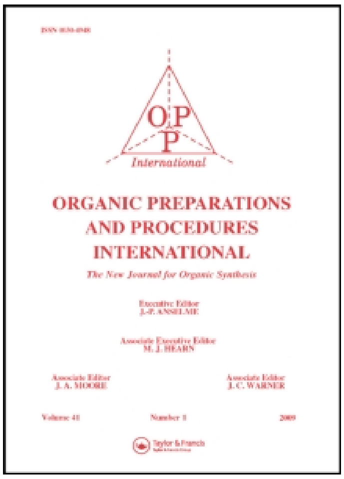
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

OXIDATIVE CLEAVAGE OF KETOXIMES WITH BENTONITIC *CLAY-SUPPORTED* COPPER (II) NITRATE

R. Sanabria[a]; P. Castaneda[a]; R. Miranda[a]; A. Tobón[b]; F. Delgado[c]; L. Velasco[d]
[a] Facultad de Estudios Superiores Cuautitlán-UNAM, MEXICO [b] SGIDTTI, Gerencia de Catálisis del IMP, MEXICO [c] Escuela National de Ciencias Biológicas-IPN, MEXICO [d] Institute de Química, UNAM, MEXICO

To cite this Article Sanabria, R. , Castaneda, P. , Miranda, R. , Tobón, A. , Delgado, F. and Velasco, L.(1995) 'OXIDATIVE CLEAVAGE OF KETOXIMES WITH BENTONITIC *CLAY-SUPPORTED* COPPER (II) NITRATE', Organic Preparations and Procedures International, 27: 4, 480 — 482

To link to this Article: DOI: 10.1080/00304949509458481

URL: http://dx.doi.org/10.1080/00304949509458481

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

OXIDATIVE CLEAVAGE OF KETOXIMES WITH BENTONITIC *CLAY-SUPPORTED* COPPER (II) NITRATE

Submitted by (06/09/94)

R. Sanabria[*†], P. Castañeda,[†] R. Miranda,[†] A. Tobón,[††] F. Delgado[†††] and L. Velasco[††††]

[†] *Facultad de Estudios Superiores Cuautitlán-UNAM, CP 54740*
[††] *SGIDTTI, Gerencia de Catálisis del IMP, CP 07730*
[†††] *Escuela Nacional de Ciencias Biológicas-IPN, CP 11340*
[††††] *Instituto de Química, UNAM, CP 04510, MEXICO*

The use of inorganic solid supports for organic synthesis has received increasing attention in recent years.[1] Various types of inorganic chemisorbed reagents have shown enhanced reactivity compared to those reagents without support.[2] Clay-supported copper (II) nitrate has been employed in order to promote the oxidation of alcohols,[3] the aromatization of 1,4-dihydropyridines,[4] the nitration of aromatic hydrocarbons,[5] the oxidative coupling of thiols,[6] as well as in the oxidative cleavage of thioacetals.[7] Several derivatives of carbonyl compounds such as ketoximes serve as important synthetic intermediates and are at the same time very useful for purification and characterization of ketones; in addition the recovery of the parent ketones has received considerable attention as evidenced by the number of methods[8] developed to bring about such cleavage. Previously, regeneration methods used either strongly oxidizing[9] or reducing conditions,[10] rather basic or acidic media,[11] or tedious work-up or expensive reagents. Recently, we reported that $AgNO_3$/bentonite,[12] is a convenient system for the cleavage of various ketoximes to the corresponding carbonyl compounds. We now report a new and efficient method for regeneration of carbonyl compounds from their corresponding ketoxime under mild conditions, using $Cu(NO_3)_2$/bentonite in dry *n*-hexane-acetone.

As indicated in the Table, all the substrates gave very satisfactory yields to the corresponding carbonyl parents (in the case of benzoin oxime, benzil was obtained as the product). This new procedure, proceeds in good yields and utilizes low cost and easily available reagents.

TABLE. Oxidative Cleavage of Ketoximes with Bentonitic Clay-supported Copper (II) Nitrate

Oxime	Yield[a] (%)	Time (min)	mp (bp [^{0}C]/torr)	
Acetophenone	80	25	(126-128/65)[b]	(119/60)[c]
Benzophenone	90	45	46-47	48[c]
Camphor	60	45	78[d]	178[c]
Cyclohexanone	70	80	(92/65)[b]	(77/60)[c]
9-Fluorenone	97	90	78-79	84[c]
Benzoin[e]	75	30	93-94	95[c]

a) Yields are of pure products which were compared with original samples. b) By Kugelrohr distillation. c) References 13-14. d) Sublimate. e) Benzil is the product.

Downloaded At: 08:44 27 January 2011

To our knowledge, the system $Cu(NO_3)_2$/bentonite has not been previously used for the cleavage of ketoximes and thus constitutes a novel and convenient reagent for the direct conversion of ketoximes to the corresponding ketone in 60-97% yields.

EXPERIMENTAL SECTION

The starting ketoximes were prepared from the corresponding carbonyl compounds by the usual methods,[15] all reagents and solvents were purified by standard methods[16] before use. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Boiling points were carried out in a Kugelrhor apparatus. TLC was performed on precoated (0.25 mm) silica gel 60-F_{254} aluminum sheets, and column chromatography using silica gel 60 (70-230 mesh), both from E. Merck. ^{1}H NMR spectra were obtained on a Varian FT-80A spectrometer; the IR spectral data were recorder on a PYE UNICAM SP3-200 spectrophotometer and mass spectral were obtained on a Hewlett Packard 5985 B GC-MS system.

Preparation of Clay-supported Copper(II) Nitrate.- A mixture of copper nitrate trihydrate (18 g) in acetone (60 mL) ions stirred vigorously until complete dissolution of the crystals; then bentonitic clay (24 g) was added in small amounts and stirring was continued for 1 hr. The solvent was removed from the resulting suspension under reduced pressure (rotatory evaporator) on a water bath, giving a clay-supported $Cu(NO_3)_2$ as a light green-blue powder: yield 40g. This reagent is stable in dry air, shows no evolution of nitrous fumes and may be stored in a closed flask for one month. Finally, we recommend to proceed to scaling-up only after appropriate safety tests.

Cleavage of Ketoximes. General Procedure.- To a solution of 9-fluorenone oxime (0.5 g; 2.56 mmol) in a mixture of 10 mL dry of *n*-hexane and 10 mL of acetone, was added a freshly prepared suspension of clay-supported copper (II) nitrate (0.75 g) in 30 mL of *n*-hexane; the addition of clay supported-copper (II) nitrate at room temperature caused an immediate green-blue coloration of the solution. The mixture was stirred at reflux until the reaction was complete (TLC; SiO_2-*n*-hexane:EtOAc [8:2], 2,4-DNFH). The green-blue colored reaction mixture gradually turned into a clear green solution and, during this period, evolution of a brown gas was observed. The solution was filtered through a pad of Celite which was washed with acetone. The combined filtrate and wash was evaporated under vacuum and the resulting residue was dissolved with 25 mL of EtOAc. The organic layer was washed with water (2 x 5 mL) and dried over (Na_2SO_4). Evaporation of the solvent under reduced pressure gave the crude product which was purified by column chromatography (silica gel, *n*-hexane-EtOAc 8:2, v/v) to give a 0.485 g (97%) of fluorenone, identified by comparison with authentic sample.

ACKNOWLEDGMENTS.- This work has been supported by Dirección General de Asuntos del Personal Acádemico de la Universidad Nacional Autónoma de México, Proyect number **(IN 301791).**

REFERENCES

1. P. Laszlo, *Preparative Chemistry Using Supported Reagents*, Academic Press (1987).

Downloaded At: 08:44 27 January 2011

2. a) A. McKillop and D. W. Young, *Synthesis*, 401 and 481 (1979); b) A. Cornelis, P. Laszlo and P. Pennetreau, *Clay Minerals,* **18**, 437 (1983); c) A. Cornelis and P. Laszlo, *Synthesis*, 909 (1985); d) P. Laszlo, *Acc. Chem. Res.*, **19**, 121 (1986); e) P. Laszlo, *Science*, **235**, 1473 (1987).

3. a) A. Cornelis and P. Laszlo, *Synthesis*, 849 (1980); b) A. Cornelis, P. Herze and P. Laszlo, *Tetrahedron Lett.*, **23**, 5035 (1982); c) T. Nishiguchi and F. Asano, *J. Org. Chem.*, **54**, 1531 (1989).

4. M. Balogh, I. Hermecz, Z. Meszaros and P. Laszlo, *Helv. Chim. Acta*, **67**, 2270 (1984).

5. A. Cornelis, L. Delaude, A. Gerstmans and P. Laszlo, *Tetrahedron Lett.*, **29,** 5657 (1988).

6. A. Cornelis, N. Depaye, A. Gerstmans and P. Laszlo, *ibid.*, **24**, 3103 (1983).

7. M. Balogh, A. Cornelis and P. Laszlo, *ibid.*, **25**, 3313 (1984).

8. N. Chidambaram, K. Satyanarayana and S. Chandrasekaran, *Synth. Commun.*, **19**, 1727 (1989); and references cited therein.

9. K. Maeda, I. Moritani, T. Hosokawa and S. Murahashi, *Tetrahedron Lett.*, 797 (**1974**).

10. H. H. Tim and E. Wildsmith, *ibid.*, 195 (**1971**).

11. a) C. H. Depuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959); b) S. H. Pines, J. M. Chermerda and M. A. Kozlowski, *J. Org. Chem.*, **31**, 3446 (1966).

12. R. Sanabria, R. Miranda, V. Lara and F. Delgado, *Synth. Commun.*, **24**, 2805 (1994).

13. D. R. Stull, *Ind. Eng. Chem.*, **39,** 517 (1979).

14. *Handbook of Chemistry and Physics*, 60th Edn; R. C. West, Ed., CRC Press, In., Boca Ratón, Florida (1979).

15. A. Y. Vogel, *Texbook of Practical Organic Chemistry*, 4th., Ed., Longmann, 1113 (1978).

16. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd., Ed., Pergamon Press LTD, Oxford, England (1992).

****

Downloaded At: 08:44 27 January 2011