

NOTE

Oxidation of Alcohols to Aldehydes and Ketones by HIO_3 in Presence of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$

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Different types of alcohols are efficiently converted to their corresponding aldehydes and ketones with HIO_3 in presence of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$. All reaction was performed in CH_3CN medium in good to high yields.

Key Words: Iodic acid, Alcohols, Aldehydes.

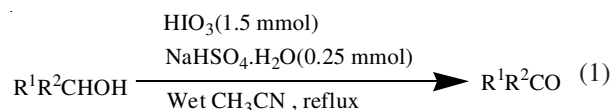
Aldehydes and ketones represent an important class of products and intermediates in the fine chemical and specialties¹. The mild oxidation of alcohols is an important transformation in organic synthesis and numerous methods using a variety of reagents and conditions have been explored²⁻⁴. Some of this method involves the use of expensive reagents, long reaction times, low yields of products and tedious work-up. Therefore, introduction of new methods and reagents for such functional group transformation is still in demand.

Application of solid acids in organic transformation have very important role because, solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems and more environmental safe disposal. Also wastes and by-products can be minimized or avoided by developing cleaner synthesis routes^{5,6} among solid acid, oxidation of alcohols with periodic acid with various catalysts has been well documented. In recent years, periodic acid has been employed for oxidation of alcohols with various catalysts such as pyridinium fluorochromate, pyridinium chlorochromate, chromium(III) acetylacetonate and Fe(III)/2-picolinic acid^{7,8}.

To the best of our knowledge all of the reported above mentioned catalysts have toxic transition metal cations or reaction condition is harsh. Therefore, we decided to choose safe and cheap catalyst for activation of periodic acid and iodic acid under mild condition.

In continuation of our studies on application of metal hydrogen sulfates in promotion of organic reaction^{9,10} and also

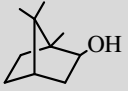
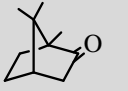
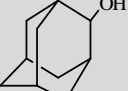
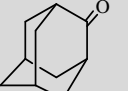
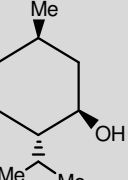
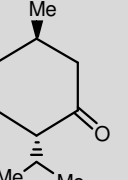
using HIO_3 in organic transformations^{11,12}, we have found that HIO_3 in the presence of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ can be oxidized alcohols to aldehydes and ketones under mild reaction conditions. In present study, we wish to report an efficient, simple and low cost method for oxidation of the above mentioned substrates to aldehydes and ketones using $\text{HIO}_3/\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ reagent system in CH_3CN medium. All reaction were performed under mild conditions in good to high yields (eqn. 1). Yields and reaction times are shown in (Table-1).



We tried to convert alcohols to their corresponding aldehydes and ketones in good to high yields. In all cases no other oxidation products were observed.

To a solution of substrate (1 mmol) in CH_3CN (3 mL), which is moisture with a drop of water, were added HIO_3 (1.5 mmol, 0.264 g) and $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.25 mmol, 0.035 g) and refluxed for the appropriate time (Table-1). The progress of the reaction was monitored by TLC. When the reaction was complete the mixture was filtered. The solid residue was washed with CH_3CN (5 mL). The solvent was evaporated and the residue was triturated with H_2O (10 mL). The product was extracted with diethyl ether (3 × 5 mL) the combined organic solution was dried over MgSO_4 and filtered. Evaporation of solvent followed by column chromatography on silica gel gave the corresponding carbonyl compounds in good to high yields.

TABLE-1
OXIDATION OF ALCOHOLS TO THEIR CORRESPONDING
CARBONYL COMPOUND USING HIO_3 IN THE
PRESENCE OF $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$

Entry	Substrate	Product	Time (h)	Yield (%)
1	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	$\text{C}_6\text{H}_5\text{CHO}$	1.5	90
2	$2\text{-ClC}_6\text{H}_4\text{CH}_2\text{OH}$	$2\text{-ClC}_6\text{H}_4\text{CHO}$	1.8	95
3	$4\text{-ClC}_6\text{H}_4\text{CH}_2\text{OH}$	$4\text{-ClC}_6\text{H}_4\text{CHO}$	0.9	95
4	$2\text{-BrC}_6\text{H}_4\text{CH}_2\text{OH}$	$2\text{-BrC}_6\text{H}_4\text{CHO}$	1.25	92
5	$4\text{-BrC}_6\text{H}_4\text{CH}_2\text{OH}$	$4\text{-BrC}_6\text{H}_4\text{CHO}$	1.5	90
6	$2\text{-MeC}_6\text{H}_4\text{CH}_2\text{OH}$	$2\text{-MeC}_6\text{H}_4\text{CHO}$	4.80	95
7	$\text{tBut-C}_6\text{H}_4\text{CH}_2\text{OH}$	$\text{tBut-C}_6\text{H}_4\text{CHO}$	1.6	95
8	$4\text{-Me}_2\text{CHC}_6\text{H}_4\text{CH}_2\text{OH}$	$4\text{-Me}_2\text{CHC}_6\text{H}_4\text{CHO}$	1.0	90
9	$4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{OH}$	$4\text{-MeOC}_6\text{H}_4\text{CHO}$	4.0	^c
10	$2\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	$2\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$	6.0	50
11	$3\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	$3\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$	8.3	50
12	PhCH(OH)Ph	PhCO Ph	1.5	70
13	$\text{Me-PhCOCH(OH)Ph-Me}$	Me-PhCOCOPh-Me	4.0	^c
14	PhCH(OH)CH_3	PhCOCH_3	1.3	90
15	$\text{PhCH(CH}_3\text{)CH}_2\text{OH}$	$\text{PhCH(CH}_3\text{)CHO}$	1.5	90
16			5.0	95
17			4.0	92
18			4.6	95

^aProduct were characterized by their physical constant, comparison with authentic samples and IR and NMR spectroscopy; ^bIsolated yield; ^cMixture of products

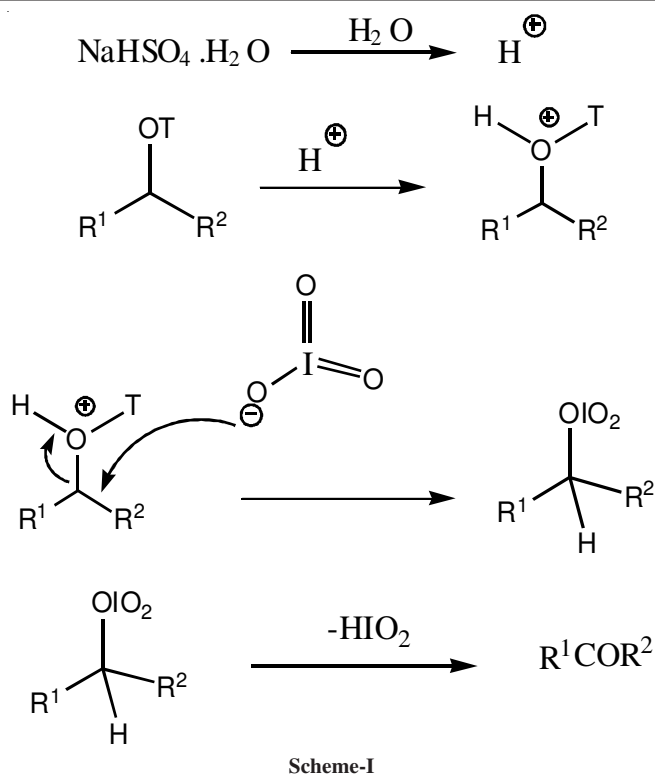
Spectra and physical data of some of the products

Benzaldehyde: Colourless liquid; IR (neat): $\nu = 1700 \text{ cm}^{-1}$; $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): $\delta = 7.48\text{-}7.52$ (m, 2H), $7.60\text{-}7.65$ (m, 1H), $7.85\text{-}7.90$ (m, 2H), 9.95 (s, 1H).

Chlorobenzaldehyde: White solide: m.p. = $45\text{-}46 \text{ }^\circ\text{C}$; IR (KBr): IR (neat): $\nu = 1703 \text{ cm}^{-1}$; $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): $\delta = 7.55$ (d, $J = 7.8 \text{ Hz}$, 2H), 7.85 (d, $J = 7.8 \text{ Hz}$, 2H), 9.95 (s, 1H).

It is important to note that reaction of alcohols with HIO_3 in the absence of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ produces undesirable product. This observation suggests the important role of sodium hydrogen sulfate monohydrate in the promotion of the oxidation reactions, and presence of water is essential for such process.

These studies clearly reveal that the described method is a suitable catalytic procedure for oxidation of benzylic and aliphatic alcohols. A plausible mechanism for the oxidation is shown in **Scheme-I**.



Conclusion

The low cost and availability of the reagents, easy and clean work-up and yields make this method suitable for multi-step synthetic chemistry. It is believed that the present methodology could be an important addition to existing methodologies.

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