A Thesis

ENTITLED

STUDIES ON THE REACTIONS BETWEEN CARBANIONS & ACTIVATED O-QUINONES

SUBMITTED By

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A T H E S I S

Entitled

"STUDIES ON THE REACTIONS BETWEEN

CARBANIONS AND ACTIVATED O-QUINONES"

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

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N O T E

Besides the work carried out in this thesis, the candidate has attended postgraduate courses in the following topics:

1. Photochemistry.
2. Microanalysis.
3. Organometallic Compounds.
4. Quantum Chemistry.
5. Spectroscopy.
6. Kinetic Chemistry.
7. Thermodynamics.

She has successfully passed a written examination in these courses, in partial fulfillment for the degree of Master of Science.

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C O N T E N T S

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SUMMARY

S U M M A R Y

In this work, the author investigated the reaction of 3,6-dibromo-9,10-phenanthrenequinone with diazoalkanes, amines, ethylacetoacetate and other reagents in order to verify the effect of the presence of bromine in position 3 and 6 in the phenanthrenequinone system.

The addition of diazomethane leads to the formation of spiro [oxiran-2,9'-phenanthrene-3',6'-dibromo-10'-one] (196); diazoethane to spiro [3-methyloxiran-2,9'-phenanthrene-3',6'-dibromo-10'-one] (197); diphenyldiazomethane to spiro [3,3-diphenyloxiran-2,9'-phenanthrene-3',6'-dibromo-10'-one] (198); phenyl benzoyl diazomethane to spiro [3-benzoyl-3-phenyloxiran-2,9'-phenanthrene-3',6'-dibromo-10'-one] (199) and with diazofluorene to spiro [3-fluorenylidene-2,9'-phenanthrene-3',6'-dibromo-10'-one] (200).

The reaction of 3,6-dibromo-9,10-phenanthrenequinone with n-butylamine leads to the formation of 2-propyl-3',6'-dibromophenanthroxazole (205), while with isopropylamine the product was the schiff's base of 3,6-dibromo-9-phenanthrol (206).

With alcoholic ammonium hydroxide 3,6-dibromo-9,10-

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phenanthrenequinone imine (207) was obtained which upon reaction with diphenyldiazomethane 2,2-diphenyl-3',6'-dibromophenanthro-2,3-dihydrooxazole (208) was formed.

The reaction of ethylacetoacetate with the quinone gives ethylic 3,6-dibromophenanthroxylene acetoacetate (210); while with alcoholic potassium hydroxide the author obtained the corresponding lactone (212), as it is the case with phenanthrenequinone.

The constitution of the products are inferred besides analytical data from infrared and electronic spectra.

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INTRODUCTION

1,3-DIPOLAR ADDITION

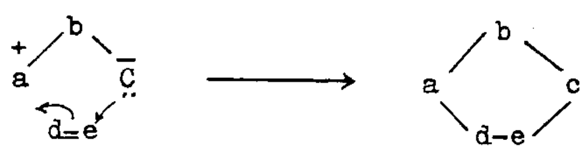
INTRODUCTION

The 1,3-dipolar cycloaddition offers a remarkably wide range of utility in the synthesis of five-membered heterocycles. Numerous individual examples of this reaction were known, some even back in the nineteenth century, yet the prediction and discovery of new classes of 1,3-dipoles and of numerous new fruitful reactions in this synthetic route, were achieved only in recent years.

Description of 1,3-Dipoles

Cycloaddition can be classified according to the number of new σ-bonds formed or according to the size of the ring which is formed. The Dieles-Alder synthesis is an important cycloaddition in which a 6-membered ring is produced.

A cycloaddition of the type $3 + 2 \longrightarrow 5$ leading to an uncharged 5-membered ring cannot possibly occur with octet stabilized reactants which have no formal charges. Accordingly, a 1,3-dipole a-b-c, must be defined such that atom "a" possesses an electron sextet, i.e., an incomplete valence shell combined with a positive formal charge and that atom "c", the negatively charged centre, has an unshare electron pair. Combination of such a 1,3-dipole with a multiple bond system d-e, termed the dipolarophile (may be any double or triple bond), by means of a cyclic electron displacement with extinction of the formal charges to give an uncharged 5-membered ring, is referred to as 1,3-dipolar cycloaddition.

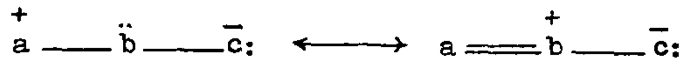


Classification of 1,3-Dipoles

A) 1,3-Dipoles with internal octet stabilization

Compounds containing an electron sextet at carbon, nitrogen or oxygen atom are not stable. The foregoing designation would therefore acquires the physical significance of a mere resonance contributor if the 1,3-dipoles were capable of isolation. Stabilization is possible if an unshared pair of electrons at atom "b" can relieve the electron deficiency at centre "a" by formation of an additional bond

$$\overset{+}{a}{=}\ddot{b}-\bar{c}: \;\leftrightarrow\; a{\equiv}\overset{+}{b}-\bar{c}: \qquad b = N$$



b = NR or O

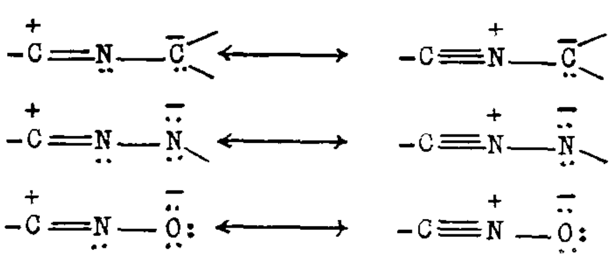
Sextet formula Octet formula

In the new mesomeric formula, in which "b" has now the positive charge, all centres have completely filled valence shells. Such systems will be designated as 1,3-dipoles with internal octet stabilization. These in turns are classified into two types.

1. 1,3-<u>Dipoles with a double bond and internal octet stabilization</u>

The sextet structure of the 1,3-dipoles contains a double bond between "a" and "b". All of these contain nitrogen as the middle atom (no other element has an extra pair of electrons available while remaining in the triply bonded neutral state) and all belong to either the nitrilium or the diazonium betaines.

<u>Nitrilium betaines</u>

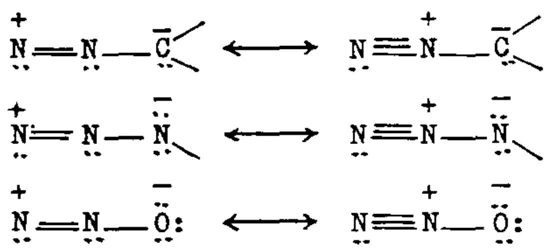


Nitrile ylides

Nitrile imines

Nitrile oxides

Diazonium betaines



Diazoalkanes

Azides

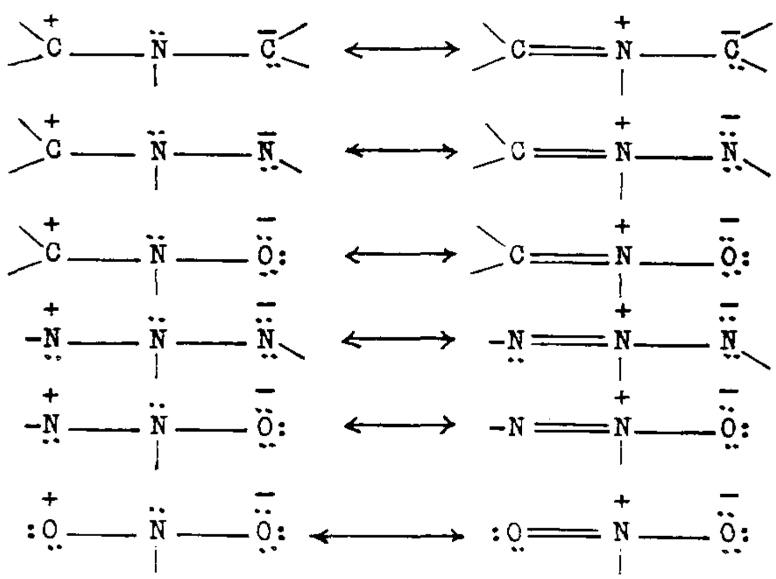
Nitrous oxides

Sextet structure   Octet structure

2) 1,3-Dipoles without a double bond but internal octet stabilization

The sextet structure of the 1,3-dipoles contains a single bond between "a" and "b". In this case either nitrogen or oxygen may occupy centre "b".

a) Nitrogen as a central atom



Azomethine ylides

Azomethine imines

Nitrones

Azimines

Azoxy compounds

Nitro compounds