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ENVIRONMENTALLY BENIGN PATHWAY FOR ORGANIC REACTIONS

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ABSTRACT

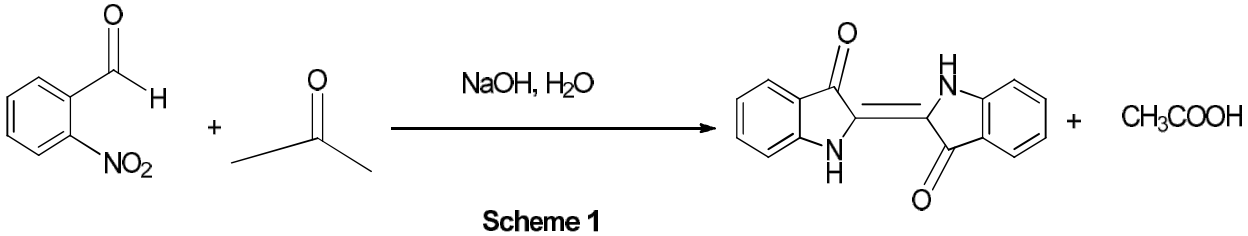
Solvents and reagents play very significant role in synthetic chemistry. The selection of these two should be environmentally benign. Use of environmentally benign chemical in organic synthesis is an important goal from an ecological point of view. Environmental benefits of using water are additionally highlighted in relation to the Twelve Principles of Green Chemistry. Using water as solvent promotes considerable rate enhancements and operational simplicity. The present article is aimed with the goal of promoting water as a solvent in organic reactions.

KEYWORDS: On Water Reactions, Green Chemistry, Knoevenagel Condensation, Aldol Condensation, DABCO Catalyst, Organocatalyst

Organic reactions that take place at the interface of water for water-insoluble compounds, and in aqueous solution for water soluble compounds, has added a potent dimension for organic synthesis under more advantageous, profitable and ecological green conditions. Terms frequently used in the literature for reactions in aqueous medium are in water and on water (Hayashi, 2006) 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 (Price and Tour, 2006). Considerable rate acceleration in on water organic synthesis can be explained on the basis of hydrophobic effects (Breslow, 2006), where non-polar reactant molecules are forced together in the rate determining transition state. The rate of on water acceleration varies in different organic moieties (Minakata and Komatsu, 2009). Besides this other advantages associated with on water reactions are ease of product isolation and safety, due to its high heat capacity (Narayan *et al.*, 2005) 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 (Chanda and Fokin, 2009). Baeyer and Drewsen in 1882 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.



Scheme 1

Various on water reactions have been frequently discussed in literature. Besides solvent, reagent and catalyst used should also be environment friendly. Many named organic reactions like the Meerwein-ponndorf-Verley reduction, Rosenmund reaction, Aldol reactions, Oppenauer oxidation etc are reported in the literature, proceeded using water as a solvent. Attempt has been made to review aldol and knoevenagel condensation reactions proceeded in solvent benign conditions.

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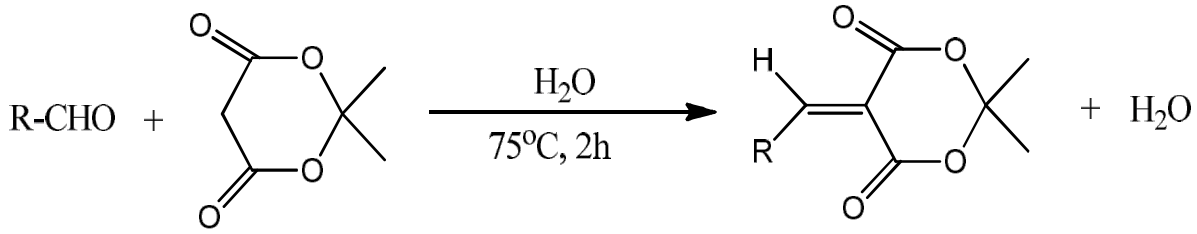
ON WATER KNOEVENAGEL CONDENSATION REACTIONS

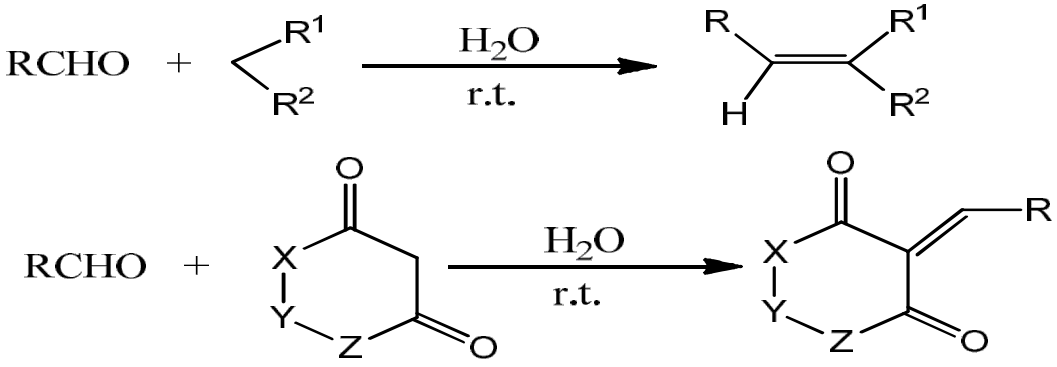
Environmentally benign, uncatalysed Knoevenagel condensation of Meldrum's acid and aldehydes in water has been performed by Bigi *et al.*, 2001 (Scheme 2).



R = aromatic, heteroaromatic

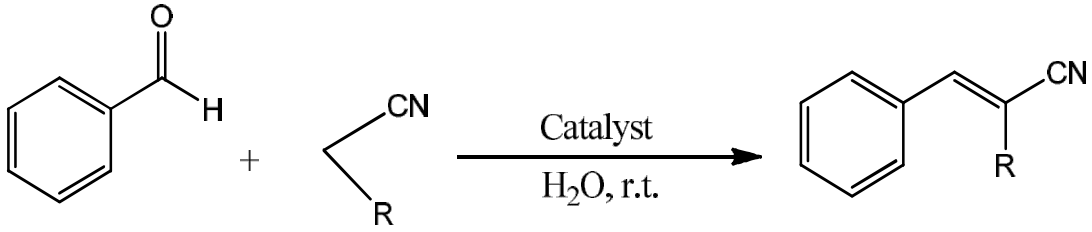
Scheme 2

Ecofriendly, convenient, uncatalysed Knoevenagel condensation of aromatic or heteroaromatic aldehydes with active methylene compounds in aqueous medium has been examined by Deb and Bhuyan, 2005 (Scheme 3). The reaction proceeded with excellent yields of the products at room temperature.



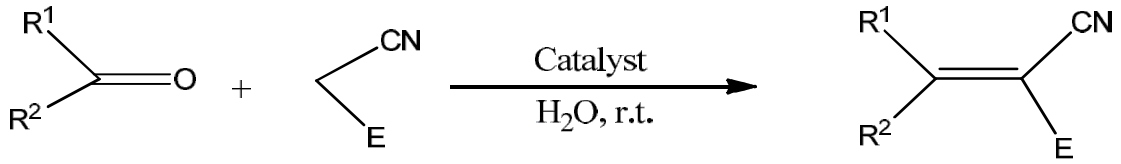
Scheme 3

The Knoevenagel condensation of aromatic aldehydes with malononitrile, efficiently accelerated by 1-aminoethyl-3-methylimidazolium hexafluorophosphate catalyst was reported by Cai *et al.*, 2006 (Scheme 4). Recyclable catalyst can be reused at least six times without loss of activity.



R = CN or CO_2Et **Scheme 4**

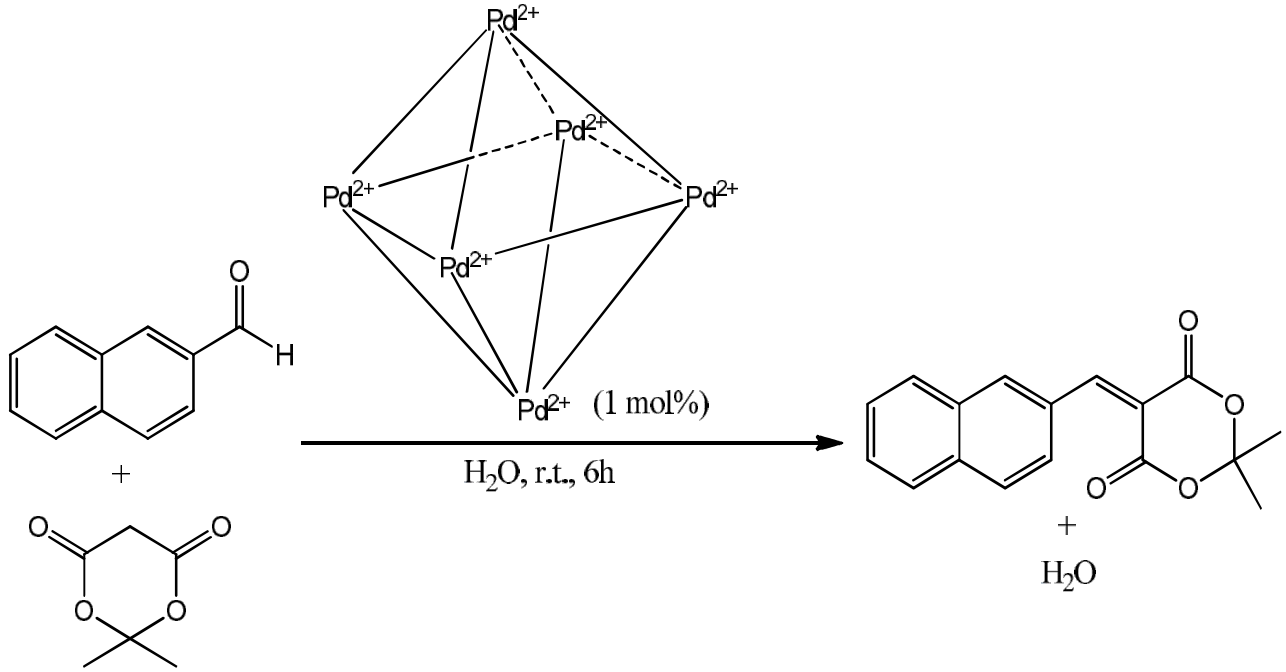
Simple and efficient green method for Knoevenagel condensation of aromatic / aliphatic / heterocyclic α, β-unsaturated aldehydes and ketones with active methylene compounds has been developed by Xu *et al.*, 2010 (Scheme 5). The method afforded corresponding substituted electrophilic alkenes up to 100% in water at room temperature. The reaction was catalysed by DABCO (1, 4-diazabicyclo [2.2.2] octane)-base ionic liquid catalysts. The catalyst could be recycled at least seven times without noticeably decreasing the catalytic activity.



Catalyst = $[C_4dabco]\ [BF_4]$ ionic liquid

Scheme 5

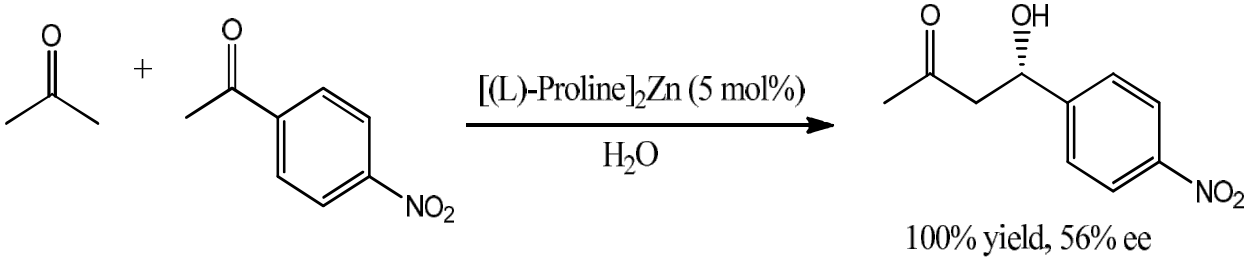
In water the Knoevenagel condensation of aromatic aldehydes under neutral conditions has been performed by Murase *et al.*, 2012 (Scheme 6). The reaction is accelerated by a catalytic quantity of cationic coordination cage catalyst and afforded the product in up to 96% yield.



Scheme 6

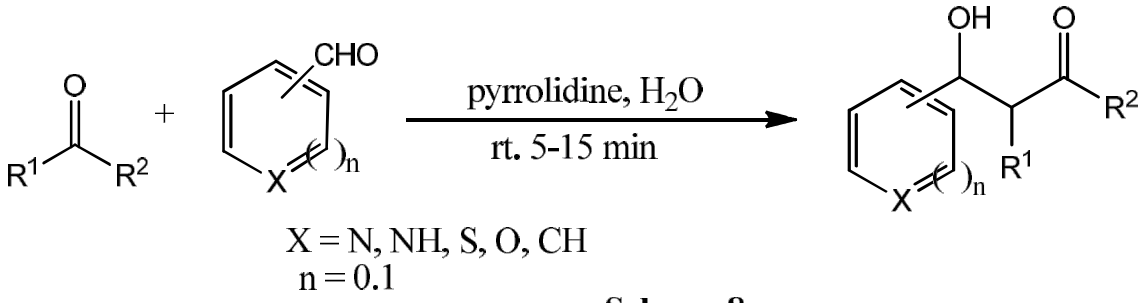
ON WATER ALDOL CONDENSATION REACTIONS

Zn-Proline catalysed direct aldol condensation of p-nitrobenzaldehyde and acetone in aqueous medium was proceeded by Darbre and Machuquerio, 2003 (Scheme 7) giving quantitative yields and enantiomeric excesses up to 56% at room temperature.



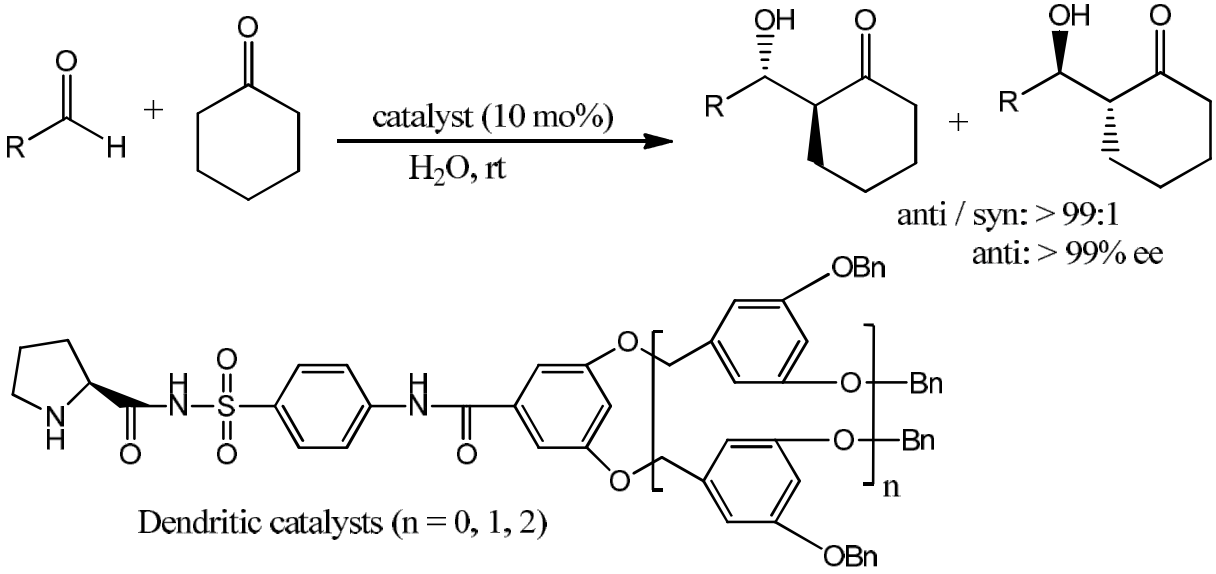
Scheme 7

Direct cross-aldol condensation of aromatic or heterocyclic aldehydes and ketones catalysed by pyrrolidine in water afforded 93% yield of the product (Scheme 8). The reaction was given by Chimni and Mahajan, 2005.



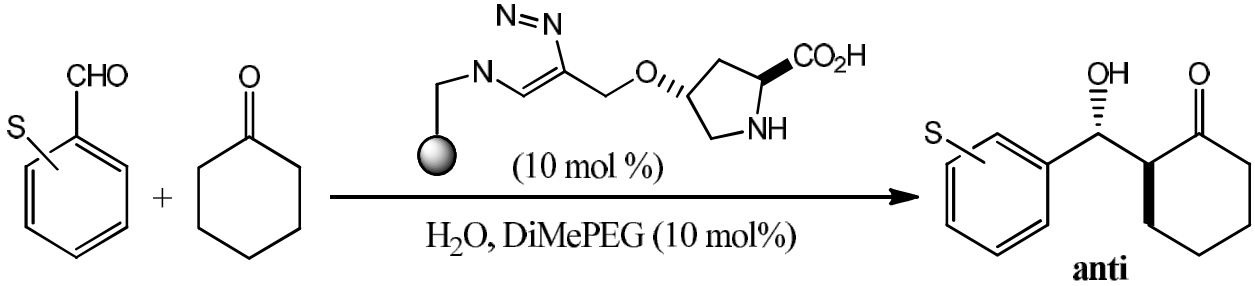
Scheme 8

Asymmetric direct aldol condensation of ketones in water catalyzed by reusable chiral dendritic catalysts derived from N- prolylsulfonamide has been afforded by Wu *et al.*, 2006 (Scheme 9). The product was isolated up to the yield of 99% with excellent anti diastereoselectivities (99:1) and enantioselectivities (> 99% ee).



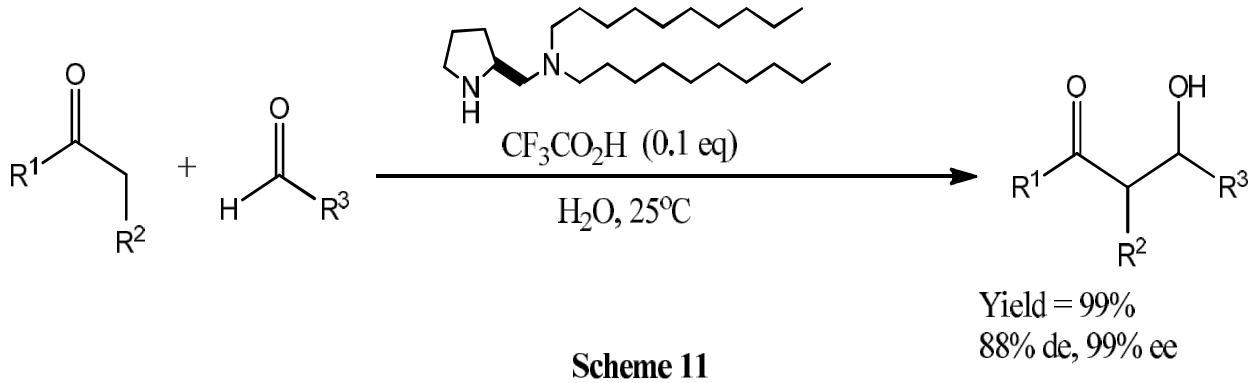
Scheme 9

Asymmetric aldol condensation between aromatic aldehydes and cyclohexanone in water has been reported by Font *et al.*, 2006 using polystyrene resin supported 4-Hydroxyproline organocatalyst. The reaction was marked with high stereoselectivity (Scheme 10) and yield was increased using catalytic amounts of DiMePEG.



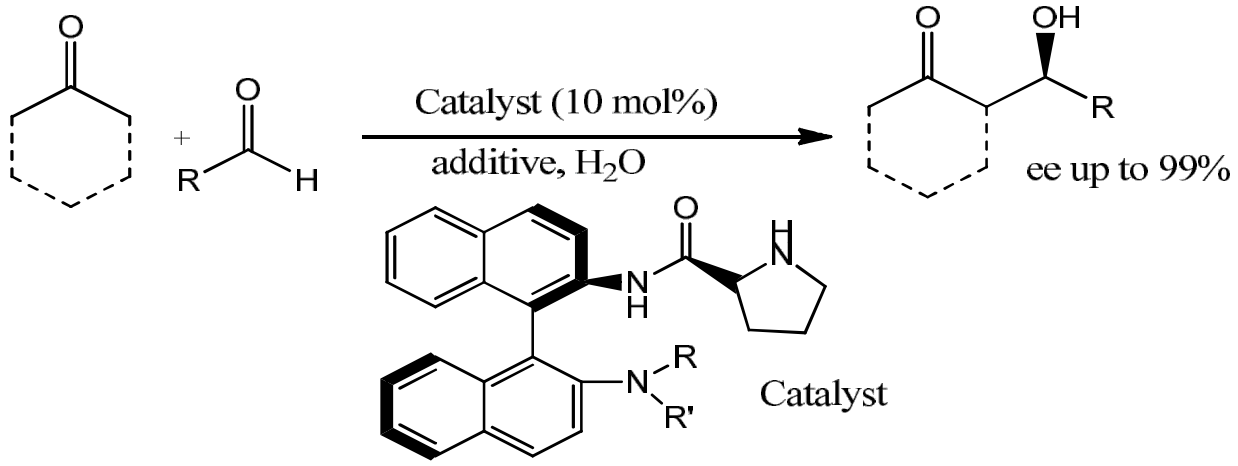
Scheme 10

Mase *et al.*, 2006 developed organocatalyst catalysed direct asymmetric cross aldol condensation reaction (Scheme 11) in water and afforded the excellent yield of products with high enantiomeric excess.



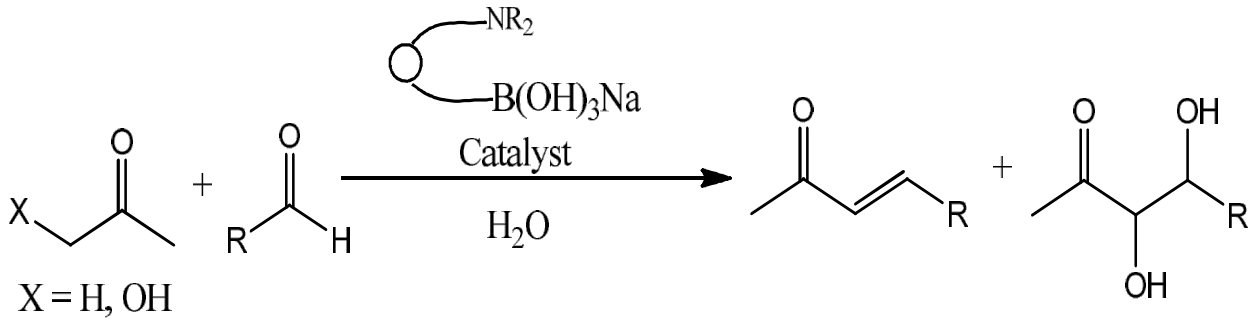
Scheme 11

On water direct aldol condensation of cyclohexanone and other ketones with different aldehydes has been reported by Guizzetti *et al.*, 2007 (Scheme 12). The reaction afforded good yield of the product with high diastereo selectivity. The reaction was promoted bychiral organocatalyst 1,1'- Binaphthyl-2,2'- diamine-based (S)-prolinamide in the presence of stearic acid.



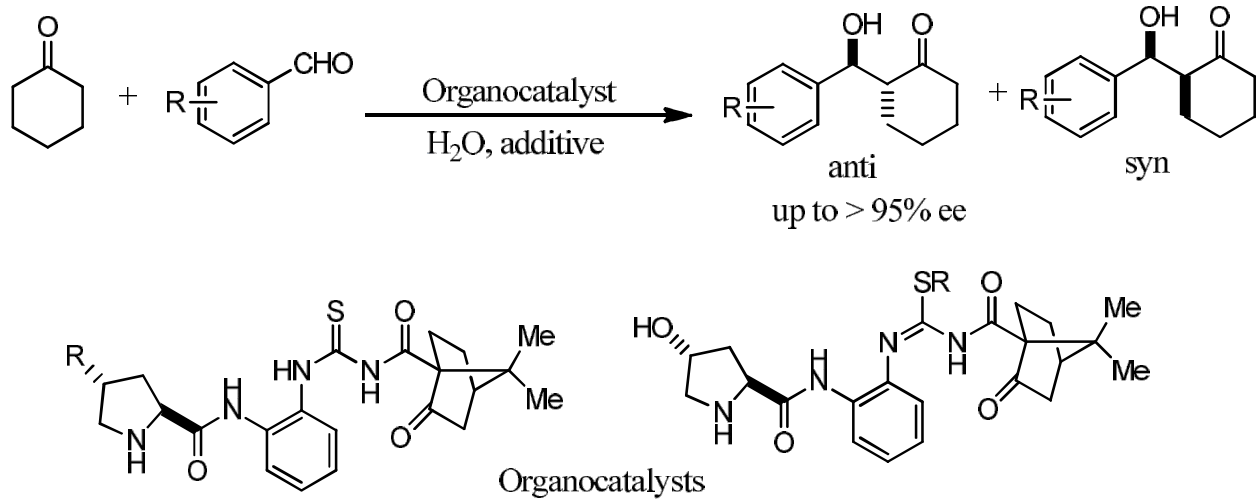
Scheme 12

The aldol condensation between hydroxy acetone or acetone with aldehyde in water catalysed by N- Butyl-1-benzimidazole-2-phenylboronic acid hydroxide complex has been reported by Aelvoet *et al.*, 2008 (Scheme 13). The reaction afforded unsaturated methyl ketones and hydroxyacetone.



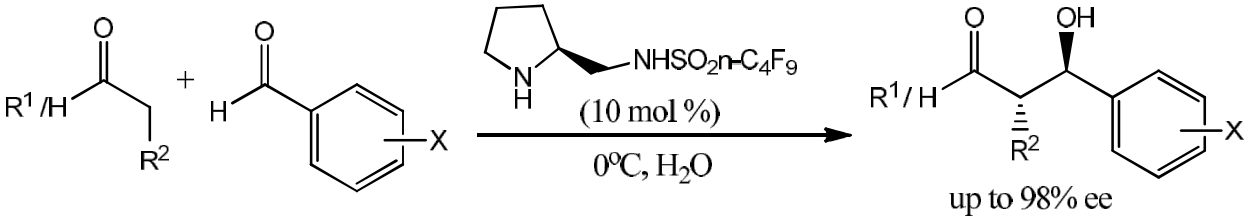
Scheme 13

On water asymmetric aldol reaction catalysed by camphor containing organocatalysts has been reported by Tzeng *et al.*, 2008 (Scheme 14). The product obtained with high to excellent diastereo- and enantioselectivities.



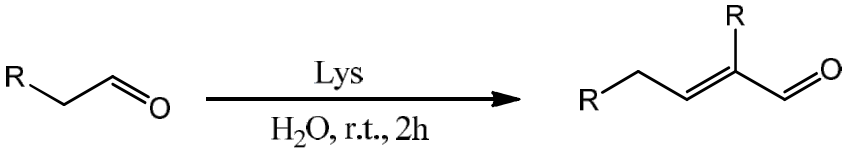
Scheme 14

Highly enantioselective on water aldol reactions of ketones or aldehydes with aromatic aldehydes has been examined by Zu *et al.*, 2008 (Scheme 15). The reaction was catalysed by recyclable fluorous (S) pyrrolidine sulfonamide organocatalyst. The reported yield was up to 92%.



Scheme 15

Solvent free green method for a self condensation of aldehydes has been accomplished by Watanabe *et al.*, 2010 (Scheme 16). The reaction was promoted by the catalytic amount of lysine in water and afforded a good yield of α,β-unsaturated aldehydes.



Scheme 16

CONCLUSION

Using water as a reaction medium has enriched the understanding of sustainable organic chemistry. Reactions in water suspensions showed great rate accelerations over homogenous solutions. A newly developed on water protocol is characterised by short reaction times, and the products are easy to isolate. The field of aqueous organic synthesis has been frequently and broadly reviewed. This article gives us a glimpse of the stimulating role of water in several Aldol and Knoevenagel condensation reactions. These on water reactions proceed with highest chemical efficiency via green pathway. Reproducible, safe procedures illustrate utility of aqueous media and the practical simplicity afforded.

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