1. Green Chemistry- Definition and Principles

What is Green Chemistry?

Green Chemistry is defined as invention, design, development and application of chemical products and processes to reduce or to eliminate the use and generation of substances hazardous to human health and environment.

Principles of Green Chemistry

1) It is better to prevent waste than to treat or clean up waste after it is formed.
2) Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3) Wherever practicable, synthetic methodologies should be designed to use and generate substances that posses little or no toxicity to human health and the environment.
4) Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5) The use of auxiliary substances (e.g. solvents, separation agents *etc.*) should be made unnecessary wherever possible and, innocuous when used.

6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7) A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.

8) Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

9) Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10) Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11) Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12) Substances and the forms of the substance used in chemical reaction should be chosen so as to minimize the potential of chemical accidents, including releases, explosions, and fires.

P. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice;* Oxford Science Publications, Oxford, 1998

19.2 THE TWELVE PRINCIPLES OF GREEN CHEMISTRY

Anastas and Warner have formulated the *twelve principles of Green Chemistry* as the guidelines or **blueprint** for practising green chemistry to save the environment. These principles are given below.

1. **Heart of Green Chemistry – to minimise the waste product formation :** It is better to prevent the formation of waste than to treat or clean up the waste after its formation.

   Illustration of the 1st Principle : The first principle aims to develop the **zero waste technology (ZWT).** In terms of ZWT, in a chemical synthesis, waste product should be zero or minimum. It also aims to use the waste product of one system as the raw material for other systems. As for example, bottom ash of thermal power station can be used as a raw material for cement and brick industry; effluent coming out from cleaning of machinery parts may be used as coolant water in thermal power station; municipal waste as a source of energy; etc. Many such examples have been discussed in Chapter 17. Such practices will reduce the waste product.

2. **Atom economy :** During the synthesis of a chemical product, the methodology should be designed in a way to maximise the incorporation of starting materials into the desired final product. *Thus it demands to minimise the formation of by-product.*

   Illustration of 2nd Principle : The concept of atom economy has been illustrated in Sec. 19.3.

3. **To avoid the use and formation of toxic materials :** If possible (both technically and economically), the synthetic methodologies should avoid the use and generation of toxic and environmentally hazardous substances.

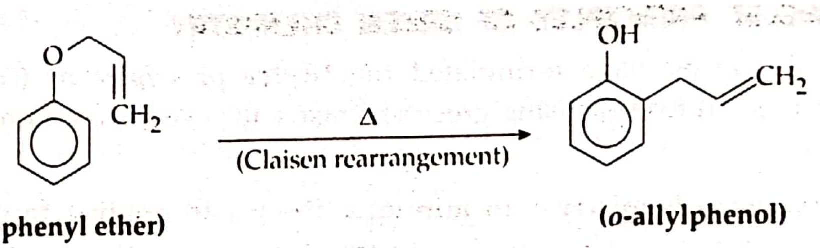
   Illustration of the 3rd Principle : This principle aims to develop the methodologies that will minimise the use and formation of toxic and hazardous substances. In other words, the synthetic methodologies should use and generate the ecofriendly substances that will show tittle or no toxicity to human health and environment.

4. **Use of nontoxic chemical products :** Chemical products to be used in different activities should have the efficacy to function but with reduced toxicity.

   Illustration of the 4th Principle : In many chemical industries, not only the waste product but the starting materials are also quite hazardous to the workers and environment. For example, **adipic acid**, $HO_2C(CH_2)_4CO_2H$ is widely used in polymer industries (*cf.* manufacture of nylon, polyurethane, lubricants, etc. Chapter 14). Benzene is the starting materials for the synthesis of adipic acid but benzene is carcinogenic and benzene being a VOC pollutes air. In green technology developed by Drath and Frost, adipic acid is enzymetically synthesised from glucose (cf. Sec. 19.5.15).

5. **Minimum use of auxiliary substances :** If possible (both technically and economically), in a chemical synthesis, the use of *auxiliary substances* like solvents, separating agents, etc. should be avoided. If, these are to be used, they should be eco-friendly.

Illustration of the 5th Principle : This principle aims to use **green solvents** (*e.g.* water, supercritical CO_2) in place of volatile halogenated organic solvents *e.g.* CH_2Cl_2, $CHCl_3$, C_2Cl_4 (perchloroethylene), CCl_4 for chemical synthesis and other purposes. If possible **solvent free synthesis** is preferred. For example, Claisen rearrangement can be carried out in solid phase.



6. **Minimum energy consumption :** In the synthesis of a chemical product, the energy consumption should be minimised to make the process more and more economic. Ideally, the synthetic methods should be carried out at ambient temperature and pressure.

Illustration of the 6th Principle : To save energy, synthetic methodologies should need more and more moderate conditions and the amibient temperature and pressure are the best choices. It needs **suitable catalysts** that will accelarate the reaction rate even at lower temperature. The **biocatalysts** (*i.e.* enzymes) can work at the ambient conditions.

Energy save can be done in many other ways : refluxing conditions require less energy; waste heat may be used for heating the reactants and other things; improving the technology of heating system; preferance for photochemical reactions (specially by using the solar radiation) instead of thermochemical reactions; extraction of energy from the waste product (*cf.* Chapter 17); use of microwave heating etc.

These practices advocate the **concept of green energy** as demanded by the 6th principle.

7. **Use of renewable sources :** If it is *technically and economically possible*, then the renewable resources (*e.g.* biomass) rather than the nonrenewable resources (*e.g.* crude oil) should be used as the raw material or feedstock.

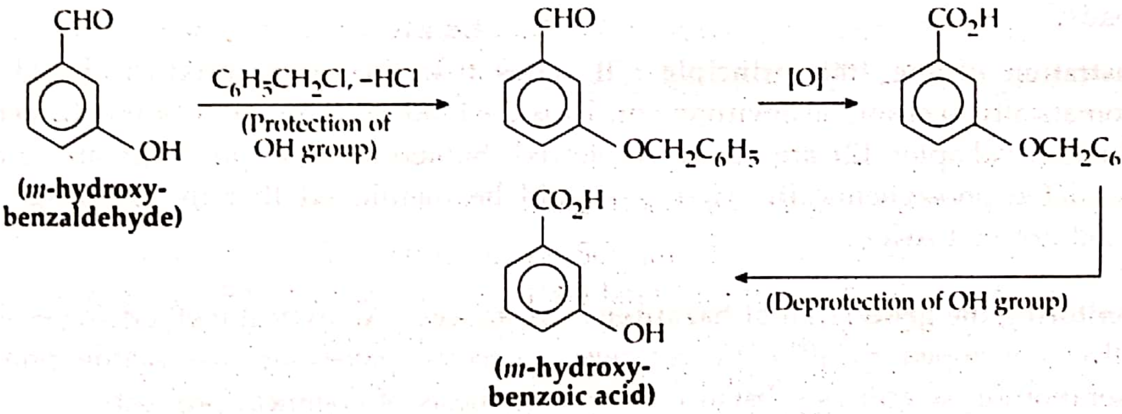
Illustration of the 7th Principle : It encourages the use of starting material (*i.e.* raw material or feedstock) which should be renewable, if technically and economically practicable. In fact, continuous use (*i.e.*overexploitation) of the nonrenewable feedstock (*e.g.* petroleum product, fossil fuel) will deplete the recource and future generation will be deprived. Moreover, use of the these nonrenewable resources puts a burden on the environment.

On the other hand, use of **sustainable** or **renewable resources** e.g. agricultural or biological product ensures the sharing of resources by future generation. Moreover, this practice generally does not put much burden on the environment. The products and wastes are generally biodegradable.

The practice of this principle has been illustrated in many cases like **bioplastics** and **biopolymers** (*e.g.* PHB, PHV, PHVB, BIOPOL, etc. Secs. 19.5.26, 14.11.1), chitin (a unique biopolymer, Sec. 19.7), biodisel (cf. Sec. 19.5.25), CO_2 feedstock in the manufacture of polycarbonate (Sec. 19.5.22), greener synthesis of furfural from biomass (Sec. 19.5.21), green synthesis of adipic acid and catechol (Sec. 19.5.15), polylactic acid (a green polymer) from biomass (Sec. 19.5.4), etc.

8. **Minimisation of steps :** If possible, the steps like blocking group, protection/deprotection of group, temporary modification of physical and chemical processes etc., should be avoided as far as possible during the synthesis of a chemical product. Thus there should be a minimum number of steps to synthesise a target product.

Illustration of the 8th principle : Specially in organic synthesis, we need very often protection of some functional groups. Finally, we again need their deprotection. It is illustrated in the following example of synthesis of *m*-hydroxybenzoic acid from *m*-hydroxybenzaldehyde.



Obviously, in such cases, atom economy is also less. The green chemistry principle aims to develop the methodology where unnecessary steps should be avoided, if practicable. Biocatalytic reactions very often need no protection of selective groups.

9. **Use of catalytic reagents :** Selective catalytic reagents are superior to stoichiometric reagents in a chemical synthesis. This will save the energy and reduce the burden of by-product.

Illustration of the 9th Principle : This principle of green chemistry states that catalytic reagents are superior to stoichiometric reagents. The use of catalysts is preferred because of the following advantages.

(i) 100% atom economy because the true catalysts are fully recovered without any change in their chemical and physical properties; (ii) the catalysed reactions are faster *i.e.* energy save is possible; (iii) reaction yields are better; (iv) selective reaction products; (v) maximum utilisation of the starting material and minium production of the waste material.

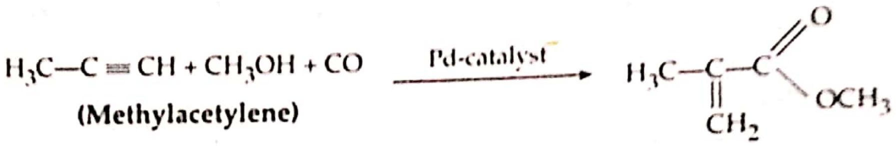
Some representative catalytic reactions (100% atom economy) are :

$$H_3C{-}CH{=}CH_2 + H_2 \xrightarrow{\text{Ni-catalyst}} H_3C{-}CH_2{-}CH_3$$

(Propene) **(Propane)**

$$H_3C{-}CH \equiv CH + H_2 \xrightarrow[\text{(Catalyt)}]{\text{Pd-BaSO}_4} CH_3{-}CH_2{=}CH_2$$

(Methylacetylene) **(Monoaddition Product)**



$$H_3C{-}C \equiv CH + CH_3OH + CO \xrightarrow{\text{Pd-catalyst}} H_3C{-}\underset{\underset{CH_2}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}OCH_3$$

(Methylacetylene)

(Methylmethacrylate, MMA)

10. **Life-time of a chemical product :** At the end of function, the chemical products (*e.g.* pesticides) should degrade easily to harmless products, *i.e.* after their function, they should not persist in the environment.

    DDT is the classic example in this area. It is an effective pesticide but its stability in the natural environment causes several environmental hazards. This aspect has been discussed already.

    Illustration of the 10th principle : It states that the waste product should degrade automatically to clean the environment. Thus the biodegradable polymers (Chapter 14) and pesticides (Chapter 12) are always preferred. Sometimes, the polymers are to be made degradable photochemically. Here it should be mentioned that the degraded products should not be toxic.

11. **Monitoring the generation of hazardous substances :** Analytical methodologies should be further developed to *allow for real-time in-process monitoring and control* prior to the generation of hazardous substances in the synthesis of chemical products.

    Illustration of the 11th Principle : Analytical methodologies should be developed or modified, so that continuous monitoring of the manufacturing and processing units is possible. This is very much important for the chemical industries and nuclear reactors. This efficient monitoring is quite essential to avoid the accident.

12. **Use of chemically safer substances :** The substances to be used in a chemical reaction should be selected in such a way that *they can minimise the occurrence of chemical accidents, explosions, fires and emissions.* In other words, the substances to be used should not be hazardous.

    Illustration of the 12th Principle : The substances used in chemical industries should be in such forms so that the possibility of accidents can be minimised.

    For example, if the chemical process works with the gaseous substances, then the possibility of accidents including explosion is relatively higher compared to the systems working with the nonvolatile liquid and solid substances. In fact, the risk is minimum if the process works with solid substances at every step.

THE PRESIDENTIAL GREEN CHEMISTRY CHALLENGE (PGCC) AWARDS

To encourage the chemists to practise the principles of green chemistry in real cases, the presitigious PGCC awards were introduced in 1995–96 by U.S. EPA (Environmental Protection Agency). Generally 5 awards are given each year for the outstanding contribution in green chemistry.

19.3 THE CONCEPT OF ATOM ECONOMY IN CHEMICAL SYNTHESIS

To synthesise a particular chemical product, all the atoms of the reactants used may not be always incorpated in the desired product. The atoms which are not incorporated in the product are involved to generate the by-product and waste product which may be environmentally hazardous. To have a quantitative idea regarding the amount of waste product and byproduct generated in a particular reaction, we can consider the idea of % **atom utilisation** defined as follows :

$$\%\ \text{Atom utilisation} = \frac{\text{Formula weight of the desired product}}{\text{Formula weight of (the desired product + the waste and by – product)}} \times 100$$

But, very oftens it is difficult to identify the waste and byproducts. To avoid this, the concept of **% atom economy** has been introduced.

The concept of atom economy also gives the measure of the unwanted product produced in a particular reaction. It is defined as follows :

$$\%\ \text{Atom economy} = \frac{\text{Formula weight of the desired product}}{\text{Sum of formula weight of the all reactants used in the reaction}} \times 100$$

The concept of % atom economy is illustrated in the following examples.

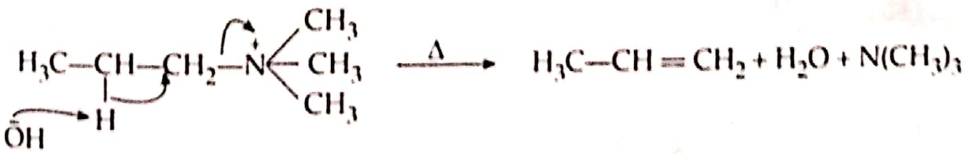
1. **Substitution reaction :** Let us consider the following reaction which aims to produce the desired product 1-bromo-butane.

-80

$$CH_3CH_2CH_2CH_2{-}OH + NaBr + H_2SO_4 \rightarrow CH_3CH_2CH_2CH_2{-}Br + NaHSO_4 + H_2O$$

$$\%\ \text{Atom economy} = 100 \times \frac{\text{Mass of } (4C + 9H + 1Br) \text{ atoms}}{\text{Mass of } (4C + 12H + 5O + 1Br + 1Na + 1S) \text{ atoms}} = 100 \times \frac{137\ \text{amu}}{275\ \text{amu}} = 50\ \%$$

2. **Elimination reaction :** Let us consider the following elimination reaction leading to the desired product propylene.



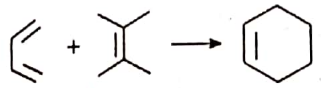
$$\%\ \text{Atom economy} = \frac{42 \times 100\ \text{amu}}{119.2\ \text{amu}} = 35.3\%$$

3. **Hydrogenation reaction :** The % atom economy in the following hydrogenation reaction is 100.

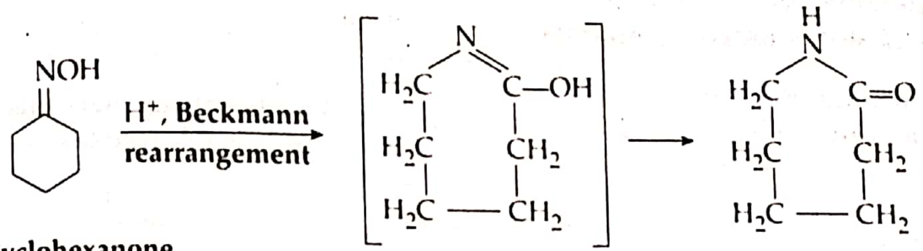
$$CH_3{-}CH{=}CH_2 + H_2 \xrightarrow{\text{Ni-catalyst}} CH_3{-}CH_2{-}CH_3$$

4. **Addition and rearrangement reactions :**

$H_3C{-}CH{=}CH_2 + Br_2 \rightarrow H_3C{-}CH(Br){-}CH_2Br$ (Bromination of propene), **(Addition reaction)**



, **(Cycloaddition** of butadiene and ethylene to cyclohexene), **(Addition reaction)**



Cyclohexanone oxime

Caprolactam

In fact, % atom economy is 100 for all addition and rearrangement reactions.

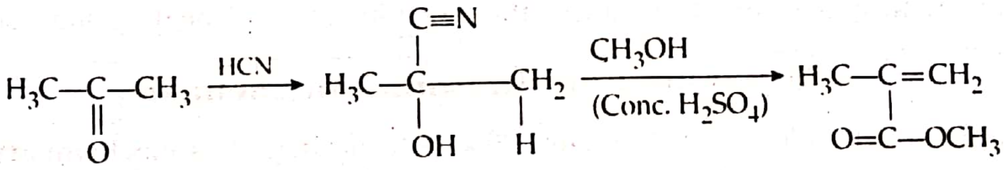
5. **Greener synthesis of ibuprofen (cf. R. A. Sheldon, Chem. Ind. 12, 1997) :** Ibuprofen is a common *analgesic and antiinflammatory drug* used widely. Its commercial synthesis was first introduced by Boots company of Nottingham, UK with atom economy only 40%. This methodology has been being used since 1960s, but BHC (a joint venture of Boots company and Hoechst Celanese) has developed a new method (Scheme 19.4.1) with atom economy 77%. For this contribution, BHC won the PGCC award in 1997.

(**Note :** About 30 million lb of ibuprofen are synthesised annually and by the original Boots method it will produce more than 35 million lb of waste product. The greener synthesis by BHC can dramatically reduce this waste product generation).

6. **Greener synthesis of methyl methacrylate (MMA) :** Methyl methacrylate (MMA) is widely used as a monomer to prepare its polymeric compound.

Let us consider the following two routes to prepare the monomer.

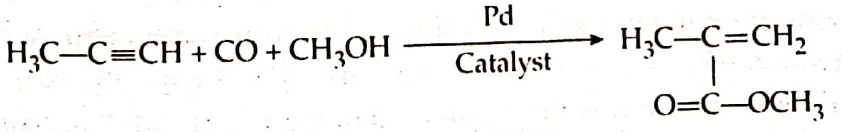
(i)



$$H_3C{-}\underset{\displaystyle O}{\overset{}{\underset{\Vert}{C}}}{-}CH_3 \xrightarrow{HCN} H_3C{-}\overset{\displaystyle C{\equiv}N}{\underset{\displaystyle OH}{C}}{-}\underset{\displaystyle H}{CH_2} \xrightarrow[(\text{Conc. } H_2SO_4)]{CH_3OH} H_3C{-}\underset{\displaystyle O{=}C{-}OCH_3}{C}{=}CH_2$$

(Atom economy = 47%)

(ii)



$$H_3C{-}C{\equiv}CH + CO + CH_3OH \xrightarrow[\text{Catalyst}]{Pd} H_3C{-}\underset{\displaystyle O{=}C{-}OCH_3}{C}{=}CH_2$$

(Atom economy = 100%) **(MMA)**

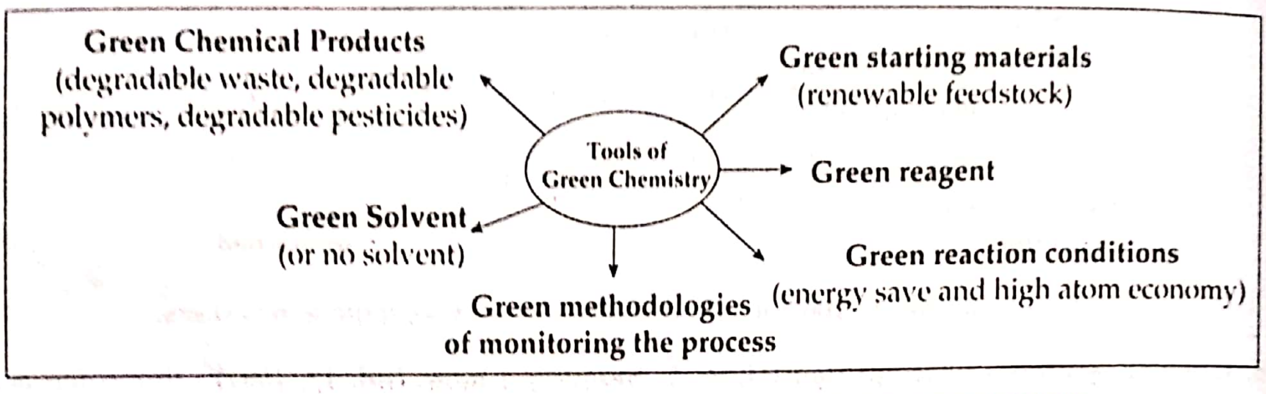
The second method enjoys the 100% atom economy. The inefficient atom economy in the first method arises from the use of ***stoichiometric amount of HCN and H_2SO_4***.

7. **Green synthesis of acetophenone :** Classical oxidation of 1-phenylethanol consumes the *stoichiometric amounts* of CrO_3 and H_2SO_4. Consequently its % atom economy is less. On the other hand, ***catalytic oxidation*** by O_2 enjoys the higher atom economy.

$3PhCH(OH)CH_3 + 2CrO_3 + 3H_2SO_4 \rightarrow 3PhCOCH_3 + Cr_2(SO_4)_3 + 6H_2O$, **Atom economy** = 42%
(Stoichimetric oxidation)

$PhCH(OH)CH_3 + \frac{1}{2}O_2 \rightarrow PhCOCH_3 + H_2O$, **Atom economy** = 87%
(Catalytic oxidation; only water is the by-product)

Thus the **catalytic reactions** (*e.g.* synthesis of methyl methacrylate, acetophenone, etc.) always possess the higher atom economy compared to the reactions consuming the reactants in **stoichiometric amounts.**



19.4 SOME IMPORTANT TECHNIQUES AND DIRECTIONS IN PRACTISING GREEN CHEMISTRY

1. **Application of microwave irradiation (MWI) in chemical process** : These unconventional energy sources are now being used in chemical transformations. Many chemical transformations can be carried out by using MWI. ***The selective absorption of microwaves (10^9–10^{11} Hz) by the polar molecules*** leads to reaction rate acceleration. In fact, the reactions experiencing ***polar transition state*** are favoured by MWI. The **advantages** in using this technique are : quick reaction; no requirement of prolonged heating or refluxing; some reactions may be done also without using any solvent (*i.e.* **solvent free microwave assisted reaction**). Solvent free reaction avoids the disposal problem of solvents very often enriched with many chemicals. * Knoevenagal
2. **Use of ultrasound in chemical process :** It is a special technique to introduce energy in chemical systems. It enhances the reaction rate and heating may be avoided.

Ultrasound or ultrasonics in chemistry

Ultrasound (not audible) covers the range 20 kHz to 10 MHz. In **sonochemistry,** it generally uses the range 20 kHz to 100 kHz. Sound wave cannot directly interact with the molecular vibration because the wavelength of sound wave is much longer than the molecular dimension. In fact, sonication in homogeneous solution produces **accoustic cavitation** which is responsible for chemical effects. A solvent medium irradiated with ultrasonic waves leads to ***production and collapse of microbubbles.*** This phenomenon is called **accustic cavitation.** During the propagation of ultrasonic waves through a solvent medium, the oscillating particles produce the regions of *compression* and *rarefaction* successively. Bubbles produced in the regions of rarefaction collapse. Collapse of these bubbles releases high energy locally to produce high temperature (*ca.* 5000°C) and high pressure (*ca.* 10^3 atm). **This gives the activation energy** to the molecules present within the bubbles and the liquid surrounding the collapsing bubbles. This accelerates the rate of chemical transformation. The symbol))))) denotes ultrasound assisted reaction.

Microwave heating

The **nonpolar molecules** fail to interact with the microwave radiation. Microwave radiation (*i.e.* electromagnetic radiation in a particular range) is selectively absorbed by the polar molecules. The **polar molecules** in an electric field will try to orient themselves parallel to the field. This *regular orientation* instead of *random orientation* (prevailing in absence of field) stores potential energy in presence of the applied field. If the direction of the field is changed slowly, the molecules will rotate properly to allign along the direction of field. If the direction of the applied field is changed quickly (*i.e.* **rapid oscillating field**), the molecules will try to orient accordingly but all the molecules may not be able to allign with the field's direction. Such molecules may bump into the other molecules. In fact, potential energy of the molecules failing to allign themselves along the field's direction does not match with the appllied field. The excess potential energy is converted into kinetic energy through collision among the molecules. **This leads to microwave heating.** Here, it may be noted that if the field oscilates too rapidly, the molecules cannot interact with the field and they remain randomly oriented. *At such frequencies, no heating will occur.*

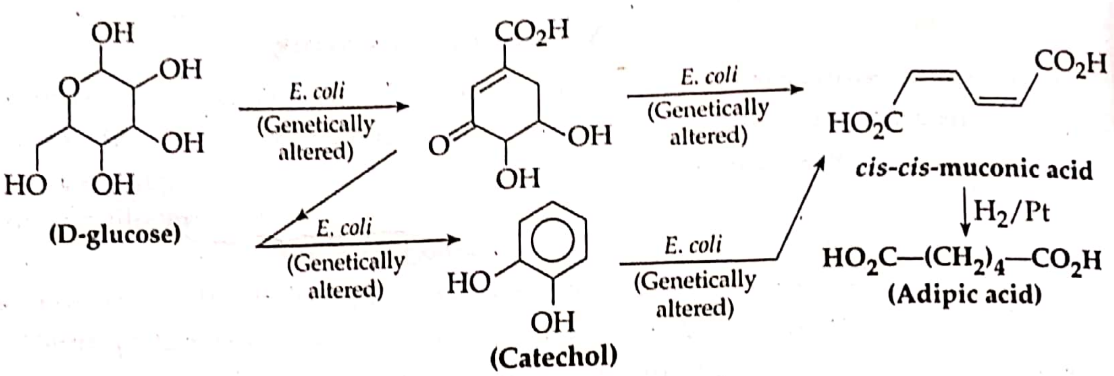
Thus microwave heating is only possible for polar molecules at a particular range of electromagnetic radiation. In domestic heating, water is commonly used as the polar medium.

The basic differece between *classical heating and microwave heating* originates from the homogeneous heating in core by microwaves. **In conventional heating, the *preheated molecules lying at the surface of container transfer heat to the bulk molecules.*** In conventional heating, the vessel walls remain hotter. The vessel (made of teflon and polystyrene and these are poor microwave absorbing material) walls in microwave heating remain cooler than the bulk solution. If microwave heating is carried out in the closed teflon vessel, the pressure developed will lead to *superheating* of the solution.

3. **Use of renewable feedstock (i.e. starting material) and biosynthesis :** Many chemical industries producing organic chemicals depend on *petroleum feedstock*. In fact, use of **biotechnology** involving biological feedstock, biocatalysts and biosynthesis is the most important aspect of green chemistry in chemical industries. The **remarkable advantages** in biotransformations are : ambient reaction conditions *i.e.* normal temperature and pressure, aqueous media, use of renewable feedstock. Some examples will be discussed in Sec. 19.5. Here we shall give some examples.

   - **Organic waste management :** Oxidation of organic compounds is very often required in both organic synthesis and treatment of waste present in the effluents of organic chemical industries. For these oxidation reactions, very often metal complexes are used as catalysts and the process produces a big burden on the environment. For this purpose, green technology considers the application of **laccase enzyme** which can oxidise many organic compounds in aqueous media by simply using atmospheric oxygen at ambient conditions.

   - **Adipic acid and catechol synthesis :** The conventional manufacture of the chemical products like *adipic acid* (used in the production of nylon polymer), *catechol*, BHT, etc. needs the consumption of petroleum based feedstock like benzene, toluene, etc. Application of green chemistry has developed an alternative process (*cf.* Sec. 19.5.15).

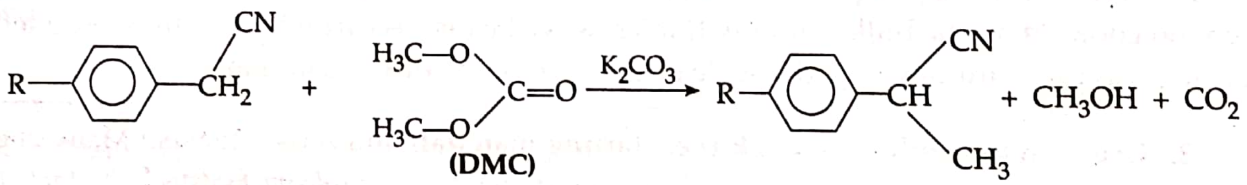


The technique consumes the agro-based product as the feedstock and the biocatalyst is the *genetically altered E. coli.* The variety producting catechol is different from the species leading to adipic acid.

- **Chitin (a biopolymer)** (cf. Sec. 19.7) it can be easity obtained from the shells of crabs and other sea-products. It can be processed into the modified polymers that find many applications including the oil-drilling industry, biomedical industry, waste mangament industry, etc.

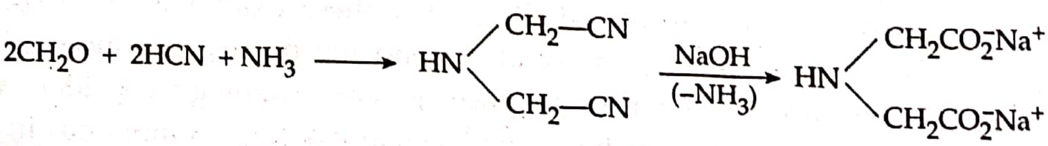
4. **Use of safer reagents :** Green Chemistry aims to replace the hazardous reagents. It is illustrated for the methylation reaction which conventionally uses the hazardous reagents like $CH_3—X$ (methyl halide), DMS (dimethylsulfate), etc. **The green alternative is DMC (*dimethylcarbonate*).**

Methylation of an active methylene group can be done by using the green reagents. It is illustrated below.



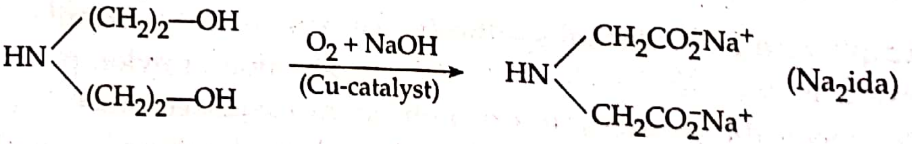
The conventional methylation process produces the hazardous toxic by-product while in the above **green methylation** reaction, the reagents are green and the by-products are also green.

Disodium iminodiacetate (Na_2ida) is an essential reactant in manufacturing a herbicide. Conventional route uses the hazardous chemicals like formaldehyde and HCN while the green synthesis (developed by Monsanto) does not use any such hazardous substance.



(Strecker process)

(Na_2ida)



(Diethanol amine) **(Green synthesis)**

K_2CO_3 is also a **green reagent** that finds uses in the synthesis of different heterocyclic compounds. It acts as a base and provides a **solvent free condition of reaction in many cases.**

Conventional synthesis of **polyurethanes** needs the use of the toxic chemical like *phosgen gas*. The green technique (Sec. 19.5.17) avoids the use of phosgen gas.

$$RNH_2 \xrightarrow[-H_2O]{+CO_2} RNCO \xrightarrow{R'OH} RNHCOOR'$$

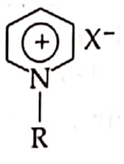
5. **Solvent free organic reactions :** Use of organic solvents is objectionable from the standpoint of environmental hazard. This is why, **solvent free reaction** condition is an important object of green chemistry. In fact, the best solvent is **no solvent** but the *'no solvent'* condition faces the problems like *heat and mass transfer, mixing of the reactants,* etc. To overcome these barriers in solvent-free reactions, the techniques like *mechanochemical mixing* (*i.e.* grinding), *microwave irradiation, solid/mineral support to the reactants, catalysis by solid surfaces of inexpensive and recyclable minerals (e.g. alumina, silica, clay, doped clay surface, etc.).* In Aldol 3,4-dimethoxybenzaldehyde and 1-indanone are used without using solvent. when *

6. **Use of green solvent :** The hazardous organic solvents need replacements. The ecofriendly reaction media are *water, polyethylene glycol, room temperature ionic liquids,* ***supercritical water*** *(SCW),* ***supercritical carbon dioxide*** *($SC\text{–}CO_2$) etc.* In fact, microwave assisted organic reactions in such green solvents are playing important roles in green chemistry. In fact, organic synthesis in aqueous media is becoming increasingly popular. Different organic reactions in aqueous media coupled with microwave/ ultrasonic irradiation have now been established. **Supercritical water** (*cf.* Chapter 17) in which organic compounds are more soluble compared to water at ordinary condition is also a potential alternative.

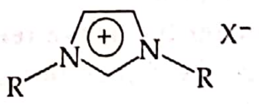
7. **Use of room temperature ionic liquids as green solvents :** Commonly used organic solvents are generally *volatile organic compounds* (VOCs) that cause several environmental hazards including *smog production in air, ozone depletion, health hazards,* etc. (*cf.* Chapter 8). The ionic liquids are the **green alternatives.** These are nonvolatile, noncoordinating but polar, immiscible with many organic solvents. These ionic liquids are generally organic salts like *alkylammonium salts, N-alkylpyridinium salts,* and *N, N'-dialkylimidazolium salts.*

$[R_xNH_{4-x}]^+X^-$

Alkylammonium Salt



N-alkylpyridinium Salt

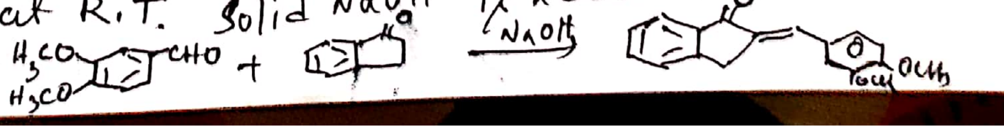


N, N'-dialkylimdazolium Salt

$X^- =$ halide, BF_4^-, PF_6^- ; R = alkyl groups of different chain length

These nonvolatile ionic liquids can be easily recovered after use. They can be recovered and purified. The product can be isolated from the ionic liquid by using some common solvent like ether in a separating funnel.

* they are mixed, their m.pts are lowered. They become liquid at R.T. Solid NaOH is added on it.



8. **Supercritical fluids as green solvents :** In fact, use of **supercritical CO_2** ($SC–CO_2$, cf. Sec. 19.5.2–3) is emerging with a great promise to substitute the VOCs. The important uses of $SC–CO_2$ are : *dry cleaning of clothes (a potential replacement of PERC,* i.e. *perchloroethylene, cleaning of semiconductor chips, extraction of caffine from coffee, preparation of nanoparticles, synthesis of organometallic compounds, enzymatic reaction* (*e.g.* lipase catalysed reactions), *polymerisation reaction* (*e.g.* polymerisation of tetrafluoroethylene), etc.

   Supercritical CO_2 may be used *to extract the organic pollutants* like MTBE, PCBs, DDT etc. present in water, soils and sediments.

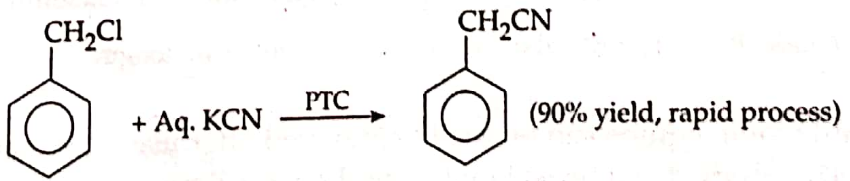
   Supercritical water ($T_c = 374°C$) (*cf.* Sec. 17.2) is too hot for many organic compounds. But ***near critical water*** appears as a *benign solvent* for many organic reactions.

9. **Catalytic reactions instead of reactions consuming stoichiometric amount :** Catalytic reactions enjoy higher atom economy. These aspects have been illustrated in Sec. 19.3 for the manufacture of methyl methacrylate and acetophenone.

10. **Use of greener catalyst :** Sometimes the used catalysts are toxic and these are accumulated in the industrial waste product. For example HF is the catalyst used in the production of linear alkylbenzenes (for the production of surfactants) and it has been replaced by the greener catalyst *i.e. fluorided silica alumina* catalyst. Other examples of greener catalysts are : *zeolites* acting as acid catalysts in Friedle-Crafts reaction, synthesis of oxime by titanium(IV) - silicate (TS-1) catalyst (*cf.* Sec. 19.5.20), dehydration of organic molecules etc. by ZSM-5 (used in the manufacture of synthetic gasoline *cf.* **Mobil process, Sec. 16.4.7**); TiO_2 (used as a photocatalyst in removing water pollutants, air pollutants, etc. Sec. 19.6) etc.

    Biocatalysts (*i.e.* enzymes) are the most ideal, green catalysts and these are finding applications in many biocatalytic transformations. These biocatalysts may be developed in the *genetically engineered bacteria* (*cf.* Sec. 19.5.15).

11. **Phase transfer catalysis (PTC) in green synthesis of organic chemicals like pharmaceuticals and agricultural chemicals** (*e.g.* insecticides, herbicides, etc.) : Organic compounds are soluble in organic solvents but the reagents (*e.g.* KF, NaCN, NaCl, NaOH, etc.) are not soluble in organic solvents. In such cases, conventionally aprotic solvents (*e.g.* DMSO, DMF) are used and vigorous stirring of the reaction mixture is required. But the process is slow; yield is low and environment faces the problem from the huge amount of organic solvent used in the process. **A *phase transfer catalyst* can transfer the active reagent which is an anion from aqueous phase to organic phase.** Thus the difficulties are overcome. The common PTCs are the *quaternary onium salts* such as ammonium salt, phosphonium salt, etc.



(90% yield, rapid process)

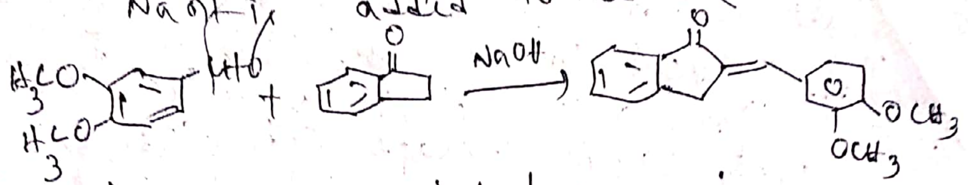
(Benzyl chloride) **(Benzyl cyanide)**

Green approaches

① Solvent free organic reaction:

a) Aldol condensation

By using 3,4-dimethoxy benzaldehyde and 1 Indanone. They themselves act as solvent. Solid NaOH is added to the mixture.

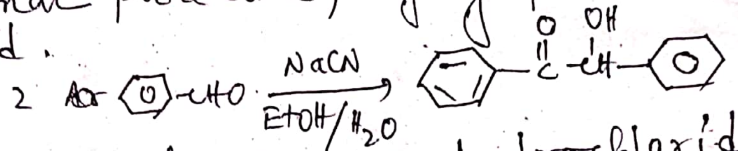


b) Microwave assisted ammonium formate mediated knoevenagal reaction.

- use of microwave energy of activation.
- solvent free reaction procedure.
- Simple workup & rapid conversion (within 90 sec)

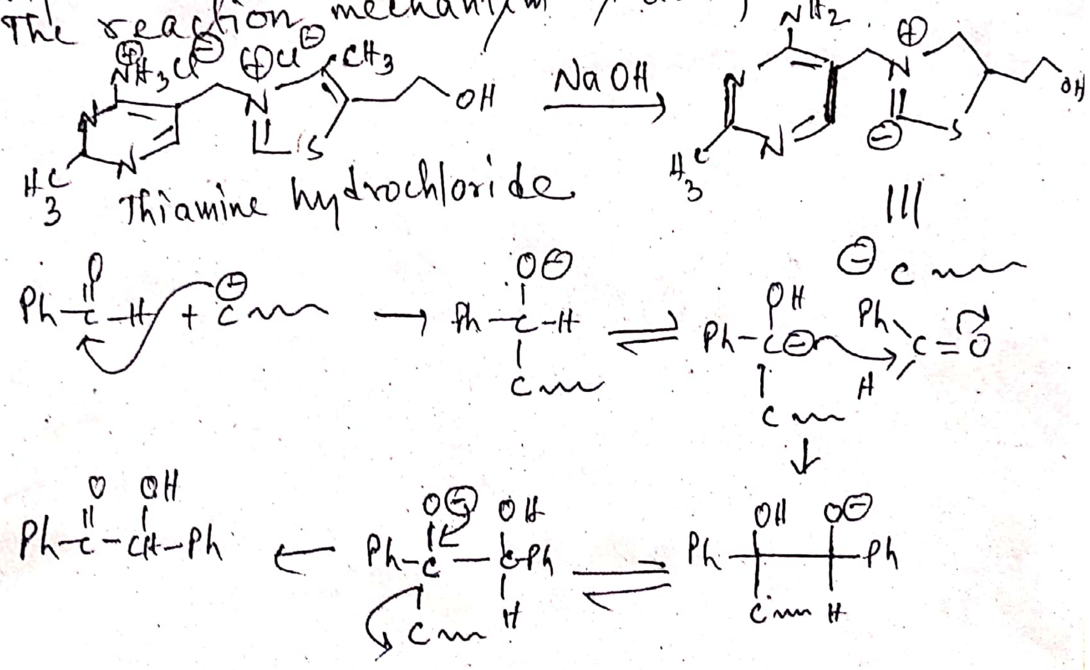
② co-enzyme catalysed benzoin condensation

In conventional procedure, highly poisonous NaCN is used.



In green approach, thiamine hydrochloride is used instead of using poisonous NaCN. The reaction is carried out comparatively at low temperature.

The reaction mechanism is as follows —



③ Use of ionic liquids in Cannizaro reaction.

Advantages of using ionic liquids

(i) They are not volatile & therefore not harmful to the environment.

(ii) They also replace volatile organic solvent and unsafe catalysts.

In normal way, strong caustic alkalies like NaOH and KOH etc are used. But, in green approach relatively milder alkali and solvent free reactions are attempted.

- Sometimes basic alumina is used in place of caustic soda along with
- LiBr ~~in presence of~~ triethyl amine are used in presence of guanidine.