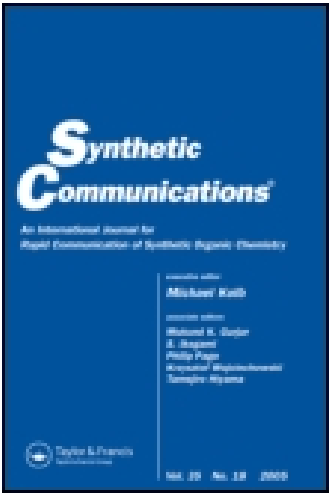

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Quinolium Dichromate Adsorbed on Alumina: A Mild, Convenient, and Inexpensive Reagent for Cleavage of C=N Under Nonaqueous Conditions

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Quinolium Dichromate Adsorbed on Alumina: A Mild, Convenient, and Inexpensive Reagent for Cleavage of C═N Under Nonaqueous Conditions

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Abstract: Oximes, hydrazones, and semicarbazones are converted to the corresponding carbonyl compounds using quinolium dichromate adsorbed on alumina (QDC/alumina) under nonaqueous conditions.

Keywords: Quinolium dichromate, alumina, oximes, hydrazones, semicarbazones, carbonyl compounds

Derivatives of carbonyl compounds such as oximes, hydrazones, and semicarbazones have played an important role in the protection of carbonyl compounds,[1] because they are very crystalline and stable compounds. Because oximes can be prepared from noncarbonyl compounds, the regeneration of carbonyl compounds from oximes is an alternative method for the preparation of aldehydes and ketones.[2] Interest in regeneration of carbonyl compounds from their derivatives under mild conditions has been growing in synthetic organic chemistry. The classical acid-hydrolytic method requires strong mineral acids, often results in low yields, and is not suitable for acid-sensitive compounds.[3] Several oxidative deoximation methods

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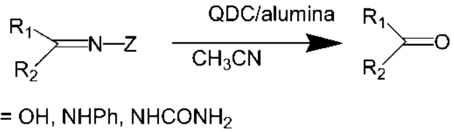
have been reported that have some advantages over the classical acid-hydrolysis method.[4–13] Recently, some microwave techniques have been developed that are valuable from a synthetic standpoint but extreme precautions have to be taken because these reactions were performed under microwave irradiation with an oxidant.[14,15] Little attention has been paid to oxidative cleavage of hydrazones and semicarbazones.[6,16] Thus, there is still a need to develop a new and facile procedure for the regeneration of carbonyl compounds from oximes, hydrazones, and semicarbazones.

Quinolium dichromate is an inexpensive reagent and was previously reported as an oxidizing agent.[17] Quinolium dichromate-adsorbed alumina is stable and easily prepared by adding alumina to a solution of quinolium dichromate in water. In recent years, the organic reactions on solid supports have attracted much attention because of their enhanced selectivity, milder reaction conditions, and associated ease of manipulation.[18] In this communication, I report a convenient and efficient method for the cleavage of carbon–nitrogen double bonds using QDC/alumina under nonaqueous conditions. Several oximes were deoximated to their corresponding aldehydes and ketones in good to excellent yields. Overoxidation of aldehydes to their carboxylic acids was not observed. In contrast, deoximation with PCC suffers from long reaction times (12–94 h);[4] PCC-hydrogen peroxide,[5] PDC-*tert*-butyl hydroperoxide,[12] and TBHP[6] alone are not suitable for aldoximes, and overoxidation products are usually produced. QDC/alumina heterogeneous system is successfully used for cleavage of semicarbazones and phenylhydrazones. The reagent has the ability to tolerate a variety of substrates. Without alumina support, oxidative cleavage takes longer to complete the reaction (Scheme 1).

In summary, the method has advantages in terms of yield, heterogeneous nature, cost and availability of reagents, reaction time, and workup.

EXPERIMENTAL

All of the products are known compounds and were checked by comparison of their spectral data (IR, ^{1}H NMR) and physical properties with an authentic



1 (see Table 1) **2**

Scheme 1. **2a**, $R_1 = R_2 = C_6H_5$; **2b**, $R_1 = C_6H_5$, $R_2 = Me$; **2c**, $R_1 = p\text{–}MeOC_6H_4$, $R_2 = H$; **2d**, $R2 = H$; **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**, $R_1 = p\text{–}ClC_6H_4$, $R_2 = Me$; **2i**, $R_1 = p\text{–}ClC_6H_4$, $R_2 = Me$; **2j**, $R_1 = p\text{–}MeOC_6H_4$, $R_2 = Me$.

Table 1. Oxidative deprotection of oximes, hydrazones, and semicarbazones with QDC/alumina in refluxing acetonitrile

Entry	Substrate (1)	Product (2)	Time (min)	Yield (%)	Mp/bp(°C) lit.[a]/obs.
1	Benzophenone oxime	**2a**	18	89	48–49/46–47
2	Acetophenone oxime	**2b**	22	92	202/200–202
3	4-Methoxybenzaldehyde oxime	**2c**	15	93	248/245–247
4	4-Bromobenzaldehyde oxime	**2d**	10	90	55–58/55–57
5	Cyclohexanone oxime	**2e**	28	93	155/150–152
6	Cyclopentanone oxime	**2f**	27	87	130–131/128–129
7	Benzaldehyde oxime	**2g**	15	95	178–179/179–180
8	4-Chloroacetophenone oxime	**2h**	25	87	232/228–230
9	Benzophenone semicarbazone	**2a**	10	92	48–49/46–47
10	4-Bromobenzaldehyde semicarbazone	**2d**	15	90	55–57/55–57
11	4-Chloroacetophenone semicarbazone	**2h**	18	92	233/228–231
12	Cyclohexanone semicarbazone	**2e**	23	81	155/150–151
13	Acetophenone semicarbazone	**2b**	20	92	202/200–201
14	Benzophenone phenylhydrazone	**2a**	27	79	48/47–49
15	4-Chloroacetophenone phenylhydrazone	**2h**	27	83	231/228–230
16	4-Bromobenzaldehyde phenylhydrazone	**2d**	16	92	57/56–58
17	4-Methoxyacetophenone phenylhydrazone	**2j**	27	91	36–38/34–35

[a] Available from Aldrich Chemical Company.

sample. The progress of the reaction was monitored by thin-layer chromatography on silica gel. All yields refer to isolated products.

Preparation of Quinolium Dichromate Adsorbed on Alumina

To a solution of quinolium dichromate (11.90 g) in water (25 mL) was added alumina (12.75 g). The reaction mixture was stirred at 50°C for 1 h. After evaporation on a rotary evaporator, the yellow solid was dried in vacuum at 50°C for 2 h. The reagent may be kept for several months in air at room temperature without losing its activity.

General Procedure for Cleavage of C=N with QDC/Alumina

A mixture of substrate (oxime or hydrazone or semicarbazone, 1 mmol) and QDC/alumina (1.5 equiv of oxidant, QDC) in acetonitrile (10 mL) was refluxed for the specified time (Table 1). After completion of the reaction, 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 (eluted hexane–ethyl acetate, 8/2) to give the pure product in good to excellent yields. All of the products are known compounds and were identified by their spectral data and physical properties (bp or mp) with those of authentic samples.

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