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Simple and economical conversion of organic compounds with H_2O_2 catalyzed by ruthenium (III) chloride

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Six aromatic aldehydes, two hydrocarbons, one cycloalcohol and one aromatic alcohol, viz. benzaldehyde, *p*-chlorobenzaldehyde, cinnamaldehyde, 4-methoxybenzaldehyde, *o*-hydroxybenzaldehyde, 4-hydroxy, 3-methoxybenzaldehyde, anthracene, phenanthrene, cyclohexanol and benzyl alcohol dissolved in acetic acid, were oxidized in quantitative to moderate yields by 50% H_2O_2 in the presence of traces of $RuCl_3$ (substrate : catalyst ratio 85 400 to 387 500 : 1). Conditions for highest yields, under most economical conditions, were obtained. Higher catalyst concentrations decreased the yield. Oxidation in aromatic aldehydes is selective at aldehydic group only, and other groups remain unaffected. The extent of oxidation in phenanthrene depends on temperature or the relative amount of substrate or both. In this new, simple and economical method, which is environmentally safe and requires less time, oxocentered carboxylate species of ruthenium (III) probably catalyze the oxidation. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: oxidation; hydrogen peroxide; ruthenium (III) chloride; catalyst; oxocentered carboxylate species

INTRODUCTION

From the synthetic point of view a large number of oxidants,[1–3] including molecular oxygen in acidic[4] or alkaline[5] media, gold on carbon,[6] etc. are frequently 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, has high active oxygen content, does not require a buffer and it is clean since the by-product formed is water. It has been used for the oxidation of aromatic aldehydes,[7] epoxidation of olefins,[8] hydroxylation of aromatics,[9] oxidation of benzyl chlorides,[10] aromatic aldehydes by magnesium monoperoxyphthalate, etc.[11] Recently oxidation of aromatic and aliphatic aldehydes in organic solvent-, halide- and metal-free conditions using $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ (PTC) with a substrate catalyst ratio of 1.1 : 2.5 has been reported.[12] Oxidation of benzyl alcohol under halide-free conditions has been reported in the presence of PTC[13] with 87% yield of benzaldehyde (alcohol–catalyst ratio 330 : 1), but the system containing dimethyl sulphate, which is used to prepare PTC, is reported to be carcinogenic.[14] Ruthenium catalyzed oxidation of alcohols by H_2O_2,[15] by peracetic acid[16] under PTC conditions and in the presence of bimetallic catalyst[17] has also been reported. In the present system good yield is obtained with substrate–catalyst ratio ranging from 85 400 to 387 500 : 1 and it oxidizes a wider range of organic compounds, is a more convenient, eco-friendly and economical compared to many other systems. The drawback is that more oxidant is required, but the system is still more economical as the cost of catalyst is nominal and the solvent and catalyst can be used again after removing the organic part. Herein, the oxidation of six aromatic aldehydes (**a**–**f**), anthracene (**g**), phenanthrene (**h** and **h***), cyclohexanol (**i**) and benzyl alcohol (**j**) by 50% hydrogen peroxide in the presence of traces of ruthenium (III) chloride has been reported.

EXPERIMENTAL

It has been reported[20] that, when heated at near reflux temperature with acetic acid, $RuCl_3$ may give rise to oxo-centered carboxylate $[Ru_3^{III}(\mu_3\text{–}O)(OOC.CH_3)_6(H_2O)_3]^+$

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Table 1. Oxidation of various organic compounds by 50% H_2O_2 in aqueous acetic acid medium in the presence of $RuCl_3$ (for **b** 7.1, **c** 7.9, **d** 8.2, **e** 9.3, **f** 7.0, **g** 0.28, **h** and **h*** 1.1 and 0.28, **i** 4.8, **j** 9.6 mmol of organic substrates given in column 1 were taken)

Organic substrate	Product	H_2O_2 mmol	Acetic acid (mmol)	$RuCl_3$ $\times 10^{-5}$ (mmol)	Temperature (°C)	Time (h)	Yyield (%)
p-Chlorobenzaldehyde	*p*-Chlorobenzoic acid (**b**)	140.6	43.7	1.2	80	1.5	100
Cinnamaldehyde	Cinnamic acid (**c**)	140.6	87.5	2.8	100	1.0	100
4-Methoxybenzaldehyde	4-Methoxybenzoic acid (**d**)	140.6	43.7	9.6	100	1.0	100
o-Hydroxybenzaldehyde	o-hydroxy benzoic acid (**e**)	159	87.5	2.4	80	1.5	14
4-Hydroxy,3-methoxybenzaldehyde	4-hydroxy,3-methoxybenzoic acid (**f**)	159	1.7	2.4	80	1.5	59
Anthracene	Anthraquinone (**g**)	70.3	350	19.6	100	0.5	98
Phenanthrene	Phenanthraquinone (**h**), diphenic acid (**h***)	70.5, 70.5	175, 170	19.2, 19.2	80, 100	2.0, 2.0	80, 90
Cyclohexanol	cyclohexanone (**i**)	28.1	17.5	9.6	80	2.0	28
Benzyl alcohol	benzaldehyde (**j**)	28.1	29.7	19.2	100	2.0	49

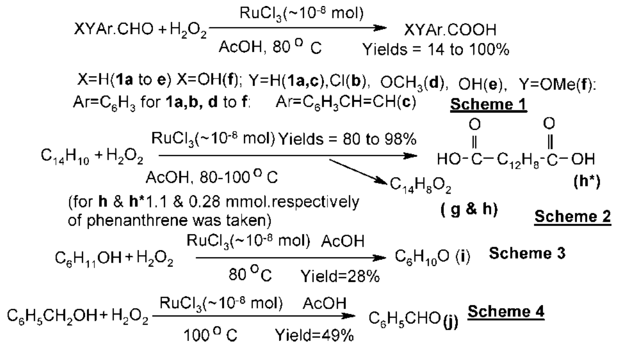
species, which may undergo reversible redox steps.[21] Trinuclear caboxylates have been reported to be effective catalysts for the aerobic oxidation of aliphatic alcohols.[22] Catalytic activities of these complexes are approximately 10 times higher than that of $RuCl_3$.[23] This also seems to be true in the present study as substrate–catalyst ratio ranging from 85 400 to 387 500 : 1 was enough for the quantitative conversion of aromatic aldehydes (**b** and **c**, Table 1) while a 50 000 : 1 ratio gave a yield of 49% in the case of benzyl alcohol (**j**, Table 1). Formation of $HO_2^{\bullet}$, $OH^{\bullet}$ and OH^- during the catalytic decomposition of H_2O_2 with metal ions is well documented.[24]

In all cases IR spectra were taken with a Brucker Vector-22 IR spectrophotometer and ^1H NMR spectra with a Xeol 400 MHz spectrophotometer in $CDCl_3$ with TMS as internal standard. GLC studies were performed with Varian Vista 6000. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Merck GF254 silica gel-coated plates. Purity and identification of products were confirmed by taking m.p., m.m.p., TLC, molecular weight determination by neutralization equivalent, preparing derivatives, and IR, NMR and GLC studies. Benzaldehyde (**a**, 10.0 mmol) was dissolved in glacial acetic acid (87.5 mmol). After adding $RuCl_3$ (2.4×10^{-5} mmol.), 50% H_2O_2 (159 mmol) was added. Mixture was kept at 80 °C for 150 min. The contents were poured on the crushed ice. The precipitate was filtered and the filtrate was extracted with 10.0 ml ether. The extract was dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure. After re-crystallization with hexane, benzoic acid (**a**) was obtained as white solid (1.19 g, 98%); mmp, 121.5 °C (reported 122 °C), ν_{max}, 3068 nm (ν_{-OH}); 1689 nm ($\nu_{C=O}$); NMR: δ 7.48 (2H t δ $J = 7.69$ Hz); δ 7.62(1H t $J = 7.43$ Hz.); δ 8.12(2H d $J = 8.39$ Hz.). *p*-Chlorobenzoic acid (**b**) prepared similarly and re-crystallization with hot ethanol gives the compound as a white solid (1.11 g, 100%); m.p., 239 °C(reported 241 °C), IR ν_{max}, 2974 nm (ν_{-OH}), 1685 nm ($\nu_{C=O}$). Cinnamic acid (**c**) was prepared in the same manner. After extracting with diethyl ether and re-crystallizing with hot water, a compound was obtained as white solid (1.15 g, 100%); m.m.p., 132 °C (reported 134 °C), compound gave the test for unsaturation, IR ν_{max}. 3060 nm (ν_{-OH}), 1683 nm ($\nu_{C=O}$), 1493 nm ($\nu_{C=C}$). 4-Methoxy benzoic acid (**d**) was prepared in the same manner. After extracting with diethyl ether and re-crystallizing with ethanol, the compound was obtained as a white solid (1.21 g, 100%); m.p., 180 °C (reported 184 °C), mol. wt, 151 (reported 152). IR ν_{max}, 2982 nm (ν_{-OH}), 1683 nm ($\nu_{C=O}$), 1601 nm ($\nu_{C=C}$), 1299 nm ($\nu_{O-C=C}$), 1165 nm (ν_{O-C}). NMR: δ 7.62–7.24 (4H m), δ 3.71(3H s). *o*-Hydroxy benzoic acid (**e**) prepared in the same manner was extracted with ethyl acetate and was dried with $MgSO_4$. The solvent was evaporated under reduced pressure. With a portion of the reddish yellow solution GLC studies were performed. Peak 11, area (%), 0.219; RT, 25.38 min. The yield obtained was 14% (0.179 g). 4-Hydroxy,3-methoxy benzoic acid (**f**), prepared in the same manner, was extracted with ethyl acetate and dried with $MgSO_4$. The solvent was evaporated under reduced pressure. With a portion of the reddish yellow solution, GLC studies were performed. Peak 7, area (%), 1.05; RT, 44.07 min. The yield obtained was 59% (0.652 g). Anthraquinone (**g**) was prepared similarly and was re-crystallized with hot glacial acetic acid to give needle-shaped yellowish crystals (0.057 g, 98%); m.p., 284 °C (reported 286 °C); IR ν_{max}, 1673 nm ($\nu_{C=O}$), 935–809 nm (ν substituted benzene ring). NMR: δ 6.8–8.5 (8Hm). Phenanthraquinone (**h**): prepared similarly as **g** to give needle-shaped yellowish orange crystals, which were identified by TLC (0.165 g, 80%); m.p., 207 °C (reported 210 °C). Diphenic acid (**h***) was prepared as above. The compound was obtained as white solid (0.062 g, 90%), m.p., 227 °C (reported 230 °C). IR ν_{max}, 3008 nm ($\nu_{-OH\ acid}$), 1695 nm ($\nu_{C=O}$ acid), 748 nm ($\nu_{subs.\ benzene\ ring}$). Cyclohexanone (**i**): the compound was prepared as above. Its hydrazone was separated and identified by TLC; m.p. of hydrazone, 157 °C (reported 162 °C), 0.133 g (product), yield 28%. NMR: δ 7.22–7.18 (3H, m), δ 0.8–2.6(10H, m), δ 3.4 (1H, s). Benzyl alcohol (**j**): compound was prepared as above (0.519 g, 49%). Its hydrazone was separated and identified by TLC; m.p. of hydrazone, 239 °C (reported 241 °C). NMR; δ 7.36–7.24 (8H, m), 5.1–5.0 (2H, s).

The present system is efficient and can also be used to oxidize a variety of functional groups in the laboratory for demonstration purposes. Above all, it is cost-effective and environmentally benign as no harmful side product is formed. The system is also effective for other organic compounds containing a variety of functional groups for which study is in progress.

DISCUSSION

This study was performed mainly to determine the efficiency and economy of the simple and novel Ru (III)-hydrogen peroxide system to oxidize various organic compounds, such as the easily oxidized aldehydes and comparatively difficult-to-oxidize cycloalcohols. To obtain the maximum yield, five to eight sets were performed by changing the concentration or conditions of each component, which can affect the yield. Addition of H_2O_2 in small fractions at regular intervals or its continuous addition drop wise showed a negligible effect on the yield, thus, the possibility of wasteful decomposition of H_2O_2 was eliminated if the whole amount was added at the beginning of the experiment. Change in the concentration of acetic acid does not affect the yield, indicating that it acts only as a solvent (entries 6 and 7, Table 2). The negligible effect of addition of $RuCl_3$ at the room temperature (entries 1 and 2, Table 2) indicated that $RuCl_3$ itself or $RuCl_6^{3-}$ species, which exists in aqueous acidic medium[18,19] 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 (entries 4 and 7, Table 2). This may be due to the unproductive decomposition of oxidant at higher concentrations of the catalyst. The electron abstracting group, when present in the benzene ring, e.g. *p*-chloro group, facilitated the yield, compared with when no such group was present (**a**, entry 3, Table 2). Thus, quantitative yield of *p*-chlorobenzoic acid (**b**, Table 1) was obtained in less time and at lower catalyst and oxidant concentrations. The double bond in the side chain or 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 (**c** and **d**, Table 1 compared with **a**, Table 2, entry 3) were required to obtain quantitative yields of corresponding acids. Poor yield in **e** (Table 1) may be due to the steric effects and in case of **i** (Table 1) may be due to a secondary alcoholic group, which is difficult to oxidize. The presence of a methoxy group at the *m*-position ($\sigma_m + 0.10$) in **f** (Table 1) decreased the effective electron density at the carbonyl carbon due to the presence of hydroxyl group at the *p*-position, which explains the better yield in case of 4-hydroxy,3-methoxy benzoic acid compared with *o*-hydroxy benzoic acid. Chromatograms of **e** and **f** show the RT only of acetic acid, corresponding aldehydes and acids according to boiling points. An additional peak (RT 20.63) in **e**, corresponding to ammonium acetate, was obtained because, after the



Scheme 1–4. Oxidation of various organic substrates under the conditions as given in Tables 1 and 2.

Table 2. Oxidation of benzaldehyde (10.0 mmol) into benzoic acid (**a**) with 50% H_2O_2 in acetic acid medium in presence of $RuCl_3$

Entry nos	H_2O_2 (mmol)	Acetic acid (mmol)	$RuCl_3 \times 10^5$ (mmol)	Temperature (°C)	Time (h)	Yield, benzoic acid (%) (**a**)
1	159	87.5	—	Room Temp.	24	<10
2	159	87.5	1.2	-do-	24	<18
3	159	87.5	2.4	80	2.5	98
4	159	87.5	2.4	80	1.5	94.5
5	159	87.5	4.8	80	2.5	87
6	159	44.0	9.6	80	1.5	65
7	159	87.5	9.6	80	1.5	65
8	55.2	87.5	1.2	80	1.5	52
9	159	87.5	9.6	70	1.5	63

completion of the reaction, the remaining acetic acid in the reaction mixture was neutralized with ammonium hydroxide. At similar oxidant concentration, the extent of oxidation in phenanthrene (**h**, Table 1) depended on the amount of substrate initially taken. Thus, higher and lower substrate concentrations (1.1 and 0.28 mmol of **h** and **h*** respectively) gave anthraquinone and diphenic acid, respectively. In all the cases, by running the TLC plates, no product other than that reported could be found, except benzoic acid in traces (<1%) in the extract of **j** after removing benzaldehyde from the reaction mixture.

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