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Short communication

TRIETHYLAMMONIUM HALOCHROMATES/SILICA GEL: AN EFFICIENT REAGENT FOR OXIDATIVE COUPLING OF THIOLS TO DISULFIDES

Shahriare Ghammamy[1], **Mohammad Kazem Mohammadi**[2], **Ali Hassani Joshaghani**[3]

[1]*Department of Chemistry, Faculty of Science, Imam Khomeini International University,*
Qazvin, Iran. P.O. Box 288
[2]*Faculty of Science, Islamic Azad University,*
Ahwaz Branch , Ahwaz , Iran
[3]*Department of Chemical Engineering, Faculty of Engineering, Islamic Azad University,*
Arak Branch, Arak, Iran.
mkmohammadi@yahoo.com

Triethylammonium halochromates, $(C_2H_5)_3NCrO_3X$, TEAXC (X = Cl, F) are easily synthesized by the reaction of triethylamine with a solution of chromium(VI) oxide in 6M hydrochloric acid, or a solution of chromium(VI) oxide in 40% hydrofluoric acid. These reagents are easily supported on common silica gel and can be used as heterogeneous oxidants. Triethylammonium halochromate(VI) is a versatile reagent for the effective and selective oxidation of organic substrates. Various aliphatic (cyclic and acyclic) and aromatic thiols are converted into the corresponding disulfides by treatment with triethylammonium fluorochromate(VI), (TEACC) or triethylammonium chlorochromate(VI), (TEAFC) supported on silica gel, in excellent yields and under mild reaction conditions.

Key words: triethylammonium fluorochromate(VI); triethylammonium chlorochromate(VI); heterogeneous oxidants; silica gel; oxidation; thiol; disulfides

ХАЛОХРОМАТИ НА ТРИЕТИЛАМОНИУМ / СИЛИКАГЕЛ: ЕФИКАСЕН РЕАГЕНС ЗА ОКСИДАТИВНО ВРЗУВАЊЕ НА ТИОЛИ СО ДИСУЛФИДИ

Халохромати на триетиламониум $(C_2H_5)_3NCrO_3X$, TEAXC (X = Cl, F) лесно се синтетизираат кога триетиламинот реагира со раствор на хром(VI)оксид во 6М хлороводородна киселина или со раствор на хром(VI)оксид во 40% флуороводородна киселина. Овие реагенси лесно се сорбираат на силика-гел и можат да бидат употребени како хетерогени оксиданти. Триетиламониумхалохроматот(VI) е погоден реагенс за ефективна и селективна оксидација на органски супстрати. Различни алифатични (циклични и ациклични) и ароматични тиоли се преведуваат во соодветни дисулфиди под дејство на триетиламониумфлуорохромат(VI), или на триетиламониумхлорохромат(VI) сорбирани на силика-гел. Условите на реакциите се благи, а приносите одлични.

Клучни зборови: триетиламониумфлуорохромат(VI); триетиламониумхлорохромат(VI); хетерогени оксиданти; силика-гел; оксидација; тиол; дисулфиди

INTRODUCTION

Disulfides are one of the most important organo-sulfur compounds possessing an exclusive chemistry both in biochemistry and in synthetic area [1]. Disulfides are also key intermediates in a wide variety of organic synthetic routes. The importance of sweetening of catalyst poisons thiols to low volatile disulfides in petroleum industries, and the industrial applications of disulfides in vulcanization of rubbers and elastomers, led us to investigate the introduction and applications of a new member of this category of reagents in oxidation of thiols to the corresponding disulfides [2].

The main type of these reactions is the oxidation of thiols in the presence of molecular oxygen [3], DMSO [4], using borohydride exchange resin [5], DMSO/alumina reagent [6], CBr_4/ solid K_2CO_3/18-crown-6/benzene [7] and $NaIO_3$/alumina [8].

However, some of the reported reagents suffer from disadvantages such as instability, hygroscopicity, low selectivity, long reaction time, difficulty of preparation and need for a large excess of the reagent. Thus a milder, more selective and inexpensive reagent is still in demand. The need for overcoming these problems, lead to the development of a good number of other oxidants, such as: pyridinium chlorochromate (PCC) by Corey and Boger [9], pyridinium fluorochromate by Bhattacharjee and co-workers [10], quinolinium dichromate by Chaubey [11]. 2,2'-bipyridinium chlorochromate by Guziec and Luzzio [12], quinolinium chlorochromate, by Jeyanthi [13] and isoquinolinium fluorochromate by Srinivasan and co-workers [14]. We have prepared tetramethylammonium fluorochromate [15] and cetyltrimethylammonium bromochromate [16], with the belief that these reagents may have oxidative properties and could be used for oxidation of organic substrates, particularly thiols.

This manuscript introduces triethylammonium fluorochromate(VI) (TEAFC) and triethylammonium chlorochromate(VI) (TEACC) absorbed on silica gel as new reagents with improved work-up efficiency and durability, for the oxidation of thiols to disulfides.

EXPERIMENTAL SECTION

Material and instruments

Chromium(VI)oxide (p.a.) was obtained from Merck, and silica gel (–150 mesh) was obtained from Aldrich. These reagents were used without further purification. The TLC plates were obtained from Merck.

Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Vis measurements were made on an Uvicon model 922 spectrophotometer. ^1H, ^{13}C, ^{19}F-NMR were carried out on a Bruker AVANCE DRX 500 spectrometer at 500, 125, 470.66 MHz, respectively. All the chemical shifts are quoted in ppm using the high-frequency positive convention; the ^1H and ^{13}C-NMR spectra were referenced to external $SiMe_4$ and the ^{19}F-NMR spectra to external $CFCl_3$. Chromium was estimated iodometrically. In the case of the reduced product of the oxidant, chromium was determined after oxidizing with acidic peroxodisulfate ($K_2S_2O_8$) solution. The percent composition of carbon, hydrogen and nitrogen were obtained from the Microanalytical Laboratories of the Department of Chemistry, OIRC, Tehran.

Triethylammonium fluorochromate (TEAFC), $(C_2H_5)_3NH^+ [CrO_3F]^-$

Chromium (VI) oxide (1.0 g, 0.01 mol) and 40% hydrofluoric acid (0.9 ml, 0.02 mol) were added to 20 ml of water in a 100 ml polyethylene beaker with stirring. After 5 min the homogeneous solution was cooled to ca. 0–2 °C. To the resultant clear orange solution, triethylamine (1.400 ml, 0.010 mol) was added drop-wise with stirring over a period of 0.5 hours and stirring was continued for additional 0.5 hours at –4 °C. The precipitated yellowish-orange solid was isolated by filtration on a polyethylene funnel, washed with petroleum ether (3 × 60 ml) and dried in vacuum for 2 hours at room temperature. Yield: (88%); mp 132 °C; $C_6H_{16}CrFNO_3$: Calc. C 32.57%, H 7.23%, N 6.33%. Found: C 32.08%, H 7.64%, N 6.44%. ^{13}C NMR (125 MHz, $CDCl_3$): δ 45.9 (CH_2), δ 8.7 (CH_3). ^1H NMR (500 MHz, $CDCl_3$): δ 7.1 (s, 1 H), δ 3.32 (q , 2 H), δ 1.58 (t, 3 H). IR (KBr): 904 cm^{-1} $\nu_1(A_1)$ or $\nu(CrO_3)$, 648 cm^{-1} $\nu_2(A_1)$ or ν(Cr–F), 948 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$,

UV-Vis: Electronic absorption at 22321 cm^{-1}, corresponded to $^1A_2 \rightarrow {}^1E$ ($\varepsilon = 270\ M^{-1}cm^{-1}$); 28735 m^{-1} to $^1E \rightarrow {}^1E$ ($\varepsilon = 845\ M^{-1}cm^{-1}$) and 36231 cm^{-1} to $^1A_2 \rightarrow {}^1E$($\varepsilon = 1233\ M^{-1}cm^{-1}$). The UV/Visible, ^{13}C NMR and ^1H NMR data was consistent with the TEAFC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution of TEAFC in water was 3.45.

Triethylammonium chlorochromate (TEACC),

$(C_2H_5)_3NH^+[CrO_3Cl]^-$

Chromium(VI) oxide (1.0 g 0.01 mol) was dissolved in water and 6 M hydrochloric acid (0.251 ml, 0.015 mol) was added with stirring at 0 °C. To the resulting orange solution, triethylamine

(0.101 ml, 0 .01 mol) was added drop-wise with stirring over a period of 30 minutes and the stirring was continued for 30 minutes at –4 °C. The precipitated orange solid was isolated by filtration, washed with petroleum ether (3×60 ml) and dried under vacuum for 2 h at room temperature. Yield: (54 %); mp 120 °C; Calcd. for $C_6H_{16}ClCrNO_3$: C 30.32%, H 6.74%, N 5.89%. Found: C 30.29%, H 6.81%, N 5.82%. ^{13}C NMR (125 MHz, $CDCl_3$): δ 44.3 (CH_2), δ 8.4 (CH_3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.0 (s, 1 H), δ 3.27 (q , 2 H), δ 1.55 (t, 3 H). IR (KBr): 900 cm^{-1} $\nu_1(A_1)$ or $\nu(CrO_3)$, 434 cm^{-1} ν_2 (A_1) or ν(Cr–Cl), 950 cm^{-1} ν_4(E) or $\nu(CrO_3)$ cm^{-1}.

Electronic absorption at 22075 cm^{-1}, corresponded to $^1A_2 \rightarrow {}^1E$ (ε =316 M^{-1} cm^{-1}); 28169 cm^{-1} to $^1E \rightarrow {}^1E$ (ε = 803 M^{-1} cm^{-1}) and 41152 cm^{-1} to $^1A_2 \rightarrow {}^1A_1$ (ε = 1327 M^{-1} cm^{-1}). The UV/Visible, ^{13}C NMR and ^{1}H NMR data was consistent with the TEACC structure. The pH of 0.01 M solution of TEACC in water was 2.4.

General procedure for preparation of silica gel supported reagents

A 500 ml suction flask equipped with a constant–pressure dropping funnel was used. The cold solution of TEAFC or TEACC, prepared by dissolving of TEAXC (X = F: 0.2 mol, 44.2 g; X = Cl: 0.2 mol, 47.4 g) in CH_2Cl_2 (10 ml), was stirred with silica gel (60 g), over a period of 30 min at room temperature. Evaporation of the solvent under low-pressure vacuum for 30 min, yielded an orange-red slurry of triethylammonium halochromate/silica gel. The slurry was completely dried on the surface of highly dried day plate in the air to give 140 g of the desired reagent.

Typical procedure for oxidation coupling of benzenethiol with Triethylammonium halochromates / Silica gel

A suspension of benzenethiol (**1f**) (0.110 g, 0.001 mol), TEAFC (0.221 g, 0.001 mol) and wet silica gel (50% (w/w), 0.2 g) in CH_2Cl_2 (10 ml) was magnetically stirred at room temperature for 114 minutes. The completion of the reaction was followed by TLC using ether/petroleum ether (6:4) as eluant. The mixture was diluted with ether (1:1 v/v) and filtered through a short column of silica gel to give a clear solution. The solution was evaporated and the residual product was purified by distillation, recrystallization or column chromatography to give 1,2 diphenyldisulfane (**2f**) in 87 % yield. m.p 57–58 °C; lit.[17] m.p 58–60 °C. For other thiols (**1a–e**, **1g–h**), the procedures were the same as above (see Table 1). The same procedure was applied for coupling of benzenethiol to 1,2–diphenyldisulfane with TEACC and above procedure could be achieved for larger scales, without any difficulties.

Spectral data for disulfides

1,2-Diisopropyldisulfane (2a), oil [17]. IR (KBr, cm^{-1}): 3000–2900 C–H (aliph. stretch), 1400–1350 C–H (aliph. bend), 1200–1100 C–S (stretch). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.7 (m, 2 H), 1.5 (d, 12 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 38.5 (CH), 24 (CH_3). HRMS Calcd. for $C_6H_{14}S_2$: M$^+$, 150.4125 amu. Found: M$^+$, 150.4117 amu (average).

1,2-Dipentyldisulfane (2b), oil [17]. IR (KBr, cm^{-1}): 3000–2900 C–H (aliph. stretch) 1200–1100 C–S (stretch). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.5 (t, 4 H) ,1.6 (m, 4 H) , 1.25 (m, 4 H) 1.3 (m , 4 H), 0.85 (t, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 36, 33, 31, 23.5, 14.5. HRMS Calcd for $C_{10}H_{22}S_2$: M$^+$, 206.8542 amu. Found: M$^+$, 206.1654 amu (average).

1,2–Dioctyldisulfane (2c), oil [17]. IR (KBr, cm^{-1}): 3000–2900 C–H (aliph. stretch), 1200–1100 C–S (stretch). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.6 (t, 4 H), 1.5 (m, 4 H), 1.2 (m, 18 H) .9 (t, 6H) . ^{13}C NMR (125 MHz, $CDCl_3$): δ 33.66, 32.5, 31.43, 31.35, 31.22, 27.03, 23.5, 15.02. HRMS Calcd for $C_{16}H_{34}S_2$: M $^+$, 290.1213. Found: *m/z* 290.3564 (average).

1,2-Dicyclohexyl disulfane (2d), oil [17]. IR (KBr, cm^{-1}): 3000–2900 C–H (aliph. stretch), 1200–1100 C–S (stretch). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.5 (m, 2 H), 1.65 (dt, 8 H), 1.4 (m, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.56, 34.52, 26.59, 25.38. HRMS Calcd for $C_{12}H_{22}S_2$: M$^+$, 230.2135 . Found: *m/z* 230.2120 (average).

Disulfanylacetic acid (2e), oil [17]. IR (KBr, cm^{-1}): 3500–3200 OH (stretch), 3000–2900 C–H (aliph. stretch), 1200–1100 C–S (stretch). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.27 (s , 4 H), 11.5 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 35 (CH_2), 179 (C=O). HRMS Calcd for $C_4H_6\ O_4S_2$: M$^+$, 182.1478. Found: *m/z* 182.342 (average).

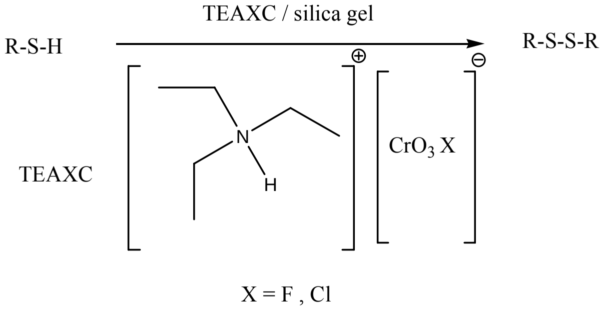
1,2-diphenyldisulfane (2f), m.p 57–58 ^{0}C, lit. [17] 58–60 ^{0}C. IR (KBr, cm^{-1}): 3200–3100 C–H (aromatic stretch), 1200–1150 C–S (stretch). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, 4 H), 7.25 (m, 6 H). ^{13}C NMR (125MHz, $CDCl_3$): δ 133.0, 131.4, 130.2, 129.53. $C_{12}H_{10}S_2$: Calc. C 66.1%, H 4.71%, S 29.37%. Found: C 66.22%, H 4.65%, S 29.2%.

Bis(4-methylphenyl)disulfide (2g), m.p 42–44 ^{0}C, lit.[18] 43–44 ^{0}C. IR (KBr, cm^{-1}): 3200–2100 C–H (aomatic stretch), 3000–2900 C–H (aliph. stretch), 1480–1400 C–H (aromatic bend), 1200– 1100 C–S (stretch). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5 (d, 4 H), 7.2 (d, 4 H), 2.5 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 130 (CH), 127 (CH), 126 (C),124 (C), 21 (CH_3). $C_{14}H_{14}S_2$: Calc. C 68.29%, H 5.70%, S 26.1%. Found: C 68.46%, H 5.60%, S 26.23%.

Bis(2-naphthyl)disulfide (2h), m.p 140–142 ^{0}C, lit. [18] 142–145 ^{0}C. IR (KBr, cm^{-1}): 3200–3100 C–H (aromatic stretch), 1200– 1150 C–S (stretch). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.1 (s , 2 H), 7.7 (d, 2 H), 7.5 (d, 6 H), 7.32 (d, 4 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 137.76, 137.11, 135.26, 134.52, 131.57, 128.92, 127.08, 126.16, 125.02, 124.87. $C_{20}H_{14}S_2$: Calc. C 75.47%, H 4.40%, S 20.12%. Found: C 75.36%, H 4.32, S 20.89%.

RESULTS AND DISCUSSION

Different thiols were subjected to oxidations with triethylammonium fluorochromate(VI) (TEAFC) and triethylammonium chlorochromate(VI) (TEACC), absorbed on silica gel, in dichloromethane (Scheme 1).

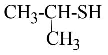
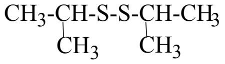
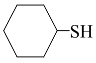
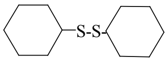
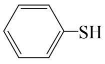
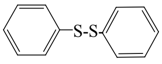
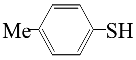
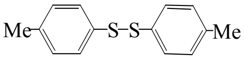
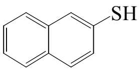
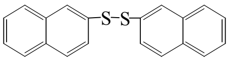


Scheme 1

These oxidations take place under mild and completely heterogeneous conditions giving excellent yields (Table 1).

Table 1

*Oxidation of thiols (**1a –h**) with TEAFC and TEACC on silica gel*

Substrate	Product	TEAFC		TEACC	
		Time (min)	Yield (%)	Time (min)	Yield (%)
 $CH_3\text{-}\underset{CH_3}{CH}\text{-}SH$ **1a**	 $CH_3\text{-}\underset{CH_3}{CH}\text{-}S\text{-}S\text{-}\underset{CH_3}{CH}\text{-}CH_3$ **2a**	92	78	145	85
n-C_5H_{11}-SH **1b**	C_5H_{11}-S-S-C_5H_{11} **2b**	90	86	108	90
n-C_8H_{17}-SH 1c	C_8H_{17}-S-S-C_8H_{17} **2c**	94	90	97	85
 **1d**	 **2d**	85	35	140	75
HOOC-CH_2-SH **1e**	HOOC-CH_2-S-S-CH_2-COOH **2e**	97	80	215	80
 **1f**	 **2f**	114	87	95	80
 **1g**	 **2g**	115	84	85	85
 **1h**	 **2h**	135	81	90	85

Oxidations may also occur using only TEAFC and TEACC, in the absence of silica gel, but considerable improvements are observed in the presence of the absorbent. This implies that the silica gel may act as a reaction medium, providing an effective heterogeneous surface area for the oxidation and at the same time making the procedure much more convenient. 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 mandated by the solubility of the products and the desired reaction temperature. The chromium(VI) contents were easily determined iodometrically. It seemed from the Table 1 that TEAFC were more effective than TEACC for saturated organic thiols (**1a** – **1d**) in terms of yields and reaction times. Overoxidation to sulfoxides and/or sulfones was not observed in the above-mentioned reactions. The IR spectra of TEAFC and TEACC are similar to that of other fluoro and chlorochromates [19]. TEAFC and TEACC are soluble in water, dimethylformamide, acetonitrile, acetone and dichloromethane; they are only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

CONCLUSION

New reagents triethylammonium fluorochromate(VI), (TEAFC) and triethylammonium chlorochromate(VI), (TEACC) absorbed on silica gel were easily synthesized. They are inexpensive, readily available oxidizing reagents for a variety of aromatic and non-aromatic thiols. Theirs advantages include higher yields, shorter reaction times, lower thiol/oxidant molar ratios, and ease of separation of products. Moreover, during the reaction, the color of the oxidants change from orange to brown, thus providing a visual means for ascertaining the progress of the oxidation. These reactions are easily scaled up without any problems. We did not perform regeneration of the reagents, but this could probably be achieved via flow in a reaction vessel. Because of phase transfer properties, availability, versatility and high adsorbance on silica gel by the quaternary ammonium cation, these reagents were suitable for oxidative coupling of thiols to disulfides. The mechanism of oxidation is probably similar to those by other quaternary ammonium reagents described by Walters and coworkers [20] and by Patel and Mishra [21]. Many functional groups are inert towards these oxidizing agents, including, sulfides and phenols, enhancing the usefulness of the oxidants and the oxidation conditions for the synthesis of highly functionalized molecules.

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REFERENCES

[1] G. Capozzi, G. Modena, S. Patai, *The Chemistry of the Thiol Group*, Wiley, New York, 1974, p. 785.

[2] D. L. Holbrook, *Handbook of Petroleum Refining Processes*, Chap. 11.3, R.A. Meyers (Ed.), McGraw Hill, 1996.

[3] K. -T. Liu, Y. C. Tong, A Facile Conversion of Thiols to Disulfides. *Synthesis*, 669 (1978).

[4] T. J. Wallace, Reactions of Thiols with Sulfoxides. I. Scope of the Reaction and Synthetic Applications. *J. Am. Chem. Soc.*, **86** (10), 2018–2021 (1964).

[5] J. Choi , N. M. Yoon, Synthesis of Disulfides by Copper-Catalyzed Disproportionation of Thiols. *J. Org. Chem.*, **60** (11), 3266 (1995).

[6] M. Hirano, S. Yakabe, H. Monobe, T. Marimoto, Alumina: an Efficient and Reusable Catalyst for the Oxidative Coupling of Thiols with DMSO. *J. Chem. Res.* **(S),** 472 (1998).

[7] E. Abele, R. Abele, E. Lukevics, Selective and Simple Phase Transfer Catalyzed Synthesis of Disulfides from Thiols, *J. Chem. Research* **(S),** 624 –625 (1999).

[8] M. Hirano, S. Yakabe, K. Ando, T. Morimoto, Simple Oxidation of Thiols with Sodium Iodate under Solid–Solution Biphasic Conditions. *J. Chem. Res.* **(S)**, 816 (1998).

[9] E. J. Corey, D. L. Boger, Oxidative cationic cyclization reactions effected by pyridinium chlorochromate , *Tetrahedron Lett.*, **19** (28) , 2461–2464 (1978).

[10] M. N. Bhattacharjee, M. K. Chauduri, H. S. Dasgupta, Pyridinium fluorochromate; A New and Efficient Oxidant for Organic Substrates, Synthesis 588–590 (1982).

[11] G. S. Chaubey, S. Das, M. K. Mahanti, Quinolinium dichromate oxidation of aliphatic aldehydes: A kinetic study, *Croatica Chemica Acta*, **76** (4), 287–291 (2003).

[12] F. S. Guziec, F. A. Luzzio, The oxidation of alcohols using 2,2'-bipyridinium chlorochromate, *Synthesis*., 691–694 (1980).

[13] G. F. Jeyanthi, G. Vijayakumar, K. P. Elango, The effect of solvent on the benzaldehydes by quinolinium chlorochromate in aqueous organic solvent media. *J. Serb. Chem. Soc.* **67** (12), 803–808 (2002).

[14] R. Srinivasan, P. Stanley, K. Balasubramanian, Isoquinolinium fluorochromate: A new and efficient oxidant for organic substrates, *Synth. Commun*., **27** (12) , 2057–2064 (1997) .

[15] A. R Mahjoub, S. Ghammami, M. Z Kassaee, Tetramethylammonium fluorochromate(VI): A new and efficient

oxidant for organic substrates, *Tetrahedron Lett.*, **44** (24), 4555–4557 (2003).

[16] Sh. Ghammamy, H. Eimanieh, M. K. Mohammady, Cetyltrimethylammonium Bromochromate: A New and Efficient Oxidant for Organic Substrates, *Synth Commun.*, **37**, 599–605 (2007).

[17] *Aldrich Catalog Handbook of Fine Chemicals*, 1996–1997, pp. 1159.

[18] M. Montazerozohori, S. Joohari, B. Karami N. Haghighat, Fast and Highly Efficient Solid State Oxidation of Thiols, *Molecules*, **12**, 694–702 (2007).

[19] K. Nakamoto, Part II, *Inorganic Compounds, Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd, Vol. 1, pp 140–150, John Wiley & Sons: New York, 1978.

[20] M. A. Walters , J. Chaparro, T. Siddiqui, F. Williams, C. Ulku, A. L Rheingold, The Formation of Disulfides by the [Fe(nta) Cl_2]2 – Catalyzed Air Oxidation of Thiols and Dithiols, *Inorg. Chimica Acta*., **359**, 3996–4000 (2006).

[21] S. Patel, B. K. Mishra, Chromium(VI) Oxidants Having Quaternary Ammonium Ions: Studies on Synthetic Applications and Oxidation Kinetics, *Tetrahedron*, **63**, 4367–4406 (2007).