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## Oxidative coupling of thiols to disulfides using two trimethylammonium halochromates (VI), $(\text{CH}_3)_3\text{NH}[\text{CrO}_3\text{X}]$ , (X = F, Cl) supported on alumina

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### ABSTRACT

Mild and efficient method for the oxidative coupling of thiols by alumina supported trimethylammonium fluorochromate (TriMFC) and trimethylammonium chlorochromate (TriMCC) are reported. Alumina supported trimethylammonium fluorochromate and trimethylammonium chlorochromate are efficient and new reagents, which prepared easily and oxidized thiols to the corresponding disulfides quickly. The reactions performed cleanly and controlled to stop at the disulfide stage without over-oxidation side products. The easy procedure, simple work-up, short reaction times, and excellent yields are another advantages of these reagents.

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### KEYWORDS

Trimethylammonium fluorochromate (VI);  
Trimethylammonium chlorochromate (VI);  
Heterogeneous oxidants;  
Alumina;  
Oxidation;  
Thiol.

### INTRODUCTION

The search for new oxidizing agents is of interest to synthetic organic chemists. Many such reagents have been developed in recent years with some success<sup>[1]</sup>. Disulfides are one of the most important organic sulfur compounds possessing an exclusive chemistry both in biochemistry<sup>[2]</sup> and in synthetic area<sup>[3]</sup>. Disulfides are also key intermediates in a wide variety of organic synthetic routes<sup>[4-6]</sup>. Sweetening of catalyst poisons thiols to low volatile disulfides in oil industries<sup>[7,8]</sup> and also industrial applications of disulfides in vulcanization of rubbers and elastomers led us to investigate the introduction and applications of new member of this category of reagents in oxidation of thiols to the corresponding disulfides.

Many stoichiometric reagents like manganese dioxide<sup>[9]</sup>, dichromates<sup>[10]</sup>, halosilane-chromium triox-

ide<sup>[11]</sup>, diethyl azodicarboxylate<sup>[12]</sup>, nickel peroxide<sup>[13]</sup>, chromium peroxide<sup>[14]</sup>, diaryl telluroxide<sup>[15]</sup>, tetrabutylammonium ceric (IV) nitrate<sup>[16]</sup>, sodium perborate<sup>[17]</sup>, silver trifluoromethane sulphonate<sup>[18]</sup> and permanganate<sup>[19]</sup> have been developed for this transformation. These reagents suffer from either one or more of the following disadvantages such as availability of the reagent, cumbersome work-up procedure, high cost of the reagent, over oxidation or oxidation of other functional groups in the presence of thiol group. As a result, there is still a need for the development of general, efficient, and new reagents to synthesize disulfides from the corresponding thiols under mild reaction conditions. These reactions are not only interest from ecological viewpoint, but also in many cases offer considerable synthetic advantages in terms of the yield, selectivity and simplicity of the reaction procedure. In this respect,

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Figure 1

we wish to report that trimethylammonium fluorochromate (TriMAFC) and trimethylammonium chlorochromate (TriMACC) absorbed on  $\text{Al}_2\text{O}_3$  able to oxidize thiols to their disulfides efficiently under different reaction conditions.

## EXPERIMENTAL

**Trimethylammonium fluorochromate (TriMAFC),  $(\text{CH}_3)_3\text{NH}[\text{CrO}_3\text{F}]$** 

A 1 g (10 mmol) sample of chromium (VI) oxide,  $\text{CrO}_3$ , and 0.9 ml (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.  $-2^\circ\text{C}$ . To the resultant orange solution, trimethylamine (0.01 mol) with hydrofluoric acid was added drop wise with stirring over a period of 0.5 h and stirring was continued for 0.5 h at  $2^\circ\text{C}$ . The precipitated clear-orange liquid was isolated by filtration on a polyethylene funnel, washed with petroleum ether ( $3 \times 60\text{ ml}$ ) and dried in vacuum for 2 h at room temperature. Yield: (86%); mp  $126^\circ\text{C}$ ,  $\text{C}_3\text{H}_{10}\text{CrFNO}_3$ ; Calc. C, 20.11; H, 5.58; N, 7.82 Found: C, 20.08; H, 5.64; N, 7.69. I.R. (KBr):  $912\text{ cm}^{-1}$   $\nu_1(\text{A}_1)$  or  $\nu(\text{CrO}_3)$ ,  $636\text{ cm}^{-1}$   $\nu_2(\text{A}_1)$  or  $\nu(\text{Cr-F})$ ,  $950\text{ cm}^{-1}$   $\nu_4(\text{E})$  or  $\nu(\text{CrO}_3)$ , Electronic absorption at  $22026\text{ cm}^{-1}$ , corresponded to  $^1\text{A}_2 \rightarrow ^1\text{E}$  ( $\epsilon = 174\text{ M}^{-1}\text{ cm}^{-1}$ );  $28735\text{ m}^{-1}$  to  $^1\text{E} \rightarrow ^1\text{E}$  ( $\epsilon = 664\text{ M}^{-1}\text{ cm}^{-1}$ ) and  $36231\text{ cm}^{-1}$  to  $^1\text{A}_2 \rightarrow ^1\text{E}$  ( $\epsilon = 1248\text{ M}^{-1}\text{ cm}^{-1}$ ). UV/Visible,  $^{13}\text{C}$  NMR,  $^1\text{H}$  NMR and  $^{19}\text{F}$  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.

**Trimethylammonium chlorochromate (TriMACC),  $(\text{CH}_3)_3\text{NH}[\text{CrO}_3\text{Cl}]$** 

Chromium (VI) oxide (1.0 g, 0.01 mol) was dissolved in water in a beaker and 6 M hydrochloric acid (0.251  $\text{cm}^3$ , 0.015 mol) was added under stirring at  $0^\circ\text{C}$ . To

the resultant clear orange solution, trimethylamine (0.059  $\text{cm}^3$ , 0.01 mol) was added drop wise under stirring over a period of 0.5 h and the stirring was continued for 0.5 h at  $-4^\circ\text{C}$ . The precipitate clear-orange crystalline solid was isolated by filtration, washed with petroleum ether ( $3 \times 60\text{ cm}^3$ ) and dried under vacuum for 2 h at room temperature. Yield: (59 %); mp  $124^\circ\text{C}$ . Calcd. for  $\text{C}_3\text{H}_{10}\text{ClCrNO}_3$ : C, 18.41; H, 5.115; N, 7.161. Found: C, 18.52; H, 5.13; N, 7.17. IR (KBr):  $902\text{ cm}^{-1}$   $\nu_1(\text{A}_1)$  or  $\nu(\text{CrO}_3)$ ,  $430\text{ cm}^{-1}$   $\nu_2(\text{A}_1)$  or  $\nu(\text{Cr-Cl})$ ,  $948\text{ cm}^{-1}$   $\nu_4(\text{E})$  or  $\nu(\text{CrO}_3)\text{ cm}^{-1}$ . UV/Visible and  $^1\text{H}$ -NMR were all consistent with the TriMACC structure. Electronic absorption at  $21881\text{ cm}^{-1}$ , corresponding to  $^1\text{A}_2 \rightarrow ^1\text{E}$  ( $\epsilon = 360\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ );  $28169\text{ cm}^{-1}$  to  $^1\text{E} \rightarrow ^1\text{E}$  ( $\epsilon = 906\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ) and  $3485\text{ cm}^{-1}$  to  $^1\text{A}_2 \rightarrow ^1\text{A}_1$  ( $\epsilon = 1157\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ). The pH of 0.01 M solution of TriMAFC in water was 2.7.

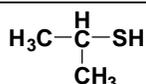
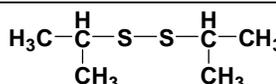
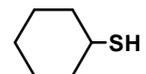
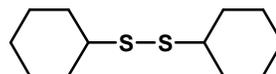
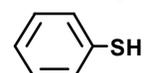
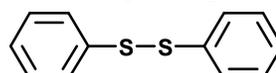
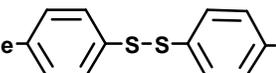
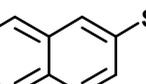
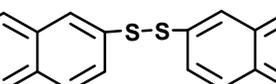
**General procedure for supporting of TriMAFC and TriMACC on alumina**

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 1-1.50 mmol of TriMAFC per 1 g of alumina 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.

**General procedure for oxidation of thiols with alumina supported TriMAFC and TriMACC**

To a stirred suspension of trimethylammonium halochromate absorbed on alumina in dichloromethane (generally 5  $\text{cm}^3$ ), a solution of the substrate in the minimum amount of dichloromethane were added drop wise (TABLE 1). The completion of the reaction was followed by TLC. The product was isolated almost in pure form by filtration chromatography of the solid reaction

TABLE 1 : Oxidations via TriMAFC and TriMACC on alumina

Substrate	Product	TriMAFC		TriMACC	
		Time (min)	Yield (%)	Time (min)	Yield (%)
1 		95	78	150	80
2 n-C <sub>5</sub> H <sub>11</sub> -SH	C <sub>5</sub> H <sub>11</sub> -S-S-C <sub>5</sub> H <sub>11</sub>	92	86	122	87
3 n-C <sub>8</sub> H <sub>17</sub> -SH	C <sub>8</sub> H <sub>17</sub> -S-S-C <sub>8</sub> H <sub>17</sub>	96	90	135	85
4 		85	35	150	67
5 HOOC-CH <sub>2</sub> -SH	HOOC-CH <sub>2</sub> -S-S-H <sub>2</sub> COOH	100	80	230	85
6 		115	87	127	83
7 		120	84	143	82
8 		137	81	154	80

mixture on a short plug of neutral silica using diethyl ether as eluent followed by evaporation of the solvent under reduced pressure. It was further purified, if required, by column chromatography over silica gel or neutral silica to yield the corresponding products as mentioned in TABLE 1. For solid thiols, ethereal solution was added followed by immediate evaporation of the solvent and then the process was followed as mentioned above.

Most of the products are known compounds as substantiated by appropriate references and they were easily identified by their spectral (IR and <sup>1</sup>HNMR) data.

## RESULTS AND DISCUSSION

Different thiols were subjected to oxidations with trimethylammonium fluorochromate (VI) (TriMAFC) and trimethylammonium chlorochromate(VI) (TriMACC) absorbed on Al<sub>2</sub>O<sub>3</sub> in dichloromethane (Figure 1). These oxidations take place under mild and completely heterogeneous conditions giving excellent yields (TABLE 1).

Oxidations may also occur using only TriMAFC and TriMACC, in the absence of Al<sub>2</sub>O<sub>3</sub>, but considerable improvements are observed in the presence of the absorbent. This implies that the Al<sub>2</sub>O<sub>3</sub> 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.<sup>[17]</sup> 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 iodo-metrically<sup>[18]</sup>. The IR spectra of TriMAFC and TriMACC are similar to that of other fluorochromate and chlorochromate.

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