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Quinaldinium Fluorochromate and Quinaldinium Dichromate: Two New and Efficient Reagents for the Oxidation of Alcohols

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Summary. Two new mild oxidizing agents, quinaldinium fluorochromate and quinaldinium dichromate, were prepared and characterized. These reagents are suitable to oxidize various primary and secondary alcohols to the corresponding carbonyl compounds and anthracene to antraquinone in good yields.

Keywords. Quinaldinium fluorochromate; Quinaldinium dichromate; Oxidation; Alcohols; Carbonyl compounds.

Introduction

Oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is most frequently accomplished by Cr(VI) reagents [1]. Some of the important entries in the list of reagents are the *Collins* reagent [2], pyridinium chlorochromate [3], pyridinium dichromate [4], pyridinium fluorochromate [5], pyridinium bromochromate [6], and 2,2′-bipyridinium chlorochromate [7]. In recent years, significant improvements have been achieved by the introduction of new oxidising agents, such as 3,5-dimethylpyrazolium fluorochromate [8], 2,6-dicarboxypyridinium chlorochromate [9], quinolinium fluorochromate [10], quinolinium dichromate [11], imidazolium fluorochromate [12], and pyrazinium dichromate [13].

Over several years our group has been involved in developing new reagents allowing oxidations to be performed under mild conditions [14]. In continuation of our studies on the development of halochromates and dichromates with heterocyclic bases we now report the preparation, characterisation, and synthetic utility of quinaldinium fluorochromate (*QnFC*) and quinaldinium dichromate (*QnDC*) with a

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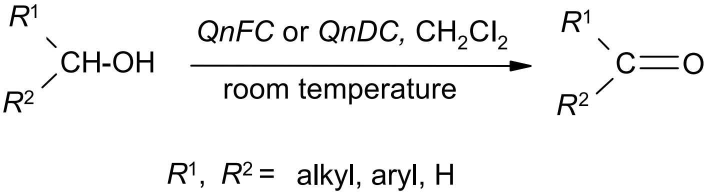
view to minimising the existing difficulties encountered in the oxidation of organic compounds with Cr(VI) based oxidants.

Results and Discussion

The two new chromate complexes can be prepared easily in good yields (85%) and (88%) by addition of aqueous solutions of CrO_3 to quinaldine; the use of 40% aqueous hydrofluoric acid causes the formation of the fluorochromate species, while the dichromate species is formed when distilled water is used. The structures of the products were confirmed by elemental analysis and their IR (KBr) spectra. Thus, the IR frequencies of the fluorochromate group at $\bar{\nu} = 948$, 870, and $617\,\mathrm{cm}^{-1}$ in quinaldinium fluorochromate are attributable to $\bar{\nu}_{\mathrm{asym}}$ (Cr=O), $\bar{\nu}_{\mathrm{sym}}$ (Cr=O), and $\bar{\nu}$ (Cr–F); these assignments are in accord with those found for $KCrO_3F$ [15]. The IR frequencies of the dichromate group at $\bar{\nu} = 948$, 891, and $785\,\mathrm{cm}^{-1}$ in quinaldinium dichromate are attributable to $\bar{\nu}_{\mathrm{asym}}$ (CrO_3), $\bar{\nu}_{\mathrm{sym}}$ (CrO_3), and $\bar{\nu}_{\mathrm{sym}}$ (Cr–O–Cr). These results are in close agreement with those found for the dichromate ion in $(NH_4)_2Cr_2O_7$ [16]. Solubility tests of *QnFC* and *QnDC* in various solvents showed that the two complexes are highly soluble in *DMSO* and *DMF*, and sparingly soluble in $CHCl_3$, CH_2Cl_2, acetonitrile, and water and insoluble in CCl_4, benzene, toluene, and ether. These results are indicative of the ionic nature of *QnFC* and *QnDC*; they are diamagnetic. *QnFC* is a 1:1 electrolyte ($\Lambda_M = 120\,\mathrm{mho\,cm^2\,mol^{-1}}$, in acetonitrile) and *QnDC* is a 2:1 electrolyte ($\Lambda_M = 295\,\mathrm{mho\,cm^2\,mol^{-1}}$, in acetonitrile). The *pH* values of 0.01 *M* aqueous solutions of *PCC*, *PFC*, *QFC*, *QxDC*, *QnFC*, and *QnDC* were found to be 1.75, 2.45, 3.35, 2.30, 3.92, and 3.80 [17]. The higher *pH* values of *QnFC* and *QnDC* compared to their companion reagents attest to their far less pronounced acidic characters. Both *QnFC* and *QnDC* are stable for prolonged periods of time (at least 18 months) when stored dry and in the absence of light.

In order to ascertain the efficacy of the reagents as oxidants, they were tested on a wide array of alcohols in CH_2Cl_2 at room temperature. Thus, *QnFC* and *QnDC* readily oxidize primary (Table 1, entries 1–6) and secondary alcohols (Table 1, entries 7–10) to their corresponding aldehydes and ketones (Scheme 1) in good to excellent yields. *QnFC* and *QnDC* in CH_2Cl_2 also oxidize anthracene to anthraquinone in good yields (Table 1, entry 11). The results (Table 1) also show that *QnFC* is a milder oxidation reagent than *QnDC*.

In conclusion, the easily accessible new reagents *QnFC* and *QnDC* are mild, efficient, and stable oxidizing agents. Their controlled acidities makes them suitable reagents for the oxidation of acid sensitive compounds. The reduced



Scheme 1

Table 1. Oxidation of organic substrates by *QnFC*[a] and *QnDC*[a]

Entry	Substrate	Product	*QnFC*		*QnDC*	
			Time/h	Yield/%[b]	Time/h	Yield/%[b]
1	1-Octanol	Octanal	4	75	4	62
2	Benzyl Alcohol	Benzaldehyde	3	79	3	70
3	4-Methoxybenzyl Alcohol	4-Methoxybenzaldehyde	2	94	3	77
4	4-Methylbenzyl Alcohol	4-Methylbenzaldehyde	2	90	3	75
5	4-Chlorobenzyl Alcohol	4-Chlorobenzaldehyde	3	74	4	69
6	4-Nitrobenzyl Alcohol	4-Nitrobenzaldehyde	3	69	3	65
7	Cyclohexanol	Cyclohexanone	3	70	4	64
8	4-*tert*-Butylcyclohexanol	4-*tert*-Butylcyclohexanone	2	60	4	61
9	Benzhydrol	Benzophenone	3	84	3	72
10	Benzoin	Benzil	2	82[c]	3	71[c]
11	Anthracene	Anthraquinone	3	81[c]	3	77[c]

[a] Oxidations were carried out in dichloromethane with a substrate to oxidant ratio 1:1.5 (1:3 for anthracene) at room temperature; [b] Yields refer to isolated 2,4-*DNP* derivatives identified by melting points; [c] Yields refer to isolated benzil and anthraquinone whose melting points were taken directly and confirmed by comparison with authentic samples (IR, TLC, and NMR)

chromium species can be trapped on a silica gel column for safe disposal. Based on all the results hitherto obtained with these reagents it may be stated that *QnFC* and *QnDC* are valuable additions to the existing palette of oxidizing agents.

Experimental

Results of elemental analysis of *QnFC* and *QnDC* agreed favourably with the calculated values.

Synthesis of Quinaldinium Fluorochromate

CrO_3 (20 g, 0.2 mol) was dissolved in 25 cm^3 of H_2O in a polyethene beaker and 11 cm^3 of 40% hydrofluoric acid (0.2 mol) were added with stirring at room temperature. To the resultant clear orange red solution, 28 cm^3 of quinaldine (0.2 mol) were added dropwise with stirring. The mixture was heated on a water bath for about 15 min, then cooled to room temperature, and allowed to stand for 1 hour. The bright yellow, crystalline quinaldinium fluorochromate was isolated by filtration. It was recrystallized from H_2O and dried *in vacuo* for about 2 h. Yield 85%; mp 146–148°C.

Synthesis of Quinaldinium Dichromate

Quinaldine (28 cm^3, 0.2 mol) was slowly added to a cooled solution of 20 g of CrO_3 (0.2 mol) in 20 cm^3 of H_2O. After 0.5 h, the reaction mixture was diluted with 40 cm^3 of acetone and cooled to -15°C. The yellow crystals were collected and washed with acetone. It was recrystallized from H_2O and dried *in vacuo* for about 2 h. Yield 88%; mp 150–151°C.

General Procedure for Oxidation

The oxidations were conducted in a dry apparatus and under efficient stirring. To a thoroughly stirred suspension of 1.5–3 mmol of *QnFC* or *QnDC* in 10 cm^3 of CH_2Cl_2 1 mmol of substrate dissolved in a small amount of the solvent was added. The mixture was stirred at room temperature for the period indicated in Table 1. The progress of the reaction was followed by *TLC* (solvent, *n*-hexane:ethylacetate, 2:1, v/v). After the completion of the reaction the solid was filtered off, washed with $10\,\mathrm{cm}^3$ of CH_2Cl_2, and the filtrate was evaporated on a rotary evaporator to furnish the product, which was isolated as the 2,4-dinitrophenylhydrazone (2,4-*DNP*).

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