MICHAEL REACTION WITH UNSATURATED KETONES

A THESIS

In Partial Fulfilment of requirement

of

MASTER OF SCIENCE DEGREE

By

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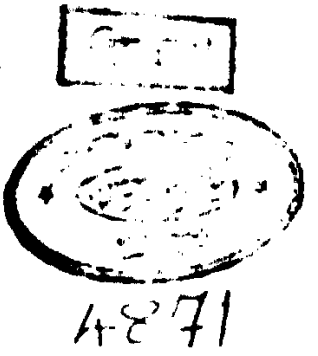

Jan. 1972

MICHAEL REACTION WITH UNSATURATED KETONES

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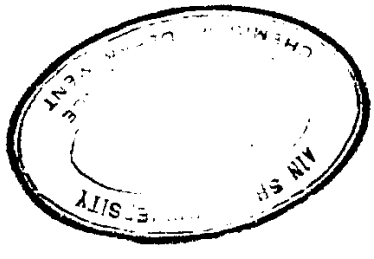

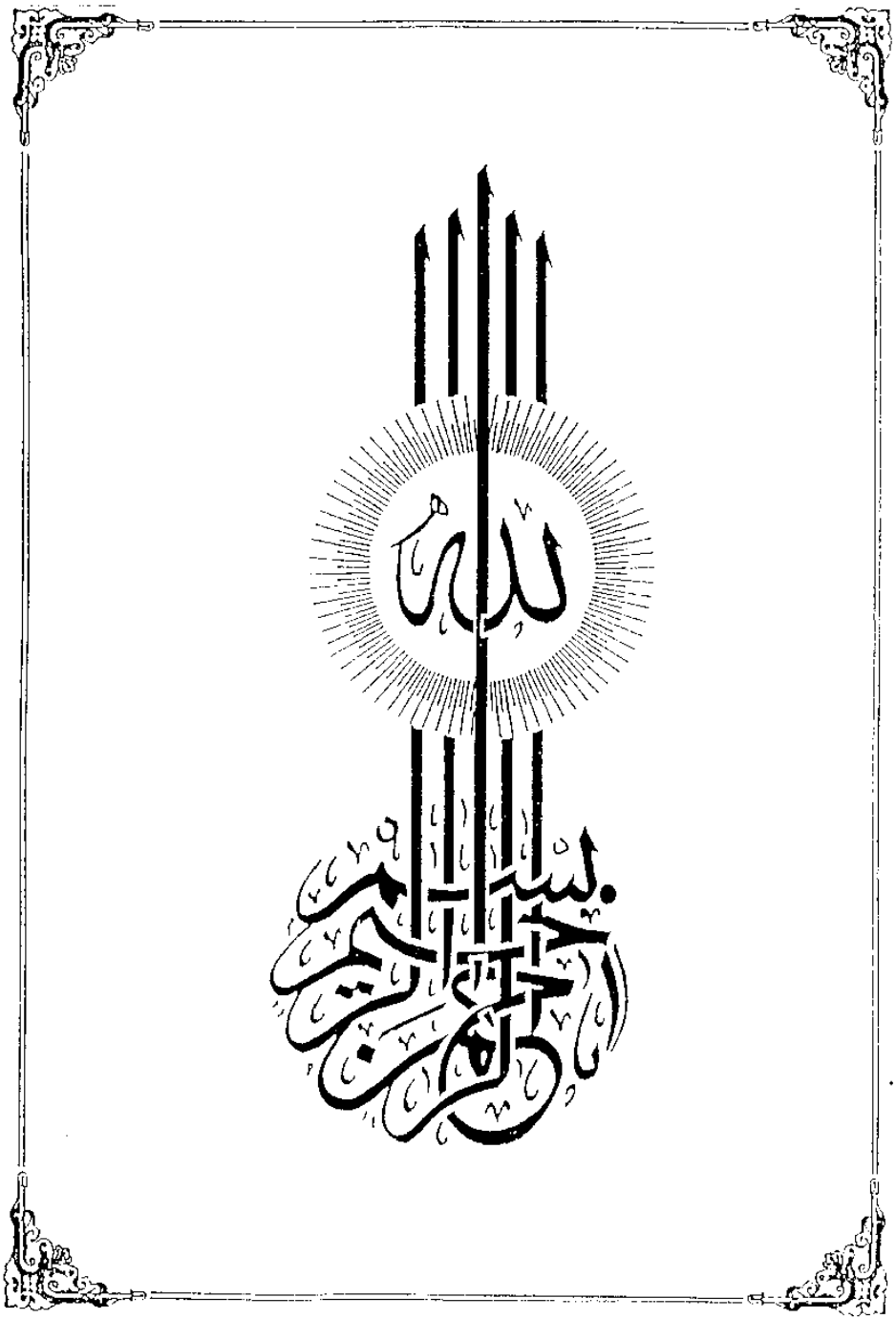

A C K N O W L E D G E M E N T

The author wishes to express his thanks and his sincere gratitude and indebtness to Dr. A. Samour, Assistant Professor; Dr. A. Abd-El Raouf, Assistant Professor and Dr. M. Elkasaby, Lecturer of Organic Chemistry, Chemistry Department, Faculty of Science. Ain Shams University. They were kind enough to suggest the lines of research investigated and to follow the progress of the work with keen interest, guidance, valuable discussion and ciriticism.

N O T E

Beside the work carried out in this thesis, the candidate has attended post graduate course for two years in organic chemistry including the following topics:

1- Reaction Mechanisms.

2- Electronic, Infrared, Raman, and N.M.R. Spectroscopy of organic Molecules.

3- Micro-analysis of organic compounds.

4- Heterocyclic compounds.

5- Reaction of organic compounds.

He has successfully passed an examination in these topics.

Prof. S. Tobia

Head of Chemistry Department

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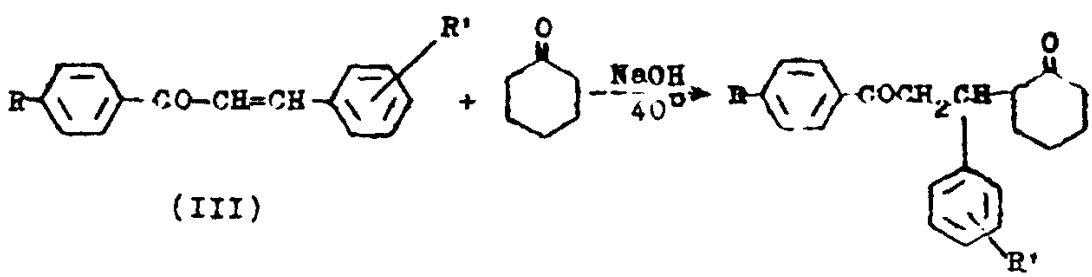
SUMMARY OF THE
ORIGINAL WORK

Summary of Original Work

Michael Reaction of Chalcones with Alicyclic Ketones, Ethyl Benzoylacetate and Dimethyl Succinate

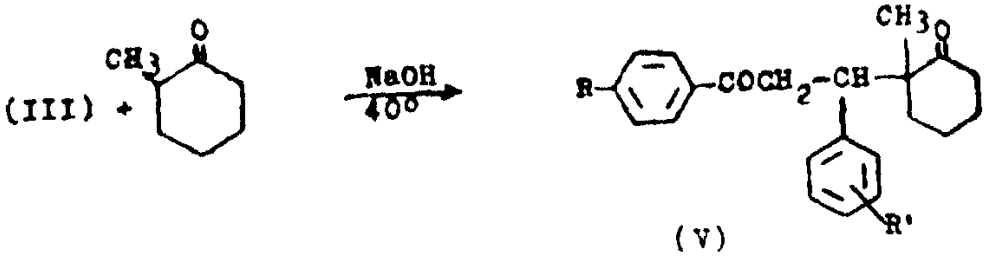
The Michael reactions of chalcones III with various donors namely cyclohexanone, 2-methylcyclohexanone, cyclopentanone, ethyl benzoylacetate and dimethylsuccinate were studied.

Chalcones III with cyclohexanone in presence of sodium hydroxide yield 2(β-aroyl-α-arylethyl) cyclohexanone IV.



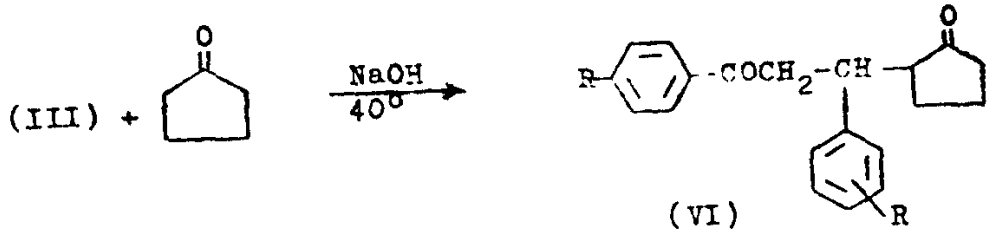
(III) (IV)

With 2-methylcyclohexanone, III yield the corresponding Michael adducts 2(β-aroyl-α-phenylethyl)α-methyl cyclohexanone V.



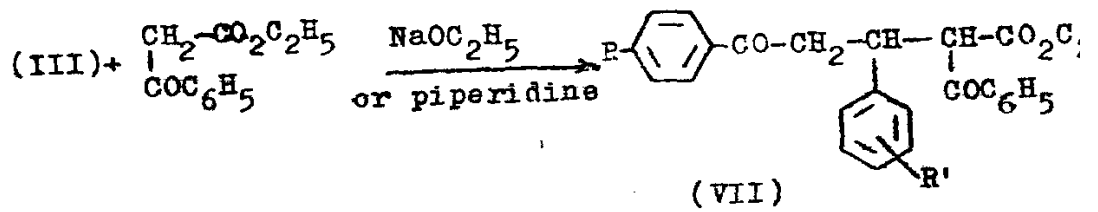
(V)

With cyclopentanone; chalcones III give 2 (β-aroyl-γ-phenylethyl) cyclopentanone VI.



(VI)

A base catalyzed Michael addition of ethyl benzoyl-acetate to chalcones III, yield ethyl (α-benzoyl-β-aryl-γ-aroyl) butyrate VII.



(VII)

Dimethyl succinate with [illegible] chalcones III in presence of piperidine or [illegible] metal alkoxide lead to the formation of VIII.

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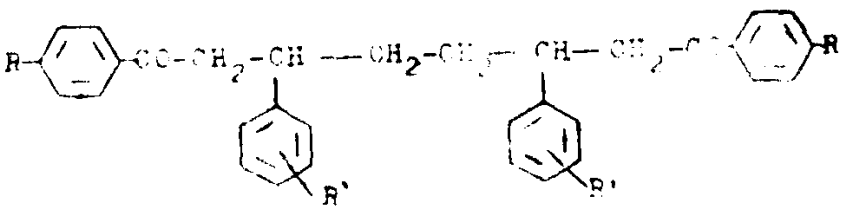

(VIII)

The reactivity of Michael adducts were studied towards a variety of reagents.

(A) With hydroxylamine hydrochloride.

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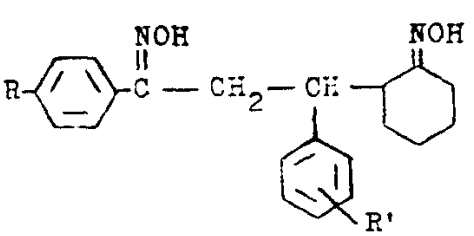
IV react with hydroxylamine hydrochloride in presence of sodium acetate to form the corresponding dioxime IX. Similarly Vb with hydroxylamine hydrochloride yields the dioxime X.



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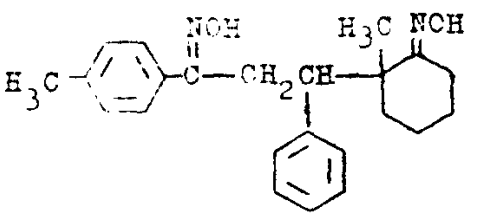

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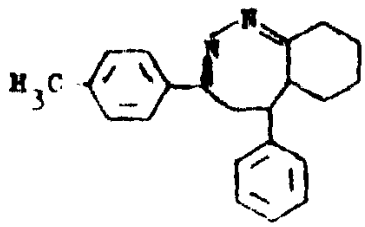
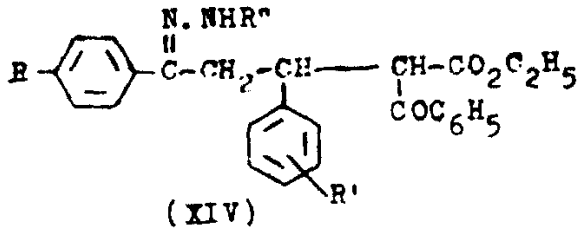


(XIII)

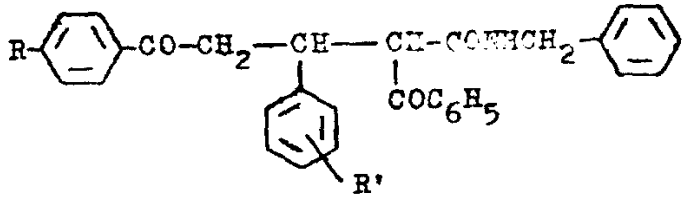
The reaction of VII with hydrazinehydrate and phenylhydrazine lead to the formation of XIV.



(XIV)

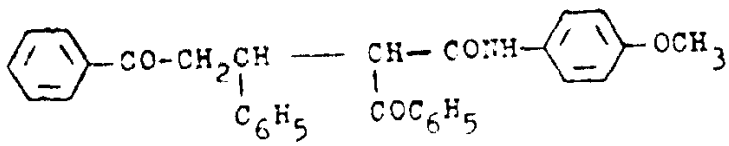
(C) Action of amines on Michael adducts.

N-Benzyl-α-aroyl-γ-benzoyl-β-arylbutyramide XV were obtained by reaction of VII with benzylamine.



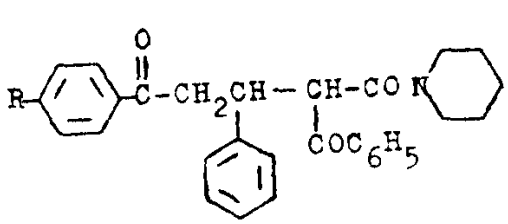
(XV)

Similarly ethyl α,β-dibenzoyl-β-phenylbutyrate VIIg reacts with p-anisidine to give the corresponding butyramide derivative XVI.



(XVI)

Compounds VII with secondary amines namely piperidine and morpholine leading to formation of XVII and XVIII respectively.



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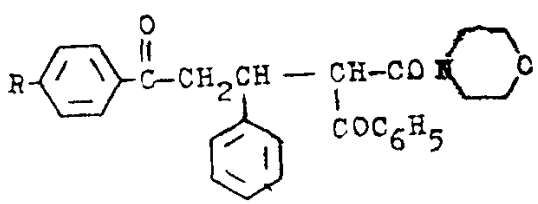
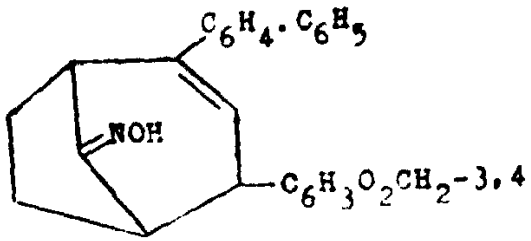


(XVIII)

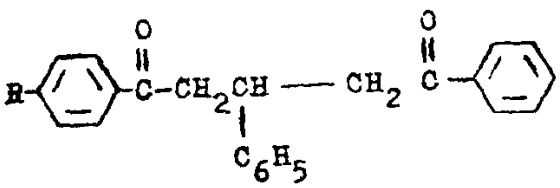
Similarly the oxime derivative XXIV was obtained by reaction of XXIIIa with hydroxylamine hydrochloride.



(XXIV)

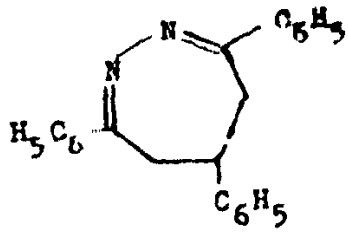
(2) Decarbethoxylation:

The diketone XXV is the product of action of AcOH/HCl acids mixture on VII and also obtained indepently by addition of acetophenone to III d,g and/or j respectivel



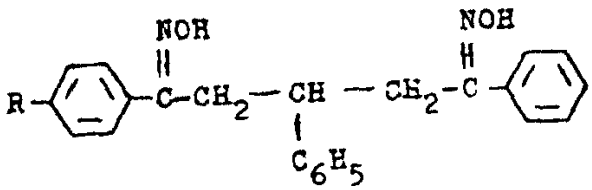
(XXV)

The 1,5-diketone XXVc reacts with hydrazinehydrate yielding the diazepine XXVI.



(XXVI)

Compounds XXV condense with hydroxylamine hydrochloride to give the dioxime derivatives XXVII.



(XXVII)