GREEN CHEMISTRY

Definition

Green Chemistry is the use of chemistry for prevention of pollution by designing proper processes that reduce or eliminate the generation of hazardous byproducts.

Goals of Green Chemistry

1) To reduce adverse environmental impacts
2) To develop processes based on renewable feed.
3) To minimize byproducts (by higher % atom economy)
4) To develop reactions involving less toxial material
5) To develop harzards free processes.
6) To ~~d~~ use environment friendly solvents & extractants rather than organic solvents.
7) To improve energy efficiency by developing low temperature, low pressure processes using improved catalysts.
8) To develop reliable methods to monitor & control processes.

Need of Green Chemistry

- ~~Before~~ In earlier days, the chemical production processes were carried out without caring ~~f~~ of environment & ~~b~~ human beings.
- The waste byproducts produced have bad effects on environment & ecosystem, the production was not necessarily less energy consuming, there were hazards & toxic releases.

- Green chemistry has proposed the philosophy for safety and well being of man and environment
- Green chemistry principles are most important for those chemical productions which are hazardous, which have impact on environment, which are energy consuming, which use non-renewable feed, which produce products of higher costs.
- Green chemistry reduces hazards of chemical processes by suggesting new chemical processes.

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Efficiency Parameters for Reactions

1) $$\text{Atom Economy} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weight of all reactants / products}} \times 100$$

- Higher atom economy is desirable.
Addition reactions have atom economy = 100

2) $$\text{Conversion (\%)} = \frac{(\text{Amount of reactant taken} - \text{Amount of reactant unconsumed})}{\text{Amount of reactant taken}} \times 100$$

3) $$\text{Reaction Yield (\%)} = \frac{\text{Amount of product formed}}{\text{Expected amount of product}} \times 100$$

4) Reaction selectivity (%) $= \dfrac{\text{Amount of desired product formed}}{\text{Amt. of product expected on the basis of amount of reactant consumed}} \times 100$

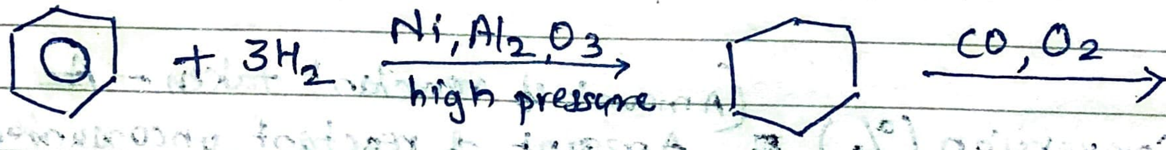
5) Environmental load factor (E) $= \dfrac{\text{Total mass of effluent generated}}{\text{Mass of desired product}}$

Traditional & Green Pathways of Synthesis

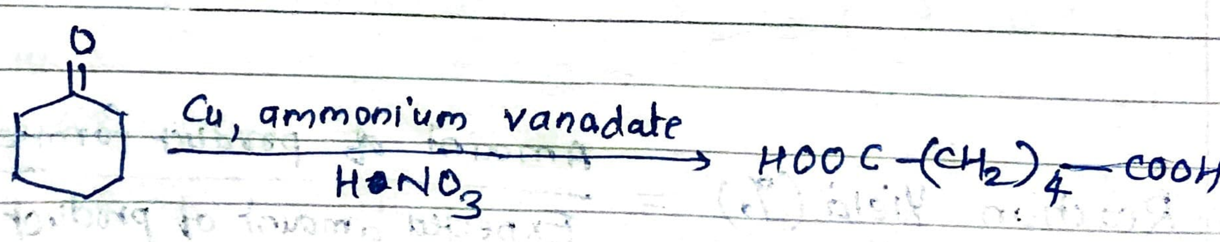
Synthesis of Adipic Acid

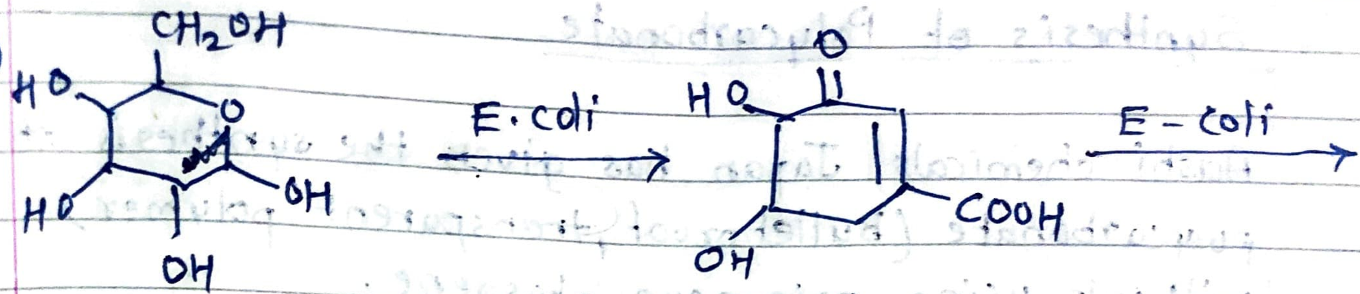
Adipic acid is required for the manufacture of nylon 66. It is prepared by traditional and green pathways.

a) Traditional Pathway

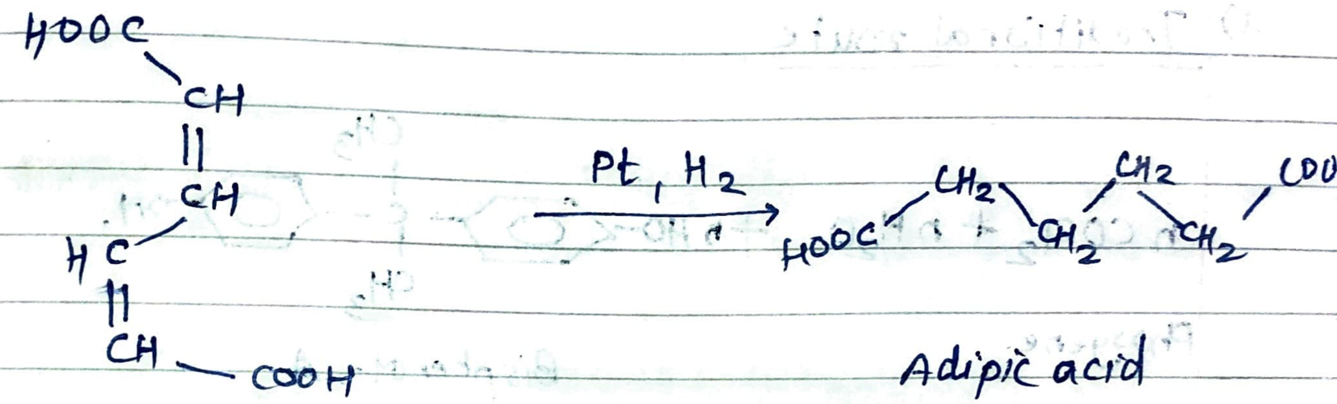


Benzene   cyclohexane



b) 

D-glucose 3-hydooshikimate.



Adipic acid

Muconic acid

- Traditional pathway uses non-renewable, carcinogenic feedstock. Benzene is carcinogenic
- Green pathway uses cheap, renewable & safer method. Green pathway requires 2-steps while traditional pathway is 3 step synthesis.

Synthesis of Polycarbonate

Traditional Route

- Uses of poisnous starting material phosgene
- Uses non-renewable CH_2Cl_2 solvent which is difficult to separate from product. Solvent is poisonous.

Green Pathway

- Does not require solvent, reaction carried out in molten state.
- Avoids use of poisonous starting material.

Synthesis of Polycarbonate

Aashi chemicals, Japan has given the synthesis of polycarbonate (bullet proof, transparent polymer) without using poisonous phosgene.

a) Traditional route

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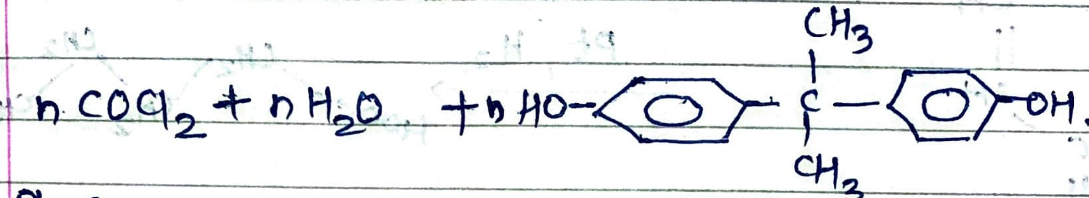
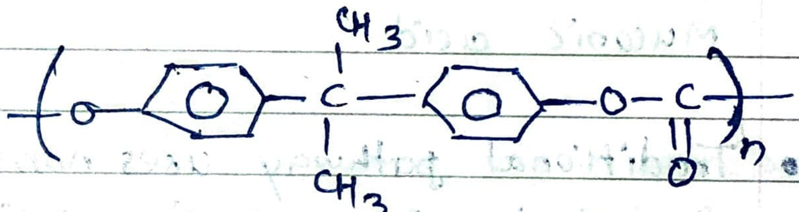


Phosgene

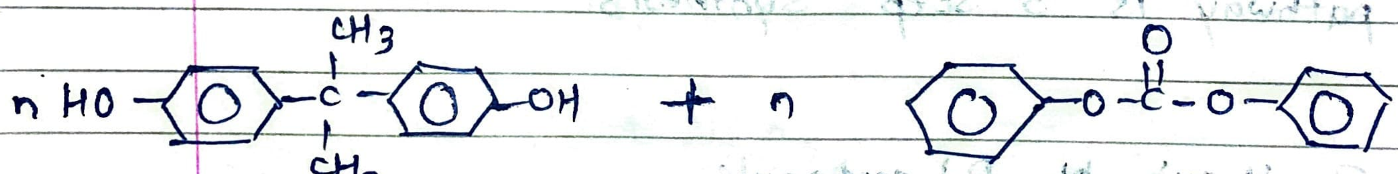
Bisphenol-A

$\xrightarrow[\text{Polymerization, by product NaCl}]{NaOH,\ CH_2Cl_2}$



Polycarbonate

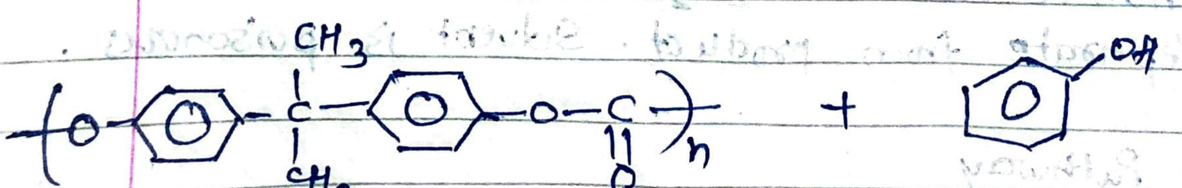
b) Green Pathway



Bisphenol-A

Diphenyl carbonate

↓ Molten State



Amorphous polycarbonate

Byproduct

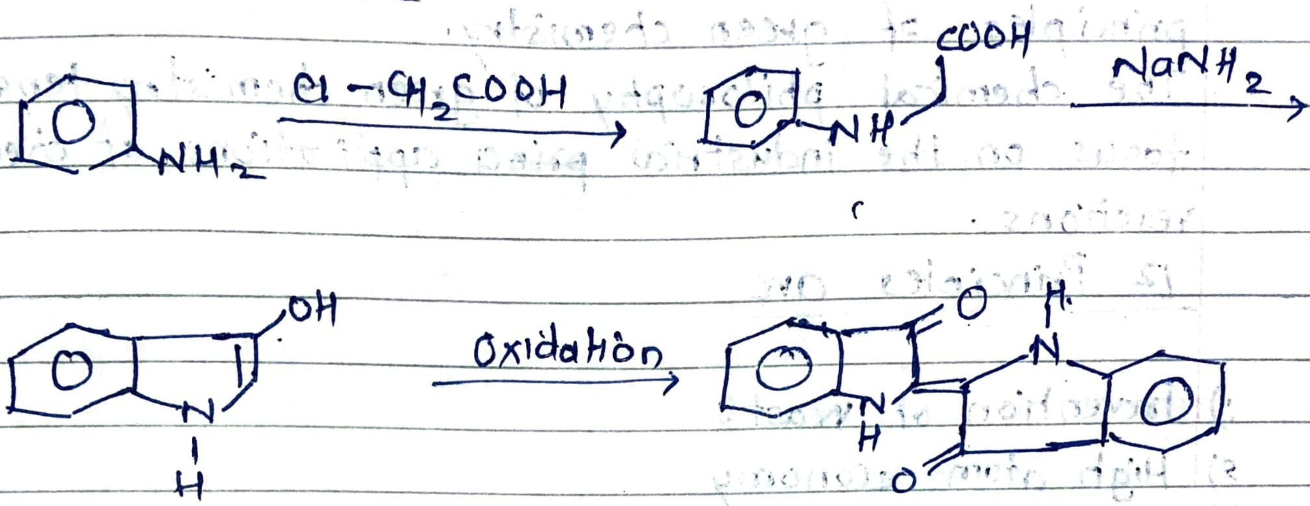
↓ Separation of byproduct, crystallisation

Crystalline Polycarbonate

Anuradha Kulkarni

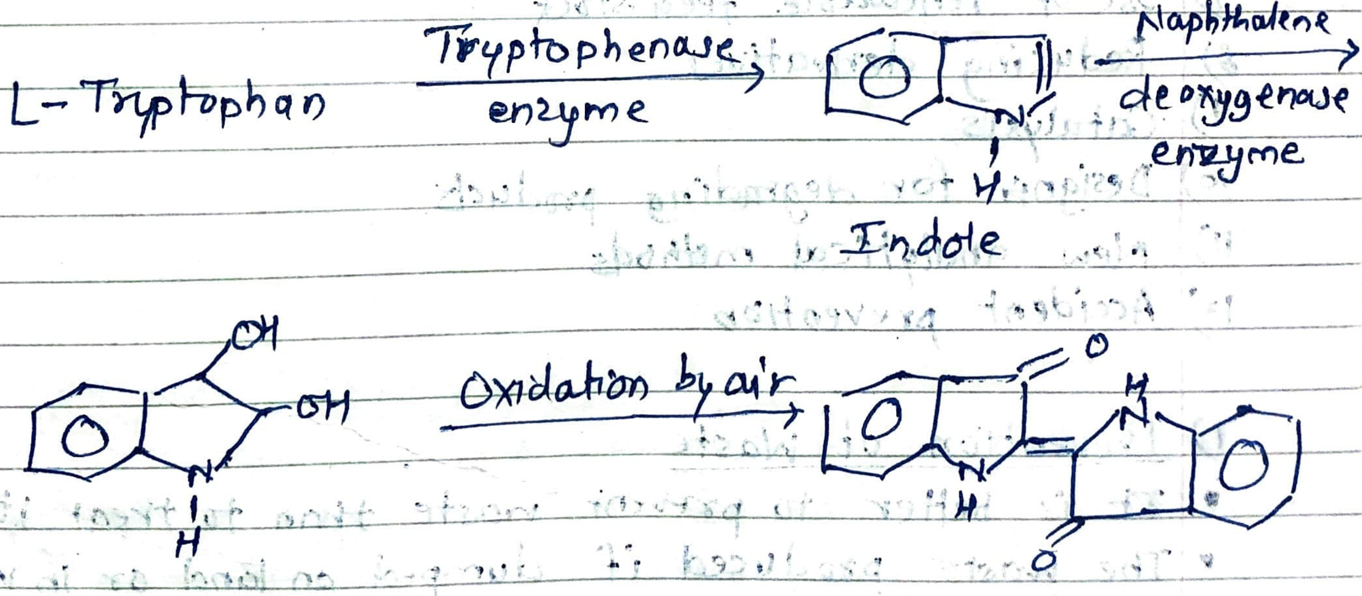
Synthesis of Indigo Dye

a) Traditional Route



Indigo Dye

b) Green Route



Indigo Dye

~~Green~~ Traditional Route	Green Route
• Starting material Non-renewable	Renewable starting material
• More steps of synthesis	Less steps
• Poisnous starting material	Ecofriendly (micro-organism process)
• Waste products produced	No waste matter

Principles of Green Chemistry

⇒ Paul Anastas & John Warner have suggested 12 principles of green chemistry.
The chemical philosophy of green chemistry tends to focus on the industrial ~~princi~~ applications of chemical reactions.

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12 Principles are

1) Prevention of waste
2) High atom economy
3) Less hazardous chemical synthesis
4) Designing safer chemicals
5) Use of safer solvents & auxillaries
6) Design for energy efficiency
7) Use of renewable feed stock
8) Reducing derivatives
9) Catalysis
10) Design for degrading products
11) New analytical methods
12) Accident prevention

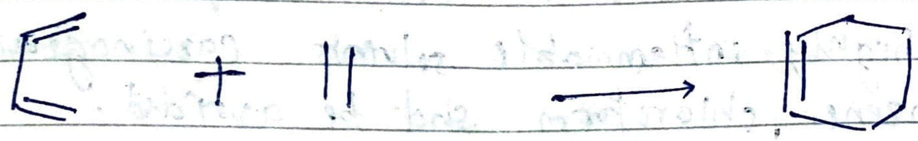
1) Prevention of Waste

- It is better to prevent waste than to treat it.
- The waste produced if dumped on land or in water or released in air, it results in pollution of soil/water/air
- Green chemistry suggest the chemical synthesis pathway for products without forming waste.

2) High Atom Economy

Green chemistry suggest ~~att~~ conversion of all reactants into 100% products & not any of byproducts.

Addition reactions, Diels-Alder reactions are having atom economy 100%.



Butadiene ethylene Cyclo~~but~~hexene.

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3) Less Hazardous Chemical Synthesis
Synthesis method shd be one which use or generate little or no toxicity to human health / environment.
e.g. Non-Phosgene Urethane Synthesis (Green Path)

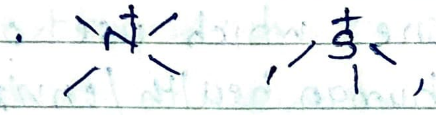
$$R-NH_2 + CO_2 \xrightarrow[-H_2O]{catalyst} R-NCO \xrightarrow{R'OH} R-NH-\underset{\underset{O}{||}}{C}-OR'$$

Traditional Path

$$R-NH_2 + \underset{\substack{\text{phosgene} \\ \text{(Toxic)}}}{COCl_2} \xrightarrow{-2HCl} R-NCO \xrightarrow{R'OH} R-NH\underset{\underset{O}{||}}{C}-OR'$$

4) Designing Safer Chemicals
- Chemical products must be designed to effect their desired function while minimizing their toxicity. Insectisides like DDT, aldrin, are toxic to humans & alternatively biological pesticides are 'green' to use.
- Another example, some antibiotics have more side effects on human body & safer antibiotics with negligible side effects are 'green' to use.

5) Safer solvents & auxillaries

Use of auxillary substances like solvents, separating agents, should be avoided whenever possible.
Use of highly inflammable solvents, carcinogenic solvents like benzene, chloroform shd be avoided.
For dry cleaning fabrics, instead of petrol, ~~CO_2~~ supercritical solvent CO_2 should be used.
~~Eo~~ Ecofriendly solvents like liquid CO_2 & ionic solvents shd be used.
e.g.  , BF_4^- , $FeCl_4^-$

Ionic solvents are polar, non-volalite, immiscible with organic solvents, thermally stable, easy to handle & eco-friendly.

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6) Design for Energy Efficiency

- Energy requirement of a reaction should be minimum considering the environment & economic impacts. Chemical synthesis should be carried out at ordinary temperature & pressure conditions.
- This can be achieved by
  1. Use of proper catalysts, enzymes.
  2. Use of micro-organisms
  3. Use of ~~non material~~ renewable starting material
- Energy efficiency is the amount of product formed per unit amount of energy.

7) Use of Renewable Feed Stock

A raw material or feed stock should be renewable
e.g. Adipic acid can be prepared from D-glucose rather than poisonous, non-renewable benzene.

8) Reduce Derivatives

Unnecessary derivatisation i.e. use of blocking groups, temporary modifications, protecting/unprotecting groups should be minimized because such steps require additional reagents, generate waste, consumes time, adds cost to product.
e.g. Preparation of ibuprofen from isobutyl benzene by Boot's route involves 5 intermediates (six steps) & by BHC route, using catalysis involves two intermediates (3 steps). Hence, BHC is greener path.
More derivatives involve
① additional reagents, ② generation of more waste products ③ more time, higher cost of product.

9) Catalysis

The catalytic reagents are superior for the process rather than stoichiometric reagents.
e.g. Toluene can be exclusively converted to p-xylene (avoiding o-xylene & m-xylene) by shape selective zeolite catalyst.

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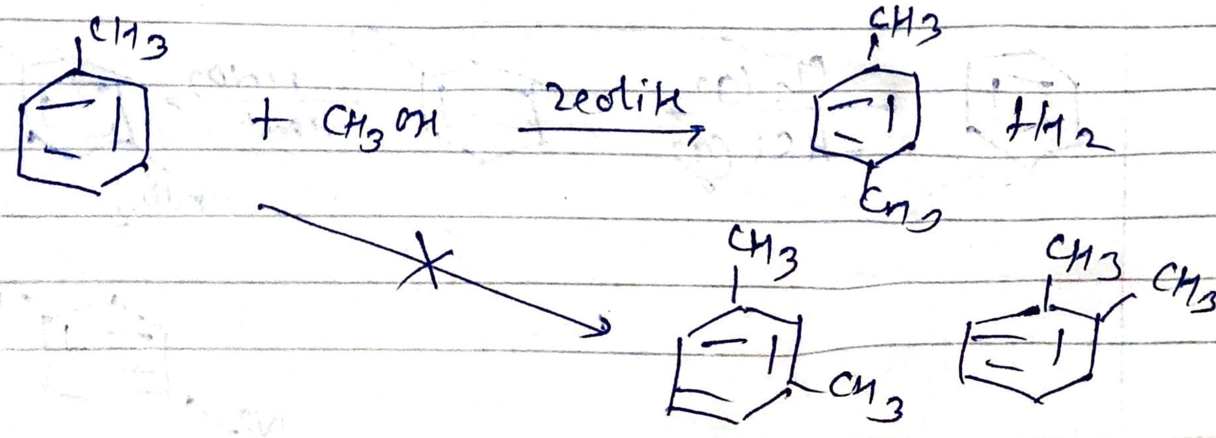


- o-xylene & ~~p~~ m-xylene are trapped ~~by~~ inside the pores of shape selective zeolite, & until they isomerize to p-xylene.
- Catalyst enhances rate of reaction.

10) Design for degrading products

The chemical products should be designed such that they undergo degradation after use & do not persist in environment for long.
Polyethylene, polystyrene are not Biodegradable but polymer like Bipol (PHBV) is degradable.

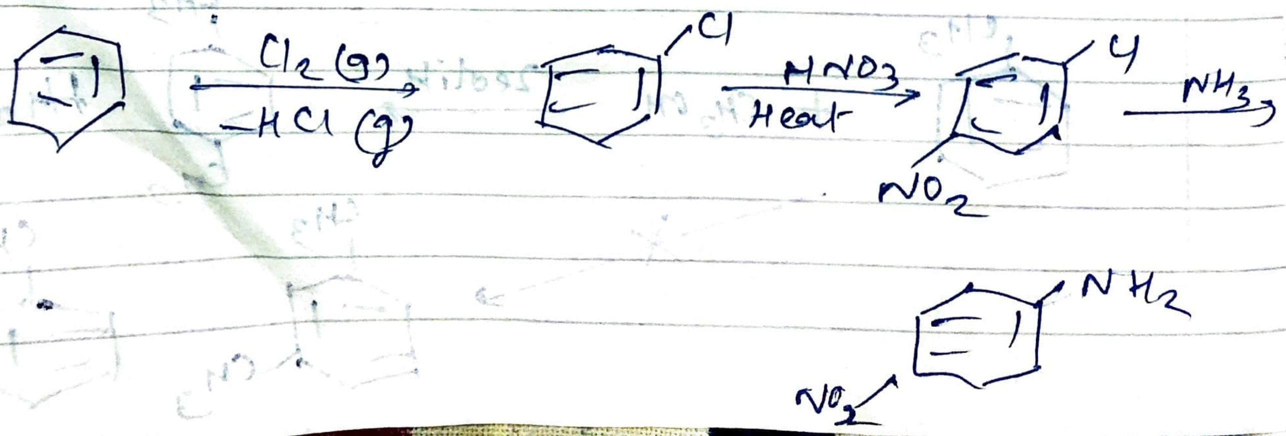
11) New analytical methods

New analytical methods have to be developed to allow monitoring & control prior to formation of hazardous substances. e.g. Preparation of ethylene glycol - In this, if reaction conditions are not monitored perfectly, toxic substances are produced.

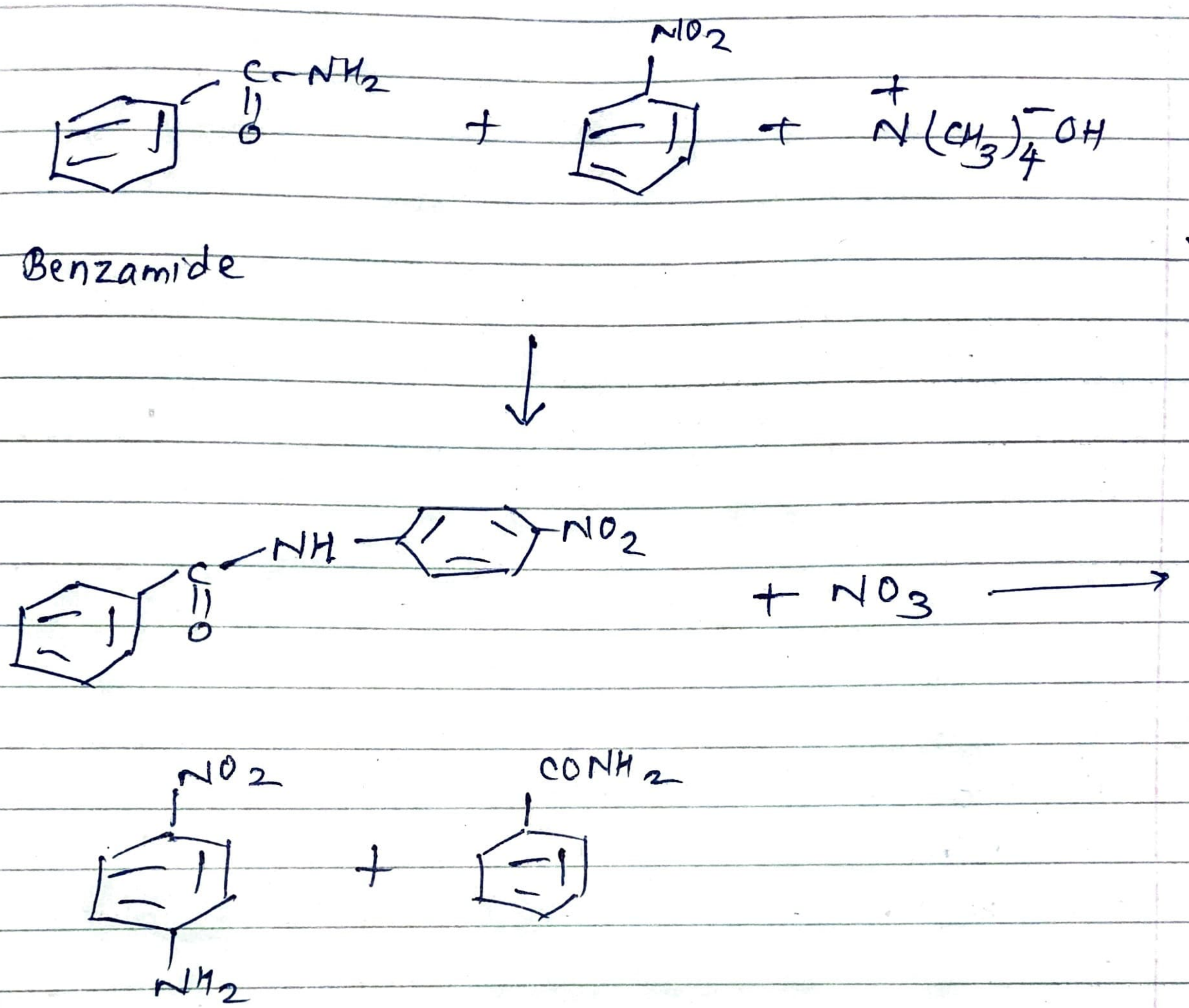
12) Safer Chemistry for Accident Prevention

The reaction conditions & reagents should be risk free in chemical process, to minimize the chemical accidents, explosions, fires & gas release.
e.g. Preparation of p-nitroaniline

Unsafe route



Safer route



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