Potassium iodate as a new reagent for the synthesis of benzaldehyde from benzyl alcohol

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Abstract

A novel reagent for the synthesis of benzaldehyde from benzyl alcohol is reported in this study. A metal free benign and an easily available cost effective agent act for direct conversion of alcohol to aldehyde in a simple way.

Keywords: Benzaldehyde, benzyl alcohol, potassium iodate.

Introduction

Selective oxidation of benzyl alcohol to produce benzaldehyde is an important reaction in the synthetic organic chemistry due to the importance of aromatic aldehydes as important scaffolds for many organic reactions. Aromatic aldehydes have gained more importance because of their applications in the synthesis of potent antimicrobial agents[1,2], anticancer agents[3], food additives, fragrances[4] and they also act as important scaffolds for liquid crystalline compounds[5,6].

Researchers have reported several methods for the direct conversion of alcohols to aldehydes viz. [$CuBr_2$(2,2A-bipyridine)] was used as catalyst in presence of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)[7], photocatalytic oxidation in presence of TiO_2 under O_2 atmosphere[8], periodinane[9], nanoparticles of Au dispersed on Al_2O_3support[10], Au/Pd-TiO_2 was also reported as catalyst.[11] Alcohols were oxidised using CH_2Cl_2 in presence of NaOCl and 4-methoxy-2,2,6,6-tetramethylpiperidine-l-oxyl[12], TEMPO in presence of [bis(acetoxy)iodo]benzene (BAIB)[13], Au/CeO_2 with various Au contents examined for the oxidation step[14] and $RuCl_2(PPh_3)_3$ in combination with TEMPO. Dijksman et al also postulated a mechanism involving hydridometal with $RuH_2(PPh_3)_3$ species as catalyst[15], 2-Iodoxybenzenesulfonic acid catalysed oxidation[16], TEMPO in presence of oxone and catalytic amount of quarternary ammonium salts as oxidizing agent.[17] Carbon-supported platinum catalysts for selective oxidation of alcohols at 100°C in dioxane medium were reported[18], dialdehyde was formed by oxidation of hydroxymethylfurfural using dioxygen and metal bromide (Co/Mn/Br, Co/Mn/Zr/Br; Co/Mn=Br/(Co+Mn)[19].

In addition, ultrasonic method in presence of H_2O_2 and a PTC is also reported[20]. Several methods using nano rods[21] and nano particles like gold supported on uranium oxide[22] have been reported.

Furthermore, TiO_2/Cu(II) as catalyst in solar pilot plant reactor[23], bimetallic catalysts gold–copper in combination supported on silica[24], non- noble transition metals hydrotalcite-like solid[25] and sulphonato-salen-chromium(III) hydrotalcites catalysts have been studied.[26] Interestingly, benzaldehyde was also produced by Mushroom Polyporustuberaster K2606[27], yeasts and Botrytis cinerea isolated from grape musts and wines[28]. All the above reported methods have the disadvantages of use of expensive compounds and nanomaterials. We have reported a simple method for the oxidation of alcohols to aldehydes using a simple metal free reagent KIO_3.

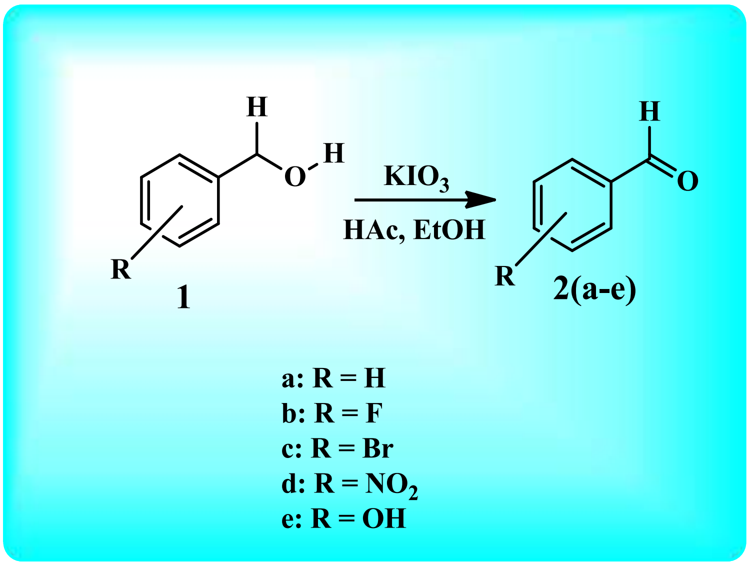

Figure 1: Synthetic pathway

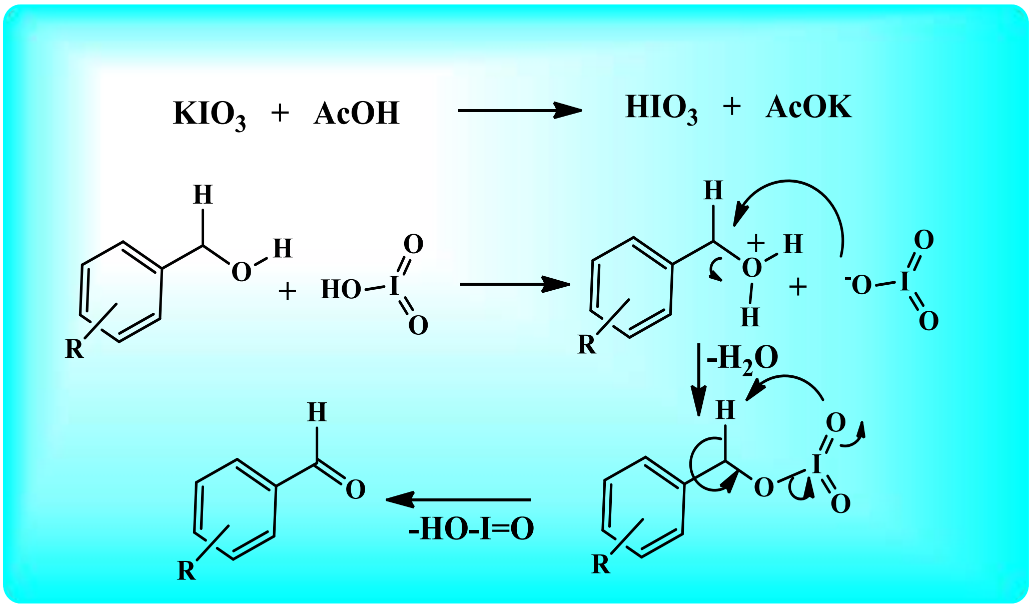

Figure 2: Scheme indicating probable mechanism

Scheme of synthesis: This method avoids the maintenance of inert atmosphere, and other difficulties encountered in the reported methods like need for excessive reagents, preparation of the complicated reagents, difficult work up.

Probable mechanism for the formation of product: *In situ* generated iodic acid undergoes esterification with alcohols which undergo disproportionation leading to the formation of aldehyde as shown in the figure 2.

Material and Methods

Benzyl alcohol was procured from RANKEM, India. Potassium iodate was procured from Merck India. Sodium sulphate, glacial acetic acid and diethyl ether were procured from SRL India, and ethanol was obtained from Changshu Yangyuan Chemical, China.

The proposed structure of product was confirmed by ^{1}H-NMR analysis carried out on AGILENT (400 MHz) NMR spectrometer, the deuterated solvent for the analysis was obtained from Sigma Aldrich, USA. The purity and formation of product were confirmed by thin layer chromatography carried out on plates obtained from Merck.

General procedure for synthesis (2a-e): Derivatives of benzyl alcohol (1mmol) were dissolved in ethanol, catalytic amount (3-4drops) of glacial acetic acid was added and to it oxidizing agent KIO_3 (1.2mmol) was added and it was refluxed for 8-10hours. Completion of the reaction was checked by TLC. After the completion of the reaction, the solvent was removed and the product was extracted into diethyl ether, the extract was washed with saturated sodium bisulphite solution.

The aqueous layer after acidification with dilute sulphuric acid, was extracted into ether, washed with water and then with brine solution and the organic layer was dried over anhydrous sodium sulphate and the crude product was purified by recrystallization. TLC and the NMR spectrum were compared with authentic samples and were found to be same. Mixed TLC was performed to confirm the formation of the desired product. The boiling point of the synthesized compound was found to be 178^{O}C. Yield: 78%.

Benzaldehyde 2a: Molecular formula: C_7H_6O
FTIR (cm^{-1}): 2821, 1697, 1598. **^{1}H NMR (400MHz, $CDCl_3$):** δ 10.010 (s, 1H), 7.870 (d, 2H, ArH, J = 8.8 Hz), 7.624 (t, 1H, ArH, J = 8.0 Hz), 7.512 (t, 2H, ArH, J = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100MHz) δ:** 192.455, 136.357, 134.470, 133.672, 130.150, 129.742, 128.457. **LCMS:** 107.177 [M+1] **Elemental Analysis:** C-79.18; H- 5.31.

4-fluorobenzaldehyde 2b: Molecular formula: C_7H_5FO
FTIR (cm^{-1}): 3016, 1710, 1610. **^{1}H NMR (400MHz, $CDCl_3$):** ∂ 9.956 (s, 1H), 7.582 (d, 2H, ArH, J = 8.0 Hz), 7.187 (d, 2H, ArH, J = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100MHz) δ:** 190.425, 167.803, 165.253, 132.971, 132.243, 116.435, 115.760. **LCMS:** 125.13 [M+1] **Elemental Analysis:** C-67.56; H- 4.02.

4-bromobenzaldehyde 2c: Molecular formula: C_7H_5BrO
FTIR (cm^{-1}): 2962, 1698, 1565. **^{1}H NMR (400MHz, $CDCl_3$):** ∂ 9.959 (s, 1H), 7.731 (d, 2H, ArH, J = 6.8 Hz), 7.668 (d, 2H, ArH, J = 6.8 Hz). **^{13}C NMR ($CDCl_3$, 100MHz) δ:** 190.964, 135.096, 132.417, 130.922, 129.731. **LCMS:** 184.22 [M+1] **Elemental Analysis:** C- 45.31; H- 2.45.

4-nitrobenzaldehyde 2d: Molecular formula: $C_7H_5NO_3$
FTIR (cm^{-1}): 2821, 1697, 1598. **^{1}H NMR (400MHz, $CDCl_3$):** ∂ 10.140 (s, 1H), 8.370 (d, 2H, ArH, J = 8.8 Hz), 8.060 (d, 2H, ArH, J = 8.8 Hz). **^{13}C NMR ($CDCl_3$, 100MHz) δ:** 190.425, 167.803, 165.253, 132.971, 132.243, 116.435, 115.540. **LCMS:** 152.18 [M+1] **Elemental Analysis:** C-55.42; H- 3.26.

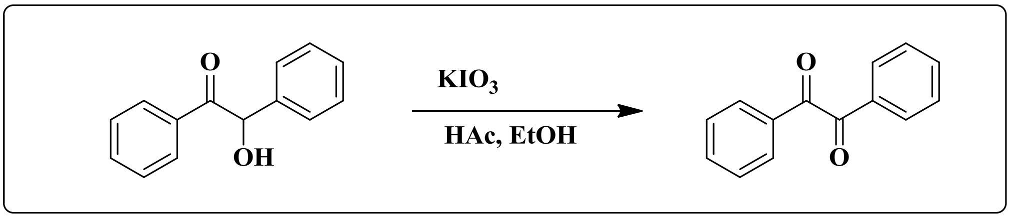

Figure 3: Scheme for conversion of benzoin to benzil

4-hydroxybenzaldehyde 2e: Molecular formula: $C_7H_6O_2$ FTIR (cm^{-1}): 3342, 1697, 1597, 1056. **^{1}H NMR (400MHz, $CDCl_3$):** ∂ 9.849 (s, 1H), 7.813 (d, 2H, ArH, J = 8.8 Hz), 6.977 (d, 2H, ArH, J = 8.8 Hz), 6.421 (s, 1H, -OH). **^{13}C NMR ($CDCl_3$, 100MHz) δ:** 191.278, 161.663, 132.524, 129.761, 115.994. **LCMS:** 123.24 [M+1] **Elemental Analysis:** C- 68.41; H- 4.71.

Application of the above proposed oxidizing agent: One of the applications of the above mentioned method is the conversion of benzoin to benzyl; this was obtained in good yields of about 90% and with good purity. Other applications are under study.

Conclusion

A cost effective, feasible, benign metal free oxidizing agent is reported for the oxidation of alcohols to aldehydes.

This new oxidizing agent will definitely find its way in the lot of organic reactions which avoid the use of expensive chemical compounds and inert atmosphere.

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