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Antimony Pentachloride-Promoted Regeneration of Carbonyl Compounds from Oximes¹

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Abstract: A simple and convenient method for the cleavage of oximes to their parent aldehydes and ketones using antimony pentachloride is described.

Key words: oximes, antimony pentachloride, cleavage reaction

Oximes are extensively used as preferred derivatives for purification and characterization of carbonyl compounds.¹ The synthesis of oximes from non-carbonyl compounds² (Barton reaction) provides an alternative pathway to aldehydes and ketones. The highly stable and readily prepared oxime derivatives play an important role in synthetic organic chemistry as protecting³ and selectively α activating⁴ groups, and for the preparation of amides via Beckman rearrangement.⁵ Therefore, there has been a continued interest in the developments of procedures for the effective regeneration of carbonyl compounds from their corresponding oximes. So far a good number of methods based on hydrolytic⁶ (acid-catalyzed), reductive⁷ and oxidative,8 clay-supported9 ferric nitrite, and microwave assisted¹⁰ reactions have been developed for regeneration of parent carbonyl compounds. Most of them are non-catalytic and require long reaction times, reflux temperature or permitted to only aldehydes. The discovery of newer, convenient, widely applicable and efficient methods is the goal of the organic chemists. In view of the current thrust on catalytic processes,11 there is a merit in developing a truly catalytic cleavage of oximes using inexpensive and mild reagents. The use of SbCl₅ as an efficient Lewis acid for the Friedel-Crafts reactions is well documented in the literature.¹²

Herein we wish to report that antimony pentachloride is a new and efficient catalyst for the cleavage of oximes under mild reaction conditions (Scheme 1).



Thus, the treatment of 3,4,5-trimethoxybenzaldoxime (1a) with SbCl₅ at ambient temperature gave the 3,4,5-trimethoxybenzaldehyde (2a) in 92% yield (Scheme 1). Similarly, various oximes were converted into their respective carbonyl compounds in 75–92% yields. The reaction proceeds efficiently in high yields at room temperature within a short period of 2–3 hours. The results summarized in Table 1 reveal the scope and generality of the reaction with respect to various oximes. We propose the mechanism given in Scheme 2 for the cleavage reaction.



Scheme 2

In conclusion, we have demonstrated a novel and highly efficient protocol for the regeneration of carbonyl compounds from their oximes using SbCl₅. The method offers several advantages over existing procedures, such as the ready availability of SbCl₅ at low cost, high yields of products, short reaction times, simple experimental and work-up procedures, which makes it a very useful and attractive process for the cleavage of oximes.

Regeneration of Carbonyl Compounds from Oximes; General Procedure

To a stirred ice-cold solution of oxime (10 mmol) in CH_2Cl_2 (15 mL) was added slowly $SbCl_5$ (0.5 mL) with a syringe and the stirring was continued for 2–3 h at r.t. After disappearance of the starting material as indicated by TLC, the reaction mixture was poured into ice water (30 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The organic layer was washed with H_2O , dried (Na₂SO₄) and the solvent was removed in vacuo to afford the crude product, which was purified by column chromatography on silica gel (Merck, 60–120 mesh) (Table 1).

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 Table 1
 Regeneration of Carbonyl Compounds with SbCl₅

Entry	Substrate ^a	Product ^b	Time (h)	Yield (%) ^c
a	MeO MeO OMe	MeO MeO MeO OMe	2.0	92
b		O ₂ N H	2.15	80
c	N-OH		3.0	80
d	N ^{OH} H	MeO	2.30	85
e	MeO' ∽ N [_] OH	о Н	2.30	87
f	N-OH CH3	СН3	2.45	82
g	✓ N·OH	() ⁰	3.0	80
h	∨ N ^{OH} ⊕ ^Щ н	О () ₆ н	3.0	75
i	N-OH		2.45	78
j	N ^{OH} H	O H	2.30	75
k	N-OH H	CI CI	2.0	88
1		C O H	3.0	78
m		√ O H O	2.30	75
n	N OH	F H	2.45	80
0	F´ >> N_OH		2.30	82

^a All substrates were prepared by known literature procedures.

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^b All products were characterized by comparison of their mps, IR and

¹H NMR spectra with those of authentic samples.

^c Yields refer to isolated pure products.