

Module - 3

Imp

- (1) 12 principles
- (2) All synthesis

Module 3

Green chemistry and Green Engineering

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An ideal chemical reaction should have a number of attributes such as
↳ 25/1

- (1) Simplicity
- (2) Safety
- (3) Selectivity
- (4) High yield
- (5) Absence of hazardous by product
- (6) Use renewable or recyclable raw materials reagents
- (7) Energy
- (8) Efficiency

Green chemistry is the
design of chemical products

and

processes that
reduce, recycle, eliminate

use and generate
of hazardous
substances

Definition:

Green chemistry is a chemical philosophy encouraging the design of product and process that reduce, recycle or eliminate the use and generation of hazardous substances.

12 principles of green chemistry:

- (1) Prevention of waste.
- (2) Atom Economy
- (3) Design safer chemical and product
- (4) Design less hazardous chemical synthesis
- (5) use of renewable feedstock
- (6) Avoid chemical derivatives
- (7)

(2) All Synthesis

(1) Prevent waste :

- It is better to design chemical synthesis to prevent waste.
rather than leaving no waste to treat or clean up.

- In most of the cases,

The cost involved in the treatment and disposal of waste adds to the overall cost production

- The unreacted starting material also form part of the waste.
- The waste if discharged in the atmosphere, sea or land not cause only pollution but also requires ^(expensive) expenditure for cleaning up.
- Hence it is truly said

"Prevention is better than cure"

or :

- because sometimes the cleaning and disposal of waste becomes so expensive and

- associated with problem

like waste storage hazards and transportation hazards

e.g disinfection of water by

Chlorination

generates harmful chlorinated compounds

this can be prevented by using

Green oxidant

like Ozone or KMnO_4

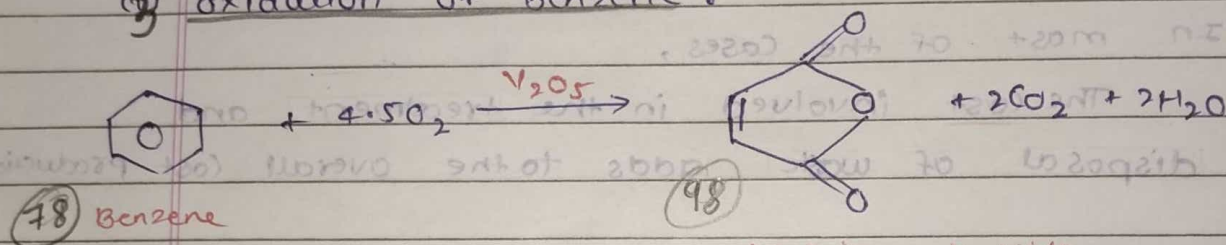
Synthetic method
 Maximize atom economy:
 or
 maximize the absorption of all the material used in the process into final product

(2) Atom Economy:-

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

$$\% \text{ Atom Economy} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weight of all reactants}} \times 100$$

① Synthesis of Maleic anhydride:
 ② oxidation of Benzene:

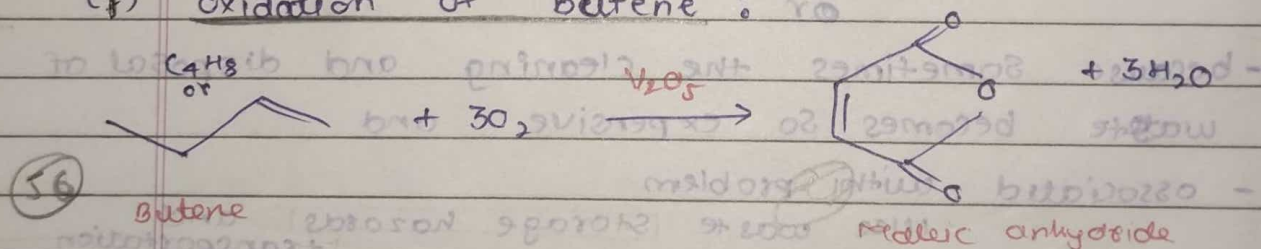


Reactants: Benzene (78) + 4.5 O₂
 = 78 + 4.5(32) = 144

Product: Maleic anhydride = 98

$$\% \text{ atom economy} = \frac{98}{144} \times 100 = 44.1\%$$

(1) oxidation of Butene:

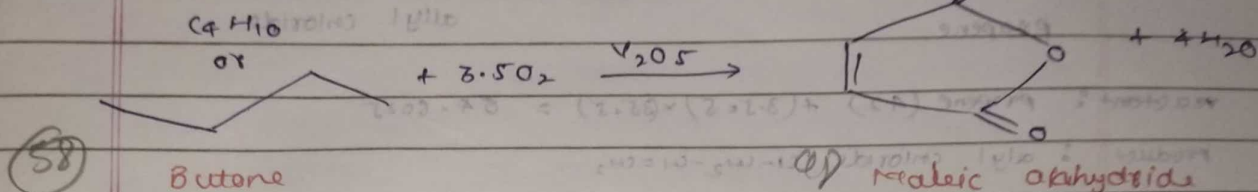


Reactants: Butene (56) + 3O₂
 = 56 + 3(32) = 152

Product: Maleic anhydride = 98

$$\% \text{ atom economy} = \frac{98}{152} \times 100 = 64.5\%$$

(3) Oxidation of Butane :



Reactant: Butane (58) + $3.5 \times 32 = 170$

Product: maleic anhydride = 98

$$\% \text{ atom economy} = \frac{98}{170} \times 100 = 57.6\%$$

Final product \nearrow
 starting material \nwarrow

- out of the above three processes for synthesis of maleic anhydride

Butane has maximum atom economy (57.6%) and hence considered as a green process.

- design chemical synthesis so that the Final product contains the maximum proportion of the starting material

Final product \nwarrow

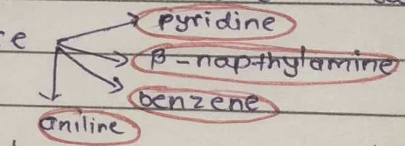
contain maximum proportion of starting material

or (minimization?)

(3) (Design) (less) hazardous chemical synthesis:
or
Non-Hazardous chemical synthesis

- Chemical Syntheses should be designed to use and generate substances which little or not toxicity to human and the environment
- one of most important principles of green chemistry is to prevent or at least minimize the formation of Hazardous product which may be toxic and or environmentally harmful.
- In case hazardous product are formed, their effect on the workers must be minimized.

- The starting material selected should be the least toxic like



} should be avoided as synth-starting material

and other aromatic compound are known as carcinogenic

Synthesis of indigo:

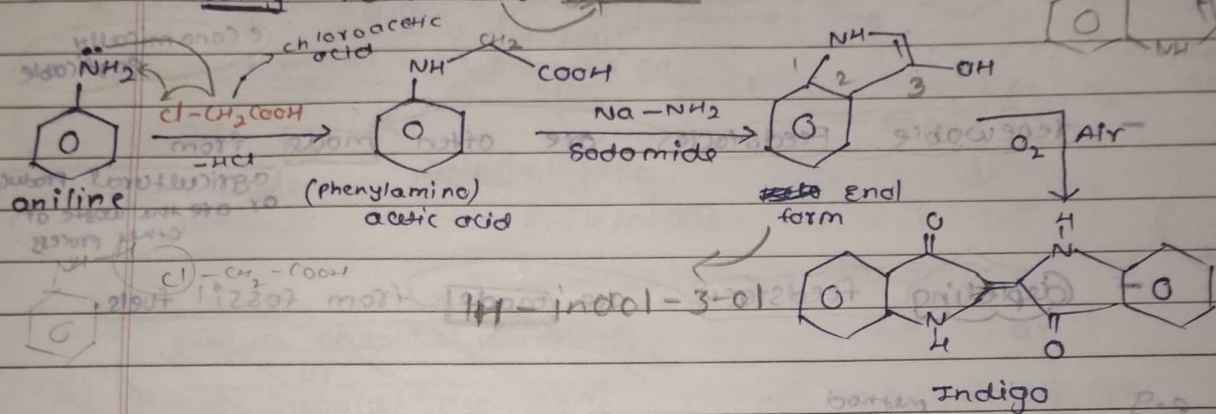
- Indigo is the dye → which is used to color blue jeans

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Synthesis of indigo

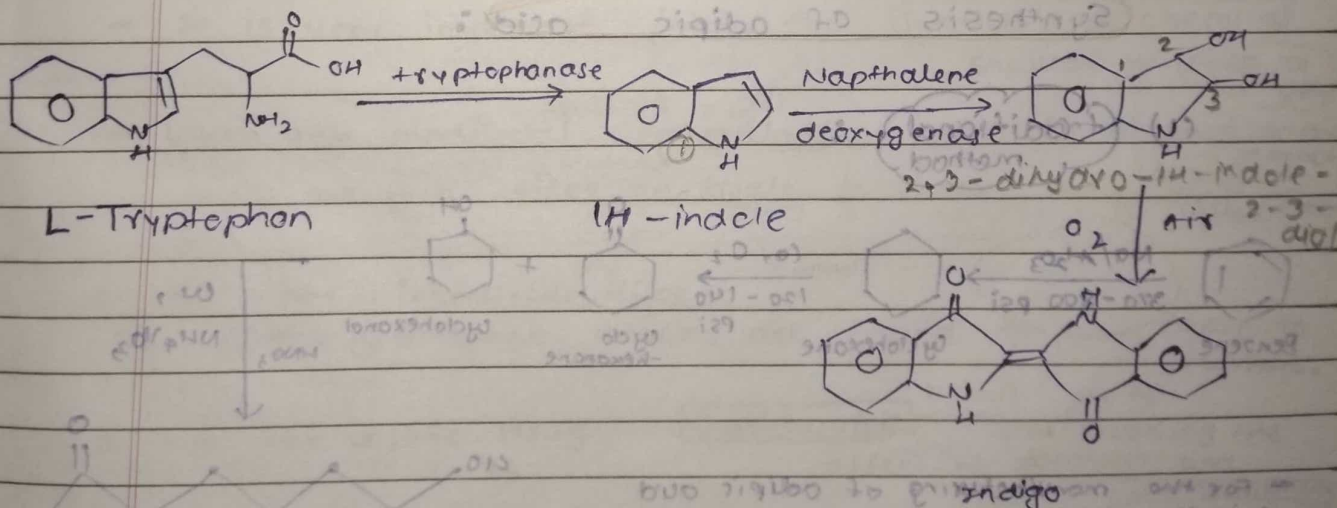
① Conventional route:

- makes use of aniline as a starting material.
- The Conventional route for the production of indigo using hazardous aniline.



② Greener route:

- use of the reaction in which side chain of tryptophan is removed enzymatically to give indole.
- It can be dehydroxylate enzymatically and then oxidized with oxygen to indigo.



(4) Use of renewable feedstock:

- Raw material and Feedstock should be renewable rather than depleting whenever technically and economically feasible.
- renewable Feedstocks are often made from agricultural products or are the waste of other process.
- Depleting feedstocks are made from fossil fuels.

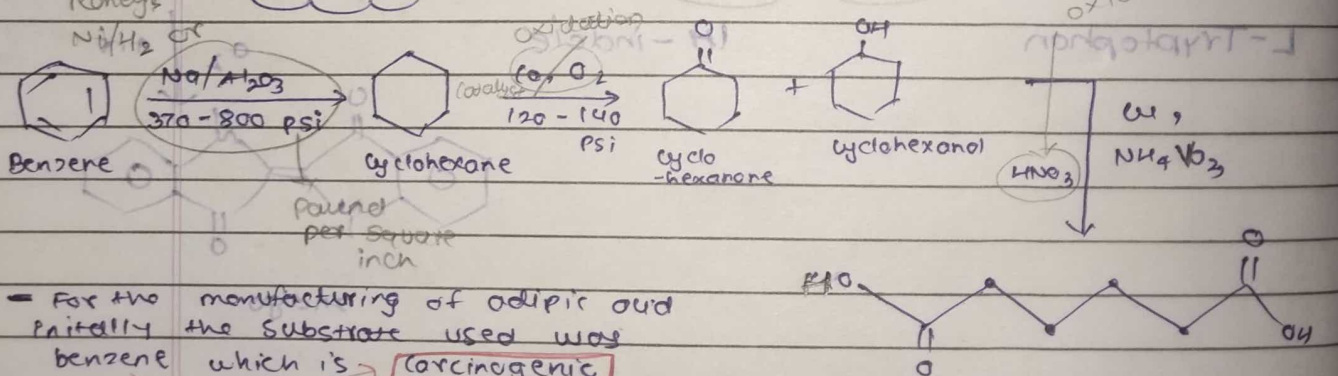
e.g.

A new method developed to prepare adipic acid from glucose obtained from cellulose.

This is green process because it replaces benzene as a starting material for the production of same product.

Synthesis of adipic acid:

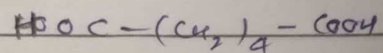
(1) Traditional method:



- For the manufacturing of adipic acid initially the substrate used was benzene which is carcinogenic.

- The continuous use of benzene affects human health.

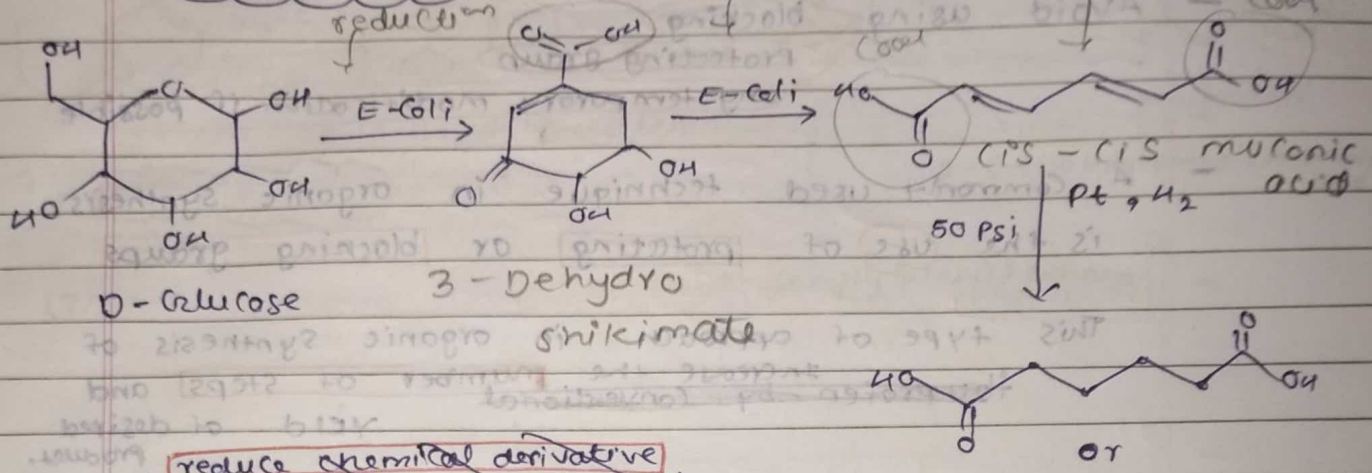
- Benzene are volatile organic compound and pollute air.



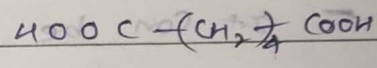
(VOC)

adipic acid

(2) Greener route :



~~reduce chemical derivative~~
or
~~Avoid chemical derivative~~



(5) Design Safer chemical and product :-

- chemical product should be designed with little or no toxicity.
- It is very important that the Synthesized chemical should be safe to use.
- when any medicinal formulations are to be put on the market, they are put first on trials to check their toxic effects.
- In many insecticide like DDT, gemoxone which are found to be toxic to humans,
- e.g the unsafe drug thalidomide \rightarrow use to reducing the effect of nausea and vomiting during pregnancy

After the birth of a child of a mother taking about thalidomide, the child suffered a birth defect.
Therefore, the usage of this drug was banned.

(5) Avoid chemical derivatives :

- Avoid using blocking protecting group only temporary modification if possible

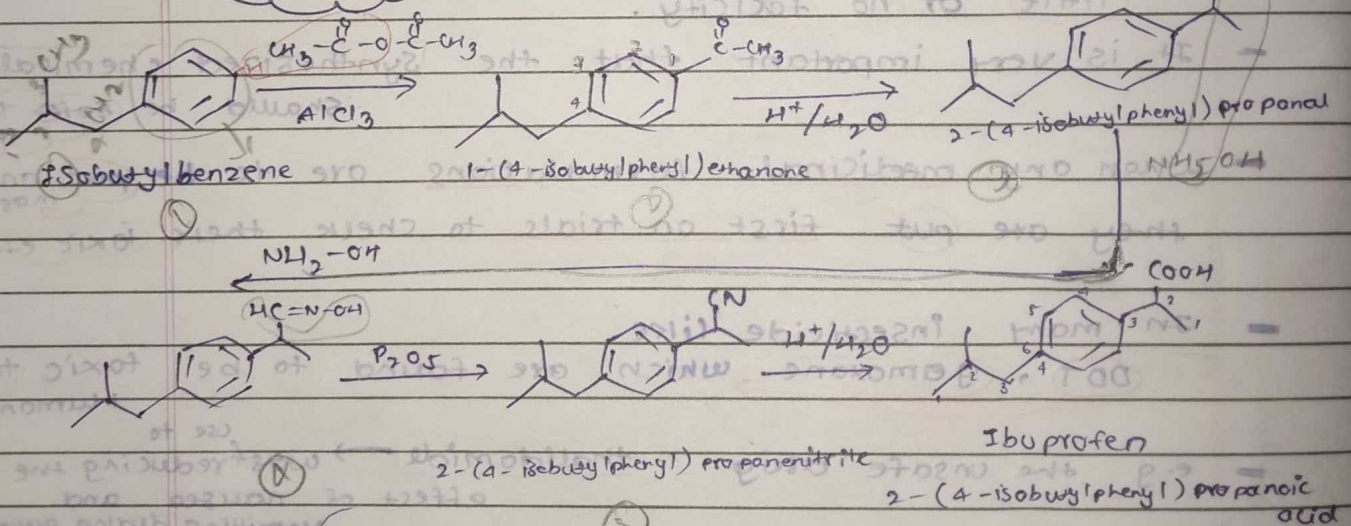
- A commonly used technique in Organic Synthesis is the use of protecting or blocking groups

This type of approach in organic synthesis of ibuprofen by conventional increase the number of steps and yield of desired product.

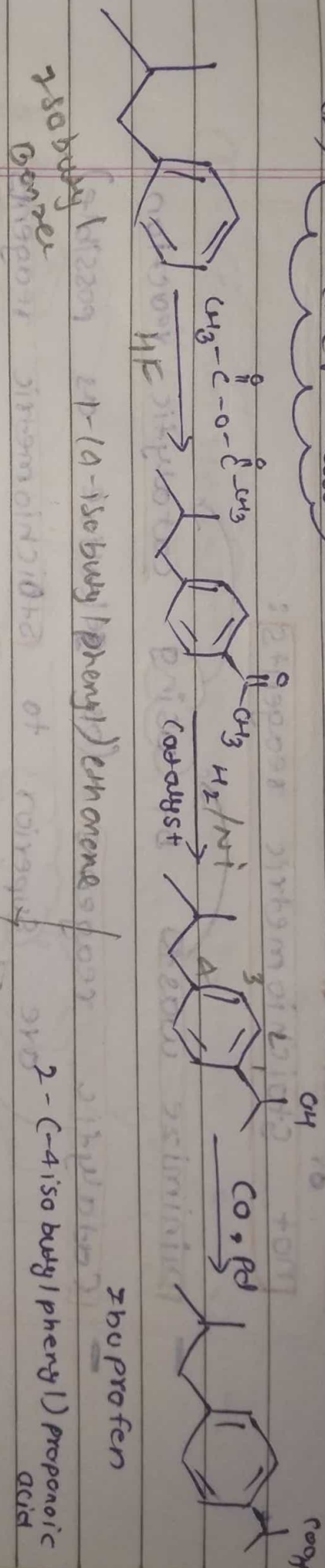
- It can be better understood by Synthesis of ibuprofen by conventional as well as Greener route

Synthesis of ibuprofen :

(1) Conventional route



(2) Greener route:



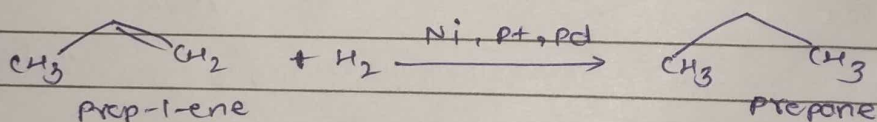
(7) 1-(4-iso butyl phenyl) ethanol

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(7) Use catalyst
or
not stoichiometric reagents:

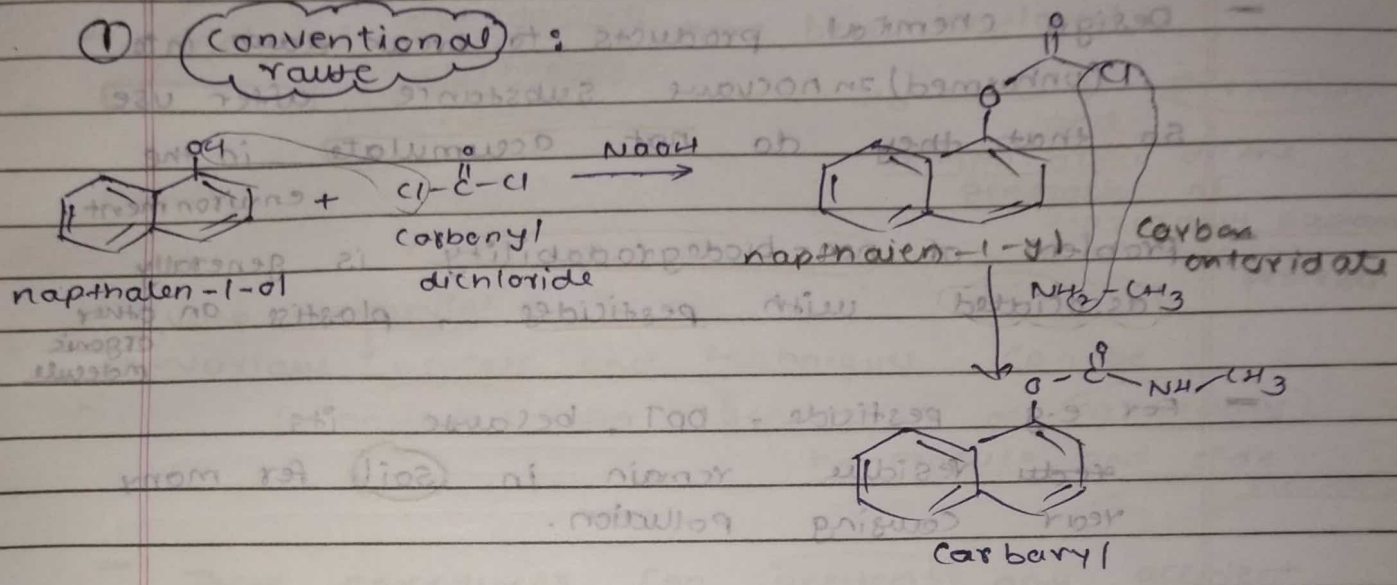
- minimize waste by using catalytic reaction
- Catalytic reagents (as selective as possible)
are superior to stoichiometric reagents
- (1) Catalysts are used in small amount and (2) can carry out a single reaction many times
- (2) stoichiometric reagents which is used in excess amount and work only once.

e.g. Hydrogenation of olefin in presence of nickel catalyst
gives much better yields

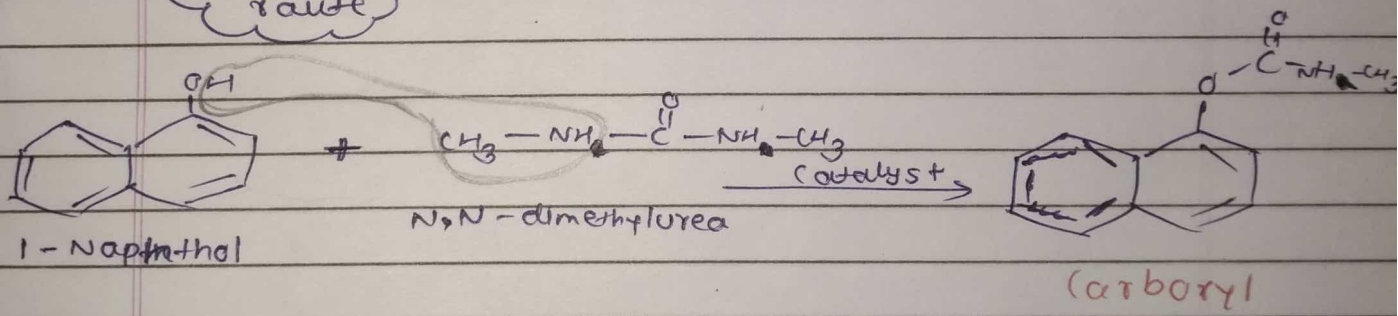


Synthesis of Carbaryl :

① Conventional route

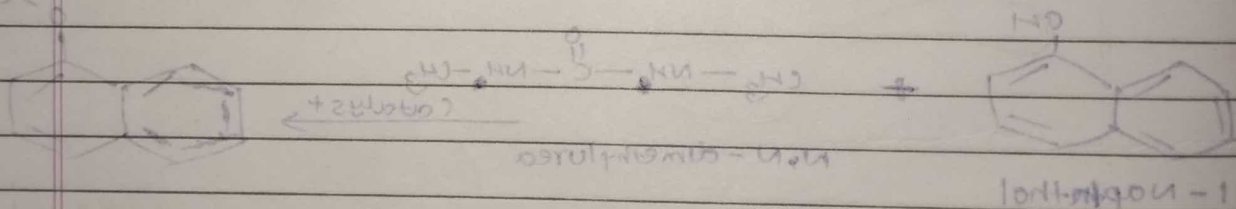


② Greener route :



(8) Design chemical and products to degrade :-
after use

- Design chemical products to break down into (unharmful) innocuous substance after use so that they do not accumulate in the environment
- problem of non-biodegradability is generally associated with pesticides, plastics and other organic molecule
- For e.g. pesticide, DDT, because its residue remain in soil for many years causing pollution.
- chemical should be taken that the biodegradating product should not be toxic.



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(10) Analyze in real time to prevent pollution :

- Analytical methodologies and technology have been developed to allow the prevention and minimization of the generation of hazardous substance in the chemical processes
- ^{using chemical} various [↓] process and techniques can be monitored for generation of hazardous by-product and side reactions
- These procedures can prevent any accident which may occur in chemical plants.