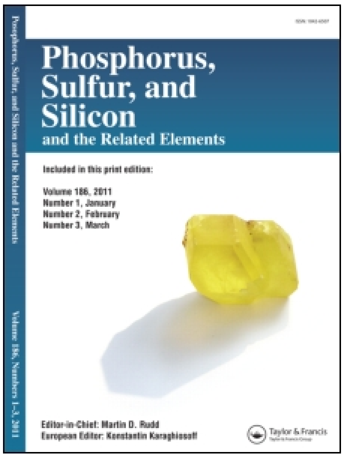


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Quinoxalinium Fluorochromate (QxFC): A New and Efficient Reagent for the Oxidation of Alcohols in Solution, Under Solvent-Free Conditions and Microwave Irradiation

Kıvılcim Şendil[a]; Beytiye Özgün[a]
[a] Gazi Üniversitesi, Fen-Edebiyat Fakültesi, Kimya Bölümü, Teknikokullar, Ankara, Türkiye

To cite this Article Şendil, Kıvılcim and Özgün, Beytiye(2006) 'Quinoxalinium Fluorochromate (QxFC): A New and Efficient Reagent for the Oxidation of Alcohols in Solution, Under Solvent-Free Conditions and Microwave Irradiation', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 4, 959 — 964

To link to this Article: DOI: 10.1080/00207450500272248

URL: http://dx.doi.org/10.1080/00207450500272248

Phosphorus, Sulfur, and Silicon, 181:959–964, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/00207450500272248

Quinoxalinium Fluorochromate (QxFC): A New and Efficient Reagent for the Oxidation of Alcohols in Solution, Under Solvent-Free Conditions and Microwave Irradiation

Kıvılcım Şendil
Beytiye Özgün
Gazi Üniversitesi, Fen-Edebiyat Fakültesi, Kimya Bölümü,
Teknikokullar, Ankara, Türkiye

The new mild oxidizing agent, quinoxalinium fluorochromate (QxFC), has been easily prepared by reacting quinoxaline with an aqueous solution of CrO_3 *and HF. This reagent is suitable for oxidizing various primary and secondary alcohols to their corresponding carbonyl compounds and anthracene to antraquinone. The reactions were carried out in solution, under solvent-free conditions and microwave irradiation. The results show that the rates of the reactions and the yields are usually highest under microwave irradiation.*

Keywords Carbonyl compounds; fluorochromate; microwave irradiation; oxidation; solvent free

INTRODUCTION

The oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is most frequently accomplished by chromium (VI) reagents. Extensive work has led to the development of a good number of these oxidants such as the Collins reagent,[1] pyridinium chlorochromate (PCC),[2] pyridinium dichromate (PDC),[3] 2,2′-bipyridinium chlorochromate (BIPCC),[4] pyridinium fluorochromate (PFC),[5,6] quinolinium fluorochromate,[7] 3,5-dimethylpyrazolium fluorochromate,[8] 2,6-dicarboxypyridinium chlorochromate,[9,16] N-methylpiperidinium chlorochromate,[11] and tetramethylammonium fluorochromate.[12]

Received March 23, 2005; accepted April 12, 2005.

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

Address correspondence to Beytiye Özgün, Gazi Üniversitesi, Fen-Edebiyat Fakültesi, Kimya Bölümü, Teknikokullar, Ankara 06500 Türkiye. E-mail:beytiye@gazi.edu.tr

However, these reagents have some limitations such as long reaction times, low yields of the products, the use of expensive reagents, and a tedious work-up procedure.

In continuation of our studies on the development of new halochromates and dichromates[13,14] with heterocyclic bases, we now report the preparation, characterization, and synthetic utility of quinoxalinium fluorochromate with a view to minimizing the existing difficulties encountered in the oxidation of organic compounds with Cr(VI) based oxidants. The oxidation reactions of alcohols were carried out in solution, under solvent-free conditions and microwave irradiation.

RESULTS AND DISCUSSION

Quinoxalinium fluorochromate can be easily prepared in an excellent yield (95%) from quinoxaline, 40% aqueous hydrofluoric acid and chromium (VI) oxide in a molar ratio of 1:1:1. The orange crystalline reagent can be stored in a sealed polythene bag for long periods without decomposition. QxFC is also a moisture-insensitive reagent. The structure of the product was confirmed by elemental analysis and IR (KBr), ^{1}H NMR, and ^{13}C NMR spectra. The infrared absorption frequencies for the fluorochromate group 948, 870, and 470 cm^{-1} in QxFC are attributable to υ_{asym} (Cr=O), υ_{sym}(Cr=O), and υ(Cr—F); these assignments are in accordance with those found for $KCrO_3F$.[15] The NMR data are consistent with the OxFC structure. The reagent QxFC is soluble in dimethylformamide, dimethylsulfoxide, and water; sparingly soluble in dichloromethane, acetone, acetonitrile, ethylacetate, and chloroform; and insoluble in benzene, ether, and toluene. These results are indicative of the ionic nature of QxFC. The reagent melts sharply at 117–118°C. It is a 1:1 electrolyte ($\Lambda_M = 124$ mho·cm^2 mol^{-1}, acetonitrile) showing a pH of 2.76 in a 0.01 M aqueous solution. The pH values of 0.01 M aqueous solutions of PCC, PFC, and QFC were found to be 1.75, 2.45, and 2.65, respectively.[2,6,16] Thus, the acidity of QxFC is less pronounced than that of PCC but comparable to PFC and QFC.

In this work, at first the oxidation of various substrates was performed in a solution. The effect of the solvent in the oxidation rate was evaluated by carrying out the oxidation reaction of benzyl alcohol with QxFC in a 1:1.5 molar ratio in n-hexane, carbon tetrachloride, dichloromethane, acetone, and dimethylformamide. The results are presented in Table I. The use of more polar solvents such as DMF and acetone resulted in moderate yields. The other solvents gave relatively good yields. Dichloromethane was chosen as a reaction medium.

TABLE I Oxidation of Benzyl Alcohol in Different Solvents using QxFC

Solvents	Substrate/oxidation (molar ratio)	Reaction period/h	Yield[a] %
n-hexane	1:1.5	2	89
Carbon tetrachloride	1:1.5	2	85
Dichloromethane	1:1.5	2	82
Acetone	1:1.5	2	74
DMF	1:1.5	2	70

[a] Yields refer to the isolated 2,4-DNP derivative.

In order to find out how the stability and activity was changed with time, we have used QxFC for the oxidation of benzyl alcohol, which was kept for different periods of storage. The percentage yield of benzaldehyde obtained in each case showed that QxFC is a quite stable compound (Table II).

The oxidation of various alcohols with 1.5 molar equivalents of QxFC was investigated in CH_2Cl_2 at r.t. As shown in Table III, substrates reacted with the reagent to afford the corresponding carbonyl compounds in 57–85% yields within 1–4 h.

The oxidation of the alcohols listed in Table III also was performed under solvent-free conditions with 1.5 molar equivalents of the reagent. Under these conditions, the carbonyl compounds were obtained in 65–97% yields within 3–120 min. It is important to note that grinding is necessary for the reactions to proceed smoothly. Finally, the transformation of alcohols to corresponding carbonyl compounds was investigated under microwave irradiation. The oxidation was carried out in the presence of 1.5 molar equivalents of QxFC with reaction periods ranging between 10 sec–3 min, and the corresponding carbonyl

TABLE II Oxidation of Benzyl Alcohol Using QxFC Stored for Different Periods

Oxidant	Storage period/week	Substrate/oxidation (molar ratio)	Reaction period/h	Yield[a] %
QxFC	1	1:1.5	2	82
	2	1:1.5	2	81
	3	1:1.5	2	81
	4	1:1.5	2	79
	6	1:1.5	2	78

[a] Yields refer to the isolated 2,4-DNP derivative.

TABLE III Oxidation of Alcohols by QxFC[a] in Solution, Under Solvent-Free Conditions, and Under Microwave Irridiation

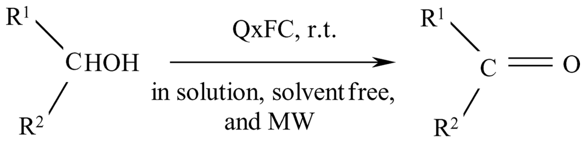
	Solution		Solvent-free condition		MW	
Substrate	Time (h)	Yield[b] (%)	Time (min)	Yield[b] (%)	Time (s)	Yield[b] (%)
1-octanol	2	66	60	97	360	98
Benzyl alcohol	3	82	120	95	108	98
4-methoxybenzyl alcohol	2	85	45	85	180	96
4-cholorobenzyl alcohol	2	70	20	88	180	93
4-nitrobenzyl alcohol	3	70	25	78	180	82
4-methylbenzyl alcohol	3	80	10	95	240	97
Cyclohexanol	1	61	45	72	480	87
4-tert-butylcyclohexanol	4	60	36	72	30	93
Benzoin	2	83[c]	60	84[c]	300	93[c]
Cinnamyl alcohol	3.5	64	3	70	10	87
Citronellol	3.5	57	90	73	20	82
Menthol	4	65	4	68	15	84
Anthracene	1.5	80[c]	30	84[c]	180	88[c]
Benzhydrol	4	75	25	86	90	94

[a] Oxidations were carried out in solution and under a solvent-free condition with a substrate-oxidant ratio. 1:1.5 (1:3 for an thracene) at r.t.

[b] Yields refer to the isolation of 2,4-DNP derivatives identified by melting points.

[c] Yields refer to isolated benzil and antraquinone whose melting points were taken directly and confirmed by comparison with authentic samples (IR, TLC).

products were obtained in 82–98% yields. The results show that the rate of the reactions and the yields are usually higher under microwave irradiation compared to solution and solvent-free reactions (Scheme 1) (Table III).



R^1, R^2= alkyl, aryl, or H

SCHEME 1

No overoxidation to carboxylic acids was observed in the case of primary alcohols. Cinnamyl alcohol was oxidized to the corresponding α,β-unsaturated aldehyde in this reaction, no trace benzaldehyde could be detected. Obviously, the oxidant can not cleave the double bond of cinnamyl alcohol. That QxFC is a relatively mild oxidation agent was illustrated by the reaction with benzoin forming benzil with no sign of bond cleavage products. During the reactions, the colour of the oxidant changes from orange to brown, providing visiual means for ascertaining the progress of the oxidation.

In conclusion, the easily preparable new reagent QxFC has a number of advantages over its companion reagents like PCC, PFC and QFC as evident from the consideration of the amount of the reagent required for the oxidation, solubility in different solvents, controlled acidity, shorter reaction time and high to very high yields of products. 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 useful reagent in synthetic organic chemistry.

EXPERIMENTAL

Preparation of Quinoxalinium Fluorochromate

Chromium (VI) oxide (20 g, 0.2 mol) was dissolved in water (25 mL) in a polythene beaker, and 40% hydrofluoric acid (11.3 mL, 0.23 mol) was added to it while stirring at r.t. Within 5 min, a clear solution resulted. To this solution, quinoxaline (26.4 g, 0.2 mol) was added slowly with stirring. The mixture was heated on a steam bath for half an hour, then cooled to r.t. and allowed to stand for 1 h. The bright orange crystalline quinoxalinium fluorochromate was isolated by filtration and dried in vacuo for 1 h. M.p.: 117–118°C, yield 95%; calcd. for $C_8N_2H_7CrO_3F$: C, 38.40; N, 11.20; H, 2.80; Cr 12.02. Found: C, 38.31; N, 11.19; H, 2.91; C, 12.12%.

General Procedure for Oxidation in Solution

The oxidations were all conducted in a dry apparatus and under efficient stirring. To the thoroughly stirred suspension of QxFC (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 r.t. for the period indicated in Table III. The progress of the reaction was followed by TLC (n-hexane:ethylacetate = 2:1). After the completion of the reaction, the solid was filtered and washed with 10 cm^3 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).

General Procedure for Oxidation Under Solvent-Free Conditions

QxFC (1.5–3 mmol) was added to the substrate (1 mmol) in a mortar. Starting materials were instantly mixed and then stored for the appropriate period at r.t. or in an oven without any further agitation (Table III). The progress of the reaction was monitored by dissolving a sample in CH_2Cl_2 and using TLC on silica gel (n-hexane:ethylacetate = 2:1). Upon completion of the reaction, HCl (20%, 30 mL) was added and extracted with Et_2O (3 × 25 mL). Evaporation of the solvent gave the corresponding carbonyl compounds in 67–97% yields.

General Procedure for Oxidation Under Microwave Irradiation

The alcohol compound (1 mmol) and 1.5 mmol of QxFC were mixed, and then 0.5 cm^3 CH_2Cl_2 was added. The mixture was subjected to microwave irradiation at 800 W. Upon completion of the reaction, HCl (20%, 30 mL) was added, and the mixture was extracted with Et_2O (3 × 25 mL). Evaporation of the solvent gave the corresponding carbonyl compounds in 82–98% yields.

REFERENCES

[1] J. C. Collins and F. J. Frank, *Tetrahedron Lett.*, **30,** 3363 (1968).
[2] E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, **16,** 2647 (1975).
[3] E. T. Corey and G. Schmidt, *Tetrahedron Lett.*, **20,** 399 (1979).
[4] F. S. Guziec and F. A. Luzzio, *Synthesis*, **9,** 691 (1980).
[5] M. N. Bhattacharjee and M. K. Chaudhuri, *Tetrahedron*, **43,** 5389 (1987).
[6] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, N. Roy, and D. T. Khathing, *Synthesis*, **7,** 588 (1982).
[7] V. Murugesan and A. Pandurangan, *Indian J. Chem. Sec. B*, **31B,** 377 (1992).
[8] U. Bora and M. K. Chaudhuri, *Tetrahedron*, **57,** 2445 (2001).
[9] M. Tajbakhsh, R Hosseinzadeh, and M. Y. Niaki, *J. Chem. Research (S)*, **10,** 508 (2002).
[10] R. Hosseinzadeh, M. Tajbakhsh, and M. Yazdani-Niaki, *Tetrahedron Lett.*, **43,** 9416 (2002).
[11] M. Tajbakhsh and M. M. Hevari, *Monatsh. Chem.*, **132,** 1229 (2001).
[12] M. K. Kassaee, A. R. Mahjob, and S. Ghammami, *Tetrahedron Lett.*, **44,** 4555 (2003).
[13] N. Değirmenbaşı and B. Özgün, *Monatsh. Chem.*, **135,** 407 (2004).
[14] N. Değirmenbaşı and B. Özgün, *Monatsh. Chem.*, **133,** 1417 (2002).
[15] M. K. Chaudhuri, H. S. Dasgupta, and N. Roy, *Indian J. Chem.*, **20A,** 1227 (1981).
[16] V. Murugesan and A. Pandurangan, *Indian J. Chem.*, **31B,** 377 (1992).