Scientific Paper

BENZYLTRIMETHYLAMMONIUM FLUOROCHROMATE(VI): A NOVEL, EFFICIENT AND SELECTIVE OXIDANT

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Abstract

Benzyltrimethylammonium fluorochromate (VI), BTMAFC, is synthesized by reacting benzyltrimethylammonium bromide with an aqueous solution of CrO_3 and HF. This new reagent, $(C_6H_5CH_2)(CH_3)_3N[CrO_3F]$, is used for almost quantitative conversion of oximes into the parent ketones or aldehydes. BTMAFC is used under mild and neutral conditions for fast and selective oxidation of primary, secondary, allylic and benzylic alcohols to their corresponding carbonyl compounds, in high yields.

Key words: Benzyltrimethylammonium fluorochromate (VI), oksidant, carbonyl compounds, alcohols.

Introduction

Significant improvements is achieved in the development of new Cr(VI) based oxidizing agents, 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 (PFC)[6,7,8,9] quinolinium fluorochromate,[10] quinolinium chlorochromate,[11] and 3,5-dimethylpyrazolium fluorochromate (DmpzHFC).[12] These oxidants are mostly used for oxidation of alcohols to their corresponding aldehydes and ketones.[1-17] Among these, PFC and DmpzHFC have an edge over others for rendering higher yields in neutral conditions.[7,12,13]

Industrial demands have led many workers reach for more ideal oxidants with a number of specifications including: lower cost, higher yields, better selectivity, milder neutral conditions, easier preparations, high solubility, less toxicity, and short reaction times. Even though, numerous oxidants for oxidation of alcohols are already reported, the growing demand for new oxidants of alcohols made us carry out the synthesis of benzyltrimethylammonium fluorochromate(VI), BTMAFC.

Results and discussion

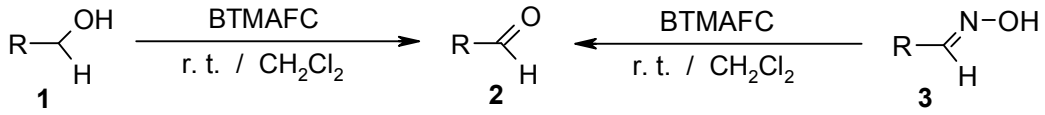
Following up on our investigation of fluorochromates (VI),[14,15] in this manuscript we are reporting the synthesis of benzyltrimethylammonium fluorochromate(VI), BTMAFC. This new oxidant efficiently oxidizes a number of organic substrates including oximes and fused ring hydrocarbons as well as primary, secondary, allylic and benzylic alcohols (Table 1, Scheme 1). Among advantages of BTMAFC is its quaternary ammonium ion, $(C_6H_5CH_2)(CH_3)_3N^+$ which is used as a phase transfer catalysts. This unsymmetrical ion clearly has an edge over symmetrical $(CH_3)_4N^+$ that we recently synthesized as a constituent of TMAFC.[14,15] As a result, BTMAFC is a more efficient and stronger oxidizing agent than those previously reported.[14,15,18,19] Also, $(C_6H_5CH_2)(CH_3)_3N^+$ serves as a crystal growing agent, which improves the quality of BTMAFC crystals.[20] Other advantages of BTMAFC over TMAFC include lack of sensitivity to moisture, which waves the requirement of a glove box purged with argon and the usage of dry acetonitrile.

BTMAFC is easily prepared, with a relatively excellent yield (98%). This is from the reaction of CrO_3 with aqueous hydrofluoric acid and benzyltrimethylammonium bromide, in the molar ratio of 1:2:1. It is obtained as orange oil, stored in a sealed bag for long periods, without any decomposition. The structure of BTMAFC is determined using elemental analyses, UV, IR and NMR spectroscopy. Its IR spectrum shows two absorptions of Cr-O at 892 cm^{-1} and 942 cm^{-1}; together with a Cr-F band at 695 cm^{-1}. The NMR data are consistent with BTMAFC structure. Moreover, ^{19}F-NMR of this oxidant gives absorption at -149.2 ppm.

Again, higher reactivity of the oxidizing reagent is linked to the extent of symmetry about the Cr for $MCrO_3F$ (M=K, Rb, Cs and NH_4),[21,22] our substitution of a benzyl group for one the methyls of tetramethylammonium fluoride introduces higher distortions of symmetry about the Cr hence making our BTMAFC more reactive.[14,23]

BTMAFC selectively oxidizes primary alcohols to their corresponding aldehydes and secondary alcohols to their respective ketones in relatively high yields (Table 1). This reagent is able to convert benzyl alcohol and its derivatives to their corresponding benzaldehydes (Table 1, Scheme 1). All oxidations are carried out in dichloromethane. Moreover, relatively higher conversions of oximes into the parent ketones and/or aldehyedes are obtained *via* BTMAFC (Table 1, Scheme 1): [Benzyl oxime to

Benzaldehyde, 88% (reported 56%)[9]; 1-Phenyl-ethanone oxime to 1-Phenyl-ethanone oxime, 98% (reported 80%)[9] and 4-Methyl benzyl oxime to 4-Methylbenzaldehyde, 84%]. Fused ring hydrocarbons such as anthracene, pyrene and phenanthrene are oxidized to 9,10-anthraquinone in 83% (reported 58%); pyrene-4,5,9,10-tetraone in 92% and 9,10-phenanthrenequinone in 92% (reported 70%).[12] In addition, BTMAFC oxidizes PPh_3 to $OPPh_3$ with a 99% yield (Table 1).



Scheme 1

This reagent has many advantages over similar oxidizing agents including: ease of preparation, involving a simple cationic exchange; high yields of the oxidized species; short reaction times; good selectivity; lower oxidant/substrate ratio and lower solvent requirement.[11,24,25] BTMAFC is highly soluble in many solvents such as dichloromethane, N,N-dimethylformamide, acetonitrile, chloroform and acetone. It is less soluble in hexane, toluene, benzene and it is very slightly soluble in ethyl acetate and water. This oxidant operates under mild and neutral conditions and can be applied to pH sensitive molecules. It does not react with acetonitrile (which may be used for studying the oxidation kinetic and mechanism). Its melting point range was found to be 53-57 °C. It is a 1:1 electrolyte (116.7 Ω^{-1} cm^2 mol^{-1}, in CH_3CN). This oxidant may be stored for long periods in the absence of air and moisture.

During the reactions, the color of the oxidant changes from orange to dark brown, providing visual means for ascertaining the progress of the oxidation. The mechanism for the present oxidation is still unclear. However, we assume it is similar to that of other fluorochromates. In addition this oxidant and the oxidation conditions can be used for the synthesis of highly functionalized molecules.

Conclusions

Our newly synthesised benzyltrimethylammonium fluorochromate(VI), BTMAFC, effectively oxidizes many organic species including alcohols and oximes. BTMAFC has many advantages over similar oxidizing agents including: ease of preparation, involving

Table 1. Oxidation of organic substrates by benzyltrimethylammonium fluorochromate (VI), BTMAFC.

Entry	Substrates	Time (min)	Substrate /Oxidant[h]	Product[a]	Yield %	mp or bp (°C) Found (Reported)
1	1-Heptanol	50 (60)[d]	1/1	Heptanal	92 (84)[d]	152.8
2	Cyclohexanol	40 (210)[d]	1/1	Cyclohexanone	86[b] (89)[d]	155.7 (156)
3	2-Phenyl-1-propanol	65	1/1	2-Phenyl-1-propanal	78	223 (222)
4	Ally alcohol	60	1/1	Acrolein	72	52.6 (53)
5	*Trans*-2-hexen-1-ol	60	1/1	*Trans*-2-hexen-1-al	80	159.6 (159)
6	Benzyl alcohol	45 (180)[c]	1/1	Benzaldehyde	98 (94)[c]	178.1 (178)
7	4-Methoxybenzyl alcohol	35 (50)[d]	1/1	4-Methoxybenzaldehyde	>99 (90)[d]	248.9 (248)
8	4-Chlorobenzyl alcohol	30	1/1	4-Chlorobenzaldehyde	>99	213.8 (213)
9	4-Bromobenzyl alcohol	40	1/1	4-Bromobenzaldehyde	>99	229.3 (228)
10	4-Nitrobenzyl alcohol	40	1/1	4-Nitrobenzaldehyde	>99 (97)[e]	107.2 (106)
11	2,4-Dichlorobenzyl alcohol	45	1/1	2,4-Dichlorobenzaldehyde	95	73.2 (71)
12	3-Methoxybenzyl alcohol	45	1/1	3-Methoxybenzaldehyde	76 (68)[b]	
13	2-Nitrobenzyl alcohol	50	1/1	2-Nitrobenzaldehyde	92 (87)[b]	45.9 (44)
14	3,4-Methylenedioxybenzyl alcohol	55 (25 h)[f]	1/1	3,4-Methylenedioxybenzaldehyde	94 (92)[f]	36 (34)
15	Antracene	3.5 h	1/2	Anthraquinone	83 (58)[g]	273 (271)
16	Phenanthrene	4 h	1/2	Phenanthrenequinone	92 (70)[g]	209.2 (206)
17	Triphenylphosphine	5 (2)[g]	1/1	Triphenylphosphine oxide	99 (90)[g]	157.9 (157)
18	2-Morpholino ethanol	60	1/1	Morpholinoacetaldehyde	96	
19	*D*(-)Mandelic acid	30	1/1	Phenylglyoxylic acid	98	67 (65)
20	Ephedrine	45	1/1	α-[1-(Methylamino)ethyl]benzaldehyde	98	
20	Pyrene	360	1/4	Pyrene-4,5,9,10-tetraone	92	
21	Furfuryl alcohol	60	1/1	Furfural	95	167 (162)
22	Benzoin	90	1/1	Benzyl	95	94 (95)
23	1-Phenyl-ethanol	45	1/1	Acetophenone	92	21 (19)
24	Benzyl oxime	60	1/2	Benzaldehyde	88 (56)[i]	179 (178)
25	4-Methyl benzyl oxime	65	1/2	4-Methylbenzaldehyde	84	104 (106)
26	1-Phenyl-ethanone oxime	60	1/2	1-Phenyl-ethanone oxime	98 (80)[i]	18 (20)

[a] Products are characteriesed by comparison with authentic samples (NMR, IR, TLC and m.p./b.p. measurement). [b] The % yield is determinated by GC analysis. [c] Quinolium fluorochromate used as the oxidant.[8] [d] Pyridinum fluorochromate used as the oxidant.[7] [e] Dipyridine-chromium(VI) oxide used as the oxidant.[1] [f] 1-(Benzoylamino)-3-methylimidazolium chlorochromate used as the oxidant.[13] [g] 3,5-Dimethyl pyrazolium used as the oxidant.[10] [h] Molar equalante ratios of substrate/oxidant are employed in our cases. Pyridinum fluorochromate used as the oxidant.[9]

a simple cationic exchange; high yields of the oxidized species; short reaction times; good selectivity; lower oxidant/substrate ratio and lower solvent requirement.

Experimental

General considerations. Melting points were obtained on an Electrothermal 9100 apparatus. IR spectra were recorded using a Shimadzu IR-460 spectrometer. NMR spectra: ^{1}H and ^{13}C NMR spectra were recorded using 90 MHz JEOL JNM-EX90A in $CDCl_3$ solutions. ^{19}F NMR spectra were performed on a Bruker DRX-500. All separations and quantization of alcohols and aldehydes were performed using a Philips 4410 gas Chromatograph. Chromatography columns were prepared from Merck silica gel.

Benzyltrimethylammonium fluorochromate(VI), $(C_6H_5CH_2)(CH_3)_3N[CrO_3F]$. To a solution of 15 g (150 mmol) CrO_3 in 12 mL water, placed in a 100 mL polyethylene beaker, 15 mL (300 mmol) 40% HF is added with stirring. An orange red solution is obtained. The reaction mixture is then cooled in an ice-bath (0-5 °C). Benzyltrimethylammonium bromide (35.7 g, 155 mmol) is added portion-wise, with stirring. An orange soft-solid, in a greenish liquid is obtained. To this mixture, 30 mL CH_2Cl_2 is added. The orange organic phase is decanted and the solvent is distilled off. A reddish orange gel is separated and stored in the refrigerator (98% Yield). IR (KBr) ν, 3420, 3005, 1690, 1471, 1216, 942 (Cr-O), 892 (Cr-O), 773, 720, 695 (Cr-F). ^{1}H NMR (90 MHz, HDO) δ 7.6 (s, 5H, ArH), 4.45 (s, 2H, CH_2), 3.16 (s, 9H, $3\times CH_3$). ^{13}C NMR (22.4 MHz, $CDCl_3$) δ 133.12, 130.54, 128.73, 127.75, 68.1, 52.21. Anal. Calcd for $(C_6H_5CH_2)(CH_3)_3NCrO_3F$: C 44.6, H 5.95, N 5.2, Found: C 44.39, H, 5.82, N, 5.13.

General procedure for the oxidation of alcohols.

Oxidation benzyl alcohol and its derivatives. To a stirred solution of each alcohol (3.7 mmol) in 5 mL of CH_2Cl_2, BTMAFC (1 g, 3.7 mmol) is added in one portion, at room temperature. The progress of the reaction is monitored by TLC. After completion of the reaction, the mixture is filtered through a short column of silica gel. The filtrate is evaporated. The product is purified by distillation, crystallization or column chromatography. Products are characterized by comparison with authentic samples

(NMR, IR, TLC and mp/bp measurement). The % yields are obtained as isolated and/or determined *via* NMR or GC analyses (Table 1).

Oxidation of anthracene. To a stirred solution of anthracene (0.65 g, 3.7 mmol) in 5 mL of CH_2Cl_2, BTMAFC (2 g, 7.4 mmol) is added in one portion, at room temperature. The reaction mixture is refluxed for 3.5 hours. The progress of the reaction is monitored by TLC. After completion, the mixture is concentrated using a rotavapor, then is washed with 30 mL of diethyl ether. The combined organic layer is passed through a short pad of Celite to trap the reduced reagent. Then it is washed thoroughly with diethyl ether (3×15 mL). The filtrate is evaporated using a rotavapor to give a crude product which is purified by column chromatography using a short pad of silica gel with ethylacetate-hexane (1:9) as eluent. 9,10-Anthraquinone is obtained as a yellow crystalline compound (Yield, 83%; mp 271 °C).

Oxidation of triphenylphosphine. In a 100 mL round-bottomed flask, under nitrogen atmosphere, is placed (1.5 g, 5.55 mmol) of BTMAFC and 2 mL of CH_2Cl_2·PPh_3 (18.5 g, 5.55 mmol), dissolved in 3 mL of CH_2Cl_2, is added in one portion. Instantaneous, exothermic oxidation is completed in 5 min. The reaction mixture is separated by centrifugation, and filtered through a short silica gel column. The filtrate is evaporated giving highly crystalline $OPPh_3$ in 99% yield. The product is characterized by TLC, boiling points, NMR, and by comparison with authentic sample.

Oxidation of Benzoin. To a stirred solution of benzoin (1.18 g, 5.6 mmol) in 5 mL of CH_2Cl_2, BTMAFC (1.5 g, 5.6 mmol) is added in one portion, at room temperature. The reaction mixture is refluxed for 45 min. The progress of the reaction is monitored by TLC. After completion, the mixture is concentrated using a rotovapor, then is washed with 15 mL of diethyl ether. The combined organic layer is passed through a short pad of Celite to trap the reduced reagent. Then it is washed thoroughly with diethyl ether (3×15 mL). The filtrate is evaporated using a rotavapor to give a crude product which is purified by column chromatography using a short pad of silica gel with ethylacetate-hexane (1:4) as eluent. Benzyl is obtained as a yellow crystalline compound (Yield, 90%).

Oxidation Benzyl oxime and its derivatives. To a stirred solution of each oxime (3.7 mmol) in 5 mL of CH_2Cl_2, BTMAFC (2 g, 7.4 mmol) is added in one portion, at room temperature. The progress of the reaction is monitored by TLC. After completion of the reaction, the mixture is filtered through a short column of silica gel. The filtrate is evaporated. The product is purified by distillation, crystallization or column chromatography. Products are characterized by comparison with authentic samples (NMR, IR, TLC and m.p./b.p. measurement). The % yields are obtained as isolated and/or determined *via* NMR or GC analyses (Table 1).

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Povzetek

Benziltrimetilamonijev fluorokromat(VI), BTMAFC, je bil pripravljen pri reakciji med benziltrimetilamonijevim bromidom in vodno raztopino CrO_3 in HF. Ta nov reagent, $(C_6H_5CH_2)(CH_3)_3N[CrO_3F]$, je bil uporabljen za skoraj kvantitetivno pretvorbo oksimov v ustrezne ketone in aldehide. BTMAFC je bil uporabljen pod milimi in nevtralnimi pogoji za hitro in selektivno oksidacijo primarnih, sekundarnih, alilnih in benzilnih alkoholov v ustrezne karbonilne spojine z visokimi izkoristki.