Note

Regeneration of carbonyl compounds from oximes, semicarbazones and tosylhydrazones with calcium hypochlorite and moist montmorillonite K-10

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Oximes, semicarbazones and tosylhydrazones are converted into the corresponding carbonyl compounds in the presence of calcium hypochlorite and moist montmorillonite K-10 under mild and heterogeneous conditions.
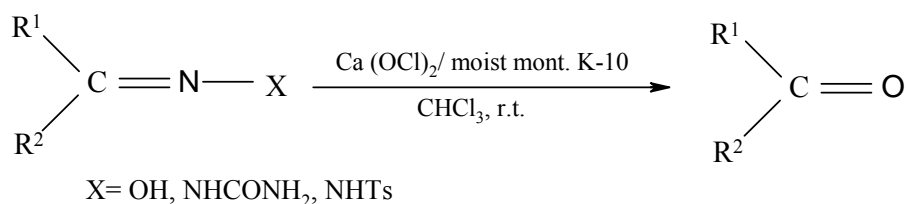
Derivatives of carbonyl compounds such as oximes, semicarbazones and tosylhydrazones are important in organic chemistry. These compounds are very useful for isolation, purification and characterization of aldehydes and ketones[1]. From the synthetic point of view, such derivatives not only serve as protective groups of aldehydes and ketones[2] but also have other uses. For instance, oximes can be prepared from non carbonyl compounds (i.e. Barton reaction[3] or nitrosation of alkenes[4] and enols[5]) and, therefore, deoximation of such oximes provides an alternative method for the synthesis of carbonyl compounds. On the other hand, tosylhydrazones serve as intermediates for the synthesis of olefins[6] and the creation of carbenes[7]. Thus, regeneration of the parent carbonyl compounds from these protecting groups under mild conditions is an important process. Most of the reported methods require strongly oxidative or reducing, acidic or basic media, hazardous or very toxic reagents, long reaction times, and tedious procedures[8-16]. These limitations prompted us to investigate further new convenient methodology for the deprotection of oximes, semicarbazones and tosylhydrazones.

Results and Discussion

Oxyhalogen acids and their organic and inorganic derivatives have been employed as versatile oxidizing and halogenating agents[17]. However, despite the attractive properties of calcium hypochlorite, $Ca(OCl)_2$, including commercially ready availability, good stability, ease of handling, and inexpensiveness, there are a few reports of synthetic applications for this reagent[18].

We describe in this note a simple method for the regeneration of carbonyl compounds from their oximes, semicarbazones and tosylhydrazones (**Scheme I**) using moist montmorillonite K-10 clay. The results illustrated in **Table I** indicate that the reaction is successful for a variety of oximes, semicarbazones and tosylhydrazones. The reaction is carried out by stirring a mixture of the substrate, calcium hypochlorite [substrate: $Ca(OCl)_2$ molar ratio, 2:1], and moist montmorillonite K-10 in chloroform at room temperature for 2-4 hr; the products were obtained through filtration and removal of the solvent. In the case of aldehyde derivatives, the filtrate was washed with 5% sodium hydroxide solution, and the separated aqueous layer was acidified with concentrated hydrochloric acid, extracted with ether, dried (Na_2SO_4), and evaporated to afford traces of carboxylic acids formed during the reaction.

Previously, calcium hypochlorite has been used to transform aldehydes to the corresponding carboxylic acids[18a]; this oxidation was carried out at ambient temperature in aqueous acetonitrile-acetic acid solution for 16 hr. Under our reaction conditions, for example, conversion of benzaldehyde semicarbazone, butyraldehyde semicarbazone, 4-methoxybenzaldehyde semicarbazone, 2,4-dichlorobenzaldoxime, 2-hydroxy-5-bromo-benzaldoxime, and 2-nitrobenzaldoxime to the corresponding aldehydes (**Table I**, entries 2, 9, 10, 15, 16, and 19, respectively) gave respectively, 5.7, 3.8, 6.1, 2.3, 2.5 and 3% of the corresponding carboxylic acid. These results clearly show the greater tendency of calcium hypochlorite for C=N→CHO conversion in comparison to CHO→COOH transformation under our reaction conditions.

X= OH, NHCONH$_2$, NHTs

Scheme I

Table I — Oxidative cleavage of carbon-nitrogen double bonds with Ca(OCl)$_2$/moist mont. K10

Entry	Substrate	Product	Time (hr)	Yield[a] (%)
1	Acetophenone semicarbazone	Acetophenone	2	91
2	Benzaldehyde semicarbazone	Benzaldehyde	2.1	84
3	Propiophenone semicarbazone	Propiophenone	2	91
4	*iso*-Butyl methyl ketone semicarbazone	*iso*-Butyl methyl ketone	2.75	81
5	Cyclohexanone semicarbazone	Cyclohexanone	2.7	85
6	Benzophenone semicarbazone	Benzophenone	2	96
7	Methyl vinyl ketone semicarbazone	Methyl vinyl ketone	3	81
8	2-Pentanone semicarbazone	2- Pentanone	2.75	82
9	Butyraldehyde semicarbazone	Butyraldehyde	2.5	80
10	4-Methoxybenzaldehyde semicarbazone	4- Methoxybenzaldehyde	2.65	85
11	Propiophenone oxime	Propiophenone	2	89
12	Methyl vinyl ketone oxime	Methyl vinyl ketone	3	81
13	Benzaldoxime	Benzaldehyde	2.15	82
14	Benzophenone oxime	Benzophenone	2	94
15	2,4-Dichlorobenzaldoxime	2,4-Dichlorobenzaldehyde	3.3	68
16	2-Hydroxy-5-bromobenzaldoxime	2-Hydroxy-5-bromobenzaldehyde	4	69
17	*iso*-Butyl methyl ketone oxime	*iso*-Butyl methyl ketone	3	81
18	Acetophenone oxime	Acetophenone	2.25	89
19	2-Nitrobenzaldoxime	2-Nitrobenzaldehyde	3.65	76
20	Benzophenone tosylhydrazone	Benzophenone	2	83
21	Cyclohexanone tosylhydrazone	Cyclohexanone	3	59
22	Benzaldehyde tosylhydrazone	Benzaldehyde	2.5	63
23	2-Pentanone tosylhydrazone	2- Pentanone	3	55

[a] Yields are of the pure isolated products.

In conclusion, the reagent combination of Ca(OCl)$_2$ and moist montmorillonite K-10 has proven to be useful for conversion of oximes, semicarbazones and tosylhydrazones to the corresponding carbonyl compounds. Thus, the current system may be added to the list of efficient oxidizing agents in view of the easy availability and low cost of the reagents, operational simplicity, mild conditions, and high yields of the products.

Experimental Section

Oximes, semicarbazones and tosylhydrazones were prepared by known literature procedures[19]. Calcium hypochlorite and montmorillonite K-10 were purchased from Merck company. Addition of distilled water (0.2 g) to carcinated (350ºC, 2hr) montmorillonite K-10 (2 g) in portions followed by vigorous shaking of the mixture for a few minutes upon every addition afforded a free-flowing powder moist montmorillonite. All compounds are known and were identified by comparison of their physical data, IR and ^{1}H NMR spectra with those of authentic samples.

General procedure. A mixture of the neat substrate (2 mmoles), CHCl$_3$ (15 mL), Ca(OCl)$_2$ (1 mmole) and moist montmorillonite K-10 (2 g) was

stirred at room temperature for appropriate time period (**Table I**). After completion of the reaction (monitored by TLC, *n*-hexane- pet. benzene- AcOEt; 2:2:1), the reaction mixture was filtered and the solid residue was washed with $CHCl_3$ (20 mL). Evaporation of the solvent, followed by column chromatography on silica gel, gave the corresponding carbonyl compounds.

Acknowledgement

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