



Trade Science Inc.

# Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 4(5), 2008 [355-358]

## A convenient synthesis of secondary amines from imines by using $\text{NaBH}_4$

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Received: 14<sup>th</sup> July, 2008 ; Accepted: 19<sup>th</sup> July, 2008

### ABSTRACT

The secondary amines have been prepared by the reaction of various Schiff bases by using sodium borohydride as a selective reducing agent. The Schiff bases were synthesized by the condensation of 2-Chloro-6-methyl quinoline-3-carboxyaldehyde with substituted iodoanilines. The structures of compounds have been confirmed by elemental analysis and spectral data. The antibacterial activity of the synthesized compound has also been screened. © 2008 Trade Science Inc. - INDIA

### KEYWORDS

Iodoanilines;  
Schiff bases;  
Secondary amines;  
Antibacterial activity.

### INTRODUCTION

A variety of secondary amines were found to possess antibacterial, fungicidal and anti-inflammatory activities<sup>[1]</sup>. An interesting feature of Schiff bases<sup>[2]</sup>, is that they serve on reduction afforded reduced products due to the presence of  $-\text{CH}=\text{N}$  moiety. The reduction of Schiff bases with Lithium Aluminium Hydride has not been very comfortable often the yields are accompanied by tarry material.

Amongst several reducing agents, Schiff bases smoothly reduced to secondary amines by using sodium borohydride<sup>[3-7]</sup> in good yield under mild condition. A less powerful complex metal hydride is  $\text{NaBH}_4$  which will not reduce carboxylic, nitro groups if present in the same. Thus, sodium borohydride is the selective reducing agent for the reduction of Schiff bases<sup>[8-9]</sup>.

### EXPERIMENTAL

All the melting points were taken in open capillary tube and are correct. The IR spectra were recorded

with KBr pellets on Perkin-Elmer 157 spectrophotometer. <sup>1</sup>HNMR spectra on Bruker WN-400 FTMHz. NMR instrument using  $\text{CDCl}_3$  on a reference (chemical shift in  $\delta$  ppm).

### General procedure

A Schiff base (0.01 mole) was dissolved in methanol and sodium borohydride (0.37 gm, 0.01 mole) was added in small installments within 10 min.

The reaction mixture was allowed to stand for 1 hr. The excess of solvent was removed by evaporation. The residue was washed with cold water and crystallized from ethanol. The purity of compound were checked by T.L.C. and structure of compounds were assigned on the bases of elemental analysis and spectral study (IR, <sup>1</sup>HNMR).

### Reduction of N-(4-nitro-6-iodo-phenyl)-2-chloro-6-methyl quinoline-3yl azomethine. (Ia)

Yield 85%, mp 140°C IR ( $\text{cm}^{-1}$ ) 3377 (NH), 1566, 1494, 1406 (C=C), 1540, 1360 (C-NO<sub>2</sub>), <sup>1</sup>HNMR ( $\text{CDCl}_3$ )  $\delta$ ppm: 2.55 (s, 3H, CH<sub>3</sub>), 4.95 (s, 1H, CH<sub>2</sub>-N),

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6.1(s,1H,NH),7.3-8.4(m,7H,ArH), Mole. Formula:  $C_{17}H_{13}N_3O_2ICl$ . Anal. Calcd. C=44.93, H=2.86, N=9.25, Found; C=44.80, H=2.55, N=9.22,

### Reduction of N-(4-iodo-6-nitro-phenyl)-2-chloro-6-methyl quinoline-3yl azomethine.(Ib)

Yield 87%, mp. 120°C IR ( $cm^{-1}$ ) 3377 (NH), 1566, 1494, 1406 (C=C), 1540,1360 (C-NO<sub>2</sub>), <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm: 2.55 (s,3H,CH<sub>3</sub>),4.95(s,1H,CH<sub>2</sub>-N), 6.1(s,1H,NH), 7.3-8.4(m,7H,ArH), Mole.Formula:  $C_{17}H_{13}N_3O_2ICl$ . Anal. Calcd. C=44.93, H=2.86, N=9.25, Found; C=44.80, H=2.55, N=9.22,

### Reduction of N-(4-iodo 6-chloro,-phenyl)-2-chloro-6-methyl quinoline-3yl azom ethine.(Ic)

Yield; 78%, mp. 135°C IR ( $cm^{-1}$ ) 3380 (NH) , 1560, 1490, 1400 (C=C) , 2930 (C-H). <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm: 2.45 (s,3H ,CH<sub>3</sub>),4.84(s,1H,CH<sub>2</sub>-N),6.2 (s,1H,NH) 7.5-8.9(m,7H,ArH). Mole.Formula:  $C_{17}H_{13}N_2ICl_2$ . Anal. Calcd. C=46.04, H=2.93, N=6.32, Found; C=45.00, H=5.95, N=6.55.

### Reduction of N-(4-chloro-6-iodo-phenyl)-2-chloro-6-methyl quinoline-3yl azom ethine (Id).

Yield 75%, mp. 142°C IR ( $cm^{-1}$ ) 3340 (NH), 2985 (CH<sub>3</sub>), 1580,1470,1400 (C=C) <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm: 2.5 (s,3H,CH<sub>3</sub>), 4.0 (s,1H,CH<sub>2</sub>-N),6.3 (s,1H, NH) 7.1-8.5(m,7H,ArH), Mole.Formula:  $C_{17}H_{13}N_2ICl_2$ . Anal. Calcd. C=46.04, H=2.93, N=6.32, Found; C=45.00, H=5.95, N=6.55.

### Reduction of N-(4- methyl- 2,6- di-iodo,-phenyl)-2-chloro-6-methyl quinoline-3yl azomethine(Ie)

Yield; 80%, mp.110°C IR ( $cm^{-1}$ ) 3325 (NH), 2967, 2890 (CH<sub>3</sub>), 1590,1500,1445 (C=C),. <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm: 2.6(s,3H,CH<sub>3</sub>), 2.5 (s,3H,CH<sub>3</sub>) 3.9 (s,2H,CH<sub>2</sub>-N), 6.3(s,1H,NH) 7.1-8.7(m,7H,ArH), Mole.Formula:  $C_{18}H_{15}N_2I_2Cl$ . Anal. Calcd. C=39.38, H=3.73, N=5.10 Found; C=39.55, H=3.88, N=5.22.

### Reduction of N-(4-nitro-2,6-di-iodo,-phenyl)-2-chloro-6-methyl quinoline-3yl azomethine(If)

Yield; 85%, mp. 105°C IR ( $cm^{-1}$ ) 3340 (NH), 2970, 2890 (CH<sub>3</sub>), 1600,1560,1400 (C=C),1560,1380 (NO<sub>2</sub>). <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm: 2.6(s,3H,CH<sub>3</sub>), 4.0(s,2H,CH<sub>2</sub>-N),6.1(s,1H,NH)6.58.2(m,6H,ArH), Mole. Formula:  $C_{17}H_{12}N_3O_2I_2Cl$ . Anal. Calcd. C=35.20,

H=2.07, N=7.24, Found; C=35.28, H=2.15, N=7.18.

### Reduction of N-(2-methyl-3-iodo-5-nitrophenyl) -2-chloro-6-methylquinoline-3yl-azomethine(Ig)

Yield; 80%, mp.115°C IR ( $cm^{-1}$ ) 3377 (NH), 2950, 2895 (CH<sub>3</sub>), 1566, 1494, 1406 (C=C), 1145, 1390 (NO<sub>2</sub>). <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm:2.3(s,3H,CH<sub>3</sub>) 2.55 (s,3H,CH<sub>3</sub>), 4.7(s,2H,CH<sub>2</sub>-N), 6.1(s,1H,NH) 7.2-8.1 (m,6H,ArH). Mole.Formula:  $C_{18}H_{15}N_3O_2ICl$ . Anal. Calcd. C=35.20, H=2.07, N=7.24. Found; C=35.22, H=2.12, N=7.35.

### Reduction of N-(4-carboxylic-6-iodo-phenyl) -2-chloro-6-methylquinoline-3yl-azomethine (Ih)

Yield; 75%, mp. 110°C IR ( $cm^{-1}$ ) 3300 (NH), 3320, 3400(-OH) 2920,2900 (CH<sub>3</sub>), 1610,1545, 1500, (C=C), 1735 (C=O). <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm: 11.1 (s,1H,OH), 2.5(s,3H,CH<sub>3</sub>), 4.2(s,2H,CH<sub>2</sub>-N), 6.5 (s,1H,NH), 7.3-8.5(m,7H,ArH). Mole.Formula:  $C_{18}H_{14}N_2O_2ICl$ . Anal. Calcd. C=47.73, H=3.09, N=6.18. Found; C=45.55, H=2.99, N=6.22.

### Reduction of N-(4-carboxylic-2,6-di-iodo-phenyl) -2-chloro-6methylquinoline-3yl-azomethine.(Ii)

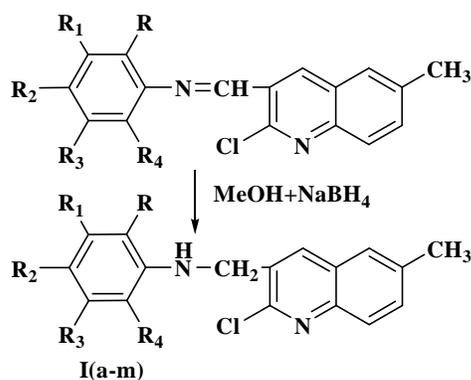
Yield; 70%, mp.118°C IR ( $cm^{-1}$ ) 3378 (NH), 3395 (-OH), 2935 (CH<sub>3</sub>), 1600,1590, 1445, (C=C), 1739 (C=O), <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm: 11.1(s,1H,-OH), 2.3 (s,3H,CH<sub>3</sub>), 4.3(s,2H,CH<sub>2</sub>-N), 6.5(s,1H,NH), 7.3-8.5 (m,6H,ArH), Mole.Formula:  $C_{18}H_{13}N_2O_2I_2Cl$  Anal. Calcd. C=37.33, H=2.24, N=4.84. Found; C=37.40, H=2.35, N=4.99.

### Reduction of N-(2-iodo-5-nitro-phenyl)-2-chloro-6methyl quinoline-3yl-azomethine(Ij)

Yield; 75%, mp.132°C IR ( $cm^{-1}$ ) 3350 (NH), 2930 (CH<sub>3</sub>), 1600,1560, 1480, (C=C) , 1550,1480 (N-O). <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm: 2.3(s,3H,-CH<sub>3</sub>), 4.1 (s,2H,CH<sub>2</sub>-N), 6.4(s,1H,NH), 7.1-8.5(m,7H,ArH). Mole.Formula:  $C_{17}H_{13}N_2O_2ICl$ . Anal. Calcd. C=44.93, H=2.86, N=9.25. Found; C=44.55, H=2.50, N=9.44.

### Reduction of N-(5-chloro-6-iodo-phenyl)-2-chloro-6methylquinoline-3yl-azomethine (Ik)

Yield; 85%, mp.148°C IR ( $cm^{-1}$ ) 3360 (NH), 2965 (CH<sub>3</sub>), 1590,1515, 1450, (C=C), <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm: 2.4(s,3H,-CH<sub>3</sub>), 4.1(s,2H,CH<sub>2</sub>-N), 6.1 (s,1H, NH), 6.9-8.2(m,7H,ArH), Mole.Formula:  $C_{17}H_{13}N_2$



Entry	R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
Ia	H	H	NO <sub>2</sub>	H	I
Ib	H	H	I	H	NO <sub>2</sub>
Ic	H	H	I	H	Cl
Id	H	H	Cl	H	I
Ie	I	H	CH <sub>3</sub>	H	I
If	I	H	NO <sub>2</sub>	H	I
Ig	CH <sub>3</sub>	I	H	NO <sub>2</sub>	H
Ih	H	H	COOH	H	I
Ii	I	H	COOH	H	I
Ij	I	H	H	NO <sub>2</sub>	H
Ik	H	H	H	Cl	I
Il	H	H	I	H	COOH
Im	Cl	H	I	H	Cl

SCHEME 1

ICl<sub>3</sub> Anal. Calcd. C=46.04, H=2.93, N=6.32. Found; C=45.00, H=5.95, N=6.55.

### Reduction of N-(4-iodo-6-caboxylic-phenyl)-2-chloro-6-methyl quinoline-3yl azomethine.(II)

Yield; 75%, mp.130°C IR (cm<sup>-1</sup>3350 (NH), 3323(OH), 1610,1584,1420 (C=C), 2980(CH<sub>3</sub>), 1735(C=O). <sup>1</sup>HNMR (CDCl<sub>3</sub>) δppm: 2.5 (s,3H,CH<sub>3</sub>), 4.1 (s,2H, CH<sub>2</sub>-N), 6.2(s,1H,NH), 7.3-8.5(m,7H,ArH), 11.2 (s,1H,OH). Mole.Formula: C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>ICl. Anal. Calcd.C=47.73, H=3.09, N=6.18, Found; C=45.55, H=2.99, N=6.22.

### Reduction of N-(4-iodo-2,6-dichloro-phenyl)-2-chloro-6-methyl quinoline-3yl azomethine.(Im)

Yield; 80%, mp.122°C, IR (cm<sup>-1</sup>) 3340 (NH), 2950 (CH<sub>3</sub>), 1625,1590,1450 (C=C). <sup>1</sup>HNMR (CDCl<sub>3</sub>) δ ppm: 2.3(s,1H,CH<sub>3</sub>), 4.2(s,2H,CH<sub>2</sub>-N), 6.1(s,1H,NH), 7.1-8.9(m,6H,ArH), Mole.Formula: C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>ICl<sub>3</sub>. Anal.Calcd.C=42.72, H=2.51, N=5.86. Found; C=42.55, H=5.88, N=6.55.

## RESULT AND DISCUSSION

Structures of compounds have been elucidated by elemental analysis. IR spectra of compounds were scanned on the Bruker-Elmer FTIR spectrometer. <sup>1</sup>H NMR spectra were recorded on the Bruker FT 200 MHz instrument using TMS as an internal standard (chemical shift are given in δ ppm).

**IR:**IR spectra of secondary amines showed band at near 1566-1494, 1406cm<sup>-1</sup> for C=C stretching vibration.

TABLE 1:Antibacterial activity of compounds -I (a -m)

Entry	<i>Xc</i>	<i>E.coli.</i>	<i>Ec.</i>	<i>Bs.</i>
Ia	04.20	04.00	02.00	04.02
Ib	03.20	03.50	05.50	02.50
Ic	10.00	12.02	12.00	00.00
Id	15.00	17.00	14.50	00.00
Ie	01.70	02.00	01.70	00.00
If	12.00	10.00	11.20	00.00
Ig	02.00	03.00	01.90	00.00
Ih	03.50	04.00	03.20	01.90
Ii	20.00	17.00	12.00	00.00
Ij	02.00	04.00	02.50	01.50
Ik	07.00	08.00	07.10	04.00
Il	04.00	03.50	03.50	00.00
Im	20.00	23.00	20.50	00.00
Ampicilin (200ppm)	18.00	20.00	21.00	17.00
Streptomycin (200ppm)	19.00	24.00	16.00	22.00
Penicillin (200ppm)	21.00	22.00	19.00	23.00

All the compounds showed absorption due to N-H stretching vibrations in the region at near 3377 cm<sup>-1</sup>.

**<sup>1</sup>H NMR:** <sup>1</sup>H NMR spectra of secondary amines were studied in CDCl<sub>3</sub> showed characteristics signals at δ 2.73 of singlet due to methyl. The singlet at 4.85 due to CH<sub>2</sub> group and aromatic protons gives multiplets in the region of δ 7.72-8.4.

### Antibacterial activity

The newly synthesized compounds were screened for their antibacterial activity<sup>[10]</sup> using *E.coli*, *X.citri*, *E.carotovora* and *B.subtilis* as bacteria. The activities of these compounds were tested using disc diffusion method at 200 ppm concentration using 5 mm filter paper disc Ampicillin, streptomycin and penicillin antibiotics were used as a standard for comparison. The

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zone of inhibition was measured compounds (**Ib, Id, If, Ii, Ik, Im**). Shows significant antibacterial activity and remaining other compounds showed moderate to less activity.

### CONCLUSION

Secondary amines have been synthesized and tested for antibacterial activity. Some of the compounds (**Ib, Id, If, Ii, Ik, Im**) were found to be nearly equal or more active than standard antibiotics use for comparison (TABLE 1). Hence, further microbial activity study may become fruitful.

### ACKNOWLEDGEMENTS

The authors are thankful to Principal, Yeshwant Mahavidyalaya, Nanded for providing laboratory facilities. The Director of IICT, Hyderabad and Dept. of Chemistry, Pune University, Pune for providing I.R, <sup>1</sup>H NMR.

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