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A facile conversion of oximes to their parent carbonyl compounds with sodium chlorite

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ABSTRACT

Oxidative cleavage of oximes to their parent ketones by sodium chlorite as oxidant in acetonitrile at room temperature with high yields is described. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Sodium chlorite; Deoximation; Oxidation; Oxime.

INTRODUCTION

Carbonyl compounds is a important class of compounds in organic synthesis which can be used to prepared many other compounds. But it often compete the reactions with other functional groups for its high reactivity, so we need protect it when reaction and remove protecting groups after the reaction finish.

An approach for the protection of carbonyl is the converting the carbonyl into oxime which are stable in many conditions^[1,2] and would not interfere the reactions of the other functional groups. oxime are easy to prepare with high yield, so the study for removing oximes is of high practicability. Oximes also can be prepared from non-carbonyl compounds^[3,4] so deoximation is a method to prepare carbondyl compounds.

There are many methods for deoximation, for instance hydrolysis, oxidation, reduction, electrochemical and so on. The hydrolysis deoximation^[5] need long reaction time and catalysed by heavy metal compounds. Reductive deoximation^[6,7] is a useful method, but it is easy to obtain amine to reduce yield.

Oxidative deoximation is practical procedure with high yield but some method are not satisfactory, the method using ozone^[8] as oxidant need low temperature(-78°C). The use of $Tl(\phi \acute{0})^{[9]}$ or $(CH_3)_3N(CH_2)_{15}$ CH₂MnO₄^[10] is expensive and toxic.

In the study of prepare nitro compounds from ketoxime, we found sodium chlorite had good effect on deximation. Sodium chlorite is cheap and easy to obtain, so deep study is carried out and satisfactory result are obtained. (The results are shown in TABLE 1).

RESULT AND DISCUSSION

Oxidative deoximation to their parent carbonyl compounds with sodium chlorite in acetonitrile was an effectient and fast method with high yield. The dosage of oxidant had a great infection on yield. When the ratio of oxime and sodium chlorite was 1:1, the oximes did not react completely as there were some side reactions and when the ratio was 1:1.2, the oxime react completely, so the best ratio of oxime and sodium chlorite was 1:1.2.

The reaction rate was slow when the temperature was low, with the temperature run up, the reaction rate was stepped up obviously, in view of the high reactivity of oxidant at high temperature, we choice room temperature($20-25^{\circ}C$) as reaction temperature.

As shown in TABLE 1, the electron-donating

Substrate

N-OH

Entry

1

2

3

4

5

6

7

Br N-OH	1.2	Br	96
O ₂ N N ^{-OH}	2.5	O ₂ N O	84
но-	0.7	но-	*
Н₃С-√М-ОН	0.6	H ₃ C-	86
	0.5	○ =0	88
,OH N ↓	0.5	O	83

9
$$\bigcirc$$
 - CH=N 1 \bigcirc - CHO 42
10 \bigcirc - CH=N OH 0.7 \bigcirc - CHO 83
11 H₃C - \bigcirc - CH=N 1 H C - \bigcirc - CHO 82

groups shorten the reaction time of remove oxime. The electron-withdrawing groups prolonged the reaction time of removing oximes and reduce the yield.

Ketoxime obtain higher yield than aldehydroxime for the aldehyde was easy to be oxidative.

For the strong oxidation of sodium chlorite, the method was not fit to the compounds with fuctional groups susceptible to oxidation.

EXPERIMENTAL

All the used oximes were prepared according to reference^[11] melting points were determined by SGW X-4 apparatus.IR spectra recorded on FTIR-8400S(SHIMADZU)

General procedure of the experiment: a mixture of oximes(0.01mol), ethionine (10ml), sodium chlorite (0.012mol) were put into a 25ml flask, with mechanical stirrer. The reaction was carried through at room temperature and monitored by TCL. The reaction mixture was filtrated, distilled to remove solvent, purified by vacuum distillation or recrystallizition and identified by the comparison of bp or mp and ir with the corresponding carbonyl compounds.

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