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Selective oxidation of primary and secondary alcohols with chromium trioxide in ionic liquid

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The oxidation of primary and secondary alcohols to corresponding aldehydes and ketones by CrO_3 in room temperature ionic liquids is an efficient and low flammability method with fast rate, facile procedure and high yields.

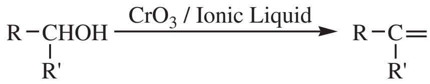
Keywords: primary and secondary alcohols, chromium trioxide, ionic liquid

The oxidation of alcohols to carbonyl compounds plays an important role in synthetic organic synthesis. Numerous reagents and methods have been developed to carry out this important conversion under various reaction conditions.[1] Chromium trioxide (CrO_3)-based oxidants are one of the most widely used[2] because they are cheap, readily available and easy to handle. They have been modified to improve selectivity. The Jones (CrO_3–H_2SO_4–acetone), Collins (CrO_3–pyridine), and PCC (CrO_3–pyridine–HCl) reagents are well-known oxidation reagents in homogeneous liquid systems. More recent modifications include CrO_3 supported on resin,[3] on graphite,[4] on silica gel,[5] on aluminium silicate,[6] and on zirconium(IV) oxide;[7] CrO_3 with diethyl ether,[8] with crown ether,[9] and with *t*-butyl hydroperoxide;[10] CrO_3 in dimethyl sulfoxide (DMSO) systems[11] and just CrO_3 with no solvents[12]. However, serious drawbacks still exist in some of the methodologies, for example, the running scale is limited to far less than 1g of substrate and potentially hazardous reactions.

Ionic liquids are environmentally benign excellent solvent for a number of purposes. Various organic reactions have been performed in ionic liquids.[13] Ionic liquids, possess high thermal stability, negligible vapor pressure and lack of flammability. They are recyclable and have a high loading capacity and tunable polarity.

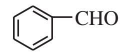
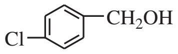
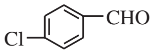
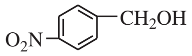
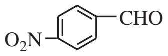
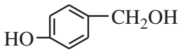
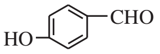
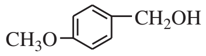
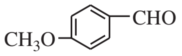
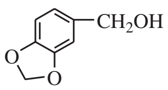
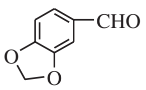
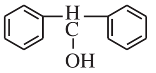
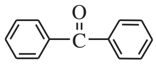
Addition of CrO_3 to [bmim]BF_4 showed that it dissolved gradually. Alcohols were oxidised by this system. As a test we added a little benzyl alcohol to [bmim]BF_4–CrO_3 system and found it was oxidised to benzaldehyde in less than 1h at room temperature. Encouraged by the reaction we oxidised a series of alcohols by this method. The results are summarised in Table 1. We found it to be a facile and very efficient procedure. Under the anhydrous and neutral condition primary and secondary alcohols are all oxidised to carbonyl compounds.

We chose more popular [emim][BF_4]$^-$ (1-ethyl-3-methylimidazolium tetrafluoroborate) as the reaction media and obtained a high yield of carbonyl compounds from corresponding alcohols. For benzylic alcohols the oxidation is very fast at room temperature. The yield is excellent for the substrates with an electron-withdrawing groups on the benzene ring (Table, Entries 2,3). However for aliphatic alcohols the reaction must be conducted at higher temperature and only a moderate yield was obtained. The work up procedure is very simple and convenient as the products can be separated from the reaction mixture by extraction. The remaining ionic liquids could be almost quantitatively recovered by a simple procedure. After the product was extracted with ether, a little acetone was added to the rest of the ionic liquid and the mixture was filtered, and then thoroughly washed with ether. The recovered ionic liquids were concentrated *in vaccuo* (5.0 torr for 6 h at room temperature). The same procedure was repeated up to 4 times using recovered ionic liquids. It seems that there is little effect on the rate or yield of the reaction.



$$\underset{R'}{R-CHOH} \xrightarrow{CrO_3\ /\ \text{Ionic Liquid}} \underset{R'}{R-C{=}O}$$

Table 1 Oxidation of alcohols by CrO_3 in ionic liquid

Entry	Substrate	Product	Temp/ Time	Yield/ %[a]
1			r.t./2h	88
2			r.t./2h	95
3			r.t./2h	92
4			r.t./2h	87
5			r.t./2h	86
6			r.t./2h	82
7	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	60°C/6h	55
8			60°C/6h	78

[a]Isolated yield

In summary, in room temperature ionic liquids the oxidation of primary and secondary alcohols to corresponding aldehydes and ketones by CrO_3 is a novel, efficient and low flammability method. Fast rate, recycling of solvent, facile procedure and high yields make it an appealing methodology.

Experimental

Reactions were carried out in a 25ml flask equipped with a magnetic stir bar with no special precaution in the fume cupboard. All the compounds were characterised by NMR, IR and physical constants and gave satisfactory results in comparison with authentic samples. Melting points are in good agreement with literature.

General Procedure: The solution of benzyl alcohol (0.22 g, 2 mmol) and chromium trioxide (0.22 g 2 mmol) in [bmim]$^+$$BF_4^-$ (3 ml) was stirred at room temperature for 2h. The reaction mixture was extracted with ether (3×5ml). The ether layer was separated. The lower ionic liquid phase can be reused. The product was further purified by column chromatography (5:1, petroleum ether/ethyl acetate), yield: 0.19g(88%).

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Product

Benzaldehyde: Oil; ^{1}H NMR (CDCl$_3$/TMS): δ_H 10.00 (s,1H), 7.87 (dd, 2H, J = 1.20, 8.15Hz); 7.65–7.59 (m,1H), 7.54–7.25 (m,2H), IR: 3060, 2934, 2852, 2814, 2727, 1696, 1653, 1596, 1583, 1455, 1390cm^{-1}.

p-Chlorobenzaldehyde: M.p. 45–46°C (lit.[14] m.p. 47°C); ^{1}H NMR (CDCl$_3$): 9.91 (s, 1H), 7.40 (d, 2H), 7.73 (d, 2H); IR: 3101, 2935, 2864, 1702, 1602, 1525, 1428 cm^{-1}.

p-Nitrobenzaldehyde: M.p. 106–107°C (lit.[14] m.p.107°C); ^{1}H-NMR (CDCl$_3$/TMS): δ_H 10.16 (s,1H), 8.40 (d, 2H, J = 8.67Hz), 8.08 (d, 2H, J = 8.67Hz); IR: 3106, 2923, 2850, 1709, 1606, 1539, 1346 cm^{-1}.

p-Hydroxybenzaldehyde: M.p. 116–117°C (lit.[14] m.p.118°C); ^{1}H NMR (CDCl$_3$/TMS): δ_H 9.87(s,1H), 7.81(d. 2H, J = 8.61Hz), 6.95(d, 2H, J = 8.61Hz), 5.59(s, 1H, OH); IR: 3431, 3171, 2923, 2847, 1668, 1602, 1518, 1455 cm^{-1}.

p-Methoxybenzaldehyde: Oil;[14] ^{1}H NMR (CDCl$_3$/TMS): δ_H 9.87(s,1H), 7.83(d, 2H, J = 8.79Hz), 6.99(d, 2H, J = 8.79Hz), 3.88(s,3H); IR: 3107, 2940, 2836, 1678, 1593, 1574, 1509, 1427cm^{-1}.

Piperonal: M.p. 35–37°C; (lit.[14] m.p. 37°C); ^{1}H NMR (CDCl$_3$/TMS): δ_H 9.81 (s, 1H), 7.41(dd, 1H, J = 1.56, 7.93Hz), 7.33(d, 1H, J = 1.56Hz), 6.93(d, 1H, J = 7.93Hz), 6.08(s,2H); IR: 3086, 2923, 2847, 1683, 1596, 1487, 1448 cm^{-1}.

Octyl aldehyde: Oil; ^{1}H NMR: (CDCl$_3$/TMS): δ_H 9.76 (1H, t, J = 1.84Hz), 2.42 (2H, tt, J = 1.84, 7.40Hz), 1.64–1.58 (m, 2H), 1.28–1.24 (m, 8H), 0.87 (t, 3H, J = 7.14Hz), IR: 2922, 2852, 1732, 1463 cm^{-1}.

Benzophenone: M.p. 48–49°C (lit.[14] m.p. 48.5–49°C); ^{1}H NMR (CDCl$_3$/TMS): δ_H 7.82–7.79 (m, 4H), 7.61–7.56 (m, 2H), 7.50–7.45 (m, 4H), IR: 3060, 2855, 1652, 1597, 1576, 1446 cm^{-1}

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