

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

HEXAMETHYL ENETETR AMMONIUM FLUOROCHROMATE. A NEW REAGENT FOR OXIDATION OF ORGANIC SUBSTRATES

Ersan Turunc^a; Fatma Aydin^a

^a Department of Chemistry, Mersin University, Mersin, TURKEY

To cite this Article Turunc, Ersan and Aydin, Fatma(2004) 'HEXAMETHYL ENETETR AMMONIUM FLUOROCHROMATE. A NEW REAGENT FOR OXIDATION OF ORGANIC SUBSTRATES', *Organic Preparations and Procedures International*, 36: 4, 363 – 366

To link to this Article: DOI: 10.1080/00304940409458680

URL: <http://dx.doi.org/10.1080/00304940409458680>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

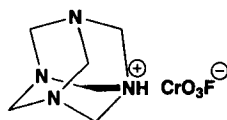
**HEXAMETHYLENETETRAMMONIUM FLUOROCHROMATE.
A NEW REAGENT FOR OXIDATION OF ORGANIC SUBSTRATES**

Submitted by Ersan Turunc and Fatma Aydin*
(02/03/04)

Department of Chemistry, Mersin University
33342 Mersin, TURKEY
**e-mail: faydin@mersin.edu.tr*

Chromium(VI) reagents have been widely used for the oxidation of primary and secondary alcohols to carbonyl compounds.¹ Some of the important reagents²⁻⁸ are Collins' reagent, chromium trioxide-3,5-dimethylpyrazole complex, pyridinium chlorochromate (PCC), pyridinium fluorochromate (PFC), pyridinium dichromate (PDC), quinolinium chlorochromate (QCC) and quinolinium fluorochromate (QFC). Some Cr (VI)-based oxidants suffer from disadvantages such as hygroscopicity, low selectivity, long reaction time, difficulty of preparation and need for a large excess of the reagent. Therefore, there is a continued interest in the development of a milder, more selective, inexpensive and non-toxic reagent. For this reason in this study we examined a new oxidizing agent, hexamethylenetetrammonium fluorochromate (HMTAFC). Hexamethylenetetraamine (urotropine) which is used for the synthesis of HMTAFC is a very cheap and, most importantly, non-toxic compound. Accordingly HMTAFC is potentially superior to some other frequently used chromium reagents such as PFC and QFC.

Hexamethylenetetrammonium fluorochromate (HMTAFC) is a yellowish orange solid, easily prepared in 70% yield by reaction of CrO₃ with aqueous hydrofluoric acid and hexamethylenetetramine. It is highly soluble in dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide



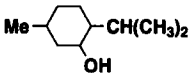
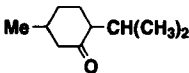




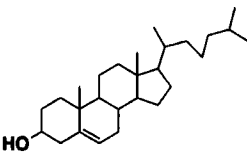
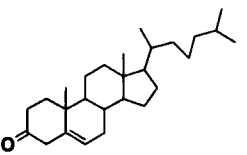
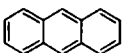
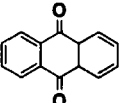

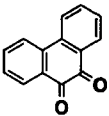
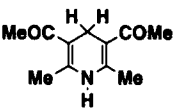
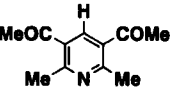
(DMF), sparingly soluble in methylene chloride and in chloroform and insoluble in toluene, benzene, ether and ethyl acetate. The structure of the new reagent was confirmed by elemental analyses and IR (KBr) spectrum which exhibited bands at 988, 936 cm⁻¹ (Cr=O stretching vibration of FCrO₃⁻ ion) and 654 cm⁻¹ (Cr-F). All of our experiments were carried out in DMF. Its molar conductance in water at 25°C is 132 Ω⁻¹ cm² mol⁻¹. The acidity of HMTAFC (4.30, 0.01 M aqueous solution) is less than that of PCC, PFC and QFC (0.01 M aqueous solution 1.75, 2.45 and 3.35 respectively). This reagent can be stored in sealed polyethylene bags as a dry solid for long periods without decomposition under anhydrous conditions.

Primary, secondary and benzylic alcohols are converted to their corresponding aldehydes and ketones in good to high yields by HMTAFC in dimethylformamide. Fused ring hydro-

carbons such as anthracene and phenanthrene are oxidized to quinones by this reagent. The reagent is found to be quite effective for the oxidation of Δ^5 -steroid system like cholesterol to the corresponding α,β -unsaturated ketone, of a thiol to the disulfide and of a 1,4-dihydropyridine to the corresponding pyridine derivative.

In conclusion, the easily prepared new reagent HMTAFC is very similar to related reagents such as PFC, QFC in terms of oxidizing properties, solubility in organic solvents, short reaction times. In addition, like these reagents, it is non-hygroscopic and stable. However, the

Table 1. Oxidation of Alcohols and Other Organic Compounds with HMTAFC

Substrate ^a	Time (h)	Product ^b	Yield (%)	mp. (°C)			
				Product		2,4-DNP	
				Found	Lit. ¹²	Found	Lit. ¹²
PhCH ₂ OH	4 h	PhCHO	75	----	----	236-237	237
	4 h		70	----	----	146-147	146
	7 h		71	----	----	160-161	162
	8 h		90	95-96	95-96	----	----
	6 h		67	125-126	127	----	----
PhSH	4 h	PhSSPh	64	62-63	61-62	----	----
	4 h		90	287-288	286	----	----
	4 h		70	207-208	208	----	----
	6 h		83	64-65	c	----	----

a) All reactions were carried out with equimolar amounts of HMTAFC at room temp. in DMF

b) The products were characterized by comparison with authentic samples by ¹H-NMR, FT-IR and mp. determinations (except for benzaldehyde, menthone and cyclohexanone which were identified with 2,4-dinitrophenylhydrazones)

c) ¹H-NMR (CDCl₃): δ 2.53 (s, 6H, CH₃-arom.); 2.67 (s, 6H, CH₃C=O), 8.13 (s, 1H, arom.), IR (KBr): 1680 (C=O), 3000 (arom. C-H), 2922-2985 (aliph. C-H) cm⁻¹.

Anal. Calcd. for C₁₁H₁₃NO₂: C, 69.11; H, 6.87; N, 7.40. Found: C, 69.13; H, 6.83; N, 7.38.

present investigation revealed that HMTAFC has a number of advantages. First of all, it is less acidic than PFC, QFC and PCC for example. The results also showed that the yields of oxidation are high despite the use of a molar ratio 1:1 of oxidant to substrate at room temperature. Thus the ratio of oxidant to substrate required to afford high yields of product is lower for HMTAFC than that of the other reagents. Furthermore, hexamethylenetetramine (urotropine) used for the synthesis of HMTAFC is relatively inexpensive and non-toxic in comparison to pyridine. Finally, since the reduced chromium species is converted into black granules in the course of oxidation, the product can readily be extracted from the black granules. Hence, working with HMTAFC is easier than is the case with other reagents.

EXPERIMENTAL SECTION

Mps were determined on Electrothermal 9100[®] apparatus. IR spectra were recorded on a Win First Satellite[®] model spectrophotometer. ¹H-NMR spectra were obtained using a 400 MHz Bruker DPX[®] instrument. Chromium and fluoride analyses were performed using UV-1601 Shimadzu[®] and Jenway-3025[®] and with a specific fluoride electrode, respectively.

Preparation of Hexamethylenetetrammonium Fluorochromate.- A solution of chromium trioxide (15 g, 0.15 mol) in water (10 mL) cooled to 0°C was added 40% aqueous hydrofluoric acid (11.25 mL, 1.225 mol) in a 50 mL polyethylene beaker. The mixture was stirred for 3-5 min to give a red-orange solution. The solution was then cooled in an ice bath (0-5°C) for 15 min. and hexamethylenetetramine (21 g, 0.15 mol) was added portionwise with mechanical stirring until a yellowish-orange solid precipitated. It was collected, washed with petroleum ether (3 x 10 mL) and dried in a vacuum desiccator over P₂O₅ to give 30 g (70%) of HMTAFC as a yellowish-orange solid, mp. 210-215°C (dec.).

The amount of chromium(VI) was determined by colorimetric methods using diphenylcarbazide solution.⁹ The amount of fluoride was determined by electrometric methods using a specific fluoride electrode.¹⁰ Pyridinium fluorochromate C₅H₅NHCrO₃F (PFC), was synthesized and recrystallized by the method described elsewhere.⁴ In both methods, PFC was used as a reference compound.

Anal. Calcd for C₆H₁₃CrFN₄O₃: Cr, 20.45; F, 7.54. Found: Cr, 20.00; F, 7.30

CAUTION.- *Hydrofluoric acid is toxic and causes severe skin and eye burns. Protective gloves and goggles should be worn when handling it. The synthesis should be carried out in a well-ventilated fume hood.*

General Procedure for Oxidations.- A solution of the substrate (10 mmol) in 5 mL of DMF was added in one portion to a solution of HMTAFC (2.6 g, 10 mmol) in DMF (15 mL). The progress of the reaction was monitored by TLC analysis. After completion of the reaction (4-6 hrs), 50 mL of water was added to the reaction mixture which was then extracted with ether (3 x 20 mL). The combined organic layer was dried over MgSO₄ and evaporated on a rotary evapo-

rator under reduced pressure. Then the product was chromatographed over silica gel using ethyl acetate-hexane (1:4) as the eluent. Evaporation of the solvent gave fairly pure solids which were crystallized; the liquid carbonyl compounds were derivatized with 2,4-dinitrophenylhydrazine.¹¹

REFERENCES

1. a) G. Cainelli and G. Cardillo, "*Chromium Oxidation in Organic Chemistry*", Springer-Verlag, Berlin, 118 (1984); b) J. Muzart, *Chem. Rev.*, **92**, 113 (1992).
2. a) J. C. Collins, W. W. Hess and F. J. Frank, *Tetrahedron Lett.* **9**, 3363 (1968); b) E. J. Corey and G. W. J. Fleet, *Tetrahedron Lett.*, **14**, 4499 (1973); c) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, **16**, 2647 (1975); d) M. K. Chaudhuri, S. K. Chettri, S. Lyndem, P. C. Paul and P. Srinavas, *Bull. Chem. Soc. Jpn.*, **67**, 1894 (1994); e) E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, **20**, 399 (1979); f) J. Singh, S. P. Kalsi, G. S. Jawanda and B. R. Chhabra, *Chem. and Ind.(London)*, 751 (1986).
3. F. A. Luzzio and F. S. Guziec, *Org. Prep. Proced. Int.*, **20**, 533 (1988).
4. M. N. Bhattacharjee, M. K. Chaudhuri, H. S Dasgupta, N. Roy, and D. T Khathing, *Synthesis*, 588 (1982).
5. F. S. Guziec and F. A. Luzzio *Synthesis*, 691 (1968).
6. F. S. Guziec, Jr., and F. A. Luzzio, *J. Org. Chem.* **47**, 1787 (1982).
7. E. J. Parish and A. D. Scott, *J. Org. Chem.* **48**, 4766 (1983).
8. F. Shirini, I. Mohammadpoor-Baltork, Z. Hejazi and P. Heravi, *Bull. Korean Chem. Soc.* **24**, 517 (2003).
9. T. L. Allen, *Anal. Chem.*, **30**, 447 (1958).
10. T. S. Light and C. C. Cappuccino, *J. Chem. Educ.*, **52**, 247 (1975).
11. A. I. Vogel, "*Textbook of Practical Organic Chemistry*", 5th ed., Longman Group UK Ltd., 1218 (1989).
12. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 72 nd Edition, 1991-1992, CRC Press, Inc., Physical Constants of Organic Compounds (Section 3).
