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Efficient and Mild Regeneration of Carbonyl Compounds from Oximes and Hydrazones by Manganese(III) Porphyrin–Periodate†

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The periodate–manganese tetraphenylporphyrin, Mn(tpp)/IO_4^-, catalytic system is efficient in regenerating the parent carbonyl compounds from oximes and phenylhydrazones at room temperature.

Oxidation reactions catalysed by metalloporphyrins, especially iron-(III) and manganese(III) complexes, that mimic cytochrome P-450 dependent monooxygenases, are attracting continuing interest.[1] The conversion of oximes and hydrazones into the parent carbonyl compounds under mild conditions is an important process in organic chemistry. A number of methods have been reported for the oxidative cleavage of oximes and phenylhydrazones,[2–7] which frequently necessitate relatively forceful reaction conditions.

Recently we have introduced $NaIO_4$ and Bu_4NIO_4 as effective oxygen atom donors for the epoxidation of olefins, catalysed by manganese tetraphenylporphyrin.[8,9] We now report the use of sodium periodate in the presence of manganese(III) tetraphenylporphyrin for oxidative regeneration of carbonyl compounds from oximes and phenylhydrazones in a two-phase system, CH_2Cl_2/H_2O, at room temperature. As far as we know, this type of reaction is novel in oxidation systems catalysed by metalloporphyrins. Most aromatic aldoximes and ketoximes were easily converted into their corresponding aldehydes and ketones in high yields within 1–3 h at room temperature (Table 1). Further oxidation of aldehydes to their carboxylic acids was not observed. Tetrabutylammonium periodate was employed as an effective source of oxygen atom donor for oxidative deoximation in the presence of catalytic amounts of manganese tetraphenylporphyrin in a single phase system at room temperature.

Comparison of the two systems showed that Mn(tpp)Cl/Bu_4NIO_4 was milder than Mn(tpp)Cl/$NaIO_4$.

Phenylhydrazones and *p*-nitrophenylhydrazones are also transformed to their carbonyl compounds by Mn(tpp)Cl/$NaIO_4$ system at room temperature (Table 2). However, the homogeneous Mn(tpp)Cl/Bu_4NIO_4 system was less efficient.

In the absence of manganese(III) tetraphenylporphyrin catalyst, $NaIO_4$ and Bu_4NIO_4 were much less efficient in regeneration of carbonyl compounds from oximes and hydrazones at room temperature.

Table 1 Regeneration of aldehydes and ketones by Mn(tpp)Cl/$NaIO_4$ and Mn(tpp)Cl/Bu_4NIO_4 systems

Run	Substrate	Product[a]	% Yield[b] (Time/h)	
			Mn(tpp)Cl/$NaIO_4$	Mn(tpp)Cl/Bu_4NIO_4
1	Anisaldoxime	Anisaldehyde	90 (2)	94 (2.5)
2	2,6-Dimethoxybenzaldoxime	2,6-Dimethoxybenzaldehyde	85 (2)	90 (3.5)
3	Salicylaldoxime	Salicyaldehyde	60 (3)	60 (4)
4	Acetophenone oxime	Acetophenone	80 (2.5)	82 (3.5)
5	Benzophenone oxime	Benzophenone	85 (1)	88 (1.5)
6	9-Fluorenone oxime	9-Fluorenone	83 (2)	86 (2.5)
7	*p*-Phenylacetophenone oxime	*p*-Phenylacetophenone	85 (1)	92 (2)

[a]All products were identified by comparison with authentic samples (IR, NMR, mp). [b]Isolated yield.

Table 2 Regeneration of aldehydes and ketones from phenylhydrazones and *p*-nitrophenylhydrazones by Mn(tpp)Cl/$NaIO_4$

Run	Substrate	Product[a]	Time (h)	Yield (%)[b]
1	Anisaldehyde phenylhydrazone	Anisaldehyde	5	82
2	2-Nitrobenzaldehyde phenylhydrazone	2-Nitrobenzaldehyde	8	40
3	Benzophenone phenylhydrazone	Benzophenone	3.5	80
4	Acetophenone phenylhydrazone	Acetophenone	3	82
5	*p*-Chloroacetophenone phenylhydrazone	*p*-Chloroacetophenone	4	80
6	*p*-Phenylacetophenone phenylhydrazone	*p*-Phenylacetophenone	3	80
7	*m*-Nitrobenzaldehyde phenylhydrazone	*m*-Nitrobenzaldehyde	8	35
8	Anisaldehyde 4-NPH[c]	Anisaldehyde	5	75
9	Acetophenone 4-NPH	Acetophenone	3	75
10	Benzophenone 4-NPH	Benzophenone	3.5	73
11	*p*-Phenylacetophenone 4-NPH	*p*-Phenylacetophenone	3	80
12	*p*-Chloroacetophenone 4-NPH	*p*-Chloroacetophenone	4	45

[a]All products were identified by comparison with authentic samples (IR, NMR, mp). [b]Isolated yield. [c]4-NPH stands for 4-nitrophenylhydrazone.

Experimental

All chemicals used were reagent grade. The tetraphenylporphyrin was prepared and metallated according to the literature.[10,11]

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General Procedure for Regeneration of Carbonyl Compounds by $NaIO_4$.—In a 25 ml flask equipped with magnetic stirrer, oxime or phenylhydrazone (1 mmol) and CH_2Cl_2 (10 ml) were added to Mn(tpp)Cl (0.012 mmol) and tetrabutylammonium bromide (0.05 mmol). After addition of sodium periodate solution (2 mmol in 10 ml H_2O) the mixture was stirred on a magnetic stirrer at room temperature for 1 to 8 h. The progress of the reaction was monitored by TLC (eluent: CCl_4/Et_2O). The organic phase was purified on a silica gel plate or silica gel column (eluent: CCl_4/Et_2O). Evaporation of the solvent afforded the pure carbonyl compound in 35–90% yields (Tables 1 and 2).

General Procedure for The Regeneration of Carbonyl Compounds from Oximes by Bu_4NIO_4.—To a solution of oxime (1 mmol) in CH_2Cl_2 (10 ml) were added Mn(tpp)Cl (0.012 mmol) and Bu_4NIO_4 (2 mmol) and the solution stirred magnetically at room temperature for 1 to 3.5 h. The progress of the reaction was followed by TLC. Purification of crude products with a silica gel plate or silica gel column (eluent: CCl_4/Et_2O) afforded pure carbonyl compounds in 60–94% yields (Table 1).

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