

## Synthesis and Reactions of *N*-Methylbenzylammonium Fluorochromate(VI) on Silica Gel, a Selective and Efficient Heterogeneous Oxidant

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**Abstract:** *N*-Methylbenzylammonium fluorochromate(VI) (MBAFC) is easily synthesized by addition of *N*-methylbenzylamine to an aqueous solution of CrO<sub>3</sub> and HF. MBAFC shows selectivity in the oxidation of aryl alcohols to their corresponding aldehydes and ketones under mild conditions. The durability, ease of work up and efficiency of MBAFC are considerably increased upon its absorption on silica gel.

**Keywords:** *N*-Methylbenzylammonium fluorochromate(VI); heterogeneous oxidants; silica gel; oxidation; alcohols.

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### Introduction

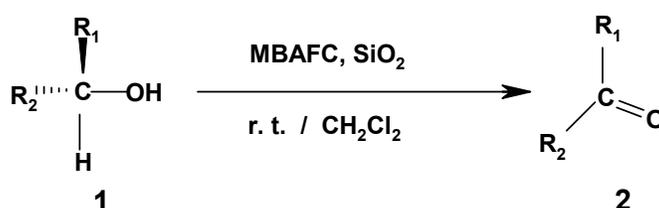
Chromium(VI) based reagents are widely used in modern organic synthesis for the oxidation of a variety of compounds under anhydrous and aprotic conditions, including primary and secondary alcohols. Extensive work has led to the development of a good number of these oxidants such as the Collins reagent [1], chromium trioxide-3,5-dimethylpyrazole complex [2], pyridinium chlorochromate (PCC) [3], pyridinium dichromate (PDC) [4], 2,2'-bipyridinium chlorochromate (BIPCC) [5], pyridinium fluorochromate [6-7], quinolinium fluorochromate [8], quinolinium chlorochromate [9], 3,5-dimethylpyrazolium fluorochromate [10], 2,6-dicarboxypyridinium chlorochromate [11-12], *N*-methylpiperidinium chlorochromate [13], tetramethylammonium fluorochromate(VI) (TMAFC) [14] and *N*-methylbenzylammonium fluorochromate(VI) (MBAFC) [15]. These reagents may all be

used for the oxidation of alcohols to corresponding aldehydes and ketones. This manuscript introduces *N*-methylbenzylammonium fluorochromate(VI) (MBAFC) 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.

## Results and Discussion

Different primary and secondary alcohols **1** were subjected to oxidations with *N*-methylbenzylammonium fluorochromate(VI) (MBAFC) absorbed on wet SiO<sub>2</sub> (50% w/w), in dichloromethane (Scheme 1). These oxidations take place under mild and completely heterogeneous conditions giving excellent yields (Table 1).

Scheme 1



The heterogeneous reaction mixtures are thoroughly stirred, at room temperature, for 10-33 minutes. The corresponding aldehyde and ketone products **2** can then be easily isolated by simple filtration and evaporation of the solvent. Yields obtained using MBAFC/silica gel are mostly higher than those reported in the literature, while both reagent ratios as well as reaction times are lower (Table 1).

Oxidations may also occur using only MBAFC, in the absence of wet SiO<sub>2</sub>, but considerable improvements of both the yields and the corresponding reaction times are observed in the presence of the absorbent. This implies that the wet SiO<sub>2</sub> may act as a reaction medium, providing an effective heterogeneous surface area for the oxidation and at the same time making the work-up much more convenient.

The selectivity of MBAFC is well demonstrated through its oxidations of 4-chlorobenzyl alcohol (yield of product: 91 %), and/or benzyl alcohol (yield of product: 93%), in the presence of equimolar amounts of 2-phenylethyl alcohol (no product detected). Neither carboxylic acids over-oxidation products nor other by-products are formed upon oxidation of alcohols *via* MBAFC (Table 1). Functional groups such as methoxy and methyl attached on the phenyl ring are inert to this reagent. In addition, we have shown that this reagent does not oxidize a variety of other substrates, including diphenyl sulfide, thiophenol, 3,5-dimethoxyphenol, 2-benzyl-3,4-dihydro-2H-pyran, benzyloxytrimethylsilane, *N*-methyl-2-phenylthioacetamide and sodium 2-hydroxyimino-malonate.

**Table 1:** Oxidations via MBAFC/Silica gel, MBAFC, PFC <sup>a</sup> and IQFC <sup>b</sup>

Alcohol	Product <sup>c</sup>	Molar Ratio ROH:OX	MBAFC/Silicagel		MBAFC		PFC		IQFC	
			Time (min)	Yield <sup>c</sup> (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
Benzyl alcohol <b>1<sub>a</sub></b>	Benzaldehyde <b>2<sub>a</sub></b>	1:1 (1:1.25) <sup>a</sup>	10	93	60	85	45	90	60	91
<i>p</i> -Chlorobenzyl alcohol, <b>1<sub>b</sub></b>	<i>p</i> -Chlorobenzaldehyde <b>2<sub>b</sub></b>	1:1	15	91	75	89	-	-	-	NR
<i>p</i> -Methoxybenzyl alcohol, <b>1<sub>c</sub></b>	<i>p</i> -Methoxybenzaldehyde <b>2<sub>c</sub></b>	1:1 (1:1.25) <sup>a</sup>	17	93	80	80	50	90	-	NR
<i>p</i> -Methylbenzyl alcohol, <b>1<sub>d</sub></b>	<i>p</i> -Methylbenzaldehyde <b>2<sub>d</sub></b>	1:1	20	92	70	89	-	-	-	NR
<i>p</i> -Nitrobenzyl alcohol, <b>1<sub>e</sub></b>	<i>p</i> -Nitrobenzaldehyde <b>2<sub>e</sub></b>	1:1	23	90	60	82	-	-	-	NR
<i>p</i> -Bromobenzyl alcohol, <b>1<sub>f</sub></b>	<i>p</i> -Bromobenzaldehyde <b>2<sub>f</sub></b>	1:1	30	91	80	75	-	-	-	NR
Cyclohexanol <b>1<sub>g</sub></b>	Cyclohexanone <b>2<sub>g</sub></b>	1:1 (1:1.5) <sup>a</sup>	24	92	75	65	210	89	240	90
Cyclopentanol <b>1<sub>h</sub></b>	Cyclopentanone <b>2<sub>h</sub></b>	1:1	19	87	95	70	-	-	-	NR
1-Phenylethanol <b>1<sub>i</sub></b>	Acetophenone <b>2<sub>i</sub></b>	1:1	33	90	180	80	-	-	-	NR
3-Phenyl-2-propen-1-ol, <b>1<sub>m</sub></b>	3-Phenylpropenal <b>2<sub>m</sub></b>	1:1 (1:1.5) <sup>a</sup>	26	89	150	80	-	-	300	70
Benzoin <b>1<sub>n</sub></b>	Benzil <b>2<sub>n</sub></b>	1:1 (1:1.25) <sup>a</sup>	30	98	80	80	150	98	180	98

<sup>a</sup> Pyridinium fluorochromate used as the oxidant [7]

<sup>b</sup> Isoquinolium fluorochromate used as the oxidant [16].

<sup>c</sup> Products were characterized by comparison (NMR, IR, TLC and m.p./b.p.) with authentic samples.

## Conclusions

A new reagent, *N*-methylbenzylammonium fluorochromate(VI) (MBAFC) absorbed on silica gel, is easily synthesized. It proves to be a low cost, readily available and highly selective oxidizing reagent for a variety of aromatic alcohols. Its advantages include higher yields, shorter reaction times, lower alcohol/oxidant molar ratios, application to pH sensitive molecules and ease of separation of products. Moreover, during the reaction, the color of the oxidant changes from orange to brown, thus providing a visual means for ascertaining the progress of the oxidation. Many functional groups are inert towards this oxidizing agent, including thiols, sulfides and phenols, enhancing the usefulness of the oxidant and the oxidation conditions for the synthesis of highly functionalized molecules.

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## Experimental

### General

*N*-Methylbenzylamine and chromium trioxide were obtained from Fluka (Buchs, Switzerland). Melting points are measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses (C, H, and N) were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded on a Bomen FT-IR-MB100 Spectrometer. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were measured on a JNM-EX90A a BRUKER-DRX500 AVANCE instrument, respectively.

### Preparation of *N*-methylbenzylammonium fluorochromate(VI)

Chromium(VI) oxide (CrO<sub>3</sub>; 1g, 0.01 mol) was dissolved in water (3 mL) in a polyethylene beaker and 40% hydrofluoric acid (0.65 mL, 0.015 mol) was added with stirring. After 5 min, the homogenous solution was cooled to 0°C. *N*-Methylbenzylamine (1.35 mL, 0.01 mol) was carefully added over 10 min. The resulting solution was stirred at 0°C for 30 minutes. A yellow-orange solid precipitated. The crystals were collected on a sintered glass funnel and dried under vacuum (yield: 85%); IR  $\nu$  (KBr): 871 cm<sup>-1</sup>(m, Cr-O), 941 cm<sup>-1</sup> (s, Cr-O), 640 cm<sup>-1</sup> (m, Cr-F); Anal. Calcd. for C<sub>8</sub>H<sub>12</sub>NCrO<sub>3</sub>F: C, 39.8; H, 5.0; N, 5.8. Found: C, 40.1; H, 5.2; N, 5.5; <sup>1</sup>H-NMR (D<sub>2</sub>O)  $\delta$ : 2.71 (s, 3H, CH<sub>3</sub>), 4.20 (s, 2H, CH<sub>2</sub>), 4.99 (s, 2H, NH<sub>2</sub>), 7.4 (s, 5H, Ph); <sup>13</sup>C-NMR (D<sub>2</sub>O)  $\delta$ : 42.09 (C methyl), 52.18 (C benzyl), 129.25 (C para), 129.61 (C ortho), 129.81 (C meta), 130.96 (C ipso).

### General Oxidation Procedure

A solution of the alcohol in the minimum amount of dichloromethane is added dropwise at room temperature to a stirred suspension of MBAFC/wet silica gel (0.5g MBAFC : 0.5g silica gel : 2 drops of H<sub>2</sub>O) in dichloromethane (typically 5 mL). The molar ratios of alcohol to the oxidant are either 1:1, 1:1.25 or 1:1.5 (Table 1). The progress of the reaction is monitored by TLC (solvent 6:1 hexane/ethyl acetate, v/v). After the completion of the reaction, the mixture is filtered through a short column of silica gel to give a clear solution. The solvent is evaporated and the crude products are purified by distillation, crystallization and/or column chromatography.

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*Sample availability:* Available from the authors