J. Iranian Chem. Res.
5 (3) (**2012**) 173-176
ISSN 2008-1030

Oxidative coupling of thiols to disulfides in solution radiation with Trimethylammonium Fluorochromate(VI), $[(CH_3)_3NH[CrO_3F]$, on Silica Gel

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Received 31 January 2012
Received in revised form 08 May 2012
Accepted 13 May 2012

A mild and efficient method for the oxidative coupling of thiols by trimethylammonium fluorochromate (TriMFC) in solution is reported. Trimethylammonium fluorochromate is efficient and new reagent, which prepares easily and oxidizes thiols to the corresponding disulfides quickly. The reactions perform cleanly and controlled to stop at the disulfide stage without over-oxidation side products.

Keywords: Trimethylammonium fluorochromate(VI); Heterogeneous oxidants; Silica gel; Oxidation

1. 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. [1] Disulfides are one of the most important organic sulfur compounds possessing an exclusive chemistry both in biochemistry [2] and in synthetic area. [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 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 azodicarboxylate, [12] nickel peroxide, [13] chromium peroxide, [14] diaryl telluroxide, [15] tetrabutylammonium ceric (IV) nitrate, [16] sodium perborate, [17] silver trifluoromethane sulphonate [18] and permanganate [19] 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, we wish to report that trimethylammonium fluorochromate (TRiMFC) able to oxidize thiols to their disulfides efficiently under different reaction conditions.

2. EXPERIMENTAL

2.1. Trimethylammonium Fluorochromate (TriMAFC), $(CH_3)_3NH[CrO_3]$

A 1g (10 mmol) sample of chromium (VI) oxide, CrO_3, and 0.9ml (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 °C. To the resultant orange solution, trimethylamine (10 mmol) 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 °C. The precipitated clear-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%); mp 126 °C, $C_3H_{10}CrFNO_3$: Calc. C, 20.11; H, 5.58; N, 7.82 Found: C, 20.08; H, 5.64; N, 7.69. I.R. (KBr): 912 cm^{-1} $\nu_1(A_1)$ or $\nu(CrO_3)$, 636 cm^{-1} $\nu_2(A_1)$ or ν(Cr-F), 950 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$, Electronic absorption at 22026 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 36231 cm^{-1} to ${}^1A_2 \rightarrow {}^1E$($\varepsilon$ = 1248 $M^{-1}cm^{-1}$). UV/Visible, 13C NMR, 1H NMR and 19F 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.

2.2. General procedure for oxidation of organic substrates with TRiMAFC

To a stirred suspension of trimethylammonium fluorochromate 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. The reaction were done under microwave irradiations.

3. RESULTS AND DISCUSSION

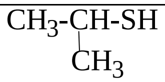
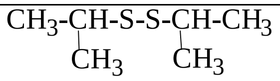
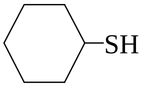
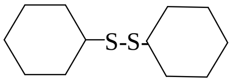
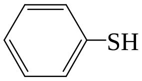
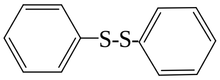
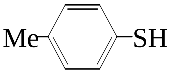
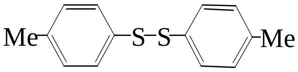
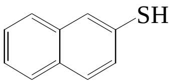
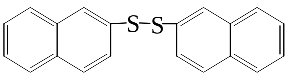
$(CH_3)_3NH[CrO_3F]$ was prepared by the reaction of $(CH_3)_3NHF$ and CrO_3 in 1:2:1 ratio in the water solvent. Different thiols were subjected to oxid:ations with trimethylammonium fluorochromate(VI) (TRiMAFC) absorbed on SiO_2 in dichloromethane. This oxidation take place under mild and completely heterogeneous conditions giving excellent yields Table 1.

Oxidation may also occur using only TRiMAFC, in the absence of SiO_2, but considerable improvement is 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 especially under irradiation.

4. CONCLUSION

Trimethylammonium fluorochromate is efficient and new reagent, which prepares easily and oxidizes thiols to the corresponding disulfides quickly. The reactions perform cleanly and controlled to stop at the disulfide stage without over-oxidation side products.

Table 1. Oxidations via TriMAFC on Silica gel**.**

	Substrate	Product	TriMAFC	
			Time (min)	Yield (%)
1	 $CH_3\text{-}\underset{CH_3}{CH}\text{-}SH$	 $CH_3\text{-}\underset{CH_3}{CH}\text{-}S\text{-}S\text{-}\underset{CH_3}{CH}\text{-}CH_3$	94	78
2	n-C_5H_{11}-SH	C_5H_{11}-S-S-C_5H_{11}	90	86
3	n-C_8H_{17}-SH	C_8H_{17}-S-S-C_8H_{17}	96	90
4			84	35
5	HOOC-CH_2-SH	HOOC-CH_2-S-S-H_2CCOOH	98	80
6			116	87
7			116	84
8			136	81

Oxidations may also occur using only TRiMAFC, in the absence of SiO_2, but considerable improvement is observed in the presence of the absorbent and irrediation. 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.

ACKNOWLEDGMENT

The author thanks Dr. A. R. Mahjoub and Mr. M. K. Mohammady and Ms. S. Khorsandtabar and Mr. S. Bagi for valuable discussion.

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