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# An Environmentally Friendly Oxidation of Thiols to Disulfides by Calcium Hypochlorite and Montmorillonite K10 in Hexane

Masao Hirano <sup>a</sup> , Shigetaka Yakabe <sup>a</sup> , Masataka Fukami <sup>a</sup> & Takashi Morimoto <sup>a</sup>

<sup>a</sup> Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo, 184, Japan Published online: 22 Aug 2006.

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### AN ENVIRONMENTALLY FRIENDLY OXIDATION OF THIOLS TO DISULFIDES BY CALCIUM HYPOCHLORITE AND MONTMORILLONITE K10 IN HEXANE

Masao Hirano,\* Shigetaka Yakabe, Masataka Fukami, and Takashi Morimoto\*

Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

**ABSTRACT**— Aromatic, aliphatic, and alicyclic thiols can be readily oxidized to the disulfides quantitatively by calcium hypochlorite and *moist* Montmorillonite K10 under mild and neutral conditions.

Oxohalogen acids and their organic and inorganic derivatives have been employed as versatile reagents in organic syntheses because of their mild oxidative and halogenating properties.<sup>1</sup> Among this class of reagents, calcium hypochlorite,  $Ca(OCl)_2$ ,<sup>2</sup> has attracted only a little attention, irrespective of its potency as a synthetic reagent in terms of stability, ease of handling, commercially ready availability, and inexpensiveness. In the course of research on the reactions in nonaqueous media, we have recently disclosed that clay minerals catalyze

<sup>\*</sup>To whom correspondence should be addressed

oxidations of various functional groups.<sup>3</sup> We have also observed that sodium bromite<sup>4</sup> and chlorite<sup>5</sup> serve as efficient oxidizing agents in aprotic solvents with the aid of solid support materials. These facts together<sup>3-5</sup> may offer the prospect of the combined use of an oxohalogen acid derivative and a clay for organic synthesis.

A plethora of methods have been available for the oxidative coupling of thiol to the disulfide and the reactions are generally believed to be readily attainable. However, literature scrutiny reveals that conventional methods frequently encounter difficulties in reaction performance and/or in production of disulfides in a simple, rapid, selective, and high-yielding manner, which, from a practical point of view, make them less than attractive.<sup>6</sup> We therefore feel that there is still a need for introduction of a new and convenient method and/or further work on technical improvements to overcome the limitations. Work is here undertaken to demonstrate the usefulness of an inexpensive and environmentally friendly reagent system, calcium hypochlorite **1** and Montmorillonite K10 in hexane, for the oxidation of thiols.

Present reactions can be readily carried out only by efficiently stirring a mixture comprising of 1, Montmorillonite K10 preloaded with a small amount of water (*moist* Mont.; *vide infra*), and thiol 2 in hexane at 20 °C under inert atmosphere (Scheme). In addition, the heterogeneous system allows a simple work-up to be performed merely by filtering off the insolubles and removing the solvent from the filtrate.

Schem

Entry	Thiol (2)	Ca(OCl) <sub>2</sub>	Time	Disulfide (3)
No.	R	(mmol)	(min)	(%)b
1	Ph	0.3	15	99
2	4-MeOC <sub>6</sub> H <sub>4</sub>	0.3	15	96
3	4-MeC <sub>6</sub> H <sub>4</sub>	0.3	5	98
4	$4-BrC_6H_4$	0.35	30	98
5	4-CIC <sub>6</sub> H <sub>4</sub>	0.3	15	98
6	4-O2NC6H4	0.4	30	97
7	PhCH <sub>2</sub>	0.35	30	96
8	1-C <sub>6</sub> H <sub>13</sub>	0.4	15	94
9	$1-C_8H_{17}$	0.4	15	98
10	$1 - C_{10}H_{21}$	0.4	15	94
11	1-C <sub>14</sub> H <sub>29</sub>	0.4	15	94
12	$\diamond$	0.35	15	93
13	$\bigcirc$ -	0.35	15	98

Table 1. Oxidative coupling of thiols (2) to the disulfides  $(3)^a$ 

a) At 20 °C, under argon; thiol 1.0 mmol, hexane 10 ml, *moist* Mont. 1.0

g. b) Isolated yield based on starting 2.

Table 1 collects the results derived from the oxidations of typical aryl (Entries 1-7), aliphatic (Entries 8-11), and alicyclic thiols (Entries 12 and 13), together with optimized reaction conditions (concentration of 1 and reaction time) which were determined on the basis of the reactivity of 2 and selectivity and yield of the disulfide 3. Thus disulfides can be readily synthesized from various thiols in substantially quantitative yields. In the absence of the clay, the reaction was sluggish, and 1 and/or its degradation product(s) adhered to the walls of the reaction vessel, making the work-up considerably tedious. In addition, GC analyses of the crude mixtures obtained from repetitive runs under otherwise similar conditions showed that the reactions not only give 3 in erratic yields, but suffer from very poor material balances (combined recovery of unreacted 2 and 3).

Consequently, *moist* Mont. is responsible for high performance of 1 as well as reproducibility of the oxidation. In the case of the related biphasic system, Montmorillonite K10 supported ferric nitrate (Clayfen),<sup>7</sup> thiol bearing an electron-withdrawing functionality, *e.g.* NO<sub>2</sub>-group, afforded the disulfide only in mediocre yield. Consequently, the current system may compare favorably to *Clayfen*, since 4-nitrobenzenethiol yielded the disulfide quantitatively (Entry 6).

Summing up, the Ca(OCl)<sub>2</sub>/moist Mont. system provides a fast and practical procedure for the high-yielding synthesis of disulfides, applicable to a wide range of thiols.

#### EXPERIMENTAL SECTION

<sup>1</sup>H NMR spectra were recorded with a JEOL PMX-60 (60 MHz) spectrometer for solutions in deuteriochloroform using TMS as an internal standard. Analytical gas chromatography was performed on a Shimadzu GC- 4CM instrument with a 2 m x 5mmØ glass column packed with 3% Silicone OV-17 on Uniport HP, with temperature programming. Melting points were determined on a Yanagimoto MP-S3 melting point apparatus. Mass spectra were measured on a JEOL SX-102A spectrometer which is coupled *via* a heated capillary column to a Hewlett Pacard 5890 Series II GC apparatus. All thiols were commercial chemicals and were purified prior to use. Calcium hypochlorite was purchased from Kokusan Chemical Works, Ltd. [Japan] and its purity (available chlorine) was determined by iodometry ( $\alpha$ . 65%); the reagent has a good shelf life without any special care. Addition of deionized water (0.1 g) to carcinated (350 °C, 5 h) Montmorillonite K10 (Aldrich: 1 g) in portions followed by vigorous shaking of the mixture for a few minutes upon every addition afforded a free-flowing powder, *moist* Mont., 1 g of which was immediately used for the oxidation.

*Oxidation Procedure.* — Oxidation of benzenethiol (Entry 1) is representative. A 30 ml round-bottom flask was charged with benzenethiol (1 mmol), hexane (10 ml), calcium hypochlorite powder (0.3 mmol), and freshly prepared *moist* Mont. (1 g) in that order. After flushing with argon, the resultant cloudy mixture was vigorously stirred at 20 °C for 15 minutes. The reaction mixture was filtered through a sintered glass funnel and the filter cake was washed thoroughly with portions of dichloromethane (total 50 ml). Rotary evaporation of the combined clear filtrate followed by chromatography on a silica gel column (Merck, Silica Gel 60; hexane/ethyl acetate) afforded pure (<sup>1</sup>H NMR, GC, and TLC) diphenyl disulfide quantitatively, mp 60 - 61 °C (reported mp<sup>8</sup> 61 - 62 °C).

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