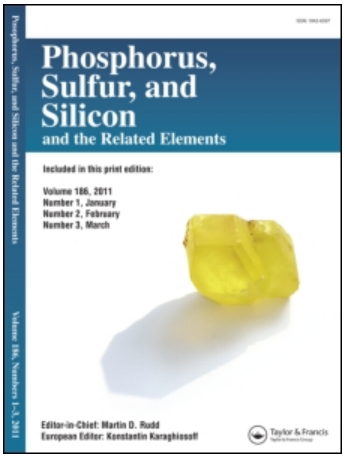


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reductive Amination of Aldehydes and Ketones with Sodium Borohydride Supported Onto HZSM-5 Zeolite Under Microwave Irradiation in a Solvent Free System

Hossein A. Oskooie[a]; Somaih Solemani Amiri[a]; Majid M. Heravi[a]; Mitra Ghassemzadeh[b]
[a] Department of Chemistry, School of Sciences, Azzahra University, Vanak, Tehran, Iran [b] Chemistry & Chemical Engineering Research Center of Iran, Tehran, Iran

To cite this Article Oskooie, Hossein A. , Amiri, Somaih Solemani , Heravi, Majid M. and Ghassemzadeh, Mitra(2005) 'Reductive Amination of Aldehydes and Ketones with Sodium Borohydride Supported Onto HZSM-5 Zeolite Under Microwave Irradiation in a Solvent Free System', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 9, 2047 — 2050

To link to this Article: DOI: 10.1080/104265090902831

URL: http://dx.doi.org/10.1080/104265090902831

Phosphorus, Sulfur, and Silicon, 180:2047–2050, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426509090902831

Taylor & Francis
Taylor & Francis Group

Reductive Amination of Aldehydes and Ketones with Sodium Borohydride Supported Onto HZSM-5 Zeolite Under Microwave Irradiation in a Solvent Free System

Hossein A. Oskooie
Somaih Solemani Amiri
Majid M. Heravi
Department of Chemistry, School of Sciences, Azzahra University, Vanak, Tehran, Iran

Mitra Ghassemzadeh
Chemistry & Chemical Engineering Research Center of Iran, Tehran, Iran

Sodium borohydride supported onto a HZSM-5 zeolite is presented as a general reducing agent for the reductive amination of aldehydes and ketones under microwave irradiation in solventless system.

Keywords Reductive amination; sodium borohydride; solventless system; zeolite

The reaction of aldehydes or ketones with ammonia, primary amines or secondary amines in the presence of reducing agents to give primary, secondary, or tertiary amines, respectively, known as reductive aminations (of the carbonyl compounds) or reductive alkylations (of the amines) are among the most useful and important tools in the synthesis of different kinds of amines.[1]

There are two commonly used direct reductive amination methods. The first method is catalytic hydrogenation with platinum, palladium or nickel catalyst.[2] Hydrogenation has limited use with compounds containing carbon-carbon multiple bonds and in the presence of reducible functional groups such as the nitro[3] and cyano groups.[4] The catalyst may be inhibited by compounds containing divalent sulfur.[5] The second method utilizes hydride reducing agents, particularly sodium cyanoborohydride ($NaBH_3CN$)[6] and sodium borohydride ($NaBH_4$)[7] for

Received September 24, 2004; accepted September 28, 2004.
Address correspondence to Hossein A. Oskooie, Azzahra University, Department of Chemistry, School of Sciences, Vanak, Tehran, Iran. E-mail: mmh1331@yahoo.com

reduction. The latter has been conducted in sulfuric acid medium. Consequently, we thought it is worthwhile to develop a manipulatively easy and eco-friendly method for the reduction of in-situ-generated Schiff's bases. In this article we wish to report that sodium borohydride supported onto HZSM-5 zeolite can be used effeciently for the reductive amination of carbonyl compounds under microwave irradiation in a solventless system. The combination of supported reagents and microwave irradiation has been used to carry out a wide range of reactions in short times and with high conversions and selectivity without the need for solvents among other advantages.[8]

The choice of solid support and linkage are important factors for success in solid phase synthesis.[9] Unlike solution phase synthesis where an optimization study will result in reproducible reactions, time consuming validation steps, usually required in solid phase synthesis, may only be specific for a particular solid support.[10] In continuation of our ongoing program using zeolites to develop environmentally benign solventless system,[11] we present a comparative study of reaction rates, yields, and purity in the reductive amination of aldehydes and ketones with sodium borohydride to assess the effectiveness of a HZSM-5 zeolite.

A number of solid supports such as silica gel, clays (such as montmorillonite K-10), HZ- and NaY zeolite and HZSM-5 zeolite were used for the simplification of this reduction. We found that the choice of the solid support is very critical to the success of reaction, since sodium borohydride should reduce imines (or iminium ions) selectively over aldehydes and ketones under the reaction conditions. We discovered among the mentioned supports HZSM-5 zeolite afforded the best results.

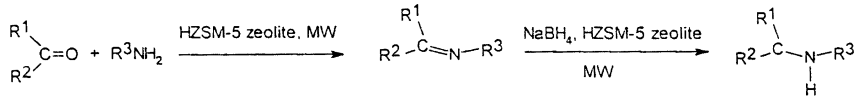
The direct reductive amination reactions were carried out by a simple mixing of the carbonyl compounds amine and HZSM-5 zeolite, irradiating this mixture in an unmodified household microwave. The progress of the reaction is followed by TLC. After completion of the reaction, 10% $NaBH_4$ in wet HZSM-5 was added and mixed thoroughly. This mixture was placed in a microwave oven. The progress of reaction was monitored by TLC. After the completion of reaction, CH_2Cl_2 was added. The mixture was filtered and the filtrate was evaporated to dryness to afford the products. The results from various reductive amination reactions of aldehydes and ketones are listed in Table I. The results in Table I showed that the reductive amination of a wide variety of aldehydes and ketones with primary and secondary amines was successful under this condition and gave the desired products in good to excellent yields. In conclusion, results presented in this communication indicate that sodium borohydride supported onto HZSM-5 zeolite is a synthetically useful reagent for reductive amination of aldehydes and ketones.

TABLE I Reduction of Carbonyl Compounds With Sodium Borohydride Supported Onto HZSM-5 Zeolite Under Microwave Irradiation in Solventless System

Entry	Carbonyl compound	Amine	Time[a] (min)	Yield[b] (%)
1	Benzaldehyde	Aniline	9	87
2	Benzaldehyde	Ethylamine	10	81
3	Benzaldehyde	Propylamine	10	85
4	Salicylaldehyde	Aniline	5	95
5	Salicylaldehyde	4-methylaniline	7	93
6	Acetophenone	Aniline	5	95
7	Acetophenone	Benzylamine	5	71
8	Cyclohexanone	Aniline	5	87
9	4-Methylcyclohexanone	Aniline	5	85

[a]Time for reduction on *in situ* generated Schiff bases in MW over.
[b]Yields reported are those of pure isolated products.

Sodium borohydride is a mild, commercially available reagent. When it is mixed with wet HZSM-5 zeolite, it can be used under microwave irradiation for the fast reaction and solventless system for the sake of an environmentally friendly condition.



EXPERIMENTAL

All compounds are known and were identified by comparison with authentic samples (physical and spectroscopic data). Yields refer to isolated products purified by column chromatography. For safety reasons, all the experiments with microwave ovens should be performed in an efficient hood to avoid contact with vapors.

REDUCTIVE AMINATION OF SALICYLALDEHYDE WITH 4-METHYLANILINE

A Typical Procedure

A mixture of 4-methylaniline (0.107 g, 1 mmol) and HZSM-5 zeolite (0.02 g) was thoroughly grinded using a pestle and mortar. To this mixture salicylaldehyde was added in a beaker. The beaker was placed in a microwave oven and irradiated for 2 min. The in-situ-generated Schiff's

base was mixed thoroughly with freshly prepared $NaBH_4$-HZSM-5 zeolite (0.038 g, 1 mmol $NaBH_4$ on 0.334 g zeolite) and water (1 mL). The reaction mixture was again irradiated for 5 min. The progress of reaction was monitored by TLC. Upon completion of the reaction, the product was extracted by CH_2Cl_2. The removal of solvent and crystallization from EtOH afforded the product in a 93% yield.

REFERENCES

[1] A. F. Abdel-Majid, K. G. Carson, B. D. Harris, C. A. Maryanoff, and R. D. Shoh, *J. Org. Chem.*, **61,** 3849 (1996).
[2] (a) W. S. Emerson, *Org. React.* **4,** 174 (1948) and references cited therein; (b) W. S. Emerson and C. A. Uraneck, *J. Am. Chem. Soc.*, **63,** 749 (1941); (c) H. E. Jahnson and D. G. Crosly, *J. Org. Chem.*, **27,** 2205 (1962); (d) M. V. Klyver and M. L. Khidekel, *Russ. Chem. Rev.*, **49,** 14 (1980).
[3] N. Rylander, In *Catalytic Hydrogenation over Platinum Metals*, New York: Academic Press, p. 128 (1967).
[4] Ibid, 128.
[5] Ibid, 21.
[6] (a) C. F. Lane, *Synthesis*, 135 (1975); (b) B. N. Trost and I. Fleming, In *Comprehensive Organic Synthesis*, 1 ed., New York: Pergamon Press, vol. 8 (1991).
[7] V. Giancarlo, A. G. Giumanini, P. Strazzolini, and M. Poiana, *Synthesis*, 121 (1993).
[8] R. S. Varma, *Green Chemistry*, 43 (1999) and references cited therein.
[9] W. Li and B. Yan, *J. Org. Chem.*, **63,** 4092 (1998).
[10] K. Bergers and D. Lim, *Chem. Commun.*, 785 (1997).
[11] M. M. Heravi and M. Ghassemzadeh, *Phosphorus, Sulfur, and Silicon*, **178,** 119 (2003) and references cited therein.