

SHORT
COMMUNICATIONS

Chemoselective Solvent-free Deoximation by $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
in the Presence of ZrCl_4 on Wet SiO_2

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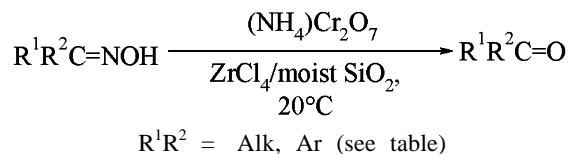
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Protection of carbonyl compounds as oximes is of great interest to synthetic chemists for the oximes are readily prepared highly stable compounds [1, 2]. Oximes are also extensively used for characterization of carbonyl compounds and in preparation of amides via the Beckmann rearrangement [3]. Since oximes can be prepared from noncarbonyl compounds, such as alcohols [4], olefins [5], primary aliphatic amines [6], and nitriles [7] the recovery of carbonyl compounds from oximes provides an alternative method for aldehydes and ketones preparation. Some of the reagents applied for deoximation [1, 8, 9] are toxic, expensive, or not readily available, they need to be freshly prepared, or the reaction requires drastic conditions, long time, and tedious workup.

In this paper we report on a convenient method for deoximation of aldehydes and ketones oximes into their corresponding carbonyl compounds using am-

monium dichromate in the presence of ZrCl_2 and wet SiO_2 under solvent-free conditions (see table).

Our experiments show that oximes are converted into their corresponding carbonyl compounds in good to high yields at room temperature. Semicarbazones do not undergo the cleavage of the C=N bonds by this method (see table, runs nos. 8-14). Therefore this procedure is suitable for selective deprotection of oximes leaving the semicarbazones intact. This fact was proved by a competitive reaction of 4-methylacetophenone oxime and acetophenone semicarbazone: Within 2.8 h all 4-methylacetophenone oxime



Oximes deoximation by ammonium dichromate in the presence of ZrCl_2 and wet SiO_2 at room temperature

Run no.	Substrate	Reaction product	Time, h	Yield, % ^a
1	4-Nitrobenzaloxime	4-Nitrobenzaldehyde	4	72
2	3-Nitrobenzaloxime	3-Nitrobenzaldehyde	4	75
3	4-Chlorobenzaloxime	4-Chlorobenzaldehyde	1	78
4	4-Methylbenzaloxime	4-Methylbenzaldehyde	1	85
5	Acetophenone oxime	Acetophenone	4	70
6	4-Methylacetophenone oxime	4-Methylacetophenone	2.7	85
7	Cyclohexanone oxime	Cyclohexanone	0.5	83
8	Benzaldehyde semicarbazone	Benzaldehyde	4	0
9	3-Nitrobenzaldehyde semicarbazone	3-Nitrobenzaldehyde	4	0
10	4-Methoxybenzaldehyde semicarbazone	4-Methoxybenzaldehyde	4	0
11	Benzophenone semicarbazone	Benzophenone	4	0
12	Acetophenone semicarbazone	Acetophenone	4	0
13	1-Naphthaldehyde semicarbazone	1-Naphthaldehyde	4	0
14	Cyclohexanone semicarbazone	Cyclohexanone	4	0

^a Yield of the isolated reaction product.

was converted into 4-methylacetophenone whereas the acetophenone semicarbazone was recovered unchanged.

It should be noted that these deoxygenation reactions did not proceed at the use either of ammonium dichromate, $ZrCl_4$, or wet SiO_2 alone.

In conclusion we can state that a mild, efficient, and chemoselective deoxygenation method has been developed. The deoxygenation occurs at room temperature under solvent-free conditions.

EXPERIMENTAL

Oximes deoxygenation (general procedure). To a mixture of $ZrCl_4$ (0.69 g, 3 mmol) and 0.4 g of wet SiO_2 (SiO_2 to H_2O 4:1 by weight) and ammonium dichromate (0.252 g, 1 mmol) was added an appropriate oxime (1 mmol). The resulting mixture was stirred at room temperature for a time specified in the table (TLC or GLC monitoring). After completion of the reaction CH_2Cl_2 (5 ml) was added to the mixture, and 15 min later the solution obtained was filtered and dried on anhydrous $MgSO_4$. The solution was filtered off, the solvent was evaporated, and the carbonyl compound formed was isolated by column

chromatography on silica gel in a yield indicated in the table. We gratefully acknowledge the Research Council of Guilan University for partial support of this study.

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