GREEN ALTERNATIVES –TO TRADITIONAL ORGANIC SOLVENTS

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Abstract: *Current objective of green chemistry is to reduce environmental harm by traditional organic solvents by finding new solvents which are desirable green alternatives .The main purpose of this review is to explain how green solvents can be prudently and ecologically profitable over classical processes.The trait of these solvents called green solvent is: They are less toxic, easily accessible, can be reused and also have very good efficiency. Which is essential purpose organic synthesis and separation processes.The use of green solvents can furnish supplemental control over activity and selectivity in catalysis such as bio-catalysis, homogeneous and heterogeneous catalysis. Vegetable oil is an alternative to organic solvents derived from petroleum having comparatively good properties and is more eco-friendly. As large quantity of solvents are used in polymer and plastic industries.So,the polymerization methods using green solvents are under research. Water, liquid CO_2 ,fluorous solvents, organic carbonates, ionic liquids and biosolvents are other alternative eco-friendly solvents.*

Keywords :*Green alternatives, bio-catalysis, fluorous solvents, organic carbonates, biosolvents.*

INTRODUCTION:

Most of the chemical reactions involved in organic synthesis and purification process, considerable quantity of solvents are used[1-2].These solvents include mostly VOCs which cost approximately 482,694,000,000.00 Rs./year globally [3-4].For dissolution purposes, cleaning purposes, extraction, crystallization and to reduce concentrations solvents are essential[5].Approximately,15-20 million ton of VOCs is released every year into atmosphere from industries[6]which comprises solvents such as volatile

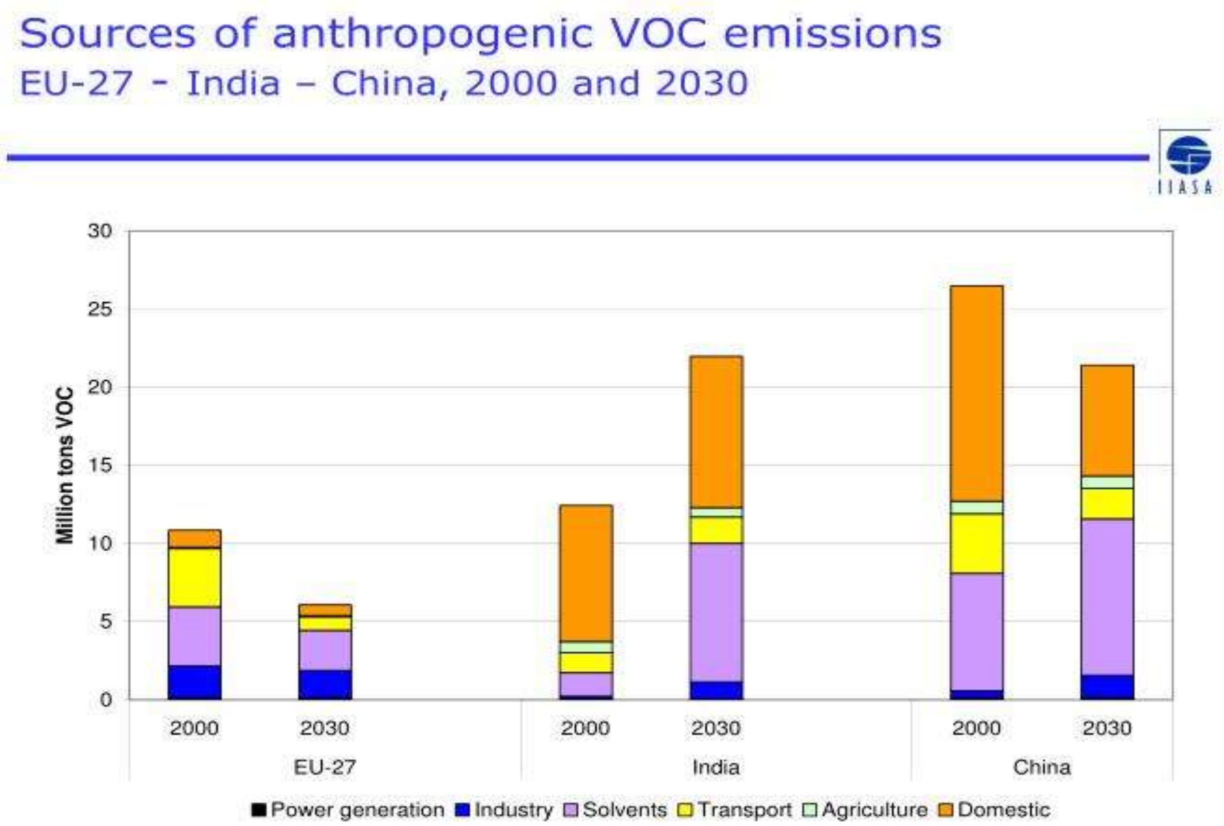


figure.1-sources of anthropogenic VOC emissions [7].

liquids in large amount causing environmental pollution and superfluous wastage[5].Furthermore, protracted exposure to hazardous solvents like CCl_4 and $CHCl_3$ has damaging influence on living beings mainly on respiratory and nervous system. On the basis of data published by WHO, protracted exposure to environmental pollutants cause approximately ¼ of the ailments existing at the moment[8-9].Prime objective of green chemistry is to reduce environmental harm by traditional organic solvents by finding new desirable green alternatives.One of the best solution is solvent- free processes. But the use of solvents is inevitable due to their crucial role. Consequently, there are two main plans: (i)Replacement of organic solvents derived from petroleum with solvents from sustainable resources, (ii)replacement of solvents which are hazardous ones with eco-friendly solvents having comparatively good EHS*[10-11].Green solvents comprises water, supercritical CO_2, ionic liquids, organic carbonates, biosolvents, fluorous solvents and non- toxic liquid polymers[12-15].

EHS*- Environmental, health and safety

GREEN ALTERNATIVES:

Solventless process- A greener reaction:

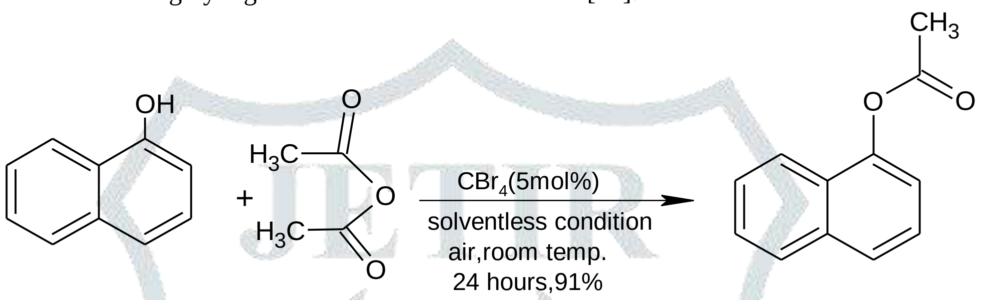
Previously, It was believed that reaction is impossible without using solvent. But nowadays, many reactions can be done in solid state without using solvent and are comparatively efficient and selective to greater extent. Usage and production of hazardous substances is reduced or abolished in such reactions . These type of reactions are in accordance with the 5^{th} principle of green chemistry and comprises following factors[16].

- Highly economic.
- Removal of solvent after completion of reaction is not required i.e no need for purification.
- As the reactants are in excess so that rate of reaction is quite high.
- No use of solvents is more eco-friendly.

Some organic reactions under solvent-free conditions are:

Carbon tetrabromide catalyzed acylation reaction:

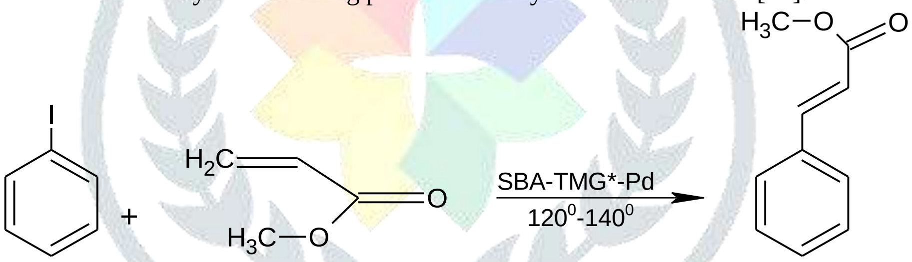
CBr_4 acts as mild lewis base and is highly regioselective and chemoselective[17].



Scheme-1: CBr_4 catalyzed acylation reaction of alpha-naphthol

Palladium catalyzed Heck reaction:

In this reaction, alkenes are reacted with aryl halides using palladium catalyst based on SBA-15[18].

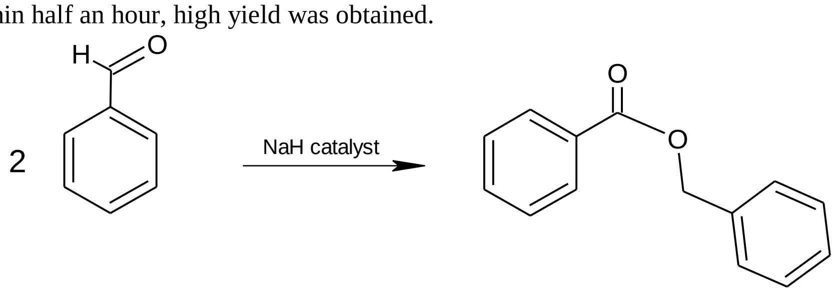


Scheme-2: Heck reaction

TMG*- 1,1,3,3-Tetramethylguanidium

Tischenko reaction:

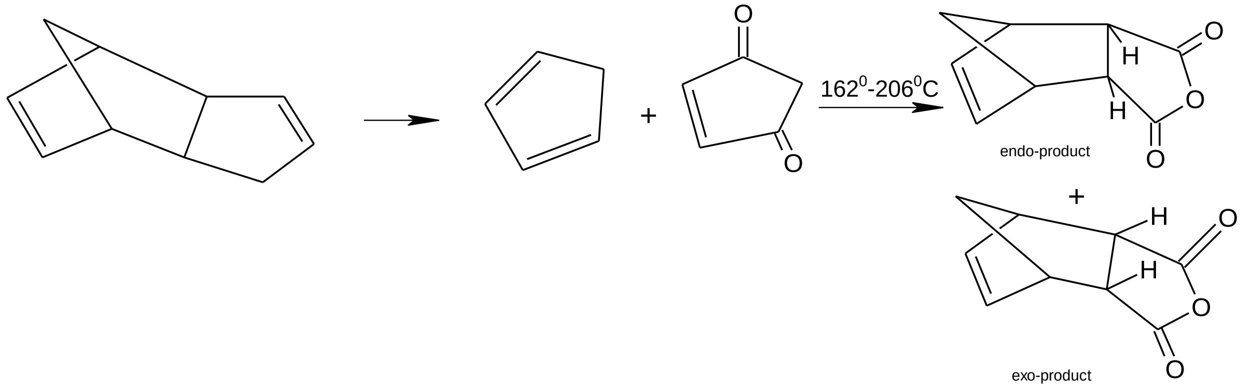
In this reaction, aldehydes are converted into esters by using NaH catalyst and high speed ball milling. Tischenko reaction of aromatic aldehydes was performed. Within half an hour, high yield was obtained.



Scheme-3: Tischenko Reaction

Diels-Alder reaction: A thermodynamically controlled solvent-free reaction

In this, mixture of dicyclopentadiene and dienophile was heated by Huertas et al.in 2009. Cyclopentadiene was formed in situ[19]. Majority of exo and endo product is time dependent.



Scheme-4: Diels Alder Reaction

Reformatsky reaction:

Tanaka et al. in 1990 performed this reaction by mixing aldehyde/ketone, a bromoester and zinc-ammonium chloride in pestle and mortar and was kept at room temperature for few hours[20].

$$C_6H_5CHO + BrCH_2COOC_6H_5 \xrightarrow[NH_4Cl]{Zinc} C_6H_5CH(OH)CH_2COOC_6H_5$$

Scheme-5: Reformatsky Reaction

Separation processes done by mechanical extraction are solventless. But work without solvent is not always possible. So use of less toxic solvents which can be regain without deficiency is requested.

Water as a green solvent:

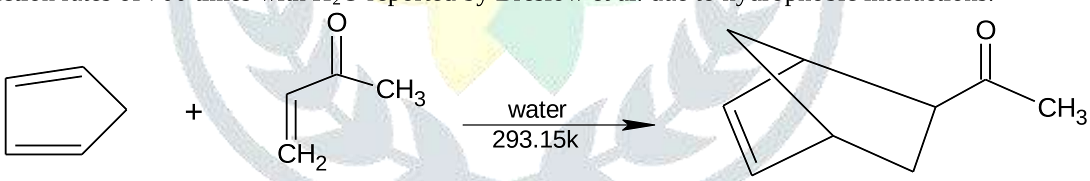
Use of water as a green solvent is one more solution to diminish an effect of solvent emission. Water can be used as a reaction medium for reaction and is eco-friendly. Water is available in ample amount and is cheapest. Furthermore, water is incombustible, non poisonous, having no odor and color. Moreover, insolubility of oxygen in water can be beneficial for metal catalysts.

In all chemical processes occurring in living organisms, water is the most useful solvent[21-23].At temperature above 647.15K and pressure above 218.11 atm. Supercritical water act as a non polar solvent due to H-bonding. So O_2 and non polar solvents becomes soluble in it[24].

Using water as a solvent, efficiency of the reaction involving conversion of 3^0 benzyl alcohols into their vicinal halogen substituted derivatives in the presence of N-halosuccinimides is increased[25].Some other reactions accompanied by increased reaction rates by using water are:

Diels-Alder reaction:

An increased reaction rates of 700 times with H_2O reported by Breslow et al. due to hydrophobic interactions.

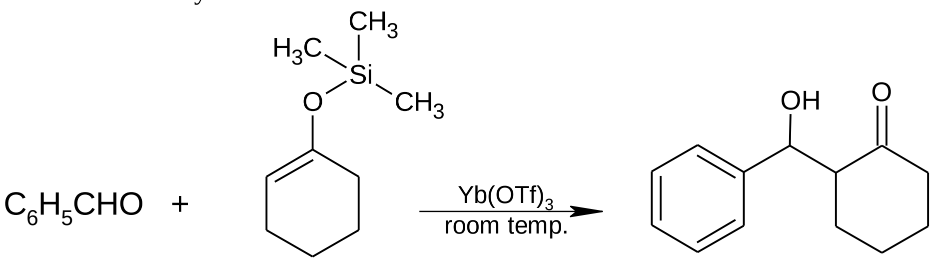


Reactions involving formation of carbocations:

• These reactions generally requires lewis acids/protic acids and are sensitive to moisture. But the replacement of these acids with metallic salts such as $Yb(OTf)_3$ and $Sc(OTf)_3$ and their activation by water increases the yield of the reaction as:

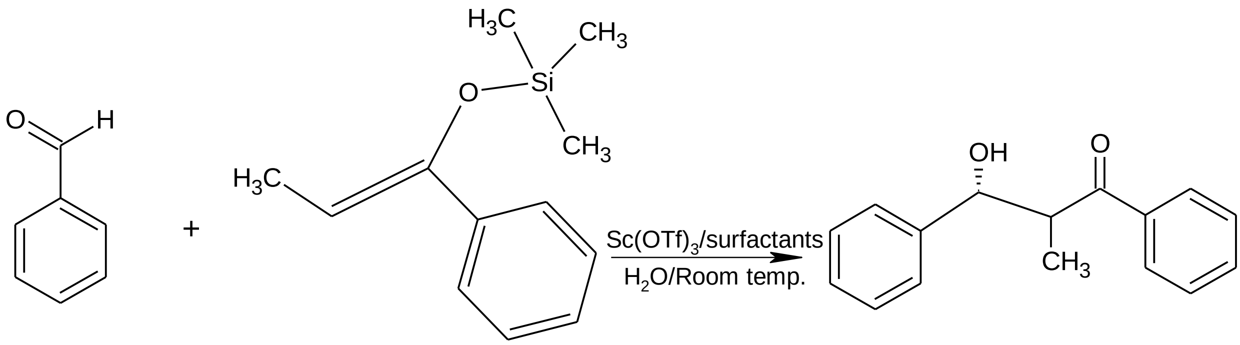
Aldol reaction:

Water increases the yield of the reaction by 9 times.



With dry THF, yield is 10% and with H_2O/THF(1:4), yield is 91%.

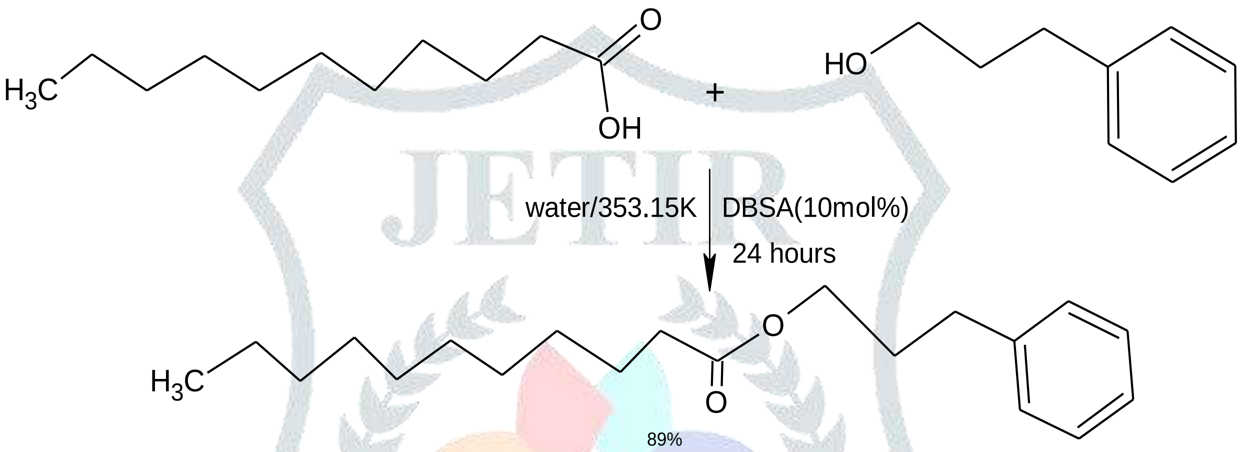
• Yields of the reactions can also be enhanced by using surfactants because they increases solubility, when such reactions are performed in water.



• The yield is further enhanced by a recently developed catalyst $Sc(DC)_3$ which have properties of both lewis acids and surfactants combined known as "LASC".

• In some cases, 'DBSA'(Dodecylbenzenesulphonic acid) is used, which is Bronsted acid-surfactant combined catalyst(BASC).

Formation of esters by using DBSA in H_2O:



89%

Formation of ethers by using DBSA in H_2O:

$$CH_2(CH_2)_{11}OH \;+\; HOCHPh_2 \xrightarrow[\text{water/80}^0\text{C,24hours}]{\text{DBSA(10mol\%)}} CH_3(CH_2)_{11}OCHPh_2$$

89%

Thus, water is unique solvent due to its characteristic properties which can be modified as per desire for chemical reaction[26-29].Nevertheless, low solubility of organic compounds in water and high reactivity of water with organometallic compounds limits its applications. Furthermore, in dyeing of cotton, water can not be used as a solvent because of various side reactions takes place which lower the quality of the dyestuff[3].

Supercritical CO_2 as a green solvent:

A supercritical fluid can transit solid materials like gas and also has dissolution properties like liquids. Supercritical carbon dioxide is a green solvent and is frequently used as supercritical fluid[21]. Polymer industries are also using supercritical carbon dioxide in place of traditional organic solvents on account of their high solubility[30] and less energy requirements. Supercritical $C0_2$ as a green solvent has wide applications in extraction of caffeine from coffee, hop oil extraction, essential oil formation, homogeneous and heterogeneous catalysis etc. Critical temp. and critical pressure of supercritical CO_2 are 304.15k and 73.0323 atm respectively. These parameters are in accordance with the requirements in enzymatic reactions. So, $scCO_2$ is the excellent solvent in biocatalysis. It is nonpoisonous and not easily recycled(prevent global warming). It is highly soluble in gases which makes it excellent solvent for hydrogen transfer and hydrogenation reactions. Furthermore, it is non polar and is an appropriate solvent for non polar compounds and also for the compounds having low polarity such as caffeine which is on account of quadripole moment of its molecules[31] and it makes it a worthy alternative over traditional organic solvents. $ScCO_2$ is very useful to synthesize and extract the molecules which are biologically active and also a very good solvent in natural products separation like proteins and carbohydrates [32].

In spite of above advantages, it has some drawbacks also. Prime drawback is its poor solubility for polar compounds and for a lot of polymers excluding fluoropolymers. So the use of co-solvents like $CHCl_3$ and CH_3OH is recommended.

Ionic liquids as a green solvent:

One of the most captivating area of research today is 'ionic liquids'(eco-friendly green alternatives) for synthetic processes. Applications of ionic liquids (ILs) and their synthesis have shown a rapid growth since last 15 years. As the definition suggests, ionic liquids are entirely made up of cations & anions and their5 melting point is either less than or equal to 373.15K [33] and which is influenced by the size and asymmetry of cations [34] and in addition due to H-bonding between cations and anions [35].Polarity of ILs is influenced by their capability to donate and accept hydrogen . This shows their good solvent properties for organic and inorganic compounds. ILs are not volatile, stable and non-combustible which makes them safer and environmentally friendly solvents over traditional organic solvents [36-37]. Thus, ILs are used in Diels-Alder reactions in place of H_2O [38], in alkylation reactions of beta-naphthol and indole in place of organic solvents [39], also in hydrogenation reactions for immobilization of catalysts [40], in polymerization [41], heck reaction [42] and in hydroformylation reactions [43]. ILs also have many industrial applications but separation of products needs distillation into organic solvents.

Organic carbonates as a green solvent:

Esters of carbonic acids known as organic carbonates have wide range of applications due to their unexpected properties. Organic carbonates are cheap, less poisonous, present in sufficient amount and are easily decomposed by biological activities. Organic carbonates have number of application in medicinal, pharmaceutical fields, in extraction, and also in batteries. Out of open & cyclic organic carbonates, cyclic carbonates in liquid state are more appropriate solvents because of their extensive temperature range and serves as green solvent [44]. No waste is produced in reactions involving organic carbonates excluding alcohols and alcohols are used to synthesize dialkyl organic carbonates and carbon dioxide. Borner et al. lately surveyed the use of dialkyl organic carbonates like ethylene, propylene & butylenes carbonates, glycerol carbonate and diethyl & dimethyl carbonates as solvents for extractions and organic reactions [45].

Biosolvent as a green solvent:

Another alternative to volatile organic compounds is biosolvents. Glycerol derivatives, terpenic compounds, esters of naturally occurring fatty acids etc. are some examples of biosolvents [46]. Biosolvents are extensively used in paints, inks, cosmetics and agricultural chemicals [46-47].

Fluorous solvent as a green solvent:

Horvath reported highly fluorinated alkanes, 3^0 amines and ethers as fluorous solvents having some special characteristics to use in biphasic systems [48].These solvents are not soluble in organic & aqueous solvents. Their soluble properties depends upon temperature. Their biphasic systems are used in biocatalytic reactions and extractions [49]. As cellulose is soluble in fluorous solvents, so it is very good method to trecover glucose [50]. Another applications on industrial scale are for cosmetics, food packaging and fire fighting foams etc. Perfluorinated compounds are chemically and thermodynamically stable i.e chemically inert than non-fluorinated compounds due to less polarizability of C-F bonds. But the cost of these solvents is very high and thrie long term environmental effect is the topic of concern.

Non-toxic liquid polymer as a green solvent:

Non-toxic liquid polymers are used with supercritical CO_2 in conjunction for catalytic reactions. Liquid polymers work like ionic liquids and are less polar than ionic liquids. So these can't replace ionic liquids, rather deemed as a supplement to ILs. Polyethylene glycol and polypropylene glycol are two known liquid polymers called green solvents because these are non-volatile, non-poisonous and are biodegradable by bacteria present in the soil & sewage [51-58]

Conclusion:

From the above discussion it is clear that we can substitute traditional organic solvents in number of ways with green solvents to reduce their environmental effect and selection of these solvents depends upon reaction conditions. Green alternatives discussed above such as solventless processes, water, supercritical carbon dioxide, ionic liquids, organic carbonates, biosolvents, fluorous solvents and non-toxic liquid polymers provide either identical results or at times even far better than obtained by using traditional organic solvents. But green solvent research is still lagging behind to satisfy the requirements for solvents to lower environmental damage. Advancement in research for green solvents and their adoption in chemical industries is recommended.

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