SHORT PAPER

J. Chem. Research (S),
2000, 24–25

A mild and versatile method for the preparation of oximes by use of calcium oxide[†]

Hashem Sharghi* and Mona Hosseini Sarvari

Department of Chemistry, Shiraz University, Shiraz 71454, I.R. Iran

A convenient method for the cleavage of aldehydes and ketones to their corresponding oximes with CaO is described.

Protection of carbonyl compounds as oximes is of great interest to organic chemists, as they are readily prepared and highly stable compounds.[1] Further, oximes of aldehydes and ketones served as protecting,[1] selective α-activating[2] groups and intermediates for many reactions such as the preparation of amides by Beckmann rearrangement.[3] Oximes are extensively used for the purification and characterization of carbonyl compounds.[3]

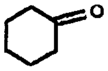
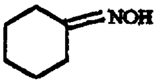
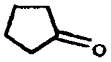
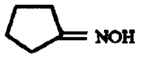
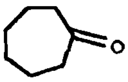
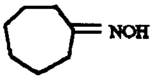
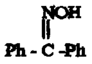
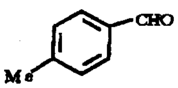
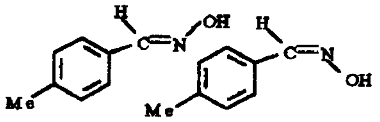
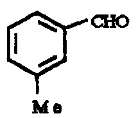
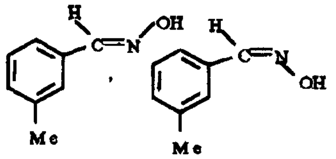
The formation of oximes, is usually catalysed by both acids and general bases. The classical process for oximes production starts from ketones and aldehydes[4] and has many disadvantages related to the use of hydroxylamin as reactant and sulfuric acid as catalyst,[5] Recently, it was patented as a process for the production of the cyclohexanone oxime by liquid-phase ‘ammoximation’ of cyclohexanone using ammonia hydrogen peroxide as the oxidizing agent and titanium silicalite as the catalyst[6]. The ammoximation reaction is suitable for the synthesis of several oximes[7-12] but the economic attractiveness of this process, however, may be limited by the use of H_2O_2. Allied Chemical Corp. patented a heterogenously catalysed gas-phase route employing ammonia with molecular oxygen as the oxidant[13], but the yields were relatively low. And also, amberlyst A-21 was used for the preparation of cyclohexanone oxime in liquid-phase[14].

In connection with our interest in solid-state reactions, the use of CaO for preparation of oximes was examined and it was found that CaO react with various types of ketones and aldehydes under mild condition to give the corresponding oximes in a quantitative yield. Herein, for the first time, we wish to report CaO as an efficient reagent for the production of oximes from ketones and aldehydes in solid rate.

Cyclohexanone oxime is a key intermediate for the production of nylon [6].[5] In an attempt to examine the property of CaO in the solid state, cyclohexanone was mixed with CaO and hydroxylamine hydrochloride in an oil bath at 130 °C. Working up and monitoring the reaction mixture by TLC showed one spot in approximately 80% that was characterized as cyclohexanone oxime.

Adopting the above method, various oximes have been prepared by use of the corresponding ketones and aldehydes (Table 1). Except in the case of symmetric ketones, two isomeric oximes are generated, syn and anti, which have

Table 1 Preparation of oximes by use CaO

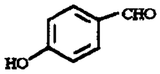
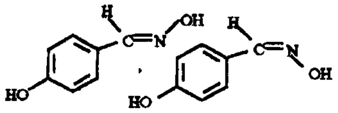
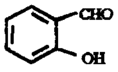
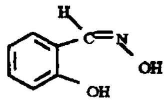
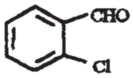
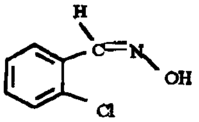
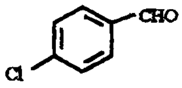
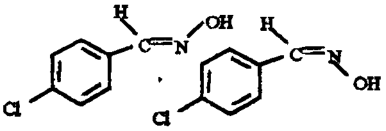
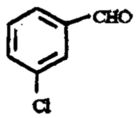
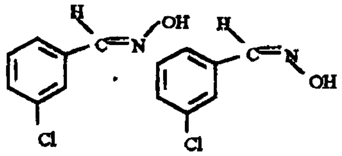
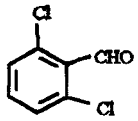
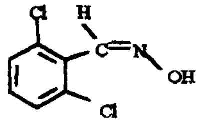
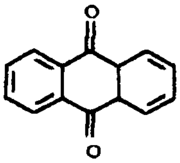
Entry	Substances	Temp.°C/Time	Products[a]	(% Yield)[b]
1.		130/1 min		(80)
2.		130/1 min		(80)
3.		130/1 min		(80)
4.		130/2 h		(> 90)
5.		130/1 min		(90), (10)
6.		130/1 min		(20), (80)
7.		130/1 min		(20), (80)

---

* To receive any correspondence.

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 *(continued)*

Entry	Substances	Temp.°C/Time	Products[a]	(% Yield)[b]
8.		130/1 min		(20), (80)
9.		130/1 min		(90)
10.		130/1 min		(> 90)
11.		130/1 min		(20), (80)
12.		130/1 min		(20), (80)
13.		130/1 min		(90)
14.		110/6 h	no reaction	

[a]Products were characterized by their melting points, IR, NMR spectra.
[b]Yields refer to pure isolated products.

different physical properties and biological activities.[15] It is known that with some aldehydes only one oxime prepared. For example, in the case of *ortho*- hydroxy and chloro benzaldehyde (Entry 9,10) only *syn ortho*- hydroxy and chlorobenzaldoxime were prepared.

In conclusion, the preparation of oximes was achieved effectively by CaO under mild condition. Generally, the oximation is achieved in solvent free condition (dry media). So, it is also environmentally benign protocol. The reagent (CaO) is inexpensive, CaO can be used for several times, the reaction is very fast, the work-up is easy, and the yields are very good when compared to other methods.

Experimental

Starting materials were obtained from Fluka company. Melting points were determined by Buchi 510 apparatus and are uncorrected. IR spectra recorded on Perkin-Elmer spectrometer. Proton NMR spectra were recorded on a Bruker Advanced DPX FT 250 MHz instrument. Calcium oxide (CaO) was purchased from Fluka company and powdered effectively.

A mixture of ketone or aldehyde (1 mmol), fine powder of CaO (0.5 g, 8.9 mmol) were heated in an oil bath for a few minutes. Then hydroxylamine hydrochloride (0.208 g, 3 mmol) was added and the mixture was stirred with a magnetic stirrer in the presence of air for appropriate time (Table 1). Afterward, the reaction mixture was mixed with ethylacetate, filtrate to remove CaO then mixed with water and extracted. The ethylacetate solution was dried over Na_2SO_4. The solvent was removed *in vaccuo* to give the product.

Received 8 September 1999; accepted 11 October 1999
Paper 9/07271C

References

1 T.W. Greene and P.G.M. Wuts, *Protective Group in Organic Synthesis*, 2nd Ed., John Wiley and Sons, New York, 1991, p.175.
2 J.K. Whitesell and M.A. Whitesell, *Synthesis*, 1983, 517.
3 L.G. Donaruma and W.Z. Heldt, *Organic Reactions*, 1960, **11**, 1.
4 A.I. Vogels, *Text Book of Practical Organic Chemistry*, Longman, New York, 1986, 1113.
5 K. Weissermer and H.J. Arpe, *Industrial Organic Chemistry*, Springer Verlag, 1978, p.222.
6 U.S. Pat. 4 794 198, 1988, to P. Roffia, N. Padovan, G. Leofanti, M.A. Mantagazza, G. DeAlberti and G.R. Tauszik.
7 M.A. Mantegazza, A. Cesana and M. Pastori, *Chem. Ind.*, 1996, **68**, 97–106.
8 Z. Tvaruzkova, K. Habersberger, N. Zilkovo and P. Jiru, *Appl. Catal.*, 1991, **79(1)**, 105.
9 G. Pertrini and G. Leofanti, *ACS Symp. Ser.*, 1996, **626**, 33.
10 J. LaBars, J. Dakka and R.A. Sheldon, *Appl. Catal.*, 1996, **36(1)**, 69–80.
11 Eur. Pat. 208 311, 1987 to Roffia, Paolo, Padovan, and Mario. (C.A.- 106:P155944s).
12 Eur. Pat. 299 430, 1989, to Padovan and Mario. (C.A.- 110:P175517r)
13 U.S. Pat. 4 163 756, 1979, to J.N. Armor.
14 R. Ballin, L. Barboni, P. Filippone, *Chem. Lett.*, 1997, **5**, 475.
15 (a) J.V. Burakevich, A.M. Lore and G.P. Volpp, *J. Org. Chem.*, 1971, **36**, 1. (b) U. Brandt and G. Vonjagow, *FEBS Lett*, 1991, **287**, 215. (c) H. Tecle, D.J. Lauffer, T. Mirzadegan, W.H. Moreland, M.R. Pava, R.D. Schwarz and R.E. Davis, *Life Sci.*, 1993, **52**, 505.