Efficient oxidative cleavage of C=N using chromium trioxide supported on $NaHSO_4{\cdot}H_2O$

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Abstract
$NaHSO_4{\cdot}H_2O$ - supported CrO_3 is used for the efficient oxidative cleavage of oximes, hydrazones, semicarbazones and azines to their corresponding carbonyl compounds under mild and completely heterogeneous reaction conditions with good to high yields.

Keywords: Chromium trioxide, oximes, hydrazones, semicarbazones, azines

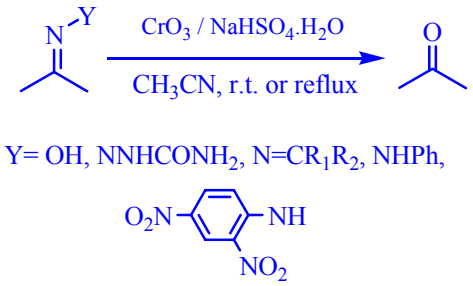
Introduction

Oximes, hydrazones, semicarbazones and azines are useful protecting groups[1] and are widely used for purification and characterization of carbonyl compounds. Since oximes can be prepared from non-carbonyl compounds,[2-4] their deoximation provides an alternative pathway to the aldehydes and ketones. Therefore, there has been considerable interest in the development of mild techniques for the conversion of oximes into their corresponding carbonyl compounds.[5-10] Although some of the known methods are carried out under mild reaction conditions, most of them require drastic conditions, high temperature, long reaction times, toxic or not- readily available reagents; they need to be freshly prepared, and have tedious work-up procedures. Little attention has been paid to the regeneration of carbonyl compounds from hydrazones, semicarbazones and azines.[11-13]

Results and Discussion

Recently, we have reported an efficient method for the oxidation of alcohols and trimethylsilyl ethers to their corresponding carbonyl compounds by using $NaHSO_4{\cdot}H_2O$ supported CrO_3 in solution and under solvent free conditions.[14, 15] In continuation of this study, we were interested in extending the applicability of this reagent system to the oxidation of other functional groups.

Here, and in continuation of our ongoing research program on the development of new methods for the cleavage of carbon-nitrogen double bonds,[16-18] we wish to report an efficient method for the oxidative cleavage of oximes, hydrazones, semicarbazones and azines to their corresponding carbonyl compounds using $NaHSO_4{\cdot}H_2O$ - supported CrO_3 under mild and completely heterogeneous reaction conditions (Scheme 1).

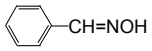
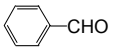
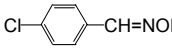
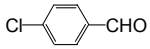
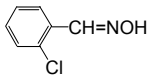
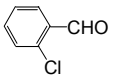
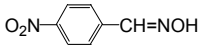
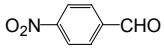
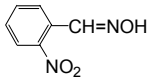
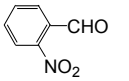
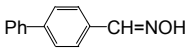
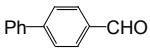
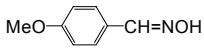
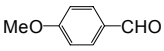
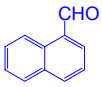
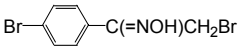
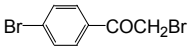
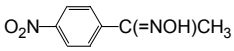
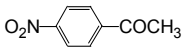
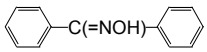
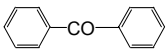
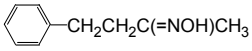
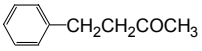
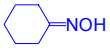
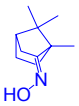
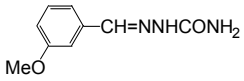
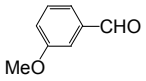
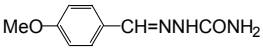
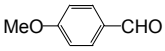
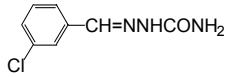
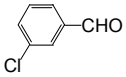
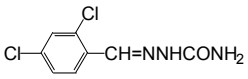
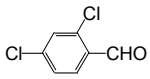
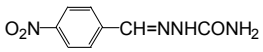
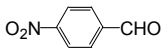
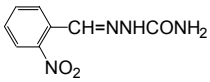
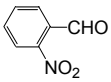


Scheme 1

Table 1 summarizes the results of the conversion of various oximes, hydrazones, semicarbazones and azines to their corresponding aldehydes and ketones. The cleavage of C=N bonds of semicarbazones using this method proceeds very rapidly at room temperature, while other reactions proceed in refluxing acetonitrile. The products of the above-mentioned reactions were isolated simply by filtering the mixture and evaporating the solvent from filtrate. It should be noted that the reaction did not proceed in the presence of CrO_3 or $NaHSO_4.H_2O$ alone, even after prolonged heating.

The method has advantages in terms of yields, heterogeneous nature, low cost and availability of reagents, short reaction times and easy work-up and will make a useful and important addition to the present methodologies.

Table 1. Oxidative deprotection of oximes, hydrazones, semicarbazones and azines with $NaHSO_4{\cdot}H_2O$ - supported CrO_3[a]

Entry	Substrate	Product	Time (min)	Yield % [b]
1			4	85
2			6	82
3			12	85
4			4	90
5			3	82
6			2	85
7			8	80
8			2	85
9			6	85
10			2	85
11			3	90
12			3	90
13			10	85
14			2	85
15			2	80
16			15	85
17			3	85
18			2	90
19			4	90
20			2	80
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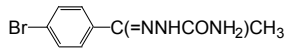
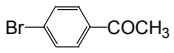
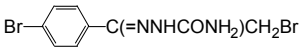
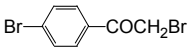
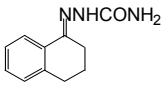
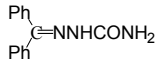
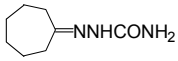
24			10	80
25			2	90
26			2	85
27			2	90
28			3	90
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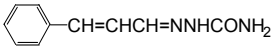
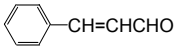
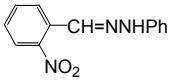
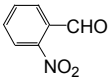
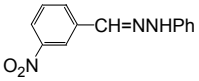
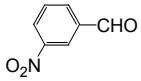
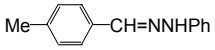
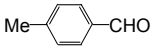
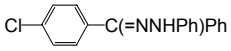
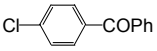
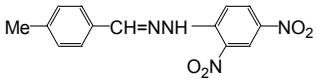
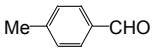
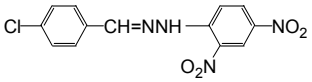
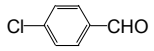
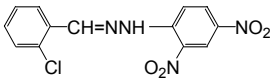
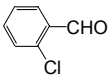
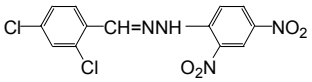
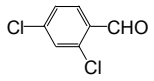
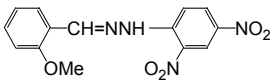
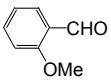
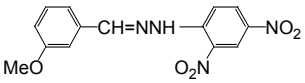
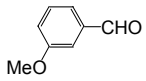
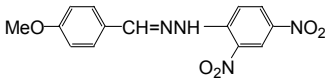
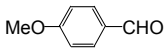
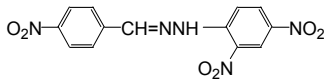
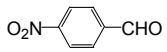
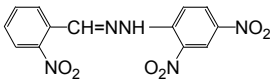
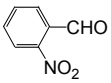
30			2	75
31			2	85
32			2	90
33			5	90
34			2	90
35			2	85
36			2	90
37			2	90
38			6	83
39			2	85
40			2	90
41			2	84
42			25	90
43			2	92
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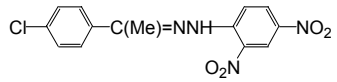
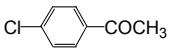
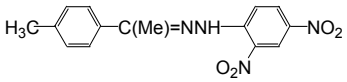
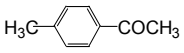
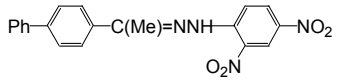
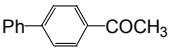
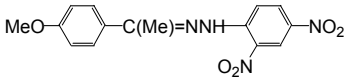
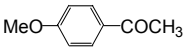
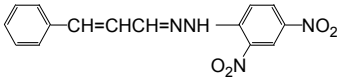
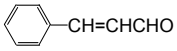
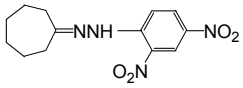
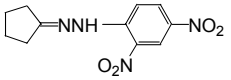
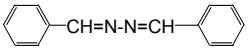
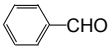
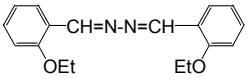
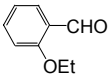
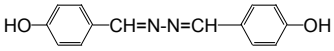
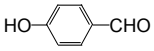
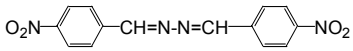
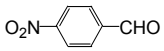
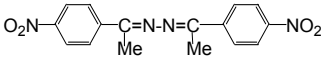
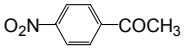
46			2	90
47			2	80
48			5	80
49			2	85
50			2	80
51			10	90
52			6	85
53			4	85
54			3	82
55			10	85
56			15	85
57			3	84

[a] Products were characterized by their physical constants, comparison with authentic samples, and IR and NMR spectroscopy. [b] Isolated yield.

Experimental Section

General Procedures. Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. Products were separated and purified by different chromatographic techniques, and were identified by the comparison of their mp, IR and NMR with those reported for the authentic samples. All yields refer to the isolated products. The purity determination of the substrates and reaction monitoring were accompanied by TLC on silica gel PolyGram SILG/UV 254 plates. Column chromatography was carried out on Merck Kieselgel 60H.

General experimental procedure. A mixture of the substrate (1 mmol) and $NaHSO_4{\cdot}H_2O$ - supported CrO_3 (0.37 g, content 0.75 mmol CrO_3) in CH_3CN (3 mL) was stirred at room

temperature, or under reflux conditions, for the specified time (Table 1). The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the solid residue was washed with CH_3CN (10 mL). Evaporation of the solvent followed by column chromatography on silica gel, gave the corresponding carbonyl compounds in good to high yield.

Acknowledgements

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