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Der Pharma Chemica, 2010, 2(6): 139-143
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X

Synthesis of New Bis-Schiff bases via environmentally benign grindstone technique

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ABSTRACT

Grindstone chemistry was used for the preparation of new bis-Schiff bases from 1,2-ethylene diamine and substituted benzaldehyde/acetophenones. Time required for formation of the bis-Schiff bases and yield of the products were compaired with conventional method. This method provides several advantages such as environmental friendliness, simple work-up procedure, and short reaction time with excellent yield.

Keywords: - Ethylene diamine, substituted benzaldehydes/acetophenones, Bis-Schiff bases, Grindstone technique.

INTRODUCTION

An environmentally benign synthesis method has received considerable attention. Verma etal[1] reported synthesis of Schiff bases using water as a solvent. Jarrahpour etal[2] has prepaired bis-schiff bases of Isatin by conventional method using ethanol solvent. Tania etal[3] reported synthesis of bis-imine Schiff bases under solvent free conditions and also in polypropelene glycol (PPG) as a recyclable reaction medium. Naqvi etal[4] have synthesized Schiff bases using (A) water based synthesis, (B) Microwave synthesis and (C) Grindstone synthesis. Laulloo etal[5] synthesised bis-Schiff bases under solvent free conditions. Jarrahpour and khaili[6] reported synthesis of bis-schiff bases of isatin and 5-Fluoroisatin in a water suspension medium. All these reported synthetic protocols are simple and giving high yield of products.

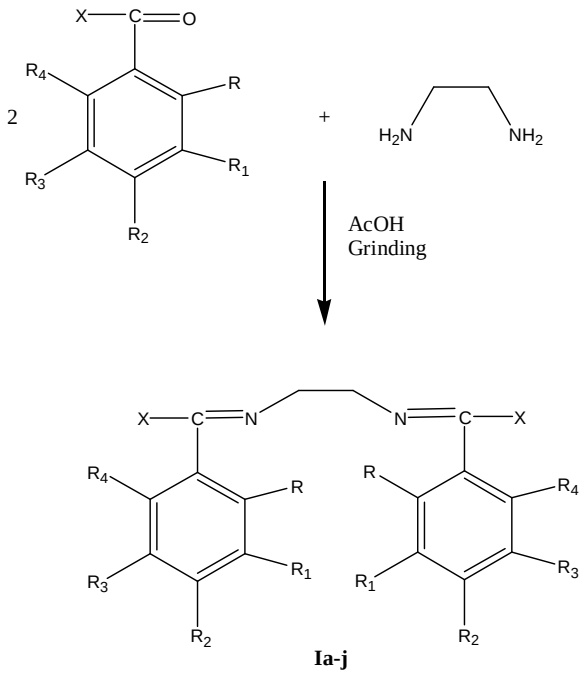
Metal-Salen Schiff bases complexes are useful as a catalyst in organic synthesis[7]. Schiff bases are well known for their biological activities like insecticidal[8], antibacterial[9], antituber culosis[10], antimicrobial[11], anticonvulsent[12], antifeedent[13], Schiff bases are used as amino protective groups in organic synthesis[13-16]. Based on these observations we decided to synthesis some new bis-schiff bases by reacting ethylene diamine with substituted benzaldehydes/acetophenones using grind-stone technique.

RESULT AND DISCUSSION

In the previous paper we have reported synthesis of number of bis-schiff bases[17], by using conventional heating method. Here in we report the synthesis of new bis-schiff bases using grindstone technique and by conventional method (scheme-I). 1,2-ethylene diamine and substituted benzaldehydes/acetophenones in the molar ratio of 1:2 respectively were taken in a porcilin mortar two drops of acetic acid was added and grinded by pistle for appropriate time (Table 1). Reaction mixture changes to pale yellow pasty mass. Reaction was monitered on TLC. After complition of reaction, water (20-30 ml) was added and stirred. Separated solid was filtered and purified by crystallizations. Structures of the synthesized products were characterized by IR, NMR and Mass and elemental analysis. IR spectra of bis Schiff bases showed a peak at 1610-1625 cm^{-1} duet to C = N stretching. All the Schiff bases showed negative test for aldehyde ^1H NMR spectra exhibited a single peak at near δ8.5 due to proton of azomethine. Structures were further confirmed by mass spectrum. All the bis-Schiff bases were synthesized by conventional method M.P. and Mixed M.P. with the product obtained by both method was not depressed. (Table1). A result shows that grindstone technique is superior as compaired to conventional method. No organic solvent required reaction completed within 3-10 minute with giving pure products and high percent yield.

Materials methods:-

Melting points are uncorrected, taken in open capillary tube. The purity of the compounds was checked by T.L.C. IR spectra were recoreded with KBr pellets on Shimadzu spectrophotometer and ^1H NMR spectra on Bruker WN-4OO FTMHz NMR instrument using DMSO (chemical shift are in δ ppm).



Ia-j

Scheme 1: Synthesis of some new bis-schiff bases.

General procedure for synthesis of bis-schiff bases by Grind stone (method A):-

1,2-ethylene diamine (0.01 mole) and substituted benzaldehydes/acetophenones (0.002 moles) were taken in a mortar. Acetic acid (0.2ml) was added and grinded by pistal for 1-10 min. Pasty mass with pale yellow/yellow orange colour separated out. Water (20-25 ml) was added and

stirred. Solid separated was filtered washed with water and crystallized from ethanol.

General procedure for synthesis of bis-schiff bases by conventional method (method B):-
1,2-ethylene diamine (0.001 mole) and aldehyde/ketone (0.002 mole) were dissolved in ethanol (15 ml). Acetic acid (0.2 ml) was added and reaction mixture was refluxed for 2-15 min. Reaction was monitored on TLC. Half of the solvent was evaporated and cooled. Separated solid was filtered washed with water and crystallized from ethanol. Time required for completion of reaction was compaired with method A (Table).

Spectral data and some bis-schiff bases:-
1. Bis(4-hydroxy-3-iodo-5-methoxy) benzylidene-1,2-ethylene diamine (1a):
IR (KBr, cm^{-1}): 1614(C=N), 1604 (C=C); **^{1}HNMR :** δ 3.91 (s, 4H, 2 x CH_2); 4.01 (s, 6H, 2 x OCH_3); 6.90 (s, 2H, Ar-H), 7.95 (s, 2H, ArH); 8.45 (s, 2H, 2x = CH);15.52 (s,2H, 2 x OH) . **MS (m/z) :** 580 (M^+), 563,326,277,191,175,91,77,51.

2. **Bis(3,5-diiodo-2-hydroxy) benzylidene-1,2-ethylene diamine(1e):**
IR (KBr, cm^{-1}): 1621(C=N), 1605 (C=C); **^{1}HNMR :** δ 3.97 (s, 4H, 2 x CH_2); 7.75 (s, 2H, Ar-H), 8.58 (s, 2H, 2 x = CH), 14.45 (s,2H, 2 x OH); **MS (m/z) :** 772 (M^+), 755, 678, 646, 554, 413, 399, 384,373,274,231,104,99,77.

3. Bis(2-hydroxy-5-chloro)benzylidene-1,2-ethylene diamine (1f):
IR (KBr, cm^{-1}): 1618 (C=N), 1595 (C=C); **^{1}HNMR :** δ 3.95 (s,4H, 2 x CH_2) δ 6.90 – 7.61(m,6H, Ar-H), δ 8.60 (s, 2H, 2 x = CH); 13.45 (s, 2H, 2 x OH); **MS (m/z) :** 326 (M^+), 265, 227, 209, 183, 171, 168, 155, 141, 91, 77.

4. **Bis(2-hydroxy-5-methyl)benzylidene-1,2-ethylene diamine (1j):**
IR (KBr, cm^{-1}): 1605 (C=N), 1555 (C=C); **^{1}HNMR :** δ 2. 5 (s,6H, 2 x CH_3); 3.9 (s, 4H, 2 x CH_2), 6.75 – 7.53 (m, 6H, Ar-H); δ 8.62 (s, 2H, 2 x = CH), 15.65 (s,2H, 2 x OH); **MS (m/z) :** 304 (M^+), 307,279,264,191,175,160,91,77.

Table – 1 : Physical and Analytical Data of Bis-Schiff bases

Entry Comp	X	R	R^1	R^2	R^3	R^4	M.P. ^0C	Crystal Appearance	Yield (%)		Time (In min.)		Mol.Formula	Eleemntal analysis Calculated(Found)			
									A	B	A	B		C	H	N	X
Ia	H	H	I	OH	OCH_3	H	142	Pale Yellow	75	-	10	15	$C_{18}H_{18}O_4N_2I_2$	37.26 (37.55)	3.13 (3.43)	4.83 (4.53)	43.75 (44.05)
Ib	H	H	Br	OH	OCH_3	H	132	Colourless	72	-	10	15	$C_{18}H_{18}O_4N_2Br_2$	44.47 (44.17)	3.73 (3.43)	5.76 (6.06)	32.84 (32.54)
Ic	H	OH	Br	H	Br	H	182	Yellow orange	83	-	01	02	$C_{16}H_{12}O_2N_2Br_4$	32.91 (33.21)	2.07 (2.37)	4.80 (4.50)	54.74 (54.44)
Id	H	OH	H	H	H	H	122	Colourless	85	-	02	02	$C_{16}H_{16}O_2N_2$	71.62 (71.32)	6.01 (6.31)	10.44 (10.14)	---
Ie	H	OH	I	H	I	H	220	Yellow orange	89	-	01	02	$C_{16}H_{12}O_2N_2I_4$	24.90 (24.60)	1.57 (1.27)	3.63 (3.93)	65.76 (65.46)
If	H	OH	H	H	Cl	H	168	Pale Yellow	81	-	02	15	$C_{16}H_{14}O_2N_2Cl_2$	56.99 (56.69)	4.18 (4.48)	8.31 (8.01)	21.03 (21.33)
Ig	CH_3	OH	I	H	CH_3	H	228	Yellow	80	-	03	13	$C_{20}H_{22}O_2N_2I_4$	41.69 (41.39)	3.85 (3.55)	4.86 (5.16)	44.05 (44.30)
Ih	CH_3	OH	H	H	CH_3	H	198	Pale Yellow	88	-	02	15	$C_{20}H_{24}O_2N_2$	74.04 (73.70)	7.46 (7.16)	8.64 (8.94)	---
Ii	CH_3	OH	Br	H	Cl	H	250	Pale Yellow	76	-	03	15	$C_{18}H_{16}O_2N_2Cl_2Br_2$	41.33 (41.03)	3.08 (3.38)	5.36 (5.06)	44.11 (44.41)

CONCLUSION

We report the synthesis of some new bis-schiff bases under organic solvent free condition and using grindstone technique. The advantages of this method include easy and simple procedure, no need of organic solvent, nearly quantitative yield, environmentally friendly synthesis.

Acknowledgement
The Authors are thankful to the Principal, Yeshwant Mahavidyalaya, Nanded, for providing Laboratory facilities. The Authors are also thankful to University Grant Commission New Delhi for providing Major Research Grant and IICT, Hyderabad for providing spectra.

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