

Synthesis of some Schiff bases of cinnamaldehyde by employing microwave irradiation

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Abstract: A series of Schiff bases have been synthesized by the reaction of Cinnamaldehyde with some substituted amines namely o-toluidine, m-toluidine, p-toluidine, p-chloroaniline and p-aminophenol by microwave irradiation method. Structures of the synthesized products were confirmed by using spectroscopic techniques (FT-IR and ¹H-NMR) and elemental analysis CHN.

Introduction:

Compounds containing an azomethine group (-C=N-) are known as Schiff base. They are usually formed by condensation of primary amine with carbonyl compounds ⁽¹⁾ according to the following equation:



Where R may be an aliphatic group, aromatic, or hetero. Schiff base of aromatic aldehydes having an effective conjugated system, are more stable ⁽²⁾. Cinnamaldehyde is an aromatic aldehydes and main component of bark extract of cinnamon ⁽³⁾. The main profit of cinnamaldehyde is that direct contact needful for organism active as antimicrobial. Cinnamaldehyde has been shown to be active against arrange of borne pathogens bacteria ⁽⁴⁾.

The important uses of cinnamaldehyde are fungicide, antimicrobial ⁽⁵⁾, anti-inflammatory ⁽⁶⁾. Recent advance in technology have now made microwave energy a more efficient means of heating reaction, chemical transformation that took hours, or even day, to complete their organic reaction can now be completed in minutes. Microwave irradiation is well known to promote the synthesis of variety of organic and inorganic compounds, where chemical reactions are accelerated

because of selective absorption of microwave by polar molecules⁽⁷⁻¹¹⁾. Microwaves have been employment in organic chemistry to reduce the reaction time, increase yields and selectivity. Under the work of green chemistry on the application of microwave in organic synthesis, we have developed an environmentally benignant method for synthesizing cinnamaldehyde analogs⁽¹²⁾.

Experimental:

Material: Cinnamaldehyde was purchased from Fluka , all other amines from Merck and used without purification . TLC plate 20 × 20 cm type silica gel 60 GF 254 (Aluminium) from Merck, all solvents used were of analytical grade.

Measurements:

Melting points were determined on a thermo fisher. IR spectra were measure using KBr pellets on a shimadzu - 84005, FT-IR spectrophotometer. ¹HNMR spectra were recorder on Brucker 400 (400 MHz) in DMSO-d₆ as solvent and TMS an internal standard. Elemental analysis (CHN) was performed in a CHNS – 932 LECO apparatus. KENWOOD, Multifunction microwave oven 780.

Preparation method (microwave method) :⁽¹³⁻¹⁵⁾

The compounds were prepared by the general procedure as follow 2mmole (0.264 g) of cinnamaldehyde and 2mmole of substituted amines [(0.216 g) m-toluidine (**Ha1**), (0.22g) p-aminophenol(**Ha2**), (0.216 g) p-toluidine(**Ha3**), (0.216 g) o-toluidine(**Ha4**), (0.257 g) p-chloroaniline (**Ha5**)]. Were grinding in 25 ml beaker and subjected to microwave irradiation for about 2-5 minutes. The reactions monitored by TLC (CHCl₃: EtOH) (9 : 1) as eluent . The crude product washed with hexane and then dried in air, and recrystallized from ethanol – water (1:3). The physical properties data with CHN analysis are summarized in table 1:

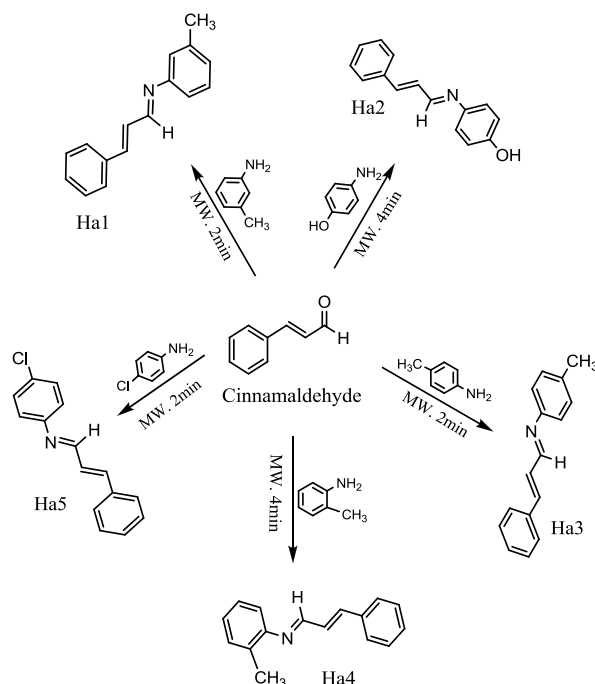
Comp.	Ti me min .	m.p (°C)	R _f	Colour and physical state	Elemental analysis % Calculated(found)		
					C	H	N
Ha1	2	121-123	0.45	Yellow powder	86.84 (86.90)	6.83 (6.79)	6.33 (6.36)
Ha2	4	192-	0.51	Yellow	80.69	5.87	6.27

		193		powder	(80.58)	(5.90)	(6.30)
Ha3	2	75-77	0.72	brown powder	86.84 (86.76)	6.83 (6.89)	6.33 (6.21)
Ha4	5	72-74	0.62	Yellow powder	86.84 (86.71)	6.83 (6.74)	6.33 (6.29)
Ha5	2	98-100	0.55	brown needle crystal	74.53 (74.41)	5.00 (5.10)	5.79 (5.71)

Table 1: physical properties and elemental analysis

Results and discussion:

All the synthesized compounds are stable in air and no hygroscopic soluble in DMF and DMSO. The molecular structures are represented in scheme 1. The result of elemental analysis are in agreement with theoretical calculation.



Scheme 1

IR spectra analysis:

IR spectra of compounds showed strong band at 1624-1627^(16, 17) cm⁻¹ that attributed to azomethine group which indicated the formation of Schiff base together with the totally absence of carbonyl group stretching near 1700 cm⁻¹ the other important bands are listed in table 2 and Fig (1,2) :

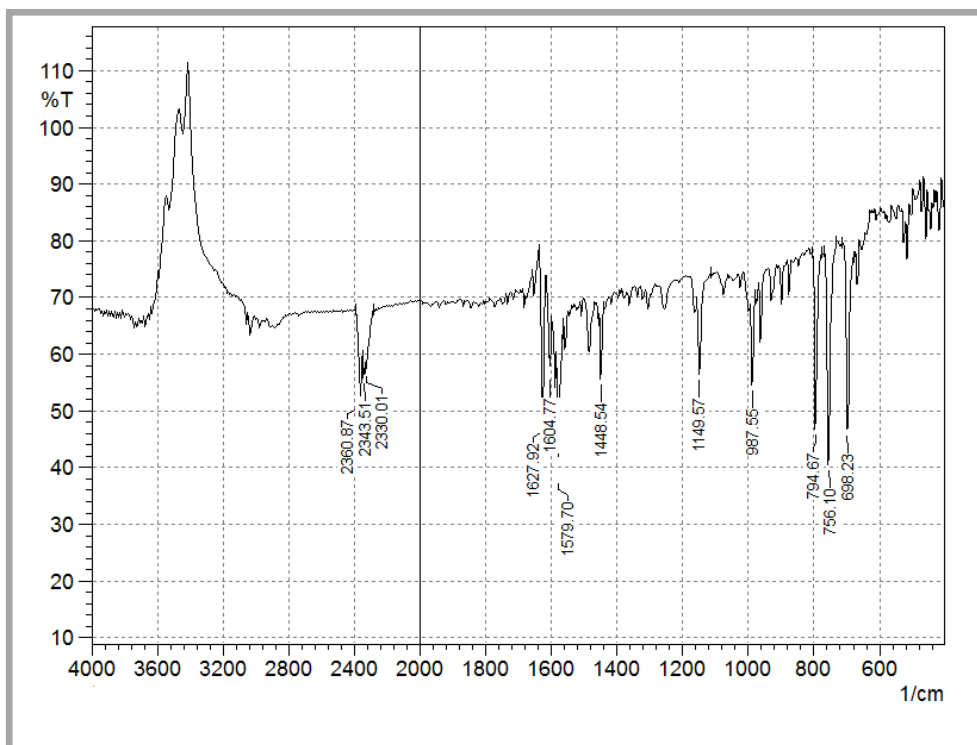


Figure 1: IR Spectrum of Ha1

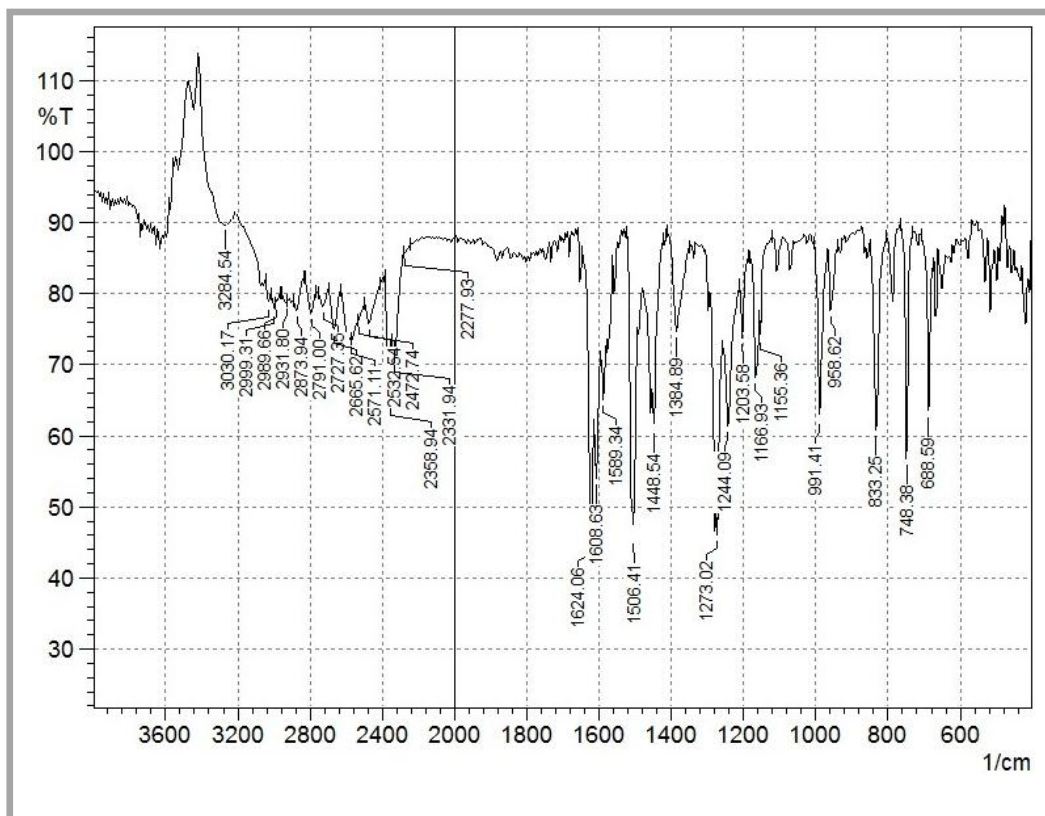


Figure 2: IR Spectrum of Ha2

¹HNMR spectra:

The spectra of all compounds in DMSO-d₆ show the azomethine proton singlet signal at δ 8.48 ppm⁽¹⁸⁻²⁰⁾ Fig (3, 4). The aromatic proton signal appear in expected region δ 6.86 – 7.78 ppm⁽²¹⁾, the CH₃ signal appear in δ 2.427 ppm⁽¹⁹⁾ in all toluidine Schiff bases. The Ha2 spectrum shows a signal at δ 9.612⁽¹⁷⁾ ppm attributed to OH Fig (4).

Table 2: IR and ¹HNMR data

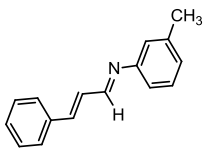
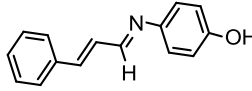
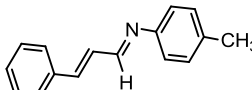
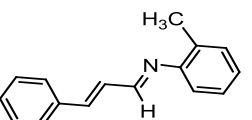
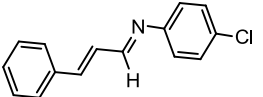
Comp.	structure	IR ν (cm ⁻¹)	¹ H-NMR (ppm)
Ha1		ν C=N (1627) ν C=C Aroma. (1579) ν C-H Aliphatic(2989-2931)	2.427 (s,3H,CH ₃) 7.09-7.78 (m,9H Arom. and 2H vinyl) 8.48 (s,1H, -HC=N-)
Ha2		ν C=N (1624) ν C=C Aroma.(1506,1589) ν C-O (1273) ν OH Phenol (3284)	6.86-7.75 (m, 9H Arom. and 2H vinyl) 8.48 (s,1H, -HC=N-) 9.612 (s,1H,OH)
Ha3		ν C=N (1625) ν C=C Aroma.(1581) ν C-H Aliphatic (2980-2923)	2.427 (s,3H,CH ₃) 6.89-7.78 (m, 9H Arom. and 2H vinyl) 8.48 (s,1H, -HC=N-)
Ha4		ν C=N (1627), ν C=C Aroma.(1573,1589) ν C-H Aliphatic (2978-2933)	2.427 (s,3H,CH ₃) 6.86-7.60 (m, 9H Arom. and 2H vinyl) 8.46 (s,1H, -HC=N-)
Ha5		ν C=N (1625), ν C=C Aroma.(1573)	6.88-7.66 (m, 9H Arom. and 2H vinyl) 8.41 (s,1H, -HC=N-)

Figure 4: $^1\text{H-NMR}$ Spectrum of Ha2

Conclusion:

From this work we can conclude that the formation of Schiff bases between cinnamaldehyde and substituted aromatic amines under microwave irradiation and solvent free suggest an effective strategy to prepared in short time with high yield, simple purification as well as the procedure consider a commercial method.

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تخليق بعض قواعد شف للسينماليديهايد بأستخدام الاشعة المايكروية

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الخلاصة :

تعد طريقة التحضير باستخدام الاشعة المايكروية من الطرق الصديقة للبيئة لعدم استخدام المذيبات والتي تسمى حالياً بالكيمياء الخضراء . حضرت سلسلة من قواعد شف بهذه الطريقة في هذه الدراسة مشتقة من السينماليديهايد ومجموعة من الامينات المعوضة وشخصت باستخدام تقنيات $^1\text{H-NMR}$ و FT-IR. وتحليل العناصر الدقيق .