STUDIES ON CHROMONES

A THESIS

Submitted in Partial Fulfilment
of the Requirements of
M. Sc. Degree

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(B. Sc.)

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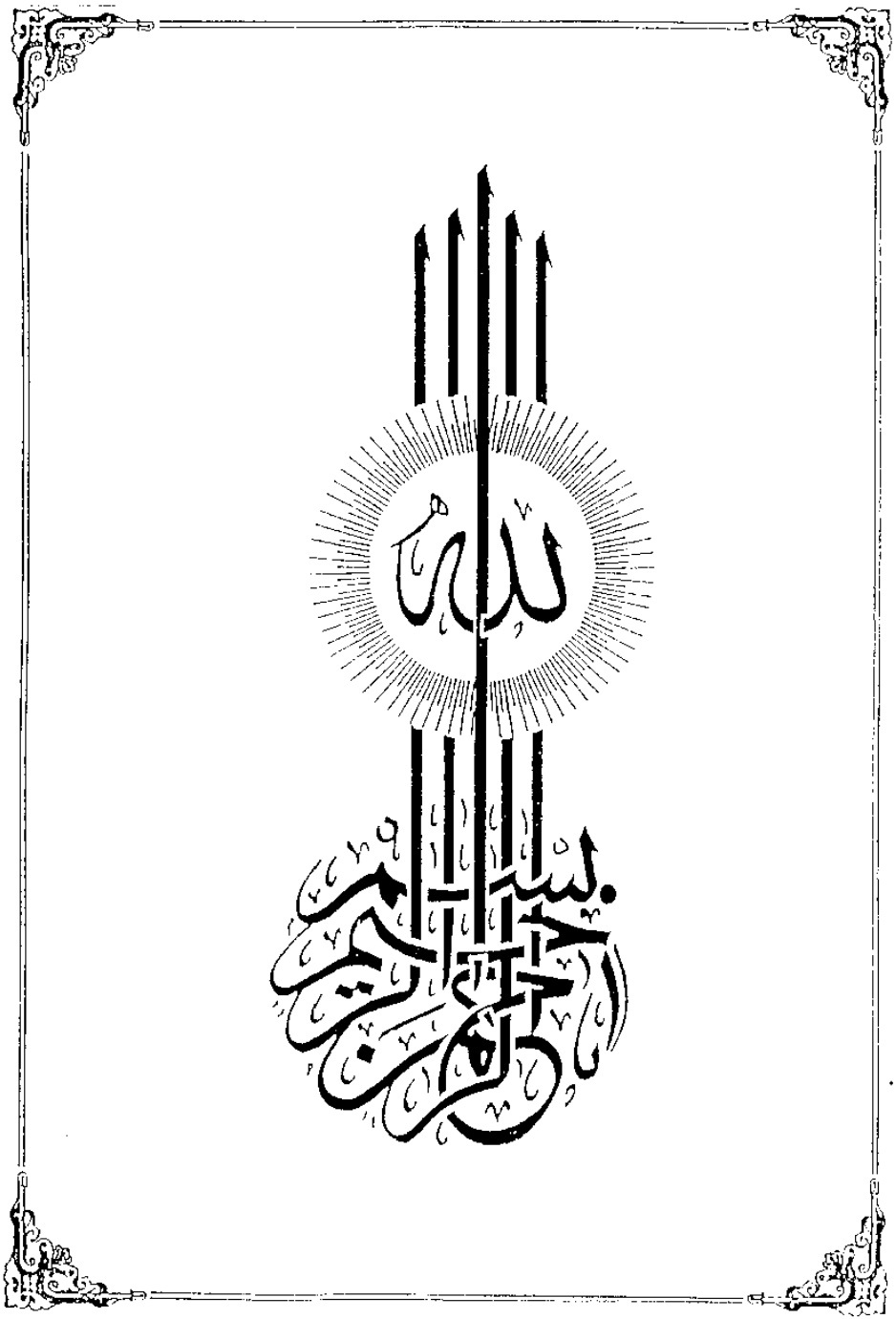
1971

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

The author wishes to acknowledge his sincere gratitude and indebtness to Dr. A. Sammour, Assistant Professor, Faculty of Science, Ain Shams University, and to Dr. M.T. El Zimaity, Chemical Department. They were kind enough to suggest the lines of research investigated and to follow the progress of the work with keen interest, guidance and valuable criticism.

The author is also indebted to Dr. Z. Sawires, General Director of the Chemical Department for the kind encouragement and facilities offered by him.



NOTE

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 :

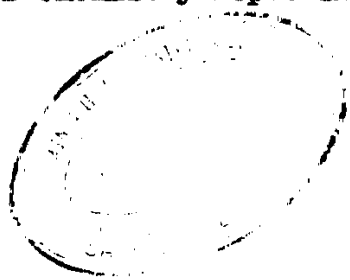
(1) Reaction Mechanisms.
(2) Electronic, Infrared, Raman and N.M.R. Spectroscopy of Organic Molecules.
(3) Microanalysis of Organic Compounds.
(4) Heterocyclic Compounds.
(5) Reactions of Organic Compounds.

He had successfully passed an examination in these topics.

F.G.Baddar

Prof. F.G. Baddar

Head of Chemistry Department



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Thesis Advisors

Approved

Prof. F.G. Baddar

Head of Chemistry Department

C O N T E N T S

Page

Special Part

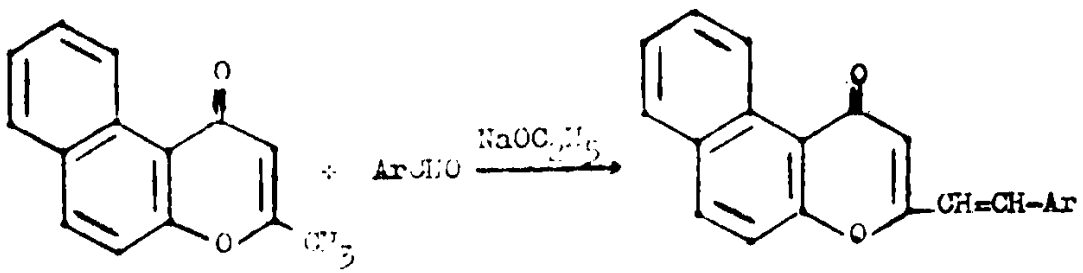
SUMMARY OF THE ORIGINAL WORK

CONTRIBUTION TO THE CHEMISTRY OF 2-METHYL-1,4-β-NAPHTHOPYRONE

SUMMARY OF THE ORIGINAL WORK

CONTRIBUTION TO THE CHEMISTRY OF 2-METHYL-1,4-β-NAPHTHOPYRONE

2- Methyl-1,4-β-naphthopyrone (I) was condensed with several aromatic aldehydes giving 2-styryl-1,4-β-naphthopyrones (II).

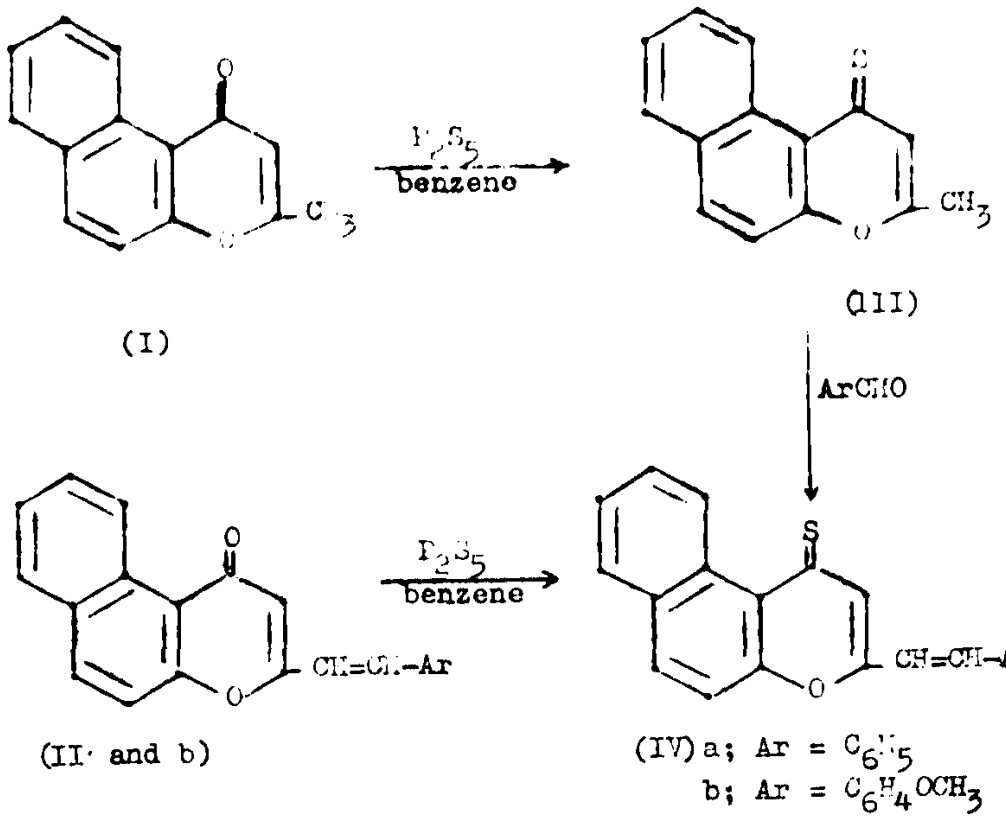


(I) (II)

IIa; Ar = C_6H_5
b; Ar = C_6H_4-OCH_3 (p)
c; Ar = $C_6H_3O_2CH_2$ (piperonyl)
d; Ar = $C_6H_4N(CH_3)_2$ (p)
e; Ar = $C_6H_4NO_2$ (p)
f; Ar = $C_6H_4NO_2$ (o)

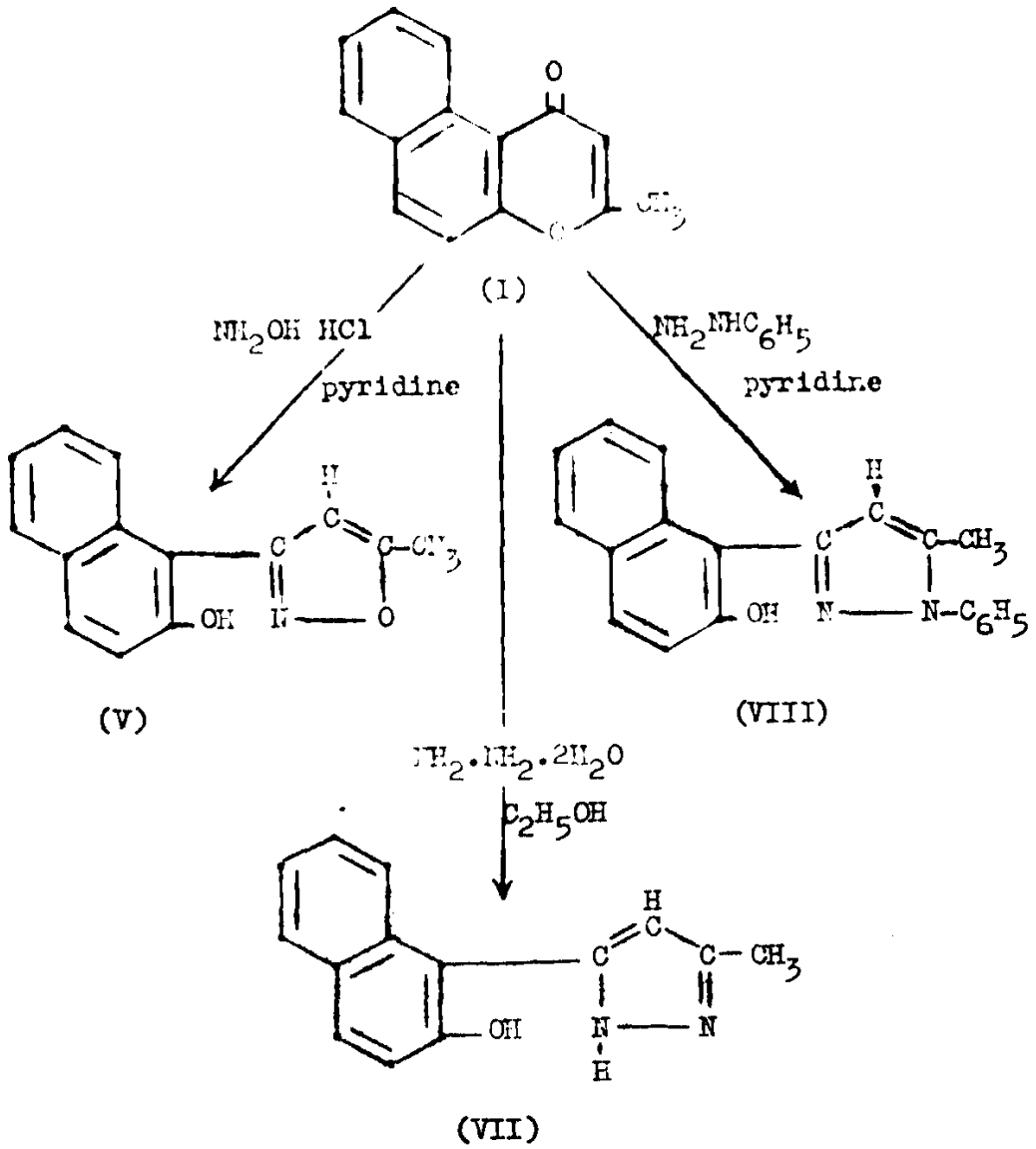
On heating the naphthopyrone (I) with phosphorous pentasulphide in benzene, the corresponding 2-methyl-1,4-β-naphtho-4-thiopyrone (III) was obtained. This thiopyrone when condensed with aromatic aldehyde, gave 2-styryl-1,4-β-naphtho-4-thiopyrones(IV). The same styrylthiopyrones

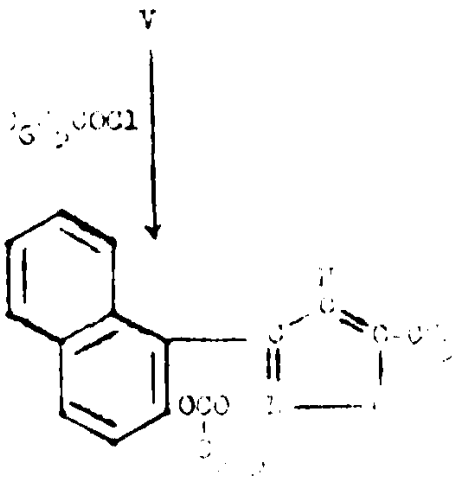
were obtained by heating styrylnaphthopyrones (II) with phosphorous pentasulphide in benzene.



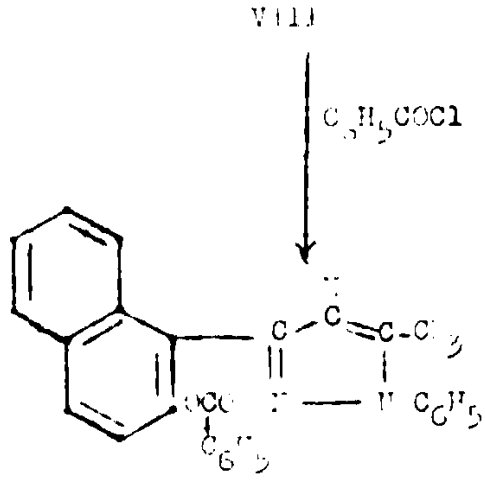
The pyrone ring in methylnaphthopyrone was cleaved when boiled with hydroxylamine hydrochloride, hydrazine hydrate and phenylhydrazine to give 3(2'-hydroxynaphthyl)-5-methylisoxazole (V), 3(2'-hydroxynaphthyl)-5-methylpyrazole (VII), and 3(2'-hydroxynaphthyl)-5-methyl-1-phenylpyrazole (VIII) respectively. The products obtained gave colours

with ferric chloride solution indicating the presence of free phenolic hydroxyl group. Besides, the corresponding benzoyl derivatives were prepared.



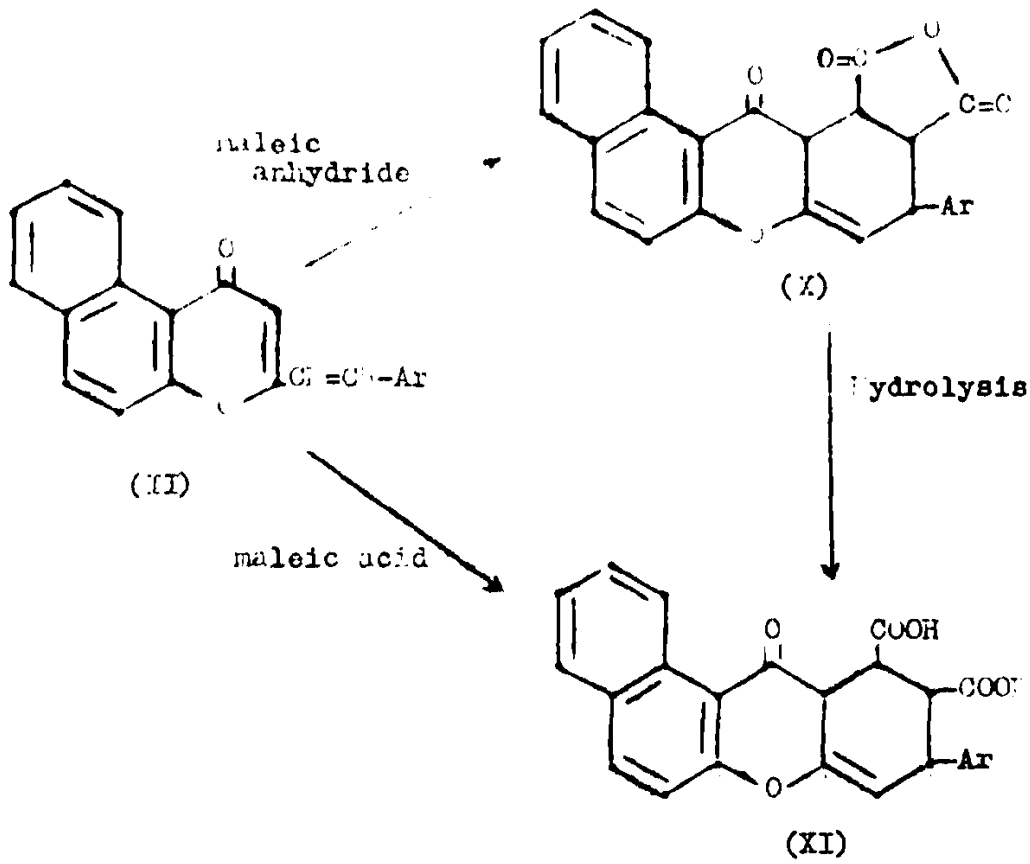


(VI)



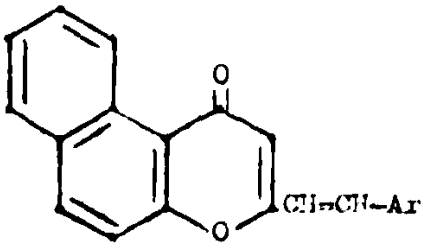
(IX)

Styrylnaphthopyrone (II) being a diene reacted with maleic anhydride in a Diels-Alder reaction. The adduct (X) on hydrolysis gave the xanthone dicarboxylic acid derivative (XI). The dicarboxylic acid (XI) was obtained by direct reaction of the styrylnaphthopyrone (II) and maleic acid.

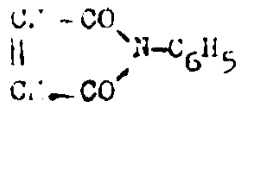


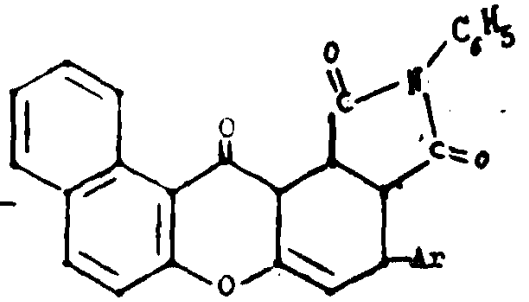
II, X and XI, a; Ar = C_6H_5
b; Ar = C_6H_4-OCH_3

On changing the dienophile to N-phenylmaleimide, we got the xanthone dicarboxylic acidimide derivative (XII) which on hydrolysis gave the previously prepared xanthone dicarboxylic acid derivative (XI) and aniline.



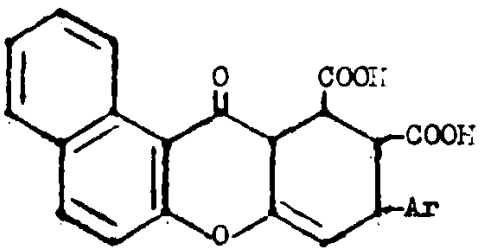
(II)



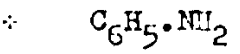


(XII)

hydrolysis



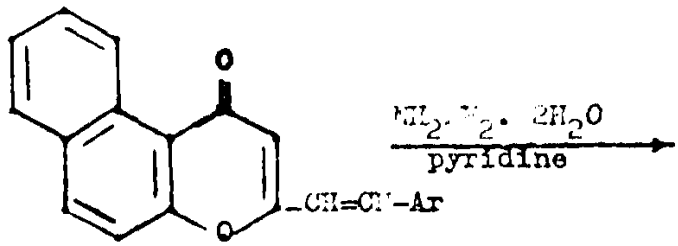
(XI)



II, XI and XII **a**; Ar = C_6H_5

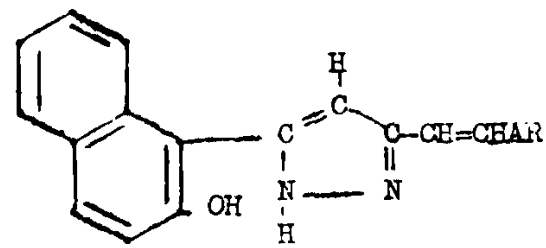
b; Ar = $C_6H_4OCH_3$(p)

The pyrone ring of styrylnaphthopyrone was cleaved by heating with hydrazine hydrate in pyridine and gave 3(2'-hydroxynaphthyl)-5-styrylpyrazole (XIV). The products obtained gave dark colour with ferric chloride solution indicating the presence of free phenolic hydroxyl group. They also gave a benzoyl derivative (XV).



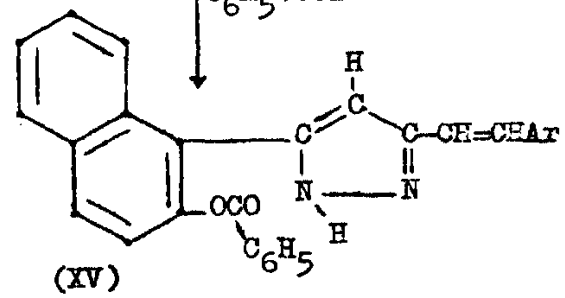
(II)

II and XIV a; Ar = C_6H_5
b; Ar = $C_6H_4OCH_3$-p



(XIV)

C_6H_5COCl



(XV)