

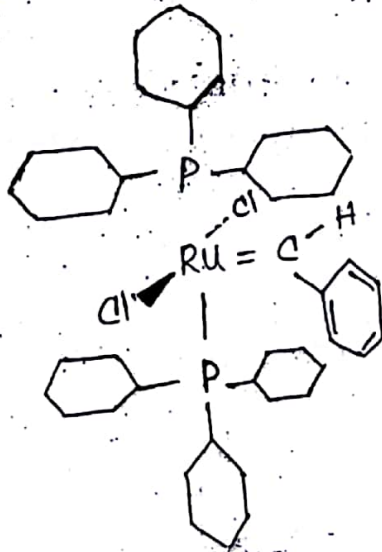
UNIT - I

Advanced named reactions in organic synthesis

Unit - I New Sample Questions
 1) Olefine - metathesis:- (or)
write about Grubbs catalyst with suitable
examples. (or) write about ROM

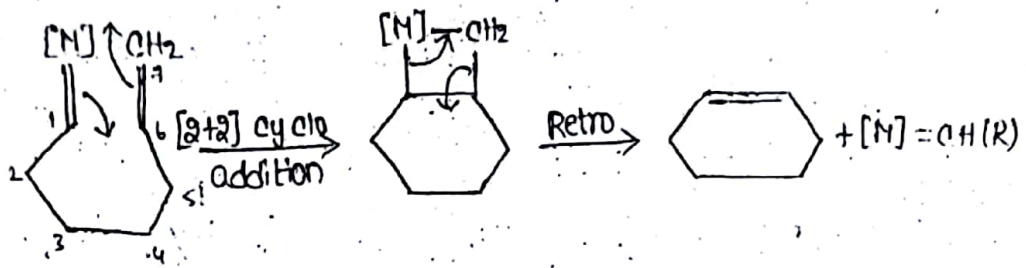
Grubbs catalyst:- Alkene metathesis reaction was developed by Grubbs using the catalyst known as Grubbs catalyst. And he also won the nobel prize in 2005. Grubbs using olefine - metathesis to form polymers that are being used to create materials for bathroom sinks, strong base ball bats.

Grubbs catalyst is an organo metallic compound containing Ruthenium metal.



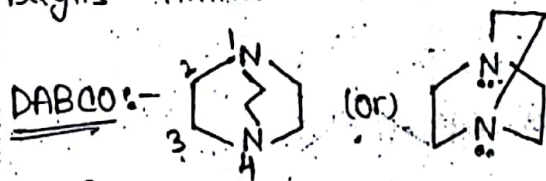
Benzylidene - bis (tri cyclo hexyl phosphene) di
 chloro Ruthenium

Step-2:-

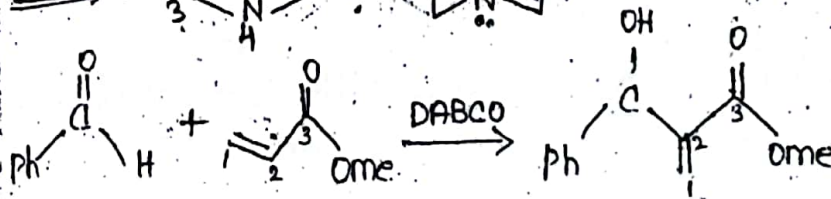


8) Baylis-Hillman reaction:-

Carbonyl compounds react with activated olefins (alkenes) in presence of a base catalyst like tertiary amine (or) DABCO to form coupling product. This reaction is known as Baylis-Hillman reaction.

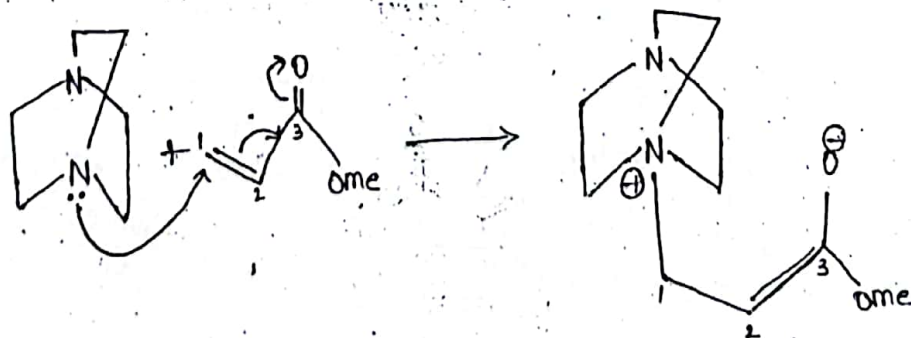


note:- DABCO
= ↓
(1,4-diazabicyclo octane)



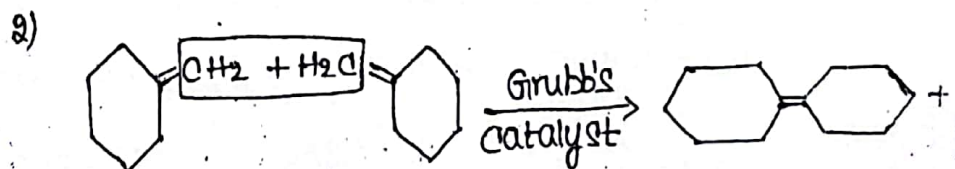
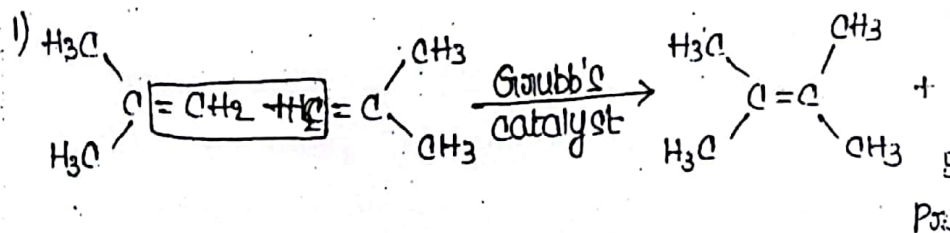
Mechanism:-

Step-1:- Michael type nucleophilic addition of tertiary amine (catalyst) to the activated alkene gives zwitter ionic enolate.

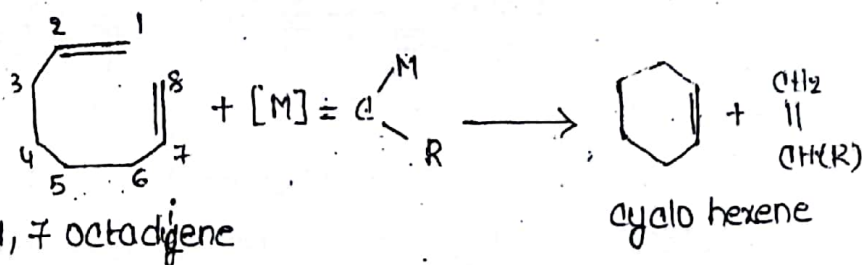


Preparation:- (Olefin - Metathesis)

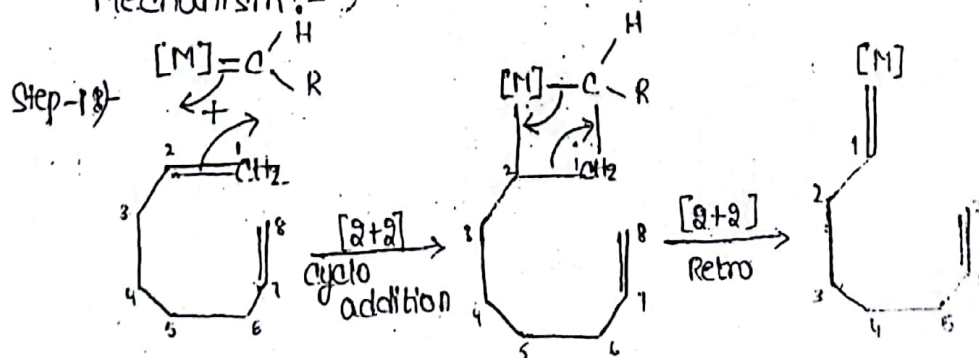
When two different olefines react in presence of Grubb's catalyst to form new olefine by breaking and rejoining of fragments of double bonds is known as Metathesis



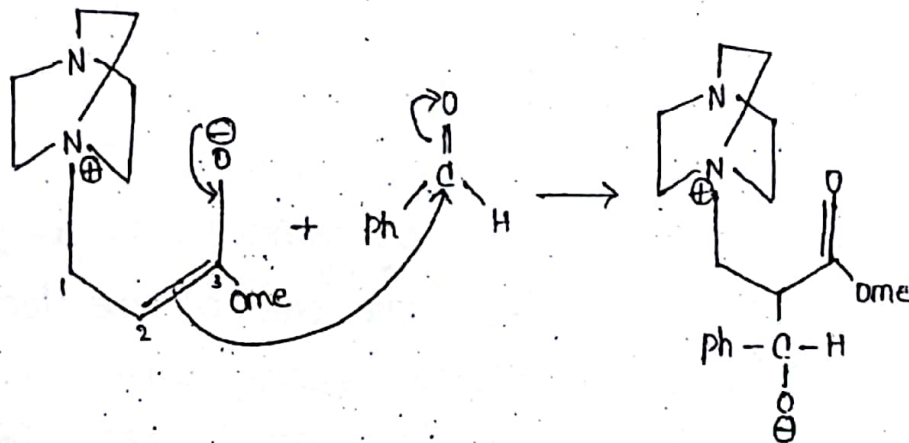
Ring closing metathesis (RCM):- (or) Grubb's catalyst



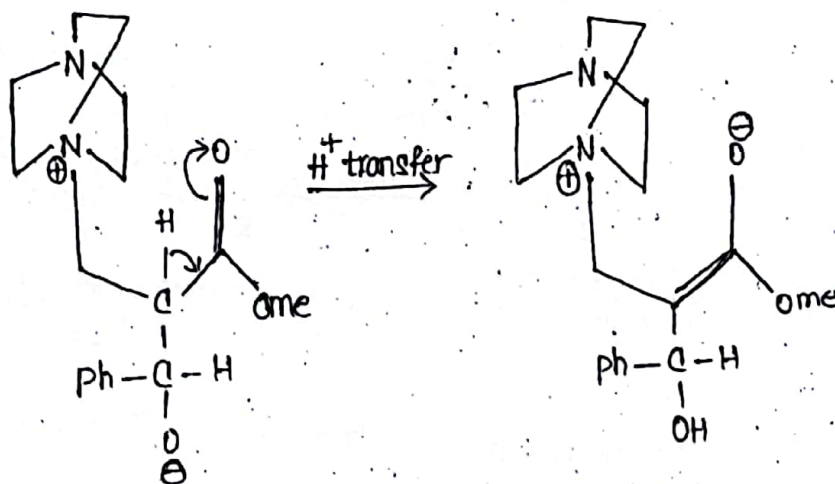
Mechanism:-



Step-II:- Nucleophilic addition of zwitter ionic enolate on to the aldehyde in aldol type reaction.

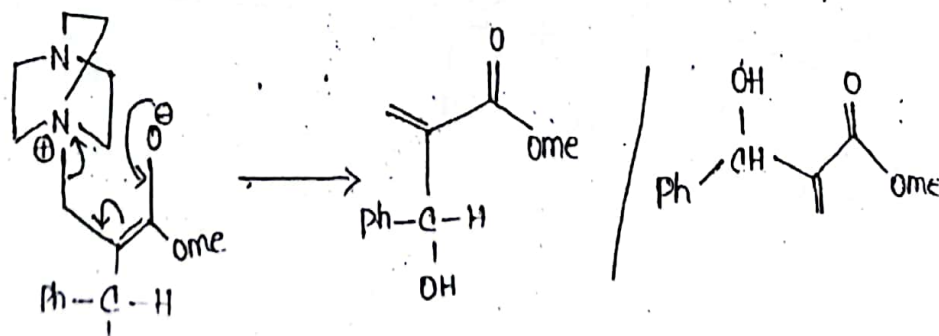


Step-III:- Proton transfer



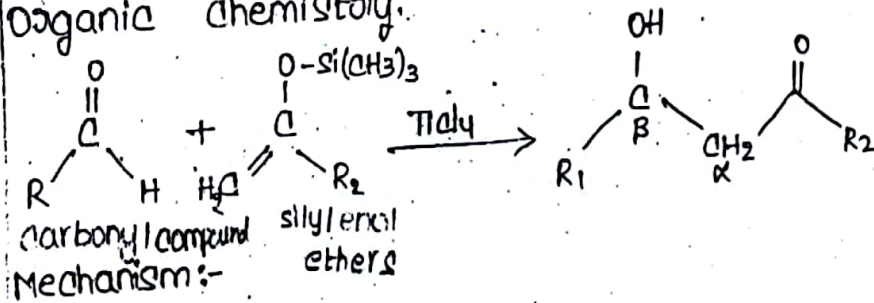
Step-IV:-

Finally, release of catalyst generates desired multi functional molecule



3) Mukaiyama-aldol reaction:-

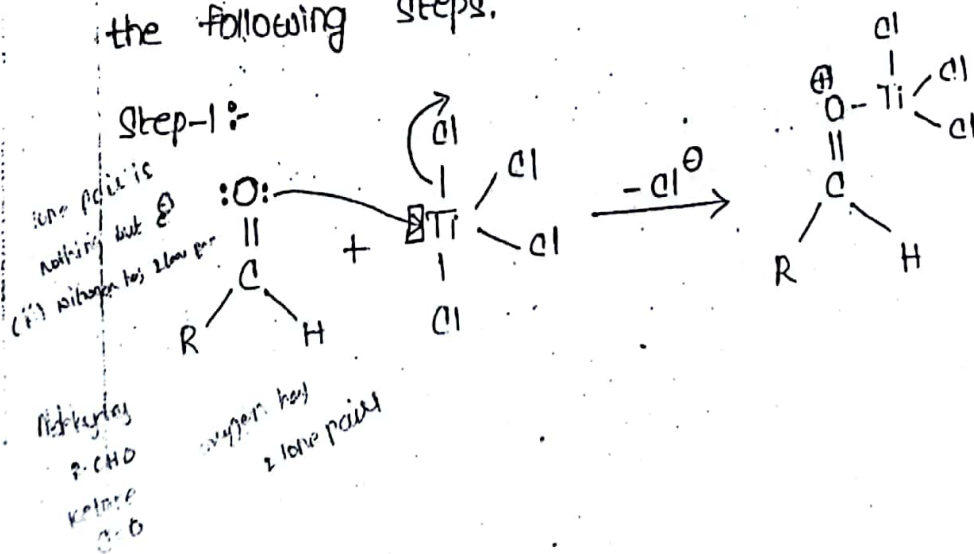
It is a nucleophilic addition of silyl enol ethers and carbonyl compounds catalysed by Lewis acids such as $AlCl_3$, BF_3 , $TiCl_4$ etc to form β -hydroxy carbonyl compound. This reaction was discovered by Mukaiyama a professor Tokyo university was one of the famous Japanese chemists, whose work had a scientific impact on the development of the aldol reaction and other areas of synthetic organic chemistry.



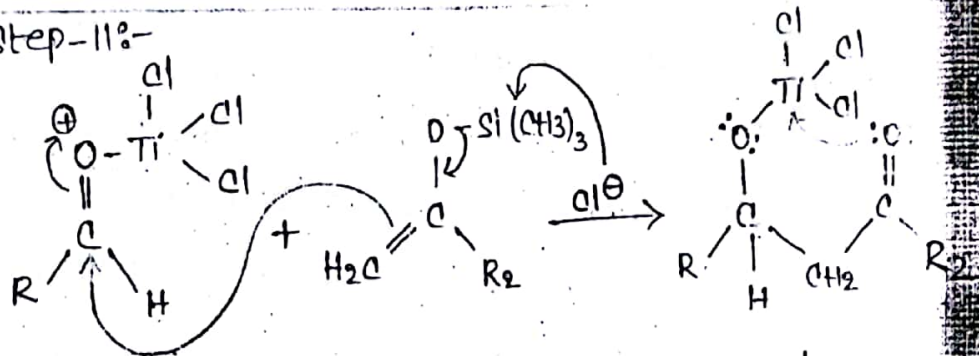
Mechanism:-

Step-1:-

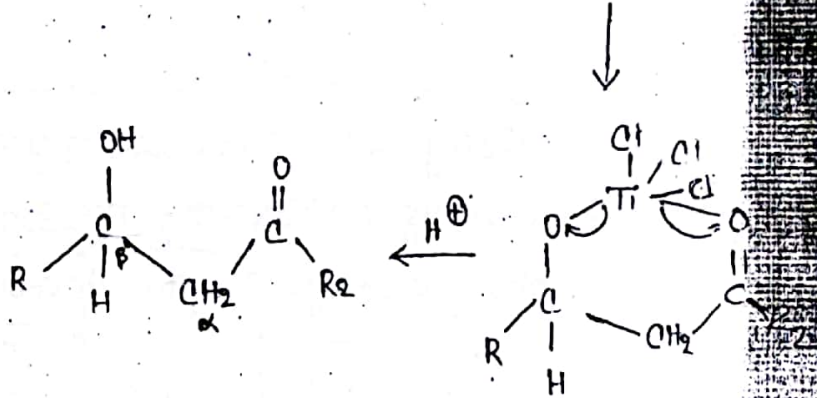
The mechanism of the above reaction involves the following steps.



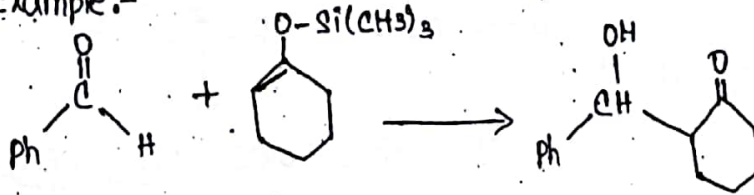
Step-11:-



α - γ bonds form

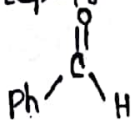


Example:-



Mechanism:-

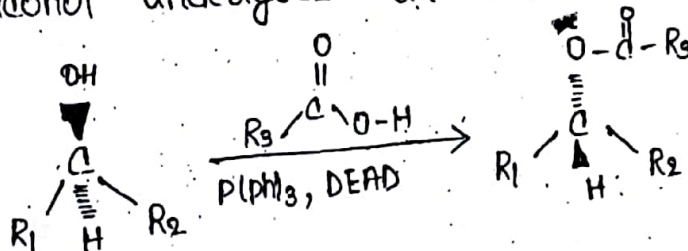
Step-1:-



4) Mitsunobu reactions

The Mitsunobu reaction was named from a Japanese chemist Mitsunobu in the year 1967. He worked at the Gakuin University in Tokyo.

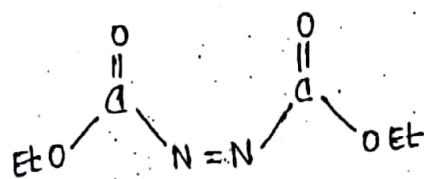
The Mitsunobu reaction is an organic reaction that converts an alcohol into a variety of functional groups like esters and it is an S_N2 type reaction in which the alcohol undergoes an inversion of stereochemistry.



In this reaction there are other two reagents

1. $P(Ph)_3 \Rightarrow$ Tri phenyl phosphine

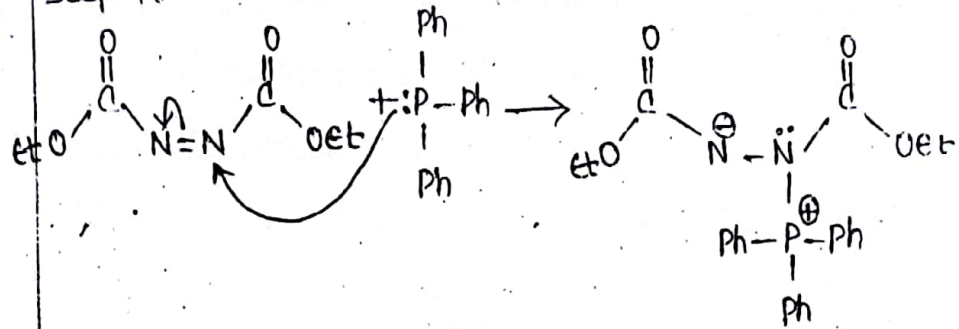
2. DEAD \Rightarrow Diethyl Azo Dicarboxylate



Mechanism:-

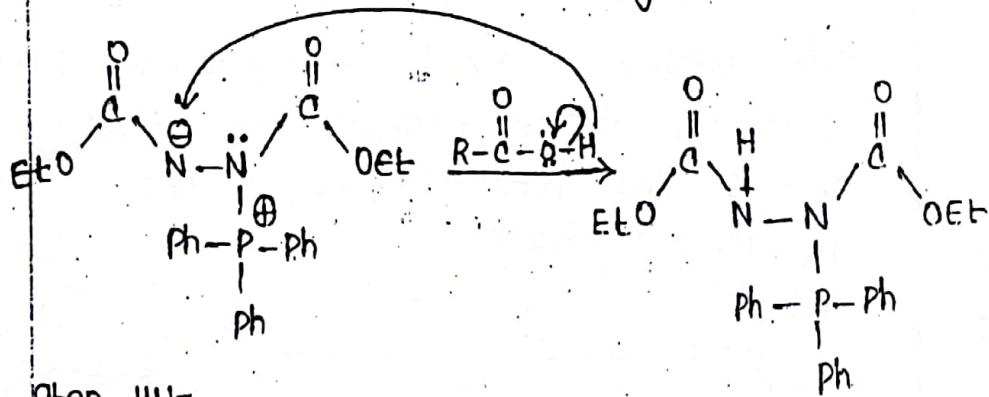
The first stage of the reaction involves neither the alcohol nor nucleophile, but the phosphine adds to the weak $N=N$ to give an anion.

Step-I:-

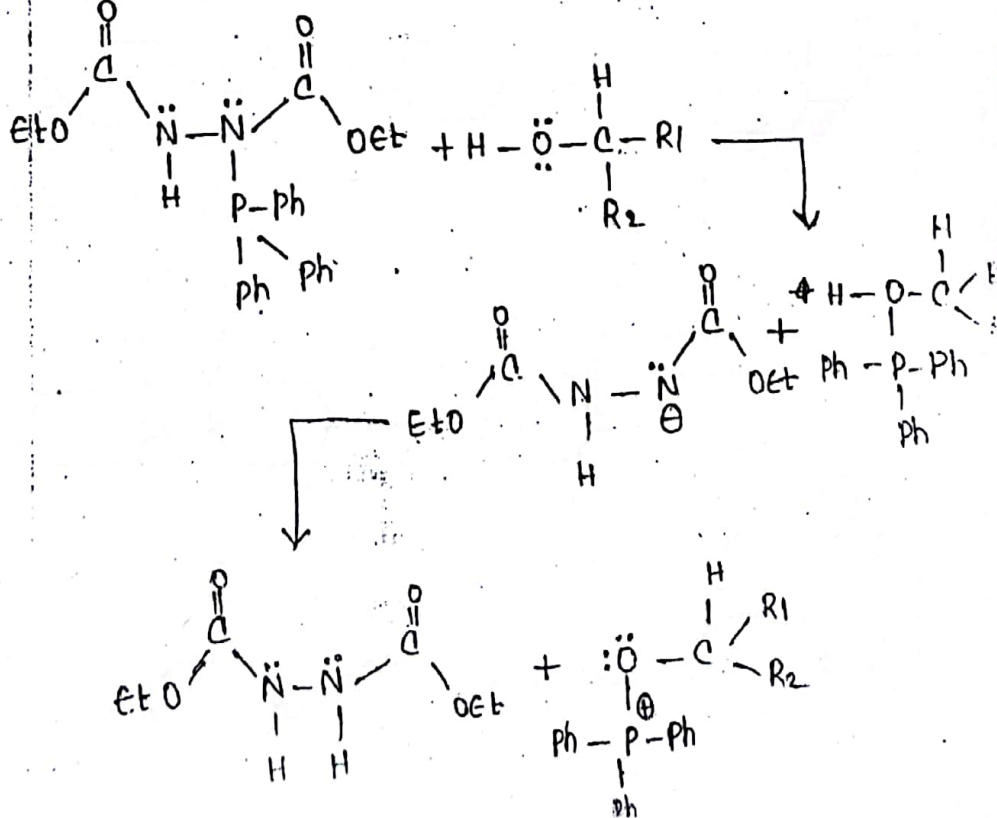


Step-II:-

The anion produced in the first step acts as a nucleophile and abstracts a proton from the acid generating nucleophile.

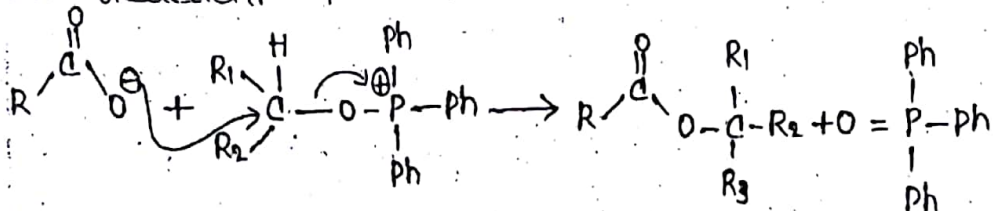


Step-III:-



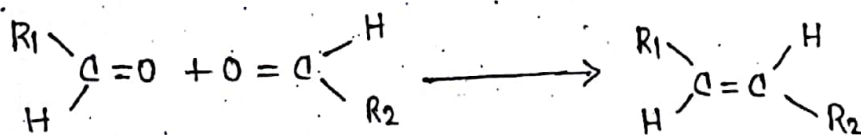
In the third step the positively charged phosphorus is now attacked by the alcohol.

Step-IV:- Anion of the nucleophile can now attack this phosphorus derivative of the alcohol in normal S_N2 reaction.



5) Mc Muray Reaction:-

The reduction coupling of carbonyl compound with low valent titanium in presence of reducing agents like potassium, Mg, Zn etc is called Mc Muray reaction.



In this reaction E-alkenes (trans) are major products.

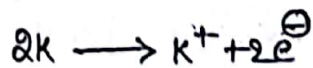
Mechanism:-

The mechanism of the above reaction involve the following steps.

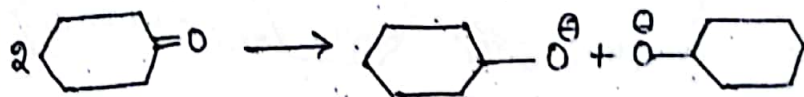
Step-I:-



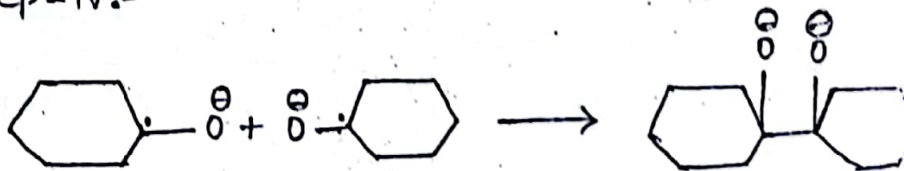
Step-II:-



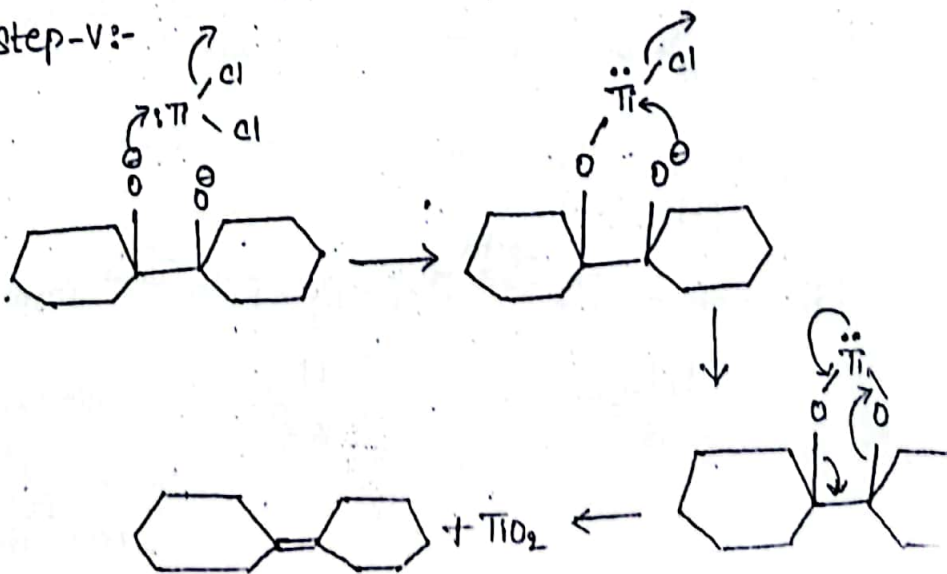
Step-III:-



Step-IV:-



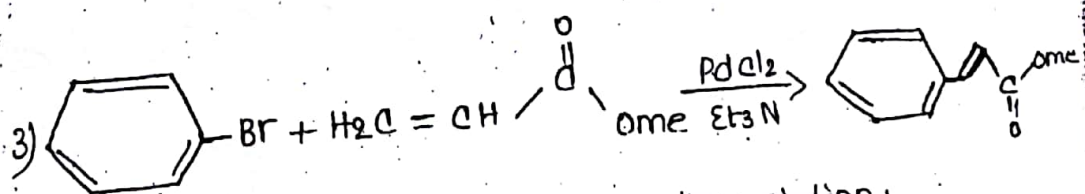
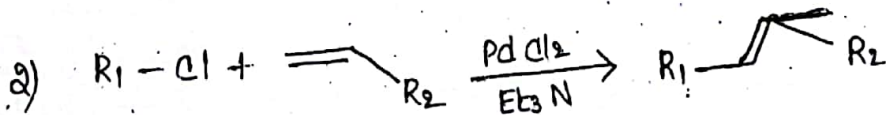
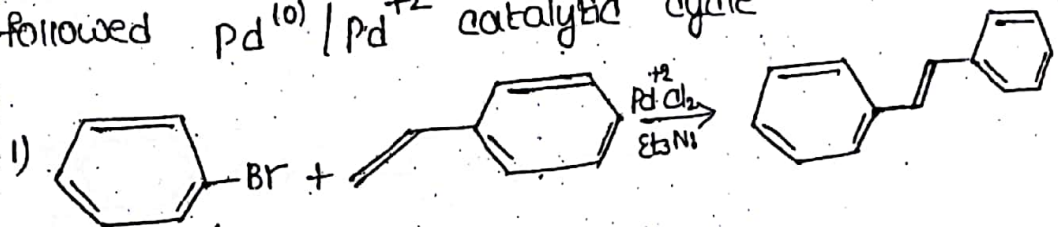
Step-V:-



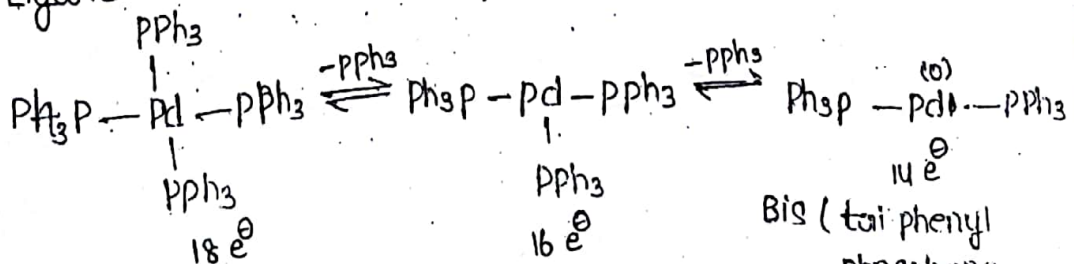
6) Heck-reaction:-

It is a chemical reaction of unsaturated halide with an alkene in presence of a base and palladium catalyst to form substituted alkene.

Heck was awarded the nobel prize in 2010 for the discovery and development of this reaction. It was the first example of a C-C bond formation reaction that followed $Pd^{(0)} / Pd^{+2}$ catalytic cycle



Ligand dissociation (or) catalytic dissociation:-



Bis (tri phenyl phosphine) palladium (0) complex only undergoes oxidative addition.

Mechanism:-

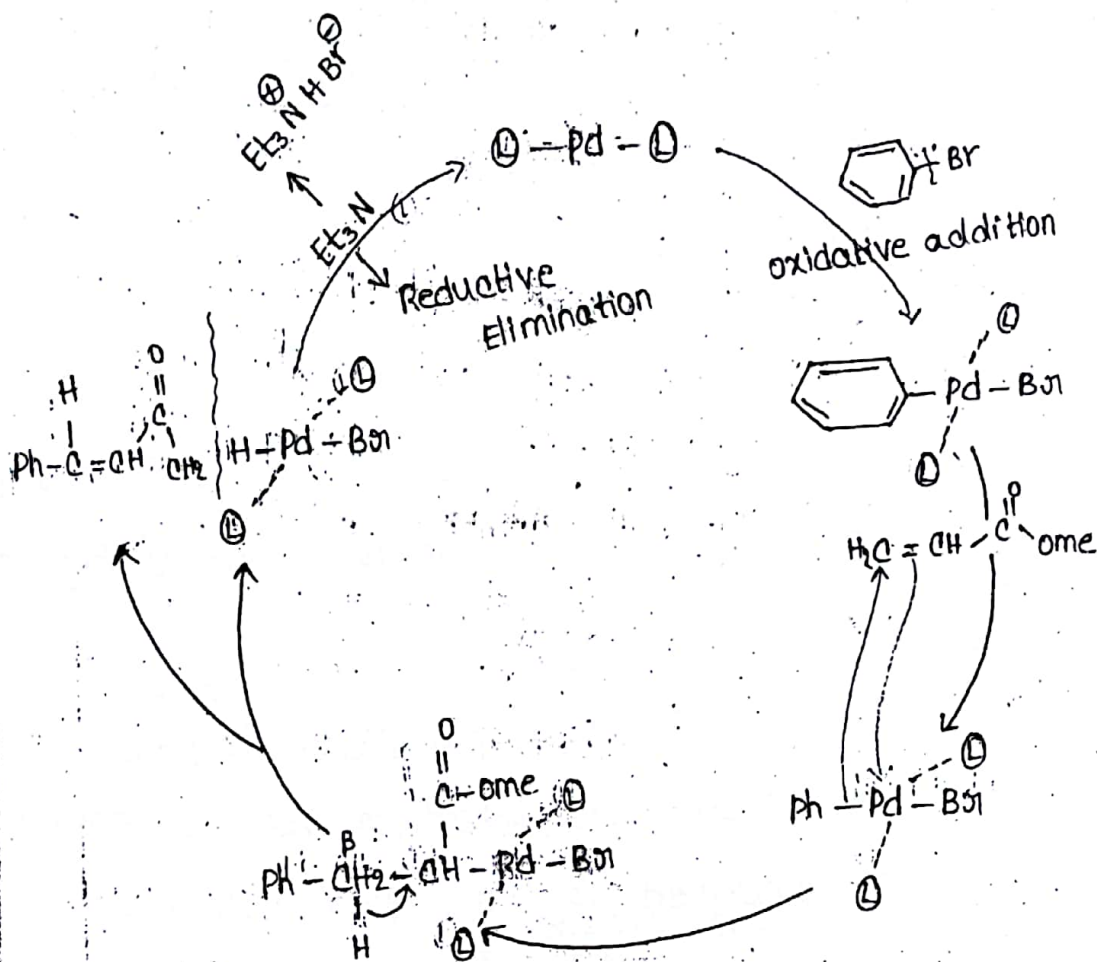
Step-I:- An oxidative addition where the palladium is inserted into the acyl bromide bond, forming a complex.

Step-II:- The alkene is inserted in the acyl palladium bond on the same side of the double bond which is known as syn addition.

Step-III:- A β hydrogen elimination takes place resulting in the formation of another palladium-alkene complex.

Step-IV:- The new palladium complex is destroyed and palladium zero compound is regenerated by reductive elimination of palladium +2 compound with the help of base (Et_3N).

Take Benzene as (Ph)

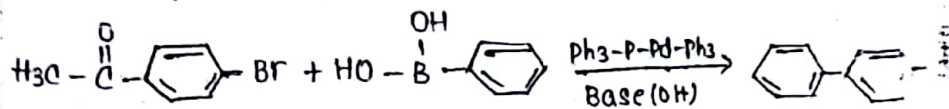


7) Suzuki coupling reaction:

This reaction is named after noble laureate a Japanese chemist Akira Suzuki who first published work on this reaction, in 1979.

It is a coupling of an organo borane compounds with aryl and vinyl halides in presence of palladium complex and a base.

Ex-coupling of an aryl bromides (bromo benzene) with aryl boronic acid to produce a biphenyl.



Mechanism:-

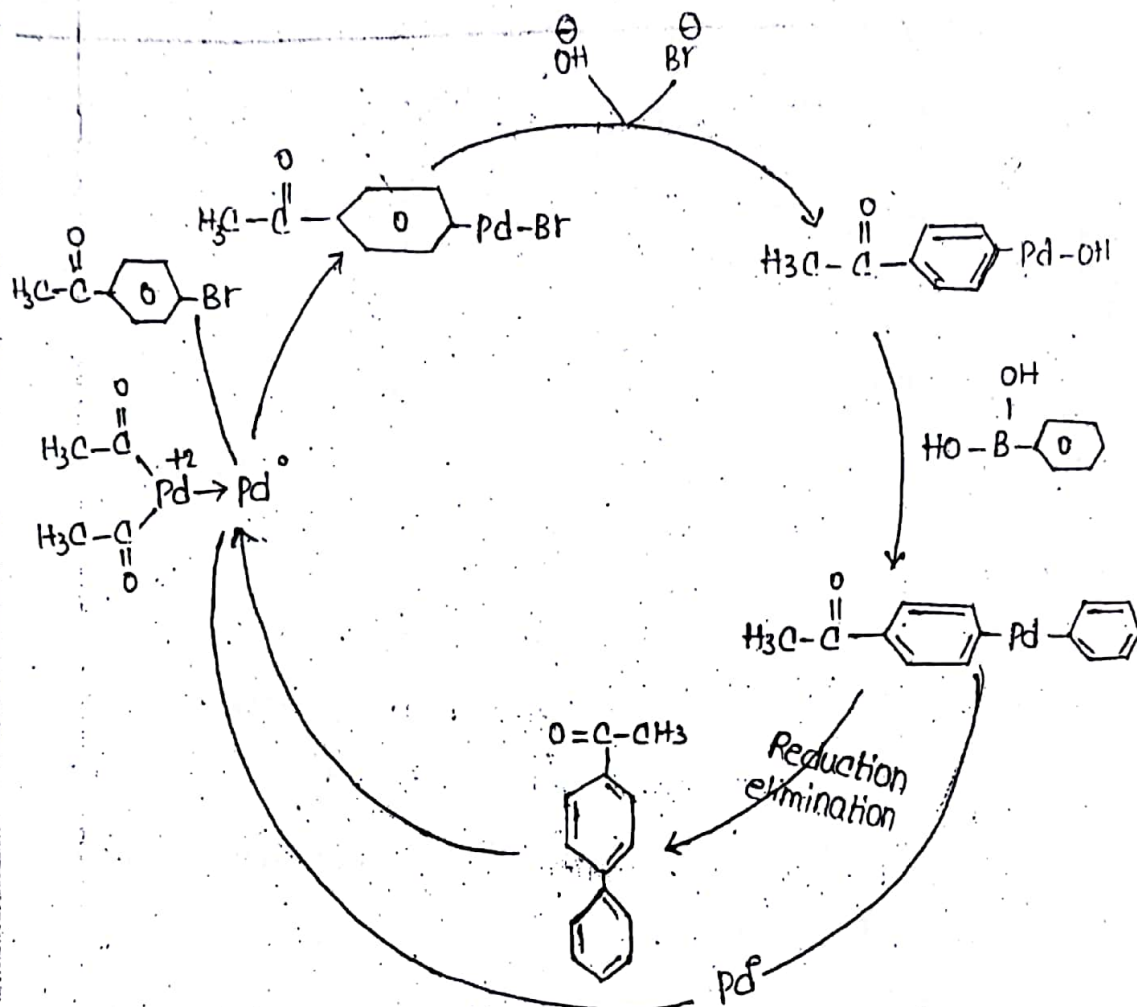
Step-I:- The reaction begins with palladium catalyst. Palladium reduces from +2 oxidation state to zero by gaining of electrons.

Step-II:- The catalyst combine with 4-bromo aceto phenone through a process of oxidative addition, the palladium catalyst reacts to form a bromo palladium aceto phenone complex.

Step-III:- A ligand substitution in the basic medium produces a hydroxy palladium aceto phenone complex.

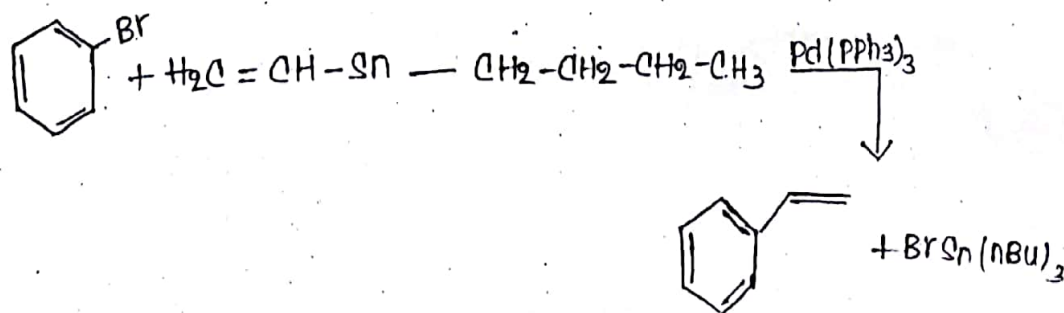
Step-IV:- Hydroxy palladium aceto phenone complex undergoes trans metalation to form phenyl palladium aceto phenone complex with phenyl boronic acid.

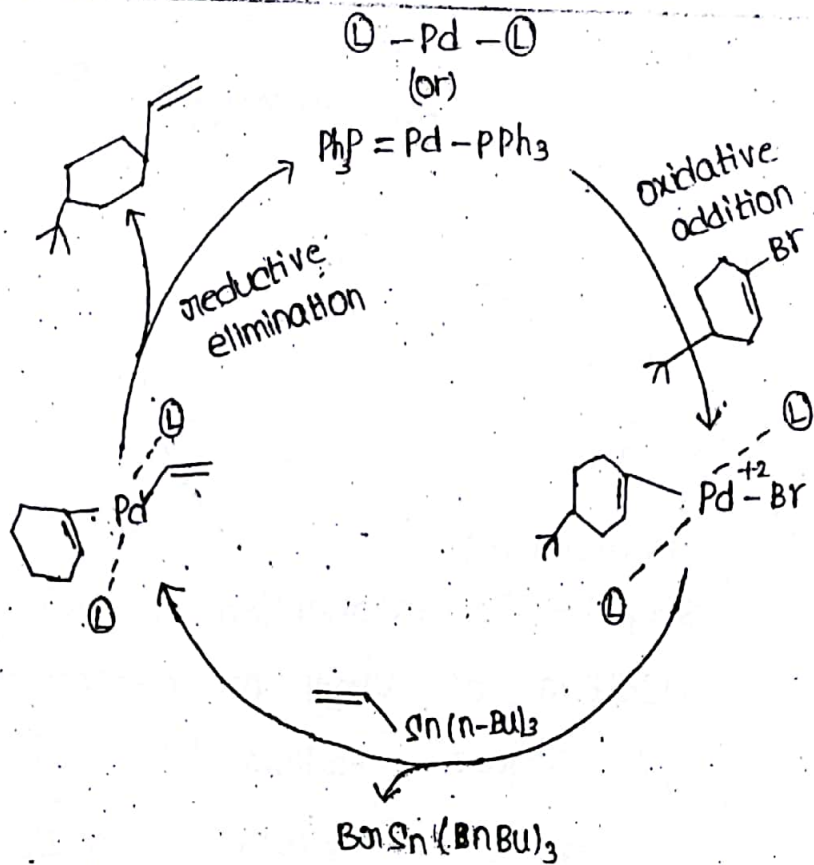
Step-V:- Finally palladium is removed through reductive elimination producing final phenyl aceto phenone.



8) Stille - coupling reaction:-

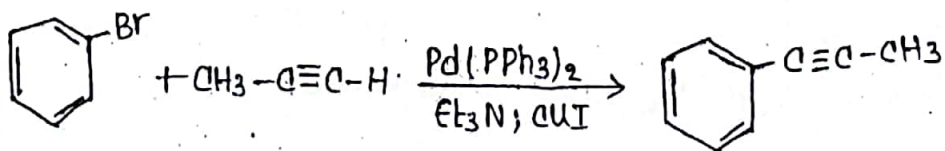
In this reaction aryl stannanes reacts with aryl or aliphatic halides in presence of palladium catalyst gives a new C-C bond formation coupling compound and it is widely used in the natural products.

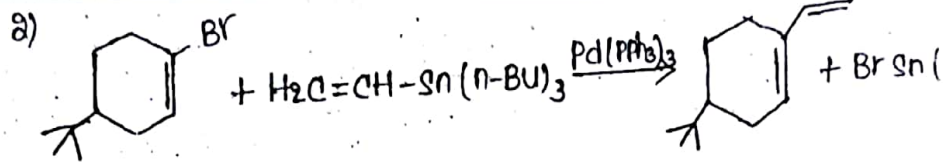




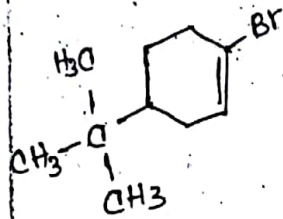
9) Sonogashira coupling reaction:-

It is the coupling of terminal alkynes with vinyl or aryl halides in presence of palladium catalyst, copper as a co-catalyst and amine base as a solvent. It is also called as sp^2 - sp coupling.





(or)



Mechanism:-

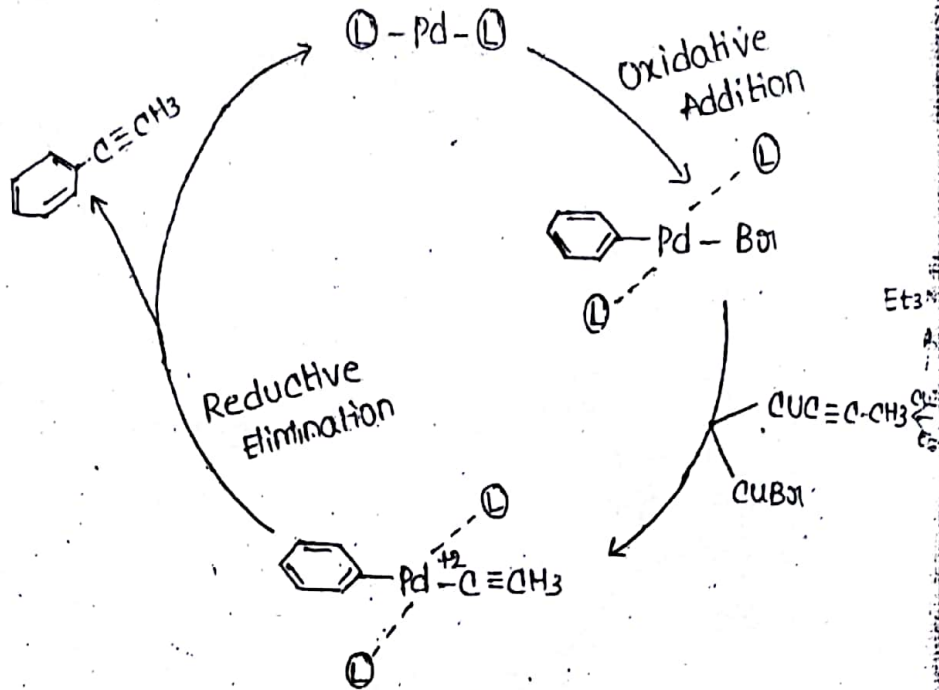
Step-I:- The mechanism involves the oxidative addition of vinyl or aromatic halides to give organo palladium intermediate.

Step-II:- Trans metalation with organo stannane forms another organo palladium intermediate with σ -palladium carbon (σ) sigma bond.

Step-III:-

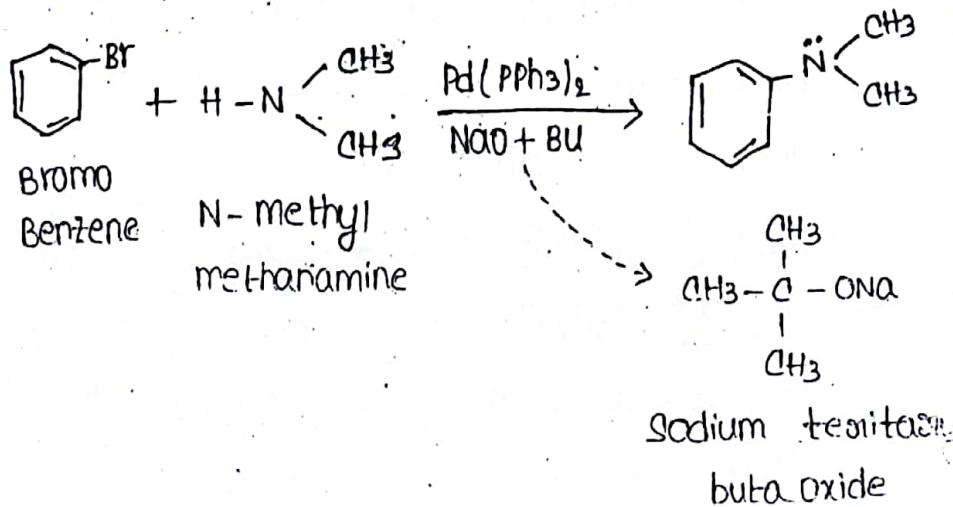
Reductive elimination releases the product and regenerate palladium product.

Mechanism:-

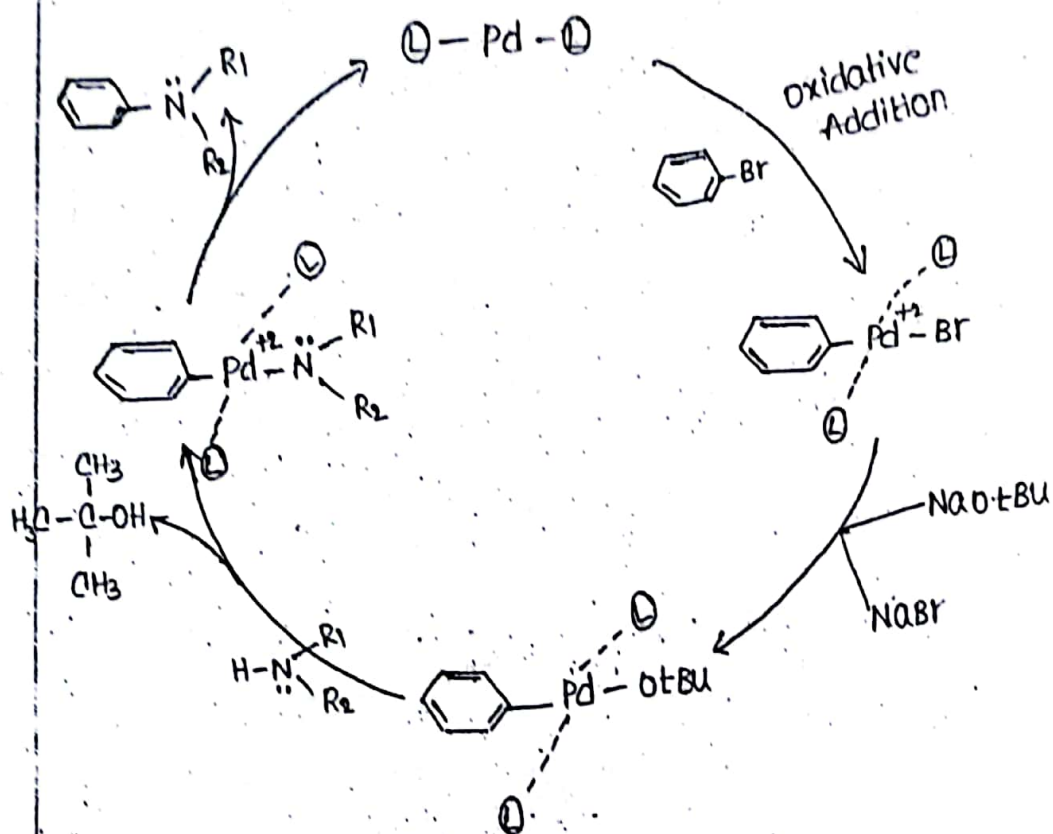


10) Buchwald Hasting Coupling Reaction:-

It is a chemical reaction in organic chemistry for the synthesis of carbon nitrogen bond compounds by the coupling reaction of amines with aryl halides in presence of palladium catalyst.



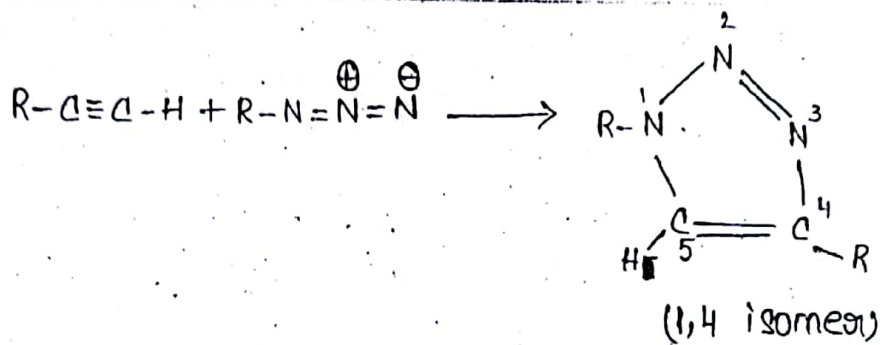
Mechanism:-



11) click reaction:-

The term click chemistry applies to reactions that are highly efficient wide in scope and product isolation is easy, the reactions are simple to perform using inexpensive reagents and can be conducted in simple solvents such as water.

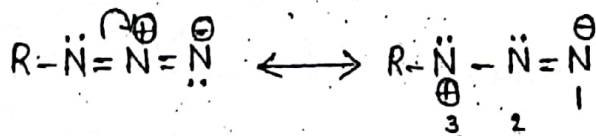
Definition:- 1-3 Dipolar cyclo addition of terminal alkynes with alkyl azide in presence of copper catalyst gives cyclic compound (1,4 Isomer)



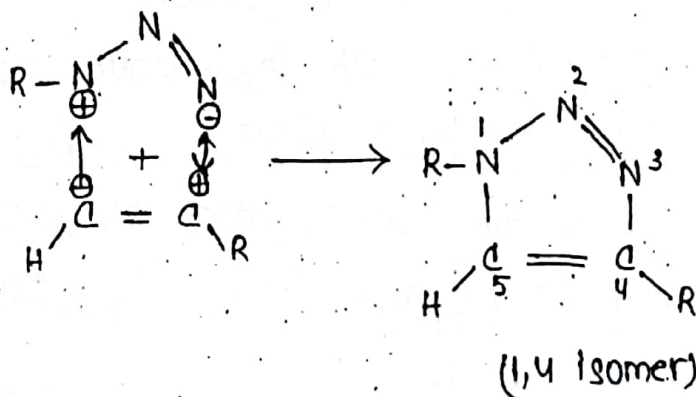
Mechanism:-

The mechanism of the click reaction involves the following steps,

Step-1:-



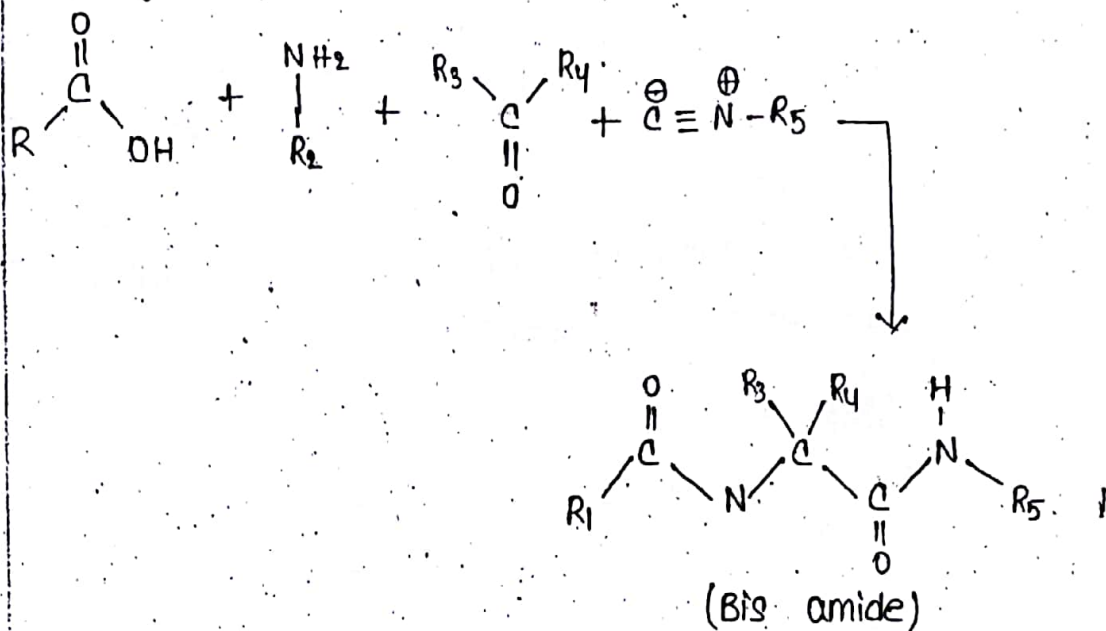
Step-II:-



B. Benzenes
terminal
of
is
puno.

reported this reaction
powerful tool in drug

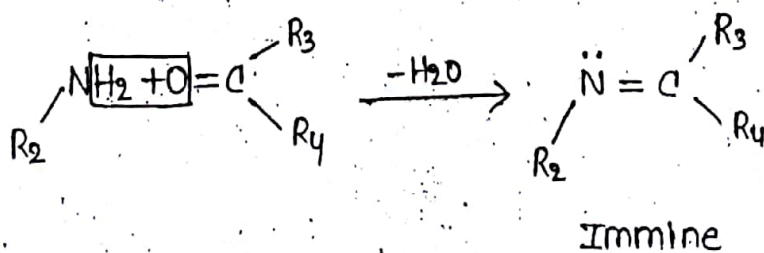
a ketone or Aldehyde amine, Isocyanide and carboxylic acid to form a Bis amide.



Mechanism:-

The mechanism of the above reaction involves the following four steps.

Step-1:- Nucleophilic addition of amine on carbonyl compounds forms ~~an~~ Imine.



Step-11:- The imine accepts the proton from acid gives Imminium ion and carboxylate ion.

Organic photochemistry

Introduction- The branch of chemistry which deals with study of chemical as well as physical changes initiated by light is known as photochemistry.

Chemical change:-

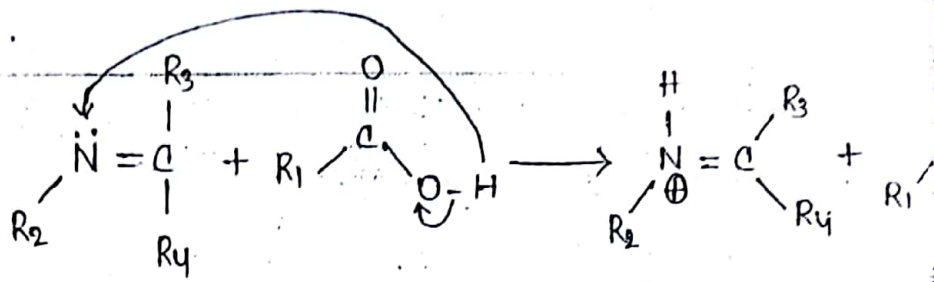
The formation of new chemical species by the consumption of reacting ones.

Principle

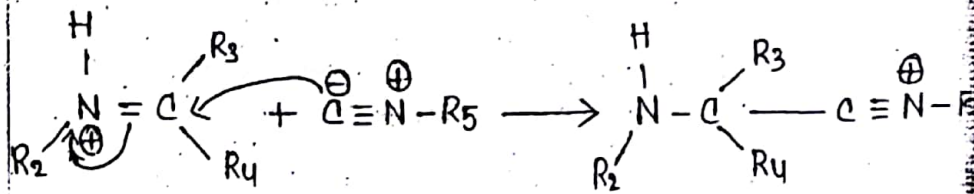
The phenomena in which energy get released in different ways (fluorescence, phosphorescence, photosensitization) other than chemical change.

Photochemistry have a no. of applications in the field of science and technology. A lot of synthetically important reactions which cannot be carried out in dark proceed photochemically.

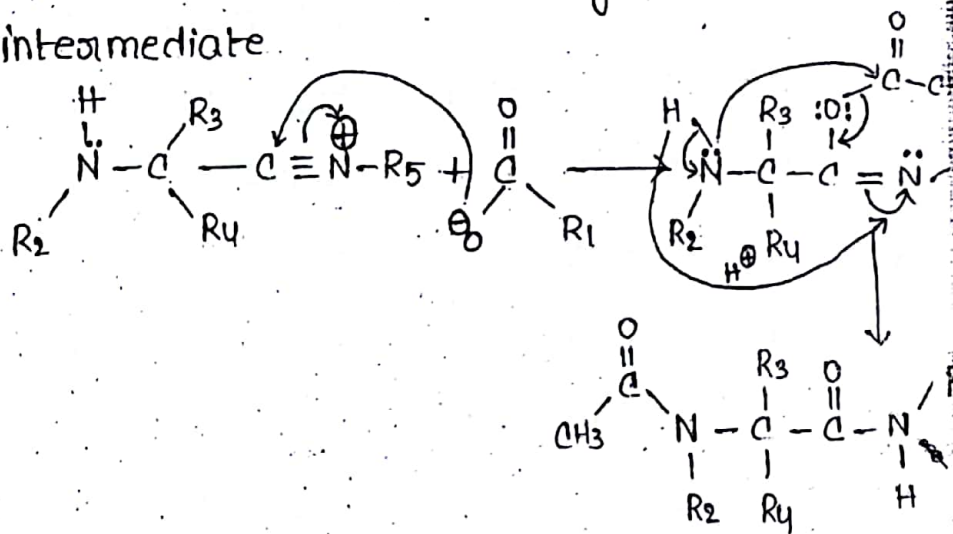
Ex:- Synthesis of Vitamin D with in the body, it is formed in the presence of sunlight only.



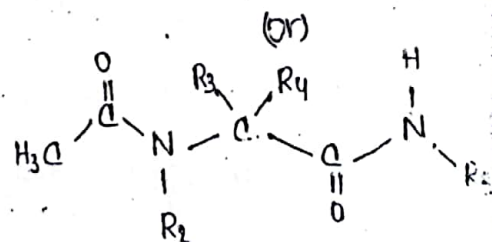
Step-III:- The nucleophilic attack of isocyanide ion on imine gives an intermediate compound.



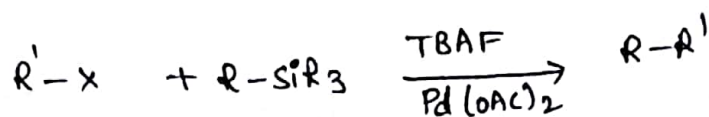
Step-IV:- Attack of carboxylate ion on intermediate.



Pudis
NE-21 shi coupling,
Hi Yamu coupling



* Hiyama coupling :- The Hiyama coupling is a palladium-catalysed cross-coupling reaction of organosilanes with organic halides used in organic chemistry to form carbon-carbon bonds (C-C bonds).



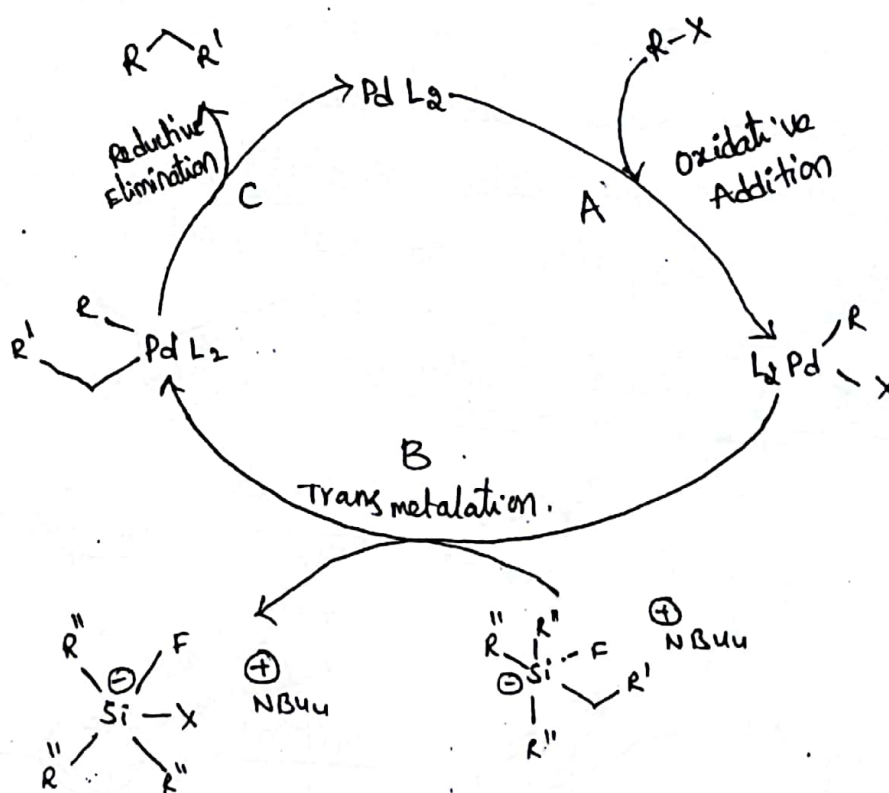
R = Aryl

R' = Aryl

X = Br

SiR₃ = SiMe₃.

Mechanism:-



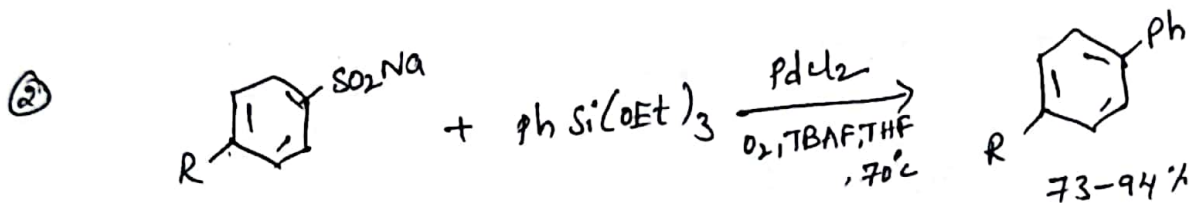
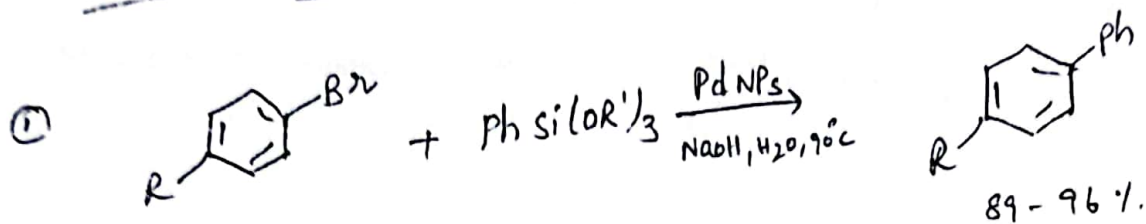
Named after:- Tamejiro Hiyama

Reaction type:- coupling reaction

RSC ontology ID:- RXNO:0000193.

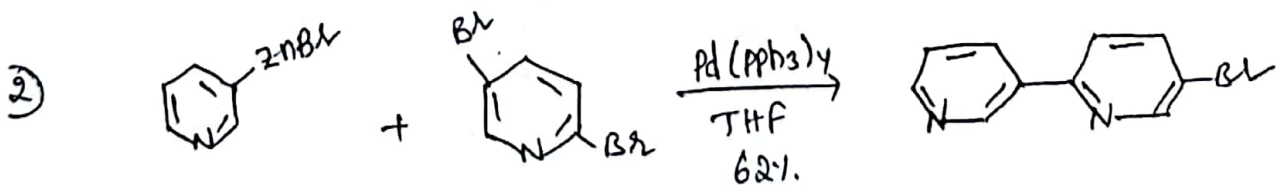
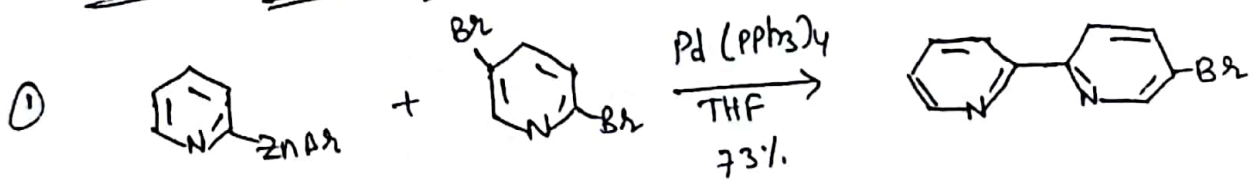
Similar reaction:- Hiyama-Denmark coupling.

* Application of Miyama coupling :-

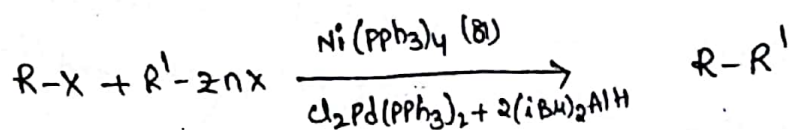


The Miyama coupling can be applied to the formation of $C_{sp^2} - C_{sp^2}$ (e.g.:- aryl-aryl) bonds as well as $C_{sp^2} - C_{sp^3}$ (e.g.:- aryl-alkyl) bonds. Good synthetic yields are obtained with couplings of aryl halides, vinyl halides, and allylic halides, and organo iodides afford the best yields.

* Application of Negishi coupling :-



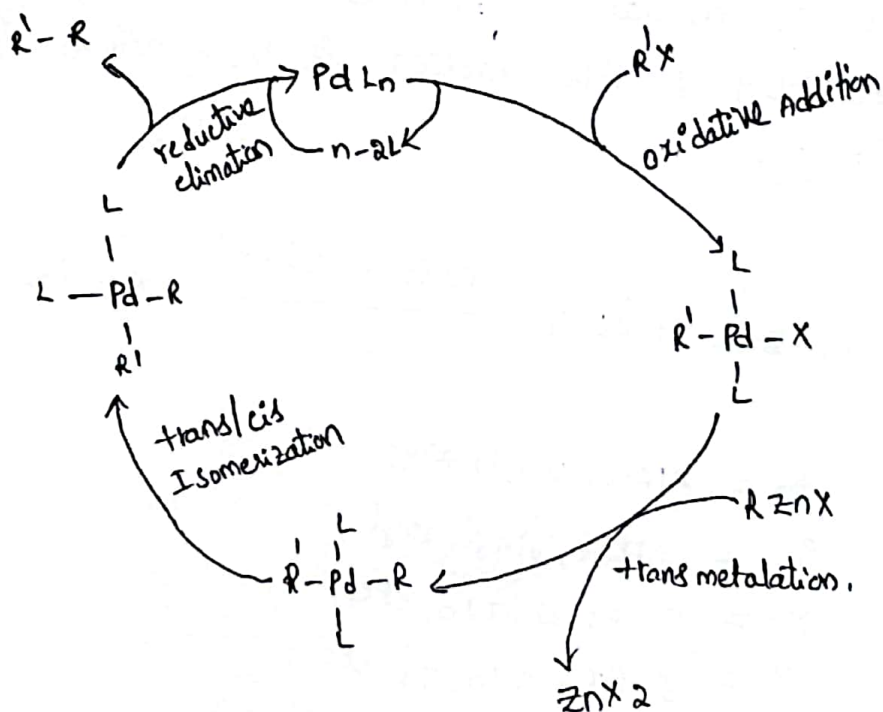
Negishi coupling :- The Negishi coupling, published in 1977, was the 1st reaction that allowed the preparation of unsymmetrical biaryls in good yields. The versatile nickel (or) palladium catalyzed coupling of organozinc compounds with various halides (aryl, vinyl, benzyl, & allyl) has broad scope, and is not restricted to the formation of biaryls.



R = alkenyl, aryl, allyl, benzyl, propargyl

R' = alkenyl, aryl, alkynyl, alkyl, benzyl, allyl.

Mechanism of Negishi coupling :-

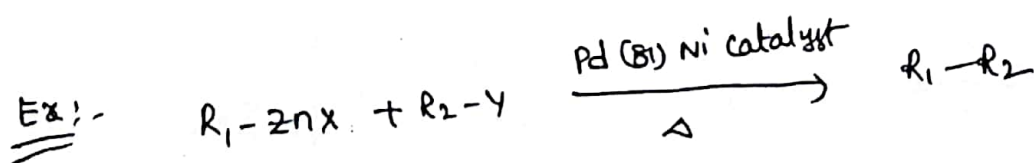


Industrial applications :- The Negishi coupling was used as an alternative to the Suzuki reaction providing improved yields, 73% on a 4.5 kg scale, of the desired benzodioxazole synthetic intermediate.

Examples of nickel catalyzed Negishi couplings include sp^2-sp^2 , sp^2-sp^3 , and sp^3-sp^3 systems. In the system first studied by Negishi aryl-aryl cross coupling was catalyzed by $Ni(PPh_3)_4$ generated in situ through reduction of $Ni(acac)_2$ with PPh_3 and $(i-Bu)_2AlH$.

Application :-

Negishi coupling reaction is not only restricted to the formation of biaryls rather it's been widely used for the synthesis of natural & pharmaceutical products. It is due to the potentiality of this reaction for the formation of carbon-carbon bonds.



where,
 $R_1 = \text{Alkyl, vinyl, aryl}$
 $R_2 = \text{Alkyl, vinyl, aryl}$
 $X = I, Br, Cl, Tfo, etc$
 $Y = I, Br, Tfo, Ts etc.$

IVth sem

UNIT-II

NANO CHEMISTRY

Synthesis of CNT's :-

To produce CNT's the following techniques have been developed.

They are: 1. Arc discharge (or) Arc evaporation

2. Laser ablation (or) Laser vapourisation

3. Chemical vapour deposition (CVD).

1. Most of the process takes place in vacuum (or) at atmospheric pressure with process gases.
2. CVD growth of CNT's can occur in vacuum or at atmospheric pressure.
3. Large quantities of nanotubes can be synthesised by these methods.
4. CNT's can be modified during post-growth treatment such as purification and annealing.

① @ Arc evaporation synthesis of MWCNT's :-

1. In this method, electrodes are two graphite rods with high purity.
2. The anode is a long rod of approximately 6mm in diameter and cathode is a short rod of 4mm in diameter.

→ 70

5. To producing good quality of nanotubes, it efficient water cooling of the cathode is essential.
4. The position of anode is usually adjustable from outside the chamber to maintain constant parameters during arc or evaporation.
5. Arc-discharge or discharge is carried out at 20V (with current in the range of 50-100 Amp).
6. A key factor in producing high yield of CNT is the pressure of "He".
7. If the pressure of "He" is below 100 Torr, the rate is optimum cond. for the production of C₆₀.
At a pressure of 100 Torr, the yields of nanotubes improved.
8. At finally (or) as a result deposition of fullerene soot takes place on the walls of vessel, and the formation of a hard cylindrical CNT deposit on the cathodic rod.
9. It is the central part of the depositor that contains CNT.

① Arc evaporation synthesis of single walled nano tubes :-

- ① SWNT's are formed by arc-evaporation; when a metal catalyst (Co, Fe, Ni) is added to one of the graphite electrodes.
- ② SWNT's are deposited on the walls of arc-evaporation vessel. SWNT's have diameters of around "1nm".
SWNT's are much more uniform in size than MWNT's
- ③ SWNT's which are produced by arc-evaporation, are invariably accompanied by amorphous "carbon" and "metal" particles.
- ④ Higher yields of SWCNT's are obtained (achieved) by using "Ni/Yt" mixture as a catalyst. than pure metal.
- ⑤ Ratio of metals in bimetallic catalyst (metal mixture) can have strong effect on both yield & diameter distribution of CNT's.

~~② The Arc evaporation vessel~~

- ⑥ The gas pressure in arc-evaporation vessel can, also have strong influence on SWNT yield.

② Laser-vapourisation synthesis (Laser ablation) :-

- ① The furnace is heated to a temperature of approximately 1200°C .
- ② And inert gas (Argon) flows through the 5cm diameter tube at a constant pressure of 500 Torr.
- ③ A cylindrical graphite target (rod) doped with small amount of metal catalyst (0.5 - 1% each of Ni & Co) is mounted (placed) at the centre of the furnace.
- ④ vapourisation of the target is performed by a Nd: YAG (Neodymium - yttrium - Aluminium - Garnet) laser.
- ⑤ In a refinement of the process a double laser pulse is used. (To provide more vapourisation of target).
- ⑥ Several groups have studied the effect of over temp. on NT yield.
All have shown that the yield is very low at temp below 6°

but $1100-1200^{\circ}\text{C}$ is the optimum temp. for the production of good yield of CNT's

③ (a) Synthesis by Chemical Vapor Deposition: (CVD method)

Principle: This method is based on the thermal decomposition of hydrocarbon gas over a transition metal catalyst to grow nanotubes in a reactor

1. In CVD process, A substrate is prepared with a layer of metal catalyst particles.
(most commonly used catalysts Ni, Co, Fe or combination)
2. metal nano particles can also be produced by, redⁿ of oxides or solid solⁿ of oxides
3. The diameters of nanotubes related to size of metal particles.
4. This can be controlled by (patterned) deposition of the metal, by annealing, or by plasma etching of metal layer.
5. The substrate is heated to approximately 700°C .
6. To initiate growth of nanotubes two gases are bled (send) into the reactor.
a process gas (NH_3 , N_2 or H_2) and carbon containing gas ($\text{CH}\equiv\text{CH}$, $\text{C}_2\text{H}_2=\text{CH}_2$, $\text{C}_2\text{H}_5\text{OH}$, or C_2H_4).
7. Nanotubes grow at the sites of the metal catalyst.
8. Carbon containing gas is broken apart at the surface of the catalyst particle and carbon is transported to the edges of the particle, where it forms nanotubes.
9. Thermal catalytic decomposition of hydrocarbon has become an active area of research and for the bulk production of CNT's.

II. SWNT growth in Arc-evaporation and Laser - vapourisation: catalyst activated growth:

1. The mechanisms of SWNT formation in Arc-evaporation and laser vapourisation process are similar.
2. Both use similar starting materials namely a graphite-metal mixture, and both involve the vapourisation of this mixture followed by condensation in an inert atmosphere.
3. The nanotube containing soot produced by both methods is identical in appearance. (bundles of SWNT's together with disordered C & metal particles)
4. Hence the mechanisms proposed for one process are applicable to both.
5. Although many different models have been put forward for the growth of SWNT's but most probably preferred method is that "root growth" rather than "tip growth".
6. ^{***} The popularly VLS ^{method} was put forward by "Saito" in 1995 to explain SWCNT growth in the arc-evaporation.
7. The first stage involves the co condensation of carbon and metal atoms from vapour phase to form a liquid metal-carbide particle.
- ∴ When the particles are super saturated, solid phase nanotubes begin to grow.

9. The first evidence for solid state growth of SWNT was given by Geohagan in 2001.
10. When they were preparing SWNTs by Nd:YAG laser vapourisation of a graphite/Ni-Co target ✓
- (11. They observed, NT growth did not occur in early stages when carbon was in vapour phase, but at a later stages, it occurs as clusters, nanoparticles. (during)
12. The ~~other~~ ^{Gorbunov} groups also prepared SWNT by using laser-vapourisation, at low temp. to induce NT formation. This SWNT was annealed at 1200°C in "Ar" atmosphere.
13. On the basis of above observation, they put forward a growth model in which (a) which involves the conversion of solid "disordered carbon" into NTs. (via liquid phase metal particles).
14. The mechanism named as SLS (Solid-liquid-solida).
- * 15. (a) The first stage involves a molten catalyst nanoparticle penetrating a disordered carbon aggregate dissolving it.
 - (b) And precipitating carbon atoms at the opp. surface.
 - (c) These atoms then form a graphene sheet whose orientation is // to super saturated ^{metal} _{carbon} melt.

is not energetically favourable

③ ⑥. In Super-growth CVD (water-assisted chemical vapour deposition) process, the activity and lifetime of the catalyst are enhanced by addⁿ of water into CVD reactor.

2. Dense millimetre-tall nanotube growths (forests), aligned normal to substrate were produced.
3. The synthesis efficiency is about 100 times higher than the laser ablation method.
4. The Super-growth CVD method is basically variation of CVD. The SWNTs, DWNTs, & MWNTs growth can be changed by (alter their ratios by tuning growth condⁿs). Change of ratios by the thickness of the catalyst.

④ Synthesis with controlled orientation :-

- ① In CVD method, if a plasma is generated by the application of a strong electric field during growth process (plasma enhanced CVD).
- ② Then the nanotube growth "will ^{follow} flow" in the direction of electric field.
- ③ By adjusting the geometry of reactor it is possible to synthesise vertically aligned CNTs (↑ r to substrate)
- ④ Without plasma, the resulting nanotubes are randomly oriented.

- (5) In Super-growth CVD process, the activity and lifetime of the catalyst are enhanced by addⁿ of water into CVD reactor, and also dense millimetre-tall nanotube forests aligned normal to the substrate, were produced.
- (6) These SWNT forests can be easily separated from the catalyst, yielding clean SWNT material (>99.98% purity) without further purification.
- (7) By the Super-growth technique, patterned highly organised SWNT structures were successfully generated.

Growth mechanisms of CNT's :-

(1) Multi-walled nanotube growth by arc-evaporation :-
 - Catalyst free growth :-

(a) Vapour phase growth :-

1. The most detailed analysis of the gas phase nucleation and growth of MWCNT's in the arc was given by Gamaly and "Ebbesen" in 1995.
2. They assumed that the nanotubes and nanoparticles are formed in the region of the arc (next to the cathode surface)
3. They suggested that in this layer, vapour of carbon particles will be 2 groups of carbon particles with different velocity distributions.
4. One group of carbon particles will have an isotropic velocity distribution corresponding to the temp. of the arc (~3700°C).
5. The other group (of particles) is composed of ions accelerated in the gap b/w +ve space (anode) & -ve space (cathode).

6. The velocity of these carbon particles will be much greater than those of the thermal particles (and in this case flux will be directed rather than isotropic)
7. The process of nanotube formation is considered to occur in three stages:
 8. In the first stage, the isotropic velocity distribution results in the formation of equiaxed structures such as nanoparticles.
 9. As the current becomes more directed open structures begin to form. (which are considered to be seeds for NT growth).
 10. In the second stage, a stream of carbon ions flows in a direction \perp to the cathode surface results in a rapid growth of NTs.
 11. In 3rd stage, finally instabilities in the arc-discharge lead to abrupt termination of NT growth (by the formation of caps)
12. Vapour phase growth mechanism suggested that, nanoparticles form in the early stages of arcing, (when the velocity distribution of carbon particles is isotropic).
13. It is well established that MWCNT's very similar structure to those produced by arc-evaporation (which can be formed from pure carbon by simple heating).

(b) Liquid phase growth :-

1. The liquid phase model of MWNT growth was put forward by De Heer et al in 2005.
2. When the arc discharge is initiated, the carbon anode is locally heated by electron bombardment from the cathode.
3. Resulting the surface to locally liquify and liquid carbon "globules" to be ejected from anode.
4. Initially becoz of high vapour pressure of liquid carbon, the surface of globules will evaporate, cooling rapidly.
5. However, the cooling of the interior of the "globule" occurs much more slowly.
6. This causes the liquid carbon to super cool.
7. It is within this super cooled liquid carbon that CNT's & nano particles are "envisaged" to homogeneously nucleate & grow.

(c) Solid phase growth :- (Arc - evaporation)

1. In the initial stages, carbon is in the vapour phase (C_2 species).
2. This vapour phase carbon condense onto the cathode as a fullerene soot like material.
3. This condensed carbon then experiences extremely high temp. as the arcing process continues, results in the formation of nanotube seeds and then MWNT.
4. Growth of MWNT's terminates when the sample of carbon exhausted (or) when arcing finishes.
5. It requires rapid heating to high temp. slow heating of fullerene soot results in formation of C₆₀ nano part.

1. The third study of SWCNTS by solid phase growth described by "Kataura"

2. Here soot was obtained by laser-ablation of Ni-Co-graphite composite targets at the temp. in the range of 25-700°C

3. The soot was then heated to 1200°C in Ar. gas.

4. The soot formed at or after 1200°C is original (before low temp did not)

5. on the basis of these observations, "Kataura" proposed a model for SWCNT growth which is similar to "Geohagan" mechanism)

1. In the first phase occurs at very high temp 2000-3000°C a small carbon clusters nucleate. these have fullerene-like structure, rich in pentagonal rings.

2. At this stage, metal atoms are still in the gas phase, as the system cools, metal atoms condense, forming particles & droplets

3. And becomes super saturated with carbon at around eutectic temp.

4. The particles then became covered with fullerene like carbon fragments.

5. The 'C' atoms then act as precursors for growth of SWCNT, with 'C' atoms being supplied by pptating from the particles or from disordered 'C' which surrounds the particle.

* Properties of CNT's

① Mechanical properties :-

- 1) Carbon nanotubes are long hollow cylinders of graphite sheets of 10^{-9} m diameter.
- 2) They have different properties in axial and radial directions.

② Axial properties :-

- 1) These are very strong in axial direction with a strength per weight ratio.
- 2) Strength per weight ratio is greater than any engineering material.
- 3) CNT's has high tensile strength.
- 4) Even impure materials can be used, to make them as light weight fibres and for strengthening of plastic & also used to prepare ceramic and metal composites.
- 5) Due to high tensile strength, the microscopic or macroscopic bundles of CNT's are used in satellites in future.
- 6) They can deform & they undergo deformation, when force is applied and they regain its original position after removing force. (Strain).

Radial properties :-

- 1) These are soft in the radial direction.
- 2) These undergoes deformation very easily by vander Waals forces in radial direction.
- 3) vander Waals forces can also deform the two adjacent NT's in radial direction.

Electrical properties :-

1. The CNT with helical twist in structure are acting as exhibits semiconducting properties.
2. Achiral CNT are metallic in nature & exhibit metallic properties.
3. SWCNTs are used in the molecular electronics.
4. SWCNT with a length of 100nm are used in field effect transistors.

Optical properties :-

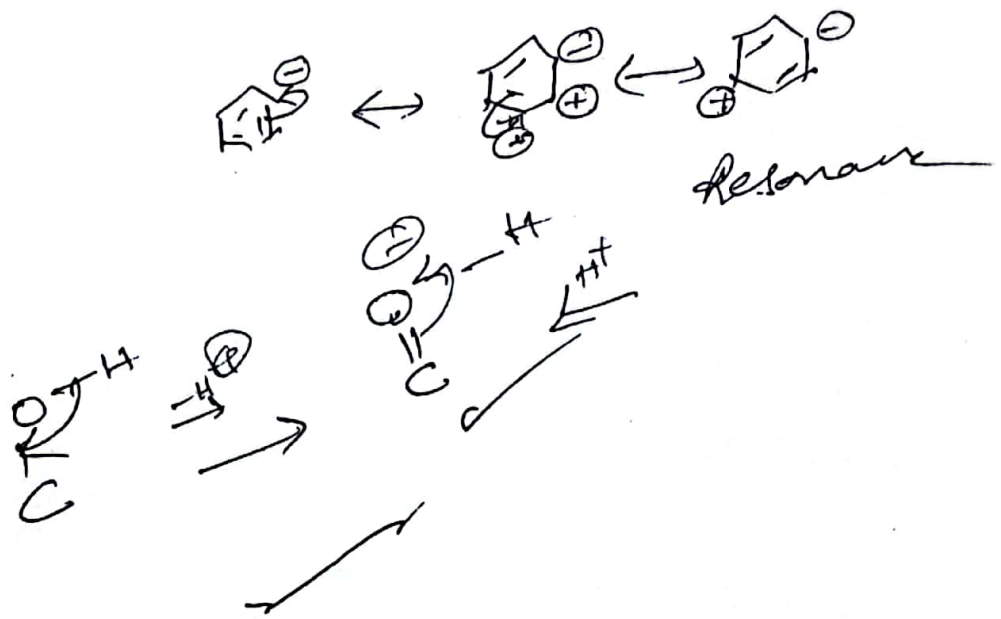
1. CNTs are used in the, absorption spectra, photoluminescence, and in Raman spectroscopy.
2. SWCNTs are used in the optics, & photonics.
3. particularly in light emitting diode (LED's) & in photodetectors.
4. These are used for selectivity in wave length of emission & detection of light.
5. The bundling of NT's has strongly effects on photoluminescence and weaker effect on optical absorption & raman scattering.

6. optical absorption is used to quantify quality of NT's powders.

7. NT's ^{related} peaks spectrum is analysed in terms of intensities.

Reactivity of CNT's :-

- ① NT's can be dispersed in a solvent using ultra sound but strong Vanderwaals interacting between walls make them quickly precipitate.
- ② Oxidⁿ using nitric acid & other strong acid open the end of NT's. & introduce carboxylate functionalities.
- ③ This process gives solubility in polar solvents.
- ④ Several chemical reagents can be done to functionalise the walls of CNT's. but these reagents causes to atomic defects in their structures.
- ⑤ To functionalise CNT's, with minimum disruption of their properties; non covalent methods have been advantages.
- ⑥ A simple & inexpensive method for is, treating of CNT's with starch, when NT's are exposed to starch solⁿ.
- ⑦ This starch biomolecules surrounds to CNT's by Vander ~~walls~~ waals forces for maintaining in solubilised state. for extended period of time.
- ⑧ The reprecipitation of CNT's can be done by adding ^{of} enzyme amylase which breaks down the bonds b/w starch & NT's.



The overall chemical reactivity of CNTs should strongly depend on the way they are synthesized.

Ex: SWNTs prepared by the electric-arc discharge method are supposed to contain less structural defects compared to CCVD-synthesized SWNTs which have a higher chemical reactivity.

→ The reactivity of MWNTs is very higher due to the occurrence of graphene edges at the nanotube surface.

Applications of carbon nanotubes

Applications of nanochemistry

→ Structural applications

① Because of carbon nanotube's mechanical properties, many structures have been proposed ranging from everyday items like clothes & sports wear to combat jackets, space elevators (i.e. a space elevator is used to transport a material from earth's surface into the space).

② CNTs are also a material as building blocks in bio-matrix composite materials.

③ Because of high mechanical structure of CNTs used in the manufacture of stab-proof & bulletproof clothing, the nanotubes would effectively stop the bullet from penetrating the body although the bullet's kinetic energy.

Carbon nanotubes have great potential applications in making ballistic-resistance materials.

→ ~~the next~~

Yamajō

→ Electronic applications :-

- ① Nanotube based transistor known as CNT field-effect transistors (CNFETs) have been made that are capable of digital switching.
- ② Depending on surface features a nanotube may act as a plain conductor or as a semiconductor.
- ③ Large structures of CNTs can be used for thermal management of electronic circuits. ~ 1mm thick CNT layer was used as a special material to fabricate overall, incorporating CNTs as transistors in to logic-gate circuits.

→ Electrical applications

- ① wires for carrying electric current may be fabricated from pure nanotubes & nanotube-polymer composites. Recently, small wires have been fabricated with high specific conductivity than Cu & Al.
- ② these cables are the highest conducting CNTs & also highest conductivity non-metal cables.

→ The CNTs act as electrodes in batteries, allowing the storage devices to conduct electricity. This battery functions as both a lithium ion & a super capacitor & can provide a long, steady power output than the normal batteries & normal super capacitors.

④ Solar cells

A mixture of CNTs & carbon buckyballs (fullerens) to form snake like structures used in the solar cells. Bucky balls trap e^- & stops the e^- flow. The sunlight excites the polymer & ^{then} buckyballs will hold the e^- . CNTs behaving like Cu wires then they able to make the current flow.

⑤ Medical applications

① In the cancer therapy, SWNTs are inserted around the cancerous cells, then excited with radio waves, which causes them to heat up & kill the surrounding cancerous cell. This method is useful in Bone cancer therapy & Kaposi's cancer therapy.

② Some nanodrugs, medical devices, ~~biomaterials~~ which are used widely in medical fields now a days.

③ There are many researches are undergoing in nanobiotechnology.

⑧ Engineering applications

- ① CNTs have been used in nanoelectromechanical systems & nanoscale electric motors (nanomotors).
- ② Electrical conductive films of CNTs to replace Indium tin oxide (ITO) making them ideal for high reliability touch screens & flexible displays. These nanotube films are used in computers, cellphones, ATM, personal digital assistant (PDA)
- ③ printable water-based inks of CNTs are desired to enable the production of these films.
- ④ Nanoradio, a radio receiver consisting a single nanotube can operate as loudspeaker, if an AC is applied.
- ⑤ A flywheel made of CNTs has extremely high velocity which can potentially store energy at a density nearly similar to fossil fuels used in the electrical power grids.

⑦ Fuel cell

- Nitrogen doped CNTs may replace Pt catalyst used to reduce O_2 in fuel cells.
- vertically aligned CNTs can reduce O_2 in alkaline soln more effectively than Pt.

⑧ Military & security applications

- CNTs have important applications in the manufacturing

of bio-sensors, weapons & bullet proof jackets & bullet proof vehicles used by the ~~scans~~ military people.

⑨ Chemicals & materials :-

- CNTs are used in the manufacturing of nanoscale chemicals & compounds, paints, coating materials, biopolymers etc.
- Nanochemistry will focus on all aspects of fuel production, mainly on fuel cells & biofuels with greater fuel efficiency.
- High power magnets, Longer-lasting satellites, Ductile & machinable ceramics, Tougher & harder cutting tools & catalysis fields are some other major applications of CNTs in different industries.

SEMESTER - IV

UNIT - III

V.R.S. & Y.R.N. COLLEGE : CHIRALA.

M.Sc. Chemistry - Semester IV - Paper-II (From 2010-11)

Organic Synthesis, Mechanisms & Green Chemistry
microwave Organic synthesis.
UNIT-III : Green Chemistry & Photochemistry

Green Chemistry

1. Introduction

Green Chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances. Thus, it seeks to reduce and prevent pollution at its source.

The term "Green Chemistry" was coined by Paul Anastas in 1991. It is defined by Paul Anastas and John Warner as "the utilization of a set of principles that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and application of chemical products".

In 2005 Ryoji Nozori identified three key developments in green chemistry: use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations and the use of hydrogen in asymmetric synthesis. Examples of applied green chemistry are supercritical water oxidation, on water reactions, and dry media reactions.

The green chemistry stands to contribute critical tools for redesigning production, and for putting into practice a philosophy of sustainability. New materials and technologies for industrial and consumer uses are already routinely developed on the molecular level by chemists.

The next step is to learn how to simultaneously consider

toxicity, safety, environmental fate and lifecycle along with function, use and cost when developing new substances and technologies; to learn how to eliminate waste before it is generated, by developing materials that are integrated into material cycles by design. With common consumer products increasingly being implicated as health hazards, and with global chemical production occurring on the scale of billions of tons per year, green chemistry and sustainable design are highly relevant research areas that have a great potential for beneficial impact.

2. Principles

Paul Anastas and John Warner developed 12 principles of green chemistry which help to explain what the definition means in practice. The principles cover such concepts as:

- the design of processes to maximize the amount of raw material that ends up in the product;
- the use of safe, environment-benign substances, including solvents, whenever possible;
- the design of energy efficient processes;
- the best form of waste disposal: not to create it in the first place.

The 12 principles are:

1. Prevent waste: Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. Design safer chemicals and products: Design chemical products to be fully effective, yet have little or no toxicity.
3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to humans and the environment.

4. Use renewable feedstock: Use raw materials and feedstock that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

5. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.

6. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

7. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.

8. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals. If a solvent is necessary, water is a good medium as well as certain eco-friendly solvents that do not contribute to smog formation or destroy the ozone.

9. Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible.

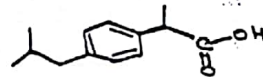
10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

11. Analyse in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

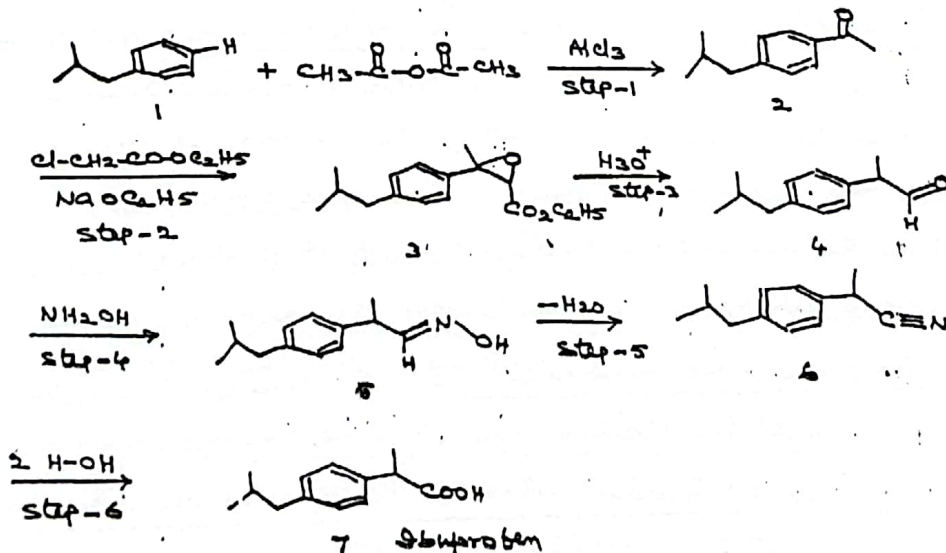
13. Examples of Green Reactions

(i) Synthesis of Ibuprofen



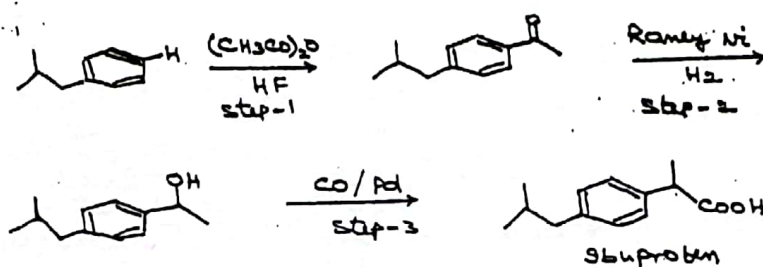
The Boots Company synthesis - The Brown synthesis 2-(4-isobutyl phenyl) Propionic acid

The synthesis of Ibuprofen is a popular case study in green chemistry. The original Boots synthesis (conventional method) of ibuprofen consisted of six steps, started with the Friedel-Crafts acylation of isobutyl benzene. Reaction with ethyl chloroacetate gave the α, β -epoxy ester, which was hydrolysed and decarboxylated to the aldehyde. Reaction with hydroxylamine gave the oxime, which was converted to the nitrile, then hydrolysed to the desired acid.



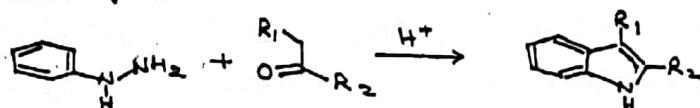
The Green Synthesis of Ibuprofen

The green synthesis of ibuprofen required only three steps. After a similar acetylation of isobutyl benzene, hydrogenation with Raney nickel gave the alcohol, which underwent palladium-catalysed carbonylation to form ibuprofen.



(ii) Fischer-Indole Synthesis

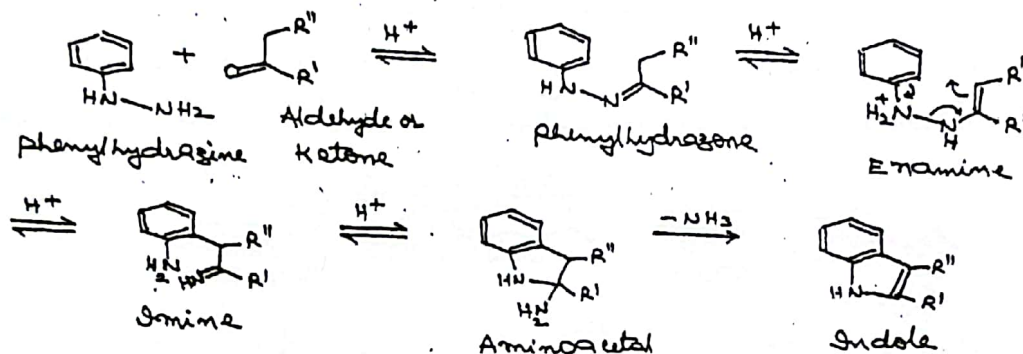
The Fischer-indole synthesis is a chemical reaction that produces the aromatic heterocycle indole from a (substituted) phenylhydrazine and an aldehyde or ketone under acidic conditions. The reaction was discovered in 1883 by Emil Fischer.



The choice of acid catalyst is very important. Brønsted acids such as HCl, H_2SO_4 , polyphosphoric acid and p-toluene sulphonic acid have been used successfully. Lewis acids such as boron trifluoride, zinc chloride, iron chloride, and aluminium chloride are also useful catalysts.

Reaction Mechanism: The reaction of a (substituted) phenylhydrazine with an aldehyde or ketone initially forms a phenylhydrazone which isomerises to the respective enamine (or 'ene-hydrazone'). After protonation, a cyclic

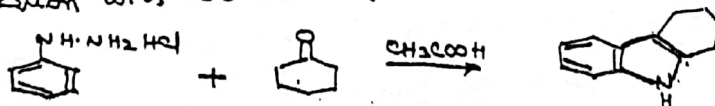
[1,3]-sigmatropic rearrangement occurs producing an imine. The resulting imine forms a cyclic aminoacetal (or aminol), which under mild catalysis ~~eliminates~~ NH_3 resulting in the energetically favourable aromatic indole.



Isotopic labelling studies show that the aryl nitrogen (N1) of the starting phenylhydrazine is incorporated into the resulting indole.

Green Fischer indole synthesis (1) clean Fischer indole synthesis

Fischer indole cyclization reaction has been conducted in three different ways in a MW oven. The Villamin group utilized montmorillonite as the absorption medium for phenylhydrazine and ketone which is then irradiated for 5 min. at 160 W to get the product. The Abramovitch group has found irradiation of preformed hydrazone in formic acid producing indoles in excellent yields. There is another report by Sridar wherein acetic acid is used as the medium and the reaction proceeds in 28 sec. with 385 fold rate acceleration with excellent yields.



Comparison of green synthesis with conventional methods

The empirical observation is that some organic reactions proceed much faster and with higher yields under microwave irradiation compared to conventional heating. Less hazardous chemicals are employed in green synthesis.

4. Introduction to Microwave Organic Synthesis

The use of microwave (MW) irradiation to carry out chemical synthesis is an upcoming field of research. The microwave region of the electromagnetic spectrum lies between IR and radio-frequency regions corresponding to wavelengths 1 cm to 1 m (frequencies of 30 GHz to 300 MHz, respectively; Giga, G = 10^9 and Mega, M = 10^6). In order not to interfere with Radar transmissions and telecommunications, domestic and industrial microwave heaters are required to operate at either 12.2 cm (2.45 GHz) or 32.3 cm (900 MHz). Microwave heating provides an alternative to conventional conductive heating for introducing energy into reaction.

Interaction of different materials with microwave irradiation plays an important role in application and designing of a chemical reaction. These materials can be part of apparatus and oven. They are of three types - Metals which tend to reflect microwaves; materials such as Quartz, Teflon, glass are practically transparent to microwaves and can be penetrated by them; dielectric materials which interact with microwaves to different extents, such as water, graphite etc.

Heating of Liquids

polar solvents with permanent dipoles such as water, acetic acid, DMSO, dioxan, diglyme, ethylene glycol have high dielectric constant and are good solvents for microwave assisted chemical synthesis. DMF (dimethylformamide) with its high dielectric constant ($\epsilon = 36.7$, b.p. = 154) is an efficient microwave energy transferring agent and a convenient solvent because it is claimed that they become superheated even at atmospheric pressure. This superheating of upto 25°C greater than the boiling point is caused because heating occurs not at the surface, but within the solvent. The solvent

Heating is so rapid that convection and vaporisation cannot dissipate the excess energy sufficiently.

The presence of salts in polar solvents can increase the dielectric loss and hence heating effects. Therefore addition of salts to polar solvent can also be used to get maximum heat during a chemical reaction under microwave heating.

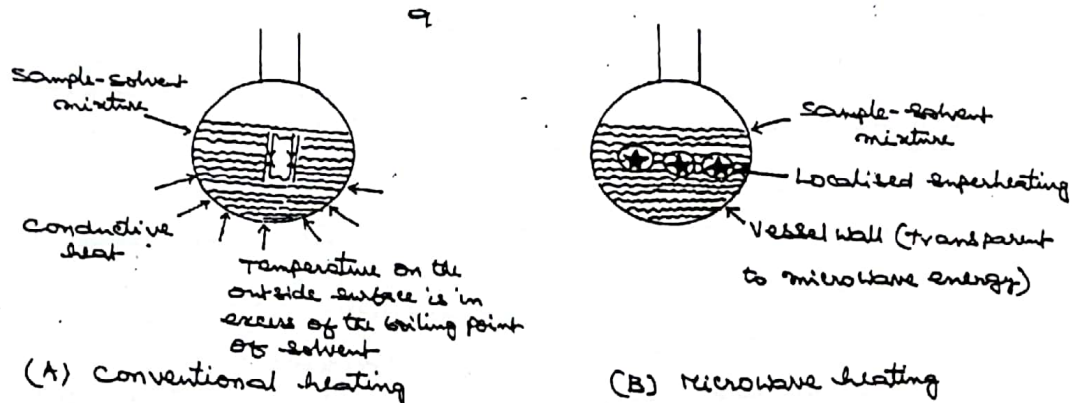
The non-polar solvents, which have no permanent dipole moment, are microwave transparent. When exposed to microwave irradiation they do not increase the temperature. Examples are benzene, petroleum ether, hexane, carbon tetrachloride, xylene etc. But these solvents can be used as microwave coolants for removing excess heat from microwave cavity. However, when a small amount of a solvent which interacts with microwave is added to these transparent solvents, it can lead to a dramatic increase in temperature of the reaction mixture, hence very useful for chemical manipulation during chemical reactions.

Heating of Solids

Dielectric properties are dependent on both the chemical composition and on the physical state of the solid material. For example, impurities, crystal defects, and the chemical nature of the material can give rise to high dielectric constants and results in strong microwave coupling. We may note that microwave frequencies correspond to rotational excitation energies in materials. Thus the incident microwave may cause rotational excitation in a material.

The difference between microwave heating and conventional heating

Microwave heating is totally different from conventional heating. In case of conventional heating the heat gradient is from the heating device to the medium while in case of microwave heating the heat is dissipated inside the irradiated medium (mass heating) and heat transfers from the medium to outside.



Again in case of conventional heating the heat transfer depends on thermal conductivity, on the temperature difference across the material and on convection currents, therefore the temperature increase is often rather slow. While in microwave heating due to the mass heating effect much faster temperature increase can be obtained depending on microwave power and the loss factor of the material being irradiated.

Microwaves heating solvents above their normal boiling points

It has been observed that liquids are superheated under microwave irradiation by 13-26°C above their conventional boiling points at atmospheric pressure. Water for example, hits 105°C instead of 100°C before boiling, and acetonitrile, another popular solvent, gets to 120°C, an amazing 38°C higher than its usual boiling point. Although microwave affords a mass heating, it is known that the field distribution is not even in the irradiated material; therefore energy is not homogeneously dissipated. This results in the formation of 'hot spots'. Hot spots occur if generation of heat is faster than heat transfer. Hot spots have actually been observed in poorly conductive solids, but could possibly occur in liquids also.

Experimental consideration

A substance can be heated by applying energy to it in the form of microwaves. In a microwave oven, radiation is generated by a magnetron. The microwaves are generated into the cavity by a waveguide and are reflected by the

walls of the cavity. If the microwaves are not absorbed, they may be reflected back down the waveguide and damage the magnetron. Thus it is essential to have a microwave active "dummy load" which will absorb excess microwaves and avoid such damage. There are a variety of methods for carrying out microwave assisted organic reactions using domestic or commercial ovens.

Type of reactions

(a) Solid-state Reactions (b) (solvent free reactions)

There are generally two types of microwave assisted dry reactions, in one of which the reagents are "supported" on a microwave inactive (or poorly active) material such as alumina or silica. In this type of reaction at least one of the reagents must be polar if the reaction is to take place by microwave irradiation. The second type of dry reaction will utilize a microwave active solid support, thus the reactants do not have to be active.

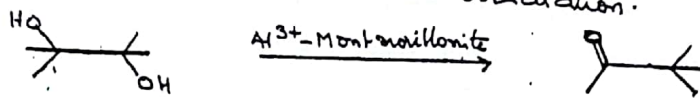
Solid-state reactions are of course very convenient from a practical viewpoint, in general the reagents and solid supports are efficiently mixed in an appropriate solvent, which is then evaporated. The adsorbed reagents are then placed in a vessel and subjected to microwave irradiation. After which the organic products are simply extracted from the support by washing and filtration. The absence of solvent coupled with high fields and short reaction times often associated with reactions of this type make these procedures very attractive syntheses.

Examples

1. Pinacol-Pinacolone rearrangement

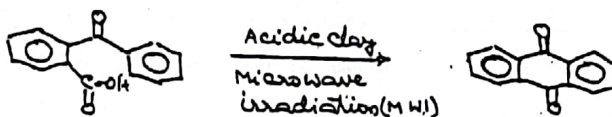
Conversion of pinacol pinacolone was carried out on a phyllosilicate (Al^{3+} -montmorillonite) as a solid support. Rearrangement took place in the intercrystalline space of sil

Charged phyllosilicates. It took 15 hrs. for conventional heating and 15 minutes for microwave irradiation.



(ii) Ring closure

It has been observed that the microwave assisted acid catalyzed cyclodehydration of *o*-benzoylbenzoic acid could be carried out to obtain anthraquinone using the same batch of catalyst without a reduction in yields (12 reactions) whereas using conventional heating the yield was around 50% after 4 reactions by using the same batch of catalyst.



(b) Solution-state reactions

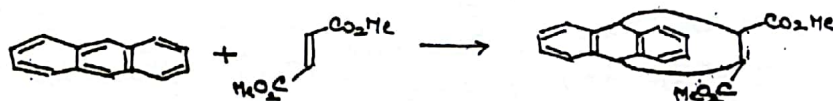
In this type of reactions, the reagents are dissolved in an organic solvent and subjected to microwave irradiation. The experimental procedure is extremely simple. The reactions could be carried out in open Erlenmeyer flasks and subjected to short periods of irradiation. This procedure could only be carried out if neither the solvent nor the reactants/products are inflammable, otherwise there is a serious risk of fire or explosion due to sparking. If one wishes to carry out a thermally driven reaction in microwave oven then one of the components must be microwave active. If neither the reagents nor solvents couple with microwaves, then we have to add a microwave active additive or supported metal catalyst to generate heat.

It is customary to choose organic solvents as a reaction medium and conduct reactions under reflux to control the temperature of the reaction. For microwave induced reactions the solvent of choice is one which absorbs microwave energy efficiently and is therefore heated rapidly under microwave

irradiation (MWI) and which has a boiling point that is at least 20-30°C higher than that of the desired reaction temperature. Any solvent having high dielectric constant and high boiling point is excellent transfer medium for a variety of microwave induced organic reactions. N,N-Dimethylformamide (DMF) is an excellent example. Using DMF as solvent ($\epsilon = 2.67$ & b.p. = 160°C) the reaction temperature can be raised to about 140°C without much vaporization of solvent. Other commonly used solvents are water, ethyl acetate, acetone, acetic acid, methanol, dichloromethane etc. ~~Hydrocarbon solvents such as hexane, benzene, toluene and xylene are unsuitable as reaction media since they absorb microwave irradiations poorly.~~

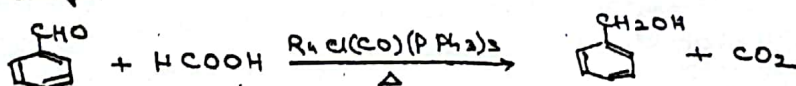
Examples

1. Diels-Alder Reaction: Diels-Alder reaction of anthracene with dimethyl fumarate proceed in 10 minutes in p-xylene (87%) whereas under conventional thermolysis conditions the reaction proceeds in 4 hours (67%).



(II) Catalytic Transfer Hydrogenation

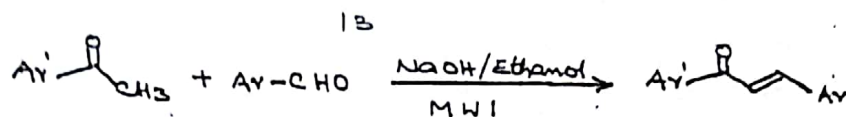
Hydrogenation of benzaldehyde has been carried out using HCOOH as the hydrogen donor and RuCl(CO)(PPh₃)₃ as the catalyst.



It has been found that with constant microwave irradiation the reaction was completed in 7 minutes as compared with 4 hrs. under standard reflux (conventional reflux).

(III) Synthesis of Chalcones and related Enones

Various chalcones and related enones have been synthesized in unsealed vessels in a domestic microwave oven using ethanol as energy transfer medium.



5. Application of Microwave Heating

1. In Material Chemistry. The use of microwave for synthesis of inorganic solid is very efficient and useful technique in material chemistry. Microwave has been used in the preparation of ceramics. SiC is a large volume ceramic and is extensively used for industrial application such as for grinding wheels and in the manufacture of abrasion tools. It is obtained when Si and C (charcoal) in their powder form are taken in a silica crucible and exposed to microwave for 4-10 min. in domestic microwave oven operating at 2.45 GHz.

2. In Catalyst Preparation

Microwaves are put to use in preparing catalysts and reagents. The growing interest in MW processing can be attributed to several attractive factors such as significant savings in time and energy costs due to shorter processing times. The MW heating gives more homogeneous structure to the catalysts and reagents. In MW heating the material absorbs MW and this electromagnetic energy is converted to heat.

For example, a high permeance NaA zeolite $\gamma \text{Ba}_2 \text{Cu}_3 \text{O}_{7-x}$ membrane was prepared from an aluminate and silicate solution in a modified domestic microwave oven operating at 2450 MHz in 15 min. It was observed that the permeance of the zeolite membrane synthesized by the MW heating is 4 times higher than that of the zeolite membrane synthesized conventional heating.

3. In nanotechnology. Nanoscale materials have been attracting increasing interest for their unique chemical and physical properties and their potential technical applications in catalysis, magnetism and electronics.

The application of microwave dielectric heating technology for synthesis of nanomaterial with definite structures in such shorter time is gaining prevalence.

Microwave heating is a reliable methodology for the fabrication of new nanoscale objects and it is a faster and efficient way of nanoscale synthesis.

4. In Polymer Synthesis. Application of microwave dielectric heating technology has widely been accepted in polymer chemistry for carrying out polymer synthesis for its advantages such as faster heating rates with high quality and better yields of the products than the conventional thermal methods of heating. The synthesis of polyacrylamide (PAM) for example, was studied under microwave irradiation. PAM is used as a flocculating agent in waste water treatment.

Polymerisation reaction such as radical polymerisation in a polar solvent can be carried out rapidly and conveniently using microwave heating in glass reactors. It was found that a significant saving of energy and time was possible in preparation of polystyrene. The heating rate was found to be influenced by monomer to water ratio, magnetron power and the volume of the reaction mixture and the geometry of the container.

5. In Analytical Chemistry. The applications of MW irradiation are immense in the field of analytical chemistry. Microwave irradiations are routinely used for sample digestion and solvent extraction techniques. They have also been put to use for gravimetry, moisture determination and to find out enthalpy of vaporisation of solvents. They are illustrated with some examples-

(i) MW Digestion: Development of high pressure Asher focused microwave (HPAFM) is a novel approach to microwave digestion.

The system has focused MW operating at 2.45 GHz at 650W power. The pressure reaction vessels are made up of quartz and pressure and temperature can be raised to 130 bar and 320°C respectively. Using this apparatus the method has developed for digestion of biological reference material such as bovine liver.

(II) MW Extraction. MW heating has been applied to the extraction of large number of organic materials from the matrices.

(III) MW Drying. Microwave is also used for drying materials. Application of MW technique in determination of the loss on drying the chemicals such as Na_2CO_3 and CaSO_4 consisting of free water was determined by MW technique. The method was found to be accurate, precise and economical.

6. In Waste Management

Microwave heating is playing an important role in the treatment of domestic and hazardous industrial and nuclear waste. Microwave heating can be advantageously used for waste management in areas where human exposure can cause health problems. The MW and high-frequency technology needed for handling such type of hazardous waste is ready to use.

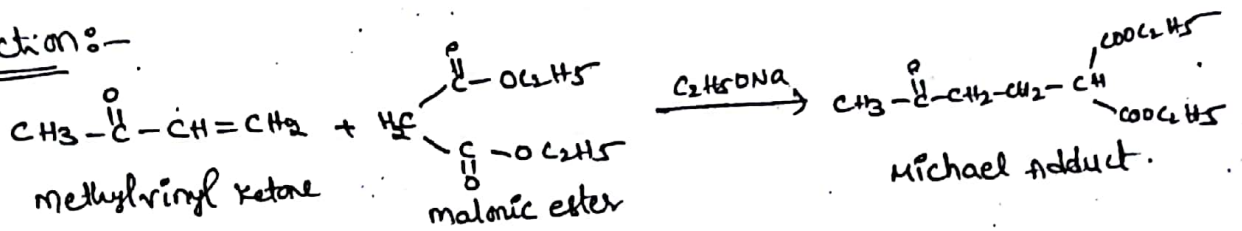
A. Process for carbonisation of organic waste for manufacturing of activated carbon using MW heating has been patented by Kasai et al. Activated carbon can be manufactured from organic waste such as used paper, wood, waste plastic etc. in high carbonisation efficiency using MW heating.

Microwaves are also very useful in the radioactive environment which requires remote handling and control. MW enables direct electronic heat control, which could lead to safer and more efficient processing of all types of wastes including radioactive waste.

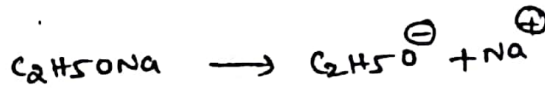
* Michael Addition :- (80) Michael Addition Reaction :-

Methyl vinyl ketone (α, β unsaturated ketone) reacts with Malonic Ester (Active methylene compound) in presence of Base to form an Additional Product i.e. Michael Adduct. This reaction is called Michael Addition Reaction.

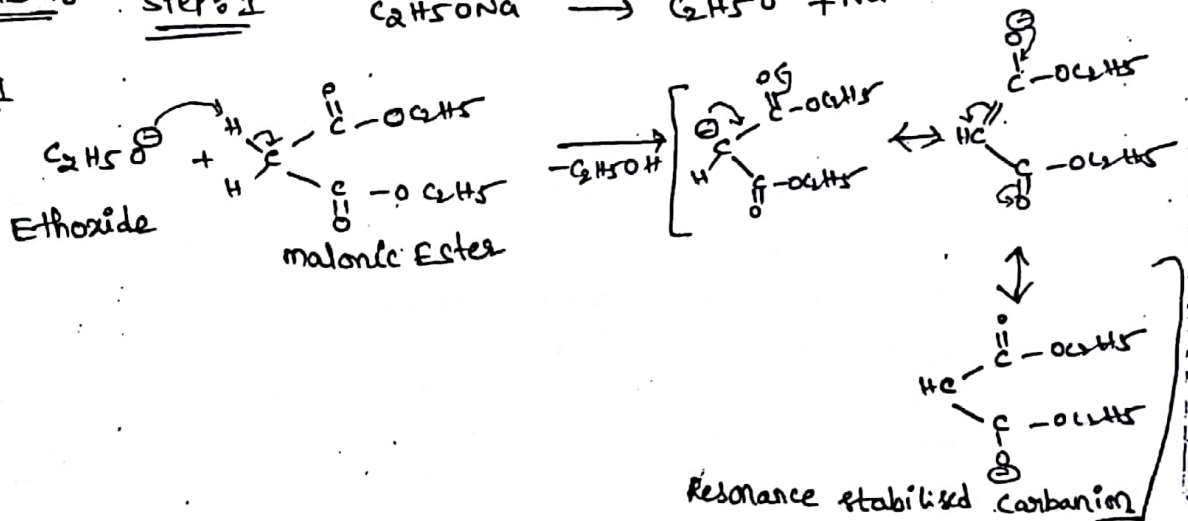
Reaction :-



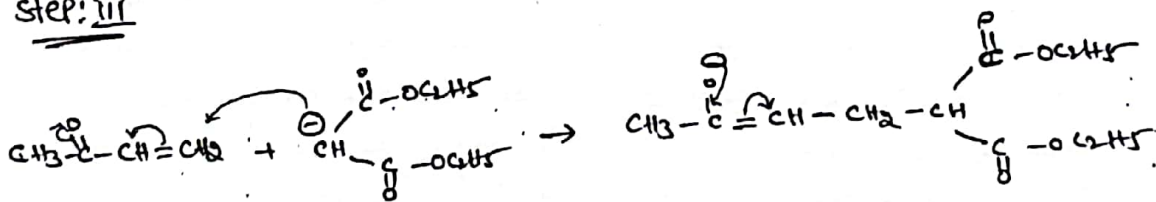
Mechanism :- Step I



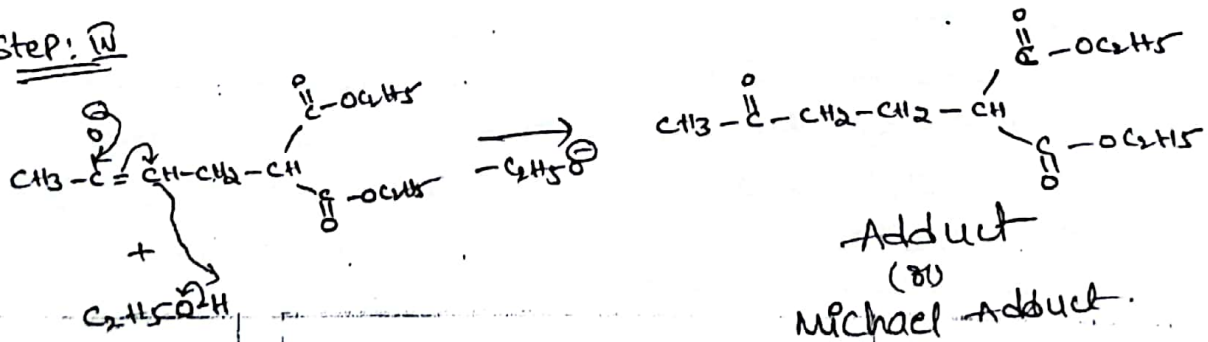
Step II



Step III



Step IV

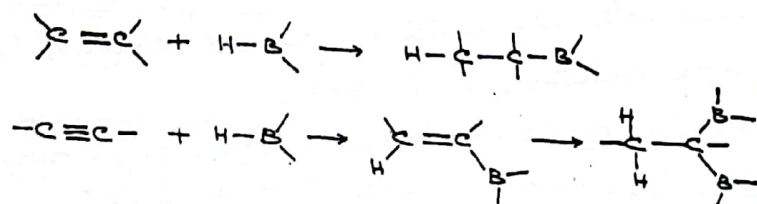


UNIT - IV1. ORGANOBORANES

Organoboranes undergo a wide variety of reactions many of which are of value in organic synthesis

1. Preparation of alkyl and alkenyl boranes - Hydroboration

Alkyl and alkenyl boranes are obtained by the addition of borane, BH_3 (which exists as a gaseous dimer diborane, B_2H_6) to alkenes and alkynes respectively. The process of addition of borane to alkenes and alkynes to form organoboranes is known as hydroboration.

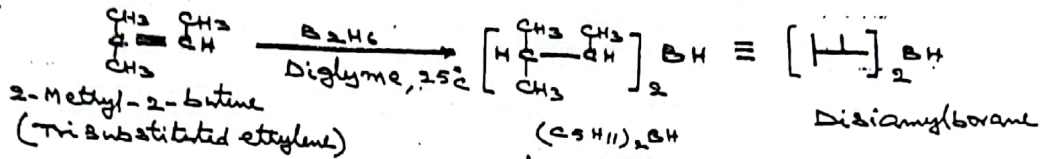


This reaction has been applied to a large number of alkenes of widely different structures. In nearly all cases the addition proceeds rapidly at room temperature, and only the most hindered alkenes do not react.

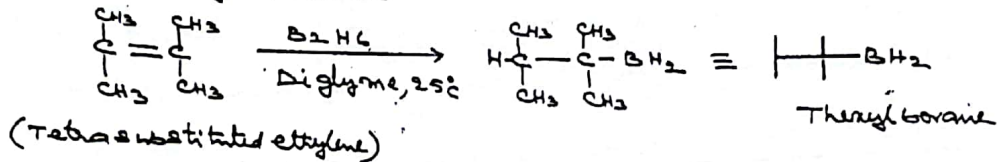
With simple alkenes (mono- and di-substituted ethylenes) a trialkyl borane is produced. But tri-substituted ethylenes normally give the dialkyl borane and tetra-substituted alkenes form only monoalkyl boranes. This has been exploited in the preparation of a number of mono- and di-alkyl boranes which are less reactive and more selective than borane itself.

Particularly important in this respect are disiamylborane, t-butylborane and 9-borabicyclo [3.3.1] nonane, 9-BBN.

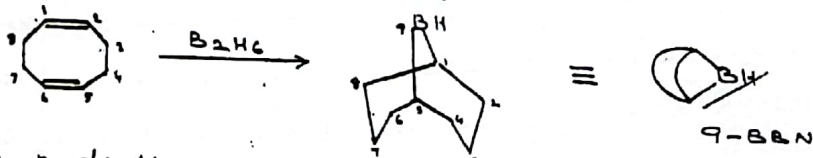
(I). Disiamylborane is prepared by the addition of borane to 2-methyl-2-butene.



(II). Terthylborane is prepared by the addition of borane to 2,3-dimethyl-2-butene.

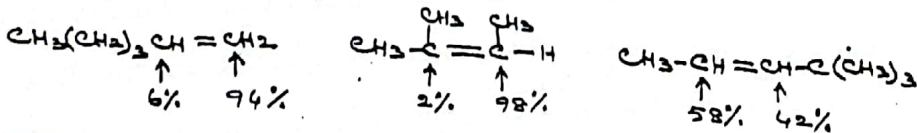


(III). 9-Bora bicyclo [3.3.1] nonane, 9-BBN is prepared by the addition of borane to 1,5-cyclooctadiene.

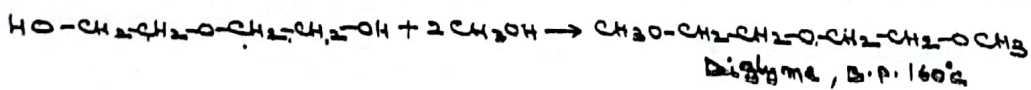


These partially alkylated boranes may themselves be used to hydroborate less hindered alkenes. They are less reactive and more selective than borane.

Addition of borane to an unsymmetrical alkene could of course, give rise to two different products by addition of the boron at either end of the double bond. It is found in practice, however, that in the absence of strongly polar neighbouring substituents, the reactions are highly selective and give predominantly the isomer in which boron is bound to the less highly substituted carbon atom (i.e., carbon atom containing more hydrogens - Markovnikov's addition, boron being the positive part of B-H bond)



Diglyme: Dimethylether of diethylene glycol. It is used as a solvent.



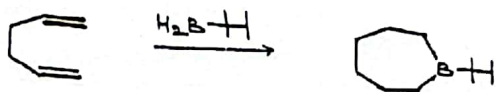
with disubstituted internal alkenes, however, there is little discrimination in reactions with borane itself.

All the available evidence suggests that hydroboration is a concerted process and takes place through a four-membered cyclic transition state formed by addition to the double bond of a polarised B-H bond in which the boron atom is the more positive.

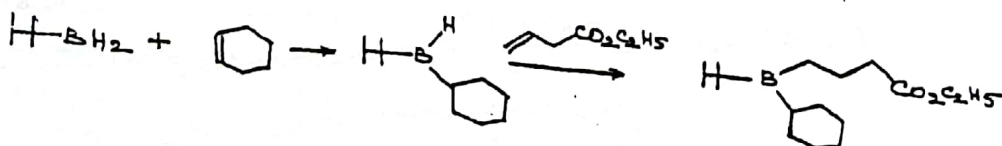


Hydroboration of alkenes and alkynes is highly stereoselective and takes place by syn addition to the less hindered side of the multiple bond.

(IV). Triethyl borane is useful for the cyclic hydroboration of dienes. 1,5-Hexadiene, for example, is converted by triethyl borane mainly into the boracycloheptane.



(V). Triethyl borane has also been used to make trialkylboranes containing three different alkyl groups by stepwise addition to two different alkenes as shown below.

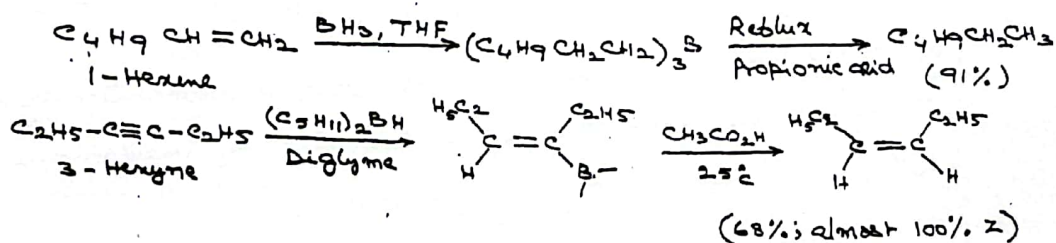


2. Synthetic applications of Organoboranes (Reactions of organoboranes)

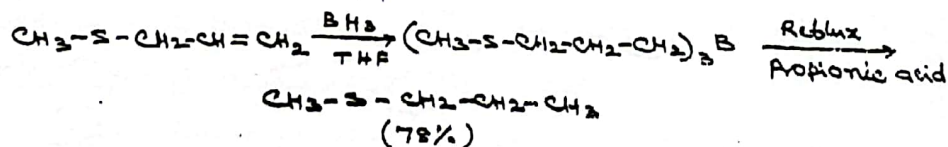
The usefulness of the hydroboration reaction in synthesis arises from the fact that the alkylboranes formed can be converted by further reaction into a variety of other products. On protomolysis (hydrolysis), for example, the boron atom is replaced by hydrogen, and under appropriate conditions boranes are readily oxidised to alcohols or carbonyl compounds. A practical advantage of these reactions is that it is often unnecessary to isolate the intermediate organoborane.

1. Protonolysis

Protonolysis of organoboranes is best effected with an organic carboxylic acid and provides a convenient method for the reduction of carbon-carbon multiple bonds. Boiling propionic acid is often used with alkyl boranes but alkenylboranes are much more reactive and often undergo rapid protonolysis with acetic acid at room temperature. The reaction takes place with retention of configuration at the carbon atoms concerned, and in accordance with the proposed mechanism of hydroboration alkynes are cleanly converted into *Z*-alkenes.

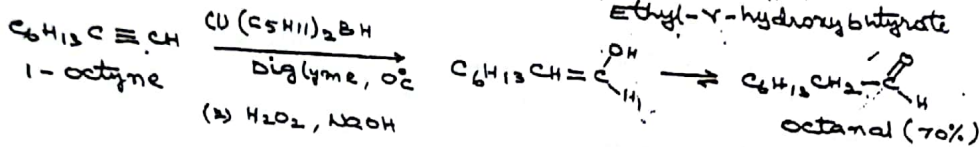
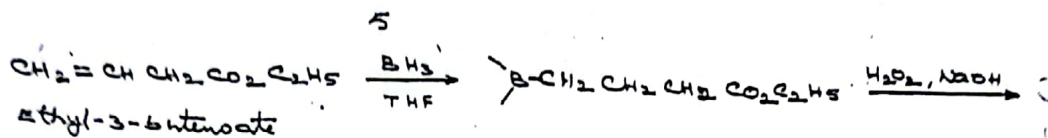


An advantage of the hydroboration-protonolysis procedure is that it can sometimes be used for the reduction of double or triple bonds in compounds which contain other easily reducible groups. Allyl methyl sulphide, for example, is converted into methyl propyl sulphide in 78% yield.

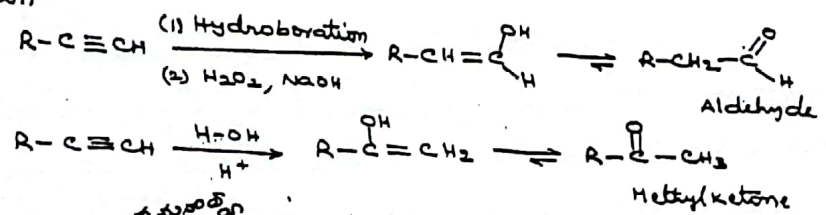


11. Oxidation

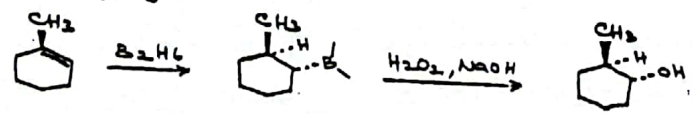
Oxidation of organoboranes to alcohols is usually effected with alkaline hydrogen peroxide although other methods can be used. The reaction is of wide applicability and many functional groups are unaffected by the reaction conditions, so that a variety of substituted alkenes can be converted into alcohols by this procedure.



A valuable feature of the reaction is that it results in overall anti-Markovnikov addition of water to the double or triple bond, and it thus complements the more usual acid-catalyzed hydration. This follows from the fact that in the hydroboration step the boron atom adds to the less substituted carbon of the multiple bond. Terminal alkynes, for example, give aldehydes in contrast to the methyl ketones obtained by acid-catalyzed hydration.

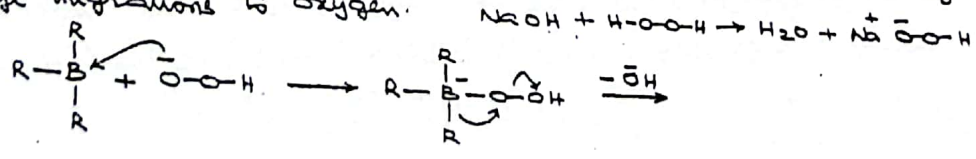


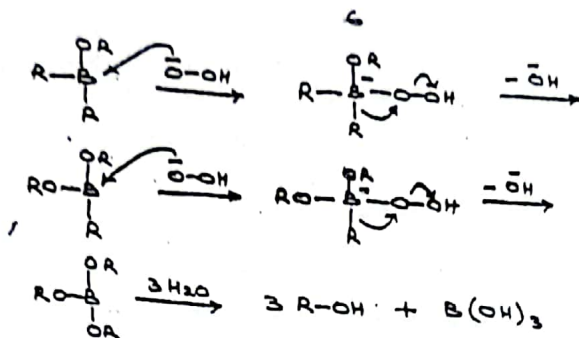
Another noteworthy feature of the reaction is that it leads to *cis* addition of the elements of water to the double bond. Thus, hydroboration-oxidation of 1-methylcyclohexene affords (E)-2-methylcyclohexanol.



The *syn* addition of B-H to less hindered side of the double bond is followed by oxidation of the carbon-boron bond with retention of configuration.

Mechanism: The mechanism of oxidation of alkyl boranes involves the following sequence and consists of a number of alkyl migrations to oxygen.



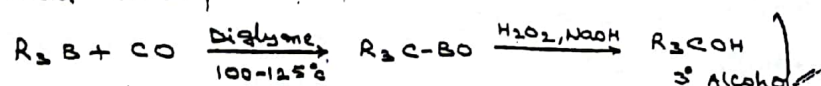


In the final step, hydrolysis of B(OA)_3 results in the formation of alcohol and boric acid.

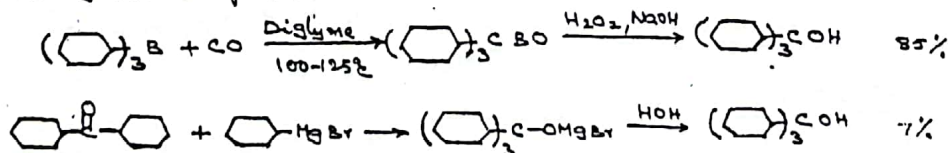
III. Carbonylation

One of the most useful reactions of organoboranes in synthesis is their reaction with carbon monoxide, which under appropriate conditions, can be directed to give primary, secondary and tertiary alcohols, aldehydes and open chain, cyclic and polycyclic ketones!

At a temperature of $100-125^\circ\text{C}$ in diglyme solution many organoboranes absorb one molecule of carbon monoxide at atmospheric pressure to form intermediates which are oxidized to tertiary alcohols by alkaline hydrogen peroxide in excellent yield.

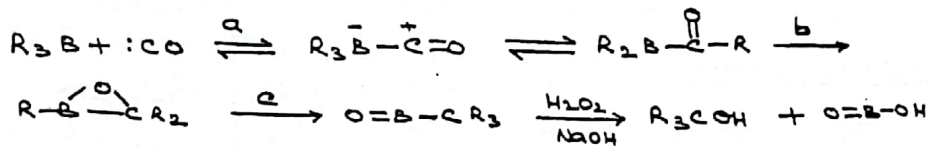


The reaction is of wide applicability, and for trialkyl-carbinols containing bulky groups gives much higher yields than any other method. Tricyclohexylcarbinol, for example, is obtained from cyclohexene in 85% yield, whereas the Grignard method gives only 7%.

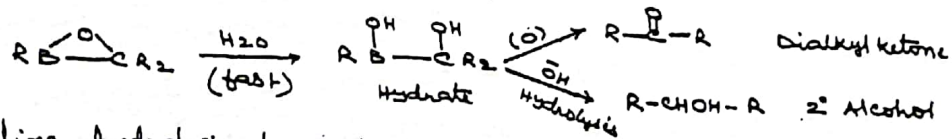


Mechanism: The reaction obviously involves migration of alkyl groups from boron to the carbon atom of carbon monoxide,

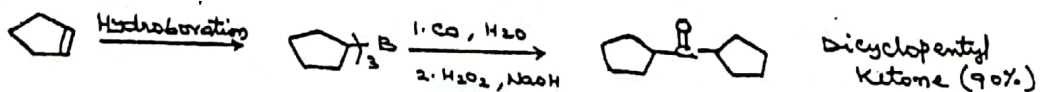
and this was shown to occur intramolecularly by the fact that carbonylation of an equimolar mixture of triethyl borane and tributyl borane gave, after oxidation, only triethyl carbinol and tributyl carbinol; no 'mixed' carbinols were formed. Similarly, dicyclohexyloctyl borane gave only dicyclohexyloctyl carbinol. The stepwise reaction pathway involving three successive intramolecular transfers has been proposed.



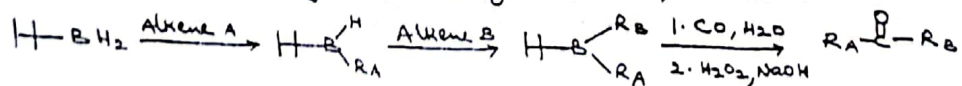
If the carbonylation is conducted in the presence of a small amount of water, migration of the third alkyl group (step c) is inhibited. Oxidation of the hydrate produced then gives the dialkyl ketone instead of the trialkyl carbinol.



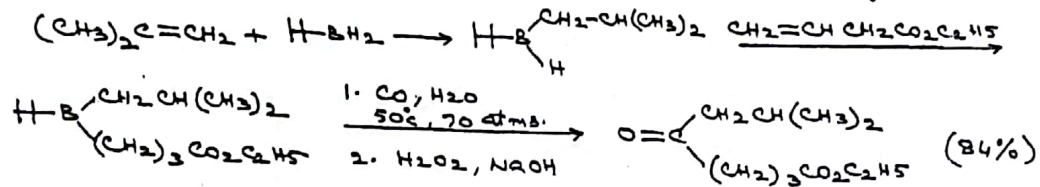
Alkaline hydrolysis leads to the secondary alcohol. Yields obtained are generally high, and the sequence provides a very convenient synthetic route to ketones. 1-octene, for example, was smoothly converted into dioctyl ketone in 80% yield, and cyclopentene gave dicyclopentyl ketone in 90% yield.



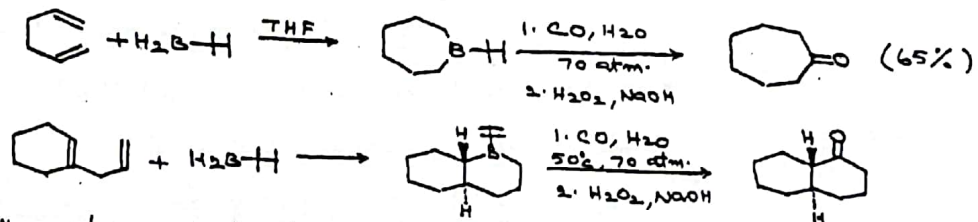
Unsymmetrical ketones. Unsymmetrical ketones can be synthesized by using 'mixed' organoboranes prepared from therylborane or therylchloroborane. The theryl group shows an exceptionally low aptitude for migration, and carbonylation of trialkylboranes containing a theryl group, in presence of water, followed by oxidation, leads to high yields of the ketone, $R_A CO R_B$.



Because of the bulky nature of the t-butyl group, carbonylation of these compounds requires more vigorous conditions than usual, and generally has to be effected under pressure. Functional groups in the alkene do not interfere with the reaction, and the procedure can be used to synthesize a ketone from almost any two alkenes.



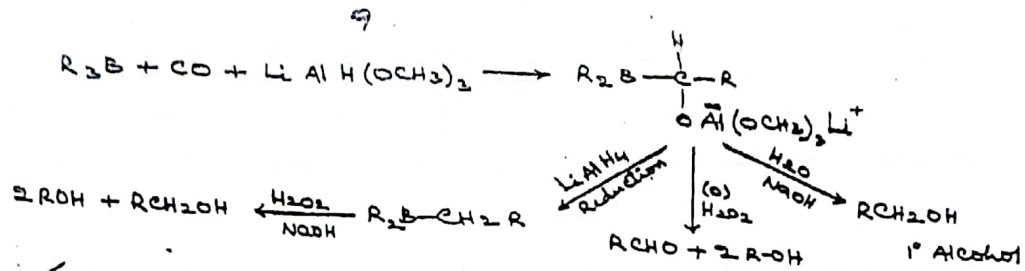
Cyclic Ketones. Diene similarly yield cyclic ketones, and in a notable extension of the reaction bicyclic ketones have been prepared. Thus, trans-1-decalone is obtained from 1-allylcyclohexene:



The stereo selectivity of the reactions, leading exclusively to the trans fused compounds, is a result of the mechanism of hydroxylation which requires *syn* addition of the B-H group to the double bond of the alkene.

Aldehydes and Primary alcohols

The carbonylation reaction can be adapted to the preparation of aldehydes and primary alcohols. In the presence of certain hydride reducing agents, such as lithium hydrido-trimethoxy-aluminate, the rate of reaction of carbon monoxide with organoboranes is greatly increased and the products, on oxidation with buffered H_2O_2 afford aldehydes. Alkaline hydrolysis gives the corresponding primary alcohol containing one more carbon atom than the original alkene, and thus differing from the product obtained on direct oxidation of the original alkyl borane.

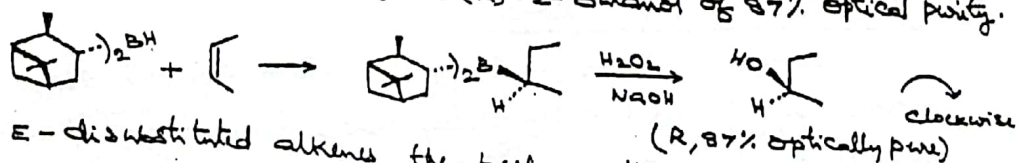


2/4. Enantioselective synthesis of secondary alcohols from alkenes

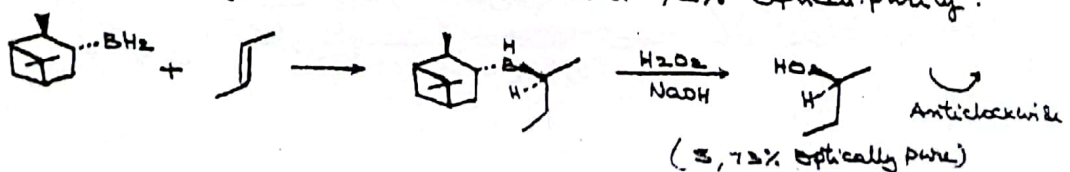
Hydroboration of alkenes with an optically active alkylborane followed by oxidation, has been used in the asymmetric synthesis of optically active secondary alcohols. The best results are obtained with mono-isopinocampheyl borane, IPC_1BH_2 and diisopinocampheyl borane, IPC_2BH . These are readily prepared in either (+) or (-) form by reaction of borane with α -pinene under the appropriate conditions.



Optically active secondary alcohols of high optical purity have been obtained from several disubstituted z-alkenes by initial hydroboration with IPC_2BH . Thus reaction of (z)-2-butene with $(-)$ IPC_2BH followed by oxidation with alkaline hydrogen peroxide gave (R)-2-butanol of 87% optical purity.



With E-disubstituted alkenes the best results have been obtained using IPC_1BH_2 , but as with z-alkenes, the success of the reactions is strongly dependent on the bulk of the alkyl substituents on the double bond of the alkene. (E)-2-butene, for example, gave (S)-2-butanol of 73% optical purity, but with (E)-di-t-butylethene the corresponding alcohol obtained had 92% optical purity.

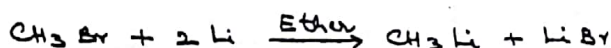


2. ORGANOLITHIUM COMPOUNDS

Organolithium compounds contain a polar Li-C bond because of the electronegativity difference; the bonding pair of electrons is located closer to the carbon atom.

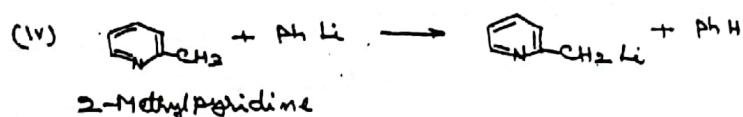
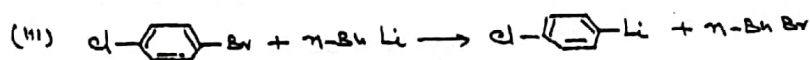
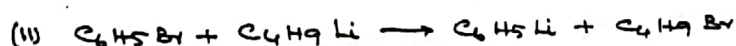
1. Preparation of organolithium compounds

(1) The alkyl lithiums can be prepared conveniently by the reaction of lithium metal with an appropriate organic halide in an inert solvent like ether.



Diethylether provides an inert medium in which the organometallic compounds are usually soluble. The reactivity of an organic halide is $\text{RI} > \text{RBr} > \text{RCl}$.

(2) Organolithiums that are not obtained directly from lithium and an alkyl halide can be prepared by an alternative method called the metal-halogen exchange or simply metallation.



2. Synthetic Applications

Organolithiums are very reactive reagents and are strong bases and powerful nucleophiles. They have found extensive applications in organic synthesis and in many cases provide better methods than other organometallic derivatives.

1. Preparation of Alcohols

Primary, secondary and tertiary alcohols can be prepared by the action of organolithium compounds on formaldehyde, other aldehydes and ketones respectively.

UNIT - IV

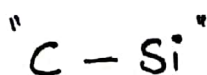
PART - II

ORGANO SILANES

Introduction:-

organo silicon chemistry is the science of the preparation and properties of organo silicon compounds, which are organo metallic compounds containing carbon - silicon bonds.

Most organo silicon compounds are similar to the ordinary organic compounds, being colourless, flammable, hydrophobic, and stable to air. Silicon carbide is an inorganic compound.



A carbon - silicon bond present in all organo silicon compounds.

Organosilanes are monomeric silicone-based chemicals, similar to hydrocarbons, which have at least one direct bond between a silicon atom and a carbon atom in the molecule. The structure of a typical organosilane molecule is shown in Figure.

Fig (a)

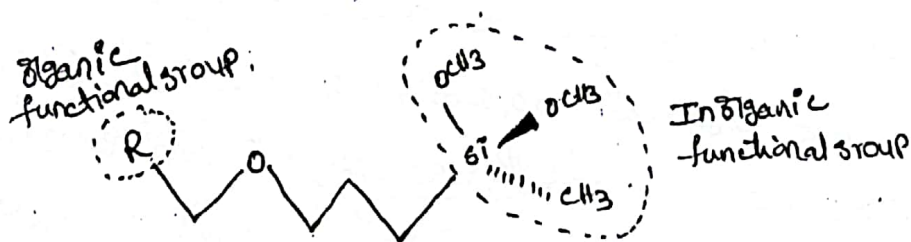


Fig (b)

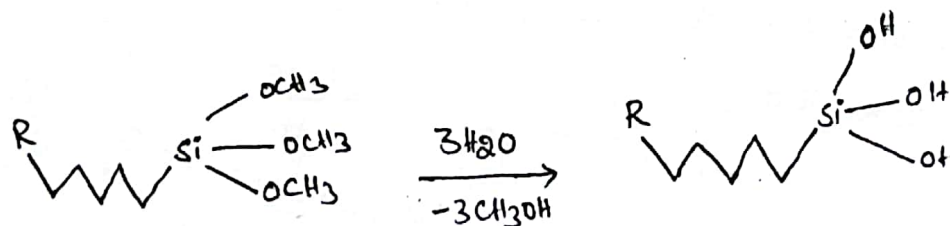
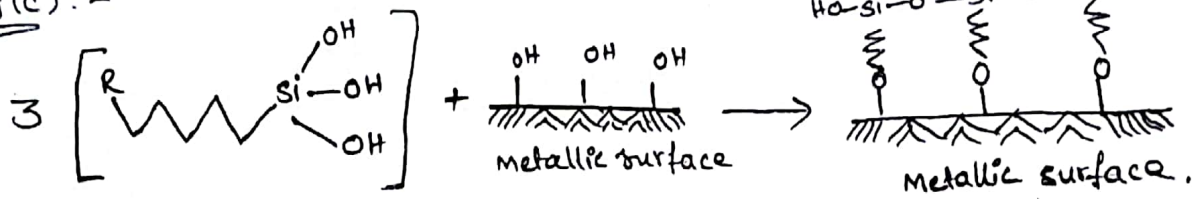


Fig (c): -



* It has larger size (atomic radius - 117 pm), more electropositive (Si - 1.64)

* Silicon has lower electronegativity in compare to C, so Si-C bond is polar in nature, so they are easily attacked by nucleophile.

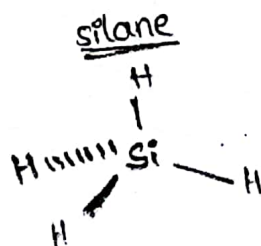
* Silicon forms very strong bond with electronegative atoms such as F &

* These are used as silylating reagents for alcohols, acids, amines & thiols, silylation is also carried out for alcohol protection.

* These are used to activate the alkyl group & reacts with electrophile to form new C-C, C-X bonds.

Ex: - allyltrimethylsilane & silyl end ethers.

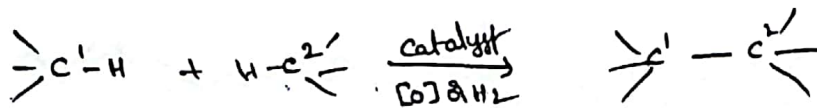
* Organosilanes are the important building blocks in organic synthesis and have significant applications in the field of materials science, medicinal chemistry and agrisciences. Organosilanes are found in a wide range of goods, including industrial, cosmetic, and personal care items.



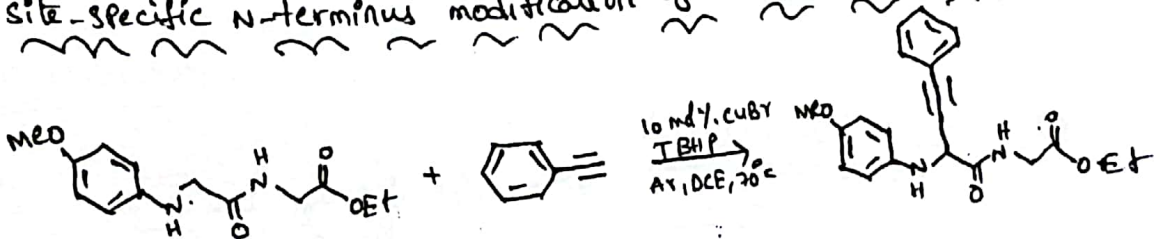
General features of C-C bond-forming reactions of organosilicon compounds ⁽³⁾

Carbon-carbon bond formation is the core of organic synthesis, in which organometallic reagents play the key role in the forms of 1,2-nucleophilic additions, conjugate additions, and transition-metal catalysed cross-couplings.

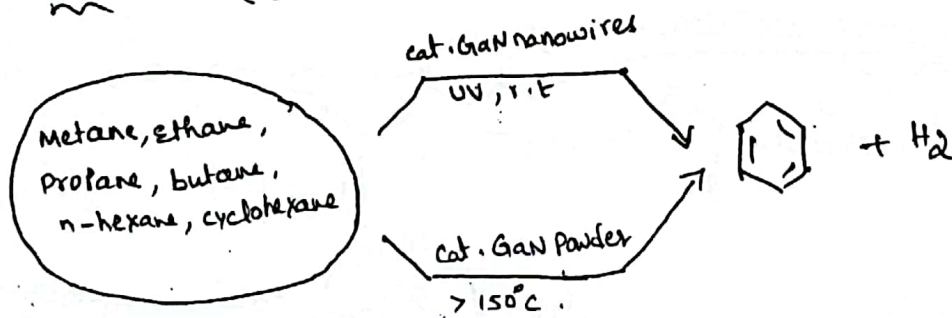
* (a) General concept for cross-dehydrogenative coupling (CDC): -



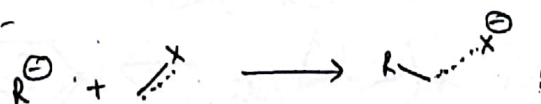
* (b) Site-specific N-terminus modification of amino acids & peptides: -



* (c) catalytic dehydrogenative conversion of methane: -



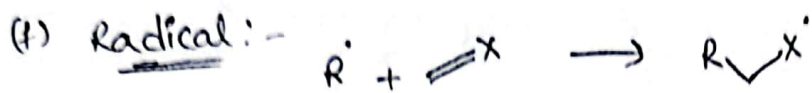
* (d) Anionic: -



* (e)

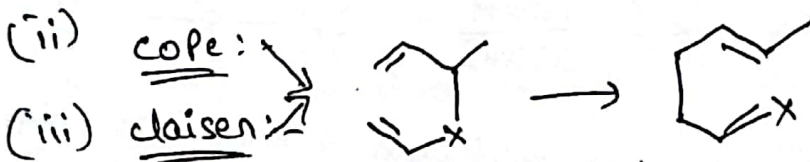
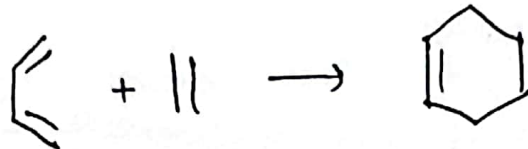
cationic: -



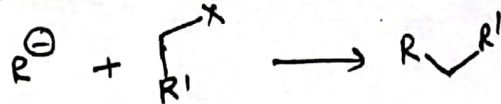


(g) Electrocyclic: -

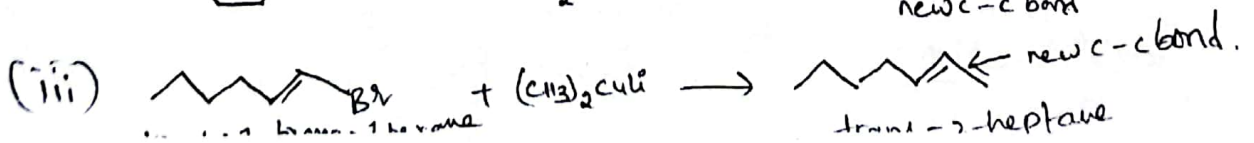
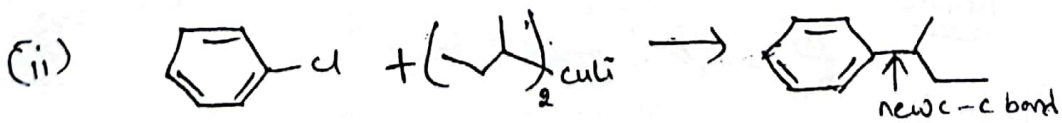
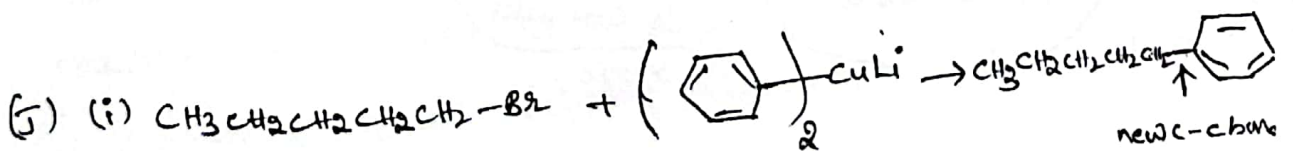
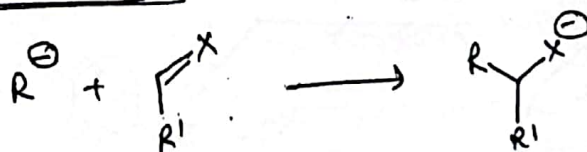
(i) Diels Alder: -



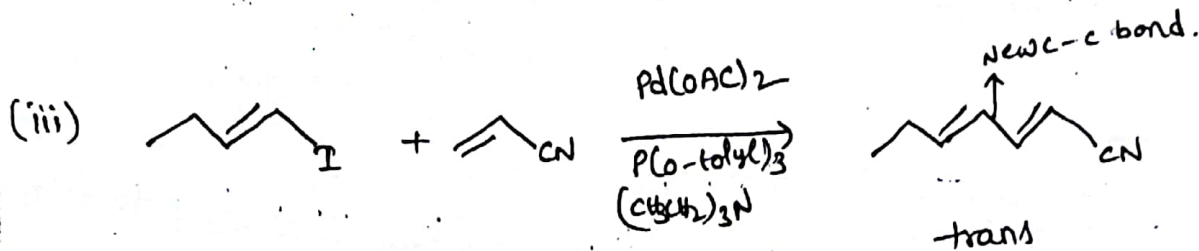
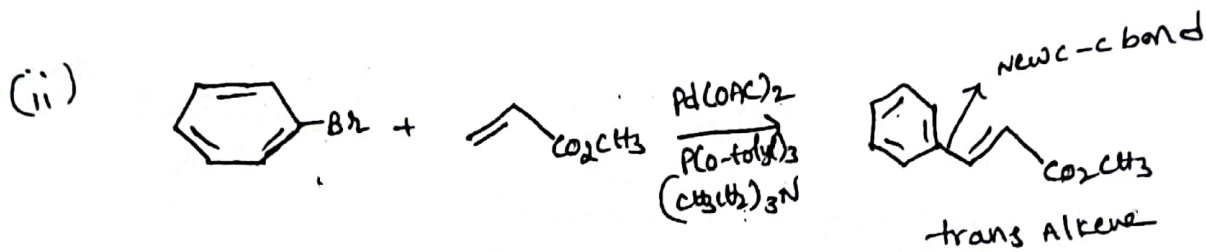
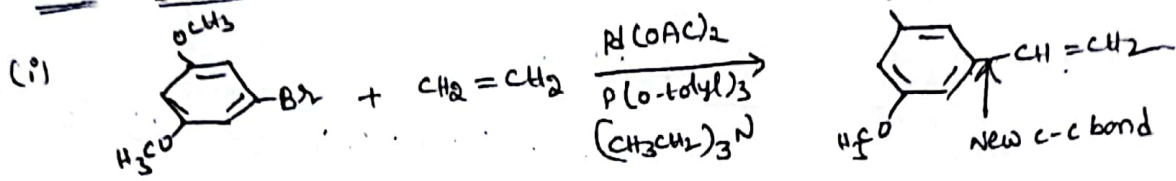
(h) substitution reaction: -



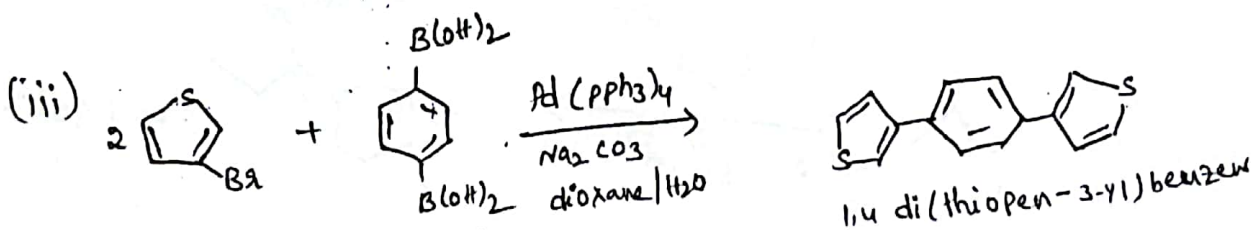
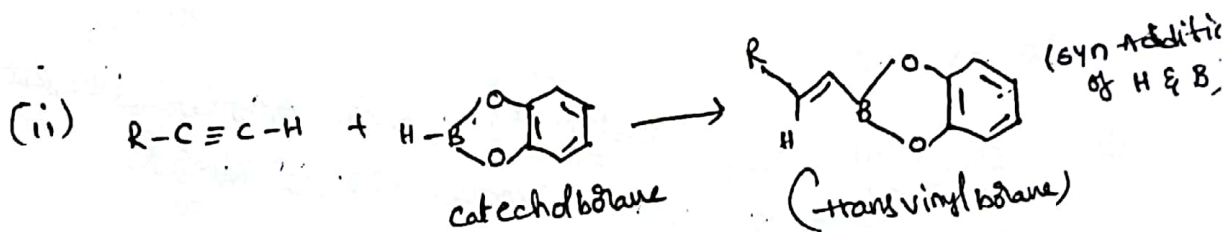
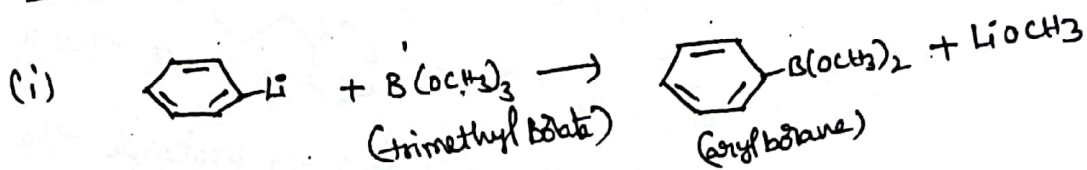
(I) Addition Reaction: -



* Heck reaction :-



* Suzuki reaction :-

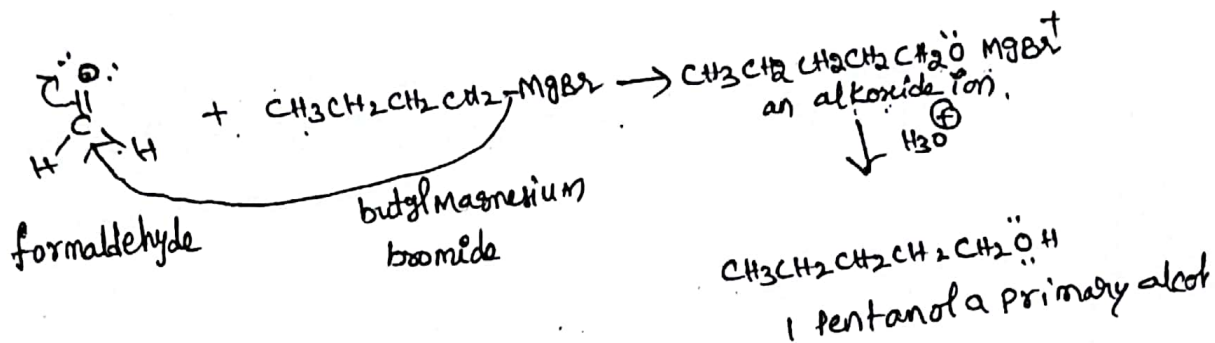


* Addition Reaction with Aldehydes & Ketones :-

(6)

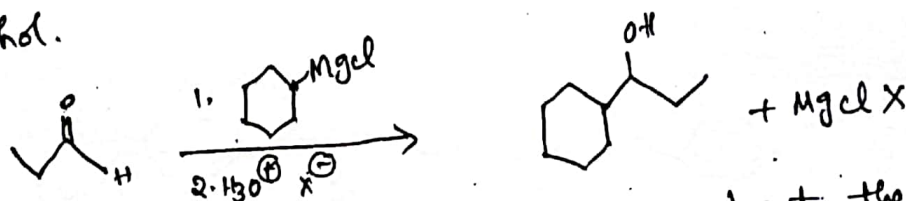
(i) Reaction with formaldehyde :-

Grignard reagent reacts with formaldehyde to form 1° alcohol.



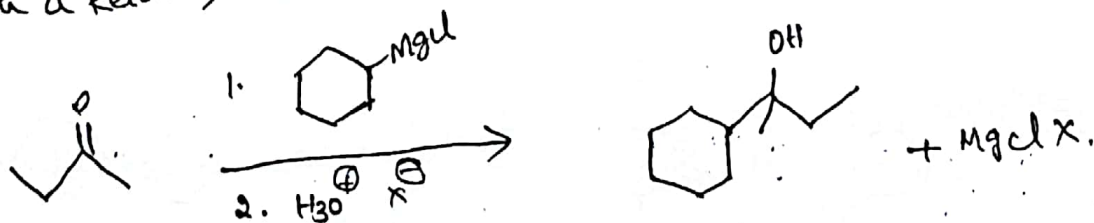
* Reaction with other Aldehydes :-

Grignard reagent with aldehydes other than formaldehyde to form 2° Alcohol.



Acid is added in the 2nd step to protonate the negatively charged oxygen.

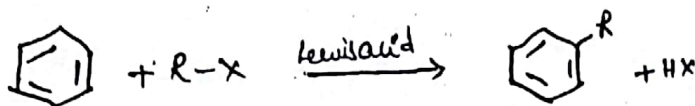
* Reaction with ketones :- when Grignard reagent reacts with a ketone, the addition product is 3° Alcohol.



* Acylation reactions:-

(i) Friedelcraft alkylation:-

Generic Example:-



Note:-

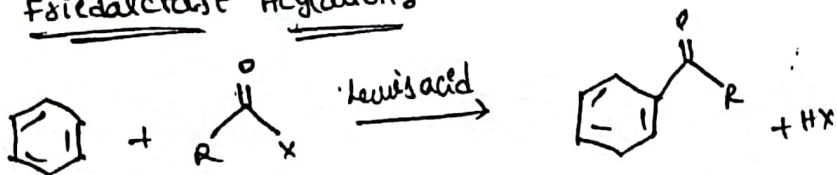
Bonds formed	Bonds Broke
C-C	C-H
H-X	C-

* R-X must be an alkyl halide

* Lewis acid often AlCl₃ but can vary widely (EX: FeCl₃, ZrCl₄)

* carbocation rearrangements can occur.

(ii) Friedelcraft acylation:-



Note:-

Bonds formed	Bonds Broke
C-C	C-H
H-X	C-O



⇒ X is usually a halogen

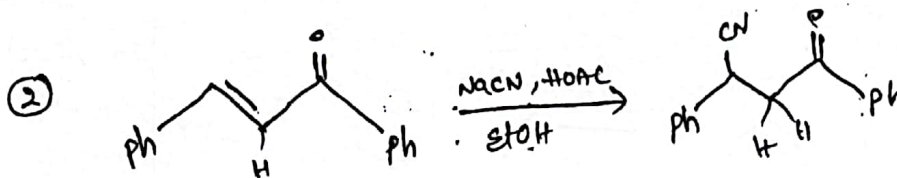
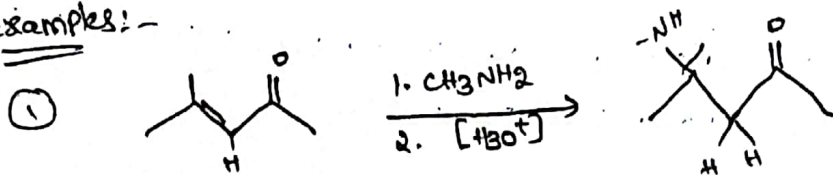
eg:- Cl, Br, I

(although anhydrides can also be used)

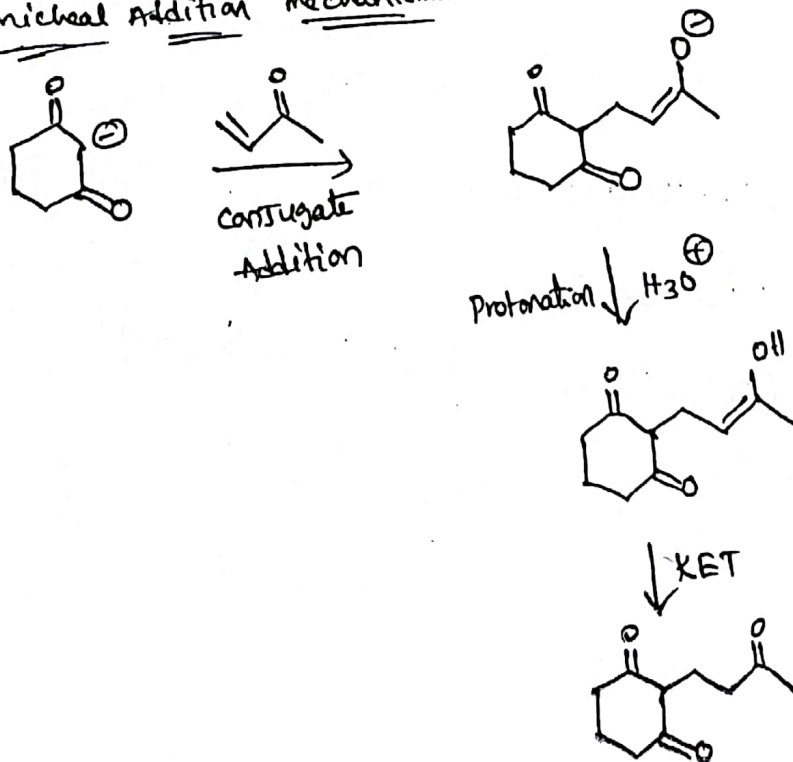
* Conjugate Addition Reaction:-

Conjugate Addition is the vinylogous counterpart of direct nucleophilic addition. A nucleophile reacts with an α, β -unsaturated carbonyl compound in the β -position. The negative charge carried by the nucleophile is now delocalized in the alkoxide anion and the α carbon carbanion by resonance.

Examples:-

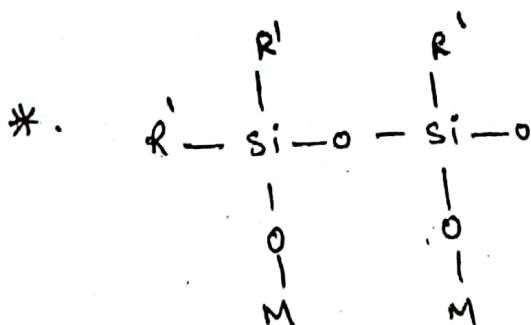
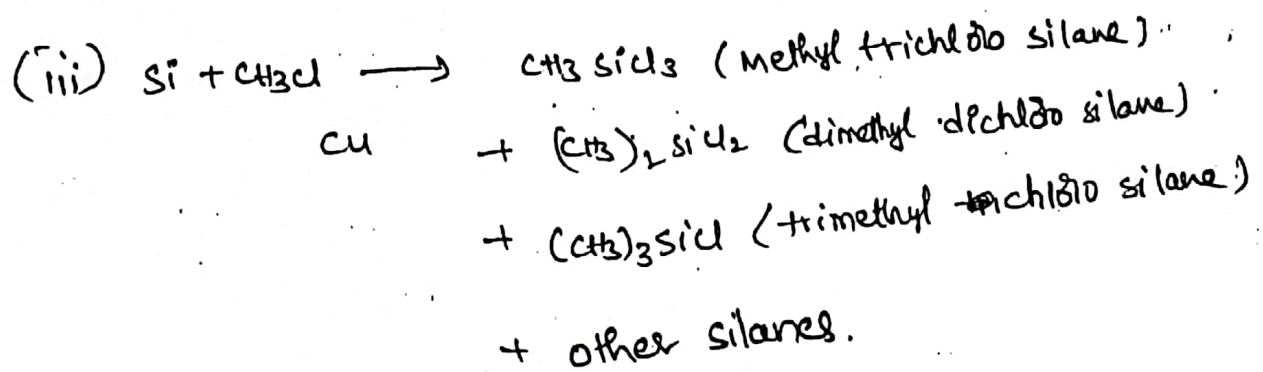
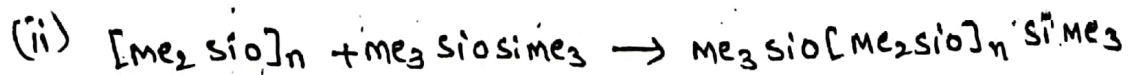
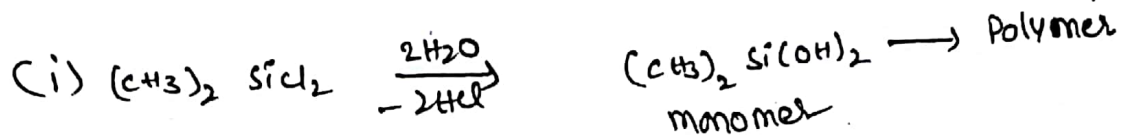


③ Michael Addition Mechanism:-



Synthesis of organo silanes:

silicon is a major constituent of sand & rocks - very durable inorganic materials. silicon bonds tenaciously to other inorganics such as glass & steel. silicon will bond tenaciously to organic polymers as well as when an organic group, such as amino propyl, is attached to the silicon, this is because the reactivity of organic groups attached to silicon is similar to



Silane Applications - Silanes are versatile materials used in a wide range of applications including adhesion promoters, coupling agents, cross linking agents, dispersing agents, and surface modification. (10)

* Adhesion Promoters - when added to adhesive (B) used as a primer on substrates, silanes often provide dramatic improvement in adhesion, by reducing moisture attack at the interface the results in improved.

* moisture resistance, temperature resistance, chemical resistance.

* Cross-linking agents - silanes can be used to cross link polymers such as acrylates, polyethers, polyurethanes and polyesters, to improve.

* Tear resistance; elongation at the break, Tear Propagation resistance
Abrasion resistance.

* Water scavengers - since silanes react very rapidly with water, they can be used in a formulation to capture excess moisture to :-

* prevent premature cure during compounding

* Enhance uniform curing.

* Improve package stability.

* Coupling Agents - They are defined as chemical substances capable of reacting with both the reinforcement and the resin matrix of composite material. It may also bond inorganic fillers (a) fibres to organic resins.