WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 8.074
Volume 7, Issue 05, 373-376. Review Article ISSN 2277–7105

A HIGHLY EFFICIENT, AND SELECTIVE CLEAVAGE OF SULFONAMIDES BY MCM-41 (H) IN MEOH

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Article Received on
04 Jan. 2018,
Revised on 25 Jan. 2018,
Accepted on 14 Feb. 2018
DOI: 10.20959/wjpr20185-11211

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ABSTRACT

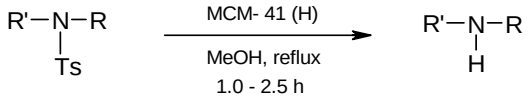
A simple and efficient method for selective cleavage of sulphonamides has been achieved for the first time using MCM-41 (H) zeolite. The procedure is applicable to a wide variety of sulphonamides and the catalyst can be recycled and reused.

KEYWORDS: solid acid, zeolites, cleavage of sulfonamide, secondary amines.

Zeolites promoted reactions are advantageous in many ways over conventional approaches, especially due to shorter times, the routine cleanliness of the processes and simple work-up procedures. For a long time, aromatic sulphonic acids have been used in the derivatization of amines and the protection of amino functions[1] and the resultant crystalline sulphonamides are very resistant to nucleophillic attack. Recently, the use of inorganic solid supports as catalysts has been developed for dry media reactions[2] resulting in higher selectivity, milder conditions and ease of handling. Toluenesulfonyl groups are widely used as protecting agents for hydroxyl groups[3,4] and amines.[1] These groups are highly stable and require drastic deprotection conditions.

In the literature, a limited number of methods are available for the cleavage of sulphonamides utilizing a variety of reagents such as sodium in liquid ammonia[4], sodium naphthanilide[5] or Mg-MeOH[6] and hydrogenolysis with Nickel[7] and KF-Al_2O_3 under microwave irradiation. Furthermore, aryl toluene sulphonamides are more stable than alkyl toluene sulphonamides and require refluxing aqueous alcoholic KOH for their deprotection.

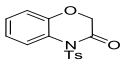
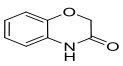
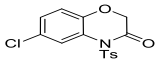
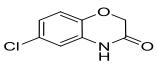
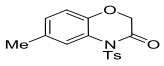
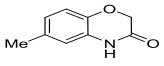
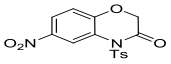
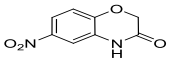
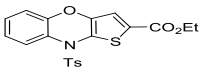
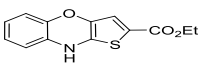
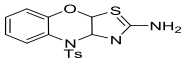
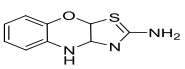
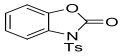
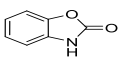
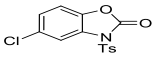
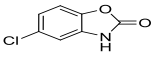
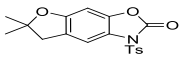
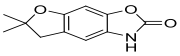
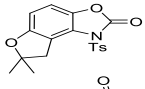
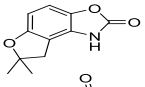
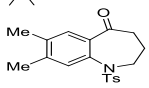
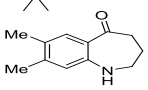
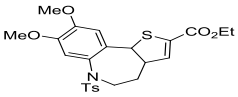
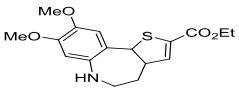
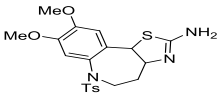
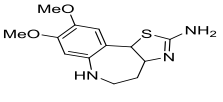
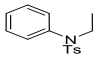
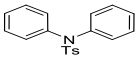
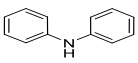
In this article, we wish to report a simple and efficient cleavage method for sulphonamides using MCM-41 (H) Zeolite[9–11] (Scheme 1).



Scheme 1

This method is general and applicable for the cleavage of aryl as well as alkyl toluene sulphonamides (See Table 1).

Table 1. Clevage of sulfonamides to amines using MCM-41 (H)a

Entry	Substrate	Amine	Time/h	Yield/%b	m.p.c
A			1.15	90	173
B			1.00	91	214
C			1.10	92	210
D			1.30	90	230
E			2.00	88	186
F			2.50	89	299
G			1.30	89	196
H			1.15	91	193
I			1.45	83	197
J			2.00	86	271
K			1.10	92	106
L			1.00	91	272
M			2.30	83	283
N			1.45	80	204d
O			1.30	78	305d

aMolar ratio of substrate: MCM-41(H) = 1.0:0.15
bYield refers to isolated and purified product.
cAll products were known compounds and characterized by ^{1}H NMR, IR and mass spectroscopy.
dmelting point

Reductive cleavage of sulphonamides with SmI_2[12], Mg/MeOH, Na/liquid ammonia and Sodium/naphthalide results in the reduction of the other functional groups such as halides, nitro, azide, carbonyl and α,β-unsaturated systems.[13] The use of HBr/AcOH[14] is highly acidic and it does not tolerate acid sensitive functionalities like Boc, Cbz and ethers. Na in liquid NH_3 affords low yields associated with cumbersome experimental and tedious isolation procedures. Present reaction conditions have been shown to be compatible with a range of these functional groups (Table). An advantage over existing methodologies was achieved by MCM-41 (H) zeolite, wherein the products were obtained in 78-92%. Important features of the reaction are that the MCM- 41(H) zeolite was recovered and reused for four cycles without substantial loss in the yields.

In conclusion, we have developed a simple, convenient and efficient method for the deprotection of sulfonamides. This method offers significant advantages such as improved yields, operational simplicity, shorter reaction times and easy workup.

ACKNOWLEDGEMENT

One of the authors (BS) is thankful to the CSIR, New Delhi, for award of SRF.

REFERENCES AND NOTES

1. T. W. Greene, P. G. M. Wuts, "*Protecting Groups in Organic Chemistry*" Wiley-Interscience, Newyork, 2nd edition. 1991; P. J. Kocienski, *"Protecting Groups"* Thieme, Newyork, 1994.
2. G. Brin, A. loupy, D. Villemin, S*olid Supports and Catalyst in Organic Synthesis*, K. Smith, Ed. Ellis Horwood and Prentice hall, Chicheser, 1992; Chapter 12.
3. H. J. E. Loewenthal, *Tetrahedron*, 1959; *6*: 269.
4. D. B. Denney, B. Goldstein, *J. Org. Chem*, 1956; *21*: 479; J. Kovacs, U. K. Ghatk, *J. Org. Chem*. 1996; *31*: 119.
5. W. D. Closson, P. Wriede, S.Bank, *J. Am. Chem. Soc*, 1966; *88*: 1581; J. Sungchul, I. E. Gortler, A. Waring, A. Batisti, S. Bnk, W. D. Closon, P. Wfiede, *J. Am Chem. Soc*, 1967; *89*: 5311.
6. M. Sridhar, B. Ashok Kumar, R. Narender, *Tetrhedron Lett*, 1998; *39*: 2847; B. Nyasse, L. Grehn, U. Ragnarsson, *J. Chem. Soc. Chem. Comm*, 1997; 1017.
7. G. W. Kenner, M. A. Murray, *J. Chem. Soc*, 1949; 5178.
8. G. Sabitha, S. Abraham, B. V. Subbareddy, J. S. Yadav, *Synlett*, 1999; *11*: 1745.

9. J. S. Beck, C. Vartuli, J. W. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc*, 1992; *114*: 10834.
10. C. T. Kresge, M. E. Leonociwicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature*, 1992; *359*: 710.
11. X. S. Zhao, G. Q. Lu, G. J. Millar, *Ind. Eng. Chem. Res*, 1996; *35*: 2075.
12. E. Vedejs, S. Lin, *J. Org. Chem*, 1994; *59*: 1602; C. Goulaouic-Dubois, A. Guggisberg, M. Hesse, *J. Org. Chem*, 1995; *60*: 5969; C. Goulaouic-Dubois, A. Guggisberg, M. Hesse, *Tetrahedron*, 1995; *51*: 12573; E. V. Vedejs, S. Lin, A. Klapars, J. Wang, *J. Chem. Soc*, 1996; *118*: 9796.
13. Zarecki, J. Wicha, *Synthesis*, 1996; 455.
14. R. C. Roemmele, H. J. Rapaport, *J. Org. Chem*, 1988; *53*: 2367.
15. Typical procedure. A mixture of *N*-tosyl-2*H*-1,4-benzoxazin-3-one (1.0g, 3.3 mmol), and MCM-41 (H) (0.15 g) in acetonitrile (10 mL) was heated at reflux for 1.15 h. The reaction mixture was allowed to cool room temperature, and was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by column chromatography on silica gel (Merck, 100–200 mesh, ethyl acetate-hexane, 2:8) to afford the pure 2*H*-1,4-bezoxazin-3-one (2A, 90 % yield) as a white crystalline solid.[6]
16. N. Lingaiah, R. Narender, *Heterocyclic Commun*, 2000; 6: 515.