بسم اللّه الرحمن الرحيم

شبكة المعلومات الجامعية

سامية محمد مصطفى

شبكة المعلومات الجامعية

التوثيق الالكتروني والميكروفيلم

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جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
علي هذه الأقراص المدمجة قد أعدت دون أية تغيرات

يجب أن

تحفظ هذه الأقراص المدمجة بعيدا عن الغبار

بِسْمِ اللهِ الرَّحمٰنِ الرَّحِيمِ

وَمَآ أُوتِيتُم مِنَ العِلمِ إلاَ قَلِيلاً

صدق الله العظيم

CHEMICAL REACTIVITY OF SOME VINYLIC KETONES TOWARDS DIFFERENT NUCLEOPHILES

A Thesis
Submitted to the Faculty of Science
Alexandria University
In Partial Fulfillment for the Degree of
Master of Science

By

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1998

TO MY HUSBAND
MOHAMED
AND MY SON
AHMED

NOTE

Beside the work carried out in this thesis ,the candidate ***Aziza Abd El-Fattah Mohamed*** has succeeded in the following post graduate courses in partial fulfillment of the ***M.Sc***. degree.

1. Electrochemistry .
2. Effect of solvents on reaction rates and mechanisms.
3. Electronic , molecular ,and nuclear magnetic resonance spectrometry.
4. Basic principles of physical organic chemistry .
5. Investigation of reaction meachanisms and the chemistry of reactive intermediates .
6. Advanced course in the chemistry of carbohydrates.
7. Mechanisms of elimination and nucleophilic aromatic substitution reactions .
8. Advanced course in the chemistry of steroids and polyterpenoids.
9. New advances in the chemistry of amino acids and proteins .
10. Elementary course in BASIC computer language.
11. Elementary German language course.

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CONTENTS

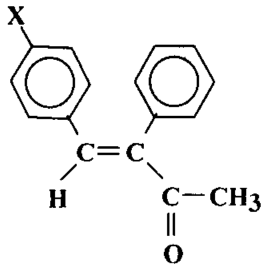
SUMMARY

This thesis includes three chapters and ends with a list of references.

The first chapter covers the most up-to-date literature of the reactions of some α,β-unsaturated ketones with different nucleophiles.

The second chapter is divided into two parts:

The first part describes the method of preparation of (E)-4-(*p*-substitutedphenyl)-3-phenyl-3-buten-2-ones $\underline{1}_{a-d}$.



(E)

$\underline{1}_{a-d}$

a, X = H; b, X = OCH_3; c, X = Cl; d, X = NO_2

This part describes the reaction of $\underline{1}_{a-d}$ with hydrazine hydrate, aroylhydrazine and phenylhydrazine in absolute ethanol in the presence of catalytic amount of acetic acid. It also includes the method of cyclization of some open-chain aroylhydrazones $\underline{3}_{c,g,k,o}$.

The second part includes the kinetic data and the kinetic procedure used for determining the rate constants for the reaction of $\underline{1}_{a-c}$ with phenylhydrazine in acetonitrile at four different temperatures as well as the kinetics of the reaction of $\underline{1}_{c}$ with phenylhydrazine in acetonitrile-ethanol mixture in different ratios at four different temperatures.

The third chapter deals with the discussion and interpretation of the results obtained from the above mentioned reactions. It provides the reaction of

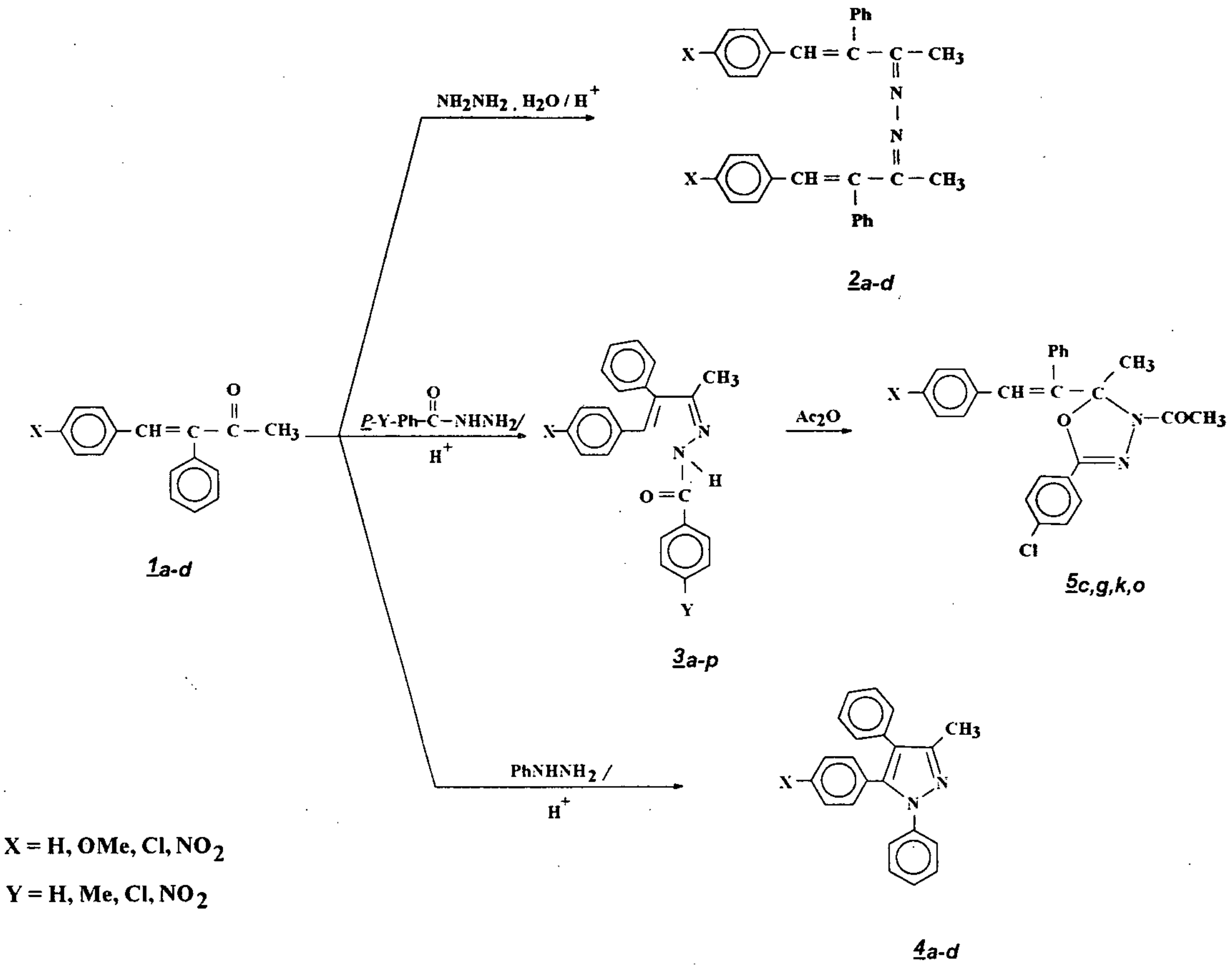
(E)-4-(p-substitutedphenyl)-3-phenyl-3-buten-2-ones $\underline{1}_{a-d}$ with hydrazine hydrate (1:1 molar ratio) in absolute ethanol in the presence of catalytic amount of acetic acid at room temperature which gave the corresponding 4-aryl-3-phenyl but-3-en-2-one azine $\underline{2}_{a-d}$ as a final product. While the refluxing of $\underline{1}_{a-d}$ with aroylhydrazine (1:2 molar ratio) in absolute ethanol and few drops of acetic acid led to the formation of the corresponding 4-(p-substitutedphenyl)-3-phenyl but-3-en-2-one-p-substitutedbenzoylhydrazone $\underline{3}_{a-p}$. Furthermore, refluxing of some of these aroylhydrazone $\underline{3}_{c,g,k,o}$ with acetic anhydride for $1^{1}/_{2}$ hour afforded the corresponding cyclic 3-acetyl-5-(p-chlorophenyl)-2-methyl-2-[$1^{\prime}$-phenyl-$2^{\prime}$-(p-substitutedphenyl) ethen-$1^{\prime}$-yl]-1,3,4-oxadiazoline $\underline{5}_{c,g,k,o}$.

However, the reaction of $\underline{1}_{a-d}$ with phenylhydrazine (1:1 molar ratio) in absolute ethanol in the presence of acetic acid at room temperature afforded the corresponding 1,4-diphenyl-3-methyl-5-(p-substitutedphenyl) pyrazole $\underline{4}_{a-d}$ as shown in Scheme (I). Assignment of the chemical structure of all products $\underline{2}_{a-d}$, $\underline{3}_{a-p}$, $\underline{4}_{a-d}$ and $\underline{5}_{c,g,k,o}$ was achieved using IR, UV, ^{1}H-NMR and mass spectra as well as elemental analysis.

The kinetic measurements of the reaction of $\underline{1}_{a-c}$ with phenylhydrazine in acetonitrile in the presence of catalytic amount of acetic acid as well as the measurements of the reaction of $\underline{1}_{c}$ with phenylhydrazine in acetonitrile-ethanol mixture with different ratios have been studied. The rate constants were measured at four different temperatures and the activation parameters were calculated by Microsoft Excel with correlation factor (r) of 0.99 in all cases.

The main governing factor is the activation enthalpy $\Delta H^{\#}$ (enthalpic control) which can be explained as arising from consecutive process, where the nucleophilic addition step on the carbonyl group affording the hydrazone is not alone.

The kinetic data reveal that the rate increases with the increase in acetonitrile content until a maximum was obtained in pure acetonitrile which attributed to the formation of more effective transition state solvation.



X = H, OMe, Cl, NO_2

Y = H, Me, Cl, NO_2

Scheme (I)