

Selective Oxidative Cleavage of Benzylic and Allylic Oximes to Their Carbonyl Compounds with Strontium Manganate in the Presence of Aluminium Chloride in Solution and under Solvent-Free Conditions

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Derivatives of carbonyl compounds such as oximes serve as effective protecting groups for aldehydes and ketones in organic synthesis.¹ Oximes are also extensively used for the purification and characterization of carbonyl compounds. Since oximes can be prepared from non-carbonyl compounds,² the regeneration of carbonyl compounds from oximes provides an alternative method for the preparation of aldehydes and ketones. Several oxidative methods have been developed for deoxygenation in the literature.³⁻¹⁹ However, some of these methods suffer from disadvantages such as long reaction times, low yields of the products and tedious work up. Also many of the reports either do not describe the deoxygenation of aldoximes or give low yields of aldehydes or the liberated aldehydes are overoxidized. Selective oxidation of benzylic and allylic oximes in the presence of aliphatic oximes and other derivatives such as semicarbazones, phenylhydrazones and 2,4-dinitrophenylhydrazones is of practical importance and only a few reports are available in the literature for this purpose.²⁰ These methods suffer from drawbacks such as long reaction times, the use of large excess of the reagents and low yields of the desired products. Therefore, introduction of a new efficient and selective method for deoxygenation is desirable.

We have previously reported that SrMnO₄/AlCl₃ can be used as a convenient reagent for the selective oxidation of benzylic and allylic alcohols to their carbonyl compounds.²¹ In the course of further exploration on the application in synthetic organic chemistry, herein, we wish to disclose that benzylic and allylic oximes are efficiently converted to their corresponding carbonyl compounds with SrMnO₄/AlCl₃ in solution and under solvent-free conditions (Scheme 1).

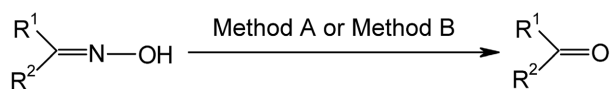
At first, the oxidation of 4-bromobenzaldoxime was examined with SrMnO₄ alone in refluxing acetonitrile and only 20% of 4-bromobenzaldehyde was obtained after 2 h. Once again, we attempted this reaction with SrMnO₄ in the

presence of several Lewis acids such as AlCl₃, FeCl₃, BiCl₃ and ZnCl₂ and found that AlCl₃ is the most suitable one. Among the various solvents such as CH₃CN, THF, CH₂Cl₂ and *n*-hexane, it was observed that CH₃CN is the only solvent of choice for this transformation. The optimum molar ratio of oxime to SrMnO₄ to AlCl₃ is found to be 1 : 1.5 : 1. The reaction of 4-chlorobenzaldoxime with AlCl₃ in the absence of SrMnO₄ was also investigated and only 10% 4-chlorobenzaldehyde was obtained from the reaction mixture.

As shown in Table 1, different types of benzylic and allylic aldoximes and ketoximes are transformed to their corresponding aldehydes and ketones in excellent yields with SrMnO₄ in the presence of AlCl₃ in refluxing acetonitrile (entries 1-11). It is pertinent to mention that over-oxidation of the resulting aldehydes, the major drawback of other oxidative hydrolytic methods, is not observed under the reaction conditions. α,β -Unsaturated oximes underwent deoxygenation very efficiently without affecting the olefinic bond and the reaction is essentially chemoselective (entries 12 and 13). It is worth mentioning that the reaction were performed under heterogenous conditions and the products were isolated by simple filtration of the mixture and evaporation of the solvent from the filtrate. Benzylic oximes with nitro-substituent and aliphatic oximes are more resistant under these conditions and the corresponding carbonyl compounds were isolated in low yields (entries 14-17).

Deoxygenation reactions were also investigated with SrMnO₄ in the presence of AlCl₃ under solvent-free conditions. The process involves simply mixing of oxime, SrMnO₄ and AlCl₃ and heating the mixture at 70 °C for the time specified in Table 1. Extraction of the reaction mixture with Et₂O gave almost pure products. The results illustrated in Table 1 indicate that under solvent-free conditions, the yields of the products are comparable with the solution reactions, but the reaction times are longer.

In order to show the chemoselectivity of the described method, we have also performed several competitive oxidation reactions. The experimental results show that benzylic and allylic oximes are oxidized selectively in the presence of aliphatic oximes, semicarbazones, phenylhydrazones and 2,4-dinitrophenylhydrazones (Scheme 2). These selectivities



Method A = SrMnO₄/AlCl₃, CH₃CN, reflux

Method B = SrMnO₄/AlCl₃, solvent-free

Scheme 1

are useful achievements in organic synthesis.

In conclusion, the paper describes an efficient method for oxidative cleavage of benzylic and allylic oximes. Short reaction times, heterogeneous reaction conditions, excellent yields, easy work up and excellent chemoselectivity offer significant improvements over many existing methods.

Experimental Section

Oxidative cleavage of 4-chlorobenzaldoxime in solution. To a solution of 4-chlorobenzaldoxime (1 mmol, 0.156 g) in CH₃CN (15 mL), SrMnO₄ (1.5 mmol, 0.310 g) and AlCl₃ (1 mmol, 0.133 g) were added and the mixture was stirred under reflux conditions for 30 min. The progress of the reaction was monitored by TLC (eluent: *n*-hexane/EtOAc, 3 : 1). The reaction mixture was filtered and the solid material was washed with CH₃CN (15 mL). Evaporation of the solvent gave the crude product. Purification of the crude product by chromatography on silica gel with appropriate eluent afforded the pure 4-chlorobenzaldehyde in 98% yield (0.138 g). Mp 47-48 °C (Lit.²² 47-50 °C). ¹H NMR (CDCl₃): δ 7.45 (d, 2H, ArH), 7.8 (d, 2H, ArH), 10 (s, 1H, CHO). IR (KBr): 3080, 2860, 1694, 1588, 1485, 1385, 1203, 1090, 1010, 838, 811 cm⁻¹ (Table 1, entry 5).

Oxidative cleavage of 2,4-dichlorobenzaldoxime under solvent-free conditions. A mixture of 2,4-dichlorobenzaldoxime (1 mmol, 0.190 g), SrMnO₄ (1.5 mmol, 0.310 g) and AlCl₃ (1 mmol, 0.133 g) was heated on an oil bath (70 °C) for 90 min. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and extracted with Et₂O (2 × 15 mL). Evaporation of the solvent followed by chromatography on silica gel with appropriate eluent afforded the pure 2,4-dichlorobenzaldehyde in 99% yield (0.173 g). Mp 70-72 °C (Lit.²² 69-73 °C). ¹H NMR (CDCl₃): δ 7.2-7.5 (m, 2H, ArH), 7.8 (d, 1H, ArH), 10.4 (s, 1H, CHO). IR (KBr): 3072, 2883, 1680, 1574, 1455, 1372, 1244, 1092, 812, 750 cm⁻¹ (Table 1, entry 4).

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