

Synthesis of Schiff bases via eco-friendly and energy efficient greener methodologies

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ABSTRACT

The present paper deals with the synthesis of Schiff bases from substituted anilines and several benzaldehydes using Non-Classical methods such as water based reactions, microwave irradiation and grindstone chemistry. The raw materials were allowed to react in water as solvent, under microwave irradiation and grindstone friction activated synthesis. These methodologies involves an energy efficient greener chemistry version of the Classical condensation reactions of Schiff bases formation. The synthesized compounds are characterized on the basis of elemental analysis and spectral data such as IR, NMR, UV, Mass etc.

Key words: Schiff Bases, MWI, Grinding, Green Chemistry, Classical Condensation reaction.

INTRODUCTION

By identifying alternative reaction conditions and solvents for much improved selectivity, energy conservation and less or no toxic waste generation and inherently safer chemical products, the chemists has accepted challenges for the synthesis of novel and simple environmentally safe chemical processes for selective synthesis. Therefore, it is just urgent to adopt so called "greener technologies" to make chemical agents for well being of human health. Schiff's bases are reported to show characteristics biological activities including antibacterial, antifungal, antiradar and herbicidal properties¹⁻⁶. Other applications of Schiff bases induces industrial synthesis of high value life saving beta lactam⁷ antibiotics from class of penicillin's and cephalosporins.

In recent years, environmentally benign synthetic methods have received considerable

attention. Verma et al⁸ reported synthesis of enemies and imines under microware irradiation accompanied with solvent less condition. Kappa et al.,⁹ reported the synthesis of Schiff bases using water as a solvent Arshi Naqvi et al.,¹⁰ reported the synthesis of Schiff bases by environmentally benign synthetic methods. It was thought worthwhile to synthesize Schiff bases using greener methodologies.

EXPERIMENTAL

Melting points were determined in open capillary tube using Precision Digital Melting Point Apparatus Model MP-D and are uncorrected Shimadzu Make –Japan-8101. The NMR spectra were recorded on AMX-400 MHz, FT-NMR high resolution NMR spectrometer in DMSO using TMS as an internal standard. Chemical shifts are given in δ ppm. Nitrogen was estimated by Kjeldhals method. Microware irradiations were carried out in

an unmodified IFB domestic microwave oven. All chemicals were of analytical grade. The values are recorded in Table 2.

General Procedure

The three different greener methodologies that were adopted and studies for preparing Schiff bases are given below –

Method A : Water based synthesis

A mixture of aniline (5mmol) and substituted benzaldehyde¹⁻⁹ (5 mmol) was stirred in 10 ml H₂O for 30 min. at R.T. in few minutes, the temperature of the reaction mixture rises due to the heat evolved during this exothermic reaction, but it should not allowed to exceed 20°C above the R.T. The crystalline product so obtained was filtered, washed with water and dried . The product was obtained in good yield (80-90%)

Method B : Microwave synthesis

A mixture of sub aniline (1.0 mmo1) , substituted benzaldehyde¹⁻⁹ (0.1 mmo1) and piperidine (0.02 mmo1) was taken in DMSO (3ml) in a round bottom flask. Reaction mixture was irradiated in MW over for 3-6 min. On cooling the reaction mixture , a good yield (73 – 86%) of Schiff bases was obtained which was recrystallized from absolute ethanol.

Method C : Grind stone synthesis

A mix of substituted aniline (1mmo1) &

substituted benzaldehyde¹⁻⁹ (1mmo1) was grinded in a mortar with a pestle made of porcelain for 5-10 min The mixture turns pasty after few minutes of grinding. Leave the reaction mixture for overnight. The solid product thus obtained (53-70%) was recrystallized from ethanol.

RESULTS AND DISCUSSION

Formation of Schiff base is an exothermic reaction. So rather than providing energy in the form of heat, their synthesis has been scaled up towards green chemistry domain by circumventing the use of water as a solvent , microwave irradiations, and friction activated synthesis by grinding. Out of the above adopted greener methodologies , water based reaction has a great virtue as water is the abundantly available solvent and cheaper medium for reactions. Reactions in aqueous media are not only environmentally benign but also easy to handle and devoid of any corrosive or carcinogenic effect. More over by this method the products obtained are in high yield pure and easily isolable.

In conclusion from our point of view water has proved here as a suitable solvent for the synthesis of Schiff bases and increase in % yield is in following order:

Method A > Method B > Method C

Table 1: Analytical data of compounds

S. No.	Aldehydes	m.p. (°C)	Colour	N (%)		Yield (%)		
				Found	Cal.	A	B	C
1	3,4-Di-OCH ₃ BD	108	White	4.38	4.43	81.37	73.64	57.00
2	2-Cl BD	61	Pale Yellow	2.96	2.98	82.00	77.10	53.72
3	4-Cl BD	120	White	2.96	2.99	90.00	79.52	68.40
4	Piperonal	86	White	3.22	3.24	89.36	84.30	65.16
5	Vanillin	84	White	5.57	5.52	87.20	85.12	69.23
6	2 - OH BD	136	Yellow	3.58	3.60	87.79	79.00	70.25
7	4 - OH BD	170	Cream	3.58	3.62	84.65	83.42	63.80
8	3 – NO ₂ BD	138	White	10.05	9.98	89.72	84.42	64.32
9	2 – OH – 1- ND	120	Yellow	4.63	4.68	85.81	84.89	55.93
10	4 – NO ₂ BD	150	Cream	10.05	9.97	82.13	86.14	63.38

BD – Benzaldehyde ND - Naphthaldehyde

Table 2: NMR spectral data of compounds

Compound No.	2R (μ in cm^{-1})	NMR (δ ppm)
1	1020(C-C1),1262-1136(C-F) 1572(-CH = N) , 1624 (Ar – C – C), 2938 (-OCH ₃)	2.51(DMSO), 3.36(s,3H,OCH ₃) 3.83 (s,3H,OCH ₃) , 7.54 – 7.24 (m, 6H , Ar – H) , 8.54 (s, 1H, -CH = N-)
3	1056 (C – C1) , 1410 – 1175 (C-F), 1576 (-CH=N) , 1610 (Ar – C- C)	2.51 (DMSO) 7.33 – 7.395 (m, 7H , Ar – H) 8.67 (s,1H,-CH = N-)
6	975 (C-O) , 1057 (C- C1), 1270 – 1150 (C-F) , 1496 (-OH), 1512 (-CH = N) , 1617 (Ar – C – C)	2.51 (DMSO) , 6.96 – 7.54 (m, 7H, Ar – H) 8.96 (s, 1H , - CH = N) 12.50 (s, 1H , - OH)

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