

Triton B mediated green protocol for epoxide cleavage

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ABSTRACT

Ionic liquids are liquids at room temperature (RTIL) and have high thermal stability, low vapour pressure, immiscibility with organic products, high kinetic control. They are used for synthesis, catalysis and extraction. Present study encompasses use of Triton B (IL) for epoxide cleavage to produce various alcohols. Characterization of product was done using H-NMR, C-NMR and GCMS. So, this route provides simple, efficient, environmentally benign way of preparing 1, 2 - methoxy alcohol from epoxide. After carrying out many reactions using Triton B as catalyst and reaction medium, it can be concluded that this ionic liquid is recyclable, reusable reaction medium and catalyst for C-O, C-C bond formation and epoxide cleavage.

Keywords: Ionic Liquid, epoxide, Triton B.

INTRODUCTION

Organic synthesis has its place in classical and applied research, it is constantly encountered with certain problems of separation of materials other than products, huge solvent usage, protection and deprotection of functional groups, low absolute yield etc. These limitations are grave in synthesis of fine and specialty chemicals. [1-2] So there is a growing need for more environmentally acceptable processes in the chemical industry. This trend has become known as 'Green Chemistry'.

Strategies of green chemistry include replacing stoichiometric reagents with recyclable solid acid (zeolites, acidic clays) or base in catalytic amounts, biocatalysis, white biotechnology, enantioselective synthesis, one pot multistep catalytic cascade process, ionic liquids as catalytic medium.

Ionic liquids are salts which are liquid < 1000c and are melting point around room temperature so these are known as RTIL. It's cation may be organic or inorganic but anion should be inorganic. There are several reasons why ionic liquids are considered as "green solvents". It's speciality lies in it's unusual physico-chemical properties such as low vapor pressure, high thermal and electrochemical stability, high solvating power [7] These properties are also significant in view of health and safety associated with many applications. Properties of molten salt are different from aqueous and organic solvents from chemical process. Application of ionic liquids in organic reactions such as acylation, alkylation, condensation, esterification, hydrogenation and oxidation are notable [2].

Epoxide are valuable intermediates in organic synthesis partly because their nucleophilic opening leads to 1,2- difunctionalized systems and partly because such cleavage usually occur specifically with regioselectivity. It also gives β hydroxy alcohol with variety of nucleophilic species. Ring opening fluorination of epoxide has been a convenient method for preparation of fluorohydrin. The direct way may be treatment of epoxide with anhydrous hydrogen fluoride, but in some cases, it has a drawback due to its toxicity and difficulty for handle. Alternative fluorine sources have been employed successfully to avoid this problem. HF-amine complex, potassium dihydrogen trifluoride or potassium hydrogen difluoride, silicon tetrafluoride, titanium tetrafluoride, tetrabutylammonium dihydrogen trifluoride, were reported as effective reagents for ring opening fluorination of epoxide. Certain ionic liquids are proved in helping nucleophile generation and its attack [3,4,5,6,7,8]. Present work includes study of Triton B (Benzyl trimethylammonium hydroxide, also known as or trimethyl benzyl ammonium hydroxide, is a quaternary ammonium salt that functions as an organic base.) as catalyst and medium in epoxide cleavage to alcohols.

METHODOLOGY

The present work investigates the innovative use of Triton B (RTIL) as reaction medium and catalyst. It is employed for synthesis of alcohol using epoxide as starting material. (Fig. 1)

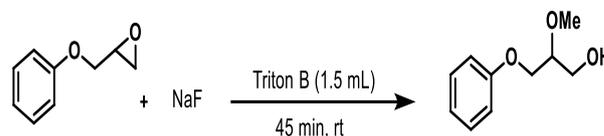


Fig. 1

The reaction mixture was extracted using diethyl ether nearly for 4-5 times and supernatant was collected. In the collected supernatant, saturated NaCl (brine solution) was added so as to remove any junk and leftover Triton-B is reused for further batch of reaction. It was separated using separating funnel since it forms two layers. A TLC was taken and found single spot. So separation of product alcohol was done using silica column and later it is concentrated using rotary evaporator. Characterization of obtained product was done using H-NMR (Fig. 6) and GCMS. (Fig. 7).

RESULTS AND DISCUSSION

In the present work I used solid acid, ionic liquids as either reaction medium or catalyst. First I carried this opening using cesium fluoride as fluoride source and amberlyst as solid acid. [Fig 2]

Before carried out the reaction quoted in Fig. 1, similar reactions are also carried out using Amberlyst-15 as catalyst and DCM as solvent. But expected alcohol was not obtained. [Fig.2] It was not also working at 800C.

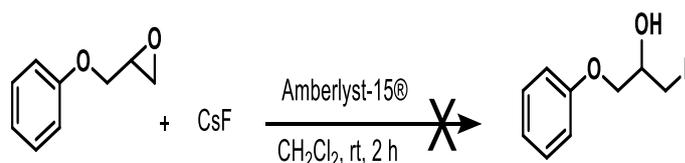
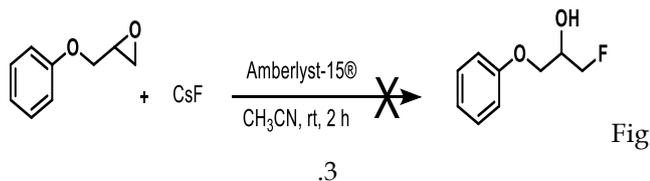


Fig.2

The above mentioned quantities of reactants are taken along with catalytic amount of amberlyst and DCM as solvent. Progress of the reaction was monitored by TLC every 30 minutes upto 2 hrs. but no progress was observed.

Same reaction was carried out in similar fashion except changing DCM by ACN. [Fig 3] But reactant conversion was not found even after heating for hours together.



Fig

Reaction was not leading to expected product since fluoride was not made available. It is probably due to insolubility of CsF in DCM and highly hygroscopic nature of CsF. After having no successful reaction even in ACN, out solubility test of CsF in various solvents like DMSO, DMF were carried out. But CsF found insoluble in all these solvents.

Triton B mediated green protocol for epoxide ring opening



Entry	Substrate	Product	Time in minutes	Yield(%)
1			45	90
2			50	85
3			40	80
4			45	95

Fig.4

So the reaction in Fig.1 proves the simple, efficient, environmentally benign way of preparing 1,2 - methoxy alcohol from epoxide. Reaction was little modified by reducing the amount of Triton-B up to catalytic amount and added DCM as solvent [Fig. 1]. It remains effective, fast without changing product nature as earlier one. This proves that Triton -B can act as catalyst in cleavage epoxide by nucleophile. The reaction in Fig. 1 is optimized using temperature, reaction time, solvents. It is then carried out using different epoxides. To the expectation all products were obtained in good yields. Results of all these reactions are consolidated in following table. (Fig.4)

Plausible Mechanism: [Fig 5]

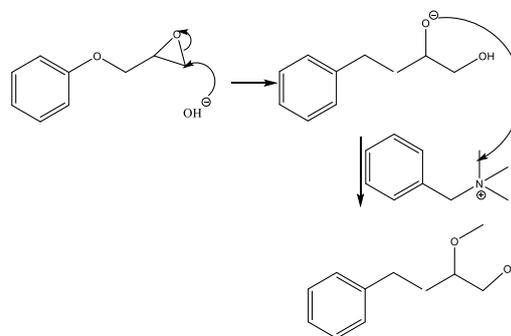


Fig: 5-Mechanism for epoxide cleavage

Characterization

H-NMR

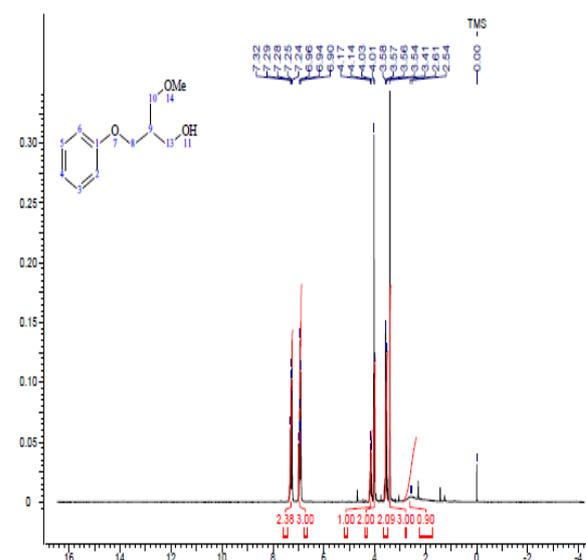


Fig.6

GCMS

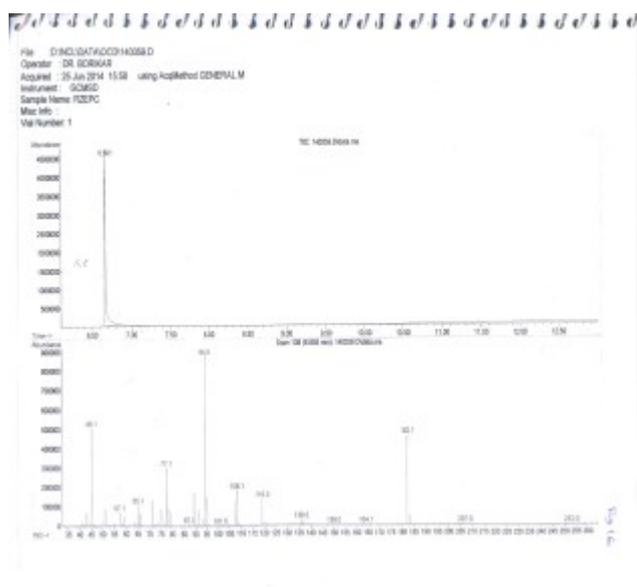


Fig.7

CONCLUSION

Epoxide cleavage is an important reaction due to its product utility in various application. Though it was studied by various scientists applying various routes, this route is quite easy, economic and environment benign due to use of Triton B as catalyst as well as reaction medium. This route also gives comparative good yield without hassle of volatile organic solvents and easy product separation.

Conflicts of interest: The authors stated that no conflicts of interest.

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