STUDIES ON SOME WITTIG REACTIONS

A THESIS

Presented to
University Collage for Women
Ain Shams University

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(B. Sc. Special Chemistry)

In Partial Fulfillment
of the Requirements for the
MASTER OF SCIENCE DEGREE



1987

STUDIES ON SOME WITTIG REACTIONS

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ACKNOWLED GEMENT

The author wishes to express her deepest thanks and gratitude to Prof. Dr. William I, Awad, D.Sc., professor of Chemistry, University College for women, Ain Shams University, not only for suggesting the subjects investigated, but also for his continuous advice and valuable criticism during the course of this work.

The author also expressess her thanks to Dr. Nadia G. Kandile, Ass. Prof. of organic chemistry and Dr. W.N. Wassef, Ass. Prof. of organic Chemistry University College for women, Ain Shams University, for their great help and continuous encouragement.

The author wishes also to thank prof. Dr.Saleh A. Awad, Head of Chemistry Dept., University College for women, Ain Shams University, for the facilities at his disposal.

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.
- 7. Microanalysis.

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SUMMARY

SUMMARY

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)- %-phenylitaconic acid (108a) and (E)- %-phenylitaconic acid (107a).

- (Z)- % -phenylitaconic acid (108a) is easily transformed to the corresponding (Z)- % -anhydride (109a) by the action of acetylchloride. Methanolysis of the latter (Z)- % -anhydride (109a) with boiling methanol gives the (Z)- %-%-half ester: Methyl-bydrogen(Z)- %-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 -p-

methoxyphenylitaconic acid (107_b) . (Z)- %-p-methoxyphenyl itaconic acid (108_b) is easily transformed to the corresponding (Z)- %-anhydride (109_b) by the action of acetyl chloride. Methanolysis of the latter (Z)- %- anhydride with boiling methanol gives (Z)- %-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) ($106_{\rm C}$). Alkaline hydrolysis of the stereoisomeric mixture gives the corresponding (E and Z) diacidS: (Z)- γ -p-nitrophenyl itaconic acid ($108_{\rm C}$) and (E)- γ -p-nitrophenyl itaconic acid ($108_{\rm C}$) and (E)- γ -p-nitrophenyl itaconic acid ($108_{\rm C}$) is easily transformed to the corresponding (Z)- γ -anhydride ($109_{\rm C}$) by the action of acetyl chloride. Methanolysis of the latter (Z)- γ -anhydride ($109_{\rm C}$) with boiling methanol gives (Z)- γ -p-halfester: Methyl-hydrogen (Z)- γ -p-nitrophenylitaconate ($110_{\rm C}$).
- 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)- % -m-nitrophenylitaconic acid (108_d) and (E)- % -m-nitrophenylitaconic acid (107_d). (Z)- % -m-nitrophenylitaconic acid (108_d) is easily transformed to the corresponding (z)- % -anhydride (109_d) by the action of acetyl chloride. Methanolysis of the latter (z)- % -anhydride (109_d) with boiling methanol gives (Z)- % -B-halfester: Methyl hydrogen (Z)- % -m-nitrophenyl-itaconate (110_d).

e) 1-Naphthaldehyde with 1,2-bis-(ethoxycarbony1) 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)- % -1-Naphthyl itaconic acid (108_e) and (E) - % -1-Naphthylitaconic acid (107_e). (Z)- % -1-Naphthylitaconic acid (108_e) is easily transformed to the corresponding (z)- % -anhydride (109_e) by the action of acetyl chloride. Methanolysis of the latter (z)- % -anhydride (109_e) with boiling methanol gives (z)- % -B-half ester: Methyl-hydrogen (z)- % -1-naphthylitaconate (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)- χ -2-Naphthylitaconic acid (108 $_{\rm f}$) and (E)- χ -2-Naphthylitaconic acid (107 $_{
m f}$). (z)- χ -2-Naphthylitaconic acid (108 $_{
m f}$) is easily transformed to the corresponding (z)- χ - anhydride (109 $_{\mathrm{f}}$) by the action of acetyl chloride. Methanolysis of the latter (z)- χ -anhydride (109 $_{\mathrm{f}}$) with methanol gives (z)- % - β -halfester: Methyl-hydrogen (z)- χ -2-naphthylitaconate (110_f). Cyclisation reaction of the (z) $\mbox{$\chi$-$B$-halfester}$ of 2-Maphthaldehyde (110 $_{
m f}$) 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

INTRODUCTION

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.

$$R^{1}$$
 $C = 0 + \text{Ha Img-CH}_{2} - R^{3} \xrightarrow{H^{+}} R^{1}$
 R^{2}
 $C - CH_{2} - R^{3} \xrightarrow{H^{+}} R^{2}$
 $C = CH - R^{3}$

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 wittig¹, 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.