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Quinaldinium Chlorochromate Supported on Alumina: A New and Efficient Reagent for the Oxidation of Alcohols

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Summary. The new, mild chromium(VI) oxidizing agent, quinaldinium chlorochromate supported on neutral alumina, was prepared as a stable yellow solid. The reagent is suitable to oxidize various primary and secondary alcohols to the corresponding carbonyl compounds and anthracene to anthraquinone in good yields.

Keywords. Quinaldinium chlorochromate; Oxidation; Alcohols; Carbonyl compounds.

Introduction

Oxidation of alcohols to carbonyl compounds is one of the most important reactions in organic chemistry [1–2]. Chromium(VI) reagents are widely utilized in the oxidation of alcohols to carbonyl compounds. Some of the important entries in the list of the reagents are pyridinium chlorochromate [3], pyridinium dichromate [4], pyridinium fluorochromate [5], pyridinium bromochromate [6], quinolinium fluorochromate [7], and prolinium chlorochromate [8]. However, most of these reagents that have been developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, tedious work-up procedures, or requirement of large excess of reagent.

Over several years our group has been involved in developing reagents allowing oxidations to be performed under mild conditions [9]. In extension of our studies on development of new reagents based on chromium(VI) we present here quinaldinium chlorochromate (*QnCC*) on alumina as a mild and efficient oxidant for alcohols and anthracene.

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Results and Discussion

The reagent *QnCC* can be easily prepared in good yield (72%) by reaction of quinaldine with chromium trioxide in $6M$ hydrochloric acid. The structure of the product was confirmed by elemental analysis and its IR (KBr) spectrum. The infrared absorption frequencies for the chlorochromate group at $\bar{\nu} = 949$, 876, and $466\,\mathrm{cm}^{-1}$ in quinaldinium chlorochromate are attributable to $\bar{\nu}_{\mathrm{asym}}$ (Cr=O), $\bar{\nu}_{\mathrm{sym}}$ (Cr=O), and $\bar{\nu}$ (Cr–Cl); these assignments are in accord with those found for $KCrO_3Cl$ [10]. It is soluble in *DMF* and *DMSO*, sparingly soluble in chloroform, dichloromethane, acetonitrile, and water, and insoluble in carbontetrachloride, benzene, toluene, and ether. These results are indicative of the ionic nature of *QnCC*. The compound is diamagnetic. It is a 1:1 electrolyte ($\Lambda_M = 150\,\mathrm{mho\,cm^2\,mol^{-1}}$, in acetonitrile). The *pH* of $0.01\,M$ solutions of *PCC*, zinc chlorochromate monohydrate [11], and *QnCC* were found to be 1.75, 2.30, and 3.79. A higher *pH* value of *QnCC* compared to its companion reagents attests its far less acidic character.

Preliminary investigations demonstrated that some primary and secondary alcohols can be oxidized to the corresponding aldehydes and ketones with *QnCC*. Although oxidation of benzyl alcohol to benzaldehyde smoothly proceeded using this reagent in CH_2Cl_2, the oxidation of other benzylic alcohols did not occur in good yield. Other primary and secondary alcohols did not give considerable amounts of the corresponding carbonyl compounds. For example, when 1-octanol was subjected to oxidation with *QnCC*, only 22% of octanal were obtained. Since organic synthesis by solid phase methods is a powerful tool [12] and chromium oxidants like pyridinium chlorochromate adsorbed on alumina [13], chromic acid on silica [14], and chromyl chloride on silica-alumina have been reported to give better yields under milder conditions as compared to the parent oxidants, we tried to follow this road for *QnCC*.

Thus, *QnCC* adsorbed on alumina was prepared by adding alumina to a solution of *QnCC* in CH_2Cl_2 and evaporation to dryness. The yellow solid was kept in vacuum at room temperature and stored in the dark before use.

The effect of solvent in the oxidation reaction was evaluated by carrying out the oxidation in a series of solvents with varying polarity. Oxidation of benzyl alcohol with *QnCC* supported on alumina in a 1:1.5 ratio was carried out in *n*-hexane, carbon tetrachloride, dichloromethane, acetone, and dimethylformamide (Table 1). Use of more polar solvents such as *DMF* and acetone (in which the reagent is soluble) resulted in moderate yields. The best results were obtained with the other solvents. Dichloromethane was chosen as the standard solvent.

The stability and activity of this supported reagent was compared with that of the unsupported *QnCC* by carrying out the oxidation of benzyl alcohol with both

Table 1. Oxidation of benzyl alcohol in different solvents using *QnCC*/alumina

Solvent	Substrate/Oxidant (molar ratio)	Reaction period/h	Yield[a]/%
n-Hexane	1:1.5	2	97
Carbon tetrachloride	1:1.5	2	95
Dichloromethane	1:1.5	2	94
Acetone	1:1.5	2	77
Dimethylformamide	1:1.5	2	69

[a] Yields refer to isolation of 2,4-*DNP* derivative

Table 2. Oxidation of benzyl alcohol using *QnCC* and *QnCC*/alumina stored for different periods

Oxidant	Storage period/week	Substrate/Oxidant (molar ratio)	Reaction period/h	Yield[a]/%
QnCC	1	1:1.5	4	78
	2	1:1.5	4	76
	4	1:1.5	4	71
	6	1:1.5	4	62
QnCC/alumina	1	1:1.5	2	94
	2	1:1.5	2	92
	4	1:1.5	2	91
	6	1:1.5	2	89

[a] Yields refer to isolation of 2,4-*DNP* derivative

Table 3. Oxidation of organic substrates with *QnCC*[a]/alumina

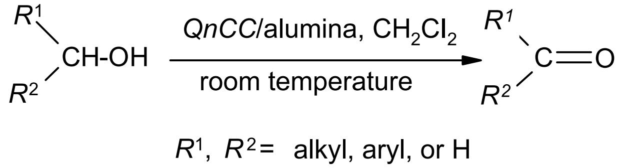
Entry	Substrate	Product	Time/h	Yield/%[b]	2,4-*DNP* (m.p./°C)	
					Obs.	Ref. [15]
1	1-Octanol	Octanal	2	71	103–105	106
2	Benzyl Alcohol	Benzaldehyde	2	94	235–236	237
3	4-Methoxybenzyl Alcohol	4-Methoxybenzaldehyde	2	73	253–254	254
4	4-Methylbenzyl Alcohol	4-Methylbenzaldehyde	2	73	231–233	233
5	4-Chlorobenzyl Alcohol	4-Chlorobenzaldehyde	2	61	263–265	265
6	4-Nitrobenzyl Alcohol	4-Nitrobenzaldehyde	2	54	318–319	320
7	Cyclohexanol	Cyclohexanone	2	53	160–162	162
8	4-*tert*-Butylcyclohexanol	4-*tert*-Butylcyclohexanone	2	60	155–156	156
9	Benzhydrol	Benzophenone	2	72	236–238	238
10	Benzoin	Benzil	2	92[c]	–	–
11	Anthracene	Anthraquinone	3	89[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)

reagents after different periods of storage. It was found that the supported reagent was more stable and active than the unsupported *QnCC* (Table 2).

In order to ascertain the efficacy of the reagent as an oxidant, it was tested on a wide array of alcohols in dichloromethane at room temperature.

Thus, *QnCC*/alumina readily oxidizes primary (Table 3, entries 1–6) and secondary alcohols (Table 3, entries 7–10) to their corresponding aldehydes and ketones (Scheme 1) in good yields.



Scheme 1

QnCC/alumina in dichloromethane also oxidizes anthracene to anthraquinone in good yield (Table 3, entry 11).

In conclusion, *QnCC*/alumina is an efficient reagent for the oxidation of various types of alcohols into the corresponding carbonyl compounds. *QnCC*/alumina has advantages in terms of ease of preparation, lower acidity, reaction period, and yield of products. We envisaged that this oxidant system, in addition to its mildness, would have the additional advantage of trapping the reduced chromium species in the alumina matrix for safe disposal and making isolation of products of oxidation easier. Moreover, this reagent is very stable, and can be stored for longer periods without much loss in its activity and hence turns out to be a very useful reagent in synthetic organic chemistry.

Experimental

Synthesis of Quinaldinium Chlorochromate (QnCC)

A solution of 10.0 g of CrO_3 (0.10 mol) in 18.4 cm^3 of 6 *M* HCl (0.10 mol) was cooled to 0°C and to this 13.9 cm^3 of quinaldine (0.10 mol) were added dropwise during 30 min. The reaction mixture was cooled for 2 h. The resulting yellow solid was collected and washed with ether, kept under suction until moderately dry, and placed under vacuum pump pressure until it became a dry powder, yield 72%, mp 139°C dec. Anal. calc. for $C_{10}H_9NHCrO_3Cl$: C 42.93, H 3.58, N 5.01, Cr 18.60%; Found: C 42.96, H 3.56, N 5.02, Cr 18.94%.

Preparation of QnCC/Alumina

To an ice cold mixture of 15 g of CrO_3 (0.15 mol) and 25 cm^3 of 6 *M* HCl (0.15 mol), 45 g of Al_2O_3 (neutral, *Brockmann* II–III) were added with stirring. Quinaldine, 22 cm^3 (0.15 mol), was then added dropwise and the resulting yellow solid was filtered, washed with water and cold acetone, and dried *in vacuo* for 3 h. The average capacity of the reagent as estimated by iodometry was found to be 1.2–1.6 mmol of *QnCC* per g of Al_2O_3.

General Procedure for Oxidation

The oxidations were all conducted in dry apparatus and under efficient stirring. To a thoroughly stirred suspension of *QnCC* and *QnCC*/alumina (1.5–3 mmol) in 10 cm^3 of CH_2Cl_2 1 mmol of the 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 (*n*-hexane:ethylacetate = 2:1). After the completion of the reaction the solid was filtered off and washed with 10 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-dinitrophenyl hydrazone (2,4-*DNP*).

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