A THESIS

Entitled

Reactions of Conjugated Double Bonds (Naphthofuchsones)

Submitted to

Ain Shams University

[illegible] fulfilment for the requirements of the degree of M.Sc.

By

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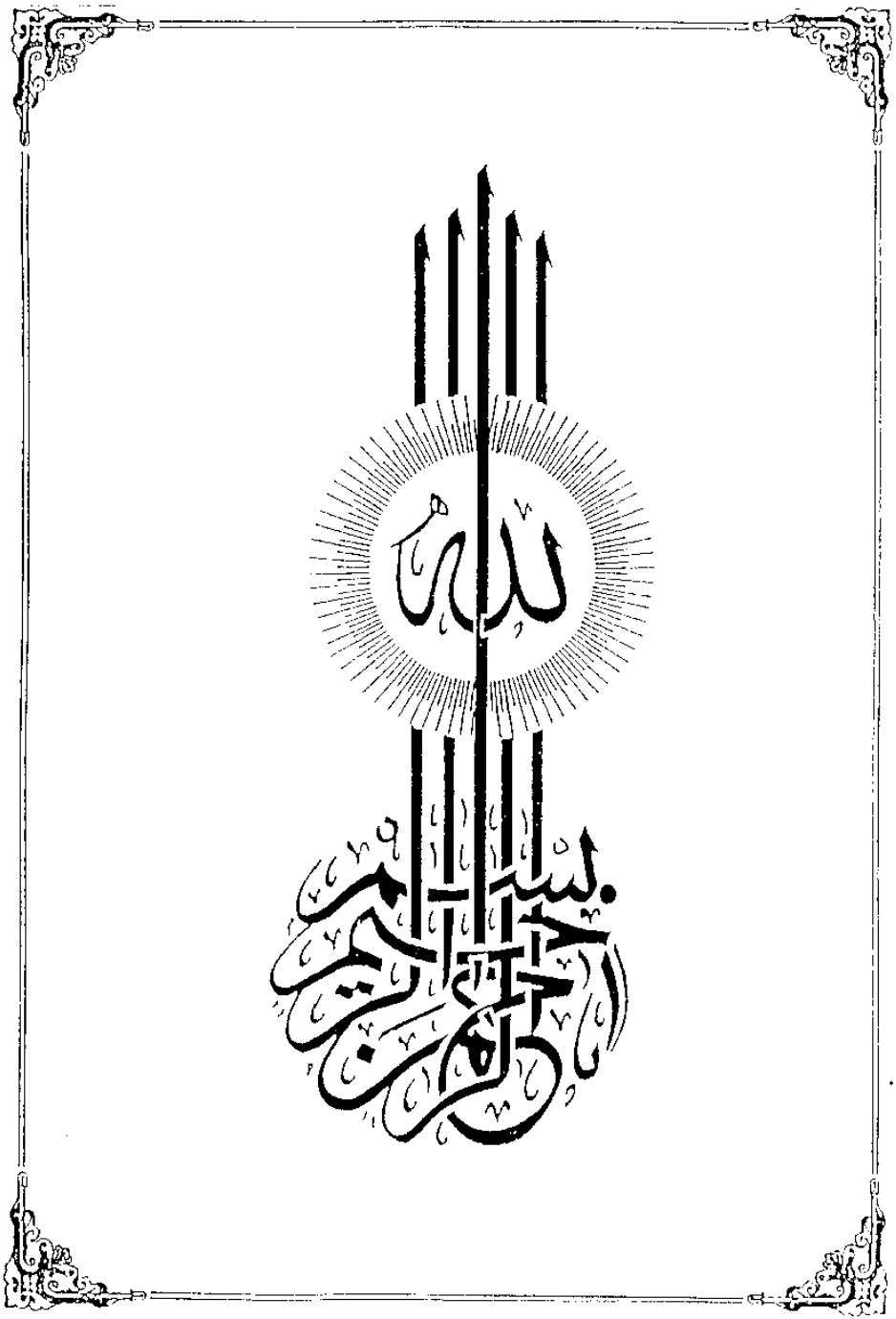


N O T E

Besides the work carried out in this thesis, the candidate has attended post graduate courses for two years in organic chemistry including the following topics:

1-Reaction Mechanism.

2-Electronic, Infrared, Raman and N.M.R. Spectroscopy of Organic molecules.

3-Microanalysis of Organic Compounds.

4-Organic Reactions.

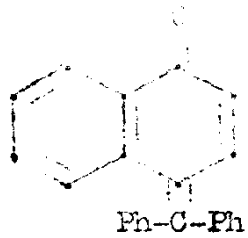
He successfully passed an examination in these topics.

C O N T E N T S

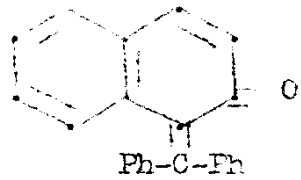
S U M M A R Y

Reactions of Conjugated Double Bonds

(Naphthofuchsones)



I



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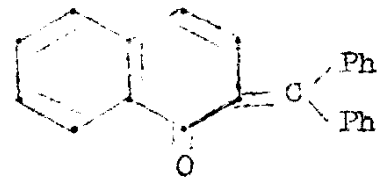
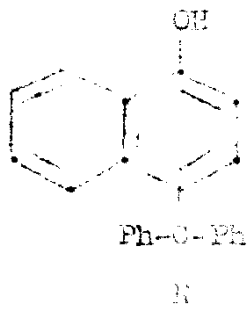


III

With Organometallic Compounds.

Methylmagnesium iodide, phenylmagnesium bromide and phenyllithium reacted with 1,2-naphthoquinone diphenylmethides by 1,4 addition to give the corresponding hydroxynaphthylalkanes (V a,b) and (VI a,b).



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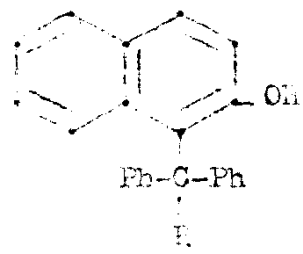
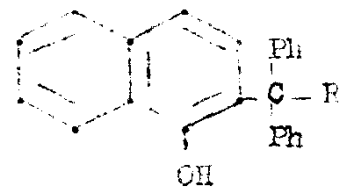


V



VI

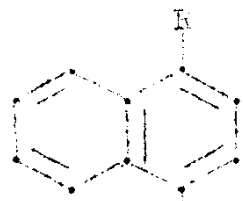
a, R = Me, b, R = Ph , c, R = OH , d, R = NHMe , e, R = $NHNH_2$

f, R = NHNHPh , g, R = NHOH , h, R = $C_{10}H_7$( ) .

With 1-naphthyl-lithium however they gave a double substitution (cf. VII and VIII).

Naph(1) VII VIII

1,4-Naphthoquinone diphenylmethide with phenylmagnesium bromide or phenyl-lithium , and 1-naphthyl-lithium gave compounds (I b,h) respectively by a first 1,2 addition reaction and migration of the OH group.



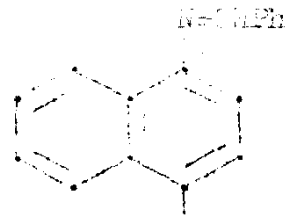
IX

The structures assigned to the above compounds are supported by i.r. and u.v. spectra , reactions with $FeCl_3$ and conc. H_2SO_4.

With Amines.

Normally the amines underwent a 1,4 addition with (II) and (III) to give (V a-f) and (VI a-t)on the cold, on fusion or heating the isolated compounds ~~they~~ reverted to the initial naphthoquinone diphenylmethides (II) and (III). ,4-Naphthoquinone diphenylmethide gave no stable amino compounds. The stable amino compounds were prepared from 1-methoxynaphthyldiphenylmethylchloride. The amino compounds according to their u.v. spectra have the structure of the corresponding triarylmethanes.

[illegible] was reacted [illegible] phenylmethane while with benzylamine [illegible] methane (X).

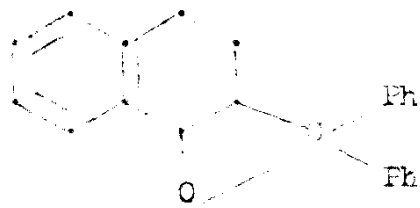


X

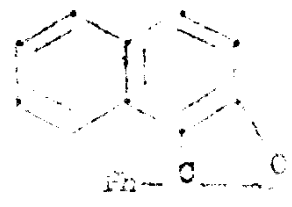
Heating with excess of hydrazine hydrate, phenylhydrazine or hydroxylamine gave hydrazone and diphenylketazine , phenylhydrazone, or oxime together with the corresponding naphthols.

With Diazomethane

(II) and (III) gave the corresponding dihydrofuran derivatives (XI) and (XII).



XI



XII

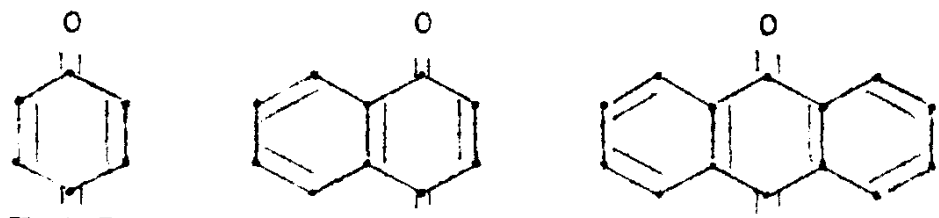
The reaction mechanisms of all the above reactions are discussed.

G E N E R A L P A R T

NAPHTHOQUINONE DIPHENYLMETHIDES

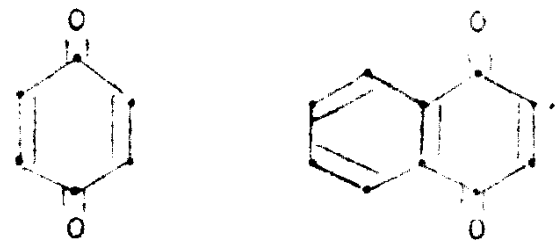
(NAPHTHOFUCHSONES)

Naphthoquinone diphenylmethides are a group of compounds containing a carbonyl group and an ethylenic bond attached to an isocyclic ring which assumes a quinonoid structure, e.g., 1,4-quinone diphenylmethide (fuchsone) (I), naphthoquinone diphenylmethide (naphthofuchsone) (II), and 9,10-anthraquinone diphenylmethide (anthrafuchsone) (III).

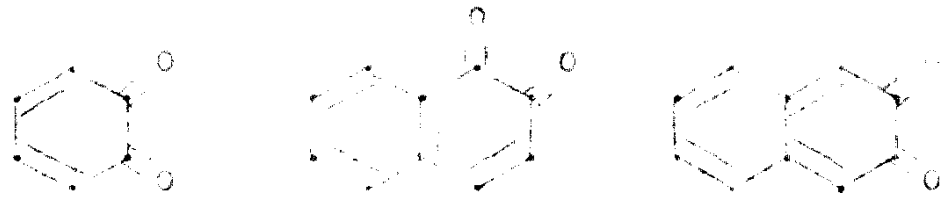


I II III

Quinone methides bear a relation in structure to quinones, and as we get para- and ortho- quinones, we get also para- and ortho- quinone methides.

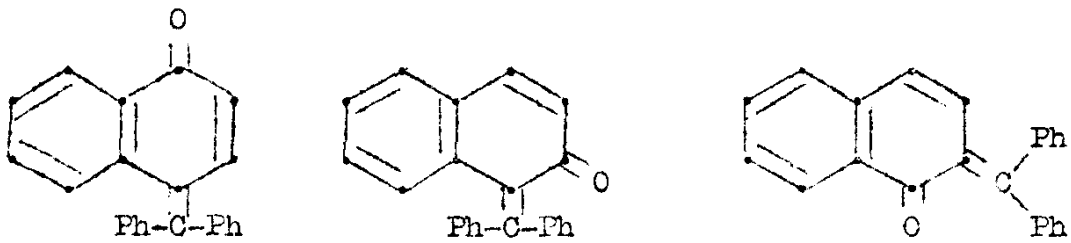


p-Quinones

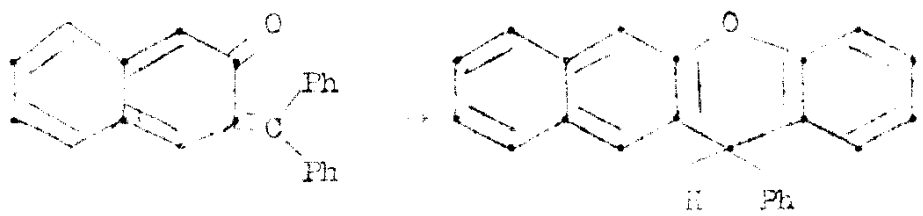


o-Quinones

Naphthoquinone diphenylmethides, where the position of the ethylenic and carbonyl groups can interchange their positions, can theoretically give four types (IV-VII) of quinone methides.



IV V VI



VII VIII

The fourth naphthoquinone diphenylmethide (VII) is unstable and changes spontaneously into xanthene (VIII).

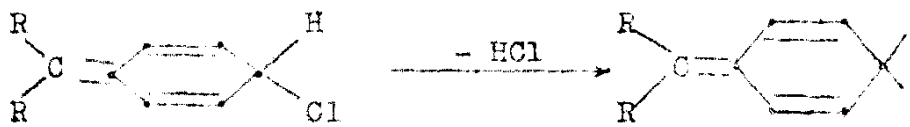
In the quinonoid structure; the resonance integral of C=O is clearly higher than C=C bonding and thus the C=C is fixed and will have a higher bond order which leads to the stability of the quinonoid structure[1].

1- C. Sandorfy, Compt.rend., 232, 633 (1951).

NATURE OF COLOUR IN TRIARYLMETHANES

The appearance of colour on treatment of triarylmethanol and its derivatives with acids, and the nature of colour in their respective coloured compounds aroused much controversies for a long time. Many scientists trying to explain the cause of the colour, put various theories of which may be cited the idea of Armstrong[1] and Nietzcki[2], stating that the colouration is due to the appearance of a quinonoid nucleus.

Kehrmann and Wenzel[3] suggested that the coloured compounds must have a quinonoid structure and that the ion having a bivalent carbon (b) is basic in character as the free radical of Norris[4]. The salts (a) and (c) having the same structure were called "quinocarbonium ion".



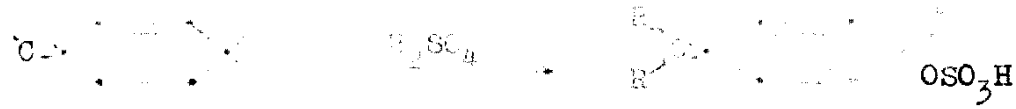
(a) (b)

1- H.A. Armstrong, Proc.Chem.Soc., 27 (1888).

2- R.Nietzcki, Organische Farbstoffe, Spreuger, Berlin (1888).

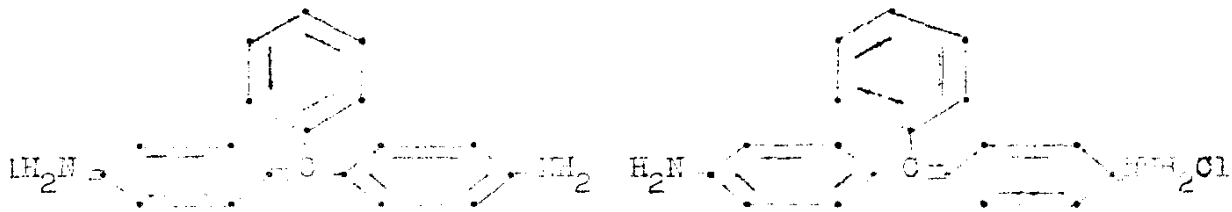
3- F.Kehrmann and F.Wenzel, Ber., 34, 3815 (1901).

4- J.F.Norris, Amer. Chem. J., 25, 117 (1901).



(b) (c)

Later, Baeyer[1] developed this idea into the "oscillation theory" which includes oscillation of an atom in the molecule, e.g., in Dobner's violet (the chlorine atom) was considered to be in a state of oscillation between the following two forms:



However, the first successful attempt towards the interpretation of the structure of coloured compounds was done by Adams and Rosenstein[2] who reported, basing on the electromagnetic theory, "absorption of light results only from the

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1 - A. Baeyer, Ber., 36, 3013(1903), Lieb.Ann., 354, 139 (1907).

2 - C. Adams and L. Rosenstein, J.Amer.Chem.Soc., 36, 1472(1914).