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Efficient Reductive Deoximation by Tungsten(VI) Chloride (WCl_6) or Molybdenum(V) Chloride ($MoCl_5$) in the Presence of Zn Powder in CH_3CN

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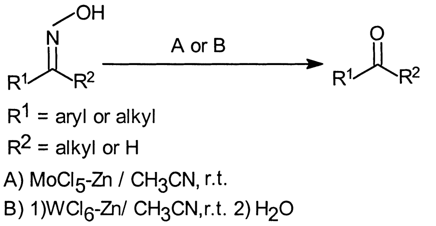
Tungsten(VI) chloride (WCl_6) or molybdenum(V) chloride ($MoCl_5$) in the presence of zinc powder in CH_3CN provides an efficient and facile procedure for the deprotection of oximes to their corresponding aldehydes and ketones in high yields.

Oximes are highly stable and readily prepared compounds which are used extensively for the protection of carbonyl groups,[1] for the purification and characterization of carbonyl compounds,[2] and also in the preparation of amides via Beckmann rearrangement.[3,4] Oximes represent a series of derivatives for the classical identification of carbonyl compounds, as exemplified in the synthesis of erythromycin derivatives.[5] Since oximes could be prepared from non-carbonyl starting materials, such as the Barton reaction,[6] their conversion to carbonyl functionality is important from a synthetic point of view. Although quite a number of methods for converting oximes to carbonyl compounds are available, the discovery of newer efficient methods is of practical importance. Some of the methods reported for deoximation involve periodic acid,[7] PCC,[8] PCC/H_2O_2,[9] triethylammonium chlorochromate,[10] bispyridinesilver permanganate,[11] Raney nickel,[12] CrO_3/TMCS,[13] N_2O_4,[14] Dowex-50,[15] dimethyldioxirane,[16] *t*-BuOOH,[17] $(NH_4)_2S_2O_8$/silica,[18] $Mn(OAc)_3$,[19] *N*-haloamides,[20] $NaIO_4$/silica,[21] Des-Martin periodinane,[22] $NaBiO_3$/silica,[23] IBX,[24] $Zn(NO_3)_2$/silica gel,[25] Zn/AcOH,[26] alumina supported $KMnO_4$.[27] The preparation of carbonyl compounds from their oxime derivatives by conventional methods have several limitations; i.e. the reagents used are often hazardous along with reactions requiring long reaction times or reflux temperatures. In addition, some of the methods cited in the literature do not describe the deoximation of aldoximes,[16,28,29] or they give low yields of aldehydes.[30] Some of the oxidative deoximation of oximes are accompanied by the further oxidation of carbonyl compounds.[8] Moreover, Des-Martin periodinane causes an explosion under excessive heating during preparation.[22]

Low-valent oxophilic *d*-block metals have become important in the deoxygenation of different types of organic substrates. Recently, we have reported that WCl_6/NaI and WCl_6/Zn are efficient reagents for the coupling of sulfonic and sulfinic acid derivatives.[31] We have also reported that $MoCl_5$ in the presence of NaI or Zn powder can be used for the coupling of sulfonic and sulfinic acid derivatives, the deoxygenation of sulfoxides and the reductive coupling of sulfonyl chlorides.[32] Deoximation by the in situ low-valent generation of titanium by the $TiCl_4$/NaI system has been reported.[33] In this procedure the ratio of the reagents is 1:2:2, and also requires successive washings with an aqueous solution of sodium thiosulfate and water in order to destroy any liberated iodine in the reaction process. In continuation of our interest to develop new applications of WCl_6 and $MoCl_5$ in organic synthesis, we now report on new reductive deoximation reactions by the in situ generation of low-valent tungsten and molybdenum species from WCl_6 and $MoCl_5$ in the presence of zinc powder (Scheme 1).

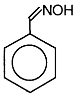
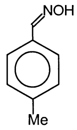
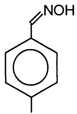
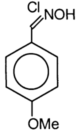
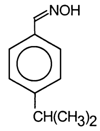
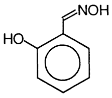
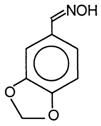
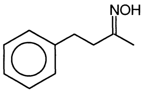
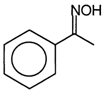
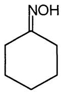
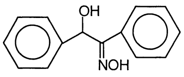
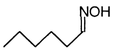
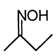


Scheme 1.

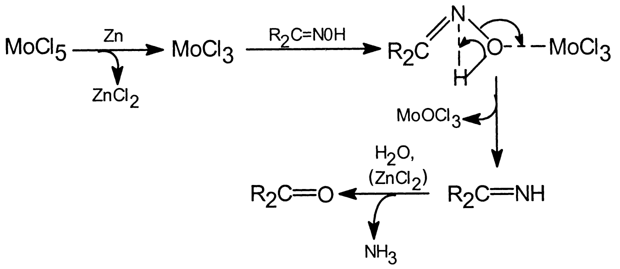
Results and Discussion

Various types of benzaldehyde oximes were efficiently converted to their benzaldehydes with WCl_6 (1 equiv) and Zn powder (3 equiv) in good-to-excellent yields (Table 1, entries 1–7). The deprotection of different types of ketoximes were also achieved in moderate-to-good yields (Table 1, entries 8–10). This method was also applied for the deprotection of an acyloin ketoxime (Table 1, entry 11); only 50% of the corresponding acyloin was obtained. This method was also successfully applied for the deoximation of oximes derived from aldehydes and ketones bearing enolizable hydrogens (Table 1, entries 8,10, 12–14). We have also applied $MoCl_5$ (0.6–0.8 equiv) and Zn powder (2–3 equiv) for the deoximation of different aromatic and saturated aliphatic oximes to their corresponding carbonyl compounds in good-to-excellent yields (Table 2). The deprotection of an acyloin ketoxime (Table 2, entry 10) was also tried with a lesser amount of $MoCl_5$/Zn compared with WCl_6/Zn, that produced the corresponding acyloin in 70% (Table 2, entry 10), and was higher than that ob-

Table 1. Deprotection of Oximes with WCl_6 and Zn Powder in CH_3CN

Entry	Substrate	Subst./ WCl_6/Zn	Time min	Yield[a)] %
1		1:1:3	15	91
2		1:1:3	20	88
3		1:1.4:4	16	95
4		1:1.2:4	15	93
5		1:1.1:4	20	92
6		1:1:3	15	75
7		1:1.2:4	15	94
8		1:1:3	25	88
9		1:1.2:4	40	93
10		1:1.1:4	20	75
11		1:1.2:4	15	50
12		1:1.2:4	25	73
13		1:1.2:4	25	77
14		1:1.1:4	30	70

a) Isolated yields.



Scheme 2.

tained in 50% using WCl_6/Zn . We believe that in these reactions low-valent molybdenum or tungsten is responsible for a deoxygenation reaction which occures occurring by an attack of the low-valent metal to the oxygen of oximes. The generated imines in the presence of $MoCl_5$, $MoCl_3$, and $ZnCl_2$ are easily hydrolyzed during the work-up to produce the corresponding carbonyl compounds. We have shown this proposal by the mechanism given above (Scheme 2). The work-up of the deoximation reactions with WCl_6/Zn and $MoCl_5$/Zn could easily proceed under both aqueous and non-aqueous conditions, whereas, an aqueous work-up for similar reactions with $TiCl_4$/NaI is an obligatory process.[33]

Conclusion

In this study, new applications of tungsten(VI) chloride (WCl_6) and molybdenum(V) chloride ($MoCl_5$) were introduced for the reductive deprotection of oximes to their parent carbonyl compounds. We found that $MoCl_5$/Zn system is more efficient than WCl_6/Zn for this purpose. The mildness of the reaction conditions, easy and non-aqueous work-up, and high yields of the products are worth mentioning concerning the presented methods.

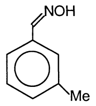
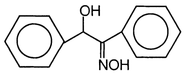
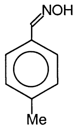
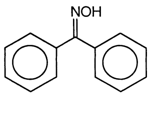
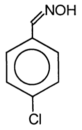
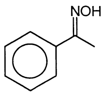
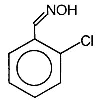
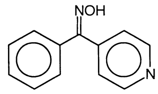
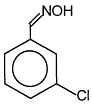
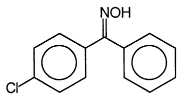
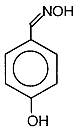
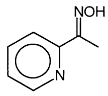
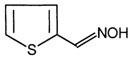
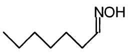
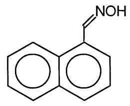
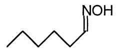
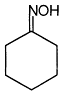
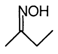
Experimental

General: All yields refer to isolated pure products, unless otherwise stated. Because all of the products are known compounds, elemental analyses are not given. Most of the products were purified by column chromatography or recrystallization and were identified by a comparison of their mp, bp, IR, MS, and NMR with those reported for authentic samples.[34] All of the solvents were completely dried and redistilled.

General Procedure for the Deprotection of Oximes Using the $MoCl_5$–Zn System (Non-Aqueous Work-Up). To a suspension of oxime (1 mmol) and zinc powder (2–3 mmol) in dry acetonitrile (10 mL), $MoCl_5$ (0.6–0.7 mmol) was added; the resulting mixture was stirred at room temperature. After completion of the reaction (5–40 min), silica-gel (1 g) was added to the mixture and the solvent was evaporated under reduced pressure. The resulting powder was added on a silica-gel pad (3 cm thick) and washed with petroleum ether (100 mL). Evaporation of the solvent afforded the corresponding pure carbonyl compound (Table 2). In the case of benzaldehyde oxime the yield was determined by its 2,4-dinitrophenylhydrazone derivative.

General Procedure for the Deprotection of Oximes Using the WCl_6–Zn System (Aqueous Work-Up). To a suspension of oxime (1 mmol) and zinc powder (3–4 mmol) in dry acetonitrile (10 mL), WCl_6 (1–1.4 mmol) was added; the resulting mixture was stirred at room temperature. After completion of the reaction (15–40 min), aqueous NaOH (10%, 25 mL) was added and the mixture was extracted with ether (2 × 25 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. Removal of the solvent gave an almost pure product. Further purification was achieved by column chromatography on silica-gel using petroleum ether as an eluent or by recrystallization from an appropriate sol-

Table 2. Deprotection of Oximes with $MoCl_5$ and Zn Powder in CH_3CN

Entry	Substrate	Subst./ $MoCl_5$/Zn	Time min	Yield[a)] %	Entry	Substrate	Subst./ $MoCl_5$/Zn	Time min	Yield[a)] %
1		1:0.6:2	5	94	10		1:0.6:2	12	70
2		1:0.6:2	5	92	11		1:0.7:2	25	92
3		1:0.6:2	10	91	12		1:0.6:2	15	93
4		1:0.6:2	10	95	13		1:0.8:3	40	65
5		1:0.6:2	10	94	14		1:0.7:2	30	78
6		1:0.6:2	10	86	15		1:0.7:3	30	85
7		1:0.6:2	7	90	16		1:0.7:2	20	81
8		1:0.6:2	7	97	17		1:0.7:2	20	78
9		1:0.7:2	15	84	18		1:0.7:2	25	74

a) Isolated yields.

vent (Table 1).

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