Green Chemistry

-greener chemistry

Chemical disasters

- The Cuyahoga River in Ohio became so polluted with chemicals it caught fire (1969).

River in which a person "does not drown but decays"

- ❑ The surface was covered with the brown oily film
- ❑ Large quantities of black heavy oil floating in slicks, sometimes several inches thick.
- ❑ No animal life and very minute concentration of dissolved oxygen
- ❑ Sparks from a passing train set fire to oil-soaked debris floating on the water's surface.
- ❑ Fire caused $1 million in damage to boats, a bridge, and a riverfront office building

- A plant accident in Bhopal, India, released methyl isocyanate. Nearly 4000 people died (1984).

558,125 injuries including 38,478 temporary partial injuries and approximately 3,900 severely and permanently disabling injuries

- An accidental release of chemicals, including dioxin, in Seveso, Italy, in 1976 resulted in death of farm animals and long-term health problems for many local residents.

- Flixborough Disaster (1974): Explosion due to the leakage of cyclohexane. 28 died and several injured

- Panipat tragedy: Liquid ammonia burst out at the high pressure. 11 died

- Endosulfan disaster: The pesticide polluted the drinking water and the consumption of this water by the people and animals resulted in diseases ranging from physical deformities, cancers, birth disorders and damages to brain and nervous system.

- Carbon disulfide (CS_2) leakage at Hindustan Insecticides Ltd, Kochi: 1 died and 11 injured

In last decade, 130 significant chemical accidents reported in India: 259 deaths and 563 number of major injured.

Environmental disasters

❑ DDT

- banned in U.S about 40 years ago and worldwide under Stockholm Convention on Persistent Organic Pollutants 2001 but we continue to live with its long-lasting effects.
- persists for a long time in the environment and accumulates in the food chain and in the tissues of living organisms.

❑CFCs

- Montreal Protocol to Protect the Ozone Layer (1989)

❑ Love Canal

Canal digged between the upper and lower Niagara Rivers to generate power cheaply. But the project was unsuccessful and the canal was turned into a municipal and industrial chemical dumpsite.

Chemists Must Place a Major Focus on the Environmental Consequences of Chemical Products and the Processes by which these Products are Made.

We must consider our chemical ecological footprint.

Origin & Evolution of Green Chemistry

- Silent Spring by Rachel Carson (1962): Harmful effects of synthetic pesticides

- President John F. Kennedy ordered the President’s Science Advisory Committee to examine the issues raised by the book.

- In 1969, Congress recognized the importance of the issue and passed the National Environmental Policy Act (NEPA). The law's goal was to "create and maintain conditions under which man and nature can exist in productive harmony,"

- US Environmental Protection Agency (EPA) was created in 1970 by President Richard Nixon for the purpose of protecting human health and the environment by writing and enforcing regulations based on laws.

Origin & Evolution of Green Chemistry

- The EPA's first major decision was to ban the use of DDT and other chemical pesticides. Congress passed a series of regulatory laws to stem the environmental impact of pollution.

Risk=f(Hazard, ~~Exposure~~)

Until 1980's Environmental Laws Attempt To Control Exposure

Controlling Exposure =

"end of the pipe solution"

Sustainable Development

United Nations 1987,

"...... Meeting the needs of the present without compromising the ability of future generations to meet their own needs."

1. Economic sustainability
2. Social sustainability
3. Environmental sustainability ✓

Origin & Evolution of Green Chemistry

- EPA established the Office of Pollution Prevention and Toxics in 1988 recognizing the need to shift from end-of-pipeline control to pollution prevention.
- The Pollution Prevention Act stating that the first choice for preventing pollution is to design industrial processes that do not lead to waste production was passed in 1990 under the George H.W. Bush Administration.

Risk=f(~~HAZARD~~, Exposure)

Eliminate the hazard, no need to worry about the exposure!

Evolution of Green Chemistry

- Prof. Paul T. Anastas of the EPA Office of Pollution Prevention and Toxins, coined the phrase "Green Chemistry" and sowed the seeds of productive collaboration between government, industry, and academia.
- EPA introduced Green Chemistry which seeks to reduce and prevent pollution at its source, as a formal area of work in 1991.
- The first symposium, "Benign by Design: Alternative Synthetic Design for Pollution Prevention," was held in 1994 in Chicago.
- In 1995, President Bill Clinton established the Presidential Green Chemical Challenge Awards.
- In 1997 The Green Chemistry Institute was launched by Joe Breen.
- Twelve Principles of Green Chemistry" was published by Paul Anastas and John Warner in 1998.

Evolution of Green Chemistry

- The Royal Society of Chemistry in London formed “The Green Chemistry Network” and started to publish the paper “Green Chemistry”
- In 2001, the Green Chemistry Institute became a part of the American Chemical Society (ACS).
- The Nobel Prize in Chemistry was won for research in areas of chemistry that were largely seen as being green chemistry in both 2001 (Knowles, Noyori, Sharpless) and 2005 (Chauvin, Grubbs, Schrock).
- In 2005, the ACS GCI established an industrial roundtable for the Pharmaceutical industry, to catalyze and enable green and engineering into chemical businesses

GREEN CHEMISTRY

PREVENTING POLLUTION

SUSTAINING THE EARTH

Aims at reducing

cost

materials

waste

risk

hazard

energy

GREEN CHEMISTRY MEANS…

- Preventing pollution before it happens rather than cleaning up the mess later.

- Saving companies money by using less energy and fewer/safer chemicals, thus reducing costs & impacts of pollution.

- Mitigating climate change, water & resource depletion, & growing demands for safer food and cleaner energy

12 Principles of Green Chemistry

1. **Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
2. **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
5. **Safer Solvents and Auxiliaries.** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
6. **Design for Energy Efficiency.** 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. **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.
8. **Reduce Derivatives.** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible .
9. **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation.** Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.
11. **Real-time Analysis for Pollution Prevention.** 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. **Inherently Safer Chemistry for Accident Prevention.** Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Anastas, P. T.; Warner, J.C. Green Chemistry: Theory and Practice, Oxford University Press,1998.

1. Waste prevention

- It is better to prevent the formation of waste than to treat or clean up the waste.
- Chemical wastes are undesirable products and are usually hazardous to the environment. Waste disposal in expensive as well.

For chemical reaction of the type

$$A + B \longrightarrow P + W$$

Find alternate A or B to avoid W

- Industrial processes should be designed to minimize the generation of waste.
- Make sure that the reagents are getting completely converted into the products during the course of the reaction and there is no unreacted reagent as waste
- Experiments in micro scale can reduce the waste and cost of disposal of waste in Universities and colleges.

2. Maximizing atom economy

- Traditionally, the success of a chemical reaction is judged by the percentage yield of product.

$$\text{Percentage yield} = \frac{\text{Actual yield to the product}}{\text{Theoretical yield to the product}} \text{ X } 100$$

If 1 mole of reagent produces 1 mole of the product, yield is 100%

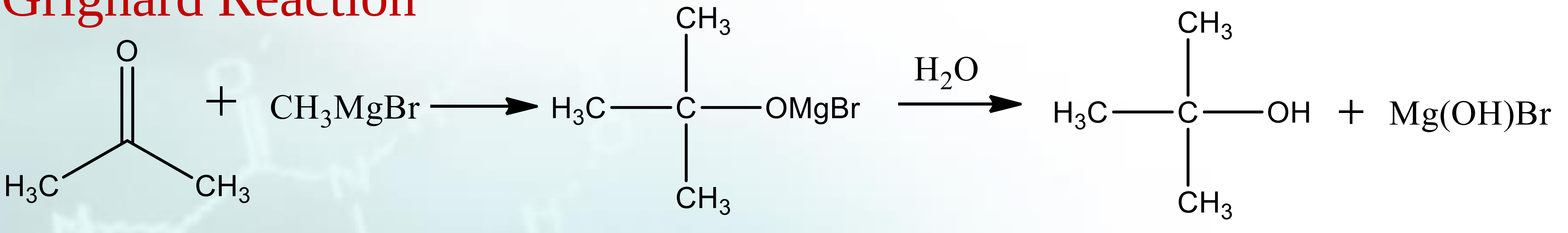
What is missing?

- ○ What are the by products?
- ○ How much waste is generated?
- ○ Is the waste environmental friendly?
- ○ Are the by products benign and/or useable?
- ○ Are purification steps needed?
- ○ What are the solvents used?
- ○ Is the catalyst stoichiometric or catalytic?

Example

Hofmann elimination, Witting reaction and Grignard reaction proceed with 100% yield but,

Grignard Reaction

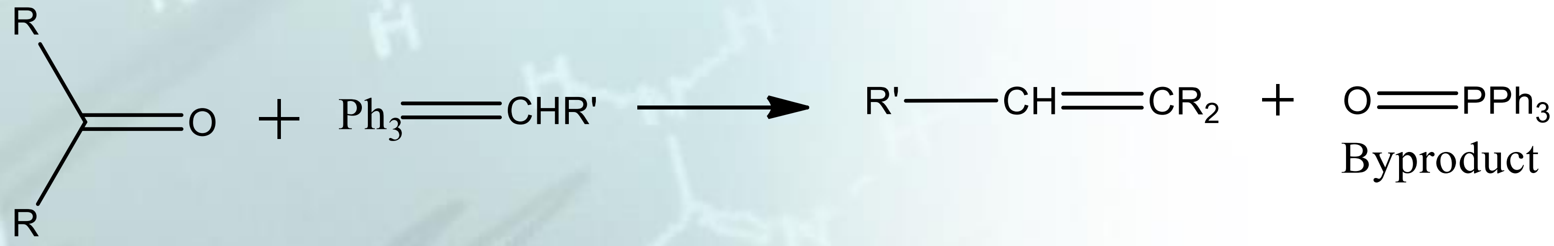


1 mole, 58g

1 mole, 74g

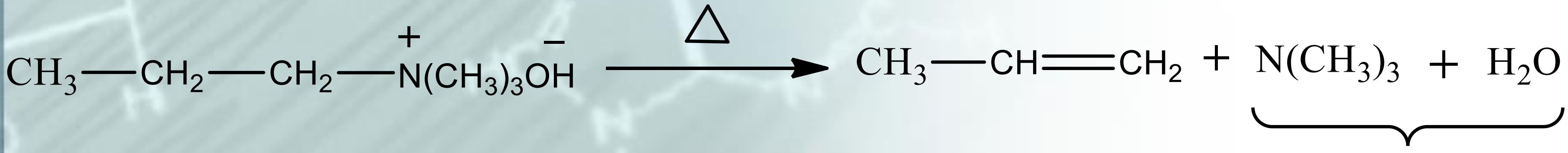
1mole, 121.2g

Witting Reaction



Byproduct

Hoffmann Elimination



$$CH_3{-}CH_2{-}CH_2{-}\overset{+}{N}(CH_3)_3\overset{-}{O}H \xrightarrow{\Delta} CH_3{-}CH{=}CH_2 + \underbrace{N(CH_3)_3 + H_2O}_{\text{Byproducts}}$$

Concept of atom economy

-developed by Barry Trost of Stanford University

$$\% \, Atom \; Utilization = \frac{MW \; of \; desired \; product}{MW \; of \; all \; products} \; \mathrm{X} \, 100$$

Concept of Atom Economy was quantified by Roger A. Sheldon

$$\% \, Atom \; Economy = \frac{FW \; of \; atoms \; utilized}{FW \; of \; all \; reactants} \; \mathrm{X} \, 100$$

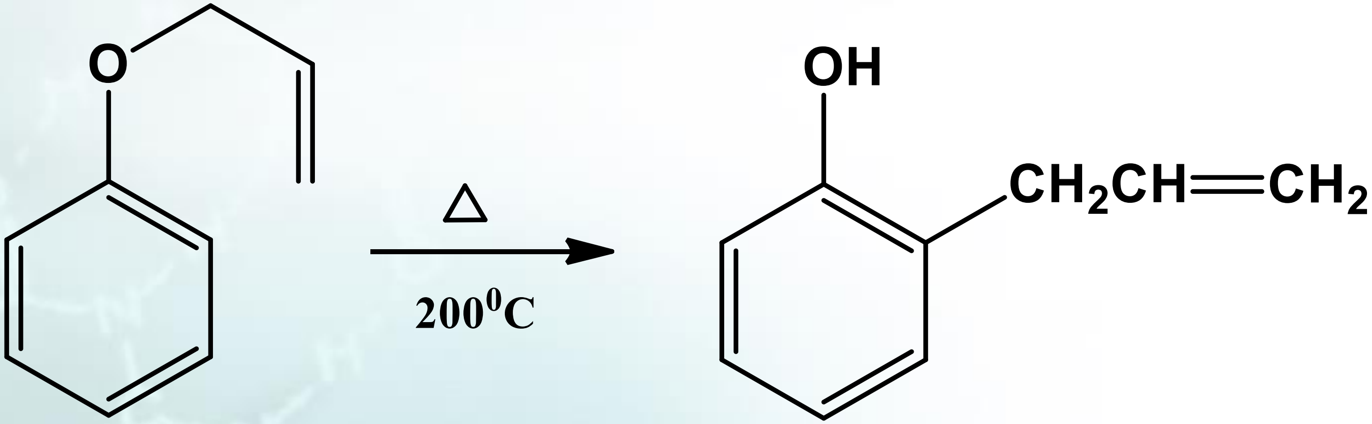
Higher the value of the atom economy, the better is the reaction to convert all the reactant atoms to the desired product. ⇒ Less waste

Common type of organic reactions are:

❑ Rearrangement reactions	Greener Reactions
❑ Addition reaction	Greener Reactions
❑ Substitution reactions	Less atom economic
❑ Elimination reaction	Less atom economic

Rearrangement reactions

Claisen rearrangement



Allyl phenyl ether

o-Allyl phenol

	Reagent formula	FW (g/mole)	Utilized formula	FW	Unutilized formula	FW
	$C_9H_{10}O$	134.173	$C_9H_{10}O$	134.173	-	-
Total	$C_9H_{10}O$	134.173	$C_9H_{10}O$	134.173	-	-

$$\% \text{ Atom Economy} = \frac{134.173}{134.173} \text{ X } 100$$

Addition reactions

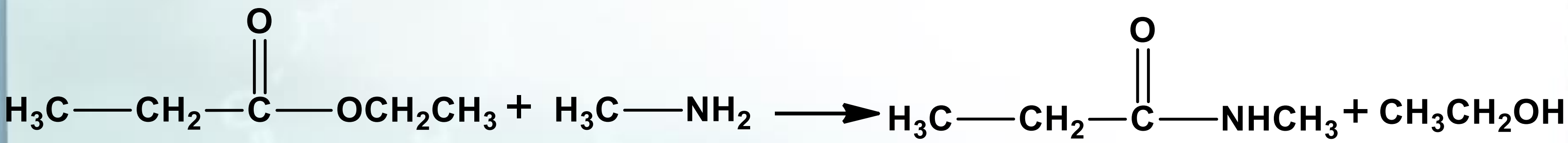
Catalytic hydrogenation of propene

$$CH_3CH{=}CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3$$

Cycloaddition of butadiene and ethene

Substitution reactions

Reaction of ethyl propionate with methyl amine



$$H_3C-CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_3 + H_3C-NH_2 \longrightarrow H_3C-CH_2-\overset{\overset{O}{\|}}{C}-NHCH_3 + CH_3CH_2OH$$

Ethyl propionate

N-methyl propamide

	Reagent formula	**FW (g/mole)**	**Utilized formula**	**FW**	**Unutilized formula**	**FW**
	$C_5H_{10}O_2$	102.132	C_3H_5O	57.057	C_2H_5O	46.061
	CH_5N	31.057	CH_4N	30.049	H	1.008
Total	$C_6H_{15}NO_2$	133.189	C_4H_9NO	87.120	C_2H_6O	46.069

$$\%\ \text{Atom Economy} = \frac{87.120}{133.189} \times 100 = 65.41\ \%$$

Calculate the atom economy of each of the following conversions

$C_4H_9OH + KBr + H_2SO_4 \rightarrow C_4H_9Br + KHSO_4 + H_2O$

136.9 136.2 18.0

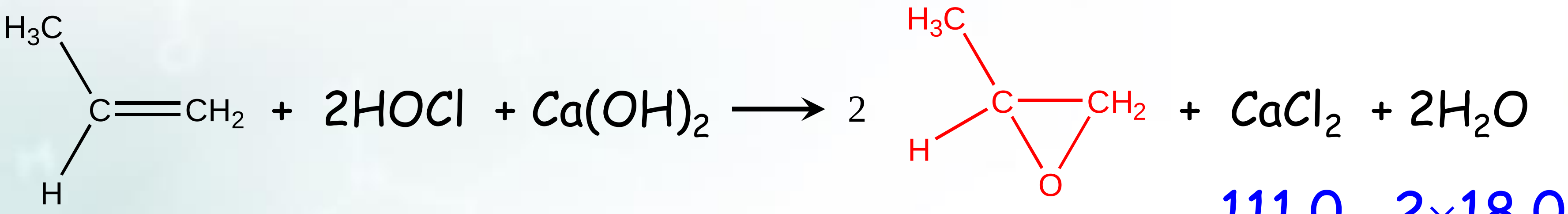
$$AE = \frac{136.9}{136.9 + 136.2 + 18.0} \times 100\%$$ = 47.0%

$3C_4H_9OH + PBr_3 \rightarrow 3C_4H_9Br + H_3PO_3$

3×136.9 82.0

$$AE = \frac{3 \times 136.9}{3 \times 136.9 + 82.0} \times 100\%$$ = 83.4%

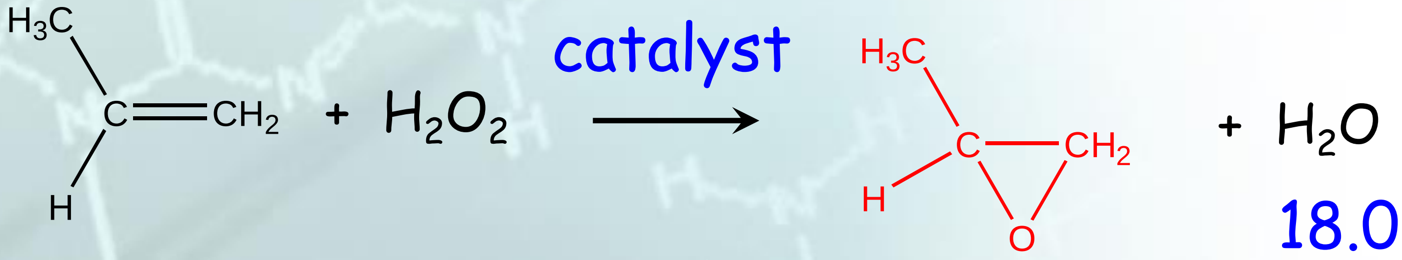
Greener



111.0 2×18.0

2×58.0

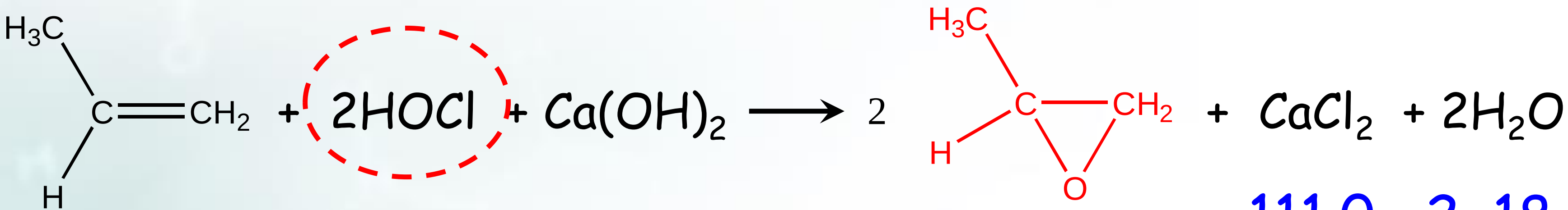
$$AE=\frac{2\times58.0}{2\times58.0+111.0+2\times18.0}\times100\% = 44.1\%$$



18.0

58.0

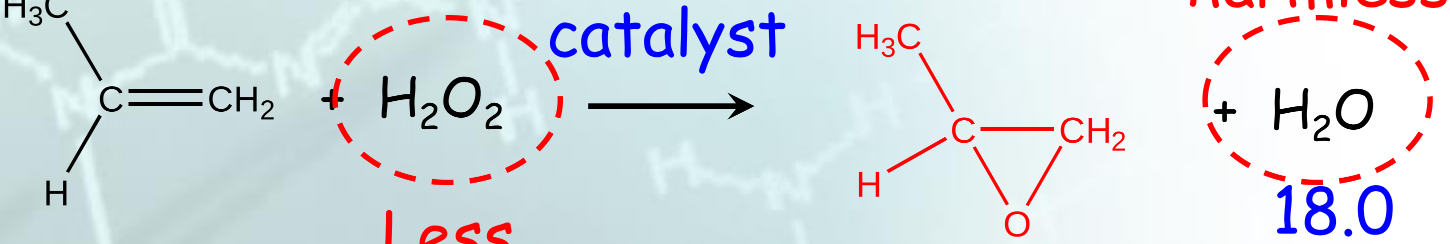
$$AE=\frac{58.0}{58.0+18.0}\times100\% = 76.3\%$$



More harmful

2×58.0

111.0 2×18.0



Less harmful

harmless

58.0

18.0

Greener

3. Using less hazardous chemical syntheses

- Chemical syntheses should be designed to use or generate substances that possess little or no toxicity to humans and the environment.

❖ **No hazardous starting material**

❖ **No hazardous byproducts**

❖ **Workers using the toxic materials should wear protective clothing and respirators**

- Consider the synthesis of adipic acid ($HOOC(CH_2)_4COOH$).

- Adipic acid is the essential feedstock for making synthetic fibres such as nylon.

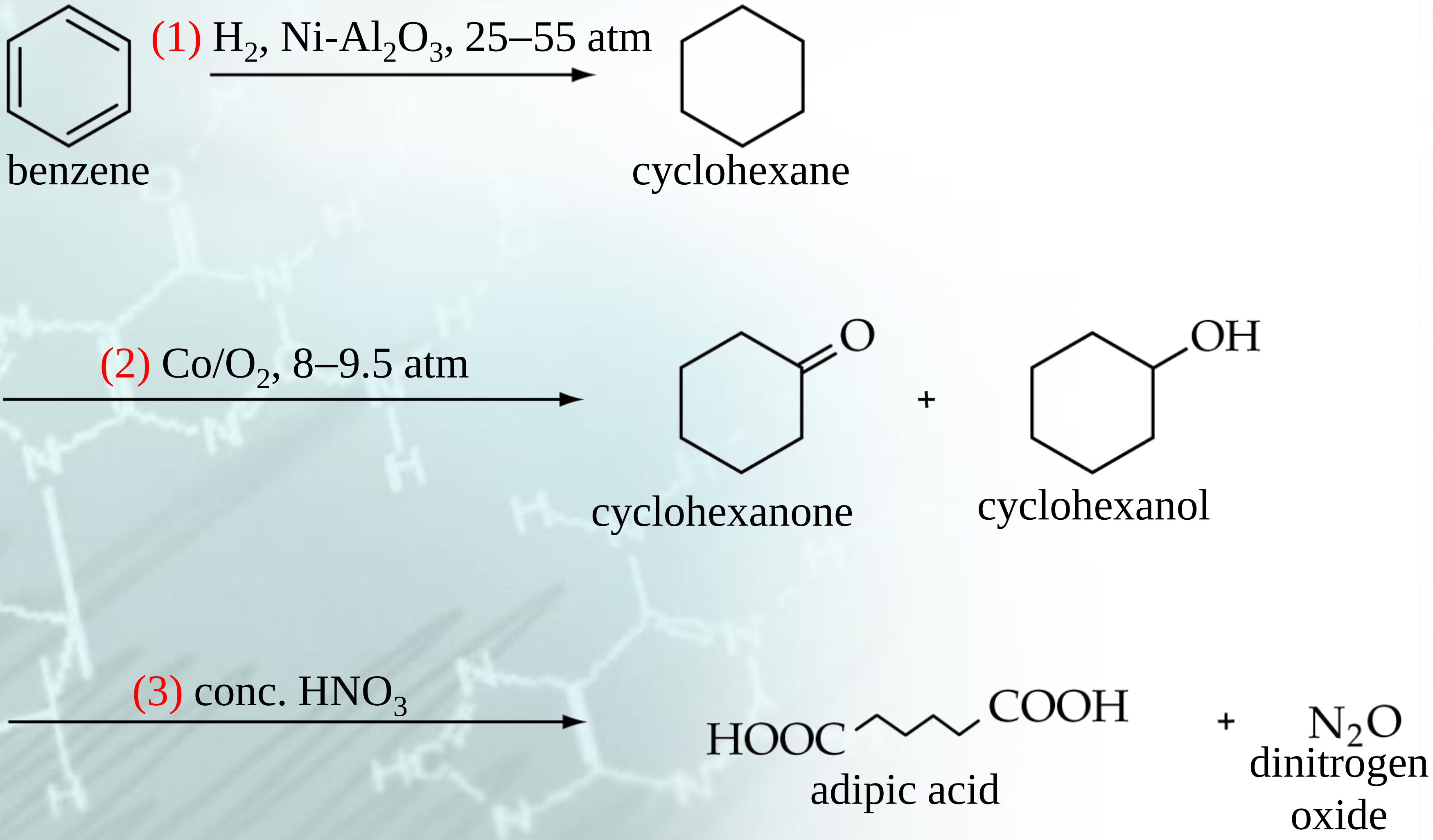
Traditional method

$$C_6H_6 \longrightarrow HOOC(CH_2)_4COOH$$

New method

$$C_6H_{12}O_6 \longrightarrow HOOC(CH_2)_4COOH$$

Traditional Method



benzene

(1) H_2, Ni-Al_2O_3, 25–55 atm

cyclohexane

(2) Co/O_2, 8–9.5 atm

cyclohexanone

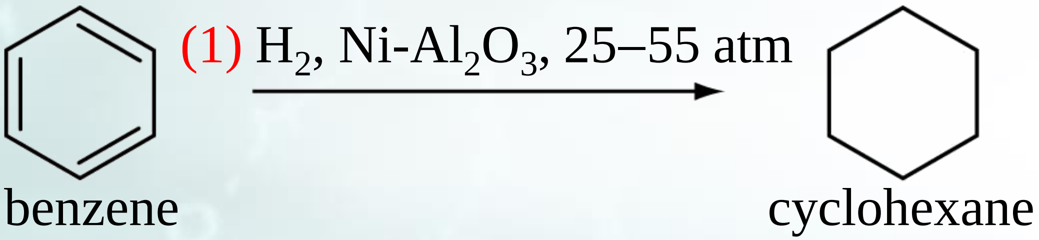
cyclohexanol

(3) conc. HNO_3

adipic acid

N_2O
dinitrogen
oxide

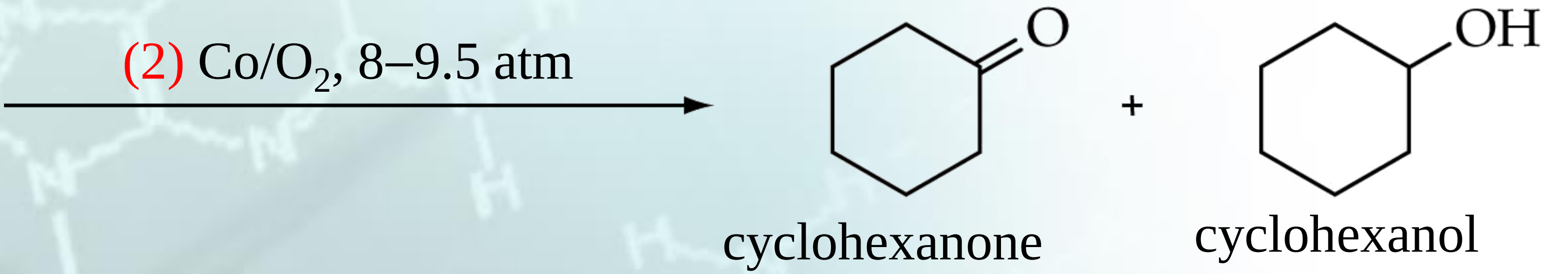
Traditional Method



- The synthesis has the following risks and hazards:
  - In step 1, the starting material for the synthesis is benzene, which is a known carcinogen.

Traditional Method

- In step 2, the oxidation of cyclohexane with air may lead to an uncontrolled reaction. It has the risk of explosion.

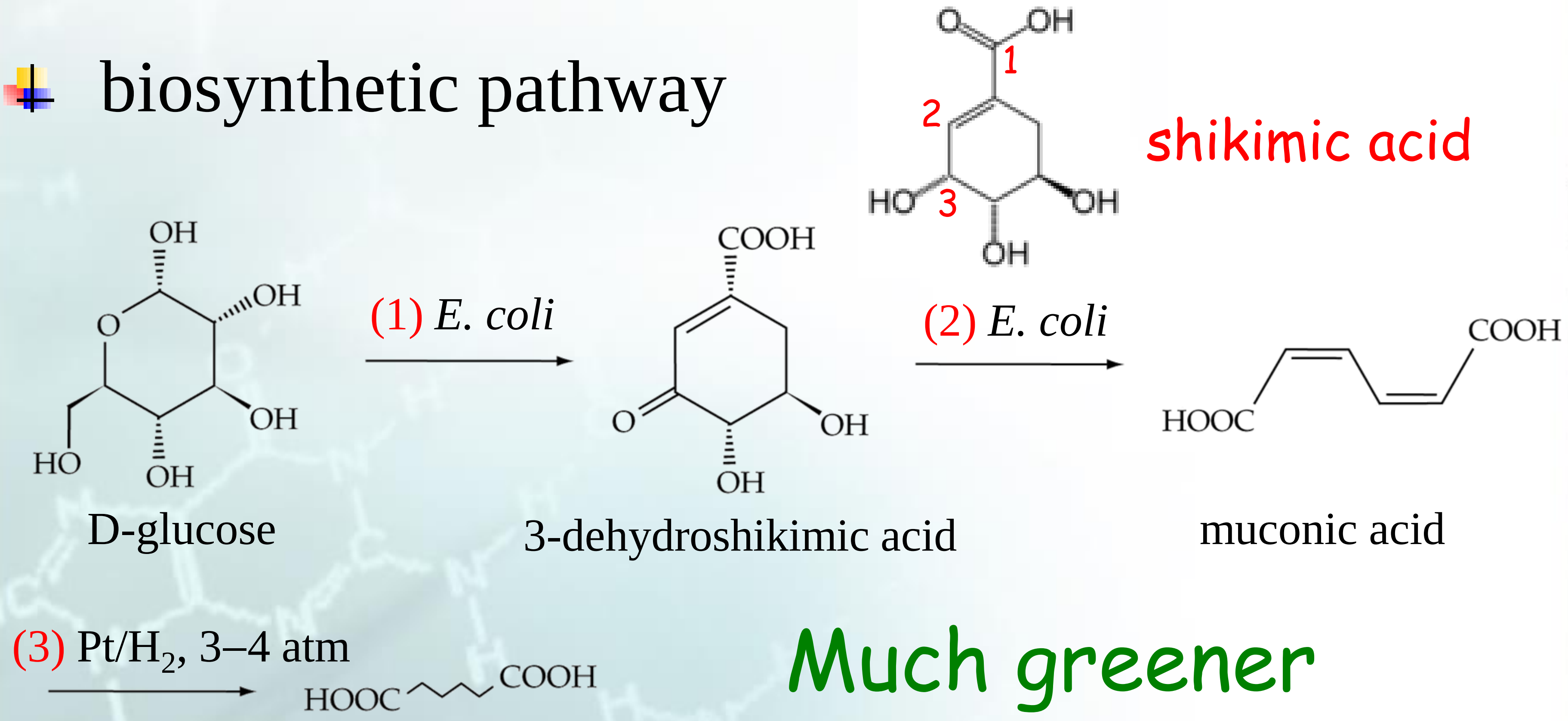


- Not all of the cobalt catalysts can be recovered. This may lead to the disposal of a heavy metal to the environment.

Traditional Method

- In step 3, dinitrogen oxide or nitrous oxide (N_2O) gas is produced as a by-product. It is a greenhouse gas with an effect which is 200 times the effect of carbon dioxide.

biosynthetic pathway



shikimic acid

(1) *E. coli*

(2) *E. coli*

(3) Pt/H_2, 3–4 atm

D-glucose

3-dehydroshikimic acid

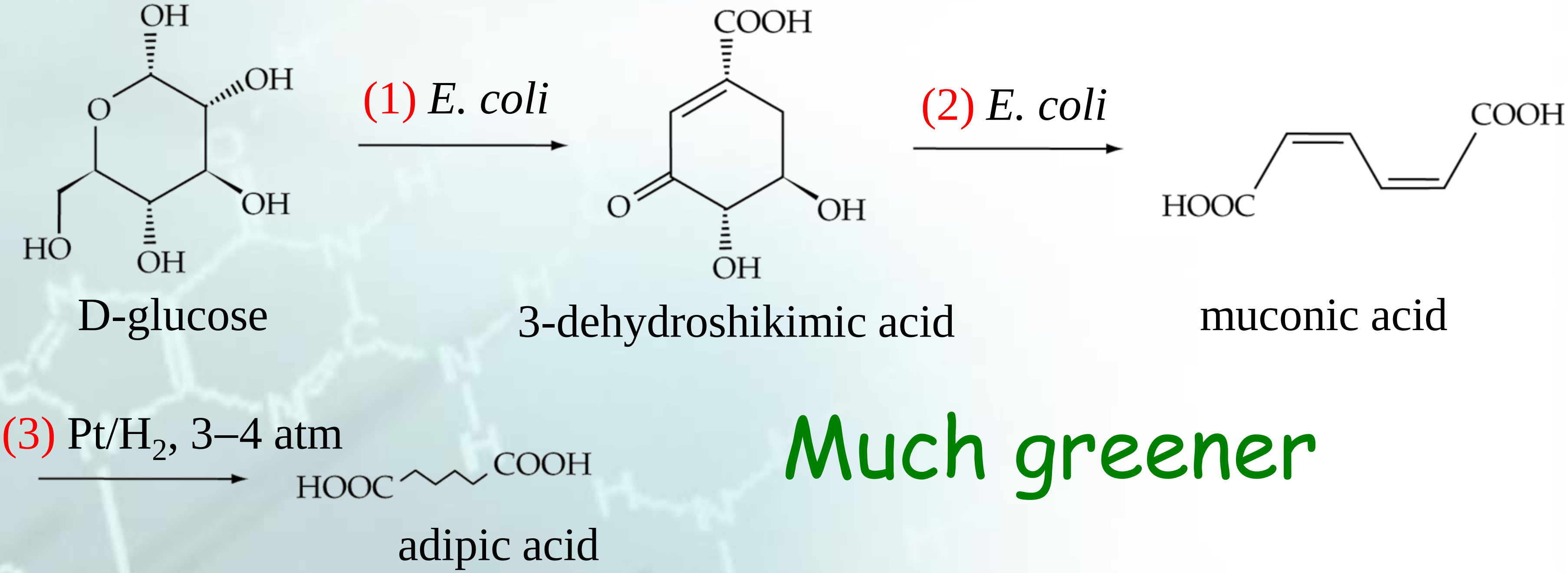
muconic acid

adipic acid

Much greener

1. the starting material, glucose, is harmless.

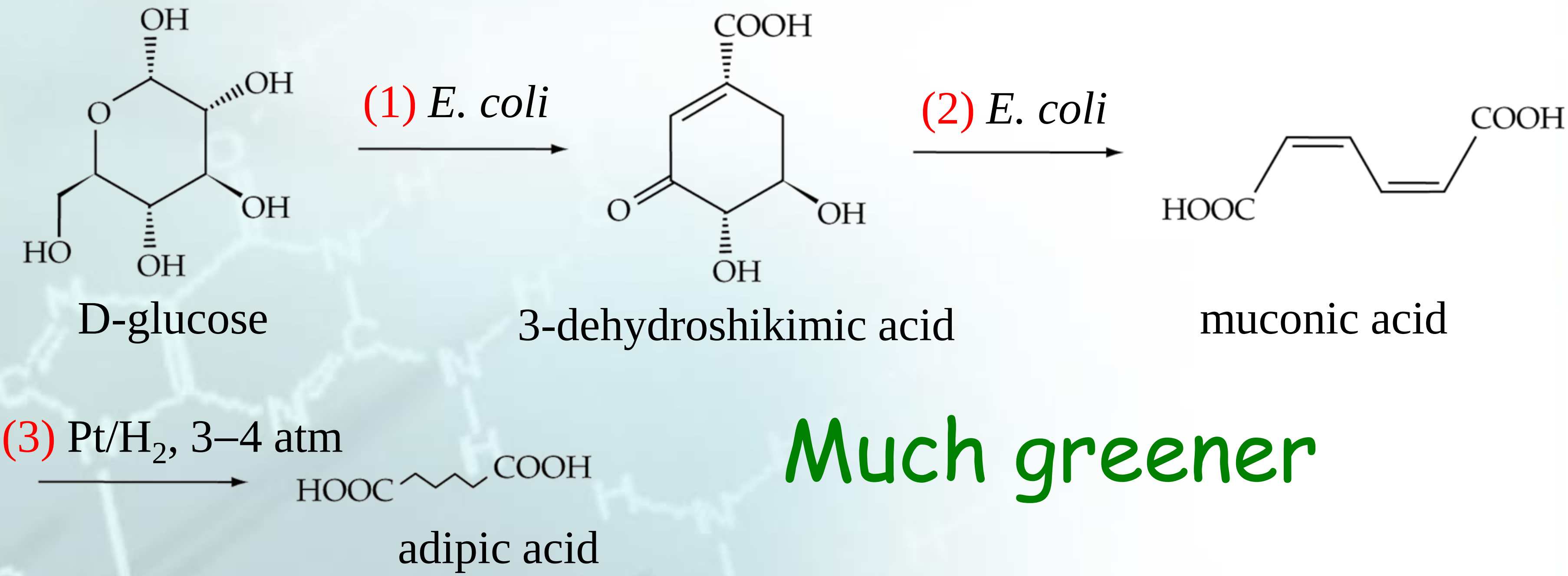
biosynthetic pathway



Much greener

2. E. coli is used to catalyse two steps of the reaction. This reduces the use of certain chemical reagents with significant toxicity.

biosynthetic pathway



(1) *E. coli*

(2) *E. coli*

(3) Pt/H_2, 3–4 atm

D-glucose

3-dehydroshikimic acid

muconic acid

adipic acid

Much greener

3. there are no by-products generated during the synthesis.

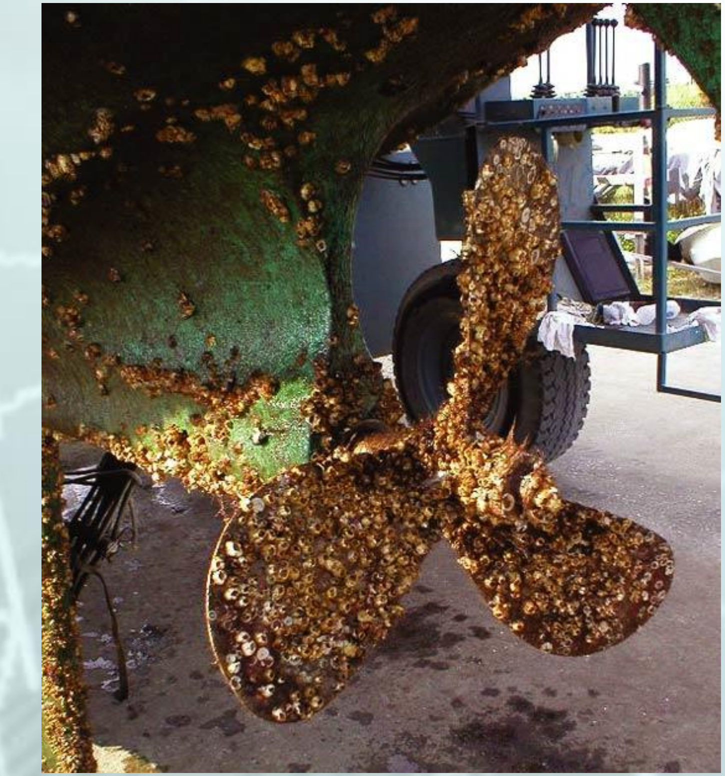
4. Producing safer chemical products

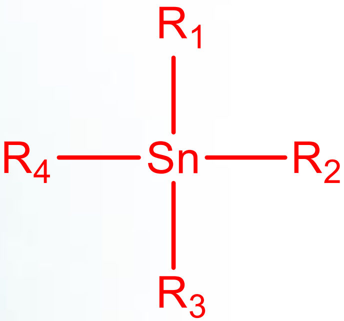
- The chemical products should be designed to preserve efficacy of function while reducing toxicity.

- Products showing toxicity, carcinogenicity, mutagenicity, neurotoxicity and reproductive and developmental toxicity must be avoided.
- Structure and its activity should be studied and functionality related to toxicity should be avoided.
- Minimize the bioavailability of toxic substances

- Thalidomide: A drug for reducing the effects of nausea and vomiting during pregnancy
- Birth defects in children born to women taking this drug.
- Drug banned and withdrawn
- Later found Thalidomide is a chiral drug
- One enantiomer act as drug and other enantiomer causes birth defect
- Thalidomide now approved under strict regulations for treatment of severe leprosy

- Organotin compounds (Anti-biofouling agent) were used in large ships to prevent accumulation of barnacles and marine plants traditionally.





The accumulation of barnacle on the ship may increase the resistance to its movement.

- However, organotin compounds are highly toxic to the surrounding marine life.
- Then, Rohm and Haas Company developed a non-toxic alternative called Sea-Nine^{TM}. It degrades quickly in the marine environment and is not toxic to the surrounding marine life.
- Sea-Nine gained the first ever Green Chemistry Challenge Award in the category for Designing Safer Chemical Products awarded by the U.S EPA

5. Using safer solvents and auxiliaries

- The solvents and auxiliaries (e.g. drying agent, blowing agent, etc.) used in chemical syntheses will become part of the wastes.
- They may cause environmental pollution and health hazard.
- Besides using safer solvents pathway for a reaction could be such that there is no need for purification and separation

CFCs : - *Miracle Compound*

unreactive

volatile liquids or easily liquefied gases

low flammability

low toxicity

⇒ Cleaning solvents

Propellants

Refrigerants

Blowing agents

- They were eventually banned because they deplete the ozone layer.

Screening of UV radiations by ozone layer

Formation of Ozone

$$O_2 \xrightarrow[242\ \mathrm{nm}]{h\upsilon} O + O$$

$$O_2 + O \longrightarrow O_3$$

Decomposition of Ozone

$$O_3 \xrightarrow{215\text{ -}295\ \mathrm{nm}} O + O_2$$

$$O + O_3 \longrightarrow O_2 + O_2$$

~99% of UV radiation from the sun are screened out

$$\mathrm{CFCl_3} \xrightarrow{\mathrm{UV}} \overset{\bullet}{\mathrm{CFCl_2}} + \overset{\bullet}{\mathrm{Cl}}$$

$$\left.\begin{array}{l} \overset{\bullet}{\mathrm{Cl}} + O_3 \longrightarrow \mathrm{ClO} + O_2 \\ \mathrm{ClO} + O_3 \longrightarrow \overset{\bullet}{\mathrm{Cl}} + 2O_2 \end{array}\right\} \text{chain reaction}$$

One $\overset{\bullet}{\mathrm{Cl}}$ free radical can destroy 100000 ozone molecules

- Nowadays, CO_2 is used to replace CFCs as the blowing agent.
- CO_2 is non-toxic and non-flammable. It does not deplete the ozone layer.

STYROFOAM produced with carbon dioxide as the blowing agent

- Many solvents currently used in the chemical industry are harmful and Volatile Organic Compounds (VOCs) difficult to dispose.

E.g. Propanone, benzene, dichloromethane, dibromomethane, chloroform and carbon tetrachloride.

$$VOCs + NO_x \xrightarrow{UV} \text{photochemical smog}$$

Safer Alternatives ?

- ☐ Use of water as an environmentally innocuous solvent
- ☐ Use of liquid or supercritical carbon dioxide
- ☐ Use of non-volatile solvents: ionic liquids
- ☐ Use of hybrid solvent systems of the three above
- ☐ Solvent-less reactions

1. Aqueous Media as Solvents for Chemical Synthesis and Processes.

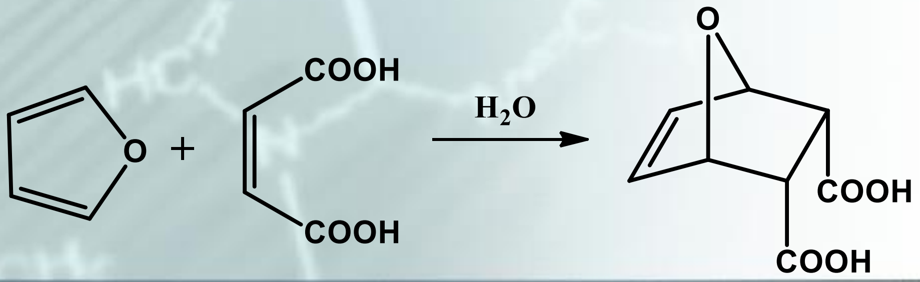
Advantages:

- Non-toxic
- Non-flammable
- Inexpensive
- Environmentally benign

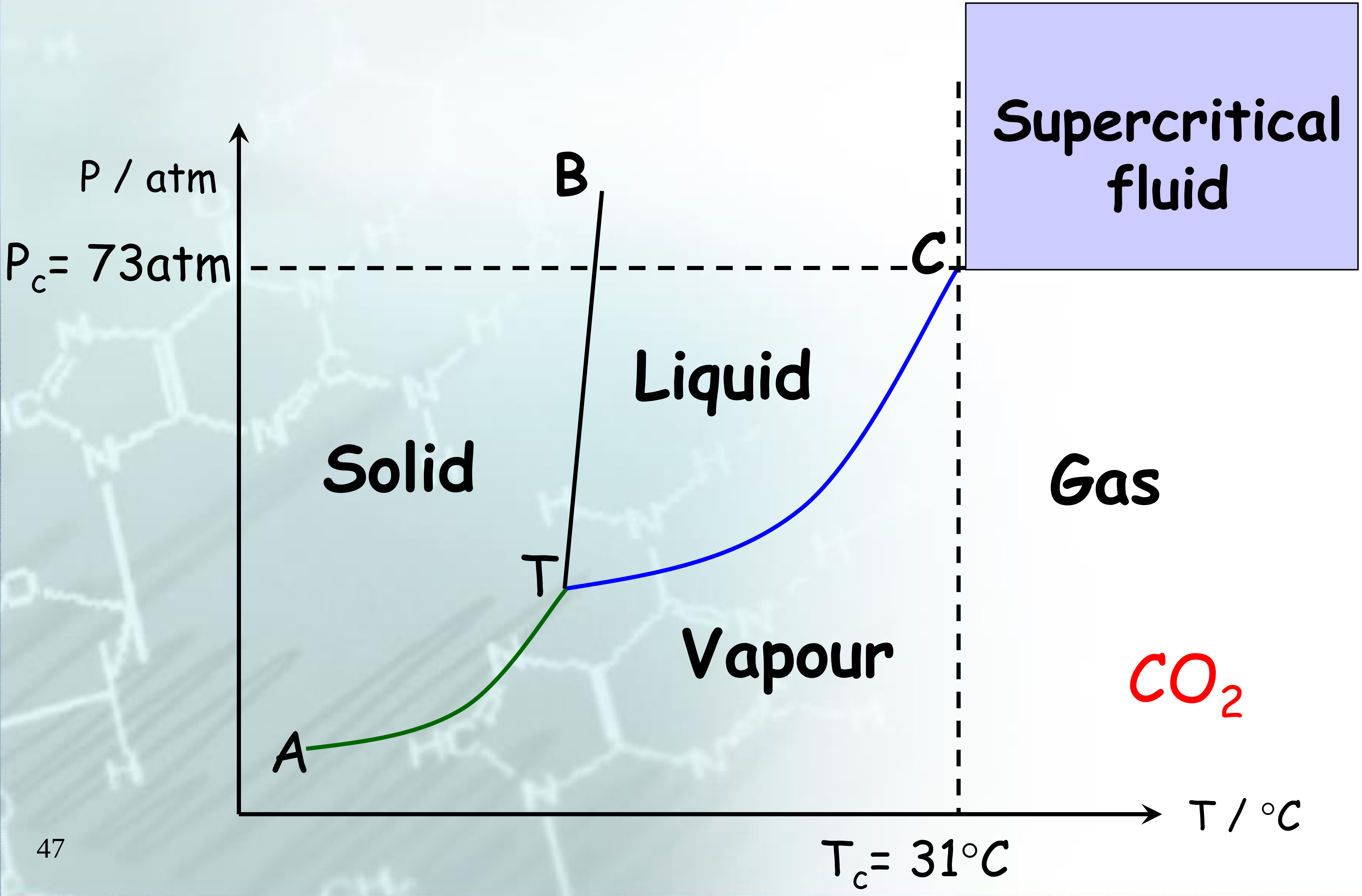
Disadvantages:

- Many organic compounds are not soluble in water

E.g. Diel’s Alder reaction of furan with maleic acid



2. Use of liquid or supercritical carbon dioxide



Advantages:

- ✓ Non-toxic
- ✓ Readily Available
- ✓ Non-flammable
- ✓ Inexpensive
- ✓ Recyclable
- ✓ Solvent properties can be tuned by changing temperature and pressure
- ✓ Can penetrate a solid sample faster than liquid solvents because of it's high diffusion rates

Disadvantages:

- ✓ Low viscosity
- ✓ Low dielectric constant and surface tension
- ✓ Difficult to dissolve polar and ionic species

Using supercritical CO_2 as solvent in decaffeination

$$\underset{\text{with caffeine}}{\text{Coffee beans}} \xrightarrow[\text{Supercritical } CO_2]{\text{decaffenation}} \underset{\text{without caffeine}}{\text{Coffee beans}}$$

In the past, solvents used for decaffeination are harmful to the environment and human beings E.g. $CHCl_3$, CH_2Cl_2, benzene

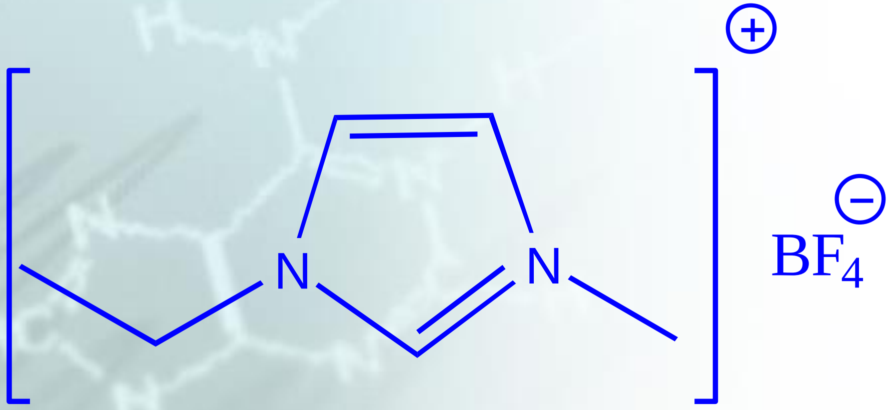
Supercritical CO_2 has:

1. the high diffusion of a gas that allows it to penetrate deep into the beans
2. the high density of a liquid that dissolves 97–99% of the caffeine
3. Will not reinforce the greenhouse effect since $scCO_2$ comes from the atmospheric CO_2

3. Using ionic liquids as solvents

- Salts having a low melting point hence liquid at room temperature.
- The ions are poorly coordinated.
- Low M.P. due to poor packing between ions of significantly different sizes.
- At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice.
- High B.P. due to ionic nature: Low volatility

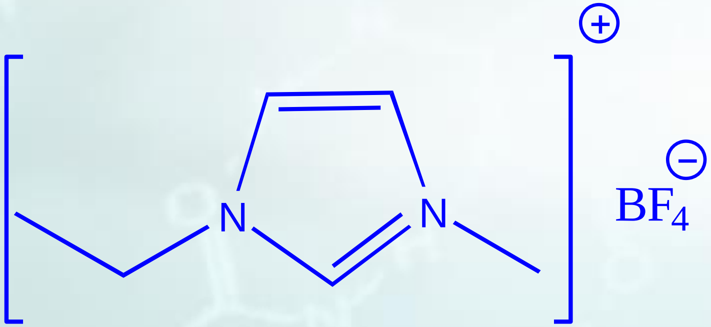
E.g.



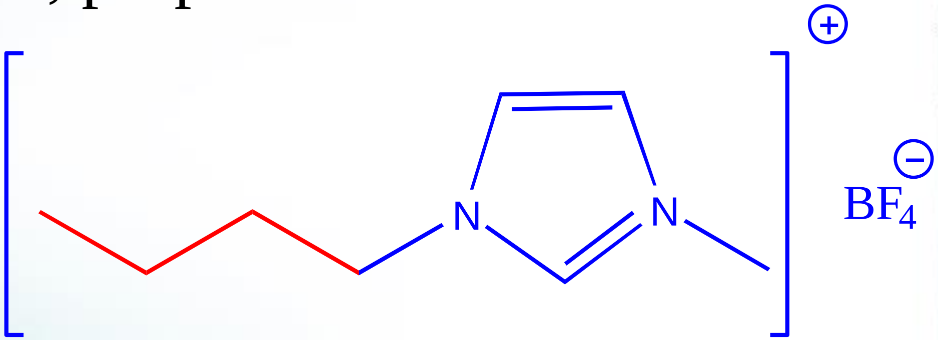
$[emim][BF_4]$

e – ethyl
m – methyl
im - imidazolium

By modifying the structures, substituents on the organic part, counterion or charges of the ions, properties can be tuned



[emim][BF_4]



More viscous

[bmim][BF_4]

Ionic liquids can exhibit specific properties such as m.p., viscosity, volatility & hydrophobicity to meet the particular needs of a synthesis.

Designer solvents

Advantages of using ionic liquids over using VOCs as solvents

1. Tailor-made
2. High b.p.

- Not easily escape to the environment
- Volatile organic reactants/products can be easily removed by simple distillation.
- The solvents can be easily recycled and reused

3. Low flammability due to their low vapour pressure
4. Wide liquid range due to low m.p. and high b.p.

   Organic syntheses can occur at higher temperatures

5. Ionic nature can allow organic syntheses involving ionic species.

4. Synthesis in solid state (Solventless reactions)

- Reactions in solid state are simple to handle, reduce pollution, and cheaper to operate.
- Not easy for reactions involving heating as heat exchange is difficult without a solvent
- Alternatively reactant in suitable solvent can be adsorbed on solid support (polymer) and carry out reaction under microwave irradiation.
  - Polmer supported reagents can be recycled
  - Purification is simpler
- Microwave heating is suitable only for polar reactants which are active to microwave.

E.g. Aldol Condensation, Beckmann rearrangement, Claisen rearrangement

6. Designing for energy efficiency

- Chemical syntheses should be designed to minimize the use of energy.

- Energy is used to
  - raise the temperature of reactants so that a reaction starts or goes on.
  - heat liquid mixtures for separating and purifying products by distillation.
  - Cool the reaction mixture in case of exothermic reaction

Drawbacks of Conventional heating techniques

- Heating is rather slow
- Develops a temperature within sample.
- Local overheating may lead to product, substrate or reagent decomposition

Ways to conserve energy:

- Using catalysts

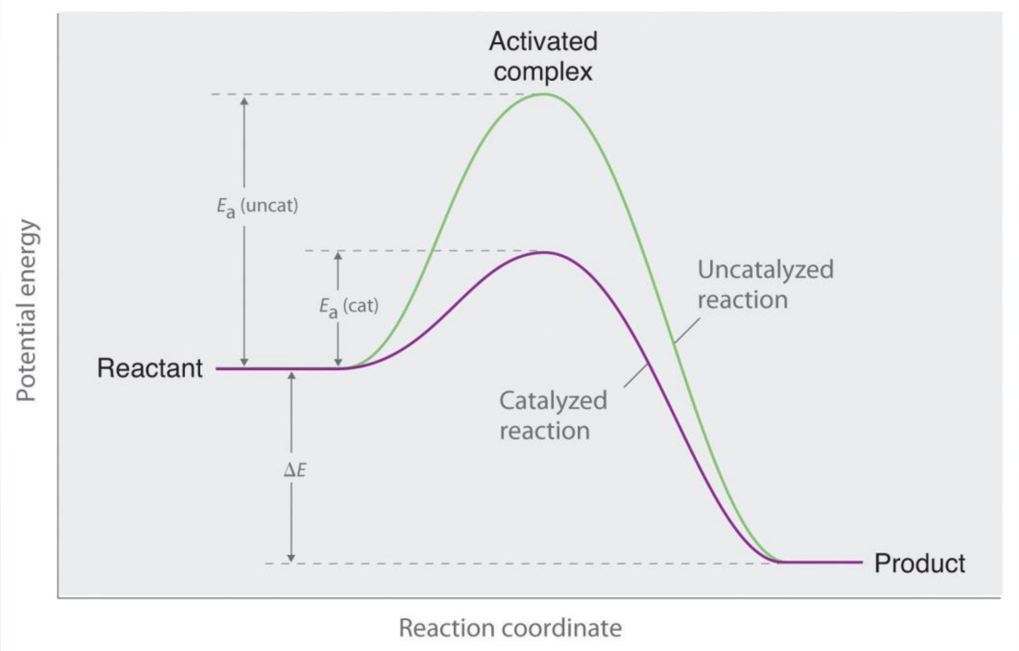
  - reactions at lower T & P
- Using microwave heating

  - more efficient
- Using biosynthetic pathways

  - reaction at ambient T & P

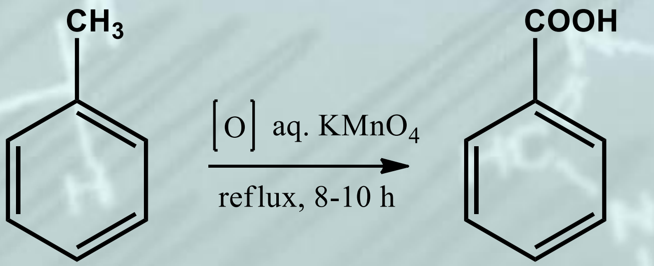
1. Catalysts

Catalyst lower the activation energy needed for a particular reaction thereby minimize the amount of energy needed



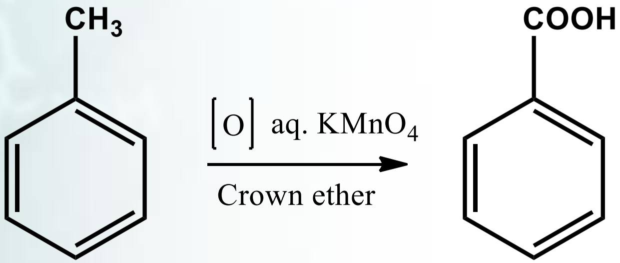
E.g. Oxidation of toluene to benzoic acid

Non-catalytic reaction



10-15% yield

Catalytic reaction

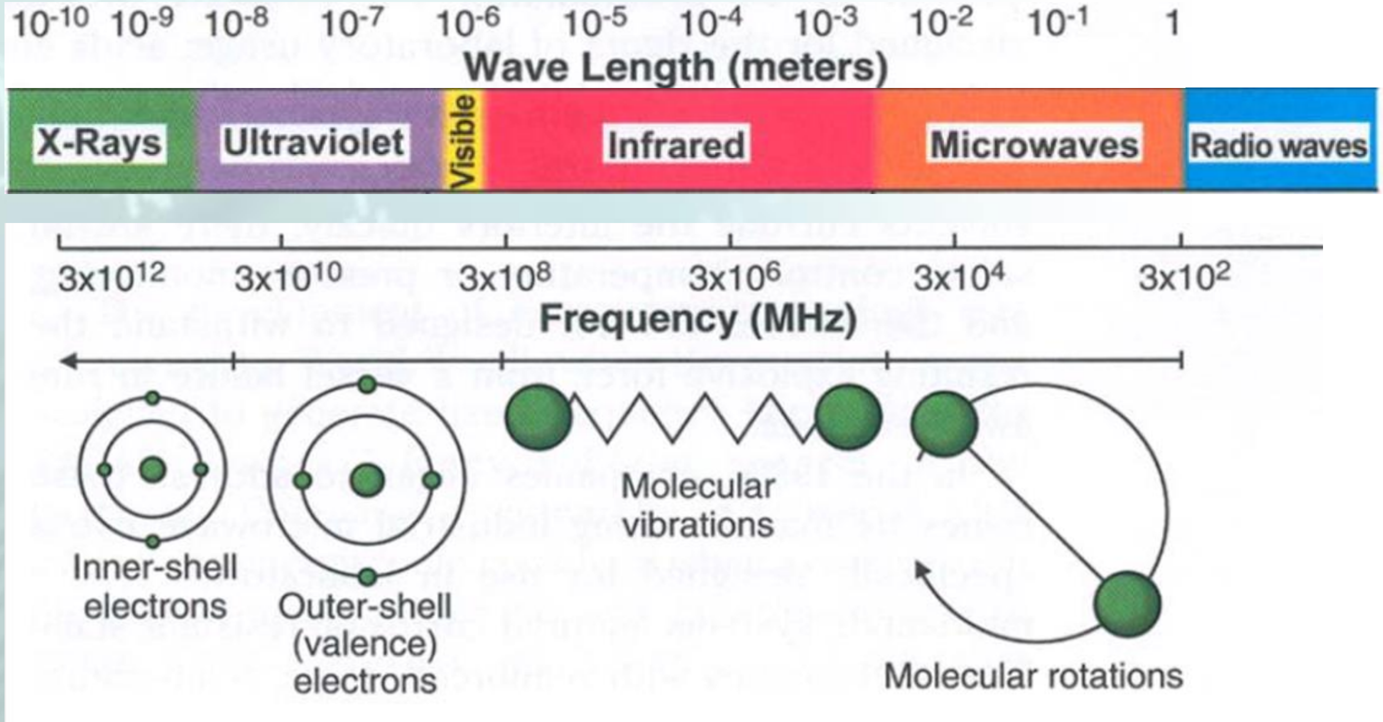


> 85% yield

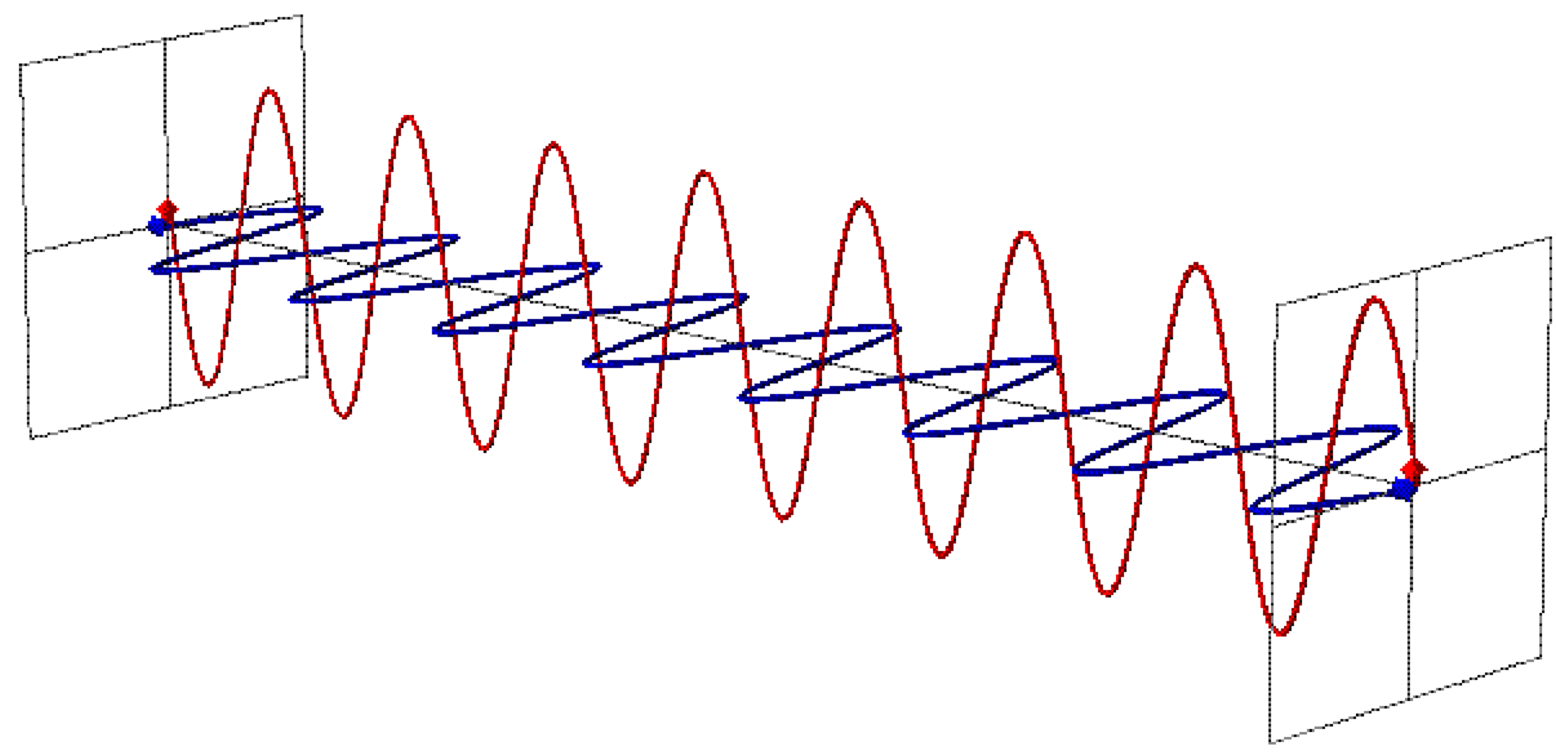
2. Microwave heating

MW are electromagnetic radiation located between IR radiation and radiowaves.

Wavelength: 0.01m to 1m
Frequency: 0.3 to 300 GHz



- EMR with electric and magnetic field perpendicular to each other



Mechanism of heating

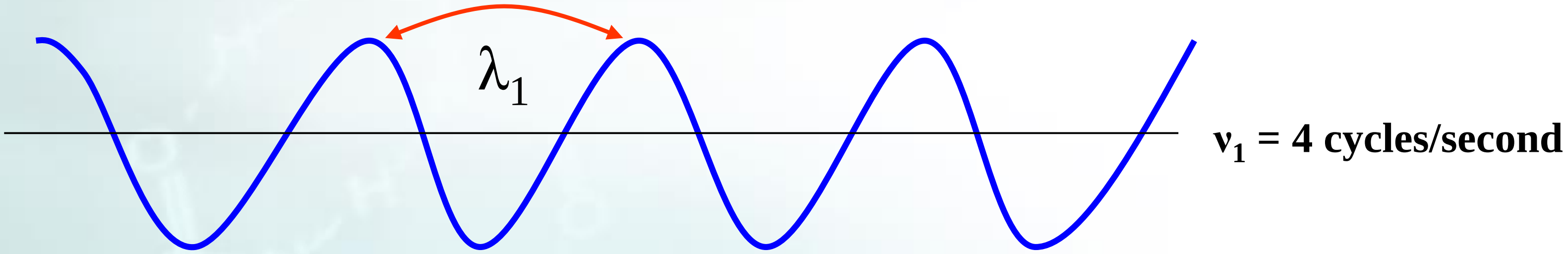
The heating arises from the interaction of electric field component of the wave with charge particle in the material.

Dipolar Polarization mechanism

- Process by which heat is generated in polar molecules
- Dipole is sensitive to the external electric field
- Dipole will attempt to align itself with the field by rotation

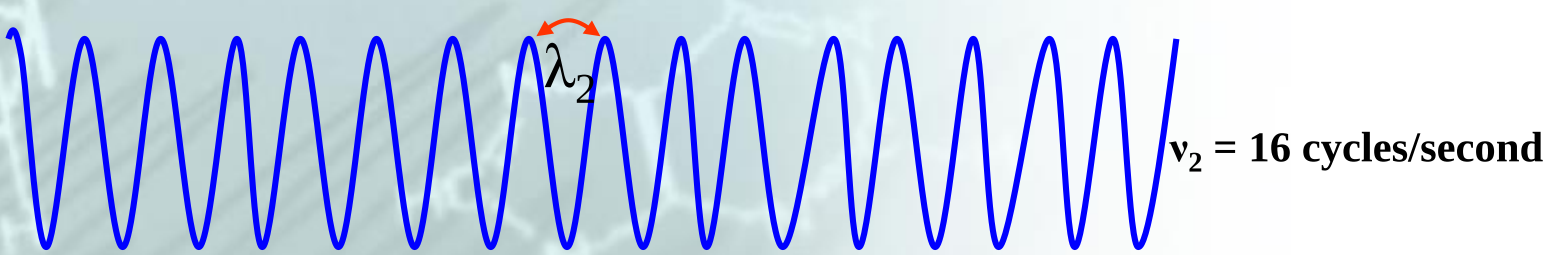
- The applied field provides the energy for rotation
- Unlike gases, the instantaneous alignment is prohibited in liquid by the presence of other molecules.

With low frequency radiation, molecule will rotate in phase with oscillating electric field



Molecule gain some energy but the overall energy is small

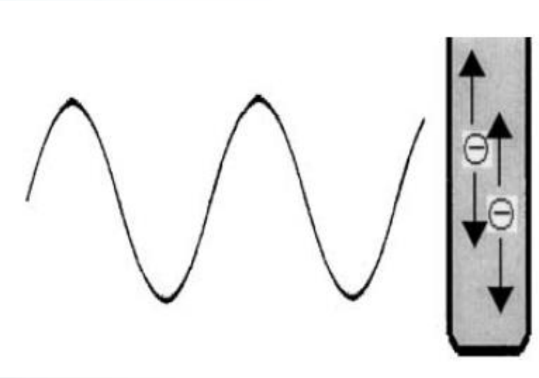
Under high frequency radiation, dipoles do not have time to respond to oscillating field and do not rotate.



- The frequency of MW radiation is low enough, so that dipoles have time to respond to alternating electric field and therefore rotate but rotation does not precisely follow the field.
- When dipole re-orientates to align itself with the alternating electric field, there generates a phase difference between the orientation of field and that of dipole
- Phase difference causes energy to be lost from the dipole by collision and friction and leads to dielectric heating.

Conduction Mechanism

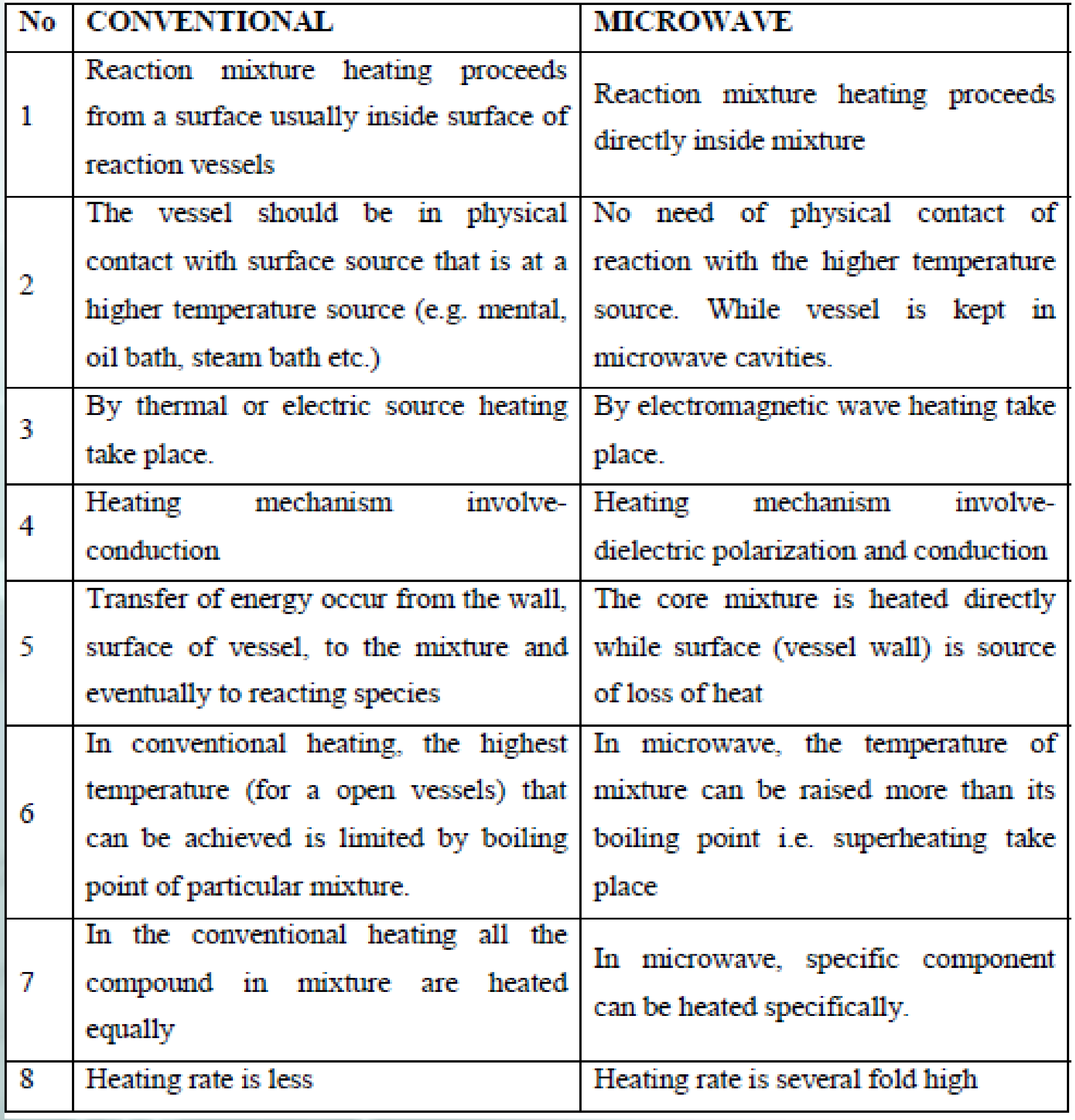
- Ions will move through the solution under the influence of electric current resulting in the expenditure of heat due to increased collision. Kinetic energy is converted into heat.



Advantages of MW heating over conventional methods

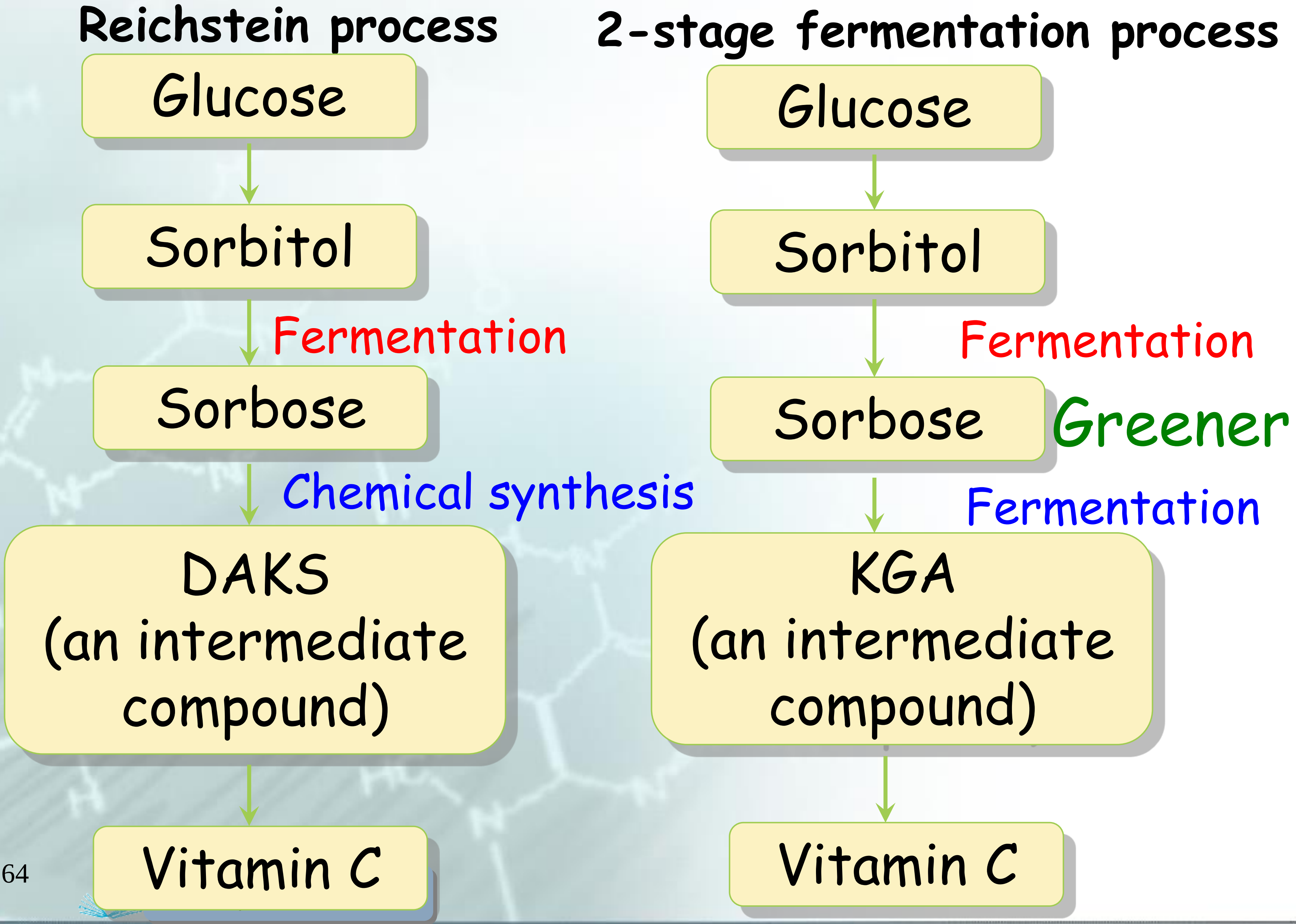
- More efficient than conventional source since energy is directly imparted to reaction mixture rather than through walls
- Heating by MW is rapid and instantaneous hence save both energy and time.
- Temperature increase is uniform throughout the sample hence less by-products or decomposition products.
- MW irradiation reduces the reaction time for completion of reaction with an improvement in the yield and quality of the product and minimizing the waste.
- Non-Polar solvents can be heated with MW adding a small amount of polar solvent to the mixture.
- An excellent solvent for MW heating is N,N-dimethylformamide (DMF).

Comparison of MW heating and conventional heating



No	CONVENTIONAL	MICROWAVE
1	Reaction mixture heating proceeds from a surface usually inside surface of reaction vessels	Reaction mixture heating proceeds directly inside mixture
2	The vessel should be in physical contact with surface source that is at a higher temperature source (e.g. mental, oil bath, steam bath etc.)	No need of physical contact of reaction with the higher temperature source. While vessel is kept in microwave cavities.
3	By thermal or electric source heating take place.	By electromagnetic wave heating take place.
4	Heating mechanism involve- conduction	Heating mechanism involve- dielectric polarization and conduction
5	Transfer of energy occur from the wall, surface of vessel, to the mixture and eventually to reacting species	The core mixture is heated directly while surface (vessel wall) is source of loss of heat
6	In conventional heating, the highest temperature (for a open vessels) that can be achieved is limited by boiling point of particular mixture.	In microwave, the temperature of mixture can be raised more than its boiling point i.e. superheating take place
7	In the conventional heating all the compound in mixture are heated equally	In microwave, specific component can be heated specifically.
8	Heating rate is less	Heating rate is several fold high

3. Biosynthetic Pathways



Reichstein process

Glucose

Sorbitol

Fermentation

Sorbose

Chemical synthesis

DAKS
(an intermediate
compound)

Vitamin C

2-stage fermentation process

Glucose

Sorbitol

Fermentation

Sorbose

Greener

Fermentation

KGA
(an intermediate
compound)

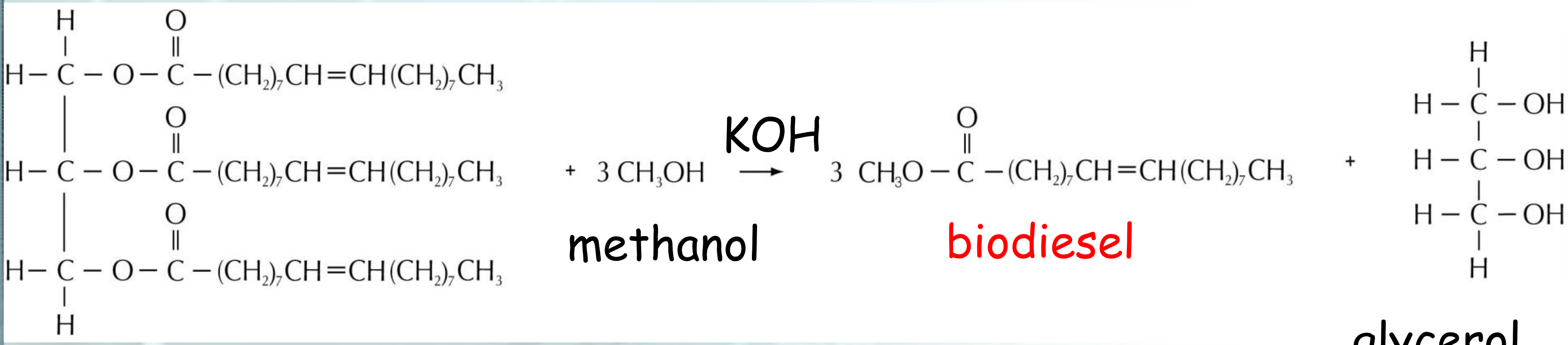
Vitamin C

7. Using renewable raw materials

Renewable raw materials

- They are often made from agricultural products.

  E.g. glucose for making adipic acid and vitamin C, biodiesel for motor vehicles



renewable

Diesel comes from petroleum which is non-renewable

Burns more completely than diesel due to its higher oxygen.

- In the production of synthesis gas, natural gas is used as the raw material for the steam-methane reforming process.

$$\underbrace{CH_4(g) + H_2O(g)}_{\textbf{From natural gas}} \xrightleftharpoons[\text{NiO}]{700\text{–}1000^{\circ}C,\ 10\text{–}20\ \text{atm}} \underbrace{3H_2(g) + CO(g)}_{\textbf{Synthesis gas}\text{ (or }\textbf{syngas}\text{)}}$$

Uses of Syngas

$$N_2(g) + 3H_2(g) \xrightleftharpoons[\text{Finely divided Fe}]{450^{\circ}C,\ 200\ \text{atm}} 2NH_3(g)$$

$$2H_2(g) + CO(g) \xrightleftharpoons[Cu/ZnO/Al_2O_3]{250^{\circ}C,\ 50\text{-}100\ \text{atm}} CH_3OH(g)$$

$$CH_3OH(g) + CO(g) \xrightleftharpoons[\text{Cativa process}]{\text{Ir based catalyst, HI}} CH_3COOH(g)$$

- In the production of synthesis gas, natural gas is used as the raw material for the steam-methane reforming process.

Non-renewable raw material

Natural gas

Replaced by

Renewable raw materials

Landfill methane gas

Pig's manure

Paper & wood waste

Seaweed

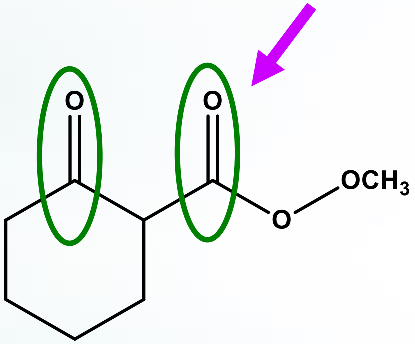
Shredded paper (left) and seaweed (right) can be used as the raw materials for the production of synthesis gas

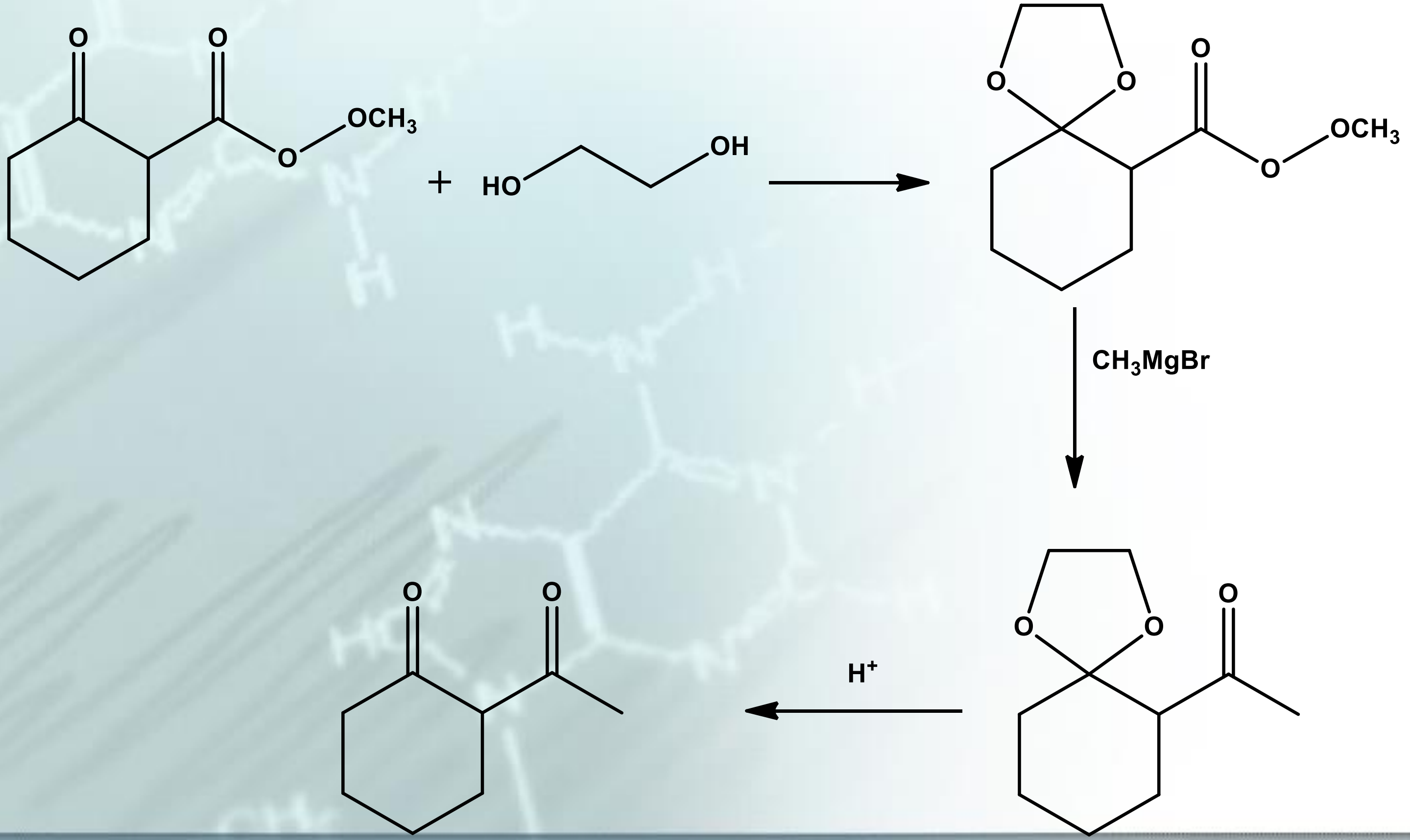
8. Reducing derivatives

- We should avoid unnecessary use of synthetic steps in order to reduce the **derivatives** of the desired product.

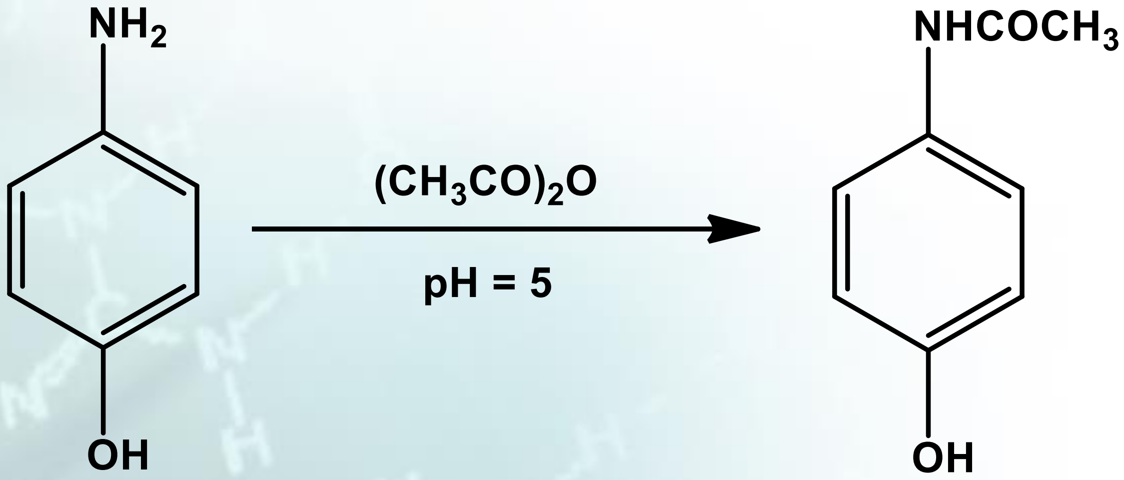
- Otherwise, more reagents are needed and more waste will be generated.

Reaction of methyl cyclohexanone 2 carboxylate with Grignard reagent





Synthesis of Analgesic tylenol



p-Aminophenol

p-Acetylaminophenol (tylenol)

9. Using catalysts

Bleaching of wood pulp in paper manufacturing

1. $H_2O_2 + \text{dye} \longrightarrow H_2O + (\text{dye} + O)$

2. $OCl^- + \text{dye} \longrightarrow Cl^- + (\text{dye} + O)$

Reaction 1 is greener because
it has a higher atom economy
it involves less harmful chemicals

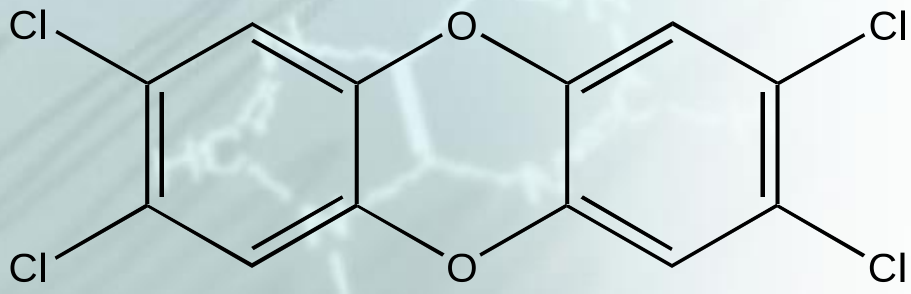
9. Using catalysts

Bleaching of wood pulp in paper manufacturing

1. $H_2O_2 + \text{dye} \longrightarrow H_2O + (\text{dye} + O)$

2. $OCl^- + \text{dye} \longrightarrow Cl^- + (\text{dye} + O)$

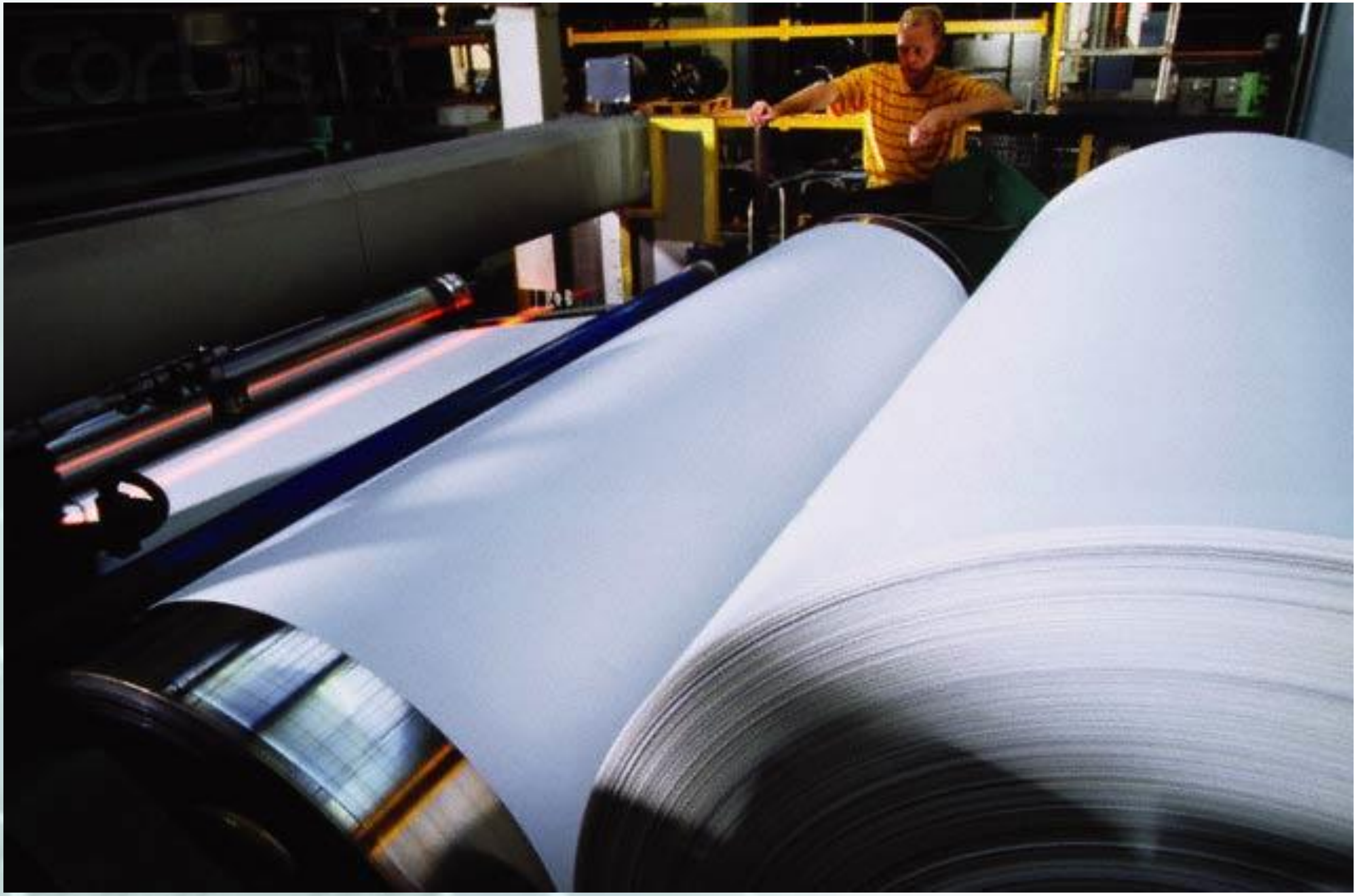
Bleaching with Cl_2 may lead to the formation of dioxin which is an accumulative carcinogen



$$H_2O_2 + \text{dye} \xrightarrow{\text{TAML}^{\text{TM}}\text{ catalyst}} H_2O + (\text{dye} + O)$$

Tetra-Amido Macrocyclic Ligand (TAML)

- non-toxic iron-based ‘green’ catalysts.
- promote the conversion of hydrogen peroxide into hydroxyl radicals that are involved in the bleaching process
- catalyse the oxidation of organic substances in wastewater.



TAML^{TM} catalysts can be used to clean up wastewater streams in the pulp and paper industry

Environmental benefits of using TAML™ catalysts in wastewater treatment

Decrease in energy requirements

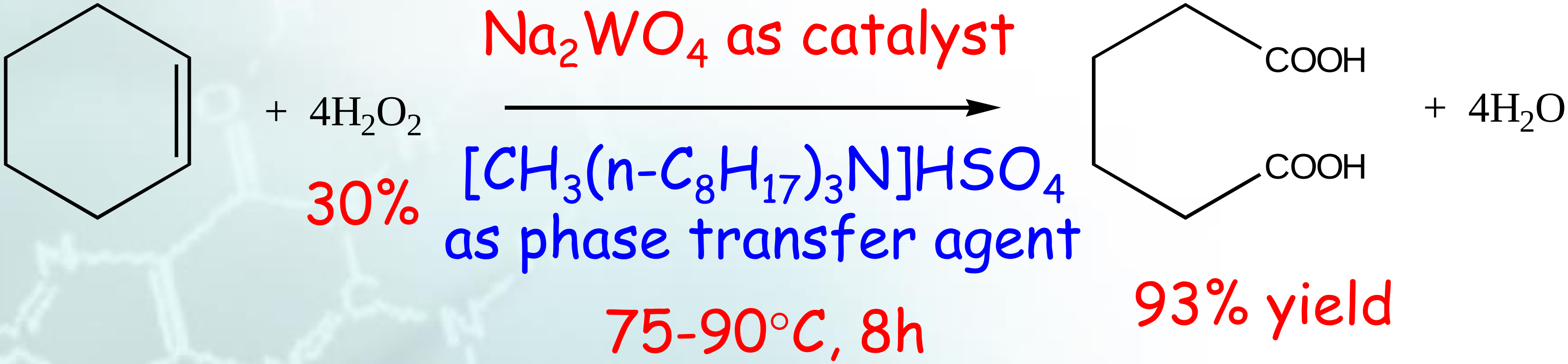
Elimination of chlorinated organic substances

Reduction in water usage

Degradable catalysts

A “Greener” Route to Adipic Acid.

Sato, K.; Aoki, M.; Noyori, **1998**



+ $4H_2O_2$

30%

Na_2WO_4 as catalyst

$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ as phase transfer agent

75-90°C, 8h

COOH

COOH

+ $4H_2O$

93% yield

1. One-step synthesis with high yield
2. Proceeds in aqueous medium at relatively low T
3. Reagents and by-product are environmentally benign

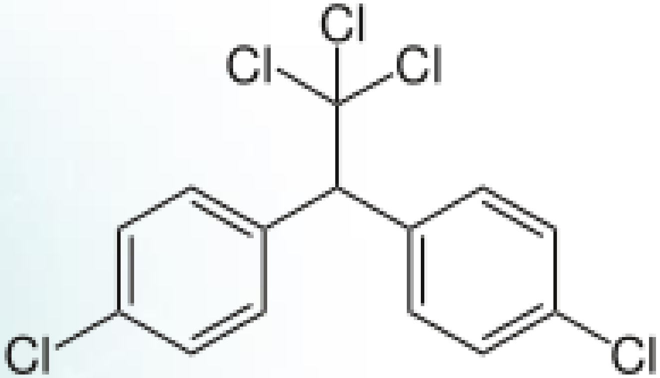
10. Designing degradable chemical products

- Many chemical products persist in the environment after use.

- They should be designed so that they can be broken down into harmless substances.

Pesticides

- E.g. DDT, they accumulate in plants and animals, causing damage to the final consumers — humans.



- Designing degradable pesticides that can be decomposed by water, sunlight or micro-organisms.

Degradable Plastics

- Several types of degradable plastics:
  - ➔ biopolymers
  - ➔ photodegradable plastics
  - ➔ synthetic biodegradable plastics

Biodegradable plastic utensils.

Photodegradable plastic bag.

11. Developing real-time analysis for pollution prevention

Real-time monitoring system for monitoring sulphur dioxide (SO_2) level

When coal is burnt in industrial boilers, SO_2 (a pollutant) is formed.

If the temperature of the boilers is too high, a large amount of SO_2 will be generated.

Real-time monitoring system for monitoring sulphur dioxide (SO_2) level

Using real-time monitoring, the amount of SO_2 generated can be measured all the time.

Once it reaches an unacceptable level, an alarming signal will be generated. Then the temperature will be lowered immediately.

12. Minimizing the potential for chemical accidents

Chemical accidents include leakages, explosions and fires.

Minimize the use of volatile liquids or gases which are associated with the majority of chemical accidents.

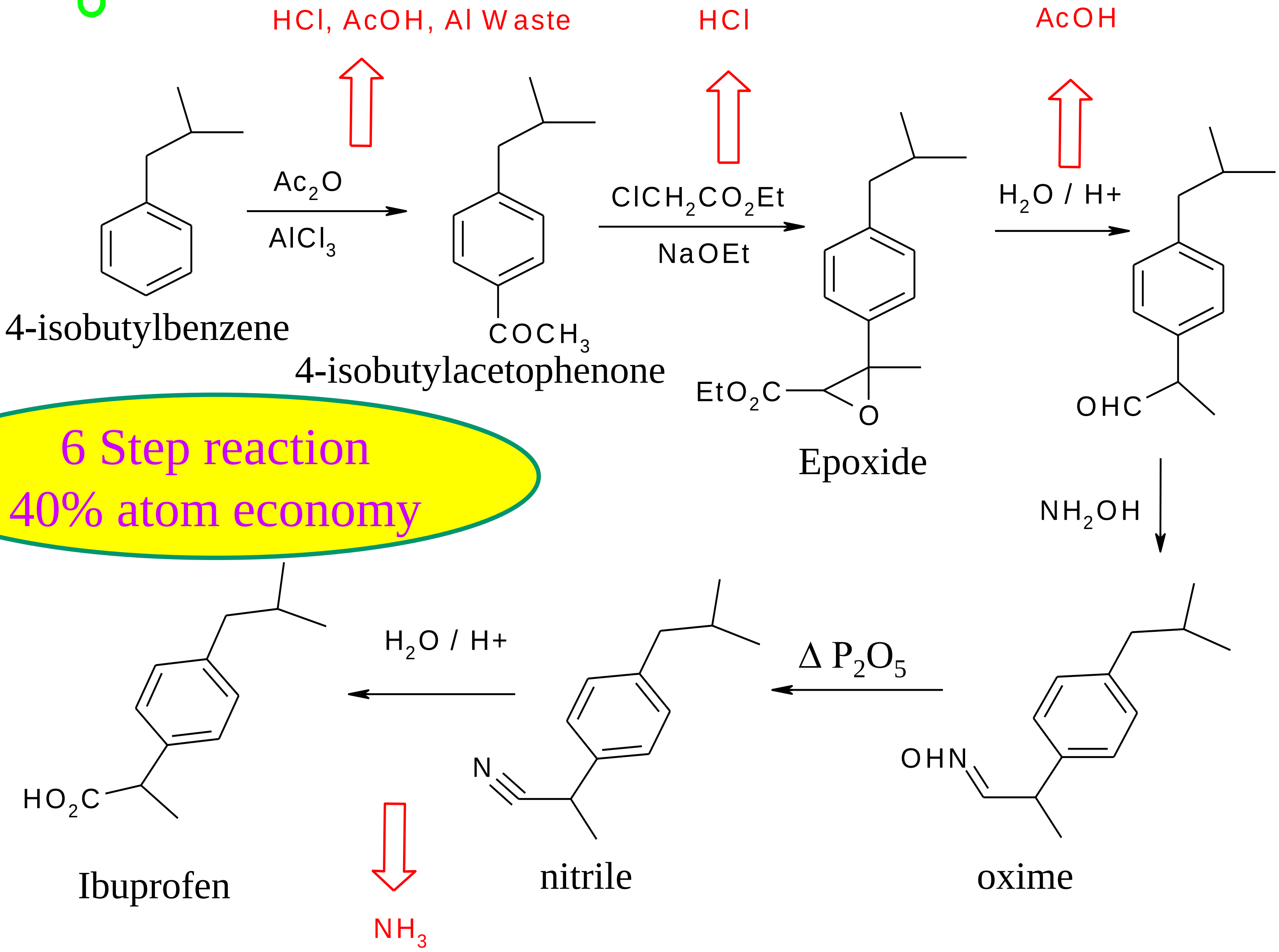
If possible, allow reactions to proceed under ambient T & P.

12 Principles of Green Chemistry

1. **Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
2. **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
5. **Safer Solvents and Auxiliaries.** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
6. **Design for Energy Efficiency.** 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. **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.
8. **Reduce Derivatives.** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible .
9. **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation.** Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.
11. **Real-time Analysis for Pollution Prevention.** 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. **Inherently Safer Chemistry for Accident Prevention.** Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Anastas, P. T.; Warner, J.C. Green Chemistry: Theory and Practice, Oxford University Press,1998.

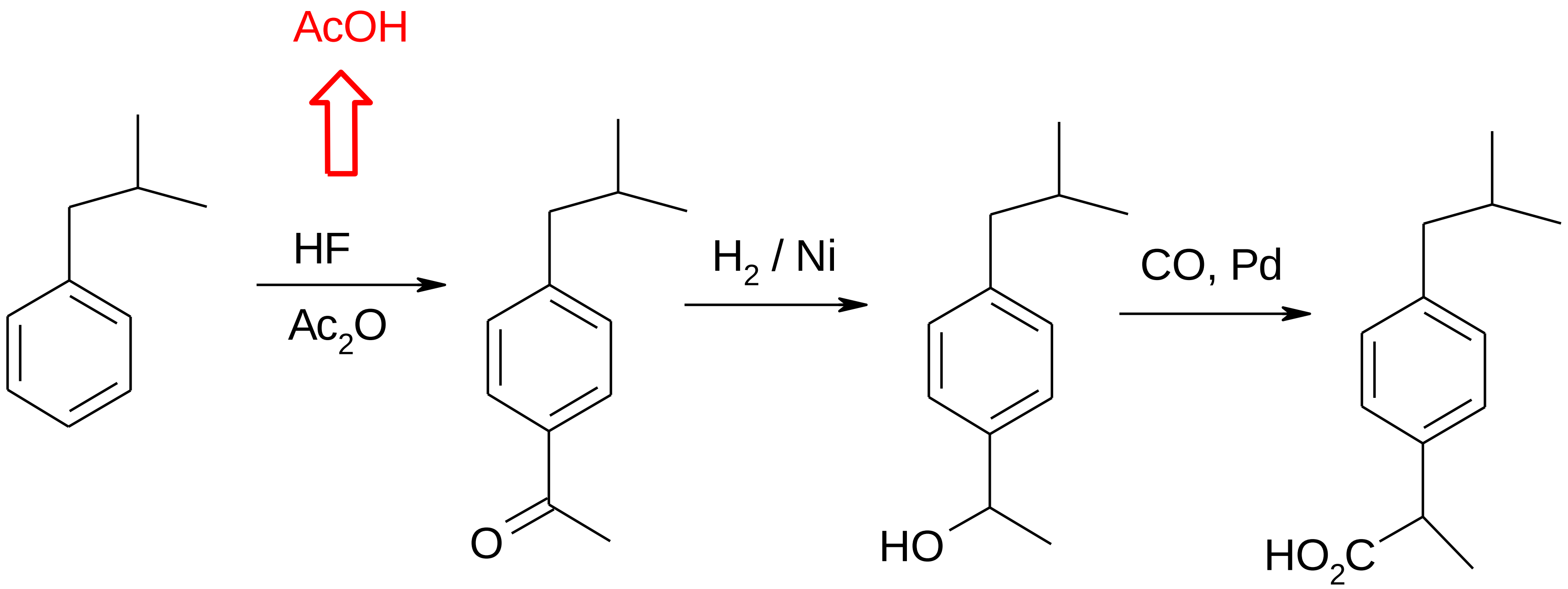
Classic Route to Ibuprofen



6 Step reaction

40% atom economy

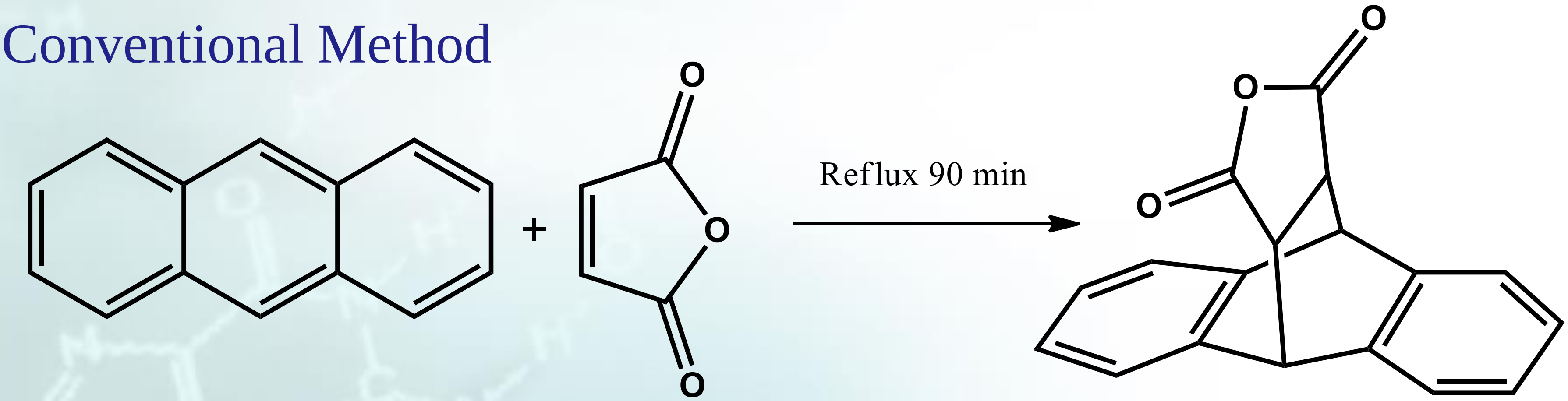
Hoechst Route To Ibuprofen



3 Step reaction
77% atom economy

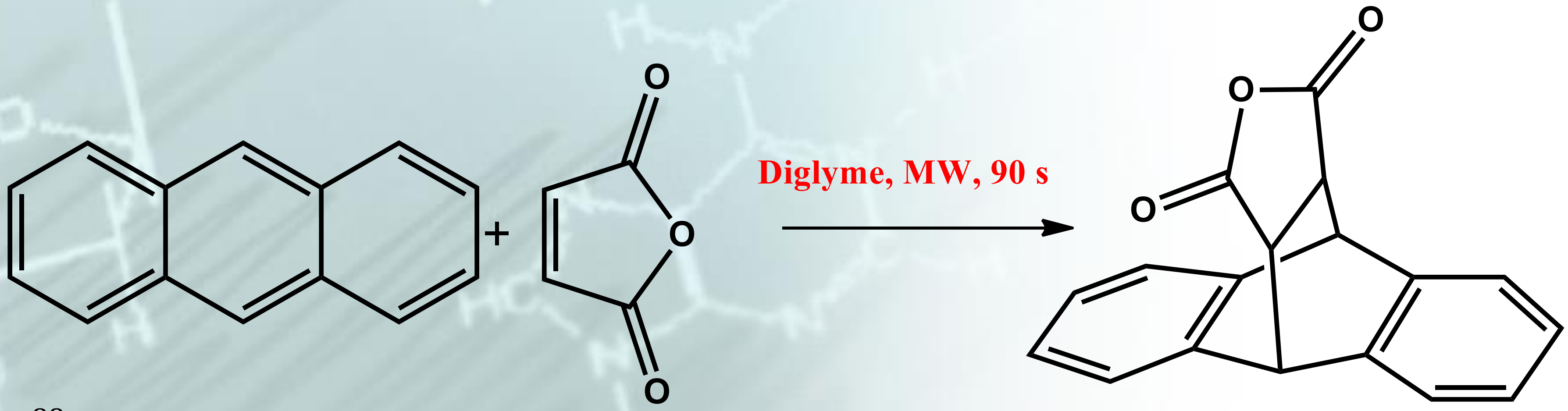
Microwave assisted Diels-Alder Reaction

Conventional Method



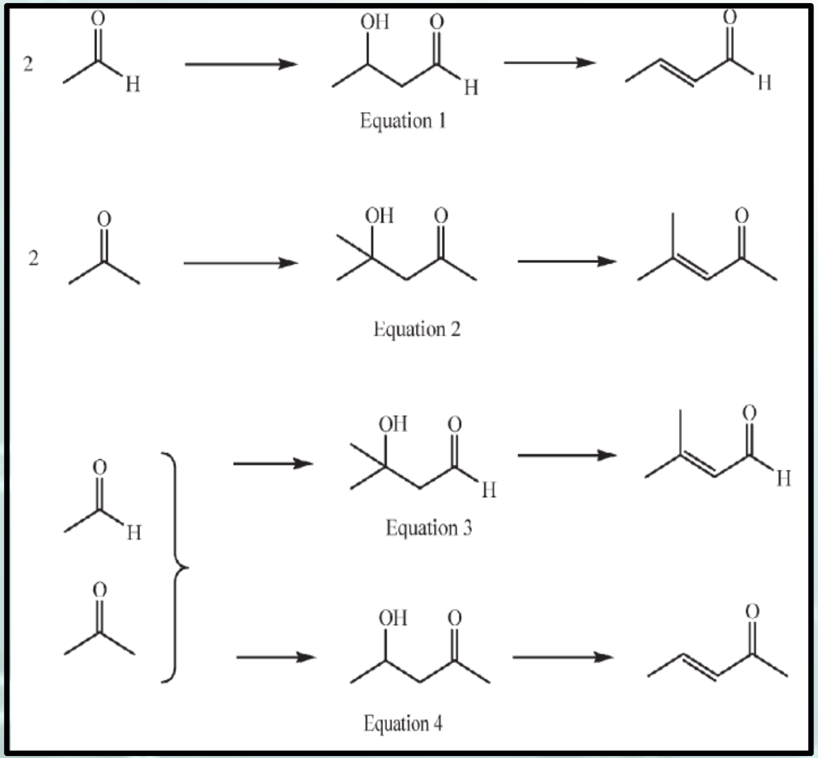
Reflux 90 min

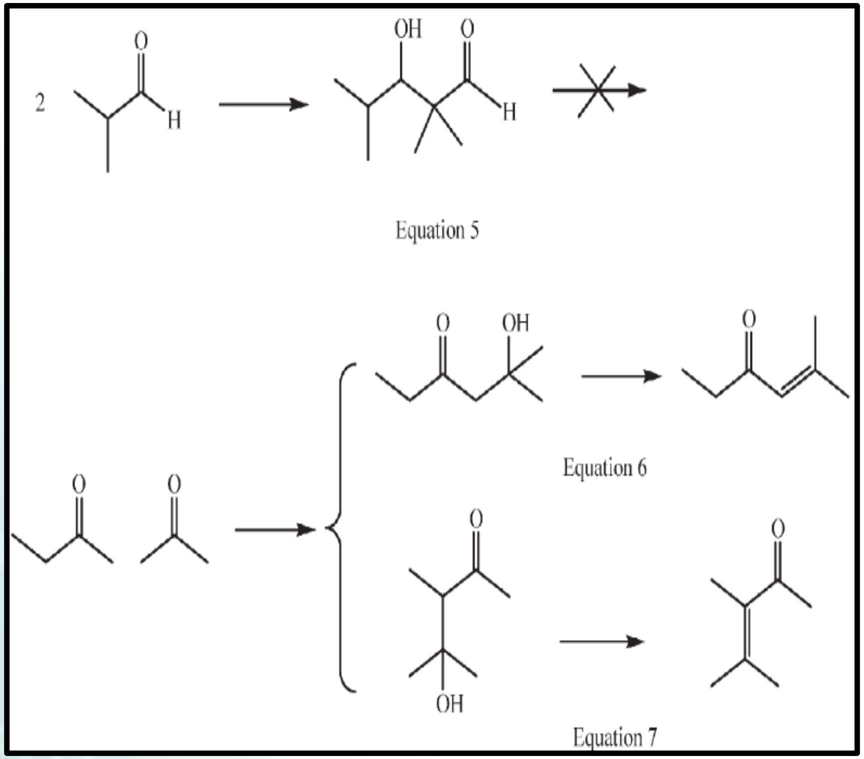
Microwave assisted



Diglyme, MW, 90 s

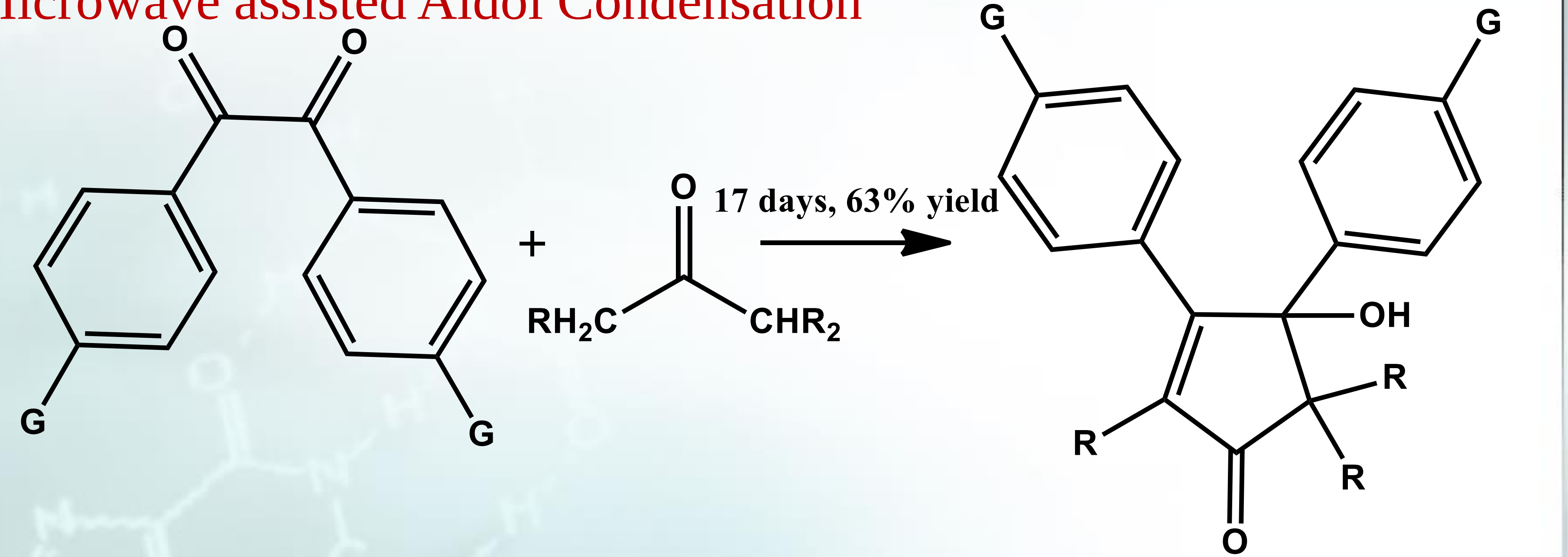
Microwave assisted Aldol Condensation

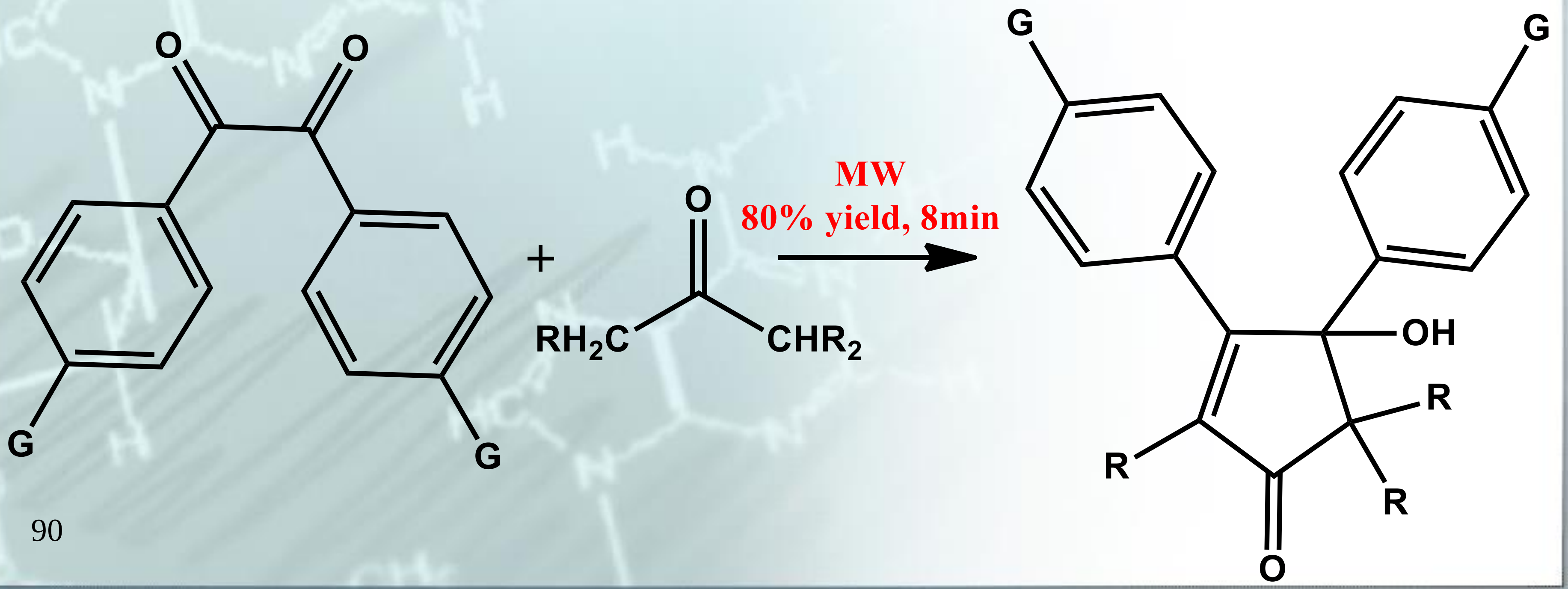




The aldol reaction of aldehydes and ketones, generally conducted under basic conditions but conversions are usually sluggish as the equilibrium lies well to the left, even with strong bases

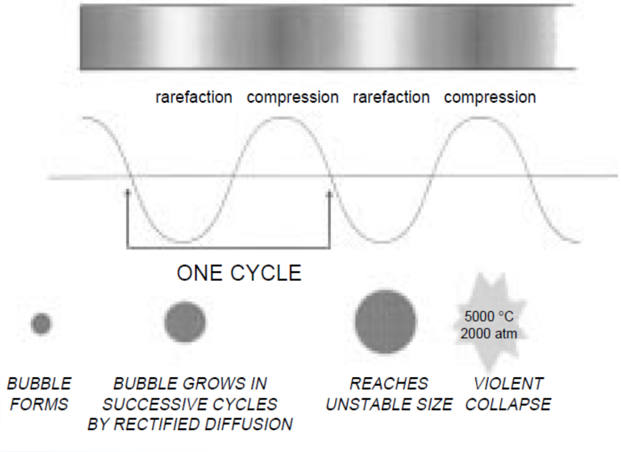
Microwave assisted Aldol Condensation





Ultrasound assisted green Synthesis

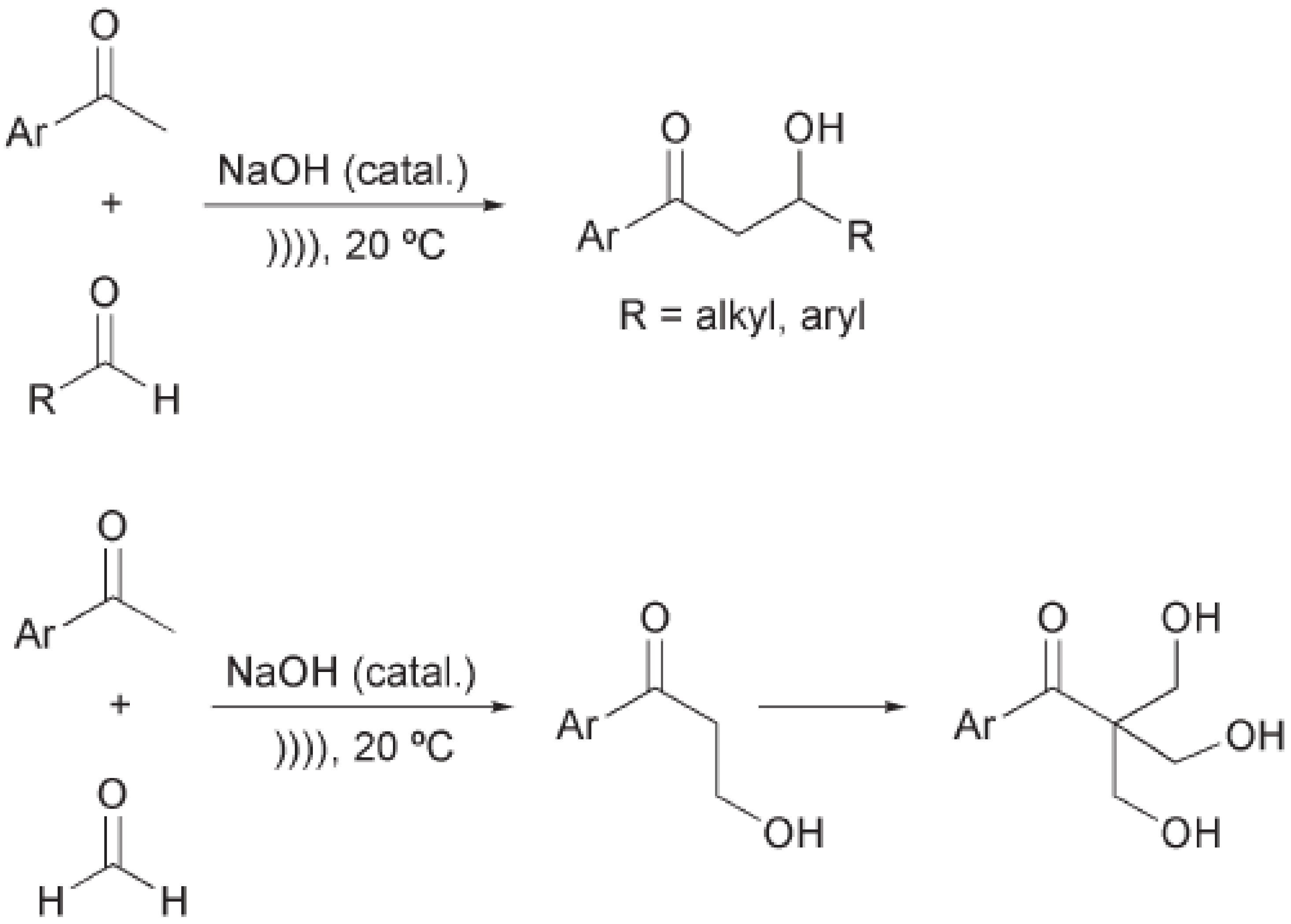
- Sound waves are propagated by a series of compression (high pressure) and rarefaction (low pressure) cycles
- When passed through a liquid medium sound waves cause the molecules to oscillate around their mean path



- Compression cycle: Average distance molecules is reduced

  Rarefaction Cycle: Average distance between molecule is increased
- During the rarefaction cycle, the molecules of the liquid overcome intermolecular process and create small vacuum bubbles or voids in the liquid.
- When the bubbles attain a volume at which they can no longer absorb energy, they collapse violently during a compression cycle creating high temperature and pressure (Cavitation).
- This high temperature and pressure initiates chemical reaction.

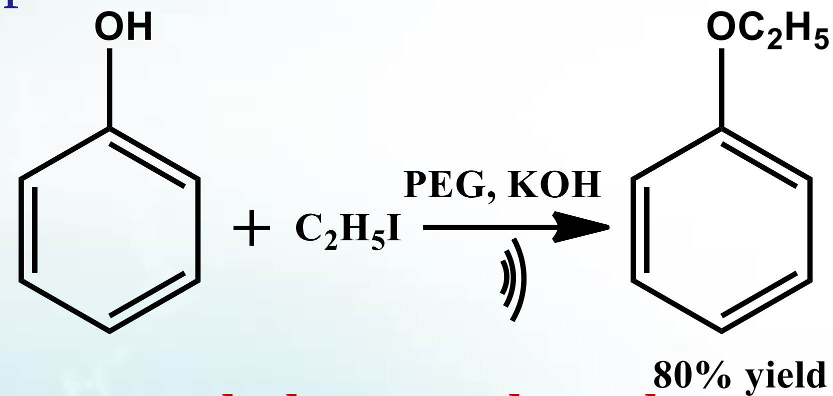
Ultrasound assisted Aldol Condensation



Good yield in short reaction time and less side products

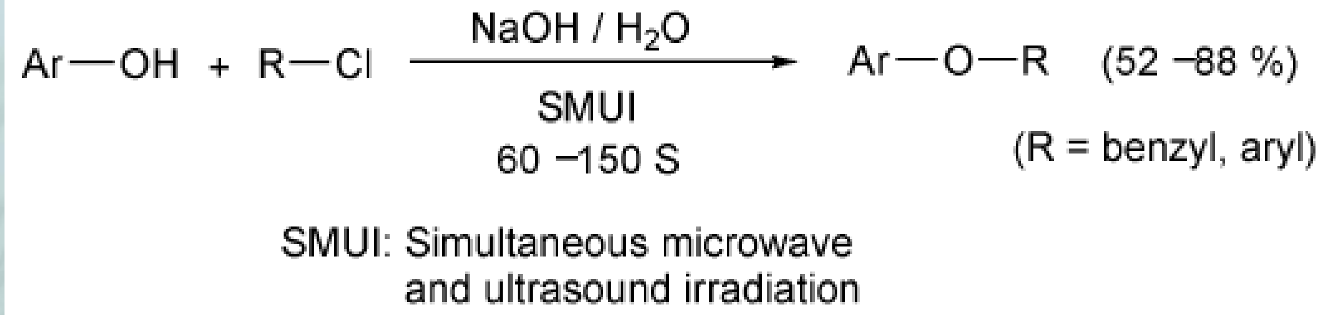
Ultrasound assisted Williamson’s Synthesis

Conventional Williamson’s synthesis require several hours of heating at relatively high temperature



Simultaneous microwave and ultrasound irradiation (SMUI)

- ❖ provides an efficient, economical and eco-friendly method for preparing useful ethers without any auxiliary substances



- ❖ SMUI provides highly efficient dielectric heating along with intensive mass transport in heterogeneous systems, resulting in dramatic reaction rate enhancement

Conclusion

Green chemistry **Not** a solution to all environmental problems **But** the most fundamental approach to preventing pollution.

Thank you