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A novel and selective oxidation of benzylic alcohols with polymer-supported periodic acid under mild aprotic conditions

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Abstract

A new polymeric oxidizing reagent was prepared by supporting periodic acid on poly(1,4-phenylene-2,5-pyridine dicarboxyamide). This polymeric reagent was used for the selective oxidation of primary benzylic alcohols to the corresponding benzaldehydes in CH_3CN at reflux conditions. Excellent selectivity was observed between primary benzyl alcohols and secondary ones as well as non-benzylic alcohols in the oxidation reactions. Allylic alcohols were also converted to the corresponding aldehydes with good yields.

Keywords: Oxidation; Benzylic alcohol; Polymer-supported reagent; Periodate

The selective oxidation of benzylic alcohols in the presence of saturated alcohols is very important in organic chemistry and can be achieved by many reagents such as MnO_2, DDQ, bis(benzyltriethylammonium)dichromate and K_2FeO_4 under phase-transfer conditions [1,2]. Also, many supported reagents [3] or catalysts [4] have been used for selective oxidation of benzylic alcohols. Recently palladium-loaded oxidized diamond catalysis for the selective oxidation of alcohols has been reported by Suzouki *et al*. [5]. Periodic acid has been used as oxidant in several selective oxidations of alcohols [6]. Pyridinium chlorochromate [6a], pyridinium fluorochromate [6b], chromium trioxide [6c], chromium (III) acetylacetonate [6d], copper on boehmite [6e], Fe(III)/2-picolinic acid [6f], [Ru(acetylacetonate)$_2$(CH_3CN)$_2$]PF_6 [6g] have been used as catalysts for the oxidation of alcohols with periodic acid. All of these reactions utilized transition metal contained catalysts that have some disadvantages such as toxicity, difficulty in the preparation of catalyst or using expensive catalysts. The immobilization of oxidizing reagents onto polymer supports provides potential for extending the benefits of heterogeneous catalysts to homogeneous systems in organic syntheses [7].

To continue our previous works on the preparation and application of polymer-supported reagents in organic synthesis [8], we now report a novel method for the selective oxidation of alcohols using polymer-supported periodic acid as a new polymeric oxidizing agent under aprotic conditions. We first supported periodic acid on the poly(1,4-phenylene-2,5-pyridinedicarboxyamide) by reacting them in water. It was stirred at room temperature for 48 h. Then it was filtered and washed with H_2O to remove unsupported periodates. The obtained polymeric reagent was dried to afford polymer-supported periodic acid (Scheme 1). By having weight of the polymeric reagent, we found that each

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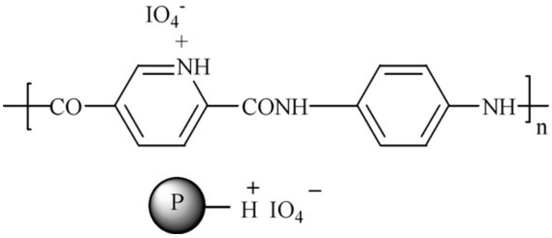
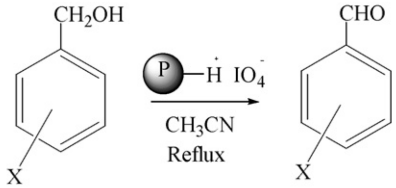


Scheme 1. Structure of polymer-supported periodic acid.



Scheme 2. Oxidation of benzylic alcohols.

gram of the reagent contains 1.75 mmol HIO_4. Thus, we used 0.60 g (1.05 mmol) of the polymeric reagent for the oxidation of 1 mmol alcohol.

We have studied the selective conversion of benzylic alcohols to the corresponding carbonyl compound using this polymeric reagent under mild conditions in CH_3CN as an aprotic solvent (Scheme 2).

We selected *p*-methoxybenzyl alcohol as a model and the oxidation was carried out in different solvents and conditions (Table 1). Reaction progress was monitored by thin layer chromatography (TLC). We used 0.3 g of polymer-supported periodic acid for the conversion of 0.5 mmol of *p*-methoxybenzyl alcohol. When the reaction mixture was stirred in acetonitrile at reflux conditions for 3 h, *p*-methoxy benzaldehyde was obtained in excellent (98%) isolated yield (Table 1, entry 5).

We used the same conditions for the conversion of other alcohols to the corresponding carbonyl compounds in good to excellent yields (Table 2). Primary benzyl alcohols without strong electron withdrawing groups such as NO_2 had excellent isolated yields (Table 2, entries 1–8), while non-benzylic alcohols (Table 2, entries 10–12) and secondary benzyl alcohols (entries 13–15) had poor yields. Allylic alcohols were also converted to the corresponding aldehydes with good yields (Table 2, entries 16–17).

For investigating the selectivity of polymeric agent between primary and secondary benzyl alcohols, a competition reaction was performed between benzyl alcohol (1 mmol) and benzhydrol (1 mmol) with 0.6 g polymer-supported periodic acid in acetonitrile at reflux conditions (Scheme 3). After 2.25 h, benzyl alcohol was converted to benzaldehyde with 90% isolated yield while benzylhydrol was recovered completely.

Also this polymeric reagent was showed another excellent selectivity between primary benzyl alcohols and non-benzylic alcohols in the reaction of benzyl alcohol (1 mmol) and 2-phenyl ethanol (1 mmol) with 0.6 g polymer-supported periodic acid in the same conditions (Scheme 4). After 2 h, benzyl alcohol was converted to benzaldehyde with 95% isolated yield while 2-phenyl ethanol was recovered completely.

Table 1
Oxidation of 4-methoxybenzyl alcohol to 4-methoxybezaldehyde by polymer-supported periodic acid in different solvents.

Entry	Solvent	Condition	Time (h)	Conversion (%)
1	Diethyl ether	Reflux	3	20
2	Dichloromethane	Reflux	3	40
3	*n*-Hexane	Reflux	20	30
4	Acetonitrile	r.t.	6	20
5	Acetonitrile	Reflux	3	98

Table 2
Selective oxidation of alcohols to carbonyl compounds withpolymer-supported periodic acid in acetonitrile at reflux conditions.

Entry	Substrate	Product	Time (h)	Isolated yield (%)
1	4-MeO$C_6H_4CH_2OH$	4-MeOC_6H_4CHO	3	98
2	$C_6H_5CH_2OH$	C_6H_5CHO	1.6	95
3	2-Me$C_6H_4CH_2OH$	2-MeC_6H_4CHO	1.25	96
4	2-*t*-Bu$C_6H_4CH_2OH$	2-*t*-BuC_6H_4CHO	1.25	95
5	3-MeO$C_6H_4CH_2OH$	3-MeOC_6H_4CHO	6	85
6	2-Cl$C_6H_4CH_2OH$	2-ClC_6H_4CHO	1.15	90
7	4-Cl$C_6H_4CH_2OH$	4-ClC_6H_4CHO	1	95
8	2,4-Cl$C_6H_3CH_2OH$	2,4- ClC_6H_3CHO	1.25	90
9	4-$NO_2C_6H_4CH_2OH$	4-$NO_2C_6H_4CHO$	1	40
10	$C_6H_5CH(CH_3)CH_2OH$	$C_6H_5CH(CH_3)CHO$	1	20
11	$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CHO$	13	10
12	$C_6H_5CH_2CH_2CH_2OH$	$C_6H_5CH_2CH_2CHO$	0.75	5
13	$C_6H_5CH(CH_3)OH$	$C_6H_5COCH_3$	2	40
14	$C_6H_5CH(OH)C_6H_5$	$C_6H_5COC_6H_5$	1.75	30
15	$C_6H_5CH(OH)CH_2CH_3$	$C_6H_5COCH_2CH_3$	1.5	50
16	$CH_2{=}CHCH_2OH$	$CH_2{=}CHCHO$	1.5	85
17	$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH{=}CHCHO$	2	70

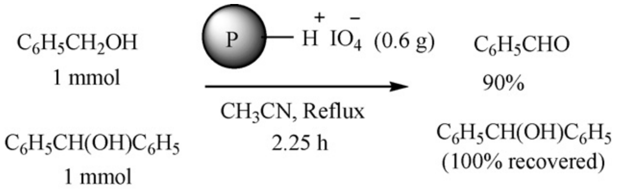
In conclusion, various primary benzylic alcohols were efficiently converted to the corresponding aldehydes using polymer-supported periodic acid under mild conditions in CH_3CN as an aprotic solvent. This method is a novel, selective and efficient route for preparation of carbonyl compounds. Furthermore, it has other advantages such as regenerability of the reagent, mildness, simple work up and simple experimental procedure.

1. Experimental

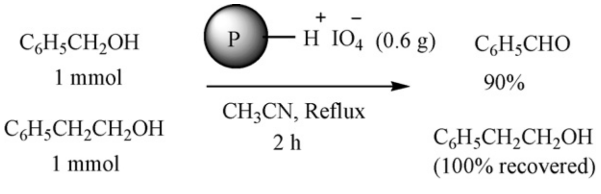
Chemicals were obtained from Merck and Fluka chemical companies. All compounds were known and are identified by comparison of their physical and spectroscopic data with those of authentic samples. Melting points were determined in open capillary tubes with a Buchi 510 apparatus. FT-IR spectra were recorded on a PerkinElmer RXI spectrometer. NMR spectra were recorded on a Brucker Advance DPX 250 MHz instrument.

Preparation of poly(1,4-phenylene-2,5-pyridinedicarboxyamide) was accomplished using 2,5-pyridine dicarboxylic acid, thionyl chloride and *p*-phenylenediamine according to literature [9].

To a solution of *p*-methoxy benzyl alcohol (0.5 mmol, 0.069 g) in acetonitrile (5 mL), was added polymer-supported periodic acid (0.3 g). The mixture was refluxed and reaction progress was monitored by thin layer



Scheme 3. Selective oxidation of benzyl alcohol in the presence of benzhydrol.



Scheme 4. Selective oxidation of benzyl alcohol in the presence of 2-phenyl ethanol.

chromatography (TLC) using mixture of ethyl acetate and *n*-hexane (1:4, v/v) as solvent. After 3 h, the mixture was filtered and polymeric reagent was washed with acetone (10 mL). The organic phases was mixed and evaporated by rotary evaporator at reduced pressure. The obtained crude product was purified by short column chromatography using silica-gel with n-hexane and ethyl acetate (4:1, v/v) as eluent, then obtained *p*-methoxy benzaldehyde (0.066 g, 98%); b.p. 247-249 °C (Lit [3a] b.p. 247–250 °C). The used reagent can be re-generated by reacting with a solution of HIO_4 as preliminary preparation of the reagent.

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