Asian Journal of Chemistry Vol. 20, No. 4 (2008), 2822-2826

Study of Oxidant Ionic Liquid with the Help of Soluble Support

Fariba Heidarizadeh* and Ghader Allahverdi
Department of Chemistry, Shahid Chamran University, Ahvaz, Iran
E-mail: heidarizadeh@scu.ac.ir

A new strategy using a soluble support for oxidation has been developed. The efficiency of this new system has been demonstrated by the use of starch as the support in oxidation of benzylic alcohols to the corresponding aldehydes. Due to the use of soluble support, oxidation reaction has been easier and no overoxidation to carboxylic acids or esters formation was detected. The purification time of the crude product has been considerably shortened.

Key Words: Ionic liquid, Soluble support, Oxidation, Alcohol.

INTRODUCTION

Ionic liquids (ILs) are non-volatile, non-flammable and thermally stable solvents and promising replacements for the traditional volatile organic solvents[1]. Ionic liquids are generally defined as salts that melt at or below 100 °C to afford liquids composed solely of cations and anions. In some cases, the ionic liquids are free-flowing liquids at room temperature, in which case they can be called ambient temperature ionic liquids. Of course, these latter liquids have real advantages over higher melting salts in terms of the handling.

The number of ionic liquids grows daily, but the cations are generally bulky, asymmetric ammonium or phosphonium salts or heteroaromatics, with low symmetry, weak intermolecular interactions and low charge densities. The 1,3-dialkylimidazolium salts remain the most intensively investigated, although this could well change in the future as more affordable alternatives arrive on the scene. However, if one wishes to generate a low-melting salt of any particular anion, an unsymmetrical 1,3-dialkylimidazolium still appears to be the best place to start. Typically, the anions are inorganic and include $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$ and $[(CF_3SO_2)_2N]^-$ although more recently, organic anions (*e.g.*, $[RCO_2]^-$) have also been introduced. The physical and chemical properties of the ionic liquid, including their melting points, are dependent on both the nature of the cations and the anions[2].

The introduction of the Merrifield method for solid-phase synthesis, insoluble polymer supports have been incorporated into numerous synthetic methodologies to facilitate product purification[3]. Although highly successful, solid-phase synthesis still exhibits several shortcomings due to the nature of heterogeneous reaction conditions. Non-linear kinetic behaviour, unequal distribution and/or access to the chemical reaction, solvation problems and pure synthetic problems associated with solid-phase synthesis have led several laboratories to pursue alternative methodologies to restore homogeneous reaction conditions. By replacing insoluble cross-linked resins with soluble polymer supports, the familiar reactions conditions of classical organic chemistry are reinstated and yet product purification is still facilitated through application of macromolecular properties. This methodology, termed liquid-phase synthesis, in essence avoids the difficulties of solid-phase synthesis while preserving its positive aspects.

The term 'liquid phase' synthesis was first used to contrast the differences between solid-phase peptide synthesis and a method of synthesis on soluble polyethylene glycol[4,5]. Although 'soluble polymer supported' synthesis might be a less ambiguous label than 'liquid- phase' synthesis, the latter term is more prevalent in the literature. In keeping with previous, the phrases 'classical' or 'solution' synthesis will be used to describe homogenous reaction schemes that do not employ polymer supports while 'liquid-phase' synthesis will be reserved for methodologies incorporating a soluble macromolecular carrier to facilitate product isolation. It should be noted that although the starting material and subsequent product is kept soluble by the attached polymer, some reactions in liquid-phase synthesis may in fact be heterogeneous due to the presence of insoluble catalysts or reagents (*e.g.*, catalytic hydrogenation)[6-9].

We have previously found that butylmethylimidazolium dichromate and nitrate are successful as oxidant ionic liquids for oxidation of alcohols to the corresponding aldehydes, because of some difficulties associated with purification, we immobilized these ionic liquids on starch gel as soluble support.

EXPERIMENTAL

Products were isolated and identified by comparison of their physical and spectral data with those of authentic samples. IR spectra were recorded on a Bomem FT-IR spectrometer and ^{1}H NMRspectra were obtained with a 400 MHz Bruker spectrometer. Melting points were uncorrected. The purity of products and reaction monitoring were accomplished by thin layer chromatography (TLC) on silica gel PolyGram SILG/UV 254 plates. All the reagents and solvents used were of AR grade.

Preparation of 1-butyl-3-methyl imidazolium dichromate: Equimolar sodium dichromate was added to a dichloromethane solution of 1-butyl-3-methyl imidazolium bromide and refluxed for approximately 24 h. The solid precipitate (NaBr and excess sodium dichromate) was filtered off and the water removed by rotary evaporation. The resultant sample was dissolved in dichloromethane to precipitate a small quantity of impurities, which was filtered off and the filtrate evaporated to dryness. 1-Butyl-3-methylimidazolium dichromate was then dried *in vacuo* for 2 d.

Preparation of 1-butyl-3-methylimidazolium nitrate: Equimolar nitric acid was added to a dichloromethane solution of 1-butyl-3-methyl imidazolium bromide and refluxed for *ca.* 5-6 h and the hydrogen bromide was collected in water. 1-Butyl-3-methylimidazolium nitrate was then dried *in vacuo*.

Preparation of starch as soluble support: 4 g of powdered starch was dissolved in minimum cold water and then 300 mL of boiled water was added. The mixture was stirred until it hardened.

Immobilized [BMIM] Cr_2O_7 on starch gel: 0.011 mol [BMIM] Cr_2O_7 was added to 3 g of starch gel. The mixture was stirred and the orange gel was used as oxidant.

Immobilized [BMIM] NO_3 on starch gel: 0.03 mol [BMIM]NO_3 was added to 3 g of starch gel. The mixture was stirred and the yellow gel was used as oxidant.

Oxidation of benzylic alcohols with immobilized dichromate (nitrate) ionic liquid on starch gel: 0.004 mol benzylic alcohol, 3 g IL-soluble support and 1-2 drops Hydrochloric acid were mixed together and stirred. The progress of the reaction is monitored by TLC (plates:aluminum-backed silica gel Merck 60 GF_{254}) using hexane-ethyl acetate (8:2) as eluent. The reaction mixture was then washed with dichloromethane (3 × 5 mL). The combined filtrates were evaporated to give crude product, which is purified by preparative TLC with hexane-ethyl acetate (8:2). IR spectrum has shown ν(C=O) of aldehyde at 1685-1680 cm^{-1}. The yields are summarized in Tables 1 and 2.

RESULTS AND DISCUSSION

Oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones plays a central role in organic chemistry, hence a wide variety of methods have been developed[1,2]. Despite progress on the catalytic oxidation of alcohols with various metal complexes and the use of environmentally friendly systems, there are still sever limitations with respect to the chemo-, regio and steroselectivity of this reaction[10-17].

Recently, employment of solid supported reagents in the oxidation of alcohols to carbonyl compound has generated interest[18]. In most cases solid supported reagents have been found superior to the non supported reagents. Solid supports modify activity of the reagent, improve selectivity and make product isolation easier.

TABLE-1
OXIDATION WITH IMMOBILIZED IONIC LIQUID
DICHROMATE ON STARCH IN 0.5 h

Alcohol	Aldehyde	Yield (%)
Benzyl alcohol	Benzaldehyde	80
2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	85
2-Hydroxybenzyl alcohol	2-Hydroxybenzaldehyde	80
2-Nitrobenzyl alcohol	2-Nitrobenzaldehyde	85
3-Methoxy benzyl alcohol	3-Metoxybenzaldehyde	80
4-Methoxybenzyl alcohol	4-Metoxybenzaldehyde	80-85
1-Phenylethanol	Acetophenone	80
Cinamyl alcohol	Cinamaldehyde	75
Crotone alcohol	Crotonaldehyde	70-75

TABLE-2
OXIDATION WITH IMMOBILIZED IONIC LIQUID
NITRATE ON STARCH IN 0.5 h

Alcohol	Aldehyde	Yield (%)
Benzyl alcohol	Benzaldehyde	80
2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	85
2-Hydroxybenzyl alcohol	2-Hydroxybenzaldehyde	80
2-Nitrobenzyl alcohol	2-Nitrobenzaldehyde	85
3-Methoxybenzyl alcohol	3-Methoxybezaldehyde	80
4-Methoxybenzyl alcohol	4-Metoxybenzaldehyde	75
1-Phenylethanol	Acetophenone	75
Cinamyl alcohol	Cinamaldehyde	70
Crotone alcohol	Crotonaldehyde	70

On the other hand industrially performed catalytic oxidation reactions also suffer from drawbacks such as poor conversion and selectivity due to over-oxidation, corrosive reaction media, lack of solvent and catalyst recycling and negative environmental impact due to evaporation of the solvents. In order to provide a methodology that addresses these problems, ionic liquids have been investigated as reaction media.

As a part of our research aimed at developing green chemistry methods specially ILs, we have prepared [BMIM]Cr_2O_7 and [BMIM]NO_3 and applied them in the oxidation of various benzylic alcohols. Besides, we describe here the use of starch as a cheap and versatile support where the substrates are not covalently attached but instead simply absorbed onto it. Supported dichromate and nitrate ionic liquid combines the advantages of ionic liquid media with support materials which enables the application of fixed-bed technology and the usage of significantly reduced amount of ionic liquid. As compared to those observed in conventional oxidation, oxidation in ionic liquids has presented enhanced activity and selectivity. Moreover, the high polarity permits ionic liquids to be used as the reaction medium for oxidation of a wide range of substrates, especially those highly polar ones, which are sparingly soluble in common organic solvents.

With an ever increasing quest for the exploration of newer reactions in ionic liquids, herein we wish to report, for the first time, the use of immobilized ionic liquids on starch. In no case could carboxylic acid or ester formation be detected using these ionic liquids and workup is greatly simplified. Purification and extraction of product is easier and one step of purification in oxidation with dichromate that celite column was eliminated.

In conclusion, the concept of supported dichromate and nitrate ionic liquids has successfully been used for oxidation of various benzylic alcohols to their aldehydes without further overoxidation. Other important advantage of this work is that impurities could be trapped in support and product can be easily separated by filtration.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support of this research by Shahid Chamran (Ahvaz) University.

REFERENCES

1. J.G. Huddleston, A.N. Visser and W.M. Reichert, *Green Chem.*, **3**, 156 (2001).
2. T. Welton, *Chem. Rev.*, **99**, 2071 (1999).
3. L.A. Thompson and J.A. Ellman, *Chem. Rev.*, **96**, 555 (1996).
4. M. Mutter, H. Hagenmaier and E. Bayer, *Angew. Chem. Int. Ed. Engl.*, **10**, 811 (1971).
5. E. Bayer and M. Mutter, *Nature (London)*, **237**, 512 (1972).
6. K.E. Geckeler, *Adv. Polym. Sci.*, **121**, 31 (1995).
7. M. Mutter and E. Bayer, In The Peptides, Academic, New York, Vol. 2, p. 285 (1979).
8. K.E. Geckeler, V.N.R. Pillai and M. Mutter, *Adv. Polym. Sci.*, **39**, 65 (1980).
9. K.E. Geckeler, *Adv. Polym. Sci.*, **121**, 31 (1995).
10. L.F. Fieser and M. Fieser, In: Reagents for Organic Synthesis 1, John Wiley & Sons, New York, pp. 144-147 (1967).
11. F. Freeman, in eds.: W.J. Mijs and C.R.H.I. de Jonge, Organic Synthesis by Oxidation with Metal Compounds, Plenum Press, New York, pp. 68-81 (1986).
12. A.H. Haines, In: Methods for the Oxidation of Organic Compounds, Alcohols, Alcohol Derivatives, Alkyl halides, Nitroalkanes, Alkyl Azides, Carbonyl Compounds, Hydroxyarenes and Aminoarenes, Academic Press, London, pp. 17-41 (1988).
13. S.V. Ley and A. Madin, in eds.: B.M. Trost and I. Fleming, Comprehensive Organic Synthesis 7, Pergamon Press, London, pp. 251-289 (1991).
14. E. Santaniello and P. Ferraboschi, *Nouv. J. Chim.*, **4**, 279 (1980).
15. M.S. Climent, J.M. Marinas and J.V. Sinisterra, *React. Kinet. Catal. Lett.*, **38**, 13 (1989).
16. E. Santaniello, P. Ferraboschi and P. Sozzani, *Synthesis*, 646 (1980).
17. J.-D. Lou, L.-H. Lu and W. Liu, *Synth. Commun.*, **27**, 3 (1997).
18. R.O. Hutchins, N.R. Natale, W.J. Cook and J. Ohr, *Tetrahedron Lett.*, **18**, 4167 (1977).

(*Received*: 30 May 2007; *Accepted*: 9 January 2008) AJC-6185