SHORT PAPER

J. Chem. Research (S),
2003, 710–711

Quinolinium fluorochromate as a reagent for selective oxidative cleavage of oximes and phenylhydrazones to their parent carbonyl compounds under non-aqueous and aprotic conditions[†]

Mahmood Tajbakhsh[a]*, Iraj Mohammadpoor-Baltork[b] and Farhad Ramzanian – Lehmali[a]

[a] *Department of Chemistry, School of Sciences, University of Mazandaran, Babolsar, Iran*

[b] *Department of Chemistry, School of Sciences, University of Isfahan, Isfahan, Iran*

Deprotection of oximes and phenylhydrazones to their parent aldehydes and ketones in high yields has been carried out by using quinolinium fluorochromate as a selective oxidant under mild conditions.

Keywords: fluorochromate, oximes, phenylhydrazones

Derivatives of carbonyl compounds such as oximes and phenylhydrazones not only are used for the characterisation and purification of carbonyl compounds but also play an important role in the protection of carbonyl compounds, as they are highly crystalline and stable compounds. Thus, the regeneration of carbonyl compounds from their derivatives under mild condition is an important process in organic synthetic chemistry.

The classical method for the cleavage of oximes to aldehydes and ketones includes acid hydrolysis which is not suitable for acid sensitive compounds.[1] Several oxidative deoximation methods have been developed that have some advantages over the classical hydrolysis methods.[2-13]

Little attention has been paid to the oxidative cleavage of phenylhydrazones and only a few reports are available dealing with the conversion of these derivatives to their corresponding carbonyl compounds.[14-15]

We report here a new and efficient method for the cleavage of oximes and phenylhydrazones using quinolinium fluorochromate (QFC). This reagent has recently been used for the oxidation of alcohols and has certain advantages over similar oxidising agents.[17]

Our experiments show that oximes and phenylhydrazones are converted to their corresponding aldehydes and ketones in suitable solvent. Further oxidation of aldehydes to their carboxylic acids is not observed. It is important to note that the reaction medium was almost neutral, so that some of the sensitive functionalities such as the carbon–carbon double bond, chloro, methoxy and alkyl substituents remained intact and no byproduct formation was observed (Table 1).

Table 1 Oxidative deprotection of oximes [a] and phenylhydrazones [b] with QFC

Run	Substrate	*t*/h	Products	Yield/%[c]
1	$C_6H_5CHNNHC_6H_5$	0.6	C_6H_5CHO	91
2	$(C_6H_5)_2CNNHC_6H_5$	1	$(C_6H_5)_2CO$	93
3	*o*-$ClC_6H_4CHNNHC_6H_5$	0.8	*o*-ClC_6H_4CHO	89
4	*p*-$ClC_6H_4CHNNHC_6H_5$	0.75	*p*-ClC_6H_4CHO	92
5	*m*-$MeOC_6H_4CHNNHC_6H_5$	0.8	*m*-$MeOC_6H_4CHO$	93
6	*p*-$MeOC_6H_4CHNNHC_6H_5$	1.25	*p*-$MeOC_6H_4CHO$	94
7	*o*-$MeOC_6H_4CHNNHC_6H_5$	0.8	*o*-$MeOC_6H_4CHO$	94
8	$C_6H_5C($*p*-$ClC_6H_4)NNHC_6H_5$	1	$C_6H_5C($*p*-$ClC_6H_4)O$	95
9	*p*-$MeC_6H_4CHNNHC_6H_5$	1.5	*p*-MeC_6H_4CHO	91
10	$C_6H_5CH_2CH_2CHNNHC_6H_5$	1.2	$C_6H_5CH_2CH_2CHO$	90
11	Cyclohexanone phenylhydrazone	1.5	Cyclohexanone	89
12	Camphor phenylhydrazone	1.4	Camphor	92
13	Cinnamaldehyde phenylhydrazone	1	Cinnamaldehyde	89
14	C_6H_5CHNOH	5	C_6H_5CHO	88
15	*p*-MeC_6H_4CHNOH	4	*p*-MeC_6H_4CHO	84
16	*o*-$MeOC_6H_4CHNOH$	4.5	*o*-$MeOC_6H_4CHO$	87
17	$C_6H_5C($*p*-$ClC_6H_4)NOH$	4	$C_6H_5C($*p*-$ClC_6H_4)O$	80
18	$(C_6H_5)_2CNOH$	4.5	$(C_6H_5)_2CO$	85
19	*p*-$ClC_6H_4C(CH_3)NOH$	5	*p*-$ClC_6H_4COCH_3$	80
20	$C_6H_5CH_2CH_2CHNOH$	5	$C_6H_5CH_2CH_2CHO$	75
21	Cyclohexanone oxime	5	Cyclohexanone	78
22	Camphor oxime	5	Camphor	78
23	Cinnamaldehyde oxime	5	Cinnamaldehyde	81

[a] Reflux, solvent: ether/cyclohexan(1:1).
[b] Room temperature, solvent: CH_2Cl_2.
[c] Yields refer to isolated products.

---

* To receive any correspondence. E-mail: ramzanian2002@yahoo.com

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Oxidative deprotection of phenylhydrazones in the presence of oximes with QFC in CH_2Cl_2 at 25 °C

Run	Substrate[a]	Product	t/min	Yield/%[b]
1	o-$MeOC_6H_4CHNNHC_6H_5$	o-$MeOC_6H_4CHO$	40	91
	C_6H_5CHNOH	C_6H_5CHO		3
2	$(C_6H_5)_2CNNHC_6H_5$	$(C_6H_5)_2CO$	60	90
	p-$ClC_6H_4C(CH_3)NOH$	p-$ClC_6H_4COCH_3$		4
3	$(C_6H_5)_2CNNHC_6H_5$	$(C_6H_5)_2CO$	60	91
	C_6H_5CHNOH	C_6H_5CHO		4
4	$C_6H_5CHNNHC_6H_5$	C_6H_5CHO	55	90
	(C6H5)2CNOH	$(C_6H_5)_2CO$		3
5	o-$ClC_6H_4CHNNHC_6H_5$	o-ClC_6H_4CHO	50	92
	o-MeOC6H4CHNOH	o-MeOC6H4CHO		5
6	m-$MeOC_6H_4CHNNHC_6H_5$	m-$MeOC_6H_4CHO$		92
	p-MeC_6H_4CHNOH	p-MeC6H4CHO	55	4

[a]Substrates/oxidant (1:1:1). [b]GLC yields.

Table 3 Oxidative deprotection of benzaldehyde phenylhydrazone in different solvents using QFC at room temperature.

Run	Solvent	t/min	Yield/%[a]
1	CH_2Cl_2	40	91
2	$CHCl_3$	60	25
3	THF	60	20
4	c-C_6H_{12}	60	30
5	CCl_4	60	30

[a]Yields refer to isolated products.

In order to show the selectivity of the described method, we have also performed several competitive oxidative deprotection reactions. We found that phenylhydrazones are deprotected selectively in the presence of oximes (Table 2). These selectivities are of value in organic synthesis.

The effect of solvent in the oxidation reaction was evaluated by carrying out the oxidation in a series of solvents with varying polarity. Deprotection of benzaldehyde phenylhydrazone with QFC in a 1:1 ratio was carried out in dichloromethane, chloroform, tetrahydrofuran, cyclohexan and carbon tetrachloride at room temperature. The experimental results show that dichloromethane is suitable solvent for these oxidation (Table 3).

In conclusion, we have developed a mild method for the regeneration of carbonyl compounds from oximes and phenylhydrazones that possesses significant advantages over the existing methods such as simple procedure, high yield, selective deprotection of phenylhydrazones in the presence of oximes and mild conditions.

Experimental

Products were isolated and their physical data were compared with those of known samples. Solvents were freshly distilled. Oximes and phenylhydrazones were prepared according to the described procedure.[16] QFC was prepared according to the literature.[17]

General procedure for the regeneration of carbonyl compounds from oximes and phenylhydrazones: Phenylhydrazone or oxime (1 mmols) was added to a stirred suspension of QFC (0.249g, 1 mmol) in dicholoromethane (15 ml) (solvent for oxime diethylether/cyclohexane, 1:1). The reaction mixture was stirred at room temperature (refluxed for oxime) for 0.6-5 h. The progress of the reaction was monitored by TLC (eluent: *n*-hexane/EtOAc, 5:1). After the reaction was complete the mixture was filtered, and the solid material was washed with diethylether several times. The combined filtrate was evaporated under reduced pressure and the resulting crude material was purified on a silica-gel plate or silica-gel column with appropriate eluent. Pure compounds were obtained in 75-95 % yields (Table 1).

We thank the Mazandaran and Isfahan University Research Councils for partial support of this work.

Received 28 July 2003; accepted 15 September 2003
Paper 03/2027

References

1 E.B. Hersberg, *J. Org. Chem.*, 1948, **13**, 542.
2 N. Kirkd and J. Sladec, *Tetrahedron Lett.*, 1980, **21**, 651.
3 E.J. Eisenbraum, R.P. Wesely, R.S. Budhram and B. Dewprasad, *Chem. Ind*., 1989, 584.
4 R.N. Ram and N. Varshak, *Tetrahedron Lett.*, 1991, **32**, 5829.
5 M. Curini, O. Rosayi, E. Pisani and U. Costantino, *Synthesis.*, 1996, 333.
6 M. Slamon, R. Miranda and E. Angeles, *Synth. Commun.*, 1986, **16**, 1827.
7 I. Mohammadpoor-Baltork and Sh. Pouranshirvani, *Synth. Commun.*, 1996, **15**, 261.
8 H. Firouzabadi, M. Seddighi, A. Ahmadi and A.R. Sardarian, *Synth. Commun.*, 1989, **19**, 3385.
9 G.S. Zhang, D.H. Yang, H.K. Chen and K. Cai, *Synth. Commun.*, 1995, **28**, 2221.
10 G.S. Zhang, D.H. Yang and M. Chen, *Synth. Commun.*, 1998, **28**, 721.
11 H. Firouzabadi, N. Iranpoor, F. Kiaeezadeh and J. Toofan, *Tetrahedron.*, 1986, **42**, 719.
12 H. Firouzabadi and I. Mohammadpoor-Baltork, *Synth. Commun.*, 1994, **24**, 489.
13 H. Firouzabadi, E. Mottaghinejed and M. Seddighi, *Synth. Commun.*, 1989, **19**, 469.
14 Z. Gui-Sheng and Y. De-Hong, *Synth. Commun.*, 1998, **28**, 607.
15 Z. Gui-Sheng and C. Bing, *Synth. Commun.*, 2000, **30**, 2507.
16 A.I.A. Vogel, *Textbook of Practical Organic Chemistry*, 4th ed., Longmans, London, 1978.
17 V. Murugesan and A. Padurangan, *Ind. J. Chem.*, 1992, **31** B, 377.