This article was downloaded by: [Stony Brook University] On: 06 October 2014, At: 07:20 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Quinolinium Fluorochromate (QFC) Supported on Alumina as a Selective Oxidant for Alcohols

G. Abraham Rajkumar $^{\rm a}$, Banumathi Arabindoo $^{\rm a}$ &

V. Murugesan^a

^a Department of Chemistry , Anna University , Chennai, 600 025, INDIA Published online: 17 Sep 2007.

To cite this article: G. Abraham Rajkumar , Banumathi Arabindoo & V. Murugesan (1999) Quinolinium Fluorochromate (QFC) Supported on Alumina as a Selective Oxidant for Alcohols, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 29:12, 2105-2114, DOI: 10.1080/00397919908086204

To link to this article: http://dx.doi.org/10.1080/00397919908086204

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and

are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <u>http://www.tandfonline.com/page/terms-and-conditions</u>

QUINOLINIUM FLUOROCHROMATE (QFC) SUPPORTED ON ALUMINA AS A SELECTIVE OXIDANT FOR ALCOHOLS

G. Abraham Rajkumar, Banumathi Arabindoo and V. Murugesan* Department of Chemistry, Anna University, Chennai-600 025, INDIA.

ABSTRACT

Quinolinium fluorochromate(QFC) supported on alumina (neutral) prepared by a new method oxidises selectively aliphatic primary and secondary alcohols, substituted benzylic alcohols and alicyclic alcohols to their corresponding carbonyl compounds in good yield.

Reagents supported on solid supports^{1a,b} have gained importance in organic synthesis because of their enhanced selectivity, associated ease of manipulation and milder reaction conditions. This concept of utilizing reagents supported on inert inorganic supports and on polymeric matrices have been applied especially to chromium(VI) based oxidants. A number of chromium(VI) oxidants supported on various solid supports²⁻¹³ have been reported. Though these reagents have advantages, they suffer from the following drawbacks: difficulties associated with their preparation *i.e* they may require adequate solvent removal and prolonged drying²⁻⁶ or may involve difficult method for their preparation¹³, rapid deactivation on storage^{2,3}, long reaction times⁵⁻⁸ and the need for the large excess of the

Copyright © 1999 by Marcel Dekker, Inc.

To whom correspondence should be addressed

reagent²⁻⁷. Thus there still exists a need for a reagent that can be easily prepared with good stability and better selectivity.

In our continued interest to develop novel heterocyclic halochromates¹⁴ supported on inorganic supports¹⁵, we now report the preparation of quinolinium fluorochromate (QFC) supported on alumina and evaluation of its synthetic utility. The reagent was prepared by a method similar to the preparation of silver carbonate on celite¹⁶. The average capacity of the reagent was estimated by following iodometric procedure.

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 QFC supported on alumina in a 1:1.5 ratio was carried out in dichloromethane, chloroform, benzene, tetrahydrofuran and hexane. The results are presented in Table I. The period for maximum conversion was found to be minimum in hexane. Although the oxidation reaction proceeded smoothly in dichloromethane, hexane was chosen as the solvent for the entire oxidation process keeping in view of the environmental hazards associated with chlorinated hydrocarbons.

The selectivity of the reagent was ascertained by conducting the oxidation of a mixture of alcohols with a two fold excess of the reagent at room temperature in hexane. The results are summarised in Table II. The results reveal that an aliphatic primary alcohol could be oxidised preferentially in the presence of an aliphatic secondary alcohol, and benzyl alcohol could be oxidised easily in the presence of a aliphatic primary alcohol and a cyclic alcohol such as cyclohexanol.

Solvent	Substrate/oxidant	Reaction period *	% Yield ^a
	mole ratio	hr	
Dichloromethane	1:1.5	3	87
Chloroform	1:1.5	3	80
Benzene	1:1.5	3.5	68
Tetrahydrofuran ^b	1:1.5	4	56
Hexane	1:1.5	2	91

Table-I Oxidation* of benzyl alcohol in different solvents using QFC- alumina#

 at room temperature carried out with 20 millimoles of the alcohol and QFC-alumina (20.6g); solvent: hexane

- # average capacity: 1.46 millimoles of QFC/gram of alumina
- a determined by GC analysis after every one hour
- b after completion of reaction, reaction mixture was poured into water and extracted with diethyl ether

Thus the reagent shows good selectivity towards the oxidation of primary hydroxyl group especially when it is attached to an aromatic ring.

A comparative study of the oxidation by this reagent and the one already reported¹⁵ (prepared by a different method) was carried out with a series of aliphatic primary alcohols, benzyl alcohol, furfurol, cyclohexanol and benzoin. The studies reveal that the present reagent is a better one in terms of reaction period and percentage yield. The results are summarised in Table III. Besides these the present supported reagent oxidises a set of substituted benzylic and cyclic alcohols under reflux conditions. The oxidation was found to be smooth and afforded the products in good yield. The results are given in Table IV.

The stability and activity of this supported reagent was compared with that of the unsupported QFC by carrying out the oxidation of benzyl alcohol with both Downloaded by [Stony Brook University] at 07:20 06 October 2014

	Substrate		Quantity		Products [*]	Reaction	% Yield
	/oxidant mole					period	
	Iauo	QFC- alumina	Alcohol	Solvent		1	
		ũ	millimoles	'n			
anol	1:2	14.5	10	30	1- Heptanal		51
					+	9	
anol					2-Heptanone		18
lou	1:2	14.5	10	30	1- Octanal		48
					+	9	
lou					2-Octanone		14
anol	1:2	14.5	10	35	1- Heptanal		28
					+	S	
cohol					Benzaldehyde		62
Icohol	1:2	14.5	10	35	Benzaldehyde	L	68(52)
					+	0	
xanol					Cyclohexanone		11(26)

Table-II Oxidation* of mixture of alcohols using QFC- alumina#

*- at room temperature, solvent : hexane

- average capacity: 1.38 millimoles of QFC/gram of alumina

a - were identified by GC analysis

b - determined by GC analysis after every one hour

yields in brackets refer to yields obtained when reaction was conducted under reflux conditions

Downloaded by [Stony Brook University] at 07:20 06 October 2014

<u> </u>			<u> </u>							<u> </u>	T	r —	T			
lumina	method)		% Yield		57	12	63	62	78	76	78	74	76	72	16	86
QFC- al (present n		Reaction	period		4	4	4	5.5	6	5.5	3	4.5	6	2	3.5	
ılumina	method ¹⁵)		% Yield		15	10	54	50	61	60	68	70	72	58	87	36
QFC- 2	(previous		Reaction	period	4	۲	2	5	7	5	5	3	5	∞	2.5	7
Product ^a					1- Rittanal	1 - Dumiai	2- Butanone	1- Pentanal	1- Heptanal	2- Octanone	1-Decanal	2-Ethyl-1- hexanal	Furfural	Cyclohexanone	Benzaldehyde	Benzil
			Solvent	1	30	2	30	40	25	30	30	30	40	25	45	30
Quantity			Alcohol	a a la millione	20	2	20	20	10	10	10	10	20	10	20	10
			QFC-	alumina	B ^{III}		11.7	20.6	10.3	10.3	7	10.3	20.6	10.3	20.6	10.3
Substrate/	oxidant	mole ratio		-			1:1	1:1.5	1:1.5	1:1.5	1:1	1:1.5	1:1.5	1:1.5	1:1.5	1:1.5
Substrate					1- Butanol		2- Butanol	1- Pentanol	1- Heptanol	2- Octanol	1-Decanol	2-Ethyl-1-hexanol	Furfurol	Cyclohexanol	Benzyl alcohol	Benzoin

Table-III- Comparison of oxidation* of alcohols using QFC- alumina prepared by different methods

&- at room temperature, solvent : hexane

- average capacity: 1.46 millimoles of QFC/gram of alumina

a - were identified by GC analysis ; b - determined by GC analysis after every one hour

Downloaded by [Stony Brook University] at 07:20 06 October 2014

ate	Substrate/		Quantity		Product ^a	Reaction	%	b.p/m
	oxidant					period hr	Yiel d	ġ.
_	mole ratio					-		ç
		QFC-	Alcohol	Solvent				
		alumina						
		mg	millimoles	m				
	1:1.5	10.7	10	26	1- Nonanal	9	61	94
	1:1.5	10.7	10	30	2-Heptanone	6	11	152
	1:2	14.2	10	35	2-Decanone	6.5	60	213
zyl alcohol	1:2	10.7	10	35	4- Nitro benzaldehyde	2.5	85	103
benzyl alcohol	1:1.5	10.7	10	30	4- Methoxy benzaldehyde	3.5	87	249
enzyl alcohol	1:1.5	10.7	10	30	4- Methyl benzaldehyde	3	16	201
cohol	1:1.5	10.7	10	35	Cinnamaldehyde	3	62	254
lol	1:1.5	10.7	10	30	Cyclopentanone	4.5	84	132
yclohexanol	1:1.5	10.7	10	35	2- Methyl cyclohexanone	5	73	166
lol	1:1.5	10.7	10	35	Cycloheptanone	5	61	182
1	1:1.5	10.7	10	35	Cyclooctanone	6	62	196
	1:2	14.2	10	40	Menthone	2.5	74	209

Table-IV Oxidation* of alcohols with QFC- alumina#

*- at room temperature, solvent : hexane

- average capacity: 1.41 millimoles of QFC/gram of alumina

a - were identified by GC analysis ; b - determined by GC analysis after every one hour

Oxidant	Storage period	Substrate/Oxidant	Reaction period ^a	% Yield ^a
	week	mole ratio	hr	
	1	1:1.5	3	90
QFC	2	1:1.5	3	89
	4	1:1.5	3	85
	6	1:1.5	3	71
	1	1:1.5	2	91
QFC- alumina	2	1:1.5	2	91
	4	1:1.5	2	89
	6	1:1.5	2	88

Table-V Oxidation* of benzyl alcohol using QFC and QFC-alumina during storage#

*- at room temperature, carried out with 20 millimoles of the alcohol and QFC-alumina (21.4g); solvent : hexane (45 ml)

- average capacity: 1.41 millimoles of QFC/gram of alumina

a - determined by GC analysis after every one hour

the reagents during different period of their storage. The percentage yield of benzaldehyde obtained in each case was compared and it was found that the supported reagent was found to be more stable and active than the unsupported QFC. The results are summarised in Table V.

Thus QFC- alumina prepared by the new method has advantages in terms of ease of preparation, reaction period and yield of products. Moreover this reagent has very good stability 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

General: Alcohols used in the present work were of extrapure quality (E.Merck, Fluka & Aldrich) and were distilled under reduced pressure as and when required. The products of oxidation were identified by comparison with authentic samples (IR, GC analysis, boiling point and melting point). IR spectra were recorded in Perkin- Elmer infrared spectrophotometer (model: Hitachi 270-50) and GC analyses were carried out on a Hewlett packard 5890A gas chromatograph using flame ionisation detector and a carbowax column.

Preparation of quinolinium fluorochromate (QFC) supported on alumina : Typical procedure

To a ice cold mixture of chromium(VI) oxide (15g.0.15 mole) and 40% hydrofluoric acid (11.3 ml, 0.23 mole), alumina (neutral, Brockmann grade I,45g) was added with stirring using a mechanical stirrer. Quinoline (17.7ml,0.15 mole) was then added dropwise and the resulting yellow orange solid was filtered, washed with water and cold acetone, dried in vacuo for 2 hours (yield 75.2 g). The average capacity of the reagent as estimated by iodometry was found to be 1-1.5 millimoles of QFC per gram of alumina.

General procedure for the oxidation of alcohols

To a stirred slurry of QFC- alumina in hexane (approximately 2ml per gram of the supported reagent), a solution of the alcohol in hexane was added and the reaction mixture was stirred vigorously at room temperature (the reaction mixture was refluxed for cyclic alcohols and substituted benzylic alcohols). The course of the reaction was followed by GC analysis after every one hour. After completion of the reaction, the reaction mixture was diluted with dry diethyl ether (30-40ml) and filtered through a short column of silica gel (2cm). The solid residues were thoroughly washed with dry diethyl ether (4x 20 ml). The combined filtrate on evaporation in a rotary evaporator gave the crude product which was purified by distillation under reduced pressure (or) by recrystallisation in the case of solid products.

Typical Reaction Procedure:

QFC-alumina (20.6 g, 30 millimoles) is made into a slurry with hexane (35 ml) in a two necked round bottom flask of 100ml capacity fitted with a reflux condenser and a mechanical stirrer. A solution of 1-pentanol (1.8g, 20 millimoles) in hexane (3ml) was added to the slurry and the mixture was stirred vigorously at room temperature. The corse of the reaction was followed by GC analsis after every one hour. After the completion of the reaction (minimum period in which maximum conversion was achieved), the reaction mixture was stirred for a further period of 30 minutes, diluted with dry diethyl ether (40 ml) and filtered through a short column of silicagel (2 cm). The solid residue was thoroughly washed with dry diethyl ether (4X20ml). The combined filtrate on evaporation gave the crude product which was distilled through a short vigereux column. Yield of 1- pentanal (b.p. 61°C/30mm Hg) was 1.42g (79%).

ACKNOWLEDGEMENT

This work was supported by a research grant from the CSIR, New Delhi. One of the authors (GAR) thanks the CSIR, New Delhi for the award of JRF.

REFERENCES

- 1(a) McKillop, A., and Young, D.W. Synthesis, 1979,401 & 481.
- (b) Preparative chemistry using supported reagents, Ed. by Laszlo, Academic press Inc., San Diego, 1987.
- 2 Santiniello, E., Ponti, F., and Manzocchi, A. Synthesis, 1978, 534.
- 3 Lou, J.D., and Wu, Y.Y. Chem & Ind., 1987,531.
- Frechet, J.M.J., Warnock, J., and Farall, M.J. J. Org. Chem., 43, 1978, 2618.
- Frechet, J.M.J., Darling, P., and Farall, M.J. J. Org. Chem., 46, 1981, 1728.
- Abraham, S., Rajan, P. K., and Sreekumar, K. Proc. Indian Acad. Sci., 108(5), 1996, 437.
- Abraham, S., Rajan, P. K., and Sreekumar, K. Indian J. Chem., 37B, 1997, 769.
- Hirano, M., Kobayashi, and Morimoto, T. Synth. Commun., 24(13), 1994, 1823.
- 9. Cheng, Y.S., Liu, W.L., and Chen, S.H. Synthesis, 1980, 223.
- 10. Lee, J.G., Lee, J.A., and Sohn, S.Y. Synth. Commun., 26(3), 1996, 543.
- 11. Lou, J.D., and Wu, Y.Y. Synth. Commun., 17(14), 1987, 1717.
- 12. Lou, J.D. Synth. Commun., 19(11& 12), 1989, 1841.
- 13. Lalancette, J.M., Rollin, G., and Dumas, P. Can. J. Chem., 50, 1972, 3058.
- 14. Murugesan, V., and Pandurangan, A. Indian J. Chem 31B, 1992, 377.
- Abraham Rajkumar, G., Banumathi Arabindoo, and Murugesan, V. Indian J. Chem 37B,1998, 596.
- 16. Balogh, V., Fetizon, M., and Golfier, M. J. Org. Chem., 36, 1976, 1339.

(Received in Japan 28 September 1998)