## CONTENTS

STATEMENT iv
CERTIFICATE v
ACKNOWLEDGEMENTS vi
LIST OF PUBLICATIONS viii
SYNOPSIS x

### PART A

**CYCLOADDITION AND OXIDATIVE ADDITION REACTIONS OF PHOSPHORUS(III) COMPOUNDS**

Chapter 1  **INTRODUCTION**  1

1.1 Reaction of P\textsuperscript{III} compounds with dialkyl azodicarboxylates  3
1.11 Synthetic applications of Mitsunobu reaction  8
1.2 Dipolar cycloaddition reactions of P\textsuperscript{III} compounds  11
1.3 Pentacoordinate phosphorus compounds  13
1.31 General Introduction  13
1.32 Reaction of P\textsuperscript{III} compounds with o-chloranil –
Formation of pentacoordinate phosphorus compounds  17
1.4 Hexacoordinate phosphorus compounds  22
1.41 General Introduction  22
1.42 Anionic and cationic hexacoordinate phosphorus compounds  22
1.43 Neutral hexacoordinate phosphorus compounds  24
1.5 Organophosphates and their involvement in hydrogen bonding  30

Objectives of the present work  34

Chapter 2  **RESULTS AND DISCUSSION**  35

2.1 Synthesis of phosphorus(III) compounds  35
2.2 Reactions of phosphorus(III) compounds with dialkyl azodicarboxylates and o-chloranil  39
2.21 Formation of pentacoordinate phosphorus compounds  39
2.22 Formation of tetracoordinate phosphorus compounds with unusual structures  53
2.23 Formation of hexacoordinate phosphorus compounds  58
2.24 Solution state NMR spectra of hexacoordinate compounds  70
2.25 Theoretical calculations  74
2.3 Involvement of cyclic phosphates in hydrogen bonding  75
2.4 Summary  82
Chapter 3  EXPERIMENTAL SECTION  

3.1 Preparation of P(III) derivatives  
3.2 Reactions of phosphorus(III) compounds with D1AD/ DEAD and o-chloranil: Reactivity of the products  
   3.21 Formation of pentacordinate phosphorus compounds  
   3.22 Formation of tetracordinate phosphorus compounds  
   3.23 Formation of hexacordinate phosphorus compounds  
3.3 Synthesis of phosphate salts  
3.4 X-ray crystallography  

REFERENCES  

PART B  

(I) PHOSPHONATES - SYNTHESIS AND UTILITY  
(II) SYNTHESIS OF ANTHRACENE DERIVATIVES WITH EXTENDED CONJUGATION  

Chapter 4  INTRODUCTION  

4.1 General Introduction  
4.2 Synthesis of α-bromo- and α-chloro-phosphonates  
   4.21 Synthesis of α-bromophosphonates  
   4.22 Synthesis of α-chlorophosphonates  
4.3 Synthetic utility of phosphonates  
4.4 Synthesis of anthracene derivatives with extended conjugation  
4.5 Addition of phosphonates to α,β-unsaturated esters–  
   Formation of cyclopropyl P substituted phosphonate derivatives  

Objectives of the present work  

Chapter 5  RESULTS AND DISCUSSION  

5.1 Synthesis of phosphites  
5.2 Synthesis of phosphonates  
   5.21 Synthesis of α-hydroxyphosphonates  
   5.22 Synthesis of bromophosphonates  
5.3 Synthetic utility of phosphonates  
5.4 Sonogashira coupling of compound 17 with terminal alkynes  
   5.41 Fluorescence spectroscopy of anthracenyl derivatives  
5.5 Synthesis of cyclopropyl phosphonates from α-chloro/bromo Phosphonates  
5.6 Synthetic utility of Mitsunobu reaction in phosphonate chemistry
Chapter 6  EXPERIMENTAL SECTION  

6.1 Synthesis of α-hydroxyphosphonates  
6.2 Synthesis and utility of bromophosphonates  
   6.21 Synthesis of bromophosphonates  
   6.22 HWE reaction of the bromophosphonate 7 with aldehydes  
   6.23 Sonogashira coupling of compound 17 with terminal alkynes  
6.3 Synthesis of cyclopropyl phosphonates  
6.4 Alkylation of adenine using Mitsunobu reaction  
6.5 X-ray crystallography  

REFERENCES  

APPENDIX 1  CCDC Reference codes/ publication numbers and atomic coordinates for X-ray structures reported in this thesis  

I-VII