THESIS
ON
SOME REACTIONS WITH DIAZOALKANES

# STUDIES ON THE STRUCTURE OF THE PRODUCTS OF DIAZOALKANES WITH o-QUINONOID SYSTEMS

Presented by

**SOAD MOHAMMED SHENDY**
B.Sc. (Hons)

In Partial Fulfilment of the Degree of

*MASTER OF SCIENCE*

University College for Women
Ain Shams University

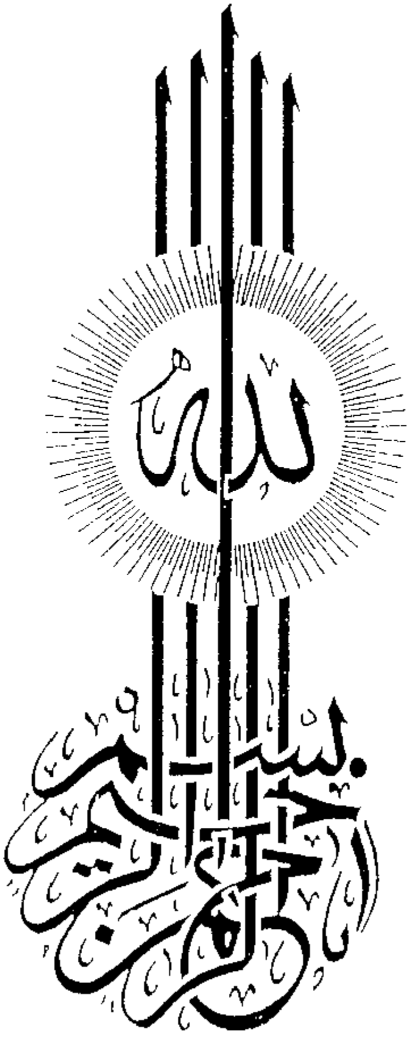
1973

# ACKNOWLEDGEMENT

The author wishes to express her deepest thanks and gratitude to Professor William Ibrahim Awad, D.Sc., Head of Chemistry Department, University College for Women, Ain Shams University, not only for suggesting the problem investigated, but also for kindly supervising the subject, continuous encouragement and helpful advice throughout all stages.

The author is also thankful to Dr. Ahmed Ismail Hashem, Lecturer of Organic Chemistry, Faculty of Science, Ain Shams University for his continuous encouragement and help.

Thanks are also due to Dr. M. Wassef, University College for Women, for measuring the I.R. and U.V. Spectra.


بسم الله الرحمن الرحيم

# NOTE

Besides the work carried out in this thesis, the candidate has attended postgraduate courses for one year in organic chemistry including the following topics.

1) Reaction mechanisms.
2) Electronic, Infrared, Raman, N.M.R. and Mass Spectral studies of organic compounds.
3) Advanced topics in organic chemistry.
4) Organic Microanalysis.
5) Quantum chemistry.
6) Chemistry of heterocyclic compounds.

She has successfully passed an examination in these topics.

Prof. Dr. W.I. Awad

Head of Chemistry Department

# CONTENTS

Page

Page

# SUMMARY

In this investigation the reactions of diazoalkanes with the following compounds are studied:

(a) Phenanthrenequinone (b) Chrysenequinone
(c) Indantrione (d) periNaphthindan-2,3,4-trione
and (e) Coumarandione.

(a) With Phenanthrenequinone:- Diphenyldiazomethane, p,p'-dichlorodiphenyldiazomethane and p-nitrophenylphenyldiazomethane react with phenanthrenequinone to give the α-ketoepoxides (XCII) and (XCVa,b) (cf. page 42,44). Such products have been previously described as methylenedioxy derivatives (ILa) and (XCIV) (cf. page 41 and 43). p,p'-Dimethoxydiphenyldiazomethane fails to react with phenanthrenequinone.

(b) With Chrysenequinone:- When diazomethane was allowed to react with chrysenequinone ring expansion and epoxide formation occured with the formation of (XCVIIa) (cf. page 48). The reaction of diphenyldiazomethane and p,p'-dichlorodiphenyldiazomethane with this quinone gives methylenedioxy derivatives (XCVIIIa) and (XCVIIIb) (cf. page 51). Diazoethane and p,p'-dimethoxydiphenyldiazomethane fail to react with chrysenequinone. These negative results are of special interest and are discussed thoroughly (cf. page 52).

(c) With Indantrione:- Diazomethane reacts with indantrione to give a mixture of 2-methoxy-1,4-naphthoquinone (XC) (cf. page 54) and another product to which the hemimethalal structure (CIIa) is given (cf. page 56).

(d) With periNaphthindan-2,3,4-trione :- The reaction of diazomethane with perinaphthindan-2,3,4-trione affords a ring expansion product (CIII) (cf. page 59).

(e) With Coumarandione:- Diazomethane reacts with coumarandione with the formation of a mixture of 3-methoxycoumarin (LXXXVIII) (cf. page 60) and another product whose data is not sufficient to verify reasonable structure for it

The structures of these products are discussed in the light of their chemical and spectroscopic properties.

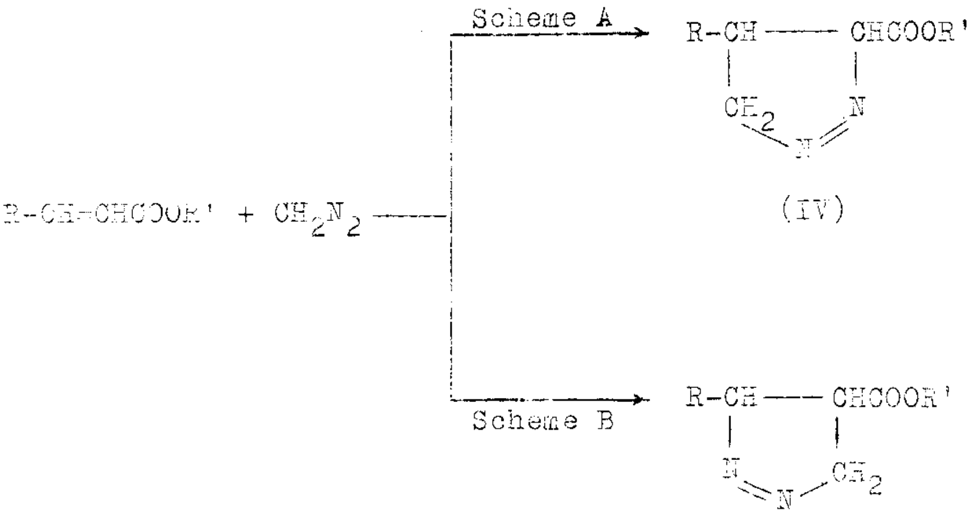
# INTRODUCTION

## REACTIONS OF DIAZOALKANES

### (A) 1,3-ADDITION TO ALKENES:-

1) Reactions with α, β-unsaturated ketones and carboxylic esters:-

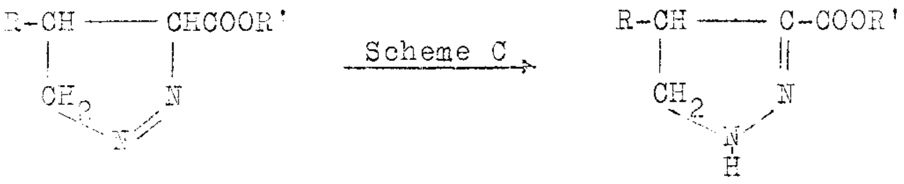
V. Auwers[2a,b,c] stated that the addition of diazomethane to α , β-unsaturated esters follows Scheme A rather than Scheme (B).



(IV)

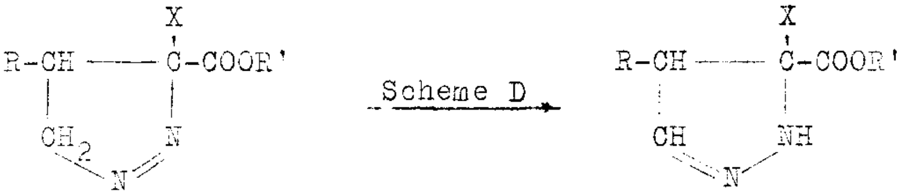
(V)

The same authors[2a,b,c] showed also that the initial products of addition of diazoalkanes are $\Delta^1$-pyrazolines (IV), which mostly isomerize rapidly to the more stable[3] isomeric $\Delta^2$-pyrazolines (VI), particulary if this change resulted in the formation of a conjugated system (Scheme C).



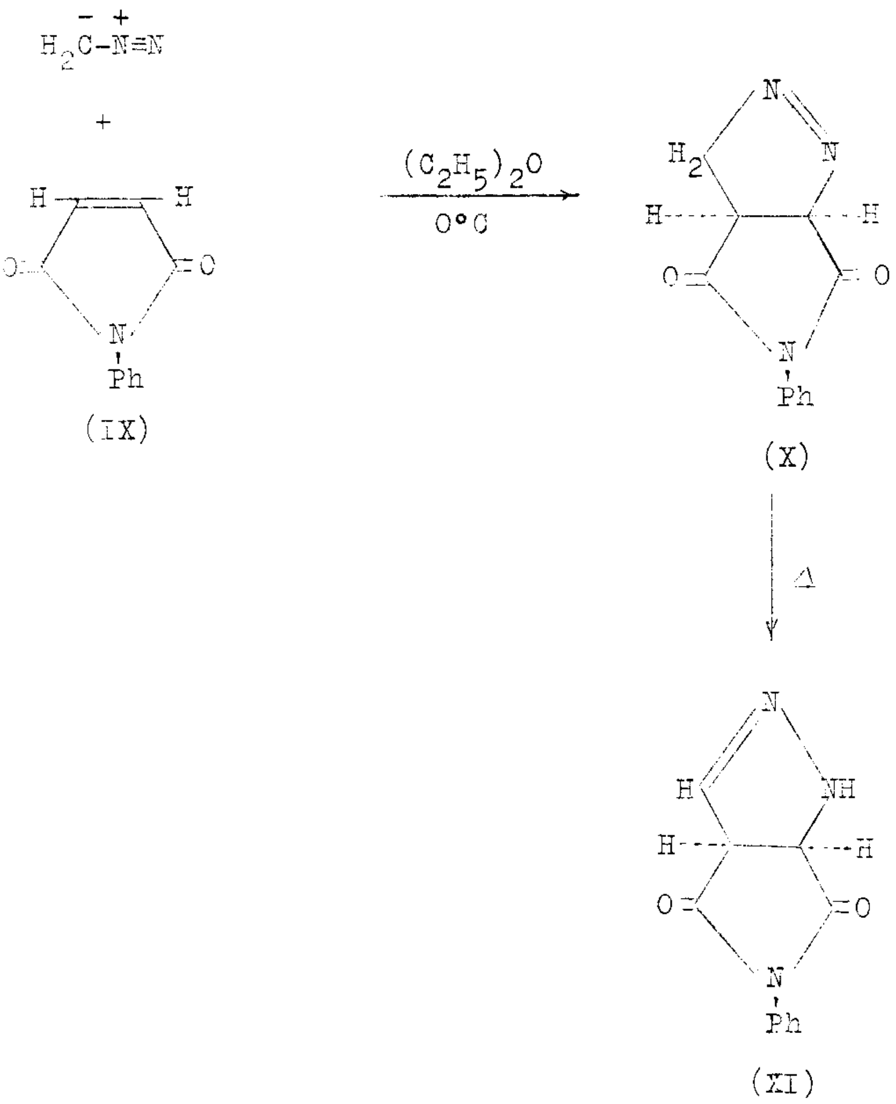
(IV) (VI)

However, in the case of substituted pyrazolines, the reaction follows Scheme (D).

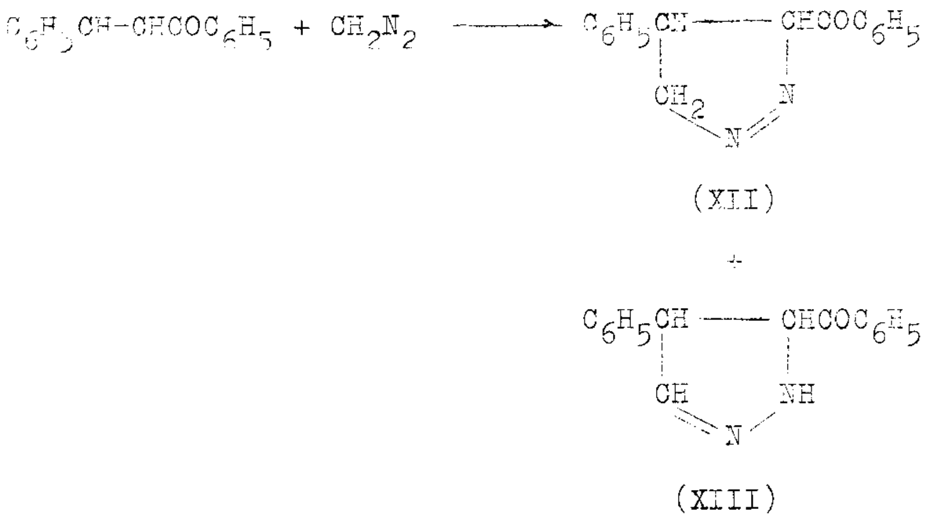


(VII) (VIII)

Awad *et al.*,[4] investigated the action of diazomethane on N-phenylmaleimide (IX) and found that the product is a derivative of $\Delta^1$-pyrazoline (X) and not $\Delta^2$-pyrazoline (XI), as previously claimed[5], (XI) was only obtained as a pyrolysis product of (X). Such rearrangement was also observed in similar cases[6].



Diazomethane was found[7] to add readily to benzalacetophenone in cold ethereal solution giving two isomeric pyrazolines, m.p. 92-93°C and 127°C respectively. The lower melting point product (XII) could be transformed into the isomer (XIII) by gentle heating slightly above its melting point.


$C_6H_5CH{=}CHCOC_6H_5 + CH_2N_2 \longrightarrow$

(XII)

+

(XIII)

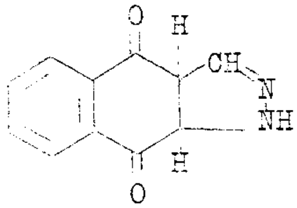
In certain cases[8] only $\Delta^2$-pyrazolines were formed in the reaction of diazomethane with $\alpha,\beta$-unsaturated ketones.

## 2) Reactions with p-quinones:-

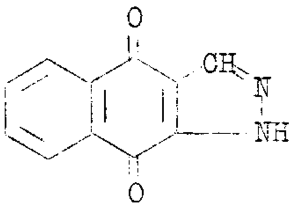
### a) Action of diazoalkanes on 1,4-naphthoquinone:-

Fieser and Peters[9] studied the addition of diazomethane and other derivatives to 1,4-naphthoquinone. Diazomethane adds to 1,4-naphthoquinone[9] to give first in quantitative yield a yellow intermediate compound which has the composition $C_{11}H_8O_2N_2$ (XIV). It was unstable and on crystallisation or dissolution in alkali, it changed over into a colourless substance having the formula $C_{11}H_6O_2N_2$ (XV) which has two hydrogen atoms less than the previous compound.

According to this, the yellow substance becomes oxidised to the colourless compound on crystallisation.

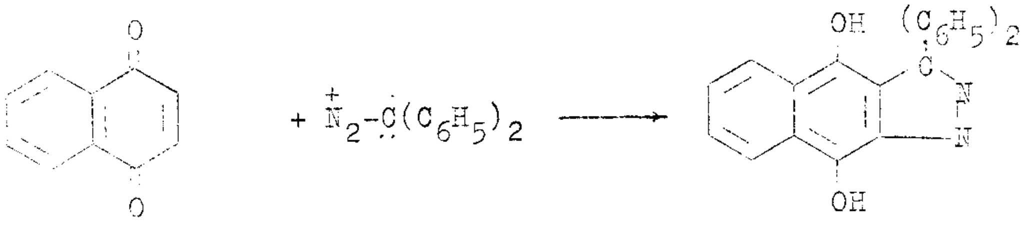


(XIV)



(XV)

The reaction of diphenyldiazomethane with 1,4-naphthoquinone was found[9] to give an orange coloured compound having the composition of the sum of the reactants (XVI).

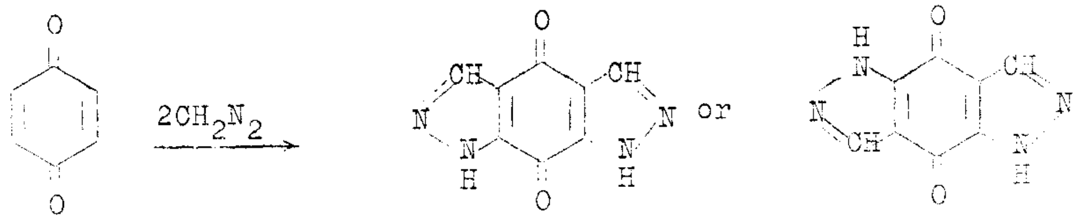


(XVI)

This product decomposes on pyrolysis with loss of nitrogen.[9,10]

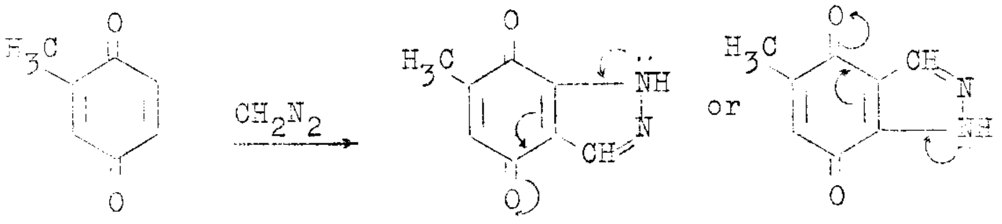
### b) Action of diazoalkanes on p-benzoquinone and toluquinone.

The reaction of p-benzoquinone with diazomethane was found to yield pyrazoline derivatives[9,11], the addition taking place at the quinonoid ethylene linkage. Fieser et al.,[9] reported that p-benzoquinone adds ordinarily two molecules of the reagent and there are two possible modes of addition.



(XVII)

In case of toluquinone, only one molecule of diazomethane was added[12] to give (XVIII).



(XVIII)

This is attributed[12] to the electron repeling character of the methyl group which increases the electron density at the double bond where it is attached, as compared with the other double bond in the same molecule. Diazomethane which is believed to react here as a carbanion $:\overset{-}{C}H_2-\overset{+}{N}\equiv N:$, seeking a low electron density on the toluquinone molecule is expected to add on the side of toluquinone free from the methyl group. This was further confirmed by the observation reported by Macbeth and Winzor[13] that the presence of an alkyl substituent