthyl is kept precisely at 6.82×10^{-4} (mole/ml).

Titanium dioxide described in experimental section was used to produce freshly precipitated TiO$_2$. This material showed comparable catalytic power to that for Aldrich anatase (see Table 11).

5.3.5.2 Rutile materials

We also examined the catalytical effect of rutile from Alfa Chemical Co., but found out that this material did not catalyze the racemization of binaphthyl under any conditions employed for the anatase case.

5.3.6 COLLOIDAL TITANIUM DIOXIDE

As stated previously, titanium dioxide was uneffective in the racemization unless the colloidal solution was used. Therefore, one could ask this question: is there a difference between two individual particles in terms of catalytic activity, provided we could separate finer particles from previously stirred solution by filtration? At one point, it was decided to prepare several batches of colloidal solutions and then filter the larger particles thus obtaining a "true" colloidal catalyst solution, which presumably would be better catalysts.

Experimentally, we filtered the stirred suspensions of titanium dioxide, stripped the solvent of the filtrate, weighed the catalyst, added 25.00ml acetone, and then stirred the solution for 1 hr before use. In any event, it has shown that the assumption was correct. The value of Kobs/[TiO$_2$] is higher than that of non-filtered reaction solution at the similar concentration of titanium dioxide (see Table 11, compared to the usual Kobs = 4.1×10^{-4}min^{-1} at [TiO$_2$] = 5.0mg/ml). Indeed, the catalytic activity is enhanced with the smaller titanium dioxide powder.

5.4 SPECULATION ON THE CATALYTIC MECHANISM ON THE BASIS OF PREVIOUS AND PRESENT KINETIC RESULTS

So far, it has been shown that, our attempt on modifying titanium dioxide in order to increase the kinetic activity and then to understand this catalysis better, seems to be unsatisfactory, but does provide a few interesting points into understanding of this heterogeneous catalysis.

Despite the fact that the catalytic activity of titanium dioxide towards this reaction has been compared to that for other catalysts throughtout the proceeding sections, an additional comparison of catalytic activity is compiled in Table 12.

Table 12 Catalytic activity of four heterogeneous inorganic solids towards the racemization of optically active binaphthyl ($*$ K=Kcat/Kuncat)

Cat.	[Cat.] (mg/ml)	[Bina.] (10^{4}xM)	t($^\circ$C)	K*	K/[Cat.] (mg^{-1})	Solvent
TiO$_2$	10.0	6.82	10.0	3.5	0.35	acetone
Ni	37.7	25.0	25.0	5.0	0.13	n-heptane
Pt	1.0	5.0	25.0	8.0	8.0	ethanol
C	1.0	250	25.0	14.0	14.0	chloroform

The most important feature drawn from Table 12 is that the four catalyst are all electron-donating type catalysts and the catalytic activity is obviously related to the electron-donating ability of the catalyst. Hattori et al[61] reported that the exposure of TiO$_2$ surfaces to nitrobenzene result in the formation of the anion radical of nitrobenzene (confirmed by ESR spectrum) in a course of identifying the intermediate of the TiO$_2$ catalyzed isomerization of butenes. This relevant finding definitely favours the arguement that an anion radical of binaphthyl is likely formed in the colloidal TiO$_2$ solution and probably plays an intermediate role in the

catalysis. It is then reasonable to guess that at least one of catalytic pathways does involve the radical anion intermediate mechanism regardless which of the catalysts is concerned.

Moreover, one can see that titanium dioxide is in some sense as good catalyst as other ones. Since the rate of the racemization also depends on the solvent[51,69], the temperature and the concentration of binaphthyl, it would be improper to list those catalysts in the order of the catalytic activity. But it is certain that the carbon is the most active catalyst and the most successful catalyst as applied to the racemization of binaphthyl.

Also, it is worth noting that preliminary studies on other semiconductor such as MoS_2 showed similar catalytic results to that for TiO_2 (the investigation was carried out by a summer undergraduate in this lab).

5.5 CONCLUSION

Until the completion of this thesis, four common heterogeneous catalysts have been discovered to be catalytically active towards the racemization of binaphthyl in virtually the same ways. It was therefore believed that this catalytic phenomeon is not unusual at all, and it suggested that many heterogeneous catalysts possessing properties similar to or different from those four catalysts might also be catalytically active in faciliating simple organic reactions like the racemization of binaphthyl. As far as the mechanistic process is concerned, the radical anion intermediate is the favorite one. All present and previous kinetic studies do not exclude this possiblity.

In particlular, observed first order rate constants increase with the concentration of the catalyst TiO_2, decrease with binaphthyl concentration, and are sensitive to small amounts of polynuclear aromatic compouds (poison increases in the order of benzene, naphthalene, anthrance, and pyrene). Also, it appears that the finer anatase particles catalyze the racemization more efficiently. Meanwhile, it is unfortunate that more precise experimental method has not been found to determine the nature of the potential titanium dioxide photocatalytic racemization.

6. EXPERIMENTAL

6.1 GENERAL

Melting points were determined with a Thomas Unimelt Capillary Melting Point Apparatus using open tube capillary and are corrected. Gas-liquid Chromotagraph (glc) was performed using a Hewlett Packard 5830A Gas Chromotagraphy equipped with a flame ionization detector and using nitrogen as carrier gas with a 6' by 0.125" stainless steel column packed with 3% OV-17 on Chromosorb WAW-DMSC, 80/100 mesh.

Optical rotation was determined using a Perkin Elmer 241 MC polarimeter with a 1dc or 1cm quartz-faced jacketed cell. Specific rotation ([α]) was calculated using the equation: [α]=observed rotation/[(path length in dm) times (concentration in g per ml)].

Solvents for kinetic and adsorption studies were spectrograde with the exception of ethanol and acetone. Ethanol "100%" was used as received. Two methods were adopted for purifying the technical grade acetone. The first one was that, acetone was treated with anhydrous magnesium sulfate, followed by distilling from anhydrous phosphorous pentoxide. Due to a reproducibility problem that occured in the kinetic studies at one time, acetone was then treated as following: acetone was first dried with type 3A Linde molecular sieve, and succesive small portions of $KMnO_4$ were added to acetone at reflux, until the violet colour persisted, followed by drying with Linda 3A sieve again and distilling. Gases (N_2, O_2, H_2, Ar) were reagent grade and dried through a column of calcium sulphate. Anthrance, pyrene and naphthalene were recrystallized before being used in the additive experiment.

6.2 SYNTHESIS OF RACEMIC 1,1'-BINAPHTHYL

The procedure used was analogous to that of Sakellerios and Kryrinis[70]. To a dry 3-necked flask fitted with overheaded stirrer and condenser was added 9.6g magnesium turnings, 72ml anhydrous ether, 56 ml ɑ-bromonaphthalene and a single crystal of iodine. The stirred mixture was heated to reflux to start the reaction, which proceeded without further heating for 20 min. The reaction mixture was then heated to reflux for 6 hours, with the addition of up to 200 ml dry benzene to thin the slurry when necessary. The reaction mixture was cooled to room temperature and added slowly to a stirred suspension of 54g anhydrous cupic chloride(prepared by drying the dihydrate salt for 4 h at 100 °C) in 200ml anhydrous ether. After the insuing vigorous reaction occurred the mixture was then stirred overnight at room temperature. The reaction mixture was quenched by slow addition of 100ml 10% hydrochloric acid and ice. The ether-benzene layer was extracted successively with several portions of 10% hydochloric acid, water, and dried over anhydrous magnesium sulfate. The solvents were removed in vacuo to afford an oil, which crystallized on cooling to 0°C. The brown material was transferred to a Bunchner funnel, washed with a small amount of cold petroleum ether (30-60°C), and recrystallized once from petroleum (65-110°C). The crude 1,1'-binaphthyl (20.9g) was then recrystallized from acetone three times to yield 10.0g of white crystals. mp: 143.5-144.5°C. mp in literature: 144-145°C.

6.3 PREPARATION OF OPTICALLY ACTIVE 1,1'-BINAPHTHYL

The procedure used was similar to that of Pincock and Wilson[71]. A solution of 0.133g of active 1,1'-binaphthyl in 400ml acetone (freshly distilled from potassium permagnate) was filtered into a 1000ml round

bottom flask. The solution was then cooled in a dry ice acetone bath (-78°C) for 10 min with swirling, during which time crystallization began. Without completing the crystallization, the flask was removed and immediately placed on a rotary evaporator (Buchi Rotovapor R). The flask was rotated in air while the full vacuum of a water aspirator was being established (5 min), it was then lowered into the water bath, maintained between 20°C and 25°C. As the flask warmed, some (but not all) of the crystals dissolved, then reprecipiated with the loss of solvent. The evaporation was taken to dryness, and any residual acetone was removed on the high vacuum pump. The material, which was 100% recovered, resolved to $[\alpha] = -174°$ (at 589nm, $\underline{c}$ 3.7mg/ml acetone) on heating at temperature 135°C.

6.4 KINETICS OF UNCATALYZED AND TITANIUM DIOXIDE CATALYZED REACTIONS

Oxide semiconductor (0.25g) was placed in a 100ml R. B. flask fitted with a magnetic stirrer and 25.0ml of dry acetone was added. After 24 hr intensive stirring, a highly divided titanium dioxide acetone solution was formed. Then the flask was fitted with a underwater magnetic stirrer and was immersed into a 10.0°C water bath. A sample of optically active binaphthyl (0.00435g) was next added into the solution, and after about 5 min (for completely dissolving the substrate and equilibrating the temperature of the solution), the kinetic run was started.

A sample (app. 2ml each time) was extracted from the solution at various reaction times by using a Pasteur pipette. This was filtered through about 0.7g Celite 530A into a one dc long polarimeter cell. The reading was measured at the Mercury line at 456nm. The cell was next placed into

the polarimeter and the reading was taken with <u>integration sec</u> set at 5 sec. The cell was then rinsed with acetone and shaken three times followed by drying with a stream of dry air.

6.5 <u>PROCEDURE FOR ATTEMPTED TITANIUM DIOXIDE PHOTOCATALYTIC REACTIONS</u>

Oxide semiconductor (0.025g) was placed in a 100ml R.B. flask fitted with a magnetic stirrer and 25.0ml of dry acteone was added. After 24 hr intensive stirring, a highly divided titanium dioxide acetone solution was formed. Then the flask fitted with a under-water magnetic stirrer was immersed into a 10.0°C water bath. A sample of optically active binaphthyl (0.00435g) was next added into the solution, and after about 5 minutes (for equilibrating the temperature of the solution), the kinetic run was started.

A solution (app. 5ml) was extracted from the above solution by using a Pasteur pipette. Two samples (app. 2.5ml each) were obtained from this solution. One was immediately measured of the optical rotation, and the other one was placed into a quartz tube, which was fitted with a magnetic stirrer and immersed in a 10°C bath beside a high-pressure mercury lamp (450 watts). After $\underline{t}$ time, the optical rotation of this sample was measured and then compared to the initial optical rotation of the identical solution. Repeating the above procedure by only changing the reaction time $(\underline{t})$ made up the kinetic data.

If a solution was needed to be saturated with one of three gasses (O_2, N_2 or He), a very small stream of gas, previously passed through a dehumidified apparatus, was bubbled through the solution for 30 minutes before the solution was divided into two parts.

6.6 PRODUCT ANALYSIS AND ADSORPTION EXPERIMENTS USING GLC

The conditions used were as follows: the gas chromatography runs started at a temperature of $170^{\circ}C$ and this increased up to $250^{\circ}C$ at a rising rate of $20^{\circ}C/min$ and completed within 20 minutes. Binaphthyl appeared at the retention time of 12.29 minutes. In all experiments done, only the binaphthyl signal and solvent signal (retention time $= 0.30$ min) were present. This indicated that there was no side reaction such as a reduction reaction occured during the catalytic racemization.

In order to know exactly what minimal concentration of binaphthyl the glc was able to detect, a solution of binaphthyl (6.82×10^{-4}mole/l, the usual concentration in the kinetic studies) was compared to a series of dilute binaphthyl solutions made up by diluting the initial solution (10.00 ml) with $\underline{a}$ ml acetone. (6.82×10^{-4}mole/l$\times$[10.00ml/(10.00ml $+$ $\underline{a}$ ml)]. It was then found that even $\underline{a}$ was down to 0.50 ml, the glc still could tell the difference of above two samples tested. In other words, the glc could identify 0.33×10^{-4} mole/l binaphthyl concentration difference.

6.7 PREPARATION OF TITANIUM DIOXIDE FROM TITANIUM TETRACHLORIDE

Hydrochloric acid (1.0M, 50 ml) was charged into a two-necked flask fitted with a condenser, a hotplate-magnetic stirrer combination and a pressure equalizing funnel. After the stirring was started, 50 ml titanium tetrachloride was added dropwise to the flask through the funnel over a period of 25 minutes, and was then heated to reflux for 2 h. Centrifuging, followed by washing the precipitate with deionized water, was repeated three times, in which the liquid was then removed with a Pasteur pipette. The precipitate was ground in a mortor and pestle into a fine powder before heating again at $700^{\circ}C$ in a furance for 12 h. The final product was

a white powder.

6.8 REDUCTION OF TITANIUM DIOXIDE

Aldrich titanium dioxide 0.80g was placed in the hydrogenation apparatus. A slow stream of hydrogen after bubbled through the concentrated H_2SO_4 solution and calcium chloride was passed over the titanium dioxide powder during the reduction process. The procedure was operated at $380^\circ C$ for times of 1 hr to 18 hr. Reduced titanium dioxide appeared greyer as the duration of the treatment increased.

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