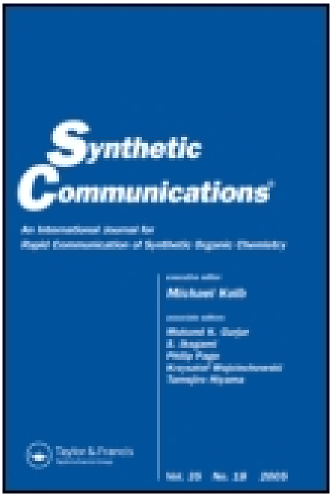

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$Mo(Co)_6$ Induced Cleavage of Oximes

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$Mo(CO)_6$ INDUCED CLEAVAGE OF OXIMES

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Abstract: The conversion of oximes to the corresponding ketones and aldehydes is obtained conveniently using $Mo(CO)_6$ 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. [1] The latter reaction usually involve non-selective acid hydrolysis and various oxidative or reductive cleavages ; [1,2] enzymatic deoximations by baker's yeast had also been investigated. [3] $Mo(CO)_6$ have been used to cleave isoxazoles to β-aminoenones, [4] as well as isoxazolines - as cyclic oximes - to β-hydroxy ketones. [5] 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/$Mo(CO)_6$ 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

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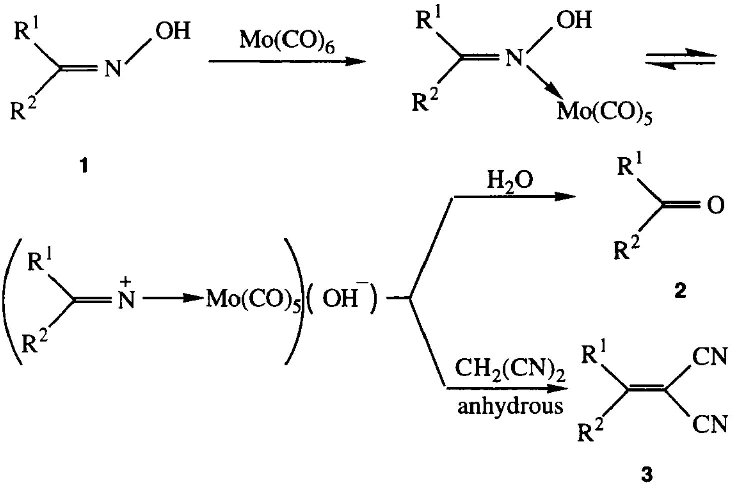
Scheme



a: R^1, R^2= $-(CH_2)_5-$
b: R^1= H, R^2= C_6H_5-
c: R^1= H, R^2= $CH_3(CH_2)_6-$
d: R^1= R^2= C_6H_5-
e: R^1= CH_3, R^2= C_6H_5-
f: R^1, R^2= $-(CH_2)_4-$

hydroxides [6], 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. [7]

These deoximation reactions are best effected in acetonitrile with molar ratios of 1 : 0.35 to 0.4 (oxime/$Mo(CO)_6$). 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 $Mo(CO)_6$ with various otherwise acid sensitive groups, this process is very convenient to cleave the oxime groups.

Table : Oximes **1** and their $Mo(CO)_6$ mediated reaction products **2** and **3**.

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

[a] *(i) see : Typical procedure ; (ii) Mo(CO)₆/1f and malonitrile (1/2/4) refluxed in anhydrous acetonitrile;* [b] *The products were identified by comparison with authentic samples, and the yields were determined by GC with internal standarts.*

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

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 $Mo(CO)_6$ (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 $MgSO_4$, ether evaporated and the carbonyl compounds **2** isolated by bulb to bulb distillation under vacuum.

Acknowledgments:

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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.

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