



# Oxidation of Aryl Alcohols by Morpholinium Fluorochromate(VI) on Silica Gel, a Selective and Efficient Heterogeneous Reagent

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**Abstract:** Morpholinium fluorochromate(VI), MFC, is easily synthesized by reacting morpholine to an aqueous solution of  $\text{CrO}_3$  and HF. This reagent selectively oxidizes aryl alcohols to their corresponding aldehydes and ketones under mild conditions. Moreover, it is inert towards aldehydes, ketones, oximes, thiols, sulfides, phenols, pyrans, trimethylsilanes, malonates and thioacetamides. The durability, reaction rate, ease of filtration and efficiency of MFC are considerably increased upon its absorption on silica gel.

**Keywords:** Morpholinium fluorochromate(VI), Heterogeneous oxidants, Aryl alcohols.

## Introduction

In modern organic synthesis are widely used chromium(VI) based oxidizing reagents for oxidation of a variety of compounds under anhydrous and aprotic conditions, including primary and secondary alcohols. Many oxidizing agents have been developed in recent years such as the Collins reagent<sup>1</sup>, chromium trioxide-3,5-dimethylpyrazole complex<sup>2</sup>, pyridinium fluorochromate (PFC)<sup>3,4</sup>, pyridinium chlorochromate (PCC)<sup>5</sup>, pyridinium dichromate (PDC)<sup>6</sup>, 2,2'-bipyridinium chlorochromate (BiPCC)<sup>7</sup>, quinolinium fluorochromate (QFC)<sup>8</sup>, quinolinium chlorochromate<sup>9</sup>, isoquinolinium fluorochromate (IQFC)<sup>10</sup>, 3,5-dimethylpyrazolium fluorochromate<sup>11</sup>, 2,6-dicarboxypyridinium chlorochromate<sup>12,13</sup>, *N*-methylpiperidinium chlorochromate<sup>14</sup>, tetramethylammonium fluorochromate(VI) (TMAFC)<sup>15</sup>, tetrabutylammonium fluorochromate(VI) (TBAFC)<sup>16</sup>, morpholinium chlorochromate (MCC)<sup>17</sup> and benzyltrimethyl ammonium fluorochromate(VI)<sup>18</sup>, *etc.* We have recently reported new reagents such as *N*-methylbenzylammonium fluorochromate(VI) (MBAFC)<sup>19</sup> and morpholinium fluorochromate(VI) (MFC)<sup>20</sup>. These reagents are mostly used for the oxidation of alcohols to corresponding aldehydes and ketones.

Many workers have been carried out for preparation of oxidants with a number of specifications including: lower cost, higher yields, better selectivity, milder neutral conditions, easier preparations, less toxicity and short reaction times. Although, because of the growing demands is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of alcohols under mild conditions. In this manuscript, we are reporting morpholinium fluorochromate(VI) (MFC) absorbed on silica gel as a new promising reagent with improved efficiency, selectivity and durability for the oxidation of aryl alcohols to their corresponding aldehydes and ketones under mild conditions.

## Experimental

Morpholinie and chromium trioxide (CrO<sub>3</sub>) were obtained from Fluka (Buchs, Switzerland). Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses were performed for C, H and N using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded on a Bomem FT-IR-MB100 Spectrometer. <sup>1</sup>H NMR was recorded using 90 MHz JEOL JNM-EX90A instrument. <sup>13</sup>C and <sup>19</sup>F NMR spectra were determined on a BRUKER-DRX500 AVANCE instrument.

### *Synthesis of morpholinium fluorochromate(VI)*

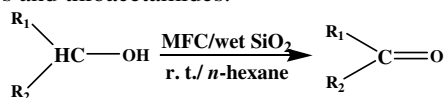
Chromium(VI) oxide (CrO<sub>3</sub>; 2 g, 0.02 mol) was dissolved in water (5 mL) in a polythene beaker and 40% hydrofluoric acid (1.05 mL, 0.03 mol) was added with stirring. After 5 min, the homogenous solution was cooled to 0 °C. Morpholine (1.74 mL, 0.02 mol) was carefully added over 10 min. The resulting solution was stirred at 0 °C for 30 minutes. An orange solid obtained. The crystals were collected on a sintered glass funnel and dried in vacuum (Yield: 3.64 g, 88%; m.p. 120-121 °C). IR  $\nu$  (KBr): 842 cm<sup>-1</sup> (m, Cr-O), 923 cm<sup>-1</sup> (s, Cr-O), 641 cm<sup>-1</sup> (m, Cr-F). Anal. Calc for C<sub>4</sub>H<sub>10</sub>NCrO<sub>4</sub>F: C, 27.01; H, 9.96; N, 6.53%. Found: C, 27.05; H, 9.85; N, 6.76. <sup>1</sup>H NMR (90 MHz, D<sub>2</sub>O)  $\delta$  3.30 (t, 2H, CH<sub>2</sub>), 4.15 (t, 2H, CH<sub>2</sub>), 4.99 (s, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR spectrum (125 MHz, D<sub>2</sub>O)  $\delta$  43.38, 63.70.

### *General procedure for oxidation of alcohols*

A solution of the alcohol in the minimum amount of *n*-hexane was added drop wise at room temperature to a stirred suspension of MFC/wet silica gel (0.5 g MFC: 0.5 g silica gel/4 drops H<sub>2</sub>O) in *n*-hexane (5 mL). The molar ratio of alcohol to the oxidant was used 1:1 (Table 1). The progress of the reaction was monitored by TLC (solvent, 4:1, *n*-hexane/ethylacetate, v/v). After the completion of the reaction, the mixture was passed through a previously prepared short column of silica gel to give a clear solution. The solvent was evaporated and the products were purified by distillation, crystallization and/or column chromatography. Products were characterized by with authentic samples (NMR, IR, TLC and m.p./b.p. measurement). The % yields were found as isolated and/or determined by NMR analyses (Table 1).

## Results and Discussion

In this paper we are reporting the synthesis of MFC. Different primary and secondary alcohols (**1**) were efficiently oxidized with MFC absorbed on wet SiO<sub>2</sub> (50% w/w) to their corresponding aldehydes and ketones (**2**), in *n*-hexane (Scheme 1). These oxidations take place under mild and completely heterogeneous conditions giving excellent yields (Table 1). Moreover, this oxidant is inert to aldehydes, ketons, oximes, thiols, sulfids, phenols, pyrans, trimethylsilanes, malonates and thioacetamides.



**Scheme 1**

**Table 1.** Oxidations by MFC/silica gel, MFC, PFC<sup>a</sup> and IQFC<sup>b</sup>

Alcohol	Product <sup>c</sup>	Molar Ratio (ROH/Ox)	MFC/silica gel		MFC		PFC		IQFC	
			Time min	Yield <sup>c</sup> %	Time min	Yield %	Time min	Yield %	Time min	Yield %
Benzyl Alcohol, <b>1a</b>	Benzaldehyde, <b>2a</b>	1:1 (1:1.25) <sup>a</sup>	20	95	65	80	45	90	60	91
<i>p</i> -Chlorobenzyl alcohol, <b>1b</b>	<i>p</i> -Chlorobenzaldehyde <b>2b</b>	1:1	25	98	75	83	-	-	-	NR
<i>p</i> -Methoxybenzyl alcohol, <b>1c</b>	<i>p</i> -Methoxybenzaldehyde <b>2c</b>	1:1 (1:1.25) <sup>a</sup>	26	95	75	79	50	90	-	NR
<i>p</i> -Methylbenzyl Alcohol, <b>1d</b>	<i>p</i> -Methylbenzaldehyde <b>2d</b>	1:1	18	96	75	85	-	-	-	NR
<i>p</i> -Nitrobenzyl alcohol, <b>1e</b>	<i>p</i> -Nitrobenzaldehyde <b>2e</b>	1:1	33	90	65	80	-	-	-	NR
<i>p</i> -Bromobenzyl alcohol, <b>1f</b>	<i>p</i> -Bromobenzaldehyde <b>2f</b>	1:1	35	92	60	75	-	-	-	NR
Cyclohexanol, <b>1g</b>	Cyclohexanone, <b>2g</b>	1:1 (1:1.5) <sup>a</sup>	20	93	85	65	210	89	240	90
Cyclopentanol, <b>1h</b>	Cyclopentanone, <b>2h</b>	1:1	21	89	86	62	-	-	-	NR
1-Phenylethanol, <b>1i</b>	Acetophenone, <b>2i</b>	1:1	35	94	150	78	-	-	-	NR
3-Phenyl-2-propen-1-ol, <b>1j</b>	3-Phenylpropanal, <b>2j</b>	1:1 (1:1.5) <sup>a</sup>	26	85	110	80	-	-	300	70
Benzoin, <b>1k</b>	Benzil, <b>2k</b>	1:1 (1:1.25) <sup>a</sup>	30	96	90	75	150	98	180	98

PFC- Pyridinium fluorochromate used as oxidant<sup>8</sup>. IQFC-Isoquinolium fluorochromate used as oxidant<sup>10</sup>.<sup>c</sup> Products were characterized by comparison with authentic samples (NMR, IR, TLC and *m.p./b.p.* measurement)

Oxidations may also occur using only MFC, in the absence of wet SiO<sub>2</sub>, but considerable improvements of both the yields and the corresponding reaction times were observed in the presence of the absorbent. The wet SiO<sub>2</sub> can act as a reactions medium, providing an effective heterogeneous surface area for the oxidation and at the same time making the simple work-up.

The selectivity of MFC absorbed on wet SiO<sub>2</sub> (50% w/w) is well proved through its oxidations of 4-chlorobenzyl alcohol 98%, and/or benzyl alcohol 95% (reported 90%)<sup>8</sup>, in the presence of equimolar amounts of 2-phenylethyl alcohol (no product detected). Neither carboxylic acids nor other by-products were formed upon oxidation of alcohols *via* MFC (Table 1). Groups such as methoxy and methyl that attached are inert to this oxidant. Moreover, the results show that this oxidant does not oxidize a variety of other substrates, including benzylaldehyde, acetophenone, diphenyl sulfide, thiophenol, 3,5-dimethoxyphenol, 2-benzyl-3,4-dihydro-2*H*-pyran, benzyloxytrimethylsilane, *N*-methyl-2-phenylthioacetamide, 1-phenyl-ethanone oxime and sodium 2-hydroxyimino-malonate.

This oxidant proves to be many advantages as compared with similar oxidizing reagents including: easier preparations, application to pH sensitive molecules, good selectivity, high yields, short reaction times, lower oxidant/substrate ratio, lower solvent requirement and simple work-up.

## Conclusion

A new reagent, morpholinium fluorochromate(VI) absorbed on silica gel, MFC/wet SiO<sub>2</sub>, selectively oxidizes aromatic alcohols. Many functional groups are inert towards this reagent,

including aldehydes, ketons, oximes, thiols, sulfids, phenols, pyrans, trimethylsilanes, malonates and thioacetamides. Thus, this oxidant can not be used for the synthesis of highly functionalized molecules. Its advantages over similar oxidizing reagents include ease of synthesis and work-up, high yields, short reaction times, good selectivity, application to pH sensitive molecules, lower oxidant/substrate ratio and lower solvent requirement.

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