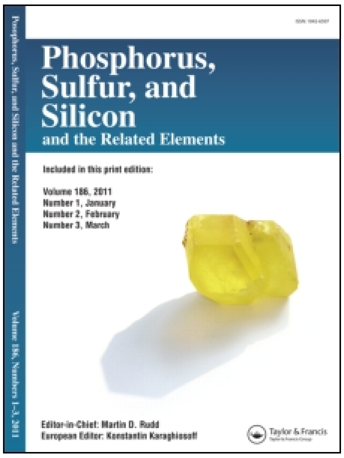

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Chemoselective Oxidation of Benzylic Alcohols and Hydroquinones with bis-(2,4,6-Trimethylpyridinium) Dichromate (BTMPDC) as an Efficient and New Oxidizing Agent

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Ilam, Iran

A simple, efficient, and chemoselective oxidation of benzylic alcohols to the corresponding aldehydes and ketones and also hydroquinones to the benzoquinones using bis-(2,4,6-trimethylpyridinium) dichromate (BTMPDC) in acetonitrile is described. A good range of primary and secondary benzylic alcohols and a limited range of hydroquinones were selectively oxidized under reflux conditions in reasonable yields.

Keywords Alcohols; bis-(2,4,6-trimethylpyridinium) dichromate; hydroquinone; oxidation

INTRODUCTION

Oxidation of alcohols is the foundation of synthetic chemistry and a fundamental transformation in organic synthesis. The conversion of primary and secondary alcohols to the corresponding carbonyl compounds is essential for the preparation of fragrances and food additives as well as of many synthetic intermediates in organic chemistry.[1] It is of interest to use heterogeneous systems for performing oxidation in industry and technologies.[2,3] A number of methods for the oxidation of alcohols have emerged in the recent years,[4–24] but low selectivity, long reaction times, low yields of products, expensive reagents, and overoxidation to carboxylic acid are still serious obstacles for this transformation.

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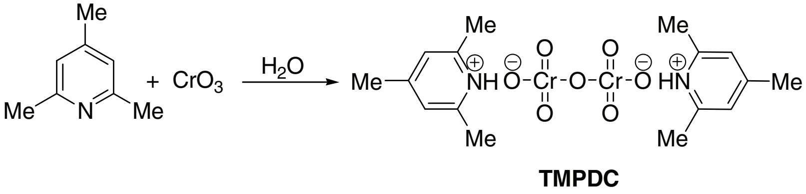
RESULTS AND DISCUSSIONS

Consequently, we decided to introduce a new reagent to overcome the above limitations. In continuation of our ongoing program on the application of new oxidizing reagents in organic functional group transformations,[25–32] we were interested to synthesize bis-(2,4,6-trimethylpyridinum) dichromate (BTMPDC) I as a new and efficient oxidizing reagent. It is interesting to note that the production of BTMPDC is easy and clean without difficult workup procedure, and pure reagent can be obtained only with crystallization in water (Scheme 1).

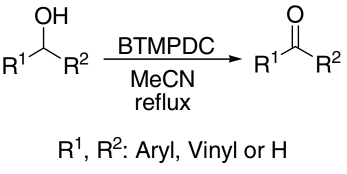


SCHEME 1

In addition, there is current research of general interest in heterogeneous systems[33–39] because of the importance such systems have in industry and in developing technologies. Thereforeherein we disclose an effective and mild procedure for the oxidation of a variety of primary and secondary benzylic alcohols to the corresponding carbonyl compounds using BTMPDC under reflux conditions in acetonitrile.

Initially, we screened different solvents for the oxidation of 2-chlorobenzyl alcohol to 2-chlorobenzaldehyde, as a typical example, using BTMPDC and found that acetonitrile is the best solvent in term of activity and selectivity (Table I).

Eventually, different types of primary and secondary benzylic alcohols **1** were subjected to the oxidation reaction in the presence of bis-(2,4,6-trimethylpyridinium) dichromate (BTMPDC) in acetonitrile under reflux conditions (Scheme 2); the results for this transformation are summarized in Table II.



SCHEME 2

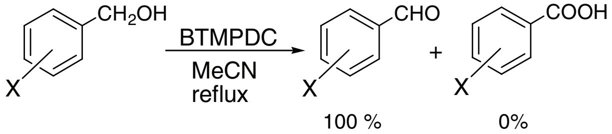
TABLE I Oxidation of 2-Chlorobenzyl Alcohol Using BTMPDC in Different Solvents Under Reflux Conditions[a]

Entry	Solvent	Time (Min)	Yield (%)[b]
1	Acetonitrile	10	100
2	Acetone	120	50
3	Chloroform	120	65
4	Dichloromethane	120	26
5	Tetrahydrofurane	120	30
6	Diethyl ether	120	12

[a] 2-chlorobenzyl alcohol : BTMPDC = 1 mmol : 1 mmol. [b] Yield was determined by 2,4-dinitrophenyl hydrazone derivatives.

To show the chemoselectivity of the described system, cinnamyl alcohol was converted to the cinnamaldehyde in good yields and a carbon–carbon double bond was intact in the course of the reaction (Table II, entry 13).

It is of interest that this oxidizing system chemoselectively oxidized all primary benzylic alcohols to the corresponding aldehydes, and overoxidation did not occur (Table II, entries 1–7, Scheme 3).



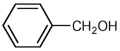
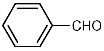
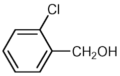
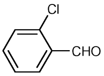
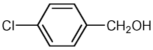
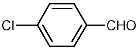
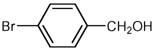
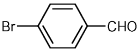
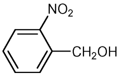
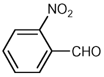
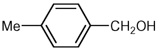
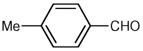
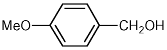
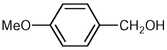
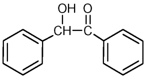
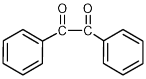
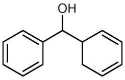
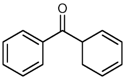
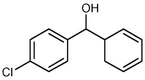
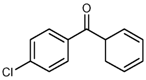
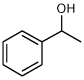
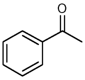
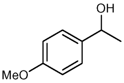
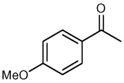
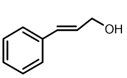
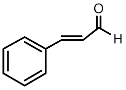
SCHEME 3

The oxidation of phenols constitutes an interesting issue from the biological and chemical point of view.[40] Various phenol derivatives exhibit biological properties and are important intermediates in industrial chemical and pharmaceutical synthesis.[41–43]

Therefore, to show the capability of BTMPDC as an effective oxidizing agent, three hydroquinones were subjected to the oxidation reaction to produce the corresponding benzoquinones under same conditions (Scheme 4).

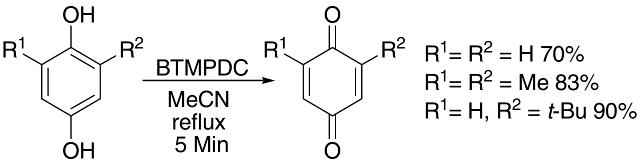
We hoped that BTMPDC would be an excellent oxidant reagent for all of the oxidation reactions. In summary, the cheapness and availability of the reagents, easy and clean workup, good conversion of alcohols, and acceptable yields make this an attractive methodology. We believe that

TABLE II Oxidation of Primary and Secondary Benzylic Alcohols 1 to Their Corresponding Carbonyl Compounds 2 with BTMPDC Under Reflux Conditions in Acetonitrile

Entry	Substrate[a]	Product	Time (Min)	Yield (%)[b]
1			10	78
2			10	80
3			5	75
4			20	82
5			60	70
6			10	85
7			10	74
8			60	82
9			40	80
10			45	82
11			35	70
12			30	75
13			30	96

[a]substrate : BTMPDC (1 : 1 mmol), [b]Isolated yields.

the present methodology could be an important addition to existing methodologies.



SCHEME 4

EXPERIMENTAL

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. The oxidation products were characterized by comparison of their spectral (IR, ^{1}H NMR, and ^{13}C NMR) and physical data with authentic samples.

General Procedure

Preparation of bis-(2,4,6-trimethylpyridinium) dichromate

A 100 mL round-bottomed flask was equipped with a dropping funnel containing 2,4,6-trimethylpyridine (26.8 mL, 0.2 mol). The flask was charged with CrO_3(20 g, 0.2 mol) and H_2O (20 mL). Then 2,4,6-trimethylpyridine was added dropwise for 10 min at room temperature. After the addition, the mixture was shaken for 15 min then kept in the freezer for 24 h. Orange jelly sediment was obtained. The jelly reagent was discolored with active charcoal and crystallized in water then dried. Bis-(2,4,6-trimethylpyridinum) dichromate as orange solid was obtained quantitatively.

Oxidation of Benzyl Alcohol to the Benzaldehyde as a Typical Procedure

A suspension of benzyl alcohol (0.108 g, 1 mmol) and bis-(2,4,6-trimethylpyridinium) dichromate (1 mmol, 0.460 g) in MeCN (15 mL) was stirred under reflux conditions for 10 min (the progress of the reaction was monitored by TLC). After reaction completion, the reaction mixture was cooled down to room temperature then filtered off. The residue was washed with diethyl ether (3 × 10 mL), then solvents were removed using rotary evaporation. The product was purified by short column chromatography using diethyl ether as elution. Benzaldehyde was obtained in 78% yield (0.083 g).

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