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Eco-Friendly Liquid Phase Oxidation of Some Aromatic Aldehydes With Sodium Perborate Catalyzed by Iridium (III)

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Seven aromatic aldehydes dissolved in aqueous acetic acid were oxidized in quantitative to good yields by sodium perborate in presence of traces of IrCl₃. Conditions were obtained for getting the highest yields under the experimental conditions.

Introduction

A large number of oxidants have frequently been used for the oxidation of organic compounds. The cheapest oxidizing agents are air, chlorine and nitric acid, all of which have important uses. Each also has associated disadvantages and limitations. However, in this eco-conscious era, development of green oxidative methodology has become a prime area of research interest. In this context sodium perborate is a desirable green oxidant due to its easy availability, high oxygen content and formation of water as a ultimate by product.¹ Sodium per-borate has reported to be an excellent reagent for the oxidation of thiols and selenols to disulfides and diselenides ², and of sulfides to either sulfoxides or sulfones ³⁻¹⁰. Acetic acid is

normally used as solvent but methanol and ethanol can also be used and yields are close to quantitative in many cases. Gupton et.al. found that treatment of 1-alkynes with sodium perborate and a catalytic amount of mercury (II) acetate in acetic acid at 60-95^oC gave good to excellent yield of 1-acetoxy alkan -2-ones.¹¹ Iridium(III) chloride shows sluggish catalytic activity in alkaline medium and thus it has been given little attention until now.¹²⁻¹³ During kinetic studies we observed ¹⁴⁻¹⁶ that iridium(III) chloride in an acidic medium, is more efficient than ruthenium(III) chloride in acidic medium ¹⁷ or osmium tetroxide in alkaline medium.¹⁸ In the present work, we report that sodium perborate oxidation of benzaldehyde, p-

methoxy benzaldehyde, trimethoxy benzaldehyde, dimethoxy benzaldehyde, p-hydroxy benzaldehyde, p-chlorobenzaldehyde and p-nitrobenzaldehyde in aqueous acetic acid medium catalyzed by iridium trichloride gives the corresponding carboxylic acids in good yields. Despite of vital role of women in the socio economic development, it is evident from the following figures that women in India in specific and throughout on globe in general don't enjoy equal footing in economic activities with men. With this broad object in view the present investigation was undertaken to know the personal and socio-economic characteristics of farm women in Parbhani district.

Experimental

Sodium perborate tetrahydrate, benzaldehyde, p-chlorobenzaldehyde, p-hydroxybenzaldehyde, p-nitrobenzaldehyde (E.merck) and p-methoxybenzaldehyde, dimethoxy benzaldehyde and trimethoxy benzaldehyde (Lancaster) were used as such without further purification. Solution of iridium(III) chloride was prepared by dissolving sodium hexa chloroiridate (Johnson matthey and Co.) in a minimum amount of concentrated HCl (A.R). Final strengths of acid and catalyst were 0.00624 M and 3.35×10^{-3} M respectively.

All other chemicals used were either AR or chemically pure substances. For getting the maximum yield, four to eight sets were performed by changing the concentration or condition of each component, which can affect the yield. Table 1, for example, shows the affect of change of various parameters on the yield of p-nitrobenzoic acid from p-nitrobenzaldehyde. For performing the reaction in the solution phase, a calculated amount of aromatic aldehyde dissolved in

acetic acid was stirred in a round-bottom flask to which known amounts of iridium (III) chloride and sodium perborate were added. The flask fitted with water condenser was kept in a magnetically stirred water bath at fixed temperature for the desired time. The resulting solution was cooled to room temperature and was extracted with appropriate solvents. The extract was dried over anhydrous magnesium sulphate (MgSO_4). The solvent was removed under reduced pressure and the obtained product was identified by appropriate methods. Purity and identification of the products were confirmed by TLC (Merck GF 254 silica gel coated plates), by checking their mp and mmp and with the help of their IR (in KBr Brucker-Vector-22 IR spectrophotometer) and ^1H NMR (Xeol 400 MHz in CdCl_2 with TMS as internal standard).

Result and Discussion

On running the TLC plate with the organic part, only one spot corresponding to the product was obtained. Reaction conditions of various experiments are summarized in Table 2, and the general procedure for performing the reactions is given in the experimental section. In all the cases after completion of the reaction contents were extracted three times with diethyl ether ($3 \times 25\text{ml}$). The organic part was washed three times with ice-cold double distilled water to remove acetic acid. After removal of extra solvent under reduced pressure, sodium hydroxide (2N) was added to the crude product and the solution was filtered. Filtrate was then acidified with HCl (2N). The precipitate was filtered with ice cold water, dried, and was weighed. Benzoic acid (a^1) (94 % yield) was obtained from benzaldehyde (a). Melting point of the product was found to be 121.6°C (reported

122°C). Finally the product was confirmed by taking its IR spectrum in which following peaks were obtained. IR ν_{\max} , 3024nm ($\nu_{\text{O-H}}$) 1683 nm ($\nu_{\text{C=O}}$).

Dimethoxy benzoic acid (b) (82% yield) was prepared in the same manner from dimethoxy benzaldehyde (b, 1.0 mmol.). Mp. of the product was found to be 178.6 °C (reported 181 °C), NMR δ 9.86 (1H, Str.), δ 7.85 to 7.58 (1 H, dd), δ 6.90 to 6.93 (2H, dd), δ 3.94 (6H Str.) IR ν_{\max} . 2841 nm (ν_{CH_3} str), 1692 nm ($\nu_{\text{C=O}}$), 2951 nm ($\nu_{\text{O-H}}$ str.), 1584nm ($\nu_{\text{C=C}}$), 1509nm ($\nu_{\text{benzene ring}}$), 846nm ($\nu_{\text{C-C}}$ str), and 1238nm ($\nu_{\text{C-O}}$).

Trimethoxy benzoic acid (C) was prepared similarly from trimethoxy benzaldehyde (C, 1mmol) which gave 58.4% yield. Mp. of trimethoxybenzoic acid was found to be 142°C (reported 144°C), NMR, δ 9.86 (1H, Str.), 7.16 (2H, Str.), δ 3.92 (9H, Str.).

p-methoxy benzoic acid (d) from p-methoxybenzaldehyde (d, 1mmol) prepared as described previously gave 84.2% yield. Mp. of p-methoxybenzoic acid was found to be 180°C (reported 184°C). IR ν_{\max} , 2980 nm ($\nu_{\text{O-H}}$), 1612 nm ($\nu_{\text{C=C}}$), 1688 nm ($\nu_{\text{C=O}}$), 1298 nm ($\nu_{\text{O-C=C}}$) and 1168 nm ($\nu_{\text{O-C}}$).

p-hydroxybenzoic acid (e) was also prepared in the similar way. After extraction and recrystallization, the product was obtained as a white solid (63.5% yield), Mp. of the product was 239°C (reported 241°C). IR ν_{\max} 3384 nm ($\nu_{\text{O-H phenolic}}$), 1684nm ($\nu_{\text{C=O}}$), 2994 nm ($\nu_{\text{O-H}}$) and 786nm ($\nu_{\text{disubstituted benzene}}$).

p-chlorobenzoic acid (f) from p-chlorobenzaldehyde (f) prepared in the same way. Product was obtained as white solid (96.3% yield). Mp. of the product was found to be 239°C (reported 241°C). IR

ν_{\max} , 3100-2558 nm (broad $\nu_{\text{O-H}}$), 1688 nm ($\nu_{\text{C=O}}$), 758nm ($\nu_{\text{C-Cl}}$).

p-nitrobenzoic acid (g) from p-nitrobenzaldehyde (g) prepared as described above. The product was obtained as white solid 84.62% yield. Mp. of the product was found to be 241°C (reported 243°C). Finally the identity of the product was confirmed by taking its IR spectrum in which following peaks were obtained, IR ν_{\max} 1686 nm ($\nu_{\text{C=O}}$), 3126-2516 nm ($\nu_{\text{O-H}}$ str.), 1278 nm ($\nu_{\text{C-N}}$), 1557nm and 1348nm ($\nu_{\text{N-O}}$ asy & sym).

The study was performed mainly to determine the efficiency and selectivity of the novel environmentally benign and effective method for the oxidation of aromatic aldehydes employing sodium perborate in aqueous acetic medium catalyzed by iridium (III) chloride. It was observed that catalyst-substrate ratio ranging from 1:151515 to 1:299401 was enough for the conversion of aromatic aldehyde (table2). Four to eight sets were performed to obtain the maximum yield by changing concentration or conditions of each substrate (Table1). Change in concentration of acetic acid does not affect the yield (entries 4&7, Table 1) indicating that it acts as a solvent to dissolve the organic substrates. Yield in all the cases reached a maximum and then started to decrease with further increase in the concentration of the catalyst (entries 7, 9-11 Table 1). This may be due to unproductive decomposition of H₂O₂ obtained from sodium perborate at higher concentration of the catalyst. Increase in temperature (entries 7, & 12 -14 Table 1) showed positive effect on the yield, but after 50°C the yield become almost constant. Increase in the duration of the experiment increased the yield, but after a certain limit, yield becomes constant (entries 7, 15-17 Table 1).

Table.1 Effect of various factors on the yield of p-nitrobenzoic acid (g') from p-nitrobenzaldehyde (g) (1.0 mmol) with sodium perborate in aqueous acetic acid medium in the presence of iridium (III) chloride

Entry No.	SPB (mmol)	Acetic acid (mmol)	IrCl ₃ X10 ⁶ (mmol)	Temperature (°C)	Time (h)	Yield % of p-nitrobenzoic acid
1	2.50	175	-	50	4	>25
2	-	175	3.34	50	4	0.0
3	2.50	175	3.34	Room Temp.	48	>8
4	2.50	350	3.34	50	4	82.5
5	1.00	175	3.34	50	4	46.84
6	2.00	175	3.34	50	4	68.40
7	2.50	175	3.34	50	4	84.62
8	3.00	175	3.34	50	4	75.24
9	1.00	175	1.00	50	4	17.54
10	1.00	175	1.67	50	4	36.42
11	1.00	175	5.00	50	4	41.20
12	2.50	175	3.34	30	4	22.54
13	2.50	175	3.34	40	4	46.86
14	2.50	175	3.34	60	4	86.32
15	2.50	175	3.34	50	3	72.00
16	2.50	175	3.34	50	5	86.64

Table.2 Oxidation of various aromatic aldehyde by sodium perborate in aqueous acetic acid medium in the presence of iridium(III) chloride (amount of aromatic aldehyde in all the cases is 1.0 mmol)

Aromatic aldehyde	Product	SPB (mmol)	Acetic acid (mmol)	IrCl ₃ X 10 ⁶ (mmol)	Temp. (°C)	Time (h)	Yield (%)
Benzaldehyde (a)	Benzoic acid (a')	2.0	140	3.34	50	3	94
Dimethoxy benzaldehyde (b)	Dimethoxy benzoic acid (b')	2.5	175	3.34	50	5	82
Trimethoxy benzaldehyde (c)	Trimethoxy benzoic acid (c')	3.0	250	6.6	60	6	58.4
p-methoxy benzaldehyde (d)	p-methoxy benzoic acid (d')	2.5	175	3.34	50	4	84.2
p-hydroxy benzaldehyde (e)	p-hydroxy benzoic acid (e')	2.5	175	6.6	50	4	63.5
p-chloro benzaldehyde (f)	p-chloro benzoic acid (f')	2.5	175	3.34	50	2	96.3
p-nitro benzaldehyde (g)	p-nitro benzoic acid (g')	2.5	175	3.34	50	4	84.62

Results indicated that for particular aromatic aldehydes, optimum conditions are required to get the highest yield with minimum expenditure of energy or chemicals. Negligible or no formation of the desired product, after prolonged heating in the absence of oxidant (entry 2, Table 1) or leaving the mixture for 48 hour at the room temperature (entry 3, Table 1) excludes aerial oxidation of substrate under experimental conditions and indicates that control of reaction conditions is necessary for obtaining the product with maximum yield. It is known that IrCl_3 in HCl medium gives IrCl_6^{3-} species¹⁹. Further, the aquation of $[\text{IrCl}_6]^{3-}$ gives $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$, $[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$ and $[\text{IrCl}_3(\text{H}_2\text{O})_3]$ species^{20,21}. In the present case also for preparing the catalyst, sodium hexachloro iridate (III) was dissolved in aqueous hydrochloric acid, and the concentration of acetic acid did not affect the yield, indicating that acetic acid probably does not change the species of the catalyst in the medium. Therefore, an active species of Iridium taking part in the solution phase reaction may will be considered to be $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$.

Reaction of acetic acid with solid perborate believed to be contains available oxygen in hydroperoxide form. Recent studies on application of sodium perborate-acetic acid system to organic synthesis have shown that it behaves essentially as a nucleophilic oxidant, consistent with the generation of AcOO^- as an active species. In the present study the presence of Ir(III) probably facilitate the generation of AcOO^- . Our experimental finding reveals that steric effect also plays an important role in oxidation of aromatic aldehyde. Thus *p*-methoxy benzaldehyde and dimethoxy benzaldehyde gave good yields but trimethoxybenzaldehyde gave poor yield (Table 2). The electron abstracting group when present in the benzene ring, they

facilitated the yield, compared with when no such group was present. The presence of an electron donating group in the ring made oxidation difficult due to decreased electron density at the carbonyl carbon atom. Thus slight increase in concentration of catalyst and temperature were required to obtain quantitative yield of corresponding acids (Table, 2)

In conclusion we report a new efficient and environmentally friendly protocol for oxidation of aromatic aldehydes to corresponding aromatic carboxylic acids with the reagent combination of sodium perborate and iridium (III) chloride in aqueous acetic acid medium. The reported system is easy and efficient and can be used to oxidize a variety of functional groups from the synthetic point of view.

References

1. Mc Killop, A. Sanderson, W.R. Tetrahedron 1995 , 51, 6145.
2. Mc Killop, A. Koyuncu, D. Krief, A. Dumont, W. Renier, P. Trabelski, M. Tetrahedron Lett. 1990,31,5007-5010.
3. Mc Killop, A. Tarbin, J.A. Tetrahedron 1987,43,1753-1758.
4. Mc Killop, A. Tarbin, J.A. Tetrahedron Lett. 1983, 24, 1505-1508.
5. Mc Killop, A. Sanderson, W.R., Tetrahedron 1995, 51,22,6145-6166.
6. Ding, X. Ge, Y Teng, Z. Fan, J. Yiyao Gongye 1987,18,193-194.
7. Ding, X. Ge, Y Teng, Z. Zhang, L. Youji Huaxue 1988,8,141-142.
8. Zhou, W. Zhang, L. Xu, X. Zhang, Z. Wuji Huaxue Xuebao 1990,6,83-86.
9. Zhou. W. Zhang, L. Xu, X. Zhang, Z. Wuji Huaxue Xuebao 1992,8,88-90.
10. Aggarwal, V.K. Davies, I.W. Franklin, R. Maddock, J Mahon, M.F. Molloy, K.C., J.chem. Soc. Perkin Trans. 1,1994, 2363-2368.

11. Reed, K.L. Gupton, J.T., McFarlane, K.L., Synth.Comm. 1989,19,2595-2602.
12. Manibala Singh, H.S Krishna, B. Tandon, P.K. J.Indian Chem.. Soc. 1985, 62, 434-437.
13. Singh M.P. Tandon, P.K. Singh, R.M. Mehrotra, A., J.Indian Chem.. Soc. 1990, 67, 458-462.
14. Tandon, P.K. Singh Alok K Baboo, R. Dwivedi, P.B., Transition Met. Chem.. 2004, 29, 663-670.
15. Tandon, P.K. Sahgal, S. Singh Alok K. Gayatri Purwar J. Mol. Catal .A : Chem. 2005, 232, 83-88.
16. Tandon, P.K. Sahgal, S. Singh, Alok K. Kumar, S. Dhusia, M., J. Mol Catal, A. Chem:, 2006, 258, 320-326.
17. Singh, M.P. Singh H.S. Verma , M.K., J. Phy.Chem. 1980,84,256-259.
18. Singh, V.N. Singh H.S. Saxena, B.B. L., J.Am.Chem.Soc. 1969,91,2643-2648.
19. Chang, J.C. Garner, C.S. Inorg. Chem. 1965,4,209-215.
20. Poulsen, I.A. Garner, C.S. J.Am. Chem.. Soc., 1962, 84,2032-2037.
21. Domingos, A.P.J. Domingos, A.M.T.S. Cabral, J.M.P., J. Inorg. Nucl. Chem.,1969, 31, 2563-2573.