STUDIES ON SOME WITTIG REACTIONS

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STUDIES ON SOME WITTIG REACTIONS

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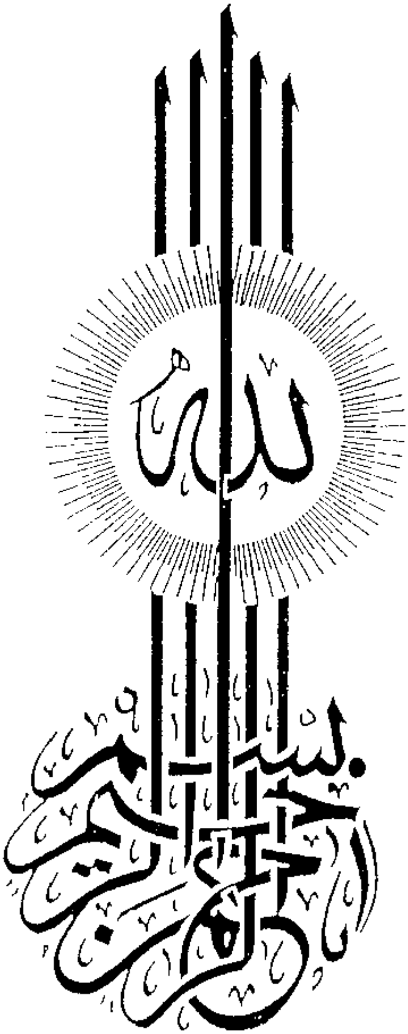
بسم الله الرحمن الرحيم

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"سُبحٰنك لَا عِلمَ لنآ إِلَّا ما علَّمتنآ

إِنّك أَنت ٱلعليم ٱلحكيم"

صدق الله العظيم

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NOTE

The Candidate has attended Courses for one year, covering the following topics:-

1. Photochemistry.
2. Spectroscopy.
3. Organometallic compounds.
4. Quantum Chemistry.
5. Thermodynamics.
6. Kinetics.
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Approved

vice dean for Graduate
studies.

CONTENTS

SUMMARY

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I: Wittig's reaction of aromatic aldehydes with 1,2-bis-(ethoxycarbonyl) ethylidene triphenyl phosphorane:

The Wittig reaction of a) Benzaldehyde with 1,2-bis-(ethoxycarbonyl) ethylidene triphenyl phsophorane in boiling benzene yields a stereoisomeric mixture of the full esters: E/Z-Diethylphenylitaconate (Oil) (106a). Alkaline hydrolysis of the stereoisomeric mixture gives the corresponding (E and Z) diacids: (Z)- γ-phenylitaconic acid (108a) and (E)- γ -phenylitaconic acid (107a).

(Z)- γ -phenylitaconic acid (108a) is easily transformed to the corresponding (Z)- γ -anhydride (109a) by the action of acetylchloride. Methanolysis of the latter (Z)- γ -anhydride (109a) with boiling methanol gives the (Z)- γ -β-half ester: Methyl-hydrogen(Z)- γ -phenylitaconate (110a).

b) p-Methoxy benzaldehyde with 1, 2- bis-(exthoxy-carbonyl) ethylidene-triphenyl phosphorane in boiling benzene yields a stereoisomeric mixture of the full esters: E/Z Diethyl p-methoxyphenylitaconate (oil) (106_b). Alkaline hydrolysis of the stereoisomeric mixture gives the corresponding (E and Z) diacids: (Z)- - γ -p-methoxyphenyl itaconic acid (108_b) and (E)- γ -pmethoxyphenylitaconic acid (107_b). (Z)- γ -p-methoxy phenyl itaconic acid (108_b) is easily transformed to the corresponding (Z)- γ -anhydride (109_b) by the action of acetyl chloride. Methanolysis of the latter (Z)- γ - anhydride with boiling methanol gives (Z)- γ--β-half ester: Methyl-hydrogen (Z)- γ -p-methoxy-phenyl itaconate (110_b).

c) p-Nitro benzaldehyde with 1,2-bis-(ethoxycarbonyl) ethylidene triphenyl phosphorane in boiling benzene yields a stereoisomeric mixture of the full esters: E/Z Diethyl-p-nitrophenyl itaconate (solid) (106_c). Alkaline hydrolysis of the stereoisomeric mixture gives the corresponding (E and Z) diacidS: (Z)- γ -p-nitrophenyl itaconic acid (108_c) and (E)- γ -p-nitrophenyl itaconic acid (107_c). (Z)- γ -p-nitrophenylitaconic acid (108_c) is easily transformed to the corresponding (Z)- γ -anhydride (109_c) by the action of acetyl chloride. Methanolysis of the latter (Z)- γ -anhydride (109_c) with boiling methanol gives (Z)- γ -β-halfester: Methyl-hydrogen (Z)- γ -p-nitrophenylitaconate (110_c).

d) m-Nitro benzaldehyde with 1,2-bis-(ethoxycarbonyl) ethylidene triphenyl phosphorane in boiling benzene yields a stereoisomeric mixture of the full esters: E:/Z Diethyl m-nitrophenylitaconate (oil) (106_d). Alkaline hydrolysis of the stereoisomeric mixture gives the corresponding (E and Z) diacids: (Z)- γ -m-nitrophenylitaconic acid (108_d) and (E)- γ -m-nitrophenylitaconic acid (107_d). (Z)- γ -m-nitrophenylitaconic acid (108_d) is easily transformed to the corresponding (z)- γ -anhydride (109_d) by the action of acetyl chloride. Methanolysis of the latter (z)- γ --anhydride (109_d) with boiling methanol gives (Z)- γ -β-halfester: Methyl hydrogen (Z)- γ -m-nitrophenyl itaconate (110_d).

e) 1-Naphthaldehyde with 1,2-bis-(ethoxycarbonyl) ethylidenetriphenylphosphorane in boiling benzene yields a stereoisomeric mixture of the full esters: E/Z Diethyl-1-naphthyl itaconate (oil) (106_e). Alkaline hydrolysis of the stereoisomeric mixture gives the corresponding (E and Z) diacids: (Z)- γ -1-Naphthyl itaconic acid (108_e) and (E) - γ -1-Naphthylitaconic acid (107_e). (Z)- γ -1-Naphthylitaconic acid (108_e) is easily transformed to the corresponding (z)- γ -anhydride (109_e) by the action of acetyl chloride. Methanolysis of the latter (z)- γ -anhydride (109_e) with boiling methanol gives (z)- γ -β-half ester: Methyl-hydrogen (z)- γ -1-naphthyl itaconate (110_e).

f) 2-Naphthaldehyde with 1,2-bis-(ethoxycarbonyl) ethylidene triphenylphosphorane in boiling benzene yields a stereoisomeric mixture of the full esters: E/Z Diethyl-2-naphthylitaconate (oil) (106_f). Alkaline hydrolysis of the stereoisomeric mixture gives the corresponding (E and Z) diacids: (z)- γ -2-Naphthylitaconic acid (108_f) and (E)- γ -2-Naphthylitaconic acid (107_f). (z)- γ -2-Naphthylitaconic acid (108_f) is easily transformed to the corresponding (z)- γ - anhydride (109_f) by the action of acetyl chloride. Methanolysis of the latter (z)- γ -anhydride (109_f) with methanol gives (z)- γ -β-halfester: Methyl-hydrogen (z)- γ -2-naphthylitaconate (110_f). Cyclisation reaction of the (z) γ-β-halfester of 2-Naphthaldehyde (110_f) with sodium acetate catalyste in boiling acetic anhydride gives a product which is identified as: Methyl-4 acetoxyphenanthrene-2-carboxylate (111_f). (6-membered ring cyclisation)

CHAPTER I

INTRODUCTION

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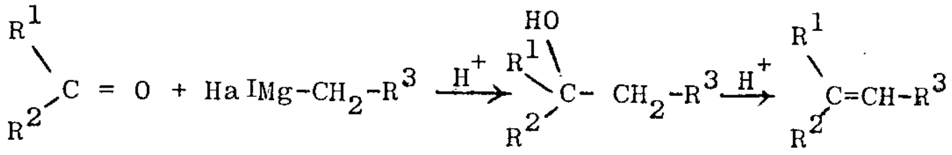
1. General Consideration:

The usual procedure followed in the conversion of a C = 0 into a C=C bond (Carbonyl olefin transformation) consits of adding a Grignard reagent to the Carbonyl and eliminating a molecule of water from the Carbinol intermediate thus formed.



This classical method does not, however, permit the uniform conversion of aliphatic aldehydes or ketones into olefins with the double bond in a definit and unambiguous location. In the case of secondary and tertiary aliphatic, water elimination can proceed in two or three directions.

In such cases the method worked out by wittig[1], utilizing triphenylphosphine methylenes is applied to advantage. These derivatives of pentavalent phosphorus are capable of exchanging their methylene group with the double bonded oxygen of a carbonyl group.