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Oxidation of Organic Substrates by Trimethylammonium Halochromates(VI), $(CH_3)_3NH[CrO_3X]$, (X = F, Cl) on Silica Gel

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Silica gel absorbed trimethylammonium fluorochromate (VI), (TriMAFC), $(CH_3)_3NHCrO_3F$ and trimethylammonium chlorochromate(VI), (TriMACC), $(CH_3)_3NHCrO_3Cl$ are efficient and new reagents, which prepare easily and oxidize thiols to the corresponding disulfides quickly. The reactions perform 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.

Key Words: Trimethylammonium fluorochromate(VI), Trimethylammonium chlorochromate(VI), Heterogeneous oxidants, Silica gel, Oxidative coupling, Thiol.

INTRODUCTION

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. Disulfides are the key intermediates in a wide variety of organic synthetic routes[1-6]. Sweetening of catalyst poisons thiols to low volatile disulfides in oil industries[7,8] 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[9], dichromates[10], halosilane-chromium trioxide[11], diethyl azo dicarboxylate[12], nickel peroxide[13], chromium peroxide[14], diaryl telluroxide[15], tetrabutylammonium ceric(IV) nitrate[16], sodium perborate[17], silver

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trifluoromethane sulphonate[18] and permangenate[19] have been developed for this transformation. Silica gel supported trimethylammonium fluorochromate(VI), (TriMAFC) and trimethylammonium chlorochromate(VI), (TriMACC) were synthesized in the belief that these reagents could be used for the oxidation of organic substrates.

EXPERIMENTAL

Trimethylammonium fluorochromate (TriMAFC), $(CH_3)_3NH[CrO_3F]$: A 1 g (10 mmol) sample of chromium(VI) oxide, 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.* 0-2 °C. To the resultant orange solution, trimethylamine (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 clear precipitated 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 %); m.p. 126 °C, $C_3H_{10}FNO_3Cr$: Calcd. C, 20.11; H, 5.58; N, 7.82 Found: C, 20.08; H, 5.64; N, 7.69. IR (KBr, cm^{-1}): 912 $\nu_1(A_1)$ or $\nu(CrO_3)$, 636 $\nu_2(A_1)$ or ν(Cr-F), 950 $\nu_4(E)$ or $\nu(CrO_3)$, electronic absorption at 22321 cm^{-1}, corresponded to $^1A_2 \rightarrow {}^1E$ (ε = 174 M^{-1} cm^{-1}); 28735 m^{-1} to $^1E \rightarrow {}^1E$ (ε = 664 M^{-1} cm^{-1}) and 35971 cm^{-1} to $^1A_2 \rightarrow {}^1E$ (ε = 1248 M^{-1} cm^{-1}). UV/Visible, ^{13}C NMR, ^1H NMR and ^{19}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), $(CH_3)_3NH[CrO_3Cl]$: Chromium(VI) oxide (1.0 g. 0.01 mol) was dissolved in water in a beaker and 6 M hydrochloric acid (0.251 cm^3, 0.015 mol) was added under stirring at 0 °C. To the resultant clear orange solution, trimethylamine (0.059 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 °C. The clear precipitated orange crystalline solid was isolated by filtration, washed with petroleum ether (3 × 60 cm^3) and dried under vacuum for 2 h at room temperature. Yield: (59 %); m.p. 127 °C. Calcd. for $C_3H_{10}ClCrNO_3$: C, 18.41; H, 5.115; N, 7.161. Found: C, 18.52; H, 5.13; N, 7.17. IR (KBr, cm^{-1}): 902 $\nu_1(A_1)$ or $\nu(CrO_3)$, 430 $\nu_2(A_1)$ or ν(Cr-Cl), 948 $\nu_4(E)$ or $\nu(CrO_3)$. UV/Visible and ^1H NMR were all consistent with the TriMACC structure. Electronic absorption at 21881 cm^{-1}, corresponding to $^1A_2 \rightarrow {}^1E$ (ε = 360 dm^3 mol^{-1} cm^{-1}); 28169 cm^{-1} to $^1E \rightarrow {}^1E$ (ε = 906 dm^3 mol^{-1} cm^{-1}) and 34965 cm^{-1} to $^1A_2 \rightarrow {}^1A_1$ (ε = 1157 dm^3 mol^{-1} cm^{-1}). The pH of 0.01 M solution of TriMACC in water was 2.7.

General procedure for silica gel supporting of TriMAFC and TriMACC: For supporting of the TriMAFC and TriMACC on silica gel, in synthesizing process silica gel (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 1.0-1.5 mmol of TriMAFC per 1 g of silica gel and 1.3-1.6 mmol of TriMACC per 1 g of silica gel. 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 organic substrates with TriMAFC and TriMACC: To a stirred suspension of trimethylammonium halochromate absorbed on silica gel in dichloromethane (generally 5 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 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 silica gel to give a clear solution. The solution was evaporated and the residual product purified by distillation, recrystallization or column chromatography.

RESULTS AND DISCUSSION

$(CH_3)_3NH[CrO_3F]$ and $(CH_3)_3NH[CrO_3Cl]$ were prepared by the reaction of $(CH_3)_3N$, CrO_3 and related HX in 1:1:2 and 1:1:1.5 ratios, respectively.

Different thiols were subjected to oxidations with trimethylammonium fluorochromate(VI) (TriMAFC) and trimethylammonium chlorochromate (VI) (TriMACC) supported on SiO_2 in dichloromethane (**Scheme-I**). These oxidations take place under mild and completely heterogeneous conditions giving excellent yields (Table-1).

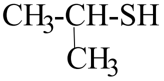
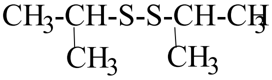
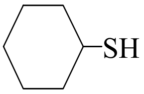
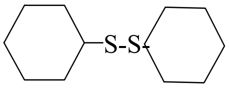
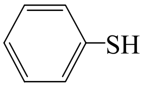
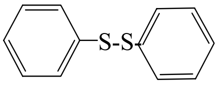
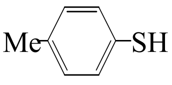
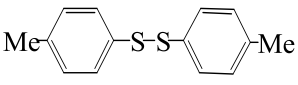
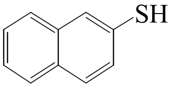
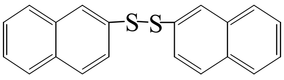
$$\mathbf{RSH \xrightarrow{TriMAHC/SiO_2} RSSR}$$

TriMAHC: $(CH_3)_3NH[CrO_3F]$ **or** $(CH_3)_3NH[CrO_3Cl]$

Scheme-I

Oxidations may also occur using only TriMAFC and TriMACC, in the absence of SiO_2, but considerable improvements are observed in the presence of the absorbent. This implies that the SiO_2 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.

TABLE-1
OXIDATIVE COUPLING OF THIOLS *VIA* TriMAFC AND TriMACC ON SILICA GEL

Substrate	Product	TriMAFC		TriMACC	
		Time (min)	Yield (%)	Time (min)	Yield (%)
 $CH_3\text{-}CH(CH_3)\text{-}SH$	 $CH_3\text{-}CH(CH_3)\text{-}S\text{-}S\text{-}CH(CH_3)\text{-}CH_3$	54	78	140	80
n-C_5H_{11}-SH	C_5H_{11}-S-S-C_5H_{11}	51	86	110	87
n-C_8H_{17}-SH	C_8H_{17}-S-S-C_8H_{17}	54	90	90	85
		48	35	135	67
HOOC-CH_2-SH	HOOC-CH_2-S-S-H_2COOH	52	80	190	85
		57	87	45	83
		62	84	35	82
		67	81	50	80

In conclusion, the silica gel supported TriMAFC and TriMACC act as simple, efficient and fast oxidizing reagents for coupling thiols. The easy procedure, simple work-up, the easy preparation of the reagents, short reaction times and excellent yields of the products will make these reagents useful additions to available oxidant. It should also be emphasized that the reactions could be performed cleanly and controlled to stop at the disulfide stage. Over-oxidation has not been observed, even when the reactions were carried out in different conditions.

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