

Preparation and Study the Spectroscopic Properties of (15*E*)-4-((4*E*)-4-((*E*)-3-Phenylallylideneamino) Phenylsulfonyl)-*N*-((*E*)-3 Phenylallylidene) Benzenamine and (15*E*)-4-((4*E*)-4-((*Z*)-2-Bromo-3 Phenylallylideneamino) Phenylsulfonyl)-*N*-((*Z*)-2-Bromo-3 Phenylallylidene) Benzenamine: as Schiff Bases

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Abstract: Schiff bases derived by condensation reaction from cinnamaldehyde and/or -bromocinnamaldehyde and 4-(4-aminophenylsulfonyl)benzenamine are reported and characterized based on elemental analyses, IR, ¹H NMR, ¹³C NMR and thermal analysis (TG/DTA).

Key words: Schiff base • α -bromocinnamaldehyde α 4-(4-aminophenylsulfonyl)benzenamine

INTRODUCTION

The synthesis and structure of Schiff bases have attracted much attention in chemistry and biology [1, 2]. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, *e.g.*, biological, inorganic and analytical chemistry [3-7]. Some of azomethines (Schiff bases) show properties

such as antiviral, antibacterial, anticancer therapeutics, antiinflammatory, anticonvulsant, antimicrobial and biological activities [8-17]. They are also applied in optical and electrochemical sensors, as well as in various chromatographic methods as enable detection of enhance selectivity and sensitivity [18-20]. They can also bind with different metal centers involving various coordination sites and lead to successful synthesis of

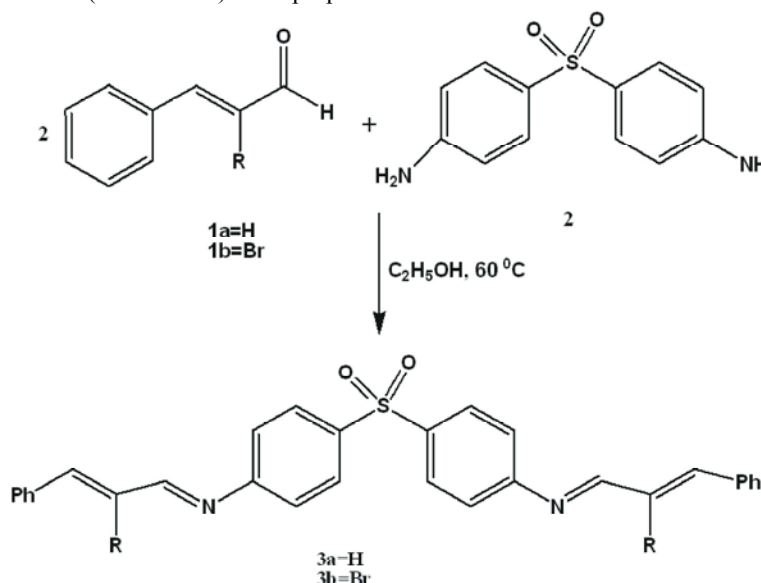


Fig. 1: Synthesis of (15*E*)-4-((4*E*)-4-((*E*/*Z*)-2-alkyl-3-phenylallylideneamino)phenylsulfonyl)-*N*-((*E*)-3-phenylallylidene) benzenamine

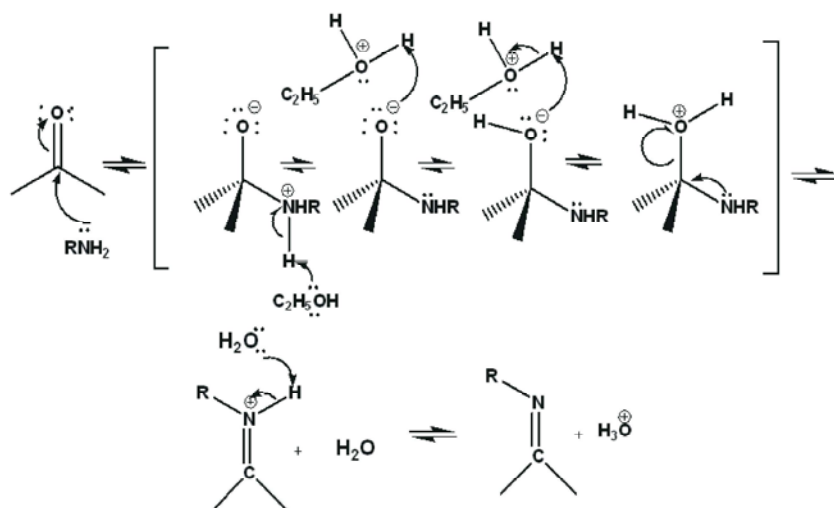


Fig. 2: General mechanism of reactions

metallic complexes with interesting stereochemistry [21-23]. Therefore, the synthesis of Schiff bases still is important and interesting for chemists.

We describe synthesis of two new Schiff bases, (15*E*)-4-((4*E*)-4-((*E*)-3-phenylallylideneamino) phenylsulfonyl)-*N*-((*E*)-3-phenylallylidene)benzenamine **3a** and (15*E*)-4-((4*E*)-4-((*Z*)-2-bromo-3-phenylallylideneamino) phenylsulfonyl)-*N*-((*Z*)-2-bromo-3-phenylallylidene) benzenamine **3b**, through the reaction cinnamaldehyde **1a** and α -bromocinnamaldehyde **1b** with 4-(4-aminophenylsulfonyl)benzenamine **2** at 60°C temperature in ethanol solvent, respectively (Fig. 1).

MATERIALS AND METHODS

Compounds were obtained from Merk and were used without further purification. Elemental analyses were performed for C, H and N using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded on a Bomen FT-IR-MB100 Spectrometer. ¹H NMR and ¹³C NMR spectra was determined using BRUKER-DRX500 AVANCE instrument (in DMSO at 500 and 125 MHz, respectively). The results were agreed favorably with the calculated values. Thermal analysis was performed using a Diamond Perkin-Elmer simultaneous TG/DTA analyser in the temperature range 29-700°C in a nitrogen atmosphere with a heating rate of 10°C/min.

Synthesis of (15*e*)-4-((4*e*)-4-((*E*)-3-phenylallylideneamino) Phenylsulfonyl)-*n*-((*E*)-3-Phenylallylidene) Benzenamine **3a:** For synthesis of this Schiff base, cinnamaldehyde (0.264 g, 2 mmol) was

dissolved in 10 ml ethanol and was carefully added 4-(4-aminophenylsulfonyl)benzenamine (0.281 g, 1 mmol) dissolved in 10 ml ethanol over 5 min with stirring at 60°C. After 2h, a brown solid precipitated and were collected on a sintered glass funnel. The solid was washed with ethanol several times and dried under vacuum. The purity of synthesized compounds was checked by TLC using silica gel G (Yield: 0.415 g, 87%). FT-IR ν_{\max} (KBr) 1688, 1609, 1597, 1456 cm⁻¹; ¹H NMR (DMSO-*d*₆, 500 MHz) δ 6.4 (2H, dd, *CH=CH-Ph), 6.6 (2H, d, ³J_{H-H}=8.5 Hz, CH=CH*-Ph), 7.1-7.4 (10H, m, -Ph), 7.5-7.8 (8H, m, -Ar-SO₂-), 8.3 (2H, d, -N=CH). ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 118.1 (C=*CH), 124-148 (-Ar-SO₂-), 128-135 (-Ph), 135.4 (-C=C*-Ph), 156.3 (C=N), *Anal.* C 75.65%, H 5.11%, N 6.63%, Calcd for C₃₀H₂₄N₂O₂S, C 75.61%, H 5.08%, N 6.71%.

Synthesis of (15*e*)-4-((4*e*)-4-((*Z*)-2-Bromo-3-Phenylallylideneamino) Phenylsulfonyl)-*n*-((*Z*)-2-Bromo-3-Phenylallylidene) Benzenamine **3b:** For synthesis of this Schiff base, α -bromocinnamaldehyde (0.422 g, 2 mmol) was dissolved in 20 ml ethanol and was carefully added to 4-(4-aminophenylsulfonyl)benzenamine (0.281 g, 1 mmol) dissolved in 10 ml ethanol over 5 min with stirring at 60°C. After 2h, a brown bloated solid precipitated. The solid were collected on a sintered glass funnel. That was washed with ethanol several times and dried under vacuum. The purity of synthesized compounds was checked by TLC using silica gel G (Yield: 0.564 g, 89%). FT-IR ν_{\max} (KBr) 1654, 1611, 1586, 1451, 654 cm⁻¹; ¹H NMR (DMSO-*d*₆, 500 MHz) δ 6.5 (2H, s, -C=CH*-Ph), 7.0 (4H, dd, -Ar-SO₂-), 7.2 (4H, dd, -Ar-SO₂-), 7.3-8.0 (10H, m, -Ph), 8.5 (2H, s, -N=CH). ¹³C NMR (DMSO-*d*₆, 125 MHz)

δ 112.2 (Br*C=C), 123-149 (-Ar-SO₂-), 128-135 (-Ph), 138 (BrC=C*-Ph), 157.3 (C=N). Anal. C 56.52%, H 3.47%, N 4.43%, Calcd for C₃₀H₂₂Br₂N₂O₂S, C 56.80%, H 3.50%, N 4.42%.

RESULTS AND DISCUSSION

The reactions led to generation of Schiff bases **3a** and **3b** in 87 and 89% yields, respectively (scheme 1). Structures of compounds **3** were assigned by elemental analyses, FT-IR, ¹H NMR, ¹³C NMR and thermal analysis (TGA).

(15*E*)-4-((4*E*)-4-((*E*)-3-phenylallylideneamino)phenylsulfonyl)-*N*-((*E*)-3-phenylallylidene)benzenamine **3a** was easily synthesized, with a relatively excellent yield (87%). This Schiff base formed of the reaction of cinnamaldehyde **1a** with 4-(4-aminophenylsulfonyl)benzenamine **2** (neutral PH), in the molar ratio 2:1 (scheme 1). The obtained compound **3a** was a brown solid. The structure of **3a** was determined by elemental analyses, FT-IR and NMR spectroscopy. Its FT-IR spectrum appeared one absorption of C=N at 1609 cm⁻¹. The NMR data were agreement with **3a** structure. The ¹H NMR spectrum of **3a** appeared one doublet peak related to hydrogen of CH=CH*-Ph in δ =6.6 ppm with ³J_{H-H}=8.5 Hz. This split (³J_{H-H}=8.5 Hz) displayed presence of trans isomer **3a**. The ¹³C NMR spectrum of **3a** showed C=N (d=156.3 ppm) and aromatic carbons (s=134.7, 141.5 and 147.9; d=132.6, 127.5, 126.1, 123.8 and 123.3 ppm) (scheme 1). The TG/DTA response curve was for the **3a** powder sample in the temperature range from 29-700°C at the heating rate of 10°C/min in nitrogen atmosphere. In the DTA curve, an endothermic peak at 257.83°C was due to melting of the sample. The weight loss around 206.45°C in the TG curve represented the decomposition of the **3a**. This compound is highly soluble in solvents such as DMSO. It is not soluble in methanol and ethanol. It may be stored for long period in the absence air and moisture.

(15*E*)-4-((4*E*)-4-((*Z*)-2-bromo-3-phenylallylideneamino)phenylsulfonyl)-*N*-((*Z*)-2-bromo-3-phenylallylidene)benzenamine **3b** was easily synthesized, with a relatively excellent yield (89%). This Schiff base prepared by the reaction of α -bromocinnamaldehyde **1b** with 4-(4-aminophenylsulfonyl)benzenamine **2** (neutral PH), in the molar ratio 2:1 (scheme 1). The obtained compound was a brown solid. The structure of **3b** was determined by elemental analyses, FT-IR and NMR spectroscopy. Its FT-IR spectrum appeared one absorption of C=N at 1611 cm⁻¹. The NMR data were agreement with **3b** structure. The ¹³C NMR spectrum of **3b**

showed C=N (d=157.3 ppm), aromatic carbons (s=134.9, 140.8 and 148.8; d=131.5, 127.9, 126.5, 124.8 and 123.5 ppm). The TG/DTA response curve was for the **3b** powder sample in the temperature range from 29-700°C at the heating rate of 10°C/min in nitrogen atmosphere. In the DTA curve, an endothermic peak at 283.65°C was due to melting of the sample. The weight loss around 223.90°C in the TG curve represented the decomposition of the **3b**. This compound is highly soluble in solvents such as DMSO. It is not soluble in methanol and ethanol. It may be stored for long period in the absence air and moisture.

The reaction mixtures were thoroughly stirred for 120 minutes at 60°C temperature and neutral PH. The neutral PH is suitable for these reactions because amines are basic compounds. If amines are protonated, they become non-nucleophilic and carbinolamine formation (as intermediate) cannot occur. During the reaction, the color of mixture changed from colorless to brown, providing visual means for ascertaining the progress of imine formation. The Schiff bases **3a** and **3b** afforded higher yields with shorter reaction times. The Schiff base products (**3a** and **3b**) can be easily isolated by simple filtration and evaporation of solvent.

Schiff bases usually form a sequence of two types of reactions, addition followed by elimination. A tentative mechanism for this transformation is proposed in Scheme 2. 4-(4-aminophenylsulfonyl)benzenamine **2** as a nucleophile molecule were attacked to cinnamaldehyde **1a** and/or α -bromocinnamaldehyde **1b**. They (as amine) are a stronger nucleophile than ethanol (as an alcohol). These reactions were progressed through the intermediate formation of a carbinolamine. These reactions were completed by separation of productions (**3a** and **3b**) and removal of water.

These Schiff bases can be used as potential ligands for complexation with metal ions. They prove to be many advantages as compared with similar Schiff bases including: easier preparations, application to pH sensitive molecules, high yields, short reaction times, lower aldehyde/amine ratio, lower solvent requirement and simple work-up.

CONCLUSION

Two new Schiff base, (15*E*)-4-((4*E*)-4-((*E*)-3-phenylallylideneamino)phenylsulfonyl)-*N*-((*E*)-3-phenylallylidene)benzenamine and (15*E*)-4-((4*E*)-4-((*Z*)-2-bromo-3-phenylallylideneamino)phenylsulfonyl)-*N*-((*Z*)-2-bromo-3-phenylallylidene)benzenamine, easily synthesized

with a relatively excellent yield (87-89%). The elemental analyses, FT-IR, ^1H -NMR and ^{13}C -NMR spectroscopy were agreed with two new Schiff bases structures. Strong vibrational band at 1609 and 1611 cm^{-1} were confirmed the presence of imine bonds ($-\text{C}=\text{N}$) in **3a** and **3b**, respectively. The TG/DTA revealed that **3a** and **3b** samples were stable up to 206.45 and 223.90°C, respectively.

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