

# Imidazolium Dichromate Adsorbed on Alumina: A Convenient and Inexpensive Reagent for the Cleavage of C=N Functionalities

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**Abstract:** Oximes, hydrazones and semicarbazones are converted to the corresponding carbonyl compounds using imidazolium dichromate adsorbed on alumina (IDC/alumina).

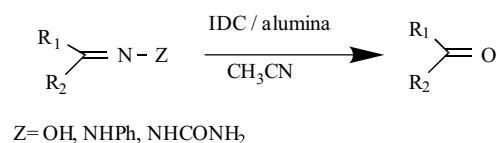
**Keywords:** Imidazolium dichromate, oximes, hydrazones, semicarbazone, carbonyl compounds.

Derivatives of carbonyl compounds such as oximes, hydrazones and semicarbazones have played an important role in the protection of carbonyl compounds [1], as they are highly crystalline and stable compounds. There has been considerable interest growing in the development of mild and novel procedures for the regeneration of carbonyl compounds from oximes. The classical acid hydrolysis method [2] is not suitable for acid sensitive compounds. Several oxidative deoxygenation methods [3-10] have been developed, which are found to have some advantages over the classical acid hydrolysis method. Although some of the known methods are carried out under mild conditions, most of them require drastic conditions, high temperature, long reaction times, and expensive, toxic or not readily available reagents. Little attention has been paid to oxidative cleavage [8,11] of hydrazones and semicarbazones.

In recent years, organic reactions on solid supports [12] have attracted much attention because of their enhanced selectivity, milder reaction conditions and associated ease of manipulation. Imidazolium dichromate is an inexpensive reagent and commercially available. Imidazolium dichromate adsorbed on alumina is stable and easily prepared by adding an amount of alumina to a solution of imidazolium dichromate in water. The reagent may be kept for several months in air at room temperature without losing its activity. Hydrazones and semicarbazones were deprotected rapidly with IDC/alumina (Scheme 1). The reagent has the ability to tolerate a variety of substrates (Table 1). Several aromatic and aliphatic oximes were reconverted to their parent aldehydes and ketones in good to excellent yields. Acid sensitive methoxy group remained intact and  $\alpha$ ,  $\beta$ -unsaturated, cinnamaldehyde was reconverted without any difficulty. Over oxidation of aldehydes to their carboxylic acids is not observed. In contrast, deoxygenation with PCC suffers from long reaction times (12-94 h) [3]. Additionally, PCC-hydrogen peroxide [4], PDC-TBHP [5], or TBHP [8] alone are not suitable for aldoximes, and overoxidation products are usually produced.

IDC/alumina heterogeneous system is successfully used for the cleavage of oximes, hydrazones and semicarbazones

(Table 1). Among the various mineral supports examined, such as alumina, clay, silica gel, etc, alumina was found to give the best results. It should be mentioned that no carbonyl compounds were produced using alumina alone even after prolonged heating. Imidazolium dichromate alone takes a longer time (6 times longer than IDC/alumina system) to complete the reaction. Thus, a new, convenient and efficient heterogeneous method for regeneration of carbonyl compounds from oximes, hydrazones and semicarbazones using imidazolium dichromate on adsorbed alumina has been developed.



Scheme 1.

## EXPERIMENTAL

All products were known and identified by comparison with authentic samples. Yields refer to isolated products. The progress of reaction was monitored by TLC.

### Preparation of IDC/Alumina

To a solution of imidazolium dichromate (8.85 g) in water (25 mL) was added alumina (12.75 g). The resulting mixture was stirred at 60 °C for 3 h. After evaporation of the solvent on a rotary evaporator, the solid was dried in vacuum at 40 °C for 2 h.

### General Procedure for the Cleavage of C=N Functionalities with IDC/Alumina System

A mixture of substrate (oxime or hydrazone or semicarbazone, 5 mmol) and IDC/alumina (1.5 equiv of oxidant, IDC) was refluxed in acetonitrile (25 mL) for the specified time (Table 1). After completion of the reaction (TLC monitored), the reaction mixture was filtered, and the solid material was washed with acetonitrile several times. The combined filtrate was evaporated and residue was chromatographed over silica gel, (eluant hexane-ethyl acetate = 8/2) to give pure product in good to excellent yield.

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**Table 1. Deprotection of Oximes, Hydrazones, and Semicarbazones with IDC/Alumina in Refluxing Acetonitrile**

Entry	Substrate	Product	Time (min)	Yield (%)
1	Benzophenone oxime	Benzophenone	40	90
2	Acetophenone oxime	Acetophenone	58	92
3	4-Methoxybenzaldehyde oxime	4-Methoxybenzaldehyde	35	87
4	4-Bromobenzaldehyde oxime	4-Bromobenzaldehyde	36	89
5	Cyclohexanone oxime	Cyclohexanone	44	90
6	Cyclopentanone oxime	Cyclopentanone	35	84
7	Benzaldehyde oxime	Benzaldehyde	34	88
8	Cinnamaldehyde oxime	Cinnamaldehyde	30	79
9	Camphor oxime	Camphor	53	85
10	3-Pentanone oxime	3-Pentanone	39	83
11	Benzophenone semicarbazone	Benzophenone	41	90
12	4-Bromobenzaldehyde semicarbazone	4-Bromobenzaldehyde	29	89
13	4-Chloroacetophenone semicarbazone	4-Chloroacetophenone	40	90
14	Cyclohexanone semicarbazone	Cyclohexanone	32	88
15	Acetophenone semicarbazone	Acetophenone	43	86
16	Benzophenone phenylhydrazone	Benzophenone	32	83
17	4-Chloroacetophenone phenylhydrazone	4-Chloroacetophenone	36	79
18	4-Bromobenzaldehyde phenylhydrazone	4-Bromobenzaldehyde	33	90
19	4-Methoxyacetophenone phenylhydrazone	4-methoxyacetophenone	35	88

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