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by

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24

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## Reaction of Enamines With Quinones

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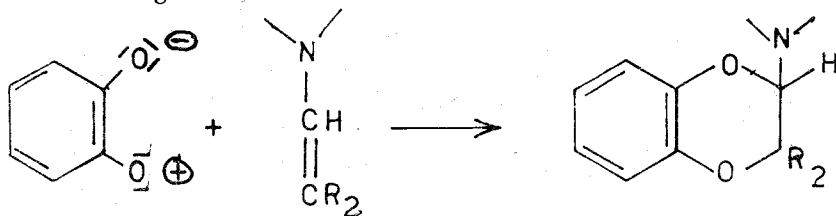
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### ABSTRACT

Phenanthrenequinone reacts with morpholinocyclopentene piperidinocyclohexene, morpholinocyclohexene and piperidinocyclopentene to give p-dioxine derivatives (IIa-d), while at room temperature only piperidinocyclopentene reacts with phenanthrenequinone to give (III). Chrysenequinone reacts with piperidinocyclopentene, morpholinocyclopentene, piperidinocyclohexene and morpholinocyclohexene to give (IVa-d) and not p-dioxine derivatives as reported before<sup>1</sup>. p-Benzoquinone reacts with morpholinocyclopentene to give (V) while p-benzoquinone reacts with piperidinocyclohexene and morpholinocyclohexene to give (VIa & b).

The reaction between some o-quinones and enamines was reported by Ried and Torok<sup>1,2</sup> to give p-dioxines (I) at 0° to -20°C according to the following mechanism.

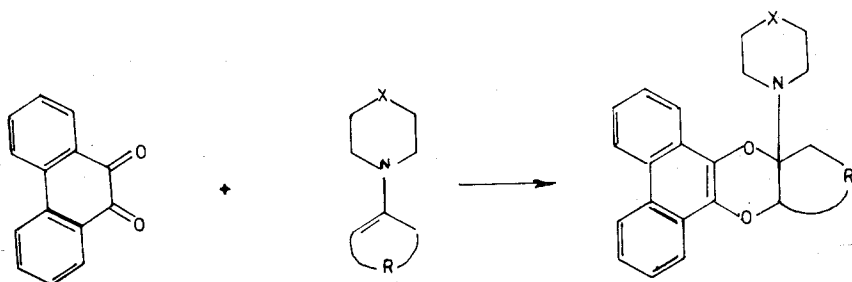


(I)

The structure of the p-dioxine products are inferred from i) analytical data (mainly carbon and hydrogen only) ii) Their infrared and N.M.R. spectra.

We reported here that phenanthrenequinone in contrast to Ried et al<sup>1,2</sup> failed to react at 0°C or even at room temperature (~25°C) when left for 24 hours. Only the starting materials were recovered unchanged.

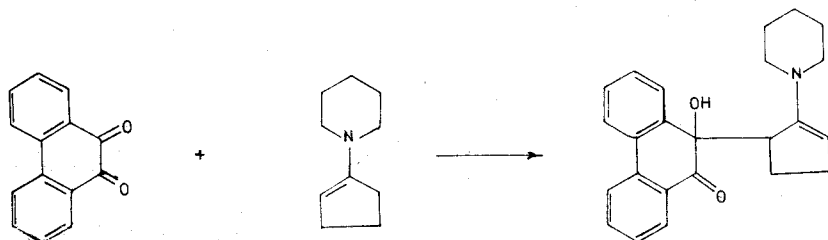
However, phenanthrenequinone reacts with morpholinocyclopentene, morpholinocyclohexene, piperidinocyclopentene and piperidinocyclohexene after the reaction mixture was refluxed for few hours to give p-dioxine derivative (II) with melting points identical with (Lit)<sup>1,2</sup> except the melting point of morpholinocyclopentene (cf. expt. part). The structure of these products are inferred from i) analytical data ii) Their infrared and U.V. spectra.



(II)

- |   |       |
|---|-------|
| a) R = -CH <sub>2</sub> CH <sub>2</sub> - | X = 0 |
| b) R = (-CH <sub>2</sub> ) <sub>3</sub>   | X = C |
| c) R = (-CH <sub>2</sub> ) <sub>3</sub>   | X = 0 |
| d) R = -CH <sub>2</sub> CH <sub>2</sub> - | X = C |

Phenanthrenequinone reacts with piperidinocyclopentene (only) under the same condition of the reaction but at room temperature to give (1:1) addition product (III) mainly and (IIc) in very poor yield<sup>3</sup>. The structure of (III) is inferred from i) analytical data ii) Their infrared and U.V. spectra.



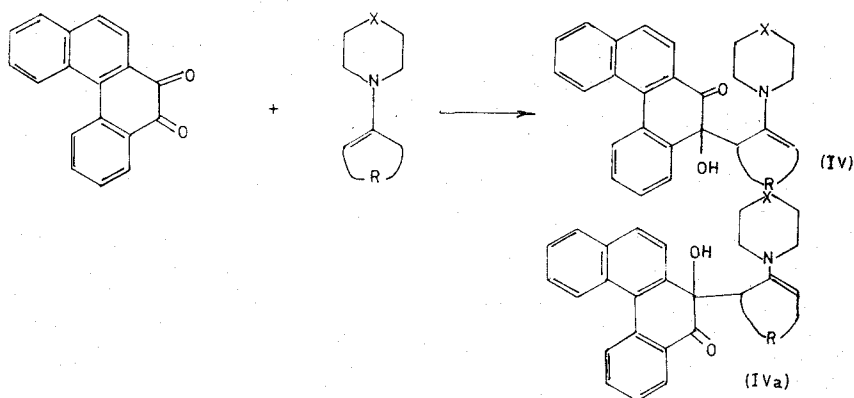
(III)

This behaviour of piperidinocyclopentene could be due to the high reactivity of this enamine as compared with the other ones<sup>3</sup>. This type of addition is similar to the addition of chloralhydrate to enamines<sup>4</sup>.

It could be concluded that the product formed at room temperature (viz III) could be a sort of intermediate stage to the one formed at higher temperature (viz II).

Also Ried and Torok<sup>1,2</sup> reported that chrysenequinone reacts with morpholinocyclohexene and piperidinocyclohexene to give p-dioxine derivatives similar to their claimed work on phenanthrenequinone<sup>1,2</sup>.

We here report that chrysenequinone fails to react with enamines under the condition reported before<sup>1,2</sup>, but it reacts after the reaction mixture is refluxed for (2-12) hours to give (IV) and not p-dioxine derivatives as previously claimed<sup>1,2</sup>. The following mechanism is proposed.

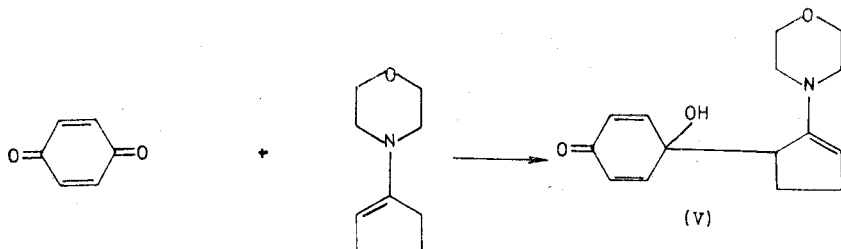


- |   |       |
|---|-------|
| a) R = -CH <sub>2</sub> CH <sub>2</sub> -                 | X = C |
| b) R = -CH <sub>2</sub> CH <sub>2</sub> -                 | X = O |
| c) R = -CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> - | X = C |
| d) R = -CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> - | X = O |

The structure of (IV) is inferred, other than from analytical data, from a study of their infrared spectra which show the carbonyl and hydroxyl (OH) stretching frequencies (cf. expt. part).

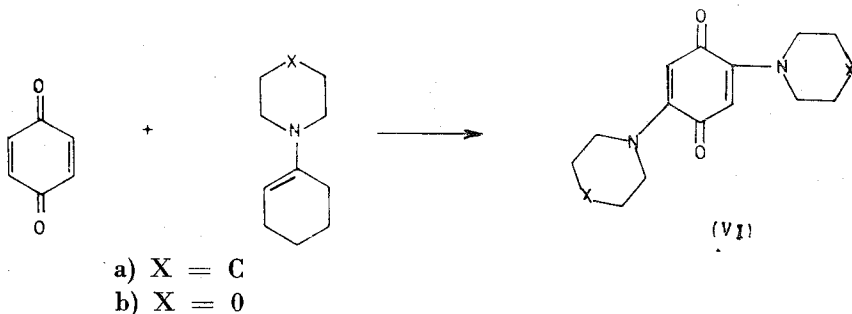
It is to be mentioned that chrysenequinone is more reactive than phenanthrenequinone<sup>5</sup>. Furthermore, one of the carbonyl groups in chrysenequinone is more reactive than the other<sup>6</sup> and that is the reason for the proposed structure (IV) and not (IVa).

During the course of this work interesting data are obtained when the reaction between *p*-benzoquinone and enamines is investigated. *p*-Benzoquinone reacts with morpholinocyclopentene at room temperature to give (1:1) addition product (V).



The structure of (V) is inferred, other than analytical data, from i.r.  $\nu_{OH}$  (at  $3320\text{ cm}^{-1}$ ) and  $\nu_{C=O}$  (at  $1630\text{ cm}^{-1}$ ) in its infrared spectrum.

However, the interaction between *p*-benzoquinone with piperidino cyclohexene and morpholinocyclohexene, proceeds in a different way and no (1:1) addition product is isolated. The products (VIa & b) contains nitrogen (cf. expt. part). It proved to be 2,5 - dipiperidylbenzoquinone and 2,5 - dimorpholino benzoquinone, respectively by melting and mixed melting point with an authentic specimen<sup>7</sup>. It seems that these two enamines decompose under the reaction conditions and the negatively charged divalent nitrogen attacks at the 2- and 5- positions of the quinone with the subsequent extraction of the proton from the reaction medium followed by oxidation. These two products were also obtained from the reaction of piperidine and morpholine with *p*-benzoquinone



## EXPERIMENTAL

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

*Reaction between phenanthrenequinone and piperidinocyclopentene*

A mixture of enamine (.02 moles) and phenanthrenequinone (0.01 mole) in (50 ml) benzene was left overnight in a refrigerator. The reaction mixture was concentrated at room temperature. The oily product obtained was dissolved in methanol and left overnight. The solid product was filtered off and crystallised from benzene to give (III) as colourless crystals m.p. 193–7°C, yield 80 %.

$C_{24}H_{25}NO_2$	Calcd	C	80.22	H	6.9	N	3.89
	Found	C	80.3	H	6.5	N	3.90

I.r.  $\nu_{OH}$  at  $3480\text{ cm}^{-1}$ ,  $\nu_{C=O}$  at  $1740\text{ cm}^{-1}$

U.V. shows  $\lambda_{max}$  250 nm ( $\epsilon_{max} = 33.107 \times 10^3$ ),  $\lambda_{max}$  272 nm ( $\epsilon_{max} = 8.6 \times 10^3$ ) and  $\lambda_{max}$  313 nm ( $\epsilon_{max} = 3.31 \times 10^3$ ) in acetonitrile.

*Reaction between phenanthrenequinone and enamines to give (II a-d)*

A mixture of enamine (0.02 moles) and phenanthrenequinone (0.01 mole) in (100 ml) benzene was refluxed for 6 hours and left at room temperature for one day, the reaction mixture was concentrated at room temperature, the solid product was filtered off and crystallised from petroleum (b.p. 100–120°C) to give (II).

(IIa) U.V. absorption shows  $\lambda_{max}$  258 nm ( $\epsilon_{max} 48.49 \times 10^3$ ),

$\lambda_{max}$  302 nm ( $\epsilon_{max} 9 \times 10^3$ ) and  $\lambda_{max}$  317 nm ( $\epsilon_{max} 9.49 \times 10^3$ ) in acetonitrile, m.p. 144–5° (Lit 188°)<sup>1</sup> yield 23 %

$C_{23}H_{23}NO_3$	Calcd	C	76.45	H	6.37	N	3.87
	Found	C	76.57	H	6.18	N	3.80

(IIb) U.V. absorption shows  $\lambda_{max}$  251 nm ( $\epsilon_{max} 51.8 \times 10^3$ ),  $\lambda_{max}$  300 nm ( $\epsilon_{max} 9.324 \times 10^3$ ) and  $\lambda_{max}$  317 nm ( $\epsilon_{max} 9.8 \times 10^3$ ) in acetonitrile, m.p. 156° (Lit. m.p. 156°)<sup>1</sup>, yield 27 %

$C_{25}H_{27}NO_2$	Calcd	C	80.42	H	7.23	N	3.75
	Found	C	80.26	H	7.03	N	3.71

(IIc) U.V. absorption shows  $\lambda_{max}$  255 nm ( $\epsilon_{max}$   $49.78 \times 10^3$ ),  $\lambda_{max}$  302 nm ( $\epsilon_{max}$   $9.051 \times 10^3$ ) and  $\lambda_{max}$  317 nm ( $\epsilon_{max}$   $9.69 \times 10^3$ ) in acetonitrile, m.p. 168–170° (Lit, m.p. 166°)<sup>1</sup>

(lit, m.p. 171°)<sup>2</sup> yield 27 %

$C_{24}H_{25}NO_3$	Calcd	C	76.80	H	6.66	N	3.73
	Found	C	77.06	H	6.65	N	4.04

(IIId) U.V. absorption shows  $\lambda_{max}$  250 nm ( $\epsilon_{max}$   $33.107 \times 10^3$ ),  $\lambda_{max}$  272 nm ( $\epsilon_{max}$   $8.608 \times 10^3$ ) and  $\lambda_{max}$  313 nm ( $\epsilon_{max}$   $3.31 \times 10^3$ ) in acetonitrile, m.p. 190° (darkness), yield 25 %

$C_{24}H_{25}NO_2$	Calcd	N	3.8
	Found	N	3.3

*Reaction between chrysenequinone and enamines to give (IV)*

A mixture of enamine (0.02 moles) and chrysenequinone (0.01 mole) in (150 ml) benzene was refluxed (1 hour) and left at room temperature, a brown oil is obtained which solidified when triturated with methanol, the solid product was filtered off and crystallised from petroleum ether (b.p. 100–120°) to give (IV).

(IVa) U.V. absorption shows  $\lambda_{max}$  264 nm ( $\epsilon_{max}$   $76.1 \times 10^3$ ),  $\lambda_{max}$  320 nm ( $\epsilon_{max}$   $11.809 \times 10^3$ ) and  $\lambda_{max}$  340 nm ( $\epsilon_{max}$   $11.809 \times 10^3$ ) in acetonitrile, m.p. 195°, yield 60 %

$C_{28}H_{27}NO_2$	Calcd	N	3.42
	Found	N	3.80

I.r.  $\nu_{OH}$  at 3445  $cm^{-1}$ ,  $\nu_{C=O}$  at 1690  $cm^{-1}$

(IVb) *The reaction mixture was refluxed for two hours*

U.V. absorption shows  $\lambda_{max}$  268 nm ( $\epsilon_{max}$   $39.558 \times 10^3$ ),  $\lambda_{max}$  320 nm ( $\epsilon_{max}$   $6.473 \times 10^3$ ) and  $\lambda_{max}$  335 nm ( $\epsilon_{max}$   $6.473 \times 10^3$ ) in acetonitrile, m.p. 117°, yield 65 %

$C_{27}H_{25}NO_3$	Calcd	C	78.83	H	6.0	N	3.4
	Found	C	78.40	H	6.0	N	3.5

I.r.  $\nu_{OH}$  at 3450  $cm^{-1}$ ,  $\nu_{C=O}$  at 1690  $cm^{-1}$



(IVc) *The reaction mixture was refluxed for 12 hours.*

U.V. absorption shows  $\lambda_{\max}$  271 nm ( $\epsilon_{\max}$   $65.141 \times 10^3$ ),  $\lambda_{\max}$  320 nm ( $\epsilon_{\max}$   $11.942 \times 10^3$ ) and  $\lambda_{\max}$  336 nm ( $\epsilon_{\max}$   $13.028 \times 10^3$ ) in acetonitrile, m.p.  $136^\circ$ , (Lit,  $146^\circ$ )<sup>2</sup>, yield 55 %

$C_{29}H_{29}NO_2$	Calcd	C	82.26	H	6.87	N	3.3
	Found	C	82.50	H	6.70	N	2.90

I.r.  $\nu_{OH}$  at  $3445\text{ cm}^{-1}$ ,  $\nu_{C=O}$  at  $1690\text{ cm}^{-1}$

(IV)d *The reaction mixture was refluxed for 12 hours.*

U.V. absorption shows  $\lambda_{\max}$  270 nm ( $\epsilon_{\max}$   $44.27 \times 10^3$ ),  $\lambda_{\max}$  320 nm ( $\epsilon_{\max}$   $8.854 \times 10^3$ ) and  $\lambda_{\max}$  335 nm ( $\epsilon_{\max}$   $7.968 \times 10^3$ ) in acetonitrile, m.p.  $151^\circ$ , (Lit,  $181-2^\circ$ )<sup>2</sup>, (Lit,  $175-6^\circ$ )<sup>1</sup>, Yield 48 %.

$C_{28}H_{27}NO_3$	Calcd	N	3.29
	Found	N	3.7

I. r.  $\nu_{OH}$  at  $3450\text{ cm}^{-1}$ ,  $\nu_{C=O}$  at  $1690\text{ cm}^{-1}$

#### *Reaction between p-benzoquinone and enamines*

A mixture of enamine (0.02 moles) and p-benzoquinone (0.01 mole) in (100 ml) benzene was left for one day at room temperature, the reaction solution was concentrated at room temperature, the solid product was filtered off and crystallised to give (V).

(V) Pale yellow crystals from benzene, m.p.  $193^\circ\text{C}$ , yield 76 %

$C_{15}H_{19}NO_3$	Calcd	C	68.96	H	7.27	N	5.36
	Found	C	68.80	H	7.20	N	5.00

I.r.  $\nu_{OH}$  at  $3320\text{ cm}^{-1}$ ,  $\nu_{C=O}$  at  $1630\text{ cm}^{-1}$

(VIa) Violet crystals from petroleum ether (b.p.  $100-120^\circ$ ) m.p.  $177^\circ\text{C}$  (lit.  $177^\circ$ )<sup>5</sup>, yield 70 %

$C_{16}H_{22}N_2O_2$	Calcd	C	70.07	H	8.02	N	10.21
	Found	C	70.10	H	8.36	N	10.54

I.r.  $\nu_{C=O}$  at  $1620\text{ cm}^{-1}$

(VIb) Red crystals from benzene, m.p. 238° (Lit 246-7°)<sup>7</sup>, yield 75%.

$C_{14}H_{18}N_2O_4$	Calcd	C	60.43	H	6.47	N	10.07
	Found	C	59.75	H	6.56	N	9.87

I.r.  $\nu_{C=O}$  at 1630  $cm^{-1}$ .

*Reaction between p-benzoquinone and secondary amine*

A mixture of secondary amine (0.02 mole) and p-benzoquinone (0.01 mole) in (100 ml) benzene was left for one day at room temperature, the reaction solution was concentrated, filtered off and crystallised the solid product to give (VI).

(VIa) Violet crystals from petroleum ether (b.p. 100-120°) m.p. 177°C, yield % 80.

(VIb) Red crystals from benzene m.p. 238°C, yield 85 %.

REFERENCES

- [1] W. Ried and E. Torok, Naturwissens, 51 Part II, 265 (1964).
- [2] W. Ried and E. Torok, Ann. Chem., 687, 187-90 (1965).
- [3] G. Stork, A. Brizzolare, H. Landesman, J. Szmuzkoviez and R. Terrell, J. Amer. Chem. Soc., 85, 207-222 (1963).
- [4] C. Noldle and S.O. Lawesson, J. Soc. Chim. Belg. 86 / no 4 / (1977).
- [5] W.I. Awad and A.R. Abdel Raouf, J. Amer. Chem. Soc., 77, 3913 (1955).
- [6] W.I. Awad and A.R. Abdel Raouf, J. Org. Chem., 23, 282 (1958).
- [7] A.N. Makarova and A. ya. Berlin-Zhur obshechi Khim. 29, 666-72 (1959).