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Manganese Triacetate Mediated Regeneration of Carbonyl Compounds from Oximes

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Abstract: A new method for the direct conversion of oximes into aldehydes and ketones by treatment with manganese triacetate is described. Manganese triacetate can be used for an effective and mild oxidizing agent for the regeneration of carbonyl compounds from oximes in good yield. Many functional groups are tolerated under the reaction conditions.
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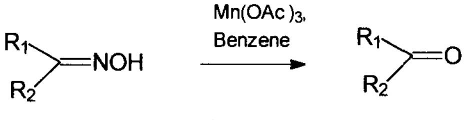
Many interesting results of the reactions with manganese triacetate have been observed in a wide variety of organic substrates[1]. In connection with our synthetic works with manganese triacetate and oximes[2], we have found a simple, inexpensive, mild procedure for the cleavage of oximes with manganese triacetate.

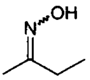
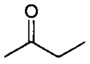
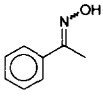
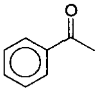
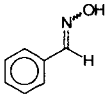
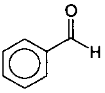
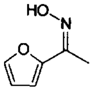
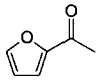
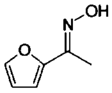
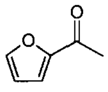
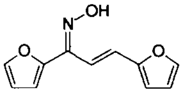
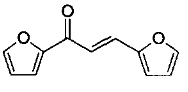
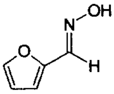
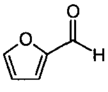
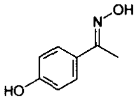
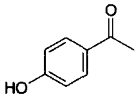
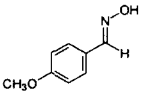
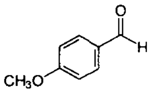
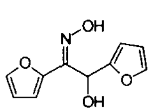
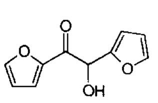
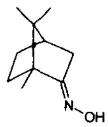
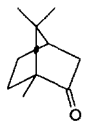
Oximes of carbonyl compounds are important, because of their use in purification and characterization of carbonyl compounds, and because of their use in synthesis. A variety of the methods have been developed for the regeneration of the carbonyl compounds from oximes[3]. However, only a limited number of methods are available for this conversion under mild reaction conditions[4]. We wish to describe in this communication a new method for the direct conversion of oximes into aldehydes and ketones by treatment with manganese triacetate (Scheme1).



Scheme 1

The following general procedure illustrates the simplicity of this method. A solution of oxime in benzene with 1 equivalent of manganese triacetate was refluxed (1-2 h, the reaction is monitored by TLC). The precipitated manganese diacetate was removed by filtration, and then washed with water . The organic layer was concentrated and purification of the crude product by distillation or crystallization afforded the pure aldehyde or ketone. Representative conversions are summarized in table 1.

Table 1. Conversion of oximes to ketones and aldehydes with $Mn(OAc)_3$

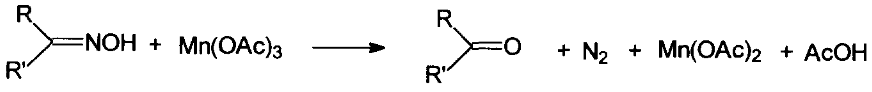
Reactant[a]	**Product**	**Yield (%)**[b,c,d]	**Time (h)**
		92	1
		96	1
		89	30 min
		93	2
		94	2
		88	1
		86	1
		96	2
		93	2
		87	1
		91	1

a) All reactions were carried out at reflux b) Yields are in pure isolated products. c) The regenerated carbonyl compounds were checked by comparison (IR, ^{1}H-NMR spectra) with an autentic sample. d) The reaction must checked by TLC because after cleavage of oximes overoxydation can occur in some cases. The regeneration of oximes of aryl-alkyl ketones produced trace amount of α-acetoxylation products.

From an examination of the reactions of a wide range of oximes with manganese triacetate under a variety of conditions, the advantages of the present method can be summarized as follows. 1) Reaction proceeds on the free oxime 2) Reaction proceeds at room temperature but refluxing of the mixture decreases the reaction time dramatically 3) Reaction tolerates many functional groups and hindered oximes underwent deoximation reaction in good yield 4) Both E-, and Z-oximes gives reaction.

Manganese triacetate was prepared according to the procedure of Heiba et al.[5] or prepared from manganese(II)nitrate and acetic anhydride and dried over phosphorus pentoxide prior to use. Using dried manganese(III)acetate improved the yields of the products.

In this reaction, manganese triacetate would act toward oximes as an oxidizing agent, but not as a hydrolyzing agent similar to lead tetraacetate oxidation[6].We suggest that the reaction of aldoximes and ketoximes with manganese triacetate proceeds smoothly, with the evolution of nitrogen, to give the corresponding carbonyl compounds and manganese diacetate as shown in scheme 2.



Scheme 2

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