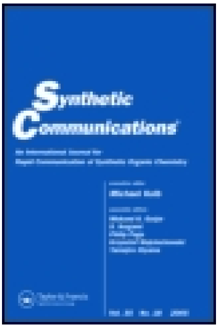

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Mild Reductive Deoximation with $TiCl_4$/NaI Reagent System

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MILD REDUCTIVE DEOXIMATION WITH $TiCl_4$/NaI REAGENT SYSTEM

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The application of the $TiCl_4$/NaI reagent system in the reductive cleavage of oximes under mild conditions is reported.

Cleavage of oxime **1** to regenerate the carbonyl compound 2 has received much attention over recent years. Since oximes can be prepared from non-carbonyl compounds or used to protect or activate the C=O group[1-3], an efficient deoximation would lead to a new route for the preparation of carbonyl compounds. The classical recovery of aldehydes or ketones from oximes consists of acid hydrolysis, which remove the hydroxylamine from the equilibrium[4]. This limits the scope of the reaction to exclude acid sensitive aldehydes or ketones.

Therefore, new methods for the oxidative[5-7] or reductive[8-10] deoximation continue to be developed. However,

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many of them required a long reaction time, the use of expensive reagents or appeared to be not suitable for the regeneration of aldehydes from aldoximes[11].

Recently, we reported that the novel $TiCl_4$/NaI system, generating low-valent titanium is a mild, efficient and selective reagent for deoxygenation of amine N-oxides[12], nitrones[12] or sulfoxides[13]. In this communication, we report the application of this extremaly versatile agent for the reductive cleavage of oximes into the corresponding carbonyl compounds.

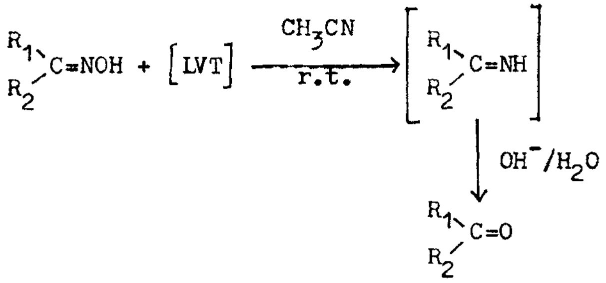
The reaction is very rapid and proceeds within 5 to 20 min. upon addition of NaI to a suspension of $TiCl_4$ and the substrate **1** in acetonitrile, at room temperature. Similar results were obtained when oxime **1** was added to the combination of $TiCl_4$/NaI in the same solvent.

The optimum solvent and molar ratio of reagents were studied using benzaldoxime as substrate. Acetonitrile was found to be the solvent of choice. The optimum ratio of reagents was found to be 1:2:2 /substrate **1** to NaI to $TiCl_4$/.

The reaction can be envisaged to proceed via the mechanism shown in the scheme. In the first atep, $TiCl_4$ is probably reduced by the iodide to form a low-valent titanium complex /LVT/. This, according to our earlier studies[14], is able to deoxygenate the substrate **1**:

Step 1: $$TiCl_4 + NaI \xrightarrow[r.t.]{CH_3CN} [LVT] + I_2$$

Step 2:



Several examples illustrating this novel and efficient procedure for reductive cleavage of oximes 1 are presented in the Table.

The selectivity of the method is demonstrated by several examples. Such reducible substituents as alkoxy, phenoxy or halogen remain unchanged.

In summary, we believe that the present procedure offers an attractive alternative to the methods for deoximation of 1 currently available. The mildness, convenience and rapidity make the present method highly practical, in particular for cleavage of (hetero)aromatic oximes. The typical procedure is as follows:

To a magnetically stirred solution of 1 /0.003 mole/ in acetonitrile /10 ml/, $TiCl_4$ /0.5 ml, 0.006 mole/ and NaI /0.9 g, 0.006 mole/ were added at room temperature. The mixture turned dark brown almost immediately, and TLC after 5-15 min. confirmed complete reaction. The whole was then decomposed with dil. aqueous KOH /5 ml/ and extracted with chloroform or ether. The combined organic layers were successively washed with an aqueous sodium thio-

Table: Reductive Cleavage of Oximes 1 to the Corresponding Carbonyl Compounds Using $TiCl_4$/NaI Reagent System[a]

Entry	Substrate 1	Time /min./	Product 2[b]	Yield[c] /%/
1	n-$C_7H_{15}CH=NOH$	20	n-$C_7H_{15}CHO$	63
2	$CH_3/C_2H_5/C=NOH$	20	$CH_3/C_2H_5/CO$	68
3	$CH_3/C_6H_5/C=NOH$	20	$CH_3/C_6H_5/CO$	70
4	$C_6H_5CH=NOH$	5	C_6H_5CHO	97
5	*m*-$/C_6H_5O/C_6H_4CH=NOH$	10	*m*-$/C_6H_5O/C_6H_4CHO$	95
6	*m*-$/CH_3O/C_6H_4CH=NOH$	10	*m*-$/CH_3O/C_6H_4CHO$	92
7	*o*-$ClC_6H_4CH=NOH$	10	*o*-ClC_6H_4CHO	96
8	*m*-$BrC_6H_4CH=NOH$	10	*m*-BrC_6H_4CHO	95
9	2-$C_4H_3OCH=NOH$[d]	10	2-C_4H_3OCHO	90
10	3-$C_5H_4NCH=NOH$	5	3-C_5H_4NCHO	97
11	4-$C_5H_4NCH=NOH$	5	4-C_5H_4NCHO	95
12	1-$C_{10}H_7CH=NOH$	10	1-$C_{10}H_7CHO$	94
13	2-$C_{10}H_7CH=NOH$	10	2-$C_{10}H_7CHO$	92
14	3-$C_9H_6NCH=NOH$[e]	5	3-C_9H_6NCHO	95

[a] The reactions were carried out at r.t. using oxime 1 /0.003 mole/, $TiCl_4$ /0.006 mole/ and NaI /0.006 mole/.

[b] All the products were characterized by comparison of their spectral and physical data with those of authentic samples.

[c] The yields reported are of pure isolated products.

[d] Furfural oxime

[e] 3-Quinolinecarbaldehyde oxime

sulfate solution and water. The solvent was then removed and the crude product was passed through a silica gel column using acetone:hexane /20:1/ as eluent to give pure carbonyl compound 2.

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