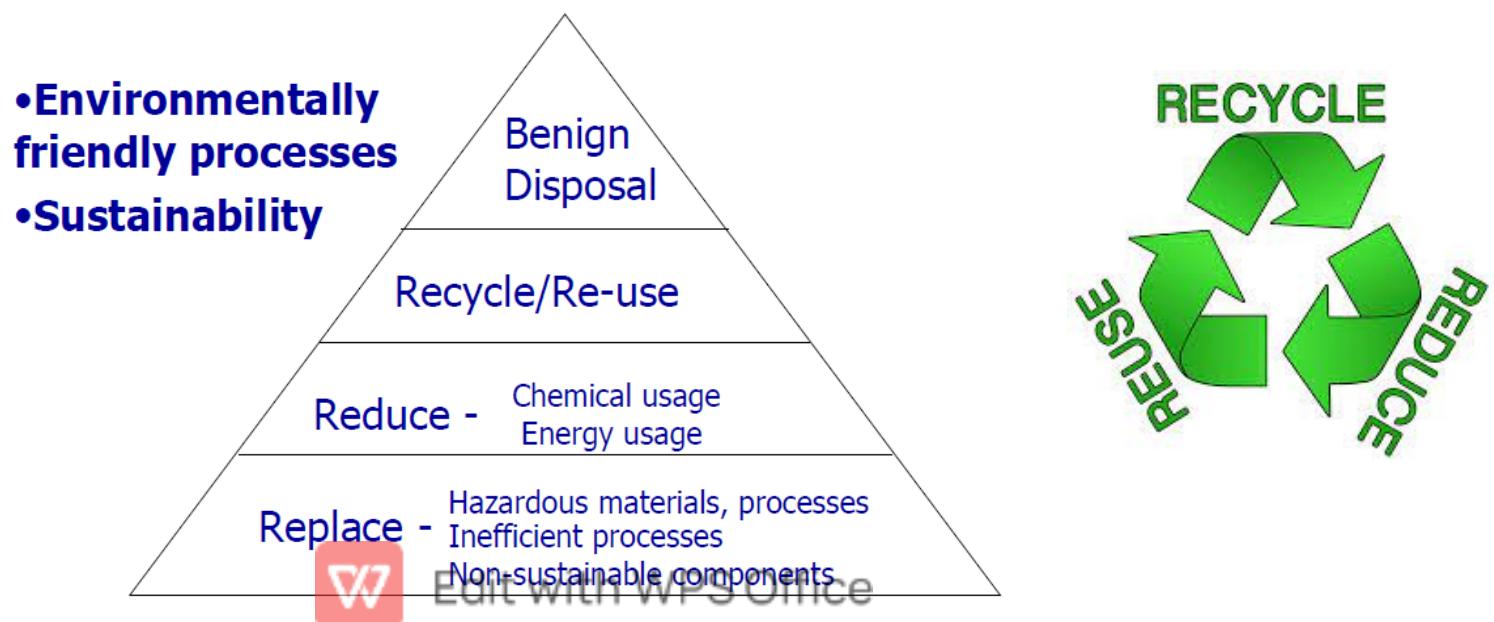


Green Chemistry

* *"Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products."*

Green Chemistry: by Paul Anastas and John Warner



Role of chemistry in making life better

- Life saving drugs
- Fertilizer & insecticides
- Composite and advanced engineering materials
- Polymers
- Cosmetics
- Preservatives
- Coatings and lacquers
- Electronics
- Fuel and batteries



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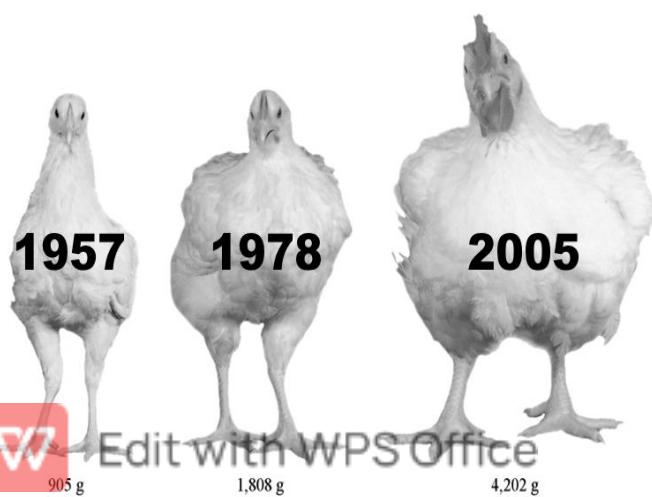
Role of chemistry in environmental problems



Air Pollution



Genetic modification



Roots of Green Chemistry in Pollution Prevention Act 1990

- * To stop creating pollution in the first place became America's official policy in 1990 with the Federal Pollution Prevention Act.
- * Reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment, or disposal.
- * The term "source reduction" includes:
 - * Modifications to equipment or technology
 - * Modifications to process or procedures
 - * Modifications, reformulation or redesign of products
 - * Substitution of raw materials



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Why do we need Green Chemistry

- * Prevents pollution at the molecular level
- * Is a philosophy that applies to all areas of chemistry, not a single discipline of chemistry
- * Applies innovative scientific solutions to real-world environmental problems
- * Results in source reduction because it prevents the generation of pollution
- * Reduces the negative impacts of chemical products and processes on human health and the environment
- * Lessens and sometimes eliminates hazard from existing products and processes
- * Designs chemical products and processes to reduce their intrinsic hazards



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Goals and Objectives of Green Chemistry

1. To reduce the adverse environmental impacts, try innovative and appropriate choice of chemicals
2. To develop process renewable rather than non renewable raw materials
3. To develop processes that are less prone to obnoxious chemical release, fire and explosion
4. To minimize by-products in chemical transformation by redesigning of chemical processes
5. To develop processes that are less toxic
6. To develop products that degrade more rapidly in environments

Contd



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7. To reduce the requirements of hazardous and persistent solvents and extractants
8. To improve energy efficiency of processes
9. To develop efficient and reliable methods to monitor the processes



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12 principles of Green Chemistry

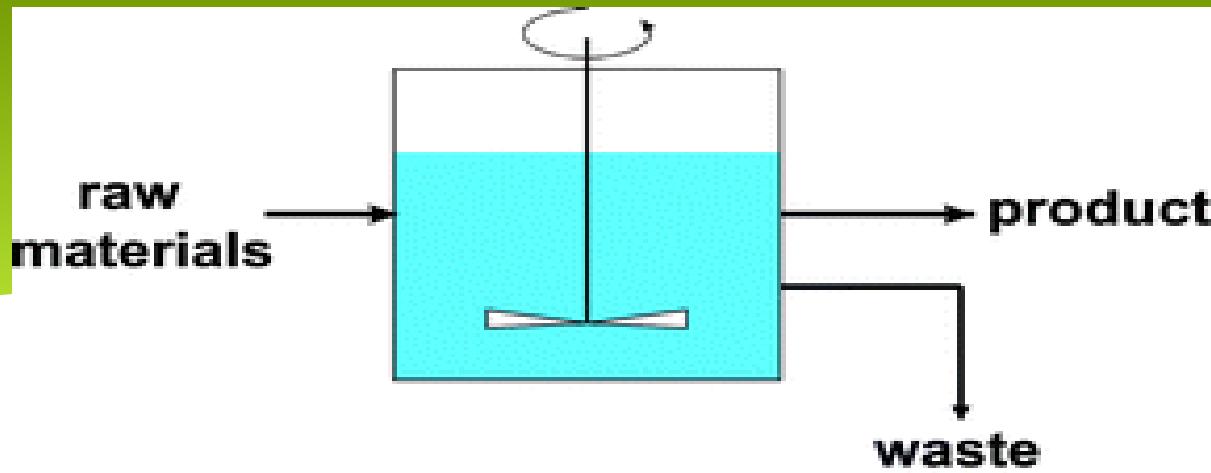


1. Prevention of waste

- * It is better to prevent waste than to treat or clean up waste after it is formed.
- * Reactant A + Reactant B -----> Product C + Waste D
- * Green chemist looks at pollution prevention at molecular level, so instead of generating the waste, focus will be on finding the alternate route of getting product without producing waste.
- * Reactant 1 + Reactant 2 -----> Product C



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$$E = \frac{\text{kg waste}}{\text{kg product}}$$

Environment Factor (E-factor) concept has played a major role in focusing the attention on the problem of waste generation in electronic manufacture.

To manufacture **computer chips**, many chemicals, large amounts of water, and energy are required. In a study conducted in 2003, the industrial estimate of chemicals and fossil fuels required to make a computer chip was a 630:1 ratio!



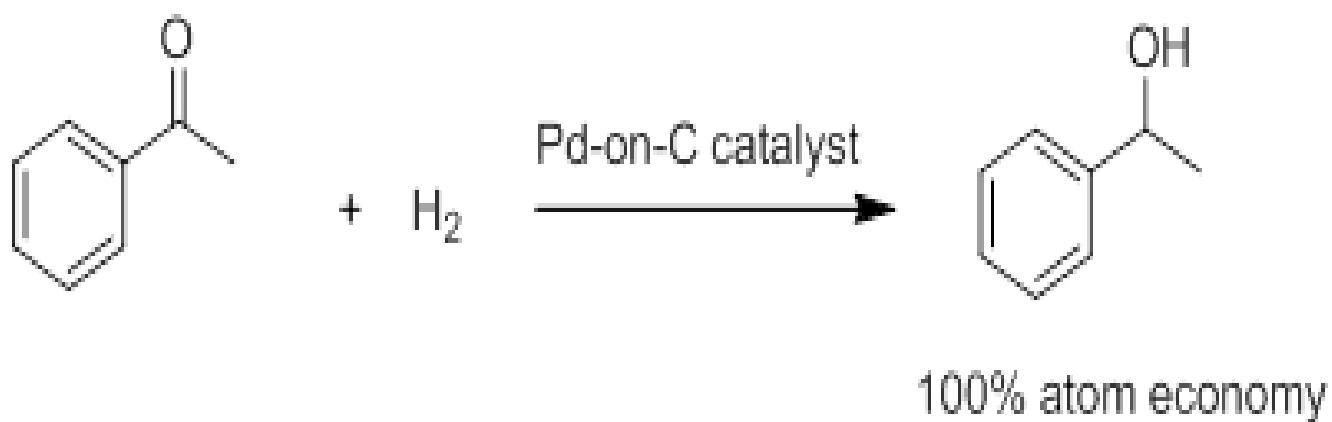
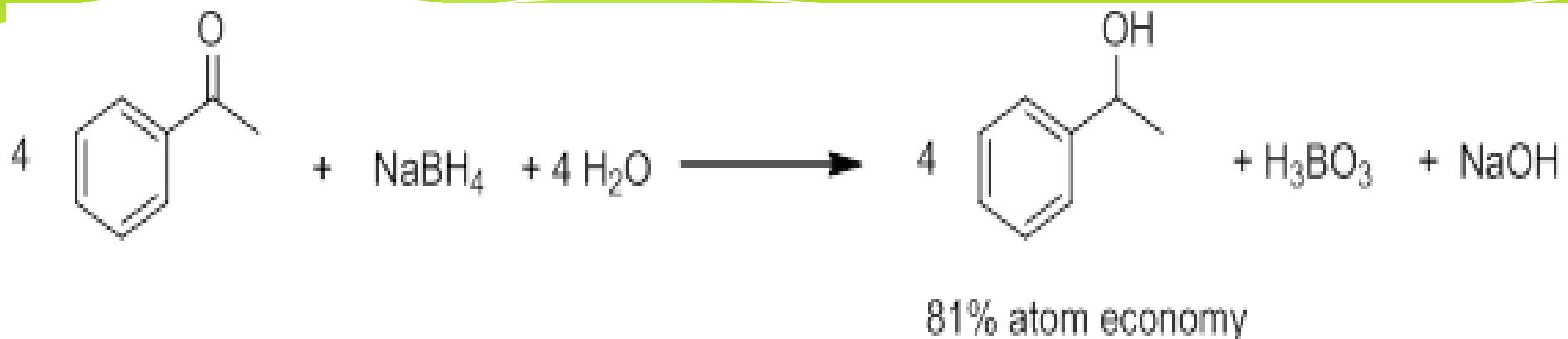


- * Serious proposals to reduce e-waste must address how electronics are manufactured in the first place. Some ways to do that include designing electronics that are more durable, repairable and recyclable.
- * Second big question is of consumer behavior.
- * **How many of our digital upgrades result from genuine obsolescence versus fashion?**
- * Stanford engineer Zhenan Bao and her team created a flexible electronic device that can easily degrade just by adding a weak acid like vinegar, according to a paper published in National Academy of Sciences.



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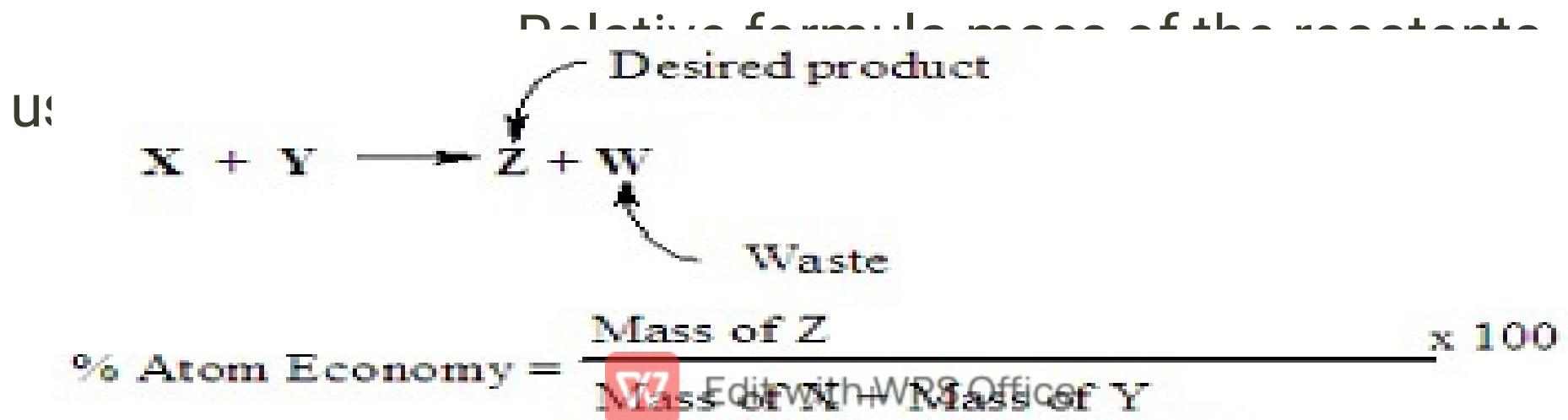
2. Atom Economy



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Increase Atom Economy

- * The concept of Atom Economy was developed by Barry Trost of Stanford University (US), for which he received the Presidential Green Chemistry Challenge Award in 1998. It is a method of expressing how efficiently a particular reaction makes use of the reactant atoms.
- * Atom economy = Relative formula mass of useful product \times 100



The theoretical yield for every reaction can be calculated as.

$$\text{Theoretical yield} = \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}} \times \text{weight of limiting reagent} \right]$$

On conducting the reaction the experimental or actual yield of the process is obtained. From this percentage yield is calculated.

$$\text{Percentage yield} = \left[\frac{\text{Actual yield}}{\text{Theoretical yield}} \right] \times 100$$

e.g. Preparation of n-propyl bromide from n-propyl alcohol (0.6 g)



Thus 1 mole of reactant gives one mole of product



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Hence

$$\begin{aligned}\text{Theoretical yield} &= \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}} \right] \\ &\quad \times \text{Weight of limiting reagent} \\ &= \frac{1}{1} \times \left[\frac{123}{60} \right] \times 0.6 \\ &= 1.23 \text{ gms}\end{aligned}$$

But actually yield of the above reaction is found to be 0.99 gms

$$\begin{aligned}\text{Hence percentage yield} &= \frac{0.99}{1.23} \times 100 \\ &= 80.49\%\end{aligned}$$



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Atom economy can be calculated by using following formula.

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

∴ In above reaction, % atom economy can be calculated as,

$$\begin{aligned}\% \text{ Atom economy} &= \frac{\text{Molecular weight of n-propyl bromide}}{\text{Molecular weight of (n-propanol + NaBr)}} \times 100 \\&= \frac{123}{60 + 103} \times 100 \\&= \frac{123}{163} \times 100 \\&= 75.5\%\end{aligned}$$

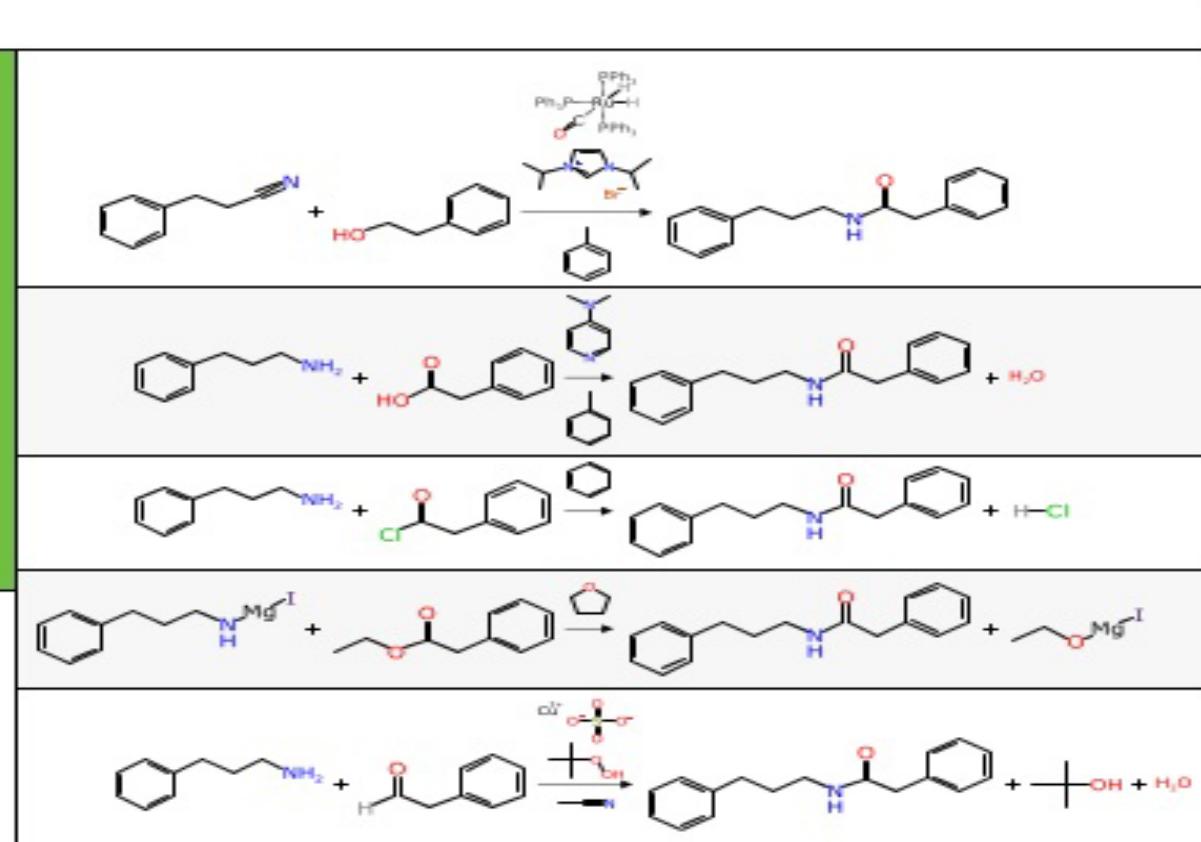


Product Search Results

MOLECULAR MATERIALS INFORMATICS

10

Decision Making



Yield	PMI	E-factor	Atom Economy
100%	2.18	1.18	100%
84%	12.49	11.49	93.3%
82%	19.17	18.17	87.4%
100%	8.26	7.26	56.3%
63%	8.93	7.93	73.3%



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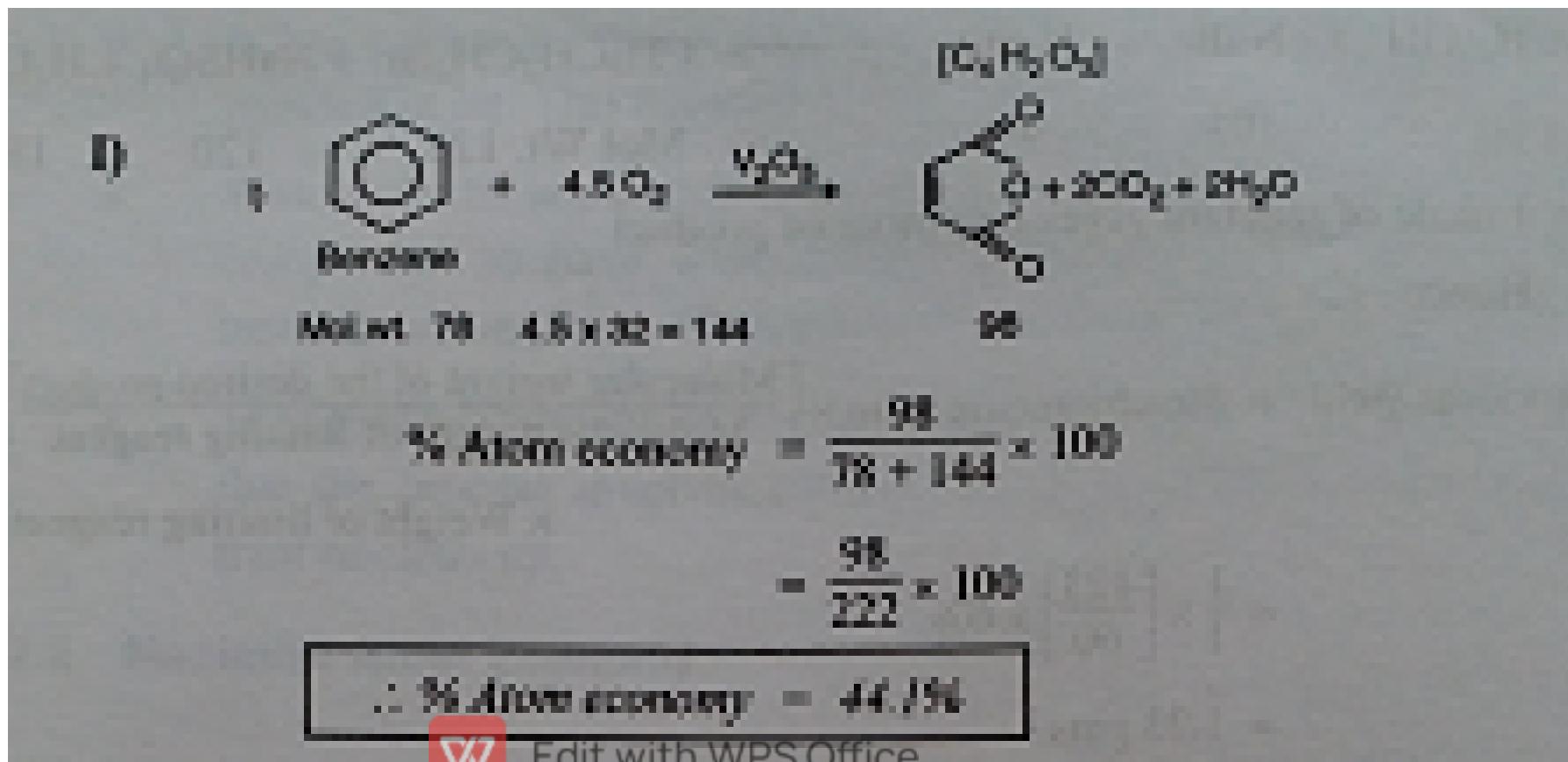
Atom Economy- Example:

Preparation of Maleic anhydride from-

Benzene

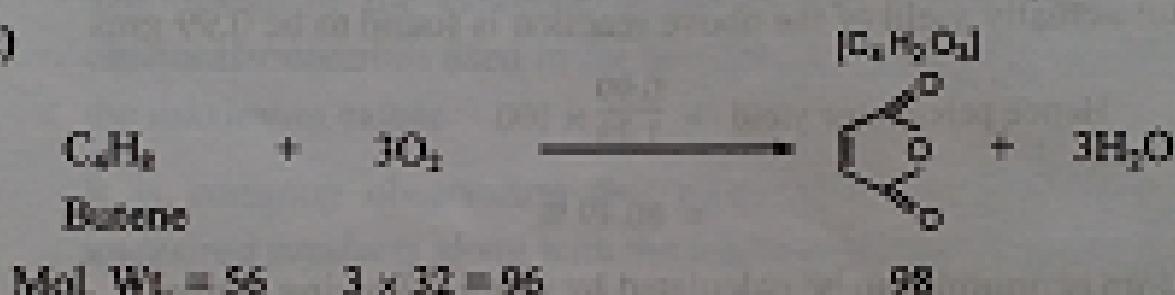
Butene

Butane



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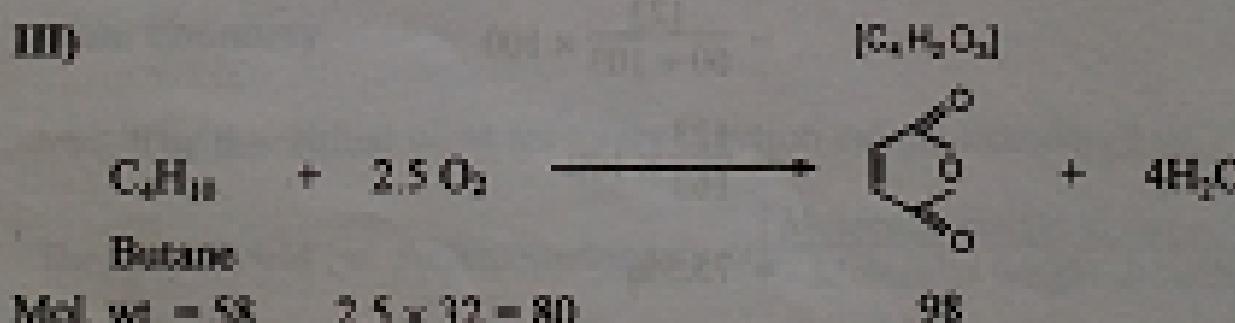
III



$$\begin{aligned}\% \text{ Atom economy} &= \frac{98}{56 + 96} \times 100 \\ &= \frac{98}{152} \times 100\end{aligned}$$

$$\therefore \% \text{ Atom economy} = 64.5 \%$$

III



$$\begin{aligned}\% \text{ Atom economy} &= \frac{98}{58 + 80} \times 100 \\ &= \frac{98}{138} \times 100\end{aligned}$$

$$\therefore \% \text{ Atom economy} = 71.0 \%$$



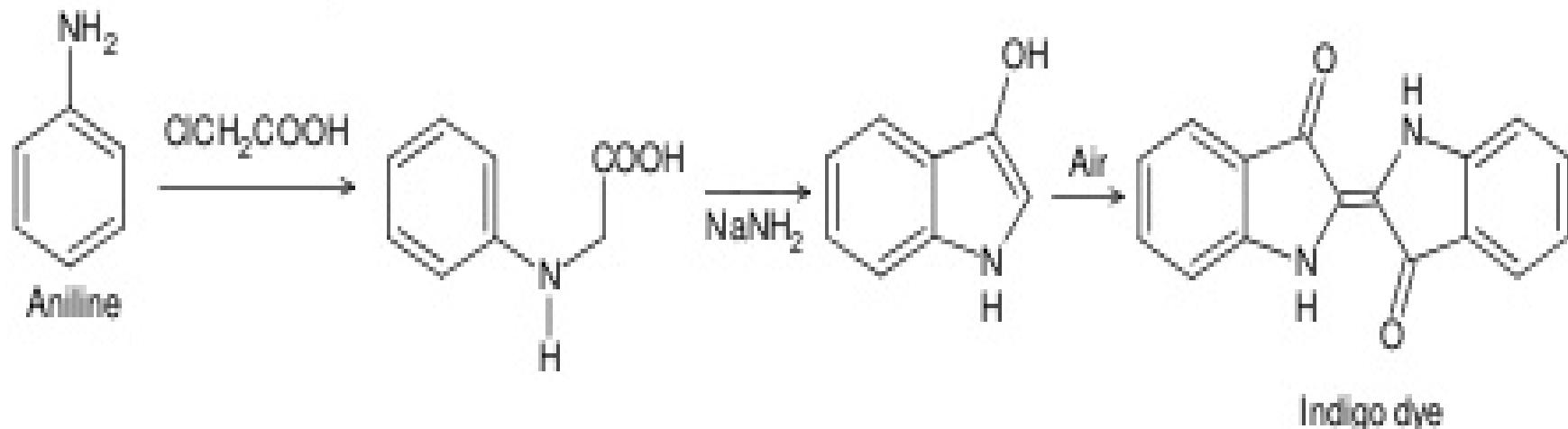
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3. Non Hazardous Synthesis

- * Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

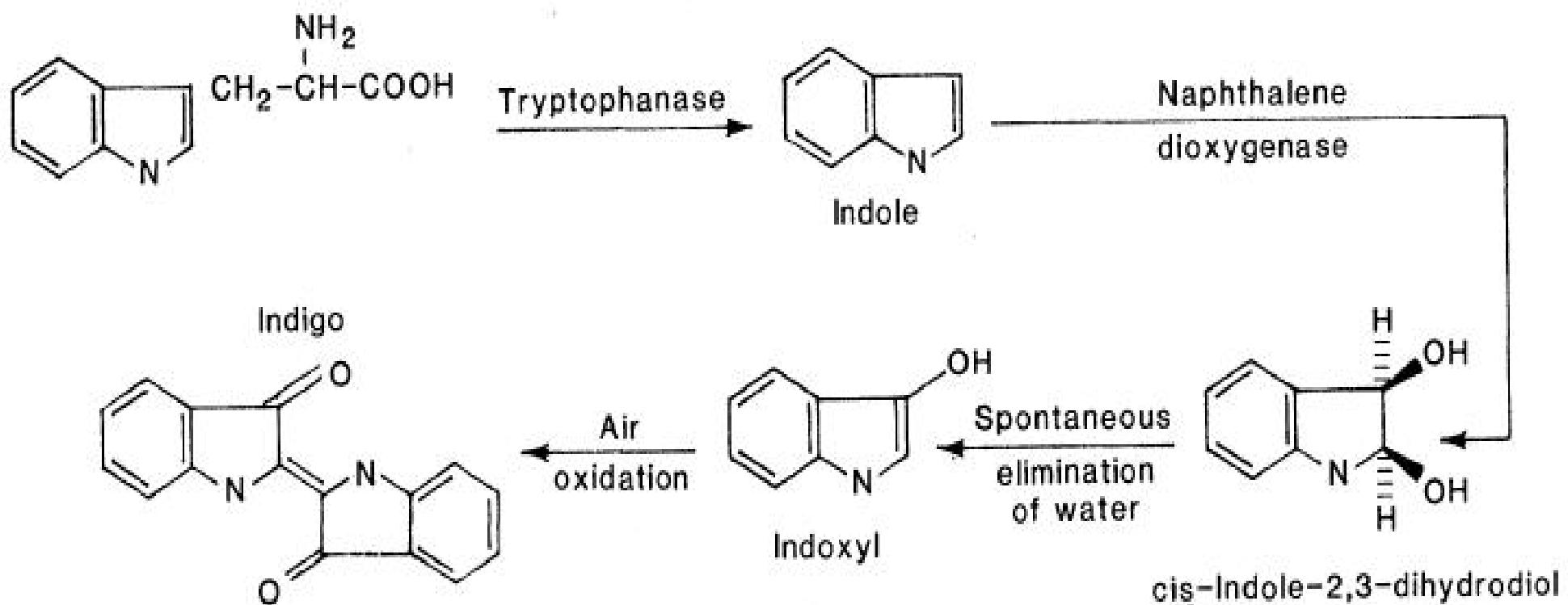
Indigo Dye:

Traditional Pathway:



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Green Synthesis of Indigo



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4. Safer Chemicals and Product

- * For reducing the toxicity, the efficiency of desired product should be preserved
- * *Chemical products should be designed to carry out their desired function, while minimizing their toxicity.*
- * Mastering the art and science of toxicology requires innovative approaches to chemical characterization that state that hazard is a design flaw and must be addressed at the genesis of molecular design. The intrinsic hazard of elements and molecules is a fundamental chemical property that must be characterized, evaluated and managed as part of a systems-based strategy for chemical design.



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- * There are two crucial elements in approaching the goal of sustainability in chemical products and processes: alternatives assessment and molecular design. To date the focus is on the first point.
- * Determining the toxicity of chemicals is necessary to identify their harmful effects on humans, animals, plants, or the environment. It is also one of the main steps in drug design. Animal models have been used for a long time for toxicity testing. However, in vivo animal tests are constrained by time, ethical considerations, and financial burden. Therefore, computational methods for estimating the toxicity of chemicals are considered useful. Computational methods to analyze, simulate, visualize, or predict the toxicity of chemicals.



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5. Use of safer Solvents

- * The solvents and separating agents should not be used unnecessarily
- * Acetone, ethers and most of organic solvents are inflammable and are avoided
- * Chloroform, carbon tetrachloride and many other chlorinated solvents are toxic and carcinogenic
- * If solvents are necessary water is good medium or some ecofriendly solvents like Supercritical CO₂ can be used.



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6. Energy Efficiency

- * The aim of green chemistry is to increase energy efficiency
- * This can be achieved by use of catalyst and by stopping the use of fossils fuels.
- * Microwave and sound waves are new alternate types of energy substitute for efficient energy processes.
- * The energy efficiency can be increased by
 - a) Proper heat transfer
 - b) minimal wastage of energy during the process.



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7. Renewable Feedstock

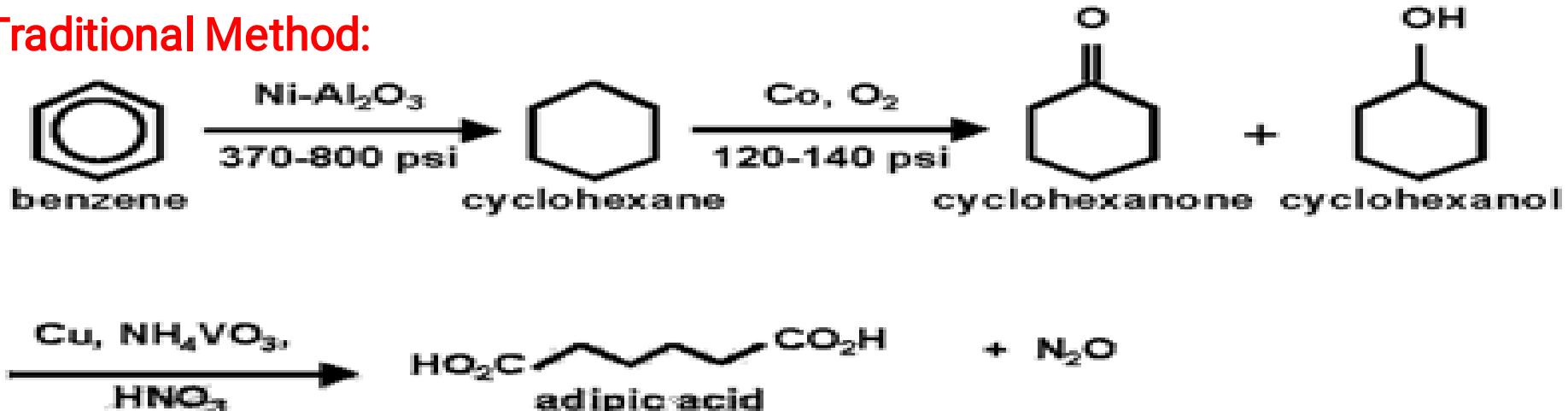
- * Adipic acid is required in large quantity as raw material for the synthesis of nylon and lubricants.
- * But Adipic acid is prepared from benzene which is toxic and carcinogenic. Also during synthesis nitrous acid is used which is a green house gas
- * Green synthesis of adipic acid uses D-Glucose as a raw material which is both non-toxic as well as renewable feedstock



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Synthesis of adipic acid

Traditional Method:



Alternate Synthesis:



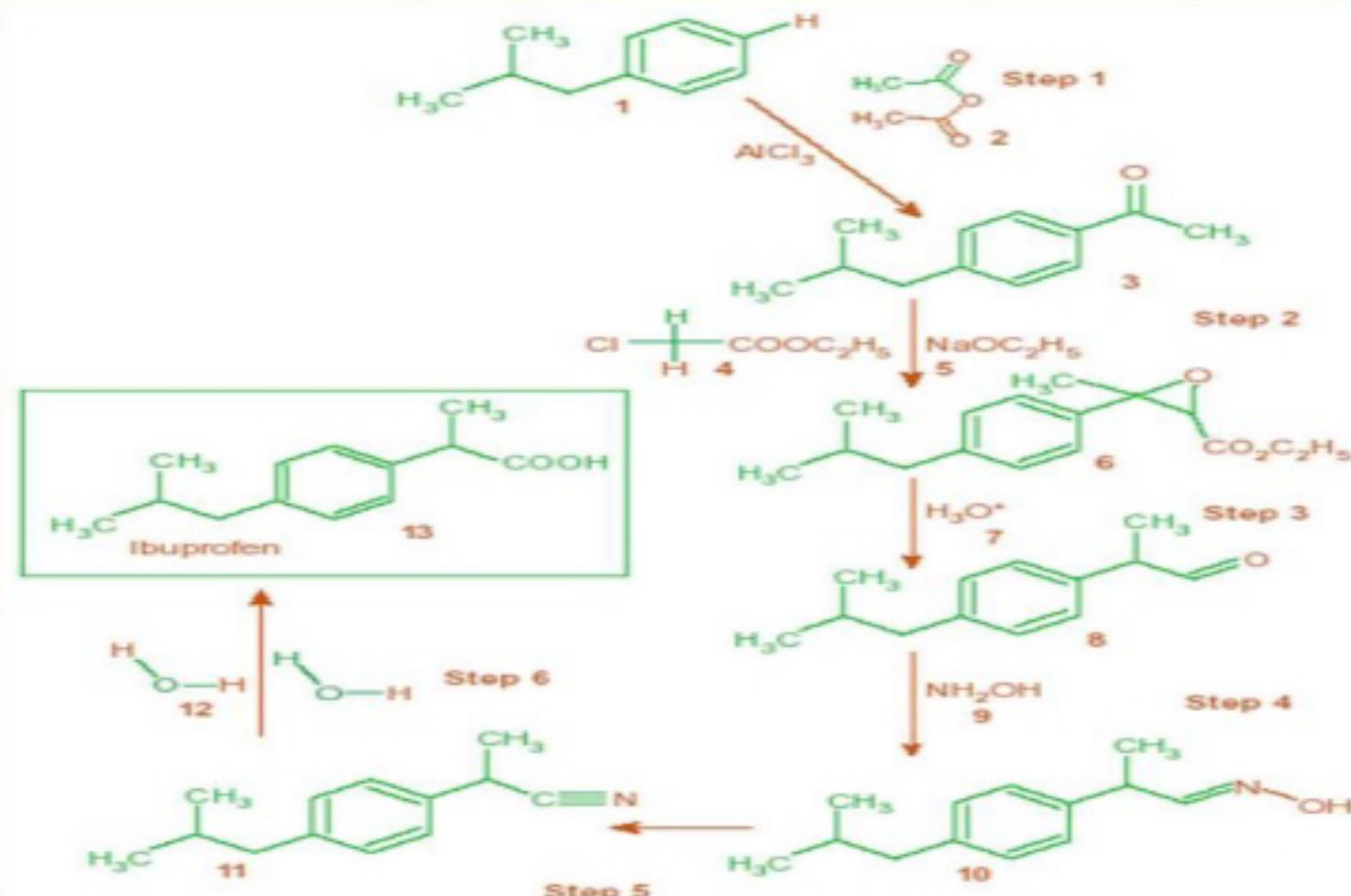
8. Avoid chemical derivatives

- * Unnecessary derivatization or temporary modifying should be avoided.
- * Derivatives increases the steps and reduces the atom economy
- * Additional reagents are required and generates more steps
- * Example
- * Synthesis of Ibuprofen in which traditionally large number of steps are involved and atom economy is only 40%
- * Whereas in alternative route product form more selectively and less number of steps. The atom economy of synthesis is 77 %



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The Boots Company Synthesis of Ibuprofen (1960)

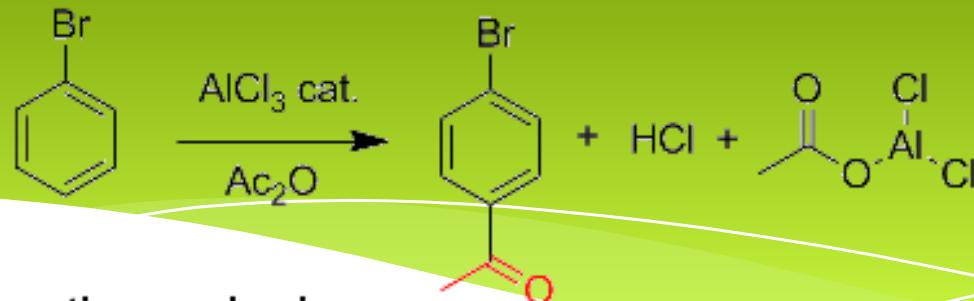


Production of 2 L of Ibuprofen generates 3 L of waste
AE = 40%



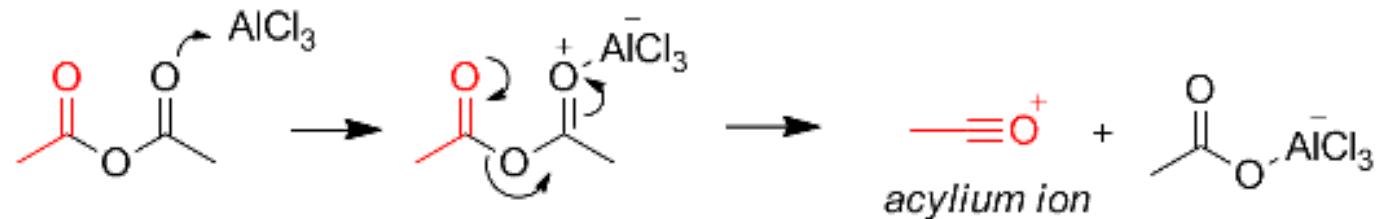
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General equation

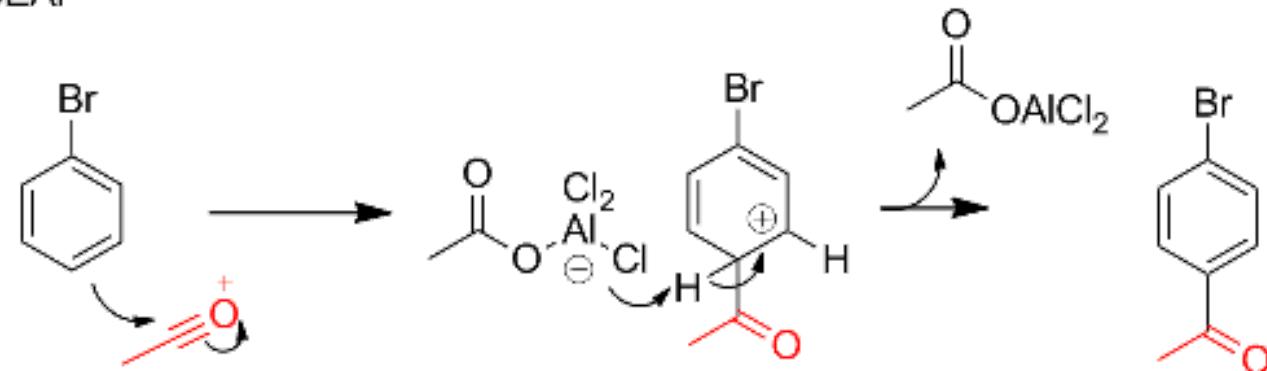


Reaction mechanism

1) generation of acylium ion



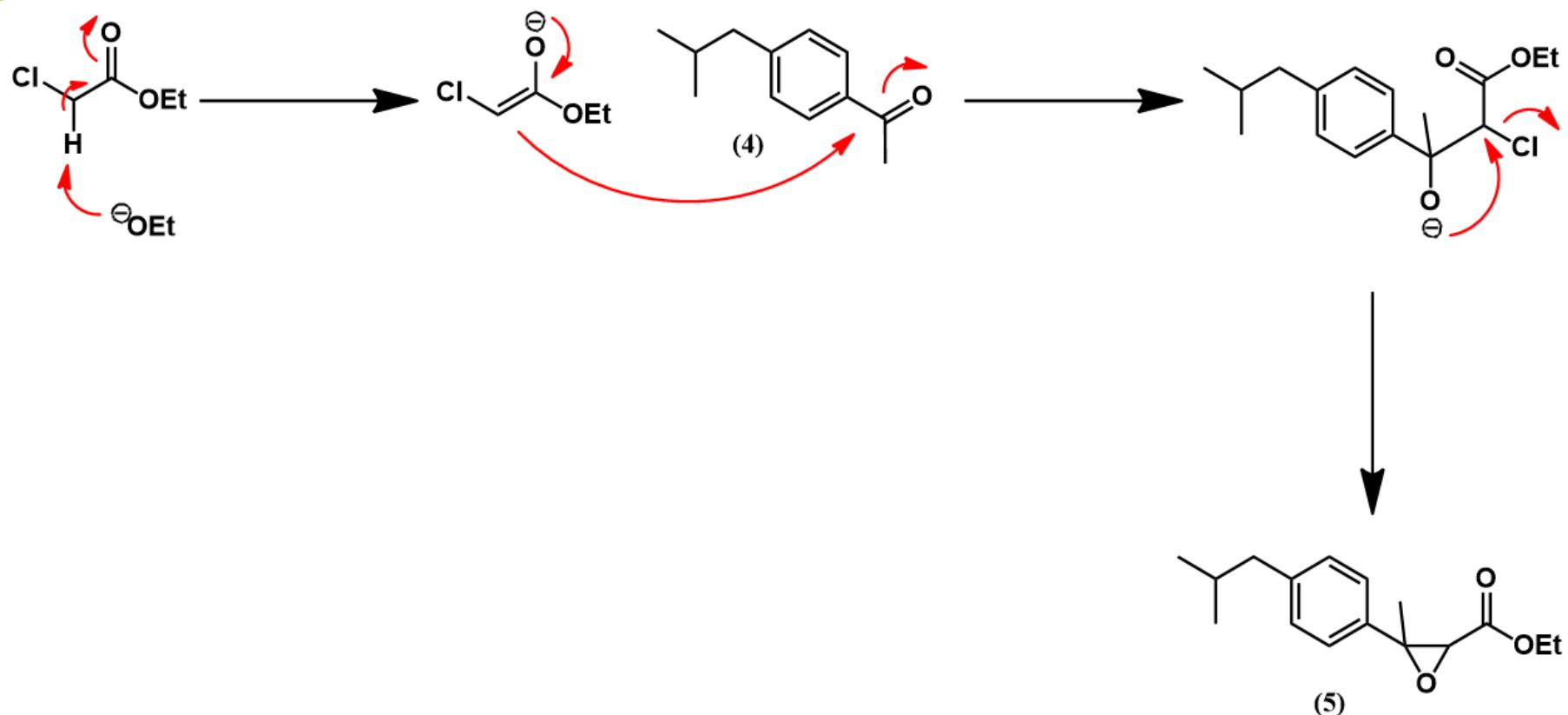
2) SEAr



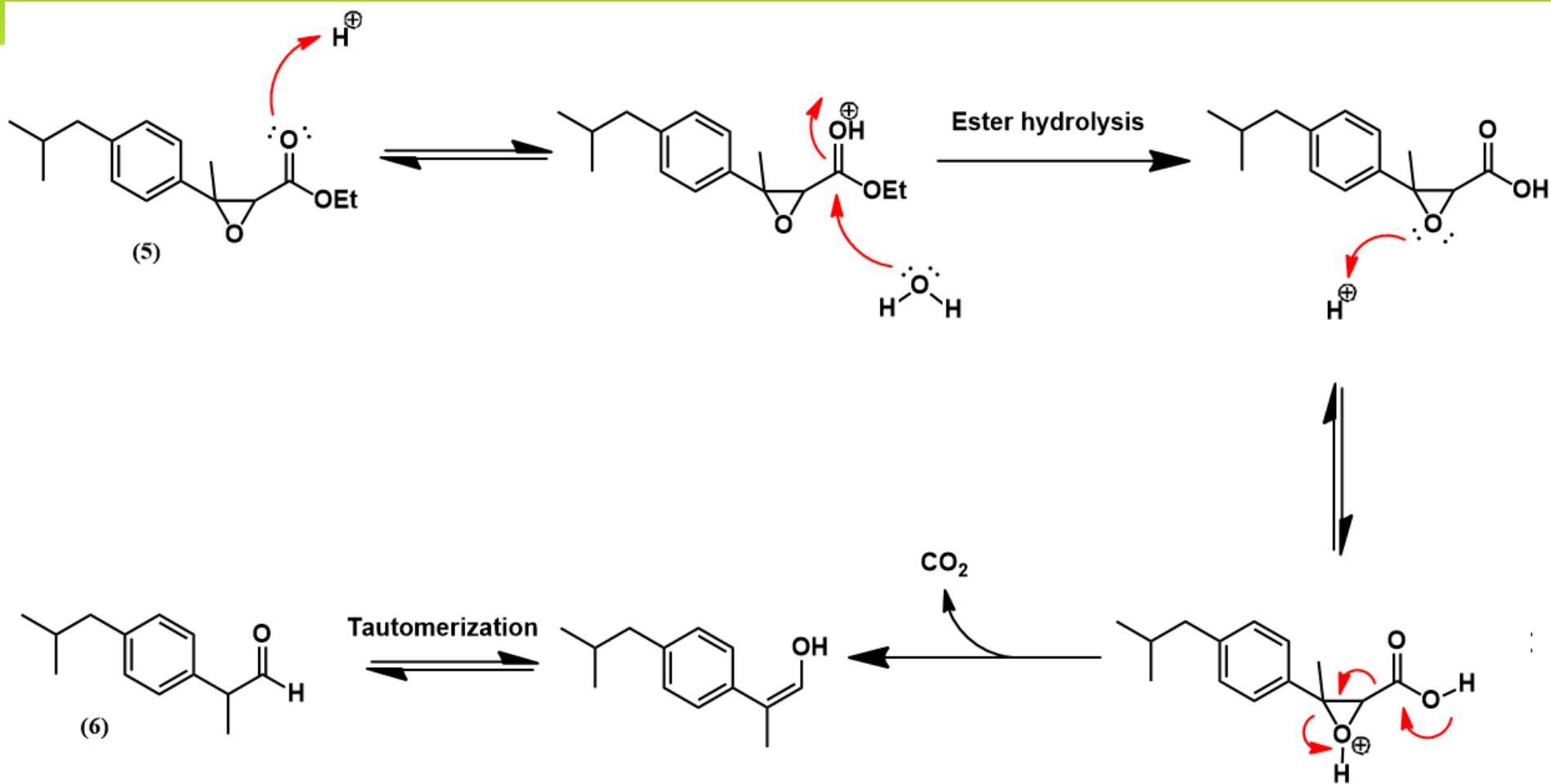
product



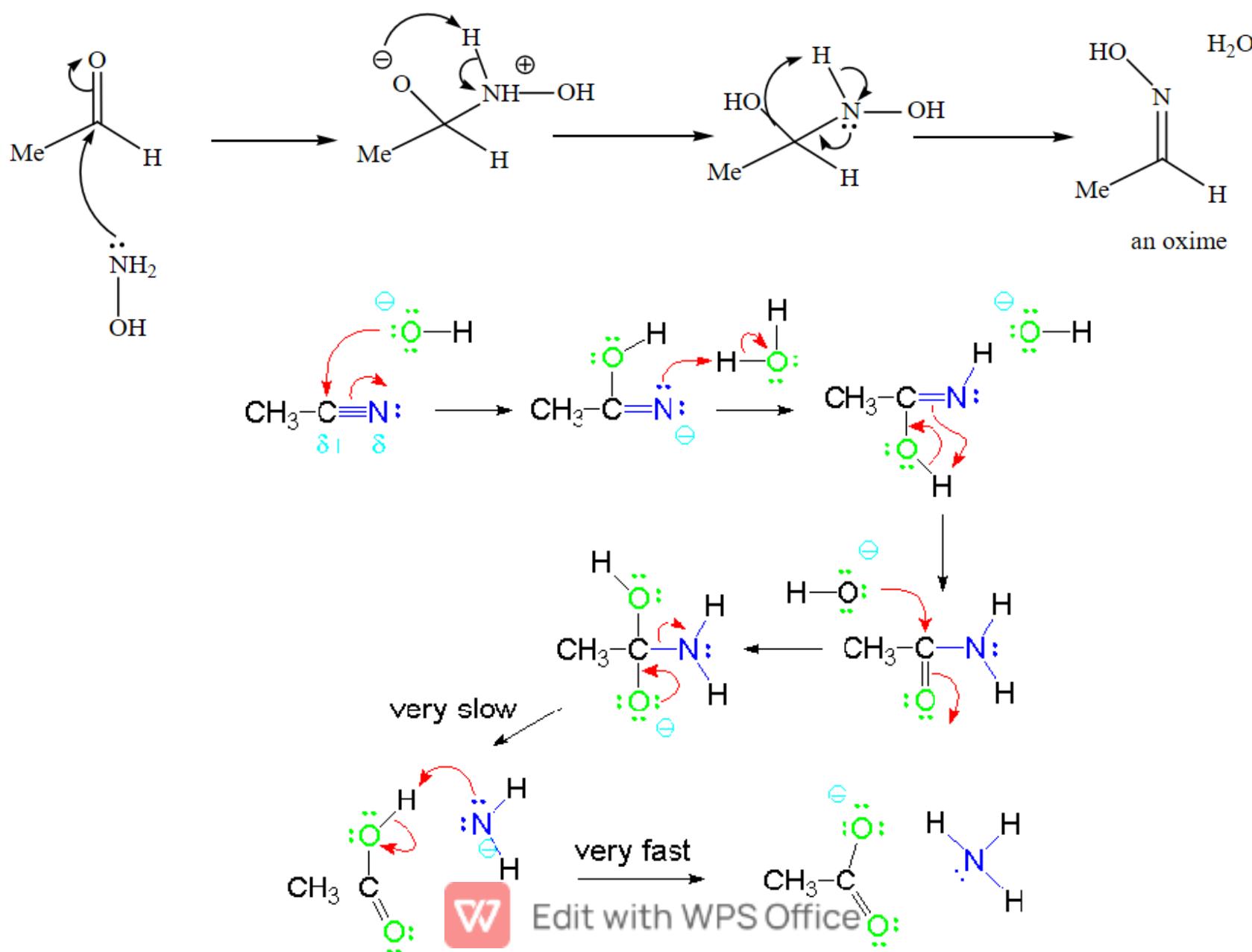
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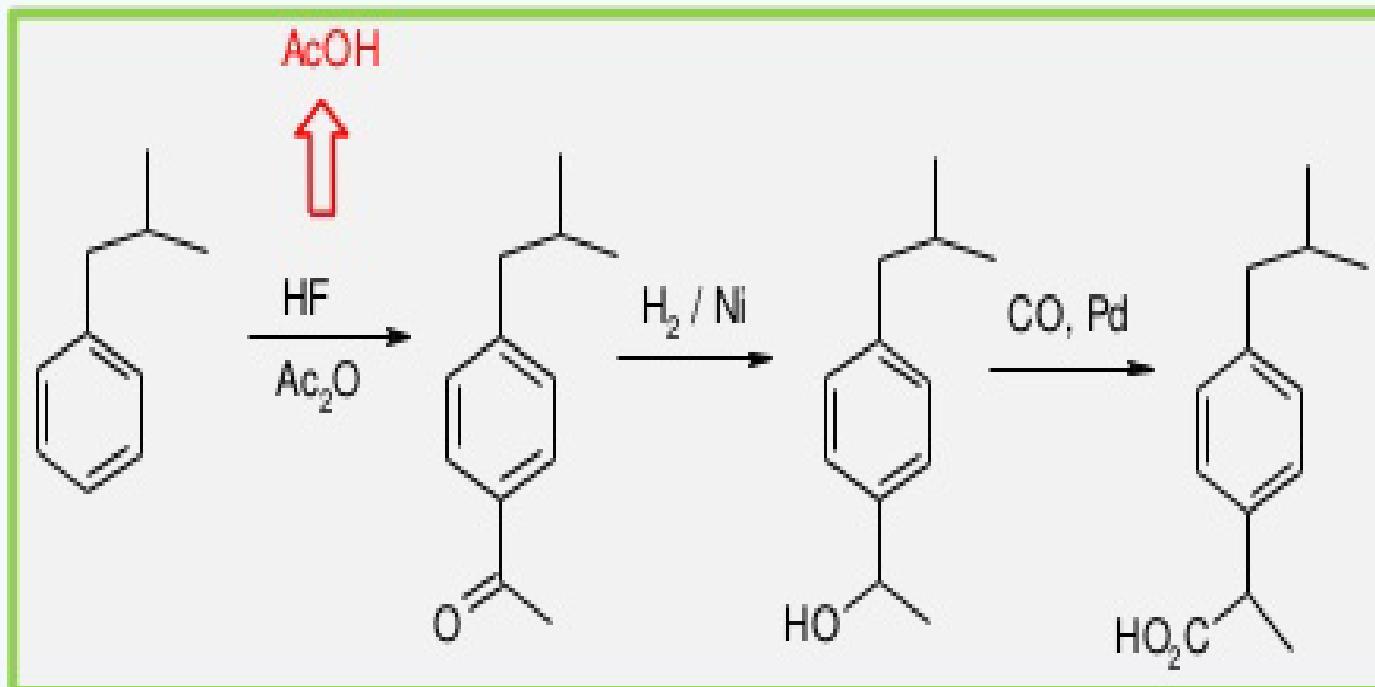


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cont...Green Synthesis Of Ibuprofen

The **BHC Company** developed a new greener synthesis of Ibuprofen that consists only of 3 steps. It results in small amount of unwanted products and has very good atom economy(77%).



Property of Amit Amra. To be used only as a reference and by consent.



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9. Catalysis

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

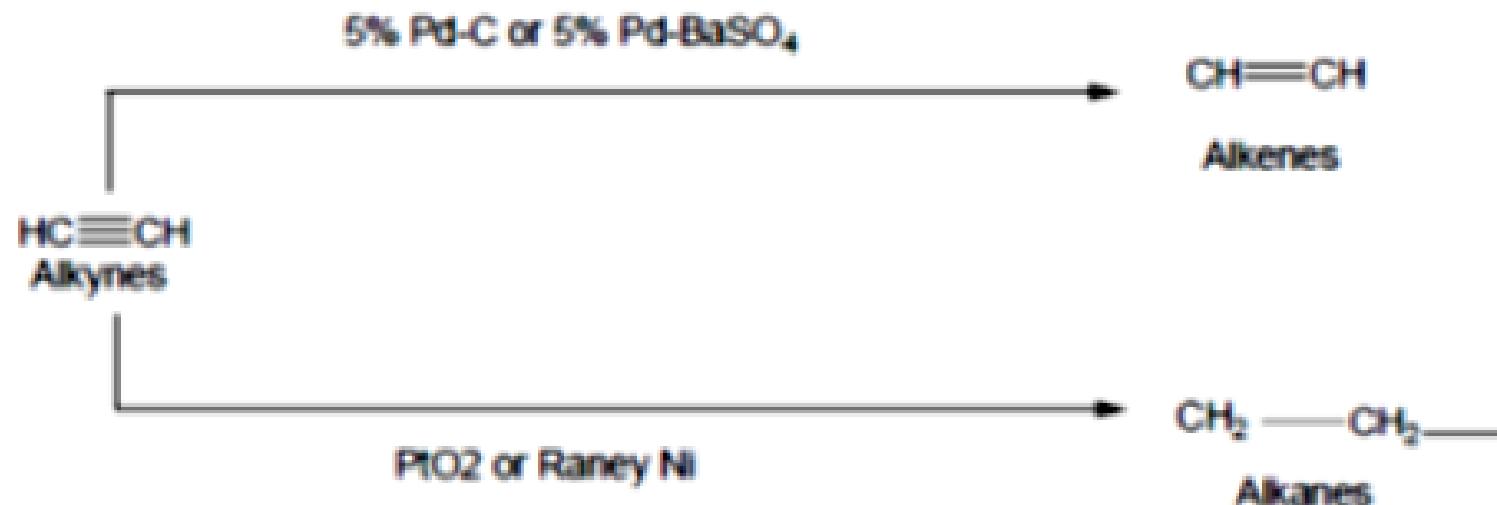
Catalyst facilitates transformation without being consumed or without being incorporated into the final product.

Catalysts are selective in their action in that the degree of reaction that takes place is controlled, e.g. mono addition v/s multiple addition.



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Example is that reduction of triple bond to a double bond or single bond.



In addition to the benefits of yield and atom economy, the catalysts are helpful in reducing consumption of energy.

Catalysts can be recycled and reused.

Catalytic reactions are faster and hence require less energy. They are preferable to stoichiometric reagents, which are used in excess and work only once.

In recent years many processes have been developed which use non-toxic recoverable catalysts and also biocatalysts.



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Heterogeneous vs Homogenous

- * Distinct solid phase
 - * Readily separated
 - * **Readily regenerated & recycled**
 - * Rates not as fast
 - * Diffusion limited
 - * Sensitive to poisons
 - * Lower selectivity
 - * **Long service life**
 - * High energy process
 - * Poor mechanistic understanding
- Green catalyst**
- * Same phase as rxn medium
 - * Difficult to separate
 - * Expensive and/or difficult to separate
 - * **Very high rates**
 - * Not diffusion controlled
 - * **Robust to poisons**
 - * **High selectivity**
 - * Short service life
 - * **Mild conditions**
 - * Mechanisms well understood



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Bio-catalysis

- * Enzymes or whole-cell micro-organisms
- * Benefits
 - * Fast rxns due to correct orientations
 - * Orientation of site gives high stereospecificity
 - * Substrate specificity
 - * Water soluble
 - * Naturally occurring
 - * Moderate conditions
 - * Possibility for tandem rxns (one-pot)



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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.

- * Sulfonated detergents
 - * Alkylbenzene sulfonates – 1950's & 60's
 - * Foam in sewage plants, rivers and streams
 - * Persistence was due to long alkyl chain
 - * **Introduction of alkene group into the chain increased degradation**
- * Chlorofluorocarbons (CFCs)
 - * Do not break down, persist in atmosphere and contribute to destruction of ozone layer
- * DDT
 - * Bioaccumulate and cause thinning of egg shells
- * DDT when used as pesticide, its residues remains in soil for many years causing pollution. **The alternative to this is biological insecticides**



Degradation of Polymers: Polylactic Acid

- ◆ Manufactured from renewable resources
 - Corn or wheat; agricultural waste in future
- ◆ Uses 20-50% fewer fossil fuels than conventional plastics
- ◆ PLA products can be recycled or composted



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Poly lactic acid (PLA) for plastics production

Examples of Green Catalys



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11. Real Time Analysis

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

- * What do you need to know, how do you get this information and how long does it take to get it?

Knowing when your product is “done” can save a lot of waste, time and energy!



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Methods and technologies should be developed so that the prevention or minimization of generation of hazardous waste is achieved.

It is necessary to have accurate and reliable reasons, monitors and other analytical methodologies to assess the hazardous that may be present in the process stream.

These can prevent any accidents which may occur in chemical plants.

Example- Preparation of ethylene glycol, in which if reaction conditions are not monitored perfectly, toxic substances are produced at higher temperature.

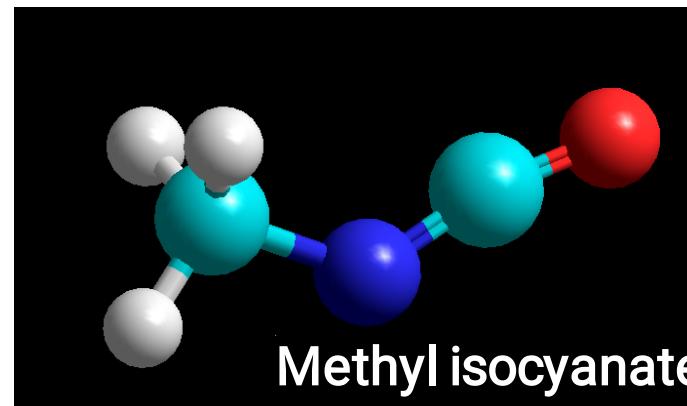


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12. Inherently Safe Chemistry

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.

Tragedy in Bhopal, India – 1984: worst industrial accident in history.



Chemists try to avoid things that explode, light on fire, are air-sensitive, etc.

In the “real world” when these things happen, lives are lost.

- * December 3, 1984 – 40 tons of poison gas leaked from a Union Carbide factory, killing thousands instantly and injuring many more (many of who died later of exposure). Up to 20,000 people have died as a result of exposure (3-8,000 instantly). More than 120,000 still suffer from ailments caused by exposure

What happened?

- * Methyl isocyanate – used to make pesticides was being stored in large quantities on-site at the plant
- * Methyl isocyanate is highly reactive, exothermic molecule
- * Most safety systems either failed or were inoperative
- * Water was released into the tank holding the methyl isocyanate
- * The reaction occurred and the methyl isocyanate rapidly boiled producing large quantities of toxic gas.



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Green Solvents

- * Solvents are substances that are liquid during application and will dissolve other substances, which can be recovered unchanged on removal of solvents.
- * Selection of solvent should be based not only on any hazards that it may possess but also on existing environmental problems that its use may cause.
- * Solvents define a major part of the environmental performance of processes in chemical industry and also impact on cost, safety and health issues.
- * The idea of 'green' solvent expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production.



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CONTI.....

- An ideal green solvent must possess following criteria:
 - i. Must have human safety.
 - ii. Reduced hazard.
 - iii. Easily degradable.
 - iv. Provide high product yield.
- Criteria for solvent selection:
 - i. Must have less human & environmental absorption.
 - ii. Its environmental toxicity should be understood.
 - iii. Environmental fate should be understood.



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Carbon Dioxide

- Similar advantages to water
 - Natural, cheap, plentiful (too much of it!)
 - Available in >99.9% pure form, £70/\$110 per 25kg.
 - By-product of brewing, ammonia synthesis, combustion
- Already being adopted in a variety of commercial processes (see later)
- Non-toxic and properties well understood
 - asphyxiant at high concentrations
- Easily removed and recycled, and can be disposed of with no net increase in global CO₂
 - Simple product isolation by evaporation, to 100% dryness.
- No solvent effluent
- Potential for product processing (extraction, particle formation, chromatography etc.)



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SUPERCritical FLUIDS

Above its critical values, a compound's liquid-vapor phase boundary no longer exists and its fluid properties can be tuned by adjusting the pressure or temperature.

Although supercritical fluid has liquid-like density, it exhibits gas-like diffusivity, surface tension and viscosity. Its gas-like viscosity results in high mass transfer. Its low surface tension and viscosity lead to greater penetration into porous solids. Because of its liquid-like density, a supercritical fluid's solvent strength is comparable to that of a liquid.

The critical temperatures and pressures of materials vary quite significantly. Generally, substances that are very polar at room temperature will have high critical temperatures since a large amount of energy is needed to overcome the polar attractive energy.



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At critical conditions, the molecular attraction in a supercritical fluid is counterbalanced by the kinetic energy. In this region, the fluid density and density-dependent properties are very sensitive to pressure and temperature changes.

The solvent power of a supercritical fluid is approximately proportional to its density. Thus, solvent power can be modified by varying the temperature and pressure. Because their properties are a strong function of temperature and pressure, supercritical fluids are considered tunable solvents.

In contrast, conventional liquid solvents require relatively large pressure changes to affect the density.



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Many reactions, extractions, separations and other operations in the chemical process industries (CPI) involve the use of organic solvents. In addition to handling and disposal issues, organic solvents can pose a number of environmental concerns, such as atmospheric and land toxicity. In many cases, conventional organic solvents are regulated as volatile organic compounds (VOCs). In addition, certain organic solvents are under restriction due to their ozone-layer-depletion potential.

Supercritical carbon dioxide is an attractive alternative in place of traditional organic solvents. CO₂ is not considered a VOC. Although CO₂ is a greenhouse gas, if it is withdrawn from the environment, used in a process, and then returned to the environment, it does not contribute to the greenhouse effect. There have been an increasing number of commercialized and potential applications for supercritical fluids.



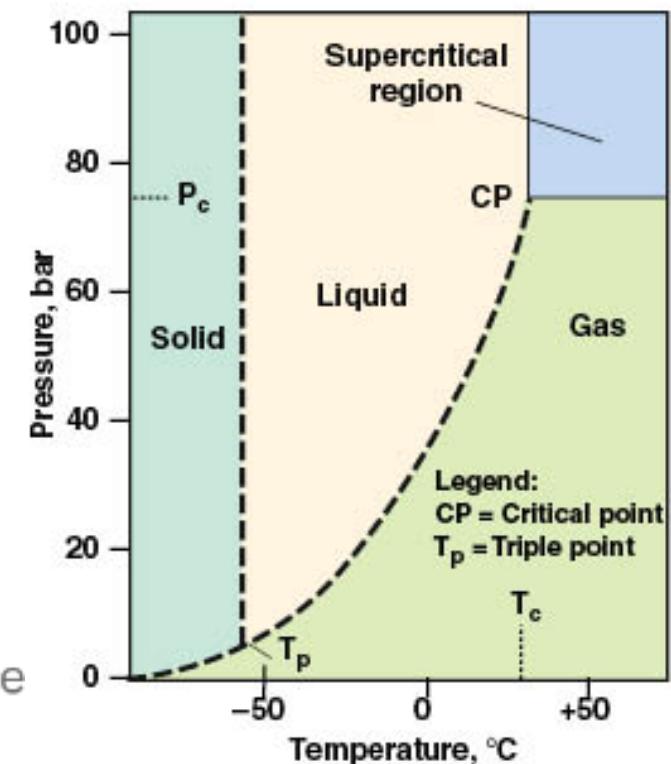
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SUPERCRITICAL CO₂ PROPERTIES

Unlike many organic solvents, supercritical CO₂ is non-flammable. It is inert, non-toxic, has a relatively low cost and has moderate critical constants. Its solvation strength can be fine-tuned by adjusting the density of the fluid. CO₂ leaves a lower amount of residue in products compared to conventional solvents, and it is available in relatively pure form and in large quantities.

CO₂'s critical temperature (T_c ; 32.1°C) is near ambient, making it an attractive solvent for temperature-sensitive materials. CO₂'s critical pressure is 73.8 bar (P_c ; 1,070 psi), as shown in its phase diagram.

The phase diagram for carbon dioxide shows its supercritical region



EXTRACTIONS USING CO₂

Currently, the widest application of supercritical CO₂ is in extraction. Total CO₂ consumption in supercritical extraction processes is estimated to have been approximately 15,000 to 25,000 ton/yr in 1994 and between 30,000 and 35,000 tons in 2002. Worldwide, over 100 facilities are estimated to use dense CO₂ for extraction and purification. Large-scale commercial plants using supercritical CO₂ extraction are found in the food industries (Table 2).

Table 2. Commercial-Scale Supercritical- CO₂ Extraction Plants and Processes

Process	Location	Manufacturer
Coffee decaffeination	Houston, Tex., U.S.	Maximus Coffee Group LP (formerly General Foods)
	Bremen, Germany	Kaffe HAG AG
	Bremen, Germany	Hermsen
	Poszillo, Italy	SKW-Trostberg AG
Tea decaffeination	Munchmuenster, Germany	SKW-Trostberg AG
Fatty acids from spent barley	Dusseldorf, Germany	Marbery, GmbH
Vitamin E oil, phytosterol, fatty acid methyl ester, ginger oil	Wuhan, Hubei, China	Wuhan Kaidi Fine Chemical Industrial Co.
Nicotine extraction	Hopewell, Va., U.S.	Philip Morris
Natural insecticide/pesticide (Pyrethrum extract)	High Wycombe, U.K.	Agropharm



Conventional processes for extracting various components from food products have limitations regarding the solvent toxicity, flammability and wastefulness. This area is where early commercial applications of supercritical CO₂ were focused. The relatively low critical temperature and low reactivity of CO₂ allow extraction without altering or damaging the product. Decaffeination of coffee was one of the first processes commercialized using supercritical CO₂.

The extraction process. Extraction of food and natural products with supercritical CO₂ consists of two steps: first, the extraction of supercritical CO₂ soluble components from the feed; and, second, the separation of the components from supercritical CO₂. The separation of supercritical CO₂ from the extract can be done by either modifying the thermodynamic conditions or by using an external agent. By modifying the thermodynamic conditions via changing the pressure or temperature, the solvent power of CO₂ is changed. If an external agent is used, separation is carried out by adsorption or absorption. If separation occurs with an external agent, no significant pressure change occurs. Therefore, the operating cost that is associated with pressure requirement is lower.



Recent extraction applications. There has been a great deal of interest in supercritical CO₂ extraction beyond caffeine extraction, particularly in the preparation of high value products, such as flavors and fragrances, food supplements and nutraceuticals.

Specialty oils, for example, are high in value and typically low in volume. They have high concentrations of bioactive lipid components that are valued because of various possible health benefits. Herbal extracts from a wide range of botanical raw materials are used as ingredients to the food-and-flavor, nutraceuticals, pharmaceuticals and the cosmetics industries. Supercritical CO₂ extraction can also be used to purify materials that are used for the production of medical devices.



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Chemical reactions. Supercritical CO₂ has been tested in a variety of industrially important reactions, such as alkylations, hydroformylations, and hydrogenation, as an alternative reaction medium.

The incentives to use supercritical CO₂ as reaction medium can include (a) replacement of the conventional organic solvent with a “green” solvent, (b) improved chemistry such as reactivity and selectivity, (c) new chemistry, and (d) improved separation and recovery of products and catalysts. Relatively high rates of molecular diffusion and heat transfer are possible with a homogenous, supercritical-CO₂ reaction-medium.

Limitations to the use of supercritical CO₂ as a reaction medium include (a) poor solubility of polar and high-molecular-weight species, (b) no observed improvement in reaction chemistry in some cases, and (c) higher capital investment cost due to higher operating pressures. For reactions not limited by reactant-gas concentrations or other mass-transfer limitations, there is no improvement in reactivity observed when using a homogeneous, supercritical CO₂ medium.



Polymer production and processing. Applications of supercritical CO₂ in polymers include polymerization, polymer composite production, polymer blending, particle production, and microcellular foaming. Several applications, particularly those involving low pressures, have been successfully commercialized.

One example of this application area is a process to produce **f luoropolymers** using supercritical CO₂ as the reaction medium that was developed by scientists at the University of North Carolina (Chapel Hill). DuPont had an exclusive license for this process until 2015. A \$40-million pilot plant was built in 2000 to produce f luoropolymers using this process technology. The pilot plant is capable of producing 1,100 metric tons per year (m.t./yr) of f luoropolymers. Several grades of melt-processable f luoropolymers produced from this process became commercially available in 2002.

Semiconductor processing. Currently, chip manufacturing involves many wet-chemical processes that use hydroxyl amines, mineral acids, elemental gases, organic solvents and large amounts of high purity water during chip fabrication. One potential application is the use of supercritical CO₂ in wafer processing. The low viscosity and surface tension of supercritical CO₂ allow for efficient cleaning of small feature sizes, which is of great importance with the continued miniaturization of integrated circuits. However, the main obstacle to the use of supercritical CO₂ in semiconductor cleaning is the high cost.

Powder production. One promising application for supercritical CO₂ is the production of micro- and nano-scale particles. The pharmaceutical industry currently uses supercritical CO₂ mainly to control the powder particle size of products during synthesis.

The use of supercritical CO₂ for micronization of pharmaceutical compounds has several potential advantages over conventional techniques such as spray drying, jet milling and grinding.

These advantages include minimum product contamination, reduced waste streams, suitability for the processing of thermally, shock or chemically sensitive compounds and the possibility of producing particles with narrow size distribution in a single-step operation.



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DMC

Carbonic esters, such as DMC- dimethyl carbonate ($\text{CH}_3\text{OCOOCH}_3$) are considered a new class of “green” solvents in many organic reaction processes.

They can replace methychlorides and dimethyl sulphate esters which are toxic and hazardous.

DMC can be used in methylation reactions of phenols, anilines and carboxylic acids.

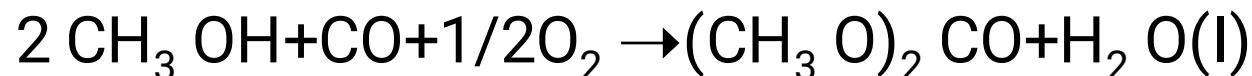
The reactivity of DMC is tunable: at $T \leq 90^\circ\text{C}$, methoxycarbonylations take place, while at higher reaction temperatures, methylation reactions are observed with a variety of nucleophiles. Besides, DMC-mediated methylations are catalytic reactions which use safe solids (alkaline carbonates) avoiding the formation of undesirable inorganic salts as byproducts. The high selectivity in methylation reactions is due to the ambident electrophilic character of DMC which reacts on its hard centre (the carbonyl group) with harder nucleophiles and on its soft one (the methyl group) with softer nucleophiles, according to the Hard-Soft Acid and Base (HSAB) theory.



DMC is produced by oxidative carbonylation of methanol with oxygen through a process developed by Enichem (Italy).

The most relevant features of this process are:

- low-cost and widely available raw materials with low toxicity;
- high production rates;
- non-toxic and easy disposable by-products (carbon dioxide and water)
- high quality product.

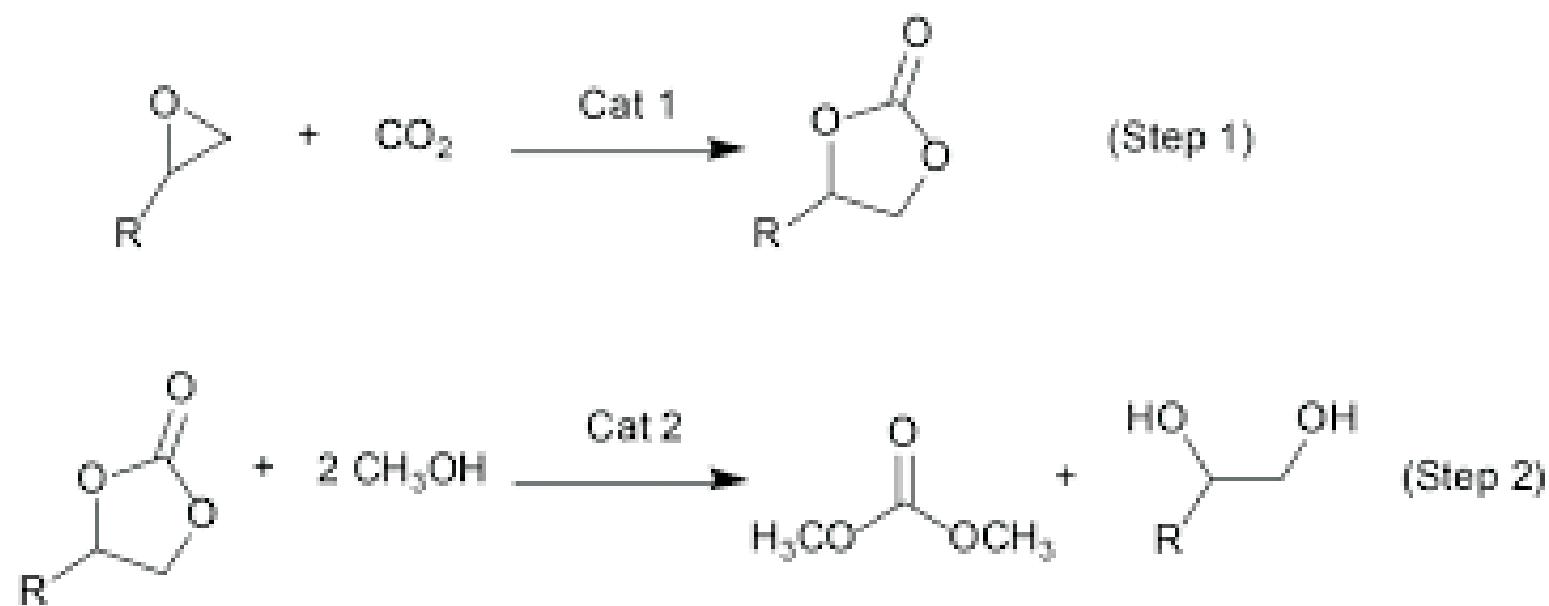


The new technology does not produce any by-products that are difficult to dispose of. The DMC obtained has also low toxicity and ecotoxicity (biodegradability >90% at 28 days OECD 301C; acute toxicity for fish; no effect at 1000 mg/l OECD 203).



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Another industrial procedure developed and recently industrialized in China is the cleavage of cyclic carbonates. Importantly, this synthesis doesn't use any chlorine.



PHYSICAL PROPERTIES OF SOLVENT'S:-

- The physical properties of solvents greatly influence the choice of solvent for a particular application.
- The solvent should be liquid under the temperature and pressure conditions at which it is employed.
- thermodynamic properties:- density & vapor pressure, temperature & pressure coefficients, as well as the heat capacity surface tension.
- transport properties:- such as viscosity, diffusion coefficient, & thermal conductivity, also need to be considered



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- Electrical, optical, and magnetic properties, such as the dipole moment, dielectric constant, refractive index, magnetic susceptibility, and electrical conductance are relevant, too.
- Molecular characteristics, such as the size, surface area, and volume, as well as orientational relaxational times, have appreciable bearing on the applicability of a solvent or on the interpretation of solvent effects.



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CHEMICAL PROPERTIES OF SOLVENT'S:-

- The chemical properties of solvents have obviously a strong bearing on their applicability for various purposes.
- Structuredness of Solvents:-The volatility, viscosity, diffusion coefficient and relaxation rates of solvents are described quantitatively by their structuredness.
- Stiffness:-expressed by the cohesive energy density
- Openness:-the difference between its molar and intrinsic volumes
- Ordering:- This is the deficit of entropy of the liquid solvent relative to the solvent vapor or the dipole orientation correlation.



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- Polarity in Molecules:-*Dispersion Forces-*
Molecules that have no permanent dipole still have their electrons in movement.
- Polarization and Polarizability:-If the molecules have a dipole but there is no applied electric field, the dipoles are randomly orientated.
- Dipole–dipole interactions between rotating dipolar molecules are small.
Only for molecules with large dipoles, and where hydrogen bonding is absent, such as DMSO (dimethyl sulfoxide) and acetonitrile, do dipole–dipole attractions contribute significantly to molecular association.



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APPLICATION OF GREEN SOLVENTS:-

- New syntheses of Ibuprofen and Zoloft.
- Integrated circuit production.
- Removing Arsenic and Chromate from pressure treated wood.
- Many new pesticides.
- New oxidants for bleaching paper and disinfecting water.
- Getting the lead out of automobile paints.
- Recyclable carpeting.
- Replacing VOCs and chlorinated solvents.
- Biodegradable polymers from renewable resources

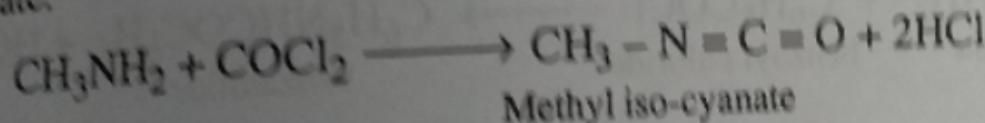


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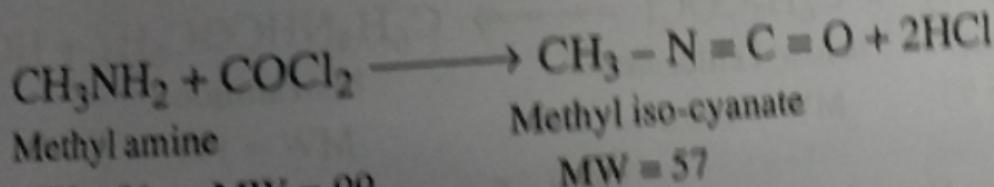
Numericals

Ques 8

Calculate percentage atom economy for the following reaction with respect to methyl iso-cyanate.
(M.U. May 2015)



Soln:



Methyl amine

MW = 31 MW = 99

MW = 57

$$\% \text{ Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactants}} \times 100$$

$$= \frac{57}{31+99} \times 100$$

$$= \frac{57}{130} \times 100 = 43.85 \%$$

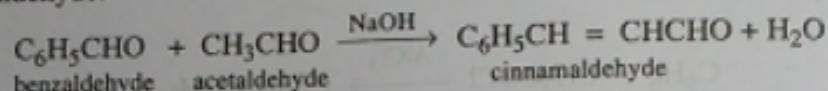
Ans. : % Atom Economy = 43.85 %



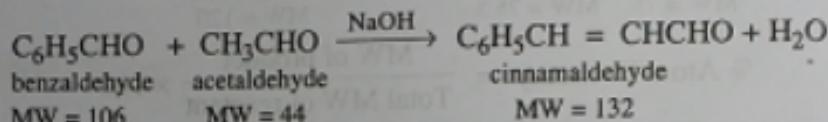
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Problem 9

Calculate percentage atom economy for the following reaction with respect to cinnamaldehyde. (M.U. Dec. 2015)



Solution :



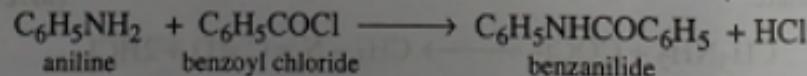
$$\% \text{ Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactants}} \times 100$$

$$\begin{aligned}\% \text{ Atom Economy} &= \frac{132}{106+44} \times 100 \\ &= \frac{132}{150} \times 100 = 88\end{aligned}$$

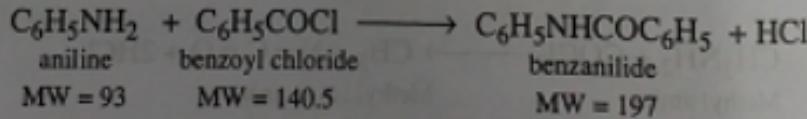
Ans. : % Atom Economy = 88 %

Problem 10

Calculate percentage atom economy for the following reaction with respect to benzalanilide. (M.U. May 2016)



Solution :



$$\% \text{ Atom Economy} = \frac{\text{MW of product}}{\text{Total MW of reactants}} \times 100$$

$$\% \text{ Atom Economy} = \frac{197}{93+140.5} \times 100$$

$$= \frac{197}{235.5} \times 100 = 83.65 \%$$

Ans. : % Atom Economy = 83.65 %

Balancing chemical reaction/ equation

- * <https://www.khanacademy.org/science/chemistry/chemical-reactions-stoichiometry/balancing-chemical-equations/v/balancing-chemical-equations-introduction>
- * <https://www.youtube.com/watch?v=yZi9URUAwIc>



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