"ON WATER" ORGANIC REACTIONS

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ABSTRACT

Solvents and reagents play an important role in synthetic chemistry. The selection of these two should be environmentally benign. Use of environmentally benign chemical in organic synthesis is an important goal from an ecological point of view. The present work is aimed with the goal of promoting water as a solvent in organic synthesis. Using water as solvent promotes considerable rate enhancements and operational simplicity.

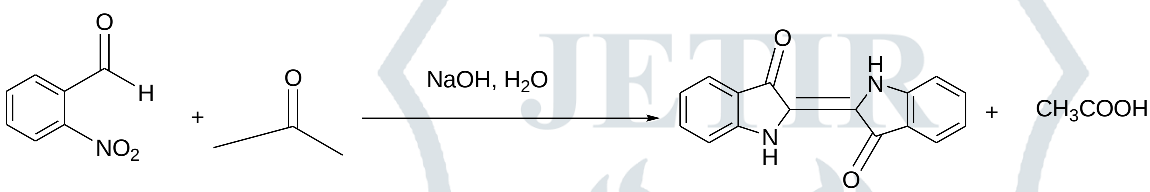
INTRODUCTION

Terms frequently used in the literature for reactions in aqueous medium are ***"in water"*** and ***"on water"***[1] according to the solubility of organic compound. When the solute is completely water soluble, then the reaction is termed as proceeding in **"in water"**. Reactions of water insoluble organic compounds, taking place in aqueous suspensions are termed as ***"on water"*** reactions.

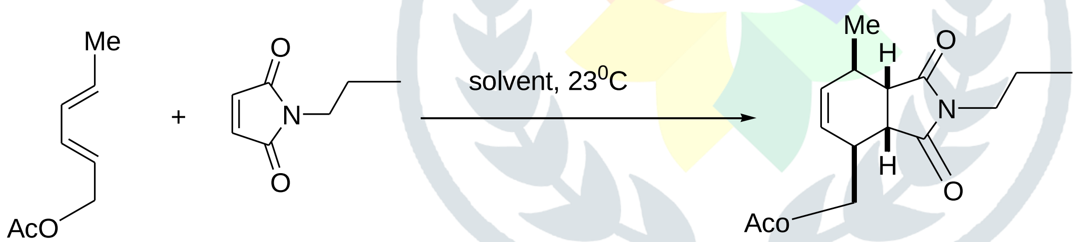
Recently, ***"on water"*** reactions have received a great deal of attention because of their high efficiency and environmentally benign synthetic protocols[2]. Considerable rate acceleration in ***"on water"*** organic synthesis can be explained on the basis of hydrophobic effects[3], where non-polar reactant molecules are forced together in the rate determining transition state. The rate of ***"on water"*** acceleration varies in different organic moities[4]. Besides this other advantages associated with "on water" reactions are ease of product isolation and safety, due to its high heat capacity[5] in case of exothermic reactions. Last but not least ***"on water"*** reactions also help in retaining the aspect of "green chemistry".

The field of aqueous organic synthesis has been frequently and broadly reviewed. The first use of water for an organic synthesis could be marked as Wohler's synthesis of urea from ammonium cyanate[6]. Baeyer and Drewsen in 1882[7] quoted the synthesis of indigo (Scheme 1). In their synthesis, a suspension of o-nitrobenzaldehyde in aqueous acetone was treated with a solution of sodium hydroxide. Immediately the characteristic blue color of indigo appeared, and the product subsequently precipitated. Various Diels-Alder reactions have been reported, which carried out efficiently in aqueous suspension with significant rate enhancement (Scheme 2)[6]. Considerable rate acceleration was observed on the rate of Claisen rearrangement by Grieco and Gajewski in aqueous phase (Scheme 3)[6]. Efficient "on-water" aminolysis was accomplished by Saidi and Azizi (Scheme 4)[6]. Many transition metal catalyzed reactions have been successfully achieved with excellent yield in aqueous suspension (Scheme 5)[6]. Highly efficient ***"on water"*** bromination was reported by Guss and Rosenthal in 1955 (Scheme 6)[6]. Various ***"on water"*** oxidation (Scheme 7)[6] and reduction (Scheme 8)[6] reactions have been frequently discussed in literature.

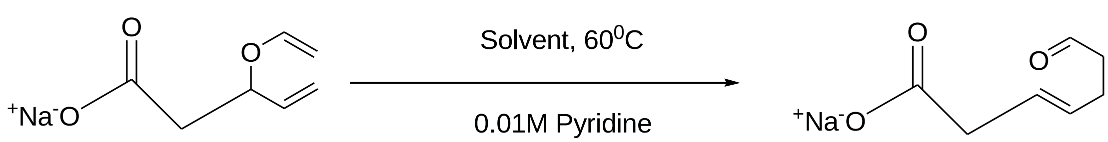
SOME REPORTED "ON WATER" REACTIONS



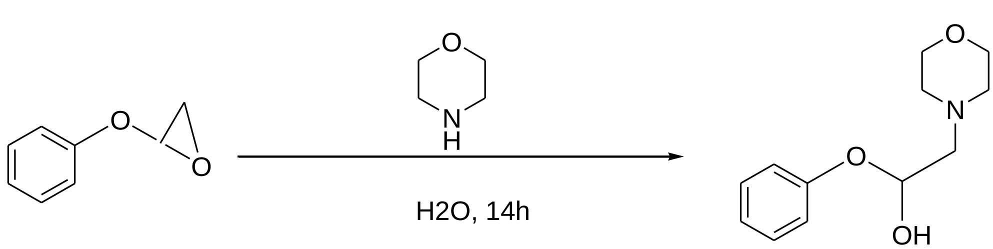
Scheme 1. Indigo synthesis by Baeyer and Drewsen



Scheme 2. *"On Water"* Diels-Alder reaction



Scheme 3. *"On water"* Claisen Rearrangement



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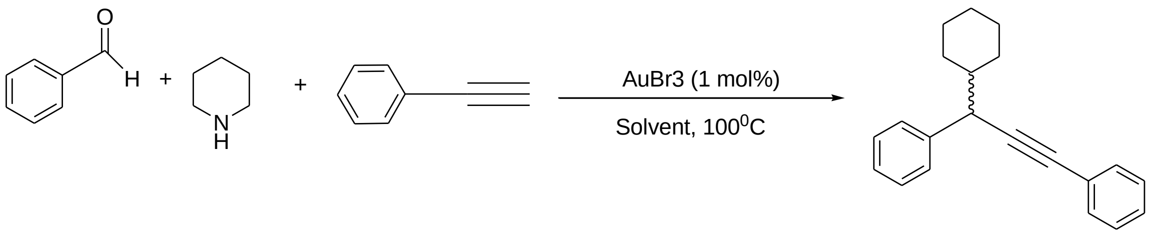
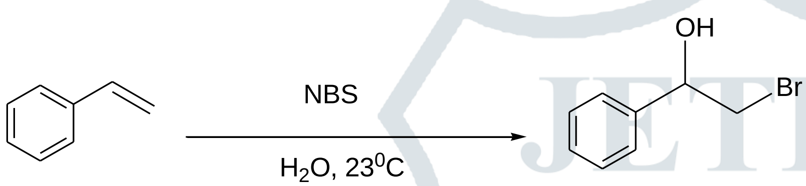
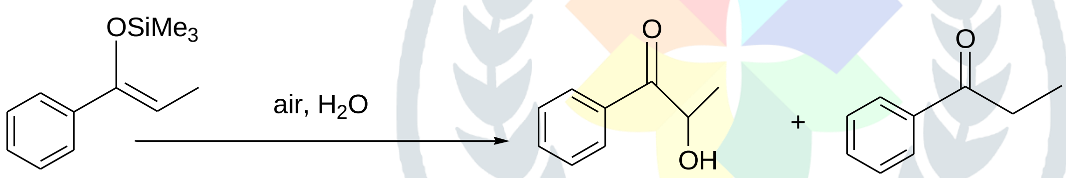
Scheme 4. *"On Water"* aminolysis



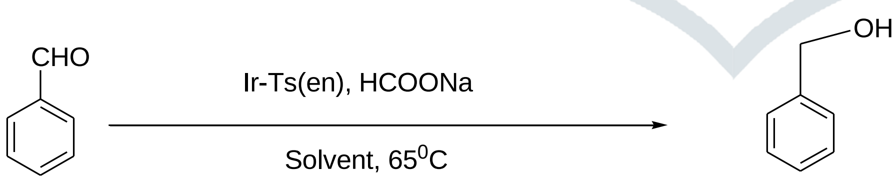
Scheme 5. *"On water"* transition metal catalyzed reaction



Scheme 6. *"On Water"* bromination



Scheme 7. *"On Water"* oxidation



Scheme 8. "On Water" reduction

Besides solvent, reagent used should also be environment friendly. Carbonyl compounds are used as important building blocks in organic synthesis. Many organic named reactions like the Meerwein-ponndorf-Verley reduction, Rosenmund reaction, Aldol reactions, Oppenauer oxidation and many other transformations reported in the literature, involve carbonyl compounds as one of the major substrates[8]. Among various known processes for the synthesis of carbonyl compounds, the most well established method is the oxidation of alcohol. Whether the resulting carbonyl compound is an aldehyde, a ketone or a carboxylic acid depends on the nature of alcohol and on the oxidizing agent. To achieve the desired carbonyl product selective oxidation of alcohols is done[9]. This method is extensively used to achieve carbonyl compounds both on the laboratory scale as well as in large scale synthesis in industry[10]. In recent years many alternate methods for the selective oxidation of alcohols and phenols to aldehydes or ketones respectively, following green and environmentally benign routes[11] were tried by chemists.

Molecular oxygen is a nonpoisonous and economical oxidant for the oxidative transformation of alcohols. In recent years, air oxygenation has attracted increasing attention. The development of air oxidation pathway for organic synthesis is highly desirable from the safety, availability and environmental friendliness point of view. It is presently used in several large scale oxidation reactions, catalyzed by chromium (VI) reagents[12].

For economical and environmental reasons, the use of selective catalyst for oxidation of alcohol into their corresponding carbonyl compounds is an essential requirement in the chemical industry[13]. Now days, metal catalyzed oxidation of organic compounds is of great interest. Various catalytic methods based on transition metals have been developed[14]. Catalytic oxidation has great significance in the chemical industry due to its green and cleaner approach.

Copper is an important metal, abundantly available in the earth's crust. It exists in various metalloprotein enzymes as haemocyanin, cytochrome c oxidase etc. These enzymes play an important role in various bio-oxidation reactions. Due to these natural bio-oxidation reactions copper has drawn particular consideration as a catalyst. However, from the industrial point of view copper can activate molecular oxygen and hydrogen peroxide with efficient catalytic activity and selectivity. Thus copper can be the attractive alternative, as a catalyst for conventional oxidation method.

Generally, the oxidation of alcohols and phenols has been achieved by the use of inorganic oxidizing agents conventionally chromates or permanganates[15]. However, the problems associated with these hazardous oxidants are there expense and production of venomous heavy metal waste in large quantities. The use of toxic substances as oxidants, in large quantities, is not acceptable from a green chemistry point of view. Thus developing an efficient system for oxidation of organic substrate is of great importance both economically as well as environmentally. Hence, much attention has been paid to the selective oxidation of phenol following the catalytic route. For environmental concern, methodologies like selective oxidation by green process are in high demands[16]. Oxygen, as an alternative to the inorganic oxidizing agent will be a better option as it is cheaper and less polluting oxidant[17]. Thus, the application of molecular oxygen for the oxidation of organic compound can be a novel green proposal. Now a day, from a green chemistry point of view, oxidation of organic compounds with the utilization of molecular oxygen is an emerging area. Hence, in the present studies my focus is directed on the oxidation reactions proceeding under environmentally benign conditions in aqueous medium, particularly employing ***"on water"*** reaction concept.

CONCLUSION

Efficient reactions in aqueous organic chemistry do not require soluble reactants, as had been thought. A newly developed "on water" protocol is characterised by short reaction times, and the products are easy to isolate. Environmental benefits of using water are additionally highlighted in relation to the Twelve Principles of Green Chemistry. The field of aqueous organic synthesis has been frequently and broadly reviewed. This project work has, therefore, been titled as "on water" reactions.

FREERENCES

1. Hayashi, Y.; In water or in the presence of water, *Angew. Chem. Int. Ed.* **45** (2006) 8103.
2. Price, B.K.; Tour, J.M.; Functionalization of single-walled carbon nanotubes "on water", *J. Am. Chem. Soc.* **128** (2006) 12899.
3. Breslow, R.J. ; The hydrophobic effect in reaction mechanism studies and in catalysis by artificial enzymes, *Phys. Org. Chem.* **19** (2006) 813.
4. Minakata, S.; Komatsu, M.; Organic reactions on silica in water, *Chem. Rev.* **109** (2009) 711.
5. Narayan, S.; Jhon, M.; Finn, M.G.; Fokin, V. V.; Kolb, C.; Sharpless, K.B.; "On Water": unique reactivity of organic compounds in aqueous suspension, *Angew. Chem. Int. Ed.* **44** (2005) 3275.
6. Chanda, A.; Fokin, V.V.; Organic synthesis "on water", *Chem. Rev.* **109** (2009) 725.
7. Baeyer, A.; Drewsen, V.; Baeyer-Drewsen indigo synthesis, *Ber.* **15** (1882) 2856.
8. Love, B.; Snader, K.M.; The Hantzsh reaction: oxidative dealkylation of certain dihydropyridines, *J. Org. Chem.* **30** (1965) 1914.
9. Balcha, T. ; Strobol, J.R.; Fowler, C.; Dash, P.; Scott, R.W.J.; Selective aerobic oxidation of crotyl alcohol using Au-Pd core-shell nanoparticles, *ACS Catal.* **1** (2011) 425.
10. Abad, A.; Almela, C.; Corma, A.; Garcia, H.; Efficient chemoselective alcohol oxidation using oxygen as oxidant, *Tetrehedron* **62** (2006) 6666.
11. Sheldon, R.A.; Arends, I.W.C.E.; Brink, G.J.; Dijksman, A.; Aqueous phase organometallic catalysis, *Acc. Chem. Res.* **35** (2002) 774.
12. Cainelli, G.; Cardillo, G.; Chromium oxidation in organic chemistry, *Springer*, Berlin 1984.
13. Arends, I.W.C.E.; Sheldon, R.A.; Modern oxidation methods, *Wiley-VCH*, Wienheim 2010.
14. Schultz, H.J.; Sigman, M.S.; Recent advances in homogenous transition metal-catalyzed aerobic alcohol oxidations, *Tetrahedron* **62** (2006) 8227.
15. Lee, D.G.; Spitzer, U.A.; Aqueous dichromate oxidation of primary alcohols, *J. Org. Chem.* **35** (1970) 3589.

16. Hoover, J.M.; Sthal, S.S.; Highly practical cooper (I)/TEMPO catalyst system for chemoselective aerobic oxidation of primary alcohols, *J. Am. Chem. Soc.* **133** (2011) 16901.

17. Xie, Y.; Mo, W.; Xu ,D.; Shen, Z.; Sun, N.; Hu, B.; Hu, X.; Efficient NO equivalent for activation of molecular oxygen and its application in transition-metal-free catalytic aerobic alcohol oxidation, *J.Org. Chem.* **72** (2007) 4288.