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Conventional to "Go Green" Approach in organic Reaction

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Abstract: In the recent times, the green method of chemical reactions becomes very popular. The scientists are now using the non–hazardous reagents and solvents to design a chemical reaction. The conventional method of most common organic rearrangements e.g Claisen, Fries etc and condensation reactions e.g Aldol, Benzoin, Knoevenegal etc. are designed successfully in greener approach. This article describes green approach of some of these reactions.

Keywords: Conventional, Green Synthesis

Introduction:

The main target of green chemistry is to minimize the environmental pollution by reducing use of toxic reagents, solvents and generation of toxic products. The emerging area of green chemistry is to design synthetic methodologies without use of toxic materials and also to eliminate the generation of toxic product. According to P. T Anastas & J. C Warner [1], "Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products". Since the last two decades, the approach of green synthesis is becoming the growing interest among the scientists. The green synthesis of the organic compounds is taken place generally by using water as solvent, supercritical fluids, ionic liquids or solid state reaction without using solvents or by microwave irradiation or by using catalysts. The pioneer of green chemistry P. T Anastas & J. C Warner [1] discussed twelve principles of green chemistry which are approved by USEPA. The 12 principles are: 1. Prevent waste 2. Design safer chemicals and products 3. Design less hazardous chemical syntheses 4. Use renewable feedstocks 5. Use catalysts, not stoichiometric reagents 6. Avoid chemical derivatives 7. Maximize atom economy 8. Use safer solvents and reaction conditions 9. Increase energy efficiency 10. Design chemicals and products to degrade after use 11. Analyze in real time to prevent pollution 12. Minimize the potential for accidents. The advantages of green methods over the conventional methods of some common organic reactions will be discussed in this paper.

Approach of Green Synthesis:

The Starting Materials in the green synthesis should be:

- Renewable
- Non-hazardous
- Simple structuring

Reaction Condition

- Preferably one-pot synthesis

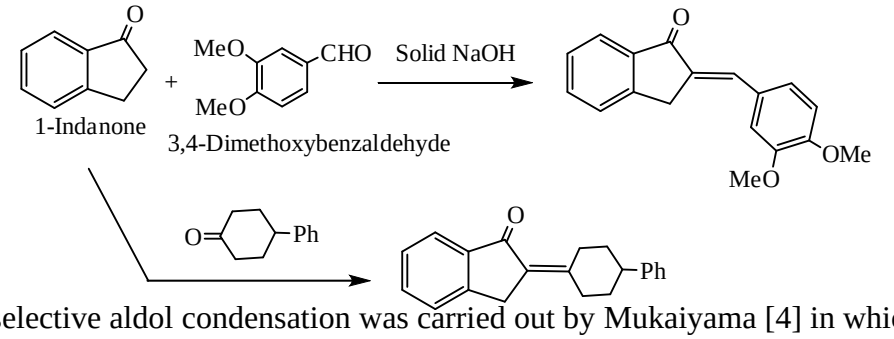
- Atom-economical, By-products should not be hazardous
- Solid state reactions preferred
- Green organic solvents/bio-based solvents should be used
- Catalyst may be used.

Products

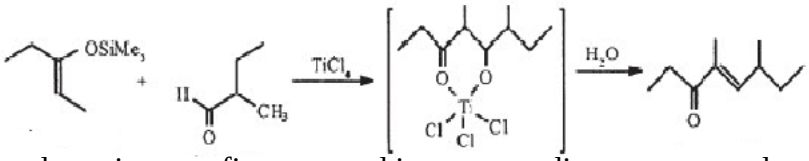
- By-products if obtained should be non-hazardous and biodegradable.

Aldol Condensation:

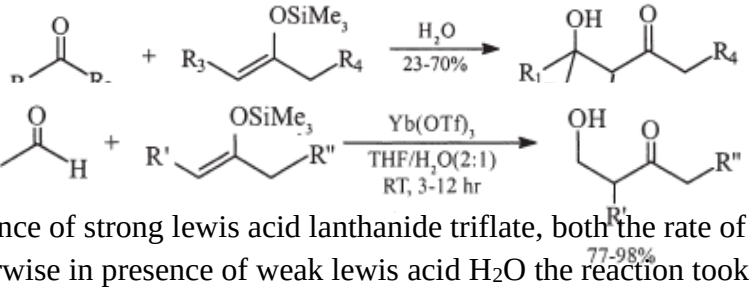
These reactions have been carried out by grinding two solids in a mortar pestle at r.t. by mechanochemical mixing until it gives yellowish brown colour. Solid NaOH is added on further stirring until solid is obtained. [2,3]



A stereoselective aldol condensation was carried out by Mukaiyama [4] in which an silyl enol ether of 3-pentanone was reacted with an aldehyde (2-methyl-butanal) in presence of $TiCl_4$ to yield an aldol product.



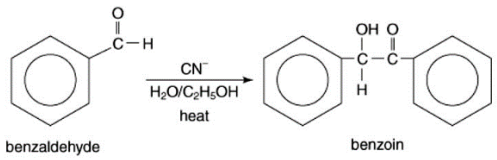
The aldol condensation was first reported in water medium as green solvent in 1986 [5].



In presence of strong lewis acid lanthanide triflate, both the rate of the reaction and the yield are increased; otherwise in presence of weak lewis acid H_2O the reaction took several days for completion [6].

Benzoin Condensation using enzymatic catalyst:

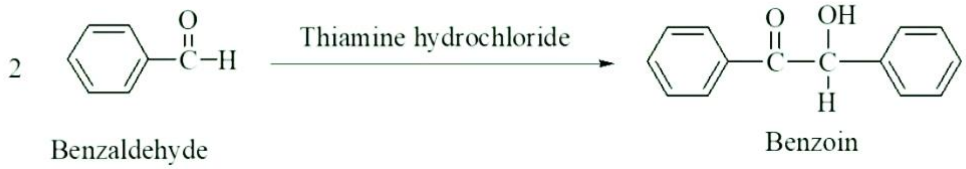
In Benzoin Condensation, two molecules of benzaldehyde undergo self-condensation to give α-hydroxyketone in presence of cyanide as catalyst.



Cyanide salts and HCN produced are hazardous and toxic.

Green Approach:

Breslow [7] in 1958 reported a safer alternative route by using a biocatalyst vitB1 thiamine hydrochloride.



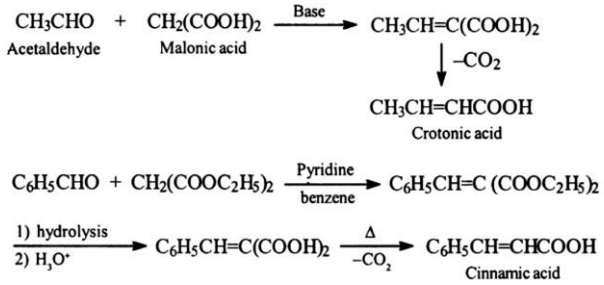
Later, Breslow found that the benzoin condensation in aqueous media using inorganic salts (e.g., LiCl) is about 200 times faster than in ethanol (without any salt). The addition of ν-cyclodextrin also accelerates the reaction, whereas the addition of β-cyclodextrin inhibits the condensation [8].

Advantages to use the biocatalyst:

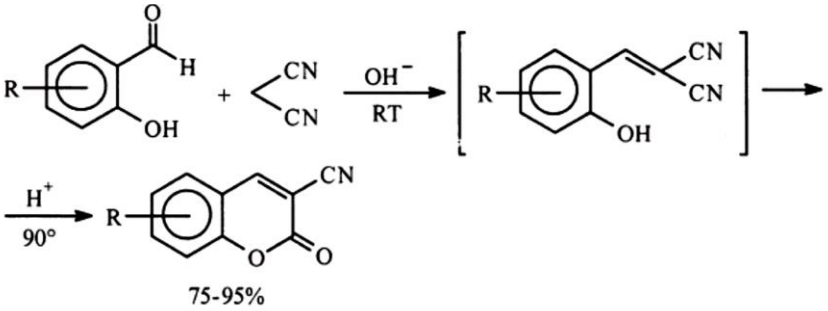
- Biocatalyst is non-hazardous and biodegradable
- Reaction takes place in mild reaction condition
- Products with high grade purity will be produced compared to the conventional chemocatalyst.

Knoevenagel Condensation:

The condensation of aldehydes or ketones, with active methylene compounds (especially malonic ester) in presence of a weak base like ammonia or amine (primary or secondary) is known as Knoevenagel reaction. However, when condensation is carried out in presence of pyridine as a base, decarboxylation usually occurs during the condensation. This is known as Doebner modification.



Green Approach

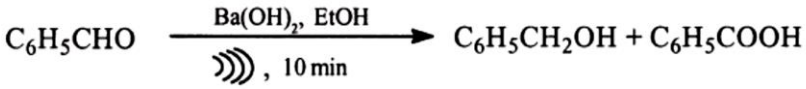


The Knoevenagel reaction has been carried out between aldehydes and acetonitrile in water. Thus, salicylaldehydes react with malononitrile at room temperature in the heterogeneous aqueous alkaline medium to give α-hydroxybenzylidene malononitriles, which are converted directly to 3-cyanocoumarins by acidification and heating [9].

Cannizaro Reaction

The aldehydes having no α-H a atom (e.g., HCHO, PhCHO, Me_3CCHO etc.) when heated with strong bases (usually 50% aqueous sodium or potassium hydroxide solution), undergo a self-oxidation-reduction reaction in which one molecule of the aldehyde oxidized to sodium salt of carboxylic acid and another molecule gets reduced to the corresponding alcohol, This reaction is known as the Cannizzaro reaction.

The Cannizarro reaction under heterogenous conditions catalysed by barium hydroxide is considerably accelerated by sonication. The yields are 100% after 10 min, whereas no reaction is observed during this period without the use of ultrasound [10].



Fries Rearrangement

Fries rearrangement is carried out by heating a mixture of substrate and aluminium chloride to produce phenolic ketones.

In the greener approach, the reaction occurs in microwave oven in enhanced rate. Thus, a mixture of p-cresyl acetate and anhydrous aluminium chloride are heated in dry chlorobenzene in a sealed tube in a microwave oven for 2 min to give 85% yield of the product [11].

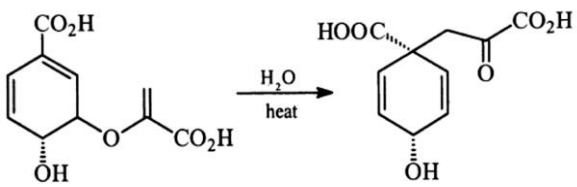
p-Cresyl acetate

2-Hydroxy-4-methyl acetophenone
85%

Claisen Rearrangement

This reaction involves the thermal rearrangement of allyl phenyl ethers to o-allyl phenol by 3,3-sigmatropic shift.

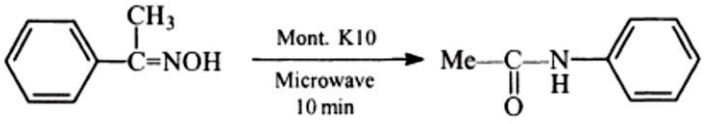
The first reported use of water in promoting Claisen rearrangements was the rearrangement of chorismic acid reported in 1970 [12].



Beckmann Rearrangement

In conventional method, Beckmann rearrangement of oximes of ketones are converted into anilides by heating with acidic reagents like PCl_5, HCOOH, $SOCl_2$ etc.

In greener approach, the oxime of a ketone is mixed with montmorillonite and irradiated for 7 min in a microwave oven to give corresponding anilide in 91 % yield [13].



Acetophenone oxime — Acetanilide (91%)

Advatages of using Green method:

- Minimization of waste (Principle 1)
- Atom Economy (Principle 2)
- Safer solvents and auxiliaries (Principle 5)
- design for energy efficiency (Principle 6)
- Use of selective catalysts (Principle 9)
- Cost effective
- Easy to collection of purified product.
- Use of energy is less
- Short time of reaction.

Conclusion:

In conclusion, green chemistry principles offer a transformative framework for the chemical synthesis which leads to safer, environment-friendly and cost-effective processes. As we confront the pressing challenges of pollution, resource depletion, and climate change, the adoption of green chemistry becomes increasingly imperative. This approach enables us to reimagine age-old practices, welcome the use of sustainable resources, and actively curb the generation of waste. This transformation paves the path towards a future characterized by resilience and prosperity.

Acknowledgement:

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