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Research Paper

Active MnO_2 As a Mild Oxidizing Reagent for the Controlled Oxidation of Benzylic and Allylic Alcohols

Chemistry

KEYWORDS : oxidation, alcohols, aldehydes, active MnO_2

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ABSTRACT

Oxidation of benzylic and allylic alcohols to their corresponding aldehydes was achieved by active MnO_2, which is prepared in situ from $KMnO_4$ and sodium hydroxide. The reaction condition is very mild and the yields of the products are excellent. The reaction was carried out in neutral solvent (petroleum ether) and the heterogeneous catalyst furnished good results.

Introduction

Use of MnO_2 as an oxidizing reagent is directed towards the syntheses of Substituted acroleins, vinyl ketones and aromatic aldehydes[1,6]. Pyridinium chlorochromate[2,7] can be used for the partial oxidation of primary alcohols to their corresponding aldehydes. The Jone's reagent also oxidizes primary allylic alcohols to the corresponding aldehydes[3]. Collin's reagent also provides other alternative path for the oxidation of primary alcohols[4]. Since aldehydes are labile to oxidizing conditions, they are distilled as soon as they are formed in the reaction pot. These reagents are effective but very costly as compared to MnO_2. These oxidizing reagents are highly reactive and nonselective for functional group interconversions. Dimethyl sulphoxide, Corey's reagent, ceric ammonium nitrate are known to be convert primary alcohols to aldehydes[5]. Active MnO_2 is a brown black solid, extensively used as an oxidizing reagent in organic synthesis. This reagent is highly efficient although it is a heterogeneous reagent. The MnO_2 can be prepared by carbon reduction of aqueous $KMnO_4$ solution. The brown-black MnO_2 is filtered, dried at 105-110 °C for 8-24 hours prior to use. Active MnO_2 is alternatively prepared by heating Manganese Carbonate/oxalate at 220-280 °C in air. The MnO_2 thus formed is washed with dilute nitric acid, water and dried at 110 °C in an oven.

Result and discussion

In the reported method, we have prepared the active MnO_2 from aqueous $KMnO_4$ solution and aqueous sodium hydroxide. The MnO_2 thus obtained is washed with water, till it is free of purple colour. It is then dried at 110-120 °C prior to use. This reagent is brownish-black powder and is highly effective for the oxidation of primary/benzylic/allylic alcohols to their corresponding carbonyl compounds i.e. aldehydes/ketones in excellent yields. The aldehydes thus formed are converted to their 2,4 dinitrophenyl hydrazone derivatives.

Experimental Section

0.250 g of pure benzyl alcohol is taken in 50 mL pet ether. This solution is shaken at room temperature for 4 hours with 0.2 g of MnO_2. The reaction mixture is filtered and the evaporation of pet ether furnished an aldehyde, which is converted into its 2,4 dinitrophenyl hydrazone derivative. The 2,4 dinitrophenyl hydrazone derivative was crystallized from ethanol. This method is very mild and highly selective. It can be used as it is, to various alcohols for partial oxidation purpose.

These derivatives are high melting solids and are characterized by IR and PMR, spectroscopic methods. The results are summarized in Table 1

Table 1 Oxidation of various alcohols

Sr. No.	Alcohol	Reaction Time (hours) at RT	% yield	Melting Point
1	Benzyl alcohol	4	82	236
2	Cinnamyl alcohol	5	86	254
3	m-Nitro benzyl alcohol	8	84	292
4	p-chloro benzyl alcohol	5	80	266
5	m-nitro benzyl alcohol	8	85	293

Spectroscopic data

IR and PMR data for 2,4 DNP derivative of benzaldehyde
MF – $C_{13}H_{10}N_4O_4$,
TLC (Rf) 0.15 pet ether
Yield 82%
Melting Point 236 °C
IR cm^{-1} 690, 827, 929, 1087, 1170, 1272, 1512, 1587, 1614, 3286
PMR ($CDCl_3$) 11.15,9.1,8.2,7.8,7.3,7.2 ppm
Cinnamyl aldehyde 2,4 DNP derivative.
IRcm^{-1} 513, 613, 746, 920, 1085, 1132, 1504, 1616, 1674, 3284
PMR ($CDCl_3$) 7.2-7.5, 9.6, 9.75, 11.1 ppm

Conclusion

The present method provides an excellent route for the oxidation of benzyllic and allylic alcohols. This method can be utilized for the oxidation of various organic compounds with variety of functionalities other than allylic and bezyllic carbons.

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