Economic synthesis of quinaldinium fluorochromate(VI), (QnFC), and solvent-free periodic acid oxidation of alcohols catalyzed by QnFC

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Economic synthesis of quinaldinium fluorochromate(VI), (QnFC), and solvent-free periodic acid oxidation of alcohols catalyzed by QnFC

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Abstract: A 1:1:1 stoichiometric reaction between CrO_3, aqueous HF, and quinaldine affords orange crystalline quinaldinium fluorochromate(VI) (QnFC) ($C_{10}H_9NH[CrO_3F]$) in 99.4% isolated yield. A highly efficient, simple, chemoselective, and environmentally benign procedure for QnFC (3 mol%) catalyzed oxidation of primary and secondary alcohols to aldehydes and ketones using 1.1 equiv of H_5IO_6 under solvent-free conditions is described.

Key words: Periodic acid, solvent-free, oxidation of alcohols, quinaldinium fluorochromate(VI)

1. Introduction

Oxidation reactions are of great interest in fine chemistry, at both the laboratory and the industrial scale.[1,2] The oxidation of alcohols to aldehydes and ketones is a fundamental process in organic synthesis.[3−5] The traditional methods for this purpose usually employ stoichiometric quantities of inorganic reagents such as chromate and permanganate. These methods are quite useful in laboratory-scale reactions but usually generate significant amounts of inorganic waste that damage the environment seriously in large-scale reactions.[6,7]

Oxochromium(VI)amine complexes such as pyridinium chlorochromate (PCC) and pyridinium fluorochromate (PFC) are extensively used in the oxidation of alcohols owing to their commendable performance under mild conditions,[8−11] but the requirement of at least a stoichiometric amount of the oxidant to complete the oxidation is a disadvantage due to the high toxicity of chromium reagents. The present concern about the toxicity and environmental implications of oxochromium(VI) has provided encouragement for the study and use of catalytic oxochromium(VI) reagents in conjunction with stoichiometric co-oxidants, particularly when applied to the large-scale preparations found in industries where the disposal of byproducts is a constant problem. Periodic acid (H_5IO_6) has been used as co-oxidant in several mild and selective oxidation reactions of alcohols catalyzed by oxochromium(VI) reagents.[12,13] These oxidation reactions are often carried out in acetonitrile and sometimes at elevated temperatures. Problems are thus encountered for the complete removal of the solvent. Of particular significance would be the establishment of solvent-free processes, which are not only of interest from an ecological point of view but avoiding the use of organic solvents during the reactions in organic synthesis leads to clean, efficient, and economical technology.

To the best of our knowledge, no chromium(VI) catalyzed oxidation reactions of alcohols have been carried out under solvent-free conditions in which periodic acid is used as the terminal oxidant. An attractive

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alternative is to carry out these oxidation reactions under solvent-free conditions. We report herein a facile and efficient oxidation of primary and secondary alcohols to aldehydes and ketones using only 3 mol % QnFC and 1.1 equiv of H_5IO_6, under solvent-free conditions at room temperature (Scheme 1).
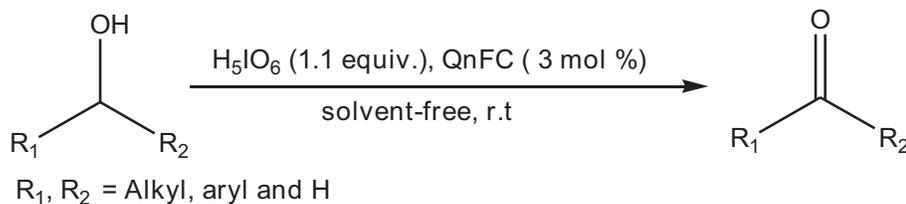
Scheme 1. QnFC catalyzed oxidation of alcohols to the corresponding aldehydes and ketones with periodic acid under solvent-free conditions.

2. Results and discussion

In continuation of our ongoing program to develop the use of solvent-free systems for environmentally benign synthetic protocols,[14−16] we examined the use of this procedure for periodic acid oxidation of alcohols catalyzed by QnFC. Although we have previously reported QnFC as a versatile reagent for various oxidative transformations,[17] the need to use an excess or at least a stoichiometric amount of QnFC to perform the oxidations is a drawback, due to all the known disadvantages of chromium-based compounds.

It was first considered worthwhile to try the atom efficient synthesis of QnFC. Apart from our previous procedure, minimal amounts of water have been used in order to enable waste minimization and prevent the loss of QnFC due to its solubility in water. Thus, a 1:1:1 stoichiometric reaction among CrO_3, aqueous HF and quinaldine affords orange crystalline quinaldinium fluorochromate(VI) in 99.4% isolated yield. QnFC thus obtained is substantially pure and crystalline and so no recrystallization is needed. QnFC melts at 146–148 °C and the results of analysis and characterization data compare very well with those reported earlier.[17]

All the oxidation reactions were carried out at room temperature under solvent-free conditions. In a control experiment, benzyl alcohol was converted into benzaldehyde with 1.1 equiv. H_5IO_6 in 15% yield after 180 min in the absence of QnFC. In order to find the catalytic amount of QnFC required for maximum yield, the oxidation reactions of benzyl alcohol were performed by using 1.1 equiv. of H_5IO_6. The use of 3 mol % QnFC maximized the yield of benzaldehyde. An increase in QnFC amount over 3 mol % does not produce more conversion. This is illustrated in Figure 1. Hence 3 mol % of QnFC was maintained during the oxidation of all the alcohols.
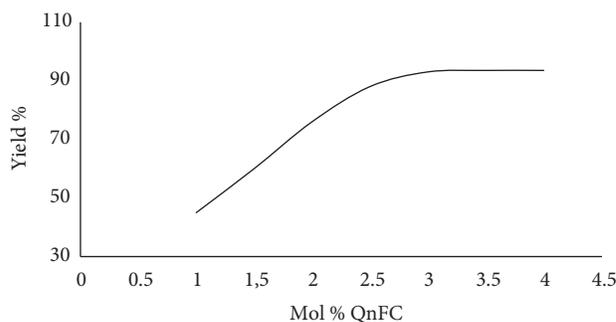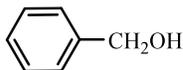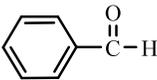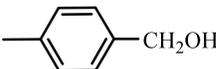

Figure 1. Effect of the catalyst amount on the oxidation of benzyl alcohol using 1.1 equiv. H_5IO_6 and benzyl alcohol for 2 min at room temperature under solvent-free conditions.

Having optimized the reaction conditions using benzyl alcohol as a model substrate, the oxidation of various aromatic and aliphatic alcohols was then examined to establish the generality of the method (Table 1). Both electron-poor (entries 3 and 4) as well as electron-rich benzylic primary alcohols (entries 1 and 2) were oxidized smoothly to give aldehydes in a short time without overoxidation to carboxylic acids. Aliphatic primary and secondary alcohols (entries 5–8) were oxidized to give the corresponding carbonyl compounds in high to excellent yields. Notable is that the oxidation of 1-octanol (entry 5) gave octanal in 84% yield, unlike PCC/H_5IO_6 oxidation, which gave a complex mixture.[13]

Table 1. Comparison of solvent-free oxidations by $QnFC/H_5IO_6$ and by QnFC.

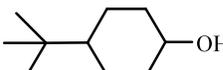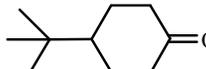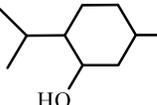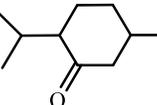| Entry	Substrate	Product [a]	$QnFC/H_5IO_6$		QnFC		Mp (°C) of DNPH	
			Time (min)	Yield (%) [b]	Time (min)	Yield (%) [b]	Found	Reported [18]
1	benzyl alcohol	benzaldehyde	2	93	180	86	237	237
2	4-methylbenzyl alcohol	4-methylbenzaldehyde	2	95	120	90	234	233
3	4-chlorobenzyl alcohol	4-chlorobenzaldehyde	4	97	120	96	265	265
4	4-nitrobenzyl alcohol	4-nitrobenzaldehyde	5	86	240	87	320	320
5	1-octanol	octanal	4	84	120	85	105	106
6	cyclohexanol	cyclohexanone	5	85	300	78	161	162
7	4-tert-butylcyclohexanol	4-tert-butylcyclohexanone	5	90	120	91	155	156
8	menthol	menthone	10	90	300	88	147	146

[a] All the aldehydes and ketones have been described previously in the literature and were identified by the IR spectra and melting points of their 2,4-dinitrophenylhydrazones. [b] isolated yields as the dinitrophenylhydrazones.

We also carried out the oxidation reactions of all the alcohols with an equimolar amount of QnFC under solvent-free conditions in the absence of H_5IO_6. The yields thus obtained are given in Table 1 in comparison with the yields obtained by the QnFC/H_5IO_6 system. Notable is that the yields of the products are either similar (entries 3–5, and 7) or a little higher (entries 1, 2, 6, and 8), but the reactions work tremendously faster with the QnFC/H_5IO_6 system than the reactions carried out with QnFC. Accordingly, periodic acid with QnFC shows a very strong oxidation power for the oxidation of alcohols to give the corresponding carbonyl compounds.

One major advantage of QnFC as a catalyst is its recyclability. The recycling of the QnFC was demonstrated for the oxidation of benzyl alcohol to benzaldehyde. After completion of the reaction, extraction of the product with diethyl ether led to the separation of the QnFC from the product and fresh charges of benzyl alcohol (1 mmol) and H_5IO_6 (1.1 mmol) were added for the subsequent oxidation of benzyl alcohol. The oxidation reactions were carried out 4 times under identical reaction conditions with recycling of the catalyst. The yields thus obtained were 93%, 91%, 90%, and 82%, respectively (Figure 2). These results demonstrate that QnFC is readily recyclable for 4 runs with no significant loss of catalytic activity.
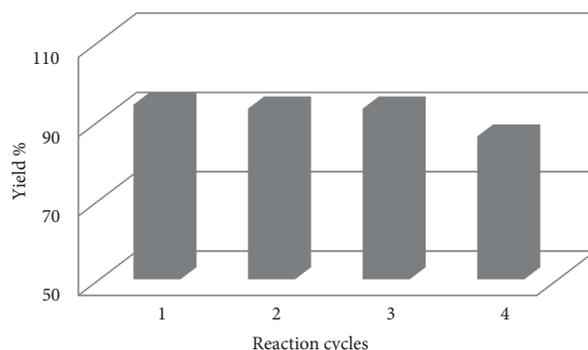

Figure 2. Recycling of the catalyst used for selective oxidation of benzyl alcohol.

In order to investigate the applicability of this modified protocol on a large scale, we carried out the oxidation of benzyl alcohol (15 mmol) under the optimum reaction conditions and obtained almost the same yield (94.0%) as in the small-scale reaction (1 mmol).

The mechanism of chromium(VI)-based oxidant catalyzed oxidation of alcohols with periodic acid is not clear. However, on the basis of the previously reported mechanisms,[12,13] we hypothesize that the QnFC/H_5IO_6 combination may form fluorochromatoperiodate (FCP), possibly a more powerful oxidizing agent than the fluorochromate (Scheme 2), and Cr may retain its +6 oxidation state throughout the reaction until all the periodic acid is consumed. We further hypothesize that the covalently attached fluoride ion may facilitate the regeneration of the catalyst.

To illustrate the catalytic activity of QnFC in the oxidation of benzyl alcohol as a model substrate we compared our results with the best of the well-known data from the literature (Table 2).

As seen in Table 2, the distinct advantages of modifying the older protocol or the characteristic aspects of the described method in this work in comparison with previous reports using PFC and PCC as catalysts are as follows: i) the use of QnFC in catalytic amount and commercially available periodic acid as co-oxidant, ii) the oxidation reaction under solvent-free conditions (no need for volatile and toxic organic solvents), iii) relatively short reaction times, and iv) high to excellent yields of the products.
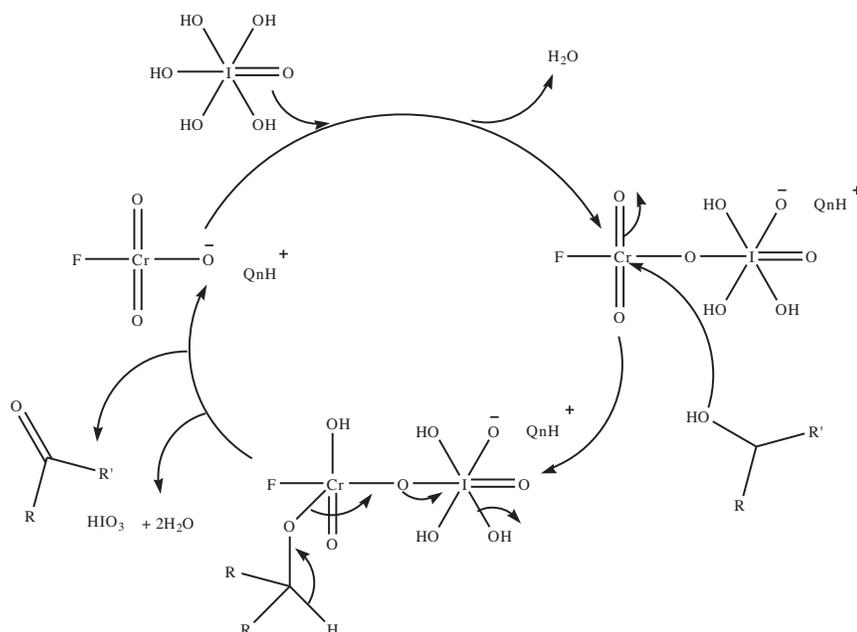
Scheme 2. Proposed mechanism for the oxidation of alcohols using H_5IO_6 in the presence of QnFC as catalyst.

Table 2. Oxidation of benzyl alcohol to benzaldehyde with various halochromate catalysts using periodic acid as terminal oxidant.

Catalyst	H_5IO_6 (equiv.)	Catalyst (mol%)	Conditions	Time (min)	Yield (%)	Ref.
QnFC	1.1	3.0	Solvent-free, rt	2	93	-
PFC	1.1	2.0	CH_3CN, 0 °C	120	67	12
PCC	1.1	2.0	CH_3CN, 0 °C to rt	120	72	13

In conclusion, we have shown that under solvent-free conditions quinaldinium fluorochromate efficiently catalyzes the oxidation of alcohols to aldehydes and ketones using periodic acid as the co-oxidant. Hence, using the chromium reagent in catalytic amount we are able to reduce the chromium waste generated while maintaining the advantages of chromium oxidation reactions. We have developed an effective and versatile oxidation system for the selective oxidation of various types of alcohols to carbonyl compounds. The new protocol is not only facile and selective but also more versatile in comparison with their solution counterparts. It is also noteworthy that the catalyst is recyclable and could be reused without significant loss of catalytic activity. Finally, owing to the fact that the reaction takes place under solvent-free conditions, the risk of combustion, the toxicity, and the environmental pollution of solvents are reduced.

3. Experimental

All reagents and solvents were obtained from Aldrich and used without further purification. The ^{1}H NMR spectrum was recorded on a Bruker Avance 300-MHz spectrometer (Germany). Elemental analysis was performed using an Elementar Micro Vario CHNS elemental analyzer (Germany), and melting points were determined with a Barnstead Electrothermal 9200 digital melting point apparatus (United Kingdom). IR spectra were recorded on a Mathson 1000 FT-IR spectrometer.

3.1. Preparation of quinaldinium fluorochromate

Chromium(VI)oxide (CrO_3) (15 mmol, 1.50 g) was taken in a polyethylene beaker and 48% hydrofluoric acid (HF) (15 mmol, 0.625 mL) was added dropwise with continuous stirring for 8–10 min. This was followed by dropwise addition of 1.0 mL of water under stirring over 15 min, leading to a clear orange colored solution. The whole was cooled in an ice-water bath for 15 min and quinaldine (15 mmol, 2.0 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. Yield: 99.4%, mp: 146–148 °C; ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.8 (s, 3H), 7.8–8.8 (m, 6H); 11.0 (s, 1H), IR (KBr): $\overline{\nu}$ = 948 cm^{-1} (Cr=O), 870 cm^{-1} (Cr=O), 617 cm^{-1} (Cr-F); Elemental Analysis (Calculated): 45.64 (C%); 3.83 (H%); 5.32 (N%); (Found): 45.62 (C%); 3.85 (H%); 5.40 (N%).

3.2. General procedure for the oxidation of alcohols with QnFC/H$_5$IO$_6$ under solvent-free conditions

A mixture of the corresponding alcohol (1 mmol) and QnFC (3 mol %) was ground in a mortar until it became homogeneous and H_5IO_6 (1.1 mmol) was introduced slowly. The progress of the reaction was monitored using TLC on silica gel (n-hexane-ethylacetate = 2:1). Upon completion of the reaction, work up with ether (3 × 15 mL) and evaporation of the solvent gave the corresponding carbonyl compounds.

3.3. General procedure for the oxidation of alcohols with QnFC under solvent-free conditions

QnFC (1 mmol) was added to the substrate (1 mmol) in a mortar. Starting materials were instantly mixed and ground and kept for the appropriate time at room temperature. The progress of the reaction was monitored by using TLC on silica gel (n-hexane:ethylacetate = 2:1). Upon completion of the reaction, work up with ether (3 × 15 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). Qualitative identification of the carbonyl products was made by comparison of the FT-IR spectra (C=N band varying between 1614 cm^{-1} and 1621 cm^{-1}) and melting points of their 2,4-dinitrophenylhydrazones with derivatives of known compounds.

Acknowledgments

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