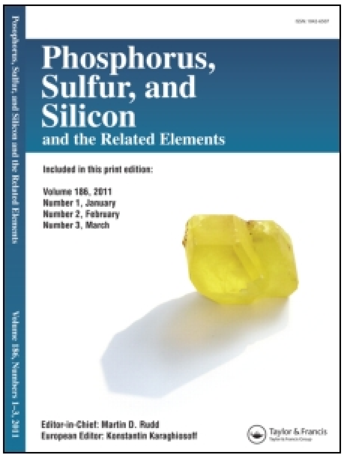

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Oxidative Coupling of Thiols to Disulfides in Solution with Tripropylammonium Halochromates, $(C_3H_7)_3NH[CrO_3X]$, (X = F, Cl) Adsorbed on Alumina

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Oxidative Coupling of Thiols to Disulfides in Solution with Tripropylammonium Halochromates, $(C_3H_7)_3NH[CrO_3X]$, (X=F, Cl) Adsorbed on Alumina

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A mild and efficient method for the oxidative coupling of thiols by tripropylammonium fluorochromate and tripropylammonium chlorochromate absorbed on alumina in solution is reported. Alumina absorbed tripropylammonium fluorochromate and tripropylammonium chlorochromate are efficient and new reagents, which are easily prepared and oxidize thiols to the corresponding disulfides quickly. The reactions are clean and readily controlled to stop at the disulfide stage without the formation of common over-oxidized side products. Thus the advantages of the easy procedure and work up, short reaction times, and excellent yields make this a viable alternative method.

Keywords Alumina; heterogeneous oxidants; thiols; tripropylammonium chlorochromate(VI); tripropylammonium fluorochromate(VI)

INTRODUCTION

The oxidation of organic substrates in aprotic solvents, under mild and neutral conditions, is important in modern organic synthesis. Therefore, the search for new oxidizing agents is of interest to synthetic

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organic chemists. Many such reagents have been developed in recent years with some success.[1]Disulfides are one of the most important organic sulfur compounds, possessing an exclusive chemistry both in biochemistry[2]and in synthetic areas.[3] Disulfides are also key intermediates in a wide variety of organic synthetic routes.[4–6] 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 are two of the most common application fields of disulfides. These applications 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. Many stoichiometric reagents such as manganese dioxide,[9] dichromates,[10] halosilane-chromium trioxide,[11] diethyl azodicarboxylate,[12] nickel peroxide,[13] chromium peroxide,[14] diaryl telluroxide,[15] tetrabutylammonium ceric(IV) nitrate,[16] sodium perborate,[17] silver trifluoromethane sulphonate,[18] and permangenate[19] have been developed for this transformation. In this respect, we wish to report that alumina-absorbed tripropylammonium fluorochromate and tripropylammonium chlorochromate are able to oxidize thiols to their disulfides efficiently under different reaction conditions.

RESULTS AND DISCUSSION

The existing 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 of 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. The results obtained with tripropylammonium fluorochromate(VI) (TriPAFC) and tripropylammonium chlorochromate(VI) (TriPACC) absorbed on alumina are very satisfactory and show the new reagents as valuable additions to the existing oxidizing agents. Different thiols were subjected to oxidations with TriPAFC and TriPACC absorbed on Al_2O_3in dichloromethane (Scheme 1). These oxidations take place under mild and completely heterogeneous conditions giving excellent yields (Table I).

Oxidations may also occur using only TriPAFC and TriPACC, in the absence of Al_2O_3, but considerable improvements are observed in the presence of the absorbent. This implies that the Al_2O_3 may act as a

$$\mathbf{RSH} \xrightarrow{\mathbf{TriPAHC/Al_2O_3}} \mathbf{RSSR}$$

TriPAHC: $(C_3H_7)_3NH[CrO_3F]$ or $(C_3H_7)_3NH[CrO_3Cl]$

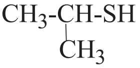
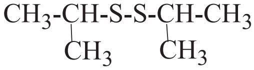
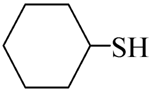
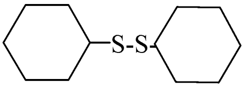
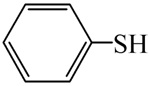
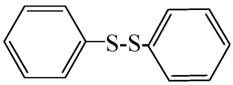
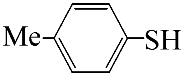
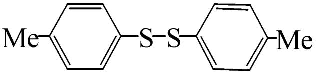
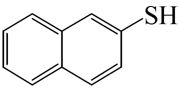
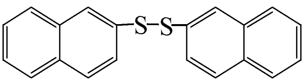
SCHEME 1

reaction medium, providing an effective heterogeneous surface area for the oxidation and at the same time making the work-up much more convenient.[20]

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 are easily determined iodometrically.

The IR spectra of TriPAFC and TriPACC are similar to that of other fluoro- and chlorochromates.[21] TriPAFC and TriPACC are soluble in water, dimethylformamide, acetonitrile, acetone, and dichloromethane; they are only sparingly soluble in benzene, carbon tetrachloride, chloroform, and hexane.

TABLE I Oxidative Coupling of Thiols via TriPACC and TriPACC on Alumina

			TriPAFC		TriPACC	
	Substrate	Product	Time (min)	Yield (%)	Time (min)	Yield (%)
1	 $CH_3\text{-}CH(CH_3)\text{-}SH$	 $CH_3\text{-}CH(CH_3)\text{-}S\text{-}S\text{-}CH(CH_3)\text{-}CH_3$	100	78	135	85
2	n-$C_{15}H_{11}$-SH	C_5H_{11}-S-S-C_5H_{11}	92	86	100	84
3	n-C_8H_{17}-SH	C_8H_{17}-S-S-C_8H_{17}	95	90	105	90
4			106	78	123	67
5	HOOC-CH_2_SH	HOOC-CH_2-S-S-CH_2-COOH	100	80	140	89
6			116	87	130	90
7			120	84	145	85
8			132	81	153	87

EXPERIMENTAL

CrO_3 (Merck, Pennsylvania, USA) was used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/visible measurements were made on an Uvicon model 922 spectrometer. ^1H, ^{13}C, and ^{19}F NMR (for TriPAFC) 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; ^1H and ^{13}C NMR spectra were referenced to external $SiMe_4$ and ^{19}F NMR spectra to external $CFCl_3$. Chromium was estimated iodometrically. Elemental analyses for carbon, hydrogen, and nitrogen were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran, Iran.

Synthesis of Tripropylammonium FluorochromateTriPAFC, $(C_3H_7)_3NH[CrO_3F]$

A 1g (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 5–7 min, the homogeneous solution was cooled to ca. 3–5°C. To the resultant clear orange solution, tripropylamine (1.4 mL, 10 mmol) was added dropwise with stirring over a period of 0.5 h and stirring was continued for 0.5 h 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 h at room temperature. Yield: (98%); mp 142°C, I.R. (KBr): 904 cm^{-1} $\nu_1(A_1)$ or $\nu(CrO_3)$, 647 cm^{-1} $\nu_2(A_1)$ or ν(Cr-F), 949 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$. Electronic absorption at 22321 cm^{-1}, corresponded to $^1A_2 \rightarrow {}^1E$ ($\varepsilon = 140\ M^{-1}cm^{-1}$); 28725 m^{-1} to $^1E \rightarrow {}^1E$ ($\varepsilon = 667\ M^{-1}cm^{-1}$) and 35971 cm^{-1} to $^1A_1 \rightarrow {}^1E$($\varepsilon = 1287\ M^{-1}cm^{-1}$). UV/Visible, ^{13}C NMR, ^1H NMR and ^{19}F NMR were all consistent with the TriPAFC structure.[22] The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution of TriPAFC in water was 3.3.

Synthesis of Tripropylammonium Chlorochromate, $(C_3H_7)_3NH[CrO_3Cl]$

Chromium(VI) oxide (1.0 g, 10 mmol) was dissolved in water in a beaker and hydrochloric acid (0.25 mL, 15 mmol) was added with stirring at 0°C. To the resultant clear orange solution, tripropylamine (1.4 mL, 10 mmol) was added dropwise with stirring over a period of 0.5 h and stirring was continued for 0.5 h at –4°C. The precipitated orange solid was isolated by filtration, washed with anhydrous ether (3 × 60 mL), and dried in vacuum for 2 h at room temperature. Yield: (95%); mp 135°C. $C_9H_{22}ClCrNO_3$: Calc. C, 38.64; H, 7.871; N, 5.008 Found: C, 37.93; H, 7.75; N, 4.88. I.R. (KBr): 901 cm^{-1} $\nu_1(A_1)$ or $\nu(CrO_3)$, 432 $cm^{-1}\nu_2(A_1)$ or ν(Cr-Cl), 949 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$. Electronic absorption at 22123 cm^{-1}, corresponded to $^1A_2 \rightarrow {}^1E$ ($\varepsilon = 351$ $M^{-1}cm^{-1}$); 28169 m^{-1} to $^1E \rightarrow {}^1E$ ($\varepsilon = 793$ $M^{-1}cm^{-1}$); 35087 cm^{-1} to $^1A_2 \rightarrow {}^1A_1$($\varepsilon = 1031$ $M^{-1}cm^{-1}$) and 41493 cm^{-1} to $^1A_1 \rightarrow {}^1E$($\varepsilon = 219$ $M^{-1}cm^{-1}$). UV/Visible, ^{13}C NMR and ^1H NMR were all consistent with the TriPACC structure. ^1H-NMR (500MHZ, CD_3CN): $\delta = 0.77$ (t, 3H, $-CH_3$), $\delta = 1.93$ ppm (m, 2H, $-CH_2-$), $\delta = 3.$ 24 ppm (t, 2H, $-CH_2-$), ^{13}C-NMR (125 MHZ, CD_3CN): δ 11.05, 20.12, 56.45. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution TriPACC in water was 2.9.

General Procedure for Alumina Supporting of TriPAFC and TriPACC

For supporting of the TriPAFC and TriPACC on alumina, the above synthetic methods were repeated, but before the tripropylamine addition step, alumina (mesh 65–250) was added. The supported reagents were separated and washed by cold water and acetone. The capacity of the supported reagents was 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 were 1–1.5 mmol of TriPAFC per 1 g of alumina and 1.3–1.6 mmol of TriPACC per 1 g of alumina. The supported reagents so obtained did not noticeably lose their activities either on storing in air at room temperature for several weeks or on refluxing for 5 h in benzene or hexane.

General Procedure for Oxidation of Organic Substrates with Alumina-Absorbed TriPAFC and TriPACC

To a stirred suspension of tripropylammonium halochromate absorbed on alumina in dichloromethane (generally 5 cm^3, 10 mmol), a solution of the substrate in the minimum amount of dichloromethane was added dropwise, the molar ratio of substrate to the oxidant being 1:2 (Table I). The completion of the reaction was followed by TLC using ether:petroleum ether (60:40) as eluant. The mixture was diluted with ether 10 mL (1:1 v/v) and filtered through a short column of alumina to give a clear solution. The solution was evaporated, and the residual product was purified by distillation, recrystallization, or column chromatography. Analysis of the reaction mixture for the corresponding disulfide compound was accomplished by the procedure reported in earlier articles 9–13.

CONCLUSIONS

New reagents tripropylammonium fluorochromate(VI) (TriPAFC) and tripropylammonium chlorochromate(VI) (TriPACC) absorbed on alumina are easily synthesized. They prove to be low cost, readily available oxidizing reagents for a variety of thiols. Theirs advantages include higher yields, shorter reaction times, lower thiol:oxidant molar ratios, application to pH sensitive molecules, and ease of separation of products. Moreover, during the reaction, the color of the oxidants changes from orange to brown, thus providing a visual means for ascertaining the progress of the oxidation. Many functional groups are inert towards these oxidizing agents, including thiols, sulfides, and phenols, enhancing the usefulness of the oxidants and the oxidation conditions for the synthesis of highly functionalized molecules.

REFERENCES

[1] L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis* (Wiley, New York, 1967–84), Vol. 1–11.
[2] D. C. Jocelyn, 1992. *Biochemistry of the Thiol Group* (Academic Press, New York, 1992), p. 1.
[3] G. Capozzi, G. Modena, and S. Patai, 1974 *The Chemistry of the Thiol Group,* (Wiley, New York, 1974), p. 785.
[4] J. Lam, H. Bildose, L. P. Christensen, and T. Thomsen, *Acta Chem. Scand. Ser B,* **43,** 799 (1989).
[5] V. Srivastav, R. Gupta, and R. R. Guptam, *Ind. J. Chem.,* **39B,** 223 (2000).
[6] P. Metzner, , *Synthesis,* 669 (1978)**.**
[7] D. L. Holbrook, *Handbook of Petroleum Refining Processes,* R. A. Meyers (Ed.) (McGraw Hill, 1996), Chap. 11.3.
[8] A. Leitao, C. Costa, and A. Rodrigues, *Chem. Eng. Sci.,* **42,** 2291 (1987).
[9] E. P. Papadopoulos, A. Jarrar, and C. H. Issidoides, *J. Org. Chem.,* **31,** 615 (1966).
[10] C. Lopez, A. Conzales, F. P. Cossio, and C. Palomo, *Synth. Commun.,* **15,** 1197 (1985).
[11] J. M. Aizpurua, M. Juaristu, B. Lecea, C. Palomo, *Tetrahedron,* **41,** 2903 (1985).
[12] F. Yoneda, K. Suzuki, and Y. Nitta, *J. Org. Chem.,* **32,** 727 (1967).
[13] K. Nakagawa, S. Shiba, M. Horikawa, K. Sato, H. Nakamura, N. Harada, and F. Harada, *Synth. Commun.,* **10,** 305 (1980).
[14] H. Firouzabadi, N. Iranpoor, F. Kiaeezadeh, and J. Toofan, *Tetrahedron,* **42,** 719 (1986).
[15] S. V. Ley, A. Meerholz, and D. H. R. Barton, *Tetrahedron,* 231 (1982).

[16] H. A. Muathen, *Ind. J. Chem.,* **30B,** 522 (1991).

[17] A. Mckillop, D. Koyuncu, A. Krief, W. Dumont, P. Renier, and M. Trabelsc,. *Tetrahedron Lett.,* **31,** 5007 (1990).

[18] H. Tamamura, A. Otaka, J. Nakamura, K. Okubo, T. Koide, K. Ikeda, and N. Fujii, *Tetrahedron Lett.,* **34,** 4931 (1993).

[19] N. A. Noureldin, M. Coldwell, J. Hendry, D. G. Lee,. *Synthesis,* 1587 (1998).

[20] G. Maier, H. P. Reisenauer, and M. D. Marco, *Angew. Chem. Int. Ed.*, **38,** 108 (1999).

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

[22] S. Ghammamy and A. Hashemzadeh, *Bulletin of Korean Chem. Soc.,* **25,** 1277 (2004).