

Heterogeneous oxidation of organic substrates by using two trimethylammonium halochromates on alumina, $(\text{CH}_3)_3\text{NH}[\text{CrO}_3\text{X}]$, (X=F, Cl)

**Shahriare Ghammamy^{*a}, Ali Moghimi^b, Zahra Sharif Nezhad^c,
Zahra Shokri Aghbolagh^a and Golam Rezaei Behbahani^a**

^a*Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran*

^b*Department of Chemistry, Varamin Campus, Islamic Azad University, Varamin, Iran*

^c*Department of Chemistry, Faculty of Science, Islamic Azad University, Arak, Iran*

ABSTRACT

Two mild, stable and new chromium (VI) reagents from trimethylamine are described. Orange trimethylammonium fluorochromate (VI) $(\text{CH}_3)_3\text{NH}[\text{CrO}_3\text{F}]$, (TriMAFC), and trimethylammonium chlorochromate (VI) $(\text{CH}_3)_3\text{NH}[\text{CrO}_3\text{Cl}]$, (TriMACC), are easily prepared in a nearly quantitative yield by the interaction of trimethylamine with CrO_3 , alumina and related acid. These reagents are versatile reagents for the effective and selective oxidation of organic substrates, in particular for alcohols, under mild conditions.

Keywords: Trimethylammonium Fluorochromate (VI); Trimethylammonium Chlorochromate (VI); Heterogeneous Oxidants; Alumina; Oxidation; Alcohols.

INTRODUCTION

The synthetic organic chemists are interested in searching new oxidizing agents. Many such reagents have been developed in recent years with some success by Fieser L.F. and Fieser M.[1], Corey E.J. and Suggs J.W.[2]. In particular, there is continued interest in the development of new chromium (VI) reagents for the effective and selective oxidation of alcohols, under mild conditions. Of the large number of "mild" chromium based oxidizing agents available, many prove impractical when the reactions are performed on a large scale (mol), although in recent years, significant improvements have been achieved by the use of new oxidizing agents by Maier G., Reisenauer H.P. and Marco M.D.[3]; Bhandari A., Sharma P.K. and Banerji K.K.[4]; Meenahshisundaram S., and Soctaugam R.[5]. Extensive works of scientists have led to the development of these oxidants such as the 4-Benzylpyridinium Fluorochromate, by Özgün B., Yaylaoglu A. and Şendil K.[6]; Quinoxalium Fluorochromate (QxFC), by Şendil K. and Özgün B.[7]; Cetyltrimethylammonium Bromochromate by Ghammamy S., Eimanieh H. and Mohammady M.K.[8]; and 2,2'-bipyridinium chlorochromate by Guzic F.S and Luzzio F.A.[9]. TriMAFC and TriMACC were synthesized with the belief that these reagents could be used for

the oxidation of organic substrates. This manuscript introduces TriMAFC and TriMACC absorbed on alumina as new promising reagents with improved work-up efficiency and durability, for the oxidation of alcohols to their corresponding aldehydes and ketones, under mild conditions.

MATERIALS AND METHODS

Experimental Section

CrO₃ (Merck, P.A.) was used as received without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. Proton, ¹³C, ¹⁹F NMR (for TriMAFC) were carried out on a Bruker AVANCE DRX 500 spectrometer at 500, 125, 470.66 MHz. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ¹H and ¹³C NMR spectra were referenced to external SiMe₄ and ¹⁹F NMR spectra to external CFCl₃. Chromium was estimated iodometrically. In the case of the reduced product of the oxidant, chromium was determined after oxidizing with acidic peroxodisulfate (K₂S₂O₈) solution. The relative concentrations of carbon, hydrogen and nitrogen were obtained from the Microanalytical laboratories, Department of Chemistry, OIRC, Tehran. Melting points were measured on Electrothermal 9100 melting point apparatus.

Synthesis of Trimethylammonium Fluorochromate (TriMAFC), (CH₃)₃NH[CrO₃]

A 1g (10 mmol) sample of chromium (VI) oxide, CrO₃, and 0.9ml (20 mmol) of 40% hydrofluoric acid were added to 20 ml of water in a 100 ml polyethylene beaker with stirring. After 7 min the homogeneous solution was cooled to ca.-2 °C. To the resultant orange solution, trimethylamine (10 mmol) with hydrofluoric acid (10 mmol) was added drop wise with stirring over a period of 0.5 h and stirring was continued for 0.5 h at 2 °C. The precipitated clear-orange liquid was isolated by filtration on a polyethylene funnel, washed with petroleum ether (3 × 60 ml) and dried in vacuum for 2 h at room temperature. Yield: (86%); mp 124 °C, C₃H₁₀CrFNO₃: Calc. C, 20.11; H, 5.58; N, 7.82 Found: C, 20.08; H, 5.64; N, 7.69. I.R. (KBr): 912 cm⁻¹ ν₁(A₁) or ν(CrO₃), 636 cm⁻¹ ν₂(A₁) or ν(Cr-F), 950 cm⁻¹ ν₄(E) or ν(CrO₃), Electronic absorption at 22026 cm⁻¹, corresponded to ¹A₂→¹E (ε = 174 M⁻¹cm⁻¹); 28735 m⁻¹ to ¹E→¹E (ε = 664 M⁻¹cm⁻¹) and 36231 cm⁻¹ to ¹A₂→¹E (ε = 1248 M⁻¹cm⁻¹). UV/Visible, ¹³C NMR, ¹H NMR and ¹⁹F NMR were all consistent with the TriMAFC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution of TriMAFC in water was 2.9.

Synthesis of Trimethylammonium chlorochromate (TriMACC), (CH₃)₃NH[CrO₃Cl]

Chromium (VI) oxide (1.0 g, 10 mmol) was dissolved in water in a beaker and 6M hydrochloric acid (0.251 cm³, 15 mmol) was added under stirring at 0 °C. To the resultant clear orange solution, trimethylamine (0.059 cm³, 10 mmol) was added drop wise under stirring over a period of 0.5 h and the stirring was continued for 0.5 h at -4°C. The precipice clear-orange solid was isolated by filtration, washed with petroleum ether (3 x 60 cm³) and dried under vacuum for 2 h at room temperature. Yield: (59 %); mp 126 °C. Calcd. for C₃H₁₀ClCrNO₃: C, 18.41; H, 5.115; N, 7.161. Found: C, 18.52; H, 5.13; N, 7.17. IR (KBr): 902 cm⁻¹ ν₁(A₁) or ν(CrO₃), 430 cm⁻¹ ν₂(A₁) or ν(Cr-Cl), 948 cm⁻¹ ν₄(E) or ν(CrO₃) cm⁻¹. UV/Visible and ¹H-NMR were all consistent with the TriMACC structure. Electronic absorption at 21881 cm⁻¹, corresponding to ¹A₂→¹E (ε = 360 dm³mol⁻¹cm⁻¹); 28169 cm⁻¹ to ¹E→¹E (ε = 906 dm³mol⁻¹cm⁻¹) and 3485 cm⁻¹ to ¹A₂→¹A₁ (ε = 1157 dm³mol⁻¹cm⁻¹). The pH of 0.01 M solution of TriMAFC in water was 2.7.

The general procedure for supporting of TriMAFC and TriMACC on alumina

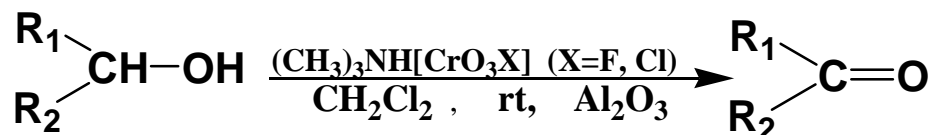
For supporting of the TriMAFC and TriMACC on alumina, in synthesizing process alumina (mesh 65-250) were added before the trimethylamine addition step. The supported reagents separated and washed by cold water and acetone. The capacity of the supported reagents were determined by stirring overnight 0.5 g of the supported reagents with 10 ml of 2 N aqueous potassium hydroxide, filtering off and titrating iodometrically the obtained chromate solution. The determined average capacity of the dried supported for the above reagents are 1-1.5 mmol of TriMAFC per 1 g of silica gel and 1.2- 1.5 mmol of TriMACC per 1 g of alumina. The supported reagents so obtained did not noticeably lose their activities neither on storing in air at room temperature for several weeks nor on refluxing for 5 h in benzene or hexane.

The general procedure for oxidation of organic substrates with TriMAFC and TriMACC on alumina

To a stirred suspension of trimethylammonium halochromate absorbed on alumina in dichloromethane (generally 5 cm³), a solution of the substrate in the minimum amount of dichloromethane were added dropwise (Table I). The completion of the reaction was followed by TLC using ether/petroleum ether (60/40) as eluant. The mixture is diluted with ether (1:1 v/v) and filtered through a short column of alumina to give a clear solution. The solution was evaporated and the residual product purified by distillation, recrystallization or column chromatography.

RESULTS AND DISCUSSION

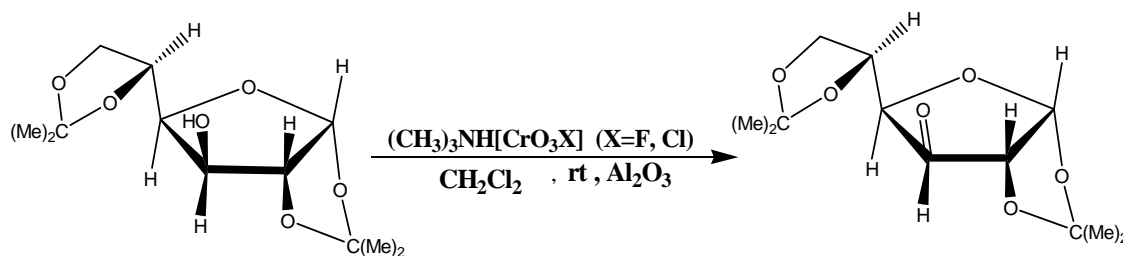
The results obtained with TriMAFC and TriMACC on alumina are very satisfactory and show the new reagents to be valuable additions to the existing oxidizing agents. Table 1 summarizes the products, yields and reaction times of TriMAFC and TriMACC on alumina with various substrates



The oxidative effects of TriMACC and TriMAFC on polycyclic rings appear more pronounced than on alcohols (Table 1).

The heterogeneous reaction mixtures are thoroughly stirred, at room temperature. The corresponding aldehyde and ketone products can then be easily isolated by simple filtration and evaporation of the solvent

TriMAFC and TriMACC on alumina have also been used for oxidation of carbohydrates such as 1, 2: 5, 6 -Di-O-isopropylidene- α -D-Glucofuranose to its relative ketosugar as other chromium reagents, by use of the equimolar ratio of the reagents.

**Table 1: Oxidations organic substrates via TriMAFC and TriMACC on alumina**

			TriMAFC		TriMACC	
Substrate		Product	Time (min)	Yield (%)	Time (min)	Yield (%)
1	$n\text{-C}_6\text{H}_{13}\text{-OH}$	$n\text{-C}_5\text{H}_{11}\text{-CHO}$	170	90	345	95
2	$n\text{-C}_8\text{H}_{17}\text{-OH}$	$n\text{-C}_7\text{H}_{15}\text{-CHO}$	210	90	250	96
3	$3\text{-C}_7\text{H}_{15}\text{-OH}$	$3\text{-C}_7\text{H}_{14}\text{O}$	240	90	295	94
4	$2\text{-C}_8\text{H}_{17}\text{-OH}$	$2\text{-C}_8\text{H}_{16}\text{O}$	235	90	275	95
5	$2\text{-C}_{11}\text{H}_{23}\text{-OH}$	$2\text{-C}_{11}\text{H}_{22}\text{O}$	115	90	240	97
6			90	85	95	99
7			12h	90	7h	91
8			6h	65	8h	95
9			6h	64	8h	96
10			20	90	26	88

Oxidations may also occur by using only TriMAFC and TriMACC, in the absence of Al_2O_3 , but considerable improvements are observed in the presence of the absorbent. This implies that the Al_2O_3 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.[10]

The nature of the solvent does not appear to be particularly critical. Hydrocarbons, benzene, ethers and chlorinated hydrocarbons are equally effective, the practical choice being oriented by

the solubility of the products and the desired reaction temperature. The chromium (VI) contents easily determined iodometrically.[11]

TriMAFC and TriMACC are easily prepared in high yields from chromium (VI) oxide, trimethylamine and aqueous related acid (HCl or HF) in a convenient molar ratio. The bright orange solid reagents can be stored in polyethylene containers for long periods without decomposition. The IR spectra of the reagents are similar to that of other halo chromates. TriMAFC and TriMACC are soluble in water, dimethylformamide¹² acetonitrile and acetone; they are less soluble in dichloromethane and only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

CONCLUSION

Two new alumina supported reagents trimethylammonium fluorochromate (VI) $(\text{CH}_3)_3\text{NH}[\text{CrO}_3\text{F}]$, (TriMAFC), and trimethylammonium chlorochromate (VI) $(\text{CH}_3)_3\text{NH}[\text{CrO}_3\text{Cl}]$, (TriMACC), are easily prepared in a nearly quantitative yield by the interaction of trimethylamine with CrO_3 , alumina and related acid. These reagents are versatile reagents for the effective and selective oxidation of organic substrates, in particular for alcohols, under mild conditions.

REFERENCES

- [1] L. F.Fieser, M.Fieser, *Reagents for Organic Synthesis*, Wiley, New York. **1967**, 1-11, 84.
- [2] E.J.Corey, J.W.Suggs, *Tetrahedron Lett*, **1975**,647, 16.
- [3] G.Maier, H. P.Reisenauer, M. D.Marco, *Angew. Chem. Int. Ed*, **1999**,08, 38.
- [4] A. Bhandari, P. K.Sharma, K. K.Banerji, *Indian J. Chem.*, **2001**,70, 40A.
- [5]S.Meenahshisundaram, R.Soctaungam, *Collect. Czech. Chem. Commun.*, **2001**, 77, 66.
- [6] B.Özgün, A.Yaylaoglu, K.Şendil, *Monatsh. Chem.*, **2007**, 38, 161.
- [7] K.Şendil, B.Özgün, *Phosphorous, Sulfur and Silicon and Related Elements*, **2006**,81, 959.
- [8] S.Ghammamy, H.Eimanieh, M. K.Mohammady, *Synthetic Commun.* **2007**, 37, 601.
- [9] F S.Guziec, F. A.Luzzio, *Synthesis*, **1980**, 91.
- [10] S.Meenahshisundaram, R.Soctaungam, *Collect. Czech. Chem. Commun.*, **2001**, 77, 66.
- [11] K.Nakamoto, Part II, Inorganic Compounds, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Third Edition, John Wiley & Sons: New York, **1978**, 40-150, 1.