

Polymer-supported dichloroiodate as a new polymeric oxidation reagent for novel and selective oxidation of benzylic alcohols under mild aprotic conditions

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ABSTRACT

A mild and efficient procedure has been proposed for oxidation of benzylic alcohols to the corresponding carbonyl compounds using polymer-supported dichloroiodate (PSDI). The oxidations were carried out in acetonitrile solution, affording the corresponding aldehydes or ketones in high substrate conversion and short reaction time under mild aprotic conditions. Excellent selectivity was observed between primary benzyl alcohols and secondary ones as well as non-benzylic alcohols in the oxidation reactions. The catalyst can be easily prepared and regenerated.

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1. Introduction

The selective oxidation of benzylic alcohols in the presence of saturated alcohols is very important in organic chemistry¹. whilst numerous reagents have been developed to effect the process, many of them use greater than stoichiometric quantities of toxic heavy metals or co-oxidants, which severely handicap their applicability to large scale industrial processes²⁻⁴. Insoluble polymer-supported reagents are convenient from the practical viewpoint for solving many problems in organic synthesis⁵⁻¹⁰. Polymer bound oxidizing agents were one of the earliest examples of polymeric reagents, which alleviate these difficulties such as toxicity, as well as in the preparation of catalyst¹¹. To continue our previous work on the preparation and application of polymer-supported reagents in oxidation of benzylic alcohols¹², we now report a novel method for the selective oxidation of alcohols using polymer-supported dichloroiodate as a new polymeric oxidizing agent under aprotic conditions. This

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new reagent is easily prepared and could be stored for months without any loss in its activity compared with previous reagent, as well as this method is inexpensive and superior to previously reported work¹² in terms of reaction time.

2. Results and Discussion

Polymer-supported reagents and scavengers are increasingly being used in the synthesis and purification of many organic reactions. In recent years, polymer-supported reagents and catalysts have been used in organic synthesis, in what is known as polymer-assisted synthesis, since they can simplify product isolation and purification¹¹.

In order to prepare the polymer-supported dichloroiodate, we prepared dichloroiodate solution by using NaClO, NaI, and HCl according to the literature¹³. For supporting dichloroiodate on the poly (1,4-phenylene-2,5-pyridine dicarboxamide), we added dichloromethane (30 mL) to polyamide (2g) in a round-bottom flask and stirred for 10 hours to afford a suspension. The prepared mixture was cooled to 0 °C and dichloroiodate solution (13.5 mL) was added and stirred for 1 hours. Stirring was continued for 40 minute at room temperature. The resin particles were collected by suction filtration, washed with chloroform (3×30 mL) and PSDI (2.48g) was obtained with 74.6% yield (**Figure 1**).

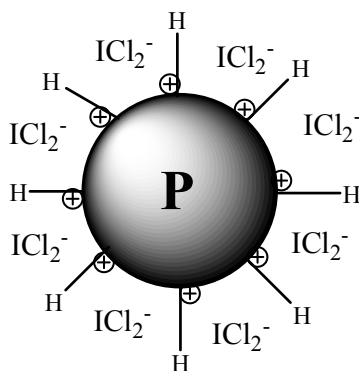
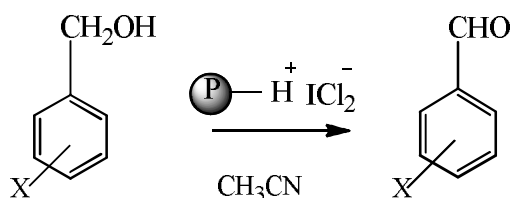


Fig. 1. The structure of polymer-supported dichloroiodate

For Estimation of polyhalide functional groups, the PSDI (200mg) was suspended in CH₃COOH for 10 hour. Then 0.5-1 g of KI was added to the suspension. The container was shaken occasionally and kept in the dark. The evolved iodine was titrated with N/20 solution of sodium thiosulfate until the disappearance of the brown color of iodine in solution occurred. This was repeated 3 times until all the complexes halogen has reacted and halogen content was calculated (1mmol/g). We have studied the selective conversion of benzylic alcohols to the corresponding carbonyl compound using this polymeric reagent under mild conditions in CH₃CN as an aprotic solvent (**Scheme 1**). We selected benzyl alcohol as a model and the oxidation was carried out in different solvents and conditions (**Table 1**).



x: OMe, Me, t Bu, Cl, NO₂

Scheme 1. The oxidation of benzylic alcohol

Table 1. The oxidation of benzyl alcohol to bezaldehyde by PSDI in different solvents

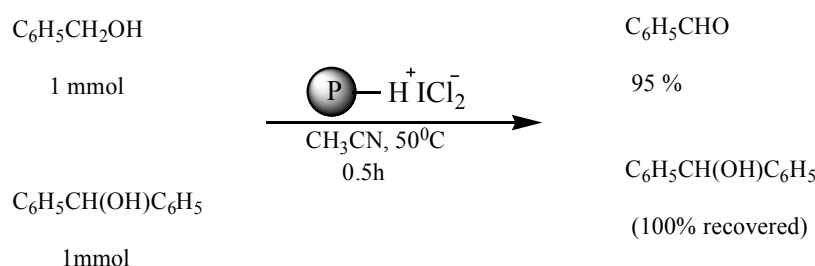
Entry	Substrate	Temperature (°C)	Time (h)	Yield (%)
1	Chloroform	50	7	40
2	Dichloromethane	50	6	30
3	n-Hexane	50	10	30
4	Acetonitrile	40	1	75
5	Acetonitrile	50	0.5	95

We used 0.5 g of PSDI for the conversion of 0.5 mmol of benzyl alcohol to related carbonyl compounds. When the reaction mixture was stirred in acetonitrile at 50 °C for 30 minute, benzaldehyde was obtained in excellent (95%) 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 NO₂ 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.

Table 2. The Selective oxidation of alcohols to carbonyl compounds PSDI in acetonitrile at 50 °C

Entry	Substrate	Product	Time (h)	Yield (%)
1	C ₆ H ₅ CH ₂ OH	PhCHO	0.5	95
2	<i>p</i> -OMeC ₆ H ₄ CH ₂ OH	<i>p</i> -OMeC ₆ H ₄ CHO	1	95
3	<i>O</i> -MeC ₆ H ₄ CH ₂ OH	<i>O</i> -MeC ₆ H ₄ CHO	1	85
4	<i>p</i> -tBuC ₆ H ₄ CH ₂ OH	<i>p</i> -tBuC ₆ H ₄ CHO	1	85
5	<i>m</i> -OMeC ₆ H ₄ CH ₂ OH	<i>m</i> -OMeC ₆ H ₄ CHO	2	87
6	<i>m</i> -ClC ₆ H ₄ CH ₂ OH	<i>m</i> -ClC ₆ H ₄ CHO	3	80
7	<i>p</i> -ClC ₆ H ₄ CH ₂ OH	<i>p</i> -ClC ₆ H ₄ CHO	3	80
8	2, 4-ClC ₆ H ₃ CH ₂ OH	2,4-ClC ₆ H ₃ CHO	3	80
9	<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ OH	<i>p</i> -NO ₂ C ₆ H ₄ CHO	3	40
10	C ₆ H ₅ CH(CH ₃)CH ₂ OH	C ₆ H ₅ CH(CH ₃)CHO	15	10
11	C ₆ H ₅ CH ₂ CH ₂ OH	C ₆ H ₅ CH ₂ CHO	20	12
12	C ₆ H ₅ CH ₂ CH ₂ CH ₂ OH	C ₆ H ₅ CH ₂ CH ₂ CHO	17	10
13	C ₆ H ₅ CH(CH ₃)OH	C ₆ H ₅ COCH ₃	26	40
14	C ₆ H ₅ CH(OH)C ₆ H ₅	C ₆ H ₅ COC ₆ H ₅	30	40
15	C ₆ H ₅ CH(OH)CH ₂ CH ₃	C ₆ H ₅ COCH ₂ CH ₃	26	40

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 1 g PSDI in acetonitrile at 50 °C conditions (**Figure 2**). After 30 minute, benzyl alcohol was converted to benzaldehyde with 95% isolated yield while benzylhydrol was recovered completely. Also this polymeric reagent showed another excellent selectivity between primary benzyl alcohols and nonbenzylic alcohols in the reaction of benzyl alcohol (1mmol) and 2-phenyl ethanol (1 mmol) with 0.6 g PSDI in the same conditions (**Figure 3**). After 30 minute, benzyl alcohol was converted to benzaldehyde with 95% isolated yield while 2-phenyl ethanol was fully recovered.

**Fig. 2.** The selective oxidation of benzyl alcohol in the presence of benzhydrol

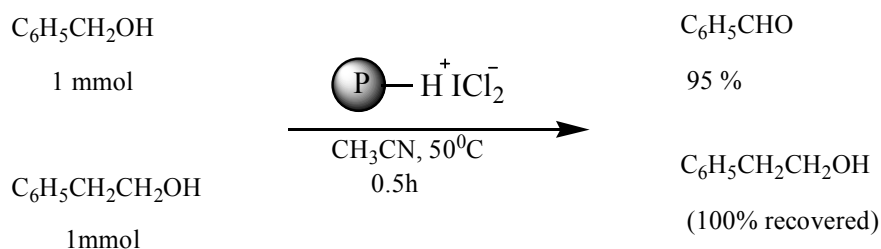
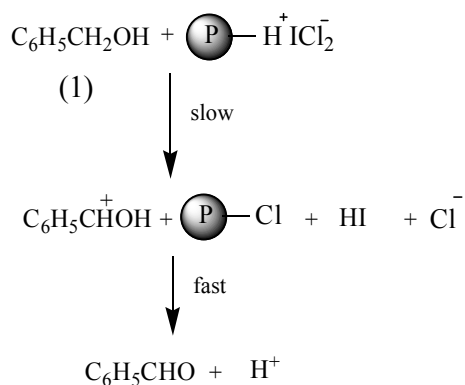


Fig. 3. The selective oxidation of benzyl alcohol in the presence of 2-phenyl ethanol

The formation of aldehyde from polymer supported dichloroiodate and alcohol can be explained by a propose mechanism which is presented in **Scheme 2**¹⁴. One molecule of alcohol (1) firstly transfers a hydride-ion to polymer reagent to provide carbocation intermediate which is named rate-determining step. The active intermediate then undergoes intramolecular dehydration to give the related aldehyde¹⁴.



Scheme 2. The mechanism of the oxidation of benzylic alcohol

3. Conclusions

In conclusion, various primary benzylic alcohols were efficiently converted to the corresponding aldehydes using PSDI 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.

Acknowledgements

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4. Experimental

4.1. Materials and Methods

Chemicals were obtained from Merck and Fluka chemical companies. All compounds were known and identified by comparison of their physical and spectroscopic data with those of authentic samples. IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and an Impact 400 Nicolet FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Bruker Advance DPX 400

MHz instrument. Melting points were determined in open capillary tubes with a Buchi 510 apparatus. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company). Preparation of poly (1,4-phenylene-2,5-pyridinedicarboxamide) was accomplished using 2,5-pyridine dicarboxylic acid, thionyl chloride and 1,4-phenylenediamine

4.2. General procedure: Oxidation of benzyl alcohol

To a solution of benzyl alcohol (0.5 mmol, 0.054 g), in CH₃CN (10 mL), PSDI (0.5 g) was added, and the mixture was stirred at 50 °C for 30 min. The progress of reaction was monitored by TLC using mixture of ethyl acetate and n-hexane (1:4, v/v) as a solvent. The reaction mixture was cooled and then filtered, and the resin was washed with chloroform. The combined filtrates were evaporated to remove the solvent. The resulting residue was purified by column chromatography on silica-gel to afford benzaldehyde with 95% isolated yield (**Table 2**, Entry 1, b.p 178 °C (lit: b.p 179 °C¹⁵).

4.3 Physical and Spectral Data

4.3.1. Poly (1,4-phenylene-2,5-pyridinedicarboxamide) dichloroiodate (PSDI):

IR (KBr, cm⁻¹): 3330 (v (N-H)), 3043 (v (C-H)), 1668 (v (C=O)), 1553 (v (N-H Bend)), 1582 (v (C-H Aromatic)) and 219, 120 (v (ICl₂)) cm⁻¹; ¹H-NMR(400 MHz, CDCl₃, δ /ppm): 6.607 (1H, s), 7.91-7.96 (4H, m), 8.04-8.12 (3H, m).

4.3.2. Benzaldehyde (**Table 2**, Entry 1):

IR (KBr, cm⁻¹): 3066 (v (C-H)), 2849 (v (C-H in Aldehyde)), 1701 (v (C=O)), 1578 (v (C-H Aromatic)) ; ¹H-NMR(400 MHz, CDCl₃, δ /ppm): 9.947 (1H, s), 7.852 (2H, d), 7.634 (2H, d), 7.413 (1H, t).

4.3.3. 3-Methoxybenzaldehyde (**Table 2**, Entry 5):

IR (KBr, cm⁻¹): 3080 (v (C-H)), 2833 (v (C-H in Aldehyde)), 1713 (v (C=O)), 1599 (v (C-H Aromatic)) and 1252 (v (C-O)) cm⁻¹; ¹H-NMR(400 MHz, CDCl₃, δ /ppm): 9.96 (1H, s), 3.65 (3H, s), 7.49 (1H, d), 7.42 (1H, t), 7.31 (1H, d), 7.25 (1H, d).

4.3.4. 4-Methoxybenzaldehyde (**Table 2**, Entry 2):

IR (KBr, cm⁻¹): 3076 (v (C-H)), 2809 (v (C-H in Aldehyde)), 1703 (v (C=O)), 1535 (v (C-H Aromatic)) and 1222 (v (C-O)) cm⁻¹; ¹H-NMR(400 MHz, CDCl₃, δ /ppm): 9.607 (1H, s), 4.36 (3H, s), 8.023 (2H, d), 8.345 (2H, d).

4.3.5. 4-Chlorobenzaldehyde (**Table 2**, Entry 7):

IR (KBr, cm⁻¹): 3012 (v (C-H)), 2810 (v (C-H in Aldehyde)), 1710 (v (C=O)), 1580 (v (C-H Aromatic)) and 685 (v (C-Cl)) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, δ /ppm): 9.45 (1H, s), 7.675 (2H, d), 7.447 (2H, d).

4.3.6. 4-t-Butylbenzaldehyde (**Table 2**, Entry 4):

IR (KBr, cm⁻¹): 3020 (v (C-H)), 2805 (v (C-H in Aldehyde)), 1712 (v (C=O)), 1566 v (C-H Aromatic) and 1394 (v (t-butyl)); ¹H-NMR(400 MHz, CDCl₃, δ /ppm): 9.567 (1H, s), 1.85 (9H, s), 7.28 (2H, d), 7.965 (2H, d).

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