



## Quinaldinium Chlorochromate(VI), (QnCC) Catalyzed Oxidation of Alcohols with Periodic Acid Under Solvent-Free Conditions and Microwave Irradiation

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**Abstract:** The atom efficient synthesis of quinaldinium chlorochromate(VI),  $C_{10}H_9NH[CrO_3Cl]$ , (QnCC) was performed by using a 1:1:1 stoichiometric amounts of  $CrO_3$ , HCl (aq) and quinaldine. QnCC was isolated in 99% yield as an orange crystalline solid and characterized with FT-IR,  $^1H$ -NMR, and  $^{13}C$ -NMR. An efficient, selective, and environmentally friendly periodic acid ( $H_5IO_6$ ) oxidation of alcohols catalyzed by QnCC (2 mol%) is described. Oxidation reactions of some primary and secondary alcohols to their corresponding aldehydes and ketones were performed under solvent-free conditions at room temperature and MW irradiation in high to excellent yields.

**Keywords:** Alcohols, quinaldinium chlorochromate, periodic acid, solvent-free, microwave irradiation.

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## INTRODUCTION

The selective oxidation of alcohols to carbonyl compounds is a foremost functional group conversion in synthetic organic chemistry, due to the key role of this process in the production of valuable compounds for pharmaceutical, dyestuff, and agrochemical industries (1–4). Thus, to date, various oxochromium(VI) amine complexes have been commonly used as stable oxidizing agents for selective oxidation of alcohols with high efficiency. Some of them are pyridinium chlorochromate, pyridinium fluorochromate, pyridinium dichromate, dipyrazinium tris(fluorotrioxochromate), 1-decyl-4-aza-1-azonia-bicyclo[2.2.2]-octane chlorochromate, 3,5-dimethylpyrazolium fluorochromate, and triethylammonium chlorochromate (5–11).

In traditional oxidation processes, volatile organic solvents and stoichiometric amounts of chromium(VI) based reagents have widely been used though these reagents are highly toxic, and environmentally polluting. Therefore, the search for effective catalytic oxidation systems that use clean, inexpensive primary oxidant with high activity and selectivity are still needed (12–18). Recently, several methods have been reported for the catalytic oxidation of various alcohols by using periodic acid ( $\text{H}_5\text{IO}_6$ ) as co-oxidant and  $\text{CrO}_3$  or oxochromium(VI) reagents as catalysts (19–22). However, these oxidation reactions are generally carried out in a solvent and long reaction times are required. Additionally, microwave-assisted oxidation reactions coupled with solvent-free conditions have gained special attention as environmentally friendly processes in recent years (23–25).

We have described for the first time the quinaldinium fluorochromate (QnFC)-catalyzed periodic acid oxidation of various alcohols under solvent-free conditions (26). Herein, in order to continue to develop environmentally benign synthetic protocols, oxidation of alcohols with periodic acid catalyzed by quinaldinium chlorochromate (QnCC) under solvent-free conditions at room temperature and under microwave irradiation has been investigated.

## MATERIAL AND METHODS

All chemicals were supplied by Aldrich, Merck, and Fluka and used without further purification. Thermo Fischer Scientific Nicolet iS10 FT-IR spectrometer was used to obtain an FT-IR spectrum of QnCC.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance III- 400 MHz spectrometer (in  $\text{DMSO-d}_6$ ). Microwave-assisted oxidation reactions were performed with professional multimode Microsynth-Milestone oven.

**Economic synthesis of quinaldinium chlorochromate**

Chromium(VI) oxide (5 mmol, 0.5 g) was taken in a beaker and hydrochloric acid (37%, 5 mmol, 0.41 mL) was added dropwise with continuous stirring for 10 min. This was followed by dropwise addition of 1.0 mL of water under stirring over a period of 15 min, leading to a clear orange colored solution. The solution was cooled in an ice-water bath for 15 min and quinaldine (5 mmol, 0.71 mL) was added dropwise to this solution with vigorous stirring. The whole was allowed to stand first in an ice-water bath for 30 min. and then at room temperature for 30 min. The compound was washed twice with hexane, kept under suction until moderately dried. Yield: 99.0%, mp: 139 °C.

FT-IR (ATR,  $\text{cm}^{-1}$ )  $\nu_{\text{max}}$  = 3292, 3030, 2884, 2610, 1645, 1603, 1546, 1492, 1412, 1382, 1307, 1231, 1150, 1047, 938, 880, 770, 726, 639, 615.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-d}_6$ , ppm):  $\delta$  = 2.85 (s, 3H); 7.77-8.15 (m, 6H); 8.78 (s, 1H) .  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-d}_6$ , ppm)  $\delta$  = 22.02; 122.45; 123.25; 126.39; 127.96; 128.60; 132.81; 142.75; 158.19.

**General procedure for oxidation of alcohols with QnCC/ $\text{H}_5\text{IO}_6$  under solvent-free conditions**

A mixture of the corresponding alcohol (1 mmol) and QnCC (2 mol%) was ground in a mortar until it became homogeneous and  $\text{H}_5\text{IO}_6$  (1.1 mmol) was introduced slowly. The progress of the reaction was monitored by using TLC on silica gel (n-hexane-ethyl acetate: 2:1). Upon completion of the reaction, work up with ether (3x15 mL) and evaporation of the solvent gave the corresponding carbonyl compounds.

**General procedure for microwave-assisted oxidation of alcohols with QnCC/ $\text{H}_5\text{IO}_6$  under solvent-free conditions**

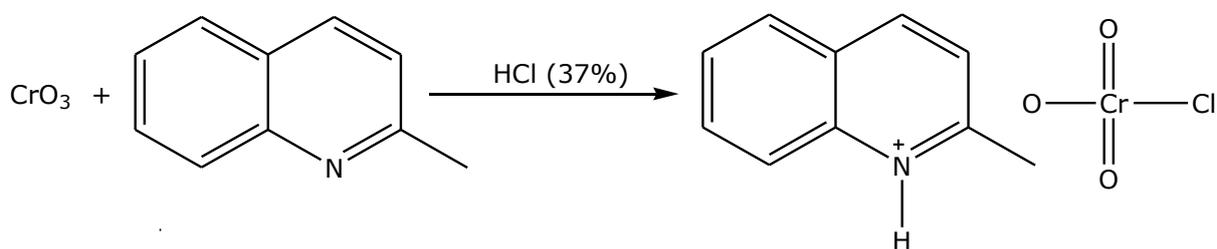
The mixture of the corresponding alcohol (1 mmol), QnCC (2 mol %), and  $\text{H}_5\text{IO}_6$  (1.1 mmol) was irradiated and heated to 50 °C in the microwave reactor by the time indicated in Table 1. The progress of the reaction was monitored by using TLC on silica gel (n-hexane-ethyl acetate: 2:1). At the end of the exposure to microwaves, the mixture was cooled to room temperature and extracted with ether (3x15 mL) and evaporation of the solvent gave the corresponding carbonyl compounds.

Yields were based on the isolation of the 2,4-dinitrophenylhydrazones (DNPH) (Table 1). Since the carbonyl compounds are all known compounds, the qualitative identification of the

products was made by comparing of the melting points of the 2,4-dinitrophenylhydrazones with those of corresponding DNPH derivatives.

## RESULTS AND DISCUSSION

An atom-efficient and environmentally benign procedure for the synthesis of quinaldinium chlorochromate was accomplished by using stoichiometric amounts of hydrochloric acid, chromium trioxide, quinaldine and minimum amount of water. Using a minimum amount of water leads to waste minimization by preventing the loss of QnCC through its solubility. Thereby, quinaldinium chlorochromate(VI) was obtained in 99.0 % isolated yield as an orange-colored crystalline solid (Scheme 1).



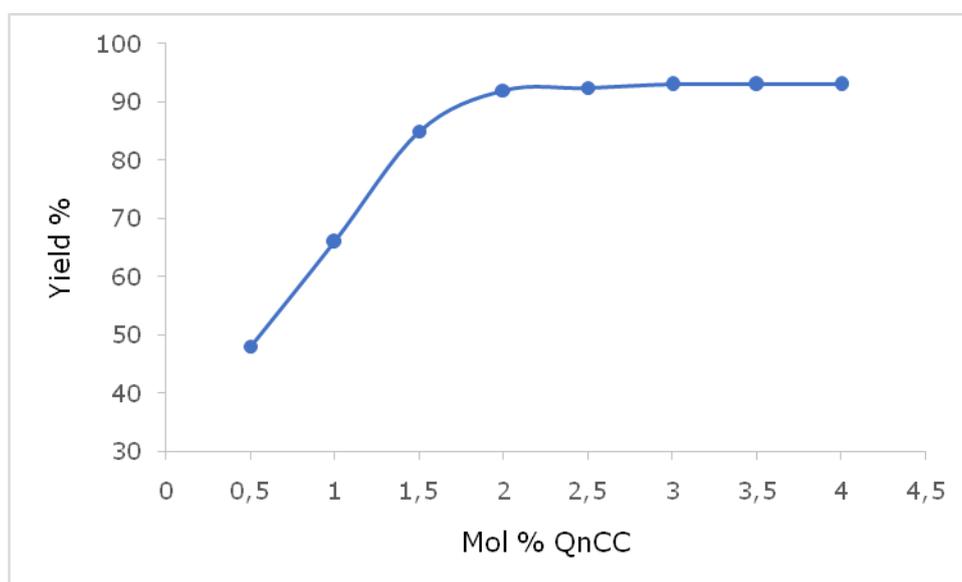
**Scheme 1:** Atom-efficient synthesis of quinaldinium chlorochromate.

The structure of QnCC was confirmed by FT-IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$ . The FTIR spectra of QnCC shows the characteristic bands of the quinaldine moiety and chlorochromate anion, where appropriate. In particular, characteristic bands of chlorochromate anion are observed at *ca.*  $\nu = 938$ , and  $880\text{ cm}^{-1}$  corresponding to  $\nu_{\text{asym}}(\text{Cr}=\text{O})$ , and  $\nu_{\text{sym}}(\text{Cr}=\text{O})$ , respectively (27). The singlet observed at  $\delta 2.85$  at the  $^1\text{H-NMR}$  spectra of QnCC proved three aliphatic protons of a methyl group and multiple peak at  $\delta 7.77\text{--}8.15$  substantiated the presence of aromatic protons of quinaldinium cation. In addition, singlet at  $\delta 8.78$  verified the N-H proton of quinaldinium cation. The obtained  $^{13}\text{C-NMR}$  spectral data for QnCC was compatible with its the structure.

Quinaldinium chlorochromate (QnCC) supported on alumina has previously been reported as a powerful oxidant for the oxidation of various alcohols (28). However, the need to use an excess amount of QnCC/alumina (alcohol to oxidant ratio 1:1.5) in  $\text{CH}_2\text{Cl}_2$  to perform the oxidation is a major drawback, due to toxicity and environmentally polluting effects of chromium based reagents and chlorinated solvents. Therefore, practical and efficient oxidation processes that produce smaller amounts of toxic chromium waste are still in demand.

In the absence of QnCC, benzyl alcohol was oxidized to benzaldehyde by using 1.1 equivalents of  $H_5IO_6$  under solvent-free conditions at room temperature, and under MW irradiation. The yields of the reactions obtained were 15% after 180 min at room temperature, and 22% after 2 min under MW irradiation.

In order to determine the optimum amount of QnCC which maximizes the yield of oxidation reaction, benzyl alcohol was oxidized to benzaldehyde by using 1.1 equivalents of  $H_5IO_6$  and 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, and 4.0% moles of QnCC under solvent-free conditions at room temperature. The use of 2.0 mol% QnCC almost maximized the yield of reaction (Figure 1). To avoid the use of excess amount of chromium compound, 2 mol% of QnCC was used for the oxidation of all the alcohols.



**Figure 1:** The influence of QnCC amount on the yield of oxidation reaction of benzyl alcohol.

Having determined the optimum QnCC amount which maximizes the yield of reaction, the oxidation reactions of various alcohols were examined. As shown in Table 1, all the primary benzylic alcohols (1-7) were almost quantitatively and selectively oxidized to corresponding aldehydes and all the secondary alcohols (8-11) to ketones with high to excellent yields in very short reaction times with the  $H_5IO_6$ /QnCC system.

In the present procedure the chemoselectivity of the oxidation reactions of some primary benzylic alcohols into the corresponding aldehydes was provided by using 1.1 equivalents of  $H_5IO_6$  and 2% mol of QnCC (Table 1). As a result, no overoxidation to carboxylic acids has been observed. On the other hand, in the oxidation reactions carried out by using with 2.2 equivalents of  $H_5IO_6$ , and catalytic (2% mol) amount of QnCC almost quantitative conversion to carboxylic acids with the yields of 85% ( 8 min), 91% (5 min), 92% (5 min), and 90%( 15

min) has been observed for the oxidation of benzyl alcohol, 4-methylbenzyl alcohol, 4-chlorobenzyl alcohol, and 4-nitrobenzyl alcohol, respectively, at room temperature under solvent-free conditions.

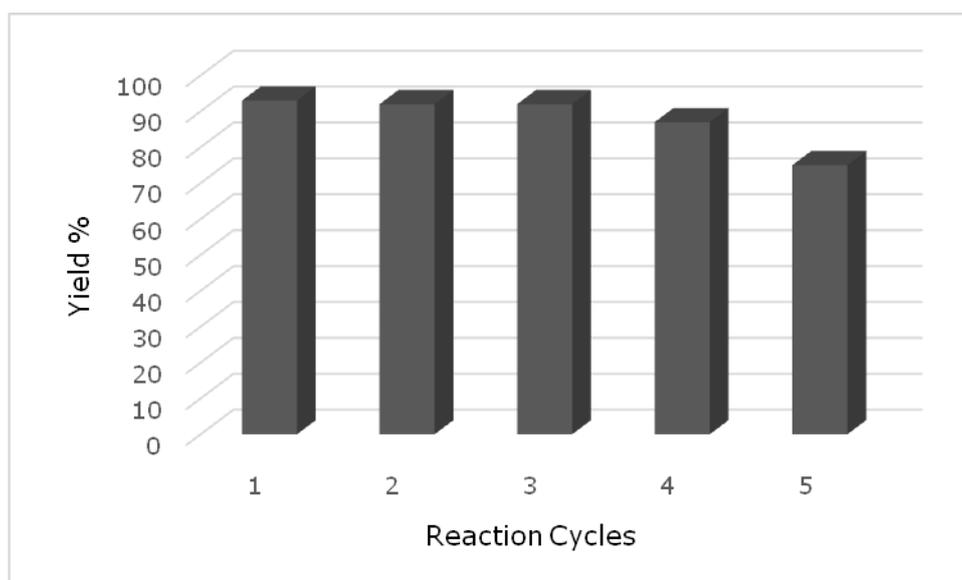
The solvent-free oxidation reactions of all the alcohols with the  $H_5IO_6/QnCC$  system were also carried out under MW irradiation at 50 °C. The results are presented in Table 1 in comparison to the results of the reactions performed at room temperature. It is notable that the yields of the products are close to each other, but the reactions which were carried out under MW irradiation occur much faster than the reactions carried out at room temperature.

**Table 1:** Solvent-free oxidation of alcohols by QnCC/H<sub>5</sub>IO<sub>6</sub> at room temperature and under MW irradiation.

Entry	Substrate	Product <sup>a</sup>	QnCC/H <sub>5</sub> IO <sub>6</sub> (RT)		QnCC/H <sub>5</sub> IO <sub>6</sub> (MW)		Mp(°C) of DNPH	
			Time (min)	Yield (%) <sup>b</sup>	Time (sec)	Yield (%) <sup>b</sup>	Found	Reported (29)
1	Benzyl alcohol	Benzaldehyde	1	92	30	96	237	237
2	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	1.5	100	20	98	232	233
3	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	2	95	30	97	265	265
4	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	2	98	10	98	254	254
5	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	5	85	40	90	319	320
6	3-Chlorobenzyl alcohol	3-Chlorobenzaldehyde	2	100	30	100	247	248
7	3-Nitrobenzyl alcohol	3-Nitrobenzaldehyde	3	83	40	90	291	292
8	4-tert-Butylcyclohexanol	4-tert-Butylcyclohexanone	6	99	30	98	155	156
9	Cyclohexanol	Cyclohexanone	6	89	40	90	162	162
10	Menthol	Menthone	12	86	40	88	146	146
11	Cycloheptanol	Cycloheptanone	3	97	20	92	148	148

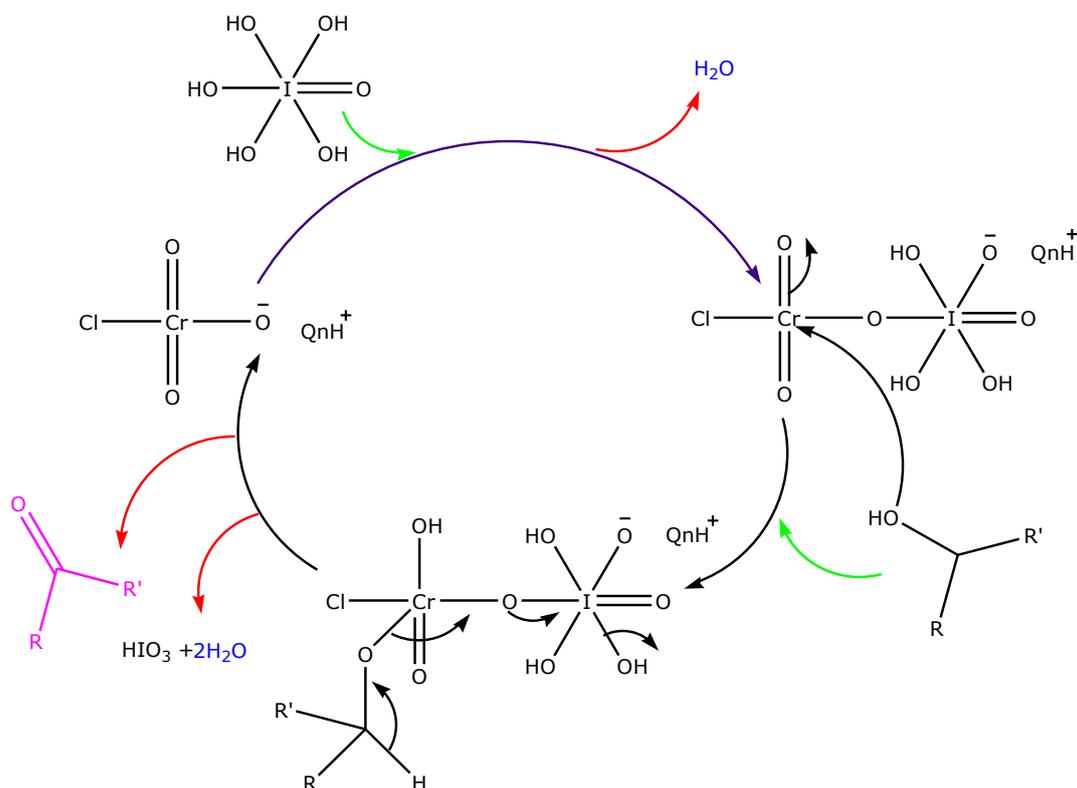
<sup>a</sup> All the products have already been reported in the literature and were defined by melting points of their 2,4-dinitrophenylhydrazones. <sup>b</sup> Isolated yields based on their corresponding dinitrophenylhydrazones.

The recyclability of QnCC was determined by performing the oxidation reaction of benzyl alcohol to benzaldehyde. Subsequent to the end of the first run of the oxidation reaction, benzaldehyde was separated from QnCC with diethyl ether extraction. Then, the fresh charges of  $\text{H}_5\text{IO}_6$  (1.1 mmol) and benzyl alcohol (1.0 mmol) were introduced for each subsequent run of the oxidation reactions. The yields thus obtained were 92%, 90%, 89%, 83%, and 70%, respectively. As shown in Figure 2, QnCC is recyclable for 4 runs without a considerable reduction in its catalytic performance.



**Figure 2:** Recyclability of the QnCC for oxidation of benzyl alcohol.

The mechanism of periodic acid oxidation reactions catalyzed by chromium(VI) reagents has not been exactly clarified. However, based on the previously reported mechanism (20,22), it may be presumed that the QnCC/ $\text{H}_5\text{IO}_6$  system may form chlorochromateperiodate which is possibly a more efficient oxidant than the chlorochromate (Scheme 2). Besides, Cr(VI) may keep its oxidation state during the reaction until all periodic acid is consumed (30).



**Scheme 2:** The recommended mechanism for QnCC catalyzed the periodic acid oxidation of alcohols.

To show the catalytic activity of QnCC/H<sub>5</sub>IO<sub>6</sub> system, we compared the results of our study with the known data from the literature for the oxidation of benzyl alcohol (Table 2). As shown in Table 2, QnCC-catalyzed periodic acid oxidation has many advantages such as the amount of chromium(VI) compound used, solvent-free conditions, relatively short reaction times, and high to excellent yields of products in comparison with previous reports. Compared to our previous work (26), a catalytic amount of QnCC (2 mol%) required for the oxidation reactions is less than that of QnFC (3 mol%), and the reactions which were carried out under MW were completed in very short reaction times with high yields.

**Table 2:** Comparison of oxidation of benzyl alcohol with periodic acid catalyzed by chromium(VI) based oxidants.

Catalyst	H <sub>5</sub> IO <sub>6</sub> (equiv.)	Catalyst (mol %)	Conditions	Time (min.)	Yield (%)	Ref.
QnCC	1.1	2	Solvent-free, rt	2	92	-
QnCC	1.1	2	Solvent-free, MW	0.5	96	-
QnFC	1.1	3	Solvent-free, rt	2	93	(26)
PCC	1.1	2	CH <sub>3</sub> CN, 0 °C to rt	120	72	(20)
Cr(acac) <sub>3</sub>	1.5	10	CH <sub>3</sub> CN, rt	180	93	(31)

## CONCLUSION

In conclusion, QnCC effectively catalyzes the selective oxidation of alcohols with periodic acid under solvent-free conditions at room temperature and under MW irradiation. The QnCC/H<sub>5</sub>IO<sub>6</sub> system is simple, effective, versatile and selectively oxidizes various alcohols in very short reaction times with high to excellent yields. In addition, this system leads to much less chromium contamination while preserving the all known advantages of chromium(VI) based oxidant. Remarkably, QnCC can be recycled for 4 times without notable loss of its catalytic performance. From the environmental point of view, this new catalytic system can be evaluated as a green protocol for the oxidation of alcohols.

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