ISSN: 0974 - 7516 Volume 11 Issue 10

Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 11(10), 2015 [367-370]

Facile preparation of symmetrical ethers from their corresponding alcohols by Prayssler acid as a mild and efficient catalyst

H.Hassani*, P.Jahandari

Department of Chemistry, Payam Noor University of Birjand, (IRAN)

E-mail: hassaniir@yahoo.com

ABSTRACT

Etherification of different classes of alcohols was performed using catalytic amounts of Prayssler acid ($H_{14}NaP_5W_{30}O_{110}$). Preparation of symmetrical dibenzyl ethers especially bis(1-methyl 1- phenyl methyl)ether also proceeded well with high yields in the presence of catalytic amounts of Prayssler acid. This compound acts as a heterogeneous, efficient and a reusable catalyst when used in organic solvents.

KEYWORDS

Symmetrical ethers;
Alcohols;
Prayssler acid;
Catalyst.

INTRODUCTION

Preparation of ethers is an important reaction for which a wide variety of procedures have been developed during the last decades. The most commonly used protocol is Williamson ether synthesis^1 which requires initial transformation of alcohols into their corresponding halides or tosylates followed by their displacement with strongly basic alkoxides or phenoxides. Strong basic condition is hazardous to complex molecules carrying base sensitive functional groups. Etherification by direct condensation of alcohols has been considered as an alternative which is conducted in the presence of catalytic amounts of organic or inorganic protic acids[2]. Lewis acids have been also used for direct etherification condensation reactions^3. In most cases, the reactions suffer from the use of steochiometric amounts of the Lewis acids which is due to their decomposition by water generated in the process of etherification reactions[3a].

Reductive etherification of carbonyl compounds by $BiBr_3/Et_3SiH$ and $BiBr_3/ClR_2SiH$ are also reported[4]. However, these systems suffer from being highly water sensitive, expensive and not easily available. We have recently reported easy etherification of different allylic and benzylic alcohols in the presence of catalytic amounts of DDQ[5a] and $Fe(ClO_4)_3$[5b].

Condensation of alcohols or their salts with aldehydes[6, 7], olefins[8], alkyloxides[9], dialkyl phosphites[10] and alcohols[11, 12] are also reported. However synthesis of bulky ethers is not possible by most of the reported methods. Furthermore some of these methods suffer from highly acidic or basic conditions or high cost of the reagent.

Polyoxometalates have proved to be good catalysts for various oxidations. They are applied in bulk or supported forms, and both homogeneous and heterogeneous catalyses are possible. Due to their acidic properties, heteropoly compounds (heteropoly acids and salts) are useful and versatile catalysts in a number of transformations. Since they exhibit weak super acidic properties, they can be used in reactions requiring electrophilic catalysis[13-16].

We now wish to report that preyssler acid ($H_{14}NaP_5W_{30}O_{110}$)[17] is as an efficient, easily available, cheap and recyclable acid for the etherification of primary and secondary alcohols at room temperature. (Scheme 1, TABLE 1).

$$\text{R-OH} \xrightarrow{NaH_{14}P_5W_{30}O_{110}} \text{R-O-R}$$

Scheme 1

RESULTS AND DISCUSSION

We first examined etherification of *p*–methoxy benzyl alcohol as a model compound in the presence of a catalytic amount (1% mol) of preyssler acid. The reaction proceeded smoothly and produced corresponding ether in 90% yield after 2 min under at room temperature. In the absence of the catalyst, similar reaction did not proceed.

Furthermore, we have studied the preparation of symmetrical dibenzyl ethers from their corresponding alcohols. We found that the reactions proceeded well at room temperature in CH_2Cl_2 in the presence of 1% mol of preyssler acid. The results of this study are summarized in TABLE 1.

In this study, we have shown that primary and secondary hydroxy groups of benzylic alcohols substituted with electron-donating and electron-withdrawing groups can be effectively converted in the presence of preyssler acid ($H_{14}NaP_5W_{30}O_{110}$) (0.01 equivalents) to their corresponding symmetric ethers in high yields. Cinnamyl alcohol was efficiently converted to the corresponding ether in excellent yields without isomerization of the C-C double bonds (entry 8). Using this method, 1-phenyl ethanol produced bis(1- methyl 1- phenyl methyl)ether in 85% yield at room temperature after 20 min in the presence of 1% mol of preyssler acid.

In addition, the preparation of bis(4-nitrobenzyl)ether from *p* -nitro-benzyl alcohol is a difficult task. However, *p*-nitrobenzyl alcohol in the presence of a catalytic amount of preyssler acid (1% mol) in CH_2Cl_2 did not produce the corresponding ether.

We also studied the reaction of 1- and 2-octanol for the preparation of their corresponding ethers in CH_2Cl_2 in the presence of preyssler acid (1 mol %). Our observations showed that the reaction did not complete and the corresponding ethers were produced 50-60% even after prolonged reaction time (3 h). Therefore, we believe, this protocol is not suitable for the preparation of aliphatic ethers.

The reactions proceeded in CH_2Cl_2 were performed heterogeneously and the isolation of the catalyst from the reaction mixture was easy and not a time consuming process and the ethers were isolated from high to excellent yields.

These comparisons clearly show the efficiency and suitability of the presented catalyst for such etherification reactions.

In conclusion, in this study we have introduced preyssler acid as a reusable and environmentally benign catalyst which has been used under heterogeneous or homogeneous conditions for the efficient etherification of benzylic alcohols and acyclic alcohols under mild traction conditions. By using this catalyst, preparation of *p*-nitrobenzyl ether which is a difficult task and the preparation of symmetrical benzyl ethers, have been achieved in excellent yields.

EXPERIMENTAL

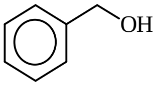
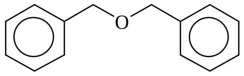
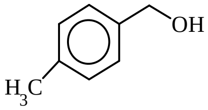
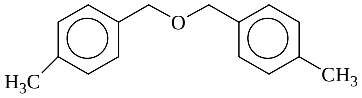
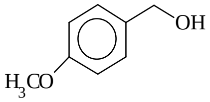
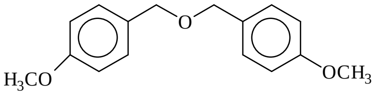
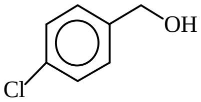
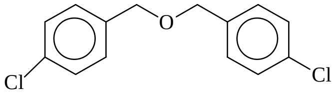
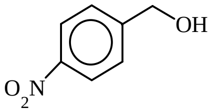
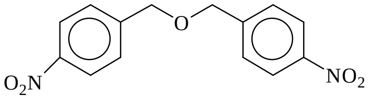
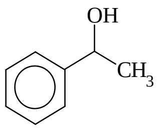
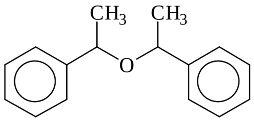
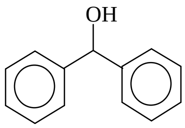
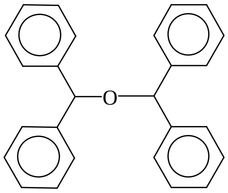
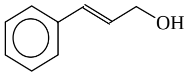
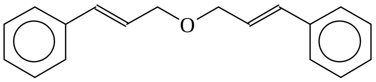
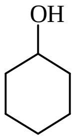
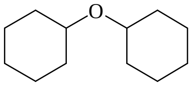
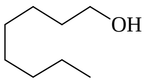
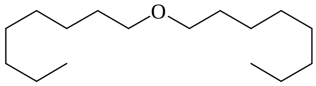
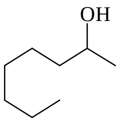
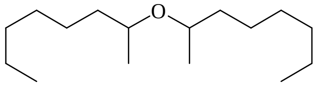
General

Chemicals were purchased from Merck and Fluka Chemical Companies. All the products are known and were characterized by comparison of their physical data with those reported in the literature. NMR spectra were recorded on a Bruker DPX-100. The purity of the products and the progress of the reactions were accomplished by TLC on silica gel poly gram SILG/UV254 plates.

Preparation of bis (*p*-methylphenyl) ether as a typically procedure

P-methyl benzyl alcohol (5 mmol), and preyssler acid (0.05 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature for 3 min. After completion of the

TABLE 1 : Etherification various alcohol with preyssler acid as a catalyst

Entry	Substrate	Product	Time (min)	Yield%
1			5	90
2			3	90
3			3	92
4			20	85
5			No Reaction	
6			20	85
7			50	85
8			10	90
9			180	60
10			180	60
11			180	50

reaction (monitored by TLC), precipitate the catalyst which was removed by filtration. After evaporation of the solvent, the almost pure product was obtained in 90% yield, 0.213 g.

REFERENCES

[1] A.W.Williamson; J.Chem.Soc., **229**, 4 **(1852)**; **(b)**

N.Bagget; in: D.Barton, W.D.Ollis, J.F.Stoddart (Eds.), Comprehensive organic synthesis, Stoddart J.F., Pergaman, Ox-ford, **1**, 799 **(1979)**.

[2] M.B.Smith, J.March, Advanced organic chemistry, fifth ed., Wiley/Inter science, New York, 479–480 **(2001)**; **(b)** R.C.Larock, Comprehensive organic transformations, 2nd Edition, Wiley/Inter science, New York, 897 **(1999)**.

[3] S.Kim, K.N.Chung, S.Yang; J.Org.Chem., and references therein, **3917**, 52 **(1987)**; **(b)** A.D.Mico, R.Margarita, G.Piancatelli; Tetrahedron Lett., **2679**, 36 **(1995)**; **(c)** T.Ooi, H.Ichikawa, Y.Itagaki, K.Maruoka; Heterocycles, **575**, 52 **(2000)**; **(d)** K.Manab, S.Limura, X.Sun, S.Kobayashi; J.Am.Chem.Soc., **11971**, 124 **(2002)**; **(e)** Z.Zhu, J.H.Espenson; J.Org.Chem., **324**, 61 **(1996)**; **(f)** J.Emert, M.Goldenberg, G.L.Chiu, A.Valeri; J.Org.Chem., **2012**, 42 **(1977)**.

[4] J.S.Bajwa, X.Jiang, J.Slade, K.Prasad, O.Repic, T.J.Black-lock; Tetrahedron Lett., **6709**, 43 **(2002)**; **(b)** X.Jiang, J.S.Bajwa, J.Slade, K.Prasad, O.Repic, T.J.Black-lock, Tetrahedron Lett., **9225**, 43 **(2002)**.

[5] N.Iranpoor, E.Mottaghinejad; Synth.Commun., **2253**, 25 **(1995)**; **(b)** P.Salehi, N.Iranpoor, F.Kargar Behbahani; Tetrahedron, **943**, 54 **(1998)**.

[6] B.H.Shoemaker, C.E.Boord; J.Am.Chem.Soc., **1505**, 53 **(1931)**.

[7] S.Torii, S.Takagishi, T.Inokuchi, H.Okumoto; Bull.Chem.Soc.Jpn., **775**, 60 **(1987)**.

[8] C D.Nenitzescu, V.Przemetzki; Chem.Ber., **2706**, 69 **(1936)**.

[9] H.C.Chitwood, B.T.Freure; J.Am.Chem.Soc., **680**, 68 **(1946)**.

[10] Y.Kashman; J.Org.Chem., **912**, 37 **(1972)**.

[11] N.Iranpoor, E.Mothaghineghad; Tetrahedron, **1859**, 50 **(1994)**.

[12] N.Iranpoor, E.Mothaghineghad; Synthetic Commun., **2253**, 25 **(1995)**.

[13] M.Misono; Stud.Surf.Sci.Catal., **69**, 75 **(1993)**.

[14] C.Izumi, Y.Urabe, M.Onaka, Zeolite; Clay and heteropoly acid in organic reactions, Kodansha: Tokyo/ VCH: New York, **3**, **(1993)**.

[15] M.H.Habibi, S.Tangestaninejad, I.Mohammadpoor-Baltork, V.Mirkhani, B.Yadollahi; Tetrahedron Lett., **2851**, 42 **(2001)**.

[16] **(a)** H.Firouzabadi, N.Iranpoor, K.Amani; Green Chem., **131**, 3 **(2001)**; **(b)** H.Firouzabadi, N.Iranpoor, K.Amani; Synthesis, 59 **(2002)**; **(c)** H.Firouzabadi, N.Iranpoor, K.Amani; Synthesis, 408 **(2003)**.

[17] C.Preyssler; Bull.Soc.Chem.Fr, 30 **(1970)**; **(b)** M.H.Alizadeh, S.P.Harmalker, Y.Jeanin, M.T.Pope; J.Am.Chem.Soc., **2662**, 107 **(1985)**; **(c)** M.H.Alizadeh, H.Razavi, F.Farrash Bamoharram, M.K.Hassanzadeh, R.Khoshnavazi, F.Mohammadizonoz; Kinetics & Catalysis, **524**, 44 **(2003)**.