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Reaction of Enamines with o-Ouinone Mononitrogenous Derivatives. Part (I)

by

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Reaction of Enamines with o-Ouinone Mononitrogenous Derivatives. Part (I)

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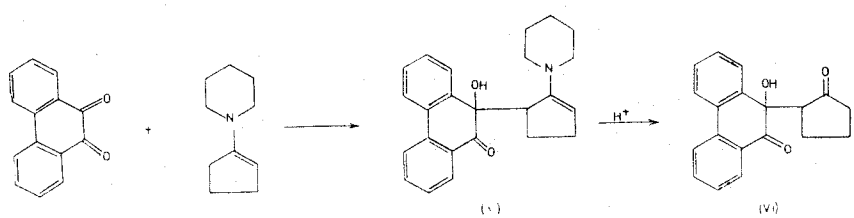
SUMMARY:

Phenanthrenequinoneimine reacts with piperidinocyclopentene, piperidinocyclohexene and morpholinocyclopentene to give (IIa-c). However, the reaction between phenantherenequinoneimine with morpholinocyclohexene yields (III). The structures of the products are discussed. Phenanthrenequinone mono-oxime reacts with piperidinocyclopentene, piperidinocyclohexene and morpholinocyclopentene to give (VIIa-c), and it reacts with morpholinocyclohexene to give (VIII).

In continuation to our previous work on enamines[1,2], it was interesting to carry out a study for the reaction of enamines with o-quinone mononitrogenous derivatives. As we reported before[1], phenanthrenequinone reacts with enamines to give p-dioxine derivatives except with piperidinocyclopentene which yields the open (1:1) addition product (I).



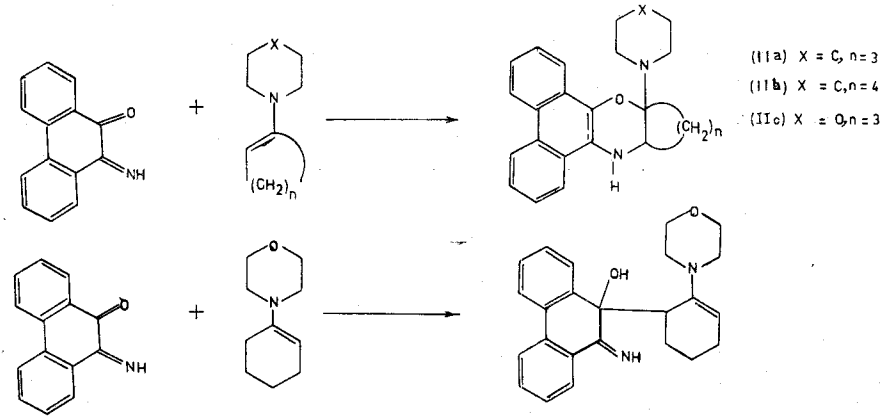
(I) (VI)

In view of the above observations, it was aimed to extend these studies on o-quinone derivatives.

Phenanthrenequinoneimine and phenanthrenequinone mono-oxime react with enamines to give different addition products depending upon the reactivity[3] of the enamine used. The reaction may proceed by

simple (1:1) addition[1,4], or it may proceed through (1:1) addition followed by cyclisation to give the cyclic product.

Phenanthrenequinoneimine reacts with piperidinocyclopentene, piperidinocyclohexene and morpholinocyclopentene to give cyclic products (IIa-c). However, morpholinocyclohexene yields (III), the open structure product.

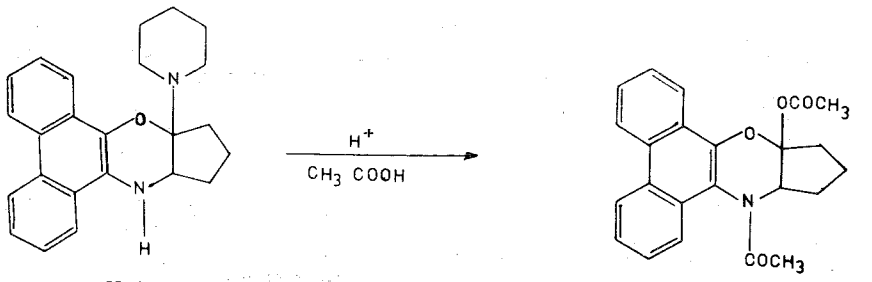


(III)

The structure of the cyclic form (IIa-c) was inferred from the following facts:

i) Analytical data (ii) The infrared spectra of the products are devoid from ν–OH.

(iii) Acid hydrolysis of (IIa) with acetic acid leads to the formation of (IV) and not the same product (VI) obtained from acid hydrolysis of (I).



(IIa) (IV)

The structure of (IV) was inferred from: i) analytical data, ii) Its infrared spectrum which shows νC=O at 1675 cm^{-1} and at 1700 cm^{-1}, iii) The electronic spectra of IIA-c bear clear resemblance which would suggest similarity of structure.

It should be noticed that if (IIa) has an open structure it would give upon hydrolysis the same compound as that of the corresponding phenanthrenequinone, i.e. (VI). This proved not to be the case.

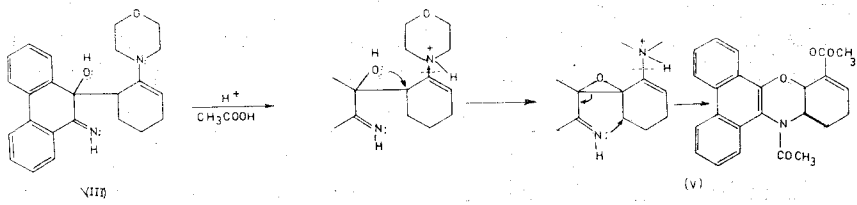
The structure of (VI) was inferred from analytical data, its i.r. spectrum which shows νC=O at 1670 cm^{-1} corresponding to carbonyl groups of quinones, νC=O at 1700 cm^{-1} of alicyclicketones and ν–OH at 3450 cm^{-1}.

On the other hand, in the reaction involving morpholinocyclohexene, the open structure (III) was more probable based on the following facts:

i) Its infrared spectrum shows sharp band at 3380 cm^{-1} characteristic of νOH, νNH_{imine} at 3080 cm^{-1} and ν C=C at 1625 cm^{-1}

ii) Its electronic spectrum is different from that of (IIa-c).

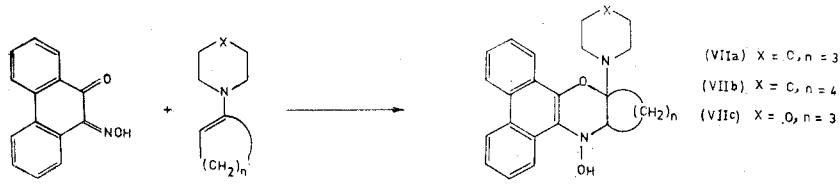
iii) Acid hydrolysis with acetic acid leads to the formation of (V). The reaction may proceed through the formation of epoxide as intermediate which rearranges to the cyclic structure (V). The epoxide rearrangement to oxazole was previously described[5].



(VIII) (V)

The structure of (V) was inferred from analytical data, from its .ir. spectrum which shows νC=O at 1675 cm^{-1} and from a study of its electronic spectrum which shows clear similarity with that of IV.

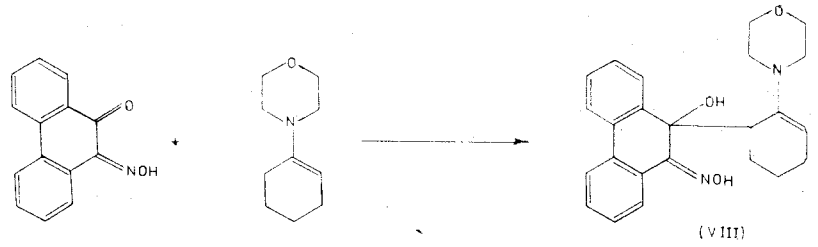
Phenanthrenequinone mono-oxime reacts with piperidinocyclopentene, piperidinocyclohexene and morpholinocyclopentene to give (VIIa-c),



The structure of (VIIa-c) was inferred from analytical data, from their i.r. and electronic spectra (cf. exp. part).

The infrared spectra of the products show νOH_{oxime} at 3070 cm^{-1}.

Phena nthrenequinone mono-oxime reacts with morpholinocyclohexene to give (VIII).



The structure of (VIII) was inferred from:

i) Analytical data.

ii) Its i.r. spectrum shows νOH at 3480 cm^{-1}, νOH_{oxime} 3070 cm^{-1} and ν C=C at 1625 cm^{-1}.

iii) The electronic spectrum of (VIII) is different from all the spectra of (VIIa-c) which bear a clear resemblance between themselves.

EXPERIMENTAL

All melting points are not corrected. Analyses were carried out in the Research Microanalytical Laboratory of Cairo University. I.r. spectra were measured on Perkin-Elmer 398 using KBr Wafer technique. Electronic spectra were carried out on Perkin-Elmer 555 U.V. Vis spectrophotometer.

Reaction between Enamines and phenanthrenequinone nitrogenous derivatives (phenanthrenequinone imine and phenanthrenequinone mono oxime), General procedure:

A mixture of enamine (0.02 mole) and nitrogenous quinone (0.01 mole) in benzene (150 ml) was refluxed for a couples of hours or left at room temperature for few days. The reaction mixture was concentrated at room temperature under reduced pressure. The product was solidified by trituration with methanol. The solid product was crystallised from a suitable solvent.

Reaction between phenanthrenequinoneimine and enamines to give (IIa,b,c).
(IIa) *The reaction mixture was left at room temperature for four days.* The solid product was crystallised from methanol to give greenish yellow crystal, m.p. 97°, yield 60 %.

$C_{24}H_{26}N_2O$ Calcd C, 80.44 H, 7.26 N, 7.82
Found C, 79.80 H, 6.70 N 7.70

U.V. absorption shows λ_{max} 372 nm (ε_{max} 3.2 x 10^3), λ_{max} 340 nm (ε_{max} 3.8 x 10^3) and λ_{max} 254 nm (ε_{max} 24.7 x 10^3) in acetonitrile.

(IIb) *The reaction mixture was refluxed for nine hours and left at room temperature for four days.*

The solid product was crystallised from benzene-pet. ether (b.p. 40–60°) mixture to give yellow crystals, m.p. 145°, yiled 65 %.

$C_{25}H_{28}N_2O$ Calcd N, 7.52
Found N, 7.60

U.V. absorption shows λ_{max} 377 nm (ε_{max} 5.9 x 10^3), λ_{max} 357 nm (ε_{max} 6.4 x 10^3) and λ_{max} 252 nm (ε_{max} 47.5 x 10^3) in acetonitrile.

(IIc) *The reaction mixture was left at room temperature for four days.* The solid product was crystallised from methanol to give buff crystals, m.p. 153°, yield 60 %.

$C_{23}H_{24}N_2O_2$ Calcd C, 76.66 H, 6.66 N, 7.77
Found C, 76.60 H, 6.30 N, 7.60

U.V. absorption shows λ_{max} 372 nm (ε_{max} 5.9 x 10^3), λ_{max} 340 nm (ε_{max} 8.3 x 10^3) and λ_{max} 254 nm (ε_{max} 53.9 x 10^3) in acetonitrile.

Reaction between phenanthrenequinoneimine and morpholinocyclohexene to give (III).

The reaction mixture was refluxed for five hours. The solid product was crystallised from benzene-pet. ether (b.p. 40–60°) mixture to give pale yellow crystals, m.p. 197°, yield 81 %.

$C_{24}H_{26}N_2O_2$	Cacld	C, 77.00	H, 6.95	N, 7.48
	Found	C, 76.70	H, 6.50	N, 7.00

U.V. absorption shows λ_{max} 330 nm (ε_{max} 7.7 x 10^3) and λ_{max} 253 nm (ε_{max} 34.1 x 10^3) in acetonitrile.

I.r. νOH at 3380 cm^{-1}, νNH_{imine} at 3080 cm^{-1} and νC=C at 1625 cm^{-1}.

Reaction between phenanthrenequinone mono-oxime and enamines to give (VIIa-c).

(*VIIa*) The reaction mixture was refluxed for two hours. The solid product was crystallised from benzene-pet. ether (b.p. 40–60°) mixture to give brown crystals, m.p. 175°, yield 60 %.

$C_{24}H_{26}N_2O_2$	Calcd	C, 77.00	H, 6.95	N, 7.48
	Found	C, 77.10	H, 7.00	N, 7.80

U.V. absorption shows λ_{max} 252 nm (ε_{max} 31.7 x 10^3) in acetonitrile.

(*VIIb*) The reaction mixture was refluxed for four hours and left at room temperature overnight. The solid product was crystallised from benzene-pet. ether (b.p. 40-60°) mixture to give brown crystals, m.p. 235°, yield 55 %.

$C_{25}H_{28}N_2O_2$	Calcd	C, 77.31	H, 7.21	N, 7.21
	Found	C, 77.30	H, 7.20	N, 6.80

U.V. absorption shows λ_{max} 250 nm (ε_{max} 23.4 x 10^3) in acetonitrile.

(*VIIc*) The reaction mixture was freluxed for three hours and left at room temperature overnight. The solid product was crystallised from benzene-pet. ether (b.p. 40–60°) mixture to give brown crystals, m.p. 245°, yield 52 %.

$C_{23}H_{24}N_2O_3$	Calcd	C, 73.40	H, 6.38	N, 7.44
	Found	C, 72.90	H, 5.90	N, 7.94

U.V. absorption shows λ_{max} 255 nm (ε_{max} 30.3 x 10^3) in acetonitrile.

Reaction between phenanthrenequinone mono-oxime and morpholinocyclohexene to give (VIII)

The reaction mixture was refluxed for eight hours and left overnight at room temperature. The solid product was crystallised from methanol to give yellow crystals, m.p. 205°, yield 65 %.

$C_{24}H_{26}N_2O_3$ Calcd N, 7.17

Found N, 7.04

U.V. absorption shows λ_{max} 225 nm (ε_{max} 42.5 x 10^3), λ_{max} 258 (ε_{max} 50.3 x 10^3) and λ_{max} 330 nm (ε_{max} 12.4 x 10^3) in acetonitrile.

I.r. ν OH at 3480 cm^{-1}, and νC=C at 1625 cm^{-1}

Acid hyrolysis

(0.3 gm) of the substance in (30 ml) acetic acid was refluxed for 30 mins. The solid product was filtered off and crystallised from the suitable solvent.

Hydrolysis of IIa *to give* (IV)

Brown crystals from benzene-methanol mixture, m.p. 160°, yield 50 %.

$C_{23}H_{21}NO_4$ Calcd C, 73.60 H, 5.60 N, 3.7

Found C, 74.00 H, 5.50 N, 3.0

U.V. absorption shows λ_{max} 248 nm (ε_{max} 24.0 x 10^3), λ_{max} 256 nm (ε_{max} 24.0 x 10^3) and λ_{max} 310 nm (ε_{max} 5.8 x 10^3).

I.r. νC=O at 1700 cm^{-1} and at 1735 cm^{-1}.

Hydrolysis of (III) *to give* (V)

Brown crystals from benzene-methanol mixture m.p. 250°, yield 47 %

$C_{24}H_{21}NO_4$ Calcd C, 74.41 H, 5.42

Found C, 74.40 H, 5.50

U.V. absorption shows λ_{max} 248 (ε_{max} 65 x 10^3), λ_{max} 255.5 nm (ε_{max} 65 x 10^3) and λ_{max} 309 nm (ε_{max} 8.8 x 10^3).

I.r. νC=O at 1675 cm^{-1}.

Hydrolysis of (I) *to give* (VI)

(0.3 gm) of the substance in (25 ml) dilute HCl was refluxed for five mins. The reaction mixture was extracted with ether. The ethereal

layer was separated, washed with water, dried (Na_2SO_4) and solvent removed. The product thus obtained was crystallised from benzene-methanol mixture to give orange crystals m.p. 165°, yield 50 %.

$C_{19}H_{16}O_3$	Calcd	C, 78.08	H, 5.47
	Found	C, 77.40	H, 4.90

U.V. absorption shows λ_{max} 252 nm (ε_{max} 48.3 x 10^3) and λ_{max} 310 nm (ε_{max} 8.8 x 10^3).

I.r. ν C=O at 1670 cm^{-1}, and ν OH at 3450 cm^{-1}

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