OXIDATIVE DEOXIMATION WITH H_2O_2 AND MCM-41

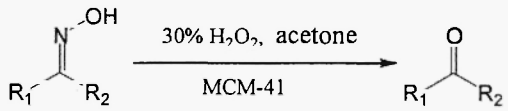
N. Vijayakumari, B. Balakrishna Reddy and Lingaiah Nagarapu*
Organic Chemistry Division-II, Indian Institute of Chemical Technology, Hyderabad, India.
E-mail : *nagarapu2@yahoo.co.in*

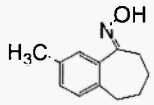
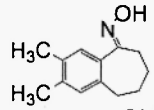
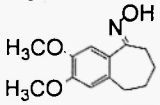
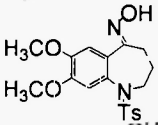
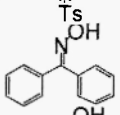
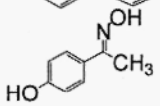
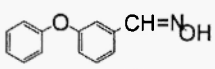
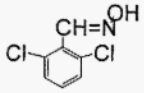
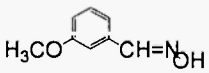
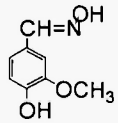
Abstract : A simple and mild method of oxidative deoximation with 30%H_2O_2 and MCM-41 is described. This method is effective for deprotection of ketones and aldehydes.
Key words : oxidative deoximation, 30%H_2O_2, MCM-41, ketones, aldehydes.

A number of carbonyl functional group equivalents are routinely employed in organic synthesis. Oximes are readily available and highly stable derivatives of carbonyl compounds that have been regarded both as protective.[1] Oximes have been used extensively for purification and charecterization of carbonyl compounds.[2] They also provide a viable route to amides from carbonyl equivalents via Beckmann rearrangement.[3] However, the utility of oximes as carbonyl equivalents is limited by the methods employed for their regeneration. Classically they are regenerated by acid hydrolysis under suitable conditions.[4] This process removes hydroxylamine from the equilibrium. There are limits to the scope of this reaction since compounds containing acid sensitive groups cannot be subjected to this hydrolysis. Recently there has been a lot of stress on the oxidative, [5] reductive [6] and microwave irradiation [7] methods for cleavage of deoximation. It has been found that most of the oxidative methods use noncatalytic amount of corrosive and carcinogenic metals such as chromium or expensive catalysts or mostly involve microwave technics. In view of the recent stress on the catalytic processes towards the development of clean and green chemical processes [8], investigation of new, less hardous chemical oxidants has become a priority for the synthetic organic chemists. Herein, we report the use of a combination of MCM-41 and hydrogen peroxide as a novel reagent system for the oxidative deoximation.

Treatment of oxime (both ketoximes and aldoximes) with 30% hydrogen peroxide in acetone, in the presence of 10 mol % of MCM-41 [9-11] at ambient temperature afforded the corresponding carbonyl compound.[12] In order to test the generality of the deoximation various types of oximes were subjected to the oxidation in the presence of 10 mol % of MCM-41 and 30% hydrogen peroxide to yield the corresponding carbonyl compounds in moderate to good yields (Table-1)

Table-1 : Physical data



Entry	Substrate	Time (h)	Yield (%)
1		3.5	70
2		3.0	69
3		4.5	66
4		4.5	63
5		6.0	67
6		3.0	72
7		8.0	68
8		4.0	76
9		6.0	68
10		6.0	62

In conclusion, we have demonstrated an efficient and inexpensive protocol for regeneration of carbonyl compounds has been realized using MCM-41 zeolite. Our presents several advantages like the stability, easy handling, shorter reaction times and moderate to good yield of products. The important feature is that MCM-41 is recovered and reused for three cycles without substantial loss in the yield of products.

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References and Notes

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12. *Typical procedure for the generation of ketones*: The oxime (2.645mmols) was dissolved in acetone (10 mL) and MCM-41 zeolite (10 mol %) was added to it. The reaction mixture was cooled to –5°C in ice-salt mixture.To a stirred mixture of the above 1.25 mL of 30% H_2O_2 was added dropwise. The reaction mixture was monitored by TLC and the solvent was removed and water added to the residue. [The reaction mixture was allowed to cool room temperature before adding water, filtered (to separate zeolite, zeolite was washed with ethyl acetate and activated for recycle)], filtrate was extracted with ether (2 x 10 mL). The combined ether extracts were washed with 5% $Na_2S_2O_3$, water and dried over anhydrous sodium sulfate. Evaporation of the solvent gives crude carbonyl compound, which is further purified by crystallization.

    3-Methyl-6,7,8,9-tetrahydro benzocyclohepten-5-one (**entry 1, Table-1**) : B.p. 168-170° C; ; ^{1}H NMR ($CDCl_3$): δ 1.72-1.90 (m, 4H, CH_2), 2.65 (t, 2H, CH_2Ar), 2.85 (t, 2H, CH_2CO), 2.35 (s, 3H, s, CH_3), 7.00 (d, 1H, *J*=9.2Hz, 1-H), 7.09 (d, 1H, *J*=9.2Hz, 2-H), 7.49 (s, 1H, 4-H). ^{13}C NMR ($CDCl_3$): δ 19.9, 20.1, 24.58, 31.1, 39.8, 128.1, 128.8, 131.8, 135.0, 137.4, 137.7, 203.5. MS : m/z 174 (M^+, 100%),

    2,3-Dimethyl-6,7,8,9-tetrahydro benzocyclohepten-5-one (**entry 2, Table-1**): m.p.52°C; ^{1}H NMR ($CDCl_3$): δ 1.70-1.95 (m, 4H, CH_2), 2.60-2.95 (m, 4H, CH_2 Ar, CH_2 CO), 2.32 (6H, s, -2 x CH_3), 6.85 (s, 1H, 1-H), 7.50 (s, 1H, 4-H). ^{13}C NMR ($CDCl_3$): δ 18.5, 19.0, 20.5, 24.0, 33.0, 40.0, 129.08, 131.5, 133.5, 136.0, 139.0, 142.1, 220.0. MS : m/z 188 (M^+, 100%), 173, 159, 145, 128, 119, 115, 105, 91, 77.

    2,3-Dimethoxy-6,7,8,9-tetrahydro benzocyclohepten-5-one (**entry 3, Table-1**) : m.p.63°C ; ^{1}H NMR ($CDCl_3$): δ 1.70-2.10 (m, 4H, -CH_2), 2.60-3.20 (m, 4H, CH_2Ar, CH_2CO), 4.00 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 6.85 (s, 1H, 1-H), 7.60 (s, 1H, 4-H). ^{13}C NMR ($CDCl_3$): δ 20.0,

24.2, 32.2, 40.2, 55.0, 115.0, 150.4, 132.2, 138.1, 148.2, 150.4, 202.4 (C=O). MS : m/z 220 ($M^{+\cdot}$ 100%), 192, 151, 121, 107, 77.

2,3,4,5-Tetrahydro-7,8-dimethoxy-1-p-toluenesulphonyl-1-benzazepin-5-one (**entry 4, Table-1**): m.p. 144°C. ^{1}H NMR ($CDCl_3$) : δ 1.82-2.00 (m, 2H, $-CH_2-$), 2.18-2.30 (t, 2H, $-COCH_2$), 3.79 (t, 2H, $-NCH_2-$), 3.90 (s, 6H, $-2OCH_3$), 2.42 (s, 3H, Ar-CH_3), 6.88 (s, 1H, Ar-H_6), 7.19 (s, 1H, Ar-H_9), 7.20 (d, 2H, Ar-H_a, *J*=9.3 Hz), 7.45 (d, 2H, Ar-H_b. *J*=9.3 Hz); ^{13}C NMR ($CDCl_3$): δ 20.1 ($C_7{}^1$), 23.0 (C_3), 29.0 (C_4), 38.0 (C_2), 49.0 (OC) 55.1 (OC), 110.1 (C_9), 112.0 (C_6), 126.1 ($C_2{}^1$+$C_6{}^1$), 128 ($C_1{}^1$), 129.9 ($C_3{}^1$+$C_5{}^1$), 132.1 ($C_4{}^1$), 138.9 (C_{10}), 143.0 (C_{11}), 148.0 (C_7), 152.0 (C_8) and 199.5 (C_5). MS : m/z 375 ($M^{+\cdot}$, 90%), 230, 220, 192 (100%), 166, 141, 104, 91 65.

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