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Potassium Permanganate Oxidation of Ketone Oximes. A Deprotective Version

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Synopsis. $KMnO_4$ in acetonitrile–water has been found to be a convenient system for regenerating ketones from ketone oximes under mild conditions.

The mechanistic duality[1] in the permanganate ion oxidation of imines prompted us to explore the effect on other easily accessible C=N compounds such as oximes. In addition, it is known that C=N bond gets oxidatively cleaved with $KMnO_4$ in the modified Nef reaction.[2] Presently however, we have found that $KMnO_4$ in acetonitrile–water converts several ketone oximes to parent ketones in good to excellent yields. These results are noteworthy from a synthetic viewpoint.

Literature records the use of a variety of reagent systems for such a conversion.[3] However, most of the available methods suffer from one or the other of the following drawbacks: poor yields, expensive and toxic reagents, unselectivity, long reaction times or drastic conditions. The present deoximation method is free of several such limitations and is thus a useful addition[4] to the existing repertoire.

Experimental

All the chemicals used were of the reagent grade. The oximes were prepared by a general method.[5] For TLC, precoated plastic backed silica gel 60 plates (Merck) were used. Melting points were recorded on Mettler FP5 apparatus and ^1H NMR spectra on JEOL JNM FX100 machine. GC analyses were done on Shimadzu 15A using 1.5% OV-17 or 15% carbowax 20M column.

$KMnO_4$ (790 mg, 5 mmol) was added to a solution of oxime (2.5 mmol) in acetonitrile (4 ml) and water (2 ml), and the mixture was stirred at room temperature (25 °C) for 1 h. Anhydrous sodium sulfate (ca. 4 g) was then added and the mixture was extracted with CH_2Cl_2 (4×15 ml). The solvent was evaporated, and the products were analyzed by GC (or TLC) and characterized by comparison with authentic samples and by ^1H NMR spectroscopy.

Results and Discussion

Evidently, oximes of benzophenone, acetophenone, cyclohexanone, cyclopentanone, and 4-methyl-2-pentanone produce the corresponding ketones in nearly quantitative yields (Table 1, Chart 1). Benzil monoxime and α-tetralone oxime gives benzil and α-tetralone, respectively in good yields. α-Benzoin oxime reacts, as expected, to provide benzil along with benzoin, albeit in low yield. However, the oxime of *dl*-camphor requires 2 h refluxing probably because of hindered steric approach. Interestingly, $KMnO_4$ in pure acetonitrile or in water alone was unreactive towards the oximes during the same reaction time.

Table 1. Regeneration of Carbonyl Compounds from Their Oximes

	Oxime	Ketone	Isolated yield (%)
1.	Benzophenone oxime	Benzophenone	95
2.	Acetophenone oxime	Acetophenone	96
3.	*p*-Methoxyacetophenone oxime	*p*-Methoxyacetophenone	85
4.	Cyclohexanone oxime	Cyclohexanone	96
5.	Cyclopentanone oxime	Cyclopentanone	96
6.	4-Methyl-2-pentanone oxime	4-Methyl-2-pentanone	95
7.	α-Tetralone oxime	α-Tetralone	65
8.	α-Benzoin oxime	α-Benzoin	25
		Benzil[a]	40
9.	α-Benzil monoxime	Benzil	80
10.	*dl*-Camphor oxime	*dl*-Camphor	95

a) Separated by column chromatography using silica gel (60—120 mesh) and petroleum ether (60—80 °C) as eluant.

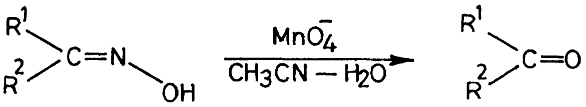

Chart 1.

The present deoximation method is applicable to compounds lacking easily oxidizable groups like –CHO, –C≡C–, and –OH unless their oxidation is a desired requirement in a given synthetic transformation. Further, a limited experimentation was designed to test the amenability of such oxidative deprotection to aldehyde oximes and to ketone hydrazones. However, the results were not synthetically appealing.

The results of the present investigation are gratifying and it's merits over some known deoximation methods[3] are evident. Thus, it is simple, inexpensive, non-toxic and above all effective in neutral medium. These reflect the reedeming features of this oxidative procedure.

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