

Environmental Friendly Conversion of Organic Compounds with H₂O₂ In The Presence Of Iridium (iii)

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Abstract: The aromatic aldehydes viz. p-chlorobenzaldehyde, p-hydroxy benzaldehyde, p-nitrobenzaldehyde, p-methoxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and benzaldehyde dissolved in aqueous acetic acid, were oxidized in quantitative to good yields by 50% H₂O₂ in presence of traces of IrCl₃. Conditions for highest yields, under most economical conditions, were obtained. Higher catalyst concentrations decrease the yield. Oxidation in aromatic aldehydes is selective at aldehydic group only, and other groups remain unaffected. In this new, simple and economical method, which is environmentally safe and requires less time, [IrCl₃H₂O]²⁻ species of iridium (III) probably catalyze the oxidation.

Key Words: aromatic aldehyde, benign, catalyst, hydrogen peroxide, iridium (III) chloride, oxidation.

I. Introduction

From the synthetic point of view, a large number of oxidants¹⁻⁵ have frequently been used for the oxidation of organic compounds. Instead of commonly used oxidants, which are harmful to the environment and require severe conditions, hydrogen peroxide is safer, cheaper and has high active oxygen content, and it does not require a buffer and is clean since the by-product formed is water. It has been used for the oxidation of aromatic aldehydes to carboxylic acids under strongly basic conditions⁶, epoxidation of olefins⁷, hydroxylation of aromatic with AlCl₃⁸, oxidation of benzyl chlorides⁹, aromatic aldehydes by magnesium monoperoxyphthalate etc¹⁰. Recently, conversion of aromatic and aliphatic aldehyde to carboxylic acid in organic solvent, halide- and metal-free conditions with [CH₃ (n-C₈H₁₇)N] HSO₄ (PTC)¹¹ and benzyl alcohol to benzaldehyde under halide-free conditions in the presence of PTC¹² have been reported. Ruthenium catalyzed oxidation of alcohols by H₂O₂¹³, by peracetic acid¹⁴, under PTC conditions and in the presence of bimetallic catalyst¹⁵ has also been reported, but the systems containing dimethyl sulfate, which is used to prepare PTC, are reported to be carcinogenic¹⁶. Homogeneous catalysis by ruthenium and osmium compounds has been reported by several workers but the use of iridium (III) chloride as homogeneous catalyst in acidic medium has not yet been reported. In the present system good yield is obtained with substrate catalyst ratio ranging from 85400 to 341250:1 and it oxidizes a wider range of organic compounds, and it is a more convenient, eco-friendly and economical compared to many other systems. To explore the potential of the present system for conversion of various other groups in aqueous acetic acid medium, here in the oxidation of p-chlorobenzaldehyde, p-hydroxybenzaldehyde, p-nitrobenzaldehyde, p-methoxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and benzaldehyde by 50% H₂O₂ in the presence of traces of iridium (III) chloride is reported.

II. Experimental

All reactions were monitored by TLC with Merck GF254 silica-gel-coated plates. Sodium hexachloroiridate (Johnson-matthey & Co.) was dissolved in a minimum amount of HCl and the final strengths of the catalyst and acid were 3.35x10⁻³ M and 6.24 x10⁻³ M respectively. In all the cases the IR spectra were taken with a Bruker Vector -22 IR spectrophotometer, and ¹HNMR spectra were taken with geol 400 MHz spectrophotometer in CdCl₂ with chromatography (GLC) studies were performed with a Varian vista 6000. Commercially obtained reagents were used without further purification. The purity and identification of the products were confirmed by melting point, mix melting point, TLC, molecular weight determination, by neutralization equivalent, preparing derivatives, IR, NMR and GLC studies. To obtain the maximum yield, five to nine sets were performed by changing the concentration or conditions of each component, which can affect the yield. In general to the mixture of aromatic aldehyde, in aqueous acetic acid and catalyst, the requisite quantity of 50% H₂O₂ was added and the mixture was heated for the required time. After completion of the reaction the contents were cooled, separated and analyzed for the products.

Table 1: Oxidation of various aromatic aldehydes by 50% H₂O₂ in aqueous acetic acid medium in the presence of IrCl₃ (Organic substrates taken: a¹, 7.3, b¹, 8.24, C¹, 0.66, d¹, 9.82, e¹, 6.8 and f¹, 9.8 m mol).

Organic substrate	Product	H ₂ O ₂ (m mol)	Acetic acid (m mol)	IrCl ₃ × 10 ⁻⁵ (m mol)	Temp (°C)	Time (H)	Yield %
p-chlorobenzaldehyde(a ¹)	p-chlorobenzoic acid(a)	48	32	1.6	100	2	90
p-hydroxybenzaldehyde(b ¹)	p-hydroxybenzoic acid(b)	91	16.5	3.4	80	2.5	18
p-nitrobenzaldehyde(c ¹)	p-nitrobenzoic acid(c)	80	16.5	1.6	80	1.5	90
p-methoxybenzaldehyde(d ¹)	4-methoxybenzoic acid (d)	96	47.8	8.2	100	3.0	22
4-hydroxy-3-methoxybenzaldehyde(e ¹)	4-hydroxy-3-methoxybenzoic acid(e)	84	36.4	1.6	80	2	48
Benzaldehyde (f ¹)	Benzoic acid (f)	80	78	1.6	80	2	78

p-chlorobenzaldehyde (a¹, 7.3mmol) was dissolved in glacial acetic acid (32mmol). After adding IrCl₃ (1.6×10⁻⁵ mmol), 50% H₂O₂ (48 m mol) was added. The mixture was kept at 100°C for 120 min. Pouring of the contents on the crushed ice resulted in a precipitate, which was filtered. The filtrate was extracted with 10.0 ml ether. The extract was dried over anhydrous MgSO₄. Solvent was removed under reduced pressure. After recrystallization with hot ethanol, p-chlorobenzoic acid (a) was obtained as a white solid (0.98g, 90%), m.p. 239°C reported (241°C). IR ν_{max} 2974 nm (ν_{OH}), 1685nm (ν_{C=O}).

p-hydroxybenzoic acid (b) was prepared similarly, and after recrystallization with hot ethanol gives the compound as a white solid (0.195g, 18%), m.p. 239°C (reported 241°C). IR ν_{max} 3387 nm (ν_{OH phenolic}), 1678 nm (ν_{C=O}), 2989 nm (ν_{OH}), 786 nm (ν_{disubstituted benzene}).

p-nitro benzoic acid (c) was prepared in some manner was extracted with ether, and after recrystallization with ethanol, p-nitro benzoic acid (c) was obtained as a white solid (98 mg, 90%); m.p. 238°C (reported 241°C). IR ν_{max} 3111 nm (ν_{OH}), 1695 nm (ν_{C=O}); 1540 nm (ν_{NO₂}).

p-methoxybenzoic acid (d) was prepared similarly and after extracting with diethyl ethers then recrystallizing with ethanol, the compound was obtained as a white solid (38mg, 22%); m.p. 180°C (reported 184°C), molecular weight 151 (reported 152). IR ν_{max} 2984 nm (ν_{OH}), 1684 nm (ν_{C=O}), 1604 nm (ν_{C=C}), 1301 nm (ν_{O-C-C}), 1165 nm (ν_{O-C}).

4-hydroxy 3-methoxybenzoic acid (e) was prepared in the same manner, was extracted with ethyl acetate and dried with MgSO₄. The solvent was evaporated under reduced pressure. With a portion of the reddish yellow solution, GLC studies were performed. The yield obtained was (0.614g).

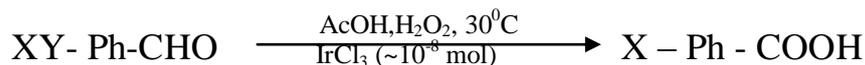
Benzoic acid (f) prepared similarly and on extraction with ether and recrystallization with hexane, the compound was obtained as a white solid (96mg, 78%) m mp, 121.5°C (reported 122°C), IR 3068 nm; 1689 nm (ν_{OH}).

III. Results and Discussion

The present system is efficient and can also be used to oxidize a variety of functional groups in the laboratory for demonstration purpose. Above all, it is cost effective and environmentally benign as no harmful side product is formed. To obtain the maximum yield, five to nine sets were performed by changing the concentration or condition of each component, which can affect the yield. Change in the concentration of acetic acid does not affect the yield, indicating that it acts only as solvent. Addition of IrCl₃ at the room temperature does not catalyze the reaction, indicating that IrCl₃ itself or IrCl₆³⁻ species, which exists in aqueous acidic medium^{17,18} at room temperature, may not be catalyzing the reactions. Yield in all the cases reached a maximum and then started to decrease with further increase in catalyst concentration. This may be due to the unproductive decomposition of oxidant at higher concentration of the catalyst. The electron abstracting group, when present in the benzene ring, e.g., p-chloro & p-nitro group facilitated the yield, compared with when no such group was present. Thus quantitative yield of p-chlorobenzoic acid was obtained in less time at lower oxidant and catalyst concentration. The presence of an electron-donating group in the ring made oxidation difficult due to decreased electron density at the carbonyl carbon atom. Thus a slight increase in concentration of catalyst and temperature (d) were required to obtain quantitative yield of corresponding acids.

The present system (scheme 1) is easy and efficient and can be used to oxidize a variety of functional groups from the synthetic point of view. Above all, it is cost-effective and environmentally benign as no harmful

by product is formed. The system is also effective for other organic compounds containing a variety of functional groups.



Yield = 18 to 90 %

X = Cl (a), . OH (b), NO₂(c) OCH₃ (d), H (f)

Y =H (a, b, c, d and f), Y = OCH₃ (e)

Scheme 1. Oxidation of various organic substrate under the condition as given in table 1.

Even with the drawback that more oxidant is required, the present system is more economical than many other methods because the cost of the catalyst is nominal (catalyst/substrate ratio is 1:85400 to 1:341250) and the catalyst and acetic acid can be regenerated.

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References

- [1] M. De Jonge. Organic Synthesis by Oxidation with Metal Compounds. Plenum: New York, 1986; 839-876.
- [2] M. Hudlicky, Oxidation in Organic Chemistry. American Chemical Society: Washington, DC, 1990; 838-840.
- [3] Z. Rappoport (ed.), Synthesis of Carboxylic Acids, Esters and Their Derivatives. Wiley: Chichester, 1991; 357-360.
- [4] G.A. Russell, Selective Oxidation Processes. American Chemical Society: Washington, DC, 1965; 112-173.
- [5] G. Sosnovsky, Organic Peroxides, Vol. I, D. Swern (ed.). Wiley Inter science : USA, Vol.I, 1970; 517-560.
- [6] JH. Birkinshaw, H. Raistrick, DJ. Ross, CE. Sticking. Biochem J. (London) 1952; 5: 610.
- [7] K. Sato, M. Aoki, M. Ogawa T. Hashimoto, D. Panyella, R. Noyori, Bull. Chem. Soc. Japan, 1997; 70:905.
- [8] ME. Kurz, GJ. Johnson. J. Org. Chem. 1971; 36:3184.
- [9] M. Shi, YS. Feng ; J. Org. Chem. 2001; 66:3235.
- [10] H. Heaney, JA. Newbold ; Tetrahedron Lett. 2001; 42:6607.
- [11] K. Sato, M. Hyodo, J. Takagi , M. Aoki, R. Noyori, Tetrahedron Lett; 2000 ;4: 1439.
- [12] K. Sato, J. Takagi , M. Aoki, R. Noyori, Tetrahedron Lett; 1998; 39:7549.
- [13] G. Barak, J. Dakka, Y. Sasson , J. Org. Chem. 1998; 53:3553.
- [14] S-1. Murahashi, T.Naota, Y.Oda, N.Hirai ,Synlett 1995; 733.
- [15] S-1. Murahashi, T.Naota, Y.Oda, N.Hirai, Org. Chem. 1993; 58:7318.
- [16] M. Hulce, DW. Marks, J. Chem. Edu. 2001; 78:66.
- [17] J.C. Chang, C.S. Garner, Inorg. Chem. 1965; 4: 209.
- [18] F.A.Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, Wiley Interscience, 1999, p. 1039.