IRANIAN JOURNAL OF CATALYSIS



Modified polyvinylpyridine

Compiled by Laleh Samavi

Laleh Samavi was born in Rasht,Iran in 1979. She received her B.Sc. (2002) and M.Sc. (2005) degrees from the university of Guilan. Presently she is working towards her Ph.D. degree under supervision of Prof. Farhad Shirini at the University of Guilan. Her research is focused on the development of synthetic rout of catalysts and their applications in organic chemistry.

The college of chemistry, University of Guilan, Rasht 41335-19141, Iran

E-mail:lsamavi79@gmail.com



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

In recent years, development of heterogeneous catalysts have become a major area of research in synthetic organic chemistry due to some potential advantages of these materials over homogeneous systems such as simplified recovery, reusability, enhanced selectivity and reactivity, easy product isolation and incorporation in continuous reactors and micro-reactors [1]. Application of solid acids in organic transformations has important roles, because these reagents do less harm to environment and have no corrosion or disposal of effluent problems [2-4]. One way to overcome the problem of recyclability of the traditional acid catalysts is to chemically anchor the reactive center onto a large surface area

Abstracts

(A) Poly(4-vinylpyridinium) hydrogen sulfate was found to be an efficient catalyst for the preparation of 1,1-diacetates at room temperature and neat conditions. Deprotection of the resulting 1,1-diacetates was achieved using the same catalyst in methanol solvent. This new method consistently has the advantages of excellent yields and short reaction times. The catalyst can be reused and recovered for several times. [8]. solid carrier [5]. Functional polymers have the potential advantages of small molecules with the same functional groups [6]. Poly(4-vinylpyridine) is an interesting material because of its stable pyridyl group and ability to form charge transfer complexes with acidic dopants [7]. Poly(4-vinylpyridine) seems to an attractive support to immobilize mineral acids because of the basic nature of pyridyl group. These catalysts have several advantages such as: green aspects by avoiding toxic catalysts and solvents, high reaction rates and excellent yields, no side reactions, ease of preparation and handling of the catalyst, effective reusability of the catalyst, use of inexpensive catalyst with lower loading and simple experimental procedure.

RCHO +
$$Ac_2O$$
 $\xrightarrow{P(4-VPH)HSO_4}$ RCH(OAc)₂
MeOH, r.t.

(B) Shirini and co-workers have found that poly(4-vinylpyridine), as a cheap and commercially available reagent, is efficiently able to catalyze the *O*-TMS protection of alcohols and phenols and *N*-Boc protection of amines. The other advantages of this methodology are relatively short reaction times, high yields of the products, high selectivity and easy and clean work-up. [9].

(C) The conversion of 1,1-diacetates to their corresponding aldehydes can be easily catalyzed in the presence of N-sulfonic acid poly(4-vinylpyridinum) chloride (NSPVPC) as a novel, efficient and reusable catalyst in methanol [10].

(**D**) Shirini and co-workers have developed a simple, efficient chemoselective protocol for the *N*-Boc protection of various amines using NSPVPC [11].

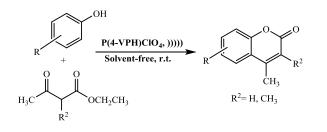
(E) Use of poly(4-vinylpyridinium) perchlorate (P(4-VPH)ClO₄) as an activator in Pechmann synthesis under solvent-free conditions and ultrasonic irradiation is reported by Shirini and co-workers for the first time. The methodology has some advantages such as green aspects by avoiding toxic catalysts and solvents, high reaction rate, excellent yields and no side reactions [12].

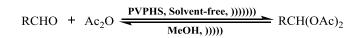
(F) The conversion of 1,1-diacetates to their corresponding aldehydes can be easily catalyzed in the presence of poly(4-vinylpyridinium)hydrogen sulfate salt in methanol. All reactions were performed at room temperature in good to high yields under ultrasonic irradiation. [13].

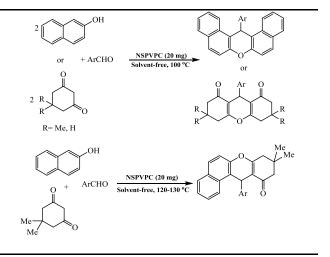
(G) A simple and efficient procedure for the preparation of xanthenes derivatives such as 14-aryl-14*H*-dibenzoxanthenes, 1,8-dioxooctahydroxanthenes and tetrahydrobenzoxanthene-11-ones is described using *N*-sulfonic acid poly(4-vinylpyridinium) chloride (NSPVPC) as a heterogeneous and efficient catalyst under solvent-free conditions [14].

ROH
$$\xrightarrow{\text{HMDS / PVP}}$$
 ROSiMe₃
PhNH₂ $\xrightarrow{\text{(Boc)}_2\text{O}/\text{PVP}}$ PhNH-Boc

$$R_1R_2NH_2 + (Boc)_2O \xrightarrow{NSPVPC} R_1R_2-N-Boc$$



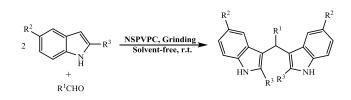




(H) Shirini and co-workers introduced *N*-sulfonic acid poly(4-vinylpyridinium) chloride (NSPVPC) catalyzed highly efficient, one-pot protocol for the synthesis of bis(indolyl)methane derivatives by the condensation of aldehydes with indole, 2-methylindole or 5-bromoindole by grinding method at room temperature under solvent-free conditions in good to excellent yields. [15].

References

- F.M. Menger, C. Lee, J. Org. Chem., 44 (1979) 3446-3448.
- [2] D. Choudhary, S. Paul, R. Gupta, J.H. Clark, Green. Chem., 8 (2006) 479-482.
- [3] A. Ghorbani-Choghamarani, S. Sardari, J. Sulfur, Chem., 32 (2011) 63-69.
- [4] R. Dalpozzo, G. Bartoli, L. Sambri, P. Melchiorre, Chem. Rev., 110 (2010) 3501-3551.
- [5] J.A. Melero, R. van Grieken, G. Morales, Chem. Rev., 106 (2006) 3790-3812.
- [6] S.V. Ley, I.R. Baxendale, R.N. Bream, P.S. Jackson, A.G. Leach, D.A. Longbottom, M. Nesi, J.S. Scott, R.I. Storer, S.J. Taylor, J. Chem. Soc., Perkin Trans. 1, (2000) 3815-4195.
- [7] V. Rao, P.V. Ashokan, M.H. Shridhar, Mater. Sci. Eng. A, 276 (2000) 266-268.



- [8] N.G.Khaligh, F. Shirini, J. Mol. Catal. A: Chem., 348 (2011) 20-29.
- [9] F. Shirini, N.G. Khaligh, J. Iran. Chem. Soc., 9 (2012) 495-502.
- [10] F. Shirini, O.G. Jolodar, J. Mol. Catal. A: Chem., 356 (2012) 61-69.
- [11] F. Shirini, N.G. Khaligh, O.G. Jolodar, J. Iran. Chem. Soc., 10(2013) 181-188.
- [12] N.G. Khaligh, F. Shirini, Ultrason. Sonochem., 20 (2012) 26-31.
- [13] N.G. Khaligh, Ultrason. Sonochem., 20 (2013) 19-25.
- [14] F. Shirini, M. Abedini, R. Pourhasan, Dyes Pigments, 99 (2013) 250-255.
- [15] F. Shirini, N.G. Khaligh, O.G. Jolodar, Dyes Pigments, 98 (2013) 290-296.