



Trade Science Inc.

Organic CHEMISTRY

An Indian Journal

Short Communication

OCAIJ, 6(1), 2010 [63-65]

Facile polyethylene glycol (PEG-400) promoted synthesis of oximes

D.Sudhakar, V.Madhava Rao, V.Siddaiah, C.Venkata Rao*

Department of Chemistry, Sri Venkateswara University, Tirupati-517 502, (INDIA)

E-mail: cvrsvu@gmail.com

Received: 9th December, 2009 ; Accepted: 19th December, 2009

ABSTRACT

A catalyst-free, high-yielding conversion of aldehydes and ketones into oximes has efficiently been carried out by treatment with $\text{NH}_2\text{OH}\cdot\text{HCl}$ at room temperature using polyethylene glycol (PEG-400) as the reaction medium. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Polyethylene glycol (PEG-400);
Carbonyl compounds;
Oximes;
Hydroxylamine hydrochloride.

INTRODUCTION

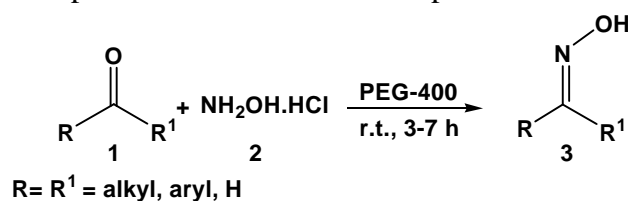
The oximes are most useful derivatives of aldehydes and ketones, both for the purposes of characterization and also as the key intermediates in the important Beckmann rearrangement^[1-3]. They are also used as precursors in the synthesis of variety of organic compounds α -phenyl-N-substituted nitrones and o-alkyl benzaldoximes^[4] and also in the preparation of 1,3-dipolar reagents^[5]. Although several methods for their synthesis^[1,2,6-8] have been reported in the literature most are associated with long reaction times, tedious reaction conditions and low yields. A typical experiment would involve heating a mixture of the carbonyl compound and hydroxylamine hydrochloride in water or ethanol, along with a base such as pyridine or sodium acetate^[1]. Few other procedures also have been reported under sol-

vent free conditions using molecular sieves^[6]. Hence there is a need for an efficient mild and environmentally friendly procedure for the synthesis of oximes.

RESULTS AND DISCUSSION

For the development of useful synthetic methodologies we have observed that aldehydes and ketones can conveniently be converted into their oximes by treatment with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in polyethylene glycol (PEG-400) at room temperature (Scheme 1), in excellent yields.

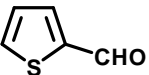
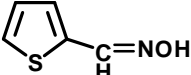
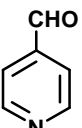
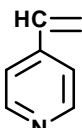
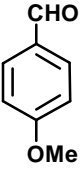
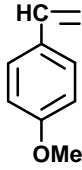
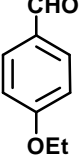
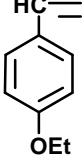
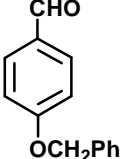
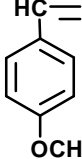
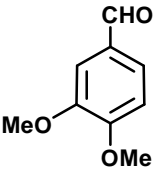
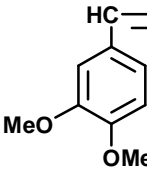
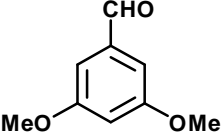
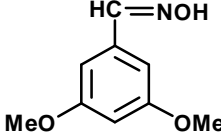
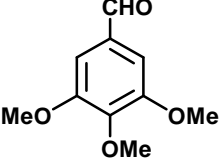
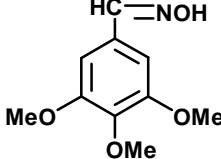
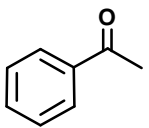
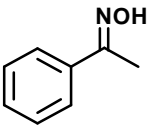
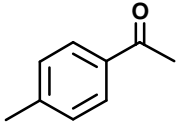
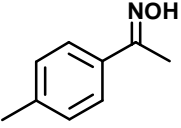
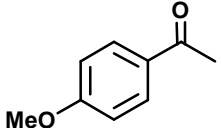
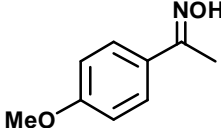
A series of oximes were prepared from several aldehydes and ketones (TABLE 1) by following the above method. No additional catalyst was required and the conversion was completed within 3-7 h. The products were obtained in good yields without any side products. The structures of the products were established by melting point comparison and spectral (¹H-NMR & GCMS) data. Polyethylene glycol (PEG-400)^[9], has been applied here as an efficient green reaction medium for the preparation of oximes. It is an inexpensive, low toxicity, eco-friendly polymer and further recycled to use without loss



Scheme 1

Short Communication

TABLE 1 : One-pot synthesis of oximes using polyethylene glycol (PEG-400) as the reaction medium

Entry	Substrate	Product ^a	Time (h)	Yield ^b (%)
1			3	98
2			5	93
3			4	95
4			4	95
5			6	92
6			5	97
7			4	96
8			5	97
9			4	96
10			3	98
11			4	97

Entry	Substrate	Product ^a	Time (h)	Yield ^b (%)
13			5	92
14			7	94
15			3	93

^aThe structures of the products were established from their spectral (m.p. ¹H NMR and GC MS) and analytical data. ^bIsolated yield of activity. Their applications as a reaction medium in organic synthesis have not yet been fully explored. for C₉H₁₁NO₃: C, 59.66; H, 10.18; N, 7.73%. Found: C, 59.50; H, 10.02; N, 7.80%.

General procedure for the synthesis of oximes

To a stirred suspension of aldehydes or ketones 1 (1 mmol) in PEG-400 (2g), NH₂OH.HCl (1.5 mmol) 2 was added and the mixture was stirred at room temperature for 3-7h (TLC showed the completion of reaction). The reaction mixture was poured into crushed ice and filtered the solid was obtained and recrystallized from aqueous ethanol to afford the pure oxime 3 product. The physical data (mp, Anal, NMR & GCMS) of the compound are present below.

Compound 2

Pyridine-4-aldoxime: Solid. m.p. 129-131°C. ¹H NMR: (200 MHz, CDCl₃), δ 8.30 (s, 1H), 7.85 (s, 1H), 8.08 (d, 2H, J=9.0), 8.84 (d, 2H, J=9.0), GCMS (m/z): 122 [M]⁺. Anal. Calcd. for C₆H₆N₂O: C, 49.18; H, 4.91; N, 22.95. Found: C, 49.12; H, 4.95; N, 22.99%.

Compound 6

2-Hydroxy-3-methoxybenzaloxime: Solid. m.p. 119-121°C. ¹H NMR: (200 MHz, CDCl₃), δ 9.9 (s, 1H, OH), 8.3 (s, 1H), 8.0 (s, 1H), 6.7-6.9 (m, 3H), 3.9 (s, 3H). GCMS: m/z 167 [M]⁺. Anal. Calcd. for C₈H₉NO₃: C, 57.48; H, 5.38; N, 8.38%. Found: C, 57.42; H, 5.50; N 8.40%.

Compound 7

3,4-Dimethoxybenzaloxime: Solid, m.p. 95°C. ¹H NMR: δ 8.15, (s, 1H), 7.9 (s, 1H), 7.25, (d, 1H, J=8.0 Hz), 7.05, (d, 1H, J=8.0 Hz), 6.9, (d, 1H, J=8.0 Hz), 3.90, (s, 6H). GCMS: (m/z) 181 [M]⁺. Anal. Calcd.

ACKNOWLEDGEMENTS

One of the authors (V.S) is grateful to CSIR for the financial assistance.

REFERENCES

- [1] 'Vogel's Textbook of Practical Organic Chemistry', 5th Ed., Addison Wesley, Longman Harlow, 1259 (1989).
- [2] J.K. Whitesell; B.M. Trost, I. Fleming, E. Winterfeldt; Ed.; 'Comprehensive Organic Synthesis', Pergamon Press, Oxford, 6, 726 (1991).
- [3] J. March; 'Advanced Organic Chemistry', John-Wiley; New York, 1095 (1992).
- [4] (a) S. Sasatani, T. Miyazaki, K. Maruoka, H. Yama Moto; Tetrahedron Lett., 24, 4711 (1983); (b) E. Buehler; J. Org. Chem., 32, 261 (1967); (c) M.W. Barennes, J.M. Patterson; J. Org. Chem., 41, 733 (1976).
- [5] (a) L. Kou-Chang, R.S. Becky, K.H. Robert; J. Org. Chem., 45, 3916 (1980); (b) J.N. Kim, K.H. Chung, E.K. Ryu; Synth. Commun., 20, 2785 (1990).
- [6] M.A. Bigdeli, M.M.A. Nikje, S. Jafari, M.M. Haravi; J. Chem. Res. (S), 1, 20 (2002).
- [7] H. Sharghi, M.H. Sarvari; Synlett., 99 (2001).
- [8] M.A. Waters, A.B. Hoem; 'Encyclopedia of Reagents for Organic Synthesis', L.A. Paquette, Ed., John-Wiley; Chichester, 14, 2760 (1995).
- [9] T.J. Dickerson, N.N. Reed, K.D. Janda; Chem. Rev., 102(10), 3325 (2002).