



Deoxygenation Using Dess-Martin Periodinane: Regeneration of Ketones from Ketoximes

Sachin S. Chaudhari and Krishnacharya G. Akamanchi*

Pharmaceuticals and Fine Chemicals Division
Department of Chemical Technology,
University of Mumbai, Matunga, Mumbai - 400 019, India.

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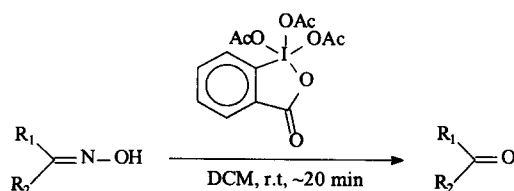
Abstract: The Dess-Martin Periodinane (DMP), [1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one], regenerates ketones from the corresponding ketoximes rapidly at room temperature in very high yields.
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Regeneration of carbonyl compounds from the corresponding oximes is a very important reaction because oximes are the preferred derivatives for purification and characterization of carbonyl compounds. Oximes are also useful as protecting group.¹ So far a good number of methods based on hydrolytic,² reductive³ and oxidative⁴ reactions have been developed for deoxygenation. The methods based on oxidative reactions make use of several oxidising agents. These include chromium reagents such as pyridinium chlorochromate,^{4a} pyridinium chlorochromate-H₂O₂,^{4b} trimethylammonium chlorochromate,^{4c} chromic anhydride-chlorotrimethylsilane,^{4d} supported reagents like clayfen,^{4e} ammonium persulphate-silica gel,^{4f} and others such as periodic acid,^{4g} dinitrogen tetroxide,^{4h} dimethyl dioxirane,⁴ⁱ manganese triacetate,^{4j} t-butylhydroperoxide,^{4k} and N-haloamines.^{4l} In spite of the many reagents available, there is still scope for newer reagents as the existing oxidative methods suffer from one or the other disadvantages like long reaction time, e.g. 18 hours in case of t-butylhydroperoxide,^{4k} need for refluxing temperature, e.g. in case of manganese triacetate,^{4j} difficulties in isolation of products, e.g. with chromium based reagents,^{4a,b,c} and formation of over oxidation products leading to low yields. A recent report on accelerated deoxygenation using ammonium persulphate-silica gel requires microwave irradiation.^{4f}

In this letter we report a new oxidative method for deoxygenation using Dess-Martin periodinane, as an oxidising agent, that overcomes many of the disadvantages associated with oxidative methods developed so far. The striking features of our method are, the reaction occurs at room temperature, with rapid rate (complete conversions within 20 minutes), formation of no over oxidation products due to high chemoselectivity and mild nature of DMP, easy work-up procedure and high yields.

DMP can be readily prepared^{5a,b} and used. It is the mildest reagent for oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones respectively⁶. This led us to consider this reagent for deoxygenation. Using DMP various ketoximes have been successfully deoxygenated⁷ to give the corresponding ketones and the results are summarized in table-1.

Table-1 : Regeneration of ketones from ketoximes using Dess-Martin periodinane.^a

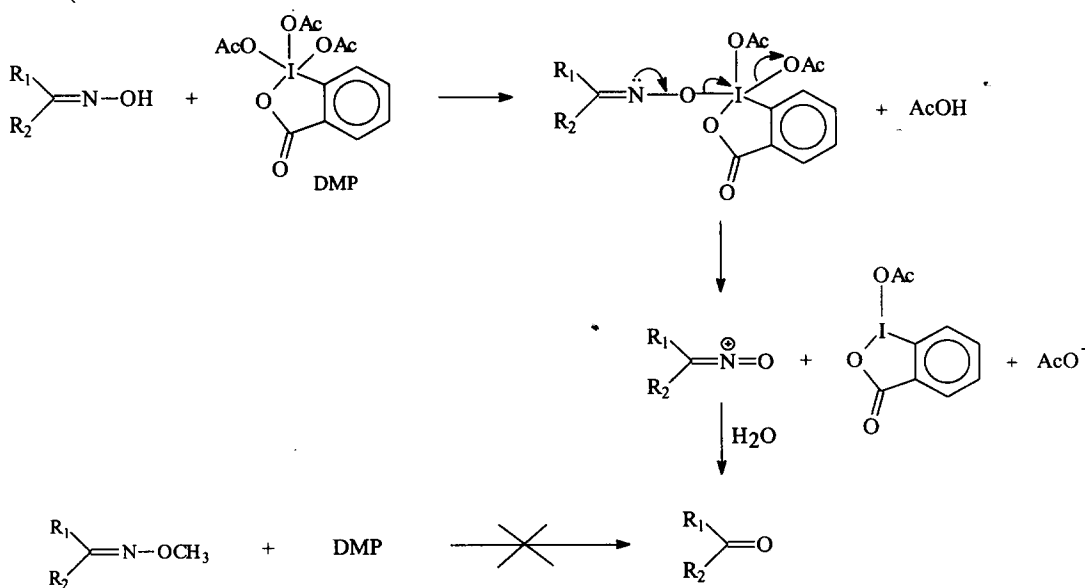


Entry	Oxime	Product	Time (min)	Yield (%) ^{b,c}
1.	Acetophenone oxime	Acetophenone	15	94
2.	4-Methylacetophenone oxime	4-Methylacetophenone	15	96
3.	4-Nitroacetophenone oxime	4-Nitroacetophenone	15	96
4.	4-Bromoacetophenone oxime	4-Bromoacetophenone	15	94
5.	Benzophenone oxime	Benzophenone	10	100
6.	4-Methoxypropiophenone oxime	4-Methoxypropiophenone	15	95
7.	Benzil monoxime	Benzil	10	100
8.	Benzil dioxime	Benzil	10	100 ^d
9.	Cyclohexanone oxime	Cyclohexanone	15	98
10.	N-Benzyl-4-piperidone oxime	N-Benzyl-4-piperidone	15	88
11.	Camphor oxime	Camphor	15	94
12.	16-Dehydropregnenolone acetate oxime	16-Dehydropregnenolone acetate	20	95
13.	2-Butanone oxime	2-Butanone	15	90
14.	Cyclohexanone O-methyloxime	NR ^e	---	---

^aAll reactions were carried out at r.t. and in DCM saturated with water. ^bYields refer to pure isolated products. ^cRegenerated ketones are characterised by IR, ¹H NMR. ^dFor benzil dioxime 2.2 molar equivalent of DMP was used. ^eNo reaction.

The rate of oxidative deoxygenation was fast in all cases requiring less than 20 minutes, including the substrates having either electron donating (entry 4,6) or electron withdrawing group (entry 3) at the para position. Even the sterically hindered camphor oxime (entry 11) was converted to camphor in very high yield in a short time. Both α,β -unsaturated oxime (entry 12) and α -keto oxime (entry 7) were also successfully deoxygenated to give the corresponding α,β -unsaturated ketones and α -diketones respectively in high yields.

As expected cyclohexanone O-methyloxime (entry 14) was recovered completely unreacted and this suggests that deoxygenation may be occurring by the mechanism as indicated in scheme 1. It is to be noted that when the reactions were carried out using DCM as it is, rather than saturated with water,⁸ some minor by-products were observed on TLC.



In addition to regenerated aldehydes aldoximes gave some other products. Investigations are still in progress and results will be communicated shortly.

In conclusion, a new expeditious and mild method for regeneration of ketones from ketoximes has been developed that may find wide applications.

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7. The deoxygenation of benzophenone oxime is representative of the general procedure employed. To a stirred solution of benzophenone oxime (0.50g, 2.53 mmole) in DCM saturated with water prior to use (25 ml, DCM was saturated by shaking with equal amount of water and allowed to settle for 30 minutes before draining the aqueous layer) was added DMP (1.18g, 2.79 mmole) at room temperature. As soon as the reaction was complete (as indicated by TLC), the reaction mixture was diluted with 5% aqueous sodium hydroxide solution (30 ml) followed by water (40 ml). The organic layer was washed with water (40 ml), dried over sodium sulphate, and concentrated to get the product in almost pure form. It was further purified by chromatography.
8. Acceleration of the Dess-Martin oxidation by water is well known, Meyer, S. D.; Schreiber, S. L. *J. Org. Chem.* **1994**, *59*, 7549.