$MoO_2(acac)_2$ catalysed oxidative deprotection of oximes

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Oximes undergo facile deprotection in acetone in the presence of a catalytic amount of $MoO_2(acac)_2$ and hydrogen peroxide.

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Oximes are extensively used for protection[1] of carbonyl compounds as they are highly crystalline and stable compounds. Since oximes can be synthesised from non-carbonyl compounds, the regeneration of carbonyl compounds from oximes provides an alternative method for preparation of aldehydes and ketones.[2] Therefore, the regeneration of carbonyl compounds from oximes has received attention. The classical acid hydrolysis[3] requires strong mineral acids and often results in low yields and is not suitable for acid sensitive compounds. Several oxidative deoximation methods have been developed which have some advantages over classical acid hydrolysis. Some examples include Dess-Martin periodane[4], PCC[5], TBHP[6], PCC-H_2O_2[7], PDC-TBHP [8], manganese acetate/benzene[9], and potassium peroxymonopersulfate[10]. However, many of these reagents or the solvent systems used are toxic, corrosive, expensive and non-catalytic. With increasing environmental concerns, it is an important to investigate a new method using less hazardous reagents and solvents.

Treatment of ketoximes with 30% hydrogen peroxide in acetone in the presence of a catalytic amount of $MoO_2(acac)_2$ (10 mol%) at room temperature gave the corresponding carbonyl compounds in excellent yields. Similarly, aldoximes gave in good yields. Presumably, the yields from ketoximes were higher order than aldoximes due to over oxidation of regenerated aldehydes. It should be noted that this method gave a much better yields for aldoximes than reported methods [6-8] at higher temperature. The method can tolerate a variety of substrates. Aromatic, aliphatic oximes were deoximated with this reagents. Acid sensitive methoxy group remained intact, and α, β-unsaturated, cinnamaldoxime was deoximated without any difficulty.

In summary, this work demonstrates a new and useful method for deprotection of oximes. The advantages include (1) operational simplicity, (2) inexpensive reagents, (3) does not need any additive for promoting the reaction, (4) the use of relatively non-toxic reagent and solvent.

Experimental

All products were known and identified by comparison with authentic samples. Yields refer to isolated products.

Deoximation of oximes (general procedure): To a mixture of oxime (5 mmol) and bis(acetylacetonato)dioxomolybdenum (10 mol%) in acetone (10 ml) was added hydrogen peroxide (30%, 3 ml) at room temperature. The reaction mixture was stirred at room temperature for specified time (Table 1). After completion of reaction (TLC), the reaction mixture was diluted with water (30 ml) and extracted with ethyl acetate. The organic layer was washed with 10% $Na_2S_2O_3$ solution, water and brine successively, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (eluted hexane-ethyl acetate, 9/1 to 8/2) to afford the pure product.

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Table 1 Deprotection of oximes with $MoO_2(acac)_2$ and hydrogen peroxide at room temperature (25 °C)

Entry	Substrate	Product	Time/h	Yield/%
1	Benzophenone oxime	Benzophenone	8	94
2	Acetophenone oxime	Acetophenone	12	91
3	4-Methoxybenzaldehyde oxime	4-Methoxybenzaldehyde	10	76
4	4-Bromobenzaldehyde oxime	4-Bromobenzaldehyde	9	75
5	Cyclohexanone oxime	Cyclohexanone	11	90
6	Cyclopentanone oxime	Cyclopentanone	10	91
7	Benzaldehyde oxime	Benzaldehyde	12	73
8	4-Chloroacetophenone oxime	4-Chloroacetophenone	8	92
9	4-Nitroacetophenone oxime	4-Nitroacetophenone	12	85
10	Camphor oxime	Camphor	11	79
11	2-Heptanone oxime	2-Heptanone	10	82
12	Cinnamaldehyde oxime	Cinnamaldehyde	11	74
13	4-Methoxyacetophenone oxime	4-Methoxyacetophenone	10	91
14	2-Methoxyacetophenone oxime	2-Methoxyacetophenone	11	88