APPROACHES TO POLYMERIC MODIFIERS OF THE LITHIUM ANODE

PhD THESIS BY IAN R. POPE

FEBRUARY 1990

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APPROACHES TO POLYMERIC MODIFIERS OF THE LITHIUM ANODE

Abstract

It is proposed that polymers containing the biphenyl group could be used to improve the cyclability of lithium anodes. The biphenyl groups would react with lithium metal to form radical anions, to give the lithium salt of an (immobilised) polymeric anion on the electrode surface. It is believed that such a material would act as a solid electrolyte interphase between the lithium metal of an electrode and the electrolyte in a cell, diminishing the rate of electrolyte degradation and improving the morphology on plating the electrodes (recharging of a secondary cell). Routes to some monomers which would generate such polymers have been examined, though with little success. The difficulties encountered were those of preparing asymmetrically substituted biphenyl derivatives, which had no benzylic hydrogens and which contained the appropriate functionality to introduce a polymerisable group. Possible routes to circumvent these problems are proposed.

ACKNOWLEDGEMENTS

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ABBREVIATIONS

Ar	Arene or aryl group
B	Biphenyl or 4-biphenylyl
bp	Boiling point
d	Doublet or density
dd	Double doublet
d.quart	Double quartet
ESCA	Electron spectroscopy for chemical analysis
ESR	Electron spin resonance spectroscopy
HMPA	Hexamethylphosphoramide
IR	Infra-red spectroscopy
J	Coupling constant
LUMO	Lowest unoccupied molecular orbital
m	Mulitplet
M	Metal
MCPBA	meta-Chloroperbenzoic acid
mp	Melting point
MTHF	2-Methyltetrahydrofuran
N	Naphthalene or 2-naphthyl
NBS	N-Bromosuccinimide
NMR	Nuclear magnetic resonance
PEO	Poly(ethylene oxide)
PS	Polystyrene
PVB	Poly(4-vinylbiphenyl)
quart.	Quartet
R	Alkyl group
RAE	Royal Aircraft Establishment (Farnborough)
s	Singlet
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
Sol.	Solvent
t	Triplet
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMEDA	N,N,N',N'-Tetramethylethylenediamine
t.t.	Triple triplet

CHAPTER 1

INTRODUCTION

The aim of this project was to develop polymeric materials that could be used to modify lithium electrodes, with the view of diminishing or eliminating the interrelated problems of electrolyte degradation, dendrite formation and poor cyclability. Before the choice of polymer materials can be considered, the nature of the difficulties encountered in lithium cells must first be examined.

1.1 Lithium Battery Technology

It is clear that, whatever the application, the smaller and lighter a battery is for a given power output, the better it is, particularly with the advent of microelectronics. The best known battery systems use heavier metals such as iron and nickel. These metals have relatively large electrochemical equivalent weights and small electrode potentials. Consequently a great deal of effort has been expended in the development of new primary (non-rechargeable) and secondary (rechargeable) battery systems, which utilise lighter, more electropositive metals as anode materials. The obvious choice of anode material is lithium metal, which has a very low equivalent weight of 6.94g and a large electrode potential of -3.04V.

There are, unfortunately, considerable problems encountered when using lithium metal (or an alloy of lithium) as the anode for a cell, all of which stem from its very high reactivity. Some difficulties are practical. To handle lithium metal, a dry inert atmosphere is required. Lithium metal is sufficiently electropositive to react with nitrogen gas at room temperature (to form a surface layer of lithium nitride),[1] so an argon atmosphere must be employed. Such a dry environment is relatively easy to achieve in a research laboratory, but is a distinct problem in a commercial process. Dry atmospheric rooms have now been developed and are used for the mass production of lithium primary cells (by Crompton Vidor, for example)[2]. Other difficulties follow from the chemical reactivity of lithium, and are considered in detail below.

Lithium thermal batteries

Lithium metal reacts with any protic medium so any cell utilising a lithium anode, unlike earlier cells, requires not just a non-aqueous but a strictly anhydrous electrolyte system. One such electrolyte system is a molten salt, or eutectic mixture of salts. This is the type of medium used in the first commercially available lithium cells, the so-called 'thermal batteries'. These batteries usually consist of a stack of disc cells, separated by thermite heat sources. To operate, the thermite is ignited electrically and melts the electrolyte; the cell then discharges until the electrode materials are exhausted or the electrolyte cools and solidifies.

The most commonly used electrolyte is a binary eutectic of lithium and potassium chlorides with a melting point of 352°C. Although the high internal temperature (400-500°C or higher) obviously poses some problems, these are easily outweighed by the advantages. The molten salt electrolytes have high ionic conductivities, are chemically stable to a molten lithium anode - which allows high anodic current densities and discharge rates - and the cells have a very long shelf-life because the system is totally inactive at room temperature. Indeed, some thermal batteries manufactured in 1960 can be discharged now and show no deterioration in their performance. To date, thermal batteries have only found use in the defence industries, for example for onboard electrical power (actuators, fuse, guidance system) in air-to-air missiles[3].

Lithium primary batteries

There are alternatives to the molten salt electrolytes. Solutions of lithium salts in aprotic organic or inorganic solvents may be used in conjunction with lithium anodes. Currently, there are five main systems available on the consumer market which employ lithium anodes. Three of the systems have a solid cathode (oxidant), namely the lithium-polycarbonmonofluoride, lithium-manganese dioxide and the lithium-copper oxide systems. The other two systems use liquid oxidants - sulphur dioxide or thionyl chloride - and a carbon cathode at which reaction occurs. In the sulphur dioxide system an organic solvent is used, but in the other system the thionyl chloride itself acts as the solvent. In both these cases, the cathode is effectively in contact with the anode. These systems are practical only because a film is deposited on the surface of the lithium metal by reaction with the electrolyte medium. Because this film is electronically insulating (in both cases) it halts reaction and prevents internal shorting of the cell. The films are, however, conductive in lithium cations which allows the anode electrochemical reaction to proceed, once the cell electrodes are brought into electrical contact. The presence of the film causes a delay in the cell achieving its full voltage, once it is switched into a closed circuit[2].

Polymer based electrolytes

All of the electolyte systems considered above are liquid at their operating temperatures. Solid electrolytes may also be employed. Crystalline materials, such as lithium nitride and lithium iodide-alumina have been investigated[4]. Their crystallinity poses a serious disadvantage as good contact between the electode and electrolyte is hard to achieve and maintain. Their brittleness also poses a problem as fractures in the solid electrolyte would decrease the ionic conductivity. A far better choice of solid electrolyte would be a 'plastic' material. A 'plastic' electrolyte medium can be achieved by using a solid polymer solution of a lithium salt. The most studied of such systems consist of a high molecular weight poly(ethylene oxide) containing $LiClO_4$ $LiCF_3SO_3$, or $LiAsF_6$ salt.

A polymer based electrolyte has a number of advantages over liquid or other solid ion-conductive media, in terms of both chemical and mechanical properties. A polymer medium is not mobile on the macroscopic scale and so the problem of electrolyte migration - which can cause inhomogeneous conductivity and shorting - is avoided. It is not brittle and is consequently more robust than other solid electrolytes. As with liquid media, polymer is decomposed at a lithium anode to form a film. In a liquid medium, if this film is mechanically displaced, by shock, vibration or by chemically induced changes of the underlying metal surface, fresh metal will be exposed and will react with more electrolyte. Such corrosion greatly reduces the shelf life of a battery. With a polymeric electrolyte, the film can not be dislodged in the same manner, and so electrolyte degradation and anode corrosion are reduced[5]. The filming phenomena of lithium anodes have proved to be a major obstruction in the development of rechargeable lithium battery systems. This point is considered in detail below.

Lithium rechargeable batteries

The main advantages a rechargeable lithium battery would have over the systems which are already available are its considerably higher power and energy densities. Another important characteristic is that with a polymer based electrolyte, batteries could be manufactured in a greater variety of shapes, designed to suit the application. For example, a flat battery pack would be most convenient for a portable television with a flat screen[4].

The most significant prospective use will be as electric vehicle traction batteries. Currently only lead/acid and nickel/iron systems are practicable. Although some battery powered vehicles are already in use (mostly urban delivery vans) with these battery systems, their performance is not sufficiently high to be accepted by the general public. The problem is that these batteries are too big and too heavy for the energy they store; the fraction of the stored energy needed to propel the battery itself is just too great. A rechargeable lithium battery with its higher energy density and power density would improve the performance of an electric vehicle considerably, making them commercially viable[4]. A number of major research projects, for example the so-called Anglo-Danish battery project[4] and the Canadian-French ACEP (polymer electrolyte battery) project[6], have been initiated in the past decade with this very aim. Preliminary investigations have shown that desired energy and power densities can be achieved[6].

1.2 Lithium Secondary Cells

Over the past 20-25 years a great many systems have been examined for use as a viable secondary cell. A wide variety of solvents have been examined; esters, ethers, polar aprotic solvents and mixtures of these. Subsequent to Fenton, Parker and Wright's discovery[7] in 1973 that solid polymer solutions can have relatively high conductivities, polymer based electrolytes have been much studied this past decade. The range of electrolyte salts employed is much narrower, generally $LiClO_4$, $LiCF_3SO_3$ or $LiAsF_6$ are used. The counter electrodes are usually composites, the electroactive component being a (mixed) metal chalcogenide. The best results have been obtained for TiS_2 and V_8O_{13} intercalation cathodes. In these materials, the transition metal cations are reduced with the simultaneous insertion of lithium cations into the chalcogenide lattice. In the anodes a wide range of metals have been used as substrate/current collector to the lithium. This work is concerned with the chemical processes occurring at the lithium anode.

Basic terminology

An electrochemical cell will usually have three electrodes; a working electrode (in this case lithium) - the one under study, a counter electrode to carry the current, and a reference electrode. If this reference electrode is not a lithium electrode, the working electrode may well remain negative of the reference under both cathodic and anodic polarization. This point needs clarification.

In an electrochemical process, the anode is the electrode at which an oxidation reaction occurs. Under anodic polarization, electrons are withdrawn from the electrode; that is, conventional current flows into the electrode. Conversely, the cathode is the electrode at which a reduction occurs, and electrons flow into the electrode on cathodic polarization.

The lithium electrode

The electrochemical behaviour of a lithium anode in a rechargeable cell is usually modelled by plating and stripping lithium metal on some substrate. The working electrode is usually cycled under conditions of constant current, the voltage monitored as a function of time. Typically, an anodic current is passed for a given time to plate lithium, and the potential is reversed to strip the metal up to a set potential limit (to prevent dissolution of the substrate). The cycle is then repeated until the electrode fails.

In a secondary cell the situation is more complex. Under a constant load, the voltage and hence current produced by the cell will diminish as the cell discharges. During the charging cycle, the current will diminish as the cell charges, and the applied potential may also vary as the cell's impedance increases during charging.

The plating efficiency may be determined by chemical analysis of a freshly plated deposit. It is usually close to 100%. The stripping efficiency is the ratio of charge passed during stripping to that passed during the plating half-cycle. The stripping efficiency is usually poor. It is the poor stripping efficiency that is the main obstacle to the development of lithium secondary cells.

1.3 The SEI Model

The electrochemical behaviour of the lithium electrode is probably best described by Peled's "Solid Electrolyte Interphase" (SEI) model[8]. When a lithium electrode is first immersed in the electrolyte of a cell, there is an immediate reaction at the surface of the lithium which forms a film over the surface of the lithium, where it contacts the electrolyte. When initially formed, it is believed to be of about 2.0 to 2.5 nm in depth. This film is composed of insolable or poorly soluble material formed by the reduction of some component(s) of the electrolyte, and it is a solid electrolyte - conductive in lithium cations - forming an interphase between the bulk metal of the electrode proper and the electrolyte. Clearly the nature of this film has a profound influence on the electrochemical behaviour of the electrode, as it affects both the deposition and dissolution processes at the electrode.

The interphase

The nature and rate of the reaction between the lithium and an electrolyte depends not only on the salt and solvent employed, but on their purity.

In a surface study of lithium electrodes[9], ESCA analysis of the surface after cycling in a $LiAsF_6$-2-methyltetrahydrofuran (MTHF) electrolyte showed that the surface layer formed contained not only arsenic and fluorine (from the salt), but relatively large amounts of magnesium and silicon. These latter were believed to be trace impurities in the salt. Other work, where the reactive materials water[10-12], sulphur dioxide and nitromethane[11,12], or gases such as oxygen and nitrogen[13] were added to the electrolyte, showed that such additives may have a dramatic effect on the cycling efficiency. The commonly used solvents propylene carbonate, THF and MTHF contain a number of contaminants (apart from moisture) which are exceedingly hard to remove (such as alcohols)[9,14]. In the case of MTHF, one of the contaminants - 2-methylfuran - has been shown to have a beneficial effect when present in MTHF based electrolytes at low concentrations[15]. The much used $LiAsF_6$ is known to react with lithium metal in both THF and MTHF to form a brown film[15-17], which consists of lithium, arsenic, fluorine and oxygen (perhaps as mixed oxyfluorides). This brown material degrades to lithium fluoride, with sublimation of arsenic oxide, on heating to about 300°C. It has been demonstrated by Eisch that THF is reduced by lithium[18], and the products of this reaction were shown to be present in THF based electrolytes degraded over lithium metal.

Deposition and dissolution

The deposition and dissolution processes depend on the migration of lithium cations through the interphase. When a lithium electrode is subject to cathodic polarization (negative of the equilibrium potential), metal cations transfer from the solvent into the interphase, migrate through the interphase, and then deposit on the metal surface. Under anodic polarization, the reverse process occurs. The rate of deposition/dissolution is limited by the rate of ion transfer at the two faces of the interphase and by the ion mobility within it.

The actual plating and stripping processes are not as straightforward as the ideal situation described above. The SEI is not uniform, but a polycrystalline composite. Lithium ion conductivity will vary with the orientation of the crystallites, and will differ from amorphous to crystalline regions, especially at grain boundaries.

Transport of lithium through the SEI may cause some breakdown of the interphase and shorting may occur, which phenomenon is discussed below. Examination by SEM and ESCA techniques[9] of the electrode surface has shown that after a stripping half cycle, pits are formed on the electrode surface, and that electrolyte degradation is centred around these pits. However these pits are not formed after a plating half cycle, and electrolyte degradation is centred along grain boundaries. This implies that there are pores or channels of relatively high conductivity present in the film, and such inhomogeneity is likely to aggravate the problem of dendrite formation - which is favoured by high local current densities. Crystallisation of amorphous regions, or transfer of anions to or from the SEI will also have an effect.

Shorting

A major problem caused by the SEI is that lithium cations can be reduced to the metal by electron tunnelling through part of the SEI, or by electrical heating causing an electronic breakdown and a semi-conductive region, leading to an electrical short. This causes lithium metal to be deposited within the bulk of the interphase where it will become electrically isolated from the bulk metal. This phenomenon might be induced by high current densities and subsequent heating at the more conductive spots on the interphase. Once a small nodule of lithium metal is formed in this way, lithium will tend to deposit there faster than at the bulk electrode nearby, due to the higher current density and its being physically closer to the electrolyte. This will increase dendrite formation. Freshly deposited metal is very reactive, so such nodules will corrode rapidly, increasing the distance between them and the actual metal surface of the electrode. This increase in separation will rapidly become sufficient to prevent the metal discharging on anodic polarization by a like mechanism, leaving the lithium nodule/dendrite isolated in the SEI. It has been observed that loose, granular or dendritic deposits are associated with low cycling efficiency, whereas compact uniform deposits are associated with high cycling efficiency[14,17,19].

Corrosion

It might be anticipated that the presence of an SEI between the lithium and the electrolyte would passivate the electrode and prevent corrosion of the lithium - that is, self-discharge - as occurs in some primary battery systems[2]. In fact the lithium metal continues to react with the electrolyte (if somewhat slowly) with a steady decrease in the amount of electrochemically available lithium at the electrode.[10-12, 14-19]

According to Peled's model[8], the SEI is in fact expected to grow in thickness, as electrons migrate through it. This electron transfer might be caused by impurities within the SEI, but there will always be a slow diffusion of electrons through the SEI via vacant anion sites in the crystallites with concomitant diffusion of lithium cations. (A net doping of the film with lithium metal). Reduction of the electrolyte will then occur with the deposition of more material at the interphase electrolyte boundary. The only way to eliminate such residual capacity loss would be to introduce an SEI material in which the reduction potential of electrons at the interface with the electrolyte will not become sufficiently large to degrade the electrolyte.

As previously mentioned, the results of an SEM study[9] implied the presence of conductive channels in the SEI. This raises an important question - is the surface film of a lithium electrode compact or porous? Thevenin and Muller investigated the use of lithium nitride as an SEI material[1]. They prepared their Li/Li_3N electrodes by exposing a freshly cut lithium surface to an atmosphere of nitrogen prior to immersing the electrode in a cell. Their impedance and mercury porosimetry studies indicated that the film formed was porous - attributed to a decrease in molar volume on reaction of lithium to form the nitride.

This point is worth closer consideration. If a material in an electrolyte reacts at a lithium electrode, there will almost always be a change in molar volume. If the molar volume decreases, contraction will lead to a porous film, if it increases, expansion will cause the film to separate from the electrode surface. In neither case will a uniform, compact SEI form.

1.4 Electrolyte Degradation

As Selim and Bro[10] pointed out, any polar solvent is intrinsically reactive towards lithium because of the electronegative heteroatom(s) responsible for the polarity of the molecule. Of the many solvents which have been employed in the electrolytes of experimental cells, the ethers are the least reactive and consequently the most important.

The first point to consider is which species at the electrode surface actually degrade the ether. The lithium metal itself is initially responsible for electrolyte degradation, but after the electrode is first filmed, not only the metal but reduction products may be responsible for decomposing the solvent. Heteroatom centred anions, such as alkoxides, are capable of attacking the electrolyte salt[16] but are not sufficiently potent to decompose ethers - even with the co-operative interactions of a (free) lithium cation. However reactive carbanionic species may be formed which can attack ethers, which reaction might be facilitated by the presence of lithium cations (from the electrolyte). The lithium cation is very small, with an ionic radius of approximately 70pm[20]. The electric field at the surface of this cation is thus of the order of $3x10^{11}$ Vm^{-1}, and 100pm from the ion the field is about $5x10^{10}$ Vm^{-1}. This exceedingly high electric field about the lithium ion makes it a very strong Lewis acid. The presence of a lithium cation solvated by the oxygen of an ether will perturb the electronic energy levels, and may render it more susceptible to reduction or attack by an anion.

The cleavage of simple ethers by alkali metals and organo-alkali metal compounds has been recently reviewed, quite comprehensively, by Maercker[21], but the reactivity of polyethers, especially poly(ethylene oxide) (PEO) has not received such attention. Polymer based electrolytes react at a lithium electrode to form a film (SEI) as do liquid electrolytes[22], but no studies of the stability to lithium metal of the polyethers themselves appear to be recorded in the literature. The major difficulty when examining polyethers is that they are far harder to purify than other solvents (except for the lower molecular weight oligomers). They can not be distilled, so contaminants such as residual polymerisation catalysts, are far harder to remove, and there may also be some uncertainty as to the nature of the end groups, which might be reactive to lithium metal.

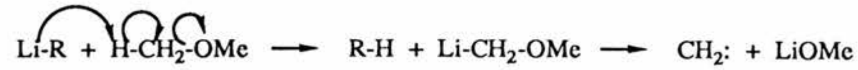
Cleavage of simple ethers

By the use of selectively deuterated diethyl ethers, Maercker[21] has demonstrated that alkyllithium compounds cleave the (undeuterated) ether predominantly by β-elimination, essentially an E2 mechanism (scheme 1.1). Most other alkyl ethyl ethers react similarly, a notable exception being ethyl methyl ether which undergoes a great deal of α-elimination.

Scheme 1.1:

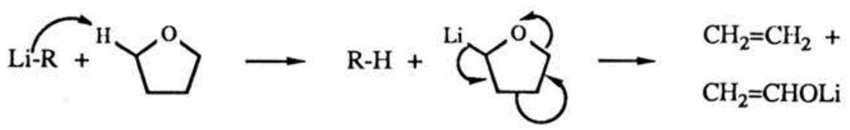
Dimethyl ether can only be cleaved by α-elimination: the ether is first metalated, and then methoxide is formed by the loss of carbene which will react further, for example by insertion into unreacted alkyllithium reagent (scheme 1.2). Most alkyl methyl ethers undergo considerable α-elimination.

Scheme 1.2:



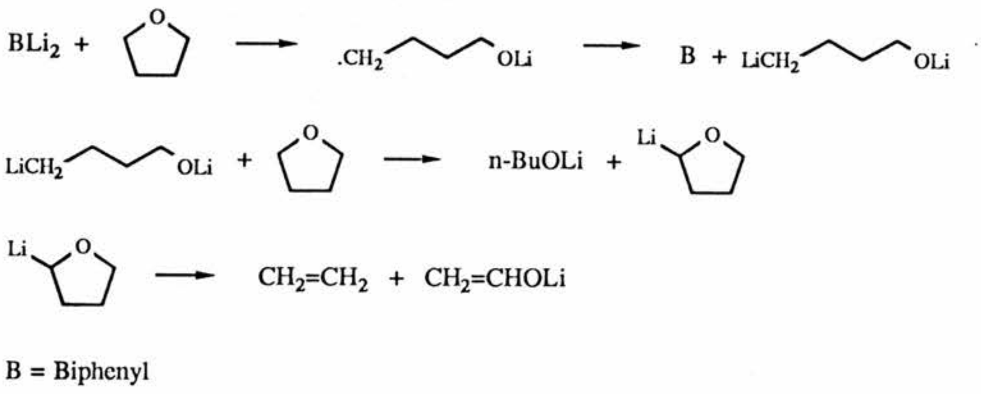
The cyclic ethers THF and MTHF, although similar in structure, react quite differently with alkyllithium compounds. The initial step in the reaction of THF is α-metalation. The metalated ether undergoes a cycloreversion to give ethylene and the lithium enolate of acetaldehyde (scheme 1.3). However MTHF undergoes a β-elimination, the carbanion abstracting a proton from the methyl group.

Scheme 1.3:



Eisch[18] found that the dilithium biphenyl adduct, which is formed by the transfer of two electrons to the LUMO (π-antibonding orbital) of the arene, will cleave THF when heated to reflux to yield 1-butanol. This presumably occurs by electron transfer into the LUMO of the ether (essentially a C-O σ-antibonding orbital) with cleavage of the C-O bond, leading to a carbon and oxygen centred dianion (scheme 1.4). This is a butyllithium derivative which will attack another THF molecule, clearing it as above (scheme 1.3), to give ethylene, lithium acetaldehyde enolate and lithium 1-butoxide. Koch[16] found 1-butanol and acetaldehyde based material present on chemical analysis of a $LiAsF_6$/THF electrolyte degraded in a lithium cell. Presumably lithium metal is reducing THF in a like manner to the biphenyl dianion.

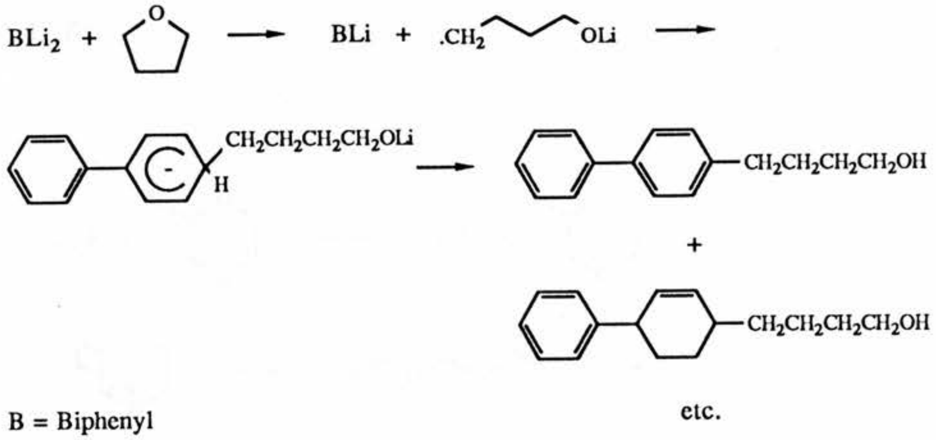
Scheme 1.4:



B = Biphenyl

Fujita, Suga and Watanabe[23], found the reaction of dilithium biphenyl to yield biphenylylbutanol derivatives, products apparently of nucleophilic cleavage. The actual process most likely results from a one-electron reduction of THF to give a C-centred radical O-centred anion and biphenyl radical anion, which could then couple (scheme 1.5). Transfer of the second electron would ultimately lead to the formation of 1-butanol which Eisch[18] notes.

Scheme 1.5.

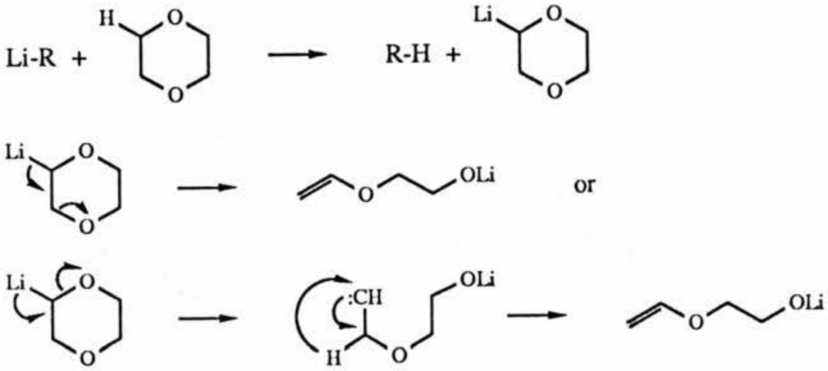


Koch, in later work with Goldman, Mank and Young[17], found that MTHF has far greater stability towards lithium than THF. Similarly $LiAsF_6$/MTHF electrolytes were found to be more stable than $LiAsF_6$/THF electrolytes. It was proposed that the methyl group raises the energy of the LUMO by inductive donation of electron density, increasing the activation energy for electron transfer and thus retarding the rate of cleavage.

Diethyl ether, and to a lesser extent THF, may be considered to model PEO, but a better model for the polymer is 1,4-dioxane. Piotrovskiy and Stotskaya[24] in a study of the reaction of butyllithium with ethers found

1,4-dioxane to undergo a ring-clearage reaction to yield 2-vinyloxyethoxide, which reacted further under the conditions they employed (scheme 1.6). The mechanism may be a β-elimination, or possibly an α-elimination followed by a hydride shift, given the geometric constraints of the ring system.

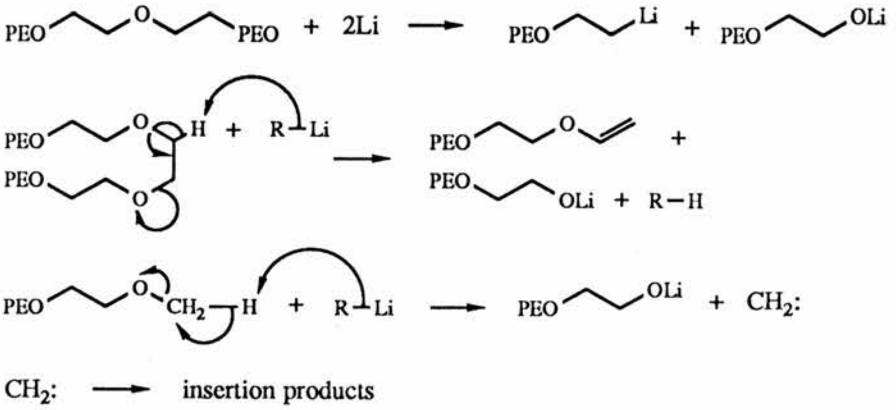
Scheme 1.6.



Polyethers

In light of the above data, it seems reasonable to propose that polymer degradation occurs by the following mechanism (scheme 1.7). The reductive cleavage of the carbon-oxygen bond of saturated ethers has only been indicated in the case of THF[16,18] and implied by analogy for MTHF[17]. This reaction might be very sensitive to conformation, which is largely fixed in the five-membered ring of the tetrahydrofurans. Acyclic ethers are unable to attain the same conformation because of steric crowding around the β-carbons. If such a reduction does not occur with a polyether, the polymer ought to be stable to lithium in the absence of organic contaminants which yield carbanions on reduction by the metal. If this cleavage does occur, or contaminants which yield carbonions are present, the polyether is expected to cleave by β-elimination along the main chain, and by α-elimination of terminal methoxy groups if they are present. This will cause a decrease in the average molecular weight and viscosity of a polymer solution, with the formation of terminal vinyl ether and alkoxide groups.

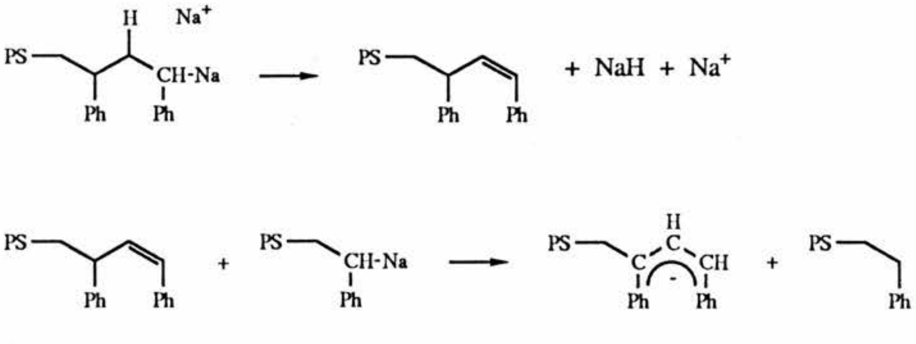
Scheme 1.7



PEO = Poly(ethylene oxide) segment

A slight digression is needed here. Spach, Levy and Szwarc[25] found that poly(styryl)sodium - the "living" polymer - undergoes slow elimination of sodium hydride (scheme 1.8), which requires the presence of a second sodium cation by the hydrogen that is lost. The rate of this reaction was found to be strongly dependent on the solvent, increasing in the order benzene < THF < 1,2-dimethoxyethane. This is expected as the rate is limited by the degree of dissociation of ion pairs to free ions - which is a solution phenomenon - to provide the (free) second sodium cation required for the elimination[26].

Scheme 1.8:

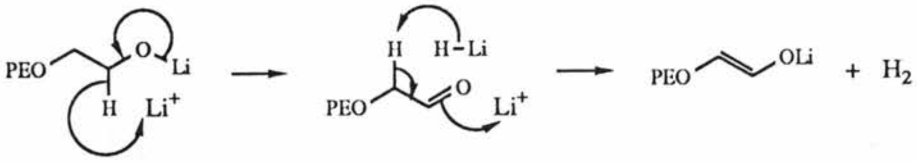


PS = Polystyrene segment

The product of elimination, a poly(styrene) with a double bond in the main chain reacts with remaining poly(styryl)sodium to give a more stable 1,3-diphenylallyl anion derivative. A corresponding transformation of poly(4-vinylbiphenyl)sodium has been noted by Al-Jarrah[27]. Brauman and Blair[28] in a study of gas phase acidities found that the benzyl anion was a weaker base than methoxide, but stronger than ethoxide. The reason for this somewhat surprising result is the great sensitivity of basicity to solvation. In the gas phase, with no solvation the stability of anions is determined by the degree of charge dispersion, which is related to their polarizability[29]. In solution this effect is swamped by solvation, the basicity being fixed by steric and inductive factors.

In the aprotic medium of polyether based electrolyte, the polymer alkoxide will be of comparable basicity to the poly(styryl) (benzylic) anion. Hence, a parallel reaction to that above may occur where lithium hydride is eliminated, forming an aldehyde end group (scheme 1.9). In this case, the hydride which is formed could react further with the aldehyde to generate an enolate. This would produce hydrogen gas which might react at the anode (where the degradation is occurring) to produce lithium hydride in the SEI, but could well lead to pressurisation in a sealed cell.

Scheme 1.9:



$H_2 + 2Li_{(m)} \longrightarrow 2LiH_{(SEI)}$

PEO = Poly(ethylene oxide) segment

CHAPTER 2

THE MODIFIED LITHIUM ELECTRODE

The characteristics of a lithium secondary cell are largely determined by the nature of the SEI that covers the electrode. As a uniform, cohesive interphase is unlikely to be formed on the direct reaction of lithium with some reactive substance, the lithium anode must be modified by coating it in a suitable ionically conductive material prior to incorporation in a cell.

The aim of this research project has been to prepare some examples of a quite narrowly defined class of polymers, which may be of use in modifying the lithium electrode. To improve the performance of the electrode, these materials must satisfy a number of demands which are outlined below.

2.1 Film Properties

Secondary lithium cells (with a polymer electrolyte) are of laminar internal construction, a sandwich of a 'plastic' electrolyte between the two electrodes. Such a design recommends itself to commercial production employing technology already developed for handling films. Consequently, it is desirable that the film modifying the electrode also be a 'plastic' material, that is that it too be a polymer based material. This means it must either be a polymer solution of a lithium salt, or consist of a polymeric anion with attendant lithium counterions, so that it has the ionic conductivity required of an SEI. The former option is excluded as it is just a polymer based electrolyte, which is exactly what the film is supposed to separate from the electrode surface, so the latter approach was adopted.

If the modifying film shields the electrode and is successful in suppressing electrolyte degradation, the major problem is then one of dendrites. Their formation appears to stem from the inhomogeneous nature of the SEI which is generated by reduction of the electrolyte. Non-uniformity in an SEI generates regions of locally high electric field which cause uneven metal deposition with the growth of dendrites. The electrical potential and surrounding field of a dendrite are higher than the neighbouring 'bulk' metal, favouring the continued development of a dendrite once formed. In the case of the modified electrode, the applied film should be quite uniform which ought to greatly diminish the problem, if not eliminate it. However, if the SEI were electronically as well as ionically conducting, any dendrite would be maintained at virtually the same potential as the rest of the metal, and the rate of its growth would be correspondingly reduced. Unfortunately, if the SEI were an electronic conductor it could easily accelerate self-discharge by carrying electrons to, and reducing the electrolyte. This is by no means certain, as reduction by electron transfer from a conductive film might have a prohibitively high activation energy, or the film's reduction potential, being lower than lithium metal, might well be insufficient to degrade the electrolyte.

Whatever the electronic properties of the film on a modified electrode, it must be a good ionic conductor or it will severely limit the charge and discharge rates of a cell. For a polymeric material with anionic side groups (lithium counterion), the side group must be carefully selected. It must form a stable lithium salt, but not bind too strongly with the cation or there will be too few free cations to carry a suitable current density. It must also be stable to the presence of lithium metal. The polymer must also be miscible with PEO (the electrolyte solvent) to avoid phase separation which would otherwise occur and impose a barrier to lithium transport.

It is also desirable that the modifying polymer film be amorphous, that is, be above its glass transition temperature under the usual operating conditions of the cell. This is not solely because crystallinity introduces anisotropy and decreases conductivity (as it does in the electrolyte), but also because an acrystalline material will maintain a better physical contact with the electrode - particularly as the metal face retreats and advances on stripping and plating respectively in the normal operation of the cell.

2.2 Modifactory Polymers

Miscibility with PEO is achieved by employing polymers with a poly ether main-chain and/or oligoether side-chains. Acrystallinity at ambient temperatures can be engineered by copolymerisation, or blending. Long, flexible side chains will also favour a low glass transition temperature. The problem is the selection of the anionic side-group. It was decided to utilise an aromatic hydrocarbon in the side chain, which would react with the lithium of the electrode to generate an anion. This approach was prompted by a paper by Freeman and Hutchison[30] concerning lithium-hydrocarbon adducts which is discussed below.

Aromatic hydrocarbon anions

Many aromatic hydrocarbons will react with alkali metals to form ionic compounds. A number of reviews have appeared in the literature concerning the physical properties of such species, but it was not until Holy's review[31] in 1974 that the chemistry of these adducts was considered in detail.

This phenomenon was first noted by Berthelot[32] in 1867 who obtained black potassium naphthalene by fusing the metal with the hydrocarbon. However it was not until 1939 than an ionic structure was proposed, by Huckel and Bretschneider[33]. The adducts are formed by the direct transfer of an electron from a metal atom into the lowest unoccupied π-orbital of the arene, to form a paramagnetic radical anion (scheme 2.1). Under the right conditions a second reduction may occur, by more metal or by disproportionation, producing a diamagnetic dianion.

Scheme 2.1:

$$\mathrm{Ar} + \mathrm{M} \rightleftharpoons \mathrm{Ar}^{-\cdot},\mathrm{M}^{+}$$

$$\mathrm{Ar}^{-\cdot},\mathrm{M}^{+} + \mathrm{M} \rightleftharpoons \mathrm{Ar}^{-2},2\mathrm{M}^{+}$$

$$2\mathrm{Ar}^{-\cdot},\mathrm{M}^{+} \rightleftharpoons \mathrm{Ar}^{-2},2\mathrm{M}^{+} + \mathrm{Ar}$$

Ar = Arene M = Metal

The equilibria are all strongly dependent on solvation effects, which vary with the different metals. For example, although lithium and potassium will react with naphthalene in diethyl ether, sodium in that solvent is unreactive, but will react quantitatively in 1, 2-dimethoxy-ethane. In general radical anion formation is favoured by ether solvents which can co-ordinate well with a metal cation. Reaction is essentially quantitative when the lower oligo(ethylene glycol) ethers (low molecular weight PEO) are used as solvent. This is because these solvents can chelate the cation, giving a large heat of solvation without a prohibitively large decrease in entropy of the solvent [34].

The solution chemistry of these compounds is complicated by ion pairing. In ethereal solution, only the cations are strongly solvated, as the positive ends of the dipoles of the ether molecules are diffuse. Usually there are three thermodynamically differentiable species present in solution; contact ion pairs, solvent-separated ion pairs and free (solvated) ions [26] (scheme 2.2). In contact pairs the metal cation interacts directly with the π-system on one face of the aromatic hydrocarbon, while in solvent-separated pairs solvent molecules co-ordinating the cation are between it and the anion.

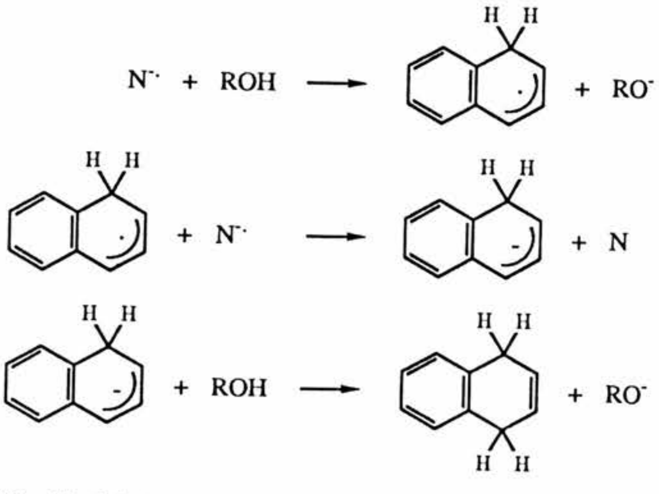
Scheme 2.2:

$$\underset{\text{contact pair}}{(Ar^{-\cdot}M^{+})sol_n} \rightleftharpoons \underset{\text{separated pair}}{(Ar^{-\cdot}[sol_nM]^{+})}$$

$$\underset{\text{separated pair}}{(Ar^{-\cdot}[sol_nM]^{+})} \rightleftharpoons \underset{\text{free ions}}{Ar^{-\cdot} + [sol_nM]^{+}}$$

These radical anions are very reactive as both reductants (by electron transfer) and strong bases. The most reactive anions, those of naphthalene and biphenyl, can abstract a proton from compounds with a pK_a of about 33 or less[31] (scheme 2.3). This process occurs during dissolving-metal reductions of aromatic compounds (Birch reduction).

Scheme 2.3:



N = Naphthalene

Electrons may be transfered from one species to another over quite large distances. In the case of radical anions, the transfer of electrons from an adduct is greatly affected by the degree of ion pairing or ion-association. If the anion is paired with a cation, the latter will introduce a strong potential gradient which will inhibit transfer except when the electron acceptor is in contact with the cation. In an ESR. study of electron transfer, Shimada and Szwarc[35] found that intramolecular exchange between naphthalene groups about 900 pm apart occurred at a frequency of about $9 \times 10^6 s^{-1}$ in the free anion (scheme 2.4).

Scheme 2.4:

N = 1-Naphthyl

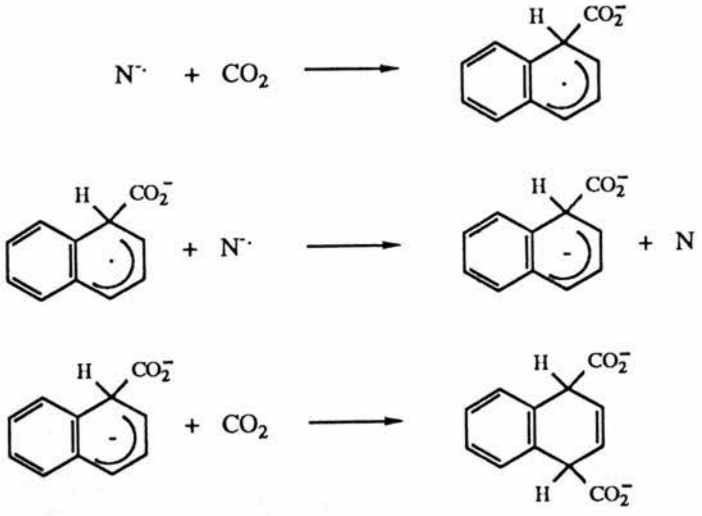
Closs et al[36] report electron transfer over even greater distances, also for the unassociated anion. Work by Shatenshtein and Petrov[34], as well as that by Szwarc[26] has shown that the oligo(ethylene glycol) dimethyl ethers are good solvents for inducing ion separation. Such solvents are, of course, just low molecular weight PEO, so ion separation of, and hence electron transfer from lithium arene adducts should be favoured in a polyether based polymer. This ion separation is essential if a polymer is to have a sufficiently high ionic conductivity to act as an SEI material.

As mentioned earlier, Eisch[18] reports the dianion of biphenyl, and Fujita, Suga and Watanabe[23] report the dianions of biphenyl and naphthalene, to attack THF. The conditions these workers employed (refluxing THF) are rather far removed from those within a lithium cell, but as arene radical anions may disproportionate in solution (scheme 2.1) to give the dianion (albeit in minute quantities), this could lead to electrolyte degradation.

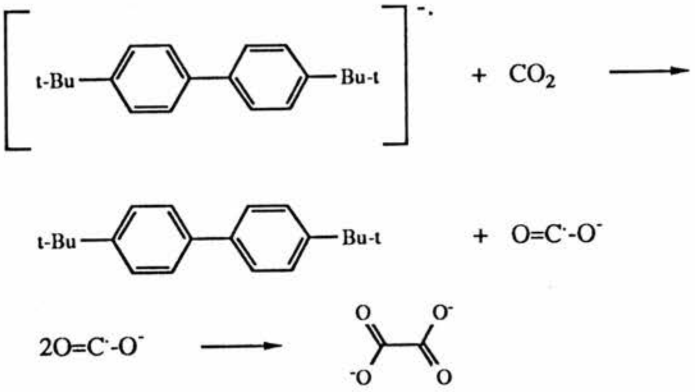
Biphenyl derivatives

In searching for a general method of preparing organolithium compounds in good yield, Freeman and Hutchinson[30] examined the use of radical anion solutions to metallate alkyl halides. They found that excellent yields of lithium alkyls could be obtained using the lithium adduct of 4,4'-di-t-butylbiphenyl as the metallating agent. In carbonation studies of the radical anions they discovered that unlike biphenyl and naphthalene which give recovered arene and dicarboxylic acids (scheme 2.5), the di-t-butylbiphenyl is recovered in 97% yield (pure) with no arene derived acids detected. In this latter case it seems likely that carbon dioxide is reduced to oxalate.

Scheme 2.5:



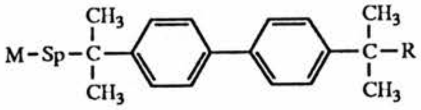
N = Naphthalene



The tertiary butyl groups are very bulky, and in this case they clearly prevent reactive intermediates - formed by electron transfer from the radical anion - from attacking the parent hydrocarbon. This is an important property because should a polymer with radical anion side-groups react with some contaminant in an electrolyte, it would be better if the arene group were not attacked in the process.

Aim

To reiterate, the aim of this project was to prepare polymers which could be used to modify the lithium anode by acting as an SEI material. The polymer structure desired is a polyether main chain and/or oligoether side chains with an electroactive side group which would determine the conductive properties of the material. In light of the above-mentioned work, it was decided that alkylated biphenyl groups would be suitable for this role, as they would react with lithium - once coated on an electrode - to generate an ionic adduct rendering the polymer conductive in lithium cations. In general terms, the target monomers can be formulated as

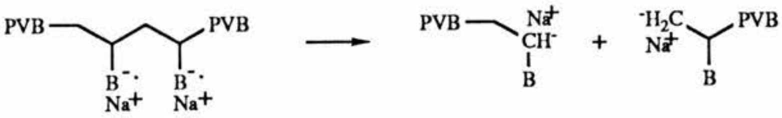


where M is the polymerisable group (an epoxide or vinyl group), Sp a spacer group (a methylene or oligoether chain), and R an alkyl or oligoether group.

2.3 Poly(4-vinylbiphenyl)

The only work recorded in the literature which is of any relevance here is that concerning the interaction of poly(4-vinylbiphenyl) (PVB) with sodium and potassium. Rembaum, Moacanin and Haack[37] report that PVB (and other polymers) will react with sodium in THF to give a poly(radical anion), but that the polymer is degraded on ageing, indicated by a steady decrease in the viscosity of the solution. The free electron spin concentration eventually drops to zero, but there is little decrease in the number of anionic species capable of initiating the polymerisation of styrene; that is, the majority of the radical anions are converted into localised carbanions. The polymer solution eventually shows the properties of a 'living' polymer solution. In a later paper, Stewart and Rembaum[38] report detecting 4-ethylbiphenyl as the radical anion by ESR among the degradation products of PVB treated with sodium or potassium in THF or 1,2-dimethoxyethane. However Marquez, Giulianelli and Eargle claim to have detected the radical anion of biphenyl itself as a reduction product of the polymer with potassium in 1,2-dimethoxyethane. All of these workers have assumed that the first step in the degradation is the direct cleavage of the polymer main chain to give benzylic and primary carbanions (scheme 2.6). Although the benzylic anion is relatively stable (compared to the radical anion) the primary carbanion is not. The charge localisation involved, the transfer of two electrons into a σ-antibonding orbital make this mechanism highly unlikely.

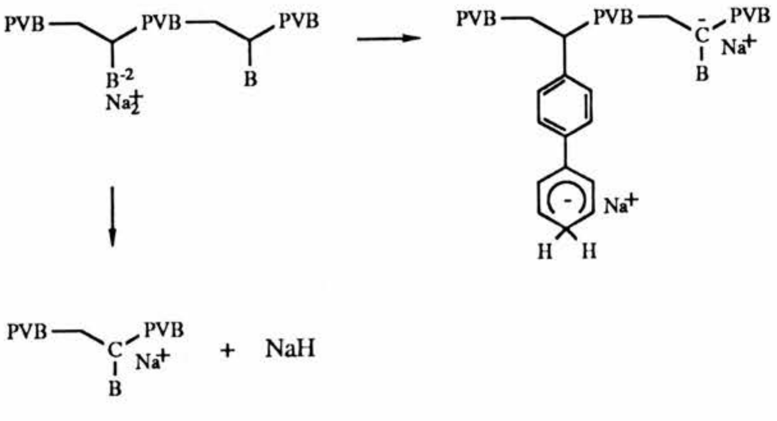
Scheme 2.6



B = 4-Biphenylyl PVB = Poly(4-vinylbiphenyl) segment

As occurs in solutions of sodium biphenyl, diamagnetic dianions will be present in the side chains of the reduced polymer to a slight degree. The dianion is a potent base and could abstract a benzylic proton from further along the macromolecule to give a benzylic anion (scheme 2.7). It might also eliminate sodium hydride directly, also to give a benzylic anion - in an analogous manner to a process which occurs in 'living' polystyrene and 'living' poly(4-vinylbiphenyl)[25,27].

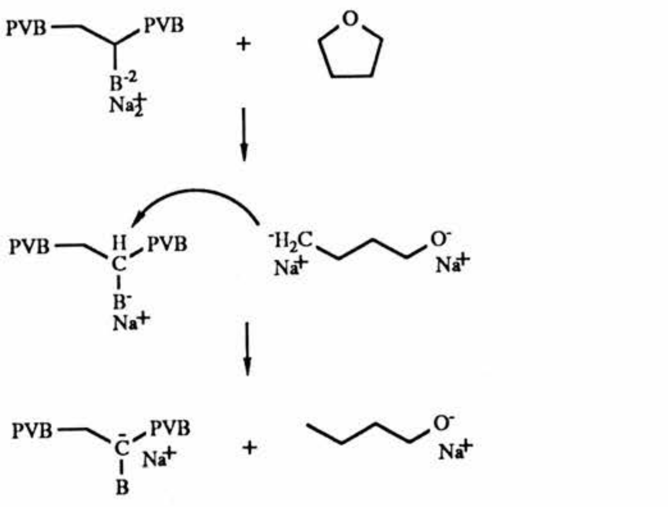
Scheme 2.7:



B = 4-Biphenylyl PVB = Poly(4-vinylbiphenyl) segment

A third possibility is that the solvent is reduced to a slight extent to give a carbanion which would be capable of deprotonating the polymer, again to give a benzylic anion (scheme 2.8). This would parallel ether reduction by lithium and its biphenyl adduct[16,18].

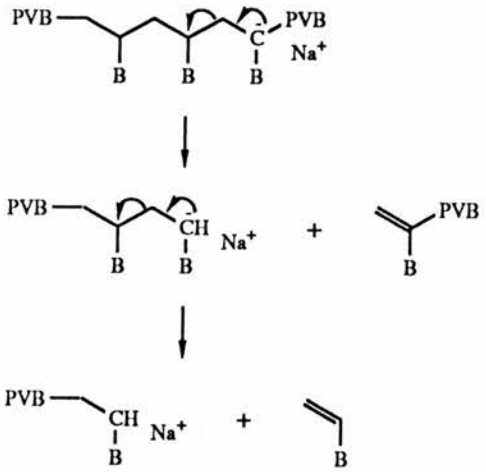
Scheme 2.8:



B = 4-Biphenylyl   PVB = Poly(4-vinylbiphenyl) segment

All of these conjectural processes lead to the formation of a benzylic polymer anion. This anion is in fact a living polymer which will depolymerise to some extent to produce a small amount of monomer (scheme 2.9) - anionic polymerisation being an equilibrium process.

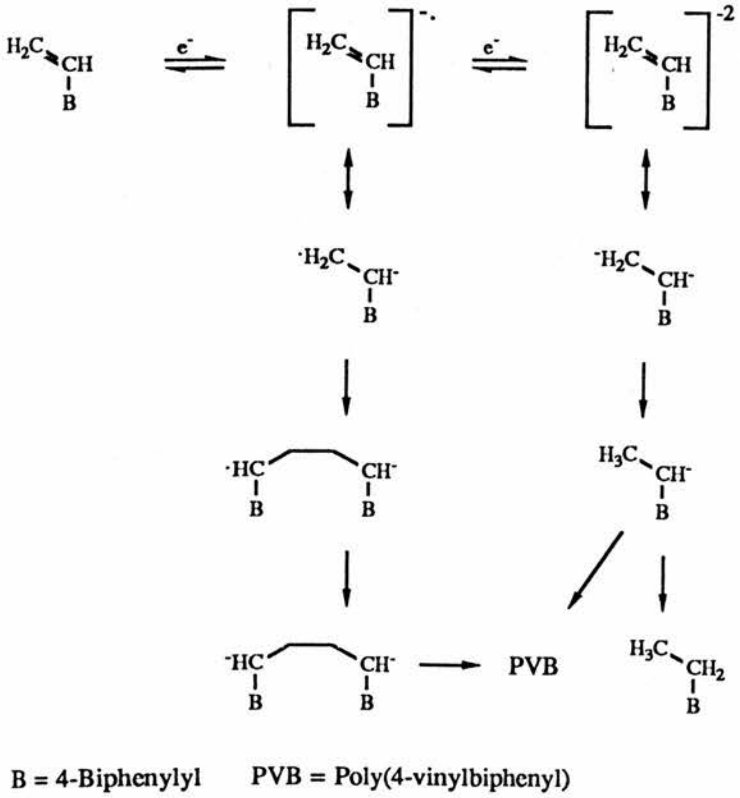
Scheme 2.9:



The free monomer which is produced will accept electrons from the remaining poly(radical anions) and start new polymer chains. Presumably the 4-vinylbiphenyl will polymerise through the dimer-dianion rather than the tetramer-dianion because of the strongly reducing nature of its environment (scheme 2.10), as does α-methylstyrene with an excess of sodium dispersion[40]. This redistribution of monomer increases the number of macromolecules present causing the decrease in the average degree of polymerisation and the viscosity. It is also possible, with the very low ratio of 4-vinylbiphenyl to 'free' electrons, that it will be reduced to the dianion.

This would be a very strong base which could deprotonate either solvent or polymer molecules to give a benzylic anion, and go on to form more PVB or 4-ethylbiphenyl as Stewart and Rembaum claim[38].

Scheme 2.10:



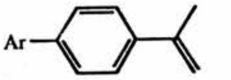
B = 4-Biphenylyl PVB = Poly(4-vinylbiphenyl)

Whatever the actual processes are, they will almost certainly be dependent on deprotonation at benzylic positions along the polymer chain. This can not occur in the compounds under consideration for the modified lithium anode because these polymers will have no benzylic hydrogens present anywhere along the molecule.

CHAPTER 3

STYRENE DERIVATIVES

Epoxides can generally be obtained from alkenes by direct oxidation, so it was decided to start by preparing some alkene monomers that would generate macromolecules in which the biphenyl sidegroup would be attached directly to the polymer main chain. These are styrene derivatives which may be formulated as 1 where Ar is a t-butylated phenyl group.



1

3.1 t-Butyl-α-methylvinylbiphenyl

The first target monomer was the unknown alkene 5 (scheme 3.1). The polymer that would be prepared from this alkene has a unit segment which may be represented by the hydrocarbon 9. This hydrocarbon was prepared by straight forward alkylation according to the method of Horne[41], and was used for preliminary stability studies. Solutions of the lithium adduct of 9 were prepared in the manner described by Freeman and Hutchinson[30], maintaining an argon atmosphere over the solution. These solutions were left standing over 2 to 3 days, during which the intense dark blue-green colour of the radical anion dissipates to leave a red residue in the base of the vessel. On work up of the solution, the only aromatic species that could be detected was recovered di-t-butylbiphenyl 9.

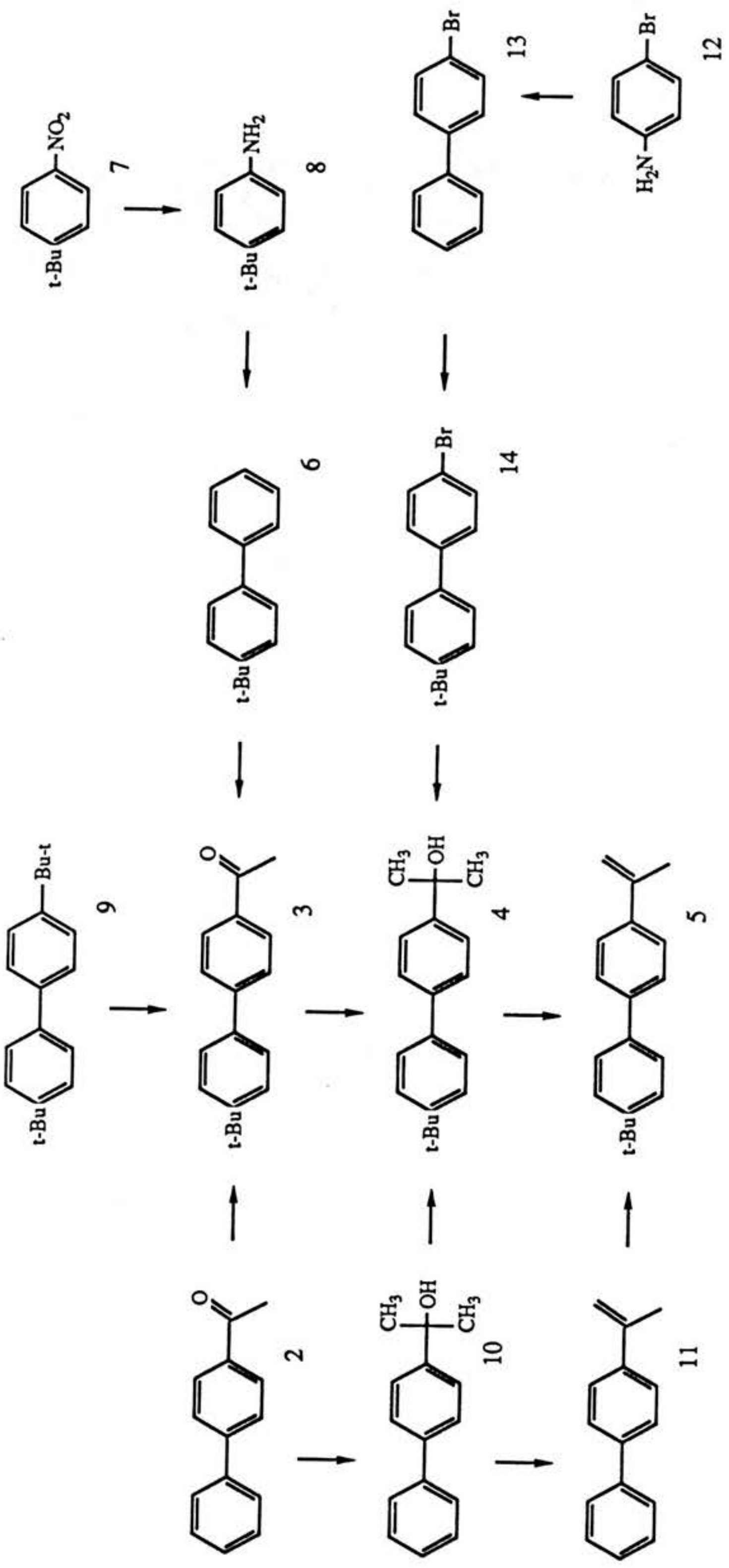
Route 1

The obvious route to the alkene 5 is from the ketone 3, by a Grignard reaction to give the carbinol 4 and then dehydration. The preparation of 3 was attempted by the direct alkylation of the ketone 2. As biphenyl undergoes substitution at the two para positions on diacetylation[42], alkylation of 2 ought to give the desired product in good yield. However, even using a large excess of t-butyl chloride with ferric chloride catalyst, only unreacted acetylbiphenyl 2 was obtained. It appears that a ketone-metal halide complex is formed very rapidly and precipitates from solution, preventing reaction of the ketone.

Route 2

The reverse order of substitution is the next obvious route to the intermediate 3. The method reported by Byron, Gray and Wilson[43] was examined. These workers prepared the hydrocarbon 6 by direct alkylation of biphenyl with one mole equivalent of t-butyl chloride in carbon disulphide, reporting a yield of 30%. Because of its toxic and inflammable nature,

Scheme 3.1



carbon disulphide was avoided and the reaction carried out in methylene chloride. This yielded mostly dialkylated material (9) and the desired hydrocarbon 6 could only be obtained impure, in a 3% yield. Curtis and Allred[44] have also carried out this alkylation, but employing a smaller quantity of t-butyl chloride in nitromethane and only obtained a 1.3% yield of pure material. The preparation of alkylbiphenyl 6 was therefore carried out by diazotisation of the aniline 8.

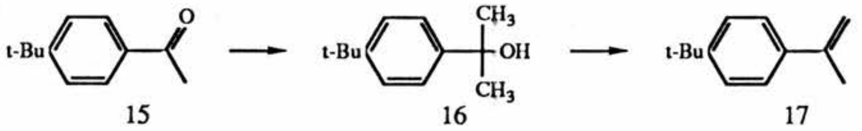
Nitration of t-butylbenzene using a mixed acid of a 1:1 mole ratio of nitric and sulphuric acids yields the nitro-compound 7 in 60% yield (isolated by column chromatography) and significant amounts of 2 dinitro-compounds. When the nitration is carried out with 70% nitric acid in acetic anhydride the desired material 7 is obtained in 84% yield after distillation. This substance gives an essentially quantitative yield of the required aniline 8 on catalytic hydrogenation if it is freshly distilled. On ageing, the nitro compound undergoes a slow degradation which causes a slight but noticeable darkening in colour. Such degraded material gives very poor yields of aniline on attempted hydrogenation - presumably the contaminants formed poison the palladium catalyst.

Diazotisation of the aniline was carried out homogeneously in benzene using iso-amyl nitrite as described by Cadogan[45]. The yield from this reaction is rather low as the product is hard to purify, recovery from crystallisation being low. The best yield, about 43% is obtained when it is isolated by column chromatography and triturated with methanol. Acylation of 6, however, proved difficult.

Byron, Gray and Wilson[43] carried out the acylation of 6 over 6 hours employing nitrobenzene as the solvent, and report a 74% yield. Because of the toxicity and the difficulty of removing this solvent, this reaction was attempted in both methylene chloride and 1,1,2,2-tetrachloroethane using acetyl chloride and aluminium chloride. In neither case could pure ketone 3 be isolated. This is probably due to the lability of the t-butyl group. Bartlett, Roha and Stiles[46] found that refluxing a mixture of benzene and 1,3,5-tri-t-butylbenzene containing aluminium chloride produced mono- and di-t-butylbenzenes. These workers also found that on bromination, 1,3,5-tri-t-butylbenzene loses one of the alkyl groups to give 1-bromo-3,5-di-t-butylbiphenyl. On the basis of these two results, it was decided to investigate the acylation of the dialkyl biphenyl 9 with the expectation that one of the alkyl groups would be displaced by the acyl group. A small scale reaction, using 1,1,2,2-tetrachloroethane as solvent did yield some of the ketone 3, but only in 14% yield after chromatographic separation and recrystallisation. A mixture of isomeric di- and tri-t-butylbiphenyls and acetyl-di-t-butylbiphenyls were also formed during this reaction.

Because of these difficulties, it was decided to examine the preparation of p-t-butyl-α-methylstyrene 17 (scheme 3.2) from t-butylbenzene as a model for the sequence 6 to 3 then to 5 (scheme 3.1).

Scheme 3.2:



The ketone 15 was prepared by the method of Mowry, Renoll and Huber[47], using the Perrier modification of the Friedel-Crafts reaction. In this method, acetyl chloride is added to aluminium chloride in carbon tetrachloride to form an adduct (which partly dissolves), and then the arene is added at a low temperature, to give an 87% yield of ketone 15 after distillation. The ketone on reaction with an excess of methyl magnesium iodide gave the crude carbinol 16 in 98% yield. This was dehydrated and azeotropically dried in toluene using an acid catalyst to give a 93% yield of alkene after distillation.

In the light of this work, the preparation of ketone 3 (scheme 3.1) was again attempted under similar conditions. The acetyl chloride-aluminium chloride adduct was formed in carbon titrachloride and alkylbiphenyl 6 added. This did produce the desired ketone in a yield of 62% after recrystallisation, but the melting point was a little low. Other work having been carried out in the interim period, there was insufficient time left to pursue this through to the alkene 5.

Route 3

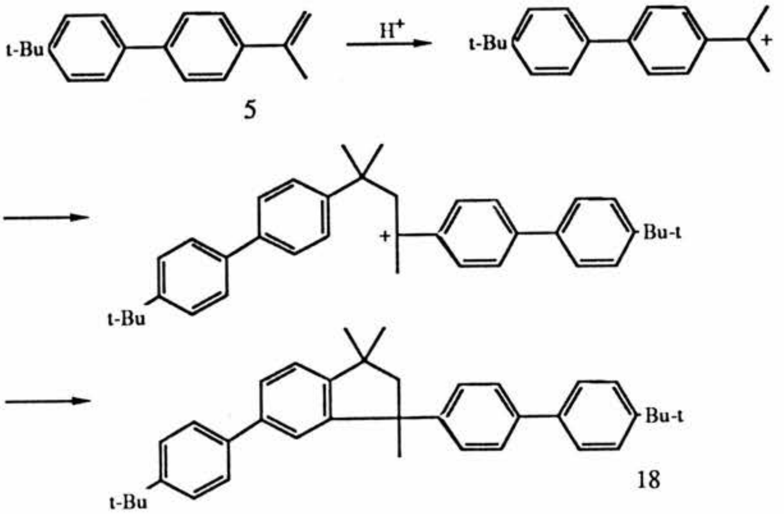
With the difficulties encountered in trying to prepare the alkylated ketone 3 (scheme 3.1) it was decided to prepare the alkene 11. The preparation of this hydrocarbon from 2 is analogous to the sequence 3 to 5, and these steps could then be optimised using the readily available ketone 2 before attempting the reaction with ketone 3. Also, the alkylation of 10 and 11 could be attempted to produce 4 or 5, and the homopolymer of 11 could be used as a reference to the homopolymer of 5 to judge the effects of the t-butyl groups.

Initial attempts were carried out using an old Koch-Light sample of the acetylbiphenyl 2. The appearance of the sample was not very good (tan rather than white) so the ketone was recrystallised from ethanol and dried in vacuo over phosphorus pentoxide prior to use. The reaction was carried out using methyl magnesium iodide in amounts varying from 5% up to a ten-fold excess of theory, using diethyl ether, THF or a mixture of the two as solvent for the Grignard reagent, adding the ketone in THF. The THF is necessary as the ketone has a very low solubility in diethyl ether. In no instance could the product carbinol 10 be detected on work-up, only the acetylbiphenyl 2 was obtained. A considerable amount of time was taken with these experiments, and as a last attempt it was decided to purify a sample of ketone 2 by column chromatography. This resulted in a sample that was white, a great deal of dark red-brown material being left on the column. This was in a reaction with a ten-fold excess of Grigmard reagent, using THF as solvent throughout. The ^{1}H-NMR spectrum of the crude product indicated a conversion to the desired carbinol 10 of about 50%. As the formation of the Grignard reagent is not as smooth in THF as it is in diethyl ether, this reaction was repeated with the methyl magnesium iodide being prepared in diethyl ether and then diluted with THF prior to adding the ketone. The ^{1}H-NMR of the crude product obtained confirmed that the reaction was successful, but after crystallisation from petroleum ether the yield of pure product was only 56%. Subsequently all samples of ketone 2 were redistilled at reduced pressure prior to use. The procedure was further modified and it was found that when 4.8 mole equivalents of methyl Grignard reagent in diethyl were used, the ketone being added in THF, and the product purified by extraction of the crude material with petroleum ether and stripping the solvent, the carbinol 10 could be obtained in high state of purity in yields of 97-99%.

The carbinol 10 was readily dehydrated and azeotropically dried in toluene with an acid catalyst to give alkene 11 in 84-86% yield after recrystallisation from ethanol.

The alkylation of carbinol 10 was attempted using t-butyl chloride with ferric chloride as catalyst. This reaction produced a mixture of a great many compounds (about 20 components by TLC). Only one substance could be isolated from the mixture. Its mass spectrum (M^+ peak at 500, accurate mass of 500.343400) and ^1H-NMR spectrum are compatible with structure 18 (scheme 3.3), a dimer of alkene 5. It appears that the HCl evolved during the alkylation reaction dehydrates the carbinol present (10 or 4) to give alkene (11 or 5) which then undergoes acid catalysed oligomerisation. The dimer 18 might be formed directly from 5, or be the product of the alkylation of the dimer formed from two molecules of 11, or one of 11 and one of 5. A similar reaction is reported by Matyjaszewski and Sigwalt[48] for p-t-butyl-α-methyl styrene 17.

Scheme 3.3:



Route 4

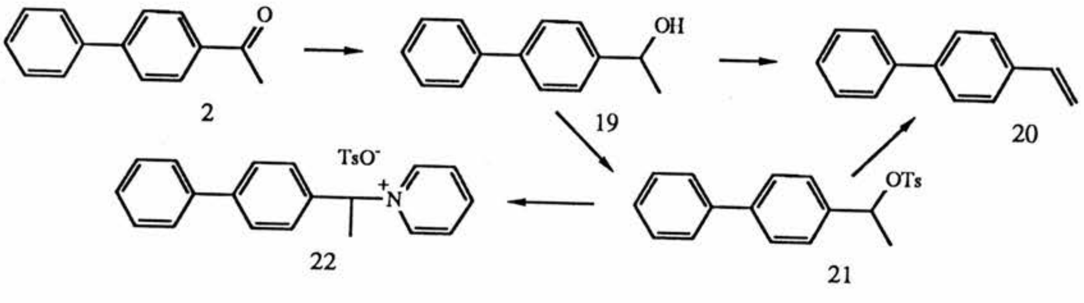
The difficulties encountered with the t-butylbiphenyl 6 in acid conditions prompted a different approach. It was decided to prepare the carbinol 4 by a Grignard reaction of the bromo-derivative 14 with acetone (scheme 3.1). The bromobiphenyl 13 was prepared from the aniline 12 by homogeneous diazotisation in benzene using iso-amyl nitrite as described by Cadogan[45] in a yield of 50-53% after recrystallisation. The bromo-compound 14 is then readily prepared by the direct alkylation of 13 with t-butyl chloride and ferric chloride catalyst in 80% yield after recrystallisation. It was also found that when impure 13 (low melting point) was alkylated, the product 14 was obtained in 93% yield when isolated by column chromatography.

Unfortunately, this bromobiphenyl derivative could not be induced to form a Grignard reagent. Jones et al.[49] report that bromobiphenyl 13 forms a Grignard reagent only with difficulty. They employed diethyl ether as solvent for the addition of 13 to a large excess of magnesium, and then added THF and distilled off the diethyl ether to leave the organomagnesium in THF. The reaction of 14 with magnesium was tried in refluxing diethyl ether, THF and 1,4-dioxan solvents, but in all cases only the bromocompound was obtained on work-up in 86-90% recovery. In a similar manner, the conversion of bromobiphenyl 13 into carbinol 10, via the organolithium reagent, but this also failed. Treating 13 with freshly cut lithium in dry, freshly redistilled THF at room temperature or at the reflux temperature, followed by dry acetone did not produce any of the designed product 10. The only aromatic compounds that could be isolated on work-up of the reaction mixture were unchanged 13 and biphenyl itself. The formation of a meta-stable radical anion of 13 may be the cause of its unreactivity.

3.2 Vinylbiphenyl Derivatives

During the period in which the difficulties preventing the preparation of intermediates 3 and 10 were being investigated, the preparation of vinylbiphenyl 20 was also examined (scheme 3.4). The obvious route to this monomer is to reduce the readily available ketone 2 to the carbinol 19 and then dehydrate.

Scheme 3.4:



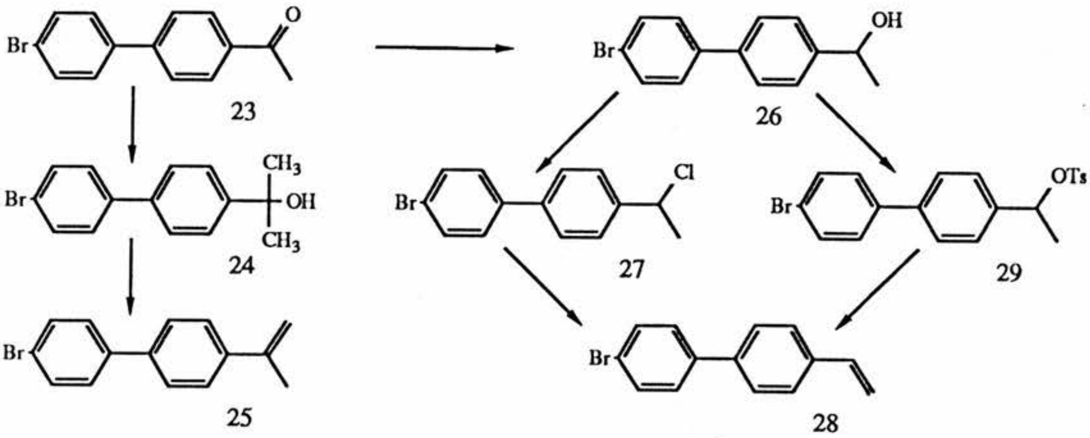
The ketone 2 was reduced to the ethanol derivative 19 with sodium borohydride in methanol solution to give a 97-98% yield of crude material of reasonable quality. Dehydration of 19 proved difficult. On refluxing in toluene with an acid catalyst, no water could be removed azeotropically. Only unreacted 19 was obtained from the reaction mixture on work-up. The preparation of 20 was repeated using t-butylbenzene as solvent instead of toluene to achieve a higher boiling point. Some polymeric material was obtained (insoluble in diethyl ether), but even after two recrystallisations the product 20 remained impure - the material is a mixture of a pale ochre solid and white lustrous flakes - and the yield was already down to 32%, so this route was not pursued.

As acid catalysed side-reactions are the most likely cause of the low yield mentioned above, alkaline dehydration was considered. The last route considered was to convert 19 into its tosylate ester, followed by elimination with base. The carbinol was added to dry, redistilled pyridine and treated with purified tosyl chloride. On work up, none of the product 21 or carbinol 19 were obtained. The precipitate in the reaction, which was assumed to be pyridine hydrochloride may have been the pyridinium tosylate 22, formed by attack of the pyridine solvent on the tosylate ester[50].

3.3 Other Styrene Derivatives

Polymers with an oligoether group in the side-chain were also of interest, so the preparation of the bromine containing monomers 25 and 28 (scheme 3.5) was examined. The bromine atom of these monomers would allow a side group to be introduced into the corresponding polymers via lithiation with butyllithium. Although it would not be possible to introduce a tertiary carbon at the ring, such polymers would be useful as a guide to the properties of polymers which did have a tertiary carbon at the 4' position.

Scheme 3.5:

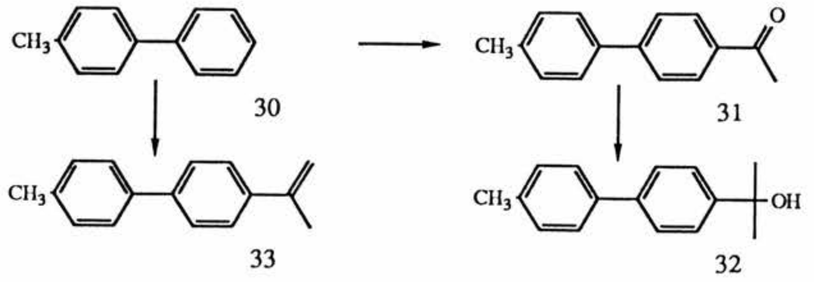


The bromo-ketone 23 (scheme 3.5) was prepared from bromobiphenyl 13 (scheme 3.1) by acylation with acetyl chloride and aluminium chloride in 84% yield after recrystallisation. This was converted to the carbinol 24 using an excess of methyl magnesium iodide, as for the conversion to 2 to 10 (scheme 3.1) in a 99% yield of crude product of reasonable quality. In a like manner to 10, the carbinol 24 (scheme 3.5) may be dehydrated using toluene and an acid catalyst, and the product 25 was obtained in a yield of 88% after recrystallisation from ethanol.

As for the preparation of 19 (scheme 3.4), the reduction of 23 was carried out with sodium borohydride in methanol, and gave crude carbinol of reasonable quality in a yield of 97%. It was decided to follow the route of Adrova, Koton and Moskvina[51] and prepare the alkene 28 via the chloro-derivative 27. However when carbinol 26 was treated with refluxing thionyl chloride and the product isolated by column chromatography, only a 10% yield of material was obtained, which proved to be a mixture of 26 and 27 so this route was abandoned. The preparation of the tosylate ester 29 was thus attempted using tosyl chloride in purified pyridine; however, as before for 21 (scheme 3.4), no ester could be isolated. The preparation was repeated, but using sodium hydride in toluene to generate the alkoxide, and then adding tosyl chloride, but again none of the ester 29 could be isolated on work up.

Another way to introduce a pendant group onto the biphenyl moieties of a polymer is through a methyl group. Such a group may be lithiated using butyllithium complexed with various tertiary amines, and most usefully with N,N,N',N'-tetramethylethylenediamine[52]. Then an oligoether halide or mesylate could be used to alkylate the benzylic site.

Scheme 3.6



The methylbiphenyl 30 (scheme 3.6) was prepared by homogeneous diazotisation of p-toluidine using iso-amyl nitrite[45]. The success of this reaction varied with yields of 47-48%, and two of 63% (impure material - coloured due to presence of some azo compound).

This hydrocarbon was acylated using acetyl chloride and aluminium chloride to give ketone 31 in a yield of 88% after recrystallisation. The ketone 31 was then treated with methyl magnesium iodide to give the carbinol 32 in a 94% yield after recrystallisation. Unfortunately there was insufficient time to prepare the corresponding alkene 33.

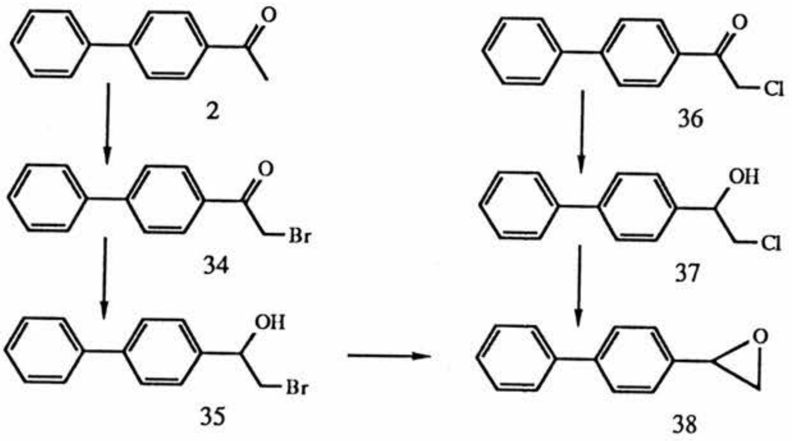
CHAPTER 4

STYRENE OXIDE DERIVATIVES

The alkenes discussed in the last chapter were investigated primarily for conversion into the corresponding epoxides by direct oxidation. The lack of success in preparing those alkenes prompted the investigation of alternative routes to the epoxide derivatives.

4.1 Hydrocarbon Epoxides

Scheme 4.1



Route 1

The preparation of the epoxide 38 (scheme 4.1) was first attempted using an old sample of 4-vinylbiphenyl (20) (scheme 3.4), after recrystallisation using m-chloroperbenzoic acid (MCPBA) in a two phase system as described by Imuta and Ziffen[53]. However, only a 24% yield of product was obtained after recrystallisation, ^{1}H NMR shows this to be a very impure sample of the desired epoxide 38. Consequently the alternative route via the α-bromoketone 34 was examined.

Route 2

The phenacyl bromide derivative 34 was prepared from 2, as described by Vogel[54] using bromine in acetic acid, in 74% yield after recrystallisation. An attempt to reduce this compound to the carbinol 35 using lithium borohydride in t-butyl alcohol, based on the method of Soai, Yamanoi and Hikima[55] proved unsuccessful. None of the desired bromohydrin 35 could be isolated on work-up. The reduction was next attempted using sodium borohydride in iso-propyl alcohol. This resulted in a mixture of at least 6 components (determined by TLC), the bromohydrin 35 clearly constituting less than 50% of the mixture. Repeating the experiment with a mixed solvent of 1:1 mixture of iso-propyl alcohol and THF produced a similar mixture, consisting of 34 and 35, the unbrominated compounds 2 and 19 (scheme 3.4) and other materials - presumably due to iso-propyl alcohol displacing the bromine - so this route was abandoned. Tamura et al.[56] claim to have prepared 38 via this route, from 34 via 35, but they do not quote the yield.

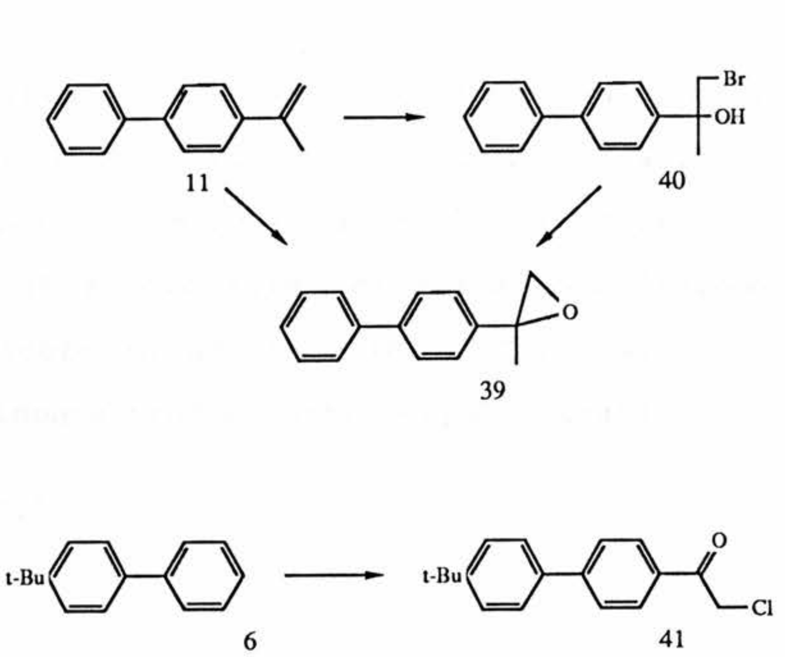
Route 3

The last approach taken to 38 was via the chloro-compound 36 (scheme 4.1). The difficulties encountered in the reduction of 34 appeared to be due to the ready elimination of bromide ion from 34 and 35. As the chloride ion is a poorer leaving group than the bromide ion it was anticipated that the phenacyl chloride derivative 36 would give a reasonable yield of the chlorohydrin 37.

The chloro-compound 36 was prepared in 85-86% yield by direct acylation of biphenyl using chloroacetyl chloride and aluminium chloride. The ketone 36 was then reduced to the chlorohydrin 37 in a 1:2 mixture of THF and methanol using sodium borohydride, to give an essentially quantitative yield of crude carbinol. The cyclisation of this compound to the epoxide 38 was carried out in THF, using sodium hydride as a non-nucleophilic base to generate the chloro-alkoxide, to gibe 38 in a yield of 75%. It was found that, although the crude carbinol 37 was shown to be of good purity by TLC, it was only when recrystallised chlorohydrin 37 was used that epoxide 38 could be isolated from the reaction mixture.

The preparation of the epoxide 39 (scheme 4.2) was attempted by direct oxidation of alkene 11, by the method of Imuta and Ziffen[53] using MCPBA in a two phase system. Unfortunately, as for the vinylbiphenyl 20 (scheme 3.4), no epoxide product could be isolated from the reaction mixture.

Scheme 4.2



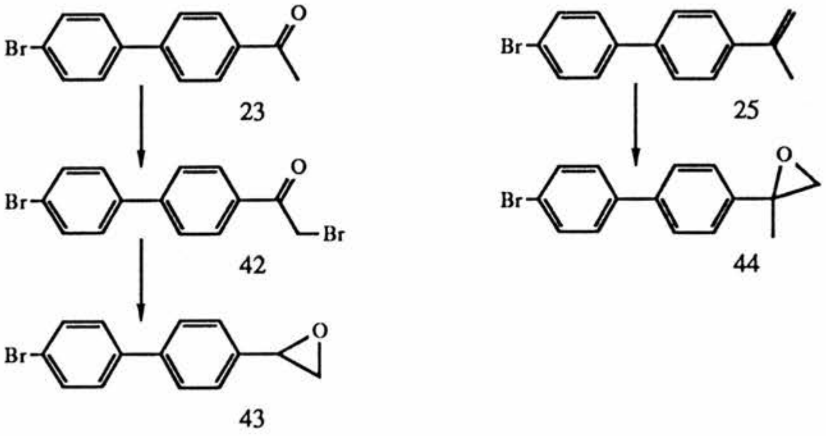
The alternative route to 39 (scheme 4.2), via bromohydrin 40 was also considered. The preparation of 40 was attempted using the method of Dalton, Hendrickson and Jones^{57}, using N-bromosuccinimide (NBS) in DMSO, but again, none of the observed product could be obtained on work-up.

The preparation of 41, an alkylated analogue of 36 (scheme 4.1) was attempted by adding hydrocarbon 6 (scheme 4.2) to a stirred mixture of the preformed adduct of chloroacetyl chloride and aluminium chloride. Unfortunately none of the desired ketone 41 could be isolated from the reaction mixture.

4.2 Bromo-derivatives

The preparation of the unknown brominated epoxides 43 and 44 (scheme 4.3) was also examined. The route chosen to 43 was from 23 via the dibromoketone 42. This compound was prepared from 23 on a small scale, using NBS in a 1:1 mixture of acetic acid and chloroform (ketone 23 is not very soluble in acetic acid). This gave a 74% yield of rather impure product after crystallisation.

Scheme 4.3



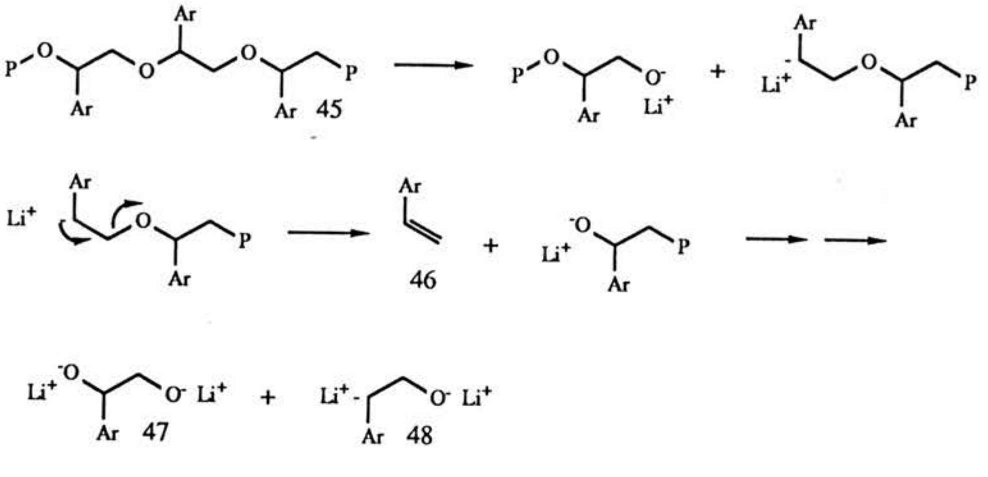
Considering the difficulties encountered in attempting to reduce bromoketone 34 to bromohydrin 35 (scheme 4.1), it was decided to attempt the reduction and cyclisation in one step by using a basic reaction medium. The ketone 42 was added to a stirred slurry of lithium borohydride and lithium t-butoxide (generated in situ with lithium metal) in t-butyl alcohol. A crude product was obtained from the resulting mixture as a paste. The ^1H NMR of this material indicates a 1:1 mixture of the desired epoxide 43 with another biphenyl derivative. This route was subsequently abandoned for reasons explained below.

The preparation of the epoxide 44 was attempted using a two phase system, based on the method of Imuta and Ziffen[53], but employing peracetic acid (generated in situ from acetic acid and hydrogen peroxide) rather than MCPBA. As with other experiments using this approach, only unreacted alkene could be obtained from the reaction mixture.

4.3 Benzyl Ether Cleavage

Other work, which was underway concurrently with the above, led to a literature search on methods of generating benzyl lithium derivatives. Papers by Gilman, Pacevitz and Baine[58], Ziegler and Dislich[59], and also Gilman and Schwebke[60] report that benzyl alkyl ethers may be readily cleaved by alkali metals. The polymers derived from the epoxides of vinyl biphenyl derivatives would have the general structure 45 (scheme 4.4).

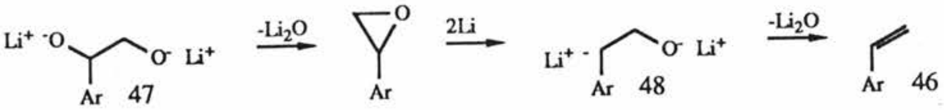
Scheme 4.4



P = Polymer segment

The polymer chain consists of benzylic ether linkages, so in the presence of lithium metal, such a polymer would be bound to undergo a rapid decomposition, presumably generating the vinyl derivative 46, and the other two anions 47 and 48. It seems likely that the two anions 47 and 48 will react further by elimination of lithium oxide, to give 46 as the ultimate cleavage product[21] (scheme 4.5). This vinyl derivative 46 would of course, commence polymerising on any excess lithium metal. Consequently all work on epoxides where the biphenyl group was bonded directly to the epoxide ring was stopped.

Scheme 4.5



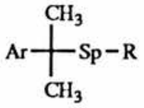
CHAPTER 5

FURTHER MONOMERS

5.1 Side Chain Polymers

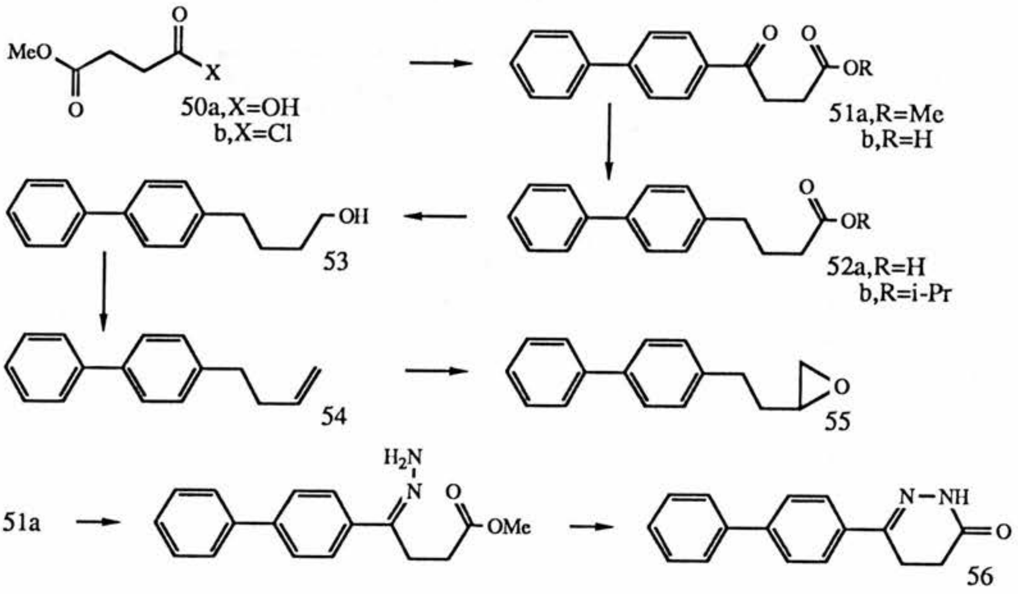
Macromolecules with relatively long, but not rigid side chains, containing biphenyl groups, are important because flexibility of the sidechains will give materials that are amorphous at ambient temperature. Some side chain polymers containing the biphenyl group, separated from the polymer main chain by 'spacer' groups (usually a methylene or poly(ethylene glycol) segment) are reported in the literature, mostly with regard to their properties as liquid crystals. For example, Gemmell et al. [61] have prepared polymers from acrylate and methacrylate esters of biphenylylalkyl alcohol derivatives; Rodriguez-Parada and Percec [62] have prepared polymers from oligo(ethylene glycol) biphenyl vinyl, propenyl and alkyl ethers. These types of polymer unfortunately are not suitable for modifying the lithium anode. The ester group of the acrylate and methacrylate polymers would react with lithium, most probably 'clipping off' some of the side chains. The other polymers mentioned above have the biphenyl groups as aryl alkyl ethers which would undergo cleavage of the aryl oxygen bond over lithium metal [21].

For a side chain polymer to be of use in modifying a lithium anode, the biphenyl group would have to be linked to the side chain through a carbon rather than an ether linkage, and the main chain would be either a polyether or a poly(vinyl ether). Such monomers may be formulated as 49, where Ar is a t-butylated biphenyl group, Sp an oligoether or methylene chain, and R is a vinyl ether or epoxy ethyl group.


$Ar-C(CH_3)_2-Sp-R$

49

Scheme 5.1



As a first step in the synthesis of such monomers, it was decided to prepare the less substituted epoxide 55 (scheme 5.1) from the alkene 54. The difficulties encountered in trying to epoxidise styrene derived monomers (chapter 4) were probably caused by the conjugation of the double bond with aromatic system, so no difficulties were envisaged in the epoxidation of 54.

The preparation of the keto acid 51b was first attempted using succinic anhydride and aluminium chloride in 1,1,2,2-tetrachloroethane, based on the method of Reinheimer and Taylor [63]. Weizmann, Bergmann and Bograchov [64] using a similar method obtained a 90% yield of product, recrystallised from acetic acid. However the best yields obtained for crude 51b were only about 55%, and there were considerable losses incurred on purifying this material. Consequently, it was decided to use the alternative route from 50a. Based on the results of later work (see below) it appears likely that the problem was in fact due to the heat of reaction.

Cason [65] prepared the ester-acid 50a by heating to reflux a mixture of succinic anyhydride with a slight excess of methanol. It was found that, using a large excess of methanol, the reaction could be carried out without heating, just stirring a slurry of succinic anhydride in methanol until dissolution was complete. In this way the product 50a was obtained in a yield of 71-74% after recrystallisation, with 18-20% of the anhydride converted to succinic acid by moisture in the methanol. (Prolonged heating of the ester-acid may result in trans-esterification to give succinic acid and its dimethyl ester in equilibrium [66]).

The acid 50a was then converted to the ester-acid chloride 50b by refluxing in excess thionyl chloride to give, after distillation a yield of 75-77%. The acid chloride 50b was then used to acylate biphenyl in the manner described by Papa, Schwenk and Hankin [67] using aluminium chloride in 1,1,2,2-tetrachloroethane, with the exception that in the initial runs the reagents were mixed at room temperature without any cooling applied. This gave 51a in 60-65% yield. The reaction mixture tended to become quite hot as the reaction proceeded. The relatively low yield of this reaction was due to the presence of a large amount of contaminating material in the crude product. It seemed likely that a side reaction between the solvent and biphenyl might be occurring in the latter stages of the reaction because of the rise in temperature. To investigate this, some biphenyl was taken up in 1,1,2,2-tetrachloroethane and aluminium chloride was added - about 20.wt.% on the biphenyl. The mixture was then heated to reflux. A black infusable material - presumably a cross-linked polymeric substance - was formed, caking the sides of the reaction flask even before reflux was achieved, with the evolution of HCl gas. When the preparation of 51a was repeated, keeping the temperature of the reaction mixture below 5°C, the product ester was obtained in 86% yield.

It was decided to carry out the reduction of the keto acid 51b to 52a, by a Huang-Minton procedure, using hydrazine hydrate and potassium hydroxide in ethylene glycol as described by Katritzky and Marson [68]. In the initial runs, the methyl ester 51a was used directly, heating it in the glycol with the potassium hydroxide. It had been expected that it would saponify in situ, and that the methanol would then be distilled off with water after the addition of the hydrazine hydrate. The yield of product 52a was rather low in these reactions, and in one reaction, some of the pyridazinone derivative 56 was isolated. It appears that saponification was slow, so that there was still some ester 51a present when the hydrazine hydrate was added, which then reacted at the ester function as well as at the ketone function (scheme 5.1). Subsequently, the ester 51a was hydrolysed to the acid with aqueous potassium hydroxide prior to reduction, the damp cake of filtered precipitated acid being used directly. When the acid 51b was used, the yields on reduction were improved. However it was found that filtering off the precipitated acid 52a, as described by Katritzky and Marson [68] was a difficult process, because of its fine particle size. Consequently the acid 52a was isolated by extraction with butanone followed by evaporation of the solvent. In this manner 52a was obtained in a yield of only 57%, whereas Katritzky and Marson [68] report a yield of 90%.

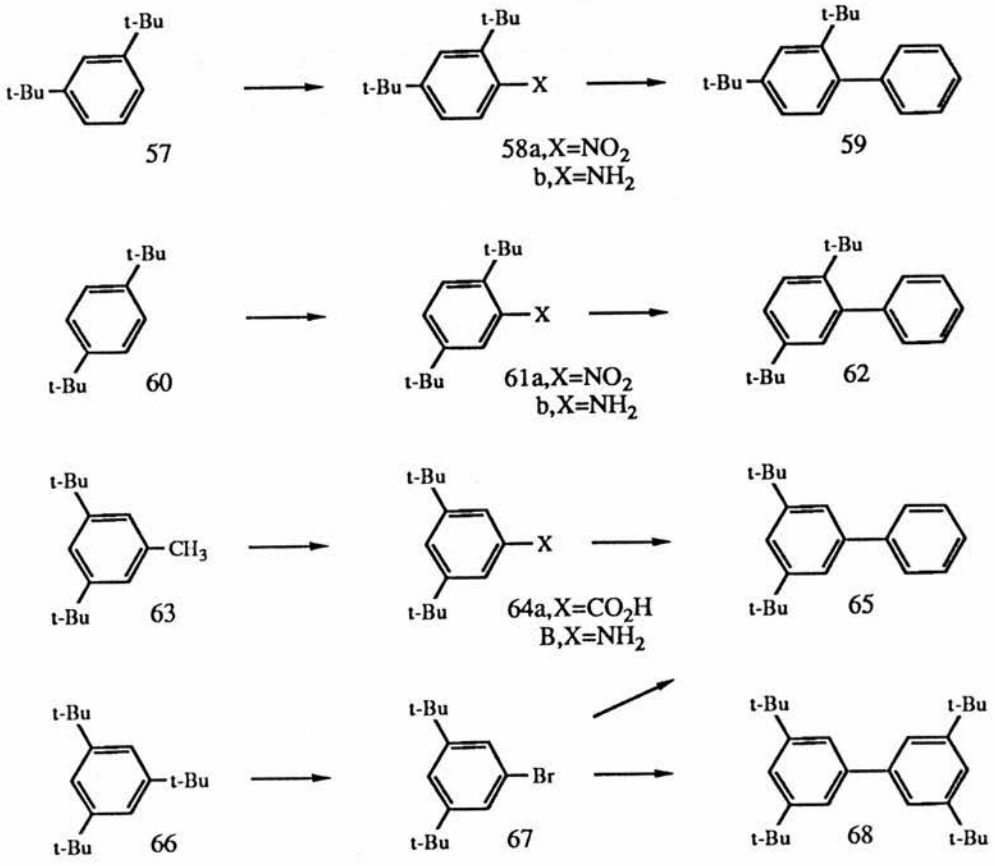
The reduction of the methyl ester of 52a using lithium aluminium hydride in THF is reported by Grovenstein and Akabori[69] to give carbinol 53 in 98% yield. The methyl ester of 52a, being a high boiling liquid, is not easy to purify as fractionation is very difficult to achieve on a small scale at low pressure, so the iso-propyl ester 52b was prepared as it is solid and may be purified by crystallisation. The reduction of 52b was attempted in the manner described by Grovenstein and

Akabori [69], but the crude product was very impure and could not be purified by column chromatography or crystallisation. Lack of time prevented further investigation of the route.

5.2 Other Butylated Biphenyls

The Royal Aircraft Establishment (R.A.E.), Farnborough, who part funded this work expressed an interest in more highly substituted biphenyl derivatives, and so routes to some di-t-butylated biphenyls were examined.

Scheme 5.2



The R.A.E. first suggested hydrocarbon 59 (scheme 5.2) as a possibility. The t-butyl group in the 2-position will prevent the two phenyl rings from approaching a co-planar orientation, and in so doing will greatly diminish the delocalisation of negative charge over the two rings in the radical anion. This would increase the reduction potential of the system, which might be better in a cell by maintaining a high electrode potential, although it could also render the radical anion too reactive if the reduction potential is raised too much.

The obvious route to 59 is from hydrocarbon 57. On nitration this should yield mostly the desired derivative 58a, which could then be reduced to the aniline 58b and then diazotised in benzene to give 59. In the mono-alkylation of toluene with t-butyl chloride, Baur [70] found that with aluminium chloride as catalyst the meta-isomer is the main product, whereas Bialobrzeski [71] found that with ferric chloride as catalyst the para-isomer is the major product. Based on these facts, the preparation of 57 was attempted by the reaction of equimolar quantities of t-butylbenzene and t-butyl chloride in 1,1,2,2-tetrachloroethane using aluminium chloride as catalyst. On both attempts to prepare 57 a mixture was obtained containing significant proportions of tri-t-butylbenzene 66. As the reaction was carried out on a small scale, there was insufficient material for efficient fractional distillation, and the mixture could not be separated by column chromatography.

Burgers et al. [72] prepared the compounds 58a and 58b by an unambiguous route from the aniline 64b. These workers converted 64b to its acetanilide and nitrated it. The 2-nitro-derivative was then isolated, hydrolysed and deaminated to give 58a of mp 52-53°C. They then reduced this compound to give the aniline 58b of mp 18.5-19°C which formed an acetanilide of mp 153.5-154.5°C. Bartlett, Roha and Stiles [46] however obtained a different compound when they prepared an aniline from 57. They obtained, after nitration and reduction of 57, an aniline of bp. 152-154°C/32 Torr, which formed an acetanilide of mp 83-84°C. The aniline also gave an anomalous result on titration with acid. Work on the preparation of 59 was suspended at this point because of the difficulties encountered in trying to prepare styrene based monomers (chapter 3).

The preparation of 62 was examined as this hydrocarbon also has a t-butyl group in the 2-position. The benzene derivative 60 was prepared from t-butylbenzene and t-butyl chloride in methylene chloride with ferric chloride as catalyst (see above) [41,71] in 64% yield after recrystallisation. This was then nitrated in acetic anhydride with concentrated nitric acid to give 61a in 55% yield after recrystallisation. Catalytic hydrogenation of 61a to give aniline 61b was attempted using 5% palladium on charcoal catalyst. However, very little hydrogen was taken up over 4 days. Whether this was due to a contaminant in the nitro compound poisoning the catalyst, or the steric bulk of the ortho t-butyl group was not determined. This work was then suspended as above.

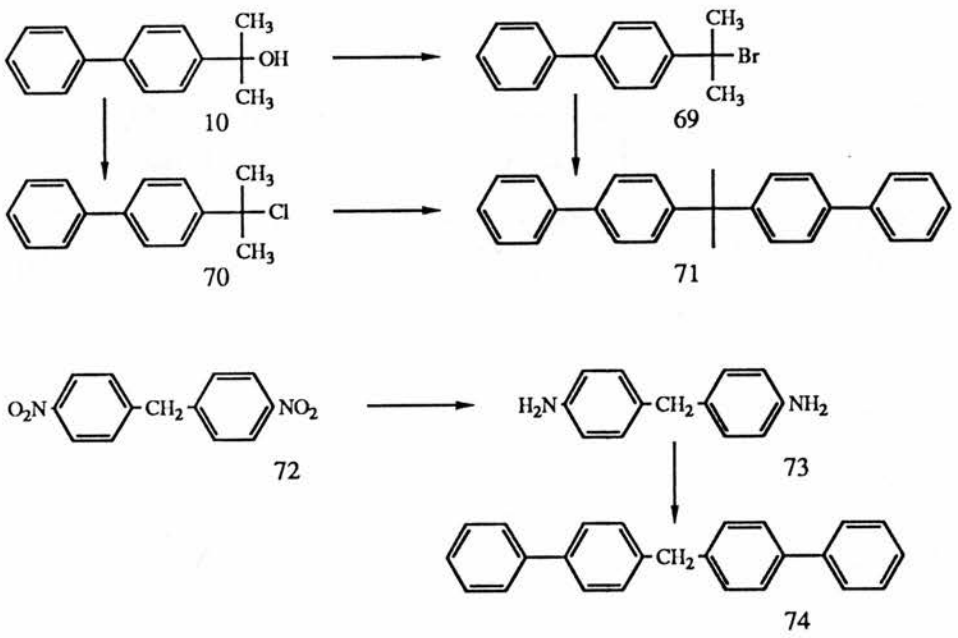
The final dialkylbiphenyl that was considered was 65. The most promising route to prepare this hydrocarbon was from 63. Geuze et al. [73] have shown that the direct dialkylation of toluene with t-butyl chloride, using either aluminium or ferric chloride gives hydrocarbon 63. Van Hartingsveldt, Verkade and Wepster [74] found that this compound may be oxidised to the acid 64a using alkaline potassium permanganate in aqueous pyridine at 95°C, in reasonable yield. They and others [72] found that acid 64a may be converted to the aniline 64b with sodium azide in a medium of chloroform and sulphuric acid at 45°C. Hydrocarbon 63 was prepared by the direct alkylation of toluene with a slight excess of t-butyl chloride with aluminium chloride catalyst in 1,1,2,2-tetrachloroethane. This was not pursued as this work, like the above, was suspended because of the problems encountered in preparing the styrene derivatives (chapter 3).

The hydrocarbon 68 was of interest as a reference compound for stability studies for the more highly substituted biphenyl derivatives. The preparation of 68 was attempted by direct alkylation of biphenyl with an excess of t-butyl chloride in 1,1,2,2-tetrachloroethane using aluminium chloride as catalyst in the hope that it would give meta-substitution as it does with toluene [70]. Unfortunately these reactions did not produce any of 68, the tarry mixture of products consisted mostly of isomeric di- and tri-t-butyl-biphenyls. Ishizu et al. [75] report preparing 68 from the hydrocarbon 6. Bartlett, Roha and Stiles [46] found that bromination of 66 results in the displacement of a t-butyl group by a bromine atom to give the derivative 67. Although these workers were unable to convert 67 to an organo-lithium or magnesium compound, Ishizu et al. [75] report forming a Grignard reagent from 67, which they then coupled to give 68. It might also be possible to prepare the hydrocarbon 65 by reaction of an organo-copper derivative of 67 with bromobenzene. The hydrocarbon 66 was prepared by the reaction of t-butylbenzene with a large excess of t-butyl chloride in 1,1,2,2-tetrachloroethane using aluminium chloride as catalyst in 46% yield after recrystallisation. At this point this work, like the above, was suspended.

5.3 Bis(biphenylyl)-Derivatives

The preparation of some biphenyl derivatives containing two biphenyl systems was also considered.

Scheme 5.3



The preparation of hydrocarbon 71 (scheme 5.3) was first considered. Direct preparation from carbinol 10 and biphenyl was not believed to be likely to give good results, as with an acid catalyst there would be competition with dehydration to alkene 11 (scheme 3.1) and oligomerisation of 11 to give indan derivatives (compare with scheme 3.3). Such an indan derivative could be used itself for a side group, but some degree of flexibility between the biphenyl groups is necessary to ensure that the final polymers would have a low glass transition temperature. Consequently it was decided to try and prepare 71 (scheme 5.3) by a Friedel-Crafts alkylation of biphenyl with one of the halides 69 or 70.

The preparation of the bromo compound 69 was attempted by treating a methylene chloride solution of 10 with concentrated hydrobromic acid, but this produced an irresolvable brown tar. It was decided to prepare the corresponding chloride 70 as it should be less reactive and hence more stable. The reaction of 10 with thionyl chloride was exceedingly vigorous, producing another irresolvable tar. Reaction of 10 in methylene chloride solution with concentrated hydrochloric acid similarly produced an irresolvable tar. Inukai[76] reports preparing 70 by treating a methylene chloride solution of carbinol 10 with dry hydrogen chloride gas at 0°C. This reaction was carried out as described by Inukai[76] but yet again an irresolvable tar was produced. It seems likely that the alkene 11 (scheme 3.1) was formed in these reactions and underwent acid catalysed oligomerisation. This work was not pursued any further.

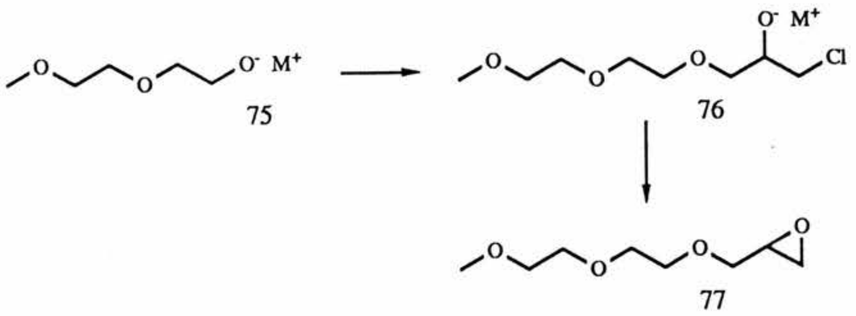
The related hydrocarbon 74 (scheme 5.3) was also considered. The first route examined was the reaction of biphenyl with methylene chloride. Adding aluminium chloride to a solution of biphenyl in methylene chloride and refluxing for 2 hours produced a mixture which was mostly biphenyl, containing the desired product 74 and 4,4'-bis(4-biphenylmethyl)biphenyl. The reaction of biphenyl with methylene chloride in 1,1,2,2-tetrachloroethane with aluminium chloride catalyst was attempted, but this produced an even lower yield of the desired product 74, most of the conversion being to polymeric material. It was decided to try another route to 74, starting from diphenylmethane, by conversion to the dinitro- compound 72, reduction to the bis(aniline) 73 and then diazotisation in benzene to give 74. The nitration of diphenylmethane in acetic anhydride using concentrated nitric acid resulted in a 2:1 mixture of the 4,4'di-nitro-derivative 72 and the 2,4'-dinitro-derivative. Nitration with concentrated nitric acid at 0°C with a little methylene chloride to keep the substrate liquid gave little conversion. Nitration using a 1:1 mixture of sulphuric and nitric acids did produce the desired product 72 slightly impure after recrystallisation in 26% yield. This work was suspended at this point and was not resumed.

The last species that was considered a possibility was bis(4-biphenyl)ether. However Eargle[77] reports that this ether is readily cleaved by lithium metal, so this line of investigation was abandoned.

5.4 Epoxide Co-monomer

While the preparation of styrene oxide derivatives (chapter 4) was being investigated, it was decided to examine the preparation of glycidyl ethers for use as co-monomers in the preparation of polyethers. In fact, because of the difficulties encountered in preparing the desired monomers, only one co-monomer 77 (scheme 5.4) was synthesised.

Scheme 5.4



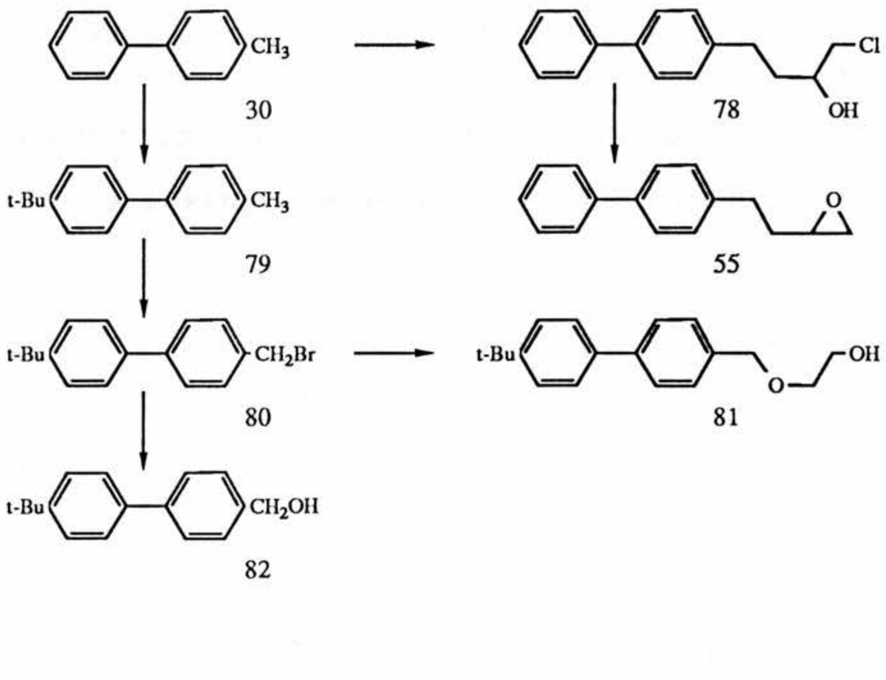
The first attempt to prepare 77 was essentially by the method of Jingle, Moore and Gandour[78] for which these workers quote a yield of 93%. Diethylene glycol monomethyl ether (methyl digol) was added to a slurry of sodium hydride in THF to form the alkoxide 75. Epichlorohydrin was then added to give the chloro-alkoxide 76, and then the solution was refluxed to cyclise 76 to the epoxide 77, which was obtained in 48% yield after distillation.

Two subsequent attempts to prepare 77 by the same method failed - the reaction mixture producing a brown sludge on reflux, from which no product could be isolated. Consequently the reaction sequence was repeated, but using potassium metal to form the alkoxide 75. The reaction of the methyl digol with the potassium was carried out at the reflux temperature of the THF. As the alcohol reacts, the reaction mixture turned a dark blue colour, which was lost when the solution was cooled. Presumably some of the excess potassium metal disolved to give potassium cations and free electrons in solution. When epichlorohydrin was added the solution turned deep burgundy in colour. After refluxing to cyclise and working up the reaction, the product 77 could only be obtained in 33-35% yield. Only a few samples of 77 were prepared.

5.5 Methylbiphenyl Derivatives

The hydrocarbon 30 (scheme 5.5) was originally prepared with the aim of using the methyl group to introduce a side chain into a polymer (section 3.3), but it may also be used to introduce a spacer group onto the biphenyl system.

Scheme 5.5



The preparation of the chloro-alcohol 78 (scheme 5.5) was examined as an alternative route to epoxide 55 (compare scheme 5.1). Hydrocarbon 30 was lithiated by butyllithium in THF in the presence of TMEDA, the solution turning dark red. Epichlorohydrin was added, the colour faded, and the reaction was worked-up by pouring into cold dilute hydrochloric acid. The reaction produced at least six components detectable by TLC. This was not pursued any further.

The synthesis of biphenyl derivatives 81 and 82 was examined for preparing monomers with ether based spacer groups. The alkylation of 30 was readily achieved, using a 32% excess of t-butyl chloride with ferric chloride catalyst gave 79 in 82.5% yield after two recrystallisations. The bromination of this hydrocarbon was carried out using a slight excess of N-bromosuccinimide in carbon tetrachloride to give 80 in a yield of 60% after two recrystallisations.

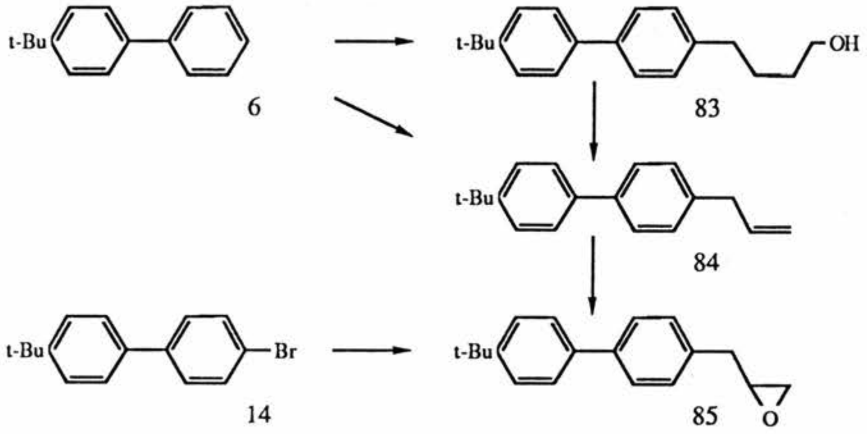
The conversion of 80 to the ether-alcohol 81 was attempted by refluxing a mixture of the bromo-compound and ethylene glycol, in which sodium metal had been dissolved to generate the alkoxide. However 80 was clearly not very soluble in ethylene glycol, and a two phase system was formed once it had melted. This reaction was repeated using ethylene glycol but adding some DMSO to homogenise the reaction mixture. The crude product contained at least three components by TLC. This work was not pursued once it was discovered that benzylic ethers undergo ready cleavage with lithium metal[58-60] (section 4.2).

The hydrolysis of 80 to give the benzyl alcohol derivative 82 was attempted using sodium hydroxide in aqueous DMSO. A two-phase system was also formed. This work, like that above, was not pursued as the benzylic ether that would eventually be formed would cleave on treatment with lithium[58-60] (section 4.2).

5.6 Other t-Butylbiphenyl Dervatives

The preparation of the 2,3-epoxypropyl derivative 85 was attempted by a number of routes.

Scehem 5.6



The conversion of the bromo-derivative 14 to 85 via an organolithium was attempted. A solution of 14 in THF was treated with a slight excess of butyllithium and to this was added epichlorohydrin. After heating to cyclise the intermediate chloro-alcohol and working up the reaction, none of the desired epoxide 85 could be isolated. Consequently the preparation of the alkene 84 was attempted as it could then be oxidised to give 85. The direct alkylation of 6 to give 84, using allyl chloride and ferric chloride catalyst, produced mostly unreacted 6, with only a trace of the desired product 84. This reaction was not repeated with the stronger Lewis acid aluminium chloride, as this would probably result in migration of the double bond to give a β-methylvinyl group. The last approach taken was to prepare the alcohol 83, which could then be dehydrated to 84 and oxidised to 85. The reaction of 6 with 3-bromo-1-propanol was attempted using aluminium chloride catalyst in 1,1,2,2-tetrachloroethane, but again, the crude product consisted mainly of unreacted hydrocarbon 6, and this work was not pursued any further.

CHAPTER 6

DISCUSSION

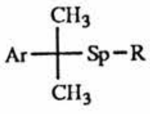
6.1 Polymers

The aim of this project, to prepare polymers (or the appropriate monomers), that could be used to modify a lithium electrode (as described in chapter 2) has clearly not been achieved.

In fact, only three monomers were obtained of reasonable purity; 4-(1-methylvinyl)biphenyl (11), 4-bromo-4'-(1-methylvinyl)biphenyl (25), and 1,2-epoxy-3-(2-(2-methoxyethoxy)ethoxy)propane (77). The alkene 11 polymerises readily with n-butyllithium in THF. However, the bromoalkene 25 on treatment with n-butyllithium in THF underwent metallation. The attempted polymerisation was worked up by adding a large excess of methyl iodide. Yellow-green crytsals were obtained after some of the solvent had evaporated. ^{1}H-NMR of this material indicates that it is 4-methyl-4'-(1-methylvinyl)biphenyl (33), clearly the product of methylation of the lithiated alkene. Cationic polymerisation was not attempted as this would only result in lower molecular weight oligomers as cyclisation to indan derivatives is possible[48] (see scheme 3.3). Radical polymerisation is also not viable because the tertiary benzylic radical formed is sufficiently stable that little propagation would occur.

6.2 Prospects

The initial work on the styrene based monomers was not as fruitful as had been hoped. Most of the problems encountered stem from the ease with which tertiary alkyl groups may be displaced from an aromatic nucleus by strong Lewis acids. Clearly the acylation and alkylation of 4-t-butylbiphenyl need closer examination. If acylation can be carried out in good yield, it would give access to the route proposed in scheme 6.2. If not then alkylation with a spacer group having a tertiary end group is still viable, as suggested in scheme 6.4. If substitution of t-alkylbiphenyls does not seem promising, then a rather more circuitous route, as described by scheme 6.1, could be adopted. There remains plenty of scope for preparing monomers of the form 49 as described in section 5.1.



$$\mathrm{Ar}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{Sp}-\mathrm{R}$$

49

It is a great pity that the cleavage of benzylic ethers by alkali metals[21,58-60], with its relevance to epoxyethylbiphenyl polymers was not discovered earlier. A considerable amount of time and effort was expended working on the styrene derivatives (chapter 3) and their epoxides (chapter 4), they being the major line of investigation.

The failure of a number of reactions to reproduce results recorded in the literature was quite disheartening.

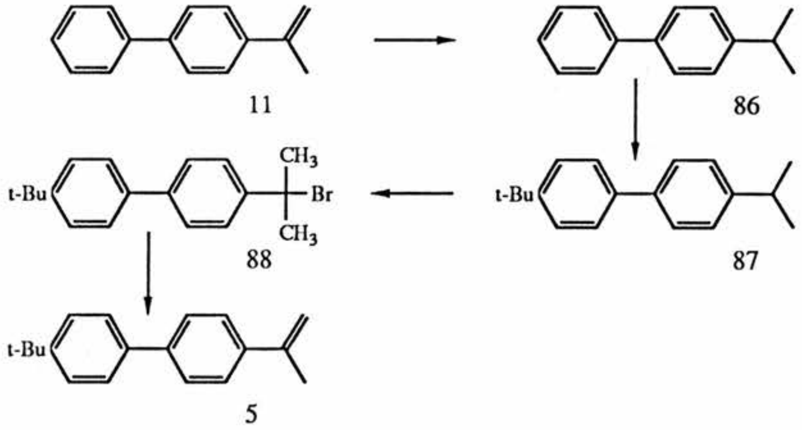
6.3 Future Work

There is clearly scope for a great deal more work to achieve the aim of this project; but the degradation of poly(4-vinylbiphenyl) over alkali metals[37-39] needs further investigation. This degradation would best be studied by modelling the system with a monomeric material, to facilitate analysis. Rembaum and his co-workers[37,38] used 4-ethylbiphenyl as a model for PVB for their ESR work. However, the polymer would in fact be better modelled by 4-iso-propylbiphenyl. The key point is the benzylic position which is the most reactive site in the polymer. In PVB all of the benzylic carbons are tertiary except for one or both of the terminal groups (depending on the method of polymerisation). The 4-ethylbiphenyl actually models the end group of PVB. The degradation of PVB over sodium would thus be modelled by ageing a solution of 4-iso-propylbiphenyl, in which only some of the biphenyl groups are present as radical anions - the same fraction of biphenyl groups as are reduced in PVB 'saturated' with sodium.

The problems encountered were mainly those of preparing asymmetrically substituted t-alkylbiphenyls. Some possible routes to the desired monomers, which were not conceived until this work had ended, are outlined below.

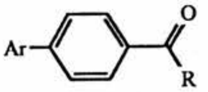
The monomer 5 (scheme 6.1) is a special case, with the double bond conjugated with the aryl system. Although the epoxide derived from this alkene would not form a useful polymer, the polyalkene itself would be of some interest.

Scheme 6.1



Alkene 11 (scheme 6.1) could be hydrogenated to 86, and alkylated to give hydrocarbon 87. Bromination with NBS would give halide 88, which would undergo elimination to give 5.

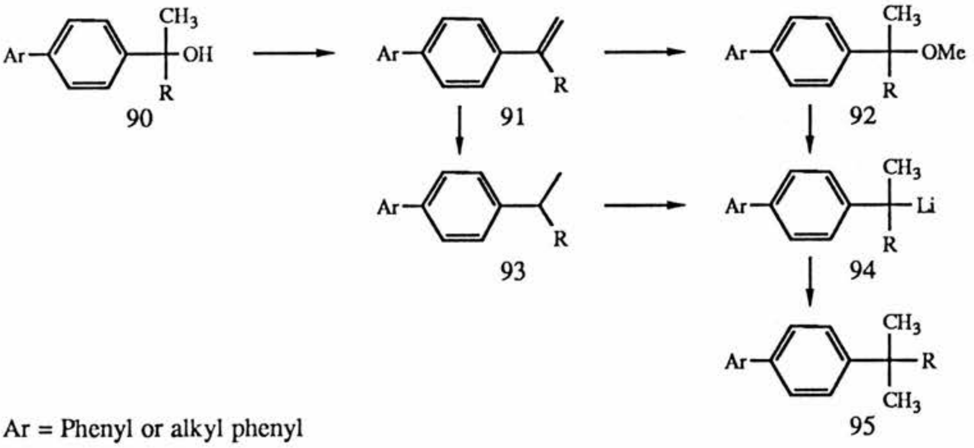
For other monomers - those with a spacer group between the biphenyl and the polymerisable group - the problems are slightly different. Monosubstitution of biphenyl itself is readily achieved by Friedel-Crafts acylation, but is not so straightforward for t-butylated biphenyls (section 3.1), while alkylation gives mostly disubstitution. If acylation is carried out, a derivative of general structure 89 is formed, where Ar is a phenyl or alkylated phenyl group and R is the 'spacer' group.



89

This ketone would then have to be converted to a material with a quaternary carbon replacing the carbonyl. A possible reaction sequence is shown below.

Scheme 6.2



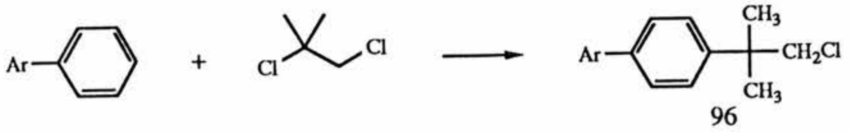
Ar = Phenyl or alkyl phenyl

Ketone 89 would be converted to carbinol 90 (scheme 6.2) by a Grignard reaction and then dehydrated. Alkene 91 would then be converted to the lithium reagent 94 either by converting 91 to the ether 92 and reacting with lithium metal[58-60], or by hydrogenation to 93 and metalation by butyllithium in the presence of TMEDA[52]. The organolithium 94 could then be methylated to give 95. The yields at each step of such a sequence would probably be quite high, but this approach greatly restricts the functionality that may be present in the side chain R, which would be necessary to introduce a polymerisable group into the molecule.

An alternative that might be considered would be to use a t-cumyllithium derivative (94, scheme 6.2, where R=Me) or an alternative organometallic (perhaps a copper reagent) derived from it, to append the biphenyl group to the end of a chain. Again the use of an organometallic compound would limit the other functionality present in the reacting molecule, but added to this it might also react as a base to give an elimination reaction.

Another possibility might be to alkylate a t-butylated biphenyl with iso-butylene dichloride in the presence of a weaker Lewis acid, such as ferric chloride (scheme 6.3) which should produce a chloro-t-butyl derivative (96).

Scheme 6.3



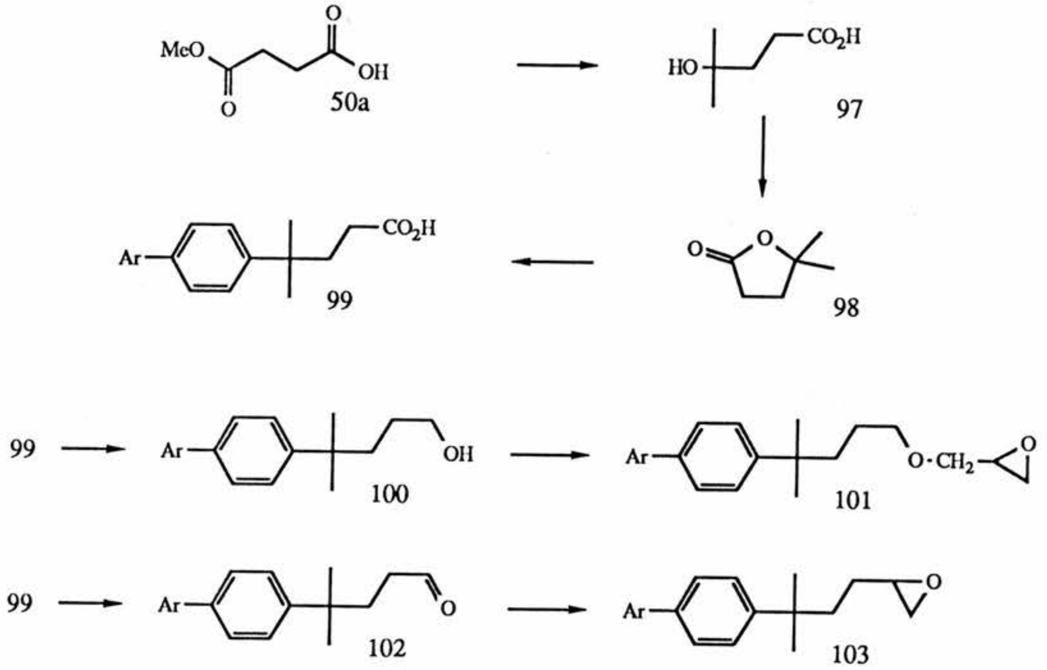
96

Ar = t-Butylated phenyl

Using a mild catalyst, the t-butyl groups already present should not be disturbed (see section 3.1). Unfortunately the chloro derivative 96 is most unlikely to undergo substitution reactions with nucleophiles because of the steric bulk of the t-cumyl group, as is known for the neopentyl halides[79]. The only use for 96 would be to prepare an organo-lithium reagent. Added to the difficulties outlined above, there is the added problem of the formation of a spiro-anion which results in a rearranged carbon skeleton[80].

The other approach is to prepare a compound which is a 'spacer' group with a tertiary halide (or equivalent) group at one end, with a precursor to the polymerisable group at the other end. This could then be used to alkylate a t-butylated biphenyl. This is illustrated below, using a lactone derived from succinic acid.

Scheme 6.4



Ar = t-Butylated phenyl

The ester-acid 50a (scheme 6.4) by a Grignard reaction, could be converted into the hydroxy acid 97, which would cyclise to lactone 98. This would be used to alkylate a t-butylated biphenyl to give intermediate 99 (compare with 52a, scheme 5.1). This acid could then for example be reduced to alcohol 100 and reacted with epichlorohydrin to give epoxy-ether 101. Alternatively, the aldehyde 102 could be prepared by selective reduction of 99 or selective oxidation of 100, to be converted to the epoxide 104 using a methylene-sulphur ylid.

CHAPTER 7

EXPERIMENTAL SECTION

Apparatus

All melting points were determined on a Gallenkamp melting point apparatus and are uncorrected.

Infra-red spectra were recorded on a Perkin Elmer 1330 infra-red spectrophotometer as nujol mulls or thin liquid films on sodium chloride discs.

^1H-NMR spectra were recorded at 80MHz on a Bruker WP80 spectrometer or (where indicated) at 300MHz on a Bruker AM300 spectrometer. ^{13}C-NMR were recorded at 20 MHz on a Varian CFT20 spectrometer. Tetramethylsilane was used as an internal reference for all NMR spectra.

Mass spectra were generated on an AEI MS-902 spectrometer operating at 70eV with a source temperature of 200°C, or on a Finnigan MAT Incos 50 mass spectrometer.

General Procedures

Glassware was dried in an oven at 105°C prior to use. In the case of Grignard reactions, the magnesium turnings were weighed into the reaction vessel prior to drying in the oven.

When argon or nitrogen gas was employed as an inert atmosphere, it was dried by passing through two Drechsel bottles filled with molecular sieves, dried overnight in an oven at 105°C.

Diethyl ether for Grignard reactions was dried over sodium wire and used without further purification.

THF was first dried over sodium wire and then redistilled. Potassium metal and benzophenone were added to the distillate which was then refluxed under nitrogen until the dark blue colour of the ketyl anion persisted. The THF was then freshly redistilled from potassium benzophenone under nitrogen and used immediately.

Abbreviations

The following abbreviations are used in describing the NMR data: s - singlet, d - doublet, t - triplet, quart - quartet, h - heptet, and combinations e.g. d.d. is a double doublet.

4-Acetylbiphenyl (2)

To a stirred mixture of 50.00g (324 mmol) of biphenyl and 47.00g (352 mmol) of anhydrous aluminium chloride in 400cm^3 of 1,1,2,2-tetrachloroethane, chilled to 5°C in an ice bath, was added dropwise a solution of 27cm^3 (382 mmol) of acetyl chloride in 100cm^3 of 1,1,2,2-tetrachloroethane, at such a rate that the temperature did not rise above 15°C. After the addition was complete the mixture was allowed to come to room temperature and left to stand overnight. The mixture was then poured onto 1700 cm^3 of ice and the organic layer was separated, washed once with 800 cm^3 water and dried over sodium sulphate. The solvent was then evaporated off at reduced pressure, and the crude product recrystallised from 50vol% ethanol in cyclohexane to yield 50.77 g (80%) of 2 product, of mp 117-119°C (lit[43] 119-120°C).

p-t-Butylnitrobenzene (7)

Method 1: A nitrating mixture was prepared by adding 40 cm^3 of nitric acid (70%, d=1.42) cautiously to 35 cm^3 of sulphuric acid (98%, d=1.84) while stirring in an ice bath. To 30 cm^3 of this mixture, vigorously stirred in an ice bath, were added 10g (74.5 mmol) of t-butylbenzene over 30 minutes. After the addition, the mixture was stirred for a further two hours and then poured onto ice. The organic material was extracted with ether, and the organic layer was washed free of acid with aqueous sodium carbonate solution, dried over sodium sulphate and the solvent evaporated off at reduced pressure. The crude product was chromatographed on 300 g of silica, eluting with 10vol% toluene in 40-60 petrol ether to give 9.12 g (68%) of 7 as a yellow oil; δ_H ($CDCl_3$) 1.37 (9H, s, t-Bu) 7.40-7.68, 8.05-8.32 (4H, AA'BB', C_6H_4)

Method 2: To a stirred solution of 50.00 g (373 mmol) of t-butylbenzene in 200 cm^3 of acetic anhydride chilled to 5^{o}C in and ice bath, was added 35 cm^3 (552 mmol) of nitric acid (70%, d=1.42) keeping the temperature below 15^{o}C, and stirring was continued for 1 hour after the addition was complete. The reaction mixture was then poured onto ice and extracted with diethyl ether. The ethereal layer was then washed with dilute sodium hydroxide solution until neutral, dried over sodium sulphate and the solvent evaporated off at reduced pressure. The crude product was distilled from a Vigreux flask to give 59.94 g (90%) of 7 as a yellow oil, bp 143-144^{o}C at water pump pressure using an air-leak (136-138^{o}C from glass wool, lit[46] 150^{o}C/21 Torr), ^{1}H-NMR as above.

p-t-Butylaniline (8)

A solution of 15.00 g (83.7 mmol) of freshly distilled 7 in 200 cm^3 ethanol was hydrogenated at slightly above ambient pressure employing 0.50 g of 5% palladium on charcoal as catalyst. Crude product was obtained, by filtering off the catalyst and evaporating the solvent off at reduced pressure, in quantitative yield (12.49 g) as a red-pink oil. The product was distilled to give 10.10 g (81%) of 8 as a colourless oil, bp 118-120^{o}C at water-pump pressure (lit[46] 125-126^{o}C/21 Torr).

4-t-Butylbiphenyl (6)

From biphenyl: To a stirred solution of 3.00 g (19.5 mmol) of biphenyl, and 1.85 g (20.0 mmol) of t-butyl chloride in 30 cm^3 of methylene chloride was added 0.05 g of anhydrous ferric chloride. After 2 hours stirring the reaction mixture was washed with 2x50 cm^3 of dilute hydrochloric acid, then with water, dried over sodium sulphate and the solvent evaporated off at reduced pressure. On standing, crystals formed from the fluorescent green oil, which were filtered off and rinsed with a little cold methanol. The filtrate was heated to dissolve the oil in the methanol and left to crystallise. The crystals obtained were filtered off and washed with a little methanol. The two solids were shown to be di-t-butylbiphenyl (9) by mass spectrometry. The filtrate of the last crystallisation was chilled in an ice bath to yield more crystals, 0.13 g (3%) impure product of mp 38-45^{o}C (lit^{81} 52.2^{o}C).

From aniline 8: A solution of 12.49 g (83.7 mmol) of crude 8 in 90 cm^3 benzene was slowly added dropwise to a stirred solution of 10.13 g (865 mmol) of iso-amylnitrite in 100 cm^3 of benzene chilled to its freezing point. This mixture was stirred for 15 minutes after the addition was complete, and then a further 700 cm^3 of benzene were added. The solution was then heated to and maintained at reflux for 3 hours, while removing water with a Dean and Stark separator. The bulk of the benzene was then distilled off, and the last of the solvent evaporated off at reduced pressure. The crude material (dark brown to black) was chromatographed on silica in 40-60 petrol ether to yield 7.57 g (43%) of 6, of mp 51-53°C (lit[81] 52.2°C). δ_H ($CDCl_3$) 1.35 (9H,s,tBu) 7.22-7.68 (9H,m,aryl-H).

4,4'-Di-t-butylbiphenyl (9)

A stirred solution of 30.00 g (195 mmol) of biphenyl and 55.00 g (594 mmol) of t-butyl chloride in 250 cm^3 of methylene chloride was chilled in an ice bath to below 5°C and then small portions of anhydrous ferric chloride were added until gas evolution commenced. Stirring was continued for 1 hour and the mixture was then poured into water, the organic layer was separated, then washed twice with dilute aqueous hydrochloric acid, and dried over sodium sulphate. The solvent was evaporated off at reduced pressure and the crude product recrystallised from ethanol to yield 36.38 g (70%) of 9 as yellowish needles of mp 124-126°C (lit[41] 127-128°C). δ_H ($CDCl_3$) 1.34 (18H,s,t-Bu) 7.32-7.61 (8H,AA'BB', aryl-H); δ_C ($CDCl_3$/$CHCl_3$) 31.40 (C-β) 34.46 (C-α) 125.58, 126.67 (C-2, C-3) 138.27 (C-1) 149.79 (C-4).

4-Acetyl-4'-t-butylbiphenyl (3)

From 4-acetylbiphenyl (2), method 1: To a stirred solution of 2.00 g (10.2 mmol) of 2 and 1.70 g (18.4 mmol) of t-butyl chloride in 20 cm^3 of methylene chloride was added 1.75 g (10.8 mmol) of anhydrous ferric chloride. Evolution of hydrogen chloride gas began, the mixture was stirred for an hour and then left to stand overnight. The mixture was poured into 50 cm^3 of water, washed with dilute hydrochloric acid (3x50 cm^3) and then dried over sodium sulphate. The solution was then treated with charcoal to remove the bulk of the colour (red-brown) and the solvent evaporated off at reduced pressure. The residue was recrystallised from ethanol to give 1.39 g of material of mp 119-121°C. ^{1}H-NMR is identical with 2, recovery is 67.5%.

From 2, method 2: To a stirred mixture of 1.70 g (18.4 mmol) of t-butyl chloride and 1.75 g (10.8 mmol) of anhydrous ferric chloride in 25 cm^3 of methylene chloride was slowly added dropwise a solution of 3.00 g (10.2 mmol) of 2 in 25 cm^3 of methylene chloride over 30 minutes. The mixture was stirred for a further 1 hour and left to stand overnight. This was worked up by pouring in 100 cm^3 of water, separating the organic layer, washing with dilute hydrochloric acid (3x100 cm^3) and drying the solution over sodium sulphate prior to evaporating the solvent off at reduced pressure. The residue was recrystallised from ethanol to give 1.28 g of material of mp 114-115°C. ^{1}H-NMR is identical with 2, recovery is 64%.

From 9: To a stirred slurry of 1.00 g (7.5 mmol) of anhydrous aluminium chloride in 20 cm^3 of 1,1,2,2-tetrachloroethane was slowly added dropwise to a solution of 2.00g (7.5 mmol) and 9 and 0.59g (7.5 mmol) of acetyl chloride in 30 cm^3 of 1,1,2,2-tetrachloroethane over hour. This was stirred for a further 2 hours, then the mixture poured into water, the organic layer separated and washed with water, dried and the solvent evaporated off at reduced pressure. Column chromatography of the crude product on silica in toluene did not give complete separation. Five components were present, unreacted 9, isomeric tri-t-butylbiphenyls, acetyldi-t-butylbiphenyl and product 3. The last two fractions obtained from the column were combined and recrystallised from ethanol to yield 0.26 g (14%) product 3 as white flakes of mp 128-129°C (lit[43] 132-133°C) δ_H ($CDCl_3$) 1.37 (9H,s,t-Bu) 2.61 (3H,s,Me) 7.37-8.13 (8H, 2 overlapping AA'BB', aryl-H).

<u>From 6, method 1</u>: To a stirred mixture of 2.10 g (10.0 mmol) of 6 and 1.40 g (10.5 mmol) of anhydrous aluminium chloride in 20 cm^3 of 1,1,2,2-tetrachloroethane was slowly added dropwise a solution of 1 cm^3 (14.1 mmol) of acetyl chloride in 10 cm^3 of 1,1,2,2-tetrachloroethane over 20 minutes. The mixture was stirred for a further hour, poured into ice-water, dried over sodium sulphate and evaporated to dryness at reduced pressure. The residue was chromatographed on silica in toluene to yield only 0.35 g (14%) of material of mp 92-100°C (lit[43] 132-133°C). TLC indicates that this is a mixture of product 3 and another material which elutes less rapidly - perhaps 4,4'-diacetylbiphenyl.

From 6, method 2: To a stirred slurry of 1.80 g (13.5 mmol) of anhydrous aluminium chloride in 15 cm^3 of carbon tetrachloride at -10°C was slowly added dropwise a solution of 1.05 g (13.4 mmol) of acetyl chloride in 15 cm^3 of carbon tetrachloride, keeping the temperature below -6°C. The adduct formed goes into solution, to which is slowly added dropwise a solution of 2.65 g (12.6 mmol) of 3 in 15 cm^3 of carbon tetrachloride, keeping the temperature below -4°C. The mixture was stirred for a further hour, poured into ice-dilute hydrochloric acid, the organic layer was separated, washed with water and evaporated to dryness at reduced pressure. The residue was crystallised from 100-120 petrol ether to give 1.96 (62%) of impure 3 of mp 122-124°C (lit[43] 132-133°C).

4-Bromobiphenyl (13)

Prior to use, 4-bromoaniline was purified by dissolution in toluene, filtration through celite to remove the insoluble material and recrystallisation, taking 2-3 crops.

To a stirred solution of 16.40 g (140 mmol) of iso-amylnitrite in 240 cm^3 of benzene, chilled to its freezing point in an ice bath, was slowly added dropwise over 1 hour a solution of 20.00g (116 mmol) of 4-bromoaniline in 160 cm^3 of benzene. The cold mixture was stirred for a further hour, then 2600 cm^3 of benzene were added and the solution was heated to and maintained at reflux for 3 hours, while removing water azeotropically. The bulk of the benzene was the distilled off and recycled. The remaining solvent and volatile side products were evaporated off at reduced pressure, and the residue was chromatographed on silica in 40-60 petrol ether to yield 17.58 g (65%) crude product (yellow-tan). Recrystallisation from ethanol gives 15.53 g (57%) of 13 as white lustrous flakes of mp 89 -90°C (lit[76] 89.5-90°C), δ_C ($CDCl_3/CHCl_3$) 121.56 (C-4) 126.92 (C-2') 127.60 (C-4') 128.71, 128.86 (C-2, C-3') 131.87 (C-3) 140.06, 140.15 (C-1, C-1').

4-Bromo-4'-t-butylbiphenyl (14)

To a stirred solution of 10.00 g (42.9 mmol) of 13 and 6.20 g (67.0 mmol) of t-butyl chloride in 80 cm^3 of methylene chloride were added small portions of anhydrous ferric chloride until effervescence commenced. The mixture was stirred for a further 2 hours and then poured into water, the organic layer was then separated, washed twice with water, dried over sodium sulphate and the solvent evaporated off at reduced pressure. Recrystallisation of the crude product from ethanol gives 9.92 g (80%) of 14 as white lustrous flakes of mp 138-139°C (lit[82] 132-133°C). δ_H ($CDCl_3$) 1.36 (9H,s,t-Bu) 7.30-7.63 (8H,m,aryl-H) δ_C ($CDCl_3/CHCl_3$) 31.32 (C-β) 34.51 (C-α) 121.21 (C-4) 125.80 (C-3') 126.56 (C-2') 128.51 (C-2) 131.80 (C-3) 137.03 (C-1') 139.96 (C-1) 150.68 (C-4').

2-(4-Biphenylyl)-2-propanol (10)

From 13: To a stirred mixture of approx. 75mg (11 mmol) of freshly cut lithium metal in 10 cm^3 of dry THF was slowly added a solution of 1.00 g (4.3 mmol) of 13 in 15 cm^3 of dry THF. The mixture slowly turned an intense black-green colour, which rapidly faded on addition of 15 cm^3 (204 mmol) of dry acetone. The solution then turned mostly solid, and a solution of 3.00 g (56 mmol) of ammonium chloride in 25 cm^3 of water was added cautiously. The two layer system was poured into 200 cm^3 of water and extracted with diethyl ether ($3x50cm^3$), the organic layer was separated, dried over sodium sulphate and the solvent evaporated off at reduced pressure. The crude material was chromatographed on silica in 40-60 petrol ether, to give 0.63 g of material. Mass spectrometry showed this to be a mixture of biphenyl and bromobiphenyl.

From 2 Method 1: A commercial sample of 2 (Koch-Light) was used after recrystallisation from ethanol. To a stirred slurry of 0.40 g (16.5 mmol) of magnesium turnings in 10 cm^3 of diethyl ether was slowly added dropwise a solution of 2.00 g (14.1 mmol) of methyl iodide in 25 cm^3 of diethyl ether to form a Grignard reagent. To this solution was slowly added dropwise a solution of 2.50 g (12.4 mmol) of 2 in 30 cm^3 of THF (2 has low solubility in diethyl ether), and the mixture was stirred for a further hour after the addition was completed. the reaction was worked up by adding aqueous acetic acid and pouring the mixture into water and extracting with diethyl ether. The organic layer was then separated, washed with water, dried over sodium sulphate and the solvent was evaporated off at reduced pressure. The residue was a red oil which slowly crystallised to give a yellow solid. The infra-red spectrum of this material showed it to be impure 2, but no O-H absorption was present, indicating that no carbinol 10 had been formed.

Method 2: A commercial sample of 2 (Koch-Light) was used after recrystallisation from ethanol.The solvent was changed to THF throughout as 2 has low solubility in ether. The above procedure was repeated the only difference being the use of THF in place of ether. The same result was obtained, a red oil which gives a yellow solid, shown to be unreacted 2 by infra-red spectrophotometry. Consequently, it was decided to increase the excess of Grignard reagent.

Method 3: A commercial sample of 2 (Koch-Light) was used after recrystallisation from ethanol. A solution of 7.38 g (52.0 mmol) of methyl iodide in 30 cm^3 of THF was slowly added dropwise to a stirred mixture of 1.39 g (57.2 mmol) of magnesium turnings in 10 cm^3 of THF to form a Grignard reagent. To this stirred mixture was then slowly added dropwise a solution of 1.00 g (5.1 mmol) of 2 in 25 cm^3 of THF, and the reaction mixture was stirred a further hour after the addition was completed. The reaction was worked up by adding aqueous acetic acid to destroy all remaining Grignard reagent and hydrolyse magnesium alkoxide. The mixture was then poured into water and extracted with diethyl ether. The ethereal layer was then separated, washed twice with water, dried over sodium sulphate and the solvent evaporated off at reduced pressure, to leave a red oil which partly crystallised to give a yellow paste. The infra-red spectrum of this paste has a broad O-H absorption at 3430 cm^{-1} indicating that the carbinol 10 was formed, but also has a strong carbonyl absorption at 1675 cm^{-1} indicating the presence of unreacted 2.

Method 4: A commercial sample of 2 (Koch-Light) was purified by column chromatography on silica in toluene prior to use. A solution of 10.85 g (76.4 mmol) of methyl iodide in 40 cm^3 of THF was slowly added dropwise to a stirred slurry of 2.04 g (83.9 mmol) of magnesium turnings in 20 cm^3 of THF. To this stirred mixture was slowly added dropwise a solution of 1.50 g (7.6 mmol) of 2 in 45 cm^3 of THF, and the mixture was stirred for a further hour. The reaction was worked up by adding aqueous acetic acid, then pouring into water and extracting with diethyl ether. The ethereal layer was separated, washed with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. Again this produced a red liquid, which slowly solidified (turning yellow). ^1H-NMR of this material indicated a 2:1 mixture of 2 to 10.

Method 5: A commercial sample of 2 purified as above (method 4) was used. To a stirred slurry of 2.04 g (83.9 mmol) of magnesium turnings in 20 cm^3 of diethyl ether was slowly added dropwise a solution of 10.85 g (76.4 mmol) of methyl iodide in 30 cm^3 of diethyl ether. When formation of the Grignard reagent was complete, 50 cm^3 of THF were then added to the solution (producing a grey-white precipitate of magnesium iodide). To this was added dropwise a solution of 1.50 g (7.6 mmol) of 2 in 50 cm^3 of THF, and the mixture was stirred for a further hour. Aqueous acetic acid was then added, the reaction mixture poured into water and extracted with diethyl ether. The organic layer was separated, washed with water, dried over sodium sulphate and evaporated to dryness at reduced pressure to give 1.32 g (82%) of crude product. Recrystallisation from 40-60 petrol afforded 0.87 g (54%) of 10 of mp 91-92 ^{o}C (lit[76] 91.5-92.5^{o}C) δ_H ($CDCl_3$) 1.60 (6H,s,Me,) 1.86 (1H, s, OH) 7.20-7.73 (9H,m,aryl-H).

Method 6: A solution of 70.00 g (492 mmol) of methyl iodide in 150 cm^3 of diethyl ether was slowly added dropwise to a stirred slurry of 13.00 g (535 mmol) of magnesium turnings in 300 cm^3 of diethyl ether to form a Grignard reagent. To this stirred solution was slowly added dropwise a solution of 20.00 g (102 mmol) of redistilled 2 in 225 cm^3 of THF. Stirring was continued for 2 hours after the addition was completed, before adding aqueous acetic acid. The mixture was then poured into water and extracted with diethyl ether, the organic layer was separated, washed, dried over sodium sulphate and evaporated to dryness at reduced pressure. The product was purified by extracting the crude material with 40-60 petrol ether, and evaporating off this solvent at reduced pressure, (leaving behind a small amount of yellow residue), giving 10 in a yield of 21.46 g (99%) as a white powder of mp 91-93°C (lit[76] 91.5-92.5°C). ^{1}H-NMR as above.

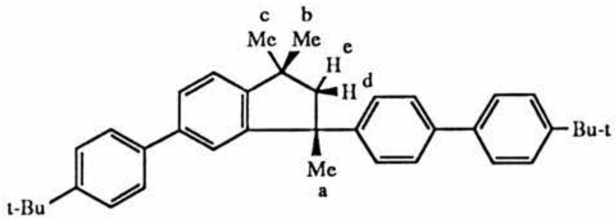
4-(1-Methylvinyl)biphenyl (11)

A small amount of p-toluenesulphonic acid was added to a solution of 20.00 g (94.2 mmol) of carbinol 10 in 200 cm^3 of toluene. The solution was heated to, and maintained at reflux until all of the water formed in the reaction had been removed azeotropically, using a Dean-Stark separator, about 1¾ hours. The reaction mixture was then washed with dilute aqueous sodium hydroxide after allowing it to cool to approx. 50°C, dried over magnesium sulphate and then evaporated to dryness. The crude product was then recrystallised from ethanol to yield 15.77 g (86%) of 11 as faintly tan lustrous flakes of mp 118-119°C (lit[83] 119.0-119.5°C).

2-(4'-t-Butyl-4-biphenyl)-2-propanol (4)

From 14: A solution of 0.80 g (2.8 mmol) of 14 in 20 cm^3 of diethyl ether was slowly added dropwise to a stirred slurry of 0.08 g (3.3 mmol) of magnesium turnings in 10 cm^3 of diethyl ether. The mixture was heated to and maintained at reflux for several hours, but no reaction occurred. Aqueous acetic acid was then added to the mixture, the organic layer was separated, washed with water, and dried over sodium sulphate. The solvent was evaporated off at reduced pressure, and the residue was recrystallised from ethanol to give 0.72 g (90% recovery) of 14 - determined by melting point and mixed melting point with reactant. The same procedure was carried out, but using THF instead of the diethyl ether. Again there was no reaction and 14 was obtained in 86% recovery. One further attempt, using 1,4-dioxan instead of diethyl ether, also failed.

From 10: To a stirred solution of 1.50 g (7.1 mmol) of 10 and a small amount of anhydrous ferric chloride in 25 cm^3 of methylene chloride was slowly added dropwise a solution of 1.30 g (14.0 mmol) of t-butyl chloride in 25 cm^3 of dry methylene chloride. No hydrogen chloride gas evolution was detectable. The reaction mixture was left standing overnight, then 1.20 g (7.4 mmol) of anhydrous ferric chloride was added. Gas evolution commenced, and the mixture was stirred for a further hour before pouring into water. The organic layer was separated, washed with dilute hydrochloric acid, dried over sodium sulphate and evaporated to dryness. The residue, about 20 components by TLC (4vol% toluene in 40-60 petrol ether) was chromatographed on silica in 4vol% toluene in 40-60 petrol ether, grading the eluant up to 100% toluene. Early fractions consisted of t-butylated biphenyls - determined by ^{1}H-NMR spectroscopy and mass spectrometry. Presumably the iso-propyl alcohol group is displaced by a t-butyl cation as protonated acetone. The third fraction obtained was a yellow-green tar, which on treating with boiling 2-propanol yielded 0.78 g (44%) of a white solid, believed to be the indan derivative 18 shown below, of mp 143-147°C.



18

Mass spectrometry shows an M^{+} peak at 500. 343400 and the 100% peak at M-15 (characteristic of t-butylbiphenyl derivatives). δ_H (CDCl$_3$) 1.11 (3H, s, Me-c) 1.33 (18H, s, 2xt-Bu) 1.39 (3H, s, Me-b) 1.77 (3H, s, Me-a) 2.27 (1H, d, J=13Hz, H-e) 2.50 (1H, d, J=13Hz, H-d) 7.13-7.70 (15H, m, aryl-H). (Assignment based on ref. 48).

4-t-Butyl-4'-(1-methylvinyl)biphenyl (5)

To a stirred mixture of approx. 0.10 g (0.6 mmol) of anhydrous ferric chloride in 15 cm^3 of methylene chloride was slowly added dropwise over ½ hour a solution of 1.00 g (5.1 mmol) of 11 and 0.55 g (5.9 mmol of t-butyl chloride in 25 cm^3 of methylene chloride. The mixture was stirred for a further ½ hour and poured into water. The organic layer was separated, washed with dilute hydrochloric acid, dried over sodium sulphate and evaporated to dryness to give a yellow-green tar. TLC (4vol% toluene in 40-60 petrol ether) showed a similar mixture to that obtained in the analagous preparation of 4 from 10, so the resolution of this mixture was not attempted.

4-t-Butylacetophenone (15)

To a stirred slurry of 42.00 g (315 mmol) of anhydrous aluminium chloride in 80 cm^3 of carbon tetrachloride chilled to -15°C, was slowly added dropwise a solution of 22 cm^3 (310 mmol) of acetyl chloride in 80 cm^3 of carbon tetrachloride over $\frac{1}{2}$ hour, the temperature rising to 0°C. At this temperature was slowly added dropwise a solution of 40.00 g (298 mmol) of t-butylbenzene in 80 cm^3 of carbon tetrachloride over $\frac{1}{2}$ hour, and the mixture was stirred a further hour before pouring onto ice. The organic layer was separated, washed twice with water, dried over magnesium sulphate and the solvent was evaporated off at reduced pressure. The crude material was distilled to give 45.71 g (87%) of 15 as a colourless liquid bp 148-150°C at water pump pressure, using an air-leak (lit[47] 137-138°C/16 Torr). δ_H ($CDCl_3$) 1.37 (9H, s, t-Bu) 2.63 (3H, s, Me) 7.52-7.80, 7.97-8.27 (4H, AA'BB', aryl-H).

2-(4-t-Butylphenyl)-2-propanol (16)

To a stirred slurry of 14.00 g (576 mmol) of magnesium turnings in 150 cm^3 of diethyl ether was slowly added dropwise a solution of 80.00 g (564 mmol) of methyl iodide in 350 cm^3 of diethyl ether to form a Grignard reagent. To the solution so formed was slowly added dropwise a solution of 45.71 g (259 mmol) of 15 in 250 cm^3 of diethyl ether. The mixture was stirred for a further hour and then aqueous acetic acid was added to give two coloured, but clear phases. The organic layer (red-brown) was separated, washed twice with water (remains coloured) then once with aqueous sodium hydroxide (becomes colourless), dried over sodium sulphate and the solvent was dried overnight in vacuo over phosphorus pentoxide to give 48.81 g (98%) of 16 as a white solid of mp 72-75°C (lit[84] mp 78.5°C). This crude material was used directly to prepare 17.

p-t-Butyl-α-methylstyrene (17)

A small amount of p-toluenesulphonic acid was added to a solution of 48.81 g (254 mmol) of crude carbinol 16 (of mp 72-75°C) in 1000 cm^3 of toluene, which was then heated to, and maintained at reflux for approx. 1 $\frac{1}{2}$ hours, removing water azeotropically using a Dean-Stark separator. The bulk of the toluene was evaporated off at reduced pressure, and the residue was redistilled from a Vigreux flask to give 41.33 g (93%) of 17 as a colourless liquid of bp 116-120°C at water pump pressure, using an air leak (lit^{48} 115°C/10 Torr). δ_H ($CDCl_3$) 1.35 (9H, s, t-Bu) 2.19 (3H, d.d, J=0.8Hz, 1.4Hz, Me) 5.15 (1H, d.quart, J=1.4Hz, 1.6Hz, Ar-C=C$\underline{H}$ trans) 5.46 (1H, d.quart, J=0.8Hz, 1.6Hz, Ar-C=C-$\underline{H}$ cis) 7.37-7.75 (4H, AA'BB', aryl-H).

1-(4-Biphenylyl)ethanol (19)

To a stirred solution of 10.00 g (51.0 mmol) of redistilled 2 in 130 cm^3 of methanol, 0.2M in sodium hydroxide was added in portions 2.00 g (52.9 mmol) of sodium borohydride over hour. The mixture was stirred a further 1 hours and was then poured into water. The organic material was extracted with diethyl ether, the ethereal layer washed twice with water, dried over sodium sulphate and the solvent evaporated off at reduced pressure to give 9.83 g (97%) of crude 19 as a white solid of mp 94-95°C (lit^{85} 98-99°C). δ_H ($CDCl_3$) 1.50 (3H, d, J=6.5Hz, CH_3) 2.07 (1H, s, OH) 4.87 (1H, quart, J=6.5Hz, CH) 7.10-7.70 (9H, m, aryl-H).

4-Vinylbiphenyl (20)

Method 1: A small amount of p-toluenesulphonic acid was added to a solution of 1.00 g (5.0 mmol) of crude 19 in 30 cm^3 of toluene, and the mixture heated to, and maintained at reflux for 3 hours with a Dean-Stark separator being employed. No water was collected. The solution was allowed to cool and was then washed with dilute sodium hydroxide solution, dried over sodium sulphate and evaporated to dryness at reduced pressure. Only unreacted 19 was obtained - determined by melting point and mixed melting point with reactant.

Method 2: A small amount of p-toluenesulphonic acid was added to a solution of 1.00 g (5.0 mmol) of crude 19 in 60 cm^3 of t-butylbenzene, and the mixture was heated to, and maintained at reflux for a total of 8 hours. The bulk of the solvent was then evaporated off in vacuo and the residue taken up in diethyl ether. The ethereal layer was washed with dilute sodium hydroxide solution after decanting off some insoluble organic material (presumably polymer), dried and evaporated to dryness at reduced pressure. The residue was recrystallised from ethanol to give 0.44 g (49%) of pale yellow-tan material of mp 110-118°C. This was again recrystallised from ethanol to give 0.29 g (32%) of solid, a mixture of pale ochre material and lustrous white flakes of mp 112-118°C. Further purification was not attempted.

1-(4-Biphenylyl)ethyl tosylate (21)

To a stirred solution of 1.89 g (9.5 mmol) of 19 in 20 cm^3 of dry pyridine at room temperature was added 1.85 (9.7 mmol) of p-toluenesulphonyl chloride. The mixture was stirred for a further 2 hours during which solid separated, and 40 cm^3 of diethyl ether were added to precipitate pyridine hydrochloride. The solid was filtered off (and not retained). The filtrate was evaporated to dryness at reduced pressure, but no product was obtained. Presumably the tosylate ester was converted to an N-alkyl pyridinium salt.

4-Acetyl-4'-bromobiphenyl (23)

To a stirred mixture of 20.00 g (85.5 mmol) of 13 and 14.00 g (105 mmol) of anhydrous aluminium chloride in 100 cm^3 of 1,1,2,2-tetrachloroethane cooled to 0^oC in an ice-salt bath, was slowly added dropwise a solution of 10.00 g (127 mmol) of acetyl chloride in 50 cm^3 of 1,1,2,2-tetrachloroethane, keeping the temperature below 5^oC. The mixture was stirred for a further 2 hours and poured onto ice. The organic layer was separated, washed three times with water, dried over sodium sulphate and the solvent was evaporated off in vacuo. The crude product was recrystallised from ethanol to give 19.76 g (84%) of 23 as white lustrous flakes of mp $127-128^oC$ (lit[43] $129-130^oC$). δ_H ($CDCl_3$) 2.62 (3H, s, Me) 7.3-7.73, 7.90-8.11 (8H, 2 overlapping AA'BB', aryl-H).

2-(4'-Bromo-4-biphenylyl)-2-propanol(24)

A solution of 51.00 g (359 mmol) of methyl iodide in 100 cm^3 of diethyl ether was slowly added dropwise to a stirred slurry of 9.50 g (391 mmol) of magnesium turnings in 650 cm^3 of ether. To the Grignard reagent so formed was slowly added dropwise a solution of 19.76 g (71.8

mmol) of 23 in 250 cm^3 of THF. The mixture was stirred for a further 1 hour after the addition was complete, and then aqueous acetic acid was added to destroy the excess of Grignard reagent. The ethereal layer was separated, washed twice with water, once with dilute sodium hydroxide solution and once more with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. This yielded 20.63 g (99%) of crude 24 of mp 138-140°C (lit[76] 143-145°C). δ_H ($CDCl_3$) 1.60 (6H, s, Me) 1.89 (1H, s, OH) 7.30-7.65 (8H, m, aryl-H).

4-Bromo-4'-(1-methylvinyl)biphenyl (25)

A small amount of p-toluenesulphonic acid was added to a solution of 20.63 g (70.8 mmol) of crude 24 in 250 cm^3 of toluene and the mixture was heated to, and maintained at reflux for 4 hours, removing water azeotropically with a Dean-Stark separator. The hot solution was then washed with dilute sodium hydroxide solution, then with water, and the solvent was evaporated off (also drying the product) at reduced pressure. The crude material was recrystallised from ethanol to give 16.98 g (88%) of 25 as white lustrous flakes of mp 138-140°C. δ_H ($CDCl_3$) 2.17 (3H, d.d., J=0.8Hz, 1.4Hz, CH_3) 5.12 (1H, d.quart., J=1.4Hz, 1.6Hz, Ar-C=C-H trans) 5.42 (1H, d.quart, J=0.8Hz, 1.6Hz, Ar-C=C-H cis) 7.33-7.68 (8H, m, aryl-H). Two further recrystallisations from ethyl acetate afforded a sample of mp 145-147°C. Analysis: calcd. for C_{15}-H_{13}Br: C, 65.95;H,4.8 Found: C,66.3; H, 4.8.

1-(4'-Bromo-4-biphenylyl)ethanol (26)

To a stirred solution of 10.00 g (36.3 mmol) of 23 in 100 cm^3 of methanol 0.2 M in sodium hydroxide, was added 1.00 g (26.4 mmol) of sodium borohydride in 3 portions over $\frac{1}{2}$ hour. The mixture was stirred for a further 1$\frac{3}{4}$ hours. The reaction mixture was then poured into water and extracted with ether, the organic layer was then washed three times with water, dried over sodium sulphate and evaporated to dryness. This yielded 9.80 g (97%) of crude 26 as a white powder of mp 145$\frac{1}{2}$-146$\frac{1}{2}$°C (lit[51] 148-150°C). The infra-red spectrum of this material shows that no ketone is present.

4-Bromo-4'-(1-chloroethyl)biphenyl (27)

To 30 cm^3 (414 mmol) of thionyl chloride was added 5.00 g (18.0 mmol) of 26, and the mixture was heated to, and maintained at reflux for an hour. The thionyl chloride was then evaporated off at reduced pressure, and the residue chromatographed on silica in 40-60 petrol ether to give 0.56 g (about 10%) of pale yellow solid of mp 98-180°C. Mass spectrometry shows the presence of 27 (lit[51] mp 110-112°C) and unreacted 26. The high melting component may well be bis(1-(4'-bromo-4-biphenylyl) ethyl)sulphite. No further purification was attempted.

1-(4'-Bromo-4-biphenylyl)ethyl tosylate (29)

Method 1: To a stirred solution of 1.00 g (3.6 mmol) of 26 in 50 cm^3 of dry pyridine at room temperature was added 0.75 g (3.9 mmol) of p-toluenesulphonyl chloride. The mixture was stirred for 1 hour and then poured into water and extracted with methylene chloride. The organic layer was separated, washed twice with water then once with dilute hydrochloric acid then once more with water, and dried over sodium sulphate. The solvent was then evaporated off at reduced pressure to leave almost no residue. Presumably a pyridinium tosylate salt was formed which was water soluble.

Method 2: To a solution of 4.84 g (17.5 mmol) of 26 in 50 cm^3 of toluene was added 1.50 g (37.5 mmol) of 60% sodium hydride dispersion and 5.00 g (26.2 mmol) of p-toluenesulphonyl chloride, and the mixture stirred a further 3 hours. Ethanol was cautiously added to destroy unreacted hydride and the solution was then washed with water and evaporated to dryness in vacuo. The crude material so obtained was shown to be impure reactant 26 by melting point and mixed melting point with 26.

4-Methylbiphenyl (30)

A solution of 35.00 g (327 mmol) of p-toluidine (recrystallised from 40-60 petrol ether) in 200 cm^3 of benzene was added dropwise to a stirred solution of 45 cm^3 (338 mmol) of iso-amyl nitrite in 150 cm^3 of benzene, chilled to its freezing point. After a further $\frac{1}{2}$ hour of stirring a further 3150 cm^3 of benzene were added and the solution was then heated to, and maintained at reflux for $3\frac{1}{2}$ hours. The bulk of the benzene was then distilled off and recovered. The remaining solvent and volatile side products were evaporated off at reduced pressure and the residue chromatographed on silica in 40-60 petrol ether. This yielded 34.88 g (63%) of impure 30, coloured red-orange by the presence of an azo compound. Considerable losses are incurred on recrystallisation. Trituration with methanol produces an almost colourless product 30 of mp 45-47°C (lit[76] 48.5-49.5°C) with the yield reduced to 28.06g (51%).

4-Acetyl-4'-methylbiphenyl (31)

A solution of 25.00 g (149 mmol) of 30 and 12.10 g (154 mmol) of acetyl chloride in 120 cm^3 of 1,1,2,2-tetrachloroethane was slowly added dropwise to a stirred slurry of 20.86 g (156 mmol) of anhydrous aluminium chloride in 80 cm^3 of 1,1,2,2-tetrachloroethane chilled to 0°C in an ice-methanol bath. The mixture was stirred a further 2 hours after the addition was completed, before pouring into ice-water. The organic layer was separated, washed twice with water, dried over sodium sulphate and the solvent evaporated off at reduced pressure. The crude product was then recrystallised from cyclohexane to yield 27.51 g (88%) of 31 as a white powder of mp 117-118 (lit[76]

122-123^{o}C), one component by TLC (toluene). δ_H (300MHz, $CDCl_3$) 2.41 (3H,s, aryl-CH_3) 2.62 (3H, s, C(O)-CH_3) 7.20-7.30, 7.47-7.56 (4H, AA'BB', Me-$C_6\underline{H}_4$), 7.60-7.70, 7.94-8.04 (4H, AA'BB', Ac-$C_6\underline{H}_4$)

2-(4'Methyl-4-biphenylyl)-2-propanol (32)

A solution of 10.00 g (70.5 mmol) of methyl iodide in 25 cm^3 of dry diethyl ether was slowly added dropwise to a stirred slurry of 1,80 g (74.1 mmol) of magnesium turnings in 50 cm^3 of dry diethyl ether to form a Grignard reagent. To this was slowly added dropwise a solution of 5.00 g (23.8 mmol) of 31 in 50 cm^3 of a 1:1 mixture of THF and diethyl ether. The mixture was stirred for 2 hours after the addition was completed, and then aqueous acetic acid was added to destroy excess Grignard reagent. Then, more water was added, the organic layer was separated, washed with dilute sodium hydroxide, then with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. The crude material was then recrystallised from 100-120 petrol ether to give 5.04 g (94%) of 32 as a pale yellow-tan powder of mp 106$\frac{3}{4}$-109^{o}C (lit^{76} 116-116.5^{o}C). δ_H ($CDCl_3$) 1.61 (6H, s, -C(OH)($C\underline{H}_3$)$_2$) 2.37 (3H, s, aryl-CH_3) 7.04-7.56 (8H, m, aryl-H).

4-(Bromoacetyl)biphenyl (34)

A mixture of 10.00 g (51.0 mmol) of 2 and 55 cm^3 of acetic acid was heated until the ketone had dissolved completely (about 60^{o}C) and was then cooled to about 40^{o}C. To this stirred solution was then slowly added dropwise 8.30g (51.9 mmol) of bromine in 5 cm^3 of acetic acid, keeping the temperature below 45^{o}C, and stirred for a further 2 hours. The reaction mixture was then cooled to 0^{o}C and the product filtered off, washed with a little acetic acid, then a little water and the damp filter cake was taken up in, and recrystallised from ethanol to yield 10.37g (74%) of 34 as faintly tan needles of mp 122-124^{o}C (lit^{54} 125.5^{o}C) δ_H ($CDCl_3$) 4.46 (2H, s, CH_2Br) 7.22-7.84, 7.93-8.22 (9H, m, aryl-H).

1-(4-Biphenylyl)-2-bromoethanol (35)

Method 1: To 75 cm^3 of t-butyl alcohol at 30^{o}C, while stirring was added 5.00 g (18.2 mmol) of 34, followed by 0.80g (36.7 mmol) of lithium borohydride (in 3 portions). The mixture effervesced and was stirred for an hour before pouring into water and extracting with diethyl ether. The organic layer was separated, washed twice with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. By TLC (20vol.% ethylacetate in cyclohexane) the crude material is a mixture of mostly unreacted 34 and some debrominated ketone 2, with a few other trace compounds.

Method 2: To a stirred mixture of 2.75 g (10.0 mmol) of 34 in 50 cm^3 of 2-propanol was added 0.20 g (5.3 mmol) of sodium borohydride, and the mixture was warmed to dissolve the ketone. This was stirred for an hour, poured into water and extracted with diethyl ether. The organic layer was separated, washed twice with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. TLC (20vol% ethyl acetate in cyclohexane) showed the crude product to consist of 2 major and 3 minor components. The crude material was chromatographed on silica in 20vol% ethyl acetate in cyclohexane. The first fraction obtained, about 0.5 g (18%) was shown to be a 1:1 mixture (perhaps a hydrogen bonded adduct) by ^{1}H-NMR of reactant 34 and product 35. δ_H ($CDCl_3$) 1.52 (1H, s, OH) 2.83 (1H, d.d., J=2.7Hz, 5.3Hz, -CH_2Br) 3.34 (1H, d.d., J=4Hz, 5.3Hz, -CH_2Br) 3.89 (1H, d.d., J=2.7Hz,4Hz, -C$\underline{H}$-CH_2Br) 7.22-7.76 (9H, m, aryl-H). The other major fraction was shown to be the debrominated alcohol 19 by TLC (20vol.% ethyl acetate in cyclohexane) against 19, and by melting point and mixed melting point with 19.

The procedure was repeated but using 1:1 mixed solvent of THF and 2-propanol. A similar mixture of products was found, containing 34, 35, 2 and 19 as major components.

4-(Chloroacetyl)biphenyl (36)

To a stirred mixture of 60.00 g (389 mmol) of biphenyl and 54.00 g (405 mol) of anhydrous aluminium chloride in 800 cm^3 of 1,1,2,2-tetrachloroethane chilled to 3°C in an ice bath, was slowly added dropwise a solution of 16.5 cm^3 (2.07 mmol) of chloroacetyl chloride in 200 cm^3 of 1,1,2,2-tetrachloroethane over 45 minutes, keeping the temperature below 10°C. The reaction mixture was stirred a further 2 hours and left to stand overnight, before pouring into a litre of ice-water. The organic layer was then separated, washed once with water, then once with dilute sodium hydroxide, dried over sodium sulphate and evaporated to dryness in vacuo. The crude product may be purified either by recrystallisation from 30vol.% ehtyl acetate in ethanol to give 77.23 g (86%) of 36 as greenish-brown crystals of mp 124-126 $^\circ$C, or by column chromatography on silica in chloroform followed by trituration with cyclohexane to give 76.31 g (85%) of 36 as tan crystals of mp 125-127°C (lit[42] 122-123°C). δ_H ($CDCl_3$) 4.70 (2H, s, CH_2Cl) .7.32-7.83, 7.92-8.15 (9H, m, aryl-H).

1-(4-Biphenylyl)-2-chloroethanol (37)

Method 1: To 50 cm^3 of methanol was added 2.00 g (8.7 mmol) of 36, and the stirred mixture was heated until the ketone had dissolved. To the stirred solution was then added 0.30 g (7.9 mmol) of sodium borohydride. After a further 1¾ hours of stirring - allowing the mixture to come to room temperature - the solution was poured into water and extracted with ethyl acetate. The organic layer was then separated, washed twice with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. TLC (20vol% ethyl acetate in cyclohexane) showed the presence of three main components; reactant 36, product 37 and the debrominated alcohol 19. The crude material was then chromatographed on silica, eluting with 20vol% ethyl acetate in cyclohexane. The second fraction obtained was recrystallised from ethanol to yield 0.57 g (28%) of 37 as a yellowish powder of mp 88-91°C.

The use of a co-solvent was then examined.

Method 2: A solution of 2.00 g (8.7 mmol) of 36 in 30 cm^3 ethyl acetate was slowly added dropwise to a stirred solution of 0.33 g (8.7 mmol) of sodium borohydride in 40 cm^3 of methanol. This mixture was stirred for a further 2 hours after the addition was completed, before pouring into water and extracting with ethyl acetate. The organic layer was separated, washed twice with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. TLC (10vol% ethyl acetate in cyclohexane on silica) showed three major components as before; unreacted 36, product 37 and side-product 19. The crude material was chromatographed on silica, eluting with 10vol% ethyl acetate in cyclohexane. The second fraction was recrystallised from ethanol to yield 0.95 g (49%) of 37 as a white powder of mp 92-95°C. (Anderson[86] obtained 37 as a yellow viscous oil by a similar method). δ_H ($CDCl_3$) 2.64 (1H, s, OH) 3.68 (1H, d.d., J=8Hz, 11Hz, $-CH_2CL$) 3.78 (1H, d.d., J=4Hz, 11Hz, $-CH_2Cl$) 4.95 (1H, d.d., J=4Hz, 8Hz, -CH- OH) 7.28-7.77 (9H, m, aryl-H).

Method 3: To a stirred solution of 10.00 g (43.3 mol) of 36 in 75 cm^3 of dry THF was added 150 cm^3 of methanol (some of the ketone precipitates), and then 1.64 g (43.4 mmol) of sodium borohydride was added in portions over 30 minutes. The mixture was stirred for a further hour before pouring into water and extracting the organic material with diethyl ether. The organic layer was separated, washed twice with water, dried over sodium sulphate and evaporated to dryness to give 10.06 g (100%) crude product. Column chromatography on silica in chloroform, followed by recrystallisation from 20vol% ethanol in cyclohexane affords 6.36 g (63%) of 37 as a faintly greenish-white powder of mp 91-92°C. ^{1}H-NMR as above.

1-(4-Biphenylyl)oxirane (38)

Method 1: A 5.00 g sample of aged 4-vinylbiphenyl (20) was recrystallised twice from ethanol to give 3.56 g of purified product. To a solution of 3.56 g (19.8 mmol) of 20 in 75 cm^3 of methylene chloride was added 75 cm^3 of 1M aqueous sodium bicarbonate solution. To the stirred mixture was then added 3.42 g (19.8 mmol) of MCPBA in three portions over 30 minutes. The mixture was left stirring overnight, and a further 3.42 g (19.8 mmol) of MCPBA was added in three portions over 30 minutes the following day. After stirring for a further 4 hours the organic layer was separated, washed once with 75 cm^3 of 1M aqueous sodium bicarbonate solution, dried over sodium sulphate and evaporated to dryness at reduced pressure. The crude material was chromatographed on silica in toluene and recrystallised from 10vol.% benzene in cyclohexane to yield 0.93 g (24%) of 38 of mp 56-60°C (lit[56] 96-97°C) ^{1}H-NMR also shows a great deal of contamination.

<u>Method 2</u>: To a stirred slurry of 0.50 g (12.5 mmol) of 60% sodium hydride dispersion in 50 cm^3 of unpurified THF was added 2.33 g (10.0 mmol) of 37. This was stirred for 30 minutes at room temperature, before heating to and maintaining at reflux for 1.5 hours. The mixture was then allowed to cool, filtered through celite and evaporated to dryness at reduced pressure. The crude material was then recrystallised from ethanol to yield 1.73 g (88%) of 38 as colourless flakes of mp 80-81°C (lit[56] 96-97°C) δ_H ($CDCl_3$) 2.85 (1H, d.d., J=2.5Hz, 5.5Hz, $-CH-C\underline{H}_2$ trans) 3.18 (1H, d.d., J=4Hz, 5.5Hz, $-CH-C\underline{H}$ cis) 3.90 (1H, d.d., J=2.5Hz, 4Hz, $ArC\underline{H}-$) 7.16-7.76 (9H, m, aryl-H). TLC (Toluene on silica) shows the presence of impurities, although these were not discernable in the ^{1}H-NMR.

When this procedure was repeated, but using 100 cm^3 of purified (dried and redistilled) THF with the same quantities of 37 and sodium hydride, product 38 was obtained in a yield of 1.48 g (75%) as slightly yellowish flakes of mp 91-92°C (lit[56] 96-97°C) δ_H (300MHz, $CDCl_3$) 2.85 (1H, d.d., J=2.5Hz, 5.3Hz, -CH-C<u>H</u>$_2$ trans) 3.18 (1H, d.d., J=4Hz, 5.3Hz, -CH-C<u>H</u> cis) 3.91 (1H, d.d., J=2.5Hz, 4Hz, ArC<u>H</u>-) 7.28-7.48 (5H, m, $-C_6H_5$) 7.53-7.63 (4H, m, $-C_6H_4-$).

When crude 37 (i.e. not recrystallised) was used, the reaction mixture turned dark brown, and none of the product 38 could be isolated from the mixture.

<u>1-(4-Biphenylyl)-1-methyloxirane (39)</u>

To a stirred solution of 1.00 g (5.1 mmol) of 11 in 25 cm^3 of methylene chloride was added 25 cm^3 of 1M aqueous sodium bicarbonate solution. To this stirred mixture was then added 0.89 g (5.2 mmol) of MCPBA, and the mixture was left stirring for 6 hours. A further 0.89 g (5.2 mmol) of MCPBA was then added and the mixture stirred for a further 6 hours. The organic layer was then separated, washed once with 25 cm^3 of 1M aqueous sodium bicarbonate solution and evaporated to dryness at reduced pressure. This yielded a fluorescent yellow-green oil which could not be induced to crystallise by trituration with a number of solvents, and could not be distilled at reduced pressure even using an oil pump and heating to 250°C.

2-(4-Biphenylyl)-1-bromo-2-propanol (40)

To a stirred solution of 2.00 g (10.3 mmol) of 11 in 50 cm^3 of dry DMSO was added 2.10 g (11.8 mmol) of NBS and 0.5 cm^3 (2.8 mmol) of water. After 30 minutes of stirring the mixture was poured into 800 cm^3 of water and was extracted with 100 cm^3 of methylene chloride. The organic layer was then washed twice with water, once with dilute hydrochloric acid, dried over sodium sulphate and evaporated to dryness at reduced pressure. This also produced a yellow-green tar which proved irresolvable.

4-t-Butyl-4'(chloroacetyl)biphenyl (41)

To a stirred slurry of 1.45 g (10.9 mmol) of anhydrous aluminium chloride in 15 cm^3 of carbon tetrachloride chilled to 0^oC was slowly added dropwise a solution of 1.20 g (10.6 mmol) of chloroacetyl chloride in 15 cm^3 of carbon tetrachloride, keeping the temperature below 5^oC. To the solution so formed was slowly added dropwise a solution of 2.10 g (10.0 mmol) of 6 in 15 cm^3 of carbon tetrachloride, keeping the temperature below 10^oC. The mixture was stirred for a further hour before pouring into ice-water. The organic layer was separated, washed twice with water, once with dilute sodium hydroxide solution, dried over sodium sulphate and evaporated to dryness at reduced pressure. TLC (toluene on silica) showed the presence of 5 components in the tarry product. The resolution of this mixture was not attempted.

4-Bromo-4'-(bromoacetyl)biphenyl (42)

To a solution of 1.87 g (6.8 mmol) of 23 in 40 cm^3 of a 1:1 (vol.) mixture of acetic acid and chloroform, was added, 1.21 g (6.8 mmol) of N-bromosuccinimide. The mixture was then heated to and maintained at reflux for 90 minutes, and then poured into water after cooling to ambient temperature and filtering off succinimide. The organic layer was then separated, washed with water, then dilute sodium hydroxide solution, dried over sodium sulphate and evaporated to dryness at reduced pressure. ^{1}H-NMR of the crude material indicated a 1:1 mixture of product 42 and reactant 23, so the above reaction sequence was repeated with this crude material. This produced 2.22 g of material which was recrystallised from cyclohexane to give 1.77 g (74%) of 42 of mp 130-135°C (lit[87] 138-140°C). ^{1}H-NMR shows the pressence of about 10% of 23. δ_H ($CDCl_3$) 4.46 (2H, s, $-CH_2Br$) 7.35-7.80, 7.92-8.18 (8H, 2 overlapping AA'BB', aryl-H).

1-(4'-Bromo-4-biphenylyl)oxirane (43)

To 25 cm^3 of t-butyl alcohol in a thermostatted oil bath at 30°C was added with stirring approx. 0.25 g (36 mmol) of lithium metal to generate lithium t-butoxide in situ. To this stirred mixture was added 0.22 g (10.1 mmol) of lithium borohydride followed by 1.77 g (contains 4.5 mmol) of impure 42. The mixture was stirred for a further hour and then poured into water and extracted with ether.

The organic layer was separated, washed twice with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. The 80MHz ^{1}H-NMR spectrum of the crude material showed that 43 was present, but the integral over the aromatic region was twice the size it ought to have been, and t-butyl alcohol was also present. The 300MHz ^{1}H-NMR spectrum of this material showed the presence of a broad peak in the aromatic region, and a broad peak around δ1.5, so presumably some polymerisation occurred. Purification of this material was not attempted. The product has the following spectrum. δ_H (300MHz, $CDCl_3$) 2.90 (1H, d.d., J=2.4Hz, 5.4Hz, -CH-C$\underline{H}_2$ trans) 3.18 (1H, d.d., J=4Hz, 5.4Hz, -CH-C$\underline{H}_2$ cis) 3.91 (1H, d.d., J=2.4Hz, 4Hz, aryl-CH) 7.51-7.59 (4H, m, aryl-H).

1-(4'-Bromo-4-biphenylyl)-1-methyloxirane (44)

To a stirred solution of 5.00 g (18.3 mmol) of 25 in 100 cm^3 of methylene chloride was added 4 cm^3 (35.6 mmol) of 100 vol. hydrogen peroxide in 100 cm^3 of 0.2 M sodium bicarbonate solution. To this stirred mixture was added 1.10 g (18.3 mmol) of glacial acetic acid. Stirring was maintained for a further 3 hours. The organic layer was then separated, washed once with water, then dilute sodium hydroxide solution, dried once over sodium sulphate and evaporated to dryness to give 4.45 g (89% recovery) of material of mp 148-153^{o}C shown to be mostly unreacted 25 by ^{1}H-NMR.

Methyl Hydrogen Succinate (50a)

To 750 cm^3 of methanol was added, with stirring, 100.0g (1 mole) of succinic anhydride. The mixture was stirred until all the succinic anhydride had dissolved - about 45 minutes - and stirring was continued for a further 30 minutes. The methanol was then evaporated off at reduced pressure. The residue was then extracted with, and crystallised from carbon tetrachloride to give 96.89g (73%) of 50a as a white powder of mp 55-57°C (lit[65] 57-58°C).

3-Methoxycarbonylpropanoyl Chloride (50b)

To 50 cm^3 of thionyl chloride was added 20.00 g (151 mmol) of 50a. The mixture was then heated to, and maintained at reflux for 2 hours. The bulk of the excess thionyl chloride was then distilled off at atmospheric pressure, and the residue was then distilled at diminished pressure. This gave 17.54 g (77%) of 50b as a colourless liquid of bp. 78-80°C at water pump pressure (lit[65] 92-93°C/18Torr).

4-(4-Biphenylyl)-4-oxobutanoic Acid (51b)

To a stirred mixture of 10.00 g (64.8 mmol) of biphenyl and 6.49 g (64.9 mmol) of succinic anhydride in 100 cm^3 of 1,1,2,2-tetrachloroethane, was slowly added in portions 17.29 g (130 mmol) of anhydrous aluminium chloride over 30 minutes. The mixture was stirred for a further 2 hours and then poured into ice-water. The organic layer was then separated, washed twice with water, then with dilute hydrochloric acid, dried over sodium sulphate and evaporated to dryness at reduced pressure. The crude material was taken up in hot toluene, and the acid extracted out with dilute potassium hydroxide solution. The aqueous layer was separated and acidified with concentrated hydrochloric acid to pH6, and the precipitated acid was filtered off, washed with water and dried in vacuo over phosphorus pentoxide to give 5.46 g (33%) of 51b of mp 175-177°C (lit[64] 183°C. δ_H ($CDCl_3$) 1.26 (1H, s, OH) 2.85 (2H, t, J=6Hz, $-C\underline{H}_2-CO_2H$) 3.36 (2H, t, J=6Hz, $Ar-CO-C\underline{H}_2-$) 7.22-7.83, 7.97-8.19 (9H, m, aryl-H).

Biphenyl Solvent Reaction

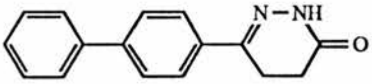
A mixture of 10.00 g of biphenyl, 2.00 g of anhydrous aluminium chloride and 200 cm^3 of 1,1,2,2,-tetrachloroethane was heated to, and maintained at reflux for 3 hours. Black material caked the inside of the flask before reflux had been achieved, and bumping was a serious problem. After allowing the mixture to cool to room temperature, the black material was filtered off and dried overnight in an oven at 100°C, yield 13.21 g. The substance is most probably a cross-linked polymer - heating above a naked flame on a spatula, it eventually burns without melting.

Methyl 4-(4-Biphenylyl)-4-oxobutanoate (51a)

To a stirred mixture of 20.05 g (130 mmol) of biphenyl and 34.67 g (260 mmol) of anhydrous aluminium chloride in 200 cm^3 of 1,1,2,2-tetrachloroethane, chilled to 5°C, was slowly added dropwise 19.59 g (130 mmol) of 50b in solution in 50 cm^3 of 1,1,2,2-tetrachloroethane, keeping the temperature below 5°C. The mixture was stirred a further 2 hours before pouring into ice-water. The organic layer was separated, washed twice with water, once with dilute hydrochloric acid, dried over sodium sulphate and evaporated to dryness in vacuo. The crude material was then recrystallised from methanol to give 29.88 g (86%) of 51a as a slightly off-white powder of mp 101-103°C (lit[68] 99-100°C. δ_H (DMSO-d_6) 2.70 (2H, t, J=6Hz, -$\underline{CH_2}$-CO_2Me) 3.36 (2H, t, J=6Hz, Ar-CO-$\underline{CH_2}$-) 3.39 (3H, s, CH_3) 7.32-8.29 (9H, m, aryl-H).

4-(4-Biphenylyl)butanoic Acid (52a)

Method 1: To a solution of 10.00 g (178 mmol) of potassium hydroxide in 110 cm^3 of ethylene glycol was added 10.09 g (37.6 mmol) of 51a and the mixture was heated to, and maintained at reflux for 1 hour. The 3.80 g (75.9 mmol) of hydrazine hydrate was added after allowing the mixture to cool. The mixture was then related to, and maintained at reflux for 1 hour, then material was distilled off until the distillate temperature reached 190°C and the remaining solution was refluxed for a further 3 hours. The mixture was then allowed to cool and was poured into water and extracted with methylene chloride. The organic layer was separated, washed twice with water, dried over sodium sulphate and evaporated to dryness. The crude material was recrystallised from glacial acetic acid to give 4.03 g of buff coloured material of mp 220-225°C (decom) (lit[68] for 52a mp 116-117°C) 2.00 g of this material was recrystallised from glacial acetic acid to give 1.33 g of pink lustrous flakes of mp 234-237 (decom). This was identified as the pyridizinone 56.



56

(lit[88] mp 248°C). δ_H (DMSO-d_6) 2.47 (2H, t, J=8Hz, -C$\underline{H}_2$-CH$_2$CO-) 3.00 (2H, t, J=8Hz, -C$\underline{H}_2$-CO-) 7.20-8.08 (9H, m, aryl-H) 11.00 (1H, s, =N-H). The mass spectrum shows M$^+$=250.

Method 2: Ester 51a was hydrolysed to acid 51b by heating to reflux a mixture of 51a with a two-fold excess of 1M potassium hydroxide solution for 2 hours, and then extracting the hot solution with toluene to remove unreacted 51a before neutralising with concentrated hydrochloric acid. The precipitated acid 51b was then reduced as follows, and the ester in the toluene extract was recycled after evaporating off the solvent.

To a solution of 6.57 g (11.7 mmol) of potassium hydroxide in 100 m^3 of ethylene glycol was added 7.00 g (27.5 mmol) of 51b and 2.84 g (56.7 mmol) of hydrazine hydrate. The mixture was heated to and maintained at reflux for 1 hour, and then material was distilled off until the temperature reached 190°C. The mixture was then maintained at reflux for a further 5 hours. The mixture was then poured into water while still hot, and the pH was taken to 6.5 with hydrochloric acid. The molten acid which separated was then extracted with hot toluene. The organic layer was then washed twice with hot water and the acid was then extracted back into the aqueous phase with potassium hydroxide solution. The aqueous phase was then separated and neutralised with hydrochloric acid, and the product was then extracted with butanone. The organic layer was separated, dried over sodium sulphate and evaporated to dryness at reduced pressure. The crude product was recrystallised from 2-propanol to yield 3.77 g (57%) of 52a as a pale tan powder of mp 114-116°C (lit[68] 116-117°C) δ_H ($CDCl_3$) 1.00 (2H, t.t., J=7Hz, 7.3Hz, $-CH_2-CH_2-CH_2-$) 2.40 (2H, t, J=7Hz, $Ar-CH_2-$) 2.72 (2H, t, J=7.3Hz, $-C\underline{H}_2-CO_2H$) 7.17-7.75 (9H, m, aryl-H) 9.75 (1H, s, $-CO_2H$).

iso-Propyl 4-(4-Biphenylyl)butanoate (52b)

The above procedure was repeated, but instead of simply recrystallising the acid 52a, hydrogen chloride gas was bubbled into a 2-propanol solution of 52a which was then maintained at reflux for 1 hour. Some of the solvent was then evaporated off at reduced pressure to concentrate the solution to crystallise the product in 2-3 crops. In this manner 52b was obtained in 52% overall yield from 51b as white flakes of mp 56-57^{o}C. A second crystallisation from methanol gave 52b as lustrous white flakes of mp 57-58^{o}C. δ_H ($CDCl_3$) 1.23 (6H, d, J=6.3Hz, $-CH(C\underline{H}_3)_2$) 1.97 (2H, t.t., J=7Hz, 7.5Hz, $-CH_2-C\underline{H}_2-CH_2$) 2.31 (2H, t, J=7.5Hz, $Ar-CH_2-$) 2.68 (2H, t, J=7Hz, $-CH_2-CO-$) 5.03 (1H, h, J=6.3Hz, -O-CH=) 7.17-7.68 (9H, m, aryl-H).

4-(4-Biphenylyl)-1-butanol (53)

A solution of 6.00 g (21.2 mmol) of 52b in 15 cm^3 of THF was slowly added dropwise to a stirred slurry of 1.00 g (26.4 mmol) of lithium aluminium hydride in 15 cm^3 of THF, maintained at reflux under nitrogen gas, over a period of 25 minutes. Reflux was maintained for a further 4 hours, and then ethyl acetate was slowly added to the mixture to destroy the excess of hydride. The mixture was then poured into water and extracted with diethyl ether. The organic layer was separated, washed once with water, dried over sodium sulphate and evaporated to dryness. TLC (toluene on silica) showed the presence of two major components. This mixture was not resolved.

1,3-Di-t-butylbenzene (57)

To a stirred mixture of 5.00 g (37.3 mmol) of t-butylbenzene and 5.00 g (37.5 mmol) of anhydrous aluminium chloride in 100 cm^3 of 1,1,2,2-tetrachloroethane, chilled in an ice bath, was slowly added dropwise a solution of 3.45 g (37.3 mmol) of t-butyl chloride in 30 cm^3 of 1,1,2,2-tetrachloroethane. The mixture was stirred for a further hour after the addition was completed, before washing with ice cold dilute hydrochloric acid. The organic layer was then separated, washed copiously with water, dried over sodium sulphate and then the solvent and unreacted t-butylbenzene were evaporated off at reduced pressure. The residue was chromatographed on silica in 40-60 petrol ether to yield 3.65 g of a yellow oil. ^{1}H-NMR indicates that this is a mixture of a desired product 57, the para-isomer 60 and tri-t-butylbenzene 66.

1,4-Di-t-butylbenzene (60)

To a stirred solution of 15,00 g (112 mmol) of t-butylbenzene and 16.00 g (173 mmol) of t-butyl chloride in 50 cm^3 of methylene chloride was added a small amount of anhydrous ferric chloride. Effervescence ensued, the mixture was stirred for a further hour and then water was added. The organic layer was separated, washed once with water, dried over sodium sulphate, and the solvent was evaporated off at reduced pressure. The crude material was recrystallised from methanol to give 15.91 g (75%) of 60 as colourless needles of mp 75-78°C (lit[89] 80-81°C).

1,4-Di-t-butyl-2-nitrobenzene (61a)

To a stirred solution of 5.00 g (26.3 mmol) of 60 in 20 cm^3 of acetic anhydride chilled to 5^oC in an ice-bath was cautiously added dropwise 3 cm^3 (47.3 mmol) of 70% nitric acid over 15 minutes keeping the temperature below 15^oC. The mixture was stirred for a further 30 minutes before pouring into ice-water. The organic material was extracted with diethyl ether, the organic layer was then separated, washed once with water, once with dilute sodium hydroxide, dried over sodium sulphate and evaporated to dryness at reduced pressure. This produced a yellow oil which crystallised on trituration with a very small amount of methanol. The solid was then recrystallised from methanol to give 3.41 g (55%) of 61a as almost colourless flakes of mp 82-85^oC (lit[46] 75-78^oC). δ_H ($CDCl_3$) 1.30 (9H, s, t-Bu) 1.38 (9H, s, t-Bu) 7.23-7.35, 7.40-7.53 (3H, m, aryl-H) δ_C ($CDCl_3/CHCl_3$) 30.69, 30.96 (CH_3) 34.46, 35.20 ($-\underline{C}(CH_3)_3$) 120.78 (C-3) 127.81, 128.31 (C-5, C-6) 138.11 (C-2) 150.43, 151.19 (C-1, C-4).

2,5-Di-t-butylaniline (61b)

To a solution of 2.00 g (8.5 mmol) of 61a in 50 cm^3 of ethanol was added 0.10 g of 5% palladium on charcoal. On attempted hydrogenation of this compound, only about 70 cm^3 of hydrogen gas was taken up in the course of 4 days, whereas approx. 600 cm^3 are required.

3,5-Di-t-butyltoluene (63)

To a stirred mixture of 7.00 g (76.0 mmol) of toluene and 1.00g (7.5 mmol) of anhydrous aluminium chloride in 25 cm^3 of 1,1,2,2-tetrachloroethane chilled to 5°C was slowly added dropwise 15.00 g (162 mmol) of t-butyl chloride keeping the temperature below 5°C. This was stirred for a further hour before washing out the aluminium chloride. The organic material was distilled at reduced pressure. This yielded 5.24 g (34%) of 63 of bp 110°C at water pump pressure (lit[73] 98°C/5.7Torr) a colourless liquid which solidified on standing after 4 days, mp 30-32°C (lit[73] 31-32°C). δ_H ($CDCl_3$) 1.32 (18H, s, t-Bu) 2.33 (3H, s, CH_3) 7.00 (2H, s, aryl-H) 7.21, 1H, s, aryl-H).

1,3,5-Tri-t-butylbenzene (66)

To a stirred mixture of 10.00g (74.5 mmol) of t-butylbenzene and 1.00 g (7.5 mmol) of anhydrous aluminium chloride in 20 cm^3 of 1,1,2,2-tetrachloroethane, chilled to 5°C, was slowly added dropwise 35.00 g (378 mmol) of t-butyl chloride. The mixture was stirred for a further hour before adding water and washing out the aluminium chloride. The organic layer was then separated, dried over sodium sulphate and solvent and unreacted t-butylbenzene were evaporated off at reduced pressure. The residue which part crystallised was triturated with methanol and the solid filtered off. The filtrate was then redistilled at reduced pressure to give a little more of the product. Combining the samples gave a yield of 8.47g (46%) of 66 as colourless flakes of mp 70-72°C (lit[74] 73-73.5°C). δ_H ($CDCl_3$) 1.33 (27H, s, t-Bu) 7.23 (3H, s, aryl-H).

3,3',5,5'-Tetra-t-butylbiphenyl (68)

To a stirred solution of 1.00 g (6.5 mmol) of biphenyl and 4.80 g (51.9 mmol) of t-butyl chloride on 50 cm^3 of 1,1,2,2-tetrachloroethane, chilled to 0°C, was added 0.40 g (3.0 mmol) of anhydrous aluminium chloride. The mixture was stirred for a further hour before adding water to wash out the aluminium chloride. The organic layer was then evaporated off at reduced pressure. This produced a green tar, which consists of mono-, di- and tri-t-butyl biphenyls: M^+ peaks at 210, 266, 322 and M-15 peaks (loss of CH_3) at 195, 251 and 307.

4-(1-Bromo-1-methylethyl)biphenyl (69)

A solution of 5.00 g (23.6 mmol) of 10 in 20 cm^3 of methylene chloride was shaken with 20 cm^3 of 47% hydrobromic acid, and then allowed to settle. The organic layer was run off, dried over sodium sulphate and evaporated to dryness. This produced a brown glass which by TLC (4vol.% toluene in 40-60 petrol ether on silica) contains about ten components.

4-(1-Chloro-1-methylethyl)biphenyl (70)

Method 1: To 25 cm^3 of thionyl chloride was cautiously added 10.00 g (47.1 mmol) of 10. The solution effervesced vigorously as the carbinol was added.

The solution was then heated to, and maintained at reflux for an hour before evaporating to dryness at reduced pressure. This produced a very thick brown tar, which by TLC (4vol.% toluene in 40-60 petrol ether on silica) contains about eight components.

Method 2: A solution of 2.00g (7.4 mmol) of 10 in 20 cm^3 of methylene chloride was shaken with 20 cm^3 of 36% hydrochloric acid, and then allowed to settle. The organic layer was run off, dried over sodium sulphate and evaporated to dryness at reduced pressure. By TLC (4vol.% toluene in 40-60 petrol ether on silica) this mixture contained about a dozen components.

Method 3: Hydrogen chloride gas was generated by adding 98% sulphuric acid dropwise into a stirred slurry of sodium chloride in 36% hydrochloric acid, the gas being dried by passing through 98% sulphuric acid.

A stirred solution of 2.00g (9.5 mmol) of 10 in 20 cm^3 of methylene chloride was treated with dry hydrogen chloride gas for 20 minutes, while maintained at 0°C in an ice-water bath.

The solution was then dried over a little sodium sulphate and evaporated to dryness at reduced pressure. TLC (4vol.% toluene in 40-60 petrol ether on silica) showed that the brown glass obtained consisted of at least six components.

1,1'-methylenebis(4-nitrobenzene) (72)

Method 1: To a stirred solution of 5.00g (29.7 mmol) of diphenylmethane in 40 cm^3 of acetic anhydride chilled to 5°C was slowly added dropwise 8.00g (88.7 mmol) of 70% nitric acid, keeping the temperature below 15°C. The mixture was stirred for an hour after the addition was completed, before pouring the mixture into water. The organic material was then extracted with diethyl ether, the organic layer was separated and then washed with water, the dilute sodium hydroxide solution, dried over sodium sulphate and evaporated to dryness at reduced pressure. The crude material was then crystallised from ethanol to yield 4.19g (55%) of golden-brown needles. ^{1}H-NMR shows this to be a 2:1 mixture of the desired product 72 and the ortho- and para-substituted isomer.

Method 2: A mixture of 10.00g (59.4 mmol) of diphenylmethane and 10 cm^3 of methylene chloride was added dropwise over 25 minutes with stirring to 50 cm^3 of 70% nitric acid chilled to 0°C in an ice-salt bath. This mixture was stirred a further hour before pouring into ice-water. The organic material was then extracted with methylene chloride, the organic layer separated, washed once with water, once with dilute sodium hydroxide, dried over sodium sulphate and the solvent evaporated off. TLC (40-60 petrol ether on silica) of the liquid obtained showed that very little conversion had occurred.

Method 3: To a stirred ice-cold mixture of 20 cm^3 of 98% sulphuric acid and 23 cm^3 of 70% nitric acid was added dropwise a mixture of 10.00g (59.4 mmol) of diphenylmethane and 15 cm^3 of methylene chloride over 30 minutes. The mixture was stirred a further 30 minutes before pouring onto ice. The mixture was then diluted with water and extracted with methylene chloride. the organic layer was separated, washed once with water, then dilute sodium hydroxide solution, dried over sodium sulphate and evaporated to dryness at reduced pressure. The crude product was twice recrystallised from ethanol to yield 4.01g (26%) of 72 as golden brown needles of mp 176-178°C (lit[90] 188°C). δ_H ($CDCl_3$) 4.21 (2H,s,CH_2) 7.13-7.56, 8.05-8.40 (8H, AA'BB', aryl-H).

4,4'-Methylenebis(biphenyl) (74)

Method : To a solution of 1.00g (6.5 mmol) of biphenyl in 50 cm^3 of methylene chloride was added 0.20g of anhydrous aluminium chloride, and the mixture was then heated to and maintained at reflux for 2 hours. The solution was then allowed to cool and water was added. The organic layer was then separated, dried over sodium sulphate and evaporated to dryness at reduced pressure to give a red tar. TLC (40-60 petrol ether on silica) of this material showed the presence of about six components. Column chromatography on silica eluting with 40-60 petrol ether gave impure samples of the first three fractions. These were identified by mass spectrometry as biphenyl (M=154), product 74 (M=320) and di-methylenetris(biphenyl) (M=486). The other components are presumably higher oligomers.

Method 2: To a stirred solution of 1.00g (11.8 mmol) of methylene chloride and 3.63g (23.5 mmol) of biphenyl in 100 cm^3 of 1,1,2,2-tetrachloroethane was added 0.35g of anhydrous aluminium chloride. The mixture was then stirred at 50°C for 90 minutes, before adding water. The organic layer was then separated, washed once with water, dried over sodium sulphate and evaporated to dryness in vacuo. TLC (40-60 petrol ether on silica) shows a similar mixture to that obtained by method 1, except that there is more unreacted biphenyl, and a higher proportion of the higher molecular weight fractions.

2-(2-(2-Methoxyethoxy)ethoxymethyl)oxirane (77)

Method 1: To a stirred slurry of 2.00g (50.0 mmol) of 60% sodium hydride dispersion in 125 cm^3 of dry THF under nitrogen was slowly added 5.00g (41.6 mmol) of 2-(2-methoxyethoxy)ethanol. The mixture was stirred until effervescence had ceased (30 minutes) and then 10.00g (108 mmol) of epichlorohydrin was added over 20 minutes. The mixture was then stirred for a further hour before heating it to, and maintaining it at reflux for 2 hours. The mixture was then allowed to cool to room temperature and was filtered through celite and the THF was evaporated off at diminished pressure. The residue was then distilled to give 3.51g (48%) of 77 as a colourless liquid of bp 120°C at water pump pressure (lit[78] 116°C/5 torr). δ_H ($CDCl_3$) 2.59 (1H, dd., J=2.5H_z, 5H_2, - $CH\text{-}C\underline{H}_2$ trans) 2.77 (1H, dd., J=5Hz, 5Hz, $CH\text{-}C\underline{H}_2$ cis) 3.13 (1H, m, $\text{-}C\underline{H}\text{-}CH_2$) 3.38 (3H, s,$CH_3$) 3.27-3.93 (10H, m, $\text{-}O\text{-}CH_2\text{-}$).

<u>Method 2</u>: To 3.60g (92.1 mmol) of (molten) potassium in 125 cm^3 of dry THF at reflux under nitrogen was was slowly added dropwise 10.00g (83.2 mmol) of 2-(2-methoxyethoxy)ethanol. Towards the end of the reaction between the metal and the alcohol, the solution turned dark-blue presumably due to free electrons in solution. The solution was maintained at reflux for 30 minutes after the addition was completed and then allowed to cool to ambient temperature. On cooling the blue colour dissipated. The solution was then quickly filtered through a glass wool plug to remove the excess of potassium metal (the colourless solution yellowed slightly on exposure to air) and blanketed in nitrogen. The solution was then chilled to 5°C in an ice bath and 10.00g (108 mmol) of epichlorohydrin was added. The mixture was then heated to and maintained at reflux for 2 hours. The solvent and excess epichlorohydrin were then evaporated off at reduced pressure. Then 125 cm^3 of toluene and 15 cm^3 of water were added. The water was then removed azeotropically using a Dean-Stark separator. This water

treatment converts the very fine precipitated potassium chloride (which can not be filtered off readily), to a coarse precipitate which was then filtered off. The toluene was then evaporated off at reduced pressure, and the resulting oil was distilled to give 5.09g (35%) of 77 as a colourless liquid of bp 120-121°C at water pump pressure (lit[78] 116°C/5 Torr). ^{1}H-NMR as above.

4-(4-Biphenylyl)-1-chloro-2-butanol (78)

Cyclohexane was dried by adding benzophenone, potassium metal and triglyme (to act as a chelating ligand) and maintaining at reflux under argon until the solution turned the dark-blue colour characteristic of the ketyl radical anion. Solvent was then distilled directly into the reaction flask under argon.

To a stirred solution of 5.00g (29.7 mmol) of 30 in approx. 50 cm^3 of dry cyclohexane, was added via syringe 9.5 cm^3 (63.8 mmol) of TMEDA followed by 20 cm^3 (32.0 mmol) of 1.6M n-butyllithium in hexanes. The mixture on stirring for 1 hour turned deep red. This solution was chilled to 5°C in an ice bath and then 5.00g (54.0 mmol) of epichlorohydrin was added. The mixture very rapidly paled and a precipitate was formed. Stirring was continued for a further hour and then the reaction mixture was poured into dilute hydrochloric acid and ethyl acetate was added. The organic layer was separated, washed with water, dried over sodium sulphate and evaporated to dryness. By TLC (4vol.% toluene on 40-60 petrol ether on silica) this material has at least six components.

4-t-Butyl-4'-methylbiphenyl (79)

To a stirred solution of 34.88g (207 mmol) of 30 and 30 cm^3 (273 mmol) of t-butylchloride in 250 cm^3 of methylene chloride were added small amounts of anhydrous ferric chloride until brisk effervescence ensued. Stirring was continued for a further 90 minutes. The reaction was then poured into water, the organic layer was separated, washed once with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. The crude material was recrystallised twice from ethanol to yield 38.37g (83%) of 79 as colourless flakes of mp 79-80^{o}C. δ_H ($CDCl_3$) 1.36 (9H,s, t-Bu) 2.38 (3H,s,CH_3) 7.13-7.65 (8H, 2 overlapping AA'BB', aryl-H). Analysis Calcd. for $C_{17}H_{20}$: C, 91.0; H,9.0 Found: C,91.4; H,8.9 (Sample recrystallised twice from ethanol mp 80-81 ^{o}C).

4-Bromomethyl-4'-t-butylbiphenyl (80)

To a solution of 20.00g (8.91 mmol) of 79 in 150 cm^3 of dry redistilled carbon tetrachloride was added 16.00g (89.9 mmol) of N-bromosuccinimide. The mixture was refluxed for 5 hours and the succinimide was filtered off after cooling to ambient temperature. The solution was then washed once with dilute sodium hydroxide solution, then twice with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. The crude material was then recrystallised twice from redistilled 100-120 petrol ether to yield 16.38g (61%) of 80 of mp 101-103 °C. δ_H ($CDCl_3$) 1.37 (9H,s,t-Bu) 4.56 (2H,s, CH_2Br) 7.40-7.75 (8H,m,aryl-H). Analysis: Calcd. for $C_{17}H_{19}Br$; C,67.3; H,6.3. Found C,67.7; H,6.3 (Sample recrystallised twice from ethanol, mp 104-106°C).

2-((4'-t-Butyl-4-biphenylyl)methoxy)ethanol (81)

Method 1: To 50 cm^3 of ethylene glycol was added approx. 0.50g (22 mmol) of sodium metal to form the alkoxide. To this was added 5.00g (16.5 mmol) of 80. The mixture was then heated to, and maintained at reflux for 30 minutes. The bromo-compound melted and formed a second phase during the reaction. The reaction mixture was then poured into water and the products were extracted with diethyl ether. The organic layer was separated, washed once with water, dried over sodium sulphate and evaporated to dryness. TLC (40-60 petrol ether on silica) shows this material to be mostly unreacted bromo-compound 80.

Method 2: To a mixture of 50 cm^3 of ethylene glycol and 50 cm^3 of DMSO was added 5.00g (16.5 mmol) of 80. This mixture was stirred at 100°C for 2 hours. The mixture was then poured into water and extracted with diethyl ether. The organic layer was separated, washed twice with water, dried over sodium sulphate and evaporated to dryness. TLC (40-60 petrol ether on silica) showed the presence of at least 3 components. Resolution of this mixture was not attempted.

4'-t-Butyl-4-biphenylylmethanol (82)

To a solution of 1.67g (41.8 mmol) of sodium hydroxide in 50 cm^3 of 40% aqueous DMSO was added 6.06g (20.0 mmol) of 80. The mixture was refluxed for 1 hour, then allowed to cool. Some yellow solid that had formed was filtered off and washed with water. The filtrate was poured into 1000 cm^3 of water and extracted with methylene chloride. The organic layer was separated, washed twice with water, dried over sodium sulphate and evaporated to dryness. The solid materials were combined and recrystallised from ethyl acetate to give 2.63g (55%) of impure 82 as a greenish-white material of mp 170-175°C. $\delta_H(CDCl_3)$ 1.40 (9H,s,t-Bu)1.55(1H,s,OH)4.73(2H,s,CH_2)7.21-7.91(8H,m,aryl-H).

3-(4'-t-Butyl-4-biphenylyl)-1-propanol (83)

To a stirred mixture of 0.20g (1.5 mmol) of anhydrous aluminium chloride in 5 cm^3 of 1,1,2,2-tetrachloroethane was slowly added dropwise a solution of 1.00g (4.8 mmol) of 6 and 0.73g (5.3 mmol) of 3-bromo-1-propanol in 15 cm^3 of 1,1,2,2-tetrachloroethane. The reaction was stirred for a further 30 minutes before pouring into water. The organic layer was separated, washed with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. Mass spectrometry of the crude material showed that it was mostly unreacted 6, di-t-butylbiphenyl 9 and biphenyl itself: M^+ peaks at 210, 266 and 154, M^+-15 peaks (loss of CH_3) at 195 and 251.

4-t-Butyl-4'-(2-propenyl)biphenyl (84)

To a stirred solution of 1.00g (4.8 mmol) of 6 and 0.37g (4.8 mmol) of allyl chloride in 30 cm^3 of methylene chloride was added a small amount of anhydrous ferric chloride. This was stirred for 1 hour before pouring into water. The organic layer was separated, washed with dilute hydrochloric acid, dried over sodium sulphate and evaporated to dryness at reduced pressure. Mass spectrometry of the crude material showed that it was mostly unreacted 6 with only a small amount of 84 present: M$^+$ peaks at 210 and 250, M$^+$-15 peaks (loss of CH_3) at 195 and 235.

2-((4'-t-Butyl-4-biphenylyl)methyl)oxirane (85)

To a stirred solution of 2.00g (6.9 mmol) of 14 in approx. 40 cm^3 of dry THF was added via syringe 4.5 cm^3 (7.2 mmol) of 1.6M n-butyllithium in hexane. This was stirred for 15 minutes before adding dropwise a solution of 1.30g (14.0 mmole) of epichlorohydrin in sodium dried diethyl ether. The mixture was then heated to and maintained at reflux for 1 hour. After cooling to ambient temperature the mixture was poured into water and extracted with diethyl ether. The organic layer was separated, washed once with water, dried over sodium sulphate and evaporated to dryness at reduced pressure. TLC (5vol.% ethyl acetate in hexane) showed that the material so obtained was mostly debrominated reactant (6).

Poly(4-(methylvinyl)biphenyl

To a stirred solution of 4.00g of 11 in 50 cm^3 of THF was slowly added via syringe 1.6M n-butyllithium until there was a persistent dark purple colour. The mixture was the chilled in a bath of ground solid carbon dioxide to below -70°C and then a large excess of methyl iodide was added. The solution was allowed to come to room temperature and was poured into a mixture of water and methylene chloride to extract the polymer, The organic layer was separated, washed three times with water, dried over sodium sulphate and the solvent was evaporated off at reduced pressure. The glass so obtained was taken up in 40 cm^3 of fresh methylene chloride and was precipiated by adding dropwise to 400 cm^3 of stirred methanol. This gave 3.95g (99%) of crude polymer. A small sample heated in the melting point apparatus appeared to undergo phase transitions at 110°C and 150°C.

Poly(4-bromo-4'-(1-methylvinyl)biphenyl)

To a stirred solution of 4.00g of 25 in 100 cm^3 of dry THF was added 1.6M n-butyllithium in hexanes via syringe. However, no strong purple colour developed as for the polymerisation of 11 above, despite the addition of a large amount of n-butyllithium. A large excess of methyl iodide was then added and the mixture was poured into water and methylene chloride was added to extract the organic material. The organic layer was separated, washed four times with water, dried over sodium sulphate and then

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