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## Reaction of Enamines With Aldehydes

by

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## Reaction of Enamines With Aldehydes

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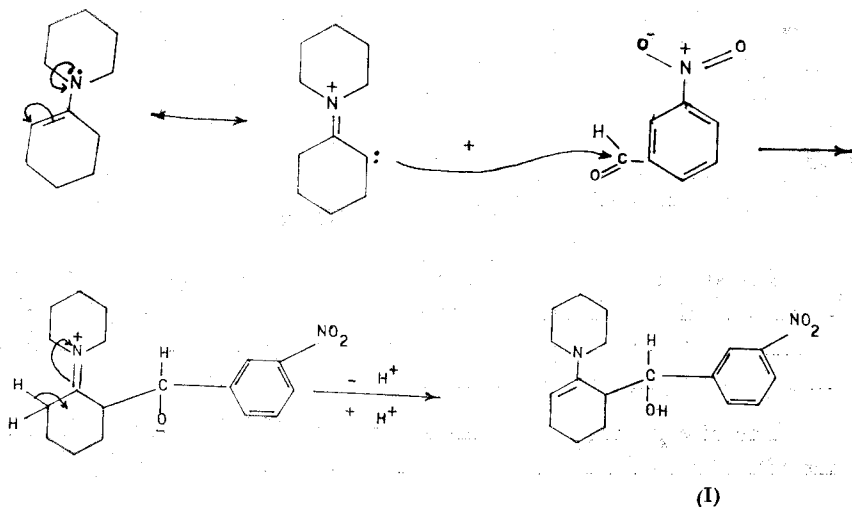
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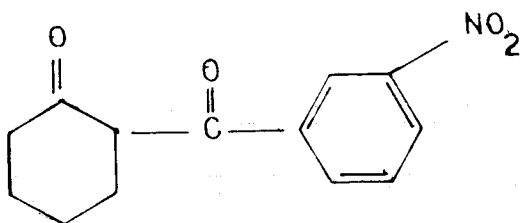
### ABSTRACT

In continuation to our previous work on enamines<sup>1</sup>, the present investigation deals with the action of morpholinocyclopentene, morpholinocyclohexene, piperidinocyclopentene and piperidinocyclohexene on aldehydes.

Piperidinocyclohexene reacts with *m*-nitrobenzaldehyde at room temperature to give (1:1) addition product (I). This type of addition is similar to the addition of chlorohydrate to enamines<sup>2</sup>. The structure of (I) is inferred from: i) analytical data, ii) Its infrared and U.V. spectra (cf. exp. part).

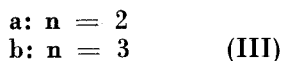
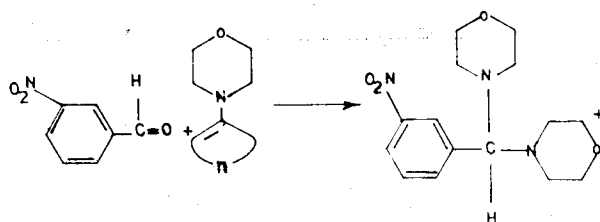


Acid hydrolysis<sup>3</sup> of (I) yields the product (II), its i.r. spectrum shows  $\nu_{C=O}$  of alicyclic ketones and  $\nu_{C=O}$  stretching frequencies.



However, the interaction between piperidinocyclopentene, morpholinocyclopentene and morpholinocyclohexene with *m*-nitrobenzaldehyde under the same conditions proceeds in a different way and no (1:1) addition product is isolated.

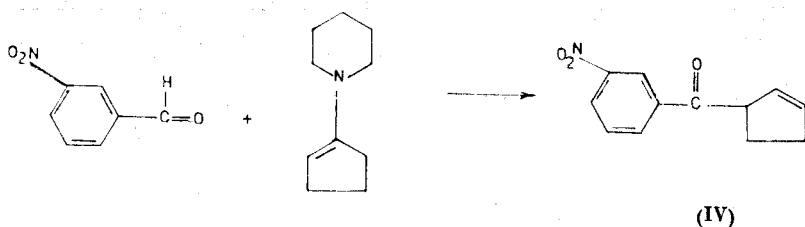
Morpholinocyclohexene and morpholinocyclopentene react with *m*-nitrobenzaldehyde to give (III) as the main product and an oily product in very poor yield.



The structure of (III) is inferred, other than analytical data, from a study of their infrared and its identity by melting point and mixed melting point with an authentic specimen prepared from direct interaction between *m*-nitrobenzaldehyde and morpholine.

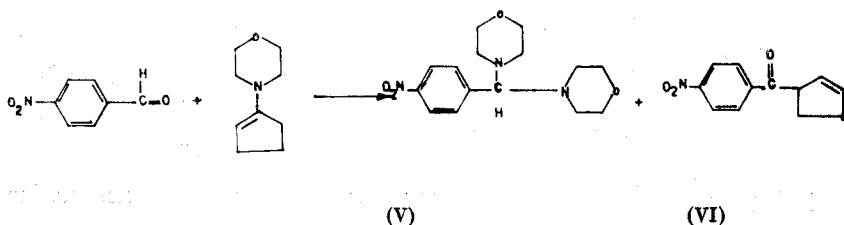
The oily product shows the following characteristics: (i) It contains nitrogen (ii) Its i.r. spectrum shows  $\nu_{C=O}$  and  $\nu_{>C=C<}$ .

Under similar conditions *m*-nitrobenzaldehyde reacts with piperidinocyclopentene to give (IV) as the only isolated product.



The structure of (IV) is inferred from (i) Analytical data ii) Its infrared spectrum does not show any absorption in the region characteristic of (OH), it also shows the carbonyl stretching frequencies at  $1690\text{ cm}^{-1}$  and  $\nu_{>C=C}<$  at  $1630\text{ cm}^{-1}$ . It seems that these enamines decompose under the condition of the reaction.

p- Nitrobenzaldehyde reacts with morpholinocyclopentene under the same conditions to give  $\alpha, \alpha$ - (N) - dimorpholino -p- nitrotoluene (V) as the main product and (VI) in very poor yield.

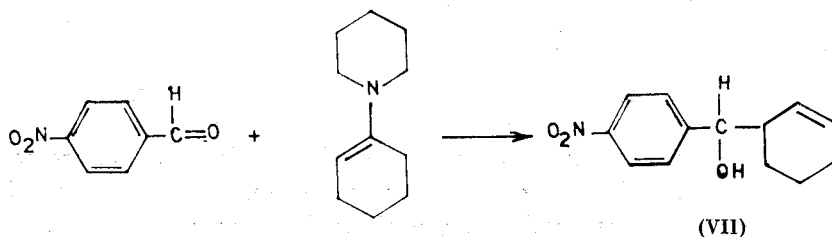


The structure of (V) is inferred, other than analytical data, from its i.r. spectrum, and its identity by melting point and mixed melting point with an authentic specimen<sup>4</sup>. Acid hydrolysis of (V) yields p-nitrobenzaldehyde.

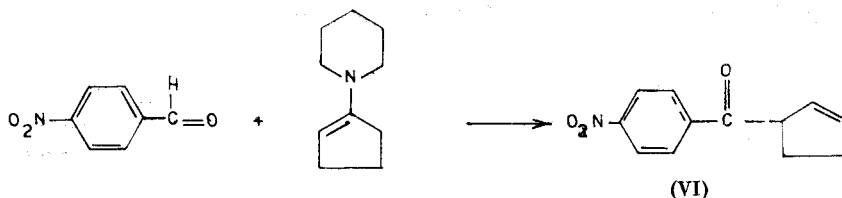
The structure of (VI) is inferred from: i) analytical data. ii) Its i.r. spectrum shows  $\nu_{C=O}$  at  $1690\text{ cm}^{-1}$  and  $\nu_{>C=C}<$  at  $1625\text{ cm}^{-1}$  and from a study of its U.V. spectrum. However, p-nitrobenzaldehyde reacts with morpholinocyclohexene under similar conditions to give (V) as the main product and an oily product in very poor yield which gives the following characteristics: i) It contains nitrogen ii) Its i.r. spectrum shows strong band in the region characteristic of  $\nu_{C=O}$  group and a strong band at  $3400\text{ cm}^{-1}$  characteristic to  $\nu_{OH}$  group.

Piperidinocyclohexene under similar conditions reacts with p-nitrobenzaldehyde to give (VII) as the only isolated product. The structure

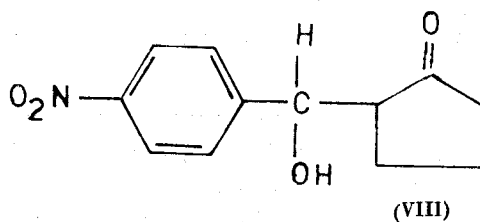
re of (VII) is referred from: i) Analytical data ii) Its i.r. spectrum shows  $\nu_{OH}$  at  $3440\text{ cm}^{-1}$  and  $\nu_{>C=C<}$  at  $1670\text{ cm}^{-1}$ . iii) From a study of its U.V. spectrum (cf. exp. part).



p-Nitrobenzaldehyde reacts with piperidinocyclopentene to give (VI) as the only isolated product. The structure of (VI) is inferred from (i) Analytical data ii) A study of its i.r. and U.V. spectra (cf. exp. part)



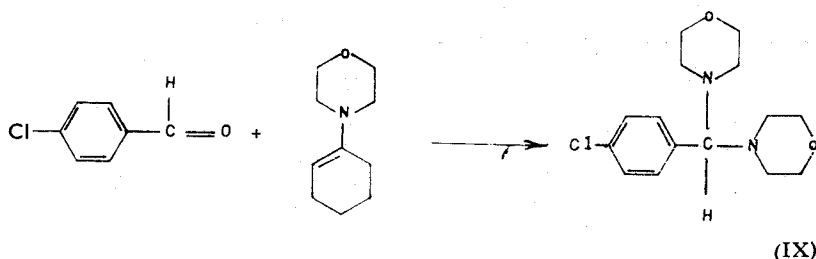
p- Nitrobenzaldehyde reacts with piperidinocyclopentene under the same conditions but in presence of water drops to yield the same product (VI) and not (VIII).



p- Chlorobenzaldehyde reacts with morpholinocyclopentene at room temperature to give  $\alpha, \alpha$ - (N)- dimorpholino -p- chlorotoluene (IX) as the only isolated product.

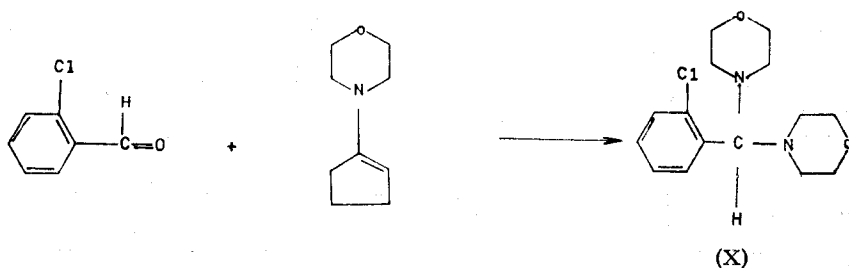
The structure of (IX) is inferred from:

i) Analytical date ii) Study of its i.r. iii) Its identity by melting point and mixed melting point with an authentic spécimen.<sup>4</sup>



Finally, *o*-chlorobenzaldehyde reacts with morpholinocyclopentene at room temperature to give (X) as the only isolated product in good yield. The structure of (X) is inferred from:

i) Analytical data ii) A study of its i.r. and U.V. spectra iii) Its identity by melting point and mixed melting point with authentic specimen which prepared from the direct interaction between morpholine and *o*-chlorobenzaldehyde.



### 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 using KBr Wafer technique. Electronic spectra were carried out on Perkin-Elmer 555 U.V. Vis Spectrophotometer.

### Reaction between Aldehydes and Enamines:

A mixture of enamine (0.02 mole) and aldehyde (0.01 mole) in (50 ml) benzene was left overnight in refrigerator. The reaction mixture was concentrated at room temperature. The oily product obtained was dissolved in methanol. The solid product separated was filtered off and crystallised from the suitable solvent [cf. Table (1)].

Table (1)

Aldehyde	Enamine	Product No.	Solvent of crystallization	m.p. °C	yield %	Analysis	ir.	u.v.
m-Nitro-benzaldehyde	piperidino cyclohexene	(I)*	Benzene/Pet. ether 40-60°C	190	85	C <sub>18</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub> Calcd C, 68.35 H, 7.59 N, 8.8 Found C, 68.30 H, 7.70 N, 8.43	ν C=C at 1660 cm <sup>-1</sup> ν OH at 3440 cm <sup>-1</sup>	λ <sub>max</sub> = 310 nm ε <sub>max</sub> 18x10 <sup>3</sup> λ <sub>max</sub> = 223 nm ε <sub>max</sub> 13x10 <sup>3</sup>
"	morpholinocyclohexene	(III)** (III) <sub>A</sub>	pet-ether (100-120°C)	130-1	80	C <sub>15</sub> H <sub>21</sub> N <sub>3</sub> O <sub>4</sub> Calcd C, 58.63 H, 6.84 N, 13.6 Found C, 58.60 H, 7.20 N, 13.9	ν C=O at 1708 cm <sup>-1</sup> ν C=C at 1638 cm <sup>-1</sup> ν OH at 3400 cm <sup>-1</sup>	λ <sub>max</sub> 267 nm ε <sub>max</sub> 11.3x10 <sup>3</sup> λ <sub>max</sub> 225 nm ε <sub>max</sub> 33.10 <sup>3</sup>
"	piperidino cyclopentene	(IV)	Benzene	oil	15	C <sub>15</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> Calcd C, 66.3 H, 5.06 N, 6.45 Found C, 65.9 H, 4.79 N, 6.80		λ <sub>max</sub> 332.5nm ε <sub>max</sub> 224x10 <sup>3</sup>
p-Nitro-benzaldehyde	morpholinocyclopentene	(V)***	pet-ether (100-120°C)	188	80	C <sub>15</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> Calcd C, 58.63 H, 6.84 N, 13.6 Found C, 59.09 H, 6.90 N, 12.99	ν C=O at 1690 cm <sup>-1</sup> ν C=C at 1630 cm <sup>-1</sup>	λ <sub>max</sub> 270 nm ε <sub>max</sub> 14.3x10 <sup>3</sup> max 220 nm ε <sub>max</sub> 17.1x10 <sup>3</sup>
"	morpholinocyclohexene	(VI) (V)****	Benzene/pet ether 40-60°C	190	15	C <sub>15</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> Calcd C, 66.3 H, 5.06 N, 6.45 Found C, 66.8 H, 5.11 N, 6.60	ν C=O at 1690 cm <sup>-1</sup> ν C=C at 1622 cm <sup>-1</sup>	λ <sub>max</sub> 355 nm ε <sub>max</sub> 20.9x10 <sup>3</sup> λ <sub>max</sub> 220 nm ε <sub>max</sub> 10.9x10 <sup>3</sup>
"	oil	oil	pet-ether (100-120°C)	188	80	C <sub>15</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> Calcd C, 58.63 H, 6.84 N, 13.6 Found C, 59.20 H, 7.20 N, 13.3	ν C=O at 1705 cm <sup>-1</sup> ν OH at 3400 cm <sup>-1</sup>	



Table 1 Continued

"	piperidino cyclohex- ene	(VII)	Benzene/pet. ether 40-60°C	145	70	C <sub>13</sub> H <sub>15</sub> NO Calc C, 66.95 H, 6.43 N, 6.00 Found C, 66.60 H, 6.60 N, 6.50 C <sub>12</sub> H <sub>14</sub> NO Calcd C, 66.3	ν C=C at 1670 cm <sup>-1</sup> ν OH at 3420 cm <sup>-1</sup>	λ <sub>max</sub> 340 nm ε <sub>max</sub> 17.5x10 <sup>3</sup> λ <sub>max</sub> 220 nm ε <sub>max</sub> 17.3x10 <sup>3</sup>
"	piperidino cyclopentene	(VI)	Benzene/pet. ether 40-60°C	190	80	H, 5.06 N, 6.45 Found C, 66.8	ν C=O at 1690 cm <sup>-1</sup>	λ <sub>max</sub> 355 nm ε <sub>max</sub> 20.9x10 <sup>3</sup>
p-Chloro- benzal- dehyde	morpholi- no cyclo- pentene	(IX)	pet-ether (40-60°C)	130	60	H, 5.10 N, 6.60 C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> Cl Calcd N, 9.40 cl, 11.82 Found N, 9.00 Cl, 11.80	ν C=C at 1622 cm <sup>-1</sup> no ν C=O, ν C=C or ν OH	λ <sub>max</sub> 220 nm ε <sub>max</sub> 10.9x10 <sup>3</sup>
o-Chloro- benzal- dehyde	morpholi- no cyclo- pentene	(X)	pet-ether (40-60°C)	88-90	60	C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> Cl Calcd C, 60.81 H, 7.09 N, 9.4 Cl, Cl, 11.82 Found C, 61.10 H, 7.60 N, 10.2 Cl, 12.00	no ν C=O, —	max 220 nm ε <sub>max</sub> 5.8x10 <sup>3</sup>
							ν C=C or ν OH	max 240 nm ε <sub>max</sub> 2.7x10 <sup>3</sup>

\* Concentration of the reaction mixture at room temperature gives yellow solid.

\*\* (III)<sub>A</sub> is the solid product and concentration of the filtrate gives oil (III)<sub>B</sub>

\*\*\* (V) is the solid product and concentration of the filtrate gives (VI)

\*\*\*\* (V) is the solid product and concentration of the filtrate gives oil.

**Acid hydrolysis of (I):**

Add to (0.5 gm) of (I) a slight excess of cold dilute hydrochloric acid. Hydrolysis was completed within a few minutes. Extraction with ether, then dry over anhydrous sodium sulphate, filtered off, evaporate under reduced pressure a greenish yellow solid formed, which crystallised from benzene-pet. ether (40-60 °C) to give (II) as greenish yellow crystals m.p. 195 °C, yield 50 %.

$C_{13}H_{15}NO_4$  Calcd. C, 63.15 H, 5.20

Found C, 62.90 H, 5.40

Its i.r. spectrum shows  $\nu_{C=O}$  at 1715  $cm^{-1}$  characteristic of alicyclic ketones and  $\nu_{C-O}$  at 1665  $cm^{-1}$ .

**Reaction between aldehydes and secondary amines:**

A mixture of (0.02 mole) amine and (0.01 mole) aldehyde was left overnight in (50 ml) benzene. The reaction mixture was concentrated at room temperature, the solid product was crystallised from the suitable solvent [cf. Table (2)].

Table (2)

Aldehyde	Amine	Product No.	m.p. °C	Yield %
m-Nitrobenzaldehyde	Morpholine	(III)	130.1	80
p-Nitrobenzaldehyde	Morpholine	(V)	188	85
o-Chlorobenzaldehyde	Morpholine	(X)	88-90	85

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