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# Oxidative transformation of alcohols and organic halides in aqueous solution†

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An efficient and new methodology for a one pot conversion of organic halides and alcohols to their corresponding aldehydes or ketones has been developed using quinolinium chlorochromate in an aqueous medium without adding any cosolvent. The same protocol has been applied for the oxidative conversion of 2-(bromomethyl)-5,7-dinitro-1*H*-indole to its corresponding aldehyde in the presence of sodium hydroxide.

## Introduction

New and alternative methods for chemical synthesis[1] are in great demand to properly harness the benefits of chemistry. A few alternatives currently available include the use of a new class of solvents such as ionic liquids, catalytic and atom economic reactions together with efficient energy techniques such as microwaves and ultrasonic irradiation. Adding to this, organic transformations in aqueous media[2] have gained much attention in the last two decades. As water is a readily available, economical and harmless solvent, it has been the focus of synthetic chemists in recent times; a lot of chemical reactions previously considered impossible in water are feasible today, including benzoin condensation,[3] allylation reactions,[4,5] Suzuki Coupling,[6] Barbier type alkylation,[7] Friedel–Crafts[8] and Mannich reactions.[9]

The oxidative transformation of halides and alcohols to their corresponding carbonyl compounds is of great importance during the synthesis of fine or special chemicals, such as medicinally or biologically active compounds, perfumes and agrochemicals.[10] Traditionally, the oxidation of alcohols was carried out using metal based oxidizing reagents[11] such as those of chromium[12] [Cr(VI)] and manganese[13] [Mn(VII)]. In addition to these, other reagents such as tertiary butyl hydroperoxide[14] (TBHP), hydrogen peroxide[15] and sodium hypochlorite[16] have recently been utilized for these reactions, particularly in association with catalysts.[17] On the contrary, oxidation of organic halides to the corresponding aldehydes and ketones is relatively difficult.[18] The classical methods for this transformation are the Hass–Bender[19] and Sommelet reactions.[20] The obvious choice for these oxidative transformations was Cr based oxidants such as the Jones, Sarrett and Collins reagents.[21] Most of these are non-selective, undergo rapid deactivation and produce carboxylic acids as an end product. The controlled oxidation of alcohols or alkyl halides to an aldehyde is a difficult task; in order to overcome these limitations organic derivatives of Cr(VI) have been prepared and are being extensively used in non aqueous solvents[21] for different synthetic endeavors.

Chlorochromate, fluorochromate and dichromate derivatives of pyridine[22] and quinoline[23] are commonly used organic derivatives of Cr(VI). These derivatives were found to be better in their reactivity and selectivity compared to the traditional Cr oxidants, and offer a benefit of solubility in organic solvents. Recently, guanidinium chlorochromate [GCC] has been used in the presence of a phase-transfer catalyst[24] for the oxidation of different benzylic and aliphatic alcohols in water. Pyridinium chlorochromate [PCC] has been used to oxidize 5,6-dihydropyrans[25] to the corresponding anhydromevalonolactone in dichloromethane in good to excellent yields. Quinolinium fluorochromate [QFC] was used for the oxidation of alcohols and phenanthrene[26] in dichloromethane. It was also used for the oxidative conversion of oximes, tosylhydrazones and *N*,*N*-dimethylhydrazones[27] to corresponding carbonyl compounds in good to excellent yields. Another analogue, quinolinium chlorochromate [QCC], was applied to the mild and selective oxidation of alcohols,[28] aromatic anils,[29] lactic and glycolic acids[30] and methionine,[31] all in non-aqueous organic solvents.

QCC is a yellow to brown solid, which is not very sensitive to moisture and is stable[32] in aqueous solutions for a considerable amount of time. Quinolinium ions in QCC provide selectivity[28] and stability to the reagent in comparison to pyridinium and isoquinolinium analogues such as PCC and isoquinolinium chlorochromate [IQCC]. In fact, quinolinium ions are better at providing selective oxidation of secondary alcohols in the presence of primary alcohols and can be used for the oxidation of a wide variety of substrates. This selectivity is probably a result

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of the different charge densities on the chromium center in various chlorochromate analogues. Quinolinium ions, being bigger in size in comparison to pyridinium ions, have a lower positive charge per unit area and hence stabilize the negative charge in the chromium center to a lesser extent. The reagent is even more selective than IQCC, which is a result of different orientations of the nitrogen atom[28] in the respective cations.

Kinetic studies during the oxidation of different substituted benzaldehydes, under pseudo-first-order conditions using QCC, have revealed that both electron-releasing and electron-withdrawing substituents can increase the rate of the reaction. This indicates that the reaction operates through two different mechanisms and the reagent is effective in performing the oxidation of electron rich and electron deficient substrates with equal ease. Certain oxidation reactions such as the oxidation of 3-methyl-2,6-diphenyl-piperidin-4-ones[33] are accelerated by the presence of electron releasing substituents, which may be due to the increase in electron density in the reaction center. QCC is also employed for the oxidation of benzaldehyde[34] in the presence of cetyl trimethylammonium bromide in acidic aqueous solutions. Kinetic studies have revealed that the reaction rate is increased by the presence of surfactant due to the formation of micelles. Furthermore, organic acids such as acetic acid decrease the rate of reaction in aqueous solutions.[35]

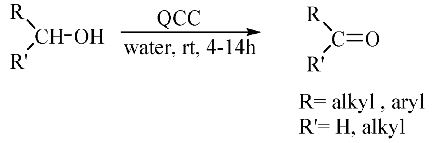
Most of the oxidation processes are either performed in organic solvents or in aquo-organic mixtures. Furthermore, methodologies describing oxidation in aquo-organic mixtures are mainly focused on kinetic studies and do not provide synthetic details. In addition, there is no work which addresses the problem of waste generation at the end of a reaction. The work described in this paper has the potential to develop a solventless synthetic procedure using QCC in aqueous solution, it is equally effective for natural product synthesis and it generates clean waste at the end of reaction. Due to the wide demand for the development of new synthetic methodologies in aqueous media, and our continuing endeavor to use new and alternative media for organic synthesis,[36,37] we are reporting to the best of our knowledge, the first use of QCC for the oxidation of different alcohols and halides in an aqueous medium, without using any co-solvent.

## Results and discussion

Organic reactions in aqueous media have attracted great attention in recent years because of the benefits water offers as a solvent, such as cost effectiveness, non-toxicity and simplified work up. Furthermore, the miscibility of different organic salts such as ionic liquids[38] and chromium salts, can be controlled by varying the cationic or anionic parts. Prompted by this thought, we have utilized a mild and selective reagent QCC for developing a new methodology for oxidative transformations in water. Herein, we are reporting the oxidation of different alcohols (Scheme 1) and halides without using any co-solvent in water at an ambient temperature using QCC.

Initially, we prepared QCC by the reported method[23] and tested its effectiveness in water for the oxidation of 1 mol equivalent of benzyl alcohol, at an ambient temperature for 3 h, and observed that its conversion to benzaldehyde was 50%, as determined by $^1$H NMR analysis. We were excited to see that the reagent worked effectively in pure water, and our focus was then to increase the solution yield further without adding any co-solvent. We therefore further increased the reaction temperature to 45–50 °C, but no appreciable change was observed. Increasing the reaction time to 12 h did not result in a change in the yield. Finally, we were able to achieve an increased yield of benzaldehyde by taking 1.5 mol equivalents of QCC at an ambient temperature (Fig. 1). We were able to oxidize a variety of alcohols (1 mmol) with QCC (1.5 mmol) in water by stirring the contents at 25–30 °C for 4–14 h, and the various results obtained are compiled in Table 1. The progress of the reaction was monitored by TLC and the isolated products were characterized by IR and $^1$H NMR spectroscopy. Water immiscible liquid products, such as benzaldehyde, formed a distinct layer on the water at the end of the reaction and were recovered by distillation without using any organic solvent for the extraction.

Oxidation processes in water are facilitated by the polar nature and stoichiometric use of QCC, which has the tendency to go into water and make the medium suitable for organic reactions by increasing the solubility. Mechanistically, the oxygen atom in alcohol coordinates to the Cr(VI) atom forming a chromate ester by displacing chlorine, which then acts as a base, abstracting a proton and finally resulting in the oxidation of alcohol to the respective carbonyl compound. Non-bonded electron pairs in organic halides may show a similar interaction with the Cr centre (Fig. 2), as shown by the oxygen atom in alcohols, resulting in the formation of an intermediate analogous to chromate esters.



Scheme 1 Oxidation of alcohols with QCC.

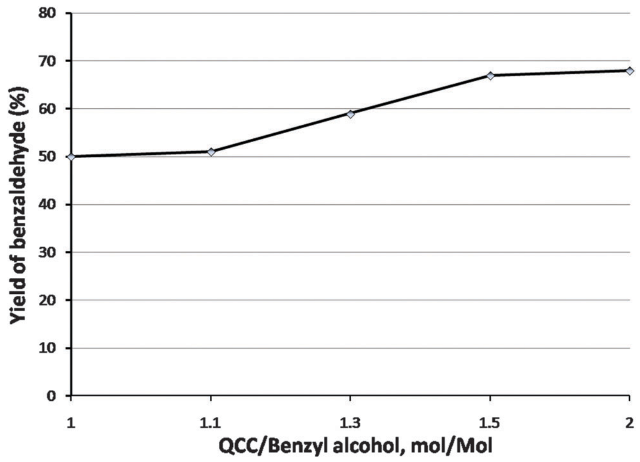


Fig. 1 Oxidation of 1 mmol of benzyl alcohol with different quantities of QCC.

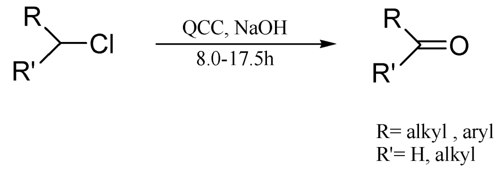
**Table 1** Comparative yields during oxidation of alcohols with QCC

| S. no. | R | R′ | Time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | $C_6H_5$ | H | 4 | 62 |
| 2 | 4-$(CH_3O)C_6H_4$ | H | 4 | 81 |
| 3 | 4-$(Cl)C_6H_4$ | H | 4 | 76 |
| 4 | 4-$(NO_2)C_6H_4$ | H | 4 | 65 |
| 5 | Cyclohexyl (including C in general formula) | — | 14 | 64 |
| 6 | $C_2H_5$ | $CH_3$ | 14 | 77[a] |
| 7 | $C_5H_{11}$ | H | 14 | 52 |

[a] Product was not isolated and only a percentage conversion from $^1H$ NMR is reported.

This can prove beneficial for the one pot conversion of halides directly to their corresponding carbonyl compounds (aldehyde or ketone), therefore we next attempted the conversion of benzyl chloride to benzaldehyde in water using QCC, by keeping all the parameters constant. Contrary to our predictions, no conversion to benzaldehyde was reported in this case. We also performed the reaction at elevated temperatures up to refluxing and by adding a co-solvent THF, but no conversion to aldehyde was reported.

The addition of an equimolar quantity of a hydroxide base may result in nucleophilic substitution of the halide to the corresponding alcohol, which may be used *in situ* for the generation of benzaldehyde. Therefore, we next performed the reaction in a basic medium using one mole equivalent of NaOH at a temperature between 45–50 °C, followed by the addition of QCC at room temperature that resulted in a much lower conversion ($<10\%$) of halide to aldehyde. Next, we doubled the molar equivalents of the base with respect to the halide and an increase in the product yield up to 38% was observed. Further optimization revealed that aromatic halides are converted into the corresponding carbonyls in 7–8 h, whereas no conversion for aliphatic chlorides such as chlorohexane and 2-chlorobutane was observed under similar conditions. Thinking that solubility might hinder the oxidation process, we also attempted it in a mixture of water–THF (8 : 2), but no change was reported in this case.



**Scheme 2** Oxidation of halides with QCC.

We were therefore able to convert the respective halide (1 mmol) into an aldehyde by stirring it with NaOH (2 mmol) in water (3 mL), at a temperature of 45–50 °C for 2.0–2.5 h, followed by the addition of QCC (1.5 mmol) at room temperature (Scheme 2). The results obtained are compiled in Table 2. The progress of the reactions was monitored *via* TLC and the isolated products were characterized with the help of IR and $^1H$ NMR spectroscopy. It is likely that the reaction involves the nucleophilic displacement of a halide with a hydroxyl group (generated from NaOH) to form an alcohol, which was used *in situ* for the oxidation.

To ascertain the efficacy of the process for organic synthesis and promote its use in process chemistry, we further applied the methodology to the oxidation of an indole derivative, namely 2-(bromomethyl)-5,7-dinitro-1*H*-indole (**3**), which was synthesized by Fischer indole synthesis.[39,40] This oxidation will in turn, open a route for the synthesis of 2-substituted indole aldehydes from the corresponding halide in aqueous media, which can be used further for the generation of a chiral centre. In the first stage we prepared 1-bromopropane-2-one by the reported method,[41] by adding bromine to acetone in the presence of $CaCO_3$ at 0–5 °C, and then stirring the contents at room temperature for 3 h to afford the crude product, which was then purified by vacuum distillation.

We next synthesized the corresponding hydrazone 1-(1-bromopropan-2-yl)-2-(2,4-dinitrophenyl) hydrazine (**2**) by reacting equimolar amounts of 2,4-dinitrophenyl hydrazine (**1**) with 1-bromopropane-2-one in ethanol in the presence of catalytic amounts of acetic acid, which was recrystallized in ethanol to afford the pure product. Finally, the corresponding halide **3** was obtained by cyclisation of **2** at an elevated temperature (115–125 °C) with polyphosphoric acid (PPA) and it was also purified by re-crystallisation in ethanol.

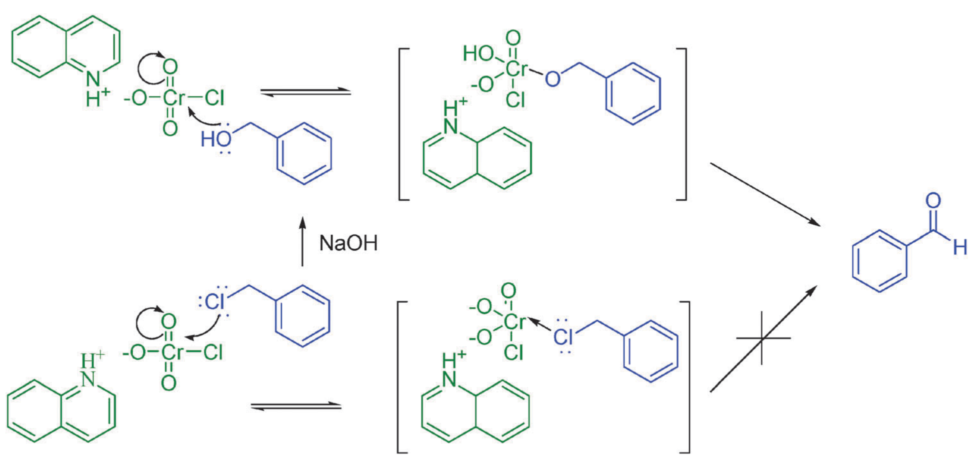


**Fig. 2** Plausible complex formation by the interaction of alcohols and halides with QCC.

Table 2 Comparative yields during oxidation of halides with QCC

| S. no. | R | R′ | Time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | $C_6H_5$ | H | 8 | 38 |
| 2 | 4-(Cl)$C_6H_4$ | H | 8 | 35 |
| 3 | Cyclohexyl (including C in general formula) | — | 18 | 37 |
| 4 | $C_2H_5$ | $CH_3$ | 18 | — |
| 5 | $C_5H_{11}$ | H | 18 | — |

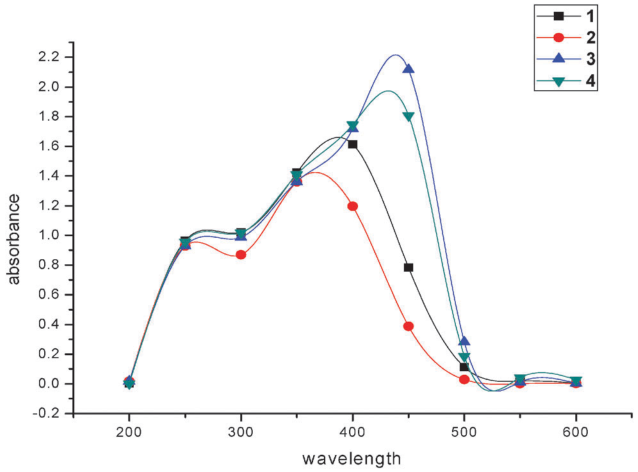


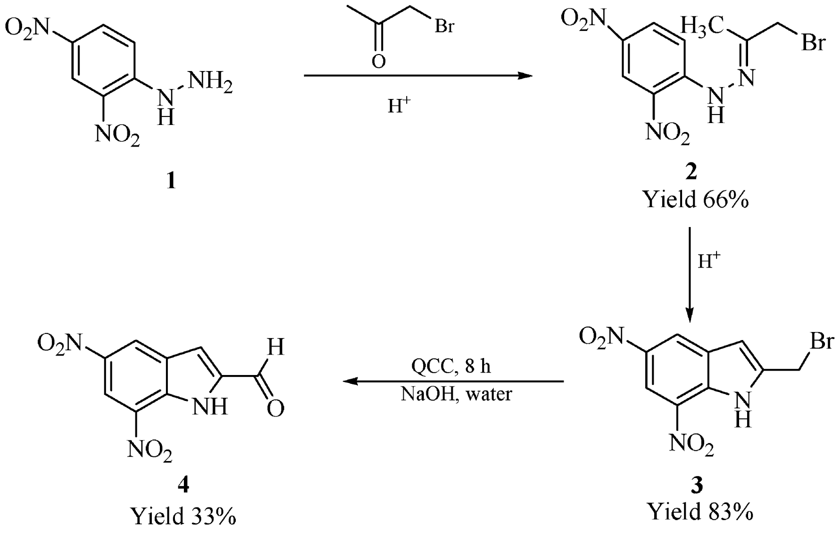
Fig. 3 Comparative UV-visible absorption spectrum of **1**, **2**, **3** and **4**.

After the synthesis of 2-(bromomethyl)-5,7-dinitro-1*H*-indole (**3**) we moved our attention towards its oxidation with QCC in an aqueous medium under the optimized conditions (Scheme 3). We were successful in obtaining the corresponding carbonyl derivative **4** by reacting **3** with QCC in an alkaline medium. Product formation at different stages was also ascertained by UV-visible absorption spectroscopy where the formation of an indole nucleus in **3** was marked with a shift towards higher wavelengths (Fig. 3). This shift is observed due to extending conjugation as we move from compound **2** to **3**. Furthermore, the mass spectrum of **3** has two peaks of equal intensity at *m*/*z* 298 and 300.

In order to increase the scope of the developed methodology, we were interested in removing the chromium ions completely from the aqueous waste. $Cr^{+6}$ has been considered as the toxic form whereas $Cr^{3+}$ has been considered as an essential nutrient component for metabolizing[42,43] fats, sugars and proteins. In the literature several methods are available for the removal of chromium, such as ion exchange,[44] reverse osmosis,[45] adsorption[46] and the most common method for the removal of $Cr^{6+}$ is its reduction to $Cr^{3+}$, followed by its coagulation and filtration. Various reducing agents including metal salts and metals themselves, including ferrous sulfate,[47] iron[48] *etc.* can be used for this purpose.

The aqueous waste obtained in the reaction was first reduced to a $Cr^{3+}$ species which was subsequently removed from water. Initially, we determined the amount of $Cr^{6+}$ leached into water[49] by dissolving a definite amount of QCC into the water. We found that 60% of the QCC remained suspended in water and 40% gets dissolved in it. The heterogeneous mixture was filtered to remove undissolved QCC. The obtained filtrate was reduced with $FeSO_4$ and coagulated by adding $Ca(OH)_2$. The precipitates were removed by filtration to remove solid waste and the aqueous solution was checked for traces of chromium ions that were found to be absent.

Once we were sure that the method was capable of removing $Cr^{6+}$ ions from water, after reduction with $FeSO_4$, we treated the waste generated at the end of the reaction. The reaction mass was first filtered to remove undissolved solid and the filtrate was then reduced with inexpensive $FeSO_4$. The solid precipitates obtained after coagulation with $Ca(OH)_2$ were removed by filtration and the mother liquor obtained was found to be acidic (pH = 3.97). It was made neutral by adding 0.1 N $Ca(OH)_2$ and was finally discarded.



**1**

**2**
Yield 66%

**4**
Yield 33%

**3**
Yield 83%

Scheme 3 Oxidation of 2-(bromomethyl)-5,7-dinitro-1*H*-indole with QCC.

# Conclusions

We have developed a new protocol for the oxidative transformation of alcohols and organic halides to aldehydes using QCC in aqueous solution. The method is efficiently used under solventless conditions for the oxidation process and generates clean waste after its reduction with $FeSO_4$. This work demonstrates an efficient use of QCC in natural product synthesis and provides an insight into the reactions that need chromium species exclusively for their transformations, such as 5-hydroxymethyl preparation[50] (5-HMF) from biomass resources.

# Experimental

## (a) General procedure for the oxidation of alcohols

Alcohol (5 mmol) was added to water (15 mL) at room temperature, followed by the addition of QCC (7.5 mmol, 2.02 g), and the mixture was then stirred for the specified time (Table 1). After completion of the reaction, as indicated by TLC, the crude product was extracted using diethyl ether (3 × 5 mL) and the combined organic layer was washed with dil. HCl solution (5 mL) and distilled water (2 × 5 mL). It was finally dried over anhydrous sodium sulphate. Evaporation of the solvent under reduced pressure, followed by chromatographic separation, afforded the pure product.

## (b) Solventless procedure for the oxidation of benzyl alcohol

QCC (15 mmol, 4.04 g) was added to a mixture of distilled water (12 mL) and benzyl alcohol (10 mmol, 1.0 mL) and stirred at room temperature for 4 h. After the completion of the reaction, as monitored by TLC, the upper organic layer of the product was separated from the aqueous layer and further washed with dil. HCl solution (5 mL) and distilled water (2 × 5 mL). The obtained crude product was further distilled to achieve pure benzaldehyde (0.53 g, 52%).

## (c) General procedure for the oxidation of halides

Sodium hydroxide (10 mmol, 0.40 g) was added to a suspension of distilled water (15 mL) and halide (5 mmol) at a temperature between 45–50 °C and stirred for 2.5 h, followed by the addition of QCC (7.5 mmol, 2.02 g) at room temperature. The reaction contents were further stirred for the specified time (Table 2) and the progress of the reaction was monitored by TLC. Finally, the crude product was extracted using diethyl ether (3 × 5 mL) and the combined organic layer was washed with dil. HCl solution (5 mL) and distilled water (2 × 5 mL), it was then dried over anhydrous sodium sulphate. Evaporation of the solvent under reduced pressure afforded the crude product, which was purified by chromatographic separation.

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# Notes and references

1 *Green Chemistry: An Introductory Text*, ed. M. Lancaster, Royal Society of Chemistry, 2010.

2 *Organic reactions in aqueous media*, ed. C. J. Li and T. H. Chan, John Wiley and Sons, New York, 1997.

3 E. T. Kool and R. J. Breslow, *J. Am. Chem. Soc.*, 1988, **110**, 1596–1597.

4 C. Petrier, J. Einhorn and J. L. Luche, *Tetrahedron Lett.*, 1985, **26**, 1449–1452.

5 C. Petrier and J. L. Luche, *J. Org. Chem.*, 1985, **50**, 910–912.

6 N. E. Leadbeater and M. Marco, *J. Org. Chem.*, 2003, **68**, 888–892.

7 Y.-S. Yang, Z.-L. Shen and T.-P. Loh, *Org. Lett.*, 2009, **11**, 1209–1212.

8 A. J. Boersma, B. L. Feringa and G. Roelfes, *Angew. Chem.*, 2009, **48**, 3396–3398.

9 V. Tychopoulos and J. H. P. Tyman, *Synth. Commun.*, 1986, **16**, 1401–1409.

10 W. W. Epstein and F. W. Sweat, *Chem. Rev.*, 1967, **67**, 247–260.

11 B. R. Travis, M. Sivakumar, G. O. Hollist and B. Borhan, *Org. Lett.*, 2003, **5**, 1031–1034.

12 *Chromium oxidations in Organic Chemistry*, ed. G. Cainelli and G. Cardillo, Springer-Verlag, Berlin, 1984.

13 F. M. Menger and C. Lee, *Tetrahedron Lett.*, 1981, **22**, 1655–1656.

14 S. K. Rout, S. Guin, K. K. Ghara, A. Banerjee and B. K. Patel, *Org. Lett.*, 2012, **14**, 3982–3985.

15 K. Sato, M. Aoki, J. Takagi, K. Zimmermann and R. Noyori, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 2287–2306.

16 S. Abramovici, R. Neumann and Y. Sasson, *J. Mol. Catal.*, 1985, **29**, 299–303.

17 A. Corma and H. Gracia, *Chem. Rev.*, 2002, **102**, 3837–3892.

18 S. W. Kshirsagar, N. R. Patil and S. D. Samant, *Tetrahedron Lett.*, 2008, **49**, 1160–1162.

19 H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, 1949, **71**, 1767–1769.

20 S. J. Angyal, P. J. Morris, J. R. Tetaz and J. G. Wilson, *J. Chem. Soc.*, 1950, **3**, 2141–2145.

21 *Oxidation of Alcohols to Aldehydes and Ketones*, ed. G. Tojo and M. Fernandez, Springer, Berlin, 2006.

22 E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 1979, **5**, 399–402.

23 J. Singh, P. S. Kalsi, G. S. Jawanda and B. R. Chhabra, *Chem. Ind.*, 1986, 751–752.

24 S. Goswami and A. Kar, *Synth. Commun.*, 2011, **41**, 2500–2504.

25 F. Bonadies, R. Di Fabio and C. Bonini, *J. Org. Chem.*, 1984, **49**, 1647–1649.

26 M. K. Chaudhuri, S. K. Chettri, S. Lyndem, P. C. Paul and P. Srinivas, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1894–1898.

27 D. S. Bose and A. V. Narasaiah, *Synth. Commun.*, 2000, **30**, 1153–1158.

28 J. Singh, G. L. Kad, S. Vig, M. Sharma and B. R. Chhabra, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.*, 1997, **36B**, 272–274.

29 G. Karthikeyan, K. P. Elango, K. Karunakaran and A. Balasubramanian, *Oxid. Commun.*, 1998, **21**, 51–54.

30 R. Gurumurthy and B. Karthikeyan, *Orient. J. Chem.*, 1998, **14**, 435–437.

31 M. Pandeeswaran, B. John, D. S. Bhuvaneshwari and K. P. Elango, *J. Serb. Chem. Soc.*, 2005, **70**, 145–151.

32 J. V. Singh, K. Mishra and A. Pandey, *Bull. Pol. Acad. Sci., Chem.*, 2003, **51**, 35–43.

33 S. S. Kanna and K. P. Elango, *Int. J. Chem. Kinet.*, 2002, **34**, 585–588.

34 K. K. Rai, R. K. Kannaujia, K. Rai and S. Singh, *Orient. J. Chem.*, 2013, **29**, 1071–1078.

35 A. A. Jameel, *J. Indian Chem. Soc.*, 1998, **75**, 439–442.

36 N. Gupta, G. L. Kad and J. Singh, *J. Mol. Catal.*, 2009, **302**, 11–14.

37 N. Gupta, G. L. Kad, V. Singh and J. Singh, *Synth. Commun.*, 2007, **37**, 3421–3428.

38 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156–164.

39 S. Wagaw, B. H. Yang and S. L. Buchwald, *J. Am. Chem. Soc.*, 1998, **120**, 6621–6622.

40 E. Fischer and O. Hess, *Chem. Ber.*, 1884, **17**, 559.

41 N. Gupta, M. Kaur, Shallu, N. Gupta, G. L. Kad and J. Singh, *Nat. Prod. Res.*, 2012, 1–6.

42 L. L. Hopkins, O. Ransome-Kuti and A. S. Majaj, *Am. J. Clin. Nutr.*, 1968, **21**, 203–211.

43 K. N. Jeejeebhoy, R. C. Chu, E. B. Marliss, G. R. Greenberg and A. Bruce-Robertson, *Am. J. Clin. Nutr.*, 1977, **30**, 531–538.

44 S. A. Cavaco, S. Fernandes, M. M. Quina and L. M. Ferreira, *J. Hazard. Mater.*, 2007, **144**, 634–638.

45 H. Ozaki, K. Sharma and W. Saktaywin, *Desalination*, 2002, **144**, 287–294.

46 M. Dakiky, M. Khamis, A. Manassra and M. Mer'eb, *Adv. Environ. Res.*, 2002, **6**, 533–540.

47 G. Qin, M. J. Mcguire, N. K. Blute, C. Seidel and L. Fong, *Environ. Sci. Technol.*, 2005, **39**, 6321–6327.

48 R. T. Wilkin, C. Su, R. G. Ford and C. J. Paul, *Environ. Sci. Technol.*, 2005, **39**, 4599–4605.

49 J. Mendham and J. Mendham, *Vogels textbook of quantitative chemical analysis*, Pearson Education India, 2006.

50 H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597.