

**STUDY ON
UNSATURATED CYCLIC CARBONYL COMPOUNDS**

A THESIS

*Submitted for the Degree of Doctor of Philosophy
(Ph.D.)*

By

And George Ibrahim George
B.Sc. (Natural Sciences) - M.Sc.

Supervised By

Prof. Dr. ABD ELMAJED SAMMOUR D.Sc.

Printed in Egypt

Ain Shams University

1974

STUDY ON

UNSATURATED CYCLIC CARBONYL COMPOUNDS

Thesis Advisor:-

Prof. Dr. A. Sammour (D.Sc.)

Thesis Approved

.....*A. Sammour*.....

Prof. Dr. S.K. Tobia

Head of Chemistry Department



A C K N O W L E D G E M E N T

The author wishes to express his thanks and deep gratitude to Prof. Dr. A. Sammour (D.Sc.), Chemistry Department, Faculty of Science, Ain Shams University not only for suggesting the problem, but also for his valuable discussion and criticism.

C O N T E N T S

	Page
List of New Compounds	1
Objective of the Study	1
Summary of the original work	2
Reactions with α -3-arylidene-5-(p-isopropyl-phenyl)spirofuran-3(2H)-2-ones	2
 General Part.	
Chemistry of butenolides	13
A) Synthesis of α -arylidene- γ -aryl- ^{β, γ} -butenolides	13
B) Reactions of butenolides	27
 Original Work.	
Reactions with α -3-arylidene-5-(p-isopropyl-phenyl)spirofuran-3(2H)-2-ones	66
I) Synthesis of α -3-arylidene-5-(p-isopropyl-phenyl)spirofuran-3(2H)-2-ones	66
II) Synthesis of pyrrolinones	76
III) Hydrolysis	83
IV) Aminolysis	87
A) Aliphatic amines	87
B) Aromatic amines	94
V) Ammonolysis	99
VI) Action of hydrazines	101
VII) Friedel-Crafts	107
A) With Furanones	107
B) With pyrrolinones	121
Experimental	123
NMR and UV. Spectra	
References	157
Summary in Arabic	

LIST OF NEW COMPOUNDS

List of New Compounds

- 1) α -3-Benzylidene-3-(p-isopropylphenyl)spirofurane-3(2H)-2-one (IIa).
- 2) α -3-Anisylidene-5-(p-isopropylphenyl)spirofuran-3(2H)-2-one (IIb).
- 3) α -3-(m-Nitrobenzylidene)-5-(p-isopropylphenyl)spirofuran-3(2H)-2-one (IIc).
- 4) α -3-Furfurylidene-5-(p-isopropylphenyl)spirofuran-3(2H)-2-one (IId).
- 5) α -3-Pipronylidene-5-(p-isopropylphenyl)spirofuran-3(2H)-2-one (IIe).
- 6) α -3-(Dimethylaminobenzylidene)-5-(p-isopropylphenyl)-spirofuran-3(2H)-2-one (IIf).
- 7) 5-(p-isopropylphenyl)-5-spirofuran-3(2H)-furanone (III).
- 8) 3-[2-oxo-5-(p-isopropylphenyl)-3(2H)furylidene]-2-indolinones (IV).
- 9) 3-[2-oxo-5-(p-isopropylphenyl)-3(2H)-furylidene]-phthalide (Va).
- 10) 5-(p-isopropylphenyl)spiro[furan-3(2H), 2'-indan]-1',2,3'-trione (VI).
- 11) 6-Chloro-3-[2-oxo-5-(p-isopropylphenyl)-3(2H)furylidene]-phthalide (Vb).
- 12) 6-Nitro-3-[2-oxo-5-(p-isopropylphenyl)-3(2H)furylidene]-phthalide (Vc).

- 13) 3-[2-oxo-5-(p-isopropylphenyl)-3(2H)-furylidene]-1-isoindolinone (VII).
- 14) α, α -Diphenyl- γ -(p-isopropylphenyl)- $\Delta^{\beta, \gamma}$ -pyrrolidenone (VIIIa).
- 15) α -Methyl- α -phenyl- γ -(p-isopropylphenyl)- $\Delta^{\beta, \gamma}$ -pyrrolidenone (VIIIb).
- 16) α -Phenyl- α -benzoyl- γ -(p-isopropylphenyl)- $\Delta^{\beta, \gamma}$ -pyrrolidenone (VIIIc).
- 17) α, α -Dibenzyl- γ -(p-isopropylphenyl)- $\Delta^{\beta, \gamma}$ -pyrrolidenone (VIIId).
- 18) α -Benzyl- α -methyl- γ -(p-isopropylphenyl)- $\Delta^{\beta, \gamma}$ -pyrrolidenone (VIIIe).
- 19) α -Benzyl- α -phenyl- γ -(p-isopropylphenyl)- $\Delta^{\beta, \gamma}$ -pyrrolidenone (VIIIf).
- 20) γ -(p-isopropylphenyl)- $\Delta^{\beta, \gamma}$ -pyrrolidenone (IX).
- 21) α -Cyclohexylidene- γ -(p-isopropylphenyl)- $\Delta^{\beta, \gamma}$ -pyrrolidenone (X).
- 22) α -Cyclopentylidene- γ -(p-isopropylphenyl)- $\Delta^{\beta, \gamma}$ -pyrrolidenone (XI).
- 23) α -(p-isopropylphenacyl)cinnamic acid (XIIa).
- 24) p-Methoxy- α -(p-isopropylphenacyl)cinnamic acid (XIIb).
- 25) 3,4-Methylenedioxy- α -(p-isopropylphenacyl)cinnamic acid (XIIc).

- 26) 1-(2'-Carboxyphenyl)-2-carboxy-4(4'-isopropylphenyl)-butane-1,4-dione (XIII).
- 27) 1,3-Dioxo-2-(p-isopropylphenacyl)-2-indan-carboxylic acid (XIV).
- 28) N-Methyl- α -(p-isopropylphenacyl)-cinnamamide (XVa).
- 29) N-Ethyl- α -(p-isopropylphenacyl)-cinnamamide (XVb).
- 30) N-(n-Butyl)- α -(p-isopropylphenacyl)-cinnamamide (XVc).
- 31) N-Benzyl- α -(p-isopropylphenacyl)-cinnamamide (XVd).
- 32) N-Methyl- α -(p-isopropylphenacyl)-p-methoxycinnamamide (XVe).
- 33) N-Ethyl- α -(p-isopropylphenacyl)-p-methoxycinnamamide (XVf).
- 34) N-(n-Butyl)- α -(p-isopropylphenacyl)-p-methoxycinnamamide (XVg).
- 35) N-Benzyl- α -(p-isopropylphenacyl)-p-methoxycinnamamide (XVh).
- 36) N-Methyl- α -(p-isopropylphenacyl)-m-nitrocinnamamide (XVi).
- 37) N-Ethyl- α -(p-isopropylphenacyl)-m-nitro-cinnamamide (XVj).
- 38) N-(n-Butyl)- α -(p-isopropylphenacyl)-m-nitro-cinnamamide (XVk).
- 39) N-Benzyl- α -(p-isopropylphenacyl)-m-nitro-cinnamamide (XVl).
- 40) N-Methyl- α -(p-isopropylphenacyl)-3,4-methylenedioxo-cinnamamide (XVn).
- 41) N-Ethyl- α -(p-isopropylphenacyl)-3,4-methylenedioxo-cinnamamide (XVo).
- 42) N-Benzyl- α -(p-isopropylphenacyl)-3,4-methylenedioxo-cinnamamide (XVp).

- 43) 4-Benzylidene-1-methyl-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XVIa).
- 44) 4-Benzylidene-1-benzyl-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XVIb).
- 45) 4-Anisylidene-1-methyl-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XVIc).
- 46) 4-Anisylidene-1-benzyl-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XVId).
- 47) 4-m-Nitrobenzylidene-1-methyl-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XVIe).
- 48) 4-m-Nitrobenzylidene-1-ethyl-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XVIf).
- 49) 4-p-Nitrobenzylidene-1-(n-butyl)-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XVIg).
- 50) 4-Benzylidene-1-p-tolyl-2-(p-isopropylphenyl)-2-pyrrolidene-5-one (XVIIa).
- 51) 4-Benzylidene-1-p-anisyl-2-(p-isopropylphenyl)-2-pyrrolidene-5-one (XVIIb).
- 52) 4-Benzylidene-1-o-chlorophenyl-2-(p-isopropylphenyl)-2-pyrrolidene-5-one (XVIIc).
- 53) 4-Anisylidene-1-p-tolyl-2-(p-isopropylphenyl)-2-pyrrolidene-5-one (XVIId).
- 54) 4-Anisylidene-1-p-anisyl-2-(p-isopropylphenyl)-2-pyrrolidene-5-one (XVIIe).

- 55) 4-Anizylidene-1-o-chlorophenyl-2-(p-isopropylphenyl)-2-pyrrolidene-5-one (XVIIIf).
- 56) 4-m-Nitrobenzylidene-1-phenyl-2-(p-isopropylphenyl)-2-pyrrolidene-5-one (XVIIIg).
- 57) 4-m-Nitrobenzylidene-1-p-tolyl-2-(p-isopropylphenyl)-2-pyrrolidene-5-one (XVIIIf).
- 58) 4-m-Nitrobenzylidene-1-p-anizyl-2-(p-isopropylphenyl)-2-pyrrolidene-5-one (XVIIIf).
- 59) 4-m-Nitrobenzylidene-1-o-chlorophenyl-2-(p-isopropylphenyl)-2-pyrrolidene-5-one (XVIIIf).
- 60) Aniline-p-isopropylphenacylcinnamate (XVIIIa).
- 61) Aniline-p-isopropylphenacyl-p-methoxycinnamate (XVIIIb).
- 62) 4-Benzylidene-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XIXa).
- 63) 4-Anizylidene-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XIXb).
- 64) 4-m-Nitrobenzylidene-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XIXc).
- 65) 4-Picronylidene-2-(p-isopropylphenyl)-2-pyrrolin-5-one (XIXd).
- 66) 4-Benzylidene-1,4-dihydro-6-(p-isopropylphenyl)-3(2H)-pyridazinone (XXa).
- 67) 4-Anizylidene-1,4-dihydro-6-(p-isopropylphenyl)-3(2H)-pyridazinone (XXb).

- 68) 4-m-Nitrobenzylidene-1,4-dihydro-6-(p-isopropylphenyl)-3(2H)-pyridazinone (XXc).
- 69) 4-Pipronylidene-1,4-dihydro-6-(p-isopropylphenyl)-3(2H)-pyridazinone (XXd).
- 70) 4-m-Nitrobenzylidene-1,4-dihydro-6-(p-isopropylphenyl)-1-phenyl-3(2H)-pyridazinone (XXI).
- 71) 4-Phthelylidene-1,4-dihydro-6-(p-isopropylphenyl)-3(2H)-pyridazinone (XXII).
- 72) 1',2'-(Dihydro)-6'-(p-isopropylphenyl)spiro-[indan-2,4'-(3'H)-pyridazin]-1,3,3'-trionedihydrazone (XXIII).
- 73) 4-(p-isopropylphenyl)-2-naphthoic acid (XXIVa).
- 74) 4-(p-isopropylphenyl)-6-methoxy-2-naphthoic acid (XXIVb).
- 75) 2-Benzylidene-1-(p-methoxyphenyl)-4-(p-isopropylphenyl)-1,4-butanedione (XXVIa).
- 76) 2-Benzylidene-1-(p-tolyl)-4-(p-isopropylphenyl)-1,4-butanedione (XXVIb).
- 77) 2-Benzylidene-1-(p-chlorotolyl)-4-(p-isopropylphenyl)-1,4-butanedione (XXVIc).
- 78) 2-Benzylidene-1-(p-ethylphenyl)-4-(p-isopropylphenyl)-1,4-butanedione (XXVI d).
- 79) 2-Benzylidene-1-(p-xylonyl)-4-(p-isopropylphenyl)-1,4-butanedione (XXVIe).

- 80) 2-Benzylidene-1-(α -methylnaphthalene)-4-(p-isopropylphenyl)-1,4-butanedione (XXVIf).
- 81) 2-Benzylidene-1-(p-chlorophenyl)-4-(p-isopropylphenyl)-1,4-butanedione (XXVIg).
- 82) p-Methoxy- α -[p-methoxy- β -(p-isopropylphenyl)styryl]-cinnamic acid (XXVIIa).
- 83) α -[p-Methyl- β -(p-isopropylphenyl)styryl]-p-methoxycinnamic acid (XXVIIb).
- 84) α -[p-Ethyl- β -(p-isopropylphenyl)styryl]-p-methoxycinnamic acid (XXVIIc).
- 85) α -[2,4-Dimethyl- β -(p-isopropylphenyl)styryl]-p-methoxycinnamic acid (XXVIId).
- 86) α -[3-Methyl-4-chloro- β -(p-isopropylphenyl)styryl]-p-methoxycinnamic acid (XXVIIe).
- 87) (XXVIII).
- 88) (XXIX).
- 89) 1-Methyl-3-(4-nitro,4'-methoxydiphenyl)methyl-5-(p-isopropylphenyl)pyrrolin-2-one (XXX).
- 90) 1-Ethyl-3-(4-nitro, 4'-ethyldiphenyl)methyl-5-(p-isopropylphenyl)pyrrolin-2-one (XXXI).

STATEMENT AND OBJECTIVES OF THE PROBLEM

The multiple functionality of the arylidene butenolides offers a potential treasure of chemical reactivity. This promoted the author to investigate the behaviour of arylidene furanones towards different reagents.

The objectives of this study are:-

- i) Synthesis of new furanones by condensation of α -p-iso-propylbenzoylpropionic acid with aromatic aldehydes, isatin, phthalimide, phthalic anhydrides.
- ii) Synthesis of new pyrrolones by condensation of β -p-iso-propylbenzoylpropionic acid with ketones in presence of ammonium acetate.
- iii) To study the behaviour of the heterocyclic ring of arylidene furanones towards the action of amines, bases, hydrazines and ammonium acetate.
- iv) To study the behaviour of the heterocyclic ring of the arylidene furanones under Friedel-Crafts conditions in both inert and reactive solvents.
- v) To study the reactivity of the furanone ring in the phthalide system towards the action of hydrazines and alkaline hydrolysis.
- vi) To study the behaviour of pyrrolin-5-ones under the Friedel-Crafts conditions.

SUMMARY OF THE ORIGINAL WORK

Reactions with α -3-Arylidene-5 (p-isopropylphenyl)-spirofuran-3(2H)-2-ones.