

PolyVinylPolyPyrrolidone-Supported Boron Trifluoride (PVPP-BF₃); Highly Efficient Catalyst for Oxidation of Aldehydes to Carboxylic Acids and Esters by H₂O₂

Mokhtary, Masoud**

Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, I.R. IRAN

Rastegar Niaki, Masoumeh

Department of Chemistry, Ayatollah Amoli Branch, Islamic Azad University, Amol, I.R. IRAN

ABSTRACT: A highly efficient method for the oxidation of aldehydes to carboxylic acids using PolyVinylPolyPyrrolidone supported - Boron Trifluoride (PVPP-BF₃) in the presence of 35% hydrogen peroxide has been developed in acetonitrile at 60 °C. This procedure cleanly oxidizes variety of aldehydes to the corresponding carboxylic acids. Oxidative esterification of benzaldehyde utilizing PVPP-BF₃/H₂O₂(35%) is also reported in good to excellent yields in acetonitrile at 60 °C.

KEY WORDS: Polyvinylpolypyrrolidone; Boron trifluoride etherate; Hydrogen peroxide; Aldehydes; Carboxylic acids; Esters.

INTRODUCTION

The use of H₂O₂ as an oxidant offers the advantages that it is a cheap, environmentally benign, and is a readily available reagent and produces water as the only byproduct [1]. There are some alternative methods for oxidation of aldehydes to carboxylic acids such as H₂O₂/[CH₃(n-C₈H₁₇)₃N]HSO₄ [2], H₂O₂/SeO₂ [3], urea/H₂O₂ [4], PB-SiO₂/KMnO₄ [5], CH₃ReO₃/H₂O₂ [6], PCF/H₅IO₆ [7], Fe(TPP)Cl/O₂ [8], CuCl/*t*-BuOOH [9], AgNO₃/H₂O₂ [10], Bi₂O₃/*t*-BuOOH [11] and Au-MgO/O₂ [12].

The transformation of aldehyds directly into the esters is often required in organic synthesis [13,14], especially in the natural products synthesis [15,16]. Several methods were reported for oxidative esterification of aldehyds

to corresponding esters, for example, molecular sieve TS-1[17], V₂O₅/H₂O₂ [18], methyltrioxorhenium/H₂O₂ [19], oxone [20], and S.SnO₂/SBA-1-H₂O₂ [21]. However, some of these methods for oxidation of aldehydes to carboxylic acids and esters involve drastic reaction conditions, costly reagents, toxic transition metal compounds and corrosive wastes, and the tedious work-up procedure. Polymer supported catalysts and reagents have become popular in organic synthesis over the past decades. The high catalytic activity, low toxicity, stability, their recyclability, and environmentally safe condition make the use of a polymer supported reagent an attractive alternative to conventional reagents. Also, the application

* To whom correspondence should be addressed.

+ E-mail: mmokhtary@iaurasht.ac.ir

1021-9986/12/1/1

7/\$/2.70

Table 1: Effect of PVPP-BF₃ loading and H₂O₂ concentration on oxidation of benzaldehyde at 60 °C.

Entry	H ₂ O ₂ (mmol)	PVPP-BF ₃ (g)	Yield (%)
1	1	0.1	62 ^a
2	2	0.2	78 ^a
3	3	0.3	96 ^a
4	1	0.1	56 ^b
5	2	0.2	71 ^b
6	3	0.3	89 ^b
7	4	0.3	95 ^b

^aYield refers to benzoic acid.^bYield refers to benzyl acetate.

Scheme 1

of polymer supported reagents and catalysts has received special attention, due to easy work up of reaction products and some selectivity which are undoubtedly attractive features of this methodology [22].

In connection of our studies on oxygenation of sulfides to sulfones by polyvinylpyrrolidone-boron trifluoride with (35%) hydrogen peroxide [23], in this research we found out the PVPP-BF₃ can be used as a heterogeneous catalyst for oxidation of aldehydes to carboxylic acids and esters in the presence of hydrogen peroxide with excellent to good yields at 60 °C (Scheme 1).

EXPERIMENTAL SECTION

PolyVinylPolyPyrrolidone (PVPP) was purchased from Fluka. Other chemicals were purchased from Merck. Melting points were recorded on an electro thermal melting point apparatus. The NMR spectra were recorded in CDCl₃ with TMS as an internal standard on a Bruker Avance DRX 400 MHz spectrometer. IR spectra were determined on a SP-1100, P-UV-Com instrument. Purity determination of the products was accomplished by TLC on silica gel poly gram SIL G/UV 254 plates. Products were separated by simple filtration, and identified by comparison IR, and ¹H NMR spectra, with those reported for authentic samples.

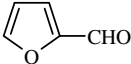
General Procedure for Oxidation of Aldehydes to Carboxylic Acids

To a suspension of aldehyde (1 mmol) and PVPP-BF₃ (0.3 g) in acetonitrile (5 mL), 35% hydrogen peroxide (3 mmol) was added drop wise. The reaction mixture was stirred for 4–6 h at 60 °C. The screening reaction temperature performed via oil bath set with thermometer and reactor fit with a condenser. After completion of the reaction (TLC), the mixture was filtered and washed with Et₂O (5 mL). The filtrate was extracted with diethyl ether (20 mL), and the combined organic fraction was washed with 3% NaHSO₃ and dried over Na₂SO₄. Evaporation of the solvent gave the corresponding carboxylic acid in 86-97% yields. The yields obtained based on isolated product.

General Procedure for Oxidation of Aldehydes to Esters

For suspending aldehyde (1 mmol) and PVPP-BF₃ (0.3 g) in alcohol (5 mL), 35% hydrogen peroxide (4 mmol) was added drop wise. The reaction mixture was stirred for 6 h at 60 °C. The screening reaction temperature performed via oil bath set with thermometer and reactor fit with a condenser. After completion of the reaction (TLC), the mixture was filtered and washed with Et₂O (5 mL). The filtrates were extracted with diethyl ether (20 mL), and the combined organic fraction was washed with 3% NaHSO₃ and dried over Na₂SO₄. Evaporation of the solvent gave the corresponding esters.

Table 2 Oxidation of aldehydes to acids^a and esters^b using of PVPP-BF₃/H₂O₂.

Entry	Aldehyde	Product	Time (h)	Yield (%) ^c
1	C ₆ H ₅ CHO	C ₆ H ₅ COOH	5	99
2	<i>p</i> -Me-C ₆ H ₄ CHO	<i>p</i> -Me-C ₆ H ₄ COOH	5	97
3	<i>p</i> -MeO-C ₆ H ₄ CHO	<i>p</i> -MeO-C ₆ H ₄ COOH	6	98
4	<i>p</i> -F-C ₆ H ₄ CHO	<i>p</i> -F-C ₆ H ₄ COOH	5	98
5	<i>p</i> -Br-C ₆ H ₄ CHO	<i>p</i> -Br-C ₆ H ₄ COOH	6	97
6	<i>p</i> -Cl-C ₆ H ₄ CHO	<i>p</i> -Cl-C ₆ H ₄ COOH	4	96
7	2,4-Cl ₂ -C ₆ H ₃ CHO	2,4-Cl ₂ -C ₆ H ₃ COOH	5	96
8	<i>p</i> -NO ₂ -C ₆ H ₄ CHO	<i>p</i> -NO ₂ -C ₆ H ₄ COOH	5	97
9	<i>p</i> -HO-C ₆ H ₄ CHO	<i>p</i> -HO-C ₆ H ₄ COOH	6	99
10	2,4-Me ₂ -C ₆ H ₃ CHO	2,4-Me ₂ -C ₆ H ₃ COOH	5	99
11			4	98
12	PhCH=CHCHO	PhCH=CHCOOH	5	97
13	CH ₃ CH ₂ CH ₂ CHO	CH ₃ CH ₂ CH ₂ COOH	5	96
14	CH ₃ (CH ₂) ₄ CHO	CH ₃ (CH ₂) ₄ COOH	5	97
15	C ₆ H ₅ CHO	C ₆ H ₅ COOCH ₂ CH ₃	6	98
16	C ₆ H ₅ CHO	C ₆ H ₅ COO(CH ₂) ₃ CH ₃	6	99
17	C ₆ H ₅ CHO	C ₆ H ₅ COOCH(CH ₃) ₂	6	0

^a Reaction Conditions: Aldehyde (1 mmol), PVPP-BF₃ (0.3 g), H₂O₂ (3 mmol), CH₃CN (5 mL), 60 °C.

^b Reaction Conditions: Aldehyde (1 mmol), alcohol (5 mL), PVPP-BF₃ (0.3 g), H₂O₂ (4 mmol), 60 °C.

^c Isolated yields.

Table 3: Comparison of our reagent with some other reagents in oxidation of benzaldehyde to benzoic acid.

Reagent	Conditions	Time (h)	Yield (%) ^a	Ref.
[CH ₃ (n-C ₈ H ₁₇)N]HSO ₄ /H ₂ O ₂	90 °C	3	85	2
SeO ₂ /H ₂ O ₂	THF/ reflux	2.5	96	3
Urea/H ₂ O ₂	HCOOH, r.t.	1.5	96	4
PB-SiO ₂ /KMnO ₄	cyclohexane, 65 °C	20	99	5
CH ₃ ReO ₃ /H ₂ O ₂	[bmim]BF ₄ , 50 °C	24	95	6
Fe(TPP)Cl/O ₂	CH ₂ Cl ₂ /r.t.	2	95	8
Bi ₂ O ₃ / <i>t</i> -BuOOH	EtOAc	2.5	90	9
Au-MgO/O ₂	120 °C	5	95	12
PVPP-BF ₃ /H ₂ O ₂	CH ₃ CN, 60 °C	5	99	This work

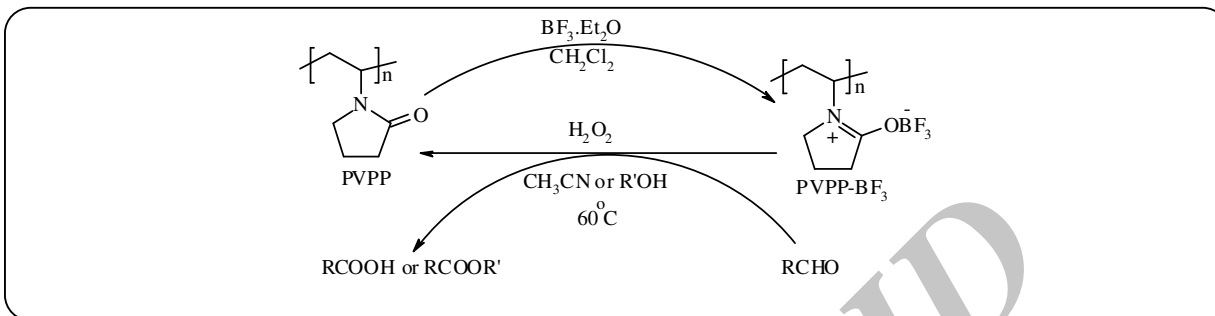
^aYield refers to the corresponding sulfone.

Table 4: The recycling of PVPP-BF₃ in the oxidation of benzaldehyde to benzoic acid.^a

Run	1	2	3	4
Yield (%) ^b	98	92	80	73

^aAll reactions were carried out using 0.1 g of the polymeric reagent, 1 mmol aldehyde and 3 mmol of H₂O₂.

^b Isolated yields.



RESULTS AND DISCUSSIONS

In this method, boron trifluoride etherate was immobilized on polyvinylpolypyrrolidone to give a stable polymeric Lewis acid catalyst according to our previous article [24]. Characterization of the Lewis-acid sites present on the polymer was performed by recording the FT-IR spectrum of PVPP-BF₃, which shows a strong broad absorption at 1000–1060 cm⁻¹ for the BF bonds and a moderate absorption at 1646 cm⁻¹ corresponds to the imine group on the backbone. The capacity of the reagent was determined by titration and found to be 10 mmol/g, whereas its silica supported analogue has a loading capacity of less than 4 mmol/g [25,26]. Despite of BF₃.Et₂O, the PVPP-BF₃ is more water tolerant, non-corrosive and stable solid catalyst with an elevated Lewis acid property. Interestingly, this reagent gives not only excellent yields of the products but also the PVPP-BF₃ is easily regenerated and can be reused and retains its activity after several months of storage (Scheme. 2). In this reaction the PVPP-BF₃ activated hydrogen peroxide, accelerates oxidative esterification and oxidation of aldehydes to carboxylic acids.

For optimizing solvent, the oxidation of benzaldehyde was studied in a variety of organic solvents such as methanol, acetonitrile, nitromethane, dioxane, and dichloromethane. Among them, acetonitrile was found to be the best solvent for oxidation of aldehydes

to carboxylic acids. In order to show the role of the polyvinylpolypyrrolidone-boron trifluoride in this oxidation reaction, the oxidation of benzaldehyde was carried out in the absence of the catalyst. The oxidation and oxidative esterification were not successful, and a low yield of corresponding carboxylic acid in longer time was formed. As seen in Table 1, the optimized stoichiometric ratio of RCHO:H₂O₂ for the conversion of aldehydes to corresponding carboxylic acid was found to be 1:3 using 0.3 g of the PVPP-BF₃ in acetonitrile at 60 °C. In the oxidative esterification, a ratio of 1:4 of aldehyde to hydrogen peroxide in the presence of 0.3 g of the reagent produces the corresponding ester in good yield at 60 °C. All reactions were carried out under the optimized conditions, and the results are summarized in Table 2. As an evidence, all aldehydes were easily converted to the corresponding acids in excellent yields (Table 2, entries 1-14). Finally, we examined the direct oxidation reaction of aldehydes with straight chain alcohols using of PVPP-BF₃/H₂O₂ system. All reactions were carried out under the optimized conditions and the corresponding esters are obtained in good yields (Table 2, entry 15, 16). However, the oxidative esterification of benzaldehyde and 2-propanol was not satisfactory (Table 2, entry 17), and no ester was detected after 6 hours. This trend indicates that steric effect is an important factor in the reaction system. In order to examine the scope and generality of our

method, the oxidation of benzaldehyde to benzoic acid was compared with some of those reported in literatures (Table 3). It is evident that the PVPP-BF₃/H₂O₂ system allows these transformations to proceed with excellent yield, appropriate time and milder conditions. To check the reusability of the catalyst, it was employed the oxidation of benzaldehyde fourth cycles under the optimum conditions. In the first run 98% of carboxylic acid was obtained. The catalyst powder was recovered by filtration, washed with dichloromethane and immediately reused for oxidation processes again, taking into account the partial loss of catalyst during the recovery. The second cycle was performed with the recovered catalyst and addition of three equimolecular amount of H₂O₂ gave corresponding acid in 92% yield. The third and fourth cycles were performed with the recovered catalyst similar to above method and 80% and 73% of acid were obtained respectively (Table 4). To improve the catalytic activity of catalyst after three cycles it is favored to separate the polyvinylpyrrolidone by filtration, washed carefully from dichloromethane and dried, then treated with boron trifluoride etherate again to prepared fresh polyvinylpyrrolidone immobilized boron trifluoride catalyst. The polymer support can be used several times for the immobilization of boron trifluoride.

CONCLUSIONS

We have developed a simple methodology that exhibits oxidation of aldehydes to carboxylic acids and esters in the presence of hydrogen peroxide using polyvinylpyrrolidone-supported boron trifluoride as a high loading of Lewis acid, which is stable, easy to prepare and handle. In addition, this method is suitable both for preparative and industrial usage because of its low cost, biocompatibility and recyclability of the polyvinylpyrrolidone as a safe polymer support.

Acknowledgments

We are grateful to Rasht Branch of Islamic Azad University for financial assistance in this work.

Received : Oct. 21, 2011 ; Accepted : Jun. 9, 2012

REFERENCES

- [1] Lane B.S., Burgess K., Iron as a Powerful Catalysts for Transition Metal-Catalyzed Reactions, *Chem. Rev.*, **103**, p. 2457 (2003).
- [2] Sato K., Hyodo M., Takagi J., Aoki M., Noyori R., Hydrogen Peroxide Oxidation of Aldehydes to Carboxylic Acids: an Organic Solvent-, Halide- and Metal-Free Procedure, *Tetrahedron Lett.*, **41**, p. 1439 (2000).
- [3] Brqszcz M., Kloc K., Maposah M., Mlochowski J., Selenium (IV) Oxide Catalyzed Oxidation of Aldehydes to Carboxylic Acids with Hydrogen Peroxide, *Synth. Commun.*, **30**, p. 4425 (2000).
- [4] Balicki R., A Mild and Convenient Procedure for the Oxidation of Aromatic Aldehyds to Carboxylic Acids Using Urea-Hydrogen Peroxide in Formic Acid, *Synth. Commun.*, **31**, p. 2195 (2001).
- [5] Takemoto T., Yasuda K., Ley S.V., Solid-Supported Reagents for the Oxidation of Aldehydes to Carboxylic acids, *Synlett*, p. 1555 (2001).
- [6] Bernini R., Coratti A., Provenzano G., Fabrizi G., Oxidation of Aromatic Aldehydes and Ketones by H₂O₂/CH₃ReO₃ in Ionic Liquids: a Catalytic Efficient Reaction to Achieve Dihydric Phenols, *Tetrahedron*, **61**, p. 1821 (2005).
- [7] Hunsen M., Fluorochromate-Catalyzed Periodic Acid Oxidation of Alcohols and Aldehydes, *J. Fluorine Chem.*, **126**, p. 1356 (2005).
- [8] Zhou X.T., Ji H.B., Yuan Q.L., Xu J.C., Pei L.X., Wang L.F., Aerobic Oxidation of Benzylic Aldehydes to Acids Catalyzed by Iron (III) Meso-Tetraphenylporphyrin Chloride Under Ambient Conditions, *Chinese Chem. Lett.*, **18**, p. 926 (2007).
- [9] Mannam S., Sekar G., CuCl Catalyzed Oxidation of Aldehydes to Carboxylic Acids with Aqueous Tert-Butyl Hydroperoxide Under Mild Conditions, *Tetrahedron Lett.*, **49**, p. 1083 (2008).
- [10] Chakraborty D., Gowda R.R., Malik P., Silver Nitrate-Catalyzed Oxidation of Aldehydes to Carboxylic Acids by H₂O₂, *Tetrahedron Lett.*, **50**, p. 6553 (2009).
- [11] Malik P., Chakraborty D., Bi₂O₃-Catalyzed Oxidation of Aldehydes with *t*-BuOOH, *Tetrahedron Lett.*, **51**, p. 3521 (2010).

- [12] Choudhary V.R., Dumbre D.K., Solvent-Free Selective Oxidation of Primary Alcohols-to-Aldehydes and Aldehydes-to-Carboxylic Acids by Molecular Oxygen Over MgO-Supported Nano-Gold Catalyst, *Catal. Commun.*, **13**, p. 82 (2011).
- [13] Williams D.R., Klingler F.D., Allen E.E., Lichtenthaler F.W., Bromine as an Oxidant for Direct Conversion of Aldehydes to Esters, *Tetrahedron Lett.*, **29**, p. 5087 (1988).
- [14] Macdonald C., Holcomb H., Kennedy K., Kirkpatrick E., The *N*-Iodosuccinimide-Mediated Conversion of Aldehydes to Methyl Esters, *J. Org. Chem.*, **54**, p. 1213 (1989).
- [15] Wilson S.R., Tofigh S., Mishram R.N., A Novel, Nonoxidative Method for the Conversion of Aldehydes to Esters, *J. Org. Chem.*, **47**, p. 1360 (1982).
- [16] Garegg P.J., Olsson L., Oscarson S., Synthesis of Methyl (Ethyl 2-O-Acyl-3,4-di-O-Benzyl-1-Thio-Beta.-D-Glucopyranosid) Urinates and Evaluation of Their Use as Reactive.Beta.-Selective Glucuronic Acid Donors, *J. Org. Chem.*, **60**, p. 2200 (1995).
- [17] Zhao R.; Ding Y., Peng Z., One-Step Synthesis of Isoamyl Butyrate from Isoamyl Alcohol and *n*-Butyraldehyde over TS-1 in Air, *Catal. Lett.*, **87**, p. 81 (2003).
- [18] Gopinath R., Patel B.K., A Catalytic Oxidative Esterification of Aldehydes Using $V_2O_5-H_2O_2$, *Org. Lett.*, **2**, p. 577 (2000).
- [19] Espenson J.H., Zhu Z., Zauche T.H., Bromide Ions and Methyltrioxorhenium as Co-Catalysts for Hydrogen Peroxide Oxidations and Brominations, *J. Org. Chem.*, **64**, p. 1191 (1999).
- [20] Travis B.R., Sivakumar M., Hollist G.O., Borhan B., Facile Oxidation of Aldehydes to Acids and Esters with Oxone, *Org. Lett.*, **5**, p. 1031 (2003).
- [21] Qian G., Zhao R., Ji D., Lu G., Qi Y., Suo J., Facile Oxidation of Aldehydes to Esters Using S. $SnO_2/SBA-1-H_2O_2$, *Chem. Lett.*, **33**, p. 834 (2004).
- [22] Ley S.V., Baxendale I.R., Bream R.N., Multi-step Organic Synthesis Using Solid-supported Reagents and Scavengers: A New Paradigm in Chemical Library Generation, *J. Chem. Soc., Perkin Trans.*, **1**, p. 3815 (2000).
- [23] Mokhtary M., Lakouraj M.M., Rastegar Niaki M., Polyvinylpolypyrrolidone-Supported Boron Trifluoride (PVPP- BF_3); Highly Efficient Catalyst for Chemoselective Oxygenation of Sulfides to Sulfones by H_2O_2 , *Phosphorus, Sulfur Silicon, Relat. Elem.*, **187**, p. 321 (2012).
- [24] Lakouraj M.M., Mokhtary M., Polyvinylpolypyrrolidone-Supported Boron Trifluoride: A High-Loaded, Polymer-Supported Lewis Acid for the Ritter Reaction, *Monatsh. Chem.*, **140**, p. 53 (2009).
- [25] Wilson K., Clark, J. H., Synthesis of a Novel Supported Solid Acid BF_3 Catalyst, *Chem. Commun.*, p. 2135 (1998).
- [26] Wilson K., Adams D.J., Rothenberg G., Clark J.H., Comparative Study of Phenol Alkylation Mechanisms Using Homogeneous and Silica-Supported Boron Trifluoride Catalysts, *J. Mol. Catal. A*, **156**, p. 309 (2000).