A review on synthesis and biological activity of Schiff Bases

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Schiff bases are versatile organic compounds, gaining importance day by day due to their wide applications. Schiff bases, containing imines or azomethine functional groups, are prepared by condensation of primary amines with carbonyl compounds or they may occur naturally in plants. They have lots of importance in industry and show numerous biological activities including antibacterial, antifungal, antiviral, anticancer, etc. The wide range of biological studies of the Schiff bases are now attracting the attention of researchers which can lead to the identification of promising lead compounds. This review consists of the recent developments and various methodologies to synthesize Schiff base as well as their biological activities covering the last 20 years.

Keywords: Amines, aldehydes, Schiff base, antibacterial, antifungal, antimalarial

Schiff Base (SB), a versatile compound discovered by chemist Hugo Schiff, is formed when condensation of primary amines with carbonyl compounds under specific reaction conditions\textsuperscript{1}. They are also termed as imine or azomethine (-C=N-). SB ligands form more readily with aldehydes than ketones. Study on SB has been done due to its very flexible character and different structures. SBs form stable complexes with metal ions\textsuperscript{2-3}. At very high temperature and in the presence of moisture many SBs show catalytic activity in various reactions. SB acts as an important intermediate in many enzymatic reactions which involves the interaction of an enzyme with carbonyl or an amino group of the substrate\textsuperscript{4,5}. In the field of organic chemistry, SB shows large number of synthetic uses. It is widely used in organic compounds such as pigment, dyes, catalysts, intermediates and polymer stabilizers\textsuperscript{6}.

Imines group can be found in a variety of natural and synthetic compounds which show diverse biological activities. SB also shows several biological properties including anti-inflammatory, antimalarial, antifungal, antibacterial, antiviral, anti-proliferative and antipyretic, etc.\textsuperscript{7-36} SBs were showed antibacterial activity against some bacterial strains like \textit{Acinetobacter baumannii}, \textit{Bacillus subtilis}, \textit{Enterococcus faecalis}, \textit{Escherichia coli}, \textit{Klebsiella Pneumonia}, \textit{M. tuberculosis}, \textit{Micrococcus luteus}, \textit{Micrococcus flavus}, \textit{Mycobacterium phlei}, \textit{Pseudomonas fluorescence}, \textit{Proteus vulgaris}, \textit{Salmonella enteric}, \textit{Staphylococcus aureus}, \textit{Streptococcus epidermidis} and \textit{S. pyogenes}, etc.\textsuperscript{14-20} SBs were reported to exhibit antifungal activity against fungal strains including \textit{Aspergillus fumigatus}, \textit{Aspergillus flavus}, \textit{Aspergillus niger}, \textit{Candida albicans}, \textit{Candida tropicalis}, \textit{Candida guillermondii}, \textit{Candida glabrata}, \textit{Cryptococcus neoformans}, \textit{Epidermophytong floccosum}, \textit{Histoplasma capsulatum}, \textit{Microsporum audouinii}, \textit{Microsporum gypseum}, \textit{Penicillium marneffei}, \textit{Trichophyton mentagrophytes} and \textit{Trichophyton rubrum}, etc.\textsuperscript{21-24}

In our review, we describe the various reported schemes to the synthesized of SBs. We also highlight the biological activities of SBs reported in the literature.

Synthesis of Schiff Bases

Imine was prepared for the first time by Schiff in 19\textsuperscript{th} century. He reported the synthesis of imines under azeotropic distillation. Dehydrating agents such as molecular sieves or magnesium sulphate are used to remove water from the system (Figure 1). Later, numerous methods have been reported for the synthesis of Schiff base.
synthesis of imines. According to Chakraborti et al. 2004, the carbonyl compounds should be highly electrophilic and amines should be strongly nucleophilic for efficiency of the methods for synthesis of SB. A SB is formed when an aldehyde or ketone react with an amine by acid or base catalysis, or upon heating with the removal of water. Due to the presence of effective conjugation, aromatic aldehydes form stable SBs in comparison to aliphatic aldehydes. Various techniques including microwave irradiation, water suspension medium, solid-state irradiation, infrared irradiation and ultrasonication have been reported. The different schemes of synthesis of SBs are listed in Table I.

Table I — The various Schiff bases

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde/ketone</th>
<th>Amine</th>
<th>Conditions</th>
<th>Products</th>
<th>Comments</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td>Aldehyde: Amine at 1:1 molar ratio; Hot ethanol; Reflux at 70°C; 6-8 h.</td>
<td><img src="image3" alt="Image" /></td>
<td>A novel SB was synthesized at reflux condition.</td>
<td>3</td>
</tr>
<tr>
<td>E2</td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td>Aldehyde: Amine at 1:1 molar ratio; Ethanol (25 mL); Reflux (2 h)</td>
<td><img src="image6" alt="Image" /></td>
<td>Three substituted SBs were synthesized. The SBs containing chloro group showed significant antibacterial activity while compounds containing benzthiazole moiety showed antifungal activity.</td>
<td>47</td>
</tr>
<tr>
<td>E3</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td>Aldehyde: Amine at 1:1 molar ratio; Absolute Ethanol; Stirring 2h and (5-10 h); 60-70°C; NaOH</td>
<td><img src="image9" alt="Image" /></td>
<td>The preparation of SBs have been carried out by stirring at 60-70°C.</td>
<td>48</td>
</tr>
</tbody>
</table>

(Contd.)
Table I — The various Schiff bases (Contd.)

<table>
<thead>
<tr>
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| E4    | ![Aldehyde](image) | ![Amine](image) | a) Aldehyde: Amine at 1:1 molar ratio; CH₃OH; Reflux (5-6 h)  
b) Aldehyde: Amine at 1:1 molar ratio; CH₃OH; M.W. (2-3 min). | ![Products](image) | The SBs preparation have been carried out by conventional and microwave methods. In conventional method, the reaction took 5-6h, whereas by microwave irradiation it took only 2-3min. The SBs were prepared in alkali absolute methanol. | 60 |
| E5    | ![Aldehyde](image) | ![Amine](image) | Aldehyde (1.0 mmol): Amine (1.2 mmol); KOH; Methanol; Reflux; 8 h. | ![Products](image) | 49 |
| E6    | ![Aldehyde](image) | ![Amine](image) | a) Aldehyde: Amine at 1:1 molar ratio; Water; 1-2 h  
b) Aldehyde: Amine at 1:1 molar ratio; Microwave/ 50-80°C; 30 sec to 2 min.  
Aldehyde: Amine at 1:1 molar ratio; Reflux 1h; Ethanol; Pouring in ice | ![Products](image) | The SBs preparation have been carried out by conventional and microwave methods. In microwave, the best yield was obtained at 70°C. | 50 |
| E7    | ![Aldehyde](image) | ![Amine](image) | ![Products](image) | 1 example (60%) | The condensation of SB was performed in reflux condition by taking equimolar amounts of furan-3-carboxaldehyde and 3-amino pyridine. | 51 |
| E8    | ![Aldehyde](image) | ![Amine](image) | ![Products](image) | 11 examples (42-75%) | The condensation of α-hydroxyl aldehyde with Ethyl 2-amino-4,5,6,7-tetrahydrobenzo(β)thiophene 3-carboxylate in 1:1 molar ratio to form SB. | 61 |
| E9    | ![Aldehyde](image) | ![Amine](image) | Aldehyde: Amine at 1:5 molar ratio; Absolute ethanol; Acetic anhydride; Reflux | ![Products](image) | 52 |
Table I — The various Schiff bases (Contd.)

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<tr>
<td>E10</td>
<td><img src="image1" alt="Aldehyde" /></td>
<td><img src="image2" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:1 molar ratio; Reflux, 3 h glacial CH$_3$COOH</td>
<td><img src="image3" alt="Product" /></td>
<td>The condensation of SB was performed in reflux condition with glacial acetic acid.</td>
<td>53</td>
</tr>
<tr>
<td>E11</td>
<td><img src="image4" alt="Aldehyde" /></td>
<td><img src="image5" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:1 molar ratio; a) Microwave irradiation; b) reflux; c) Stirring; d) Grinding; Ethanol; NaOH</td>
<td><img src="image6" alt="Product" /></td>
<td>Among the methods including Microwave, Reflux, Stirring and Grinding for SB preparation, microwave irradiation requires the least time and greatest yield (80%).</td>
<td>54</td>
</tr>
<tr>
<td>E12</td>
<td><img src="image7" alt="Aldehyde" /></td>
<td><img src="image8" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:1 molar ratio; Na$_2$SO$_4$, CHCl$_3$; Reflux 24 h</td>
<td><img src="image9" alt="Product" /></td>
<td>A novel chiral SB of (R,R)-11,12-diamino-9,10-dihydro-9,10-ethanonanthracene was synthesized.</td>
<td>62</td>
</tr>
<tr>
<td>E13</td>
<td><img src="image10" alt="Aldehyde" /></td>
<td><img src="image11" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:1 molar ratio; a) Reflux, Benzene b) Microwave Irradiation neutral alumina (1g) CH$_2$Cl$_2$ (2 mL) c) Reflux Anhydrous MgSO$_4$ DCM</td>
<td><img src="image12" alt="Product" /></td>
<td>SBs were synthesized in three reaction conditions.</td>
<td>56</td>
</tr>
<tr>
<td>E14</td>
<td><img src="image13" alt="Aldehyde" /></td>
<td><img src="image14" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:1 molar ratio; stirred, RT ethanol acetic acid</td>
<td><img src="image15" alt="Product" /></td>
<td>The condensation of SB was performed in reflux condition by taking equimolar amounts of 2-hydroxybenzaldehyde and 4-aminobenzenesulfonic acid. The SBs are yellow coloured solid with sharp melting point and insoluble in organic solvents.</td>
<td>55</td>
</tr>
<tr>
<td>E15</td>
<td><img src="image16" alt="Aldehyde" /></td>
<td><img src="image17" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:1 molar ratio; CH$_3$COOH; Stirred. 1.15- 2.00 h</td>
<td><img src="image18" alt="Product" /></td>
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<td>5</td>
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### Table I — The various Schiff bases (Contd.)

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<tr>
<td>E16</td>
<td><img src="image1" alt="Aldehyde/ketone" /></td>
<td><img src="image2" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:2 molar ratio; CH₃COOH; Stirred. 1.30-1.45 h</td>
<td><img src="image3" alt="Products" /></td>
<td>The SBs are yellow coloured solid with sharp melting point and insoluble in organic solvents.</td>
<td>5</td>
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<td>E17</td>
<td><img src="image4" alt="Aldehyde/ketone" /></td>
<td><img src="image5" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:2 molar ratio; CH₃COOH CH₂OH, M.W.</td>
<td><img src="image6" alt="Products" /></td>
<td>SBs were synthesized under conventional and microwave heating.</td>
<td>57</td>
</tr>
<tr>
<td>E18</td>
<td><img src="image7" alt="Aldehyde/ketone" /></td>
<td><img src="image8" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:2 molar ratio; H₂O</td>
<td><img src="image9" alt="Products" /></td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>E19</td>
<td><img src="image10" alt="Aldehyde/ketone" /></td>
<td><img src="image11" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:2 molar ratio; Reflux; Absolute EtOH</td>
<td><img src="image12" alt="Products" /></td>
<td></td>
<td>59</td>
</tr>
<tr>
<td>E20</td>
<td><img src="image13" alt="Aldehyde/ketone" /></td>
<td><img src="image14" alt="Amine" /></td>
<td>Aldehyde: Amine at 1:1 molar ratio; THF; Acetic acid (pH = 4-5); reflux 24 h.</td>
<td><img src="image15" alt="Products" /></td>
<td>SBs were reported as two pairs, one of which was synthesized by 2,3-dimethoxybenzaldehyde and 2-amino-1,3,4-thiadiazole couple while the other was synthesized by o-vanillin and 2-amino-1,3,4-thiadiazole couple.</td>
<td>2</td>
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<tr>
<td>Entry</td>
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<tr>
<td>E21</td>
<td>(\text{Aldehyde: Amine at 1:1 molar ratio; Reflux} )</td>
<td>[Diagram]</td>
<td></td>
<td></td>
<td>The fluorine containing SB exhibited higher antimicrobial activity than bromine and chlorine containing SBs.</td>
<td>20</td>
</tr>
<tr>
<td>E22</td>
<td>(\text{Aldehyde: Amine at 1:2 molar ratio; Reflux (4 h) Absolute EtOH} )</td>
<td>[Diagram]</td>
<td>[Diagram]</td>
<td></td>
<td>SBs exhibited Antibacterial activity.</td>
<td>21</td>
</tr>
<tr>
<td>E23</td>
<td>(\text{Aldehyde: Amine at 1:1 molar ratio; Reflux (4 h) Dil HCl, CH}_3\text{OH/Na} )</td>
<td>[Diagram]</td>
<td>[Diagram]</td>
<td></td>
<td>A novel series of SBs 2-amino-4-(o-chloroanilino)-1,3-thiazole were synthesized. SBs exhibited promising antibacterial activity. Five different molar ratios of Chitosan-Cinnamaldehyde were prepared. It was found that increasing the cinnamaldehyde ratio to chitosan increases the formation of SB. Twelve new bis-SBs of isatin, benzylisatin and 5-fluoroisatin were synthesized.</td>
<td>32, 26, 31</td>
</tr>
<tr>
<td>E24</td>
<td>(\text{Aldehyde: Amine at 1:1 molar ratio; 2% acetic acid; RT (6 h); 10 mL EtOH} )</td>
<td>[Diagram]</td>
<td>[Diagram]</td>
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(Contd.)
Biological activities of Schiff bases

Antibacterial activity

SBs have been reported to exhibit as significant antibacterial agents. There are several synthetic or plant produced Schiff bases possess antibacterial activity. Shi et al., 2007 studied antimicrobial activity of synthesized 5-chlorosalicylaldehyde Schiff base derivatives (1-10) against P. fluorescense, E. coli, B. subtilis and S. aureus. Compounds (1-10) were found most active against P. fluorescense with MIC values 2.5-5.2 µg/mL whereas reference drug kanamycin showed MIC value 3.9 µg/mL. The Schiff bases 1, 2, 4-6 and 9-10 showed antibacterial activity against E. coli with MIC value 1.6-5.7 µg/mL. Compound 9 showed antibacterial activity against B. subtilis (MIC value 1.8 µg/mL) whereas compounds 1 and 2 exhibited activity against S. aureus with MIC values 3.1 and 1.6 µg/mL respectively. Pandeya et al., 1999a, 1999b reported antibacterial activity of Isatin-derived Schiff base 11 against twenty-eight pathogenic bacteria compared with sulfamethoxazole as reference drug. According to Hearn et al., 2004 the isoniazid-derived Schiff base 12 exhibited antibacterial activity against M. tuberculosis H37Rv with MIC value of 0.03 mg/L. Panneerselvam et al., 2005 tested antibacterial activity of morpholine-derived Schiff bases (13-15) against S. aureus, M. luteus, S. epidermidis, B. cereus and E. coli. They reported that compound 13 showed activity S. aureus, M. luteus with MIC values 20 and 32 µg/mL, respectively. Compound 14 exhibited activity against S. epidermidis with MIC value 17 µg/mL. Moreover, compound 15 reported inhibition against B. cereus and E. coli with MIC values 21 and 16 µg/mL, respectively. According to Karthikeyan et al., 2006, Schiff bases with a 2,4-dichloro-5-fluorophenyl compounds (16-19) were reported to hinder the bacterial growth against S. aureus, E. coli, P. aeruginosa, and K. pneumonia with MIC values from 6.3 to 12.5 µg/mL, compared with reference drug Ciprofloxacin. The compounds are depicted in Figure 2.

The dimeric disulphide Schiff base derivatives 20-22 were studied for antimicrobial activity against A. baumannii, E. coli, K. pneumoniae, S. aureus, C. tropicalis, C. guilliermondii, C. albicans and C. glabrata by Disc diffusion method compared with standard Cefotaxime, Amoxicillin/clavulanic acid for antibacterial and Posaconazole for antifungal. SB (20) exhibited more inhibition against bacteria as compared to other SBs in which K. pneumoniae is the most sensitive bacterium. The fluorine containing SBs exhibited higher antimicrobial activity than bromine and chloride containing SBs20. SBs (23-27) were studied for antimicrobial activity against pathogenic microorganisms by disc diffusion method with test sample 250 µg/disc. The results showed zones of inhibition for the SBs ranged from 0.9 to 3 cm for Gram positive bacteria, from 0.7 to 2.5 cm for gram-negative bacteria and from 0.6 to 2.4 cm for Candida which indicate better effect against gram positive bacteria than against gram negative and Candida. A novel series of SBs 2-amino-4-(o-chloroanilino)-1,3-thiazole (28-37) exhibited promising antibacterial activity against S. aureus, B. subtilis, E. coli and K. pneumoniae. Cinnamyl chitosan SB was (38) showed to have antimicrobial activity against S. aureus, S. pyogenes, P. aeruginosa, P. vulgaris and Shigella. Salihovic et al., 2018 studied the in vitro antimicrobial activity of SBs (39-41) against bacteria S. aureus, Methicillin-resistant S. aureus: MRSA, B. subtilis, E. faecalis, S. enteric, P. aeruginosa,
E. coli, and one yeast C. albicans by Agar Well Diffusion Method. SB (39) showed maximum inhibition against the microorganisms.

Madura hydroxylactone SBs (42-47) (Figure 3) isolated from Actinomadura rubra inhibited bacterial growth of B. subtilis, M. flavus, Sa. lutea, and S. aureus, with MIC values 0.2-3.1 µg/mL. They also showed very low activity against M. phlei or P. vulgaris with MIC value 50.0 µg/mL.23-24

**Antifungal activity**

Both synthetic and naturally occurring Schiff bases reported promising antifungal activity (Figure 4). 2,4-dichloro-5-fluorophenyl Schiff bases (16, 48-51) inhibit the growth of fungi against Aspergillus fumigatus, Aspergillus flavus, Penicillium marneffei, and Trichophyton mentagrophytes with MIC values range of 6.3–12.5 µg/mL, compared with reference fluconazole19.

According to Echevarria et al., 1999, Piperonyl-derived Schiff bases (52–57) repressed the growth of fungi Trichophyton rubrum and Epidermophyton floccosum with MIC values 820–980 µM and 200–930 µM, respectively. The isatin-derived Schiff bases (11, 58–68) were found to have antifungal activity against Microsporum udouinii and Microsporum gypseum with MIC values ranging from 2.4-9.7 µg/mL and 1.2-9.7 µg/mL, respectively.15

Further, compounds (11, 58–68) also showed inhibition against Aspergillus niger, Candida albicans, Cryptococcus neoformans, E. floccosum, Histoplasma capsulatum and T. mentagrophytes at
MIC values 10-79 µg/mL. Compounds 14 and 69 exhibited antifungal activity against *C. albicans* and *A. niger* conceded by treatment at 20 and 30 µg/mL, respectively. Compound 70, a natural product derived Schiff base reported antifungal activity against *C. albicans* and *C. neoformans* at 20 µg/mL, whereas for free nystatin required a concentration of 10 µg/mL. SB (25) showed moderate activity against *Candida* (24 µg/mL) and could be a promising anti microbial agent. The SBs 2-amino-4-((o-chloroanilino)-1,3-thiazole (28-37) exhibited promising antifungal activity against *C. albicans* and *A. niger*. The hydrazone SB (71) synthesized by Pawaiya et al., 2014 exhibited antifungal activity against *C. albicans*, *A. niger*, and *Penicillium* sp.

Figure 3 — Structures of some antibacterial Schiff bases derived from plant

Figure 4 — Structures of some antifungal Schiff bases
Antimalarial activity
A series of fifteen SBs derived from aromatic sulphonamides were tested as inhibitors of Plasmodium falciparum carbonic anhydrase enzyme compared with clinical drug acetazolamide (Figure 5). SBs 72-77 inhibited parasite activity with an affinity constant (K<sub>I</sub>) ranging from 0.54-1.23 µg/mL against carbonic anhydrase enzyme<sup>27-28</sup>. SBs 78-80 exhibited good antimalarial activity against the tested 3D7 strain with IC<sub>50</sub> values ranging from 19.69 to 25.38 µg/mL. SBs 81-86 exhibited antimalarial activity inhibiting the growth of this parasite (IC<sub>50</sub>, 2.28 - 26.9 µg/mL<sup>29</sup>.

Antiviral activity
A 1-amino-3-hydroxyguanidine tosylate derived SB (87) was reported to exhibit antiviral activity against mouse hepatitis virus (MHV), by 50% inhibition in growth at concentrations of 3.2 µM<sup>30</sup> (Figure 6). Further, according to Sriram <i>et al</i>., 2006
the abacavir-derived Schiff bases (88–98) showed significant antiviral activity against HIV-1 in which compound 90 was the most potent Schiff base, being effective at 50 nM, could be a principal compound for new anti-HIV-1 (Figure 6). The new bis-Schiff bases of isatin, benzylisatin and 5-fluoroisatin (99-110) were reported having antiviral activity in human embryonic lung (HEL) and human epithelial (HeLa) cells and African green monkey kidney (Vero) cells.

Antioxidant activity
The SB (111) bearing N,N-dimethylamino benzaldehyde and 4-hydroxy benzaldehyde showed antioxidant activity with IC\(_{50}\) value 50 mM compared with curcumin using 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay (Figure 7). Vreese et al., 2016 studied antioxidant activity of thirteen new derivatives (112-124) bearing a β-enaminone by DPPH and the ferric reducing ability of plasma (FRAP) assays. SBs showed antioxidant activity by both tests (0.08–0.13% inhibition per mM by DPPH assay and 0.83–1.29 Trolox equiv. per mM by FRAP assay) compared with curcumin (0.15% inhibition per mM by DPPH assay and 1 Trolox equiv. per mM by FRAP assay)\(^3\). The new enaminone analogues (125-132) exhibited antioxidant activities comparable to curcumin\(^3\).

**Conclusion**
This article summarizes the working procedures of preparation of Schiff base since they have many important applications in organic chemistry. In this article we have also highlighted various biological activities of Schiff base.

**Acknowledgement**
The authors thank Director, Sikkim Manipal Institute of Technology and Director, CSIR-North East Institute of Science and Technology for providing facilities to carry out this review work.

**References**