

IN THE NAME OF GOD

I. VOSE



Shiraz University
Faculty of Sciences

Ph.D. Dissertation in Organic Chemistry

**NEW APPLICATIONS OF TRIETHYLPHOSPHITE AND
DIETHYL CHLOROPHOSPHATE IN ORGANIC
SYNTHESIS
&
PREPARATION OF SOME NEW EXCIPILEX SMALL
MOLECULES**

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FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF
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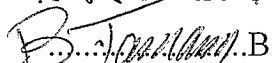
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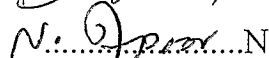
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**THIS TESIS IS DEDICATED
TO
MY
FATHER,
MOTHER
AND BROTHERS
THE BEST FREINDS OF MINE**

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Abstract

New Applications of Triethylphosphite and Diethyl Chlorophosphate in Organic Synthesis

&

Preparation of Some New Exciplex Small Molecules

By:

Zahra Shahsavari Fard

This thesis is concerned with the new applications of triethylphosphite and diethyl chlorophosphate in organic synthesis and synthesis of some new exciplex small molecules.

Development of efficient methods for preparation of β -hydroxyphosphonates via epoxide ring opening in the presence of triethylphosphite and preparation of benzoxazoles, preparation of nitriles from primary amides, preparation of nitriles from aldoximes, preparation of amides from ketoximes using Beckmann rearrangement, formylation of activated heteroaromatic rings in the presence of diethyl chlorophosphate is discussed in chapter one. In other work, according to importance of solvent free conditions in organic reactions, it is tried omitting solvent from above reactions.

Chapter two describes the synthesis of some new exciplex small molecules. In this chapter it is tried to synthesize some new exciplexes and investigate chemical structure and solvent effect on the wavelength and intensity of their fluorescence.

TABLE OF CONTENTS

CONTENTS	PAGES
LISTS OF FIGURES	
CHAPTER 1: New Applications of Triethylphosphite and Diethyl Chlorophosphate in Organic Synthesis	
Introduction	1
1.1 β -Hydroxyarylphosphonates	6
1.2 2-Substituted Benzoxazoles	10
1.3 Aliphatic and Aromatic Nitriles	14
1.3.1 Nitriles from Dehydration of Primary Amides	15
1.3.2 Nitriles from Dehydration of Aldoximes	19
1.4 Aliphatic and Aromatic Amides	21
1.4.1 Beckmann Rearrangement of Ketoximes to Amides	22
1.5 Vilsmeier Formylation	24
1.6 Solvent Free Media	27
1.7 Objective	30
Experimental	
2.1. General Procedure for the Preparation of β -Hydroxy phosphonates	33
2.2. General Procedure for the Preparation of Arylphosphates	37
2.3. General Procedure for the Preparation of Ethyl Aryl Hydrogenphosphae	39

CONTENTS	PAGES
2.4. General Procedure for the Preparation of 2-Substituted Benzoxazoles	42
2.4.1 General Procedure for Direct Acylation of Phenols in Presence of AMA	46
2.5. General Procedure for Dehydration of Aldoximes to Nitriles	46
2.6. General Procedure for Conversion of Primary Amides to Nitriles	46
2.7. General Procedure for Beckmann Rearrangement of Ketoximes to Amides	52
2.8. General Procedure for Solvent-Free Preparation of Amides, Nitriles and Benzoxazoles	55
2.9. General Procedure for Vilsmeier-Haack Formylation of Activated Aromatic Nuclei	55
 Results and Discussion	
3.1. Synthesis of β -Hydroxyphosphonates	58
3.1.1. Mechanism of the Reaction	63
3.1.2. Monoethyl Aryl Hydrogenphosphate	64
3.1.2.1 Mechanism of the Reaction	68
3.2. Synthesis of 2-Substituted Benzoxazoles	69
3.2.1 Mechanism of Conversion of 2-Hydroxyaryl Ketoximes to Benzoxazoles	73
3.3 Dehydration of Aldoximes to Nitriles	74
3.3.1 Mechanism of Dehydration of Aldoximes	79

CONTENTS	PAGES
3.4 Dehydration of Primary Amides to Nitriles	80
3.4.1 Mechanism of the Conversion of Primary Amides to Nitriles	84
3.5 Beckmann Rearrangement of Ketoximes to Amides	85
3.5.1 Mechanism of the Transformation of ketoximes to the Corresponding Amides	88
3.5.2 Beckmann Rearrangement of Benzoin Oxime	89
3.5.2.1 Mechanism of Beckmann Rearrangement of Benzoin Oxime	90
3.6 Vilsmeier-Haack Formylation	91
3.6.1 Reaction Conditions	91
3.6.1.1 Solvent Effect on the Formylation Reaction	91
3.6.1.2 Temperature Effect on the Formylation Reaction	93
3.6.1.3 Hydrolysis Conditions for the Formylation Reaction	93
3.6.2 Formylation of Aromatic and Heteroaromatic Rings	94
3.6.3 Mechanism of the Formylation Reaction	96
3.7 Solvent Free Reactions	97
3.7.1 Benzoxazole Preparation	97
3.7.2 Nitriles from Aldoxime	99
3.7.3 Nitriles from Primary Amides	101
3.7.4 Beckmann Rearrangement of Ketoximes	103
3.8. Conclusion	105

CONTENTS	PAGES
 CHAPTER 2: Preparation of Some New Exciplex Small Molecules	
Introduction	108
1.1 Excimer	108
1.2 Exciplex	108
1.2.1 Chemical Structure	111
1.2.2 Solvent	112
1.2.3 Magnetic Field	114
1.2.4 Ligand	114
1.3 Some Applications of Exciplexes	114
1.3.1 Detection of Nucleic Acid	114
1.3.2 Recognition of ATP	116
1.3.3 Indication of Reaction End Point	118
1.4 Objective	119
 Experimental	
2.1 General Procedure for Esterification of Alcohols	122
2.1.1. General Procedure for Alcohols from Aldehyde	125
 Results and Discussion	
3.1 Exciplexes	128
3.1.1 Chemical Structure Effect on Florescence Intensity	131
3.1.2 Solvent Effect on Florescence Intensity	137
3.2 Conclusion	141

CONTENTS

PAGES

References	142
Appendix	156
Abstract and Title Pages in Persian	183

LIST OF FIGURES**PAGES**

1. The ^1H NMR spectra of Diethyl 2-Hydroxy-3-phenoxypropyl Phosphate	157
2. The ^{13}C NMR spectra of Diethyl 2-Hydroxy-3-phenoxypropyl Phosphate	157
3. The IR spectra of Diethyl 2-Hydroxy-3-phenoxypropyl Phosphate	158
4. The Mass spectra of Diethyl 2-Hydroxy-3-phenoxypropyl Phosphate	158
5. The ^1H NMR spectra of Ethyl 2-Bromophenyl Hydrogen Phosphate	159
6. The ^{13}C NMR spectra of Ethyl 2-Bromophenyl Hydrogen Phosphate	159
7. The IR spectra of Ethyl 2-Bromophenyl Hydrogen Phosphate	160
8. The Mass spectra of Ethyl 2-Bromophenyl Hydrogen Phosphate	160
9. The ^1H NMR spectra of 5-Methyl-2-nonylbenzoxazole	161
10. The ^{13}C NMR spectra of 5-Methyl-2-nonylbenzoxazole	161
11. The IR spectra of 5-Methyl-2-nonylbenzoxazole	162
12. The Mass spectra of 5-Methyl-2-nonylbenzoxazole	162
13. The ^1H NMR spectra of Piperidin-2-one	163
14. The ^{13}C NMR spectra of Piperidin-2-one	163
15. The IR spectra of Piperidin-2-one	164

LIST OF FIGURES	PAGES
16. The ^1H NMR spectra of Anthracene-9-ylmethyl 4-(dimethylamino) benzoate	165
17. The ^{13}C NMR spectra of Anthracene-9-ylmethyl 4-(dimethylamino) benzoate	165
18. The IR spectra of Anthracene-9-ylmethyl 4-(dimethylamino) benzoate	166
19. The Mass spectra of Anthracene-9-ylmethyl 4-(dimethylamino) benzoate	166
20. The ^1H NMR spectra of Pyrene-1-ylmethyl 4-(dimethylamino) benzoate	167
21. The ^{13}C NMR spectra of Pyrene-1-ylmethyl 4-(dimethylamino) benzoate	167
22. The IR spectra of Pyrene-1-ylmethyl 4-(dimethylamino) benzoate	168
23. The Mass spectra of Pyrene-1-ylmethyl 4-(dimethylamino) benzoate	168
24. The ^1H NMR spectra of Phenanthren-9-ylmethyl 4-(dimethylamino) benzoate	169
25. The ^{13}C NMR spectra of Phenanthren-9-ylmethyl 4-(dimethylamino) benzoate	169
26. The IR spectra of Phenanthren-9-ylmethyl 4-(dimethylamino) benzoate	170
27. The Mass spectra of Phenanthren-9-ylmethyl 4-(dimethylamino) benzoate	170
28. The ^1H NMR spectra of Naphthalen-2-ylmethyl 4-(dimethylamino) benzoate	171

LIST OF FIGURES	PAGES
29. The ^{13}C NMR spectra of Naphthalen-2-ylmethyl 4-(dimethylamino) benzoate	171
30. The IR spectra of Naphthalen-2-ylmethyl 4-(dimethylamino) benzoate	172
31. The Mass spectra of Naphthalen-2-ylmethyl 4-(dimethylamino) benzoate	172
32. The ^1H NMR spectra of Anthracene-9-ylmethyl 4-methoxy benzoate	173
33. The ^{13}C NMR spectra of Anthracene-9-ylmethyl 4-methoxy benzoate	173
34. The IR spectra of Anthracene-9-ylmethyl 4-methoxy benzoate	174
35. The Mass spectra of Anthracene-9-ylmethyl 4-methoxy benzoate	174
36. The ^1H NMR spectra of Anthracene-9-ylmethyl Phenyl acetate	175
37. The ^{13}C NMR spectra of Anthracene-9-ylmethyl Phenyl acetate	175
38. The IR spectra of Anthracene-9-ylmethyl Phenyl acetate	176
39. The Mass spectra of Anthracene-9-ylmethyl Phenyl acetate	176
40. The ^1H NMR spectra of Anthracene-9-ylmethyl Phenyl propanoate	177
41. The ^{13}C NMR spectra of Anthracene-9-ylmethyl Phenyl propanoate	177

LIST OF FIGURES	PAGES
42. The IR spectra of Anthracene-9-ylmethyl Phenyl propanoate	178
43. The Mass spectra of Anthracene-9-ylmethyl Phenyl propanoate	178
44. The ¹ H NMR spectra of Anthracene-9-ylmethyl 4-nitro benzoate	179
45. The ¹³ C NMR spectra of Anthracene-9-ylmethyl 4-nitro benzoate	179
46. The IR spectra of Anthracene-9-ylmethyl 4-nitro benzoate	180
47. The Mass spectra of Anthracene-9-ylmethyl 4-nitro benzoate	180
48. The ¹ H NMR spectra of 4-Methoxybenzyl- 4-pyrene-1-butanoate	181
49. The ¹³ C NMR spectra of 4-Methoxybenzyl- 4-pyrene-1-butanoate	181
50. The IR spectra of 4-Methoxybenzyl- 4-pyrene-1-butanoate	182
51. The Mass spectra of 4-Methoxybenzyl- 4-pyrene-1-butanoate	182

CHAPTER 1

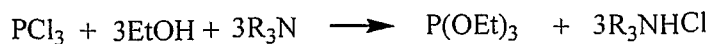
**New Applications of Triethylphosphite and Diethyl
Chlorophosphate in Organic Synthesis**

CHAPTER 1

INTRODUCTION

It is now accepted that phosphorus compounds play a vital role in living processes and are essential, not only for hereditary processes, but also for the growth, development and maintenance of all plants and animals. They are present in soil, bones, teeth, and in blood and all cellular organisms. Energy transfer processes such as photosynthesis, metabolism, nerve function and muscle action all involve phosphorus compounds. Reversible phosphorylation is the most universal mechanism employed in nature for regulation the action of enzymes and other proteins involved in biochemical processes. The 20th century expansion of all phosphorus chemistry has been enormous and it has been paralleled by a great increase in both the diversity and volume of application of manufactured phosphorus compounds.¹ In this work, it is attempted to study the application of some organophosphorus compounds in organic synthesis and then their new applications are reported.

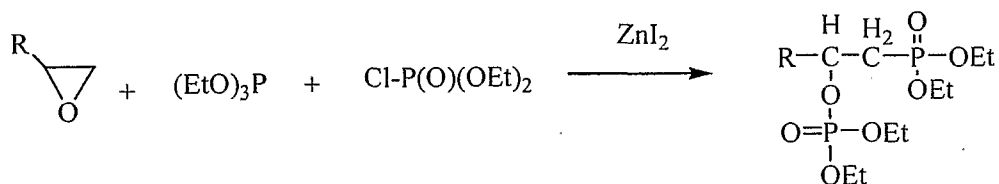
The first compound we are interested is triethylphosphite which is an organophosphorus compound with the formula of $P(OCH_2CH_3)_3$. This colorless liquid is used as a ligand in organometallic chemistry and as a reagent in organic chemistry. Triethylphosphite is prepared by treating phosphorus trichloride with ethanol in the presence of a base, typically a tertiary amine (Scheme 1.1).¹



Scheme 1.1

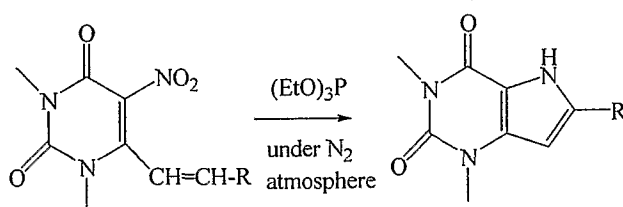
This compound has wide applications in organic reactions. Reactions of triethylphosphite with alkyl or aryl halides,^{2a} furfural oxime,^{2b} *o*-hydroxybenzyl alcohol,^{2c} iminium salts^{2d} and 2-halo anilides³ are some examples.

Synthesis of 2-(diethylphosphinyloxy) alkanephosphonates from epoxides is another application which is reported in literature (Scheme 1.2).⁴



Scheme 1.2

Pyrrolo [2, 3-d] - and pyrrolo [3, 2-d] pyrimidines are synthesized by treatment of 5-nitro-6-styryl derivatives with triethylphosphite (Scheme 1.3).⁵



Scheme 1.3

There are many other similar examples in the literature.