NEW TRENDS IN ORGANIC SYNTHESIS

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ABSTRACT

Now a day so many new methods of synthesis are find out. Due to that the pollution free Environment are produced, Low cost less energy, less solvent are techniques developed. They are a) Aqueous Phase Reactions b) Reactions in ionic liquids c) Solid support organic synthesis d) Solvent reaction e) Green catalyst f) Microwave and ultra sound assisted Green synthesis. Above process are discussed in their paper.

INTRODUCTION

Chemists felt the need for sustainable development. This includes incorporations and environmentally friendly approach to all aspects of chemical industry. After 1990 particularly chemists have started solving complicated environmental issues safe and economically profitable manner under different names like clean, environmentally, sustainable or green chemistry. The term green chemistry was coined by Paul T. Anastas. Green chemistry means the Judicious use of chemistry for prevention of environmental pollution.

Green strategies focus on i) Replace of organic solvents by water or super critical fluids or totally elimination of solvents ii) The use of environmentally friendly substances in place of toxic heavy metals iii) Development of solid support reagents and catalysts iv) Use of Starting substances that can be recycled or are safely disposable if they remain uncreative, v) Producing a hazardous chemical in the just sufficient amount using a biocatalyst is safer.

New synthesis process:

1. Aqueous phase Reactions: Diels- Alder reaction of cyclopentadience in water is 700 times faster in water than in isooctane.

2. Reaction in Ionic Liquids: The ionic liquids, comprising ions and existing in liquid state near or below room temperature like $[EtNH_3]$ $[NO_3]$ as green solvents had been developed. Ionic liquids may be a) Simple salts with one cation and one anion or b) Binary liquids which are also salts with equilibrium.

3. Solid supported Organic Synthesis: Here the reactants are mixed a suitable solvent like water, alcohol etc., The solution obtained is stirred together with a suitable adsorbent or solid support like silica gel, alumina etc., After stirring thoroughly the solvent is removed in vacuum and the dried solid support on which the reactants have been absorbed is used for carrying out the reaction under microwave irradiation.

Example: Synthesis of Porphyrin: Pyrrole and benzaldehyde are absorbed on silica gel give tetrapyrrolic product under dry media conditions with microwave activation. This takes place within ten minutes where as conventional method needs 24 hours.

4. Solvent Free Reactions (Solid Phase Reactions): though it was thought that it would not be possible to carry a reaction without solvent, the thought was proved to be wrong. It is found that a large number of reactions take place in solid state without solvent. The use of solvent is to achieve homogeneity by dissolving all the reactants in a suitable solvent. The solvent does not participate in the reaction. It allows achieving the required temperature for the given reaction and could be easily removed while isolating the product. In brief, we can say that the solvent helps heat transfer, mixing and transport of solids, liquids and gases and removal of undesired by- products through recrystallisation or by the formation of azeotropes. Solvent free reactions as on today are less common in the fine chemical and pharmaceutical industries but a number of reactions occur more effectively and selectively than those with solvents. These solvent free reactions are easy to handle, less polluting and relatively cheaper to operate. Slvent free reactions are largely green organic synthesis in solid state. They are explained in two parts as (i) Solid state synthesis without using any solvent and (ii) Solid supported organic synthesis.

5. Solid Phase Synthesis without using any Solvent: Example: The reaction between 3,5-dimethyl phenol and N-bromosuccinimide gives in solid state 45% tribromoderivative. If the reaction is carried out in solution a mixture of mono and dibromo derivatives is formed.

6. Green catalysts: Catalysis is the corner stone of green chemistry. Catalytic reactions help in reducing energy requirements due to the reduction of reaction times and decrease the separation procedures particularly, when product selectivity is enhanced. Catalysts may decrease the number of overall reaction steps and decrease the amounts of solvents to be used. The loss of reagents during the reaction is minimizes by use of catalysts. Catalyst permits the use of less toxic reagents like using H_2O_2 for oxidation in place of heavy metals as catalysts. Photocatalyst absorbs visible light and decomposes water molecules into hydrogen and oxygen. So obtained hydrogen can be used in fuel cells. These hydrogen fuel cells when used in cars would reduce air pollution by reducing the green house gases.

7. Phase Transfer Catalysis in Green Synthesis: Consider an organic synthesis involving an organic compound, soluble in organic solvent and the reagent in a polar solvent say, water. If these two reactants are allowed to react in their respective solutions the reaction would be very slow proceeding only at the interface where the two solutions are in contact. The rate of the reaction may slightly increase on stirring or by using aprotic polar solvents which solvate the cations leaving the anions free. Such solvents like dimethyl formamide are expensive and their removal is difficult. If strong bases are used, side reactions are possible. These problems are solved by using a catalyst which is soluble in water (polar solvent) as well as in organic solvent. Such catalysts are known as phase transfer catalysts (PTC). The PTC reaction is a methodology for accelerating the reaction between the water

insoluble organic compounds and water soluble reagents. The basic function of PTC is to transfer the anion from the reagent from the aqueous phase to the organic phase.

Example: The reaction between 1-chlorooctane with NaCN in water does not form 1-cyanooctane even if the reaction misture is shaken for several days. However, if a small quantity of an appropriate PTC is added the product is formed in about 2 hours giving 95% yield.

$$CH_3(CH_2)_6CH_2Cl \xrightarrow[PTC\ [CH_3(CH_2)_{15}P^+(n\text{-}Bu)^-3]]{NaCn,\ H_2O,\ decane} CH_3(CH_2)_6CH_2CN$$

1-Chlorooctane 1-cyanooctante (95%)

Phase transfer catalysts used are quaternary 'onium' slats like ammonium, phosphonium, antimonium and tertiary sulphonium salts.

Some PTC's are given below

1. Aliquat 336: methyltrioctyl ammonium chloride; $N^+CH_3(C_8H_{17})_3\ Cl^-$
2. Benzyl trimethyl ammonium chloride or bromide; $N^+(CH_3)_3\ CH_2C_6H_5\ X^-$ ($X^- = Cl^-, Br^-$) (TMBA)
3. Benzyl triphenyl phosphonium iodide; $C_6H_5CH_2(C_6H_5)_3\ P^+I^-$

PTC reactions are fast and do not require vigorous conditions. They are low cost, and they require relatively cheaper aprotic solvents. They can be carried out at low temperatures. As water is involved we need not maintain anhydrous conditions. As anions enter the organic colvent the nuvleophilicity increases. Strong bases like (RO^-, NH^-_2, H^-_2) are not used. In the presence of PTC even OH^- is a strong nucleophile.

1. Biocatalysts: The catalyst derived from the nature. Biocatalysts are clean and non-toxic. Therefore the biocatalysts are a part of green chemistry. Biocatalysts are highly selective i.e., both stereospecific and regiospecific. They need no use of protection and deprotection gropus. They give pure isomers as compared to racemic mixtures with non-biocatalysts. This efficiency alone serves in the saving of energy, time, material cost and other separation procedures. This does not mean we should use only green catalysts like biocatalysts. Biocatalysts require narrow operational parameters and the operational conditions are limited. For example biocatalysts will be easily denatured under adverse condition which causes a loss of its catalytic activity. Sometimes substrate or product in high concentration inhibits the biocatalyst.

2. Microwave and Ultrasound Assisted Green Synthesis: Microwaves have wavelengths between 1 cm and 1 m (in terms of frequencies it is 30 GHz to 300 GHz). These are similar to those of rader and tele communications. The radivative frequency emitted by house hold and industrial microwave oven is about 2.45 GHz. The microwaves are used for heating purposes. The microwave reactions involve the selective absorption of electromagnetic waves by polar molecules (Non polar molecules are inert towards microwaves). When molecules with a permanent dipole are exposed to an electric field, they get aligned and as the field oscillates, the orientation of the molecules changes rapidly. This rapid reorientation produces intense internal heating. The main difference between ordinary heating and microwave heating and classical heating is all about heat transfer by preheated molecules.

In microwave induced organic reactions, the reactions are carried out in a solvent medium or on a solid support in which no solvent is used. If a solvent is used, that solvent has dipole moment so as to absorb microwave radiation and its boiling point should be $20\text{-}30^0$C higher than the desired temperature.

An Excellent solvent in a microwave oven is N, N-dimethylformamide, (DMF) with b.pt 160^0C and dielectric constant, E=361.7. It is also retains water if any formed in the reaction.

Microwave organic reactions are classified into three types as

i. Microwave assisted reactions in water
ii. Microwave assisted reactions in organic solvents
iii. Microwave assisted solvent free reactions (solid sate reactions)

Example: Esterfication (Reaction of Carboxylic and alcohol) –in organic solvents

$$C_6H_5COOH + C_3H_7OH \xrightarrow[(Microwave,\ 6\ min)]{Conc.\ H_2SO_4} C_6H_5COOC_3H_7$$

Benzoic acid n-Propyl alcohol n-propyl benzene

Ultrasound assisted Green Synthesis: Ultra Sound refers to sound waves having frequencies higher than those to which human ear can respond ($\mu > 16$ KHz). High frequency ultra sound waves are used in medical equipments. For chemical reactions the ultra sound frequencies suitable are of 20-100 KHz much lower than those used for medical applications, but the power used is higher. Generally electrical energy is converted to ultra sound. Very high local temperature of about 5000^0C and high pressure over 100 bar may be produced. The high temperature and pressure conditions initiate the chemical reactions. 'Sonometry' is the term used to describe the effect of ultra sound waves on chemical activity.

Example: Hydrolysis: $C_6H_5CN \xrightarrow[Ultrasound]{H_2O} C_6H_5COOH$

CONCLUSION

Above process are useful along with that so many new developments also find out in everyday research.

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