CHAPTER 19

Green Chemistry and Environmental Protection

19.1 INTRODUCTION TO GREEN CHEMISTRY

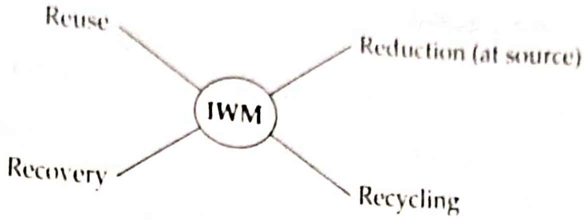
To meet the demands of modern civilisation, we need varieties types of chemical products and chemcial industries. These very often lead to the formation of hazardous substances and sometimes we are also to use the hazardous substances. To prevent or minimise the formation and use of such hazardous substances, the chemists are required to develop the *novel technologies*. This need has inspired the generation of the new branch of chemistry called **GREEN CHEMISTRY** which follows the principle, **PREVENTION IS BETTER THAN CURE.**

Green chemistry is defined as : ***it designs the chemical processes and products that reduce or eleminate the use and formation of hazardous substances.*** The main purposes of **Green Chemistry** are mentioned here.

- **Ecofriendly chemical technology :** Green chemistry aims to protect the environment and this is why it is also described as *ENVIRONMENTALLY BENIGN CHEMISTRY.*
- **Replacement of organic solvent and to minimise the waste product :** Green chemistry aims to devise *greener reaction conditions* for the synthesis of chemicals so that waste product (specially toxic waste) formation can be minimised. *It needs the replacement of organic solvent by water or complete elimination of the use of solvent.* It also needs *to minimise the formation of by-products* (specially the hazardous substances).
- **Use of renewable feedstocks :** Green chemistry aims to develop the *greener synthesis* of the required chemical products by using the *renewable resources* (*e.g.* biomass rather than petrochemical feedstocks). *It reduces the consumption of nonrenewable resources* (*e.g.* Crude Oil).
- **To minimise the energy consumption :** Green chemistry aims to develop the *greener conditions* for the synthesis of chemical products *so that energy consumption can be minimised.* For many existing chemical technologies, drastic reaction conditions (*e.g.* high temperature, high pressure, etc.) which are energy requiring are applied. Greener synthesis aims *to develop the mild or modest reaction conditions.* Idealty, the reactions should be carried out at ambient temperature and pressure.
- **Use of more ecofriendly chemical products :** *Green chemistry* aims to design the new chemical products to replace the existing hazardous chemical products provided the new

chemicals are having the same desirable properties of the existing ones (*e.g.* development of new pesticide which is only toxic to the target species and at the same time it biodegrades easily to harmless products).

- **Four R's (4R's) and integrated waste management (IWM) :** These four R's are : **reduction** (at source), **recycling, reuse** and **recovery.**



The principles of 4R's of IWM have been illustrated in Sec. 17.3.

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.

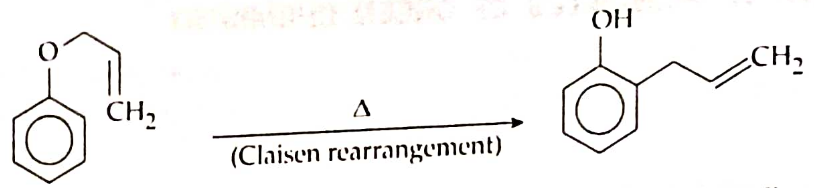
   Illustration of the 3rd Principle : This principle aims to develop the methodologies that will minimise the use and formation of toxic and hazardous substances. In other words, the synthetic methodologies should use and generate the ecofriendly substances that will show tittle or no toxicity to human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



(allylphenyl ether) **(*o*-allylphenol)**

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.

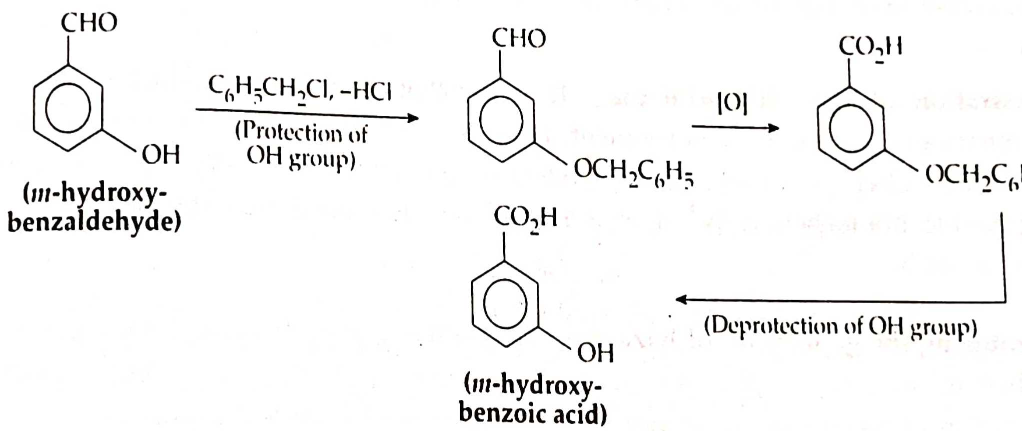
Illustration of the 7th Principle : It encourages the use of starting material (*i.e.* raw material or feedstock) which should be renewable, if technically and economically practicable. In fact, continuous use (*i.e.*overexploitation) of the nonrenewable feedstock (*e.g.* petroleum product, fossil fuel) 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 :

$$\underset{\textbf{(Propene)}}{H_3C{-}CH{=}CH_2} + H_2 \xrightarrow{\text{Ni-catalyst}} \underset{\textbf{(Propane)}}{H_3C{-}CH_2{-}CH_3}$$

$$\underset{\textbf{(Methylacetylene)}}{H_3C{-}C{\equiv}CH} + H_2 \xrightarrow[\text{(Catalyst)}]{\text{Pd-BaSO}_4} \underset{\textbf{(Monoaddition Product)}}{CH_3{-}CH_2{=}CH_2}$$

$$\underset{\textbf{(Methylacetylene)}}{H_3C{-}C{\equiv}CH + CH_3OH + CO} \xrightarrow{\text{Pd-catalyst}} \underset{\textbf{(Methylmethacrylate, MMA)}}{H_3C{-}\underset{\underset{CH_2}{\|}}{C}{-}C({=}O){-}OCH_3}$$

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 :

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

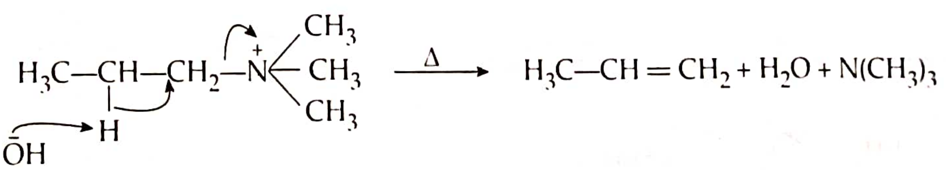
The concept of % atom economy is illustrated in the following examples.

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

$$CH_3CH_2CH_2CH_2—OH + NaBr + H_2SO_4 \rightarrow CH_3CH_2CH_2CH_2—Br + NaHSO_4 + H_2O$$

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

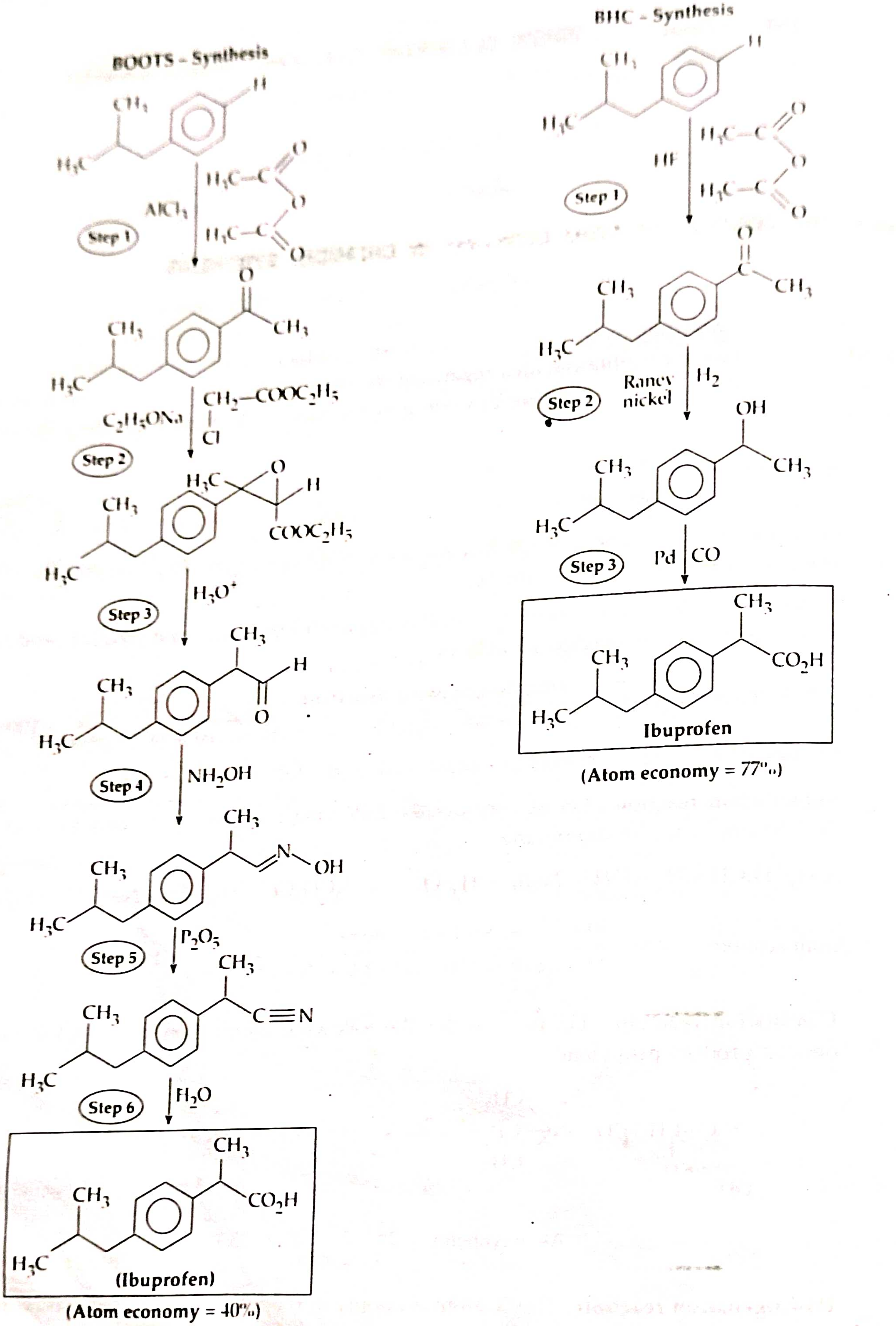
2. **Elimination reaction :** Let us consider the following elimination reaction leading to the desired product propylene.



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

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

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

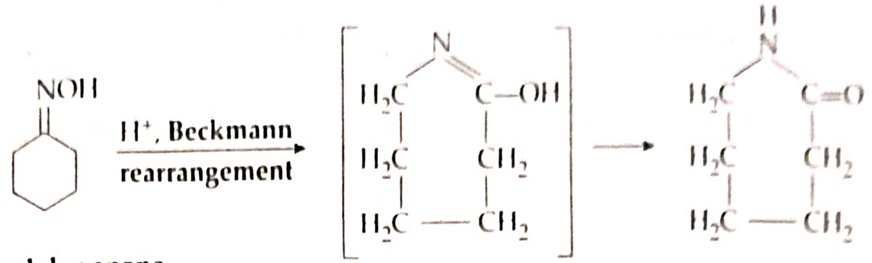


Scheme 19.4.1 : Two different routes of Ibuprofen synthesis.

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

(Atom economy = 47%)

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

(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.

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.

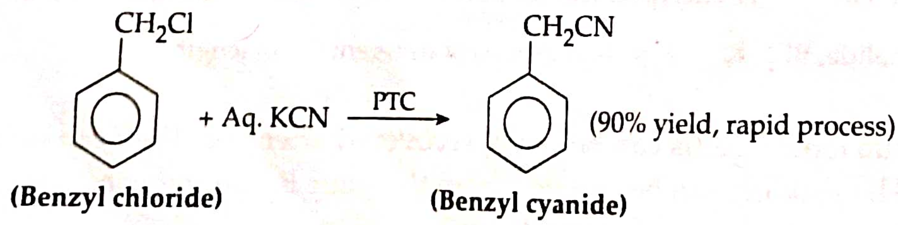
   Supercritical water (T_c = 374°C) (*cf.* Sec. 17.2) is too hot for many organic compounds. But ***near critical water*** appears as a *benign solvent* for many organic reactions.

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.

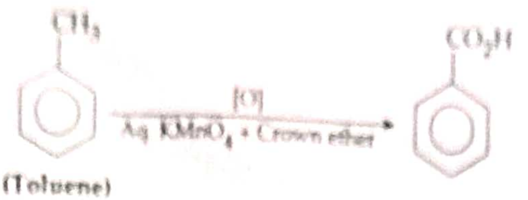
10. **Use of greener catalyst :** Sometimes the used catalysts are toxic and these are accumulated in the industrial waste product. For example HF is the catalyst used in the production of linear alkylbenzenes (for the production of surfactants) and it has been replaced by the greener catalyst *i.e. 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.



Crown ether may also act as a PTC in some cases.



(Toluene)

Here crown ether complexes with K^+ and the oxidant MnO_4^- remains outside the crown ether. Thus $KMnO_4$ is transported into the organic phase where toluene remains.

19.5 GREEN CHEMISTRY IN ACTION : REAL - WORLD CASES

19.5.1 Replacement of CFC and Hydrocarbon Blowing Agents with the Environmentally Friendly Blowing Agent Carbon Dioxide for the Production of Foamed Polystyrene

Problem : *Extruded polystyrene foam sheet* is widely used in packaging of various products. To introduce the foamlike properties in polystyrene sheet, a *blowing agent* is passed through the molten polystyrene mass. In fact, the blowing agent produces bubbles/gas packets in the polystyrene sheet.

The commonly used blowing agents are : CFCs (chloroflurocarbons), hydrochlorofluorocarbons (HCFCs) and aliphatic hydrocarbons (*i.e. volatile organic compounds VOCs*). **These blowing agents cause environmental hazards (cf. Chapter 8).**

CFCs and HCFCs ⟶ Ozone depletion and global warming (*i.e.* greenhouse effect)

Aliphatic hydrocarbons *i.e.* volatile organic compounds (VOCs) ⟶ Ground level **smog formation** and inflammable chraracter of VOCs can cause **fire accidents** at the stage of manufacture

$$\boxed{VOCs + NO \xrightarrow{h\nu} \longrightarrow O_3 + HNO_3 + \text{Organic compounds}}$$

Green Chemistry in action to solve the problems : Carbon dioxide has been chosen as the alternative blowing agent to replace the environmentally hazardous blowing agents like CFCs, HCFCs and VOCs. Use of CO_2 is more eco-friendly and more economic.

- CO_2 does not deplete ozone layer.
- CO_2 does not contribute in smog formation.
- *Global warming potential (GWP)* of CO_2 is far less than that of CFCs and HCFCs; noninflammable character of CO_2 avoids the fire accidents and consequently worker safety is enhanced.
- Use of CO_2 is more economic as it is readily available from different sources (*e.g.* as a by-product from different industries).

- Polystyrene foam sheet made with CO_2 remains flexible for a much longer period.
- Polystyrene foam sheet made with CO_2 can be easily recycled while for the other blowing agents, recycling step needs precaution.

Dow chemicals first introduced the use of CO_2 as a blowing agent in producing polystyrene foam sheets.

10.5.2 Replacement of Ozone Depleting and Smog Producing Solvents by the Surfactant Assisted Liquid or Supercritical Carbon Dioxide for Cleaning in Manufacturing and Service Industries.

Problem : A large amount of organic solvents is used in industry for various purposes like *precision cleaning in microelectronics, optics and electroplating; medical device fabrication; and dry cleaning of garments.* The representative examples of organic solvents used for these purposes are : volatile organic compounds (VOCs); halogenated organics like CFCs, HCFs and PERC ($Cl_2C{=}CCl_2$, *perchloroethylene*). The VOCs participate in ground level smog formation and they can cause fire accidents at the time of uses. The CFCs and HCFCs act as ozone depleting agents in stratosphere and they are also of high global warming potential (GWP); PERC can contaminate ground water; some of the organics including PERC are powerful carcinogens. The environmental hazards from the said organic solvents and VOCs have been discussed in Chapter 8.

Green Chemistry in action to solve the problems : Liquid or supercritical CO_2 in presence of suitable surfactants can largely replace the above mentioned hazardous organic solvents for the said purposes.

To use CO_2 as a solvent, it is brought into the liquid or supercritical state. For CO_2, the *critical temperature* (T_c) and *critical pressure* (P_c) are 31°C and 72.8 atm respectively. If the temperature is below the T_c, then by exerting pressure, a gas can be brought into its liquid state. If the temperature and pressure are kept above the T_c and P_c then the gas attains the *supercritical fluid state* that represents ***an intermediate state of gaseous and liquid state.*** In the supercritical state, because of the high pressure, the molecules are closely spaced to mimic the liquid state. **In the superciritical state, the density is close to that of liquid state while the viscosity is close to that of gaseous state.** Thus, the supercritical state possesses these unique properties to act as a solvent.

In presence of suitable surfactants, liquid and supercritical CO_2 can act as a good industrial solvent for cleaning purposes and it can replace the existing organics.

The presence of surfactants can enhance the solubility of industrial materials like waxes, greases, heavy oils, polymers, proteins, nonpolar residues, etc. in liquid and supercritical CO_2. In the surfactant molecule, there is a *polar head group* and *a nonpolar chain.* The nonpolar tails of surfactants can aggregate in a polar solvent (e.g. SC–CO_2) to produce a *nonpolar core* with a *polar surface* made by the polar groups of the surfactant molecules. Thus the **micelles** mimicking ***oil-in-water*** (o/w) are formed. In the nonpolar core of the micelles, nonpolar solutes (*e.g.* greases, waxes, oils etc.) are dissolved. For liquid or supercritical CO_2 solvent, the surfactant molecule possesses a **CO_2 phobic chain segment** (that produces the *core of the micelle*) and a **CO_2-philic chain segment** (that produces the periphery of the micelle). **The carbon chain bearing F-substituents (i.e. fluoropolymer) is CO_2–philic while the polystyrene block is CO_2–phobic.** The solubility of fluoropolymer chain in CO_2 arises due to van der Waals forces between the fluorocarbon tail and CO_2. *Bonds in both CO_2 and fluorocarbon tails are polar.* Thus