

Chemistry congress: 2018 Nitric Acid Assisted In Situ Generation of BrOH: A Selective Catalyst for Oxidation of Benzylic Alcohols- Subbarayappa Adimurthy

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Aerobic oxidation is catalyzed by hypobrominated acid generated in situ by nitric acid (15% by mole%) to benzylic alcohols in which the metal is described without aqueous conditions. Nitric acid plays a dual role as an "H + " donor and as a secondary oxidant to a convert bromide to a reactive species (BrOH) in the presence of molecular oxygen.

The oxidation of alcohols to carbonyl compounds is one of the most important and fundamental transformations of functional groups in synthetic organic chemistry. To date, many excellent catalytic methods have been developed for the oxidation of benzyl alcohols. Oxidation is catalyzed by a transition metal or a nitroxyl radical of alcohols to aldehydes or ketones. Alternating metallic catalysts, halogenated species (Cl, Br and I) are frequently used for the oxidation of alcohols. Numerous methods have been reported for the oxidation of alcohols with a variable amount (2 to 40 mol%) of bromine or bromine-based catalysts.

In addition, there are halogens or useful halide derivatives such as oxyhalogenated bromine and iodine compounds. and N-halosuccinimides. are reported for the oxidation of alcohols. Oxone has been used as an attractive oxidant and offers several advantages such as non-toxic nature, controlled addition, stability, easy handling and ease of transport. However, molecular oxygen and aqueous H₂O₂ are more environmentally friendly and economical than oxidants. Most of the alcohol oxidation protocols are based on transition metal catalysts, which suffer from multiple limitations, such as inert reaction atmosphere, temperature catalyst, high-cost precious metals, the use of co-catalysts and the elimination of reactions. with low environmental acceptance. On the other hand,

All commercially available chemicals and reagents were used without further purification, unless otherwise noted. The ¹H and ¹³C NMR spectra were recorded at 200 and 125 MHz. The spectra were recorded in CDCl₃ as solvent. The multiplicity has been as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), sp (septet) etc. and the coupling constants (J) were given in Hz. The chemical shifts are reported in ppm relative to the TMS as an internal standard. The ¹H NMR and ¹³C NMR delta values correspond to a deuterated solvent CDCl₃. The reactions of The Progress were

monitored by thin layer chromatography (TLC). All the products were purified by column chromatography using 100 to 200 mesh silica gel using hexane.

In a 25 ml round bottom flask, 2 mmol of benzyl alcohol (1 a), 10 mol% of NaBr / NaBrO₃ 5: 1 pair and 2 ml of dioxane / water (10: 1) were placed. To this reaction flask, 15 mol% of HNO₃ (27 mg) was added. The reaction flask was placed in an oil bath at 80 ° C with a condenser and maintained under stirring for 12 hours, after which the reaction mixture was left at room temperature, then extracted with 3 x 25 ml of ac 'ethyl and dried over. anhydrous sodium sulfate. Removal of the solvent under reduced pressure, the residue left behind was subjected to column chromatography on silica gel (200-400) and hexane / ethyl acetate as eluent, which gave an isol% yield of benzaldehyde.

A possible mechanism for the current transformation. Bromide-bromate and acid (H +) generate bromine in situ, under aqueous conditions, which are disproportionate to HBr and BrOH. BrOH is found to act as a mild and selective oxidizing agent for a number of organic substrates

Benzyl alcohol is used as a general solvent for inks, waxes, shellacs, paints, lacquers and epoxy resin coatings. Thus, it can be used in paint strippers, especially when combined with composite viscosity enhancers to promote the use of painted surfaces. It is a precursor to a variety of esters and ethers, used in the soap, perfume and aroma industries. For example. benzyl benzoate, benzyl salicylate, benzyl cinnamate, dibenzyl ether, benzyl butyl phthalate.

It is also used in e-liquids to enhance e-cigarettes to savers. When applied to damaged skin or mucous membranes with a concentration of 10%, it acts as a local anesthetic and antimicrobial agent. It can be used as a degreaser in carpet cleaning products. As a dyeing solvent, it is most likely the dyeing process for wool, nylon and leather. It is also used as a photographic film developer and as an insect repellent. Benzyl alcohol has almost the same refractive index as quartz and wool fiber. If a clear quartz object is immersed in benzyl alcohol, it becomes almost invisible. This test was used to determine if non-destructively an object is actually a quartz.