ADDITION REACTIONS WITH SOME UNSATURATED KETONES

A THESIS

Submitted for the Degree of Doctor of Philosophy

(Ph. D.)

By

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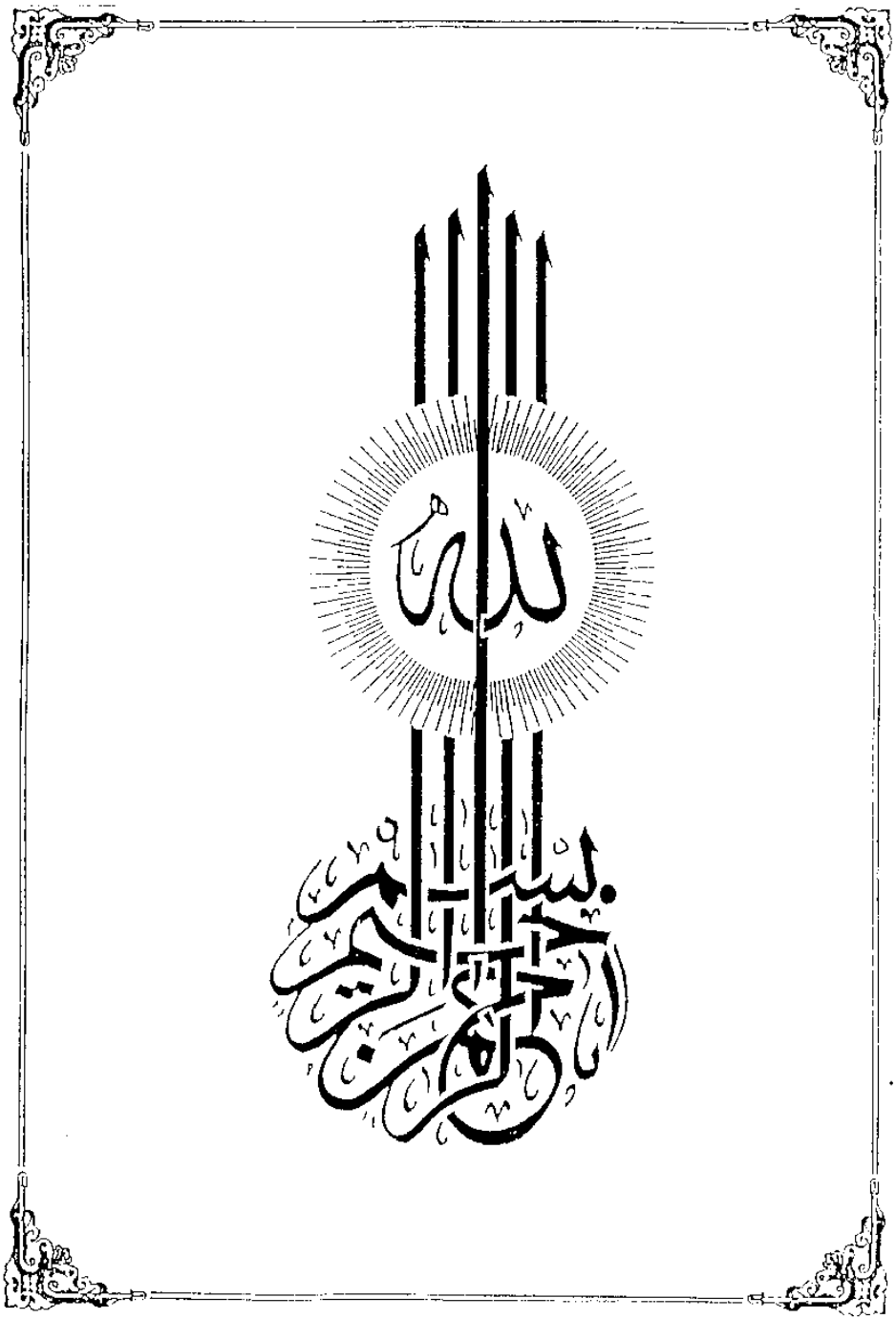

A C K N O W L E D G E M E N T

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C O N T E N T S

STATEMENT AND OBJECTIVES OF THE PROBLEM

Diaroyl ethylenes contain the olefinic double bond conjugated with two keto groups.

This olefinic double bond is subjected to attack by nucleophilic reagents since it is activated by the two carbonyl groups.

In view of this and of the continuing in the chemistry of unsaturated carbonyl compounds in our laboratory the author studied the reactivity of diaroyl ethylenes towards some reagents. The objectives of this study are:

(1) To study the reactivity of diaroyl ethylenes towards some of the active methylene substrates under Michael condition e.g. diethyl malonate, benzyl phenyl ketone, ethyl benzoyl-acetate, ethyl phenylacetate, ethyl acetoacetate and ω-cyanoacetophenone.

(2) To study the action of Grignard reagents, addition of bromine and addition of amines to diaroyl ethylenes.

(3) To study the effect of hydrazine hydrate, phenylhydrazine, hydroxylamine, amines and thiourea on the prepared Michael adducts.

(4) To study the effect of hydrazine hydrate, phenylhydrazine and hydroxylamine on Grignard addition products, dibromides and amine addition products.

SUMMARY OF THE ORIGINAL WORK

Addition Reactions With Some Unsaturated Ketones

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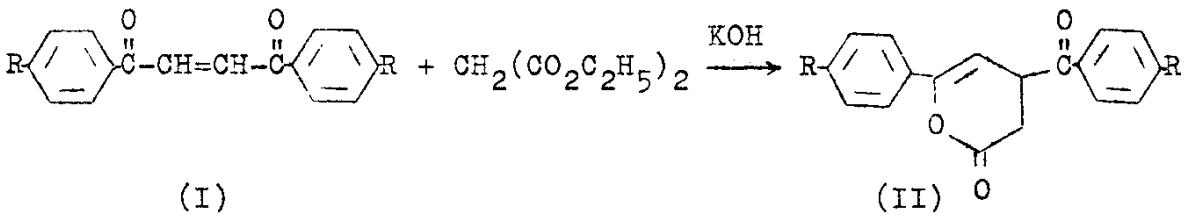
ADDITION REACTIONS WITH SOME UNSATURATED KETONES

CHAPTER I

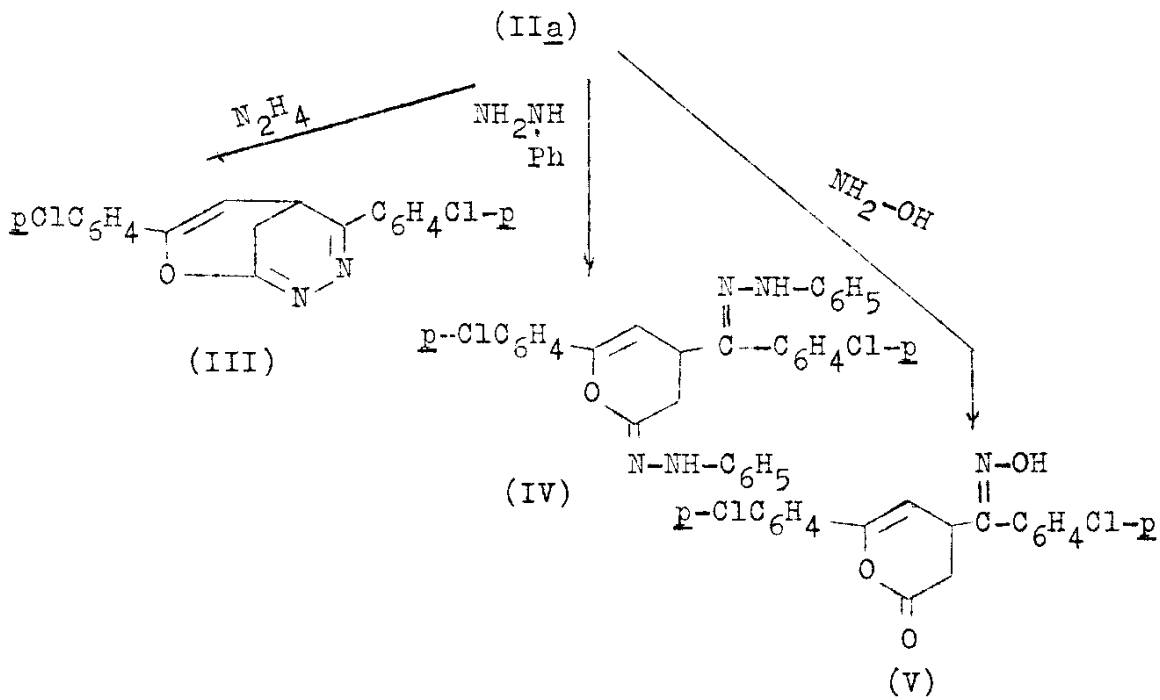
The Michael reaction of diaroyl ethylenes (I) with diethyl malonate yielded the Michael adducts (II).



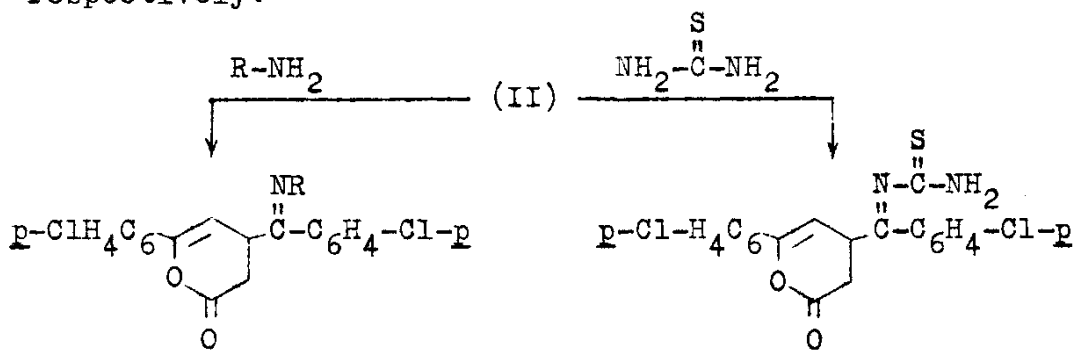
(I) (II)

a, R = Cl b, R = H

Condensation of (IIa) with hydrazine hydrate, phenylhydrazine and hydroxylamine gave (III), (IV) and (V) respectively.

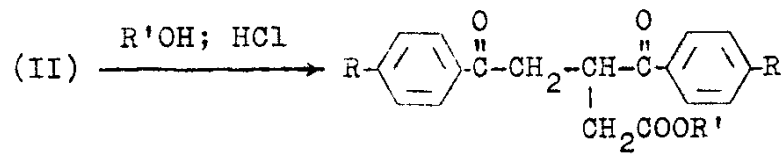


The Michael adduct (II) condensed with primary aliphatic and aromatic amines and thiourea and yielded (VI) and (VII) respectively.



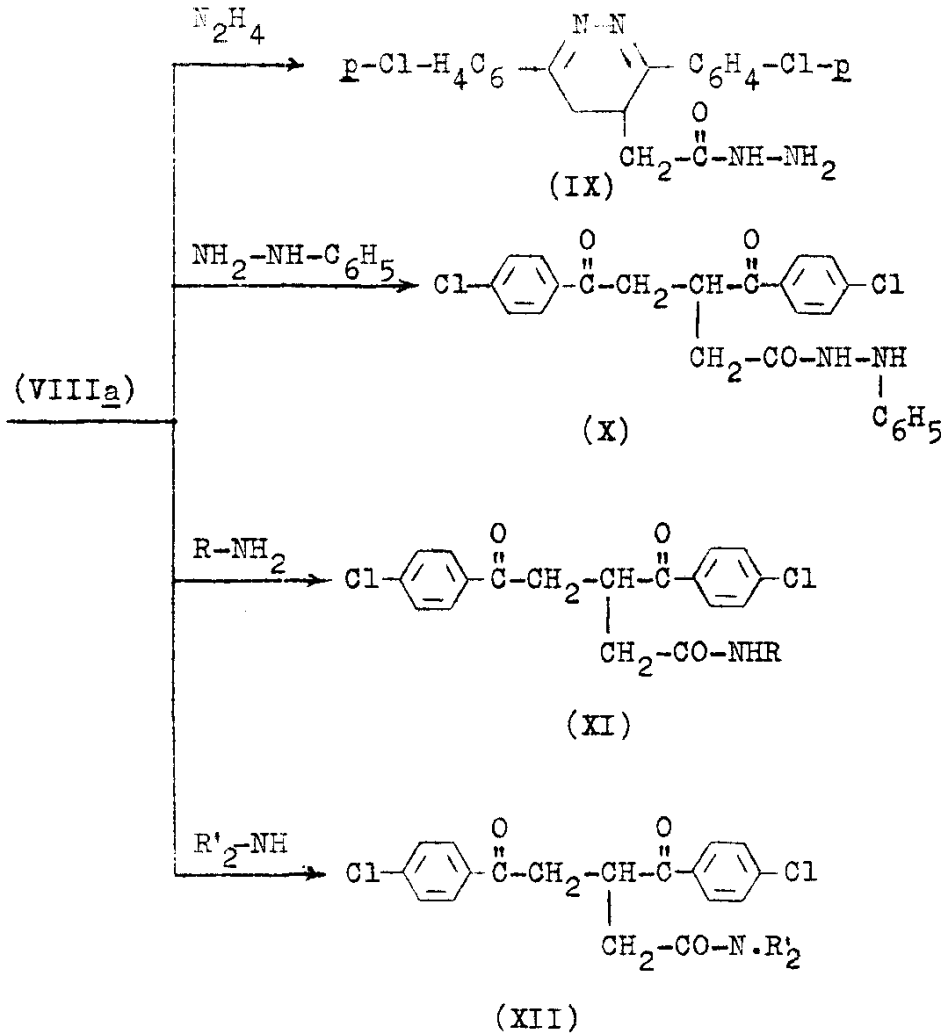
(VI) (VII)

(II) reacted with alcohols in presence of hydrogen chloride gas and gave the butyrate derivatives (VIII).

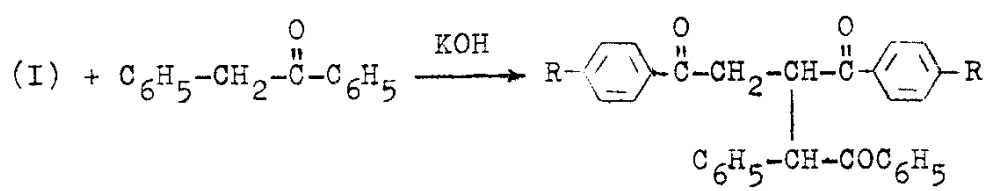


(VIII)

(VIIIa) reacted with hydrazine hydrate, phenylhydrazine, primary aliphatic, aromatic amines and secondary amines and gave the corresponding products (IX), (X), (XI) and (XII) respectively.

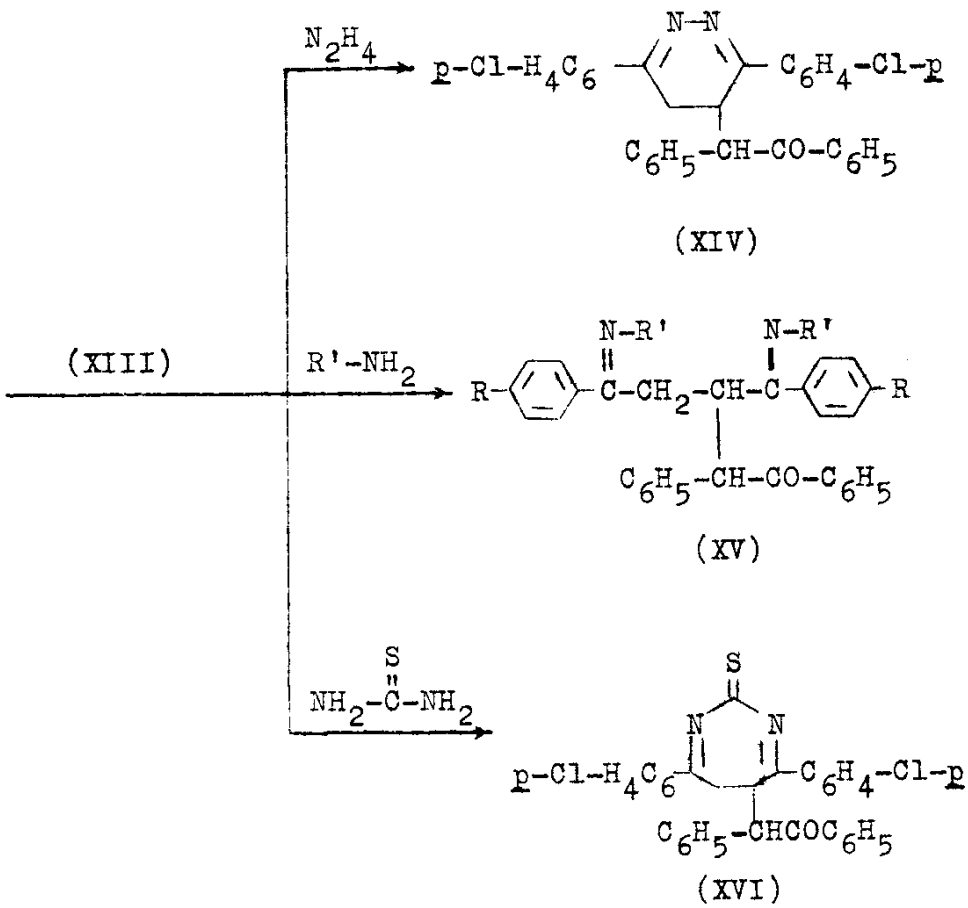


Benzyl phenyl ketone reacted with (I) under Michael conditions and gave the pentan-1,5-dione derivatives (XIII).



(XIII)

Condensation of (XIII) with hydrazine hydrate, primary aromatic amines and thiourea and gave the products (XIV), (XV) and (XVI) respectively.

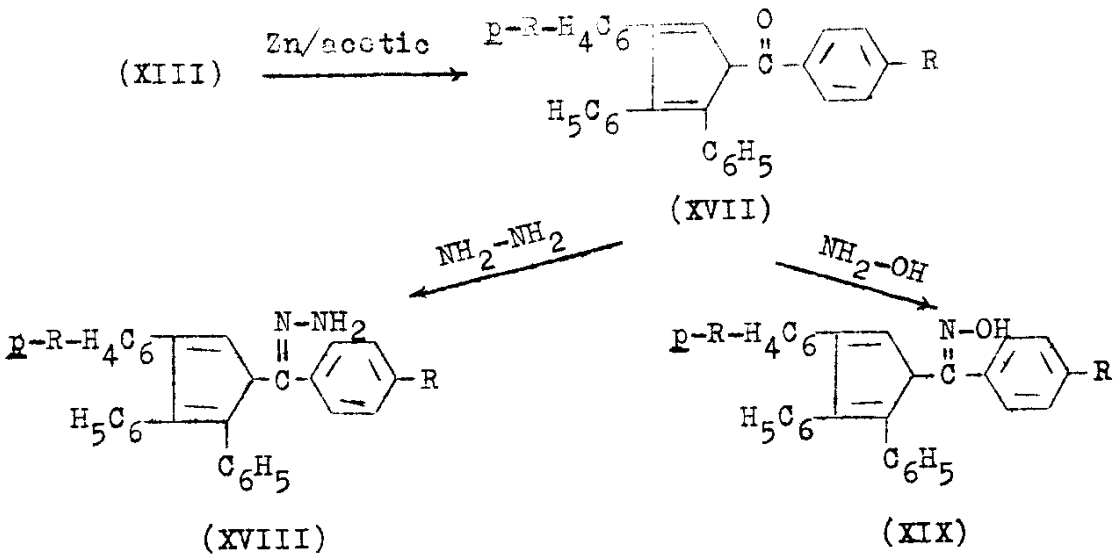


(XIV)

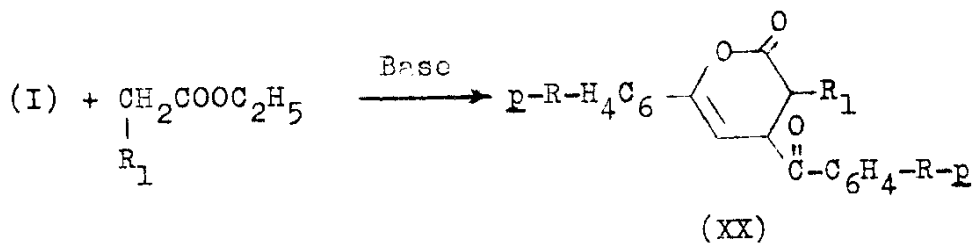
(XV)

(XVI)

The Michael adducts (XIII) were reduced with zinc/acetic acid yielded the pentadiene derivatives (XVII) which condensed with hydrazine hydrate and hydroxylamine and gave (XVIII) and (XIX) respectively.

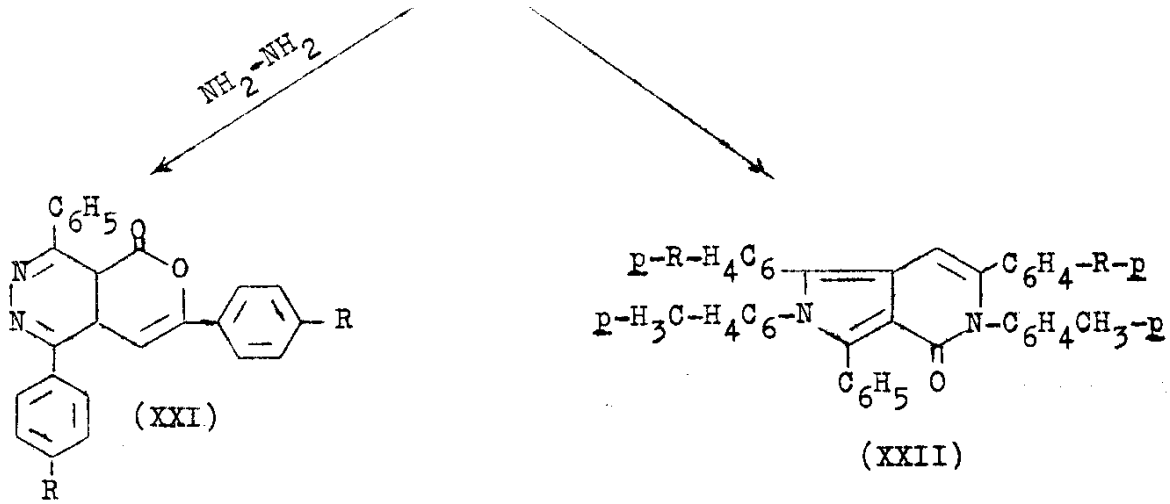


Ethyl benzoylacetate, ethyl phenylacetate and ethyl acetoacetate reacted with (I) under Michael conditions and gave the pyran-2-one derivatives (XX).



The product (XX) condensed with hydrazine hydrate and p-toluidine and gave the pyridazine and pyridone derivatives (XXI) and (XXII) respectively.

(XX)



The Michael reaction of diaroyl ethylenes (I) and chalcones (I') with ω-cyanoacetophenone yielded the corresponding cyanopyridine derivatives (XXIII) which was hydrolysed by alcoholic potash (10 %), reacted with sulphuric acid (95 %) and was reduced with zinc/acetic, hydrochloric acids to give the corresponding nicotinamides (XXIV), pyridine derivatives (XXV) and the amino-pyridine derivatives (XXVI) respectively.