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شبكة المعلومات الجامعية



شبكة المعلومات الجامعية

التوثيق الالكتروني والميكرو فيلم

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التوثيق الالكتروني والميكروفيلم

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بالرسالة صفحات
لم ترد بالأصل

Studies on Enamines

A Thesis in Chemistry

Submitted for M.Sc. Degree

By

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(B.Sc.) 1999

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Approval sheet for submission

Title of M.Sc. Thesis

Studies on Enamines

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This thesis has been approved for submission by the supervisors.

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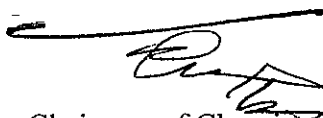
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Abstract

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Title of thesis: Studies on Enamines

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Abstract

This work has been carried out to investigate the reactivity of arylhydrazone ketones and arylhydrazonals toward electrophilic reagents as well as their potential utility as precursors of pyridazines and 1,2,3-triazoles. Quite a number of new heterocyclic compounds could be synthesized and their structure was established via inspection of spectroscopic and analytical data.

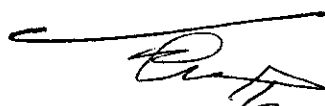
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Finally my deepest thanks to my family specially my dear husband and my son.

List of abbreviations

MS	Mass Spectroscopy
IR	Infrared Spectroscopy
NMR	Nuclear Magnetic Resonance Spectroscopy
MW	Microwave
DMF	Dimethylformamide
DMFDMA	Dimethylformamide dimethylacetal
Ac	Acetyl group
Et.	Ethyl group
Ph	phenyl group
SAMP	(s)-1-Amino-2-methoxymethyl pyrrolidine
TDSOTf	Dimethylhexylsilyl triflate
THF	Tetrahydro furan
TBAF	Tetrabutylammonium fluoride

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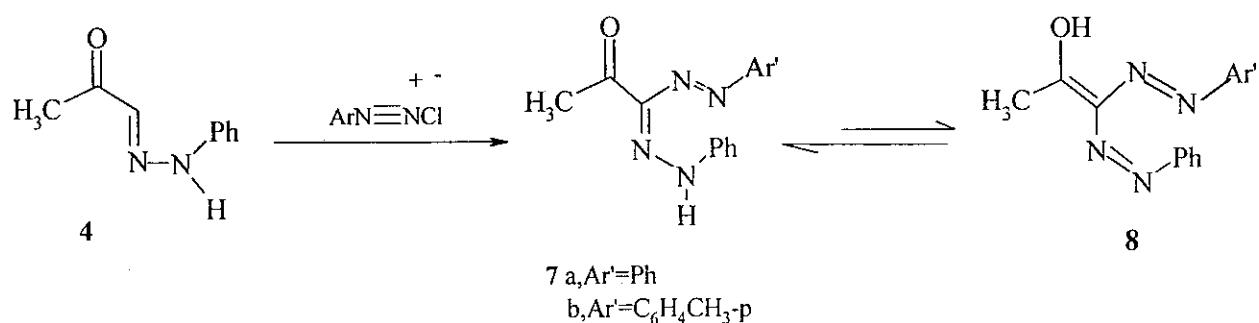
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Summary of the original work

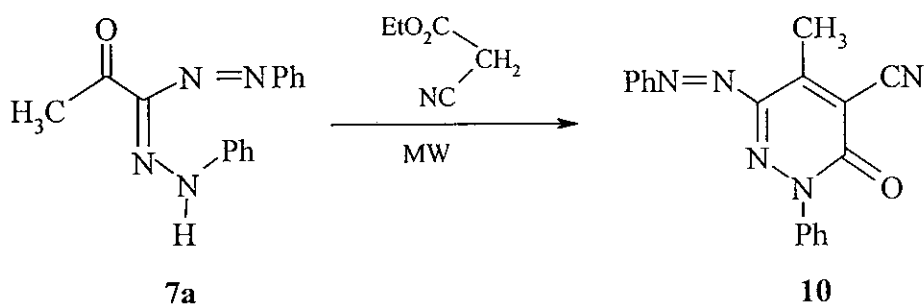
Part I: Arylhydrazonoketones and Arylhydrazonals as precursors to polyfunctionally substituted pyridazines and 1,2,3-triazoles.

This work has been done to make use of the nucleophilicity of hydrazone CH in developing new approach to pyridazines. Moreover utility of arylhydrazononitriles as precursors to 1,2,3-triazoles is further explored.

Thus when the phenylhydrazonoketone **4** was reacted with aromaticdiazonium chlorides, it afforded the formazanes **7a, b**. These may exist in theory in the enol form **8** but according to analytical data, it was concluded that the compounds exist only in the azo-hydrazone form **7**.

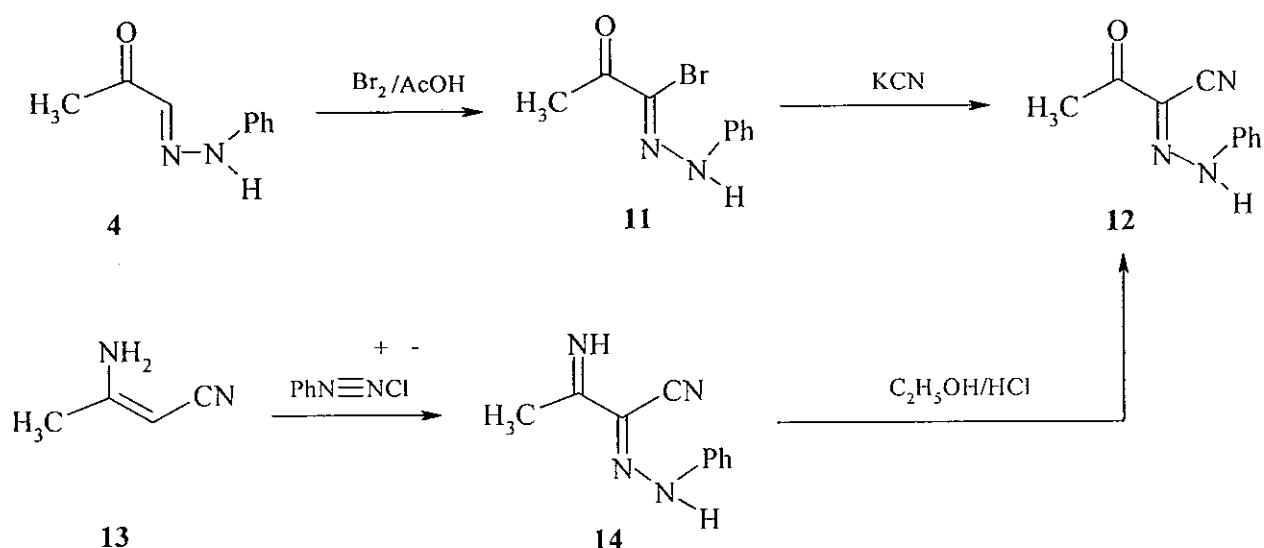


When **7a** was reacted with ethyl cyanoacetate in micro-wave oven, it afforded readily the pyridazinone **10**.



Also compound **4** reacted with bromine to give the hydrazonyl halide **11** which further reacted with potassium cyanide to give **12**.

Better yield of **12** could be obtained via coupling **13** with benzenediazonium chloride, then refluxing the formed iminohydrazone **14** in ethanolic HCl for 15 minutes.



^{13}C NMR and ^1H NMR for compound **12** support our belief that the hydrazone nitrogen lone pair is delocalized extensively at the hydrazone carbon.

^1H NMR revealed a methyl signal at δ 2.53 ppm. Hydrazone signal appeared at δ 9.66 ppm, the aromatic protons appeared at δ 7.22-7.47 ppm.

^{13}C NMR showed a carbonyl carbon at δ 193.5 ppm supporting our belief that compound **12** exists totally as hydrazone. The methyl signal appeared at δ 25.4 ppm.

The ^1H NMR spectrum for the precursor of compound **12** which is the hydrazone imine **14** supports all previous assumptions that this compound exists as hydrazone –imine and not as azo-enamine. Thus in addition to the methyl signal at δ 2.41 ppm, there are two signals; one for the hydrazone NH at δ 12.2 ppm and imine NH at δ 7.16 ppm.

Although compound **12** could be prepared from the hydrazidic halide **11** by the action of cyanide ion; the coupling procedure was preferred.

Compound **15** was synthesized via coupling **13** with p-chlorobenzenediazonium chloride and subsequent hydrolysis of the formed imine **16** by action of acetic acid-hydrochloric acid mixture utilizing procedure described earlier by Elnagdi et al on 2005. This reacted smoothly with hydroxylamine hydrochloride to yield the amidoxime **17**; possible formation of **18** was excluded based on