Journal "Fluorine Notes", Volume # 5(60), September - October 2008

Tripropylammonium and Trimethylammonium fluorotrioxomolybdate (VI) (TriPrAFM) (TriMAFM): Two mild and efficient oxidants for oxidation of organic substrates

Z. Javanshir[a], S. Ghammamy[b], K. Mehrani[a], N. Babayani[a]

aDepartment of Chemistry, Faculty of Science, Islamic Azad University, Ardebil Branch, Ardebil, Iran
[b]Department of Chemistry, Faculty of Science, Imam Khomeini International University, Ghazvin, Iran, E-mail: shghamami@ikiu.ac.ir or shghamamy@yahoo.com

Abstract

Two new mild molybdenum (VI) oxidizing agents: Tripropylammonium fluorotrioxomolybdate (VI)(TriPrAFM) and Trimethylammonium fluorotrioxomolybdate (VI) (TriMAFM) were prepared and characterized. These new compounds are effective in the oxidation of organic substrates specially alcohols to corresponding carbonyl compounds. These compounds were characterized by IR, UV/Visible, ^{13}C-NMR, ^{1}H-NMR and ^{19}F-NMR techniques. The electronic and vibrational spectra of TriPrAFM and TriMAFM have been measured and studied.

Keywords: *Molybdenum (VI), Tripropylammonium fluorotrioxomolybdate, Trimethylammonium fluorotrioxomolybdate, Oxidation, Organic substrate, Alcohols*

Introduction

In recent years, significant improvements were achieved by the use of new oxidizing agents[1-3] such as Pyridinium dichromate (PDC)[4], Pyridinium fluorochromate (PFC)[5], Triphenylmethylposphonium chlorochromate[6], Chromium trioxide-3,5- Dimethylpyrazole complex (CrO_3 3,5-DMP)[7], Tributylammonium chlorochromate (TriBACC)[8], 3,5-Dimethylpyrazolium fluorochromate (DmpzHFC)[9], Quinolinium fluorochromate (QFC)[10], 2,2'- Bipyridinium chlorochromate (BiPCC)[11]. Many of above reagent be used the ammonium cation with chromate. Now we want to use ammonium cation with molybdate. In this research Pr_3N and Me_3N with HF were used to synthesis tripropylammonium fluorotrioxomolybdate (VI) (TriPrAFM) and trimethylammonium fluorotrioxomolybdate (VI), (TriMAFM). These new compounds are efficient and have certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields.

RESULTS AND DISCUSSION

These compounds can be easily prepared in good yield, quite stable when stored dry and in the absence of light, and are active as oxidizing agents for the conversion of alcohols to carbonyl compounds.

It has been found that these reagents have certain advantages over similar oxidizing agents in terms of the amounts of oxidant and solvent required, and especially in the short reaction times required and in the higher yields of the product (Table I and Table II).[13-16]

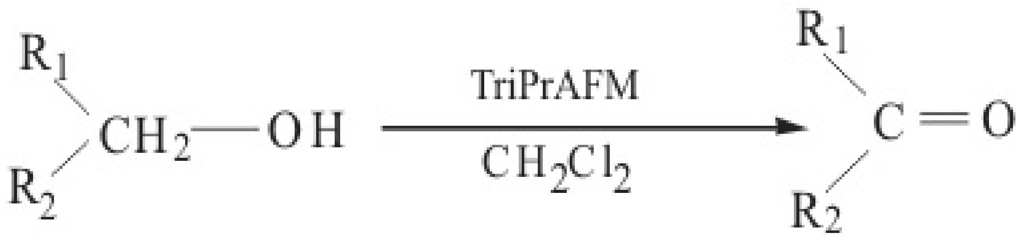
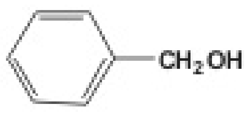
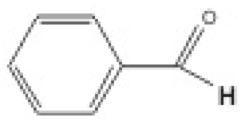


Table I. *Oxidation of alcohols and polycyclic arenes with TriPrAFM*

Substrate		Substrate /Oxidant Ratio	Time (min)	Product		Yield (%)	B.P. (°C)
1a	n-C_3H_7-OH	1/1	60	2a	n-C_2H_7-CHO	65	48-50
1b	2-C_3H_7-OH	1/1	60	2b	2-C_2H_7-CHO	70	55-57
1c	n-C_4H_9-OH	1/1	120	2c	n-C_3H_9-CHO	86	74-75
1d	2-C_4H_9-OH	1/1	120	2d	2-C_3H_9-CHO	66	79-80
1e	n-C_5H_{11}-OH	1/1	90	2e	n-C_4H_9-CHO	94	102
1f	n-C_8H_{17}-OH	1/1	180	2f	n-C_7H_{15}-CHO	90	170-172
1g		1/1	90	2g		95	177-179
							154-

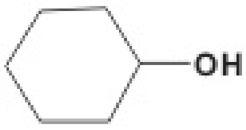
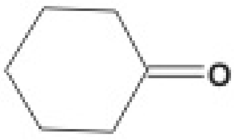
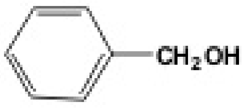
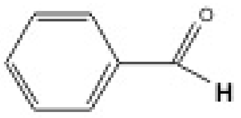
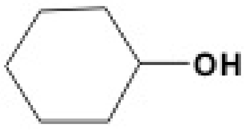
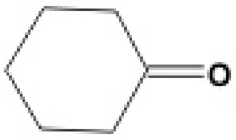
1h		1/1	5h	2h		75	156

Table II. *Oxidation of alcohols and polycyclic arenes with TriMAFM*

Substrate		Substrate /Oxidant Ratio	Time (min)	Product		Yield (%)	B.P. (°C)
1a	n-C_3H_7-OH	1/1	120	2a	n-C_2H_7-CHO	90	48-50
1b	2-C_3H_7-OH	1/1	60	2b	2-C_2H_7-CHO	70	55-57
1c	n-C_4H_9-OH	1/1	120	2c	n-C_3H_9-CHO	72	74-75
1d	2-C_4H_9-OH	1/1	180	2d	2-C_3H_9-CHO	75	79-80
1e	n-C_5H_{11}-OH	1/1	180	2e	n-C_4H_9-CHO	75	102
1f	n-C_8H_{17}-OH	1/1	180	2f	n-C_7H_{15}-CHO	60	170-172
1g		1/1	70	2g		93	177-179
1h		1/1	5h	2h		83	154-156

In conclusion, the lower acidity of these reagents, the easiness of preparation, theirs stability, non-hygroscopicity, the ease of the work up of the reaction mixture, reasonable yields of products and reaction time make them versatile and practical reagents for the oxidation of alcohols and a useful addition to the presently available reagents in organic synthesis. TriPrAFM and TriMAFM reagents are easy to handle, can be weighed and have no hazardous effects.

TriPrAFM and TriMAFM in dichloromethane also oxidize primary and secondary alcohols to, respectively, the corresponding aldehydes or ketones with high yields (Table I and Table II).

The results obtained with these reagents are very satisfactory and show the new reagents as a valuable addition to the existing oxidizing agents.

Experimental

MoO_3 (Merck, p.a.) was used without further purification. Solvents were purified by standard methods. Melting points were determined in open capillaries on "Electrothermal 9200" apparatus and are not corrected. Infrared spectra were recorded (KBr disks) on a "Shimadzu" model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. ^{1}H-NMR, ^{13}C, ^{19}F NMR 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. ^{1}H and ^{13}C NMR spectra were referenced to external $SiMe_4$ and ^{19}F NMR spectra to external $CFCl_3$. The percent composition of elements was obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Preparation of Tripropylammonium fluorotrioxomolybdate (VI), $[(C_3H_7)_3NH][MoO_3F]$, TriPrAFM

$(C_3H_7)_3NH[MoO_3F]$ was prepared by the reaction of $(C_3H_7)_3N$, MoO_3 and HF (1:1:1 ratio) in acetonitrile solvent as follows:

$$(C_3H_7)_3N + HF + MoO_3 \longrightarrow (C_3H_7)_3NH[MoO_3F]$$

Molybdenum (VI) oxide (1 g, 7 mmol) was dissolved in dry acetonitrile in a beaker and 30 % hydrofluoric acid (0.1 ml, 7mmol) was added with stirring at 0°C. To the resultant, tripropylamine (0.3 ml, 7 mmol) was added dropwise with stirring to this solution over a period of 0.5 h and stirring was continued for 2h at 0 °C. Within 5 min, a clear white solution formed gave solid TriPrAFM, which was isolated by filtration. The solid was washed with hexane and dried under vacuum for 1 h.

In the vibrational spectrum of this compound the known bands of cation and anion were seen[14,15,16] such as νMo=O(A_1) that was found at 873.16 cm^{-1} that confirmed with literature data. The expected signals were found in the ^{1}H-NMR and ^{13}C-NMR. ^{19}F-NMR shows the bond between Mo and F. IR (KBr): 873cm^{-1} $\nu_1(A_1)$ or $\nu(MoO_3)$, 918cm^{-1} $\nu_4(E)$ or $\nu(MoO_3)$, 598 cm^{-1} $\nu_2(A_1)$ or ν(Mo-F). UV/Visible ^{13}C-NMR, ^{1}H-NMR and ^{19}F-NMR were all consistent with the TriPrAFM structure. Electronic spectrum of TriPrAFM shows a transition in acetonitrile at 228nm (ε= 355.2 $mol.^{-1} lit.cm^{-1}$) that belongs to $^1A \longrightarrow {}^1E$ ($a \longrightarrow e$) transition. This transition is expected as in mono substituted molybdate ions, because of the position of molybdenum in the second series of transition metal elements and making of strong crystalline field complexes.

Preparation of Trimethylammonium fluorotrioxomolybdate (VI), $[(CH_3)_3NH][MoO_3F]$, TriMAFM

$(CH_3)_3NH[MoO_3F]$ was prepared by the reaction of $(CH_3)_3N$, MoO_3 and HF (1:1:1 ratio) in acetonitrile solvent as follows:

$$(CH_3)_3N + HF + MoO_3 \rightarrow (CH_3)_3NH[MoO_3F]$$

Molybdenum (VI) oxide (1 g, 7 mmol) was dissolved in acetonitrile in a beaker and 30 % hydrofluoric acid (0.05 ml, 7mmol) was added with stirring at 0 °C. To the resultant solution, trimethylamine (0.3 ml, 7 mmol) was added dropwise with stirring to this solution over a period of 0.5 h and stirring was continued for 2h at 0 °C. Within 5 min, a clear white solution formed gave solid TriMAFM, which was isolated by filtration. The solid was washed with hexane and dried under vacuum for 1 h.

In the vibrational spectrum of this compound the known bands of cation and anion were seen[14,15,16] such as ν Mo=O(A_1) that was found at 877 cm^{-1} that confirmed with literature data. The expected signals were found in the ^{1}H-NMR and ^{13}C-NMR. ^{19}F-NMR shows the bond between Mo and F. IR (KBr): 877cm^{-1} $\nu_1(A_1)$ or $\nu(MoO_3)$, 920cm^{-1} $\nu_4(E)$ or $\nu(MoO_3)$, 597 cm^{-1} $\nu_2(A_1)$ or ν (Mo-F). UV/Visible ^{13}C-NMR, ^{1}H-NMR and ^{19}F-NMR were all consistent with the TriMAFM structure. Electronic spectrum of TriMAFM shows a transition in acetonitrile at 230nm (ε= 360.7 $mol.^{-1}lit.cm^{-1}$) that belongs to ${}^1A \rightarrow {}^1E$ ($a \rightarrow e$) transition. This transition is expected as in mono substituted molybdate ions, because of the position of molybdenum in the second series of transition metal elements and making of strong crystalline field complexes.

Oxidation of alcohols: General Method

The alcohol (0.001 mol) dissolved in a small amount of the solvent was added to TriPrAFM (0.001 mol) in CH_2Cl_2 (25 ml) at room temperature. The mixture was stirred and refluxed for the time indicated in the Table 1 at room temperature, diluted with CH_2Cl_2 and filtered. Evaporation of solvent furnished the product. The molar ratio of substrate to oxidant was 1:1. The solution became homogeneous briefly before the black-brown reduced reagent precipitated. The progress of the reaction was monitored by TLC and UV/Visible spectrophotometery (at 228 nm).

Same as above to TriMAFM (0.001 mol) in CH_2Cl_2 (25 ml) was added the alcohol (0.001 mol) dissolved in a small amount of the solvent at room temperature. The mixture was stirred and refluxed for the time indicated in the Table 1 at room temperature, diluted with CH_2Cl_2 and filtered. Evaporation of solvent furnished the product. The molar ratio of substrate to oxidant was 1:1. The solution became homogeneous briefly before the black-brown reduced reagent precipitated. The progress of the reaction was monitored by TLC and UV/Visible spectrophotometery (at 228 nm).

Acknowledgements

The authors would like to thank Dr. Gh. Rezaei Behbahani and Dr. Mahjoub for valuable discussions.

References

1. G. Marier, H.P. Reisenauer, M.D. Marco, *Angew. Chem. Int. Ed. Engl.,* **38,** 108 (1999).
2. A. Bhandari, P.K. Sharma, K.K. Banerji, *Indian J. Chem. Sec. A.,* **40A,** 470 (2001).
3. S. Meenahshisundaram, R. Soctaungam, *Collect. Czec. Chem. Commun.,* **66,** 877

(2001).

4. M.Z. Kassaee, S.Z. Sayyed-Alangi, H. Sajjadi-Ghotbabadi, *Molecules*, **9**, 825 (2004).

5. M.N. Bhattacharjee, M.K. Chaudhuri, H.S. Dasgupta, N. Roy, *Synthesis,* 588 (1982).

6. A.R. Hajipour, L. Khazdooz, A.E. Ruoho, *J. Iranian .Chem. Soc.,* **2**, 315 (2005).

7. E.J. Corey, G.W. Fleet, *J. Tetrahedron Lett.,***14,** 4499 (1973).

8. S. Ghammamy, S.A. SeyedSadjadi, *J. Serb. Chem. Soc.,* **70**, 1243 (2005).

9. R. Srinivasan, C.V. Ramesh, W. Madhulatha, K. Balasubramanian, *Indian J. Chem. Sec. B.,* **35B**, 480 (1996).

10. U. Bora, M.K. Chaudhuri, *Tetrahedron*, **57**, 2445 (2001).

11. F.S. Guziec, F.A. Luzzio, *Synthesis,* **12**, 691 (1980).

12. W. Granier, S. Vilminot and J.D. Vidal. *J. Fluorine Chem*. **19**, 123 (1981).

13. K.M. Harmon, I. Gennick and S.L. Madeira. *J. Phys. Chem*. **78**, 2585 (1974).

14. Bahattacharjee, M. N., Chaudhuri, M. K., Das, H. S., and Roy, N., *Synthesis*, (**1982**) 588

15. A.A. Opalovskii and Z.M. Kuznetsova, IZU. *Sib. Dtd. Akad. Nauk. SSSR. Ser. Khim. Nauk*., **5**, 62, (1973).

16. J.P. Chaminade, J.M. Molltone, G. Villeneuve, M. Couzi, M. Pouchard and Hagenmuller, *J. Solid state. Chem*., **65**, 27, (1980).

17. M.N. Bahttacharjee, M.K. Chauduri and H.S. Dasgupta. Synthesis 588 (1982).

18. R. Srinivasan, P. Stanly and K. Balasubramanian. *Synth. Commun*. **27**, 2057, (1997).

19. J.C. Collins, W.W. Hess and F.J. Frank. *Tetrahedron Lett*. **9**, 3363 (1986).