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A Mild and Efficient Method for Cleavage of C=N Using Imidazolium Dichromate

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ABSTRACT

Oximes, hydrazones, and semicarbazones are converted to their corresponding carbonyl compounds by using imidazolium dichromate (IDC).

Key Words: Imidazolium dichromate; Oximes; Hydrazones; Semicarbazones.

INTRODUCTION

Oximes, hydrazones, and semicarbazones are useful intermediates in organic chemistry and are utilized for purification and characterization of

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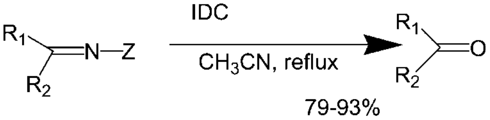
carbonyl compounds. They are also used as protecting groups for carbonyl compounds.[1] Their synthesis from noncarbonyl compounds[2] provides an alternative pathway to aldehydes and ketones. Therefore, the regeneration of carbonyl compounds from their oximes has received much attention.[3] Some chlorochromate derivatives are also used for this purpose [4–9] Although some of the known methods are carried out under mild conditions, most of them require drastic conditions, such as high temperature, long reaction times, expensive, toxic, or not readily available reagents, and they need to be freshly prepared with tedious work-up procedures. Little attention has been paid to oxidative cleavage[5,6,10] of hydrazones and semicarbazones. In this communication, author wishes to report a convenient and an efficient method for the regeneration of carbonyl compounds from oximes, hydrazones, and semicarbazones by using imidazolium dichromate (IDC).



Z = OH, NH-Ph, NHCONH$_2$

1 (see table 1) **2**

2a, $R_1 = R_2 = C_6H_5$; **2b**, $R_1 = C_6H_5$, $R_2 = Me$; **2c**, $R_1 = p$-$MeOC_6H_4$, $R_2 = H$; **2d**, $R_1 = p$-BrC_6H_4, $R_2 = H$; **2e**, $R_1 = R_2 = -(CH_2)_5-$; **2f**, $R_1 = R_2 = -(CH_2)_4-$; **2g**, $R_1 = C_6H_5$, $R_2 = H$; **2h**, $R_1 = Ph{-}CH{=}CH$, $R_2 = H$; **2i**, $R_1 = p$-ClC_6H_4, $R_2 = Me$; **2j**, $R_1 = p$-$MeOC_6H_4$, $R_2 = Me$.

IDC is an inexpensive reagent, which has been used as an oxidizing agent.[11] Author believes this is the first report of using IDC as the reagent for the deprotection of oximes, hydrazones, and semicarbazones. Several oximes were deoximated to their corresponding aldehydes and ketones in a good to excellent yields. Over-oxidation of aldehydes to their carboxylic acid was not observed. In contrast, deoximation with PCC suffers from long reaction times (12–94 hr).[4] Also, PCC-hydrogen peroxide,[12] PDC-TBHP,[13] or TBHP[14] alone are not suitable for aldoximes, over-oxidation products are usually produced. The reagent IDC has the ability to tolerate a variety of substrates. Aromatic and aliphatic oximes were deoximated with IDC. Acid sensitive methoxy group remained intact and α,ß-unsaturated, cinnamaldoxime was deoximated without any difficulty. Several phenyl hydrazones and semicarbazones were deprotected by using IDC to give the corresponding carbonyl compounds in excellent yields.

Table 1. Deprotection of oximes, hydrazones, and semicarbazones with IDC in refluxing acetonitrile.

Entry	Substrate (**1**)	Product (**2**)	Time (hr)	Yield (%)	M.p./b.p.(°C) lit. [a]/obs.
1	Benzophenone oxime	**2a**	6	94	48–49/46–47
2	Acetophenone oxime	**2b**	8	90	202/200–202
3	4-Methoxybenzaldehyde oxime	**2c**	5	84	248/245–247
4	4-Bromobenzaldehyde oxime	**2d**	5	89	55–58/55–57
5	Cyclohexanone oxime	**2e**	4	94	155/150–152
6	Cyclopentanone oxime	**2f**	5	88	130–131/128–129
7	Benzaldehyde oxime	**2g**	5	83	178–179/179–180
8	Cinnamaldehyde oxime	**2h**	6	83	248/245–246
9	Benzophenone semicarbazone	**2a**	8	91	
10	4-Bromobenzaldehyde semicarbazone	**2d**	7	82	
11	4-Chloroacetophenone semicarbazone	**2i**	8	90	232/229–231
12	Cyclohexanone semicarbazone	**2e**	5	88	
13	Acetophenone semicarbazone	**2b**	7	86	
14	Benzophenone phenylhydrazone	**2a**	8	83	
15	4-Chloroacetophenone phenylhydrazone	**2h**	4	89	
16	4-Bromobenzaldehyde phenylhydrazone	**2d**	7	91	
17	4-Methoxyacetophenone phenylhydrazone	**2j**	5	88	36–38/34–35

[a] Available from Aldrich Chemical Company.

Mildness of reaction condition, efficiency of the reagent, ease of work-up procedure and high yields of products are among the outstanding advantages of this new method.

EXPERIMENTAL

All products are known compounds and were identified by comparison of their spectral data (IR, 1H NMR) and physical properties with those of authentic samples. The progress of reaction was monitored by thin layer chromatography on silica gel. All yields refer to isolated products.

General Procedure for Regeneration of Carbonyl Compounds from Oximes, Hydrazones, and Semicarbazones with IDC

To a solution of substrate (oxime or hydrazone or semicarbazone, 5 mmol) in acetonitrile (25 mL) IDC (7.5 mmol) was added. The reaction mixture was refluxed for the specified time (Table 1). After completion of the reaction (TLC), the solvent was evaporated on rotary evaporator and the residue was chromatographed over silica gel, eluted hexane–ethyl acetate system to afford a pure product.

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