Monatshefte für Chemie 133, 1417–1421 (2002)
DOI 10.1007/s00706-002-0476-9

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Quinoxalinium Dichromate: A New and Efficient Reagent for the Oxidation of Organic Substrates

Nebahat Değirmenbaşı and **Beytiye Özgün**[*]

Gazi Üniversitesi, Fen-Edebiyat Fakültesi, Kimya Bölümü, TR-06500 Ankara, Turkey

Received February 2, 2002; accepted (revised) April 3, 2002

Summary. A new chromium(VI) reagent, quinoxalinium dichromate ($[C_8H_6N_2H]_2Cr_2O_7$, *QxDC*), was prepared by reacting quinoxaline with CrO_3 in water. *QxDC* oxidizes primary and secondary alcohols and oximes to the corresponding carbonyl compounds, and anthracene to anthraquinone.

Keywords. Quinoxalinium dichromate; Oxidation; Alcohols; Oximes; Carbonyl compounds.

Introduction

In recent years, chromium(VI)-based oxidizing reagents have been extensively worked on, leading to the development of a number of reagents which have found wide application in many types of oxidative transformations [1–2]. Pyridinium chlorochromate (*PCC*) [3], pyridinium dichromate (*PDC*) [4], pyridinium fluorochromate (*PFC*) [5], pyridinium bromochromate (*PBC*) [6], quinolinium fluorochromate (*QFC*) [7], and 3,5-dimethylpyrazolium fluorochromate (*DmpzHFC*) [8] have turned out as the most significant chromium(VI) oxidants. As part of a program aiming at new reagents allowing both oxidations and brominations to be performed under mild conditions we have recently prepared four new reagents: quinolinium bromochromate (*QBC*) [9], benzimidazolium bromochromate (*BIBC*) [10], quinaldinium bromochromate (*QnBC*) [11], and isoquinolinium bromochromate (*IQBC*) [12]. The chromium-based reagents developed so far all suffer from at least one of the following drawbacks: high acidity, photosensitivity, instability, tedious workup procedures, or requirement of large excess of reagent. Therefore, the search for a new reagent persisted which has now led to the synthesis of quinoxalinium dichromate ($[C_8H_6N_2H]_2Cr_2O_7$, *QxDC*).

---

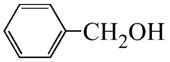
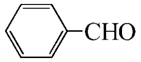
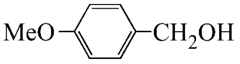
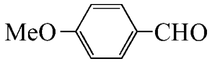
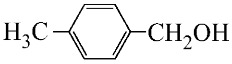
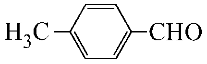
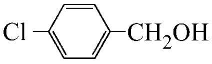
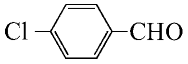
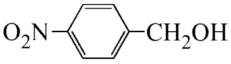
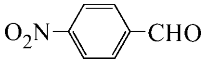
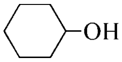
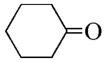
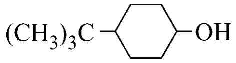
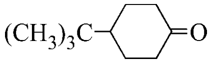
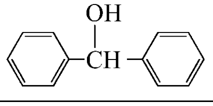
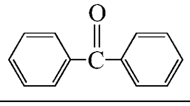
[*] Corresponding author. E-mail: beytiyeozgun@hotmail.com

Results and Discussion

Quinoxalinium dichromate (*QxDC*) can be easily prepared in good yield (78%) by addition of quinoxaline to a solution of chromium trioxide in water in a molar ratio of 1:1. *QxDC* is a yellow, non-hygroscopic, and stable solid compound which can be stored in the darkness for months without losing its activity. The structure of the product was confirmed by elemental analysis and its IR spectrum (nujol). The infrared absorption frequencies for the dichromate group at 950, 900, and 787 cm^{-1} in *QxDC* are attributable to $\upsilon_{asym}(CrO_3)$, $\upsilon_{sym}(CrO_3)$, and υ_{sym} (Cr–O–Cr); these assignments are in accordance with those found for $(NH_4)_2Cr_2O_7$ [13]. It is soluble in dimethyl formamide and dimethylsulfoxide, sparingly soluble in dichloromethane, acetonitrile, and chloroform, and insoluble in benzene, toluene, ether, nitrobenzene, and ethyl acetate. These results are indicative of the ionic nature of *QxDC*. The reagent melts sharply at 115–116°C. The compound is diamagnetic. It is a 2:1 electrolyte ($\Lambda_M = 210\,mho \cdot cm^2 \cdot mol^{-1}$, acetonitrile), showing a *pH* of 2.30 in a 0.01 *M* aqueous solution. The *pH* values of 0.01 *M* solutions of *PCC*, *PFC*, and *QFC* were found to be 1.75, 2.45, and 2.65 [3, 5, 7]. Thus, the acidity of *QxDC* is less pronounced than that of *PCC*, but comparable to that of *PFC* and *QFC*.

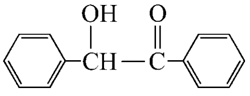
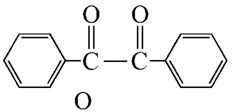
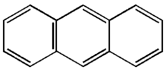
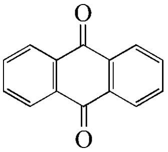
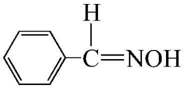
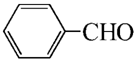
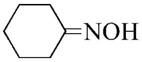
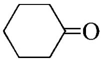
In order to ascertain the efficacy of the reagent as an oxidant, it was tested on a wide array of substrates in dichloromethane at room temperature. *QxDC* readily oxidizes primary (Table 1, entries 1–6) and secondary alcohols (Table 1, entries 7–10) to their corresponding aldehydes and ketones (Scheme 1) and was found to

Table 1. Oxidation of organic substrates with *QxDC*[a]

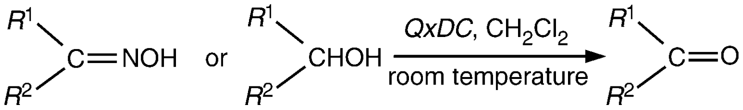
Entry	Substrate	Product[b]	Uncatalyzed		Catalyzed[d]	
			t/h	Yield/%[c]	t/h	Yield/%[c]
1	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	4	69	2	71
2			4	69	2	71
3			4	92	2	92
4			4	84	2	87
5			4	69	2	71
6			4	64	2	65
7			4	62	2	64
8			4	68	2	70
9			4	79	2	81

(*continued*)

Table 1 (*continued*)

Entry	Substrate	Product[b]	Uncatalyzed		Catalyzed[d]	
			t/h	Yield/%[c]	t/h	Yield/%[c]
10			4	71	2	73
11			4	73	2	75
12			6	74	3	74
13			6	73	3	78

[a] Oxidations were carried out in dichloromethane with a substrate to oxidant ratio of 1:1.5 (1:3 for anthracene) at room temperature; [b] all products were identified by comparison of their physical and spectroscopic data with those of authentic samples; [c] isolated yields; [d] in the presence of anhydrous acetic acid as catalyst



Scheme 1

be an effective reagent in the oxidative deoximation of several oximes to their parent carbonyl compounds (Scheme 1) in reasonably good yields (Table 1, entries 12, 13). *QxDC* in dichloromethane also oxidizes anthracene to anthraquinone in good yield (Table 1, entry 11).

The oxidation reactions for all the substrates were also performed in dichloromethane at room temperature in the presence of anhydrous acetic acid as catalyst (Table 1). The results clearly demonstrated the catalytic effect of anhydrous acetic acid. The reactions are in all cases is markedly accelerated, and the reaction time is reduced. In most cases, there is some improvement in the overall yield of the product as well.

The stability and activity of *QxDC* was investigated during different periods of its storage. The results are summarized in Table 2.

In conclusion, the easily prepared new reagent *QxDC* has a number of advantages over naphthyridinium dichromate (*NapDC*) [14], *PCC* [3], quinolinium dichromate (*QDC*) [15], and *PDC* [4] in considering the amount of oxidant, acidity, percent yield, and reaction time. The reduced chromium species can be trapped on a silica gel column for safe disposal. Moreover, it is stable and can be stored for long periods without much loss in its activity and hence turns out to be a very useful reagent in synthetic organic chemistry.

Table 2. Oxidation of benzyl alcohol using *QxDC* after various storage periods[a]

Oxidant	Storage period/week	Substrate/Oxidant (molar ratio)	Reaction period/h	Yield[b,c]/%
QxDC	1	1:1.5	4	69
	2	1:1.5	4	66
	4	1:1.5	4	62
	6	1:1.5	4	56

[a] Oxidations were carried out in dichloromethane at room temperature; [b] all products were identified by comparison of their physical and spectroscopic data with those of authentic samples; [c] isolated yields

Experimental

Preparation of quinoxalinium dichromate

A solution of 26.4 g quinoxaline (0.2 mol) in 60 cm^3 H_2O was slowly added to a cooled solution of 21.0 g CrO_3 (0.2 mol) in 20 cm^3 H_2O. After 0.5 h, the reaction mixture was diluted with 40 cm^3 acetone, cooled to -15°C, and the orange solid was filtered, washed with acetone, and dried *in vacuo*.

M.p.: 115–116°C; yield: 78%; calcd. for $[C_8H_6N_2H]_2Cr_2O_7$: C 40.32, H 2.94, N 11.76, Cr 21.73; found: C 40.17, H 2.93, N 11.72, Cr, 21.76.

General procedure for the oxidation of substrates

The oxidations were conducted in a dry apparatus and under efficient stirring. To a thoroughly stirred suspension of 1.5–3 mmol *QxDC* in 10 cm^3 CH_2Cl_2, 1 mmol of substrate dissolved in a small amount of solvent was added. The mixture was stirred at room temperature for the period indicated. The progress of the reaction was followed by TLC (*n*-hexane:ethylacetate = 2:1). After completion of the reaction, diethyl ether was added to the mixture which was then passed trough a previously prepared short column of silica gel. Elution of the carbonyl compound was effected with diethyl ether. Evaporation of the solvent afforded the pure product in 62–92% yield.

In the case of catalyzed oxidation reactions, 100 mm^3 of anhydrous acetic acid were added to the well stirred solution of *QxDC* in CH_2Cl_2. After stirring for at least 5 min, the substrate was added in neat form to the oxidant-catalyst solution. The further procedure is same as described above.

Acknowledgements

The authors are grateful to the Research Foundation of Gazi University for supporting this study.

References

[1] Cainelli G, Carbillo G (1984) Chromium Oxidation in Organic Chemistry, vol 19. Springer, Berlin

[2] Hudlicky M (1990) Oxidation in Organic Chemistry. American Chemical Society, Washington

[3] Corey EJ, Suggs JW (1975) Tetrahedron Lett 2647

[4] Corey EJ, Schmidt G (1979) Tetrahedron Lett 399

[5] Bhattacharjee MN, Chaudhuri MK, Dasgupta HS, Roy N (1982) Synthesis 588

[6] a) Narayanan N, Balasubramanian TR (1986) Indian J Chem 228; b) Durai S, Ravikumar V, Narayanan N, Balasubramanian TR, Mohan S (1987) Spectrochim Acta **43A**: 1191

[7] Murugesan V, Pandurangan A (1992) Indian J Chem **31B**: 377

[8] Bora U, Chaudhuri MK, Dey D, Kalita D, Kharmawphlang W, Mandal GC (2001) Tetrahedron **57**: 2445

[9] Özgün B, Değirmenbaşı N (1996) Synth Commun **26**(19): 3601

[10] Özgün B, Değirmenbaşı N (1999) Synth Commun **29**(5): 763

[11] Değirmenbaşı N, Özgün B (2002) Journal of the Institute of Science and Technology, Gazi University (submitted)

[12] Coşkuner Ö, Değirmenbaşı N, Özgün B (2002) Journal of the Institute of Science and Technology, Gazi University (submitted)

[13] Stammerich H, Bassi D, Sala O, Seibert H (1958) Spectrochim Acta **13**: 192

[14] Harry BD, Roger MS, William WP, Garry LG (1984) Heterocycles **22**: 2029

[15] Balasubramanian K, Prathiba V (1986) Indian J Chem **25B**: 326