*Asian Journal of Chemistry* Vol. 21, No. 9 (2009), 6727-6730

# Microwave-Assisted Solvent Free Synthesis of 1{5-[(E)-1-Aralkyl/ Arylimino ethyl]-2,4-dihydroxy phenyl}ethanones

D. ASHOK*, D. SHRAVANI and M. SARASIJA
*Department of Chemistry, Osmania University, Hyderabad-500 007, India*
*Email: ashokdou@gmail.com*

Microwave assisted condensation of 4,6-diacetyl resorcinol and aralkyl/aromatic amines under solvent free condition gave selectively 1{5-[(E)-1-aralkyl/arylimino ethyl]-2,4-dihydroxy phenyl}ethanones (mono Schiff bases) (**2a-f**) in high yields. Synthesis of Schiff bases under microwave irradiation was found much easier and faster than conventional heating. The newly synthesized compounds were characterized by IR, $^1$H NMR and Mass spectral data.

**Key Words: 4,6-Diacetyl resorcinol, Aralkyl/Aromatic amines, Selective synthesis, Microwave irradiation, Solvent free synthesis.**

## INTRODUCTION

A perusal of literature has revealed that Schiff bases belong to a widely used group of organic intermediates, important for production of specialty chemicals, such as pharmaceuticals, rubber additives[1] and as amino protective groups in organic synthesis[2-4]. They also have uses in analytical[5,6] medicinal[7] and polymer chemistry[8]. Schiff base ligands are the basis of an extensive class in the coordination chemistry of transition and main group elements[9-12]. Schiff bases and their metal complexes exhibit wide applications in biological and industrial systems[13,14]. The characterization[15-17], thermodynamic[18], theoretical[19] and catalytic aspect[20] of this class of compounds have been extensively investigated. Schiff bases have good antimicrobial and fungicidal[21] applications. The diverse and potential biological activities of Schiff bases and their enormous applications, prompted us to synthesize different new Schiff bases. The main aim of present study is to make use of these title compounds to synthesize metal complexes and mixed heterocycles of biological interest. The Schiff bases have been characterized by IR, $^1$H NMR, $^{13}$C NMR and mass spectral data.

## EXPERIMENTAL

Melting points were determined in open capillary tubes and are uncorrected. Microwave reactions were carried out in a Multisynth series microwave system (Milestone). The IR spectra were recorded in KBr on Shimadzu FTIR 8400S spectrophotometer, $^1$H NMR and $^{13}$C NMR spectra were recorded on a Gemini 300 MHz using TMS as internal standard. Mass spectra were recorded on a LCMS-2010A

Shimadzu spectrophotometer. Elemental analysis was determined by using Thermofinnigan CHNS analyzer. Purity of the compounds was checked on TLC using silica gel G-254 (Merck).

**General procedure:** The required starting material 4,6-diacetyl resorcinol (**1**) was synthesized from resorcinol under microwave irradiation. 4,6-Diacetyl resorcinol on condensation with aralkyl/aromatic amines by conventional heating and microwave irradiation gave selectively 1{5-[(E)-1-aralkyl/arylimino ethyl]-2,4-dihydroxy phenyl}-ethanones (**2a-f**).

**Conventional heating:** A mixture of 4,6-diacetyl resorcinol (0.01 mol) and benzylamine (0.01 mol) was dissolved in ethanol (10 mL) and refluxed for 10 h. The progress of the reaction was monitored with TLC. The reaction mixture was poured into ice-cold water. A yellow coloured solid compound was obtained. The solid was filtered and recrystallized from benzene.To further substantiate this result, various amines such as aniline, *o*-toluidine, *p*-toluidine, *p*-methoxyaniline, *p*-nitro aniline were treated with 4,6-diacetyl resorcinol for specified time mentioned in Table-1 to afford the corresponding Schiff bases in good yields.

TABLE-1
COMPARISION OF TIME AND YIELDS IN THE FORMATION OF 1{5-[(E)-1-ARALKYL/ARYLIMINO ETHYL]-2,4-DIHYDROXY PHENYL} ETHANONES (**2a-f**) UNDER MICROWAVE IRRADIATION AND CONVENTIONAL METHOD

| Entry | Amine | m.p. (ºC) | Microwave irradiation | | Conventional method | |
|---|---|---|---|---|---|---|
| | | | Time (min) | Yield (%) | Time (h) | Yield (%) |
| **2a** | Benzylamine | 155 | 2 | 90 | 10 | 60 |
| **2b** | Aniline | 194 | 2 | 95 | 8 | 70 |
| **2c** | *o*-Toluidine | 170 | 2 | 92 | 9 | 68 |
| **2d** | *p*-Toluidine | 120 | 2 | 94 | 10 | 70 |
| **2e** | *p*-Methoxyaniline | 166 | 3 | 90 | 8 | 72 |
| **2f** | *p*-Nitroaniline | 142 | 2 | 92 | 10 | 65 |

**Microwave irradiation:** A mixture of 4,6-diacetyl resorcinol (0.01 mol) and benzylamine (0.01 mol) was taken in a 100 mL Borosil beaker. This beaker was zapped into the microwave oven and subjected to microwave irradiation for 2 min. The completion of the reaction was checked by TLC. The reaction mixture was then cooled and poured into ice-cold water. A yellow coloured solid compound was obtained. The solid was filtered and recrystallized from benzene. To further substantiate this result, various amines such as aniline, *o*-toluidine, *p*-toluidine, *p*-methoxy aniline, *p*-nitroaniline were treated with 4,6-diacetyl resorcinol in microwave oven for specified time mentioned in Table-1 to afford the corresponding Schiff bases in good yields.

## Spectral data

**1-(5-((E)-1-(Benzylimino)ethyl)-2,4-dihydroxyphenyl)ethanone (2a):** IR (KBr, $\nu_{max}$, $cm^{-1}$): 3436, 3035, 1641, 1600; $^1H$ NMR ($CDCl_3$) δ: 2.48 (s, 3H, $CH_3$),

2.55 (s, 3H, $CH_3$), 4.79 (s, 2H, $CH_2$), 6.27 (s, 1H, $C_3$-H), 7.26-7.41 (m, 5H, Ar-H), 7.96 (s, 1H, $C_6$-H), 12.65 (s, 1H, $C_2$-OH) 17.80 (s, $C_4$-OH); Mass: $[M + H]^+$ m/z = 284.

**1-(5-((E)-1-(Phenylimino)ethyl)-2,4-dihydroxyphenyl)ethanone (2b):** IR (KBr, $\nu_{max}$, $cm^{-1}$): 3292, 1630, 1597; $^1H$ NMR ($CDCl_3$) δ: 2.35 (s, 3H, $CH_3$), 2.65 (s, 3H, $CH_3$), 6.45 (s, 1H, $C_3$-H), 6.9 (m, 2H, Ar-H), 7.3-7.4 (m, 3H, Ar-H), 8.05 (s, 1H, $C_6$-H), 12.80 (s, 1H, -OH); Mass $[M+H]^+$ m/z = 270.

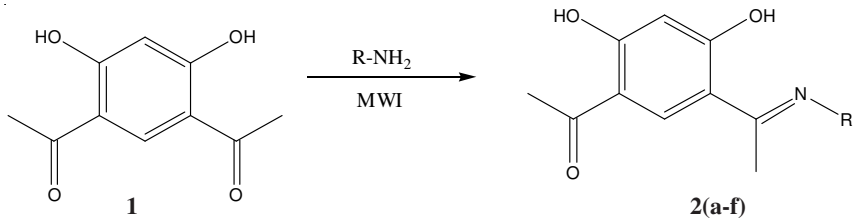
**1-(5-((E)-1-(*o*-Tolylimino)ethyl)-2,4-dihydroxyphenyl) ethanone (2c):** IR (KBr, $\nu_{max}$, $cm^{-1}$) 3440, 3061, 1640, 1604; $^1H$ NMR ($CDCl_3$) δ: 2.2 (s, 3H, $CH_3$); 2.3 ( s, 3H, $CH_3$) 2.9 (s, 3H, $CH_3$) 6.3 (s, 1H, $C_3$-H), 6.8 (m, 1H, Ar-H ), 7.0-7.3 (m, 3H Ar-H), 8.1 (s, $C_6$-H) 12.7 (s, 1H -OH): $^{13}C$ NMR ($CDCl_3$) δ: 16.21, 17.36, 25.73, 103.8, 112.30, 120.70, 125.03, 126.09, 128.73, 130.19, 134.13, 136.55, 143.80, 165.87, 169.57, 170.73, 201.99; Mass $[M+H]^+$ m/z = 284 Anal. Calcd. for $C_{17}H_{17}O_3N$. C, 72.08; H, 6.00; N, 4.94 found C, 70.94; H, 5.94; N, 4.13.

**1-(5-((E)-1-(*p*-Tolylimino)ethyl)-2,4-dihydroxyphenyl)ethanone (2d):** IR (KBr, $\nu_{max}$, $cm^{-1}$): 1634, 1598. $^1H$ NMR ($CDCl_3$) δ: 2.34 (s, 3H, $CH_3$) 2.43 (s, 3H, $CH_3$), 2.66 (s, 3H, $CH_3$); 6.22 (s, $C_3$-H) 6.8 (d, 2H, Ar-H), 7.0-7.3 (d, 2H, Ar-H), 8.1 (s, 1H, $C_6$-H), 12.65 (s, 1H, -OH); Mass $[M+H]^+$ m/z = 284.

**1-(5-((E)-1-(4-Methoxyphenlimino)ethyl)-2, 4-dihydroxyphenyl)ethanone (2e):** IR (KBr, $\nu_{max}$, $cm^{-1}$) 3450, 3020, 1630, 1595. $^1H$ NMR ($CDCl_3$) δ: 2.42 (s, 3H, $CH_3$); 2.62 (s, 3H, $CH_3$), 3.82 (s, 3H, $OCH_3$) 6.2 (s, 1H, $C_3$-H), 6.9-7.1 (m, 4H, Ar-H), 8.20 (s, 1H, $C_6$-H) 12.7 (s, 1H, OH); Mass $[M+H]^+$ m/z = 300.

## RESULTS AND DISCUSSION

4,6-Diacetyl resorcinol (**1**) was synthesized from resorcinol under microwave irradiation. 4,6-Diacetyl resorcinol on condensation with aralkyl/aryl amines gave selectively 1{5-[(E)-1-aralkyl/arylimino ethyl]-2,4-dihydroxyphenyl}ethanones (**2a-f**) by conventional heating and under microwave irradiation (**Scheme-1**). As a representative case spectral identification of **2a** is discussed. IR (KBr) spectrum of **2a** showed characteristic bands at 3436 ν(-OH), 1641 ν(C=O), 1600 $cm^{-1}$ ν(C=N). $^1H$ NMR ($CDCl_3$) spectrum of **2a** showed seven singlets. Two singlets observed at δ 2.48 and 2.55 integrating for three protons each, were assigned to protons of two methyl groups. One singlet observed at δ 4.79 integrating for two protons was assigned to protons of $CH_2$. Two singlets observed in the aromatic region at δ 6.27 and 7.96




**1** **2(a-f)**

R: **a** = benzyl; **b** = phenyl; **c** = *o*-tolyl; **d** = *p*-tolyl; **e** = *p*-methoxyphenyl; **f** = *p*-nitrophenyl

**Scheme-I**

integrating for one proton each were assigned to $C_3$-H and $C_6$-H, respectively. A multiplet in the aromatic region was observed at δ 7.26-7.41 integrating for five protons was assigned to aromatic protons of phenyl ring. At low field two more singlets were observed at δ 12.65 and 17.80 integrating for one proton each were assigned to $C_2$-OH and $C_4$-OH respectively. In the mass spectrum of **2a** $[M+H]^+$ observed at m/z = 284 (100 %).

## Conclusion

In summary, this work demonstrates a rapid, efficient and environmentally friendly method of synthesis of 1{5-[(E)-1-aralkyl/arylimino ethyl]-2,4-dihydroxy phenyl}ethanones under microwave irradiation and results obtained confirm the superiority of microwave irradiation method over the conventional method. Above all it is a selective synthesis of mono Schiff bases, which are potential intermediates for the synthesis of various mixed heterocyclic compounds and metal complexes.

## ACKNOWLEDGEMENTS

Authors wish to thank Head, Department of Chemistry, Osmania University for providing the facilities. Thanks are also due to UGC, SERO, for financial assistance.

## REFERENCES

1. V. Macho, M. Kralik, J. Hudec and J. Cingelova, *J. Mol. Catal. A: Chem.*, **209**, 69 (2004).
2. P. Bey and J.P. Vevert, *Tetahedral Lett.*, **18**, 1455 (1977).
3. R.A. Lucas, D.F. Dickel, M.J. Dziemian, B.L. Hensle and H.B. Mcphillarney, *J. Am. Chem. Soc.*, **82**, 5688 (1960).
4. B. Bezas and L. Zervas, *J. Am. Chem. Soc.*, **83**, 719 (1961).
5. J.P. Adams, *J. Chem. Soc., Perkin Trans. I*, 125 (2000).
6. (a) R.W. Layer, *Chem. Rev.*, **63**, 489 (1963); (b) A. Abbaspour, A.R. Esmaeilbeig, A.A. Jarrahpour, B. Khajeh and R. Kia, *Talanta*, **58**, 397 (2002).
7. (a) A.A. Jarrahpour, M. Motamedifar, K. Pakshir, N. Hadi and M. Zarei, *Molecules*, **9**, 851 (2004); (b) V. Alexander, *Chem. Rev.*, **95**, 273 (1995).
8. M. Higuchi and K. Yamamoto, *Org. Lett.*, **1**, 1881 (1999).
9. W.L. Liu, Y. Zou, C.L. Ni, Y.Z. Li and Q.J. Meng, *J. Mol. Struct.*, **751**, 1 (2005).
10. P. Przybylski, G. Schroeder and B. Brzezinski, *J. Mol. Struct.*, **658**, 115 (2003).
11. R. Dreos, G. Nardin, L. Randaccio, P. Siega, G. Tauzher and V. Vrdolijak, *Inorg. Chim. Acta*, **349**, 239 (2003).
12. M.T.H. Tarafder, K.B. Chew, K.A. Crouse, A.M. Ali, B.M. Yamin and H.K. Fun, *Polyheron*, **21**, 2683 (2002).
13. M.D. Cohen and S. Flavin, *J. Chem. Soc. (B)*, 317 (1967).
14. S.M. Abu-El-Wafa and R.M. Issa, *Bull. Soc. Chim. (France)*, **128**, 805 (1991).
15. Z. Hayvali, M. Hayvali, Z. Kilic, T. Hokelek and E. Weber, *J. Inc. Phenomena Mac. Chem.*, **45**, 285 (2003).
16. Z. Hayvali and M. Hayvali, *Synth. React., Inorg. Met.-Org. Chem.*, **34**, 713 (2004).
17. Z. Hayvali, *Asian J. Chem.*, **15**, 877 (2003).
18. E.C. Niederhoffer, J.H. Timmons and A.E. Martell, *Chem. Rev.*, **84**, 137 (1984).
19. I. Bytheway and M.B. Hall, *Chem. Rev.*, **94**, 639 (1994).
20. C. Bianchini and R.W. Zoellner, *Adv. Inorg. Chem.*, **44**, 263 (1997).
21. B. Dash, P.K. Mahapatra, D. Panda and J.M. Patnayak, *J. Indian Chem. Soc.*, **61**, 1061 (1984).

(*Received*: 21 August 2008; *Accepted*: 27 July 2009) AJC-7685