

Some Reactions of Enamines

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Summary: Tetrabromo-*o*-benzoquinone reacts with 1-(cyclopentenyl) piperidine and 1-(1-cyclohexenyl) piperidine to give the open (1:1) adduct (Ia,b) or (I'a,b), whereas it reacts with 4-(1-cyclopentenyl) morpholine to give the open (1:1) addition product (Ic or I'c) together with the cyclic (1:1) addition product (IIa or II'a). However, it reacts with 4-(1-cyclohexenyl) morpholine to give the cyclic (1:1) addition product (IIb or II'b).

Chloranil reacts with 4-(1-cyclopentenyl) morpholine and 1-(1-cyclohexenyl) morpholine to give the open (1:1) adduct (IIIa,b or III'a,b).

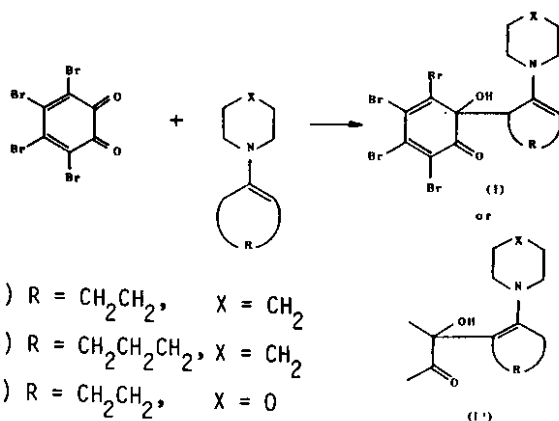
1,4-Naphthoquinone reacts with 4-(1-cyclopentenyl) morpholine to give IV in which the addition involves the C=O group, whereas it reacts with 1-(1-cyclohexenyl) morpholine to give V in which the (1:1) addition involves the C=C group. Finally, maleic anhydride reacts with 4-(1-cyclopentenyl) morpholine, 4-(1-cyclohexenyl) morpholine and 1-(1-cyclohexenyl) piperidine to give (VIa,b).

It is interesting to extend our previous work on enamines [1-4] to the study of the reaction between tetrabromo-*o*-benzoquinone, chloroanil, 1,4-naphthoquinone and maleic anhydride.

Results and Discussion

Tetrabromo-*o*-benzoquinone reacts with 1-(1-cyclopentenyl) piperidine and 1-(1-cyclohexenyl) piperidine to give the open (1:1) addition products (Ia,b or I'a,b).

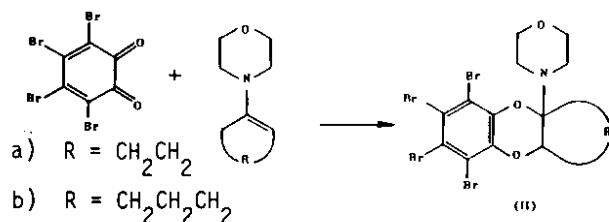
The structures of (Ia,b,c) are established from: i) Analytical data ii) Their IR spectra show $\nu_{C=O}$ at 1690 cm^{-1} and ν_{OH} at 3425 cm^{-1} iii)



Their electronic spectra show clear resemblance among themselves.

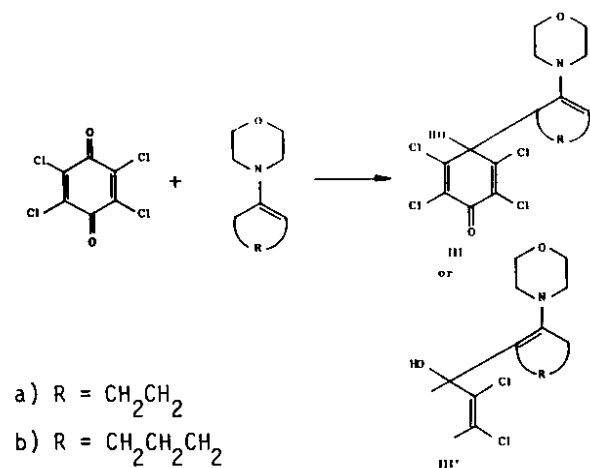
It was reported [5,6] before that 4-(1-cyclopentenyl) morpholine and 4-(1-cyclohexenyl) morpholine react with tetrabromo-*o*-benzoquinone to give the cyclic (1:1) addition product (IIa,b). In contrast to Ried and Torok [5,6] we isolated both the open adduct (Ic) besides the cyclic adduct (IIb) in case of cyclopentenyl morpholine. We confirm the previous finding [5,6] in case of 4-(1-cyclohexenyl) morpholine where only the cyclic product is obtained.

The structures of (IIa,b) are established from: i) Identity of melting point with lit. [5] ii) I.r. spectra are devoid of $\nu_{C=O}$.



It could be concluded that the open product could be a sort of intermediate stage to the cyclic one.

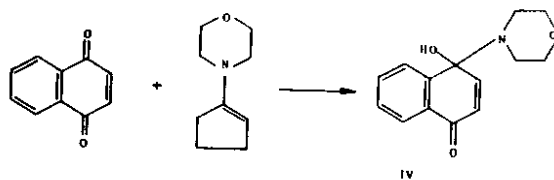
Chloranil reacts with 4-(1-cyclopentenyl) morpholine and 1-(1-cyclohexenyl) morpholine to give the open (1:1) addition product (IIIa,b or III'a,b).



The structures of (IIIa,b) are established from: i) Analytical data ii) Their IR spectra show (ν C=O 1720 cm⁻¹, ν OH 3410-3450 cm⁻¹ and ν C=C at 1625 cm⁻¹). iii) Their electronic spectra show clear resemblance among themselves.

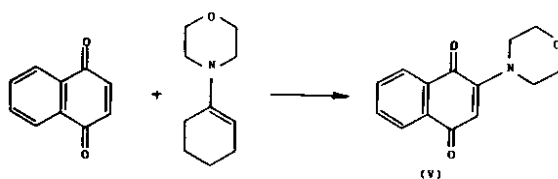
During the course of this work interesting data are obtained when the reaction between 1,4-naphthoquinone and enamines is investigated. Thus, 1,4-naphthoquinone reacts with 4-(1-cyclopentenyl) morpholine to give (1:1) addition product (IV).

The structure of (IV) is inferred, other than analytical data, from IR ν C=O 1675 cm⁻¹ and ν OH 3450 cm⁻¹.



It proved to be the same product obtained from the reaction between 1,4-naphthoquinone and morpholine.

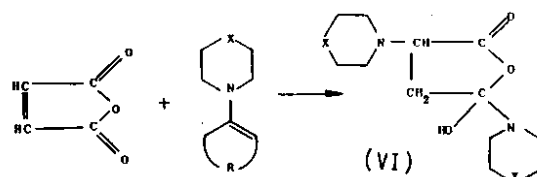
However, the interaction between 1,4-naphthoquinone and 1-(1-cyclohexenyl) morpholine proceeds in a different way to give (V).



The structure of (V) is inferred, other than analytical data, from I.R. which devoid from ν OH and shows ν C=O at 1645, 1680 cm⁻¹. It proved to be 2-morpholino-1,4-naphthoquinone by melting point and mixed melting point with an authentic specimen [7].

It seems that this enamine decomposes under the reaction conditions and the negatively charged divalent nitrogen attacks at the 2-position of the quinone with the subsequent extraction of the proton from the reaction medium followed by oxidation.

Finally, maleic anhydride reacts with 4-(1-cyclopentenyl) morpholine, 4-(1-cyclohexenyl) morpholine and 1-(1-cyclohexenyl) piperidine to give (VIa,b).



- a) X = O, R = CH₂CH₂
- b) X = CH₂, R = CH₂CH₂CH₂

The structures of (VIa,b) are established from: i) Analytical data ii) IR spectra show $\nu_{\text{C=O}}$ at 1650 cm^{-1} and ν_{OH} at 3450 cm^{-1} .

Experimental

All melting points are uncorrected. The IR spectra were measured by using Perkin-Elmer 398 (KBr Wafer technique). Electronic spectra were measured by using Perkin-Elmer 555 UV-Vis spectrophotometer. Elemental analyses were carried out in the Research Microanalytical Laboratory of Cairo University.

Material:

Enamines were prepared according to the method of Stork et al.[8].

Reactions of tetrabromo-o-benzoquinone, chloranil, 1,4-naphthoquinone and maleic anhydride with enamines:

General Procedure:

A mixture of an enamine (0.02 mole) and tetrabromo-o-benzoquinone or chloranil or 1,4-naphthoquinone or maleic anhydride (0.01 mole) in benzene (150 ml) was refluxed or left for a couple of hours or days. The reaction mixture was concentrated at room temperature under reduced pressure, it was solidified by trituration with methanol. The solid product was crystallized from a suitable solvent as shown in respective case.

(Ia):

The reaction mixture was left for one day at room temperature. The solid product was crystallized from benzene pet.ether (b.p. $40-60^\circ\text{C}$) mixture, giving yellow crystals 40%,

m.p. 125°C ; IR (KBr) 1690 ($\nu_{\text{C=O}}$), 1616 ($\nu_{\text{C=C}}$) and 3425 cm^{-1} (ν_{OH}), UV λ_{max} in (CH_3CN) 310 ($\epsilon 3.733 \times 10^3$), 264 ($\epsilon 9.706 \times 10^3$) and 224 nm ($\epsilon 28.746 \times 10^3$). Found: C, 33.40; H, 3.00; N, 2.80, Calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_2\text{Br}_4$: C, 33.41; H, 2.95; N, 2.43.

(Ib):

The reaction mixture was left for one day at room temperature. The solid product was crystallized from benzene-pet.ether (b.p. $40-60^\circ\text{C}$) mixture, giving buff crystals, 30%, m.p. 187°C ; IR (KBr) 1665 ($\nu_{\text{C=O}}$), 1625 ($\nu_{\text{C=C}}$) and 3480 cm^{-1} , (ν_{OH}), UV λ_{max} in CH_3CN , 320 ($\epsilon 4.741 \times 10^3$), 304 ($\epsilon 6.953 \times 10^3$) and 224 nm ($\epsilon 33.503 \times 10^3$), Found: N, 2.80; Br, 54.10 Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_2\text{Br}_4$: N, 2.37 Br, 54.29.

(IIa):

The reaction mixture was left three hours at ($0-4^\circ\text{C}$). The solid product was crystallized from benzene-ethanol mixture giving pale yellow crystals, 35%, m.p. 152°C (lit. 152°C) [5].

(Ic):

Concentration of methanol solution (oil trituration) of (IIa) and dilution with few drops of water giving yellow crystals, 35%, m.p. 120°C ; IR (KBr) 1700 , ($\nu_{\text{C=O}}$), 1625 , ($\nu_{\text{C=C}}$) and 3400 cm^{-1} (ν_{OH}); UV λ_{max} in CH_3CN , 304 ($\epsilon 13.193 \times 10^3$), 252 ($\epsilon 15.078 \times 10^3$) and 216 nm ($\epsilon 89.527 \times 10^3$). Found: N, 2.60; Br, 54.90; Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{Br}_4$: N, 2.42; Br, 55.42.

(IIb):

The reaction mixture was left for three hours at (0-4°C). The solid product was crystallized from ethanol giving brown crystals, 40%, m.p. 139°C (lit. 149°) [5]; IR (KBr) devoid of ($\nu\text{C}=\text{O}$) and (νOH).

(IIIa):

The reaction mixture was left for two days at (24°C). The solid product was crystallized from benzene giving dark violet crystals, 65%, m.p. 110°C; IR (KBr) 1720 ($\nu\text{C}=\text{O}$), 1625 ($\nu\text{C}=\text{C}$) and 3410 cm^{-1} (νOH); Found: N, 3.90, Cl, 35.00 calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{Cl}_4$: N, 3.50, Cl, 35.58.

(IIIb):

The reaction product was crystallized from methanol giving yellow crystals, 60%, m.p. 155°C; IR (KBr) 1720 ($\nu\text{C}=\text{O}$), 1625 ($\nu\text{C}=\text{C}$) and 3450 cm^{-1} (νOH); $\text{UV}\lambda_{\text{max}}$ CH_3CN , 430 ($\epsilon 1.5 \times 10^3$), 290 ($\epsilon 4.4 \times 10^3$) and 222 nm ($\lambda_{\text{max}} 30.2 \times 10^3$). Found: C, 45.70, H, 4.40, N, 3.60; Calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{Cl}_4$: C, 46.48, H, 4.11, N, 3.38.

(IV):

The reaction mixture was left overnight at (24°C). The dark brown solid was crystallized from pet.ether (b.p. 100-120°C) giving brown crystals, 60%, m.p. 120°C; IR (KBr) 1675 ($\nu\text{C}=\text{O}$) and 3450 cm^{-1} (νOH); $\text{UV}\lambda_{\text{max}}$ in CH_3CN , 440 ($\epsilon 2.7 \times 10^3$), 265 ($\epsilon 15.6 \times 10^3$) and 221 nm ($\epsilon 25.5 \times 10^3$). Found: N, 5.80, Calcd. for $\text{C}_{14}\text{H}_{15}\text{NO}_3$: N, 5.71.

(V):

The reaction mixture was refluxed for one hour. The solid product was crystallized from pet.ether (b.p. 100-120°C) giving orange crystals, 65%, m.p. 153°C (lit. 152-153.5°C) [8] and (lit. 164-5°C) [9]; IR (KBr) devoid of (νOH), 1645, 1680 cm^{-1} ($\nu\text{C}=\text{O}$), $\text{UV}\lambda_{\text{max}}$ CH_3CN , 447 ($\epsilon 2.8 \times 10^3$), 270 ($\epsilon 12.25 \times 10^3$) and 222.5 nm ($\epsilon 21.0 \times 10^3$). Found: C, 69.09, H, 5.50, N, 5.44 calcd. for $\text{C}_{14}\text{H}_{13}\text{NO}_3$: C, 69.13, H, 5.34; N, 5.72.

(VIa):

The reaction mixture was left for three days at (0-4°C). The solid product was crystallized from pet.ether (100-120°C) giving colourless crystals, 60%, m.p. 183°C; IR (KBr) 1650 ($\nu\text{C}=\text{O}$) and 3450 cm^{-1} (νOH). Found: C, 52.65, H, 7.56, N, 10.4. Calcd. for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2$: C, 52.94, H, 7.35, N, 10.29.

(VIb):

The reaction mixture was left at (0-4°C) for four days. The solid product was crystallized from benzene-pet.ether (40-60°C) mixture giving colourless crystals 56%, m.p. 178°C, IR (KBr) 1645 ($\nu\text{C}=\text{O}$) and 3430 cm^{-1} (νOH). Found: C, 62.90, H, 9.30, N, 10.30 Calcd. for $\text{C}_{14}\text{H}_{24}\text{N}_2\text{O}_3$: C, 62.68, H, 8.95, N, 10.44.

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