M. Sc. Chemistry

Semester II (CBCS)

C 204 Analytical chemistry

Green chemistry

Prepared by;

Rahul Talaviya

Q-What is green chemistry/Define green chemistry?

Green chemistry is the sustainable practice of chemical science and manufacturing within a **framework** of industrial ecology in a manner that is **sustainable**, safe, and non-polluting, consuming minimum amounts of energy and material resources while producing virtually no wastes.

or

The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of substances hazardous to human health and the environment.

"Sustainable chemistry" is the design, manufacture and use of efficient, effective, safe and more environmentally benign chemical products and process

12 Principles of Green Chemistry

1. Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

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 Syntheses

Wherever practicable, synthetic methods 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 affect their desired function while minimizing their toxicity.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. Design for Energy Efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstock's

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

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 break down into innocuous degradation products and do not persist in the environment.

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

Substances and the form of a substance used in a chemical process shouldbe chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

One mark question answer

Sr No	Question	Answer
1	How many principles in green chemistry	12 principle
2	Bunch of 12 principle related to prevention of hazardous chemical used and production known as	Green chemistry
3	According to Green chemistry, which type energy used in the synthesis of organic compounds	Green energy such as solar, radiation, etc

Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

- This rule is generally associated with waste generated during synthesis of desire product.
- This is an important roundtable focus because sometimes large amount of waste (coproduced) was generated during drug manufacturing - more than 100 kilos per kilo of API in many cases.
- This rule indicate that the use such path or starting material that formed less hazardous material or waste.
    - For example: love canal in Niagara Falls, NY a chemical and plastics company had used an old canal (letter known as love canal) for chemical dump from 1930s to 1950s.
    - The land was then used for a new school and housing track. The chemicals leaked through a clay cap that sealed the dump.
    - It was contaminated with at least 82 chemicals (benzene, chlorinated hydrocarbons, dioxin etc).
    - Health effects of the people living there included: high birth defect incidence and siezure-inducing nervous disease among the children.

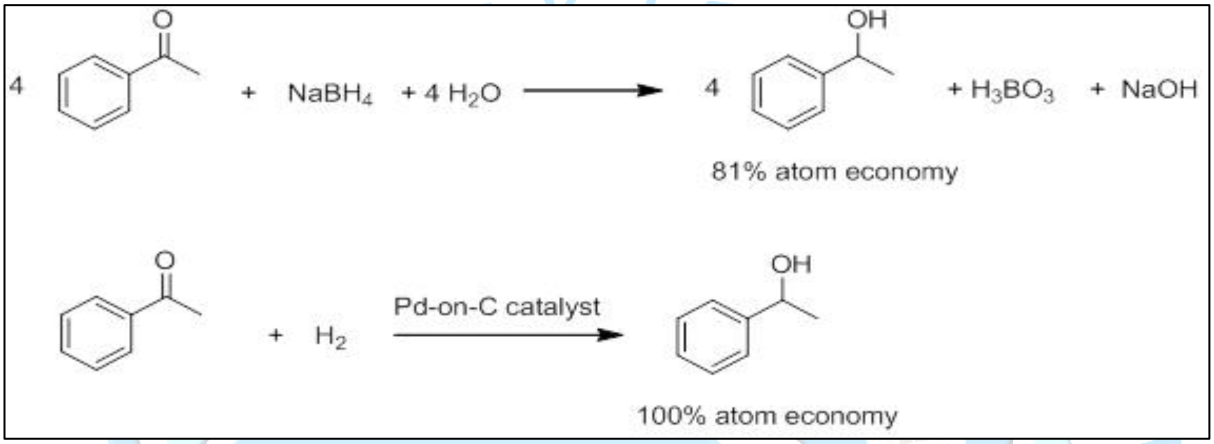
Atom economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

- The second principle of green chemistry can be simply stated as the "atom economy" of a reaction.
- It is an example of a green chemistry metric, which helps us understand the efficiency of a reaction.
- This rule indicates that the how many atoms are incorporate into final product out of taken for reaction?
- The higher the atom economy the better, since any atoms that are not incorporated into the final product are considered wasted.

$$percentage\ yield = \frac{practically\ obtined\ yield}{theoriticaly\ yield} * 100$$

For example



- For reduction of acetophenone two path are suggests.
- In the first path, for reduction sodium borohydride used which is reduce acetophenone into secondary alcohol.
- During this reaction as by product boric acid and sodium hydroxide is obtained.
- It means that in this reaction all atoms of starting materials are not incorporate into desire product. Hence, atom economy is decreases.
- However, in second path of reduction all atoms of starting materials are incorporate into final product i.e., 100 % atom economy.

One mark question answer

Sr No	Question	Answer
1	First rule of green chemistry which associated with waste generated during synthesis of desire product	Prevention of waste
2	In green chemistry, starting material completely convert into product which suggest atom economy	100 %

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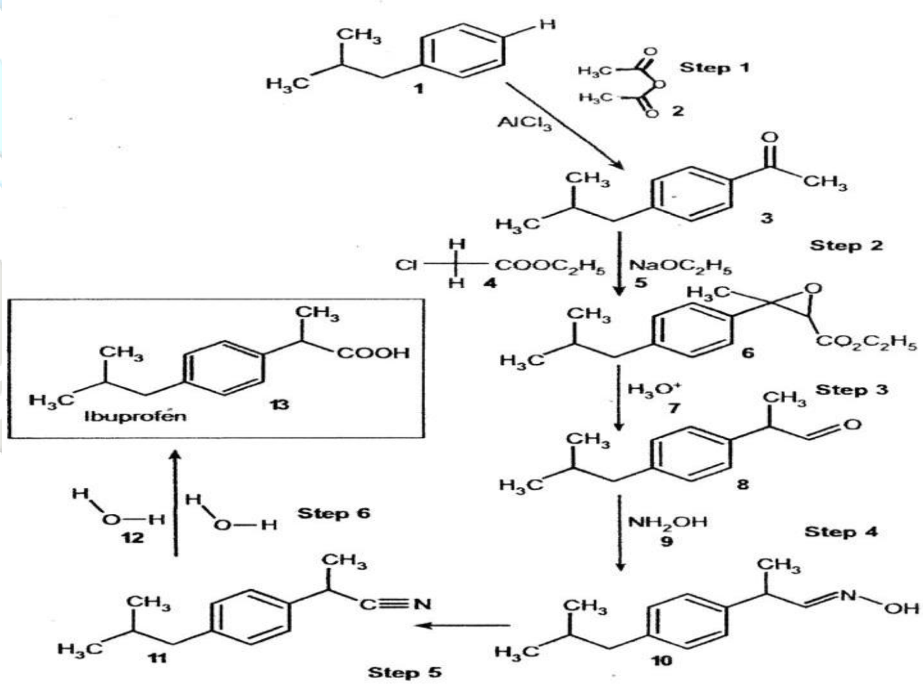
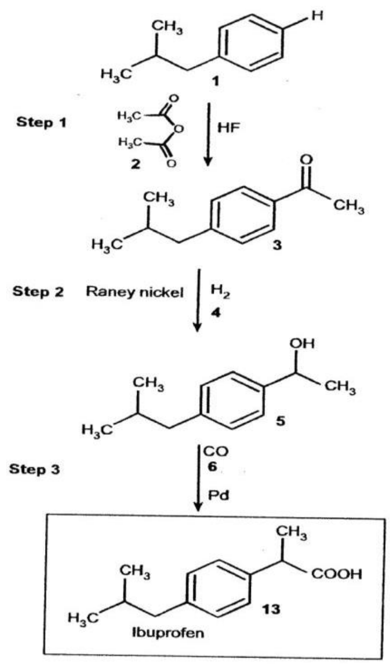
Q- Explain atom economy with example of ibuprofen

- Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- In the old synthetic route, each step had a yield of 90% so that the final product came to be 40% yield compared to the starting chemical. This resulted in the increased production of by-products as waste.
- In 1990 a new synthetic route with only three steps and increased efficiency has been founded. The atoms of the starting chemicals are incorporated into the products of the reactions and waste is minimised. In both synthetic routes the starting chemical is 2-methylpropylbenzene, which is produced from the petrochemical industry.
- In the "greener' method of three steps the final yield is 77%, whereas the Raney nickel catalyst (Nickel) can be recycled and reused.
- In the old synthetic route, the AlCl3 used as a catalyst had to be thrown away as waste. The energy requirements of the second method were much lower than the first.

Old method for the synthesis of Ibuprofen



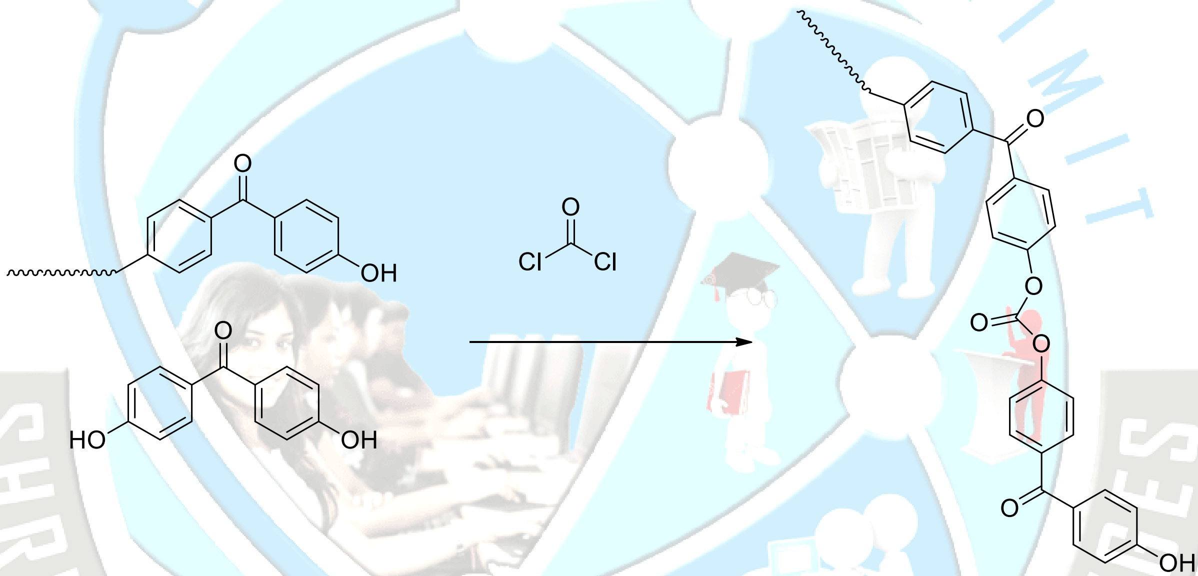
New method for the synthesis of Ibuprofen;



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 rest of the environment.

- These rules suggest that the synthesis of target molecule design in such a way that there is minimum or no use of hazardous starting materials.
- For example;
- In early, synthesis of polymer of polycarbonate was carried out by using **phosgene (COCl2)**.



- **Disadvantages**
  - **phosgene is highly toxic, corrosive**
  - **requires large amount of CH_2Cl_2**
  - **polycarbonate contaminated with Cl impurities**

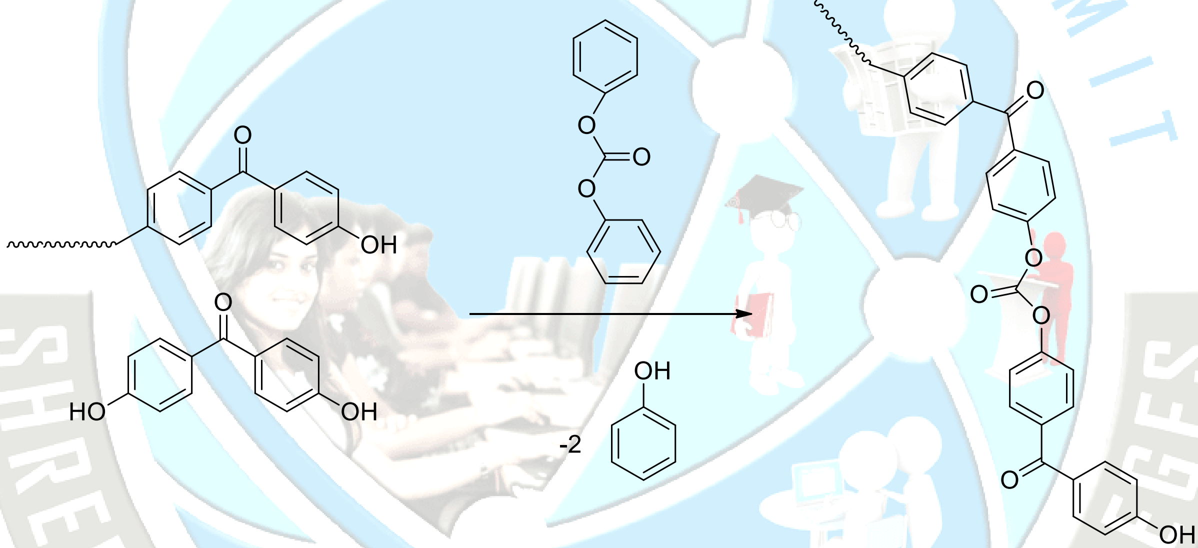
- Phosgene, which smells like moldy hay, is also an irritant but six times more deadly than chlorine gas.
- Phosgene was responsible for 85% of chemical-weapons used during World War I.
- Mustard gas, a potent blistering agent, was dubbed King of the Battle Gases.

Optional route for synthesis of this polymer

In another method for synthesis of polymer diphenylcarbonate was used. the reaction also carried out in solid state method.

Advantages

- **diphenylcarbonate synthesized without phosgene**
- **eliminates use of CH_2Cl_2**
- **higher-quality polycarbonates**



One mark question answer

Sr No	Question	Answer
1	Old method of synthesis of ibuprofen complete in how Many steps?	6 steps
2	In early, synthesis of polymer of polycarbonate was carried out in the presence of	phosgene (COCl2)
3	Now days, in place of phosgene which chemical used in the synthesis of polycarbonate polymer	diphenylcarbonate

Designing Safer Chemicals

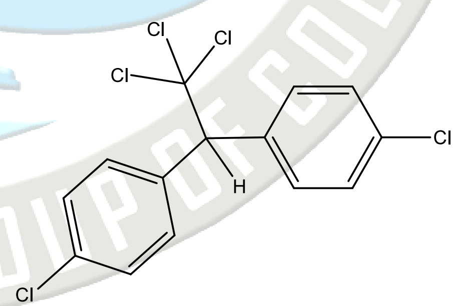
Chemical products should be designed to preserve efficacy of the function while reducing toxicity.

- This principle links closely to the previous one.
- Chemists must aim to produce chemical products that fulfill their role, be that medical, industrial, or otherwise, but which also have minimal toxicity to humans.
- The design of safer chemical targets requires knowledge of how chemicals act in our bodies and in the environment. In some cases, a degree of toxicity to animals or humans may be unavoidable, but alternatives should be sought.

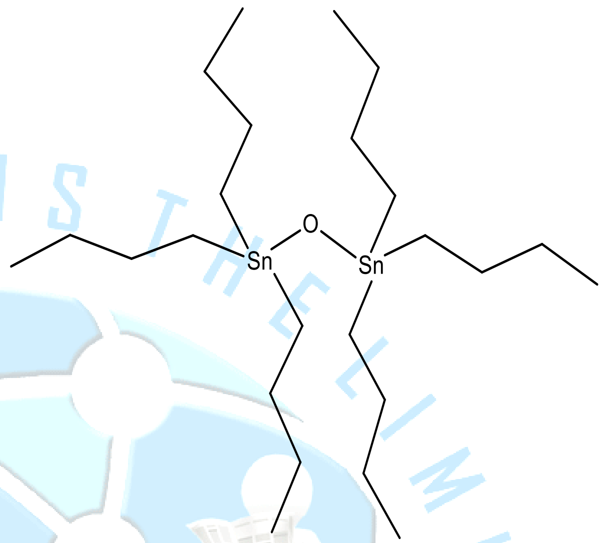
For example

Dichlorodiphenyltrichloroethane (DDT)

- commonly known as DDT,
- It is a colorless, tasteless, and almost odorless crystalline chemical compound, an organochlorine.
- Originally developed as an insecticide, it became infamous for its environmental impacts.
- DDT was first synthesized in 1874 by the Austrian chemist Othmar Zeidler.
- DDT was used in the second half of World War II to control malaria and typhus among civilians and troops.
- DDT and other pesticides had been shown to cause cancer and that their agricultural use was a threat to wildlife, particularly birds.
- A worldwide ban on agricultural use was formalized but its limited and still-controversial use in disease vector control continues, because of its effectiveness in reducing malarial infections, balanced by environmental and other health concerns.



- Organotin compounds have traditionally been used, particularly tributyltin oxide (TBTO). TBTO works by gradually leaching from the hull killing the fouling organisms in the surrounding area TBTO and other organotin antifoulants have long half-lives in the environment (half-life of TBTO in seawater is > 6 months). It is also bio-concentrate in marine organisms (the concentration of TBTO in marine organisms to be 104 times greater than in the surrounding water).



Safer Solvents and Auxiliaries

The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, non hazardous chemicals.

- Many chemical reactions require the use of solvents or other agents in order to facilitate the reaction. They can also have a number of hazards associated with them, such as flammability and volatility.
- Solvents might be unavoidable in most processes, but they should be chosen to reduce the energy needed for the reaction, should have minimal toxicity, and should be recycled if possible.

One mark question answer

Sr No	Question	Answer
1	Full form of DDT	Dichlorodiphenyltrichloroethane
2	Full form of TBTO	tributyltin oxide
3	half-life of TBTO in seawater is	> 6 months

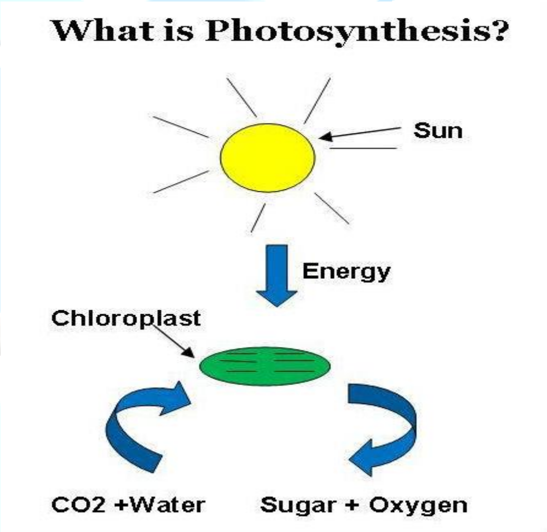
Design for Energy Efficiency

Energy-intensive processes are frowned upon in green chemistry. Where it is possible, it is better to minimize the energy used to create a chemical product, by carrying out reactions at room temperature and pressure. Considerations of reaction design also have to be made; removal of solvents, or processes to remove impurities, can increase the energy required, and by association increase the process's environmental impacts.

- We know that heating a reaction requires energy, but another energy-intensive aspect of lab work that occurs after completion of the reaction is the work-up.
- "Working up" the reaction means separating our desired product from the other components in the reaction mixture such as solvent and byproducts.
- To remove solvent conveniently we use a rotary evaporator, commonly referred to as a "rotovap," which involves the combined use of a heat source, vacuum pump, rotating motor, and chiller.
  The heat, vacuum, and rotation vaporize the solvent and the chiller condenses the solvent vapors into a flask for removal.

Use of Renewable Feedstock's

- The perspective of this principle is largely towards petrochemicals: chemical products derived from crude oil.
- These are used as starting materials in a range of chemical processes, but are non-renewable, and can be depleted.
- Processes can be made more sustainable by the use of renewable feedstocks, such as chemicals derived from biological sources.
- They use CO_2 as an example of a feedstock which plants convert into sugar via photosynthesis. We humans use this sugar as our own feedstock for many different delicious things, including cookies!
- Many common feedstocks are depleting, such as petroleum and natural gas. The petrochemical industry uses petroleum and natural gas as feedstocks to make intermediates, which are later converted to final products.



- An example of a renewable feedstock is *biomass*, which refers to any material derived from living organisms, usually plants. In contrast to depleting feedstocks like petroleum, we can much more easily grow new plants once we use them up, and maintain a continuous supply.

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Reduce Derivatives

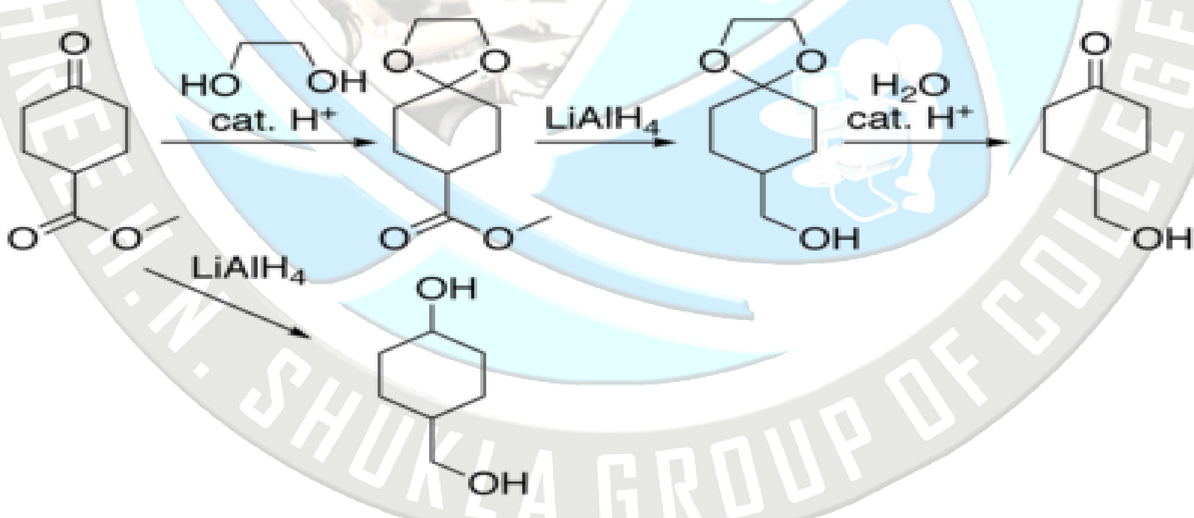
Protecting groups are often used in chemical synthesis, as they can prevent alteration of certain parts of a molecule's structure during a chemical reaction, whilst allowing transformations to be carried out on other parts of the structure.

Q-explain blocking and deblocking reagents used in reaction and its effect

Protecting groups are often used in chemical synthesis, as they can prevent alteration of certain parts of a molecule's structure during a chemical reaction, while allowing transformations to be carried out on other parts of the structure.

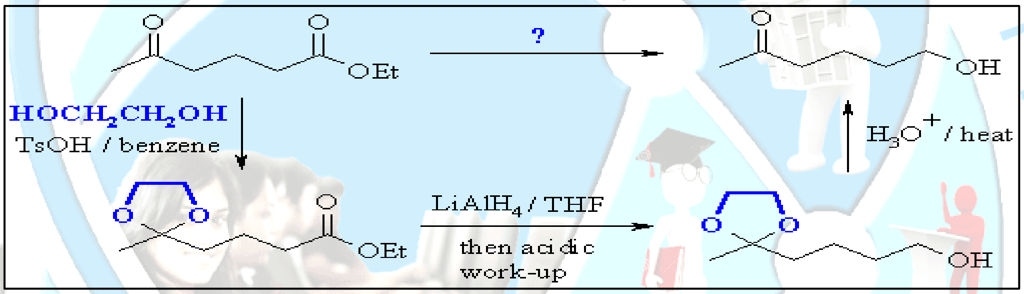
- However, these steps require extra reagents, and also increase the amount of waste a process produces.
- An alternative that has been explored in some processes is the use of enzymes.
- As enzymes are highly specific, they can be used to target particular parts of a molecule's structure without the need for the use of protecting groups or other derivatives.

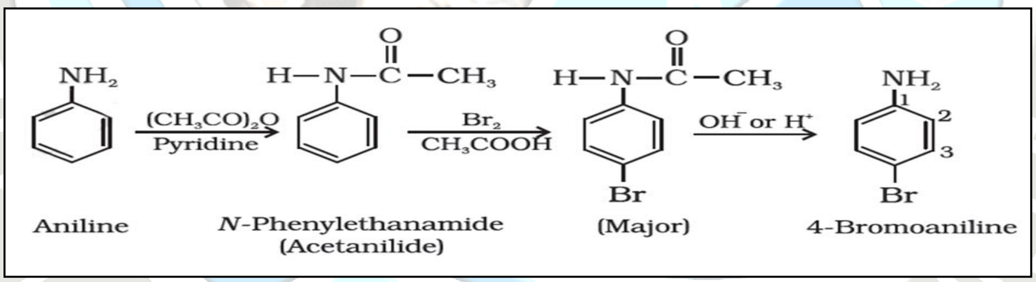
For example;



- In above reaction the specific reduction of carbonyl group was carried out by lithium aluminium hydride under alcoholic condition.

- But on direct reaction of starting material with lithium aluminium hydride, both carbonyl groups are reduced into alcoholic group.
- So in such type reaction, for the reduction of particular carbonyl group blocking-deblocking method is used. In this, method one of the carbonyl group was blocked by reaction of it with ethylene glycol. Then reduction of second carbonyl group was carried out by using lithium aluminium hydride. After reduction blocking reagent is removed by appropriate reaction.
- As a result of blocking-deblocking method, synthesis steps are increased and overall %yield decreases. Further during the process by product also formed.
- Another example;

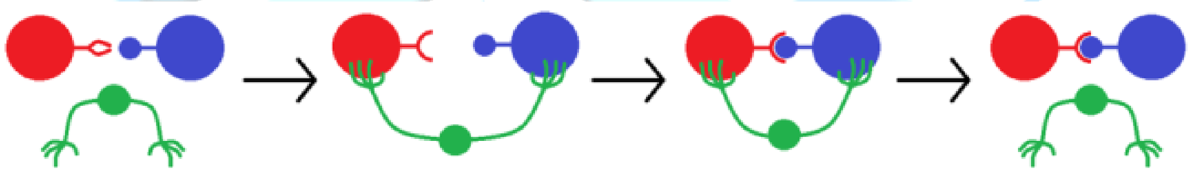


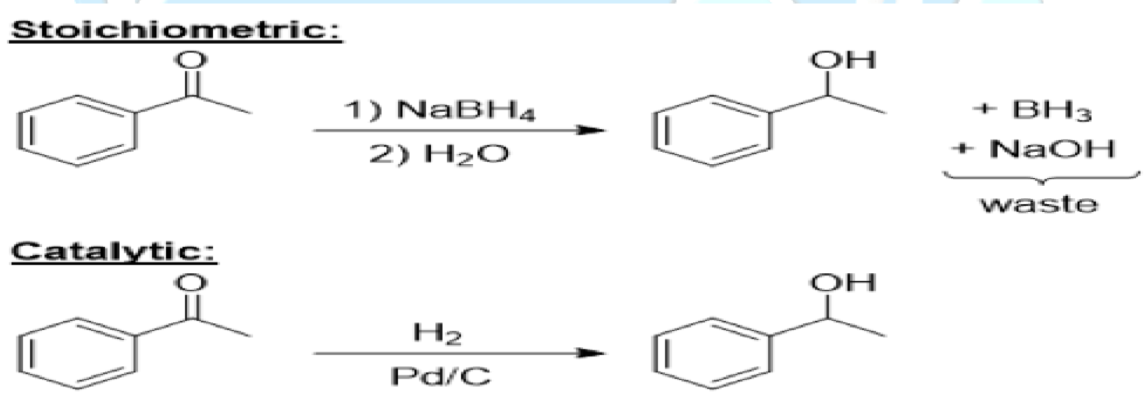


Catalysis

The use of catalysts can enable reactions with higher atom economies. Catalysts themselves aren't used up by chemical processes, and as such can be recycled many times over, and don't contribute to waste. They can allow for the utilization of reactions which would not proceed under normal conditions, but which also produce less waste

Catalyst' is defined simply as a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change.





- One common example of a catalytic reaction that is taught in introductory organic chemistry is the hydrogenation of ketones.
- The stoichiometric reaction involves the addition of sodium borohydride, followed by addition of water.
- In this reaction, borane (BH_3) and sodium hydroxide are (formally) generated as waste.
- By simply employing palladium on carbon as catalyst, the ketone can react directly with H2 to generate the same desired product without producing any waste.

Another example

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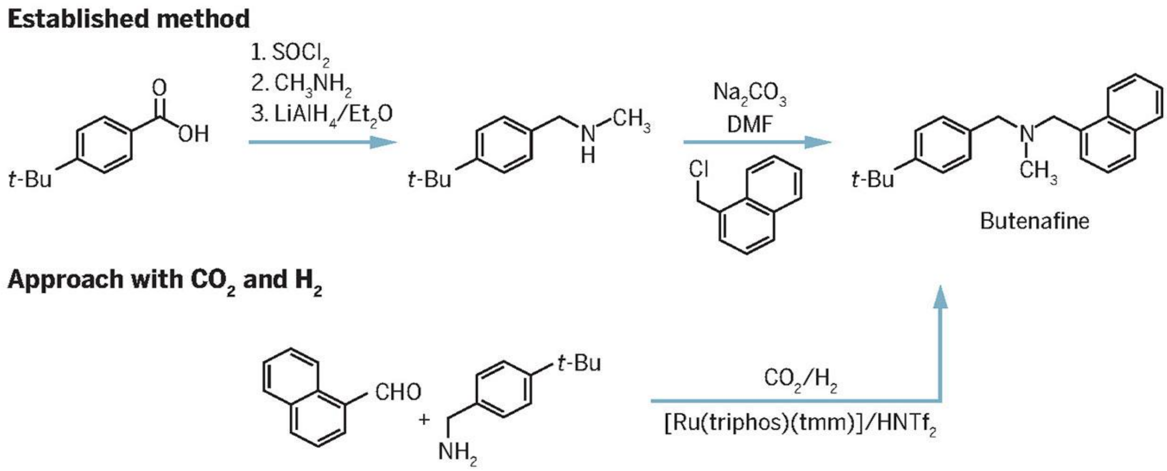

One mark question answer

Sr No	Question	Answer
1	The chemical which used in reaction to accelerate reaction rate but doesn't involve in product is known as	catalyst
2	The use of ________ can enable reactions with higher atom economies	catalyst
3	Sodium borohydride is used as ______________	Reducing agent
4	Acetophenone on catalytic reduction give ________product	Secondary alcohol

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 not harmful 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

➢ Once chemicals are done providing their main function, they might end up in a landfill or wastewater treatment plant where they can enter the waters, soil and air of our environment, or be taken up by animals or humans.

➢ The biggest challenge is making chemicals that are stable during usage, but don't persist in the environment – or in other words, chemicals that can be degraded.

➢ A common example that we hear about is biodegradation, especially with the well-known "biodegradable soaps."

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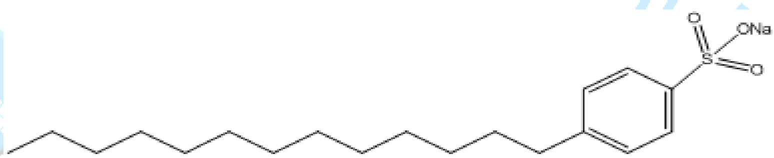
- Sodium dodecylbenzenesulfonate is a common detergent, and is often referred to as LAS, for linear alkylbenzene sulfonates.
- Looking at structure, you can see that it has a linear alkyl chain with a benzylsulfonate attached to it. It is useful as a detergent because it has a polar headgroup (sulfonate) and a non-polar alkyl group, making it a surfactant.



Alkyl benzene sulphonate
less bio degradable

- It degrades quickly in the environment under aerobic conditions, or when oxygen is present, because microbes are able to use to the linear alkyl chain as energy, via a process called β-oxidation, a process which breaks down the carbon chain.
- Once the long chain is degraded, the rest of the molecule can be degraded as well.

This molecule was also used as a detergent just like the linear version, but because of the location of the branches, microbes cannot perform β-oxidation since there are no good sites for that reaction to be initiated. Therefore, these branched detergents do not biodegrade.

- The main way these molecules are degraded is through microbes, when oxygen is present.
- This is because there are fewer microbes in water as compared to in soil. Interestingly, the branched version is 4 times less toxic than the linear version, but can cause more damage because of its persistence.
- This is one of the reasons that it is very important to consider persistence, or a molecule's resistance against degradation, and not only its toxicity

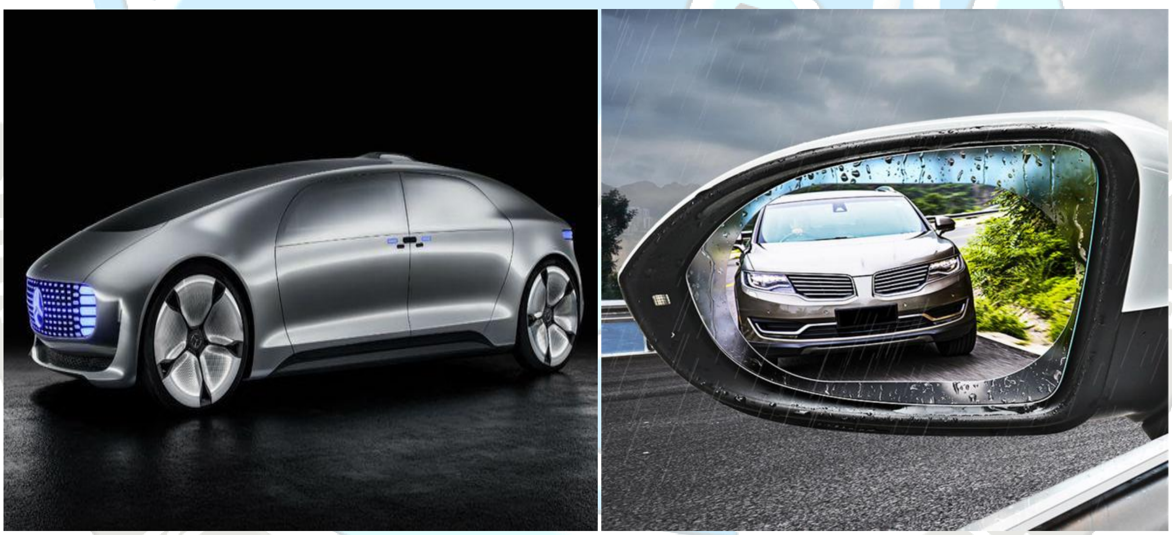
Real-time Analysis for Pollution Prevention

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

From example

- Knowing when your product is "done" can save a lot of waste, time and energy!
- Real time analysis for a chemist is the process of "checking the progress of chemical reactions as it happens."

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?



The design of analytical methodologies to monitor chemical reactions in real time and allow for adjustments. We can think of the windows and rearview mirrors as examples of such "analytical methodologies

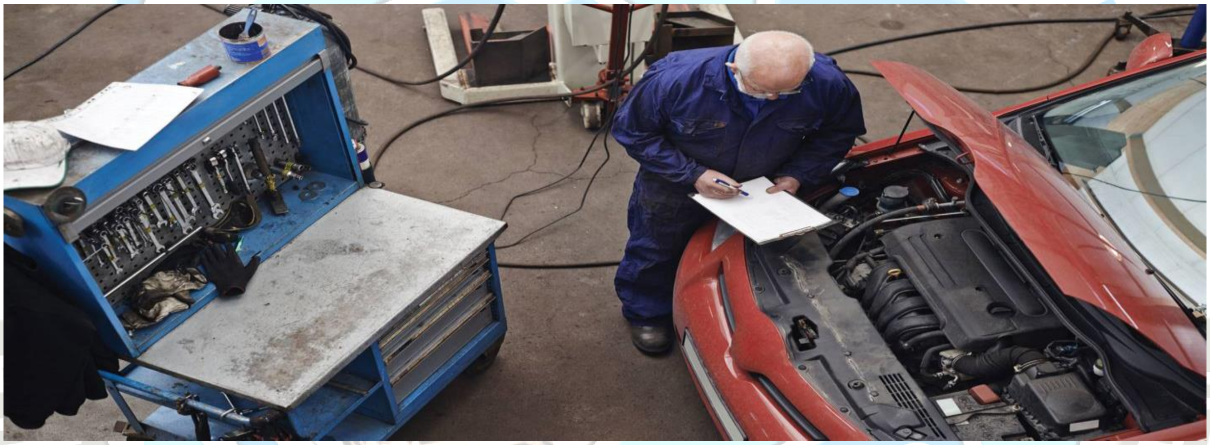
In the case of the simplest chemical reaction, reactants A and B react together to form a product C. How do we know when the reaction is complete?

Typically, we can use techniques such as NMR or TLC to see how far along the reaction has proceeded.

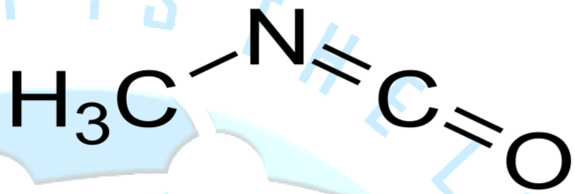
Inherently Safer Chemistry for Accident Prevention

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.

It is insuring that all aspects of the car, from the engine, to the brakes, to the steering are all in working order so that the car is less likely to get into an accident.



- Storing chemicals that are reactive together, such as oxidizers and flammable materials, leads to a risk of release and reaction.
- If these compounds leak from their containers and react, they will create a large fire. This is a hazard that could be easily avoided by storing these chemical types separately.
- In arguably the worst industrial accident in history, 40 tons of methyl isocyanate was accidentally released when a holding tank overheated at a Union Carbide pesticide plant, located in the heart of the city of Bhopal. 3900 people died and more than thousands were injured.



- 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.