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FASCINATING PROBLEMS IN ORGANIC REACTION MECHANISMS VIII: REACTIONS AND REARRANGEMENTS OF PHENANTHRAQUINONE MONOIMINE**

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Phenanthraquinone monoimine, being the only stable 1,2-diketone monoimine has contributed significantly towards the transformation of diketone monoimines to diverse types of heterocyclic systems. Additionally, the structural work relating to "Phenanthraquinoneimide Anhydride" discovered in 1879 has led to discernment of some interesting transformations associated with heterocyclic systems. This article provides an integrated account of the development in this area and incorporates our own unpublished work.

1. Phenanthraquinone monoimine
2. Structure and Reactions of Phenanthraquinoneimide Anhydride

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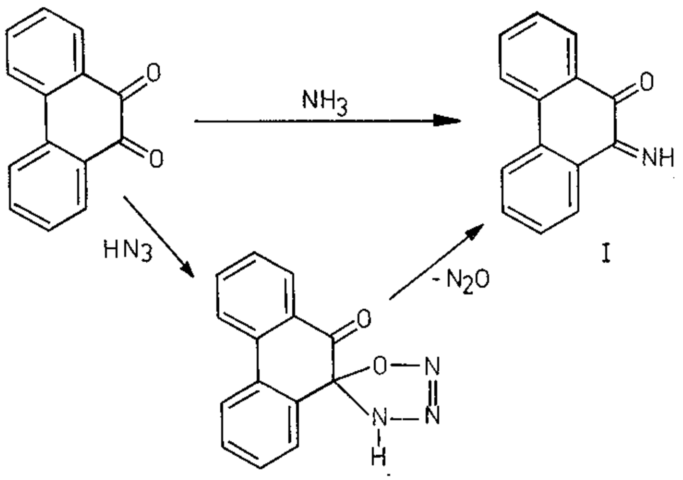
[**] Respectfully dedicated to Professor R. B. Woodward on the occasion of his sixtieth birthday.
Paper 7, Tetrahedron, 31, 1391 (1975).

3. Phenanthraquinone monoimine-Phenanthraquinoneimide Anhydride type Rearrangements
4. Aromatic Heterocyclic Systems from Phenanthraquinone monoimine and other in situ Generated quinone monoimines
5. Cyclo addition reactions of 1,2-Diketone monoimines.

The discovery of phenanthraquinoneimide anhydride in 1879 by Zincke[1] formed on pyrolysis of phenanthraquinonemonoimine (I) should be considered as a significant event in the development of heterocyclic chemistry. During the intervening century no fewer than 8 structures have been proposed for this compound.[1-5] These, culminating in the firm establishment of this structure[4,5] traces the increased understanding of the formation and reactions of heterocyclic systems. Phenanthraquinone monoimine itself occupies a unique position because of its isolable nature and the reactions of this substance in turn have helped in the synthesis of a variety of systems, some of which possessing marked anti-inflammatory properties.[6]

1. Phenanthraquinone Monoimine (I)

Compound I is best prepared by the reaction of phenanthraquinone with saturated ethanolic ammonia.[7] The reaction of phenanthrenequinone with hydrazoic acid also leads to I, involving perhaps a cyclo addition-reversal pathway:[8]

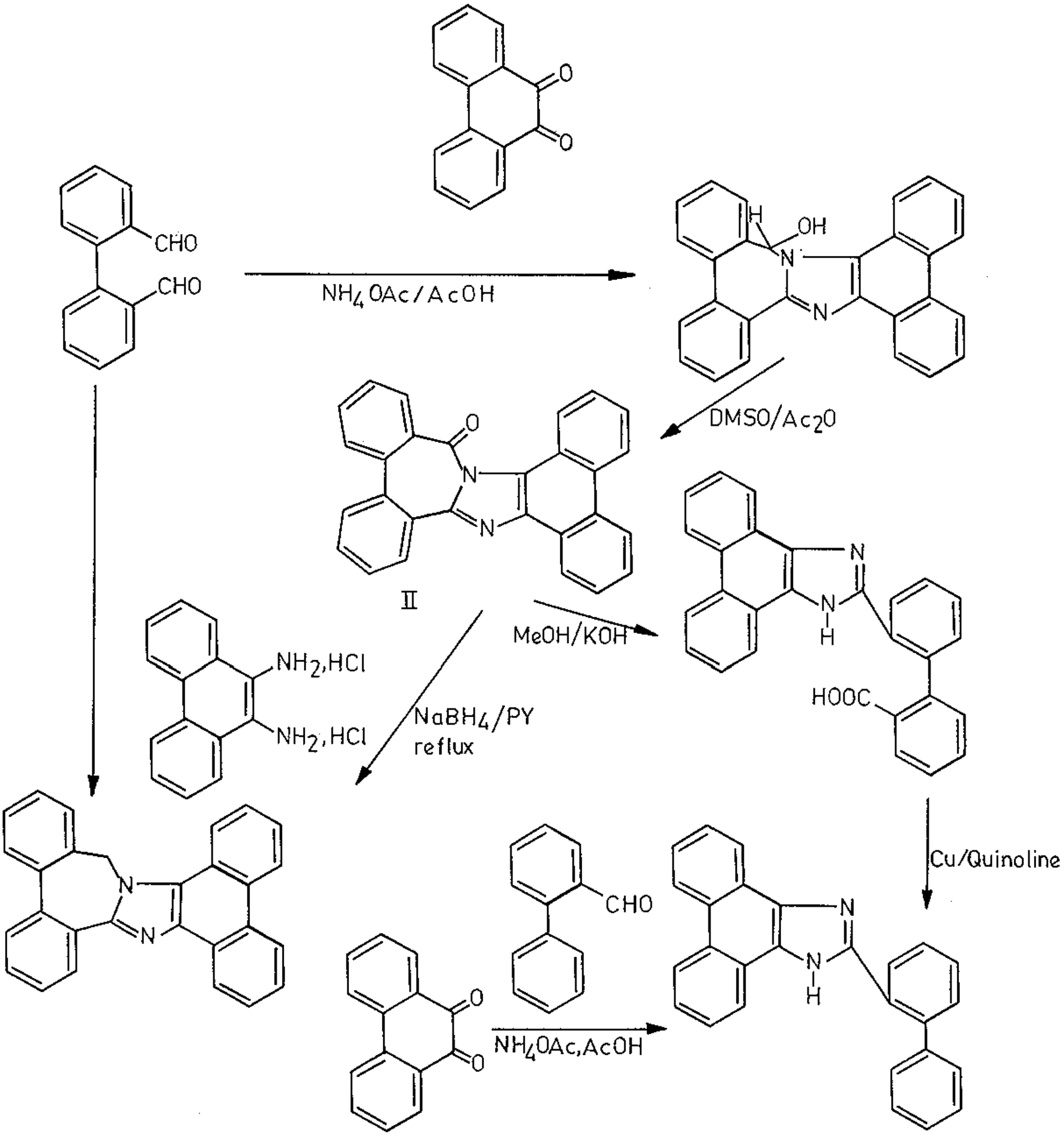


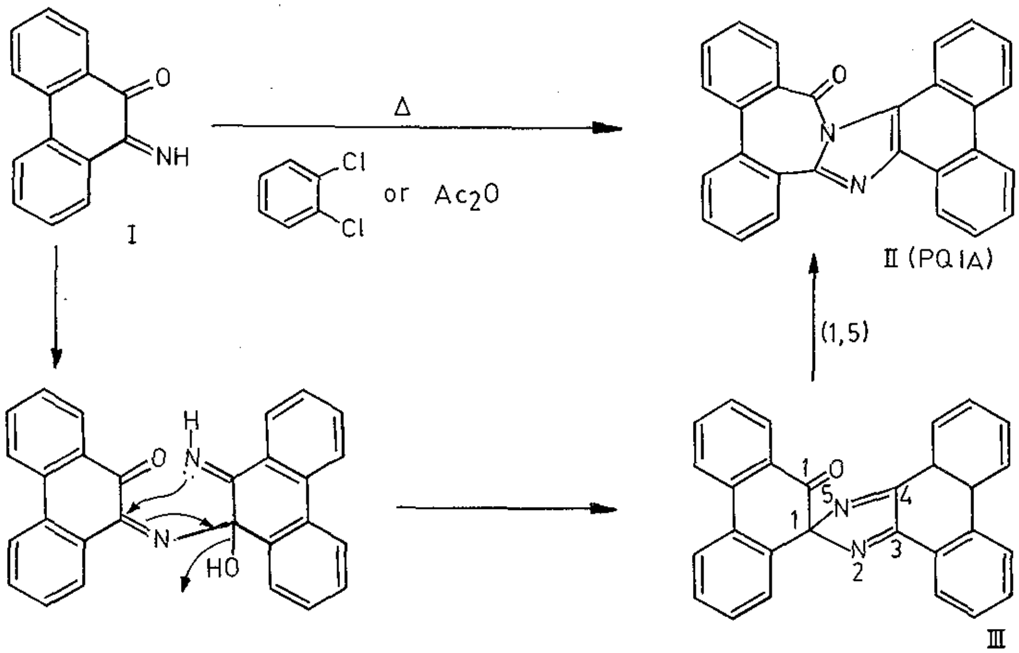
2. Structure and Reactions of Phenanthraquinoneimide Anhydride (PQIA)

The structure of PQIA, the product arising from thermolysis of I in acetic anhydride or o-dichlorobenzene or neat has now been firmly established as 10H-dibenzo(c,e)phenanthro(9',10':4,5)-imidazo-(1,2-a)azepine-10-one (II) on the basis of two independent, parallel and complementary investigations[4,5] which are summarized in Chart I.

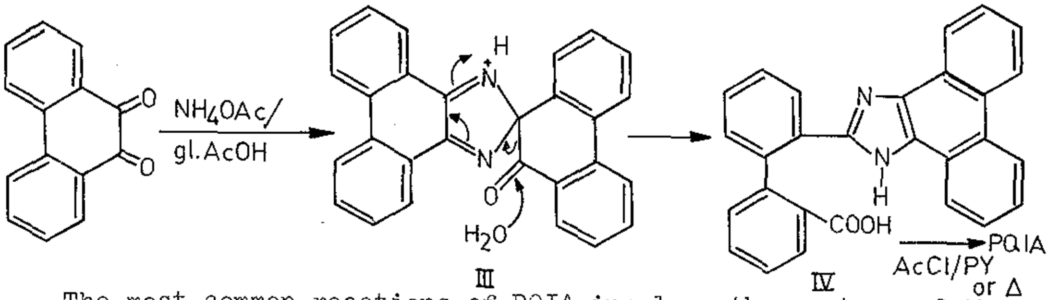
The I→PQIA change is best rationalized on the basis of a fascile 1,5-shift of the key intermediate III:

CHART I


O
O
CHO
CHO
NH4OAc/AcOH
H
OH
N
N
DMSO/Ac2O
O
N
N
II
MeOH/KOH
N
N
H
HOOC
NH2,HCl
NH2,HCl
NaBH4/PY
reflux
N
N
Cu/Quinoline
CHO
N
N
H
O
O
NH4OAc,AcOH

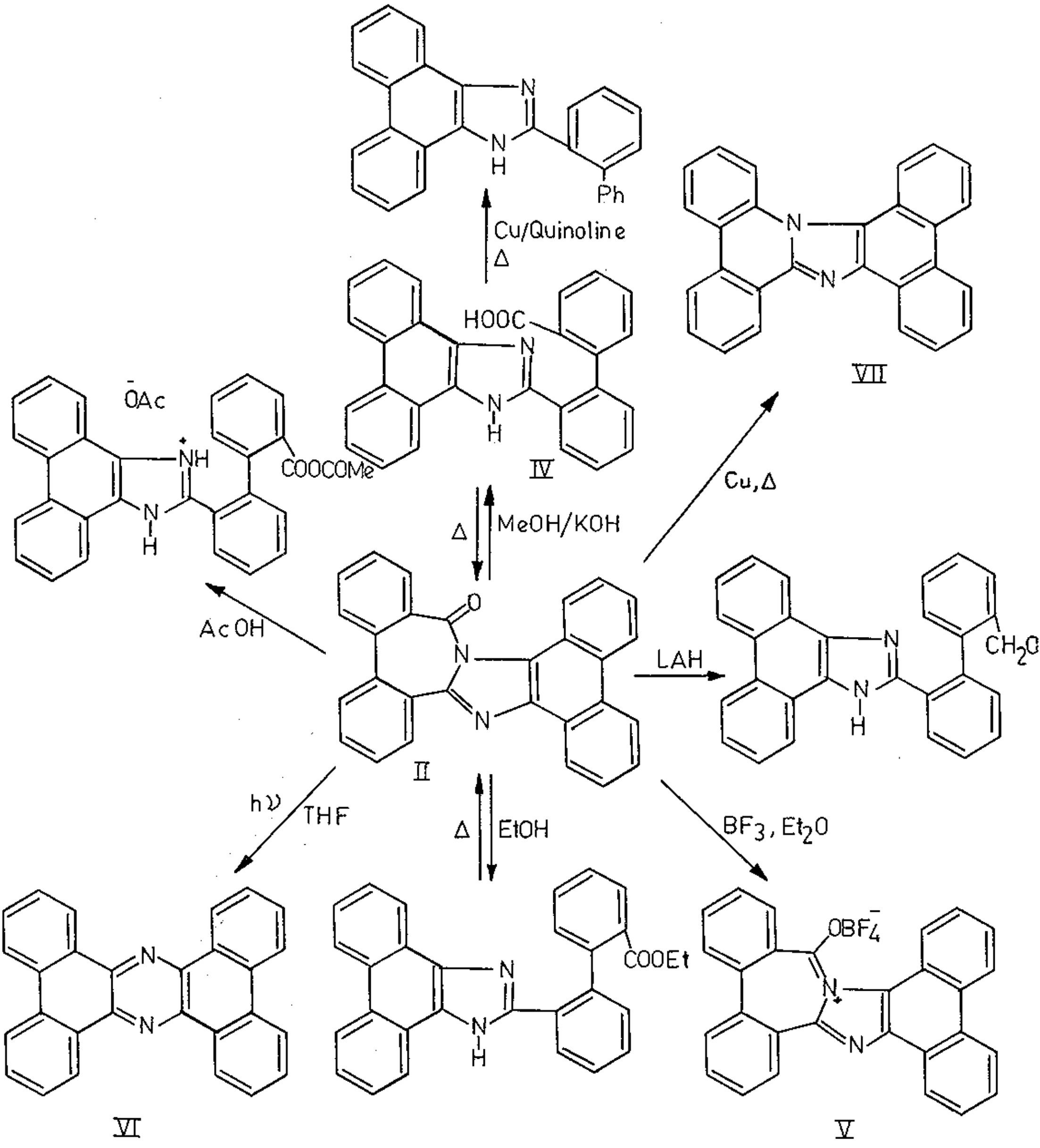


In media containing water the 1,5-shift of III can be superceded by a hydrolysis sequence leading to the acid IV:[9]

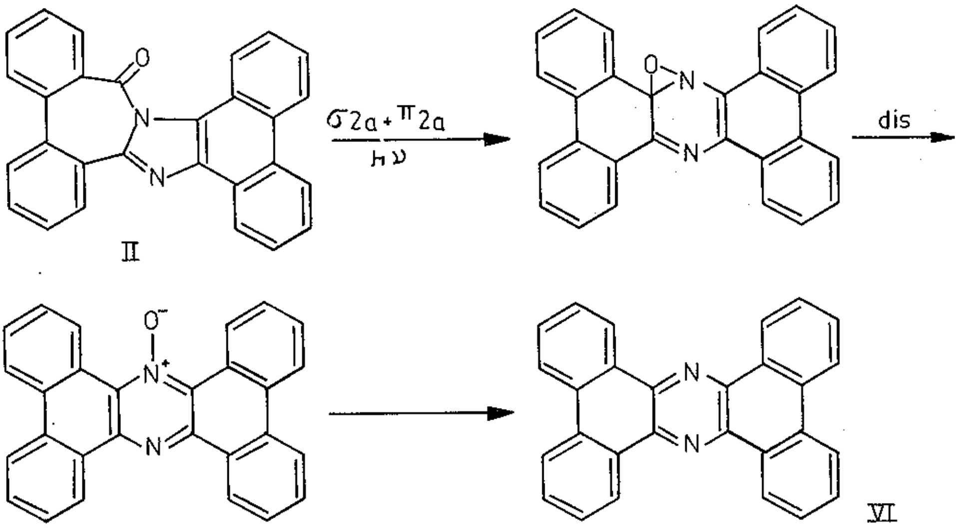


The most common reactions of PQIA involves the rupture of the amide function leading to imidazoles. Particular mention must be made relating to the formation of the aromatic systems V, VI and VII (Chart 2).

CHART II


N
N
H
Ph
Cu/Quinoline
Δ
HOOC
N
N
H
IV
N
N
VII
ŌAc
N̊H
N
H
COOCOMe
Δ
MeOH/KOH
Cu,Δ
AcOH
O
N
N
II
LAH
N
N
H
CH2OH
hν
THF
Δ
EtOH
BF3, Et2O
N
N
VI
N
N
H
COOEt
OBF4-
N+
N
V

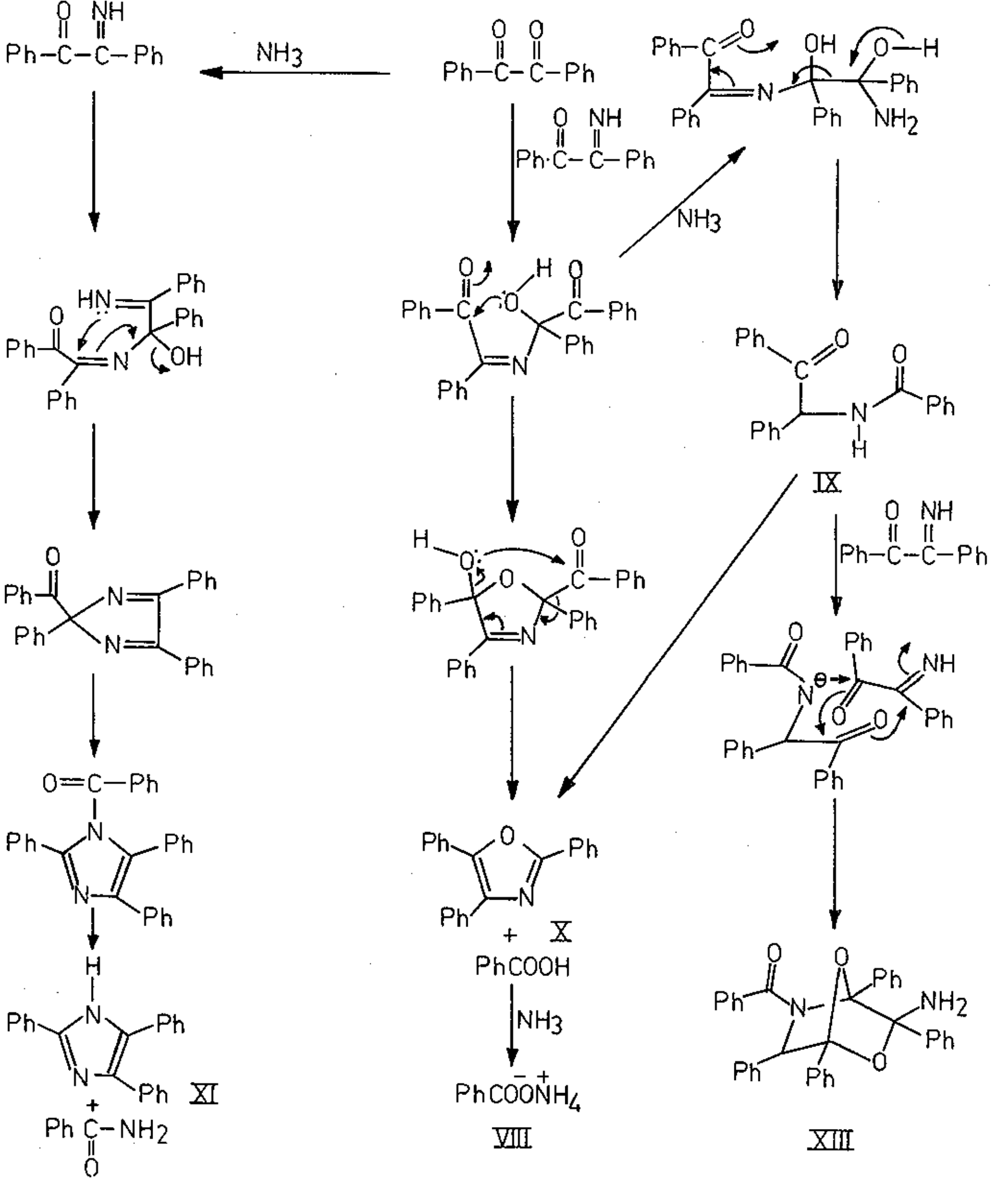
The PQIA → Tetrabenzopyrazine (VI) change is best rationalized on the basis of a $\sigma_{2a} + \pi_{2a}$ shift, dis-rotatory cyclization and oxygen loss.[10]

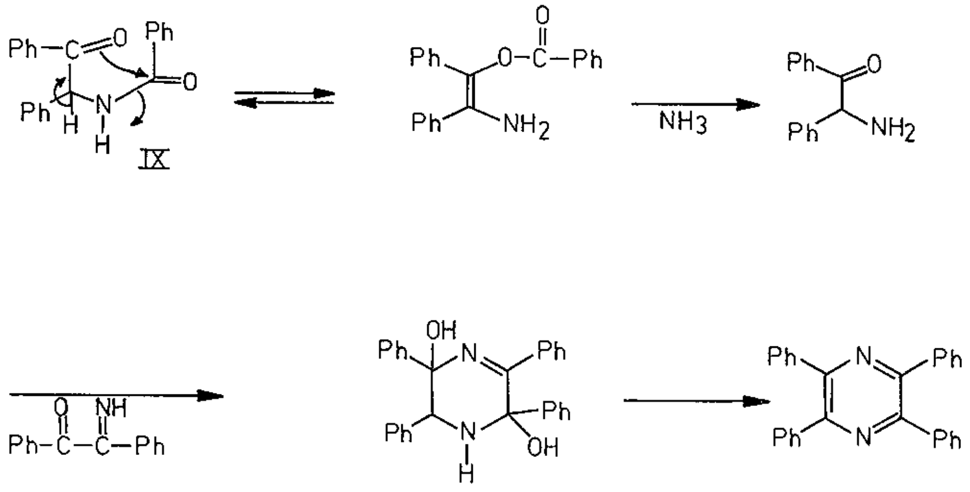


3. Phenanthraquinone Mono-imine (I)→PQIA Type Rearrangements

The rationalization of the I→PQIA change has provided a logical explanation to the formation of various types of imidazoles from 1,2-diketones, thereby demonstrating that the reaction is a general one involving as it does a facile 1,5-shift. Of particular interest is the much studied[11] and apparently trivial transformation of benzil with ammonia leading to ammonium benzoate (VIII), benzamidodesoxybenzoin (IX), triphenyl oxazole (X), triphenyl imidazole (XI), tetraphenylpyrazine (XII) and imabenzil (XIII), which we now rationalize on the basis of involvement of benzil mono-imine intermediate. The formation of the major product triphenyl imidazole (lophine) can be understood by a sequence similar to that involved in the I→PQIA change.

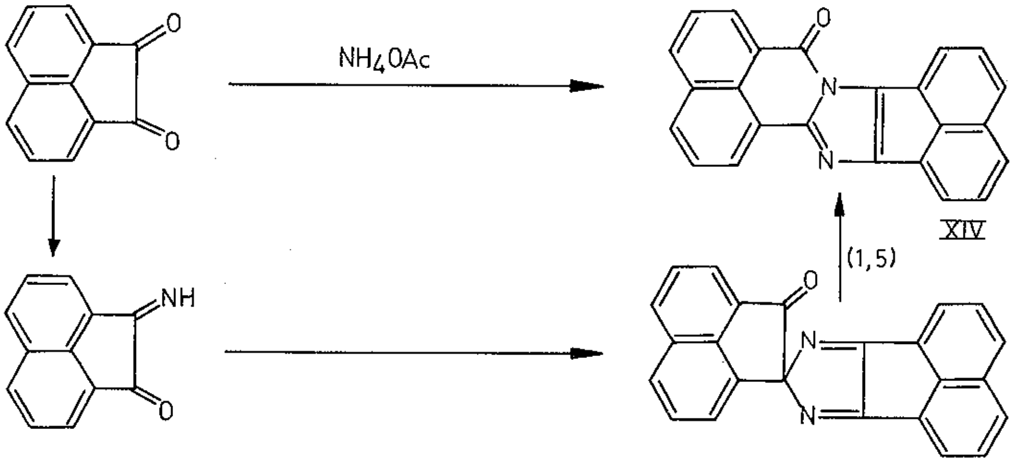
Triphenylimidazole (XI) can be obtained in a clean manner by treatment of benzil with ammmonium acetate in acetic acid.[12]





XII

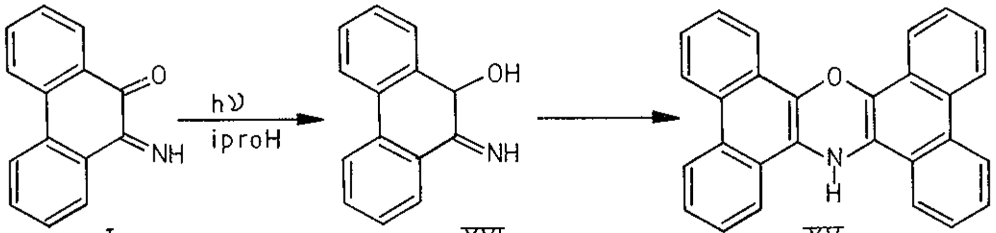
Recently it has been shown that acenaphthenequinone on thermolysis in presence of ammonium acetate is transformed to XIV[13] via pathways involved in the formation of PQIA.



XIV

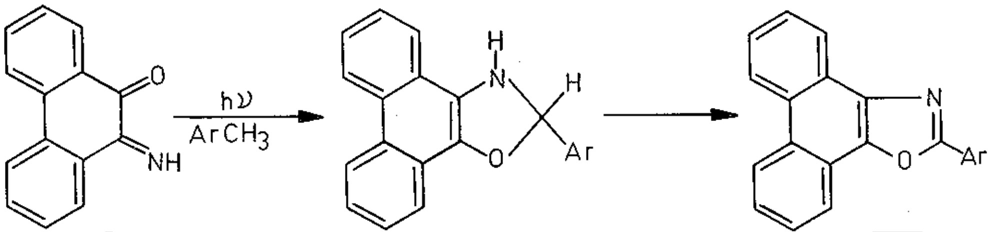
4. Aromatic Heterocyclic Systems from I and Other *in situ* Generated Quinone Monoimines

Phenanthraquinone monoimine undergoes on photolysis in isopropanol, reductive dimerization leading to the morpholine XV:[14]



I XVI XV

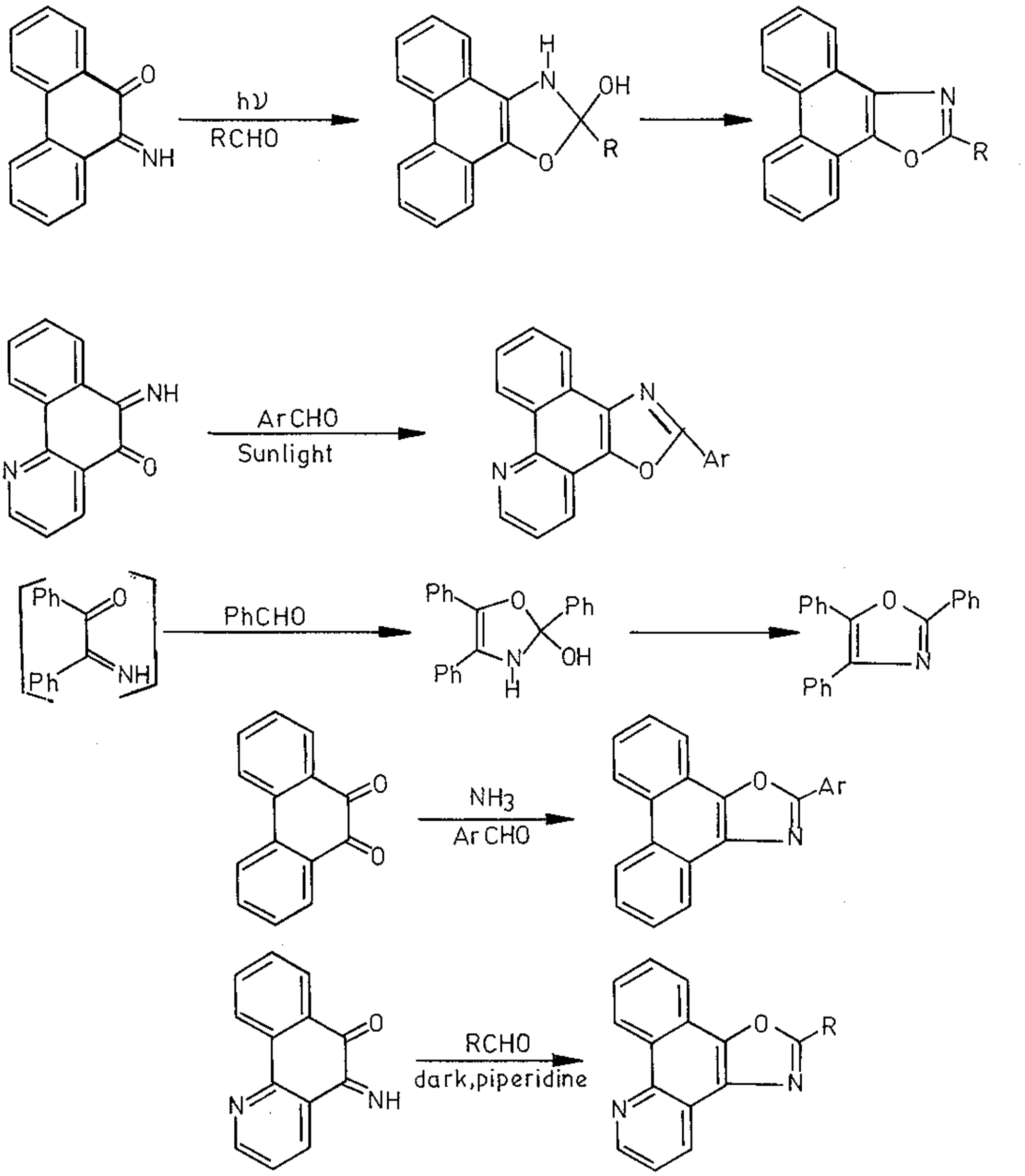
Phenanthraquinonemonoimine on photolysis in presence of substituted toluenes undergoes a remarkable change giving rise to the oxazoles[15] (XVII), necessarily involving extensive oxidation. It is believed that intermediates arising from homolytic scission of the aryl C-H bond are involved in this change:



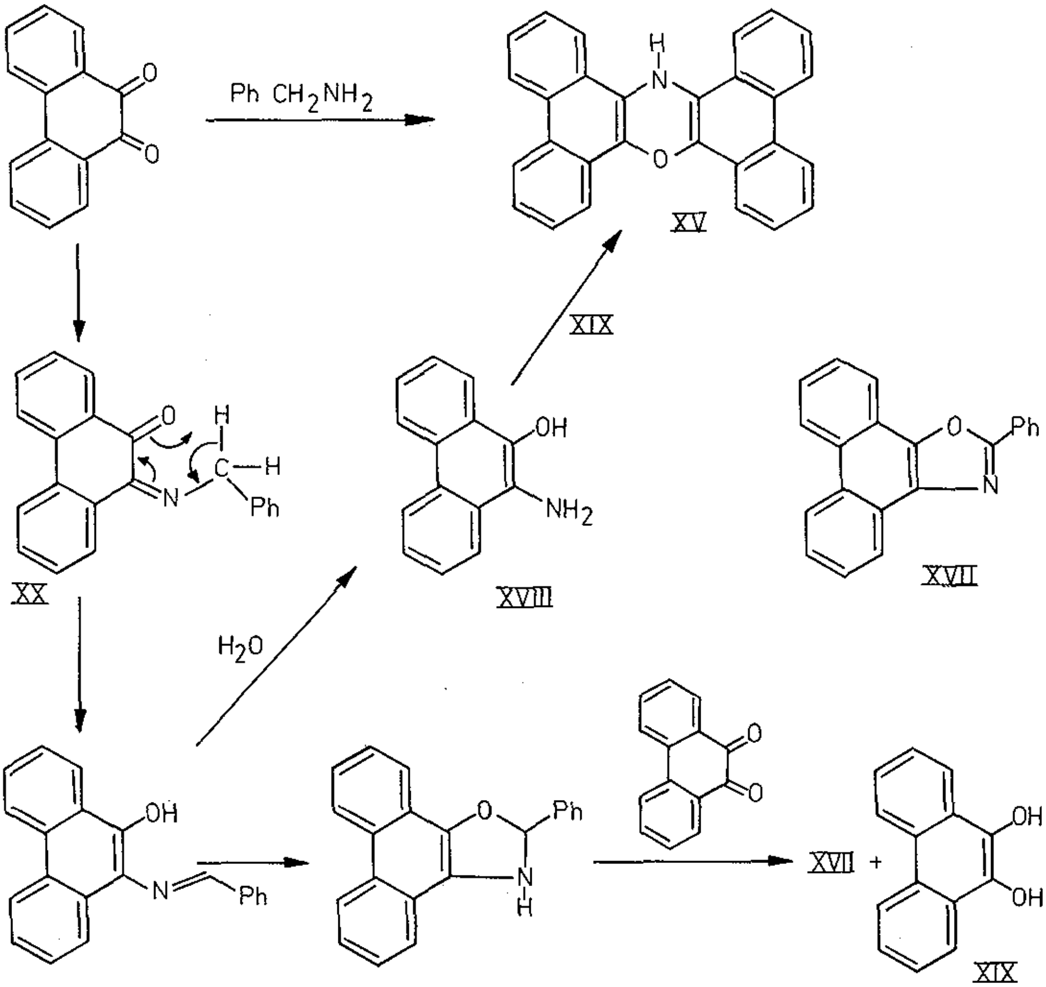
I XVII

Oxazoles are readily formed from quinone monoimines and aldehydes either photochemically or thermally[16-19] (Chart III).

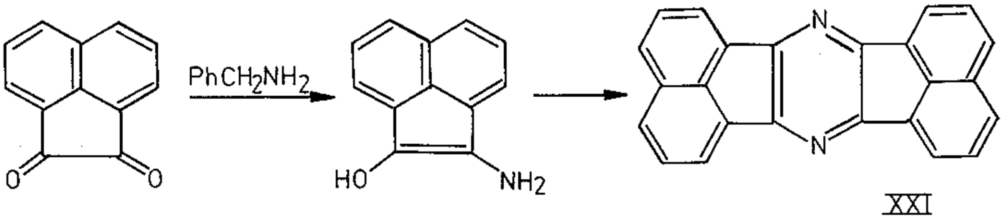
CHART III


O
NH
hν
RCHO
H
N
OH
O
R
N
O
R
NH
N
O
ArCHO
Sunlight
N
N
O
Ar
Ph
O
Ph
NH
PhCHO
Ph
O
Ph
Ph
N
H
OH
Ph
O
Ph
Ph
N
O
O
NH3
ArCHO
O
Ar
N
O
N
NH
RCHO
dark,piperidine
O
R
N
N

The apparently perplexing transformation of phenanthraquinone with benzylamine leading to XV, XVII (Ar=Ph), XVIII and XIX can now be rationalized on the basis of the quinonemonoimine intermediate XX.[20,21]

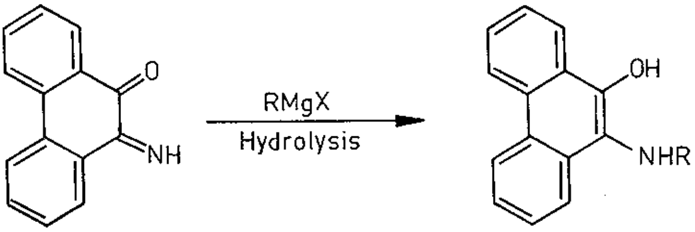


Interestingly in the reaction of acenaphthenequinone with benzylamine the intermediate related to XVIII undergoes dimerization leading to acenaphthazine XXI.[22]



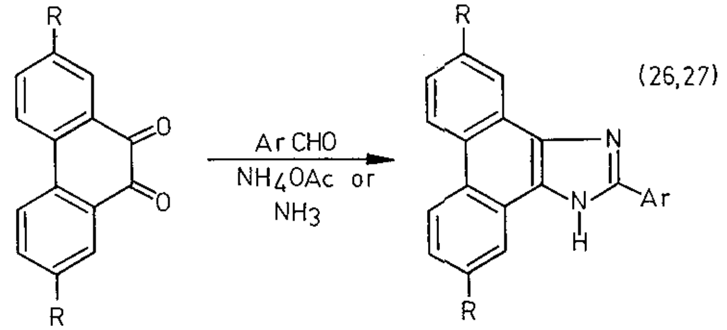
XXI

An unusual reaction of phenanthraquinone monoimine (I) is the addition of Grignard reagents which prefers a 1,4-path over the more rational 1,2-addition.[23]

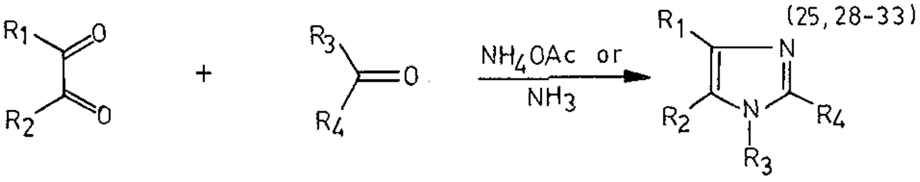


I

In contrast to the stable nature of I, attempts thus far to characterise the phenanthraquinone 9,10-diimine have not been successful. This could be attributed to the fact that the quinone-monoimines undergo transformations to products related to PQIA in preference to acceptance of another mole of ammonia.[24] Therefore, the transformation of phenanthrenequinone and other 1,2-diketones to imidazoles in presence of ammonia or ammonium salts - extensively used in the synthesis of imidazoles (vide infra) - currently believed to take place via quinone diimine intermediates[25,26] merit more detailed examination. It is quite possible that they take place involving the more established quinone monoimine intermediates.

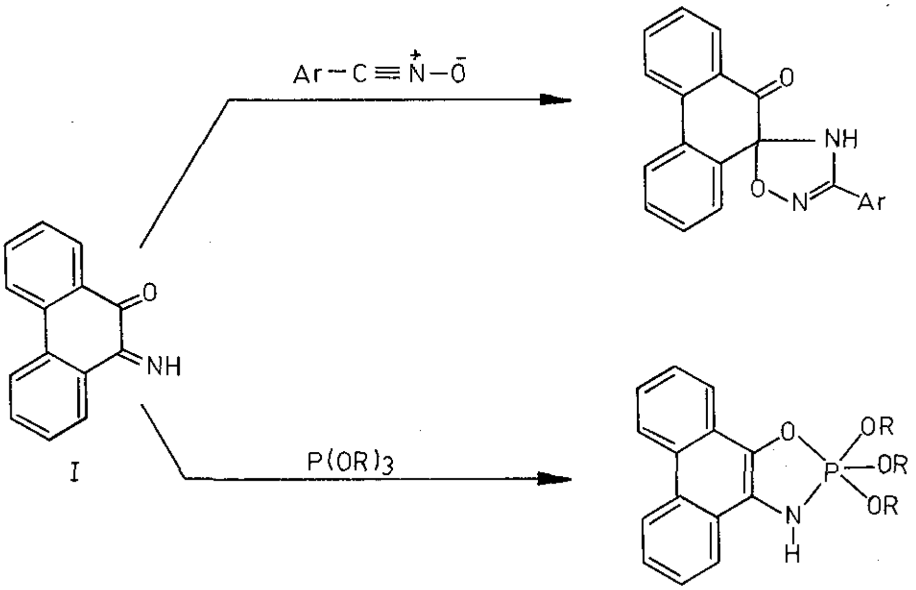


R= H ; R=Ph



5. Cycloaddition Reactions of 1,2-Diketone Monoimines

Unlike 1,2-diketones, (4+2) addition involving ketone monoimines have not been reported thus far. However, the possibilities in this area are exemplified by the following two unusual reactions of phenanthraquinone monoimine:[34,35]



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