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Transformation of Allylic and Benzylic Oximes to Their Carbonyl Compounds with Zinc Bismuthate $Zn(BiO_3)_2$[1]

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Abstract:

Benzylic and allylic oximes are selectively oxidized with zinc bismuthate in refluxing toluene or the mixture of acetonitrile-toluene to afford the corresponding carbonyl compounds.

Oximes can be prepared from non-carbonyl compounds[2-6]. Therefore, their transformation to aldehydes and ketones is important.

Acid hydrolysis of oximes to ketones and aldehydes is unsatisfactory and the method is not suitable for acid sensitive compounds[7]. Therefore, development of new methods which work under non-aqueous and aprotic condition is of synthetic importance. For this purpose several oxidative methods have been developed[7-12].

Table

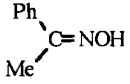
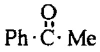
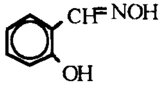
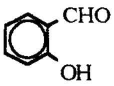
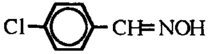
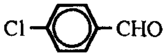
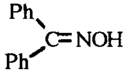
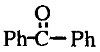
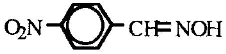
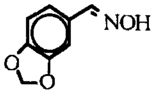
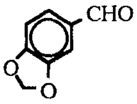
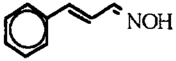
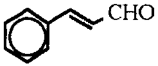
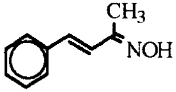
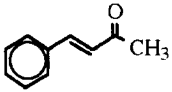
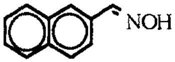
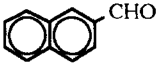
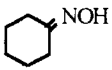
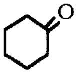
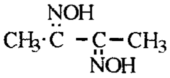
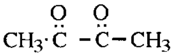
	Substrate	Product	Oxid/React	Rxn Time (hr)	Yield% (ZB)	Yield% (BPM)	Yield% (PCC)	Yield% (HSCT)
1	PhCH:NOH	PhCHO	2	1	75	85	56	72
2		 $Ph\cdot\overset{O}{\overset{\|}{C}}\cdot Me$	2	0.5	80	75	55	-
3			2.5	0.4	70	60	-	-
4			2	1	65	80	-	79
5		 $Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ph$	2	1	85	80	-	65
6			3	1	72	-	-	79
7			3	1.5	70	60	-	-

Table continued

8			3	1.5	65	-	-	-
9			3	1	56	-	-	-
10			2.5	1	56	-	-	-
11			2.5	3	10-15	trace	47	45
12	 $CH_3\cdot\overset{NOH}{\ddot{C}}-\underset{NOH}{\underset{..}{C}}-CH_3$	 $CH_3\cdot\overset{O}{\ddot{C}}-\overset{O}{\ddot{C}}-CH_3$	2	2	0	-	-	-

However, deoximation using pyridinium chlorochromate (PCC)[8] suffers from long reaction time (12-94h), low yields and low selectivity. Hydrogen peroxide-(PCC) system is not suitable for aldoximes and over oxidation products are usually produced and shows low selectivity as well[7]. The other oxidants; supported dichromates[13] and triethylammonium chlorochromate[14] are also used for the same transformation. All these methods show low selectivities for different types of oximes.

Recently we have introduced barium permanganate[15] as a useful oxidant for the selective deoximation of benzylic oximes to their corresponding carbonyl compounds.

Very recently, zinc bismuthate as a mild, stable, and easily prepared oxidant is introduced[1]. This reagent is able to affect selectively and efficiently different functional groups.

Now in this communication we wish to report that zinc bismuthate is also able to convert selectively benzylic and allylic oximes to their corresponding carbonyl compounds in refluxing toluene or toluene/acetonitrile mixture in good yields (56-85%). This method is a useful addition to the present methodologies for the transformation of oximes under non-aqueous and aprotic conditions. Our results with zinc bismuthate (Table) are compared with some of those reported with barium permanganate[16] (BPM), pyridinium chlorochromate (PCC)[8,17], and halosilanes/chromium trioxide (HSCT)[10].

EXPERIMENTAL

Preparation of Zinc Bismuthate Zn(BiO$_3$)$_2$ [1]

To a suspension of sodium bismuthate (20 g, 34.54 mmol) in water (30 ml) a solution of (15% by weight) zinc chloride hexahydrate (300 ml) was added and the resulting mixture was refluxed for 1.5 hrs. The reaction mixture was filtered and the solid material was isolated. The solid brown material was washed first with hot water (100 ml) and then with acetone (100 ml) and dried further over calcium chloride in a desiccator to afford zinc bismuthate; yield 20.5 g, 99%.

General Procedure for Oxidation of Oximes to Their Corresponding Carbonyl Compounds with Zinc Bismuthate (ZB).

In a round-bottomed flask (50 ml) equipped with a condenser and a magnetic stirrer, a solution of oxime (1 mmol) in toluene or in mixture of toluene-acetonitrile (15-20 ml) was prepared. The oxidant, zinc bismuthate, (2-3 mmol) was added to the solution and refluxed for 0.5-2 hrs. The progress of the reaction was monitored by t.l.c. (eluent: CCl_4/ether). The reaction mixture was filtered and the solid material was washed with acetonitrile (20 ml) and carbon tetrachloride (20 ml).The combined filtrates were evaporated to afford crude products. Purification of crude products with a silica gel plate or silica gel column afforded pure products in (56-85%) yields.

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