STUDIES ON SOME PYRONE DERIVATIVES

A Thesis
Submitted in Partial Fulfilment of the Requirments of
M.Sc. Degree in Chemistry

Presented By
Hesham Mahmoud Abd-Allah Hassan Rashed
B.Sc. (Good)

Department Of Chemistry
Faculty Of Science
Ain Shams University
Cairo, Egypt
1995

STUDIES ON SOME PYRONE DERIVATIVES

THESIS ADVISORS	THESIS APROVED
Prof. Dr. A. A. Afify	A. A. Afify
Prof. Dr. F. A. El-Bassiouny	F. A. El-Bassiouny
Dr. M. R. Mahmoud	Mahmoud M. R.

Head of Chemistry Department

Prof. Dr. A. F. M. Fahmy

A. F. M. Fahmy

بسم الله الرحمن الرحيم

AIN SHAMS UNIVERSITY
FACULTY OF SCIENCE
CHEMISTRY DEPARTMENT

POST GRADUATE STUDIES FOR M.Sc STUDENT IN ORGANIC CHEMISTRY (91-92)

This is to certify that *Hesham Mahmoud Abd-Allah Hassan Rashed* has attended passed successfully the following post graduate courses as partial fulfillment of the requirement for the degree of Master Science.

1-Advanced studies in physical organic chemistry
  i) Polar reaction mechanism.
  ii) Pericyclic reaction.

2-Advanced studies in heterocyclic chemistry.

3-Advanced studies in applied spectroscopic analysis.
  Electronic spectra, Infrared, ^{1}H-NMR, C^{13}-NMR, and Mass spectroscopy of organic chemistry.

4-Advanced studies in natural product

5-Advanced studies in microanalysis
6-Advanced studies in polymer chemistry.

7-Advanced studies in aromaticity.

8-Advanced studies in organic reagent.

9-Advanced studies in organometallic.

10-Advanced studies in photochemistry.

11-Advanced studies in free radical reaction mechanism.

12-Selected topics in organic reactions.

13-Courses English Language.

Prof. Dr. A. F. M. Fahmy
Head of Chemistry Department
Faculty Of Science
Ain Shams University

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ACKNOWLEDGMENT

I would like to express my sincere gratitude and indebted to ***Prof. Dr. Amin Abd-El-Maksoud Afify,*** *Professor of organic chemistry, faculty of Science, Ain Shams University,* ***Prof. Dr. Fakhry Abd-El-Aziz El-Bassiouny,*** *Professor of organic chemistry, faculty of Science, Ain Shams University and* ***Dr.Mahmoud Refai Mahmoud,*** *Associated Professor of organic chemistry, faculty of Science, Ain Shams University. They were always kind enough to suggest the lines of research and to follow the progress of the work with keen interest, guidence and valuable criticism.*

I am deeply indebted to ***Prof. Dr. Mohamed youssef El-Kady,*** *Professor of organic chemistry, faculty of Science, Ain Shams University, for his encouragement, continuous advices and for his valuable help.*

بسم الله الرحمن الرحيم

وَقُل رَّبِّ زِدْنِي عِلْماً

(سورة طه آية ١١٤)

SUMMARY

summary

3-Carboethoxy-6-nitrocoumarin 1 was synthesised with the aim of study the effect of nitro group in 6-position on the reactivity of α,β-unsaturated-δ-lactone and ester groups towards nitrogen and carbon nucleophiles.

Compound 1 was treated with cyclohexylamine in refluxing ethanol to give 4-(N-cyclohexylamino)-6-nitro-3-(N-cyclohexyl)-carboxamidocoumarin 5and 6-nitro-3-(N-cyclohexyl)carboxamidocoumarin 6.

Fusion of 1 with o-phenylenediamine in oil bath at 170°C gave the 6-nitro-3-(benzimidazole-2-yl)coumarin 7, whereas with benzidine in refluxing ethanol yielded 6-nitro-3-N-(4`-aminobiphenyl) carboxamidocoumarin 8a.

Acetylation, diazotization and coupling of 8a afforded the acetylated product 8b and the azo compound 9.

The reaction of 1 with p-aminoacetophenone in boiling ethanol gave 6-nitro-3-N-(4-acetylphenyl)carboxamidocoumarin 10 whose structure was supported chemically by its reaction with 3,4,5-trimethoxybenzaldehyde to give the chalcone 11, and with ethylcyanoacetate in the presence of ammonium acetate in an oil bath at 160-170°C to give 12 and 13.

Hydrazinolysis of 1 using hydrazinehydrate in boiling ethanol gave the two geometrical isomers E/E 15, Z/E 16 of the azine derivatives. The E/E isomer separated in pure crystalline form, while the Z/E isomer was detected in the remaining oil using the GC-MS technique.

Treatment of 1 with thiosemicarbazide gave the cyclized product 17 which condensed with 3,4,5-trimethoxybenzaldehyde to give the Schiff's base 21.

2-(6-nitro-coumarin-3-yl)-3,1-benzoxazin-4(H)one 22 was obtained when the ester 1 was submitted to react with anthranilic acid in refluxing n-butanol.

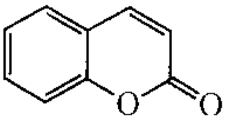
The reactivity of compound 1 as Michael acceptor was investigated via its reaction with malononitrile in the presence of sodiumethoxide to give the Michael adduct 23 which could be explained on the basis of formation of dimer of malononitrile followed by nucleophilic attack.

The configurational assignment for the synthesised compounds were discussed on the basis of i.r, ^{1}H-NMR and mass spectra, beside the microanalytical data.

INTRODUCTION

Coumarins

Coumarins represent a class of oxygen heterocyclic compounds which may be regarded as derivatives of 5,6-benzopyran-2one (I).



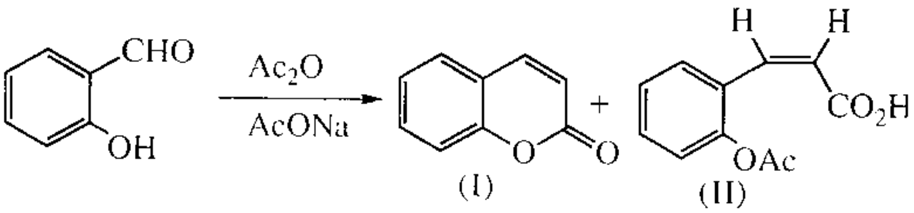
(I)

Synthesis of coumarins

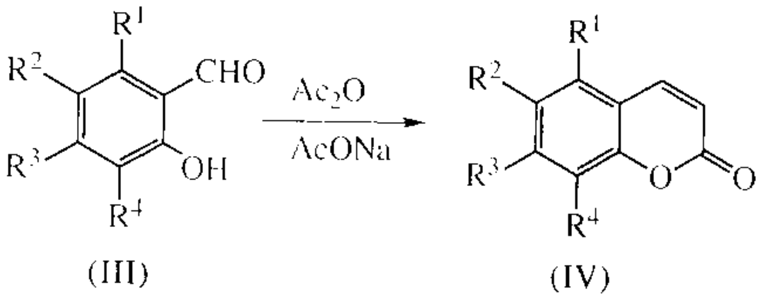
Coumarins could be synthesized by one of the following methods:

(1) Perkin synthesis :

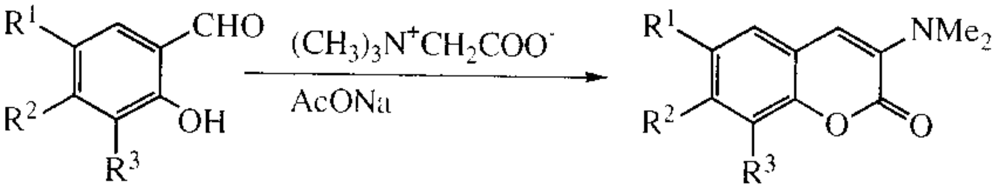
The classic synthesis was discovered by Perkin[1] who prepared coumarin (I) and acetylcoumaric acid (II) by heating salicylaldehyde with acetic anhydride in the presence of anhydrous sodium acetate.



This was the first example of the reaction which bears his name; in its more general form it involves the reaction of an aromatic aldehyde (III) with the anhydride of an aliphatic acid in the presence of the sodium salt of its acid to give the coumarin (IV) [2-5]

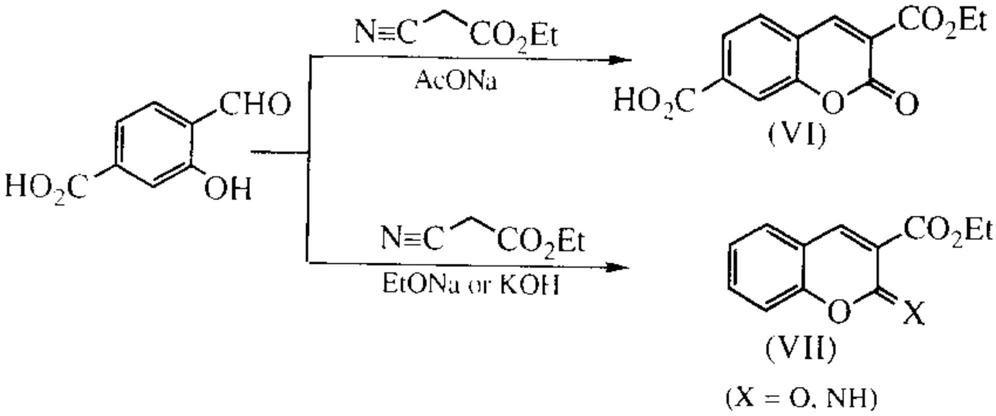


Recently, coumarin (I) was prepared in good yield by treating salicylaldehyde and acetic anhydride with anhydrous sodium fluoride as catalyst in molar ratio 1 : 3.1 : 1.6. The reaction time was reduced and the operation was simple in comparison to the classical synthesis of coumarin using sodium acetate[6]. The reaction of salicylaldehyde, betaine and acetic anhydride produced 3-dimethylamino coumarin (V)[7].

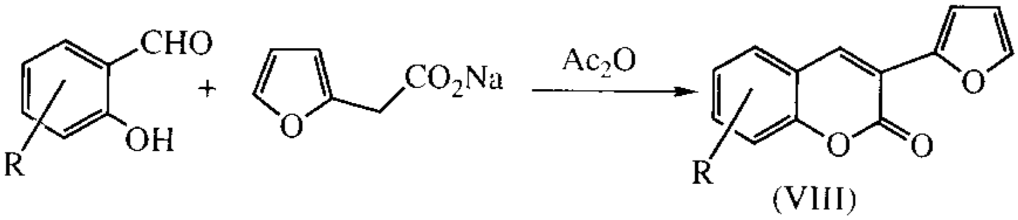


(V)

3-Hydroxy-4-formylbenzoic acid, ethyl cyanoacetate and sodium acetate gave 3-carbethoxy coumarin (VI)[8]. But the reaction of salicylaldehyde with ethyl cyanoacetate in the presence of sodium ethoxide or potassium hydroxide resulted in the derivatives (VII)[9].



Sodiumfurylacetate when added to substituted O-hydroxy benzaldehyde in the presence of acetic anhydride resulted in 3-(2-furyl)-coumarin derivatives (VIII)[10].



The benzopyranones (X) and naphthopyranones (XI) were prepared by treating the corresponding 2-hydroxy aldehyde with furandione (IX)[11].