INTRODUCTION
TO
GREEN CHEMISTRY

BY

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WHAT HAPPENED IN TWENTIETH CENTURY …

1. PRODUCTION OF GASOLINE AND DIESEL FROM PETROLEUM, FUEL ADDITIVE, CATALYTIC CONVERTER, PLASTIC TO REDUCE WEIGHT OF VEHICLE.
2. PRODUCTION OF CLOTHES- RAYON, NYLON, DYES, WATERPROOFING AND OTHER SURFACE FINISHING CHEMICALS .
3. PRODUCTION OF ALL TYPE OF MEDICINE.
4. PRODUCTION OF NEW MATERIALS.
5. PRODUCTION OF FERTILIZERS.
6. PRODUCTION OF COSMETICS.
7. PRODUCTION OF PLASTIC MATERIALS

WE HAVE CREATED LAKHS OF ORGANIC COMPOUNDS…..

ALSO TREMENDOUS POLLUTION, CHEMICAL WASTE ETC..

THAT, WE HAVE TO CLEAN UP

NEED OF GREEN CHEMISTRY

REDUCE

1. **WASTE**
2. **MATERIALS**
3. **HAZARDS**
4. **RISK**
5. **ENERGY**
6. **COST**

WHAT IS GREEN CHEMISTRY

GREEN CHEMISTRY IS THE BASIS OF DEVELOPING HEALTHY ALTERNATIVE TO THE TOXIC MATERIALS THAT MAKE UP OUR BUILT ENVIRONMENT AND OUR MANUFACTURING PROCESSES. IT'S A BUILDING BLOCK OF FUTURE.

TWELVE PRINCIPLE OF GREEN CHEMISTRY

1. **IT IS BETTER TO PREVENT WASTE THAN TO TREAT OR CLEAN UP WASTE AFTER IT IS FORM.**
2. **SYNTHETIC MATERIALS SHOULD BE DESIGNED TO MAXIMIZE THE INCORPORATION OF ALL MATERIALS USED IN THE PROCESS INTO THE FINAL PRODUCTS.**
3. **WHEREVER PRACTICABLE, SYNTHETIC METHODOLOGIES SHOULD DESIGN TO USE AND GENERATE THAT POSSESS LITTLE OR NO TOXICITY TO HUMAN HEALTH AND THE ENVIRONMENT.**
4. **CHEMICAL PRODUCT SHOULD BE DESIGNED TO PRESERVE EFFICACY OF FUNCTION WHILE REDUCING TOXICITY.**
5. **THE USE OF AUXILIARY SUBSTANCES (SOLVENTS, SEPARATION AGENT, ETC.) SHOULD BE MADE UNNECESSARY WHENEVER POSSIBLE AND, WHEN USED INNOCUOUS (NONTOXIC).**
6. **ENERGY REQUIREMENT SHOULD BE RECOGNIZED FOR THEIR ENVIRONMENTAL AND ECONOMIC IMPACTS AND SHOULD BE MINIMIZED.**
7. **A RAW MATERIAL OR FEEDSTOCK SHOULD BE RENEWABLE RATHER THAN DEPLETING WHENEVER TECHNICALLY AND ECONOMICALLY PRACTICABLE**

8. UNNECESSARY DERIVATIZATION SHOULD BE AVOIDED.

9. CATALYST REAGENTS ARE SUPERIOR TO STOICHIOMETRIC REAGENTS.

10. CHEMICAL PRODUCTS SHOULD BE DESIGNED 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 SUBSTANCE.

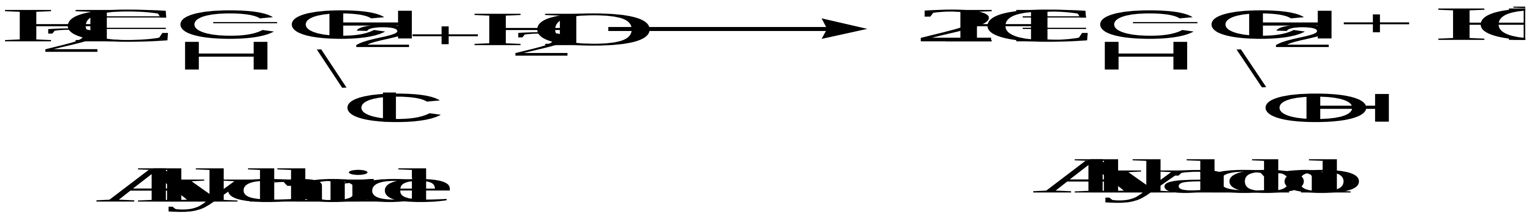
12. SUBSTANCES AND FORM OF A SUBSTANCE USED IN A CHEMICAL PROCESS SHOULD BE CHOSEN SO AS TO MINIMIZE THE POTENTIAL FOR CHEMICAL ACCIDENTS, INCLUDING RELEASES, EXPLOSIONS AND FIRES.

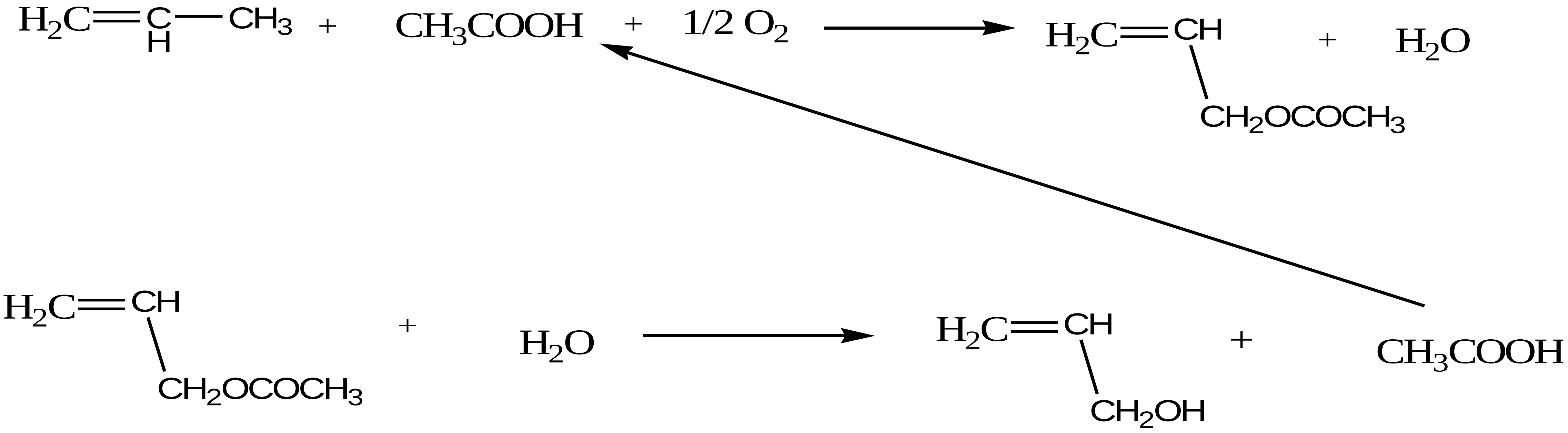
FIRST PRINCIPLE:- PREVENTION

IT IS BETTER TO PREVENT WASTE THAN TO TREAT OR CLEAN UP WASTE AFTER IT IS FORM.

- If the chemical reaction of the type

- Find alternate A or B to avoid W
- Example 1:
- Disinfection of water by chlorination. Chlorine oxidizes the pathogens there by killing them, but at the same time forms harmful chlorinated compounds.
- A remedy is to use another oxidant, such as O3 OR SUPERCRITICAL WATER OXIDATION.





H2C=CH–CH3 + CH3COOH + 1/2 O2 → H2C=CH–CH2OCOCH3 + H2O
H2C=CH–CH2OCOCH3 + H2O → H2C=CH–CH2OH + CH3COOH

SECOND PRINCIPLE:- ATOM ECONOMY

SYNTHETIC MATERIALS SHOULD BE DESIGNED TO MAXIMIZE THE INCORPORATION OF ALL MATERIALS USED IN THE PROCESS INTO THE FINAL PRODUCTS.

CONCEPT OF ATOM ECONOMY:- This is the most fundamental principle of green chemistry, Atom economy.

Consider chemical reaction

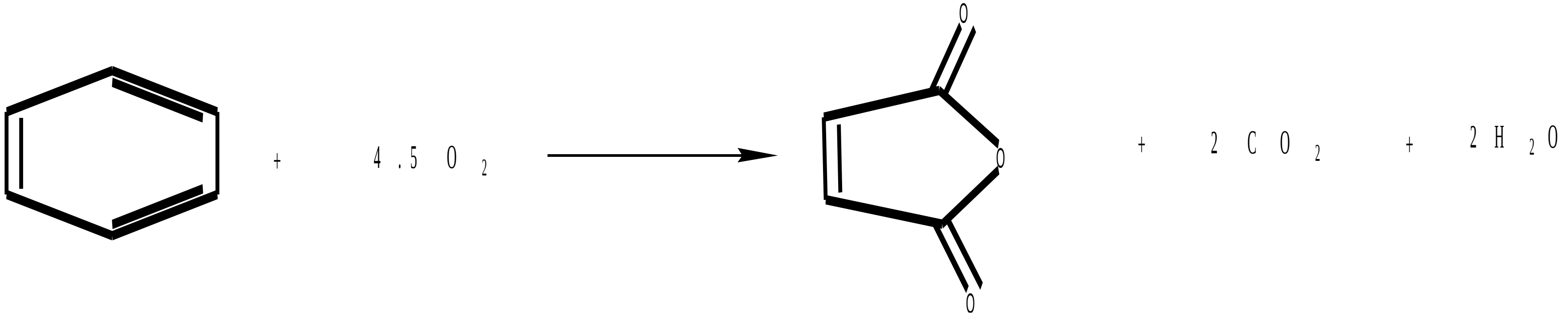
X + Y = P + U

Where, X,Y are reactant & P is product ,U is waste

Here, because of unwanted materials U its atom economy is less than 100%

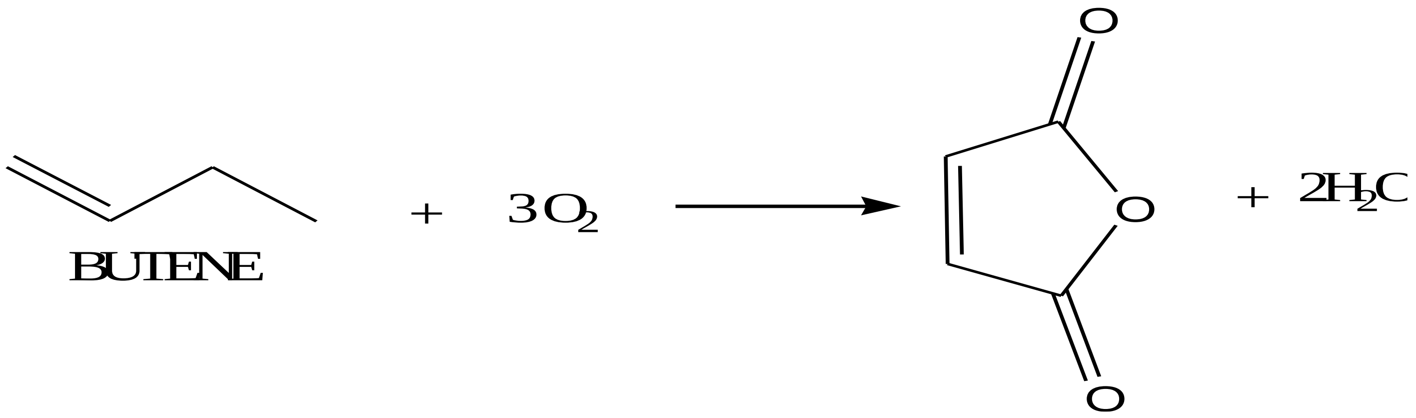
[redacted]

MALEIC ANHYDRIDE SYNTHESIS



% Atom Economy= 100* 98/(78+144)

= 44.1%



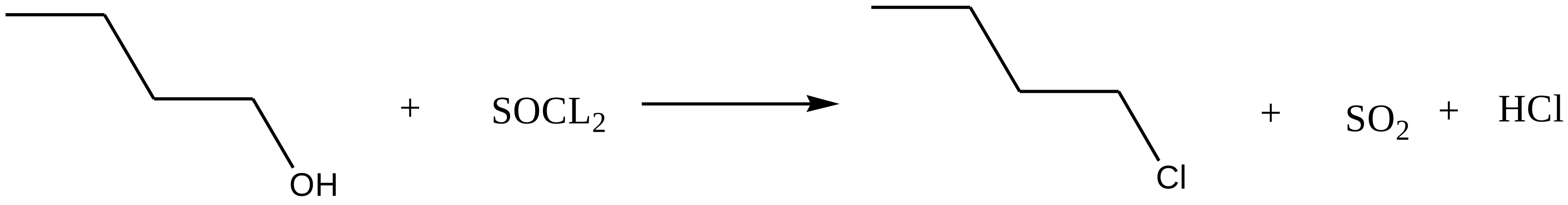
% Atom Economy= 100* 98/(56+96)

= 64.5%

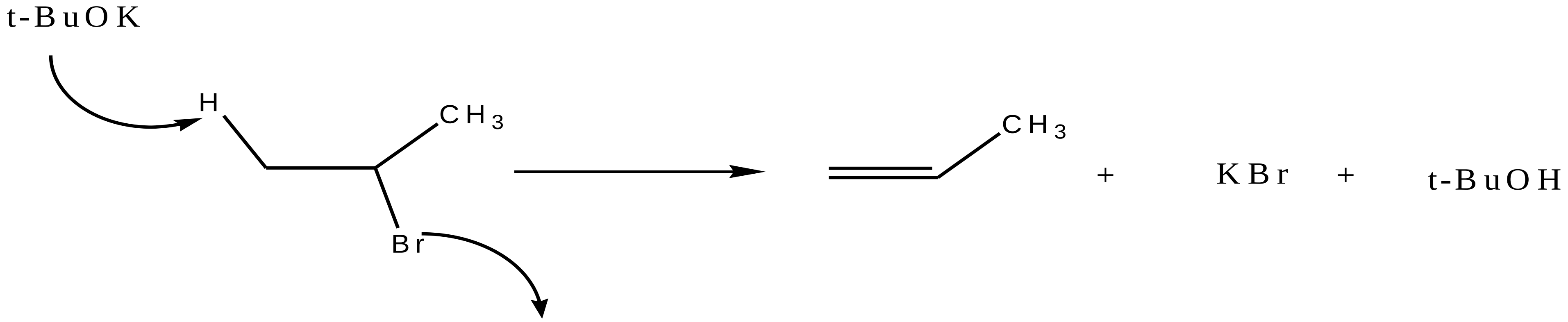
It is evident that, butene oxidation route is more atom efficient and no wasting of atoms

ATOM UN-ECONOMIC REACTION:-

1. SUBSTITUTION REACTION
2. ELIMINATION REACTION



% Atom economy=54.5%



% Atom economy=17.9%

Atom Economy in Elimination Reactions

- Equation 2

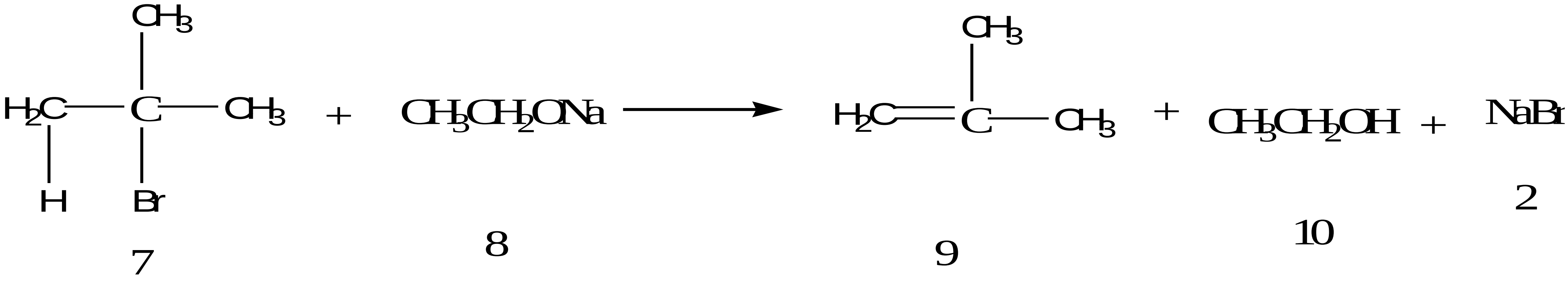
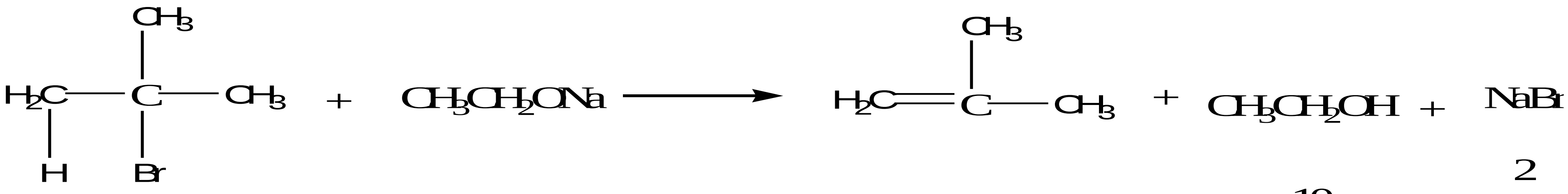


Table 5 Atom Economy Equation 2

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
7 C_4H_9Br	137	4C,8H	56	HBr	81
8 C_2H_5ONa	68	—	0	2C,5H,O,Na	68
Total 6C,14H,O,Br,Na	205	4C,8H	56	2C,6H,O,Br,Na	149

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (56/205) X 100 = 27%



7 8 9 10 2

Atom Economy in Addition Reactions

- Equation 3

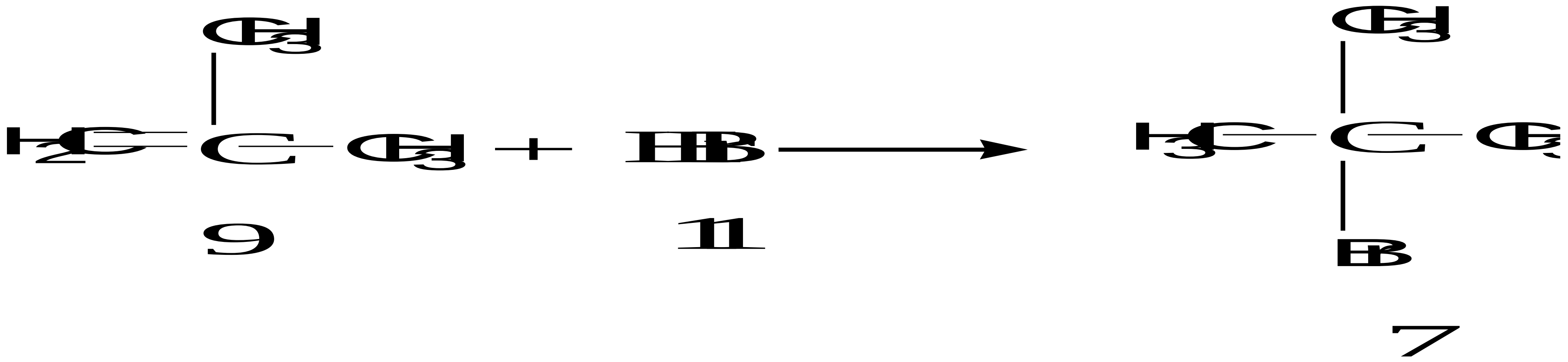
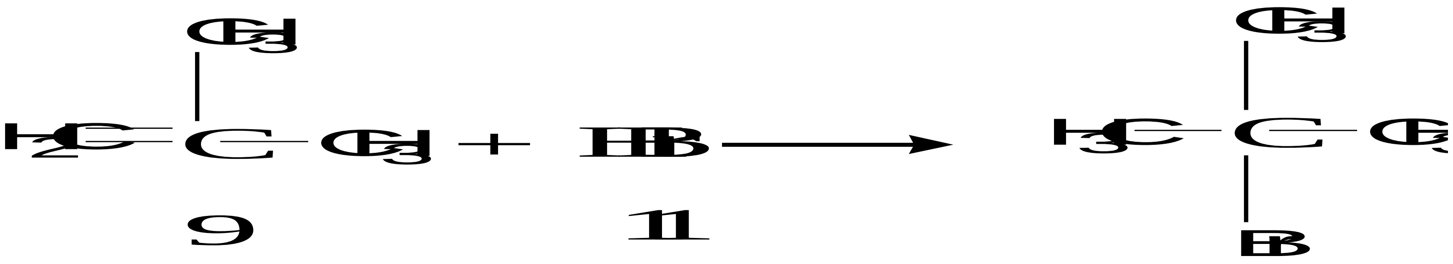


Table 6 Atom Economy Equation 3

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
9 C_4H_8	56	4C,8H	56	__	0
11 HBr	81	HBr	81	__	0
Total 4C,9H,Br	137	4C,9H,Br	137	__	0

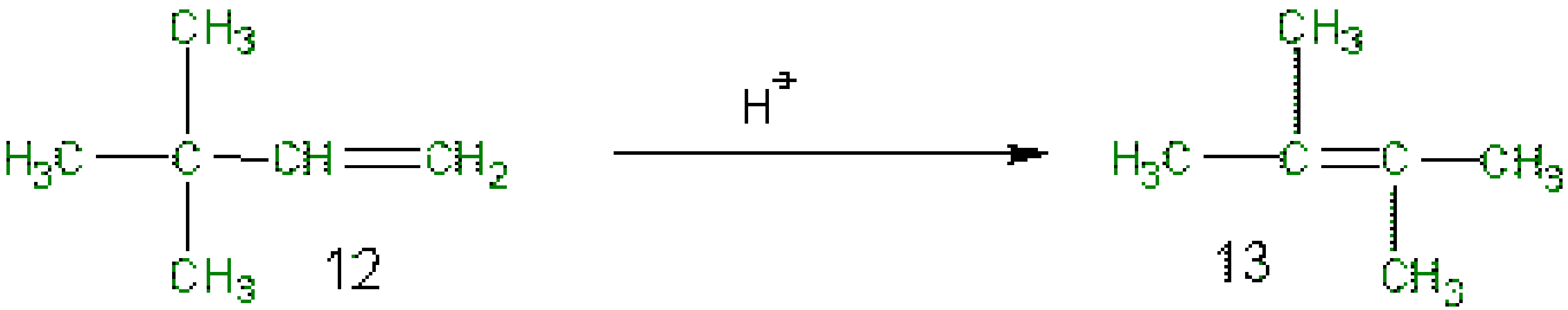
% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (137/137) X 100 = 100%



9 11 7

Atom Economy in Rearrangement Reactions

- Equation 4

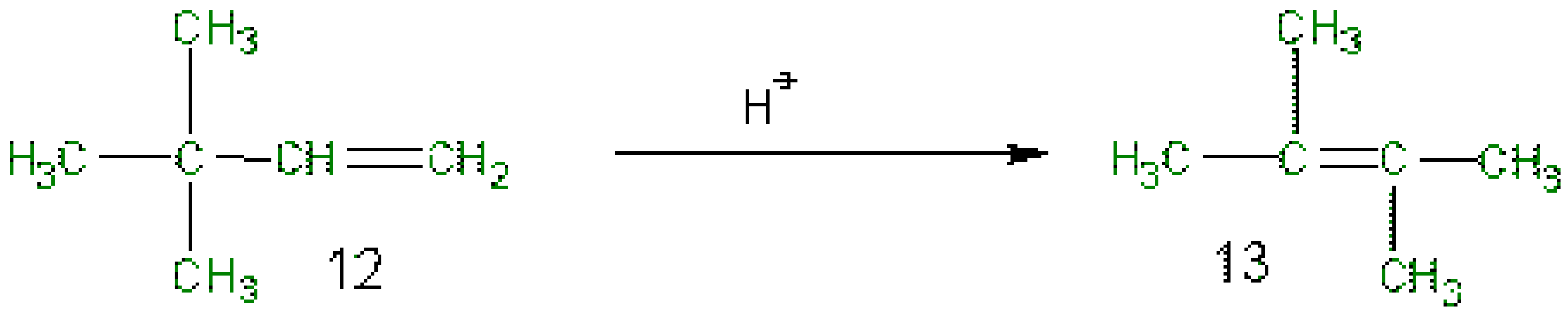


12 13

Table 7 Atom Economy Equation 4

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
12 C_6H_{12}	84	6C,12H	84	—	0
Total 6C,12H	84	6C,12H	84	—	0

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (84/84) X 100 = 100%



The Boots Synthesis of Ibuprofen

Scheme 3, Atom Economy

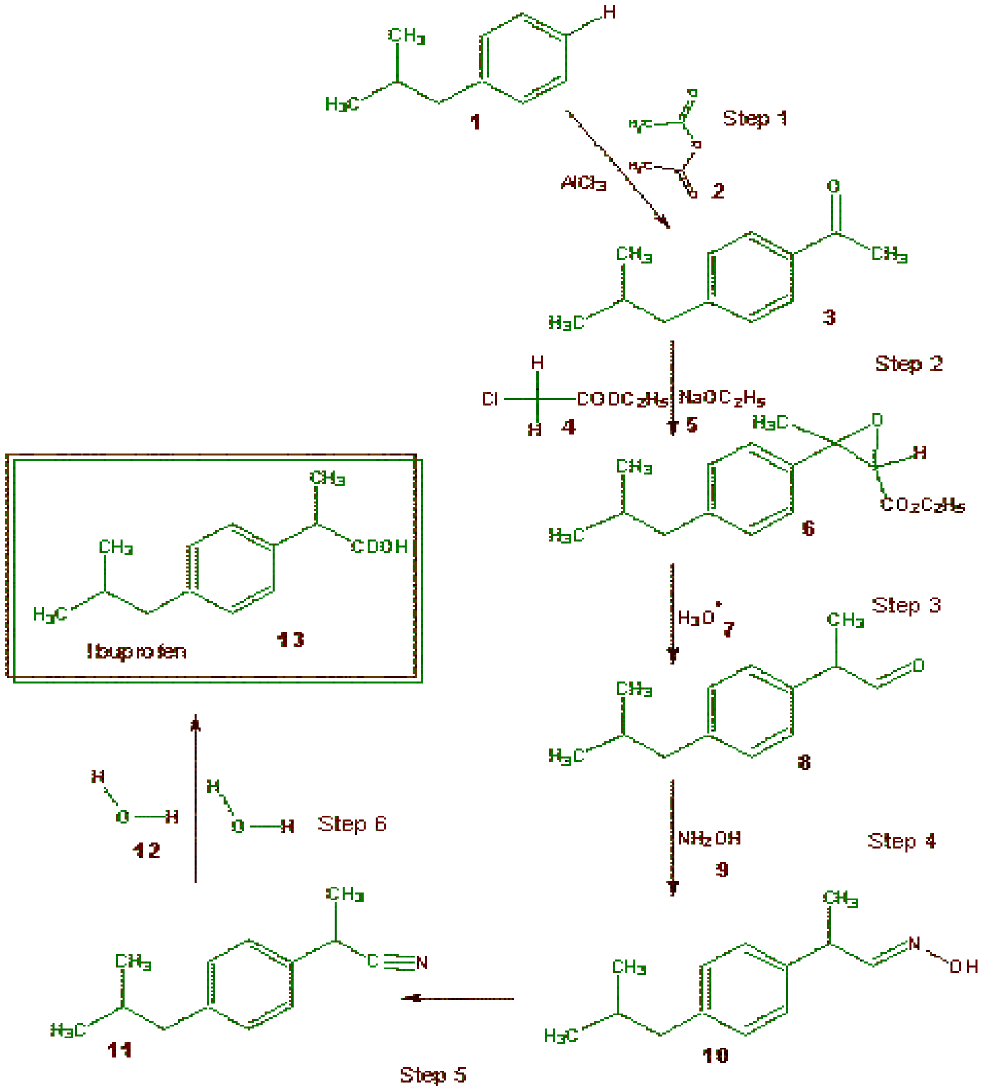


Table 10 Atom Economy of Scheme 3, the Boots Company Synthesis of Ibuprofen

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
1 $C_{10}H_{14}$	134	10C,13H	133	H	1
2 $C_4H_6O_3$	102	2C,3H	27	2C,3H,3O	75
4 $C_4H_7ClO_2$	122.5	C,H	13	3C,6H,Cl,2O	109.5
5 C_2H_5ONa	68	—	0	2C,5H,O,Na	68
7 H_3O	19	—	0	3H,O	19
9 NH_3O	33	—	0	3H,N,O	33
12 H_4O_2	36	H,2O	33	3H	3
Total 20C,42H,N,10O,Cl,Na	514.5	Ibuprofen 13C,18H,2O	Ibuprofen 206	Waste Products 7C,24H,N,8O,Cl,Na	Waste Products 308.5

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (206/514.5) X 100 = 40%

The BHC Synthesis of Ibuprofen Scheme 4, Atom Economy

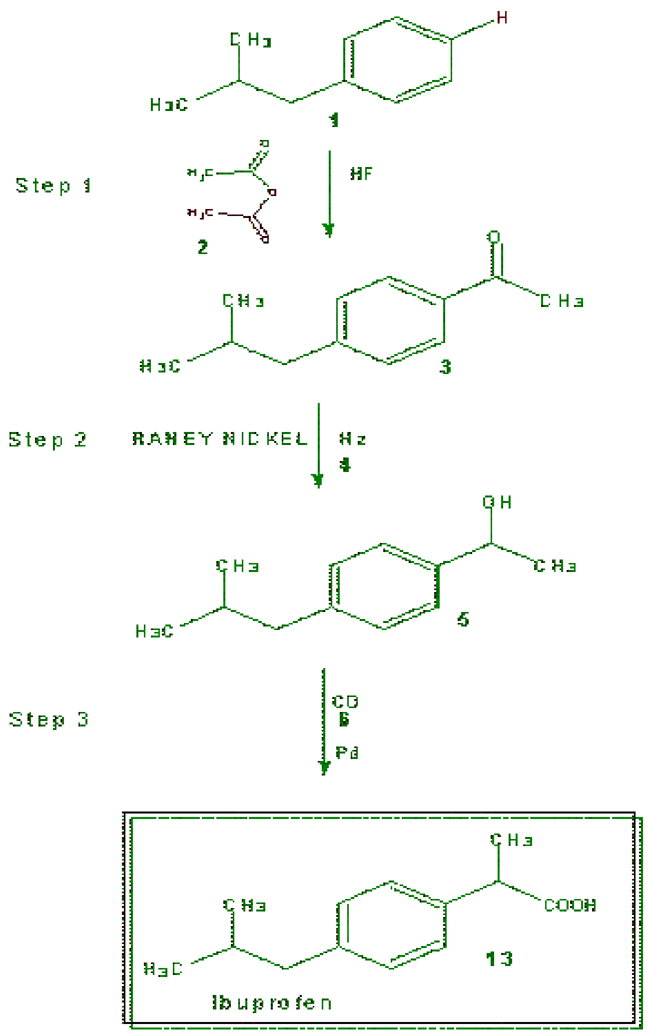


Table 11 Atom Economy of Scheme 4, the BHC Company Synthesis of Ibuprofen

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
1 $C_{10}H_{14}$	134	10C,13H	133	H	1
2 $C_4H_6O_3$	102	2C,3H,O	43	2C,3H,2O	59
4 H_2	2	2H	2	—	0
6 CO	28	CO	28	—	0
Total 15C,22H,4O	266	Ibuprofen 13C,18H,2O	206	Waste Products 2C,3H,2O	60

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (206/266) X 100 = 77%

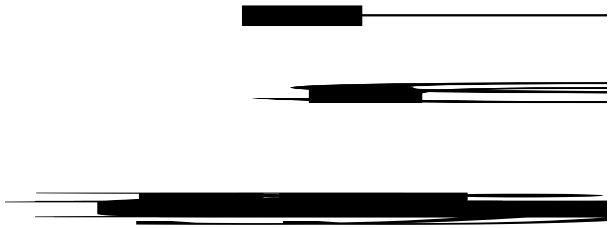
THIRD PRINCIPLE:-LESS HAZARDOUS CHEMICAL SYNTHESIS

WHEREVER PRACTICABLE, SYNTHETIC METHODOLOGIES SHOULD DESIGN TO USE AND GENERATE THAT POSSESS LITTLE OR NO TOXICITY TO HUMAN HEALTH AND THE ENVIRONMENT.

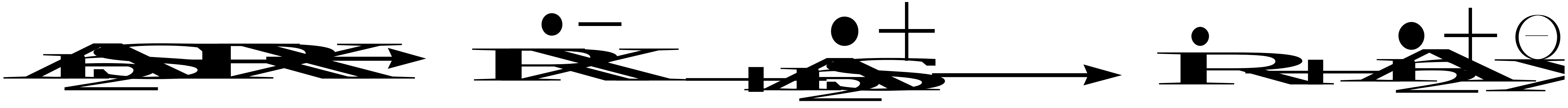
Eg. Carbon –Carbon bond formation via free radical chemistry is a very versatile method for production of range of materials of interest of pharmaceutical companies.

Traditional way of generating free radical is to use highly neurotoxic organotin compounds, especially tributyl tin hydride, as excellent radical carrier.

Whilst handling this compound is a significant hazard there is also the slight but real possibility that the trace amount of organotin compound may left in the product at the end of reaction and purification stages.



In green chemistry, this compound have been replaced by less toxic free radical carrier, sulphide which could transfer an electron to an electrophile to give a radical anion. This in turn could fragment to give an organic radical.



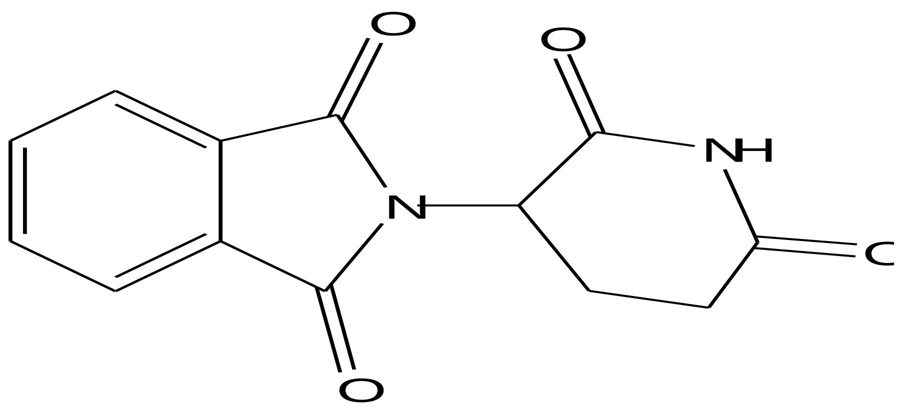
FREE RADICAL

FOURTH PRINCIPLE:- DESIGNING SAFER CHEMICALS

CHEMICAL PRODUCT SHOULD BE DESIGNED TO EFFECT THEIR DESIRED FUNCTION WHILE MINIMIZING THEIR TOXICITY.

SYNTHESIZED CHEMICAL COMPOUNDS SHOULD BE SAFE TO USE.

THOLIDOMIDE IS USED FOR REDUCE NAUSEA AND VOMITTING DURING PREGNANCY.
THE CHIEDREN BORN TO WOMEN TAKING THOLIDOMIDE SUFFERED BIRTH DEFECT. THEREFORE THE USE OF THALIDDOMIDE WAS BANNED.



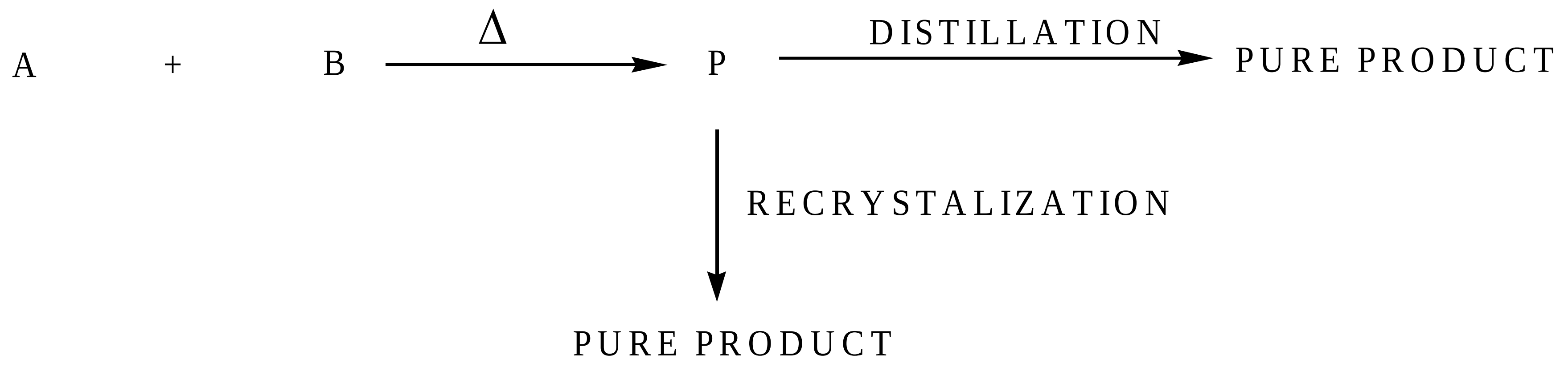
FIFTH PRINCIPLE:- SAFER SOLVENT AND AUXILARY

THE USE OF AUXILIARY SUBSTANCES (SOLVENTS, SEPARATION AGENT, ETC.) SHOULD BE MADE UNNECESSARY WHENEVER POSSIBLE AND, WHEN USED INNOCUOUS (NONTOXIC).

- In many organic reaction solvent like methylene dichloride, chloroform, perchloroethylene, carbon tetrachloride, benzene and other aromatic hydrocarbon have been used due to their excellent solvent properties.
- Halogenated solvents have been identified as human carcinogens. Also, benzene and other aromatic hydrocarbons are believed to promote cancer in human and other animals.
- The solvent selected for particular reaction should not cause any environmental pollution and health hazard.
- The use of liquid carbon dioxide should be explored.
- If possible, reaction should be carried out in aqueous phase or without the use of a solvent in solid phase.
- VOCS like carbon tetrachloride, methylene chloride etc. Which have been used as a solvent in a number of applications have disastrous effect in the atmosphere.
- As far as possible the pathway for a reaction should be such that there is a no need for separation or purification.

SIXTH PRINCIPLE:- DESIGN FOR ENERGY EFFICIENCY

ENERGY REQUIREMENT SHOULD BE RECOGNIZED FOR THEIR ENVIRONMENTAL AND ECONOMIC IMPACTS AND SHOULD BE MINIMIZED.



IF PRODUCT IS NOT PURE THEN WE NEED EXTRA STEPS LIKE RECRYSTALLIZATION AND DISTILLATION

- USE PROPER CATALYST TO MINIMIZE ENERGY REQUIREMENT
- USE PHOTOCHEMICAL REACTION
- PERFORM REACTION IN MICROWAVE OR SONICATION

SEVENTH PRINCIPLE:- USE OF RENEWABLE FEEDSTOCKS

A RAW MATERIAL OR FEEDSTOCK SHOULD BE RENEWABLE RATHER THAN DEPLETING WHENEVER TECHNICALLY AND ECONOMICALLY PRACTICABLE.

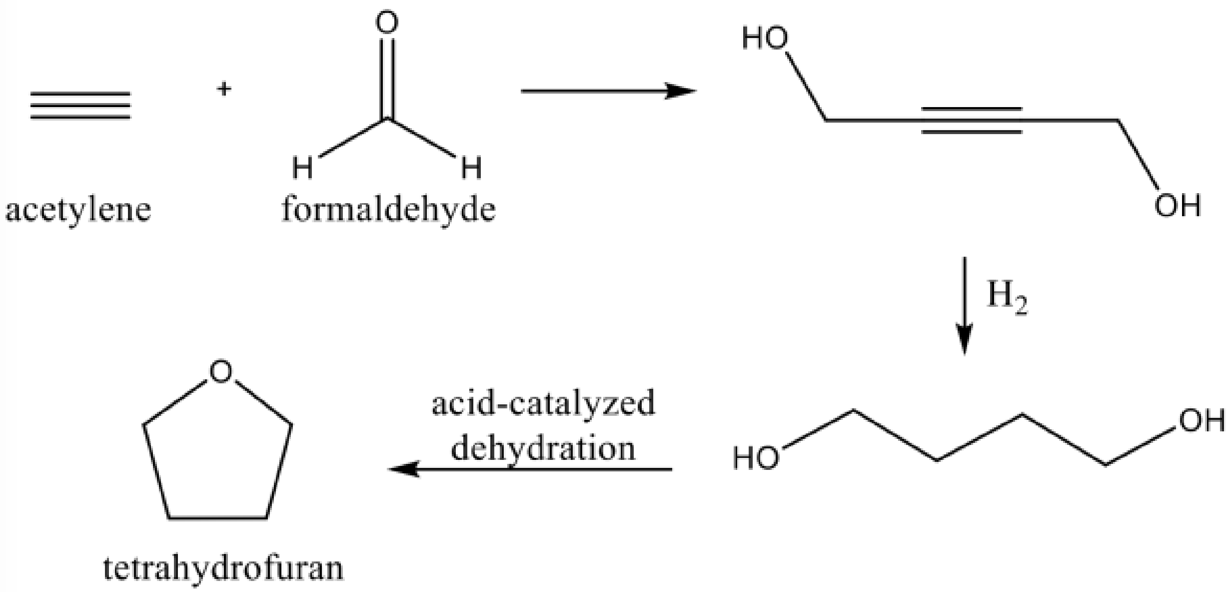
STARTING MATERIALS →

NON-RENEWABLWABLE SOURCES

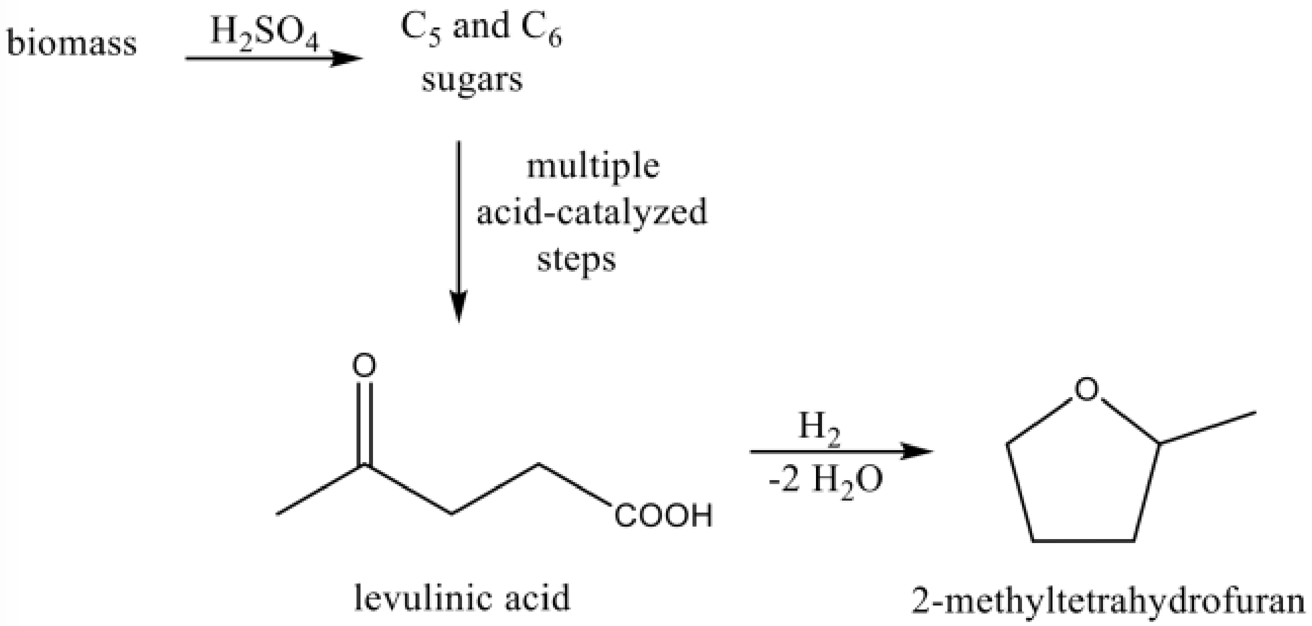
PETROCHEMICALS ARE MOSTLY OBTAINED FROM PETROLEUM OIL, WHICH IS NON-RENEWABLE

RENEWABLE SOURCES

CHEMICAL COMPOUNDS WHICH ARE OBTAINED FROM AGRICUTURE OR BIOLOGICAL SOURCES ARE RENEWABLE

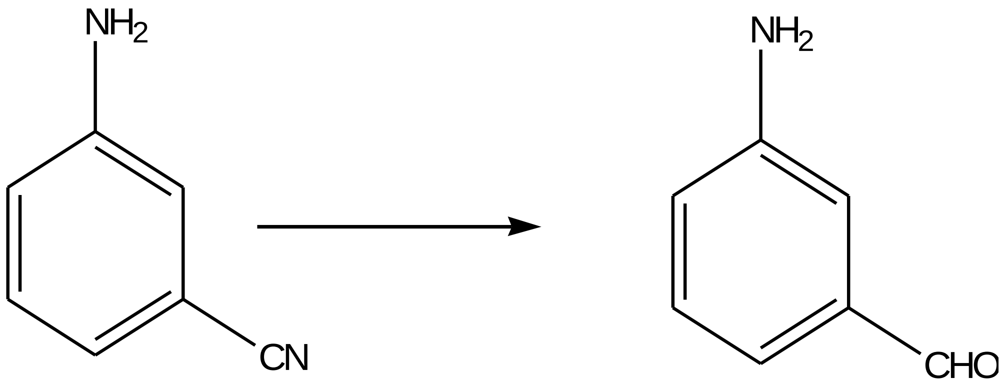


THF IS ONE OF THE BEST SOLVENT IN MOST ORGANIC REACTION

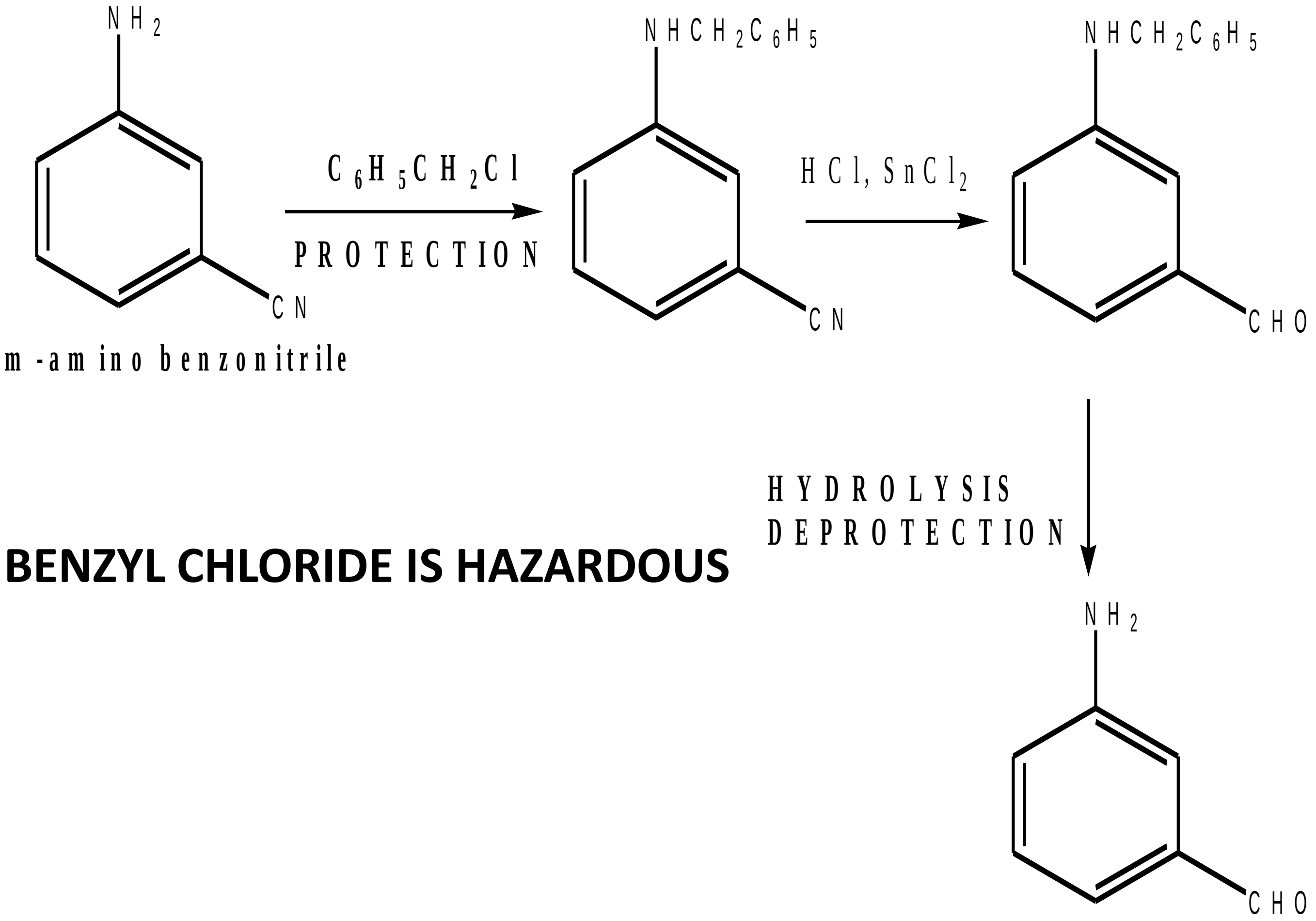


EIGHTH PRINCIPLE:- REDUCE DERIVATIVES

UNNECESSARY DERIVATIZATION SHOULD BE AVOIDED.



m-amino benzonitrile → m-amino benzaldehyde



m-amino benzaldehyde

BENZYL CHLORIDE IS HAZARDOUS

NINETH PRINCIPLE :- CATALYST

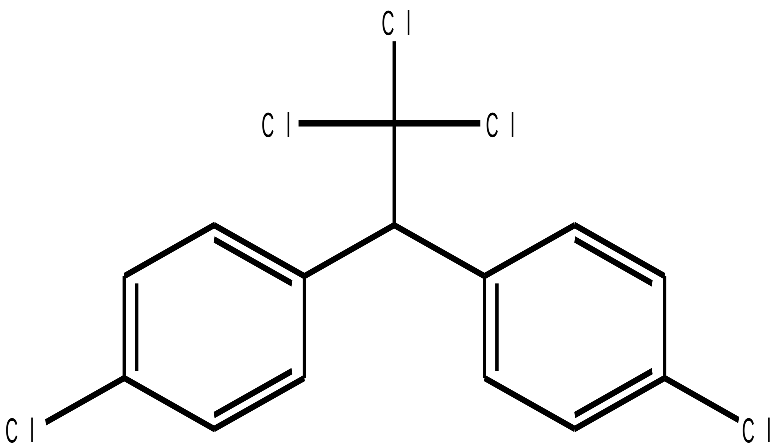
CATALYTIC REAGENTS (AS SELECTIVE AS POSSIBLE) ARE SUPERIOR TO STOICHIOMETRIC REAGENTS.

- By using catalyst starting materials utilization is enhanced and formation of waste reduced.
- Catalyst facilitates the transformation without being consumed or without being incorporated.
- An additional advantages of catalyst is that the activation energy of a reaction reduced and also the temperature necessary for reaction is also lowered. This result in saving energy.

TENTH PRINCIPLE:- DESIGN FOR DEGRADATION

CHEMICAL PRODUCTS SHOULD BE DESIGNED THAT AT THE END OF THEIR FUNCTION THEY DO NOT PERSIST IN THE ENVIRONMENT AND BREAK DOWN INTO INNOCUOUS DEGRADATION PRODUCTS.

- IT IS OF ALMOST IMPORTANT THAT THE PRODUCT THAT ARE SYNTHESIZED SHOULD BE BIODEGRADABLE, THEY SHOULD NOT BE PERSISTANT CHEMICAL OR PERSISTANT BIOACCUMULATORS.



DDT

- The pesticide DDT was one of the first pesticide tend to bio accumulated in plant and animals and produce adverse effect to them and environment.
- Whenever a chemical is being designed, it should be made sure that it will be biodegradable.
- It is now possible to place functional group and other features in the molecules which will facilitate its degradation.

11TH PRINCIPLE :-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 SUBSTANCE.

Most of us have driven a car before. Picture yourself driving down the highway in a car that doesn't have any windows or rearview mirrors. I'd imagine it would be hard to not get into some sort of accident. Now add all the windows and the mirrors. It'd probably be safer to drive now, right?

So what does this have to do with chemistry, or with green chemistry principle Windows and rearview mirrors provide the driver with means to monitor their surroundings in real time and allows them to react and adjust.

This is exactly the idea behind principle #11 – the design of analytical methodologies to monitor chemical reactions in real time and allow for adjustments.

12TH PRINCIPLE

SUBSTANCES AND 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.

- THE OCCURANCE OF ACCIDENTS IN CHEMICAL INDUSTRY MUST BE AVOIDED.
- BHOPAL INCIDENCE

ROLE OF SOLVENT IN ORGANIC REACTION

- Obviously, the solvents are the ideal medium to transport heat to and from endo- and exothermic chemical reactions.
- On dissolution of solutes, solvents break the crystal lattice of solid reactants, dissolve liquid or gaseous reactants, and exert a significant influence on reaction rates and on the positions of chemical equilibrium.
- Additionally, the reactants can interact efficiently when they are in a homogeneous solution, which facilitates stirring, shaking, or other forms of agitation, whereby the reactant molecules come together rapidly and continuously.
- Furthermore, uniform heating or cooling of the mixture in solution can be carried out easily.
- A solvent has the power to increase or decrease the speed of a reaction, sometimes extremely.
- Changing the solvent can influence the rate of reaction, and it can even alter the course of reaction. This may manifest in altered yields and ratios of products.
- Therefore, a solvent can be deeply and inseparably associated with the process of an organic reaction through the solvation of the reactants, products, transition state, or other intervening species.

ENVIRONMENTAL EFFECT OF SOLVENTS()

These solvents are characterized by high volatility and limited liquidus ranges (at atmospheric pressure, ~85–200°C).

As a result, about 20 million tons per year of volatile organic compounds (VOCs) are discharged into the atmosphere owing to industrial processes, contributing to global climatic changes, air pollution, and human health-related issues.

PROBLEMS WITH VOC'S

- **Direct**
  - Varying toxicity depending on nature of VOC, exposure method and duration.
    - E.g. DMF (teratogenic), $CHCl_3$ (suspect carcinogen)
  - Flammability (fire hazards)
  - Peroxide formation (usually ethers)

- **Indirect**
  - Ozone depletion
  - Chlorofluorocarbons (CFC's) now phased out
  - E.g. CF_3Cl, lifetime in atmosphere 640 years, GWP 14,000
  - CCl_4 – now much more limited use (35yrs, GWP 1400)
  - Global warming potential (GWP)
  - Does not have to be ozone depleting to have GWP
  - E.g. (CH_2FCF_3) used in refrigerants and air conditioning units, 14yrs, GWP 1300
  - Environmental persistence
- Use of less volatile solvents may improve environment as long as they do not lead to problems elsewhere.

STRATEGIES OF SOLVENT REPLACEMENT

- Avoid or minimise solvents in first place
- Use less toxic solvents
- Use renewable solvents (not derived from petrochemicals)
- Avoid VOC's – solvents with low vapour pressure / high boiling points may be preferable as long as this does not lead to other complications.

CURRENT APPROACHES TO SOLVENT REPLACEMENT IN SYNTHETIC CHEMISTRY

- No solvent
- Water
- Carbon dioxide
- Ionic liquids
- Lactate esters
- Fluorous phase reactions

All have advantages and disadvantages which need to be considered when assessing suitability for replacement

SOLVENT FREE REACTION:-

In many solvent-free reactions, one of the reagents is a liquid and is sometimes present in excess. This liquid is often acting as the solvent and making a homogeneous reaction solution. In other solvent free reactions, there may be a liquid, for example, water, formed during the course of the reaction, and this liquid assists the reaction at the interface between the reagents and acts like a solvent.

ADVANTAGES OF SOLVENT FREE REACTION:

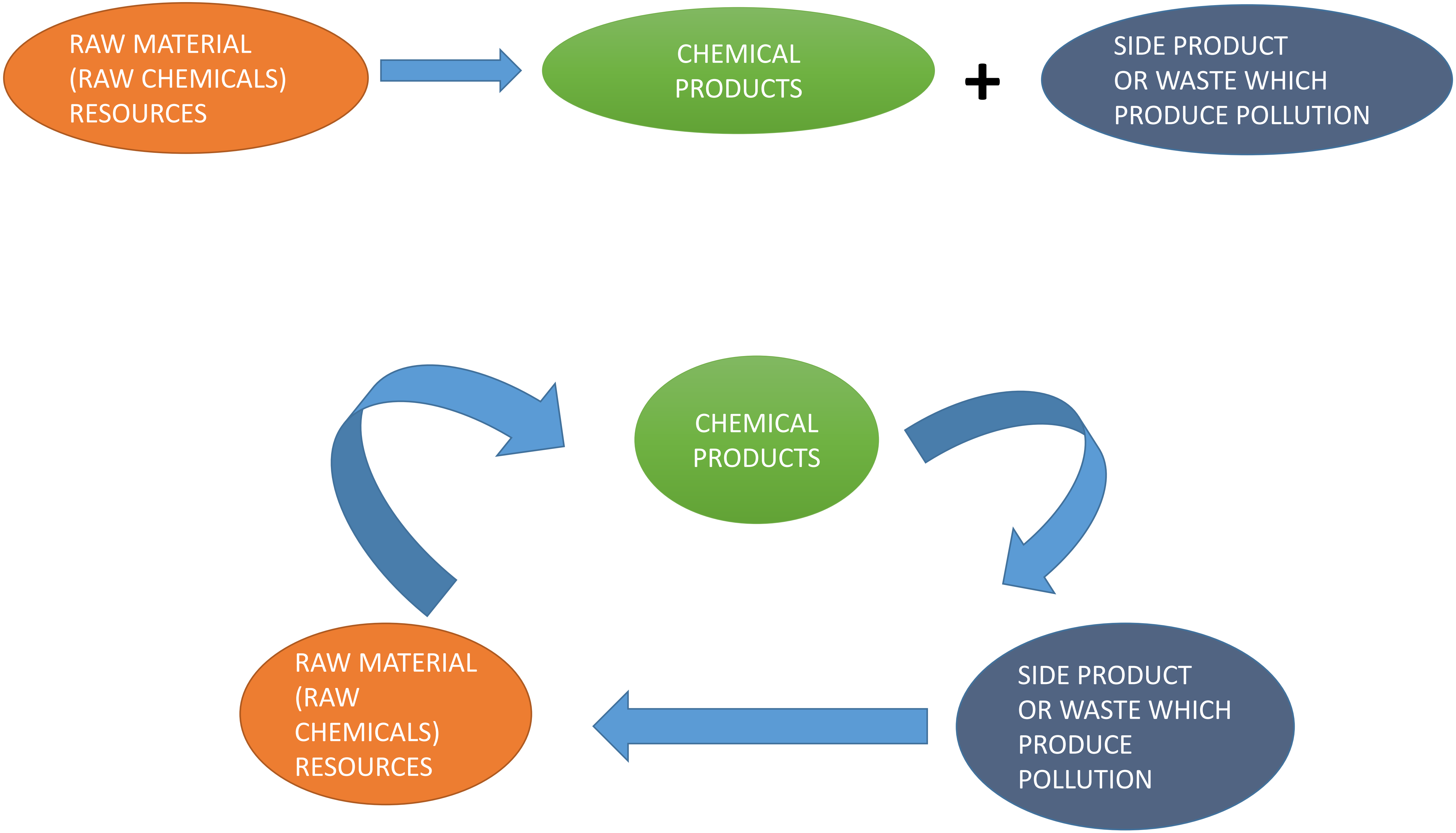
- there is no reaction medium to collect, purify, and recycle
- the compounds formed are often sufficiently pure to avoid extensive purification by chromatography, and in some cases, there is not even the require for recrystallization
- the reactions are often quick, sometimes reaching completion in several minutes as compared to hours with organic solvents
- energy usage may be considerably lower
- processing cost savings, production of solvent-free protocols is not only more environmentally benign but also more economically feasible

GREEN CHEMISTRY AND SUSTAINABLE DEVELOPMENT DESIGNING PRODUCT UNDER THE HOLISTIC APPROACH

“CRADLE TO CRADLE”

It is a sustainable business strategy that mimics the regenerative cycle of nature in which waste is reused. (Nothing is waste)

The “Waste equals food” principle is based on the nutrient cycle in nature. It leads to the elimination of the concept of waste as any unnecessary component of one system becomes nutrient for another system. This material flow system is a fundamental component of the C2C method of production. According to its composition, a product can reenter a biological cycle or a technical cycle at the end of its life.


RAW MATERIAL (RAW CHEMICALS) RESOURCES
CHEMICAL PRODUCTS
+
SIDE PRODUCT OR WASTE WHICH PRODUCE POLLUTION
CHEMICAL PRODUCTS
RAW MATERIAL (RAW CHEMICALS) RESOURCES
SIDE PRODUCT OR WASTE WHICH PRODUCE POLLUTION

THANK YOU.....