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Synthesis of Schiff Base under Solvent-free Condition: As a Green Approach

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Abstract: A new route for the synthesis of Schiff bases **(3a-g)** was developed by eco-friendly reactions to increase the yield of products by maintaining the purity of them.
By considering this a novel and green synthesis of salicylaldimine Schiff bases **(3a-g)** were successfully carried out by irradiating salicyaldehye **(1)** with substituted aryl amines (**2a-g)** respectively without using any solvent and catalysts.The justification and identification of the structure of these newly synthesized compounds have been established on the basis of elemental analysis and through spectral data.
Key words: schiff bases, microwave, amine, aldehyde.

Introduction

Schiff bases have been known since 1864 when Hugo Schiff reported the condensation of primary amines with carbonyl compounds.[1] The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R_1, where R and R_1 are alkyl, aryl, cyclo alkyl or heterocyclic groups. These compounds are also known as anils, imines or azomethines.

Schiff bases resulted from aromatic aldehydes *ortho-substituted* with a hydroxyl group have initially arouse the researchers' interest because of their ability to act as bidentate ligands for transitional metal ions.[2-6] Later, in studies concerning quantitative structure-antitumor activity relationship of a series of Schiff bases derived from variously substituted aromatic amines and aldehydes, it has been shown that azomethines from salicylaldehydes gave the best correlation.[7,8] Schiff bases of salicylaldehydes have also been reported as plant growth regulators,[9] antimicrobian[10] and antimycotic[11] activity. Schiff bases also have some analytical applications.[12] Schiff Bases are characterized by the -N=CH- (imine) group which imports in elucidating the mechanism of transamination and rasemination reaction in biological system.[13,14]

Microwave assisted synthesis, a green chemistry approach, is now a day widely practiced in the synthetic laboratories. Various green strategies have been worked out. One of the thrust areas for achieving this target is to explore alternative reaction conditions and reaction media to accomplish the desired chemical transformation with minimized by-products or waste as well as eliminating the use of conventional organic solvents, if possible.[15, 16]

Microwave reactions under solvent-free conditions are attractive in offering pollution free reaction, low cost, shorter reaction time and high yields together with simplicity in processing and handling.[17-21] The recent

introduction of single-mode technology[22] assures safe and reproducible experimental procedures and microwave synthesis has gained acceptance and popularity among the synthetic chemist community.

In the present work, some Schiff's bases were synthesized by solvent free technique using microwaves. They were purified and characterized by means of spectral data and elemental analysis.

Experimental

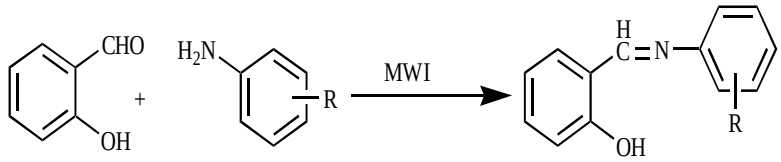
Melting points (mp) were determined using Boetieus micro heating table and are uncorrected. IR (KBr, cm^{-1}) spectra were obtained on Shimadzu-8201 spectrophotometer. ^1H NMR spectra were recorded on Bruker AMX-400 (400 MHz) spectrometer using TMS as an internal reference (Chemical shifts in δ, ppm). Elemental analyses were performed on Perkin Elmer CHN-analyzer. Mass spectra were recorded on Shimadzu GCMS-QP5050A (70 ev) mass spectrometer. For microwave irradiation a Kenstar (OM-20ESP, 2450 MHz) domestic microwave oven was used.

General method for preparation of Schiff bases (3a-g)

A mixture of respective anilines and salicylaldehyde was taken in a 50 mL beaker and mixed well. The mixture was irradiated in a microwave oven at a power of 160 W for the specified time (**Table 1**). The reaction was monitored by thin layer chromatography (TLC) and spots were visualized in iodine chamber. After completion of the reaction, the reaction mixture was poured into ice water. The yellow solid obtained was filtered, washed, dried and recrystalised from ethanol. The spectral and analytical data of the compounds are given in Table 1 & 2.

Results and Discussion

A series of salicylaldimine schiff bases are prepared from salicyladehyde and substituted aniline by microwave irradiation in appropriate time (Scheme 1). It is observed that the condensation between a carbonyl compound and an amine leading to the formation of Schiff bases should be a facile reaction due to the good electrophilic and nucleophilic characteristic properties of the carbonyl and amine groups respectively.



1 **2a-g** **3a-g**

R= 2-COOH,4-Cl, 4-NO_2, 4-CH_3, 4-OCH_3,2-CH_3, 2-OCH_3

Scheme 1

The presence of the methoxy group in 4-methoxyaniline reduces the electrophilicity of the amine through resonance and the strong electron withdrawing property of the nitro group in 4-nitroaniline decreases the nucleophilicity of the amine group. The less nucleophilic amines such as 4-nitroaniline and less electrophilic aldehydes such as 2-hydroxybenzaldehyde were employed. Good results are obtained in the later two cases (**3c, 3f**). It was also observed that if one of the reactant is deactivated by its substituent, comparatively more reaction time is required to complete (TLC) the reaction. The structures of the target compounds were well characterized by IR, ^{1}HNMR, ^{13}CNMR and MS Spectra. Analytical and spectral data of Schiff bass are depicted in Table 1 & 2.

Table 1: Analytical and IR Spectral data of Schiff bases 3a-g

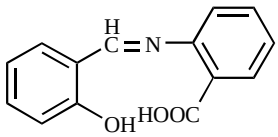
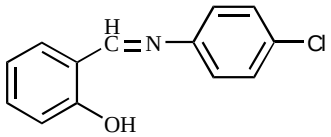
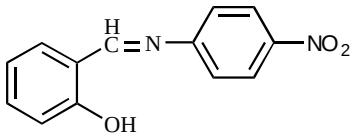
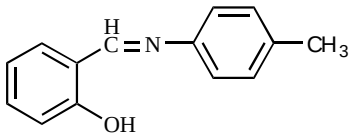
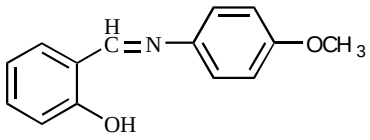
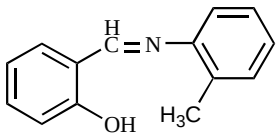
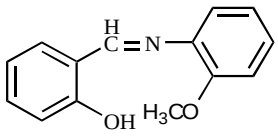
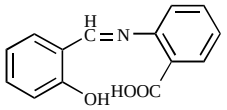
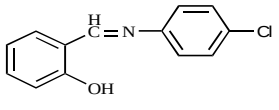
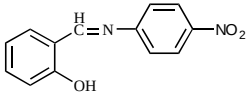
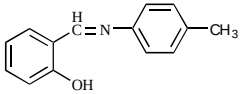
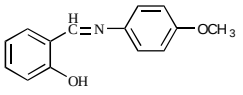
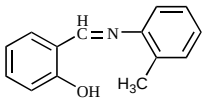
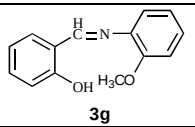
S.NO.	Compound	Physical Data			IR Spectrum (KBr,cm^{-1})		
		Reaction Time (min)	**Yield (%)**	**mp° C**	**$\nu_{C=N}$**	**ν_{C-O}**	**ν_{C-C} (aromatic stretching)**
1	 **3a**	4	92	220	1615	1230	1507 1454 1373
2	 **3b**	3	97	205	1614	1280	1588 1571 1498 1457
3	 **3c**	3	97	190	1600	1272	1565 1508 1484 1459
4	 **3d**	4	95	185	1615	1278	1560 1510 1482 1459
5	 **3e**	5	95	215	1612	1280	1575 1518 1464 1462
6	 **3f**	4	91	207	1614	1277	1572 1505 1474 1466
7	 **3g**	5	90	218	1620	1265	1561 1501 1489 1466

Table 2: Spectral data of Schiff bases 3a-g

S. NO.	Compound	^{1}HNMR Spectrum (ppm)					^{13}CNMR Spectrum (ppm)				Mass Spectrum (70 eV, *m/e*)	
		δ_{C-H}	δ_{OH}	$\delta_{CH=N}$	δ_{COOH}	δ_{CH3}	δ_{C}(Ar)	δ_{CN}	δ_{COOH}	δ_{CH3}	Molecular Formula	(M^{+})
1	 **3a**	6.6-7.4	12.94	8.59	11.06	-	117.3-163.7	76.7-77.4	196.59	-	$C_{14}H_{11}NO_3$	241
2	 **3b**	6.47-7.75	13.00	9.92	-	-	109.9-174.9	82.8-82.9	-	-	$C_{13}H_{10}NOCl$	231
3	 **3c**	6.98-8.30	12.58	9.65	-	-	117.5-165.3	76.7-77.3	-	-	$C_{13}H_{10}N_2O_3$	242
4	 **3d**	6.62-7.92	12.23	9.62	-	2.45	119.4-162.3	77.4-78.4	-	29.03	$C_{14}H_{13}NO$	211
5	 **3e**	6.78-8.02	12.52	9.78	-	3.97	111.5-172.5	82.4-82.8	-	35.66	$C_{14}H_{13}NO_2$	227
6	 **3f**	6.92-8.22	13.05	8.79	-	2.52	117.4-163.5	76.2-77.8	-	30.22	$C_{14}H_{13}NO$	211
7	 **3g**	6.88-8.15	12.88	8.92	-	3.93	115.4-164.0	76.7-77.6	-	39.56	$C_{14}H_{13}NO_2$	227

Conclusion

In this article, we are reporting a new eco-friendly route with good yield for the synthesis of Schiff bases by solvent free microwave irradiation, and the products can be purified by recrystallization using appropriate solvents. This solvent-free approach is nonpolluting and does not employ any toxic materials, quantifying it as a green approach for the synthesis of Schiff bases.

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