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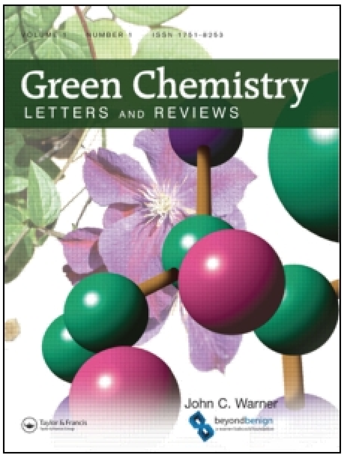

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Synthesis of Schiff's bases in aqueous medium: a green alternative approach with effective mass yield and high reaction rates

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RESEARCH LETTER

Synthesis of Schiff's bases in aqueous medium: a green alternative approach with effective mass yield and high reaction rates

V. Koteswara Rao[a], S. Subba Reddy[a], B. Satheesh Krishna[a], K. Reddi Mohan Naidu[a], C. Naga Raju[a]* and S.K. Ghosh[b]

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Schiff's bases constitute a class of pharmaceutical and medicinally important molecules. The conventional methods for the synthesis of Schiff's bases require long reaction times and use of organic solvents. We report a novel and eco-friendly condensation reaction method permitting the "green synthesis" of various Schiff's bases by stirring 1,2-diaminobenzene with various aromatic aldehydes in water as solvent. This method is experimentally simple, clean, high yielding, green, and with reduced reaction times. The product is purified by simple filtration followed by washing with water and drying processes.

Keywords: green synthesis; Schiff's bases; aromatic aldehydes; aqueous medium

Introduction

The concept of green chemistry (*1–5*) and its applications (*6–9*) in synthetic organic chemistry have emerged as major solutions for the development of clean and more benign chemical processes. Various methodologies and routes have been developed for this purpose. In recent years, environmentally benign synthetic methods have received considerable attention and some solvent-free protocols have been developed (*10,11*). Schmeyers *et al.* reported the solid-state synthesis of various kinds of benzylideneaniline derivatives by grinding together solid anilines and solid benzaldehydes (*12*). Varma *et al.* reported the clay catalyzed synthesis of imines and enamines under solvent-free conditions using microwave irradiation (*13*). There has been a large emphasis both in the chemical industry and in academic research on the development of environmentally benign solvents and reaction conditions. This is largely owed to the fact that traditional solvents, such as volatile organic solvents, have been implicated in a number of environmental problems. Organic synthetic procedures use organic solvents like benzene and chlorinated hydrocarbons, which have created havoc to the environment because of their toxic and volatile nature (*14,15*). To reduce such disasters there is a need to use a safer reaction medium like water. Water is non-toxic, safe, cheap, and never leads to menace to the environment (*16–21*). The use of water as a solvent (*22–30*) is undoubtedly the best alternative as there are generally no harsh reaction conditions and no need of vigorous drying of the solvents.

Schiff's bases have been playing vital roles in pharmaceuticals, rubber additives (*31*), as amino protective groups in the synthetic organic chemistry and several biologically active organic compounds (*32–34*). They are also used as liquid crystals (*35*) in analytical (*36*), medicinal (*37,38*), and polymer chemistry (*39,40*). Besides their utility in phosphorus chemistry Schiff's bases have been used for the preparation of α-aminophosphonate esters and *H*-phosphonate esters with repeatable Pudovik reaction (*41–45*), which possess bioactivity such as inhibitor of cancers and viruses, and as antibiotics. Particular attention has recently been paid to the synthesis and study of imino and diimino Schiff's bases and their complexes. This is due to various reasons, such as the biological functions of bacteriorhodopsin (*46*). Schiff's base complexes of small organic molecules with metal cations have found broad applications in the field of interactions with biogenic macromolecules such as DNA, RNA, and peptides (*47,48*). Considering the numerous applications of Schiff's bases in various fields of chemistry, there has been tremendous interest in developing efficient methods for their preparation. Although

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different research groups have developed various methods for different types of condensation reactions attempted so far (*49–54*), these methods suffer from drawbacks such as prolonged reaction times and low yields. In such consequences we have developed a new protocol for the preparation of Schiff's bases in aqueous media with short times and high yields.

In the present work, we report our results for the preparation of Schiff's bases in aqueous medium under the aspect of environmentally benign processes with high yields, which are superior to conventional methods. Our new method has the advantage that neither acid catalysts nor aromatic solvents for azeotropic water separation are needed. The product can be isolated simply by filtration, and it is noteworthy to mention that the condensation reactions occur very efficiently in the presence of water.

Results and discussion

Conventionally, Schiff's bases can be prepared by refluxing the amine and aldehyde in an organic solvent, for example, ethanol or methanol, with variations which are known, such as treatment of the same mixture at room temperature, refluxing the mixture in heptane in the presence of acetic acid, or azeotroping the mixture with benzene in a Dean–Stark apparatus in the presence of acid (*55*). In addition, the equilibrium must often be shifted, usually by removal of the water, either azeotropically by distillation or with suitable drying agents.

In the present method, we describe a mild, efficient, high yielding efficient process for the condensation reaction of various aromatic aldehydes and 1,2-diamino benzene in water at room temperature (Scheme 1). Using this methodology these reactions were completed in shorter reaction times (5–22 min) with excellent yields (94–98%). It is noteworthy to mention that the green route method requires simple work-up procedures, i.e. simple filtration to isolate the products as they are insoluble in water and the desired products were obtained with satisfactory yields without any further purification. Considering the reaction time with water as solvent and yield of products this process was selected as green, environmental benign, clean, and safe to promote the synthesis at room temperature of various Schiff's bases (Tables 1 and 2).

This acceleration has been attributed to many factors, including the hydrophobic effect (*56,57*), enhanced hydrogen bonding in the transition state (*58*) and the high cohesive energy density of water (550.2 cal.ml^{-1} at 25°C) (*59,60*). From previous studies (*61–63*), the above three effects are as mentioned, the first involves the notion that enforced hydrophobic interactions[1] destabilize the initial state relative to the activated complex, thereby increasing the rate of the reaction in water. Secondly, hydrogen bonding of water to the activating group(s) stabilizes the polarized activated complex, leading to a significant rate enhancement. This is due to the small size of the water molecule which allows efficient interaction with hydrogen bond acceptors by forming more hydrogen bonds than protic organic solvents; hence, the rate of the reaction was increased in water. Thirdly, the cohesive energy density of water is high (550.2 cal.ml^{-1} at 25°C) as it is able to form four hydrogen bonds with four other water molecules in a tetrahedral configuration, where as it is not possible in the case of organic solvents like methanol (204 cal.ml^{-1} at 25°C), benzene (85 cal.ml^{-1} at 25°C), tetra chloromethane (74 cal.ml^{-1} at 25°C). This facilitates faster water reactions. Recent computer simulations by Blake *et al.* (*64*) strongly support these suggestions.

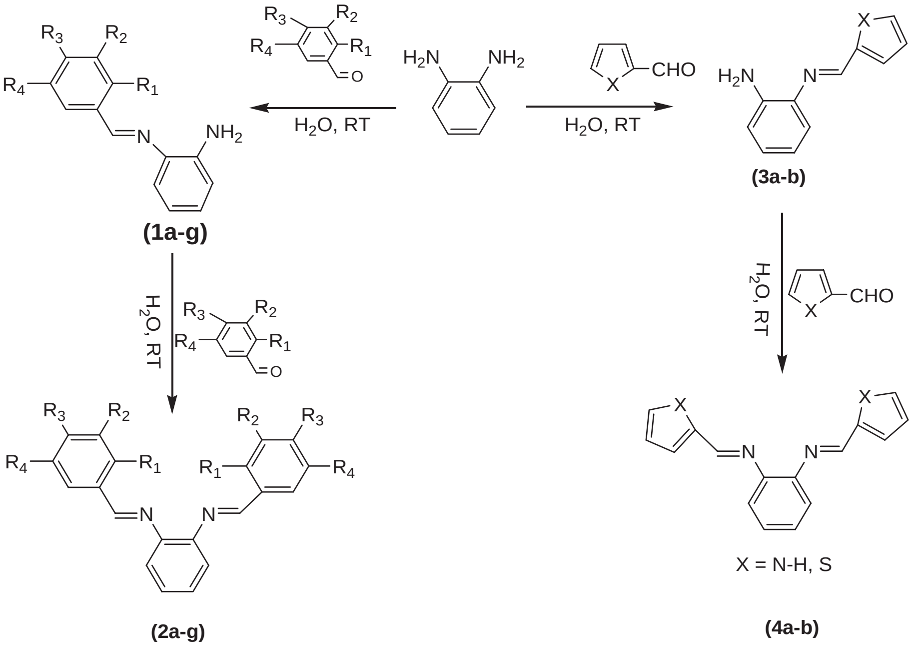
As cited above, not only does the use of water as solvent allow for rapid reactions, but also the products are often insoluble in water, facilitating their ready isolation. This method permits a rapid synthesis of compound libraries. The utility of Schiff's base reactions has been significantly expanded by conducting them in water. They can exhibit rate accelerations compared to those in organic solvents of nearly 300-fold, and the insolubility of the products in water renders isolation trivial. The crude reaction products show adequate purity for initial biological investigation.

The Schiff's bases **(1a–g)**, **(3a – b)**, and **(2a–g)**, **(4a–b)** were obtained via the condensation of 1,2-diamino benzene with various substituted aromatic aldehydes in aqueous medium in corresponding molar ratio of 1:1 and 1:2 (Table 1).

Schiff's bases **(1a–g)**, **(2a–g)**, **(3a–b),** and **(4a–b)** showed strong characteristic IR absorption bands at 3475–3392, 3386–3313, and 1632–1592 cm^{-1} for O–H, N–H, and C = N, respectively (*65,66*). In the ^{1}H NMR spectra of **(1a–g)**, **(2a–g)**, **(3a–b)**, and **(4a–b)** aromatic hydrogens of the phenylene ring were observed as multiplets (*67*) at δ 6.39–7.90. The N–H hydrogen resonated as a broad singlet at δ 4.72–5.30. The – CH = N– hydrogen resonated as a singlet at δ 8.40–8.72. ^{13}C NMR chemical shifts for compounds **(1a–g)**, **(2a–g)**, **(3a–b)**, and **(4a–b)** were observed in their expected region.

Experimental

All chemicals were obtained from Sigma-Aldrich, Merck, and Lancaster, and used as such without further purification. Melting points were determined



Scheme 1. Overall green synthetic route of Schiff's bases.

using a calibrated thermometer by Guna Digital Melting Point apparatus and are uncorrected. Elemental analyses were performed by Central Drug Research Institute, Lucknow, India. IR Spectra were recorded in the Environmental Engineering Laboratory, S.V. University, Tirupati, as KBr discs on a Nicolet 380 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ on a Bruker AMX 400 MHz spectrometer operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C. The ^{1}H and ^{13}C chemical shifts were referenced to tetramethylsilane. LC Mass spectra were recorded on LCMS 2010A Shimadzu and FAB Mass spectra were recorded on a Jeol SX 102 DA/600 Mass spectrometer (Scheme 2).

Table 1. Schiff's bases of various aromatic aldehydes.[a]

					Reaction time		Yields[b] (%)		Melting points (°C)	
Compound	R_1	R_2	R_3	R_4	Gre. (min)	Conv. (hrs)	Gre.	Conv.	Obs.	Lit.
1a	OH	H	H	H	8	2	95	65	192–194	191–197 (*55*)
1b	H	OH	H	H	5	4	98	54	111–112	111–113 (*68*)
1c	H	H	OH	H	10	2	96	66	196–197	196–197 (*69*)
1d	H	H	H	H	20	4	96	71	147–149	148–150 (*70*)
1e	H	H	Cl	H	22	5	97	90	167–168	167–169 (*71*)
1f	OH	H	H	Cl	10	2	95	74	125–127	124–126 (*68*)
1g	OH	H	H	Br	8	1	94	52	194–196	194–196 (*72*)
2a	OH	H	H	H	8	4	97	48	161–162	161–163 (*73*)
2b	H	OH	H	H	5	5	98	55	197–199	198–200 (*71*)
2c	H	H	OH	H	10	1	96	62	194–196	196–198 (*71*)
2d	H	H	H	H	20	3	95	64	195–196	195–197 (*74*)
2e	H	H	Cl	H	22	2	96	55	194–196	196–198 (*75*)
2f	OH	H	H	Cl	10	1	95	58	195–196	
2g	OH	H	H	Br	8	2	97	52	142–144	

[a] All the products were characterized by IR, ^{1}H, ^{13}C, and mass spectral data.
[b] Isolated yields based upon starting aldehyde.
Note: Gre., green route method; Conv., conventional method.

Table 2. Schiff's bases of various hetero aromatic aldehydes.[a]

		Reaction time		Yields[b] (%)		Melting points (°C)	
Compound	X	Gre.	Conv.	Gre.	Conv.	Obs.	Lit.
3a	N–H	12 min	90 min	96	65	194–196	195–197 (*37*)
3b	S	14 min	80 min	95	68	143–145	144–145 (*47*)
4a	N–H	10 min	2 hrs	94	51	241–243	241–243 (*37*)
4b	S	10 min	2 hrs	94	68	164–165	165–166 (*44*)

[a] All the products were characterized by IR, ^{1}H, ^{13}C, and mass spectral data.

[b] Isolated yields based upon starting aldehyde.

Note: Gre., green route method; Conv., conventional method.

Conventional method

To a solution of 1.08 gm of 1,2-diaminobenzene (0.01 mole) in 30 ml of ethanol, a solution of 1.22 gm of salicylaldehyde (0.01 mole) in 20 ml of ethanol was added. A few drops of 10% NaOH were added to adjust the pH and the reaction mixture then refluxed with stirring for two hours and the obtained precipitate was collected by filtration through Buchnner funnel, recrystallized from methanol, and dried at room temperature to afford yellow needles (yield 65%, mp 192–194°C).

Green route method

To a solution of 1.08 gm of 1,2-diaminobenzene (0.01 mole) in 10 ml of water, 1.22 gm of salicylaldehyde (0.01 mole) was added. The resulting mixture was then stirred for 10 min at room temperature. The yellow precipitate formed was filtered, washed with water, and dried to afford yellow needles (yield 95%, mp 192–194°C).

By following the same experimental procedure, the remaining title compounds **(1b–g)** and **(3a–b)** are prepared (Scheme 3).

The same experimental procedure was adopted for the preparation of the compound **(2a)** by taking 0.02 moles of salicylaldehyde with 0.01 mole of 1, 2-diaminobenzene. The Schiff's bases obtained by both conventional and green route methods are subjected to melting point determination and obtain the reading as 161–162°C, which are comparable to the literature value of 161–163°C, but the yields are highly varying, i.e. 52% yield in conventional method and 97% yield in the green route method.

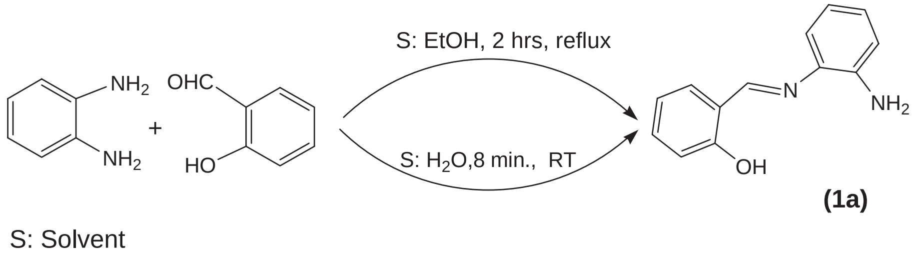
By following the same experimental procedure, the remaining title compounds **(2b–g)** and **(4a–b)** are prepared.

The structures of all the compounds were characterized by IR, ^{1}H, ^{13}C, and mass spectral data.

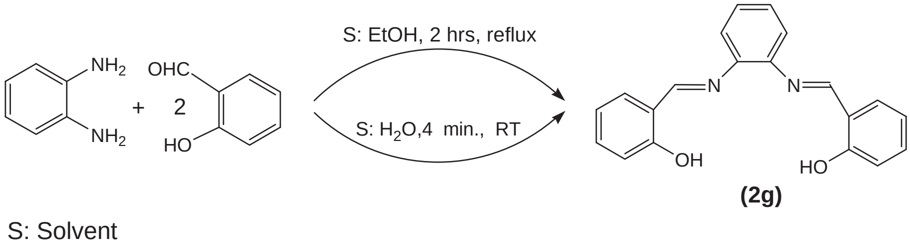
Spectral data of compounds

2-((Z)-(2-aminophenylimino) methyl) phenol ***(1a)***
IR-cm^{-1} (KBR): 3392 (O–H), 3313 (N–H), 1598 (C = N).
^{1}H NMR studies (CDCl$_3$) ppm: 10.18 (1H, s, O–H), 8.42 (1H, s, $-N=\underline{CH}-$), 6.40–7.45 (8H, m, Ar–H), and 5.02 (2H, br s, N–H).
^{13}C NMR (CDCl$_3$) ppm: 162.7, 160.1, 143.2, 141.0, 135.0, 130.5, 128.0, 121.2, 120.2, 117.1, and 116.2.
LCMS m/z (%) 214 (100%) [M + 2].

2,2'-(1E,1'E)-(1,2-phynelenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol ***(2a)***
IR-cm^{-1} (KBR): 3453 (O–H), 1628 (C = N).
^{1}H NMR studies (CDCl$_3$) ppm: 10.15 (2H, s, O–H), 8.72 (2H, s, $-N=CH-$), and 6.40–7.82 (12H, m, Ar–H).



Scheme 2. Synthesis of 2-((Z)-(2-aminophenylimino) methyl) phenol (**1a**).



Scheme 3. Synthesis of 2,2′-(1E,1'E)-(1,2-phynelenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol (**2g**).

^{13}C NMR ($CDCl_3$) ppm: 162.7, 161.7, 143.2, 141.0, 132.0, 130.5, 128.0, 121.2, 120.2, 117.1, and 116.2.
FAB m/z (%) 317 (100%) [M+1], 281 (4%), 211 (32%).

*(E)-N^1-((1H-pyrrol-2-yl) methylene) benzene-1,2-diamine **(3a)***
IR-cm^{-1} (KBR): 3380 (N–H), 1612 (C=N).
^{1}H NMR studies ($CDCl_3$) ppm: 8.56 (1H, s, $-N=CH-$), 7.25 (1H, s, N–H), 6.20–7.00 (7H, m, Ar–H), and 4.65 (2H, s, N–H).
^{13}C NMR ($CDCl_3$) ppm: 162.7, 161.7, 143.2, 141.0, 132.0, 130.5, 128.0, 121.2, 120.2, 117.1, and 116.2.LCMS m/z (%) 186 (100%) [M+1].

*(N^{1}E, N^{2}E)-N^1,N^2-bis((1H-pyrrol-2-yl) methylene) benzene-1,2-diamine**(4a)***
IR-cm^{-1} (KBR): 3375 (N–H), 1621 (C=N).
^{1}H NMR studies ($CDCl_3$) ppm: 8.52 (2H, s, $-N=\underline{CH}-$), 7.55 (2H, s, N–H), 6.20–7.00 (7H, m, Ar–H), and 4.65 (2H, s, N–H).
^{13}C NMR ($CDCl_3$) ppm: 162.7, 161.7, 143.2, 141.0, 132.0, 130.5, 128.0, 121.2, 120.2, 117.1, and 116.2.
LCMS m/z (%) 264 (20%) [M+2], 263 (100%) [M+1], 261 (25%), 246.

Conclusion

We developed a convenient, simple, efficient, and eco-friendly green procedure for the synthesis of Schiff's bases from various aldehydes and 1,2-diamino benzene under mild reaction conditions in an aqueous medium at room temperature. From the spectroscopic characterization it is concluded that the products obtained from conventional and green methods are comparable in chemical composition. Some of the major advantages of this protocol are the ambient conditions, very high yields, short reaction times, simple work-up procedure, use of water as a desirable solvent for chemical reaction for reasons of cost, safety, and environmental concerns. To our knowledge this method represents the first example of synthesis of Schiff's bases in water. All these advantages make this methodology an alternative platform to the conventional method and also make it significant under the umbrella of environmentally greener and safer processes.

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Note

1. The term enforced is used to distinguish the hydrophobic bonding of the reactant in the activated complex from hydrophobic interactions not dictated by the activation process, which may lead to complexes of different geometry.

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