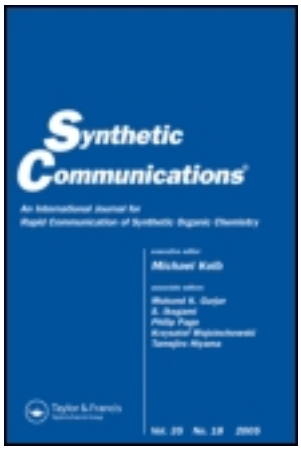


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Microwave-Assisted Synthesis of the Tetradentate Schiff-Bases Under Solvent-Free and Catalyst-Free Condition

Maryam Mirza-Aghayan [a], Mitra Ghassemzadeh [a], Maryam Hoseini [a] & Mohammad Bolourtchian [a]

[a] Chemistry and Chemical Engineering Research Center of Iran (CCERCI), Tehran, Iran

Published online: 16 Aug 2006.

To cite this article: Maryam Mirza-Aghayan, Mitra Ghassemzadeh, Maryam Hoseini & Mohammad Bolourtchian (2003) Microwave-Assisted Synthesis of the Tetradentate Schiff-Bases Under Solvent-Free and Catalyst-Free Condition, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:4, 521-525, DOI: 10.1081/SCC-120015804

To link to this article: http://dx.doi.org/10.1081/SCC-120015804

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SYNTHETIC COMMUNICATIONS®
Vol. 33, No. 4, pp. 521–525, 2003

Microwave-Assisted Synthesis of the Tetradentate Schiff-Bases Under Solvent-Free and Catalyst-Free Condition

Maryam Mirza-Aghayan,* Mitra Ghassemzadeh, Maryam Hoseini, and Mohammad Bolourtchian

Chemistry and Chemical Engineering Research Center of Iran (CCERCI), Tehran, Iran

ABSTRACT

Synthesis of tetradentate Shiff bases using microwave activation under solvent-free conditions with and without support is described. This method affords high yields in very short reaction times for synthesis of tetradentate Shiff bases.

The synthesis of tetradentate Schiff base ligands is an important reaction in organic chemistry because of their applications in chemical

*Correspondence: Maryam Mirza-Aghayan, Chemistry and Chemical Engineering Research Center of Iran (CCERCI), P.O. Box 14335-186, Tehran, Iran; Fax: +98 21 8037185; E-mail: m.mirzaaghayan@ccerci.ac.ir.

DOI: 10.1081/SCC-120015804 0039-7911 (Print); 1532-2432 (Online)

transformations.[1] The ability of the tetradentate Schiff base to form stable complexes with different cations is well known.[2]

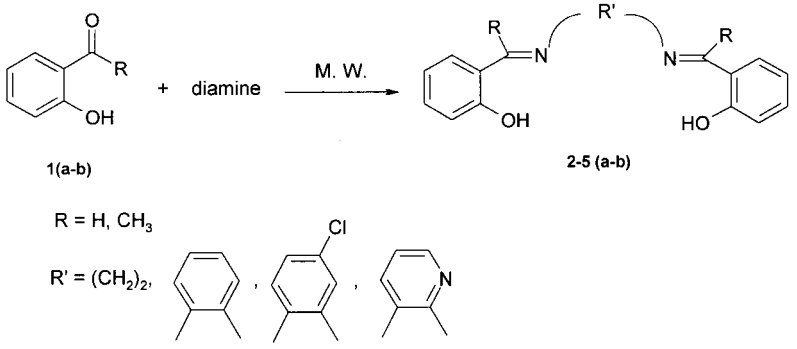
In general, the synthesis of imines has been achieved using several reagents such as zinc chloride,[3] drying agent $TiCl_4$,[4] molecular sieve[5] or alumina.[6] Although the synthesis of tetradentate Schiff bases has been extensively documented and a variety of methods being available,[7] the use of microwave irradiation with a support solid remains unknown.

Microwave (MW) enhanced chemical reaction[8] in general and on organic solid supports[9] in particular has gained popularity over the usual homogeneous and heterogeneous reaction. They can be conducted rapidly and provide pure products in quantitative yield without using solvent.

In continuation of our investigations in organic reaction in solventless systems,[10] we now report a facile preparation of tetradentate Schiff bases under solvent-free conditions using microwave irradiation. We started our studies with the synthesis of tetradentate Schiff bases **2–5(a–b)** by the reaction of salicylaldehyde (**1a**) or 2′-hydroxyacetophenone (**1b**) with the corresponding diamines supported on silica gel, which is accelerated by exposure to microwaves (Sch. 1).

However, in order to obtain better yields, an alternative procedure using no adsorbent was developed. Without the solid inorganic support (silica gel), the reaction is faster and the yields are higher (Table 1). The absence of solvent coupled with the high yield and very short reaction times make this procedure for the preparation of tetradentate Shiff bases more attractive.

In conclusion, we have developed a simple procedure for the synthesis of tetradentate Schiff base that proceeds rapidly under



Scheme 1.

Table 1. Solvent-free preparation of tetradentate Shiff bases, **2**–**5(a**–**b)**, using microwave irradiation.

		Microwave			
		With silica gel as support		Without silica gel as support	
Reagent	Product	Time (s)	Yield (%)	Time (s)	Yield (%)
Ethylenediamine	**2a**	120	90	40	98
	2b	240	90	10	98
Phenylenediamine	**3a**	180	80	120	98
	3b	360	55	480	65
4-Chlorophenylenediamine	**4a**	240	60	110	90
	4b	300	40	100	55
2,3-Diaminopyridine	**5a**	180	70	120	98
	5b	300	30	300	50

solvent-free condition. Protocol for the synthesis of tetradentate Schiff base under focused microwave irradiation in the absence of any catalyst, solid support or solvent, affords a clean, efficient and an environmentally friendly method.

EXPERIMENTAL

Nuclear magnetic resonance spectra were registered on a Bruker 80 MHz in $CDCl_3$ utilizing tetramethylsilane as internal standard. Mass spectra were obtained on a FTSONS GC 8000/Trio 1000 under 70 eV. Microwave irradiation was carried out in a National oven Model 6755 at 900 W.

General Procedure for Preparation of Compounds 2–5(a–b)

Zero point five equimolar of the diamines **2–5** were added to an equimolar amount of aldehydes **1a–b** (in condition of presence of inorganic solid support, the aldehyde was supported on 0.4 g of silicagel 60, Fluka, particle size <230 mesh ASTM). The reaction mixture was irradiated in a microwave oven for the indicated time (Table 1). The progress of reaction was monitored by TLC. After completion of the

reaction, the residue was taken into $CHCl_3$, filtered, washed with $CHCl_3$ (2×10 mL) and the filtrate was evaporated to dryness to give the corresponding compound. Fine purification was achieved by column chromatography using hexane–ethylacetate 9:1 as eluent.

REFERENCES

1. (a) Jacobsen, E.N.; Zhang, W.; Muci, A.R.; Ecker, J.R.; Deng, L. J. Am. Chem. Soc. **1991**, *113*, 7063–7064; (b) Mascarenhas, C.M.; Miller, S.P.; White, P.S.; Morken, J.P. Angew. Chem. Int. Ed. **2000**, *40* (3), 601–603; (c) Berberich, H.; Roesky, P.W. Angew. Chem. Int. Ed. **1998**, *110*, 1618; Angew. Chem. Int. Ed. **1998**, *37*, 1569; (d) Onozawa, S.Y.; Sakakura, T.; Tanaka, M.; Shiro, M. Tetrahedron **1996**, *52*, 4291; (e) Yokoo, K.; Mine, N.; Taniguchi, H.; Fujiwara, Y. J. Organomet. Chem. **1985**, *279*, C19; (f) Bachmann, S.; Mezzetti, A. Chimia **2001**, *55* (7/8), 199, 636; (g) Nakata, K.; Takeda, T.; Mihara, J.; Hamada, T.; Irie, R.; Katsuki, T. Chem. Eur. J. **2001**, *7* (17), 3776; (h) Cameron, P.A.; Gibson, V.C.; Irvine, D.J. Angew. Chem. Int. Ed. **2000**, *39* (12), 2141.
2. (a) Freire, C.; Castro, B. J. Chem. Soc., Dalton Trans. **1998**, 1491–1497; (b) Vilas-Boas, M.; Freire, C.; Castro, B.; Christensen, P.A.; Hillman, A.R. Chem. Eur. J. **2001**, *7* (1), 139–150; (c) Schon, E.; Plattner, D.; Chen, P. Chimia **2001**, *55* (7/8), 103, 612; (d) Miller, K.J.; Baag, J.H.; Abu-Omar, M.M. Inorg. Chem. **1999**, *38*, 4510; (e) Darensbourg, D.J. et al. J. Am. Chem. Soc. **1999**, *121*, 107.
3. Billman, J.H.; Tai, K.M. J. Org. Chem. **1958**, *23*, 535.
4. White, W.A.; Weingarten, H. J. Org. Chem. **1967**, *32*, 213.
5. (a) Taguchi, K.; Westheimer, F.H. J. Org. Chem. **1971**, *36*, 1570; (b) Bonnett, Emerson. J. Chem. Soc. **1965**, 4508; (c) Roelofsen; Van Bekkum. Recl. Trav. Chim. Pays-Bas 91 **1972**, 605; (d) Furegati, M.; Rippert, A.J. Chimia **2001**, *55* (7/8), 140, 621.
6. Texier-Boullet, F. Synthesis **1985**, 679.
7. Wilkinson, S.G.; Gillard, R.D.; Mc Cleverty, J.A. *Comprehansive Coordination Chemistry*; Pergamon Press, 1987; Vol. 2, 715–738 and references cited therein.
8. For recent review on microwave-assisted chemical reaction see (a) Abramovich, R.V. Org. Prep. Proced. Int. **1991**, *23*, 683; (b) Whittaker, A.G.; Mingos, D.M.P. J. Microwave Power Electromagn. Energy **1994**, *29*, 195; (c) Majetich, G.; Hicks, R. J. Microwave Power Electromagn. Energy **1995**, *30*, 27; (d) Caddick, S. Tetrahedron **1995**, *51*, 10403; (e) Varma, R.S.; Chatterjee, A.K.; Varma, M.

Tetrahedron Lett. **1993**, *34*, 3207; Tetrahedron Lett. **1993**, *34*, 4603; (f) Varma, R.S.; Chatterjee, A.K. J. Chem. Soc., Perkin Trans. **1993**, 999; (g) Varma, R.S.; Lamtur, J.B.; Varma, M. Tetrahedron Lett. **1993**, *34*, 3029; (h) Varma, R.S. Green Chem. **1999**, *1*, 43; (i) Hoz, A.; Diaz-Ortis, A.; Moreno, A.; Langa, F. Eur. J. Org. Chem. **2000**, 3659.

9. (a) Clark, J.H. *Catalysis of Organic Reactions by Supported Inorganic Reagents*; VCH Publisher, Inc.: NY, 1994; (b) Varma, R.S.; Varma, M. Tetrahedron Lett. **1992**, *33*, 5937; (c) Marrero-Terrero, A.L.; Loupy, A. Synlett. **1996**, 245; (d) Clark, J.H.; Ross, J.C.; Macquarrier, D.J.; Barlow, S.J.; Bastock, T.W. Chem. Commun. **1997**, 1203.
10. (a) Heravi, M.M.; Ajami, D.; Mojtahedi, M.M.; Ghassemzadeh, M. Tetrahedron Lett. **1999**, *40*, 561; (b) Heravi, M.M.; Mirza-Aghayan, M.Z. Naturforsch **1998**, *54b*, 815; (c) Mirza-Aghayan, M.; Heravi, M.M. Synth. Commun. **1999**, *29* (5), 785; (d) Heravi, M.M.; Ajami, D.; Ghassemzadeh, M. Synth. Commun. **1999**, *29* (5), 781.

Received in Japan November 27, 2001

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016