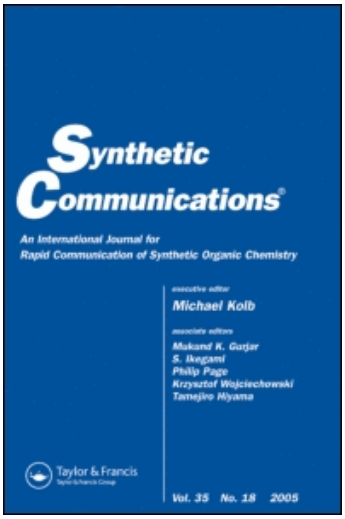

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OXIDATIVE COUPLING OF THIOLS BY PYRIDINIUM CHLOROCHROMATE IN SOLUTION AND SOLVENT FREE CONDITIONS

Peyman Salehi [ab]; Afsaneh Farrokhi [b];Mostafa Gholizadeh [c]
[a] Department of Phytochemistry, Medicinal Plants Research Institute, Shahid Beheshti University, Tehran, Iran [b] Department of Chemistry, Razi University, Kermanshah, Iran [c] Department of Chemistry, Teacher Training University, Sabzevar, Iran

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OXIDATIVE COUPLING OF THIOLS BY PYRIDINIUM CHLOROCHROMATE IN SOLUTION AND SOLVENT FREE CONDITIONS

Peyman Salehi,[1,*] Afsaneh Farrokhi,[1] and Mostafa Gholizadeh[2]

[1]Department of Chemistry, Razi University, Kermanshah, Iran
[2]Department of Chemistry, Teacher Training University, Sabzevar, Iran

ABSTRACT

Oxidative coupling of aromatic and aliphatic thiols is achieved efficiently by pyridinium chlorochromate in solution and solvent free conditions. Omitting the solvent does not change the reaction time and product yield significantly, while the need of using the solvent is suppressed and workup procedure becomes easier.

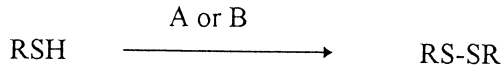
Many years have passed from the introduction of pyridinium chlorochromate (PCC) as a reagent for oxidation of primary and secondary alcohols.[1] Due to its mildness and high selectivity, this oxidant has found wide applications in organic synthesis.[2–4]

*Corresponding author. Department of Phytochemistry, Medicinal Plants Research Institute, Shahid Beheshti University, Tehran, Iran.

Oxidative coupling of thiols to disulfides under mild conditions is of importance from biological and practical points of view.[5,6] Thiols are among functional groups which can over oxidized and therefore extensive studies have been carried out for their controlled oxidation.[7–19]

In this paper we wish to report an efficient method for the conversion of thiols to disulfides by the well known reagent, pyridinium chlorochromate in solution and solvent free conditions.

Oxidative coupling of different types of mercaptans was investigated in the absence of solvent by pyridinium chlorochromate (Scheme, Table). In an easy procedure the reactants mixed together in a mortar and stood together for the appropriate period (Table) without any further agitation. Both aromatic and aliphatic thiols reacted efficiently and the corresponding disulfides isolated in good to excellent yields.



A: PCC, Solvent Free, r.t.
B: PCC, Dichloromethane, r.t.

Scheme.

In order to compare the obtained results with those performing in solution we tried to study the coupling reactions in dichloromethane. As shown in Table there are not appreciable differences between the results obtained in solution and neat conditions.

In conclusion omitting the solvent in oxidative coupling of thiols by PCC does not change the reaction time and product yield significantly while the need of using the solvent is suppressed and workup procedure becomes easier. The method could be used for the synthesis of disulfides from corresponding thiols in a preparative scale.

EXPERIMENTAL

All of the products are known compounds and were characterized by comparison of their spectral data (^{1}H NMR, IR) and physical properties with those of authentic samples. The purity determination of substrates and reaction monitoring were accomplished by TLC using silica gel polygram SIL G/UV 254 plates. All yields refer to isolated products.

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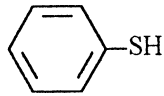
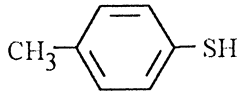
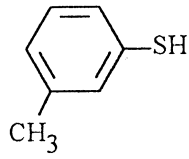
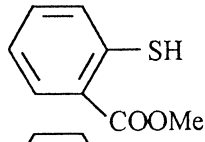
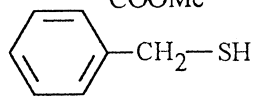
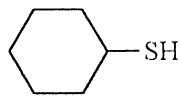
Table. Oxidative Coupling of Thiols by Pyridinium Chlorochromate in Dichloromethane or Solvent Free Conditions

		Solvent Free Oxidation		Oxidation in CH_2Cl_2	
Entry	R-SH	Time (h)	Yield (%)	Time (h)	Yield (%)
1		1.9	94	1.5	97
2		1.9	91	1.6	89
3		1.2	92	1.4	90
4		2.1	93	2	90
5		1	93	0.9	97
6		1.8	91	1.9	95
7		3	86	1.9	94
8	$CH_3(CH_2)_3SH$	4.2	88	4.4	89
9	$CH_3(CH_2)_7SH$	4	87	4.2	91
10	$HOCH_2CH_2SH$	1.3	55	1.7	62
11	$HOOCCH_2SH$	1.7	47	2.2	50

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General Procedure for Oxidative Coupling of Thiols by Pyridinium Chlorochromate Under Solvent Free Conditions

Pyridinium chlorochromate (1 mmol) was added to thiol (1 mmol) in a mortar. Starting materials were mixed and stood together for the appropriate period (Table) at room temperature. Progress of the reaction was followed by dissolving a sample in acetone and using thin layer chromatography on silica gel (MeOH/HOAc: 5/1). After completion of the reaction hydrochloric acid (20%) was added and the mixture extracted with ether (2×20 mL) and chloroform (2×20 mL). The organic layer was separated and dried ($MgSO_4$). Final evaporation of solvent gave the products in 47–94% yields. [Isolation of water soluble disulfides (Table, entries 10, 11) was achieved by washing the sticky mixture with ether and chloroform followed by chromatography on glass plates (Silica gel, CCl_4/Ether/MeOH: 3/3/1)].

General Procedure for the Conversion of Mercaptans to Disulfides by Pyridinium Chlorochromate in Dichloromethane

Pyridinium chlorochromate (1 mmol) was added to a solution of mercaptan (1 mmol) in dichloromethane (10 mL). The mixture was stirred magnetically at room temperature until the complete consumption of the substrate. Solvent was evaporated on a rotary evaporator. Water was added (40 mL) and the mixture was extracted with ether (2×20 mL) and chloroform (2×20 mL). The organic layer was dried ($MgSO_4$) and concentrated. The corresponding disulfides were obtained in 50 to 97% yields. [Water soluble products (Table, entries 10, 11) were isolated by evaporation of the solvent followed by thin layer chromatography on glass plates (Silica gel, CCl_4/Ether/MeOH: 3/3/1)].

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