

SOME REACTIONS WITH BENZOYLACRYLIC ACID DERIVATIVES

A THESIS

In Partial Fulfilment of the Requirements
of

MASTER OF SCIENCE DEGREE

By

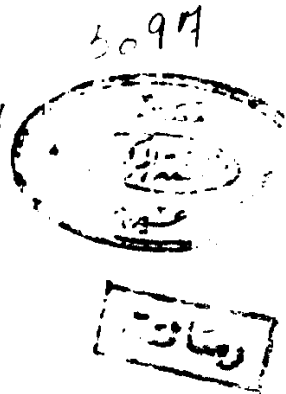
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N O T E

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, N.M.R., and Mass Spectroscopy of Organic Molecules.
- 3) Microanalysis of Organic Compounds.
- 4) Organic Reactions.
- 5) Heterocyclic Compounds.

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STATEMENT AND OBJECTIVES OF THE PROBLEM

CHAPTER I

STATEMENT AND OBJECTIVES OF THE PROBLEM

β -Aroylacrylic acids contain the olefinic double bond conjugated with a keto group and a carboxyl group.



This olefinic double bond is subject to attack by nucleophilic reagents since it is activated by both the keto and carboxyl groups. The object of the present work is to report whether β -aroylacrylic acids behave as α,β -unsaturated acids or as α,β -unsaturated ketones.

In view of this and of the continuing interest in the chemistry of unsaturated carbonyl compounds in our laboratory, the author studied the reactivity of some β -aroylacrylic acids towards some reagents.

The objectives of this study are :

- 1) To investigate the addition of amines to β -aroylacrylic acids.
- 2) To examine the behaviour of the acids towards hydrazines.
- 3) To study the cyclization behaviour of the acids when treated with thioureas. Such a reaction will

lead to the formation of aminothiazoles.

- 4) To investigate the Friedel-Crafts alkylation of aromatic hydrocarbons with β -aroylacrylic acids.
- 5) To study the addition of thiophenol to β -aroylacrylic acids.

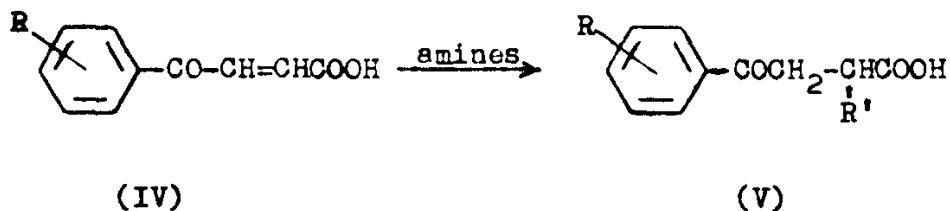
SUMMARY OF THE ORIGINAL WORK

CHAPTER II

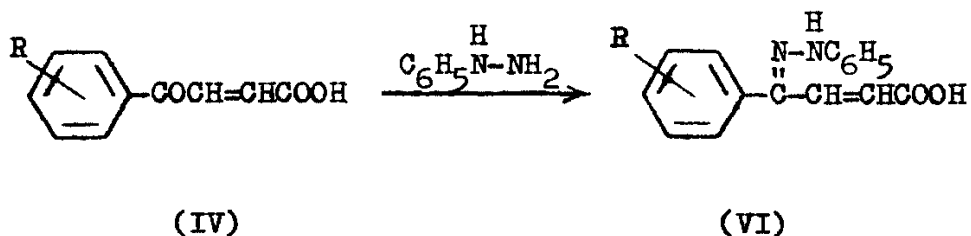
SUMMARY OF THE ORIGINAL WORK

ADDITION REACTIONS WITH β -AROYLACRYLIC ACIDS

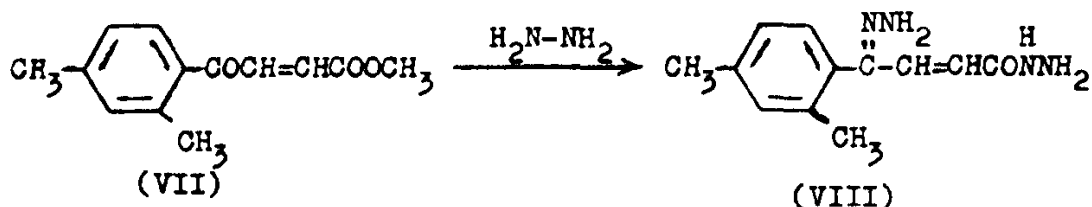
Treatment of the benzene solution of β -aroylacrylic acids (IVa-c) with amines, namely, benzylamine, piperidine, morpholine, yielded the α -alkyl amino β -aroylpropionic acids (Va-1).



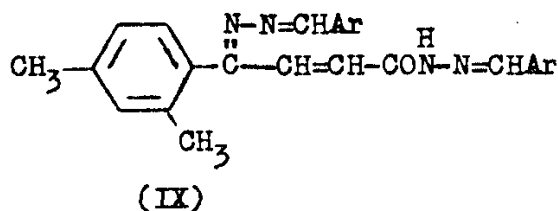
Condensation of β -2,4-dimethylbenzoyl, β -2,5-dimethylbenzoyl and β -4-isopropylbenzoyl acrylic acids (IVa-c) with phenyl hydrazine in acetic acid gave the corresponding phenyl hydrazones (VIa-c).



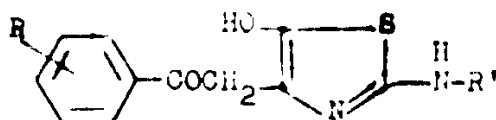
Methyl β -2,4-dimethyl benzoyl acrylic ester (VII) reacts with hydrazine hydrate to give hydrazone hydrazone derivative (VIII).



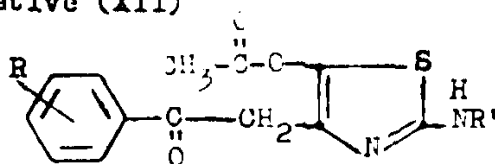
The structure of VIII was confirmed via the condensation with aromatic aldehydes to give the dihydrazones (IX)



Thiourea, benzyl thiourea and phenyl thiourea add to β -2,4-dimethyl benzoyl-, β -2,5-dimethyl benzoyl and β -4-isopropyl benzoyl acrylic acids (IVa-c) to give the corresponding 2-amino-4-hydroxy-5-aryl methyl thiazole (XIa-i).

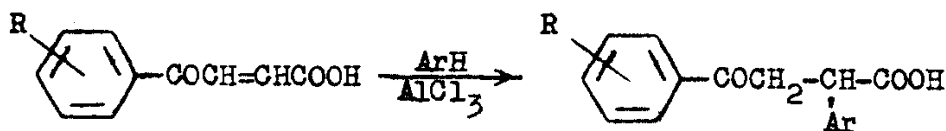


Reaction of (XI_a and g) with acetic anhydride gives α -acetyl derivative (XII)



(XII)

Acid-catalyzed 1,2-dipolar addition of aromatic hydrocarbons to β -2,4-dimethyl benzoyl, β -2,5-dimethyl benzoyl and β -4-iso-propyl benzoyl acrylic acids (IV_{a-c}) give α -aryl- β -aroyl propionic acids (XIV_{a-e}).

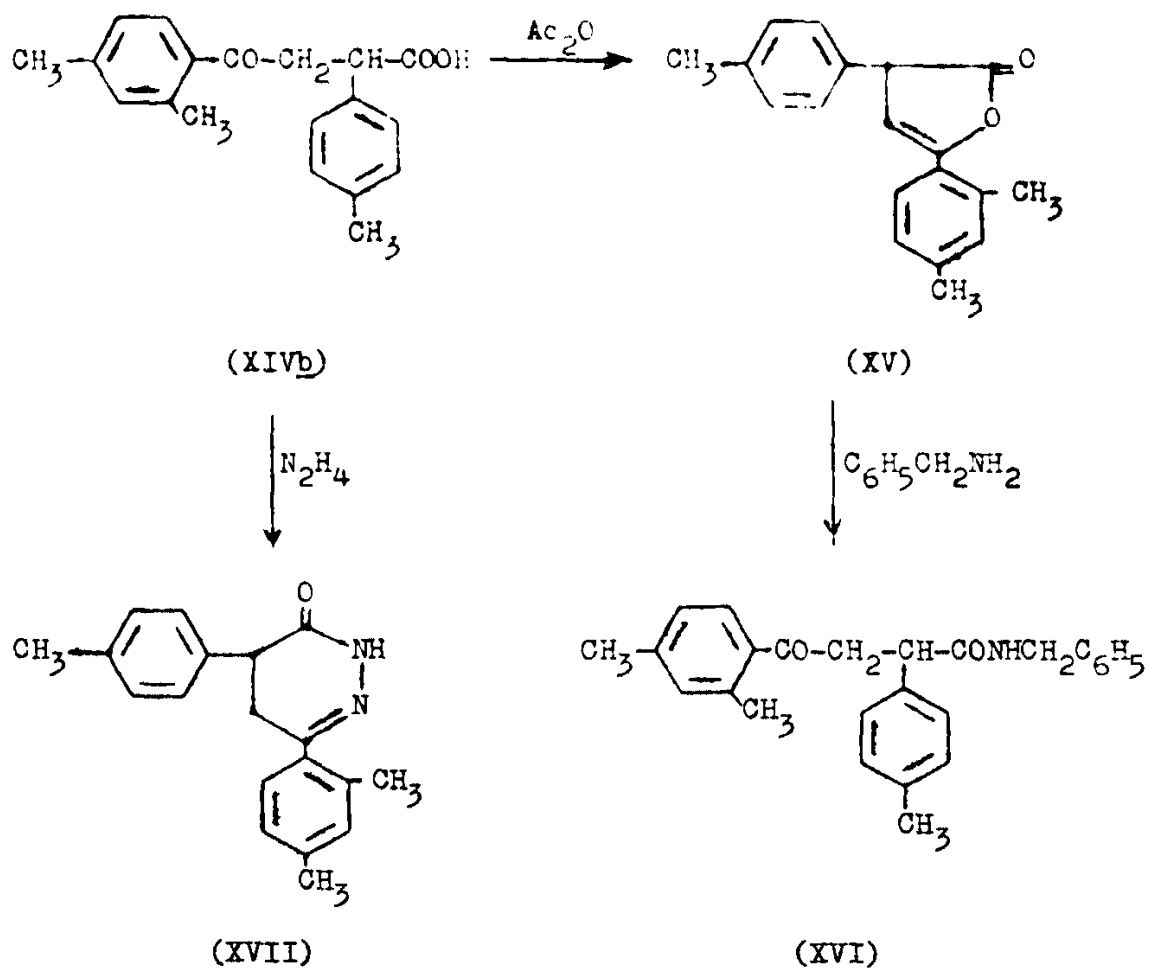


(IV)

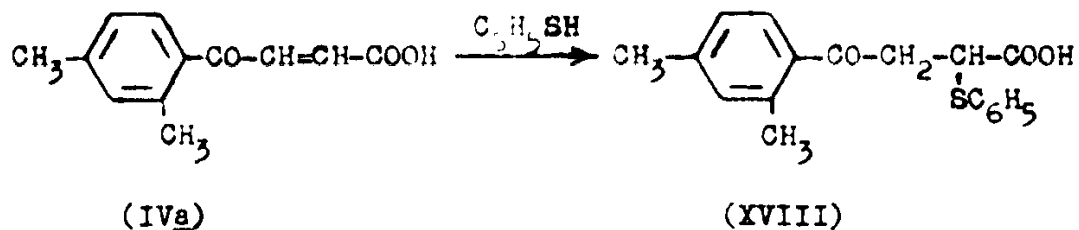
(XIV)

Dehydration of XIV_b with acetic anhydride yields the butenolide XV. Reaction of XV with benzylamine gives the amide XVI. Reaction of XIV_b with hydrazine hydrate gives

the corresponding pyridazinone (XVII).



Reaction of the acid IVa with thiophenol gives the addition product XVIII.



The above data show that β -aroyl-acrylic acids (IVa-c) behave towards the addition of amines, thioureas and aromatic hydrocarbon as α,β -unsaturated ketones and not as α,β -unsaturated acids and this appears due to the fact that the polarization of double bond by keto groups strongly outweighs that caused by the carboxyl group.