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MILD REDUCTIVE DEOXIMATION WITH TiCl,/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 group¹⁻³, 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 equilibrium⁴. 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 aldoximes¹¹.

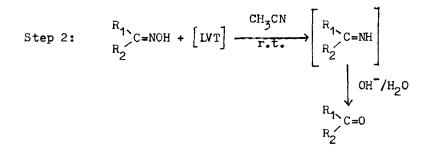
Recently, we reported that the novel TiCl₄/NaI system, generating low-valent titanium is a mild, efficient and selective reagent for deoxygenation of amine N-oxides¹², nitrones¹² or sulfoxides¹³. In this communication, we report the application of this extremaly versatile agent for the reductive cleavage 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 $TiCl_{h}/.$

The reaction can be envisaged to proceed via the mechanism shown in the scheme. In the first step, $TiCl_4$ is probably reduced by the iodide to form a low-valent titanium complex /LVT/. This, according to our earlier studies¹⁴, is able to deoxygenate the substrate 1:

Step 1: TiCl₄ + NaI
$$\xrightarrow{CH_3CN}$$
 [LVT] + I₂



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 (heter) 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-

Product 2^b Yield^C Time Entry Substrate 1 /%/ /min./ n-C7H15CHO n-C7H15CH=NOH 1 20 63 $CH_3/C_2H_5/C=NOH$ CH3/C2H5/CO 2 68 20 $CH_3/C_6H_5/C=NOH$ $CH_3/C_6H_5/CO$ 70 3 20 C6H5CH=NOH C₆H₅CHO 4 5 97 <u>m</u>-/C6H50/C6H4CH0 m-/C6H50/C6H4CH=NOH 10 5 95 m-/CH30/C6H4CH=NOH m-/CH30/C6HLCHO 6 10 92 o-ClC6H4CH=NOH o-ClC6H4CHO 7 10 96 m-BrC6H4CH=NOH 10 <u>m</u>-BrC₆H₄CHO 8 95 2-C4H3OCH=NOHd 2-C4H30CH0 9 10 90 3-C5H4NCH=NOH 3-C5H4NCHO 10 5 97 4-C₅H₄NCH=NOH 4-C5H4NCHO 11 5 95 1-C10H7CH=NOH 10 1-C10H7CH0 12 94 10 2-C₁₀H₇CHO 2-C₁₀H₇CH=NOH 13 92 3-C₉H₆NCH=NOH^e 3-C_OH₆NCHO 14 5 95

Table: Reductive Cleavage of Oximes 1 to the Corresponding Carbonyl Compounds Using TiCl₁/NaI Reagent System^a

^a The reactions were carried out at r.t. using oxime 1 /0.003 mole/, TiCl₄ /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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