

NOTE

Pyridinium Chlorochromate Supported on to Copper(II) Sulfate as a Rapid and Efficient Oxidizing Agent for Oxidation of Alcohols under Microwave Irradiation

KHODABAKHSH NIKNAM

*Department of Chemistry, Faculty of Science, Persian Gulf University, Bushehr-75168, Iran**Fax: (98)(771)4545188; Tel: (98)(771)4541494**E-mail: kh_niknam@yahoo.com; niknam@pgu.ac.ir*

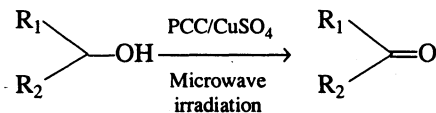
A rapid and convenient method is described for oxidizing alcohols into carbonyl compounds using pyridinium chlorochromate supported on to copper sulfate under microwave irradiation.

Key Words: Pyridinium chlorochromate, Oxidation, Copper sulfate, Alcohol, Microwave irradiation.

Pyridinium chlorochromate (PCC) (Corey's reagent¹) is well known as a versatile and very good oxidant for the conversion of primary alcohols into the corresponding aldehydes. Pyridinium chlorochromate has shown a slightly acidic character and usually it does not react with simple olefinic C—C double bonds². So, many modifications were done; for example, the chlorochromate anion has been supported on a polymeric matrix²⁻⁴. Also, Cheng and coworkers⁵ reported that pyridinium chlorochromate adsorbed on alumina is a suitable reagent for the oxidation of alcohols to aldehydes and ketones. The reagent is mild, selective and remarkably effective, the yields being equal to or greater than those obtained with pyridinium chlorochromate. The reactions are very clean and the isolation of the products is simple. Thus, this methodology allows the elimination of the problems and the side reactions, sometimes observed, due to the acidic character of pyridinium chlorochromate.

Microwave-assisted heating treatment of liquid and solid samples has become a very helpful method for organic and inorganic synthesis as well as for extraction of organic compounds or trace metals from soils, sediments, oils and biological samples^{6,7}. The early experiments were carried out using domestic microwave ovens and rudimentary vessels. Microwave heating offers many advantages over conventional forms of heating. Due to the mass heating effect, much faster temperature increase can be obtained. High temperatures required for reactions are achieved rapidly. The applications of microwave energy in organic chemistry are increasing rapidly⁸⁻¹¹.

Keeping the above facts in mind, a convenient method for oxidation of alcoholic groups into the corresponding carbonyl compounds with PCC supported on to CuSO_4 as an oxidant under microwave irradiation has been reported (Scheme-1).



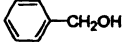

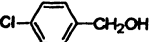

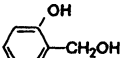

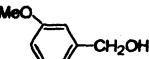

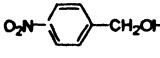

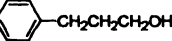
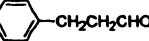
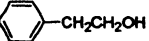
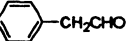
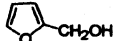

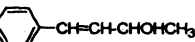

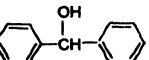
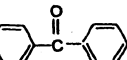
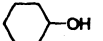

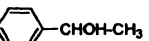
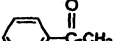
Scheme-1

Pyridinium chlorochromate was prepared according to the literature¹. Alcohols and CuSO_4 were purchased from Fluka and Merck, respectively. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates.

General procedure for the oxidation of alcohols using PCC/ CuSO_4

CuSO_4 (2 g) and pyridinium chlorochromate (PCC) (0.43 g, 2 mmol) were crushed together in a mortar so as to form an intimate mixture, then poured into a flask. Neat alcohol (1 mmol) and some drops of *t*-BuOH were added and irradiated in a domestic microwave oven at 90% power for the time specified (Table-1).

TABLE-1
CONVERSION OF ALCOHOLS TO CARBONYL COMPOUNDS USING
PCC SUPPORTED ON TO CuSO_4 ^a

Entry	Substrate	Product	Time (sec)	Yield ^{b,c} (%)
1			25	94
2			25	92
3			20	86
4			25	89
5			30	75
6			25	86
7			25	87
8			15	85
9	$\text{HC}\equiv\text{CCH}_2\text{OH}$	$\text{HC}\equiv\text{CCHO}$	10	85
10			20	88
11			25	87
12			20	89
13			25	87
14	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_4\text{CHO}$	10	87
15	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$	10	88

^aMolar ratio of reagent to substrate was 2:1. ^bYields refer to isolated products.

^cProducts were characterized by comparison of their physical data, IR, NMR spectra with known samples.

The progress of reaction was monitored by TLC using ether- CCl_4 . Then, the reaction mixture was poured into a mixture of ether (20 mL) and water (10 mL). The organic layer was passed through a small bed of alumina and evaporated to dryness using a rotary evaporator to give the pure corresponding carbonyl compound (Table-1).

As shown in Table-I, primary and secondary saturated aliphatic, benzylic, and heterocyclic alcohols were oxidized to the corresponding carbonyl compounds in very good to excellent isolated yields with very short times (10–30 s). 4-Phenyl-but-3-en-2-ol and propargyl alcohol as well as α,β -unsaturated alcohols were easily converted to the corresponding carbonyl compounds in 88 and 89% isolated yields respectively. Furfuryl alcohol was converted to furfural in 85% yield.

The rapid and selective formation of oxidation products demonstrates the efficiency of this new method. The structures of all the products were established from their analytical and spectral (IR, ^1H NMR) data and by comparison with authentic samples.

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