SHORT PAPER

J. Chem. Research (S), 2003, 28-29

Solvent free oxidation of thiols by $(NH_4)_2Cr_2O_7$ in the presence of $Mg(HSO_4)_2$ and wet SiO_2†

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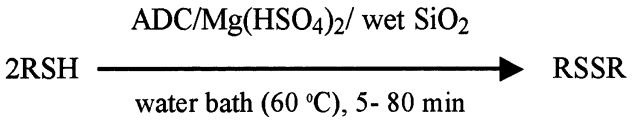
A very simple and mild reaction for the efficient coupling of thiols by ammonium dichromate (ADC) in the presence of $Mg(HSO_4)_2$ and wet SiO_2 ,under solvent free conditions, is reported.

Keywords: oxidation of thiols, ammonium dichromate, disulfides

Oxidation of thiols to disulfides is well documented and wide range of reagents have been used for this conversion.[1-9] As is usually the case for every reagents used to date, some of the reported reagents suffer from disadvantages such as: long reaction time, availability, difficult work-up, preparation and instability. Conseqently, there is a need for protocols using readily available, safe and cheap reagents, leading to general and selective oxidation of thiols in good yields.

We have already described the use of ammonium dichromate[10] (ADC) in the presence of $Mg(HSO_4)_2$ and wet SiO_2[11] for the oxidation of alcohols. Now we report that ADC in the presence of $Mg(HSO_4)_2$ and wet SiO_2 can act as a very efficient reagent for the oxidative coupling of thiols under solvent free conditions (Scheme 1, Table 1).



Scheme 1

In order to compare the obtained results with those obtained in solution we tried to study the coupling reactions in *n*-hexane. As shown in Table 1, there are appreciable difference between the results obtained in solution and neat conditions. By the ommision of the solvent the reaction time and products yields are changed significantly and the work-up procedure becomes easier.

Table 2 Comparison of some of the results obtained by our method (1) with some of those obtained by sodium perborate (2)[5] and pyridinium chlorochromate (3)[6]

Entry	Substrate	Yield/% min. (1)	(2)	(3)
1	PhSH	(90)(15)	(92)(120)	(94)(114)
2	$PhCH_2SH$	(90)(80)	(93)(120)	(91)(108)
3	p-ClC_6H_4SH	(92)(15)	(99)(120)	(91)(108)

It should be noted that the oxidation reaction did not proceed in the absence of $Mg(HSO_4)_2$. This result could be attributed to the *in situ* generation of H_2CrO_4 in low concentration at the surface of wet SiO_2 by $Mg(HSO_4)_2$ and ammonium dichromate.

In order to evaluate the efficiency of this method we compared some of the results obtained by our method with with some of those reported by the relevant reagents in the literature (Table 2).[5,6]

In conclusion, the cheapness and availability of the compounds, mildness of the reaction condition, reasonable yields of the products and easy work-up of this method are worthy of mention.

Experimental

General procedure for the oxidation of thiols under solvent free condition: A mixture of the substrate (1 mmol), $Mg(HSO_4)_2$ (0.654g, 3 mmol),wet SiO_2 (50% *ww*, 0.1g) and $(NH_4)_2Cr_2O_7$ (0.126g, 0.5 mmol), was heated in a water bath (60°C) for the specified time (Table 1). The progress of the reaction was monitored by TLC. The reaction mixture was triturated with CH_2Cl_2 (10 ml) and then filtered. Anhydrous $MgSO_4$ was added to the filtrate and filtered after 10 min. Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding disulfide from good to high yield.

General procedure for oxidation of thiols in n-hexane: A suspension of the substrate (1 mmol) $Mg(HSO_4)_2$ (0.654g, 3 mmol), wet SiO_2 (50% ww, 0.1g) and $(NH_4)_2Cr_2O_7$ (0.126g, 0.5 mmol) in *n*-hexane (5 ml) was stirred at room temperature for the specified time (Table 1). The progress of the reaction was monitored by TLC and the mixture filtered upon completion. The residue was washed with CH_2Cl_2 (10ml). Then anhydrous $MgSO_4$ was added to the filtrate and filtered after 10 min. Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding disulfide.

We are thankful to Guilan University Council for the partial support of this work.

Received 23 February 2002; accepted 15 July 2002
Paper 02/1264

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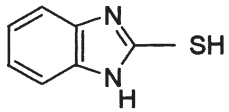
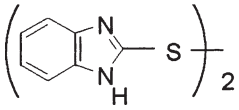
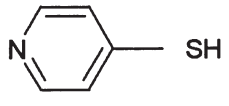
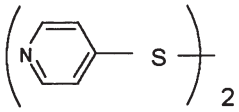
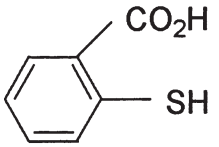
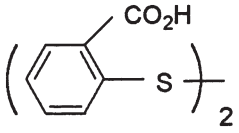
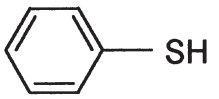
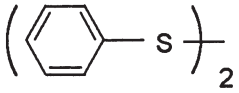
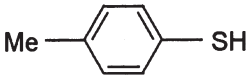
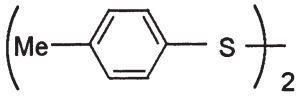
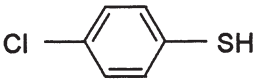
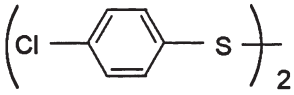
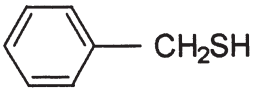
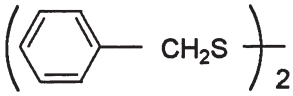
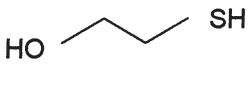
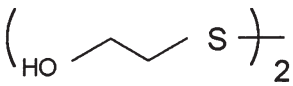
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1: Oxidation of thiols to disulfides

Entry	Substrate	Product	Solvent free oxidation		Oxidation in solvent	
			Time /min	Yield[a] /%	Time /min	Yield[a] /%
1			10	90	10	80
2			20	90	15	80
3			5	80	30	82
4			15	90	120	----[c]
5			10	82	120	----[c]
6			15	92	120	----[c]
7			80	90	120	----[c]
8		—	40[b]	----	180	----[c]
9			30	80	35	80

[a]:Isolated yield; [b]:polymerisation has occurred; [c]:reaction was not completed.

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