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A Proficient Role of Zirconium Oxychloride Octahydrate with Sodium Nitrite for Deoximation of Various Aldoximes and Ketoximes under Solvent Free Conditions

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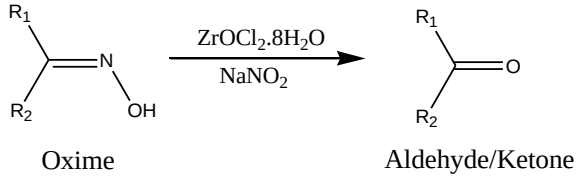
ABSTRACT

A clean protocol for effective and rapid deoximation of aldoximes and ketoximes to the corresponding aldehydes and ketones has been developed using $ZrOCl_2.8H_2O$ with $NaNO_2$ as catalytic system, under solvent free conditions using microwave irradiations. The modus adopted is mild, selective and is pertinent for both aldoximes and ketoximes substituted with diverse electron withdrawing and donating groups. Oximes of some steroidal compounds have also been deoximated under similar conditions. Structural confirmation of all the products were done on the basis of spectroscopic analyses-^{1}H NMR and FT-IR and by comparison of their melting point/boiling point with those of authentic samples.

1. Introduction

Carbonyl compounds are very useful preparatory materials for a large number of transformations in organic synthesis. Hence, it becomes essential to protect them and to deprotect them as well, when obliged. One of the simplest potential routes is by converting them to oximes [1]. Oximes are the significant derivatives of carbonyl compounds with C=N–OH functional group and are extensively used for protection and purification of carbonyl compounds. Synthesis of oximes from non-carbonyl compounds and their subsequent deoximation to carbonyl compounds provides an alternative route for synthesis of aldehyde and ketones [2]. Many methods for the regeneration of carbonyl compounds from oximes have been reported which includes the hydrolytic method, oxidative cleavage and reductive cleavage [3-10]. The classical method for cleavage of oximes to aldehydes and ketones include acid hydrolysis, which is not suitable for acid sensitive compounds. Some other reagents employed are mercuric nitrate [11], dinitrogen tetroxide [12], triethylammonium chlorochromate [13], titanium silicate [14], pyridinium chlorochromate [15], bismuth trichloride [16], zirconium sulphophenyl phosphate [17], N- halo-amides [18], silica supported sodium periodate [19], Dess Martin periodinone (DMP) [20], quinolinium flurochromate (QFC) [21], raney nickel [22] and aluminum nitrate in traces of NaBr [23]. However, these reported methods suffers from limitations of limited yields of carbonyl compounds, longer reaction times, difficulties in isolation of products, harsh reaction conditions, use of organic solvents and production of environmentally detrimental by-products. Organic solvents are highly volatile in nature and are extremely hazardous to human health and environment. With the growing awareness towards sustainable development, there is a need for developing new eco-friendly approaches to carry out such type of conversions.

In recent years organic synthesis under solvent-free conditions using microwave irradiations has become increasingly prevalent. Major advantages of the use of MW irradiations for conducting organic reactions in the absence of organic solvent includes higher yields, shorter reaction times and increased selectivity leading to clean, eco-friendly and efficient reactions. The use of zirconium oxychloride octahydrate as a catalyst in organic synthesis has attracted our attention as it is a promising Lewis acid catalyst in a variety of organic reactions [24-26] providing excellent yields with marked selectivity. Further, this hydrated salt of zirconium oxychloride is non-toxic, easy to handle, insensitive to moisture and is readily available. In continuation of our efforts towards developing clean and green methodologies for various organic transformations [27, 28], herein we report an efficient method for deoximation of aldoximes and ketoximes in the presence of $ZrOCl_2.8H_2O$ with $NaNO_2$ under solvent free conditions using microwave irradiations.



Oxime Aldehyde/Ketone

R_1, R_2 = H, alkyl, aryl

Scheme 1 Regeneration of carbonyl compounds from oximes

2. Experimental Methods

2.1 General Method

Melting points were determined in open capillaries and are uncorrected. The aldehydes, ketones, steroidal compounds and other chemicals were purchased from Sigma-Aldrich and Fluka. The reactions were carried out in a Biotage microwave reactor (power range: 0-300 W at 2.45MHz) and were monitored by analytical thin layer chromatography (TLC) performed on glass plates precoated with silica gel G as supplied by Sisco Research Laboratories (SRL). Visualization of the resulting chromatograms was done by looking under iodine chamber followed by dipping in a solution of carbon tetrachloride (CCl_4) and ethyl acetate ($CH_3COOC_2H_5$). IR spectra were recorded on Perkin-Elmer spectrum BX Series FT-IR spectrophotometer with KBr pellets. ^{1}H-NMR was recorded on a 400 MHz spectrometer (Bruker Avance Π 400 using Tetramethylsilane (TMS) as internal standard. Oximes of all carbonyl compounds were prepared according to reported procedure [26].

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2.2 General Procedure for the Deoximation of Oximes

Benzophenone oxime (0.182 g, 1 mmol), $ZrOCl_2.8H_2O$ (200 mg) and $NaNO_2$ (100 mg) were mixed thoroughly in a 10 mL Pyrex beaker and then subjected to microwave irradiations at 50 °C. The progress of reaction was monitored by TLC (CCl_4: Ethyl acetate / 38: 2) after every 10 seconds. The reaction was found to be completed after 25 sec. The reaction mixture was diluted with ice cold water. The solid thus separated out was filtered at vacuum; washed with water and recrystallized from ethanol to give benzophenone in 78% yield. Identical procedure was followed for the preparation of other carbonyl compounds from their oximes under similar reaction conditions. The products were recognized on the basis of comparison of their melting points / boiling points and spectroscopic data with those of the authentic samples which were found in good accord with literature [29-31].

2.3 Data Analysis

Benzophenone (1a): M.P. 49 °C; IR (KBr, cm^{-1}): 3054 (C-H), 1651 (C=0); ^1H NMR (400 MHz, $CDCl_3$): δ 7.81-7.78 (m, 4H), 7.59-7.55 (m, 2H), 7.48-7.44 (m, 4H).

4-Methoxyacetophenone (1b)**:** M.P. 39 °C; IR (KBr, cm^{-1}): 3063 (C-H), 1634 (C=0); ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 3.13 (s, 3H), 2.24 (s, 3H).

Cyclohexanone (1c): B.P. 157 °C; IR (KBr, cm^{-1}): 2937 (C-H), 1713 (C=0); ^1H NMR (400 MHz, $CDCl_3$): δ 2.33-2.31 (m, 4H), 1.86-1.84 (m, 4H), 1.72-1.69 (m, 2H).

4-Nitrobenzaldehyde (1d): M.P. 103 °C; IR (KBr, cm^{-1}): 3043 (C-H), 1707 (C=0); ^1H NMR (400 MHz, $CDCl_3$): δ 10.12 (s, 1H), 8.33 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.7 Hz, 2H).

4-Chlorobenzaldehyde (1e): M.P. 46 °C; IR (KBr, cm^{-1}): 3040 (C-H), 1603 (C=0); ^1H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 8.16 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H).

4-Hydroxybenzaldehyde (1f): M.P. 114 °C; IR (KBr, cm^{-1}): 3292 (O-H); 3093 (C-H), 1636 (C=0); ^1H NMR (400 MHz, $CDCl_3$): δ 10.12 (br, 1H, OH), 9.81 (s, 1H), 7.34 (d, J = 8.7 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H).

4-Bromobenzaldehyde (1g): M.P. 57 °C; IR (KBr, cm^{-1}): 3030 (C-H), 1689 (C=0); ^1H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 7.51 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H).

Testosterone propionate (1h): M.P. 154 °C; IR (KBr, cm^{-1}): 2942 (C-H), 1727 (C=0); ^1H NMR (400 MHz, $CDCl_3$): δ 5.73 (s, 1H), 4.61 (t, 1H), 2.42-2.30 (m, 6H), 2.19-2.15 (m, 1H), 2.04-2.00 (m, 1H), 1.83-1.77 (m, 2H), 1.71-1.65 (m, 2H), 1.61-1.54 (m, 3H), 1.42-1.33 (m, 2H), 1.19-1.15 (m, 4H), 1.13-1.08 (m, 3H), 1.07-1.00 (m, 2H), 0.95-0.94 (m, 1H), 0.83 (s, 3H).

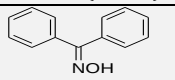
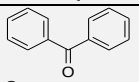
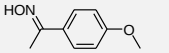
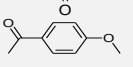
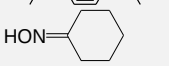
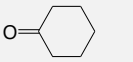
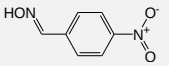
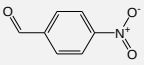
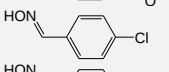
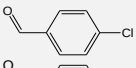
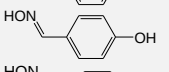
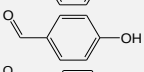
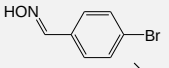
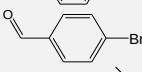
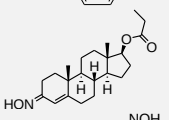
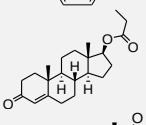
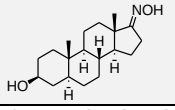
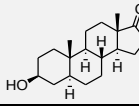
Trans-androsterone (1i): M.P. 181 °C; IR (KBr, cm^{-1}): 2934 (C-H), 1729 (C=0); ^1H NMR (400 MHz, $CDCl_3$): δ 3.59 (s, 1H, OH), 2.47-2.45 (m, 1H), 2.11-2.08 (m, 1H), 1.95-1.82 (m, 1H), 1.82-1.81 (m, 3H), 1.80-1.73 (m, 3H), 1.70-1.56 (m, 4H), 1.46-1.30 (m, 6H), 1.13-1.12 (m, 1H), 0.99-0.98 (m, 2H), 0.97-0.86 (m, 6H), 0.73-0.69 (m, 1H).

3. Results and Discussion

To start with, $ZrOCl_2.8H_2O$ alone was used in catalytic amount to explore the formation of the desired product i.e. benzophenone under microwave irradiations. It was found that low temperature ranges do not support product formation. Very high temperature ranges also does not support product formation, as the reaction mixture starts decomposing and the mixture turned black. So, the optimum temperature was found to be 50 °C. Accordingly, when Benzophenone oxime was treated with $ZrOCl_2.8H_2O$ at 50 °C under microwave irradiations in an open vessel, the desired ketone product was formed, but it was obtained in low yield of 45%. However, when the reaction was carried out in presence of a catalytic mixture of $ZrOCl_2.8H_2O$ and sodium nitrite ($NaNO_2$) the product was obtained in about 78% yield in 25 seconds under the same reaction conditions.

To examine the scope of newly developed protocol, some other structurally diverse aryl ketoximes were selected. The deoximation of these oximes was conducted in the presence of same catalytic system and corresponding ketones were obtained in good yield. Encouraged with the adequate results from the deoximation of ketoximes, we turned our consideration towards deoximation of aldoximes using the identical approach. The selected catalytic system is equally effective for the conversion of aldoximes with differently substituted electron withdrawing groups such as -NO_2, -Br, -Cl and electron releasing groups such as -OH on the aromatic ring, into the corresponding aldehydes under similar reaction conditions. Another peculiar feature of the above mentioned protocol is that the oximes of steroidal compounds like testosterone propionate and trans-androsterone also underwent deoximation under the same reaction conditions and product was obtained in good yield, without any effect on the rings of compound. Results are gathered in the table mentioned ahead (Table 1).

Table 1 Rapid deoximation of variously substituted aldoximes, ketoximes and oximes of sterically hindered compounds in the presence of $ZrOCl_2.8H_2O$ and $NaNO_2$

Entry	Substrate (Oximes)	Yield[a] (%)	Time (s)	Product (Ketones)
1a		78	25	
1b		75	40	
1c		71	40	
1d		77	40	
1e		72	35	
1f		73	45	
1g		75	35	
1h		65	40	
1i		68	45	

[a]Yields refers to isolated products

4. Conclusion

A highly efficient method for deoximation of variously substituted aldoximes and ketoximes and even for oximes of some sterically hindered compounds has been developed using zirconium oxychloride octahydrate and sodium nitrite under mild reaction conditions. The present method is fairly rapid, clean and selective and it avoids use of organic solvents at any stage of reaction.

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