



## Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcyc20>

### Mo(Co)<sub>6</sub> Induced Cleavage of Oximes

Florence Geneste<sup>a</sup>, Nadia Racelma<sup>a</sup> & Alec Moradpour<sup>a</sup>

<sup>a</sup> Laboratoire de Physique des Solides, UA 2 du CNRS, Université Paris-Sud, Bâtiment 510, F-91405, Orsay, FRANCE

Published online: 22 Aug 2006.

To cite this article: Florence Geneste, Nadia Racelma & Alec Moradpour (1997) Mo(Co)<sub>6</sub> Induced Cleavage of Oximes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:6, 957-960

To link to this article: <http://dx.doi.org/10.1080/00397919708003039>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages,

and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

## **Mo(CO)<sub>6</sub> INDUCED CLEAVAGE OF OXIMES**

Florence Geneste, Nadia Racelma, Alec Moradpour\*

Laboratoire de Physique des Solides, UA 2 du CNRS,  
Université Paris-Sud, Bâtiment 510, F-91405 Orsay, FRANCE

**Abstract:** The conversion of oximes to the corresponding ketones and aldehydes is obtained conveniently using Mo(CO)<sub>6</sub> in the presence of water ; the preparation of Knoevenagel-type condensation products is also possible, in dry media, with this process.

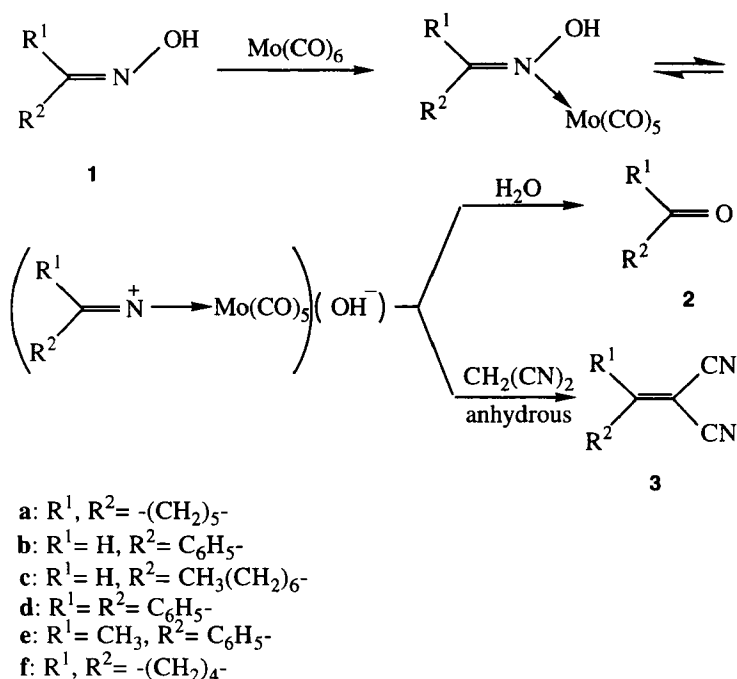
The protection of the carbonyl groups through oximes is a widely used procedure, and the deprotection step is also well documented.<sup>1</sup> The latter reaction usually involve non-selective acid hydrolysis and various oxidative or reductive cleavages ;<sup>1,2</sup> enzymatic deoximations by baker's yeast had also been investigated.<sup>3</sup> Mo(CO)<sub>6</sub> have been used to cleave isoxazoles to  $\beta$ -aminoenones,<sup>4</sup> as well as isoxazolines - as cyclic oximes - to  $\beta$ -hydroxy ketones.<sup>5</sup> Curiously, the regeneration of the carbonyl group from simple oximes had never been described with this reagent. We wish to report shortly that such transformations are in fact effected under mild conditions, with good yields, by a simple reflux of the oximes/Mo(CO)<sub>6</sub> mixtures, in solvents containing water.

The process (scheme) probably involves the initial formation of an oxime/molybdenum complex, as the precursor of the subsequent nitrene complex

---

\* To whom correspondence should be addressed

## Scheme



hydroxides <sup>6</sup>, which lead to : (i) the carbonyl compounds **2**, after hydrolysis in the medium ; (ii) the Knoevenagel-type condensation product **3**, if an anhydrous solvent is used ; the latter process is reminiscent of similar reactions of simple non-complexed imines with malonitrile. <sup>7</sup>

These deoximation reactions are best effected in acetonitrile with molar ratios of 1 : 0.35 to 0.4 (oxime/ $\text{Mo(CO)}_6$ ). Alternatively, other solvents (THF) might also be used, resulting in comparable yields, although after much longer reaction times.

Owing to the resulting good yields, and to the simplicity of the procedure, as well as the compatibility of  $\text{Mo(CO)}_6$  with various otherwise acid sensitive groups, this process is very convenient to cleave the oxime groups.

Table : Oximes **1** and their Mo(CO)<sub>6</sub> mediated reaction products **2** and **3**.

Compounds	Reaction conditions <sup>a</sup>	Reaction time (h)	Products <sup>b</sup> (yields/%)
<b>1a</b>	i	1	<b>2a</b> (73)
<b>1b</b>	i	1	<b>2b</b> (94)
<b>1c</b>	i	2	<b>2c</b> (66)
<b>1d</b>	i	1	<b>2d</b> (69)
<b>1e</b>	i	1.5	<b>2e</b> (81)
<b>1f</b>	ii	2	<b>3f</b> (59)

<sup>a</sup> (i) see : Typical procedure ; (ii) Mo(CO)<sub>6</sub>/If and malonitrile (1/2/4) refluxed in anhydrous acetonitrile; <sup>b</sup> The products were identified by comparison with authentic samples, and the yields were determined by GC with internal standards.

The starting oximes **1a-f** were prepared by standart procedures from the corresponding ketones and aldehydes, and **3f** was obtained by a described preparation. <sup>8</sup>

**Deoximations to carbonyl compounds: Typical procedure :** To a solution of the oximes **1** (20 mmol) in acetonitrile (40 ml) and water (0.4 ml) was added Mo(CO)<sub>6</sub> (7 mmol) and the mixture heated at reflux until no more starting material was detected by TLC. The solvent was removed and water (50 ml) added and extracted by ether (3 × 50 ml). The organic phase was dried over MgSO<sub>4</sub>, ether evaporated and the carbonyl compounds **2** isolated by bulb to bulb distillation under vacuum.

### Acknowledgments:

A financial support from the DRET is greatly acknowledged.

### References and notes :

- (1) Greene, T.W., Wutz, P.G.M. "Protective Group in Organic Synthesis," J. Wiley, **1991**.
- (2) (a) Olah, G.A., Ho, T.L. *Synthesis* **1976**, 610. (b) Balicki, R., Kaczmarek, L. *Synth. Comm.* **1991**, 21, 1777, and references cited therein.
- (3) Kamal, A., Rao, M.V., Meshram, H.M. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2056.
- (4) Nitta, M., Kobayashi, T. *J. Chem. Soc., Chem. Comm.* **1982**, 877.
- (5) Baraldi, P.G., Barco, A., Benetti, S., Manfredini, S., Simoni, D. *Synthesis* **1987**, 276.
- (6) The hydroxide ions are probably also coordinated through some weak acid- base adduct forms, as observed for metal carbonyl complexes, see for example : Brown, T.L., Bellus, P.A. *Inorg. Chem.* **1978**, 17, 3726.
- (7) Charles, G., *Bull. Soc. Chim. Fr.* **1963**, 1559.
- (8) Mirek, J., Adamczyk, M., Mokrosz, M. *Synthesis* **1980**, 297.

(Received in The Netherlands 25 September 1996)