Ordered polyesters and polyester-sulfones: aromatic nucleophilic substitution reactions involving diaryl ethers

Linda Hobart
ORDERED POLYESTERS AND POLYESTER-SULFONES

AROMATIC NUCLEOPHILIC SUBSTITUTION
REACTIONS INVOLVING DIARYL ETHERS

LINDA L. HOBART

June, 1985

THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

APPROVED:

Name Illegible
Project Advisor

Terence C. Morrill
Department Head

Name Illegible
Library

Rochester Institute of Technology
Rochester, New York
Department of Chemistry
Title of Thesis  Ordered Polyesters and Polyester-Sulfones

Aromatic Nucleophilic Substitution
Reactions involving Diaryl Ethers

Linda L. Hobart hereby (grant, deny) permission to the Wallace Memorial Library, of R.I.T., to reproduce my thesis in whole or in part. Any reproduction will not be for commercial use or profit.

Date  7-2-85
TO MY FAMILY,
RAY, JORDAN, AND JOHANNA
TABLE OF CONTENTS

I. ACKNOWLEDGEMENT ........................................... xi
II. ABSTRACT .................................................... xii
III. POLYESTERS .................................................. 1
   i. INTRODUCTION ............................................ 1
      Background. Polymer Chemistry ................... 1
      Ordered Polyesters ................................. 6
      Liquid Crystals ...................................... 11
      Low Molecular Weight Liquid Crystals ....... 23
      Polymers ............................................. 37
   ii. OBJECTIVES ............................................ 56
   iii. RESULTS AND DISCUSSION ......................... 60
      Phenols ............................................. 60
      Debloking of Di(methoxyphenyl) Tereph-... 67
      thalates .............................................
IV. POLY(ESTER-SULFONES) .................................. 81
   i. OBJECTIVE ............................................ 81
   ii. RESULTS AND DISCUSSION ............................ 82
      Debloking ............................................ 82
      Ullmann Ether Synthesis ............................ 91
V. AROMATIC NUCLEOPHILIC SUBSTITUTION .................. 98
   i. INTRODUCTION ........................................ 98
S_{N}Ar Mechanism

Benzyne Mechanism

Ether Cleavage

ii. DISCUSSION AND RESULTS

VI. EXPERIMENTAL

General Information

Diazotization and hydrolysis of 4-methoxy-2-methyl aniline using the procedure described by Fieser and Williamsom

Diazotization and hydrolysis of 4-methoxy-2-methyl aniline using the procedure described by Lambooy

Diazotization and hydrolysis of 4-methoxy-2-methyl aniline using the procedure described by Gottstein and co-workers

Recrystalization of terephthaloyl chloride

Preparation of di(3-methoxy-5-methylphenyl)terephthalate

Preparation of di(p-methoxyphenyl)terephthalate

Cleavage reactions of di(p-methoxyphenyl)terephthalate to give the following:

I). Terephthalic acid

II). Di(p-methoxyphenyl) terephthalate

III). Di(ethylthio) terephthalate
IV). 4-ethylthiocarboxybenzoic acid . 135
Preparation of 4,4'-sulfonyl bis(p-phenylene ether) dianisole .............. 136
Preparation of 4,4'-sulfonyl bis(p-phenylene ether) dibenzene ............ 138
Ether cleavage of 4,4'-sulfonyl bis(p-phenylene ether) dianisole ........ 139
Ether cleavage of 4,4'-sulfonyl bis(p-phenylene ether) dibenzene ......... 141
Preparation 4,4'-sulfonyl bis(p-phenylene ether) phenol (Hydrobromic acid) .... 142
(Hydrobromic acid and glacial acetic acid) 143
Treatment of 4,4'-sulfonyl bis(p-phenylene ether) dibenzene with hydrobromic acid and acetic acid ............ 144
Preparation of 4-bromo-2,6-dimethylanisole . 145
Attempted Ullmann synthesis of 4,4'-sulfonyl bis(p-phenylene ether) di(2,6-dimethyl-anisole (solvent dimethylformamide) 146
(solvent dimethyl sulfoxide) . 147
Ether cleavage reaction with sodium ethane-thiolate
4-Bromophenyl phenyl ether ............ 148
Di-phenyl ether ..................... 149
4-Phenoxyphenol ..................... 150
p-Nitrophenyl phenyl ether ............. 151
VII. APPENDIX ........................................................................ 153
VIII. REFERENCES ................................................................. 187
IX. TABLES ........................................................................... 1

1. Terminal group efficiencies in the three mesophases ................ 29
2. Thermodynamic data for semiflexible polymers 36
3. Properties of polymers of series I .... 48
4. Thermodynamic Properties for the Transitions of Series III Polymers .... 51
5. Thermal properties of polymers containing n-alkyl or polar substituents .... 52
6. Properties of Methylhydroquinone Copoly-esters .................. 54
7. Transition temperatures for the polyterphthalates ..................... 55
8. Relative rates ...................................................... 92
9. Substituent Effects on Nucleophilic Aromatic Substitution .......... 102
10. Leaving group mobility in some 1-X-2,4-dinitro-benzenes (a) With MeO- in MeOH/MeOAc (1/1 v/v) at 0°C; (b) With OMe- in MeOH/Dioxane (1/1 v/v) at 0°C; (c) with KOH inMeOH at 2°C ...... 105
11. Orientation of Reaction Products of Substituted Bromobenzenes with NH2-/NH3(liq.) ............................ 108
12. Cleavage of o-, m-, and p-Substituted Diphenyl Ethers ................ 113
13. Cleavage of 4-4′-Disubstituted Diphenyl Ethers .................... 114

X. FIGURES ........................................
1. The nematic liquid-crystal structure ...... 15
2. Possible restricted orientation of liquid crystal molecules with respect to the major direction (director) n .............. 16
3. Schematic representation of the orientational distribution function, f(θ), condensed media composed of elongated molecules ...... 17
4. The smectic liquid-crystal structure .... 19
5. The chlosteric liquid-crystal structure .. 21
6. Possible X-linkage groups ............... 24
7. Bond angles for carbon-sulfur and carbon-oxygen bonds ............... 28
8. Dipole interactions along the long axis of the mesogen ............... 30
9. Transition temperature pattern for thermotropic esters with terminal carbon chains. 31
10. Nematicogenic compounds ................. 33
11. Plot of N→I transition temperatures for structurally similar nematogenic compounds 34
12. Comb-like polymers ....................... 38
13. Polymer series prepared by Dupont Corp. . 43
14. Various mesogenic units and flexible spacers that have recently appeared in the literature .......... 44
15. Liquid crystal polyesters having mesogenic units and flexible spacers in the main chain ............... 45
16. Polyesters with poly-(p-phenylene terephthalate) linkages .................. 47
17. The structure of the polyterephthalates prepared by Kops and co-workers .... 55
18. Ordered and random polyterphthates ...... 56
19. Substituted 4-methoxyphenols to be synthesized for the ordered polyester study ... 57
20. Reaction scheme for the synthesis of ordered polyesters ...................... 58
21. The proposed reaction sequence for the preparation of 4-methoxy-2-methylphenol .. 61
22. Dropping device for the addition of the diazonium salt ................. 63
23. IR spectral data and elemental analysis for 4-(p-methoxyphenylcarboxo)-benzoic acid . 71
24. IR spectrum of di(p-methoxyphenyl) terephthalate ...................... 72
25. IR spectrum of terephthalic acid ............ 73
26. IR spectrum of 4-(p-methoxyphenylcarboxo)-benzoic acid .................. 74
27. IR spectrum of di(ethylthio) terephthalate. 79
28. IR spectrum of 4-ethylthiocarboxybenzoic acid .......................... 80
29. IR spectrum of 4,4′-[sulfonyl bis(p-phenylene ether)] dianisole ........ 85
30. IR spectrum of 4,4′-dithioethoxydiphenyl sulfone ........................ 86
31. IR spectrum of 4,4′-[sulfonyl bis(p-phenylene ether)] diphenol ........ 88
32. IR spectrum of the product from the attempted Ullmann synthesis of 4,4′-[sulfonyl bis(p-phenylene ether)] di(2,6-dimethyl anisole .......................... 97
33. SARC mechanism ............................................. 99
34. Approximate leaving order of groups .................. 104
35. Formation of aryne from monosubstituted ortho-, meta-, and para-halogeno- benzenes .......................... 107
36. Transition states for addition to substituted aryne. ................. 109
37. Cleavage pattern of diaryl ethers .................... 112
38. SARC mechanism for demethylation ........................ 116
39. Diaryl ether cleavage of 4,4′-[sulfonyl bis (p-phenylene ether)] dianisole .............. 117
40. Commercially available diaryl ethers ................ 119
41. Diaryl ether cleavage of 4,4′-[sulfonyl
(p-phenylene ether) dibenzene .......................... 120
42. IR spectrum of 4-nitrophenyl ethyl thioether .......................... 123
43. IR spectrum of the bromoderivative of acid extract .......................... 124
44. IR spectrum of di(3-methoxy-5-methylphenyl) terephthalate .......................... 154
45. NMR spectrum of di(p-methoxyphenyl) terephthalate .......................... 155
46. NMR spectrum of terephthalic acid .......................... 156
47. NMR spectrum of di(ethylthio) terephthalate 157
48. NMR spectrum of 4-ethylthiocarboxybenzoic acid .......................... 158
49. NMR spectrum of 4,4′-[sulfonyl bis(p-phenylene ether)] dianisole .......................... 159
50. NMR spectrum of 4,4′-[sulfonyl bis(p-phenylene ether)] dibenzene .......................... 160
51. IR spectrum of 4,4′-[sulfonyl bis(p-phenylene ether)] dibenzene .......................... 161
52. NMR spectrum of 4,4′-dithioethyldiphenyl sulfone .......................... 162
53. NMR spectrum of 4,4′-dithioethyldiphenyl sulfone .......................... 163
54. IR spectrum of 4,4′-dithioethyldiphenyl sulfone .......................... 164
55. NMR spectrum of 4,4′-[sulfonyl bis(p-phenylene ether)] dibenzene .......................... 160
phenylene ether)] diphenol ............ 165
56. NMR spectrum of 4,4'[(sulfonyl bis(p-
phenylene ether)] diphenol ............ 166
57. IR spectrum of 4,4'[(sulfonyl bis(p-
phenylene ether)] diphenol ............ 167
58. NMR spectrum of 4,4'-(sulfonyl bis(p-
phenylene ether)] dibenzene ............ 168
59. IR spectrum of 4,4'-(sulfonyl bis(p-
phenylene ether)] dibenzene ............ 169
60. NMR spectrum of 4-bromo-2,6-dimethylanisole 170
61. IR spectrum of 4-bromo-2,6-dimethylanisole 171
62. IR spectrum of 4,4'dihydroxydiphenyl sulfone
(recovered from the reaction mixture) .... 172
63. IR spectrum of 4-bromo-2,6-dimethylanisole
(starting material) .................. 173
64. NMR spectrum of 4-bromophenyl phenyl ether
(starting material) .................. 174
65. NMR spectrum of 4-bromophenyl phenyl ether
(recovered after reaction) ............ 175
66. IR spectrum of 4-bromophenyl phenyl ether
(starting material) .................. 176
67. IR spectrum of 4-bromophenyl phenyl ether
(recovered after reaction) ............ 177
68. NMR spectrum of diphenylether (starting
material) .......................... 178
69. NMR spectrum of diphenylether (recovered after reaction) . . . . . . . . . . . . . . . . . . . . . . . . . . . . 179
70. IR spectrum of diphenylether (starting material) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 180
71. IR spectrum of diphenylether (recovered after reaction) . . . . . . . . . . . . . . . . . . . . . . . . . . 181
72. NMR spectrum of 4-phenoxyphenol (starting material) . . . . . . . . . . . . . . . . . . . . . . . . . . 182
73. NMR spectrum of 4-phenoxyphenol (recovered after reaction) . . . . . . . . . . . . . . . . . . . . . . . . 183
74. NMR spectrum of 4-nitrophenyl ethyl thioether . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 184
75. NMR spectrum of 4-nitrophenyl phenyl ether 185
76. IR spectrum of 4-nitrophenyl phenyl ether 186
I would like to express my gratitude and appreciation to Dr. Jerry M. Adduci for his encouragement and guidance through the course of this study. Also I want to thank the members of my oral committee, Drs., Terrance C. Morrill, Laura Tubbs and Christian Reinhardt for their suggestions on the preparation of this thesis.

Much appreciation is extended to my family whose moral support and assistance made this all possible.

Financial assistance, a Teaching Fellowship and a Graduate Scholarship received from Rochester Institute of Technology and a Scholarship Award from the Community College of the Finger Lakes, are all greatly appreciated.
ABSTRACT

Synthesis of methyl substituted phenols (via various diazonium salts), to be used as a monomer in the synthesis of ordered polyesters and to study the liquid crystal continuum from monomer-to-oligomer-to-polymer, was attempted.

Deblocking of di(methoxyphenyl) terephthalates with sodium ethanethiolate in dimethylformamide resulted in the preferential cleavage of the ester linkage over the alkyl-aromatic ether linkage. A number of cleavage products resulted, depending upon the reaction conditions.

4,4′-[sulfonyl bis(p-phenylene ether)] dianisole was prepared as a model compound to be used in the ordered poly(ester-sulfone) study. Deblocking with hydrobromic and hydrobromic acid-acetic acid cosolvents was successful. However, deblocking with sodium ethanethiolate in dimethylformamide resulted in preferential cleavage of the aryl-aromatic ether linkage over the alkyl-aromatic ether linkage.

Attempts to synthesize 4,4′-[sulfonyl bis(p-phenylene ether)] dianisole by the Ullmann synthesis of diaryl ethers was unsuccessful.

The effect of para-substituents on aromatic-
nucleophic substitution reactions, in cleavage reactions of diaryl ethers by sodium ethanethiolate in diamethylformamide, was studied. Electron-withdrawing groups were found to facilitate the cleavage reaction.
INTRODUCTION

Polymer chemistry is a relatively new science. As late as the 1920's organic chemists had little concern with the synthesis of polymers. In 1929 Carothers and co-workers began their studies of addition and condensation polymers. From this work it became clear that simple condensation reactions could yield polymers with high molecular weights. The research in aliphatic polyesters by Carothers and co-workers led to the development of synthetic fibers. Polyethylene terephthalate, which is made by high temperature ester exchange, attained commercial importance. This discovery stimulated more research in the field of polyesters.

A variety of combinations of reactants and process conditions are available for polyester synthesis. Direct esterification of a diacid or diester with a diol,

\[ n\text{HO-}R\text{-OH} + n\text{HO}_2\text{C-R}\text{'-CO}_2\text{H} \longrightarrow \text{HO-}(-\text{R-CO-R}\text{'-CO0})_n\text{-H} + (2n-1)\text{H}_2\text{O} \]

or the self-condensation of a \( \omega \)-hydroxycarboxylic acid,

\[ n\text{HO-}R\text{-CO}_2\text{H} \longrightarrow \text{H-}(-\text{OR-CO-})_{n-1}\text{OH} + (n-1)\text{H}_2\text{O} \]

-1-
are two general examples of possible reactants.

Carothers overcame some of the difficulties encountered in the synthesis of crystalline high molecular weight linear fibers by an ester interchange reaction with ethylene glycol (1) and dimethyl terephthalate (2) producing polyethylene terephthalate (3)\textsuperscript{1}.

\[
\begin{align*}
\text{nH}_3C-\text{O-}-\text{C} & \quad + \quad \text{nHO(CH}_2\text{)_2OH} \\
\text{(1)} & \quad \text{(2)} \\
\text{CH}_3\text{ONa} & \xrightarrow{\Delta} \quad \text{[O-C-}-\text{C(O(CH}_2\text{)_2O)}\text{-}]_n & + & \text{2nCH}_3\text{OH} \\
\text{(3)} & 
\end{align*}
\]

This direct esterification reaction is the classic reaction for producing Dacron, Kodel, and Terylene fibers as well as Dacron film. Polyester fibers are now the world’s leading synthetic fibers.

Another example of a condensation reaction is the synthesis of Glyptal polyesters which were produced as early as 1901. These crosslinked polyesters (4) are produced by heating phthalic anhydride (5) and glycerol (6).

\[
\begin{align*}
\text{O} & \quad + \quad \text{CH}_2\text{OH} \\
\text{(5)} & \quad \text{CHOH} \quad \text{CH}_2\text{OH} \\
\text{CH}_2\text{OH} & \xrightarrow{\Delta} \quad \text{[OCH}_2\text{-CH-CH}_2\text{-O]}\text{-}]_n \\
\text{(6)} & \\
\text{(4)} & 
\end{align*}
\]
When each monomer contains just two functional groups, growth can occur in only two directions, a linear molecule is obtained as in Dacron. In the polymerization of Glyptal, since the reaction can occur at more than two positions on the glycerol, a highly cross-linked space network polymer can be formed. Dacron and Glyptal are both polyesters, but their structures and uses are quite different.

Polymerization reactions are generally classed into two types by the mechanism of their synthesis: chain reaction and step-reaction polymerizations.

In chain reaction polymerization a reactive species is produced which can be a free radical, cation or anion. These are often called initiators. The initiator reacts with the monomer producing another active species. Thus each individual reaction depends upon the previous one and the monomer is added one unit at a time. The high molecular weight polymer is formed at once. Long reaction times give high yields but have little affect on the molecular weight of the polymer.

The term step-reaction mechanism refers to polymerizations in which polymer molecular weight increases in a slow, step-like manner as the reaction proceeds. The series of reactions is independant of the preceding step. The net effect is that dimer,
trimer, tetramer, etc., molecules are formed, and along with the monomers, react rapidly without any large chains being formed until the reaction progresses toward total reaction of the chains themselves. Thus long reaction times are essential to obtain high molecular weights. The reactions involving the synthesis of Dacron and Glyptal are examples of a step-reaction polymerization.

The three main synthetic routes in the synthesis of condensation polymers are: melt, solution, and interfacial techniques.

The melt technique is an equilibrium controlled process in which the removal of the byproduct drives the reaction in the forward direction. Since high temperatures are required, the reactants and polymer must be thermally stable. The yields are high, however, long reaction times, several hours to days, are required.

Solution polymerizations are also equilibrium controlled. Like melt polymerization, the reaction kinetics are stepwise. If lower temperatures are used, fewer side reactions are likely to occur. Side reactions with the solvent and solvent entrapment may be problems.

The interfacial technique is a novel low temperature polymerization which is carried out at the
interface between two immiscible solvents, each containing one of the reactants. The reaction mechanism is usually nonequilibrium and the rates are similar to the solution technique. Lower temperature (0-50°C) eliminates possible side reactions. Another advantage is that many functional groups do not interfere. This technique requires that the acid or acid anhydride be replaced with a more reactive acid chloride. The high cost of acid chlorides rules out this technique for the industrial synthesis of polyesters.

In the laboratory the interfacial technique is often the method of choice for the synthesis of esters and polyesters. The sodium salt of the alcohol or phenol is in the aqueous phase, while the acid chloride is in the organic phase. When aqueous alkali is used to combine with the hydrochloric acid which is formed, the reaction is called the Schotten-Baumann procedure.¹

\[
\begin{align*}
n\text{ClCO-R-COCl} & + \ n\text{HO-R'-OH} \quad \longrightarrow \\
\text{-(-COR-COO-R'-O-)n-} & + \ 2n\text{HCL}
\end{align*}
\]

The interfacial polymerization is usually diffusion controlled, as the rates of diffusion of the reactants to the interface are usually slower than the rate of reaction of the two functional groups. The mechanism is
different from the step-reaction in that the monomers that diffuse to the interface will react only with the end groups of the polymer chain and not with other monomers, dimers, etc.. Stoichiometry is often unnecessary to produce high molecular weight polymers in high yields.

ORDERED POLYESTERS

One objective of this thesis work was to determine the effect of order in polyesters and polysulfones. The reaction of 2-methylhydroquinone (7) and terephthaloyl chloride (8) can be used to illustrate what is meant by order.

\[ \text{HO} \quad \text{+} \quad \text{ClC} \quad \rightarrow \]

(7) \hspace{2cm} (8)

Random polyester

The 2-methylhydroquinone monomer adds in a random order to the terephthaloyl chloride, addition
taking place at the 1 or 4 position on the hydroquinone. The position of the methyl group with respect to other 2-methylhydroquinone repeat units is random.

\[
\text{CH}_3
\]

\[
\text{CH}_3
\]

\[
\text{CH}_3
\]

Ordered Polyester

The self-condensation of a methyl substituted \(\omega\)-hydroxycarboxylic acid (9) results in the formation of an ordered polyester (10).

Much work has been done on the effect of order in aromatic amides. J. Preston\(^2\) found that order in aromatic polyamides increased their melting points. Goodman and Rhys\(^3\) confirm the significance of structural regularity in connection with physical properties. Since symmetry increases the melting point and crystallinity in homopolyesters, one would hypothesize that regularity or order in the placement of molecular units would effect the properties of polyesters in the same way.

Alternating terepolyesters (11) have been prepared by the reaction of ethylene di-\(p\)-hydroxybenzoate and
dicarboxylic acid chlorides\textsuperscript{a}.

\begin{align*}
\begin{array}{c}
\text{O} \quad \text{R} \quad \text{O} \quad \text{C} \quad \text{O} \\
\text{C} \quad \text{R} \quad \text{O} \quad \text{O} \\
\text{C} \quad \text{OCH}_2\text{CH}_2\text{O} & \quad \text{C} \\
\end{array}
\end{align*}

\textsuperscript{(11)}

The sebacate (R = (CH\textsubscript{2})\textsubscript{8}) and terephthalate (R = C\textsubscript{6}H\textsubscript{4}) members of the series were highly crystalline with melting points of 115-120\textdegree C and above 360\textdegree C respectively. The random copolyesters of the same gross composition were either a viscous syrup or an amorphous glass, as was the case with the terphthalate.

P. W. Morgan completely reviewed aromatic polyesters and noted their improved thermal and mechanical properties compared to their partially aliphatic analogs.\textsuperscript{55} These polymers were found to be high-melting but were largely insoluble in organic solvents.

Introduction of aliphatic groups on the aromatic ring increased the solubility but lowered the melting point T\textsubscript{m} of the polyester. Stevenson and Mulvaney\textsuperscript{6} prepared ordered copolymers in an attempt to increase polymer solubility without greatly decreasing the melting point. Interfacial polymerization of the diacid chloride (12) with resorcinol (13) gave the perfectly ordered block copolymer (14). The high molecular weight polymer (melting point 349\textdegree C) was soluble in a number of organic solvents.

Stevenson and Mulvaney\textsuperscript{7} incorporated hydroxybenzoyl
chloride linkages, as well as bisphenol and terphthaloyl linkages, in their block copolymers. Our objective was to use substituted bisphenols and terphthaloyl chloride to prepare polyesters, since this would minimize the number of different linkages. The polymer should have a B-C sequence instead of an A-B-A-C linkage illustrated in polymer (14).

\[
\begin{align*}
\text{(12)} & \quad \text{(13)} \\
\end{align*}
\]

(14)

Ober and Lenz prepared polymers containing either random or alternating sequences of the mesogenic dyad (15). The polymer (16) with the random head-tail orientation of the oxybenzoate units in the dyad was thermotropic, however, the compositionally identical polymer (17), an exactly alternating head-tail arrangement of mesogenic units in successive dyads, did not form a mesophase. This points out that randomness in mesogenic group orientations in the main chain can be important in
determining mesophase formation and properties. We hoped to determine the effect of order in substituted hydroquinones on mesophase properties.

![Diagram](image1)

(15)

![Diagram](image2)

(16)

![Diagram](image3)

(17)

The tendency for ester-exchange between groups in polyester chains presents another difficulty for the preparation of ordered polyesters with well-defined structures. Prasadarao evaluated the role of steric hinderance in ester-interchange reactions. The polyester synthesized from dimethyl terphthalate and bis(hydroxyethyl)tetramethyl terphthalate was found to undergo ester-exchange. Prasadarao hypothesised that steric hinderance might prevent the ester-exchange reaction. It was found that the presence of a single
group ortho to an ester group had no effect on ester-exchange reactions\textsuperscript{10}.

We hypothesised that in the interfacial polymerization of terephthaloyl chloride with a bisphenol, ester-exchange would be minimal, since there would be no aliphatic ester linkages.

**LIQUID CRYSTALS**

Although liquid crystals have been known for more than 80 years, these substances have until recently been regarded as laboratory curiosities. In the past few years, applications of the remarkable ability of liquid crystals to register small changes in temperature, mechanical stress, and the electromagnetic environment by changes in their optical properties have been numerous. The most familiar of these applications is the liquid crystal display.

An interesting recent development in polymer chemistry was the observation of liquid crystalline properties in aromatic polyesters and polyamides. This presents the challenge to prepare ultra high strength polyester fibers from anisotropic melt\textsuperscript{11}. In the late 1960's, DuPont introduced the high performance fiber, Kevlar. Kevlar and other high modulus fibers, based on lyotropic nematic polyamides\textsuperscript{12}, present practical difficulties of solvent
based lyotropic systems (sulfuric acid). Thermotropic polymers should possess similar properties, but should not require the adverse manufacturing conditions required in the manufacture of lyotropic polyamides. In 1975, Rovielli and Sirigu\textsuperscript{13} reported the first thermotropic "backbone" liquid crystalline polymer. They prepared three alkanoates of 4,4′-dihydroxy-α, α′-dimethyl-benzaline (18) with \( n = 6, 8, \) and 10.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{O} - \text{C} = \text{N} - \text{N} = \text{C} - \text{O} - \text{C} - (\text{CH}_2)_n - \text{C} \\
\text{CH}_3 \\
\end{array}
\]

Polymers and low molecular weight compounds which are highly associated over various temperatures in melts or solutions are called liquid crystalline. This intermediate state between crystalline solids and isotropic liquids is also referred to as mesomorphic or mesophase.

Until the discovery of the liquid crystalline state, matter was thought to exist in one of three distinct states. In the solid state, constituent molecules (atoms) execute small vibrations about firmly fixed lattice positions, but cannot rotate. In the liquid state, relatively unhindered rotation is observed but no long-range order exists. In the gaseous state, the particles are free to move throughout the entire
volume of their container with almost no constraint\textsuperscript{14}.

When normal solids melt, the collapse of the overall positional order of the lattice occurs abruptly and is marked by the essentially free rotation of the molecules. The mesophase of liquid crystals does not meet all the criteria for either a true liquid or a true solid. In liquid crystals, the molecules are free to move, but their rotational mobility is restricted. Sufficient thermal energy has not been supplied to allow individual molecules to rotate (except around their long axis); hence some positional order remains.

Since mesophases do not satisfy all the criteria of either a true liquid or true solid, they exhibit many physical properties that are characteristic of both phases. The mesophase is a true liquid in that it takes the shape of its container (flows) and forms a perfect sphere when a drop is placed in an immiscible liquid of equal density, but the optical properties of the mesophase are those of a solid, some with a magnitude without parallel in any true solid, liquid or gas. Other physical properties of significance are ordering, which is controlled by magnetic and/or electric fields, and birefringence, which gives rise to the color change of some liquid crystals with a change in temperature or solvent concentration.

Liquid crystals are classified into two classes,
depending on the principal way in which the order of the parent solid is destroyed. Lyotropic liquid crystals change phase by the action of the solvent on the molecule. Thermotropic liquid crystals respond to temperature changes. Since thermotropic polymers could have a great impact on the fiber industry, it is these compounds which will be addressed.

The structure of liquid crystalline polymers in the mesophase is very similar to that of low molecular weight liquid crystals in the mesophase. The differences in properties are due to the fact that the units in the polymer are covalently bonded while the units in the low molecular weight mesogen are free to act independently. Since the properties of the polymer parallel the low molecular weight mesogens, it is useful to look at these mesogens to gain insight into the organization of polymer melts.

Liquid crystal science began in 1888 with the preparation of cholesteryl benzoate by Friedrich Reinitzer, an Austrian botanist. Two interesting properties were observed. When heated, the compound’s crystal lattice collapses at 145°C to form a turbid anisotropic liquid (liquid crystal), and at 179°C, the turbid liquid disappears and an isotropic liquid is formed. The reverse process was observed on cooling. The second and even more interesting observation was
that the color of the turbid liquid changed from red to blue as its temperature increased, and from blue to red as the temperature was decreased.

Lehmann\textsuperscript{1-4} was the first to suggest the name liquid crystals to identify the anisotropic state of matter possessing properties of both liquid and solid.

Friedel, in his work with liquid crystalline compounds, found that when a liquid film was placed on a microscope with cross polarized light, the mesophases gave birefringent patterns or textures\textsuperscript{1-7}. These patterns characterize the three different basic types of mesophase; nematic, smectic, and cholesteric.

![Figure 1. The nematic liquid-crystal structure.](image)

"Nematic" comes from the Greek word for thread; nematic phases, structurally the least complex of the mesophases, have a thread-like pattern (Schlieren
texture) when viewed through a microscope with crossed-polarizers. In typical nematic liquid crystals, the molecules remain parallel to one another, but the positions of their centers of gravity are disorganized (Figure 1). The nematic phase always changes to an isotropic liquid when heated.

Although nematic liquids have an infinite-fold symmetry axis and are, therefore, uniaxial, the orientation of the individual molecules along this axis is not perfect.

![Diagram](image)

**Figure 2.** Possible restricted orientations of liquid crystal molecules with respect to the major direction (director) $n$.

A measure of the degree of internal order (or alignment) in the liquid crystal is commonly given the
order parameter, $S$, defined by

$$S = \frac{1}{2}(3\cos^2 \theta - 1)$$

where $\theta$ denotes the angle between the molecules long axis and the nematic symmetry axis (Figure 2) and the brackets indicate a thermal average. For a perfectly parallel arrangement of molecules, such as in a crystalline solid, $f(\theta)$ (the angular distribution of molecules throughout the sample) would be a highly-peaked function about an angle restricted by near neighbor interactions (Figure 3).

In this case, $S$ would be 1.0, indicating perfect order. For a completely random distribution, an isotropic liquid, $f(\theta)$ constant as all orientation angles in the sample are equally probable, and $S = 0$. Experimental

---

Figure 3. Schematic representation of the orientational distribution function, $f(\theta)$, for condensed media composed of elongated molecules.
values of S range from about 0.4 at the nematic-isotropic point to about 0.6 in the nematic liquid at lower temperatures\(^{20}\). X-ray, ultraviolet, optical, infrared, magnetic resonance and thermal analysis are routinely used to determine the order of the liquid crystalline state.

When solid \(p-n\)-propoxybenzoic acid is heated to its melting point \((T_m = 145^\circ C)\), it becomes a turbid liquid with a Schlieren texture (nematic). At 154\(^\circ C\) there is an abrupt change to a clear isotropic phase (clearing point, \(T_c\)), with all the properties of a normal liquid. The intermediate state is "solid like" in that it is not optically extinct when viewed between crossed Polaroids. The phase is a fluid in that it flows above 9\(^\circ C\).

\[ S = 0.6 \text{ at } T_m = 145^\circ C \text{ and } S = 0.4 \text{ at } T_c = 154^\circ C \text{ for } p-n\text{-propoxybenzoic acid}. \]

Thermodynamic properties of mesophases should also be considered. From thermal and volumetric measurements, it has been shown that both the change from a solid crystal to mesophase and the change from mesophase to an isotropic melt are first order transitions\(^{21}\). A substantial decrease in order can be seen in the significant change in entropy \((\Delta S = 20-50 \text{ cal/mol-K})\) when a solid crystal melts to form the nematic phase. Since, the clearing transition from the nematic phase to the isotropic melt has a much lower
value of $\Delta S$, the randomness of the mesophase is presumed to be much closer to that of the isotropic melt than to the solid.

The smectic phase is the most highly ordered mesophase. Molecules are arranged in layers much like those in soap films, with the long axes parallel to each other (Figure 4). The term "smectic" (soaplike) was coined in 1922 by Friedel, who studied the birefringent patterns of mesophases.

![Smectic liquid-crystal structure](image)

**Figure 4.** The smectic liquid-crystal structure.

The layers are not strictly rigid, but form flexible, two-dimensional molecular sheets which can slide past one another. The viscosity of the smectic phase is generally higher than the other two phases, and because of the two dimensional order, the viscosity is anisotropic.
Of the nine known smectic phases, eight have molecular packing arranged in layers. The nineth smectic structure, known as smectic D, is optically isotropic and has cubic, not layered, packing. The nine structures are designated smectic A to I, the letter subscripts assigned by the order of discovery.

Smectic phases are differentiated by the order in their layers as either structured or unstructured. The structured smectics have a crystallike arrangement of molecules in each layer (two dimensional lattices). In unstructured smectics, the molecules in each layer are positioned randomly. In orthogonol smectics (A, B, and C) the molecules are perpendicular to the layers; in tilted smectics (C, F, G, H, and I), the molecules are tilted.

Smectic layers behave as uniaxial, birefringent crystals. The velocity of light transmitted parallel to the molecular layers is greater than that transmitted perpendicularly. The fact that the birefrigence is only slightly temperature dependent indicates that very little change in internal order occurs over the smectic phase. Thus the smectic mesophase is the most "solid-like" of all the liquid crystal modifications. The melting process disrupts end-to-end molecular collisions but is not sufficient to break the lateral associations thus the layers are undisturbed. The S
value of smectic liquid crystal may be as high as 0.9.

The third type of liquid crystalline modification, the cholesteric structure, is also referred to as the chiral-nematic structure. Some scientists\textsuperscript{23} prefer to classify this mesophase as a subdivision of the nematic class. The name cholesteric was chosen because many cholesterol esters exhibit this phase.

These optically active compounds have local nematic packing, but the director is not fixed; instead, it rotates spatially about an axis perpendicular to itself. The molecules have a helical structure, presumably due to the chirality of the molecules (Figure 5).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{cholesteric_structure}
\caption{The cholesteric liquid-crystal structure.}
\end{figure}

The distance for a 360° turn of the director, commonly referred to as the pitch, may be in the order of a
wavelength of light. The spectacular color effects often observed in such structures are due to the periodicity of the structure. Physical changes in temperature, pressure, shear, foreign vapors, etc, result in color changes in these molecules. These properties make chiral liquid crystals useful as indicators.

Some liquid crystalline structures pass through more than one phase (polymorphism) as the temperature is increased. These transitions occur at definite temperatures and result in the progressive destruction of molecular order. As smectic phases possess a higher degree of order, smectic transitions always occur at lower temperatures. Smectic-to-smectic transitions, as well as smectic-to-nematic transitions are well known. Nematic-to-smectic transitions were not predicted, however, a re-entrant nematic phase has been discovered by Patricia E. Cladis of Bell Laboratories. Mixtures formed with two liquid crystals exhibited a sequence of nematic, smectic, and then nematic (re-entrant) phase on cooling.

\[
\begin{align*}
\text{C}_6\text{H}_{11}-\text{O-} & \quad \text{C-OH} \\
227.5{}^\circ\text{C} & \quad 229.5{}^\circ\text{C} & \quad 275.0{}^\circ\text{C} \\
\text{solid} & \quad \text{smectic} & \quad \text{nematic} & \quad \text{isotropic liquid}
\end{align*}
\]

-22-
Polymorphism can be illustrated in the polymesophase transitions of 4'-n-pentyloxybiphenyl-1-4-carboxylic acid (19).

LOW MOLECULAR WEIGHT LIQUID CRYSTALS

Several generalizations have been made regarding the structures of molecules which exhibit liquid crystalline properties. Gray's classic monograph suggested that the determining factor in the formation of the mesophase was the tendency for molecules to adhere to one another sideways. A hypothetical organic molecule that exhibits liquid crystalline properties is illustrated below.

\[
\begin{array}{c}
A \\
\hline
X \\
\hline
B
\end{array}
\]

The majority of the molecules have aromatic nuclei that are polarizable, planar, and rigid. The molecules must have cohesive forces which preserve the interlayer forces in the mesophase, as well as, have a rigid structure which prevents flexing in the mesophase. Para-substitution of the phenylene groups and a rigid link, X, determine the rod-like structure of the molecule. The X linkage usually contains either a multiple bond along the long axis of the molecule or a
system of conjugated double bonds, or involves a
dimerization of carbonyl groups (Figure 6).

\[
\begin{align*}
-\text{C}=\text{O}, & \quad -\text{C}-\text{NH}, & \quad -\text{N}=\text{N}, & \quad -\text{N}=-\text{N}, & \quad -\text{CH}=\text{N} \\
-\text{C}==\text{C}, & \quad -\text{R}-\text{C}==\text{OH}==\text{O}-\text{C}-\text{R}, & \quad -\text{CH}=\text{N}-\text{N}=\text{CH}-
\end{align*}
\]

Figure 6. Possible X-linkage groups

The central group constitutes a lathlike or rodlike core in the molecule. The length of the molecule must be greater than the width, since a large length-to-breadth ratio is important in the mesophase. The importance of linearity can be illustrated by looking at the cis and trans isomers of \( p-n \)-alkoxycinnamic acid. The \( \text{trans} \)-\( p-n \)-alkoxycinnamic acids (20) are mesophasic, while the \( \text{cis} \) isomers (21) are not, a result of the greater breadth of the \( \text{cis} \) isomers.

\[
\begin{align*}
\text{(20)} & \quad \text{(21)}
\end{align*}
\]

The effect of rigidity can be illustrated by the compounds below. Notice that the molecule with the dimethylenic central group (22) is not a liquid crystal
while the stilbene derivative (23) is essentially linear and mesomorphic. The double bond prevents freedom of rotation. Dewar and Goldberg\textsuperscript{26} have studied the effect of rigidity on liquid crystallinity.

\[
\text{CH}_3\text{CO}_2\text{-CH}_2\text{CH}_2\text{-CO}_2\text{CH}_3 \quad (22)
\]

\[
\text{CH}_3\text{CO}_2\text{-CH=CH-CO}_2\text{CH}_3 \quad (23)
\]

Ortho or meta linkages destroy liquid crystallinity by destroying molecular linearity; substitutions on the phenylene groups effect the liquid crystallinity as well. Substituion on the phenylene groups lowers the thermal stability of the molecule as demonstrated by a narrower temperature range in the mesophase\textsuperscript{27}, presumably by geometric interference with the necessary parallel orientation of molecules in the mesophase. As we planned to look at methyl substituted monomers, trimers, etc. we hypothesized that the small methyl groups would not destroy the mesophase. We would expect a decrease in the thermal stability of these oligomers, and polymers indicated by the narrowing of the temperature range of the mesophase.

If the length of the molecule is increased by increasing the number of monomer units, liquid crystalline properties are enhanced, especially if
conjunction or direct linkage with aromatic rings is involved. In general, modifying the length-to-breadth ratio of the mesogenic molecule will affect the mesophase behavior.

It has been shown that in addition to the rigidity, strong polarity in the linkage generally enhances the liquid crystallinity of the molecule.

Dewar and Griffen looked at the role of the central group on the stability of nematic liquid crystals. The effects of structural changes in p-methoxyphenyl terephthalate (24) were studied.

\[ \text{CH}_3\text{O-} \begin{array}{c} \text{O-} \text{C-} \text{C-} \text{O-} \text{O-} \text{CH}_3 \\
\end{array} \]

(24)

The central phenylene group was replaced with 1,4-bicyclo[2.2.2]octylene (25), a saturated group which is linear and rigid, and also with trans-1,4-cyclohexylene (26), a saturated group which is linear but flexible. The flexible group (26) had a greater damaging effect on the nematic phase (lowered the nematic-to-liquid transition temperature more significantly). This would indicate that rigidity is probably a more
important requirement for nematic mesophase stability than unsaturation.

While the double bond introduced into the bicyclo-octylene compound (27) led to an increase in the mesophase stability, the nematic-to-isotropic liquid transition temperature of (27) was 9°C less than that of (24). Dewar and Griffen suggest that the difference between (25) and (27) was due to reduced symmetry in the saturated group. Replacement of the central phenylene group in (24) with the vinylene group (-C=C-) resulted in a monotropic transition 142°C lower than that of (24). This data seems to suggest that the central molecules must be rigid and rod-shaped, have more or less uniform cross-sections, and that polarizability and conjugative effects of the \( \pi \)-systems are important.

Other data also suggests that more uniform cross-sections are important: e.g. the azoxy link (-N=N-) is thermally more stable than azo (-N=N-) as a linking group, while ester and thio-ester linkages are superior to vinylene or azo. Van Meter and Klanderman compared central linkages, \( X \), in compound (28) and found the order of increasing thermal stability for their series to be

\[-\text{NO=N} \rightarrow \text{N=N} \rightarrow \text{CH=N} \rightarrow \text{COO}\].

It has already been
pointed out that lateral substituents that project beyond the edges of the molecule lower the stability of the mesophase.

The corresponding thioesters of compounds (24-28) were also prepared. Because sulfur is less electronegative than oxygen, it was anticipated that these compounds would be less stable than their oxygen analogs. This was not the case; the thioesters had consistently higher nematic-to-isotropic transition temperatures and usually higher transition heats and entropies as well. Elser found that replacement of the oxygen atoms with sulfur in chlolestryl carbonates led to an increase in the smectic-to-chlolestric transition temperature.

A possible explanation of the more stable mesophases of thioesters is that the smaller bond angle and longer carbon-sulfur bond improve the overall linearity of the molecule (Figure 7).

---

oxygen ester  
sulfur ester

Figure 7. Bond angles for carbon-sulfur and carbon-oxygen bonds.

It is also possible that the introduction of sulfur reduces unfavorable steric interaction between the ring hydrogen and the lone pair of electrons on the carbonyl.
carbon. A more efficient packing is therefore possible. The more planar molecule should promote intermolecular attractions which would explain the higher $\Delta H_{N-x}$ for the thioesters than the esters. The greater $\Delta S$ in the thioesters is due to the greater order in the mesophase in the thioester.

Finally, weak polar groups at the ends of the molecule enhance liquid crystalinity in low molecular weight compounds. The types of terminal substituents can be divided into two groups: the compact type and the homologous series.

Terminal groups with a small compact structure such as cyano, methoxy, nitro, halogen, etc., may interact with the molecule in which they are attached or with adjacent molecules.

Work of Schroeder and Bristol and Gray is shown in Table 1. The work illustrates the efficiency order of various compact groups in all three types of mesophase.

<table>
<thead>
<tr>
<th>Type of compound</th>
<th>Phase</th>
<th>Group Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-Phenyl dibenzoates</td>
<td>Nematic</td>
<td>CH$_3$O $\succ$ NO$_2$ $\succ$ Br $\succ$ Cl $\succ$ CH$_3$ $\succ$ F $\succ$ H</td>
</tr>
<tr>
<td>Biphenyl anils</td>
<td>Smectic</td>
<td>Br $\succ$ Cl $\succ$ H $\succ$ NO$_2$ $\succ$ CH$_3$O</td>
</tr>
<tr>
<td>Active cin-namate esters</td>
<td>Cholesteric</td>
<td>CN $\succ$ CH$_3$O $\succ$ NO$_2$ $\succ$ Cl $\succ$ Br $\succ$ H</td>
</tr>
</tbody>
</table>

Table 1. Terminal group efficiencies in the three mesophases.
Highly polarizable terminal groups (–OMe, –CN, and –NO₂) tend to favor interactions along the long axis of the mesogen (Fig. 8), and as a result, these groups tend to favor nematic and cholesteric phases. For example, methoxy dipoles of neighboring molecules reinforce one another to give end to end threadlike organization of the nematic phase rather than lateral reinforcement.

![Figure 8. Dipole interactions along the long axis of the mesogen.](image)

Groups such as the halogens tend to reduce terminal interactions and thus increase the tendency to form smectic phases.

Compact, polar and polarizable groups seem to increase the clearing points \( T_\alpha \) of the low molecular weight liquid crystals\(^{36}\). Dewar and Griffen\(^{37}\) found that in a series of para substituted bisphenyl terephthalates, electron-withdrawing groups lowered clearing points of the mesophase while electron-releasing groups raised the clearing points. It is thought that electron-releasing groups increase polarity of the ester carbonyl and thus increase lateral interaction.

The second type of terminal group is the
homologous series. Studies on numerous homologous series have shown a decreasing odd-even effect between the melting and clearing temperatures with the number of methylene units in the terminal alkyl end groups\textsuperscript{3-7}. The clearing temperatures for even carbon chain members and for odd carbon chain members each fall on a smooth curve when $X = -(\text{CH}_2)_n\text{CH}_3$ or $-\text{O(}\text{CH}_2)_n\text{CH}_3$ in compound (29).

The even curve lies above the odd curve in the alkoxy series and is reversed for the homologous alkyl series. (Figure 9). The odd-even effect slowly disappears as the alkyl chain length increases and the relationship between chain length and transition temperature levels off.

Figure 9. Transition temperature pattern for thermotropic ester with terminal carbon chains.
Heats and entropies of transitions have also been determined for homologous series. The data seems to support the odd-even effect of mesophase transition temperatures. Branching in the alkyl and alkoxy groups usually lowers the clearing point. This is due to inefficient packing which weakens the intermolecular interactions.

Another objective of this thesis study was to consider the question of whether there is a continuum of mesophase behavior from small molecule to polymer in aromatic polyesters. The details of this will be discussed in greater detail in a latter section of this thesis.

Griffen and Britt investigated the question of the continuum using a series of Siamese-twin liquid crystals. The mesogenic small molecule family of 4-alkoxyphenyl 4'-benzoates (30) twin molecules (two phenyl benzoates joined through a diether linkage, i.e., tail to tail) (31), and polymeric liquid crystals (32), were compared. The polymeric structures contain rigid (a small molecule liquid crystal moiety) and flexible segments (Figure 10). The small molecule family and the Siamese twins also have rigid central cores with flexible sections. Nematic-to-isotropic transition temperatures are plotted versus alkoxy carbon number in Figure 11. Dodecyloxy compound data was used because decycloxy-
monomer data was not available.

\[
C_xH_{(2x+1)}-O-\begin{array}{c}
\text{O-C'-O-}
\end{array}OC_yH_{(2y+1)}
\]

(30)

\[
[ C_xH_{(2x+1)}-O-\begin{array}{c}
\text{Q-}
\end{array}-O(CH_2)_{10}-O-\begin{array}{c}
\text{O-}
\end{array} ]
\]

(31)

\[
\begin{array}{c}
\text{O-C'-O-}
\end{array}OC_xH_{(2x+1)}
\]

(32)

Figure 10. Nematogenic compounds

The usual odd-even effect in the nematic-to-isotropic transitions was observed. The monomeric compounds with \(-OC_{12}H_{25}\) did not show the typical random scatter of many liquid crystalline series but seem to fall on a nearly smooth curve.

Thermal properties of these polymers were investigated by Griffin and Havens\textsuperscript{42}. While no regular behavior of clearing enthalpies within the homologous
series of polymers was apparent, an odd-even alternation of the enthalpies appeared. Polymers with an even number of methylene groups in the diacid segment of their chains had a larger clearing enthalpy than those with an odd number of methylene groups. Homologous series of small molecule liquid crystals typically exhibited an alternating behavior of their nematic-to-isotropic transitions, but had increasing trends with increasing chain length.

![Graph](image)

Figure 11. Plot of N --> I transition temperatures for structurally similar nematogenic compounds.
Increasing alkoxy tail length in the monomer led to a smectic phase and often smectic polymorphism. The oligomers (twins) showed only nematic phases. It appears that smectic tendencies of the small molecules are lost on the first coupling. The continuum of properties between the small molecule --> oligomer --> polymer is through the nematic phase. The loss of the smectic phase was due to the increased nonlinearity caused by flexible units which preclude layered structures.

Order in the nematic phase of semiflexible polymers and thermal properties of monomer (33), dimer (34) and polymer (35), were studied by Sigaud, Yoon, and Griffin*3. Their data is summarized in Table 2.

The continuum is shown by this series of compounds.
The order parameter of the nematic phase at the nematic-to-isotropic transition was found to increase with chain length.

<table>
<thead>
<tr>
<th></th>
<th>$T_{N\rightarrow I}$</th>
<th>$\Delta H_{N\rightarrow I}$</th>
<th>$\Delta S_{N\rightarrow I}$</th>
<th>$S_{N\rightarrow I}$ (order)</th>
</tr>
</thead>
<tbody>
<tr>
<td>monomer</td>
<td>79</td>
<td>0.74</td>
<td>2.09</td>
<td>0.37</td>
</tr>
<tr>
<td>dimer</td>
<td>148</td>
<td>3.52</td>
<td>8.37</td>
<td>0.49</td>
</tr>
<tr>
<td>polymer</td>
<td>215-227</td>
<td>6.53</td>
<td>13.4</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Table 2. Thermodynamic data for semiflexible polymers

The nematic-isotropic transition of the polymer occurs over a broad temperature range ($\sim$12°C) compared to 1-2°C for the monomer and dimer. Two possible explanations are: (i) biphasic separation due to polydispersity of chain lengths\(^4^4\), and (ii) kinetic control analogous to crystallization of polymer melts\(^4^5\).

Polymeric liquid crystals may exhibit intrinsic differences from their monomeric counterparts because the linking of monomers inevitably causes them to lose translational and orientational independence. This has a profound effect on the dynamics of the polymer fluids. Since the properties of oligomers more closely resemble the properties of the parent polymer, it should be more useful to consider the oligomer than monomer, when projecting the properties of the polyester.

-36-
Polymers which exhibit liquid crystalline behavior in solution (lyothropic mesomorphism) have proven to be of great significance to the fiber industry. Industrial use of solvents to form lyotropic liquid crystals has been hindered by the fact that the rigid parasubstituted aromatic polyamides used will dissolve only in such solvents as fuming sulfuric acid. The corrosive environment required by these polymers has severely impeded the fiber spinning operation. Dupont Corporation’s Kevlar is an example of such a commercially available lyotropic liquid crystal polymer.

Industrial research laboratories, therefore, have developed a considerable interest in the synthesis of polymers which display liquid crystalline behavior in the melt phase (thermotropic mesomorphism). The objective is to produce a thermotropic polymer that will melt to a liquid crystal at about 250°C, an appropriate processing temperature; the polymer must also possess superior mechanical properties at ambient temperatures. Unfortunately, lowering the transition temperature by chemical modification has generally decreased the polymers mechanical properties.

A large number of liquid crystal polymers have been
prepared since the 1970's. Three classes will be discussed: cross-linked, comb-like, and semiflexible linear polymers.

Cross-linked polymers were prepared in 1975 by Blumstein and coworkers. Generally, the monomers contained two terminal vinyl groups, and free radical initiated polymerization was carried out at a temperature within the liquid crystalline range of the monomer. The polymers possessed either smectic or nematic melts. Work in this area has slowly given way to side-chain liquid crystals.

Side-chain or comb-like monomeric liquid crystals appear as a pendent side-chain attached to the main chain by flexible links (usually methylene groups \((-\text{CH}_2-)\_n\), where \(n = 1\) to \(10\) (Figure 12).

Figure 12. Comb-like polymers

The polymers, often solids, are petrified versions of the liquidcrystalline order that existed in the monomer before the polymerization. The polymer and mesogenic effects are essentially uncoupled and the latter are often predictable from those of the mesophase. The molecular conformation is not altered by
the formation of the mesophase.

Two general procedures have been developed for the synthesis of side-chain polymers: (1) The conventional method of synthesis which involves the polymerization of appropriate liquid-crystalline monomers and (2) A method reported by Paleos and coworkers\textsuperscript{48-49} which involves the interaction of reactive polymers with mesogenic compounds.

Blumstein and co-workers prepared nematic polymer products from monomers (36-39). The nature of the molecular order was established for polymers prepared from these monomers.

\begin{align*}
\text{H}_2\text{C}=\text{CH}-\text{CO}-\underset{\text{Q}}{\text{C}}\text{H}_3\quad &\text{H}_2\text{C}=\text{CH}-\text{CO}-\underset{\text{O}}{\text{C}}\text{H}_3\text{N}=(\text{CH}_2)_3\text{C}=\text{CH}_2 \quad (36) \\
\text{H}_2\text{C}=\text{C}-\text{CO}-(\text{CH}_2)_{26}\text{CH}_3 \quad &\text{H}_2\text{C}=\text{CH}-\text{N}=(\text{CH}_2)_3\text{O}-(\text{CH}_2)_3\text{C}=\text{CH}_2 \quad (37) \\
\text{H}_2\text{C}=\text{CH}-\text{N}=(\text{CH}_2)_3\text{CN} \quad &\text{H}_2\text{C}=\text{CH}-\text{N}=(\text{CH}_2)_3\text{CN} \quad (38) \\
\end{align*}

Within the layers, the side groups usually were oriented at an angle to the plane formed by the main chain. The presence of strong transverse dipoles (such as carboxy groups) probably led to well defined lamellar organization of the smectic phase. The presence of strong
longitudinal dipoles favored nematic polymers.

Inherent disorder of the polymer main chain was found to influence the melt structure, the main chain tended to coil. Flexible spacers (-(CH₂)ₙ-) were introduced between the main chain, and the mesogenic unit. This spacer group allowed greater freedom of the side group⁴⁸, permitting the formation of the mesophase. Very few polymers with pendant groups, which have no spacers, show mesophases. Ringsdorf and coworkers⁴⁹ prepared polymers based on acrylic and methacrylic acid esters with flexible spacers of polymethylene chains and various mesogens, such as biphenyl (40) and aromatic esters (41).

When Ringsdorf and co-workers prepared polymers with the same mesogen but different alkyl or alkoxy substituents two effects were observed: the polymers with the alkoxy substituents had a greater mesophase stability, and an increase in substituent length caused a higher clearing temperature. Substituting a biphenyl group in the phenyl esters resulted in a broader mesophase temperature range.

Main-chain or linear liquid crystal polymers were first reported in the mid-1970s by a group of researchers at the University of Naples⁵⁰. Inclusion of the mesogenic structures in the main chain requires condensation polymerization techniques. The main chain
is not superfluous (as in comb-like polymers), therefore considerable care must be taken to produce a high molecular polymer with a narrow distribution of chain lengths.

Typical linear thermotropic polymers have stable liquid crystal phases in the range of 100-400°C. While these polymers exhibit properties almost identical to their monomeric and oligomeric counterparts, they have very slow response times -minutes to hours- to external stimuli in electric and magnetic fields, and have unique X-ray diffraction patterns.

In main-chain polymers the molecule must adopt a conformation and packing that is compatible with the structure of the mesophase. The alternation of the repeating unit may affect the molecular packing and cause the properties of the polymeric mesophase to depart from those of the low molecular weight mesogen. The formation of the mesophase can affect the conformation of the polymer, hence the mechanical properties of the solid polymer after it is cooled from the mesophase. The theory and potential applications of these polymers cause them to be of most interest today.

Mesogenic linear polyesters are divided into three groups: rigid homopolyesters, copolymers, and semiflexible homopolyesters.

Completely rigid polyesters with high symmetry such
as poly(p-hydroxybenzoic acid) form neither thermotropic nor lyotropic mesophases due to their high transition temperatures, $T_m$, and limited solubility.

Rigid-rod polymers have been reviewed by Jin and co-workers\textsuperscript{52}. They are usually high melting polyesters with a large aromatic content. Poly-(p-phenylene terephthalate) (42) is a logical representative compound, however the $T_m$ and $T_\alpha$ (267°C and 467°C, respectively) are too high.

\begin{equation}
(-\overset{0}{C}-\overset{0}{O}-\overset{0}{C}-\overset{0}{O}-)_n
\end{equation}

(42)

Three approaches have been taken to lower these transition temperatures: (1) the use of symmetrically substituted hydroquinones and terephthalic acids; (2) the preparation of copolymers containing non-linear comonomers; and (3) the inclusion of flexible units in the main chain.

Dupont patents report the use of unsymmetrical hydroquinones and many different aromatic or cycloaliphatic diacids (Figure 13)\textsuperscript{53}.

The use of asymmetrically-substituted hydroquinones in random copolymers suppressed the melting points and enabled the melt spinning of fibers from the liquid crystal state of the polymer melt. The inclusion of limited amounts of non-linear structural units such as
those derived from resorcinol, isophthalic acid and m-hydroxybenzoic acid was chosen over the substituted monomers as a general method of approach. However, problems controlling the polymer composition, sequence distribution of structural units, and reorganization during processing were encountered.

\[
\begin{align*}
X \quad & - O - C - Y \\
\quad & - O - C - Z - O \\
X \text{ and } Y = & \quad - H, - C l, - B r, - C H_3 \\
Z = & \quad - H, - C H_3, - O C H_2 C H_2 O - , - C H_3
\end{align*}
\]

Figure 13. Polymer series prepared by Dupont Corp.

W.J. Jackson reported 2,6-naphthalene-dicarboxylic acid (43) as a comonomer effective in lowering the transition temperatures of all-aromatic copolyesters. The all-aromatic homopolyesters with similar structures melt too high to be thermally processed without thermal decomposition.

\[
\text{HOOC-} - C - \text{COOH} \quad \text{(43)}
\]
Polymers prepared with 1,4- and 1,5- oriented monomers have been reported but are not as effective as 2,6- oriented naphthalene derivatives in lowering the transition temperatures of the copolymers.

Figure 14. Various mesogenic units and flexible spacers that have recently appeared in the literature.

The phase transitions of copolyesters are expected to be biphasic (nematic and isotropic). This effects the mechanical properties, as the isotropic portion may not achieve the desired orientation during flow. An
alternative is the inclusion of flexible units to modify the behavior of the melt. The alternating pattern of flexible spacer – rigid mesogen – flexible spacer may result in better liquid crystal properties. Mesogenic groups and flexible spacers which have been incorporated into polyester polymers are listed in Figures 14 and 15.

Structure of Polymers

Mesophase

\[
\begin{align*}
&-O- \text{CH}=\text{CH}- \quad O-C-(\text{CH}_2-)_{n}-C- \quad \text{smectic} \\
&-O- \text{C}- \quad \text{O} \quad \text{C}-O-(\text{CH}_2\text{CH}_2\text{O})_4- \quad \text{smectic} \\
&-O- \text{C}- \quad \text{O} \quad (\text{CH}_2)m-0- \text{C}-0- \text{O} \quad (\text{CH}_2-)n- \\
\end{align*}
\]

where \( m = 2-10 \) and \( 12 \) \( n = 6,8,10 \) all nematic

\[
\begin{align*}
&-O- \text{C}- \quad \text{O} \quad O-(\text{CH}_2-)n- \\
\end{align*}
\]

where \( n = 2-5 \) nematic

\[
\begin{align*}
&n = 6-9 \quad \text{smectic II} \\
&n = 10 \text{ and } 11 \quad \text{and nematic} \\
&\text{smectic I & II} \\
&\text{and nematic}
\end{align*}
\]

Figure 15. Liquid Crystal Polyesters having Mesogenic Units and Flexible Spacers in the Main Chain

Polymeric liquid crystals with flexible spacers (semiflexible homopolymesters) offer the advantage of
orientation of the mesogen with respect to the main chain, as well as lowering the melting point, \( T_m \), of the polymer. Polymers with mesogenic side chains show orientation of the pendant groups perpendicular to the main chain. This property would be detrimental in the case of fiber applications because a tensile force on the sample would be borne by non-covalent bonds. Rigid-rod polymers would also have the mesogenic groups in the direction of the force. However, they do not have the advantage of reduced melting temperatures and increased solubility which make processing much easier.

Jin and co-workers\(^{59-60}\) also synthesized a series of polyesters with flexible spacers. These are of particular interest to us because of the poly-(\( p \)-phenylene terphthalate) linkage. The five polymer series is represented in Figure 16.

The melts of the polymers (Series I) derived from 4,4 ′-dihydroxy-\( \alpha \)-\( \omega \)-diphenoxalkanes and terephthalic acid all were strongly birefringent and most showed typically nematic threaded-Schlieren textures. Thermodynamic data is summarized in Table 3. The dependence of the melting points (\( T_m \)) on the number of methylene units in the flexible spacer was typical of those observed for other organic compounds and polymers; the decreasing zig-zag (odd-even) fashion with the length of the polymethylene group, and \( T_m \) was
higher for polymers having an even number of methylene
groups than those with an odd number. This was
previously noted in the section on oligomers, and
reaffirms the theory of the continuum from monomer-to
oligomer-to-polymer.

Structure of Polymer

\[
\begin{align*}
\text{Series} & \quad \text{Structure} \\
I & \quad \begin{array}{c}
-\text{O-C-CH}_3- - \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \\
n = 5-10
\end{array} \\
II & \quad \begin{array}{c}
-\text{O-C-CH}_3- - \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \\
n = 2-8 \text{ and } 10
\end{array} \\
III & \quad \begin{array}{c}
-\text{O-C-CH}_3- - \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \\
X
\end{array} \\
IV & \quad \begin{array}{c}
-\text{O-C-CH}_3- - \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \\
Y
\end{array} \\
V & \quad \begin{array}{c}
-\text{O-C-CH}_3- - \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \quad \text{O-} \\
Z
\end{array}
\end{align*}
\]

Figure 16. Polyesters with poly-(p-phenylene
terephthalate) linkages

When the length of the flexible spacer was
increased it was observed that $\Delta T (T_1 - T_m)$ decreased
and that $\Delta T$ was greater for the odd numbered methylene
units. A proper physical explanation for these
observations has not been made.

<table>
<thead>
<tr>
<th>n</th>
<th>Tm°C</th>
<th>Tc°C</th>
<th>ΔT°C</th>
<th>ΔH₄ (kcal/mol)</th>
<th>ΔS (kcal/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>242</td>
<td>355</td>
<td>113</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>267</td>
<td>330</td>
<td>63</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>239</td>
<td>326</td>
<td>85</td>
<td>0.22</td>
<td>0.37</td>
</tr>
<tr>
<td>8</td>
<td>245</td>
<td>278</td>
<td>35</td>
<td>0.34</td>
<td>0.62</td>
</tr>
<tr>
<td>9</td>
<td>229</td>
<td>298</td>
<td>68</td>
<td>0.43</td>
<td>0.75</td>
</tr>
<tr>
<td>10</td>
<td>237</td>
<td>265</td>
<td>31</td>
<td>0.67</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 3. Properties of Polymers of Series I

Table 3 summarizes the thermodynamic behavior of the polymers in relation to their transitions. The enthalpy (ΔH₄) and entropy (ΔS₄) of clearing increased with increasing spacer length. Higher values of ΔS₄ for the polymers with longer spaces indicate that these polymers have higher degrees of orientation in their mesophases than the ones with shorter methylene linkages. Enthalpy and entropy changes for the nematic-to-isotropic transitions were calculated from the area under the curve of endothermic peaks observed in DSC thermograms.

All the polymers showed broad clearing endotherms which were obscured by the decomposition of the polymers with shorter flexible spacers because of their very high melting points. The broadness of the transition was probably due to the polydispersity of the molecular weights of these polymers and kinetic effects that
affect the transitions.

The second series of polyesters were derived from terephthalic acid and 4-4'-dihydroxy-dibenzoylalkanes. In these polymers, the mesogenic units were connected with the polymethylene flexible spacers through ester linkages, whereas the first series was connected through ether linkages. The polymers all showed thermotropic behavior and the usual decreasing odd-even behavior, but as \( n \) increased from 7 to 8, the transition temperature seemed to increase. As the methylene groups increased from 3 to 8, the mesophases were nematic; \( n = 9 \) and 10 were smectic. The longer flexible spacer renders a higher degree of freedom for the mesogens to be aligned to form smectic layers. Transition temperatures were generally lower for the Series II polyesters.

The effect of colinearity and coplanarity of the mesogenic unit on the mesophase was determined by comparing polymer (IV) and the polymer in series (I) with 10 methylene units (Figure 16). The melting points, \( T_m \), were about the same (237°C and 236°C respectively). \( T_1 \) for the polymer in series (I) was 265°C, while \( T_1 \) for (IV) was 297°C. This demonstrated that greater colinearity and coplanarity of (IV) stabilizes the mesophase by producing a greater \( \Delta T \).

Polymer (V) is similar to (IV), except that a phenylene group was replaced by biphenyl (IV). \( T_m \) increased by 22°.
and $T_1$ increased by 77°. The increase in the mesophase with the addition of a phenylene linkage indicates that longer mesogenic units increase the stability of the liquid crystal phase.

Blumstein and co-workers, using azoxy mesogenic groups, also demonstrated that the molecular structure of the components and the manner in which they are assembled can have a great effect on the thermal properties of polymers. Changes of type or direction of the bonds alters the geometry and polarizability of the mesogenic units, and ultimately the liquid crystal properties of the polymer.

Griffen and Havens have reported the thermal behavior for a series of nematic liquid crystal polyesters with flexible spacers with the same general structure as the Series II polymers. There is a decreasing odd-even alternation in the clearing point transition temperatures of the homologs with short and intermediate length methylene units. The clearing points of the even and odd members line on smooth lines. As the chain length increased past a certain point the two curves merge into a single curve.

The Series III polyesters were of interest because they were synthesized from substituted hydroquinones and 4,4'-dicarboxy-1,10-di-phenoxydecane. The data in Table 4 reveals that when hydroquinone was monosubstituted
the transition temperature was very much lowered due to
the loss in symmetry. Monosubstitution also improved
solubility. Disubstituted (symmetrical) hydroquinones
had a lower $T_m$ than the unsubstituted ones, however, $T_m$
was higher than the $T_m$ for the monosubstituted form.

$$\begin{array}{cccccc}
X & Y & T_m^\circ C & T_1^\circ C & \Delta T & \Delta H_1 \\
H & H & 236 & 294 & 58 & 0.97 \\
H & Cl & 157 & 279 & 122 & 1.6 \\
H & CH_3 & 162 & 274 & 112 & 2.5 \\
H & Br & 146 & 270 & 124 & 2.8 \\
Cl & Cl & 200 & 255 & 55 & 0.94 \\
\emptyset & \emptyset & 151 & 168 & \\
\end{array}$$

<table>
<thead>
<tr>
<th>$\Delta S_1$</th>
<th>kcal/mol K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>2.9</td>
</tr>
<tr>
<td>4.6</td>
<td>5.2</td>
</tr>
<tr>
<td>1.8</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Thermodynamic Properties for the Transitions of Series III Polymers

Zhou and Lenz\textsuperscript{44} reported the properties of a
series of polyesters 44 in which $X$ is either (CH$_2$)$_n$-H
and $n = 0,1,2,...6,8,10$ or OCH$_3$, Br, CN or NO$_3$.

![Polyester Structure](image)

This was of interest to us because we had hoped to
synthesis a series of ordered polyesters which were
quite similar; the polymethylene linkage would have been
replaced with a phenylene linkage. We also considered
the incorporation of polymethylene linkages into the
main chain had the transition temperatures for the all-aromatic chain polymers been too high.

As seen in the data in Table 5, there is a decrease in $T_g$ (glass transition temperature) with increasing length of the alkyl group in the polymer. A substantial decrease in $T_m$ occurs when a hydrogen atom is substituted with a methyl group (231 to 154°C). This transition temperature further decreases in an approximately odd-even, zig-zag fashion when the methylene unit increased from $n = 1$ to 6. Further increase in $n$ had little effect on $T_m$. Methyl substitution also causes a substantial depression of the clearing temperature, $T_c$, from 267 to 190°C. For groups larger than methyl, $T_c$ continues to decrease until $n = 8$ and 10, when no mesophase is observed.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$T_g$°C</th>
<th>$T_m$°C</th>
<th>$T_c$°C</th>
<th>$\Delta T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>----</td>
<td>67</td>
<td>231</td>
<td>267</td>
<td>36</td>
</tr>
<tr>
<td>methyl</td>
<td>44</td>
<td>154</td>
<td>190</td>
<td>36</td>
</tr>
<tr>
<td>ethyl</td>
<td>35</td>
<td>71</td>
<td>127</td>
<td>56</td>
</tr>
<tr>
<td>propyl</td>
<td>27</td>
<td>97</td>
<td>110</td>
<td>13</td>
</tr>
<tr>
<td>butyl</td>
<td>35</td>
<td>75</td>
<td>103</td>
<td>28</td>
</tr>
<tr>
<td>pentyl</td>
<td>25</td>
<td>79</td>
<td>94</td>
<td>15</td>
</tr>
<tr>
<td>hexyl</td>
<td>17</td>
<td>75</td>
<td>86</td>
<td>11</td>
</tr>
<tr>
<td>octyl</td>
<td>9</td>
<td>99</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>decyl</td>
<td>4</td>
<td>98</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>bromo</td>
<td>44</td>
<td>140</td>
<td>196</td>
<td>56</td>
</tr>
<tr>
<td>cyano</td>
<td>47</td>
<td>157</td>
<td>219</td>
<td>62</td>
</tr>
<tr>
<td>nitro</td>
<td>42</td>
<td>161</td>
<td>194</td>
<td>33</td>
</tr>
<tr>
<td>methoxy</td>
<td>50</td>
<td>158</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 5. Thermal properties of polymers containing n-alkyl or polar substituents.
Polar groups which are larger than methyl and smaller than the ethyl group were also studied. It is apparent that the data of the alkyl and polar groups showed no simple relationship between size and the transition temperatures of the polymers. Instead, the polymers with larger polar substituents have as high or higher values of \( T_m \) and \( T_\alpha \) as the methyl substituted polymer, and there is little or no correlation between these transition temperatures and size within the polar series.

From this data it became apparent that if the polymers we hoped to synthesize (methyl substituted hydroquinones) were not liquid crystalline, substitution with polar groups may have resulted in a mesophase.

J.I. Jin and co-workers\(^6\) reported the properties of a series of copolyterephthalates of methylhydroquinone and bisphenol. The copolymers with the sulfone linkage were of particular interest to us since we planned to synthesis polyesters with sulfone linkages. The copolymer (45) had the following structure: \( X \) was none, \(-\text{CH}_2-\), \(-\text{C(CH}_3)_2-\), \(-\text{O}-\), \(-\text{S}-\), \(-\text{SO}_2-\), and \(-\text{CO}-\).

\[
\text{[structures shown]}
\]

The last five copolymers showed definite liquid
crystalline behavior in the melt. The copolymer with the sulfone linkage showed only borderline liquid crystal properties, Table 6. The steric and geometric factors in the structural units were the most important in controlling the liquid crystallinity of the copolymers. We might expect that the polyesters with polysulfone linkages we hope to prepare would show similar properties.

<table>
<thead>
<tr>
<th>X</th>
<th>$T_m$°C</th>
<th>Stir Opalescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>-C(CH$_3$)$_2$-</td>
<td>---</td>
<td>No</td>
</tr>
<tr>
<td>-SO$_2$-</td>
<td>354</td>
<td>Weak</td>
</tr>
<tr>
<td>-CH$_2$-</td>
<td>289</td>
<td>Strong</td>
</tr>
<tr>
<td>-S-</td>
<td>334</td>
<td>Strong</td>
</tr>
<tr>
<td>-O-</td>
<td>350</td>
<td>Strong</td>
</tr>
<tr>
<td>-CO-</td>
<td>399</td>
<td>Strong</td>
</tr>
<tr>
<td>none</td>
<td>---</td>
<td>Strong</td>
</tr>
</tbody>
</table>

Table 6. Properties of Methylhydroquinone Copolyesters.

The effect of substitution of the hydroquinone component of polyterephthalates (Figure 17) with methyl groups was investigated by Kops and co-workers. These random homopolymesters were of prime importance to us, as we planned to prepare a series of ordered homopolyesters, two of which would have the same structural units as polymers II and V.

The melting points (Table 7) of these random polymers decrease with increasing substitution. The solubility, on the other hand, increases, although all the
polymers are insoluble in common organic solvents. The additional endothermic transitions $T_4$ were observed and are attributed to thermotropic changes in the liquid crystalline state of the melt.

![Diagram of polyterephthalates structure]

**Figure 17.** The structure of the polyterephthalates prepared by Kops and co-workers.

**Table 7.** Transition temperatures for the polyterephthalates.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>#</th>
<th>$T_m^\circ\text{C}$</th>
<th>$T_i^\circ\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>I</td>
<td>387</td>
<td>426</td>
</tr>
<tr>
<td>2-Me</td>
<td>II</td>
<td>378</td>
<td>460</td>
</tr>
<tr>
<td>2,3-DiMe</td>
<td>III</td>
<td>323</td>
<td>475</td>
</tr>
<tr>
<td>2,5-DiMe</td>
<td>IV</td>
<td>317</td>
<td>423</td>
</tr>
<tr>
<td>2,6-DiMe</td>
<td>V</td>
<td>300</td>
<td>453</td>
</tr>
</tbody>
</table>

Lenz and co-workers\(^6\)\(^7\) have reported similar observations for aromatic polyester systems with spacer groups.
OBJECTIVE

Preparation and characterization of ordered polyesters was the objective of this thesis study. Figure 18 illustrates the structures of ordered and random polyesters with methylhydroquinone repeat units. The methyl groups are arranged in random order in one polyterephthalate and systematically in the other.

Figure 18. Ordered and random polyterphthlates

The first step of this investigation involves the synthesis of four substituted 4-methoxyphenols (46) as seen in Figure 19.

As substituted methoxyanilines (47) are commercially available, the phenols were to be prepared by the hydrolysis of diazonium salts.
4-methoxy-3-methylphenol, where $R_1=CH_3$, $R_2=R_3=R_4=H$
4-methoxy-2-methylphenol, " $R_2=CH_3$, $R_1=R_3=R_4=H$
4-methoxy-3,5-dimethylphenol " $R_1=R_3=CH_3$, $R_2=R_4=H$
4-methoxy-2,4-dimethylphenol " $R_2=R_4=CH_3$, $R_1=R_3=H$

Figure 19. Substituted 4-methoxyphenols to be synthesized for the ordered polyester study.

Interfacial condensation of a methyl substituted $p$-methoxyphenol with terephthaloyl chloride should yield a blocked trimer (48). The methoxy group would limit the condensation reaction to the formation of a trimer.

The next step involves the removal of the blocking group (CH$_3$) from the alkyl-aryl ether linkage to give a bisphenol (49).

Interfacial condensation of the bisphenol with terephthaloyl chloride should result in the formation of the desired ordered polyester (50). The overall reaction scheme is presented in Figure 20.

Characterization of these ordered polymers and comparison of their properties to those of the random polyesters prepared by Kops and co-workers$^{69}$ is the final step in our study of ordered polyesters.
Figure 20. Reaction scheme for the synthesis of ordered polyesters.

Since many aromatic polyesters exhibit liquid crystal properties, another objective was to study the continuum from monomer-to-oligomer-to-polymer for compounds and polymers prepared in the ordered polyester study. It is, therefore, necessary to prepare an
oligomer to complete the series. The key step is the removal of one methyl blocking group from trimer (48). Limiting the amount of deblocking agent should result in a mixture of three compounds: the original trimer (48), the bisphenol (49), and trimer (51), which has only one methyl group removed. This trimer (51) is necessary for the synthesis of the oligomer.

Isolation of compound (51) (which has one end blocked with a methoxy group), followed by condensation with terephthaloyl chloride, should yield oligomer (52), a septamer.

\[
\begin{align*}
&\text{CH}_3\text{O} - \text{O-C-} - \text{O} - \text{C-} - \text{OH} \\
&\text{R}_3 \text{R}_4
\end{align*}
\]

(51)

\[
\begin{align*}
&\text{CH}_3 - Z - \text{C} - Z - \text{CH}_3
\end{align*}
\]

(52)

when \(Z =

\[
\begin{bmatrix}
R_1 & R_2 & R_2 & R_1 \\
R_3 & R_4 & R_4 & R_3
\end{bmatrix}
\]

Monomer (48), oligomer (52), and polymer (50) are expected to possess liquid crystal properties.
Thermodynamic data from the ester series should support the theory that a continuum exists with increasing molecular weight for a given ester series.
DISCUSSION AND RESULTS

PHENOLS

In the proposed synthesis of ordered aromatic polyesters, the first step was to prepare methyl substituted 4-methoxyphenols (53, 54, 55, and 56).

Most organic chemistry texts indicate that phenols are readily prepared by the hydrolysis of diazonium salts. Primary aromatic amines react with nitrous acid to yield diazonium salts.

2,6-Dimethyl-4-methoxyphenol (56) was successfully prepared from a diazonium salt by T. C. Bruice and co-workers. They reported an unusually high yield, 88%, from the corresponding aniline.

The diazotization of 4-methoxy-2-methylaniline (57) using the procedure described by Fieser and Williamson was attempted. The proposed reaction was the conversion of the amine to a quaternary ammonium salt (58). When the salt, dissolved or suspended in cold aqueous mineral acid, was treated with sodium nitrite, a diazonium salt
was formed. Since diazonium salts decompose slowly, even at ice-bath temperatures, the solution was immediately hydrolyzed with large volumes of sulfuric acid. An acidic solution of boiling dilute sulfuric acid was used, and the diazonium salt was added dropwise to minimize the coupling of the phenol with the diazonium salt to form azo compounds. The attempt was unsuccessful (Figure 21).

\[
\begin{align*}
\text{CH}_3\text{O} & \quad \text{NH}_2 \\
(57) & \quad \text{HCl} \\
\text{CH}_3\text{O} & \quad \text{NH}_3^+\text{Cl}^- \\
(58) & \quad \text{HONO} \quad 0^\circ\text{C} \\
\text{CH}_3\text{O} & \quad \text{N}_2^+\text{Cl}^- \\
(59) & \quad \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \quad \Delta \\
\text{CH}_3\text{O} & \quad \text{OH} \\
(60) & \quad \text{CH}_3
\end{align*}
\]

Figure 21. The proposed reaction sequence for the preparation of 4-methoxy-2-methylphenol.

Sulfuric acid was then substituted for the hydrochloric acid. Hydrogen sulfates are preferred to chlorides or nitrates, since in these cases there is competition from the nucleophiles, Cl\(^-\) or NO\(_3^-\). This too was unsuccessful.

It has been cited\(^7\) that the difficult step in this preparation of phenols is the hydrolysis of the diazonium salt. Coupling of the phenol with the undecomposed diazonium compound and the formation of
tars results in very small yields of the phenol. In an effort to increase the yield of phenols, Lambooy improved the procedure for the hydrolysis of the diazonium salt. The phenol was removed immediately after its formation by steam distillation, before it coupled with the diazonium salt. The concentration of the diazonium salt was kept low to reduce the chances of the coupling side reaction. Bruice and coworkers used Lambooy's technique in their successful preparation of compound (56). They also added a solution of urea to destroy excess nitrous acid before the diazonium salt was hydrolyzed to the phenol.

As diazonium salts are stable only at low temperature, usually below 5°C, a special dropping device for adding the cooled diazonium salt had to be devised. Using a description from Lambooy's paper, we built a similar cooling apparatus; a condenser was converted into a dropping funnel and ice water was circulated through the condenser to maintain the diazonium salt at a temperature below 5°C (Figure 22). This method did not improve the yield of the desired phenol.

Some diazonium salts require a more vigorous treatment than the method described by Fieser and Williamson, i.e., boiling with aqueous sulfuric acid or with trifluoroacetic containing potassium.
trifluoracetate. Diazotization in trifluoroacetic acid and the subsequent hydrolysis of the diazonium salt was successfully used in the conversion of 4-amino-2-(1-nonenyl)quinoline (61) to 2-(1-Nonenyl)-4-quinolinol (62) by Gottstein and co-workers.\textsuperscript{75}
When we used trifluoroacetic acid under similar conditions in the diazotization of 4-methoxy-2-methylaniline, the expected phenol was not isolated.

Three alternate routes for the synthesis of methyl substituted 4-methoxyphenols could be used. The first modification involved the formation of a diazonium tetrafluoroborate. Horning and co-workers transformed aromatic amine (63) into a diazonium tetrafluoroborate (64) which, when boiled under reflux in trifluoroacetic acid and potassium trifluoroacetate gave the trifluoroacetate (65). Hydrolysis of the trifluoroacetate, upon dilution in water, gave the desired phenol (66) in high yield.
Alkali fusion of sulfonates is another method of preparation of phenols. In spite of the extreme conditions, the reaction has been reported to give good yields of the phenols, except when the substance contains groups which are also attacked by alkali under these conditions. A molten mixture of hydroxide and a little water in a copper, nickel, or iron crucible is treated with small portions of the sodium salt of a sulfonic acid. The reaction temperature is usually 300–320°C.

The potassium persulfate oxidation of phenols, with the \( p \)-position to the phenolic group free, to resorcinols, was discovered by Elbs in 1893\textsuperscript{7}. Baker and Brown\textsuperscript{79} report the synthesis of 2-hydroxy-5-methoxytoluene (53) and 5-hydroxy-2-methoxytoluene (54) from \( m \)-cresol and \( o \)-cresol respectively.

\( o \)-Cresol (67) was oxidized by alkaline potassium persulfate to a \( p \)-hydroxyphenylpotassium sulfate (68). This intermediate was isolated in the crude state and then alkylated with methyl sulfate in alkaline solution.
to give a product (69) in which the alkoxy group occupies the position of the original hydroxyl group. Acid hydrolysis then gave 5-hydroxy-2-methoxymethyltoluene (54).

\[
\begin{array}{c}
\text{OH} \quad \text{CH}_3 \quad \xrightarrow{\text{OSO}_2\text{OK}} \quad \text{OH} \quad \text{CH}_3 \\
(67) & \quad (68) & \quad (69) & \quad (54)
\end{array}
\]
DEBLOCKING OF DI(METHOXYPHENYL) TEREPTHALATES

Di(3-methoxy-5-methylphenyl) terephthalate (70) and di(p-methoxyphenyl) terephthalate (71) were prepared by condensation of the blocked phenol with terephthaloyl chloride. These compounds were to be used as model compounds in the ordered polyester and continuum studies. Both studies required cleavage of the aryl methyl ether.

![Diagram of compound (70)]

![Diagram of compound (71)]

Aryl methyl ethers are very stable to many common reagents. Originally, drastic conditions of strong acid (i.e. HI or HBr) were required for the cleavage of the ether. Acidic conditions were not possible in our case because of ester linkages in compounds (70) and (71).

The demethylation of aryl ethers under nonacidic conditions has been accomplished recently by a wide variety of nucleophiles: iodonitromethyldisilane in
chloroform, sodium-\(p\)-thiocresolate in toluene, boron tribromide in methylene chloride, sodium benzylselenolate in dimethylformamide, sodium cyanide in dimethyl sulfoxide, and sodium ethanethiolate in dimethylformamide. A comprehensive review of ether cleavages can be found in an article by Bhatt and Kulkarni. The most convenient methods are sodium ethanethiolate in hot N,N-dimethylformamide and \(p\)-thiocresolate in hot toluene containing hexamethylphosphoramide (HMPA).

The method of Feutrill and Mirrington was selected for the demethylation of blocked compounds. Sodium ethanethiolate, in N,N-dimethylformamide, removes the protecting methyl group from the blocked terephthalate. Several features make this method particularly attractive: (1) High temperatures and long reaction times are usually not required. (2) Both the excess reagent and by-product, ethyl methyl thioether, can be easily removed during evaporation of solvents. (3) A hindered ether can be demethylated without difficulty.

Di(p-methoxyphenyl) terephthalate (71) was reacted with sodium ethanethiolate in N,N-dimethylformamide under nitrogen. The reaction did not proceed as expected. Di(p-hydroxyphenyl) terephthalate (72), the expected product, was not recovered.
The original reaction, 0.010 mole of di(p-methoxyphenyl) terephthalate and excess sodium hydride (0.035 mole) and ethanethiol (0.040 mole), was heated at 105°C overnight. The ester linkage was cleaved to give terephthalic acid (73) and p-methoxyphenol, as products. It appeared that, the ethanethiolate ion preferentially attacked the carbonyl group over the methoxy group. Formation of a thioester followed by hydrolysis resulted in terephthalic acid and ethanethiol. Ethanethiol is volatile and was easily removed. Different reaction conditions were tried.
In the second attempt at the demethylation reaction, equivalent amounts (0.010 equivalents) of reactants were used and the reaction was heated at 55°C for six hours. Small amounts of terephthalic acid, p-methoxyphenol, and di(p-methoxyphenyl) terephthalate (starting material) were recovered, as well as, a high percentage of 4-(p-methoxyphenylcarboxo)-benzoic acid (75).

\[
\begin{align*}
\text{CH}_3\text{O}- & \quad \text{O} \quad \text{C} \\
& \quad \text{C} \quad \text{O}-\text{H}
\end{align*}
\]

Figure 23 compares the spectral data of di(p-methoxyphenyl) terephthalate (Figure 24), terephthalic acid (Figure 25), and the product, 4-(p-methoxyphenylcarboxo)-benzoic acid (Figure 26). The spectral data supports the hypothesis of cleavage at one of the carbonyl carbons of the original diester. The IR spectrum and elemental analysis confirm the product, 4-(p-methoxyphenylcarboxo)-benzoic acid.
IR Spectral Data

<table>
<thead>
<tr>
<th></th>
<th>Starting Material (71)</th>
<th>Terephthalic Acid (75)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H stretch</td>
<td>2940 &amp; 2820 (W)</td>
<td>1685 (S)</td>
<td>2810 (W)</td>
</tr>
<tr>
<td>C=O stretch</td>
<td>1728 (S)</td>
<td>1730 &amp; 1685</td>
<td></td>
</tr>
<tr>
<td>C-O-C Asym St</td>
<td>1200 (S)</td>
<td>1205 (S)</td>
<td></td>
</tr>
<tr>
<td>O-H stretch</td>
<td>3300-2500</td>
<td>3300-2700</td>
<td></td>
</tr>
<tr>
<td>C-O stretch</td>
<td>1280 (S&amp;B)</td>
<td>1280 (S)</td>
<td></td>
</tr>
<tr>
<td>O-H bending</td>
<td>1420 (M)</td>
<td>1420 (M)</td>
<td></td>
</tr>
</tbody>
</table>

Elemental Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Starting Material (71)</th>
<th>Terephthalic Acid (75)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>69.84</td>
<td>57.83</td>
<td>66.18 (66.24)*</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.76</td>
<td>3.61</td>
<td>4.44 (4.35)</td>
</tr>
<tr>
<td>Sulfur</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Figures in () are values determined analytically

Figure 23. IR spectral data and elemental analysis for 4-(p-methoxyphenylcarboxo)-benzoic acid.

The aqueous phase was extracted with ether. An oil, which remained after evaporation, was spotted on three thin layer sheets, and the components extracted from the strip. p-methoxyphenol was identified by IR and NMR analysis.
Figure 24

Di(p-methoxyphenyl) terephthalate
Trial three involved quadrupling the reactants. Half of the reaction mixture was worked up at the end of three hours and the other half at the end of five hours. The reaction temperature was 55°C. The products of the two reactions were not the same. They did not include the proposed product, di(p-hydroxyphenyl) terephthalate (72), but were identified to be di(ethylthio) terephthalate (76) and 4-ethylthiocarb-oxobenzoic acid (77).

\[
\begin{align*}
\text{(76)} & \quad \text{(77)}
\end{align*}
\]

Three hour reaction: After 3 hours, one half of the reaction mixture was added to hydrochloric acid and ice. A white precipitate was collected and recrystallized twice from ethyl acetate, T_m, 86-87°C. NMR and IR spectra of the product indicate di(ethylthio) terephthalate (76). The NMR spectrum indicates an ethyl thioester, quartet at 3.2 and the triplet at 1.38. Shift upfield from 4.2PPM and 1.5PPM supports a thioester over an ester.

<table>
<thead>
<tr>
<th>PPM</th>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singlet 8.0 Aromatic 10.5 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartet 3.2 -CH_2- 12 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triplet 1.35 -CH_3 15 6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The IR Spectrum (Figure 27) supports di(ethylthio)terephthalate: Absence of O-H stretch eliminates a carboxylic acid or terphthalic acid, C-H stretch at 2860, 2915, 2945, and 2970cm⁻¹ (W), as well as, C-H bending at 1375 and 1450cm⁻¹ (M) indicate an aliphatic component ([-CH₂⁻]ₙ, CH₃). A single C=O stretch at 1650cm⁻¹ (S), and C-O stretch at 1205cm⁻¹ (S) indicates the ester.

Elemental analysis calculated for C₁₀H₁₀O₃S also indicates the proposed compound:

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>56.67</td>
<td>5.55</td>
<td>25.21</td>
</tr>
<tr>
<td>Experimental</td>
<td>56.99</td>
<td>5.95</td>
<td>23.78</td>
</tr>
</tbody>
</table>

A slight contamination of 4-ethylthiocarboxobenzaic acid in the di(ethylthio)terephthalate would explain the slight discrepancy in the elemental analysis values.

The aqueous phase (filtrate) was extracted with ether and methylene chloride and the extracts evaporated. TLC and NMR spectrum of this material suggest p-methoxyphenol in DMF.

Five hour reaction: After five hours, the other half of the reaction mixture was added to hydrochloric acid and ice. A white precipitate (77), Tₘ (180-182°C), was collected. The product appears to be 4-ethylthiocarb-
oxobenzoic acid.

The NMR spectrum indicated a nonsymmetrical aromatic component, as well as, an ethyl ester. Shift upfield from 4.2PPM and 1.5PPM supports a thioester over an ester.

<table>
<thead>
<tr>
<th></th>
<th>PPM</th>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doublet</td>
<td>8.1</td>
<td>phenyl</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>Quartet</td>
<td>3.15</td>
<td>-CH₂-</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>Triplet</td>
<td>1.38</td>
<td>-CH₃</td>
<td>12</td>
<td>3</td>
</tr>
</tbody>
</table>

The IR spectrum (Figure 28) has a broad O-H stretch, two carbonyl peaks, and aliphatic and aromatic characteristics. This spectrum does not indicate di(p-methoxyphenyl)terephthalate ([71], starting material), 4-(p-methoxyphenylcarboxo)benzoic acid (75), or di(ethylthio)terephthalate (76).

<table>
<thead>
<tr>
<th>Bond</th>
<th>(71)</th>
<th>(75)</th>
<th>(76)</th>
<th>(77)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>2940, 2820(W)</td>
<td>2810(W)</td>
<td>2970, 2945,</td>
<td>2959, 2915(W)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2915, 2860(W)</td>
<td>1375(W)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1450, 1375(W)</td>
<td>1450, 1375(W)</td>
</tr>
<tr>
<td>C=O(acid)</td>
<td></td>
<td>1685(S)</td>
<td></td>
<td>1645(S)</td>
</tr>
<tr>
<td>C=O(ester)</td>
<td></td>
<td>1728(S)</td>
<td></td>
<td>1730(S)</td>
</tr>
<tr>
<td>C=O(thioester)</td>
<td></td>
<td></td>
<td>1650(S)</td>
<td>1680(S)</td>
</tr>
<tr>
<td>C-O-H</td>
<td></td>
<td></td>
<td>1430(M)</td>
<td>1440(M)</td>
</tr>
<tr>
<td>C-O-C</td>
<td></td>
<td>1200(S)</td>
<td>1205(S)</td>
<td>1280(S)</td>
</tr>
<tr>
<td>C-O</td>
<td></td>
<td>1275(S)</td>
<td>1280(S)</td>
<td>1280(S)</td>
</tr>
<tr>
<td>C-S-C</td>
<td></td>
<td></td>
<td>900(S)</td>
<td>910(S)</td>
</tr>
<tr>
<td>C-S</td>
<td></td>
<td></td>
<td>1205(S)</td>
<td>1205(S)</td>
</tr>
<tr>
<td>O-H</td>
<td>3300-2700</td>
<td></td>
<td>3300-2000</td>
<td></td>
</tr>
</tbody>
</table>

Elemental analysis calculated for C₁₀H₁₀S₀₃ also indicates the proposed compound to be 4-ethylthio-
carboxobenzoic acid. The slight discrepancy in the figures is probably due to slight contamination of the product with terephthalic acid.

**Elemental Analysis**

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>57.13</td>
<td>4.79</td>
<td>15.25</td>
</tr>
<tr>
<td>Experimental</td>
<td>58.11</td>
<td>4.86</td>
<td>14.26</td>
</tr>
</tbody>
</table>

The aqueous phase (filtrate) was extracted with ether and methylene chloride. TLC and the NMR spectrum of the material left after solvent removal suggest \( p \)-methoxy-phenol contaminated with DMF (solvent).

Preferential cleavage of the ester linkage over the ether linkage lead us to consider the preparation of ordered polyester-sulfones.
Figure 27  Di(ethylthio) terephthalate
Figure 28  4-Ethylthiocarboxybenzoic acid
OBJECTIVE

Introduction of order into poly(ester-sulfones) is a pathway to the study of ordered polyesters. Order will be introduced into the polymer through the sulfone component, thus eliminating the problem of ester cleavage in the deblocking step.

The proposed reaction sequence follows:

1) Preparation of an ordered sulfone component (78), which is blocked at both ends, condensation of a methyl substituted p-methoxyphenol with 4,4'-dichlorodiphenyl sulfone.

\[
\begin{align*}
& \text{CH}_3\text{O-} \quad \text{Cl-} \quad \text{SO}_2- \quad \text{Cl} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{O-} & \quad \text{SO}_2- \quad \text{O-} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

2) Debloking of the sulfone.

\[
\begin{align*}
\text{(78)} & \quad \text{debloking} \\
\text{(79)}
\end{align*}
\]
3) Condensation of the deblocked sulfone (79), with terephthaloyl chloride to form a poly(ester-sulfone) (80).

$$
\text{condensation} \\
\begin{array}{c}
\text{(79)} + \text{Cl-C-C-Cl} \\
\end{array}
$$

4) Characterization of the polymer.

**DISCUSSION AND RESULTS**

**DEBLOCKING**

Preparation of a model compound was the first step of our ordered poly(ester-sulfone) study. Since p-methoxyphenol and 4,4'-dichlorodiphenyl sulfone were both readily available, they were chosen to prepare the model compound, 4,4'-[sulfonyl bis(p-phenylene ether)] dianisole (81).

$$
\text{CH}_3\text{O-} -\text{SO}_2- \text{CH}_3
$$

Condensation of p-methoxyphenol and 4,4'-dichloro-
diphenyl sulfone gave the desired blocked sulfone (81), 
Tₘ, 143-145°C, with a 95% yield. NMR data supports the 
successful preparation of 4,4′-[sulfonyl bis(p-phenylene 
ether)] dianisole:

<table>
<thead>
<tr>
<th>Multiplet</th>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0-6.9</td>
<td>Aromatic</td>
<td>32.3</td>
<td>16</td>
</tr>
<tr>
<td>3.8</td>
<td>-OCH₃</td>
<td>11.5</td>
<td>6</td>
</tr>
</tbody>
</table>

IR spectral (Figure 29) information is indicative of the desired sulfone; aromatic carbon-hydrogen 
stretching band at 3050 cm⁻¹, aromatic carbon-carbon 
double bond absorption at 1580, 1500, and 1480 cm⁻¹; aliphatic carbon-hydrogen stretching bands at 2940 and 
2815 cm⁻¹; carbon-oxygen-carbon stretching bands at 1235 
and 1030 cm⁻¹; and sulfone group absorptions at 1325 and 
1147 cm⁻¹.

The next step in the reaction sequence was the 
demethylation of 4,4′-[sulfonyl bis(p-phenylene ether)] 
dianisole. Clean and rapid demethylation of aryl ethers 
attracted us to the use of sodium ethanethiolate 
dissolved in N,N-dimethylformamide (DMF). Reaction 
conditions were the same as those used in the attempted 
demethylation of esters; di(3-methoxy-5-methylphenyl) 
terephthalate (70) and di(p-methoxyphenyl) terephthalate 
(71). 4,4′-[sulfonyl bis(p-phenylene ether) diphenol 
(82) was not isolated. Instead 4,4′-dithioethyldiphenyl
sulfone (83) and p-methoxyphenol were recovered in 86% yield.

\[
\begin{align*}
\text{CH}_3\text{O} & \quad \text{-O-} & \quad \text{SO}_2 & \quad \text{-O-} & \quad \text{OCH}_3 \\
\text{expected product} & \quad \overset{\text{CH}_3\text{CH}_2\text{S}^-}{\text{DMF}} & \quad \text{HO} & \quad \text{-O-} & \quad \text{SO}_2 & \quad \text{-O-} & \quad \text{OH} \quad (82)
\end{align*}
\]

NMR and IR spectra confirm 4,4'-dithioethoxy-diphenyl sulfone. The NMR spectrum confirms the presence of an ethyl group and an aromatic component.

<table>
<thead>
<tr>
<th>PPM</th>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6</td>
<td>aromatic</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>2.9</td>
<td>-CH$_2$-</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>-CH$_3$</td>
<td>15</td>
<td>6</td>
</tr>
</tbody>
</table>

IR spectrum (Figure 30) showed aromatic carbon-hydrogen stretching at 3050 cm$^{-1}$, aromatic carbon-carbon double bond absorption at 1569 and 1475 cm$^{-1}$; aliphatic carbon-hydrogen stretching bands at 2949, 2903, 2845, 1442 and 1376 cm$^{-1}$; and sulfone group absorptions at 1314 and 1151 cm$^{-1}$, which also confirms the structure.
Figure 29  4,4'-[Sulfonyl bis(p-phenylene ether)] dianisole
Figure 30  4,4'-Dithioethoxydiphenyl sulfone
Unexpected cleavage of the diaryl ether linkages of our model compound forced us to consider an alternative cleavage reaction. The absence of the ester linkage permitted consideration of many other deblocking methods. Constant boiling hydrobromic acid, particularly with acetic acid as a co-solvent, has been extensively used to cleave ethers, dialkyl and alkyl-aryl ethers are cleaved. In the later case the alkyl-oxygen bond is preferentially cleaved.

Two demethylation reactions were carried out on 4,4′-[sulfonyl bis(p-phenylene ether)] dianisole (81), using hydrobromic acid as a demethylating agent. Ether cleavage reactions were run with and without acetic acid as a co-solvent. The sulfone was insoluble in hot hydrobromic acid, however, was soluble in the co-solvent system (hydrobromic acid-acetic acid). In both cases the alkyl-oxygen bond was cleaved to give 4,4-[sulfonyl bis(p-phenylene ether)] diphenol (84).

\[
\text{HBr} \\ \begin{array}{c}
\text{CH}_3O-O-O-SO_2O-O-OCH_3 \\
(81)
\end{array} \rightarrow \begin{array}{c}
\text{HO-O-SO}_2O-O-OH \\
(84)
\end{array}
\]
Figure 31 4,4'-[Sulfonyl bis(p-phenylene ether)] diphenol
The NMR spectrum showed the absence of a singlet at 3.82PPM (CH$_3$O- of the starting material). The IR spectrum (Figure 31) has a typical oxygen-hydrogen stretch at 3550-3000cm$^{-1}$; aromatic carbon-hydrogen stretching bands at 3075, 3045 and 3110cm$^{-1}$, aromatic carbon-carbon double bond absorption at 1588, 1505, 1487, and 1451cm$^{-1}$; carbon-oxygen stretch at 1230cm$^{-1}$ and; sulfone group absorptions at 1366 and 1145cm$^{-1}$.

Elemental analysis data of 4,4'([sulfonyl bis(p-phenylene ether)] diphenol confirms the demethylation reaction:

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>66.35</td>
<td>4.18</td>
<td>7.38</td>
</tr>
<tr>
<td>Experimental</td>
<td>66.50</td>
<td>4.06</td>
<td>5.62</td>
</tr>
</tbody>
</table>

The melting point of the product from the two demethylation reactions with hydrobromic acid was 187-189°C.

4,4'([sulfonyl bis(p-phenylene ether)] dibenzene (85) was prepared to confirm that hydrobromic and acetic acids do not cleave the diaryl ether linkage.

\[\text{(85)}\]

Also, it was to be used in the nucleophilic
aromatic substitution study which will be discussed latter in this thesis.

\[ 4,4'-[\text{sulfonyl bis}(p\text{-phenylene ether})]\] dibenzene (85) was prepared by condensation of phenol with 4,4'-dichlorodiphenyl sulfone to give product product with a melting point of 143-145°C (99% yield).

Treatment of \[ 4,4'-[\text{sulfonyl bis}(p\text{-phenylene ether})]\] dibenzene with hydrobromic and acetic acids did not cleave the diaryl ether linkage. The starting material was recovered unaltered.

Demethylation with hydrobromic acid and acetic acid as a co-solvent appears to be a useful technique in the synthesis of ordered poly(ester-sulfones).

One step in the synthesis of ordered poly(ester-sulfones) requires the preparation of methyl substituted \[ 4,4'-[\text{sulfonyl bis}(p\text{-phenylene ether})]\] dianisoles. We had previously prepared \[ 4,4'-[\text{sulfonyl bis}(p\text{-phenylene ether})]\] dianisole by condensation of \( p\)-methoxyphenol with 1 4,4'-dichlorodiphenyl sulfone. Both of these starting materials were commercially available. When it became evident that the preparation of desired methyl substituted \( p\)-methoxyphenols was nearly impossible, an alternate route for the synthesis of the desired methyl substituted sulfones became necessary. The Ullmann ether synthesis was our choice.
ULLMANN ETHER SYNTHESIS

The Ullmann condensation has been used as a synthetic tool for nearly 80 years. This method of preparation of diaryl ethers is also referred to as the Ullmann ether synthesis and should be distinguished from the Ullmann coupling reaction used to prepare biaryls from aromatic halides.

The ether synthesis involves a copper catalyzed reaction between aromatic halides and alkali metal phenoxides or anilines to yield aryl ethers of arylamines. The original reaction with phenols has been carried out by heating the phenol, potassium hydroxide and copper without solvent at about 200°C.

\[
\text{Y}+\text{C}_6\text{H}_4\text{X} + \text{C}_6\text{H}_4\text{OH} + \text{KOH} \rightarrow \text{Y}+\text{C}_6\text{H}_4\text{O}+\text{C}_6\text{H}_4\text{X}
\]

The reaction has been modified over the years. Certain organic solvents containing heteroatoms dissolve copper salts to form catalytic complexes, thus allowing the use of lower reaction temperatures. Acidic solvents destroy phenoxide ions and cannot be used; water also interferes seriously with ether condensation. A number of copper salts have been used successfully in the Ullmann reaction including CuBr₂, CuCl₂, Cu(OAc)₂ H₂O, CuI, CuBr, and CuCl. Solubility is suggested as an
important factor in the success of the reaction. Yields have been reported up to 85%.

Little is known about the mechanism of these reactions, but it may be supposed that catalysis involves the joint association of the aryl halide and the nucleophile with the surface of the copper species employed. The reaction is assumed to be nucleophilic aromatic substitution based on the observation, by Weingarten\textsuperscript{73}, that the pattern of reactivity of various halo aromatics in the Ullmann condensation closely parallels other known nucleophilic aromatic substitution reactions\textsuperscript{74}.

A series of competitive reactions between unactivated aromatic halides with potassium phenoxide in diglyme solvent (CH\textsubscript{3}OCH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{3}) catalyzed by copper salts were undertaken by Weingarten in a mechanism study. A slight retardation due to a methyl substituent, activation due to substitution of an additional halo group, and slightly higher reactivity of the meta dihalo vs. the para dihalo compounds was observed. The relative rates for these reactions are found in Table 8. This is typical of nucleophilic substitution reactions. The halogen mobilites were found to be in the order, I \sim Br > Cl \gg F.

The proposed route of synthesis for 4,4’-[sulfonyl bis(p-phenylene ether)] dianisoles started with the
methylation of commercially available halophenols. Four halophenols were found, which would be useful in our study: 4-bromo-2,6-dimethylphenol (86), 4-bromo-3,5-dimethylphenol, 4-chloro-2-methylphenol, and 4-chloro-3-methylphenol.

\[
\begin{align*}
\text{CH}_3\text{-}F & \quad 0.001 \\
\text{CH}_3\text{-}\text{Cl} & \quad 0.78 \\
\text{Cl} & \quad 1.0 \\
\text{CH}_3\text{O}\text{-}\text{Cl} & \quad 1.2 \\
\text{Cl} & \quad 1.4 \\
\text{Cl} & \quad 1.9
\end{align*}
\]

Table 8. Relative rates

Methylation of 4-bromo-2,6-dimethylphenol (86), method described by Bruice and co-workers\(^8\), gave 80% yield of 4-bromo-2,6-dimethylanisole (87), after vacuum distillation.
The NMR spectrum exhibits the characteristics of 4-bromo-2,6-dimethylanisole:

<table>
<thead>
<tr>
<th>Singlet</th>
<th>PPM</th>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singlet</td>
<td>7.1</td>
<td>Aromatic</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Singlet</td>
<td>3.68</td>
<td>CH$_3$O-</td>
<td>14</td>
<td>3</td>
</tr>
<tr>
<td>Singlet</td>
<td>2.2</td>
<td>CH$_3$-</td>
<td>30</td>
<td>6</td>
</tr>
</tbody>
</table>

The IR spectrum has aromatic carbon-carbon double bond stretch absorptions at 1673 and 1577cm$^{-1}$; aliphatic carbon-hydrogen stretches at 2973, 2926, 2850, 2816, and 1379cm$^{-1}$; carbon-oxygen stretch at 1012 and 1215cm$^{-1}$.

The boiling point (89°C at ~4mm) compares favorably with Bruice and co-workers (83 at 3mm).

Success of the Ullmann ether synthesis was the determining step in our overall synthesis of ordered poly(ester-sulfones).

Modification of an ether synthesis scheme of Weingarten was designed for our first attempt at the ether synthesis of the desired sulfones. Since solvent seems to be a key factor in the success of the ether
synthesis, we decided to use dimethylformamide instead of diglyme. We also replaced CuCl$_2$ with CuBr$_2$. The proposed product for this reaction is 4,4’-[sulfonyl bis(p-phenylene ether)] di(2,6-dimethylanisole) (88). The reactants were not completely soluble in this solvent and we recovered the original sulfone.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Br} \\
\text{CH}_3 & \quad \text{OH}
\end{align*}
\]

\[
\text{1) KOH} \\
\text{2) CuBr}_2 \\
\text{DMF, N}_2
\]

(88)

4-bromo-2,6-dimethylanisole was not recovered. It is believed to have been removed when the DMF was evaporated.

The ether synthesis was repeated, replacing dimethylformamide with dimethyl sulfoxide. Since the reactants were soluble in the solvent (DMSO). A brown precipitate was collected when the reaction mixture was combined with hydrochloric acid and ice. The precipitate was insoluble in chloroform, ether, hexane, sodium hydroxide, acetone, and benzene. Insolubility of the product prevented thin layer chromatography. It is very slightly soluble in hot DMSO and ethyl acetate.
The compound charred at temperatures above 300°C.

The appearance of the product suggests a mixture of materials. It appears to contain white and brown components. Elemental analysis of the mixture: carbon 58.11, hydrogen 4.86, sulfur 14.26, and nitrogen < 0.1.

IR spectral data (Figure 32) indicates a broad peak at 3670-2400cm⁻¹ (maximum at 3350); carbon-carbon double bond stretch at 1586 and 1490cm⁻¹; possible aliphatic carbon-hydrogen stretch at 2950, 2890, 1450, and 1350cm⁻¹; peaks at 1285, 1212, 1145 and 1090cm⁻¹ could be interpreted as carbon-oxygen stretch and sulfone group absorptions. The limited solubility of the product made it impossible to collect NMR data.

The compound does not appear to be the desired product (88). The electron withdrawing nature of the sulfone group may limit the nuleophilicity of the phenol, therefore, inhibiting the ether synthesis.

The unexpected cleavage of the diaryl ether linkage by the ethanethiolate ion of (4,4'-[sulfonyl bis(p-phenylene ether)] dianisole lead us to a third topic in this thesis, nucleophilic aromatic substitution of diaryl ethers, discussed in the next section.
AROMATIC NUCLEOPHILIC SUBSTITUTION

INTRODUCTION

The $S_{\text{NAr}}$ Mechanism

Nucleophilic aromatic substitution reactions generally proceed so slowly that they are relatively uncommon. In many simple ArX compounds such as halo-benzenes and -toluenes nucleophilic substitution reactions require either vigorous or else very basic conditions, whereas $S_N$ reactions of alkyl halides are relatively facile. However, under other conditions which cannot be applied to alkyl halides, aryl halides react rapidly with nucleophilic or basic reagents to form products of considerable interest.

Three kinds of nucleophilic aromatic substitution reactions are relatively successful: (1) reactions activated by electron-withdrawing groups ortho or para to the leaving group (nucleofuge); (2) reactions catalyzed by very strong bases which proceed through aryne intermediates; and (3) reactions in which nitrogen of a diazonium salt is replaced by a nucleophile.

Reaction (1) is one of the oldest and most useful methods of substitution at an aromatic carbon. This mechanism, which is often referred to as $S_{\text{NAr}}$ (Figure 34), and reaction (2) (the Benzyne mechanism) will be
discussed in this thesis.

Concerted nucleophilic displacement at the aromatic carbon does not occur, as is the case in $S_{N2}$ substitution at the aliphatic carbon. Evidence indicates that the nucleophile adds to the ring to give a $\sigma$-complex as an intermediate. The "new" bond between the nucleophile and aromatic carbon must be fully formed before the "old" bond to the nucleofugic group is broken. The product forms when the leaving group is eliminated with its bonding pair of electrons. The addition-elimination mechanism ($S_{NAr}$) involves two steps and a $\sigma$-complex intermediate in which a negative charge must be accommodated on the other carbon of the ring:

Step (1)

\[
\begin{align*}
\text{Step (1)} & \\
\begin{array}{c}
\text{X} \\
\uparrow \\
\text{Y}^{-} \\
\downarrow \\
\text{Y} \\
\end{array} \\
\longrightarrow & \\
\begin{array}{c}
\text{X} \\
\uparrow \\
\text{Y} \\
\downarrow \\
\text{Y} \\
\end{array} \\
\end{align*}
\]

Step (2)

\[
\begin{align*}
\text{Step (2)} & \\
\begin{array}{c}
\text{X} \\
\uparrow \\
\text{Y} \\
\downarrow \\
\text{Y} \\
\end{array} \\
\longrightarrow & \\
\begin{array}{c}
\text{X} \\
\uparrow \\
\text{Y} \\
\downarrow \\
\text{Y} \\
\end{array} \\
\end{align*}
\]

Figure 34. $S_{NAr}$ Mechanism

The first step is usually, but not always, rate-
determining.

There is a great deal of evidence supporting the SNAr mechanism. If the mechanism were similar to either SN1 or SN2 mechanisms for aliphatic compounds, the ArX bond would be broken in the rate-determining step. If this were true, a change in the leaving group should effect the rate of reaction. In the reaction between 1-X-2,4-dinitrobenzenes with piperidine (89) in MeOH at 0°C100,

\[
\begin{align*}
\text{X} & \quad \text{NO}_2 \quad \text{+} \quad \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\end{align*}
\]

the rates differed only by a factor of about 5 when X was Cl, Br, I, SO\text{Ph}, SO\text{2Ph} or p-nitrophenoxy. If the breaking of the ArX bond was the rate-determining step, these results would not be expected. When X was F or NO\text{2}, much higher rates were observed. An increase in the electronegativity of X causes a decrease in the electron density around the substrate carbon, resulting in a faster attack by a nucleophile.

The isolation of Meisenheimer salts is probably the most convincing evidence in support of the SNAr mechanism. In 1902, intermediate (90) was isolated in the
reaction between ethyl picrate (91) and methoxide ion\textsuperscript{101}

Many more Meisenheimer salts have been isolated since 1902.

\[
\begin{array}{c}
\text{O}_2\text{N} \quad \text{OEt} \\
\text{NO}_2 \quad \text{NO}_2 \\
(91)
\end{array}
\quad + \quad \begin{array}{c}
\text{OMe}^- \\
(90)
\end{array}
\quad \rightarrow \quad \begin{array}{c}
\text{EtO}^- \\
\text{OMe}^- \\
\text{N}^+ \\
\text{O}^-
\end{array}
\quad \text{etc.}
\]

This mechanism is seldom encountered with unactivated aryl halides. The few cases in which it does occur without activation, involve dipolar, aprotic solvents\textsuperscript{102}. These solvents enhance the reactivity of nucleophiles and the aryl halide\textsuperscript{103}.

There is ambiguity in consideration of substituent effects in bimolecular reactions. Electron-withdrawal favors bond-formation by the nucleophile while it hinders bond-breaking. In order to have substitution proceed at a reasonable rate under mild conditions, the presence of one or more electron-withdrawing groups or heteroatoms at annular sites is usually required. This indicates that bond-formation is more important than bond-breaking in the transition state.

In aromatic nucleophilic substitution reactions, attention is largely focused on the reactivity of one molecule compared with another and not on the...
comparision of the reactivity of different positions within the molecule. However, studies have been done on the reactivity of different positions104.

Reactions proceeding by the SNAr mechanism are accelerated by electron-withdrawing groups, especially in position ortho and para to the leaving group, and are hindered by electron-attracting groups105 (Table 9).

\[ G \text{ withdraws electrons: } G = -\text{N(CH}_3\text{)}_3^+ \]
\[ \text{stabilizes the transition state, activates} \]
\[ G = -\text{NO}_2 \]
\[ -\text{CN} \]
\[ -\text{SO}_2\text{H} \]
\[ -\text{SO}_2\text{Ar} \]
\[ -\text{COOH} \]
\[ -\text{CHO} \]
\[ -\text{COR} \]
\[ -X \]

\[ G \text{ releases electrons: } G = -\text{NH}_2 \]
\[ \text{destabilizes the transition state, deactivates} \]
\[ G = -\text{OH} \]
\[ -\text{OR} \]
\[ -R \]

Table 9. Substituent Effects on Nucleophilic Aromatic Substitution

Substituents attached by an atom bearing a positive charge withdraw electrons powerfully and stabilize a benzenide transition state. When the atom bearing the positive charge can increase its outer electronic shell beyond an octet, conjugative stabilization results and
the group is more active in activation. Miller demonstrated the activating effect, $S^+\text{Me}_2 > P^+\text{Me}_3 > N^+\text{Me}_3$.

Substituents attached by the positive end of a dipole are also effective in promoting $\text{SN}_\text{Ar}$ substitution. As well as inductive effects, these groups are able to stabilize the benzenide transition state by conjugative withdrawal of electrons into the group (resonance effects). This can be demonstrated with the nitro group. Similar resonance contributions are also observed for $-\text{CN}, -\text{COOH}, -\text{COR}, -\text{SO}_2\text{R},$ and $-\text{NO}$.

Commonly employed nucleofugic leaving groups include: $-\text{F}, -\text{Cl}, -\text{Br}, -\text{RSO}_3, -\text{RSO}_2, -\text{RSO}, -\text{RS}, -\text{R}_2\text{S}^+, -\text{RN}^+, -\text{R}_2\text{N}, -\text{RO}$ & $-\text{NO}_2$. The $-\text{NO}_2\text{OR}, -\text{OAr}, -\text{SO}_2$ and $-\text{SR}$
groups are common leaving groups in aromatic nucleophilic substitution but are not generally lost in aliphatic systems. This data supports the hypothesis that the first step (addition) of the $S_{N\text{Ar}}$ mechanism is usually rate-determining, and is promoted by groups with strong electron-withdrawing effects. The approximate order of leaving ability is listed in Figure 34. Bunnett and Zahler$^{107}$ noted that the order varies with reagent.

\[
F > NO_2 > OTs > SOPh > Cl, Br, I > N_3 > OSO_2R >
\]
\[
NR_3^+ > OAr, OR > SR, SAr, SO_2R, NR_2^{104}.
\]

Figure 34. Approximate leaving order of groups

Electronegativity is a key factor in aromatic mobilities. Although bond breaking is unimportant in these conditions, differences in bond strength between the aromatic bond of the initial state and aliphatic bond of the transition state are likely to be important.

Leaving group mobility in some 1-X-2,4-dinitrobenzenes has been reported for the cleavage of diaryl ethers and is summarized in Table $10^{109}$.

A nucleophilic reagent is one which supplies a pair of electrons to form a new bond between itself and an atom at the reactive center in the substrate. It is not possible to construct an accurate order of nucleophilicity, since different substrates and
different conditions lead to different orders of nucleophilicity. March\textsuperscript{110} compiled a list from data in Bunnett and Zahler\textsuperscript{111}, Sauer and Huisen\textsuperscript{112} and Bunnett\textsuperscript{113}.

The order of nucleophilicity is:

\[
\text{NH}_3^{-} \rightarrow \text{Ph}_3\text{C}^{-} \rightarrow \text{PhNH}^{-}\text{(aryne mechanism)} \rightarrow \text{ArS}^{-} \rightarrow \text{RO}^{-} \rightarrow \text{R}_2\text{NH}^{-}
\]
\[
\text{ArO}^{-} \rightarrow \text{OH}^{-} \rightarrow \text{ArNH}_2^{-} \rightarrow \text{NH}_3^{-} \rightarrow \text{I}^{-} \rightarrow \text{Br}^{-} \rightarrow \text{Cl}^{-} \rightarrow \text{H}_2\text{O}^{-} \rightarrow \text{ROH}.
\]

Nucleophilicity is generally dependent on base strength and generally increases as the attacking atom moves down a Family in the Periodic Table.

<table>
<thead>
<tr>
<th>Series</th>
<th>Leaving group</th>
<th>Rate Constant ( \times 10^{-3} )</th>
<th>4'-substituent effect on mobility</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) OPh</td>
<td>( \text{p-Nitrophenoxo} )</td>
<td>1.42</td>
<td>116.6</td>
</tr>
<tr>
<td></td>
<td>( \text{p-Nitrophenoxo} )</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>(b) OPh</td>
<td>( \text{p-Iodophenoxy} )</td>
<td>1.65</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>( \text{p-Phenoxyphenoxy} )</td>
<td>4.02</td>
<td>2.44</td>
</tr>
<tr>
<td></td>
<td>( \text{p-Nitrothiophenoxy} )</td>
<td>3.07</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>( \text{p-Nitrothiophenoxy} )</td>
<td>6.09</td>
<td>0.369</td>
</tr>
<tr>
<td>(c) OPh</td>
<td>( \text{p-Nitrophenoxo} )</td>
<td>4.73</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>( \text{p-Chlorophenoxy} )</td>
<td>6.46</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>( \text{p-Cresoxy} )</td>
<td>1.07</td>
<td>2.26</td>
</tr>
<tr>
<td></td>
<td>( \text{p-Cresoxy} )</td>
<td>2.84</td>
<td>0.601</td>
</tr>
</tbody>
</table>

Table 10. Leaving group mobility in some 1-X-2,4-dinitrobenzene \( (a) \) With \( \text{MeO}^{-} \) in \( \text{MeOH/MeOAc} \) (1/1 v/v) at 0°C; \( (b) \) With \( \text{OMe}^{-} \) in \( \text{MeOH/Dioxane} \) (1/1 v/v) at 0°C; \( (c) \) with KOH in \( \text{MeOH} \) at 2°C.
**Benzyne Mechanism**

Reactions catalyzed by very strong bases generally proceed by the elimination-addition (Benzyne) mechanism\(^{114}\).

**Step 1**

\[
\begin{align*}
\text{Cl} & + \text{NH}_2^- \rightarrow \text{H} + \text{NH}_3 + \text{Cl}^- \\
\end{align*}
\]

**Step 2**

\[
\begin{align*}
\text{H} & + \text{NH}_3 \rightarrow \text{NH}_2\text{H} + \text{NH}_2^- \\
\end{align*}
\]

Evidence for this mechanism:

1. Roberts and his co-workers\(^{115-116}\) showed that chlorobenzene-1-\(^{14}\)C reacts with amide ion in liquid ammonia to give nearly equal amounts of aniline-1-\(^ {14}\)-C and aniline-2-\(^ {14}\)-C. They also showed that the reactions, described by Wittig and co-workers\(^{117-118}\), of fluorobenzenes with phenyl lithium gave the same statistical results in relation to biphenyl formation.

2. When the aryl halide contains two ortho substituents, the reaction does not occur\(^{119}\).

3. S\(_{\text{Ar}}\) mechanism is not operating because Br > I > Cl \(\gg\) F\(^{120}\).

4. Aromatic nucleophilic substitution frequently occurs occasionally
results in substitution at a different position (cine substitution). In the conversion of \( o \)-bromoanisole to \( m \)-aminoanisole\(^{121} \), only the meta isomer is formed. The reason the 1:1 mixture is not formed is that the intermediate aryne is not symmetrical and the methoxy group directs the incoming group to the meta position.

Roberts and his co-workers\(^{122} \) investigated substituent effects extensively. They pointed out that an ortho-substituted compound can form only a 2,3-aryne, and a para-substituted compound only a 3,4-aryne, whereas a meta-substituted compound can form either or both as shown in Figure 35.

Figure 35. Formation of aynes from monosubstituted ortho-, meta-, and para- halogenobenzenes.

Yields were low because of side reactions, however the results are thought to be highly significant, Table -107-
<table>
<thead>
<tr>
<th>Substituent</th>
<th>Total Yield</th>
<th>Position yield as % of total yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ortho</td>
<td>meta</td>
</tr>
<tr>
<td>o-OC\textsubscript{6}H\textsubscript{5}</td>
<td>33</td>
<td>100</td>
</tr>
<tr>
<td>m-OC\textsubscript{6}H\textsubscript{5}</td>
<td>59</td>
<td>100</td>
</tr>
<tr>
<td>p-OC\textsubscript{6}H\textsubscript{5}</td>
<td>31</td>
<td>49+1</td>
</tr>
<tr>
<td>p-F</td>
<td>30</td>
<td>20+1</td>
</tr>
<tr>
<td>o-CH\textsubscript{3}</td>
<td>64</td>
<td>48.5+2</td>
</tr>
<tr>
<td>m-CH\textsubscript{3}</td>
<td>61</td>
<td>22+4</td>
</tr>
</tbody>
</table>

Table 11. Orientation of Reaction Products of Substituted Bromobenzenes with NH\textsubscript{2}/NH\textsubscript{3}(liq.).

The nucleophilic attack in the addition stage of the substitution reaction is assumed to take place at the point of lowest electron density. In terms of transition state theory, electron-withdrawing (activating) substituents favor reaction at the more distant position since at that time the partially unshared aryne bond electrons are closer to the electron deficient carbon. With electron-releasing (deactivating) substituents, reaction is preferred at the nearer carbon since the partially unshared electrons are further from the electron rich carbon. These two effects are illustrated by Figure 36.

Factors favoring the aryne or elimination-addition mechanism are:

1. the presence of a hydrogen atom ortho to a group X, which is sufficiently electronegative for the
1,2-elimination of HX to take place.

2. an appropriate solvent. In solvents such as ammonia, aryne formation tends to occur. Ammonia is not a very good proton donor, but is fairly good at solvating anions. In dipolar, aprotic solvents such as hexamethylphosphoramide (HMPA) and N,N-dimethylformamide (DMF), halide ions have a high free energy because they are so poorly solvated, and halophenyl anions therefore have little tendency to form arynes.

3. when assisted by coordination of the departing halide ion with lithium or magnesium.

4. low reactivity of the substrate via the addition-elimination $S_{N}Ar$ mechanism.

![Figure 36. Transition states for addition to substituted arynes.](image)

**Ether Cleavage**

The cleavage of ethers is a versatile reaction in organic synthesis, particularly in the degradation of
natural products and in the synthesis of polyfunctional molecules. The protection of alcholic and phenolic groups has found widespread application especially in the chemistry of steroids, sugars, glycerides, and a number of pharmaceutical drugs.

The cleavage of ethers was comprehensively reviewed by Bhatt and Kulkarni\textsuperscript{124} in 1983. The review attempts to include all ether cleavage reagents of synthetic value reported prior to 1981.

The reagents are classified into six main categories: (1) Acidic Reagents, (2) Basic Reagents, (3) Reductive Cleavage, (4) Oxidative Cleavage, (5) Photochemical Cleavage and (6) Miscellaneous.

The phenolic hydroxyl group is often protected during multistage synthesis by conversion into the methyl ether. The demethylation of aryl methyl ethers is the most common ether cleavage reaction. However, we are interested in diaryl ether cleavage.

The cleavage of alkyl aryl ethers by hydrohalic acids\textsuperscript{121} always involves alkyl-oxygen fission. However, diaryl ethers are not cleaved.

Diaryl ethers and alkyl aryl ethers are cleaved by finely divided alkali metals like sodium, potassium and lithium in the absence of solvents.\textsuperscript{126}.

Solutions of the biphenyl/lithium adduct (92) in tetrahydrofuran are effective in cleaving a variety of
alkyl aryl and diaryl ethers\textsuperscript{127}.

\[
\begin{align*}
\text{ROR} + 2\text{Li} & \rightarrow 2\text{Li}^+ \text{Re}^- + \text{RO}^{-} + 2\text{Na}^+
\text{Re}^- + \text{NH}_3 + \text{Na}^+ & \rightarrow \text{RH} + \text{NH}_2^- + \text{Na}^+
\end{align*}
\]

where (R) represents a phenyl group, and \((e^-)\) an "electron anion"\textsuperscript{136}.

It is currently believed that aromatic nucleophilic substitution by a solution of sodium in liquid ammonia proceeds by the benzyne mechanism\textsuperscript{137-138}.

In ortho, meta, and para mono-substituted diphenyl
ethers the linkage between the oxygen and the substituted phenyl group is strengthened against cleavage by sodium in liquid ammonia by the introduction of the following substituents: \( o-\text{CH}_3 < m-\text{CH}_3 < m-\text{NH}_2 < p-\text{CH}_3 < p-\text{OCH}_3 < o-\text{NH}_2 < p-\text{NH}_2 \). The linkage is weakened toward cleavage by the following substituents: \( m-\text{OCH}_3 < o-\text{OCH}_3 < m-\text{CO}_2 \text{Na} < o-\text{CO}_2 \text{Na} < p-\text{CO}_2 \text{Na} \). It was also noted that \textit{para}-subsituents were more effective in hindering or facilitating cleavage.

The pattern of cleavage of diaryl ethers (Figure 37) was shown to depend upon the substituents on the aromatic rings.

\[
\begin{align*}
&\text{Figure 37. Cleavage pattern of diaryl ethers} \\
&\text{When } R \text{ is an electron-releasing group, for example the amino group, } X\text{-type fission occurs. } Y\text{-type fission takes place when } R \text{ is an electron-withdrawing group like the carbonyl, which stabilizes the carbanion on the substituent bearing the aromatic ring. The positions arranged according to the effectiveness of the inductive influence of the methyl group are: } \text{para} > \text{meta} > \text{ortho}. \\
&\text{Table 12 summarizes the experimental results of Sowa and co-workers. Cleavage products are based in the percentage of phenols recovered. The yields are not}
\end{align*}
\]
consistent and are poor in many cases.

<table>
<thead>
<tr>
<th>Compound ROR’</th>
<th>Cleavage products as mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>R’</td>
</tr>
<tr>
<td>Phenyl</td>
<td>Phenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>4-Methylphenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>2-Methylphenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>3-Methylphenyl</td>
</tr>
<tr>
<td>2-Methylphenyl</td>
<td>4-Methylphenyl</td>
</tr>
<tr>
<td>2-Methylphenyl</td>
<td>3-Methylphenyl</td>
</tr>
<tr>
<td>3-Methylphenyl</td>
<td>4-Methylphenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>4-Methoxyphenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>3-Methoxyphenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>2-Methoxyphenyl</td>
</tr>
<tr>
<td>2-Methoxyphenyl</td>
<td>4-Methoxyphenyl</td>
</tr>
<tr>
<td>2-Methoxyphenol</td>
<td>3-Methoxyphenyl</td>
</tr>
<tr>
<td>3-Methoxyphenyl</td>
<td>4-Methoxyphenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>4-Aminophenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>2-Aminophenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>3-Aminophenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>4-Carboxyphenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>2-Carboxyphenyl</td>
</tr>
<tr>
<td>Phenyl</td>
<td>3-Carboxyphenyl</td>
</tr>
</tbody>
</table>

Table 12. Cleavage of o-, m-, and p-Substituted Diphenyl Ethers

Orientation in addition to benzyne derivatives appears to be governed mainly by inductive effects of substituents\textsuperscript{139}; steric factors are relatively unimportant\textsuperscript{140}.

The influence of various substituents upon the carbon atoms in a phenyl group consists of two factors: an inductive effect (I) and a tautomeric or resonance effect (T). As predicted by electronic theories of Ingold and Robinson, the tautomeric effect is the more
dominant effect, and is more pronounced in the para position than in the ortho or meta positions. These are the same effects observed in electrophilic aromatic substitution reactions and other nucleophilic aromatic substitution mechanisms.

Sowa and co-workers also looked at the cleavage of 4,4′-disubstituted diphenyl ethers. This has merit because comparison can be made of the effect of two dissimilar groups within the same molecule. Table 13 lists the mole percentages of the cleavage products formed in each case.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Cleavage products as mole %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R--O--R'</td>
<td>ROH</td>
</tr>
<tr>
<td>p-Tolyl</td>
<td>p′-Anisyl</td>
<td>21</td>
</tr>
<tr>
<td>p-Tolyl</td>
<td>p′-Aminophenol</td>
<td>100</td>
</tr>
<tr>
<td>p-Tolyl</td>
<td>p′-t-Butylphenyl</td>
<td>48</td>
</tr>
<tr>
<td>p-Anisyl</td>
<td>p′-Aminophenyl</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 13. Cleavage of 4-4′-Disubstituted Diphenyl Ethers

The cleavage of 4-4′-diaryl ethers depends upon the substituents present on the aromatic rings. Cleavage of the carbon-oxygen bond next to the ring which contains the substituent with the greater electron withdrawing characteristics is preferred.

The order of increasing electron-withdrawing in the cleavage of the carbon-oxygen bond in 4-4′-diaryl ethers by the benzyne mechanism is: COO-> H> Me> OMe>
NH₂. This is the same order of descending activating ability as is observed in cleavage by the SNAr mechanism: N₂⁺ > NO > NO₂ > SO₂Me > CN > CHO > COR > COOH > SO₃⁻ > Br > Cl > I > COO⁻ > H > F > CMe₃ > Me > OMe > OH > NH₂¹⁴¹.

Sodium piperidide, obtained by the reaction of sodium amide with piperidine, has been shown to cleave alyl aryl ethers, as well as diaryl ethers¹⁴².

Sodium thioethoxide dissolved in N,N-dimethylformamide (DMF) has been shown to be a powerful agent for demethylating aryl methyl ether under mild conditions¹⁴³. The reaction conditions are such that bromo substituents and isolated olefinic bonds are unaffected.

Dipolar aprotic solvents are advantageous in bimolecular reactions involving anions and uncharged species¹⁴⁴. DMF was chosen as solvent because it is an efficient solvent for ethanethiolate ion, it is stable to strong bases at reflux temperatures, and it is water soluble, allowing for easy recovery of phenolic products.

The mechanism for demethylation is SN₂, with displacement of the aryloxide ion (Figure 38).

When higher temperatures and longer reaction times were used, Feutrill and Mirrington found the SN₂ Ar reaction preceded demethylation (SN₂) of 4-bromo-3-methyl anisole.
Aryl methyl ethers which have a strong electron-withdrawing substituent (G) require milder conditions and are likely to undergo substitution (S_NAr) at the aromatic carbon rather than cleavage of the ether with strong carbon nucleophiles\textsuperscript{145}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure38}
\caption{S_N2 mechanism for demethylation.}
\end{figure}
DISCUSSION AND RESULTS

Aromatic nucleophilic substitution reactions involving diaryl ethers are relatively uncommon. The $S_{N}Ar$ mechanism requires activated reaction sites, or activation by dipolar, aprotic solvents. In the case of site activation, electron-withdrawing groups stabilize the resonance forms of the negative transition state. Polar, aprotic solvents also support the negative transition state.

Diaryl ether cleavage of 4,4'-[sulfonyl bis $(p$-phenylene ether)] dianisole (Figure 39) lead us to perform other diaryl ether cleavage reactions.

\[ \text{expected product} \quad \text{HO-} - \quad 4,4'\text{-} \quad \text{SO}_2 - \quad \text{O} - \quad \text{OH} \quad \] (82)

\[ \text{experimental products} \quad \text{CH}_3\text{CH}_2\text{S} - \quad \text{SO}_2 - \quad \text{SCH}_2\text{CH}_3 \quad \] (83)

\[ + \quad \text{CH}_3\text{O-} - \quad \text{OH} \quad \]

Figure 39. Diaryl ether cleavage of 4,4'-[sulfonyl bis $(p$-phenylene ether)] dianisole.
No information on the effect of substituents on diaryl ether cleavage by the $S_N$Ar mechanism could be found in the literature. However, Sowa and co-workers\textsuperscript{146} reported extensive studies on the effect of substituents on diaryl ether cleavage by the benzyne mechanism.

Testaferri and co-workers\textsuperscript{147-149} synthesized aryl-alkyl thioethers and aromatic thiols from unactivated aryl halides. The use of polar, aprotic solvents, such as N,N-dimethylformamide, enhanced the reaction. Hexamethylphosphoric triamide was the original solvent, however, carcinogenic properties limited its use. Testaferri and co-workers\textsuperscript{149} also reported successful syntheis of the alkyl-aryl thioethers using N,N-dimethylformamide and dimethylacetamide. These results support our observation of ether cleavage by ethanethiolate ion in N,N-dimethylformamide.

In aromatic nucleophilic substitution reactions of aryl halides, attention is focused on the reactivity of one molecule compared to another, with various substituents in the same position. Keeping with this tradition, we decided to look at the effect of para-substituents on the cleavage of diaryl ethers.

Under the same reaction conditions as those employed in the demethylation of 4,4'-[sulfonyl bis($p$-phenylene ether)] dianisole, 4,4'-[sulfonyl
bis(p-phenylene ether) dibenzene and four commercially available diaryl ethers (Figure 40) were treated with sodium ethanethiolate in N,N-dimethylformamide.

\[ \begin{align*}
(84) & \quad Y = \text{Br} \\
(85) & \quad Y = \text{H} \\
(86) & \quad Y = \text{OH} \\
(87) & \quad Y = \text{NO}_2
\end{align*} \]

Figure 40. Commercially available diaryl ethers

4-bromophenyl phenyl ether, diphenyl ether, and 4-phenoxyphenol did not undergo cleavage. 4-nitrophenyl phenyl ether, 4,4'-[sulfonyl bis(p-phenylene ether)] dianisole and 4,4'-[sulfonyl bis(p-phenylene ether)] dibenzene underwent ether cleavage. Sulfone and nitro groups activate the S_NAr cleavage reaction due to their strong electron-withdrawing ability, with stabilization of the transition state by resonance forms.

The reaction involving 4,4'-[sulfonyl bis(p-phenylene ether)] dianisole was previously discussed. Cleavage products were identified as 4,4'-dithioethoxydiphenyl sulfone (83) and p-methoxyphenol (Figure 39).

4,4'-[sulfonyl bis(p-phenylene ether)] dibenzene was cleaved by sodium ethanethiolate (Figure 41). The products were identified as 4,4'-dithioethoxydiphenyl sulfone (93) and phenol.
Figure 41. Diaryl ether cleavage of 4,4'-[sulfonyl (p-phenylene ether)] dibenzene.

TLC, solubility, melting point, and NMR and IR spectral data are the same as those observed for product (83); one of the products from the cleavage reaction of 4,4'-[sulfonyl bis(p-phenylene ether)] dianisole by the ethanethiolate ion.

The products in the ether cleavage of 4-nitrophenyl phenyl ether were 4-nitrophenyl ethyl thioether (94), phenol, and an unidentified black oil.

The NMR spectrum confirms an ethyl group.

<table>
<thead>
<tr>
<th>Quartet</th>
<th>PPM</th>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7.75</td>
<td>Aromatic</td>
<td>21</td>
<td>4</td>
</tr>
<tr>
<td>Quartet</td>
<td>3.0</td>
<td>-CH$_2$-</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Triplet</td>
<td>1.36</td>
<td>-CH$_3$</td>
<td>15</td>
<td>3</td>
</tr>
</tbody>
</table>

IR spectral data (Figure 42) has aliphathic and
aromatic characteristics and indicates a nitro group; aromatic carbon-carbon stretch at 1479cm\(^{-1}\); aliphatic carbon-hydrogen stretch at 2953, 2911, 2848cm\(^{-1}\); aliphatic carbon-hydrogen stretch (-S-CH\(_3\)-) at 1445cm\(^{-1}\); aliphatic carbon-hydrogen bend at 1090cm\(^{-1}\); and nitrogen-oxygen double bond stretch at 1578 and 1401cm\(^{-1}\).

Elemental analysis, calculated for C\(_8\)H\(_{10}\)O\(_2\)S\(_0\), does not confirm the proposed product.

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Sulfur</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>52.46</td>
<td>4.95</td>
<td>17.51</td>
<td>7.65</td>
</tr>
<tr>
<td>Experimental</td>
<td>57.78</td>
<td>5.81</td>
<td></td>
<td>9.03</td>
</tr>
</tbody>
</table>

The product was soluble in toluene, acetone, hot acetic acid and hot ethanol, insoluble in hexane and water.

The aqueous phase, from the reaction of \(p\)-nitrophenyl phenyl ether and ethanethiolate ion, was made basic and extracted with methylene chloride, a dark brown liquid remained after evaporation. This was primarily DMF. The basic phase was made acidic and extracted with methylene chloride. A brown liquid remained after evaporation. The liquid smelled like a phenol. Preparation of a bromo-derivative gave a positive test for phenol (\(T_m = 91-92^\circ\)C). The literature value is 95\(^\circ\)C. An IR spectrum of the derivative was taken and it matches perfectly with the spectrum of...
2,4,6-tribromophenol (Figure 43).

Cleavage of aryl halides by the SNAr mechanism has been studied extensively. Our data indicates the same electron-withdrawing effects by para-substituents, as observed in the aryl halide cleavage reactions by the SNAr mechanism. Electron-withdrawing groups in the para-position activate ether cleavage reactions by ethanethiolate ion in N,N-dimethylformamide, a polar, aprotic solvent.

Under extreme reaction conditions, reflux (~160°C), diphenyl ether and 4-phenoxyphenol did not undergo cleavage, however, 4-bromophenyl phenyl ether was cleaved. The products of the ether cleavage were phenol and 4-bromophenyl ether thiaether (95).

\[
\text{Br-SCH}_2\text{CH}_3 \quad (95)
\]

The effect of para-substituents on diaryl ether cleavage can be listed in the following order of decreasing activation:

\[-\text{SO}_2-\phi, -\text{NO}_2 > -\text{Br} > -\text{OH}, -\text{H}\]

This is the same order as lists compiled by Bunnett and Zahler\textsuperscript{151}, Sauer and Huisen\textsuperscript{152} and Bunnett\textsuperscript{153} for cleavage of aryl halides.
Figure 43  Bromo derivative of acid extract
EXPERIMENTAL

General Information

Starting materials used in this work were either commercially available in 98% or higher purity and used without further purification (unless otherwise noted) or prepared by standard literature procedures.

Melting points were determined on a Mel-Temp apparatus and have not been corrected. NMR and IR spectra were obtained on Hitachi-Perkin Elmer-R-20 and Perkin-Elmer 1330 spectrometers, respectively. Tetramethylsilane was used as an internal standard in the NMR calibration.

Elemental analyses were performed by Baron Consulting Company, Orange, Connecticut.

Thin layer chromatography was run on Eastman Kodak Silica Gel 13181 with fluorescent indicator.

Diazotization and hydrolysis of 4-methoxy-2-methyl aniline (57) using the procedure described by Fieser and Williamson154

To a mixture of 13.7g (0.1 mole) of 4-methoxy-2-methyl aniline in 15ml of water was added 25ml of 12M hydrochloric acid, all the material did not dissolve. The mixture was cooled in an icebath, and 7g of sodium...
nitrite (.1mole) in 20ml of water was added in 5ml portions to the hydrochloride. The diazonium salt was cooled in an icebath and then added slowly, with a syringe, to 400ml of boiling 3M sulfuric acid. The reaction mixture was cooled and extracted with benzene. The final product, a tar like material, did not appear to be a phenol.

Diazotization and hydrolysis of 4-methoxy-2-methyl aniline (57) using the procedure described by Lambooy133

To a cooled solution of 30 ml of 20% sulfuric acid and 5.0g (.036 mole) of 4-methoxy-2-methyl-aniline, 7g of sodium nitrite in 20ml of water was slowly added. The aniline mixture which was kept in an icebath to keep the temperature near 0°C. A 2000ml 3 neck flask was fitted with a steam inlet, condensor and the condensor-dropping funnel. Water (200ml) and concentrated sulfuric acid (150ml) were added and the solution brought to a boil. The diazonium salt was added slowly and 1000ml of steam distillate was collected. The distillate was extracted with 200ml of ether three times. The ether extract was washed with 250ml of 5% hydrochloric acid and 200ml of saturated sodium chloride. The ether was removed by the Rotovap. A few crystals of white solid remained in the flask. They did
not give a positive test with ferric chloride nor did they appear to be a phenol when run on thin layer chromatography.

Diazotization and hydrolysis of 4-methoxy-2-methyl aniline (57) using the procedure described by Gottstein and coworkers136.

4-methoxy-2-methylaniline (10.97g, 0.08mole) was added to 20ml of trifluoroacetic acetic acid, which was chilled in an icebath with salt. The solution was cooled to 5°C and 0.52g (.08mole) of sodium nitrite was added. The purple mixture was stirred for 0.5 hour at 5°C. Water (7ml) was added and the solution was stirred for an additional 0.5 hour. The mixture was poured into 50ml of water and extracted with ether. The ether was removed on the Rotovap. One hundred milliliters of 5% hydrochloric acid was added to the residue. This was extracted with ether. The ether extract was washed with 100ml of 10% sodium bicarbonate, final pH 8-10. The phenol should have remained in the ether layer. The ether layer was washed with 3X50ml of 1M potassium hydroxide. The aqueous layer, cooled in an icebath, was neutralized with hydrochloric acid and extracted with 3X50ml of ether. The ether layer was removed on a Rotovap and no phenol was recovered.
Recrystalization of terephthaloyl chloride.

Terephthaloyl chloride (11g) was recrystalized from 60ml of hexane, 8.1g was recovered. The melting point of the original material was 79-81°C, while the recrystalized material melted at 79-80°C.

Condensation of 3-methoxy-5-methyl phenol with terephthaloyl chloride to prepare di(3-methoxy-5-methyl-phenyl) terephthalate (70).

3-methoxy-5-methyl phenol (8.3g, 0.06mole) was mixed with 150ml of 0.47M sodium hydroxide, in a Waring blender. Terephthaloyl chloride (0.03mole) dissolved in 30ml of cyclohexanone, was added to the blender and the solutions were mixed at medium speed for about 10 minutes. A white gummy material was filtered through a sintered glass filter and dried under vacuum to give 10.2g (84% yield) of di(p-methoxyphenyl) terephthalate (70). Recrystalization from cyclohexanone gave a product which melted at 159-160°C.

Di(3-methoxy-5-methylphenyl) terephthalate was soluble in carbon tetrachloride, methylene chloride, benzene and hot cyclohexanone. It was insoluble in water, ethanol and hexane.

Elemental analysis: Calculated for C_{24}H_{22}O_6:

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>70.72</td>
<td>5.46</td>
</tr>
<tr>
<td>Found</td>
<td>69.74</td>
<td>5.43</td>
</tr>
</tbody>
</table>

-128-
**IR:** The IR Spectrum (Figure 44) supports di(3-methoxy-5-methylphenyl) terephthalate:
carbon-hydrogen stretch at 2945, 2920, 2900, and 2825\(\text{cm}^{-1}\), as well as, carbon-hydrogen bending at 1360\(\text{cm}^{-1}\) indicate an aliphatic component; absence of an oxygen-hydrogen stretch and a single carbon-oxygen double bond stretch at 1760\(\text{cm}^{-1}\) indicates an aromatic ester; aromatic carbon-hydrogen stretching at 3075\(\text{cm}^{-1}\); and aromatic carbon-carbon stretch at 1630 and 1565\(\text{cm}^{-1}\).

**Condensation of \(p\)-methoxyphenol with terephthaloyl chloride to prepare di(\(p\)-methoxyphenyl) terephthalate** (71).

Di(\(p\)-methoxyphenyl) terephthalate was prepared by the same technique as di(3-methoxy-5-methylphenyl) terephthalate. \(p\)-methoxyphenol (7.44g, 0.06mole), sodium hydroxide (2.8g, 0.07mole) and 6.09g (0.03mole) of terephthaloyl chloride were mixed in a Waring blender for 15 minutes at medium speed. A 91\% yield (10.3g) of di(\(p\)-methoxyphenyl) terephthalate was obtained.

Di(\(p\)-methoxyphenyl) terephthalate was insoluble in acetone, benzene, ether, ethanol, hexane, ethyl acetate, methylene chloride and dimethyl sulfoxide (DMSO). It was slightly soluble in chloroform, hot methylene chloride and hot cyclohexane, and soluble in hot...
chloroform.

Di(p-methoxyphenyl) terephthalate was observed to have liquid crystal properties; Maltese cross patterns were observed under a polarizing microscope equipped with a melting stage. A melting point ($T_m$), 209°C, and a clearing temperature ($T_c$), 280.3–282.6°C, were observed. The corresponding literature values are $T_m$: 210.6°C, and $T_c$: 287.6°C.

Thin layer chromatography (TLC), using the solvent system benzene-methylene chloride (7:3), gave $R_s = 0.54$ for the product (71). The starting materials gave $R_s$ values of 0 and 0.3, for terphthaloyl chloride and p-methoxyphenol, respectively. The final product, one spot on TLC, did not appear to be contaminated with starting materials.

**Elemental analysis:** Calculated for $C_{22}H_{19}O_6$:

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>69.84</td>
<td>4.76</td>
</tr>
<tr>
<td>Found</td>
<td>69.26</td>
<td>4.85</td>
</tr>
</tbody>
</table>

**NMR:** (Figure 45), Multiplet a 8.3–6.8PPM (Aromatic), Integration 16, $H = 12$, Singlet at 3.8PPM, (CH$_3$), Integration 7, $H = 6$.

**IR:** The IR Spectrum (Figure 24) supports di(p-methoxyphenyl) terephthalate: carbon-hydrogen stretch at 2965, and 2820cm$^{-1}$ indicate an aliphatic component; absence of an oxygen-hydrogen stretch and a single carbon-oxygen double bond stretch at 1727cm$^{-1}$.
indicates an aromatic ester; aromatic carbon-hydrogen stretch at 3040 cm\(^{-1}\); aromatic carbon-carbon stretch at 1505 cm\(^{-1}\) and; carbon-oxygen stretch at 1200 cm\(^{-1}\).

**Cleavage reactions involving di(p-methoxyphenyl) terephthalate and sodium ethanethiolate.**

(I) A 1-liter 3-neck flask equipped with a gas inlet, condensor with drying tube, and dropping funnel was charged with 0.83 g (0.035 mole) sodium hydride and 45 ml of DMF. The mixture was saturated with argon and cooled to below 5\(^{\circ}\)C in an ice bath with salt. Ethanethiol (2.5 g, 0.04 mole) in 5 ml of DMF was added dropwise while the temperature of the reaction mixture was kept below 5\(^{\circ}\)C. The greyish mixture cleared as it was stirred for 15 minutes.

Di(p-methoxyphenyl) terephthalate (2.0 g, 0.053 mole) and 300 ml DMF were added to the reaction mixture. The temperature was maintained at 105\(^{\circ}\)C for 15 hours.

Cold 10\% hydrochloric acid (275 ml), approximately 200 g of ice, and the reaction mixture, were mixed in a large beaker. The mixture was extracted with 150 ml of methylene chloride three times. The organic phase was washed with saturated sodium chloride solution and put on a Rotovap. An oily material was collected. A white precipitate (0.3 g), terephthalic acid, settled out. The precipitate sublimed at 301\(^{\circ}\)C. It was slightly soluble
in methylene chloride, benzene, and ether, and was soluble in cyclohexane and DMSO.

**NMR:** (Figure 46) The singlet at 8.05 indicates terphthalic acid.

**IR:** (Figure 25) The IR spectrum also indicates terphthalic acid: oxygen-hydrogen stretch between 3300 and 2500cm\(^{-1}\) and oxygen-hydrogen bending at 1420cm\(^{-1}\), as well as, a strong carbon-oxygen double bond stretch at 1685cm\(^{-1}\) and a strong carbon-oxygen stretch at 1280cm\(^{-1}\) indicate a carboxylic acid.

(II) A 1-liter 3-neck flask equipped with nitrogen inlet, condensor with drying tube, and dropping funnel was charged with 0.26g (0.0108mole) sodium hydride and 30ml of DMF. After cooling the mixture to below 5\(^\circ\)C 0.68g , (0.0109mole) of ethanethiol in 1ml of DFM was added dropwise. The temperature was held below 5\(^\circ\)C. Di(p-methoxyphenyl) terephthalate (2.0g, 0.0053mole) was added along with 200ml DMF. The reaction was maintained at 55\(^\circ\) for six hours.

Cold 10% HCl (150ml) and approximately 100g of ice were added to the reaction mixture. A white precipitate (0.9g) was removed from the solution. The precipitate, 4-(p-methoxyphenylcarboxo)-benzoic acid (75), was recrystalized from absolute ethanol twice, and melted at 208-209\(^\circ\)C.
IR: (Figure 26) The presence of two carbonyl peaks in the IR spectrum, 1685 and 1730 cm⁻¹, carbon-oxygen stretch at 1280 cm⁻¹, oxygen-hydrogen bending at 1420 cm⁻¹, a broad oxygen-hydrogen stretch (3300-2700 cm⁻¹), and carbon-oxygen-carbon asymmetric stretch at 1205 cm⁻¹ indicates a nonsymmetrical molecule, most likely an ester and a carboxylic acid. The weak peak at 2810 cm⁻¹ indicates a methyl group, probably the methoxy substituent. The spectral data supports the hypothesis of cleavage at one of the carbonyl carbons of the original diester.

**Elemental Analysis**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>69.84</td>
<td>57.83</td>
<td>66.18 (66.24)*</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.76</td>
<td>3.61</td>
<td>4.44 (4.35)</td>
</tr>
<tr>
<td>Sulfur</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Figures in () are values determined analytically.

The aqueous phase was extracted with 100ml of ether three times, and the solvent evaporated. A white precipitate and an oil were collected. The precipitate was terephthalic acid. When the oil was separated by thin layer chromatography, a major product in the oil was identified as p-methoxyphenol.

The third attempt at the demethylation reaction was carried out under slightly different reaction conditions. Di(p-methoxyphenyl) terephthalate (8.0g, 0.021mole), sodium hydride (1.04g, 0.043mole),
ethanethiol (2.72g, 0.043mole) and 280ml of DMF were combined in the reaction vessel.

(III) After three hours at 55°C one half of the reaction mixture was removed and added to 60ml of cold 10% hydrochloric acid and approximately 100g of ice. A white precipitate, di(ethylthio) terephthalate (76), weighing 1.02g was collected. The precipitate was recrystallized twice from ethyl acetate, T_m = 86-87°C

The precipitate was soluble in chloroform, ether, acetone, methylene chloride, ethyl acetate, and hot methanol. It was insoluble in water and potassium hydroxide.

NMR: (Figure 47)

<table>
<thead>
<tr>
<th>PPM</th>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>Aromatic</td>
<td>10.5</td>
<td>4</td>
</tr>
<tr>
<td>3.2</td>
<td>-CH₂⁻</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>1.35</td>
<td>-CH₃</td>
<td>15</td>
<td>6</td>
</tr>
</tbody>
</table>

IR: (Figure 27) Absence of oxygen-hydrogen stretch eliminates a carboxylic acid or terphthalic acid, carbon-hydrogen stretch at 2860, 2915, 2945, and 2970cm⁻¹ (W), as well as, carbon-hydrogen bending at 1375 and 1450cm⁻¹ (M) indicate an aliphatic component \((-\text{CH}_2\text{-})_n, \text{CH}_3\). A single carbon-oxygen double bond stretch at 1650cm⁻¹ (S) and carbon-oxygen stretch at, 1205cm⁻¹ (S) indicates the ester.
Elemental analysis calculated for C₁₀H₁₀O₃S also indicates the proposed compound, di-(ethylthio) terephthalate.

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>56.67</td>
<td>5.55</td>
<td>25.21</td>
</tr>
<tr>
<td>Experimental</td>
<td>56.99</td>
<td>5.95</td>
<td>23.78</td>
</tr>
</tbody>
</table>

Sodium fusion\textsuperscript{15\textregistered} gave a positive test for sulfur.

The aqueous phase was extracted with 80ml of ether three times, followed by three 80ml extractions with methylene chloride. The separate fractions were then evaporated. A pasty material (2.9g) was collected from the ether extract, while no products were recovered from the methylene chloride. TLC and an NMR spectrum of this mixture suggests \( p \)-methoxyphenol in DMF.

(IV) After five hours the remainder of the reaction mixture was treated with 70ml of 10\% HCl and approximately 100g of ice. 4-ethylthiocarboxybenzoic acid (77), 0.89g, was collected as a precipitate.

The precipitate is soluble in chloroform, acetone, methanol, and ethyl acetate. It is slightly soluble in ether and methylene chloride and insoluble in water.

TLC with benzene-methylene chloride (7-3):

\( \text{di}(p\text{-methoxyphenyl}) \) terephthalate, \( R_f = 0.52 \); precipitate (77), \( R_f = 0 \), slight spots as 0.52 and 0.76.
\[ T_m = 180-182^\circ C. \]

**NMR:** (Figure 48)

<table>
<thead>
<tr>
<th>PPM</th>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doublet</td>
<td>8.1</td>
<td>phenyl</td>
<td>14</td>
</tr>
<tr>
<td>Quartet</td>
<td>3.15</td>
<td>-CH\textsubscript{2}−</td>
<td>7</td>
</tr>
<tr>
<td>Triplet</td>
<td>1.38</td>
<td>-CH\textsubscript{3}</td>
<td>12</td>
</tr>
</tbody>
</table>

**IR:** The IR spectrum (Figure 28) has a broad oxygen-hydrogen stretch at 3300-2000 cm\(^{-1}\); two carbonyl peaks at 1645 cm\(^{-1}\) (acid) and 1680 cm\(^{-1}\) (thiolester); aliphatic carbon-hydrogen stretch at 2959 and 2915 cm\(^{-1}\); carbon-sulfur-carbon vibrations at 1280 cm\(^{-1}\); and carbon-sulfur vibrations at 910 cm\(^{-1}\).

**Elemental analysis** calculated for C\textsubscript{10}H\textsubscript{10}SO\textsubscript{3} also indicates the proposed compound to be 4-ethylthio-carboxobenzoic acid. The slight discrepancy in the figures is probably due to slight contamination of the product with terephthalic acid.

**Elemental Analysis**

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>57.13</td>
<td>4.79</td>
<td>15.25</td>
</tr>
<tr>
<td>Experimental</td>
<td>58.11</td>
<td>4.86</td>
<td>14.26</td>
</tr>
</tbody>
</table>

Condensation of \( p \)-methoxyphenol with 4,4′-dichloro-diphenyl sulfone to prepare 4,4′-[sulfonyl bis(\( p \)-phenyl ene ether)] dianisole (81).
A 1-liter 3-neck flask equipped with nitrogen inlet-tube, magnetic stirrer, and Dean-Stark trap was charged with 43.76g (0.35 mole) p-methoxyphenol, 140ml dimethyl sulfoxide, 95ml toluene and 28.7g (0.35 mole) 50% sodium hydroxide. The solution was saturated with nitrogen, and water was removed via a toluene/water azeotrope. Remaining toluene was distillated from the pot. The reaction mixture was cooled to 80°C and 50.61g (0.173 mole) 4,4'-dichlorodiphenyl sulfone was added slowly to prevent the resulting exotherm from producing high pot temperatures. The mixture was refluxed at 160°C for 2 hours, then cooled to room temperature. Since it was impossible to remove the salt by filtration, the mixture was added to a Waring blender and mixed with ice water and hexane three times.

The final mixture was filtered and dried under vacuum. A 95% yield of 4,4'-[sulfonyl bis(p-phenylene ether) dianisole was obtained. The sulfone was insoluble in ether, cyclohexane, and water; slightly soluble in chloroform, benzene, and ethanol; and soluble in acetone, methylene chloride and hot ethanol. The sulfone was recrystallized three times from hot ethanol-water, melting point 114-116°C.

Thin layer chromatography, hexane-ethyl acetate (4:1), gave $R_f = 0.35$ for the product, $R_f = 0.47$ for p-methoxyphenol and $R_f = 0.76$ for 4,4'-dichloro-
diphenyl sulfone. The product did not appear to be contaminated with starting material.

**NMR:** (Figure 49)

<table>
<thead>
<tr>
<th>Multiplet</th>
<th>PPM</th>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singlet</td>
<td>3.8</td>
<td>CH₃O⁻</td>
<td>11.5</td>
<td>6</td>
</tr>
<tr>
<td>Singlet</td>
<td>8.0-6.9</td>
<td>phenyl</td>
<td>32.3</td>
<td>16</td>
</tr>
</tbody>
</table>

**IR:** IR spectral (Figure 29) information is indicative of the desired sulfone; aromatic carbon-hydrogen stretching band at 3050cm⁻¹, aromatic carbon-carbon double bond absorption at 1580, 1500, and 1480cm⁻¹; aliphatic carbon-hydrogen stretching bands at 2940 and 2815cm⁻¹; carbon-oxygen-carbon stretching bands at 1235 and 1030cm⁻¹; and sulfone group absorptions at 1325 and 1147cm⁻¹.

**Condensation of phenol with 4,4'-dichlorodiphenyl sulfone to prepare 4,4'-[sulfonyl bis(p-phenylene ether)] dibenzene (85).**

The procedure described in the preparation of 4,4'-[sulfonyl bis(p-phenylene ether)] dianisole was used to prepare sulfone (85). Phenol (47.05, 0.05mole), 71.8g (0.25mole) of 4,4' dichlorodiphenyl sulfone, and 41.0g of 50% sodium hydroxide were used in the synthesis. The final product, 99% yield, was recrystallized from ethanol, melting point 143-145°C.
**NMR:** (Figure 50) The expected multiplet at 8.0-6.9PPM was observed.

**IR:** (Figure 51) The IR spectrum has a typical aromatic carbon-hydrogen stretch at 3070, 3041, and 3016cm\(^{-1}\); aromatic carbon-carbon stretch at 1573 and 1480cm\(^{-1}\); and sulfone group absorptions at 1318 and 1142cm\(^{-1}\).

**Ether cleavage of 4,4′-[sulfonyl bis(p-phenylene ether)] dianisole (81).**

A 1-liter 3-neck flask equipped with nitrogen inlet, condensor with drying tube, and dropping funnel was charged with 0.50g (0.020 mole) sodium hydride and 160ml of DMF. The mixture was saturated with nitrogen and cooled to below 5°C in an ice bath with salt. Ethanethiol (1.32g, 0.020 mole) in 5ml of DMF was added dropwise while the temperature of the reaction mixture was kept below 5°C. The greyish mixture cleared as it was stirred for 15 minutes.

4,4′-[sulfonyl bis(p-phenylene ether)] dianisole (4.45g, 0.010 mole) and 300 ml DMF were added to the reaction mixture. The temperature was maintained at 60-63°C for 5 hours. The reaction mixture, was added to a large beaker containing 200ml of cold 10% hydrochloric acid and approximately 200g of ice.

A white precipitate, 4,4′-dithioethyldiphenyl -139-
sulfone (83), was collected in a sintered glass funnel, dried in a vacuum oven, and it weighed 2.9g (86% yield). The precipitate was recrystallized from ethanol, Tm = 109-110°C. It was insoluble in acetone, ethanol and ether, soluble in chloroform and hot acetone, ethanol and ether.

Thin layer chromatography with hexane-ethyl acetate (4:1) gave one spot with a Rf = 0.53.

**Elemental analysis:** Calculated for C_{16}H_{18}S_{3}O_{2}:

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>56.77</td>
<td>5.36</td>
<td>28.41</td>
</tr>
<tr>
<td>Observed</td>
<td>56.94</td>
<td>5.56</td>
<td>26.55</td>
</tr>
</tbody>
</table>

**NMR:** (Figure 52)

<table>
<thead>
<tr>
<th>Group</th>
<th>PPM</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>aromatic</td>
<td>7.6</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>-CH_2-</td>
<td>2.9</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>-CH_3</td>
<td>1.3</td>
<td>15</td>
<td>6</td>
</tr>
</tbody>
</table>

**IR:** IR spectrum (Figure 30) showed aromatic carbon-hydrogen stretching at 3050cm^{-1}, aromatic carbon-carbon double bond absorption at 1569 and 1475cm^{-1}; aliphatic carbon-hydrogen stretching bands at 2949, 2903, 2845, 1442 and 1376cm^{-1}; and sulfone group absorptions at 1314 and 1151cm^{-1}, which also confirms the structure.

The aqueous phase was extracted three times with 100ml of methylene chloride. The combined organic layers were evaporated and 2.1g (96% yield) p-methoxy-
phenol was recovered.

The product and \( p \)-methoxyphenol both had \( R_f \) values of 0.49 in hexane-ethyl acetate (4:1) when spotted on silicia thin layer chromatography strips. A positive ferric chloride test indicated a phenol.

NMR: Singlet at 6.7 (aromatic); and a singlet at 3.7 (-CH\(_3\)). This corresponds to \( p \)-methoxyphenol.

**Ether cleavage of 4,4'-[sulfonyl bis(p-phenylene ether)] dibenzene (85).**

The same procedure as described for the ether cleavage of 4,4'-[sulfonyl bis(p-phenylene)] dianisole (81) was employed. 4,4'-[sulfonyl bis(p-phenylene)] dibenzene (3.9g, 0.099mole), 0.50g (0.020mole) of sodium hydride, 1.32g (0.0205mole) of ethanethiol in 460ml of DMF were used in the reaction mixture.

4,4'-dithioethyl diphenylsulfone (83), 2.86g, was recovered for an 87% yield. Thin layer chromatography, solubility, melting point, and NMR and IR spectral data, are the same as observed for product the cleavage product of 4,4'-[sulfonyl bis(p-phenylene ether)] dianisole. A mixed melting point with the cleavage product from the cleavage of 4-4'-[sulfonyl bis(p-phenylene ether)] dianisole, showed no depression, all three samples melted at 110-112°.

The aqueous layer was extracted three times with
150ml of ether. Solvent was removed on a Rotovap and 20ml of ether was added to the extract. The ether layer was extracted three times with 20ml of 1M sodium hydroxide. The combined aqueous phase was made acidic with 20ml of 10% HCl. This solution was extracted three times with 50ml of ether, washed once with saturated sodium chloride, and dried over anhydrous sodium sulfate. Solvent was removed on a Rotovap to yield 0.79g of phenol.

**NMR:** (Figure 53) The same as (83) above.

**IR:** (Figure 54) The same as (83) above.

**Demethylation of 4,4′-[sulfonyl bis(p-phenylene ether)] dianisole (81) with hydrobromic acid.**

A 200ml flask equipped with a condensor and a thermometer, was charged with 2.31g (0.005mole) of di(p-methoxyphenyl) diphenyl sulfone, 65ml hydrobromic acid and 12ml (0.22mole) glacial acetic acid. The reaction was heated to 110°C and left overnight. The mixture was cooled to room temperature and 30ml of 1M sodium hydroxide was added. Three 50ml portions of ether were used to extract the reaction mixture. Removal of solvent was followed by three 10ml extractions with 1M sodium hydroxide. The aqueous extract was neutralized with 10% HCl and extracted three times with 50ml of ether. 4,4′-[sulfonyl bis(p-phenylene ether)] diphenol (84), 1.82g, was
recovered after solvent removal.

The product (84) was recrystallized from ethanol-water (1-1). $T_m$ was 187-189°C. It was soluble in acetone, DMSO, hot ethanol and sodium hydroxide, slightly soluble in ethanol and ether and insoluble in chloroform.

**NMR:** (Figure 55) The NMR spectrum showed the absence of a singlet at 3.82PPM (CH$_3$O of the starting material). A multiplet at 7.5PPM (aromatic) was observed.

**IR:** The IR spectrum (Figure 31) has a typical oxygen-hydrogen stretch at 3550-3000cm$^{-1}$; aromatic carbon-hydrogen stretching bands at 3075, 3045 and 3110cm$^{-1}$; aromatic carbon-carbon double bond absorption at 1588, 1505, 1487, and 1451cm$^{-1}$; carbon-oxygen stretch at 1230cm$^{-1}$ and; sulfone group absorptions at 1366 and 1145cm$^{-1}$.

**Elemental analysis:**

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calculated</strong></td>
<td>66.35</td>
<td>4.18</td>
<td>7.38</td>
</tr>
<tr>
<td><strong>Experimental</strong></td>
<td>66.50</td>
<td>4.06</td>
<td>5.62</td>
</tr>
</tbody>
</table>

**Synthesis of 4,4'-(sulfonyl bis(p-phenylene ether)) diphenol by demethylation of 4,4'-(sulfonyl bis(p-phenylene ether)) dibenzene (81) with hydrobromic acid and acetic acid.**

-143-
A 200ml flask equipped with a condensor and a thermometer, was charged with 2.05g (0.0044) of 4,4′-[sulfonyl bis (p-phenylene ether)] dianisole, 58ml (0.50) of hydrobromic acid and 12ml (0.22mole) of glacial acetic acid. The reaction was heated under reflux (about 120°C) for six hours. Forty milliliters of 1M sodium hydroxide was added, and the mixture was extracted four times with 100ml of ether. Evaporation of the solvent left a very small amount of solid.

The aqueous phase was acidified with 15ml concentrated hydrochloric acid and extracted three times with 100ml of ether, 1.4g of (84) after solvent removal. The precipitate was recrystalized from ethanol–water (1:1). It is soluble in acetone and sodium hydroxide, insoluble in chloroform.

The melting point was 187-189°C. A mixed melting point determination with the product collected from the previous reaction (demethylation without acetic acid) was also 187-189°C.

NMR: (Figure 56) Same as the above demethylation with HBr.

IR: (Figure 57) Same as the above demethylation with HBr.

Treatment of 4,4′-[sulfonyl bis(p-phenylene ether)] dibenzene (85) with hydrobromic acid and acetic acid
The procedure used in this reaction was the same as the demethylation of 4,4′-[sulfonyl bis(p-phenylene ether)] dianisole with hydrobromic acid and acetic acid. 4,4′-[sulfonyl bis(p-phenylene ether)] dibenzene (2.42g, 0.006mole), 79ml (0.69mole) of hydrobromic acid and 16ml (0.29 mole) of glacial acetic acid were combined at 120°C for six hours. Starting material (2.0g) was recovered.

NMR: (Figure 58)

IR: (Figure 59)

Preparation of 4-bromo-2,6-dimethylanisole

A 500ml round bottom flask equipped with a condenser was charged with 12.0g (0.06mole) 4-bromo-2,6-dimethylphenol and 12ml of absolute ethanol. To the stirred, refluxing solution, there was slowly added a solution of sodium ethoxide (made from 2.8g sodium in 54ml of absolute ethanol) and methyl sulfate. The addition was made in small alternate proportions. After refluxing for four hours, the procedure of adding the sodium ethoxide and methyl sulfate was repeated exactly as above. The mixture was refluxed and stirred for 17 hours.

Most of the remaining alcohol was distilled from the reaction flask before the slurry was added to 450ml of water. After extraction with 300ml of chloroform, the chloroform was removed on a Rotovap. The product
was treated with 40ml of 2.5M NaOH and extracted with methylene chloride. Thin layer chromatography in benzene-methylene chloride (7:3) indicated a slight contamination with starting material. The product was then vacuum distilled at 89°C and 4mm.

**NMR: (Figure 60)**

<table>
<thead>
<tr>
<th>PPM</th>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Aromatic</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>3.68</td>
<td>CH₃O⁻</td>
<td>14</td>
<td>3</td>
</tr>
<tr>
<td>2.2</td>
<td>CH₃⁻</td>
<td>30</td>
<td>6</td>
</tr>
</tbody>
</table>

**IR: (Figure 61)**

The IR spectrum has aromatic carbon-carbon double bond stretch absorptions at 1673 and 1577cm⁻¹; aliphatic carbon-hydrogen stretches at 2973, 2926, 2850, 2816, and 1379cm⁻¹; carbon-oxygen stretch at 1012 and 1215cm⁻¹.

**Attempted Ullmann ether synthesis of 4,4'-(sulfonyl)bis(p-phenylene ether) di(2,6-dimethylanisole) (solvent dimethylformamide)**

In a flask equipped with a stirrer, condenser (fitted with a Dean-Stark azeotrope adapter), thermometer, and a gas inlet were placed 0.025mole of potassium hydroxide, 12.5g (0.05mole) 4,4'-dihydroxy-diphenyl sulfone, and 60ml of toluene. The mixture was heated under a nitrogen flow at 100-115°C until all the...
water was removed. All but approximately 10ml of the 
toluene was distilled off. Fifty milliliters of 
dimethylformamide was added to the reaction mixture 
followed by slow addition of 21.5g (0.1mole) 
of 4-bromo-2,6-dimethylanisole. Cupric bromide 
(0.1g) was added and the solution was refluxed at 160°C 
for 19 hours.

Dimethylformamide was distilled off. The reaction 
mixture was added to 100ml 10% hydrochloric acid and 
ice, and 10.8g of 4,4’dihydroxydiphenyl sulfate was 
recovered. This was recrystalized from ethanol-water. 
The melting point was determined to be 243°C.

The IR spectrum was the same as the starting 
4,4-dihydroxydiphenyl sulfate (Figures 62 and 63, 
respectively).

4-bromo-2,6-dimethylanisole was not recovered. We 
believe that it was removed when the dimethylformamide 
was distilled off.

Attempted Ullman ether synthesis of 4,4’[sulfonyl 
bis(p-phenylene ether) di(2,6-dimethylanisole) 
(solvent dimethyl sulfoxide)

The reaction procedure as described for the 
previous reaction was followed except dimethylformamide 
was replaced with dimethyl sulfoxide. The reactants were 
soluble in the solvent (DMSO). A brown precipitate was
collected when the reaction mixture was combined with hydrochloric acid and ice. The precipitate was insoluble in chloroform, ether, hexane, sodium hydroxide, acetone, and benzene. It is very slightly soluble in hot DMSO and ethyl acetate. The compound charred at temperatures above 300°C.

The appearance of the product suggests a mixture of materials. It appears to contain white and brown components. Elemental analysis of the mixture: carbon 58.11, hydrogen 4.86, sulfur 14.26, and nitrogen < 0.1.

IR: IR spectral data (Figure 32) indicates a broad peak at 3670-2400cm⁻¹ (maximum at 3350); carbon-carbon double bond stretch at 1586 and 1490cm⁻¹; possible aliphatic carbon-hydrogen stretch at 2950, 2890, 1450, and 1350cm⁻¹; peaks at 1285, 1212, 1145 and 1090cm⁻¹ could be interpreted as carbon-oxygen stretch and sulfone group absorptions.

Limited solubility of the product made it impossible to collect NMR data.

Ether cleavage reaction of 4-bromophenyl phenyl ether by sodium ethanethiolate.

A 1-liter 3-neck flask equipped with nitrogen inlet, condenser with drying tube, and dropping funnel was charged with 0.75g (0.030 mole) sodium hydride and 160ml of DMF. The mixture was saturated with nitrogen
and cooled to below 5°C in an ice bath with salt. Ethanethiol (1.98g, 0.030 mole) in 5ml of DMF was added dropwise while the temperature of the reaction mixture was kept below 5°C. The greyish mixture cleared as it was stirred for 15 minutes.

4-bromophenyl phenyl ether (3.75g, 0.015 mole) and 300 ml DMF were added to the reaction mixture. The temperature was maintained at 60-63° for six hours. The reaction mixture, was added to a large beaker containing 200ml of cold 10% hydrochloric acid and approximately 200g of ice.

A precipitate was observed after the addition of ice and hydrochloric acid. However, it was impossible to remove the product by filtration, as it had a melting point of 18°C.

The aqueous solution was extracted three times with 100ml of methylene chloride. The solvent was removed on a Rotovap. 98% of the starting material was recovered after vacuum distillation.

Thin layer chromatography with hexane-ethyl acetate (4:1), indicated one spot (Rf = 0.83), the same as the starting material. There was no indication of phenol or 4-bromophenol. The IR and NMR spectra matched those of the starting material.

NMR: (Figures 64 and 65)
IR: (Figures 66 and 67)
Ether cleavage reaction of diphenyl ether by sodium ethanethiolate.

The reaction procedure described for the ether cleavage of 4-bromophenyl phenyl ether was followed: 2.55g (0.015mole) of diphenyl ether, 0.75g (0.030mole) of sodium hydride, and 1.98g (0.030mole) of ethanethiol, were heated at 65°C for six hours.

A precipitate was collected after the addition of ice and hydrochloric acid. 95% of the starting material was recovered. This was varified by NMR and IR spectra, and thin layer chromatography with hexane-ethyl acetate (10:1), one spot at Rf = 0.56 for phenyl ether and the recovered phenyl ether. Phenol had an Rf = 0.25.

NMR: (Figures 68 and 69)
IR: (Figures 70 and 71)

Ether cleavage reaction of 4-phenoxyphenol by sodium ethanethiolate.

The reaction procedure described for the ether cleavage of 4-bromophenyl phenyl ether was followed: 2.55g (0.015mole) of 4-phenoxyphenol, 0.75g (0.030mole) of sodium hydride, and 1.98g (0.030mole) of ethanethiol, were heated at 65°C for six hours.

Starting material (2.37g, 93% recovery) was collected after the addition of ice and hydrochloric acid.
acid. This was recrystalized from hexane. The melting point was 82-84°C. Thin layer chromatography and, NMR and IR spectra indicate starting as the final product. No phenol or hydroquinone was detected.

NMR: (Figures 72 and 73)

Ether cleavage reaction of p-nitrophenyl phenyl ether by sodium ethanethiolate.

The reaction procedure described for the ether cleavage of 4-bromophenyl phenyl ether was followed: 3.23g (0.015mole) of p-nitrophenyl phenyl ether, 0.75g (0.030mole) of sodium hydride, and 1.98g (0.030mole) of ethanethiol, were heated at 65°C for six hours.

A yellowish brown precipitate (1.14g) was collected after the addition of ice and hydrochloric acid. The precipitate was crystalized twice from absolute ethanol. The yellow needlelike crystals melted at 96-98°C. They were soluble in toluene, acetone, hot acetic acid and hot ethanol; insoluble in hexane and water.

TLC: Hexane-ethyl acetate (10:1)

4-Nitrophenyl ethyl thioether, \( R_\equiv = 0.54 \)
Phenol \( R_\equiv = 0.32 \)
4-Nitrophenyl phenyl ether \( R_\equiv = 0.63 \)

NMR: (Figure 73)

<table>
<thead>
<tr>
<th>Group</th>
<th>Integration</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartet</td>
<td>7.75</td>
<td>Aromatic</td>
</tr>
<tr>
<td>Quartet</td>
<td>3.0</td>
<td>-CH₂-</td>
</tr>
<tr>
<td>Triplet</td>
<td>1.36</td>
<td>-CH₃</td>
</tr>
</tbody>
</table>
IR:  (Figure 42)

IR spectral data has aliphatic and aromatic characteristics and indicates a nitro group; aromatic carbon-carbon stretch at 1479 cm\(^{-1}\); aliphatic carbon-hydrogen stretch at 2953, 2911, 2848 cm\(^{-1}\); aliphatic carbon-hydrogen stretch (-S-CH\(_3\)-) at 1445 cm\(^{-1}\); aliphatic carbon-hydrogen bend at 1090 cm\(^{-1}\); and nitrogen-oxygen double bond stretch at 1578 and 1401 cm\(^{-1}\).

Ten milliliters of 10% sodium hydroxide was added to the aqueous phase (basic), followed by three extractions with 50 ml of methylene chloride. Evaporation of the solvent on a Rotovap, followed by distillation resulted in 2.07 g of dark brown liquid left in the pot. This turned out to be primarily DMF.

The basic aqueous extract was acidified with 10% hydrochloric acid (pH $>$ 2). This was extracted three times with 50 ml of methylene chloride. A brown liquid remained after evaporation. The liquid smelled like a phenol. Preparation of a bromo-derivative gave a positive test for phenol ($T_m = 91-92^\circ$C). The literature value is 95°C. An IR spectrum of the derivative was taken and it matches perfectly with the spectrum of 2,4,6-tribromophenol (Figure 43).
Figure 45  Di(p-methoxyphenyl) terephthalate
Figure 47   Di(ethylthio) terephthalate
Figure 48  4-Ethylthiocarboxybenzoic acid
Figure 49 4,4'-[Sulfonyl bis(p-phenylene ether)] dianisole
Figure 50  4,4'-[Sulfonyl bis(p-phenylene ether)] dibenzene
Figure 52  4,4'-Dithioethyldiphenyl sulfone
Figure 55 4,4'-[Sulfonyl bis(p-phenylene ether)] diphenol
Figure 56  4,4'-[Sulfonyl bis(p-phenylene ether)] diphenol
Figure 58  4,4'-[Sulfonyl bis(p-phenylene ether)] dibenzene
Figure 60  4-Bromo-2,6-dimethylanisole
Figure 61  4-Bromo-2,6-dimethylanisole
Figure 62
4,4'-Dihydroxydiphenyl sulfone (recovered from reaction mixture)
Figure 63 4,4'-Dihydroxydiphenyl sulfone (starting material)
Figure 64  4-Bromodiphenyl ether (starting material)
Figure 65  4-Bromodiphenyl ether (recovered after reaction)
Figure 67  4-Bromodiphenyl ether (recovered after reaction)
Figure 68  Diphenyl ether (starting material)
Figure 69  Diphenyl ether (recovered from reaction)
Figure 70
Diphenyl ether (starting material)
Figure 71  Diphenyl ether (recovered from reaction)
Figure 72  4-Phenoxyphenol (starting material)
Figure 73  4-Phenoxophenol (recovered after reaction)
Figure 74  4-Nitrophenyl ethyl thioether
Figure 75  4-Nitrophenyl phenyl ether
Figure 76  4-Nitrophenyl phenyl ether


7. S.R. Stevenson, Ibid.


10. M. Presadarao, Ibid.


23. G.H. Brown, Ibid.

24. G.H. Brown, Ibid.

25. G.W. Gray, see reference 11.


29. M.J.S. Dewar and A.C. Griffin, Ibid.

30. M.J.S. Dewar and A.C. Griffin, Ibid.


36. J.P. Schroeder and D.W. Bristol, see reference 34.
38. M.J.S. Dewar and A.S. Griffin, Ibid.
59. J.I. Jin, as cited in reference 52.
63. S. Antoun, see reference 60.
65. J.I. Jin, see reference 52.
67. R.W. Lenz, see references 52 and 60.
68. J. Kops, see reference 66.
72. T.C. Bruice, see reference 69.
73. J.P. Lambooy, see reference 71
74. L.F. Fieser, see reference 70.
80. L.F. Fieser, see reference 70.
81. J.P. Lambooy, see reference 71.
82. W.J. Gottstein, see reference 75.
91. G.I. Feutrill, Ibid.


96. T.C. Bruice, see reference 95.

97. H. Weingarten, see reference 93.


110. J. March, see reference 98.
114. J. March, see reference 1.
118. G. Wittig, and H. Witt, *Ber.*, 74, 1474 (1941), as sited in reference 106.
119. J.D. Roberts, see reference 116.
120. J.D. Roberts, see reference 116.
122. J.D. Roberts and co-workers, see reference 116.
123. J. Miller, see reference 106.

-193-


136. P.A. Saroretto and F.J. Sowa, see reference 133.

137. J.D. Roberts, see references 115 and 116.


139. Wittig *et al.*, *Ber.*, 40, 1193 (1940), as sited in reference 106.


141. J. March, as sited in reference 1.


146. F.J. Sowa, see references 133-136.


152. Sauer and Huisen, see reference 112.

153. J.F. Bunnett, see reference 113.

154. L.F. Fieser, see reference 70.

155. J.P. Lambooy, see reference 71.

156. W.J. Gottstein, see reference 75.


158. R.L. Shriner, see reference 150.