

Semester VI
Paper No. XV
(Organic Chemistry)

Unit I. Name reactions. [08]

Statement, General Reaction, Mechanism and Synthetic applications

1. Diels -Alder reaction
2. Oppenauer Oxidation
3. Meerwein –Pondorff-Verley reduction
4. Schmidt rearrangement
5. Hofmann rearrangement
6. Wittig reaction
7. Wagner- Meerwein rearrangement
8. Favorskii rearrangement
9. Michael reaction
10. Dieckmann's reaction or condensation
11. Problem based on above reactions.

Name Reactions

Introduction:

A **name reaction** is a chemical reaction named after its discoverers or developers. Well known examples include the Wittig reaction, the Claisen condensation, the Friedel-Crafts acylation, and the Diels-Alder reaction etc. Among the tens of thousands of organic reactions that are known, hundreds of such reactions are well-known enough to be named after people. Books have been published devoted exclusively to name reactions; the Merck Index, a chemical encyclopaedia, also includes an appendix on name reactions.

As organic chemistry developed during the 20th century, chemists started associating synthetically useful reactions with the names of the discoverers or developers; in many cases, the name is merely a mnemonic. Some cases of reactions were not really discovered by their

namesakes are known. Examples include the Pummerer rearrangement, the Pinnick oxidation and the Birch reduction.

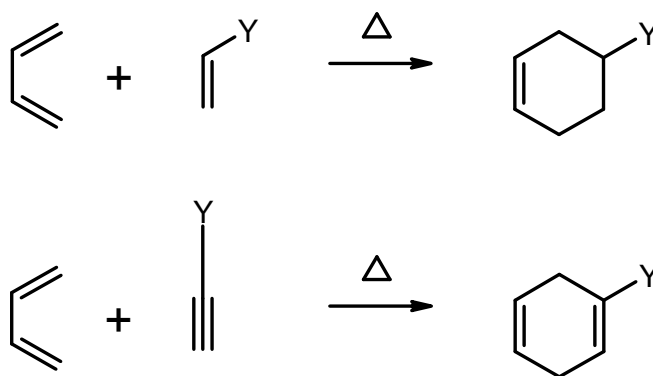
1.1 Diels -Alder reaction

Statement:

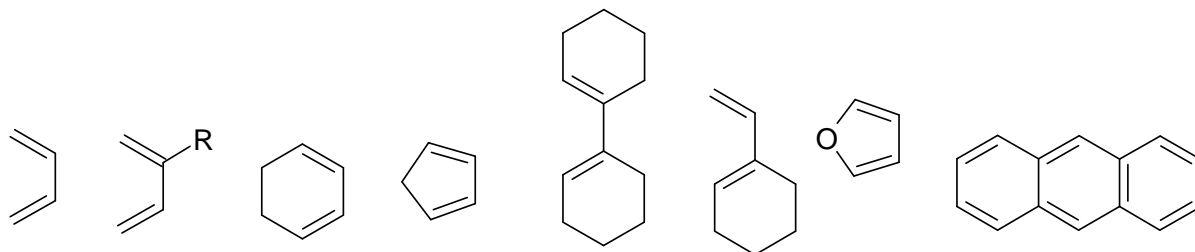
The reaction between conjugated diene and an alkene to produce a cyclohexene derivative is called Diels-Alder reaction.

General reaction:

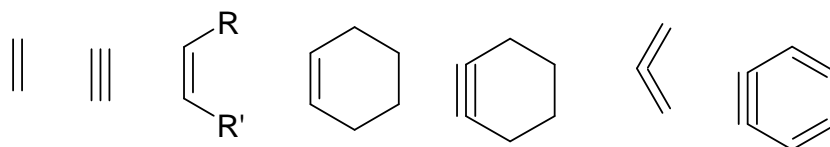
It is the [4+2]-cycloaddition of a conjugated diene and a dienophile (an alkene or alkyne). It involves the 4 π -electrons of the diene and 2 π -electrons of the dienophile. There is the formation of new σ -bonds, which are energetically more stable than the π -bonds. Diels-Alder is the most powerful synthetic method for unsaturated six-membered rings.



The reaction involves two main constituents as diene and dienophile. A diene is any conjugated diene capable of existing in a cis form (i.e. both double bonds are to the same side of the C-C single bond between them). So such system in any aliphatic alicyclic aromatic or heterocyclic compounds can take part in the Diels-Alder reaction as diene. Some examples are as below.



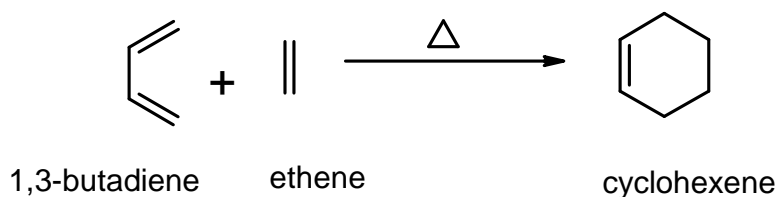
Whereas, the species reacting with a diene is called dienophile. It can be any compound having a double or triple bond, activated by presence of an electron withdrawing group, an allene or benzyne as given below.



Where the groups R and R' can be C=O, -CHO, -COOR, -CN, -NO₂ etc.

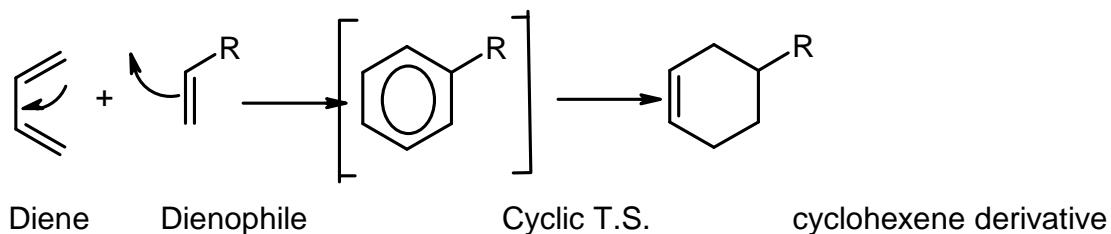
Example:

The simplest example of Diels-Alder reaction is reaction between 1,3-butadiene and ethene. However, due to lack of any electron withdrawing group on ethane, the reaction occurs at high temperature (473K)



Mechanism:

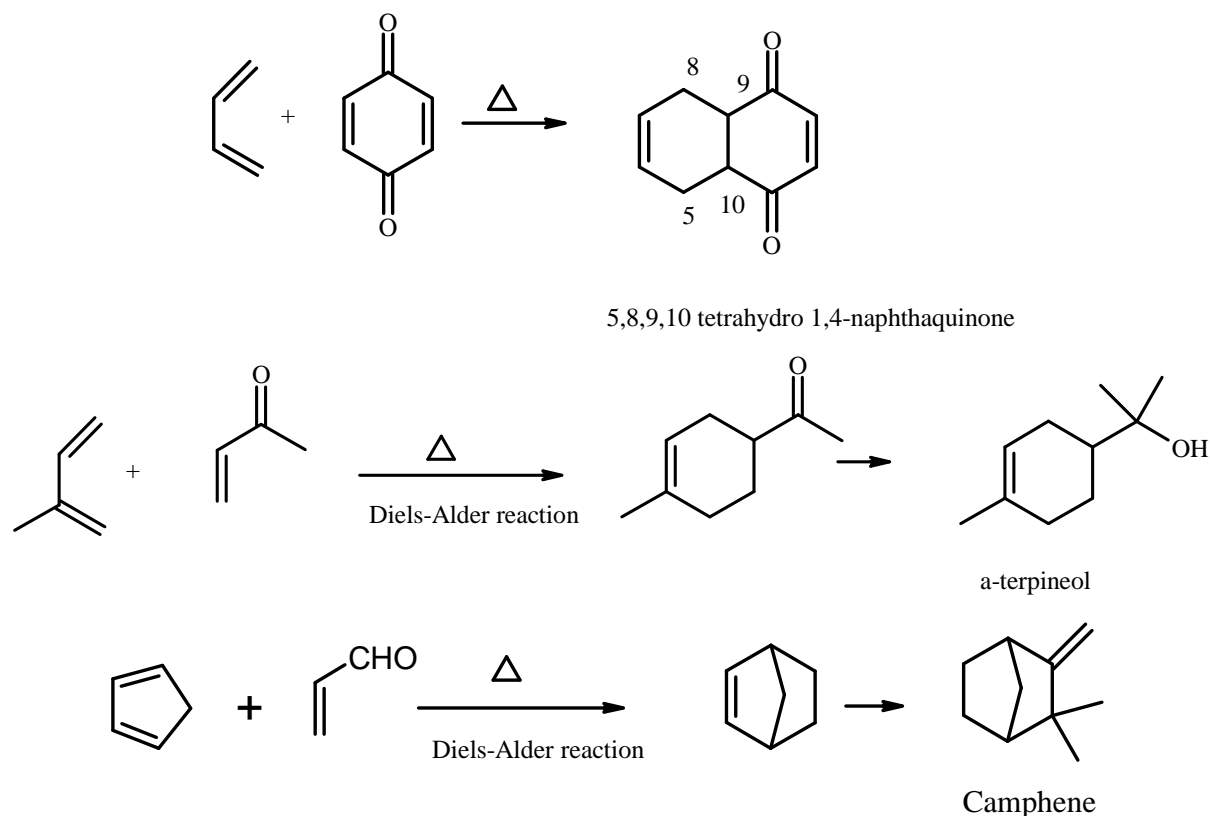
Diels-Alder reaction is a cycloaddition reaction also called pericyclic reaction which occurs in a single step, hence called as following a concerted mechanism. It involves simultaneous breaking and making of bonds by cyclic redistribution of bonding electrons, leading to a six membered transition state.



The reaction is favoured by electron donating groups on diene and electron deficient dienophiles.

Synthetic applications:

Due to its high stereoselective nature, the reaction is of much synthetic importance. It is mainly used in synthesis of unsaturated cyclic products such as polynuclear quinones, natural products such as alpha-terpineol, camphene etc.



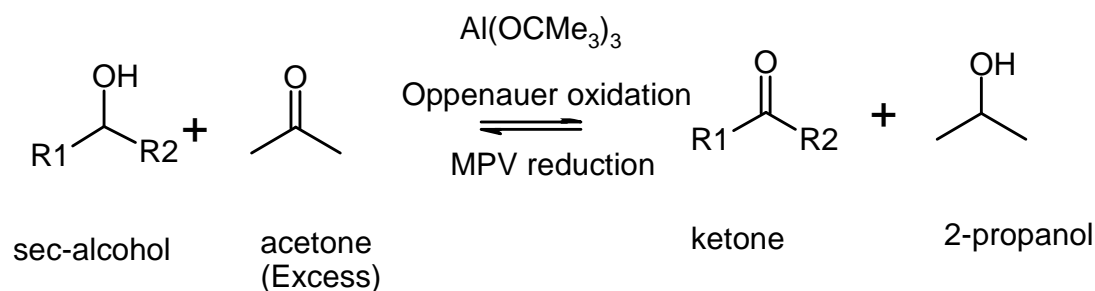
1.2 . Oppenauer Oxidation

Statement:

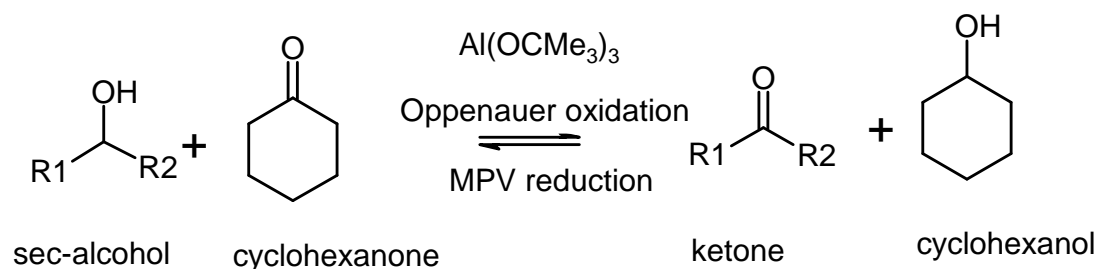
Oppenauer oxidation is reaction named after Rupert Viktor Oppenauer. It is a gentle method for selectively oxidizing secondary alcohols to ketones

General reaction:

The reaction is the opposite of Meerwein-Ponndorf-Verley reduction. The secondary alcohol is oxidized with aluminium tert-butoxide in excess acetone. The excess of acetone shifts the equilibrium toward the product side, where the secondary alcohol is converted in ketone it is oxidation reaction.

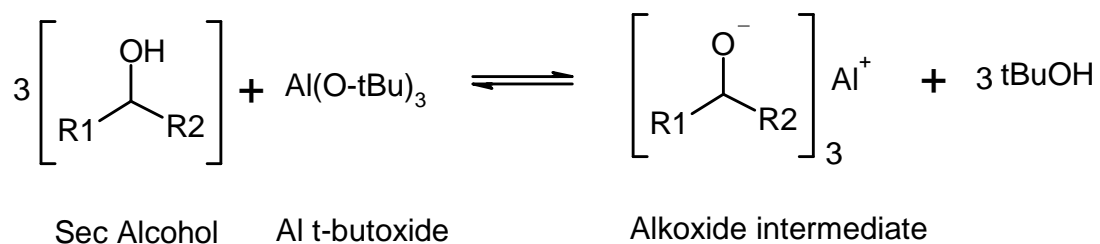


The same reaction can be carried out in presence of excess cyclohexanone too.

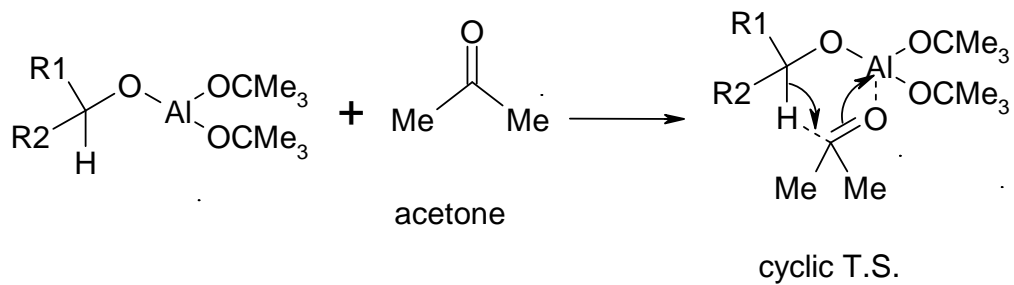


Mechanism:

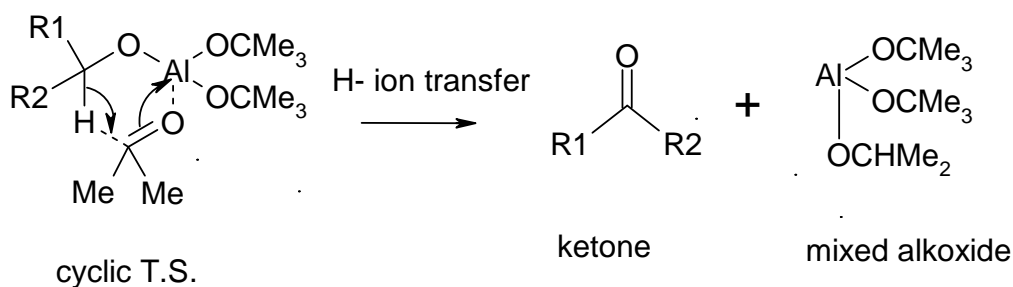
In the first step of the mechanism, the secondary alcohol gets deprotonated by aluminium tert-butoxide to generate an alkoxide intermediate.



In the next step, both the oxidant acetone and the substrate alcohol are bound to the aluminium. The acetone is coordinated to the aluminium which activates it for the hydride transfer from the alkoxide.

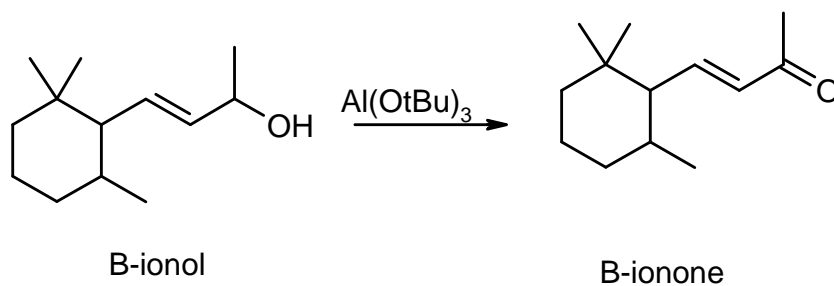


The aluminium-catalyzed hydride shift from the α -carbon of the alcohol to the carbonyl carbon of acetone proceeds over a six-membered transition state. The desired ketone is formed after the hydride transfer.

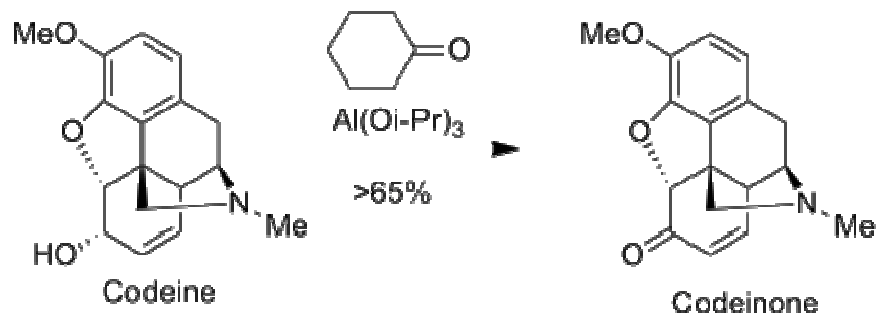


Synthetic applications:

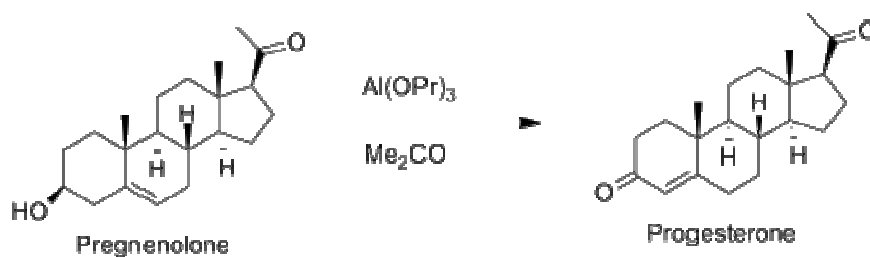
Oppenauer oxidation does not affect other oxidisable groups like double bond, phenolic OH group etc in the substrate if present. It oxidises selectively only secondary alcoholic group. Hence it is used in synthesis of many macromolecules.



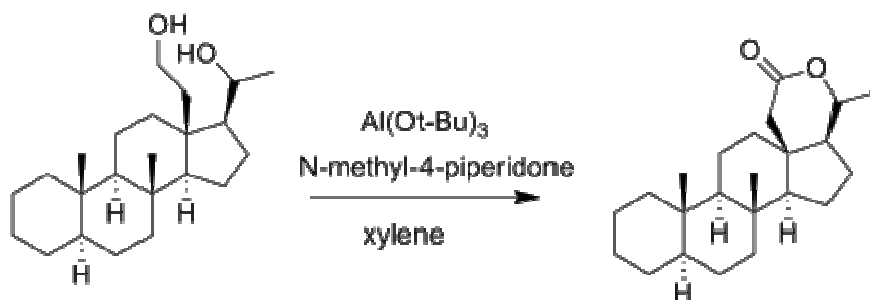
The Oppenauer oxidation is used to prepare analgesics in the pharmaceutical industry such as morphine and codeine. For instance, codeinone is prepared by the Oppenauer oxidation of codeine.



The Oppenauer oxidation is also used to synthesize hormones. Progesterone is prepared by the Oppenauer oxidation of pregnenolone.

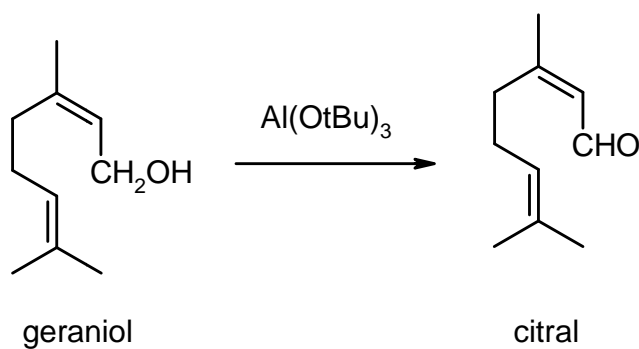


The Oppenauer oxidation is also used in the synthesis of lactones from 1,4 and 1,5 diols.



With some modifications in reaction conditions like temperature and use of solvent like p-benzoquinone it can be used for oxidation of primary alcohol to aldehyde.

Eg. Synthesis of citral

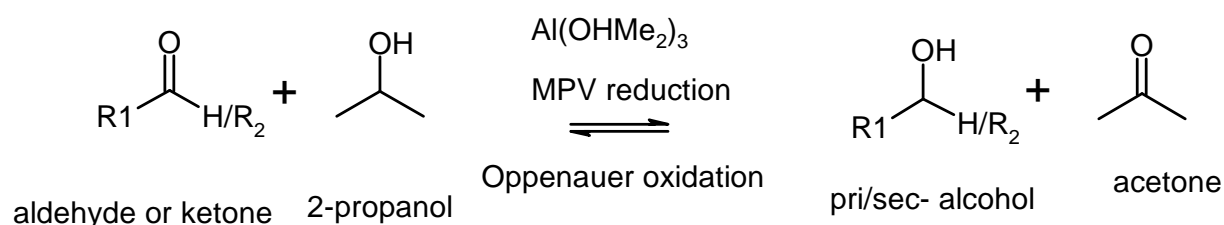


1.3 Meerwein –Pondorff-Verley reduction

Statement:

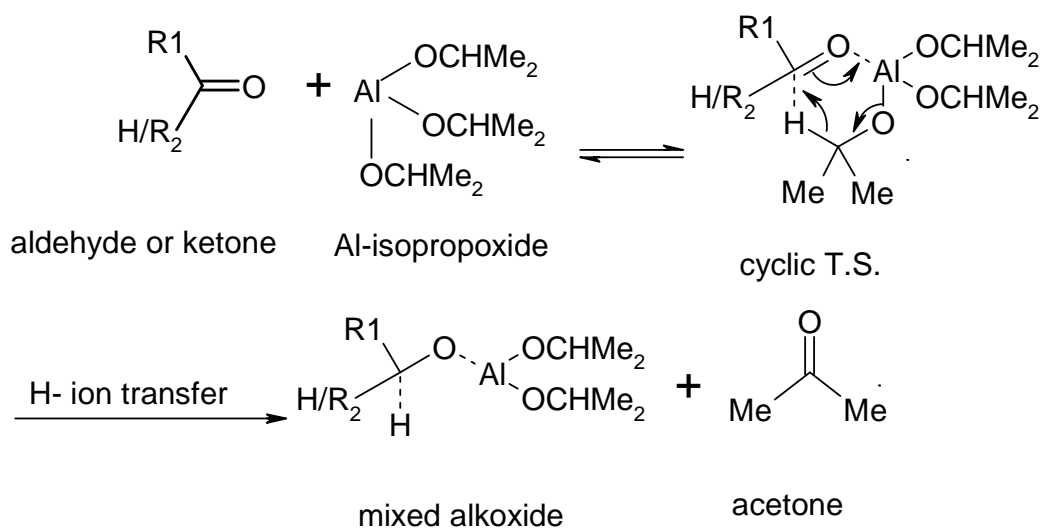
The **Meerwein–Ponndorf–Verley (MPV) reduction** in organic chemistry is the reduction of ketones and aldehydes to their corresponding alcohols utilizing aluminium alkoxide catalysis in the presence of an excess secondary alcohol.

General reaction: Aldehyde or ketones are reduced selectively to primary or secondary alcohol respectively in the presence of an excess of 2-propanol by reagent as aluminium tert-butoxide or isopropoxide.

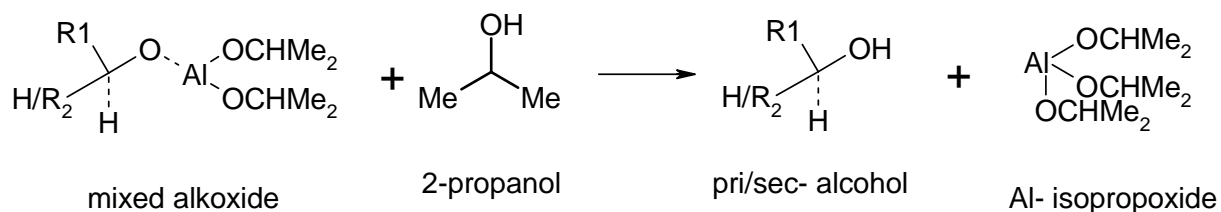


The reduction is so specific that the other reducible groups remain unaffected such as $-\text{C}=\text{C}-$, $-\text{NO}_2$, $-\text{COOR}$ etc and only the carbonyl group is reduced to alcohol.

Mechanism: The isopropoxide or tert-butoxide gives hydride to the carbonyl group through a cyclic six-membered transition state as given below.



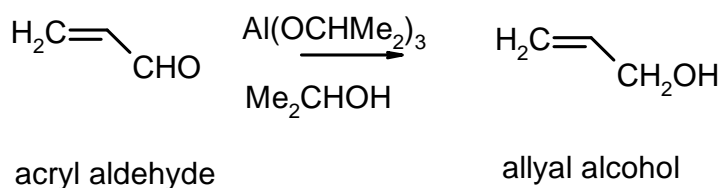
when the excess of isopropyl alcohol is present in the reaction medium, it acts as a source of proton to the mixed alkoxide and thus there is a formation of alcohol and the Aluminium isopropoxide is regenerated.



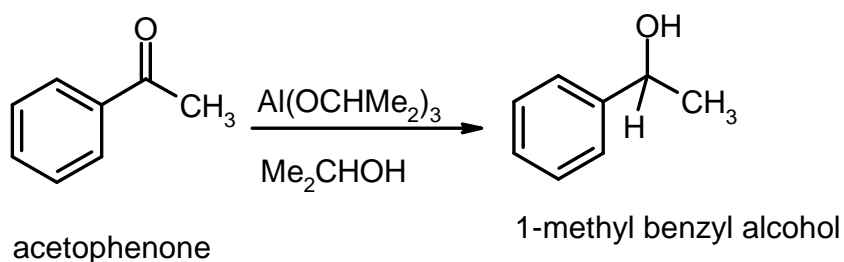
Synthetic applications:

Due to its selective nature the MPV reduction is used in synthesis of various compounds which require a substrates such as unsaturated aldehydes, aromatic ketones, alicyclic ketones, nitro aldehydes etc which contains other reducible groups.

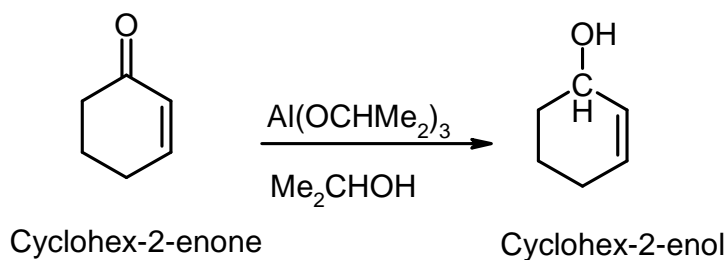
1. unsaturated aldehydes



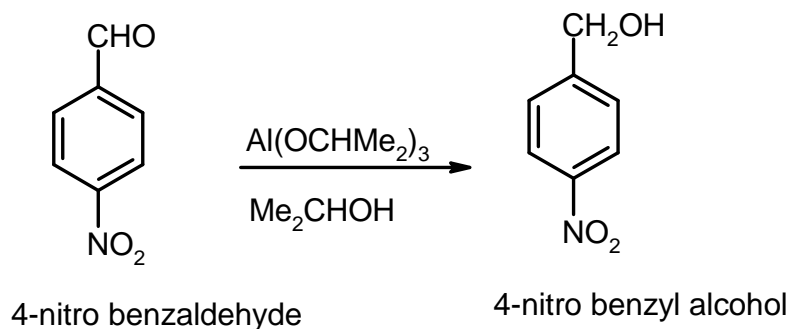
2. aromatic ketones



3. alicyclic ketones



4. nitro aldehydes



1.4 Schmidt rearrangement

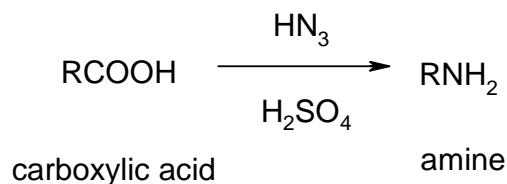
Statement:

The Schmidt reaction is an organic reaction involving alkyl migration over the carbon nitrogen bond in an azide with expulsion of nitrogen. The acid catalysed reaction of hydrogen azide with electrophiles such as carboxylic acid, aldehyde or ketones, tertiary alcohols or alkenes to produce amines, nitriles, amides or imines after a rearrangement and extrusion of N₂.

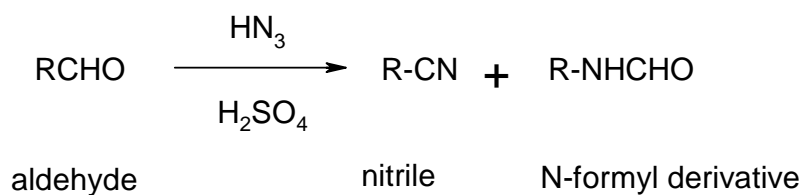
General reaction:

The nature of product formed depends on the type of reactant used in the reaction.

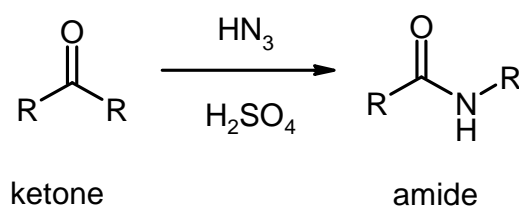
1. Carboxylic acid gives amine



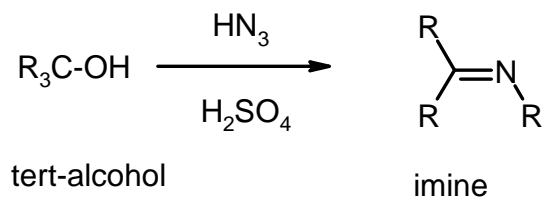
2. Aldehydes give mixture of nitrile and N-formyl derivatives



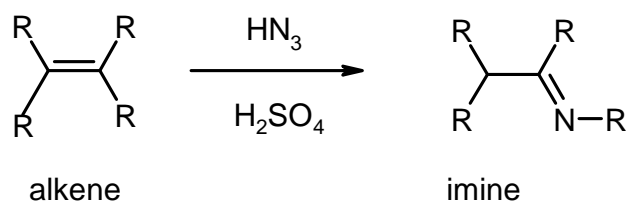
3. Ketones give amide



4. Tertiary alcohols give imine



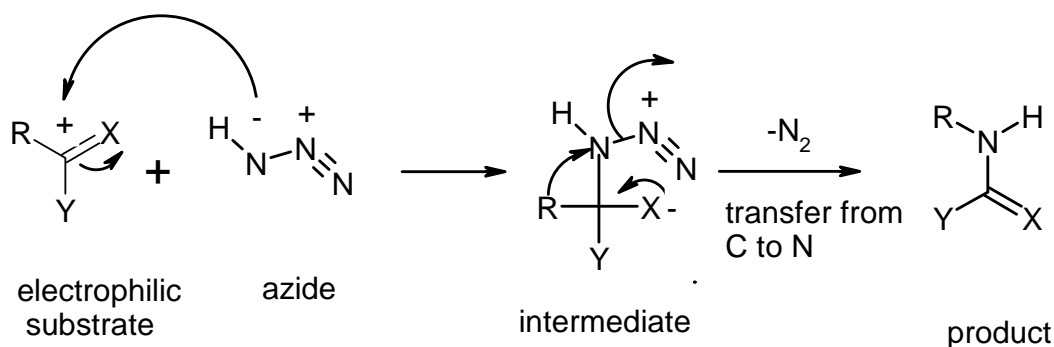
5. Alkenes give imine



Mechanism:

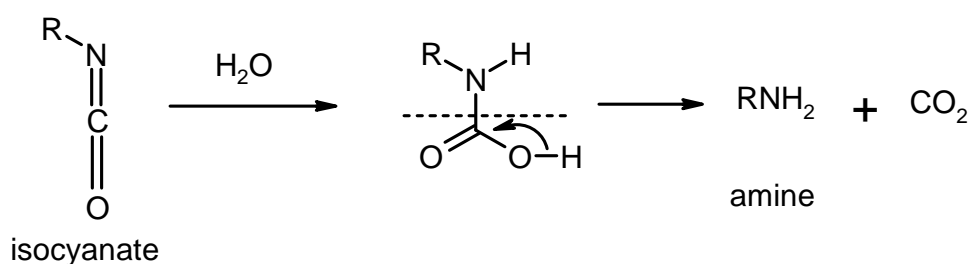
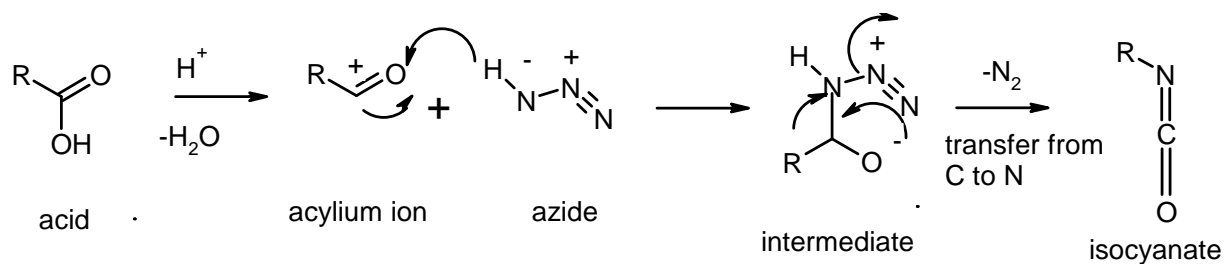
The reaction involves the formation of isocyanate intermediate through the migration of a group from Carbon to Nitrogen. The intermediate formed depends on the substrate as well. The azide nitrogen is electron rich which attacks the electron deficient carbon to form a intermediate which on further shift of group from carbon to nitrogen.

However for the sake of understanding the general mechanism can be written as follows: The attack of electron rich N from azide on the electron deficient center mostly the carbon in various substrates mentioned above, cause formation of an intermediate which on transfer of group from C to N and extrusion of N₂ gives a product.

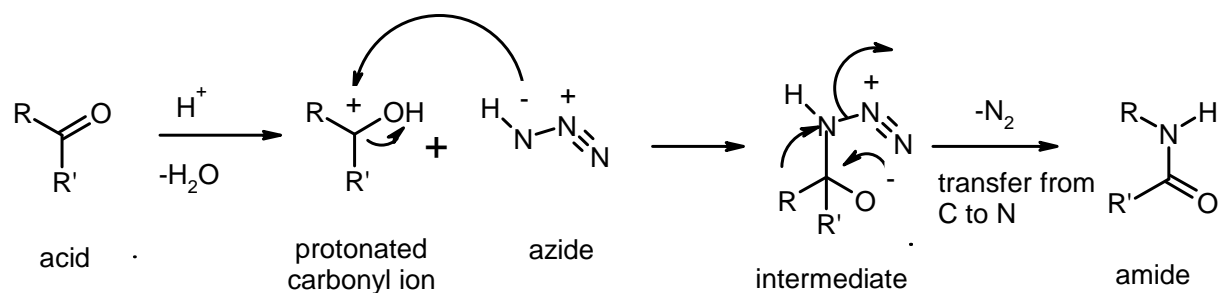


However the reactions actually does not follow this path exactly. It differs a little from substrate to substrate. The reactions of acids and carbonyl compounds are discussed below.

1. Acids form acylium ion on protonation and dehydration in first step which is attacked by azide to form the intermediate which then undergoes rearrangement to isocyanate. Which on hydrolysis yields amine and CO_2



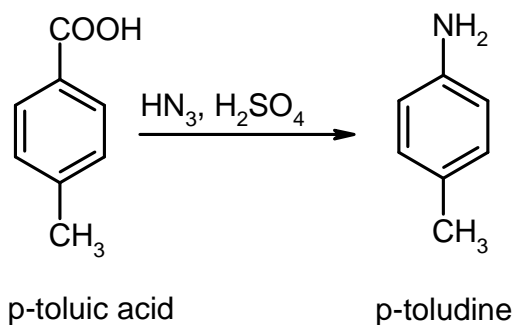
2. Carbonyl compounds undergo protonation to give a cation which is attacked by azide to form the intermediate which then undergoes rearrangement and extrusion of N_2 to amide.



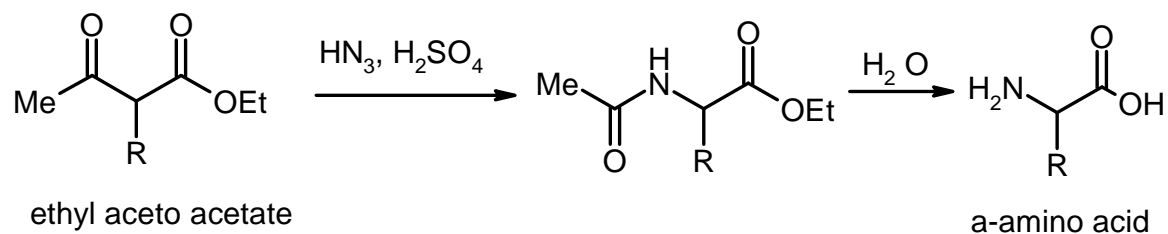
Synthetic applications:

Variety of substrates undergo Schmidt reaction as mentioned above. Hence Schmidt reaction is applied to synthesize number of compounds such as amines, amides, imides, amino acids etc.

Eg. P-toluidine is formed from p-toluic acid



Similarly the alpha amino acid is produced when ethyl aceto acetate undergoes Schmidt reaction.



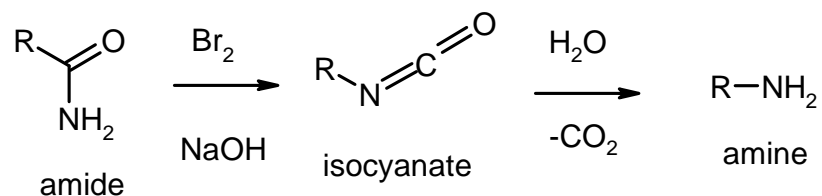
1.5 Hofmann rearrangement

Statement:

The Hofmann rearrangement is the organic reaction of a primary amide to a primary amine with one carbon atom less. This is also called Hoffmann degradation due to loss of one carbon.

General reaction:

Acid amides when warmed with bromine and concentrated aqueous alkali gives amine, sodium bromide, sodium carbonate and water.

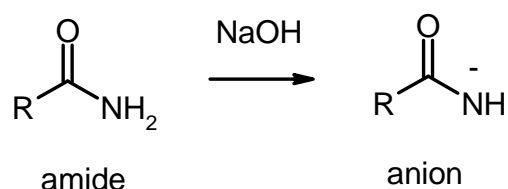


Where, R may be alkyl, aryl or heterocyclic group. However higher amides with more than eight carbon atoms give nitriles instead of 1°-amines.

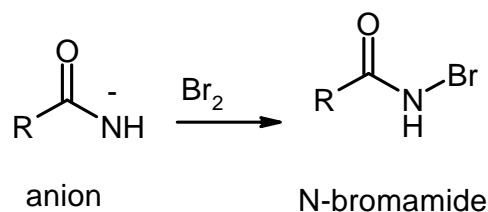
The reaction is also called Hoffmann rearrangement as the product is formed by rearrangement of an isocyanate intermediate. The reaction proceeds through the formation of N-bromamide intermediate when Bromine is the halide used commonly. Hence, the reaction is also named as Hoffmann bromamide reaction too.

Mechanism:

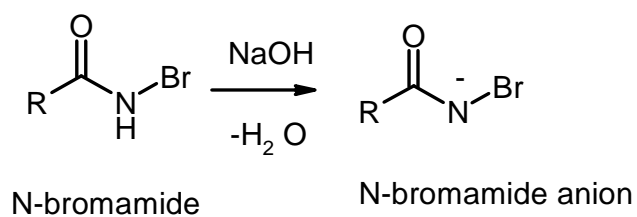
1. Base abstracts an acidic N-H proton, yielding an anion.



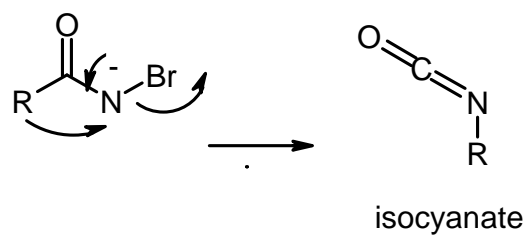
2. The anion reacts with bromine in α -substitution reaction to give an N-bromoamide.



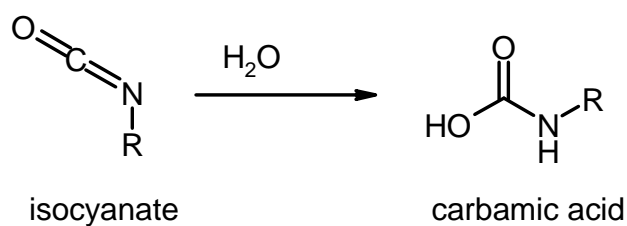
3. Base abstraction of the remaining amide proton gives a bromoamide anion.



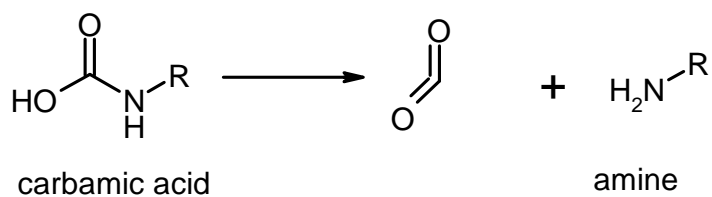
4. The bromoamide anion rearranges as the R group attached to the carbonyl carbon migrates to nitrogen at the same time the bromide ion leaves, giving an isocyanate.



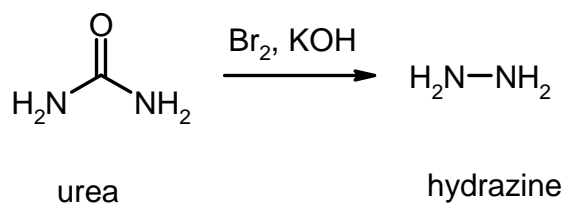
5. The isocyanate adds water in a nucleophilic addition step to yield a carbamic acid (aka urethane).



6. The carbamic acid spontaneously loses CO₂, yielding the amine product.



This mechanism can be summarized as follows:



1.6 Wittig reaction

Statement:

Organophosphorus ylides react with aldehydes or ketones to give substituted alkenes in a transformation called the Wittig reaction.

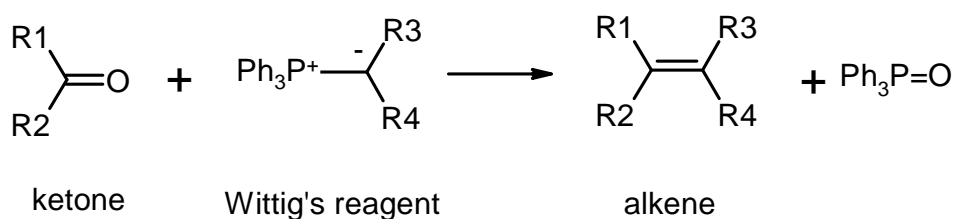
[An ylide is defined as a compound with opposite charges on the adjacent atoms both of which have complete octet.]

The **Wittig reaction** or Wittig olefination is a chemical reaction of an aldehyde or ketone with a triphenyl phosphonium ylide (often called a **Wittig reagent**) to give an alkene and triphenylphosphine oxide.

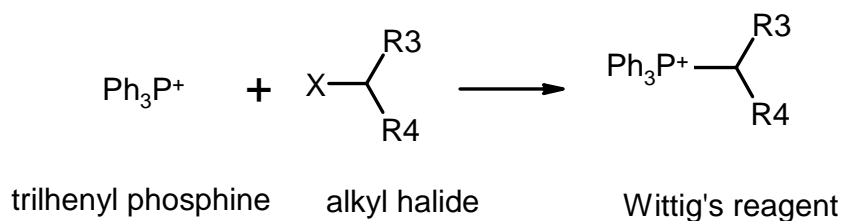
The Wittig reaction was discovered in 1954 by Georg Wittig, for which he was awarded the Nobel Prize in Chemistry in 1979. It is widely used in organic synthesis for the preparation of alkenes. It should not be confused with the Wittig rearrangement.

General reaction:

Aldehydes and ketones on treatment of ethereal solution of Wittig reagent form substituted alkenes.

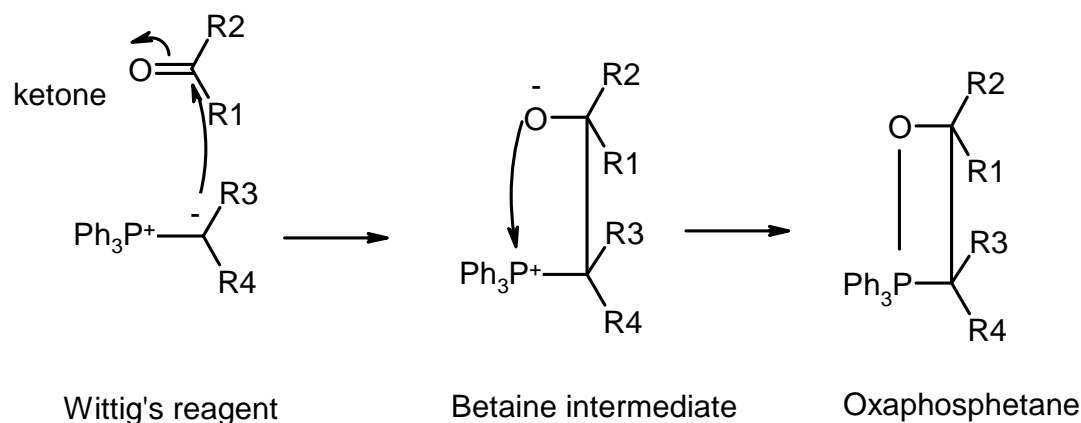


Wittig reagent is alkylidene or arylidene triphenyl phosphorane. This ylide is prepared by reaction of alkyl halide with triphenyl phosphine.

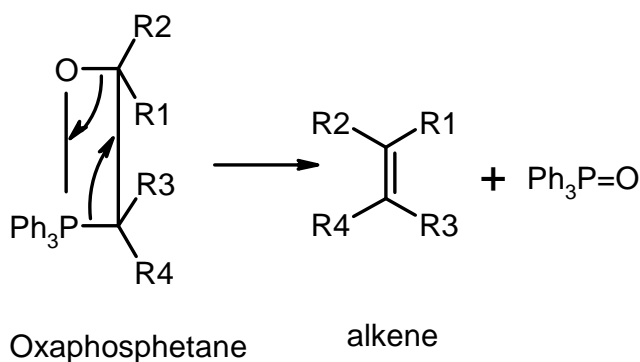


Mechanism:

Step I: ylide nucleophile attacks on the carbonyl carbon of aldehyde or ketone to give Betaine a dipolar intermediate which is stabilized by cyclic 4 membered structure called Oxaphosphetane.

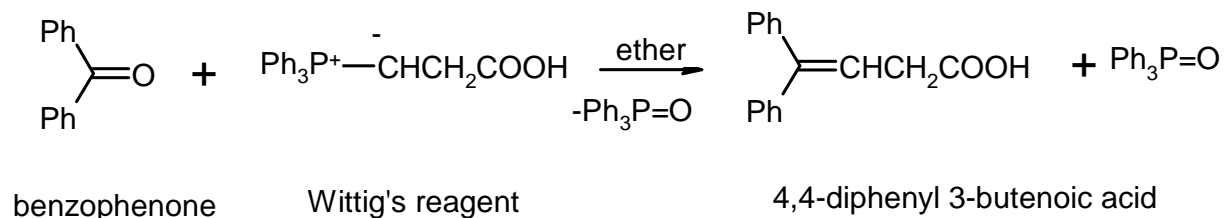


Step II: The Oxaphosphetane is a four membered heterocycle which eliminates triphenyl phosphene to give product alkene.

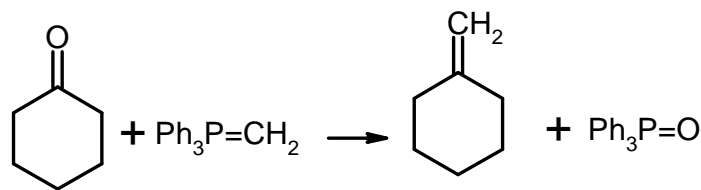


Synthetic applications:

1. Preparation of α - β unsaturated acids. As the reaction proceeds through a cyclic intermediate, the reaction produces stereo-chemically pure isomer.



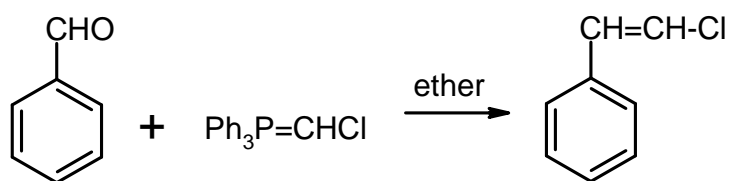
2. Exocyclic methylene derivatives required in the synthesis of steroids.



cyclohexanone

methylene
cyclohexane

3. Synthesis of vinyl halides by using chloromethylene triphenyl phosphorane as Wittig reagent.



benzaldehyde

styryl chloride

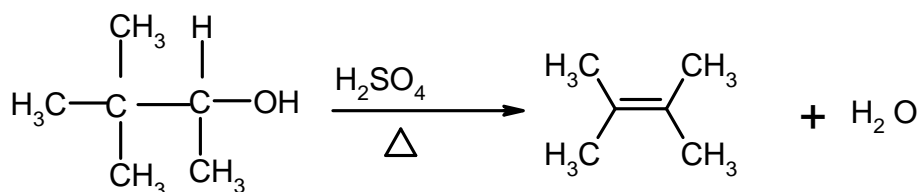
1.7 Wagner- Meerwein rearrangement

Statement:

The Wagner-Meerwein rearrangement is an organic reaction used to convert an alcohol to an olefin using an acid catalyst. A Wagner-Meerwein rearrangement is any reaction in which the carbon skeleton of a reactant changes due to one or more rearrangements involving carbocations.

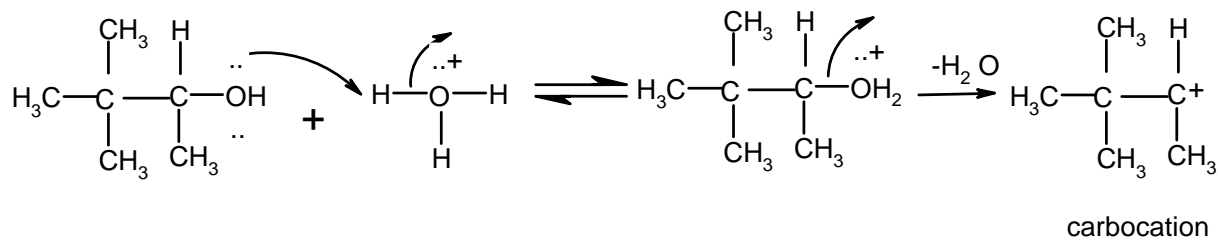
General reaction: Any highly branched or bridged bicyclic compound undergoes Wagner-Meerwein rearrangement to an olefin where there occurs the shift of alkyl, aryl group or the sigma bond of ring. There is a change in the carbon skeleton of the substrate.

Eg. 2,3,3-trimethyl 2-butanol is converted to 2,3-dimethyl but-2-ene when treated with sulfuric acid.



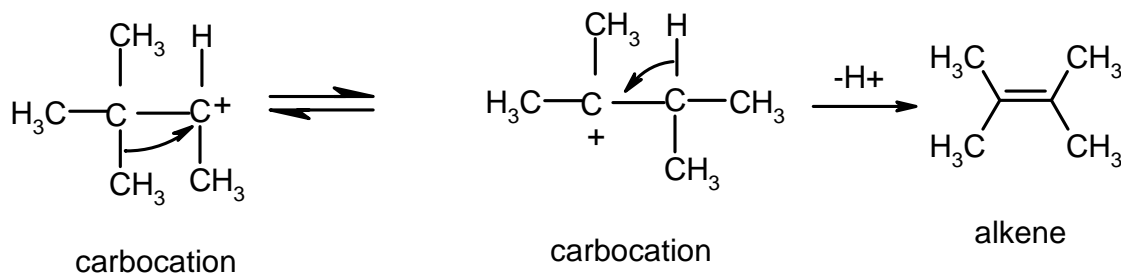
Mechanism:

The mechanism begins with protonation of the alcohol by the acid which is then released as water to form a carbocation.



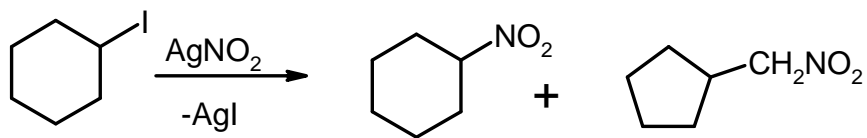
A 1,2-shift then occurs to form a more substituted and stabilized carbo-cation.

A final deprotonation with water produces the final olefin product and regenerates the acid catalyst.



Synthetic applications:

1. Wagner-Meerwein rearrangement is used for synthesis of compounds with ring contraction.

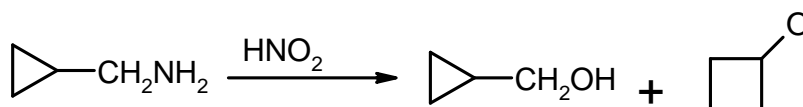


iodo cyclohexane

nitro cyclohexane

Nitromethyl-cyclopentane

2. Wagner-Meerwein rearrangement is used for synthesis of compounds with ring expansion too.

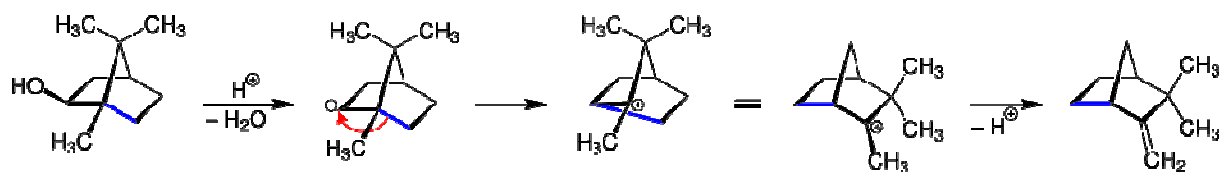


C-Cyclopropyl-methylamine

Cyclopropyl-methanol

Cyclobutanol

3. The conversion of isoborneol to camphene:



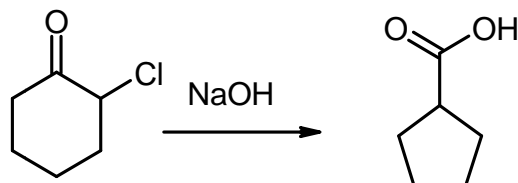
1.8 Favorskii rearrangement

Statement:

The Favorskii rearrangement, is most principally a rearrangement of cyclopropanones and α -halo ketones which leads to carboxylic acid derivatives. In the case of cyclic α -halo ketones, the Favorskii rearrangement constitutes a ring contraction. This rearrangement takes place in the presence of a base, sometimes hydroxide, to yield a carboxylic acid but most of the time either an alkoxide base or an amine to yield an ester or an amide, respectively. α, α' -Dihalo ketones eliminate HX under the reaction conditions to give α, β -unsaturated carbonyl compounds.

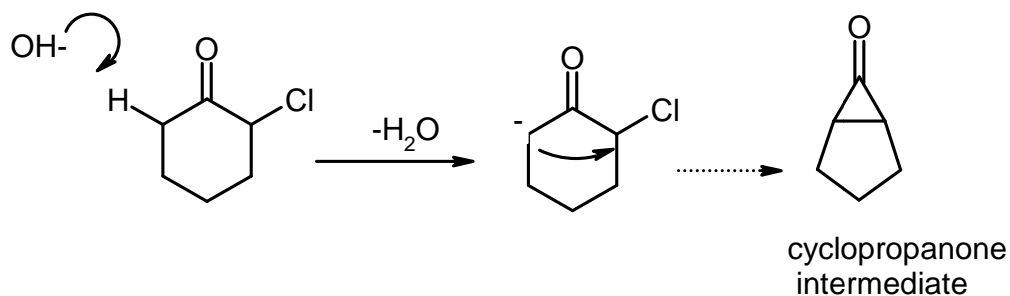
General reaction:

2-Chloro cyclohexanone when treated with sodium hydroxide undergoes Favorskii rearrangement resulting in a ring contraction to produce cyclopentane carboxylic acid.

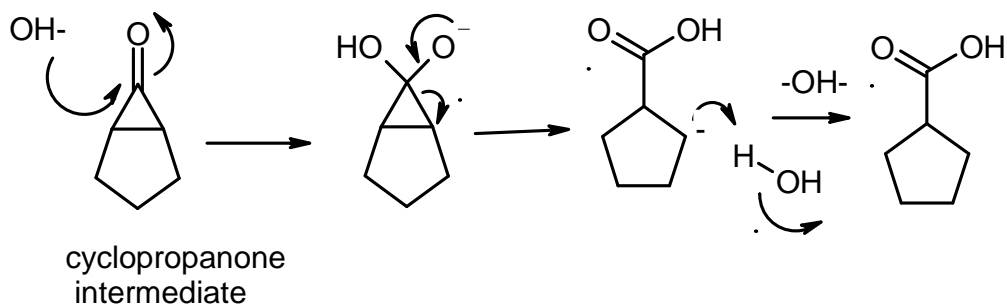


Mechanism:

The reaction mechanism is thought to involve the formation of an enolate on the side of the ketone away from the chlorine atom. This enolate cyclizes to a cyclopropanone intermediate.



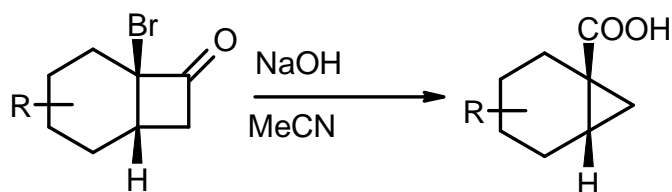
The cyclopropanone intermediate is then attacked by the hydroxide nucleophile. Further redistribution of the electrons and shift of sigma bond alpha to the carbonyl carbon to next carbon opening the cyclopropane ring to stable five membered ring produce the cyclopentane carboxylic acid.



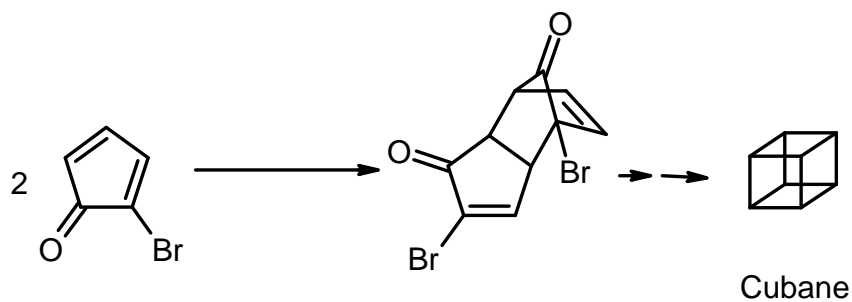
Use of alkoxide anions such as sodium methoxide, instead of sodium hydroxide, yields the ring-contracted ester product.

Synthetic applications:

It is used specifically to generate useful structural patterns.



Synthesis of cubane:



1.9 Michael reaction

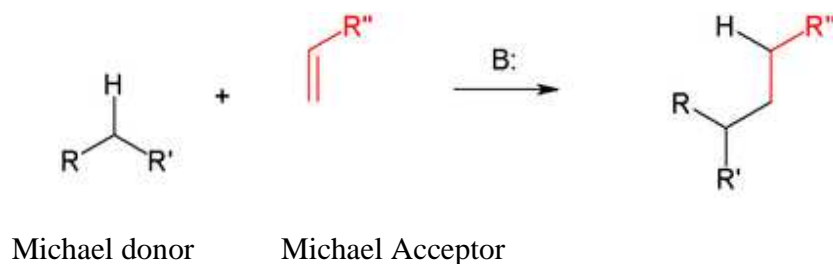
Statement:

The Michael reaction or **Michael addition** is the nucleophilic addition of a carbanion or another nucleophile to an α,β -unsaturated carbonyl compound. It belongs to the larger class of conjugate additions. This is one of the most useful methods for the mild formation of C–C bonds.

In this reaction, the substituents on the Michael donor a nucleophile are electron-withdrawing groups such as acyl and cyano which make the methylene hydrogen acidic and thus form the carbanion on reaction with base B:. The substituent on the activated alkene, also called a Michael acceptor, is usually a ketone making it an enone, but it can also be a nitro group.

The reaction donors are active methylenes such as malonates and nitroalkanes and the acceptors are activated olefins such as α,β -unsaturated carbonyl compounds.

General reaction:



Classical examples of the Michael reaction are the reaction between Michael donor and Michael acceptor pairs as given below:

Michael donor	Michael acceptor
diethyl malonate	diethyl fumarate
mesityl oxide	diethyl malonate
diethyl malonate	methyl crotonate
2-nitropropane	methyl acrylate
<i>ethyl phenylcyanoacetate</i>	acrylonitrile

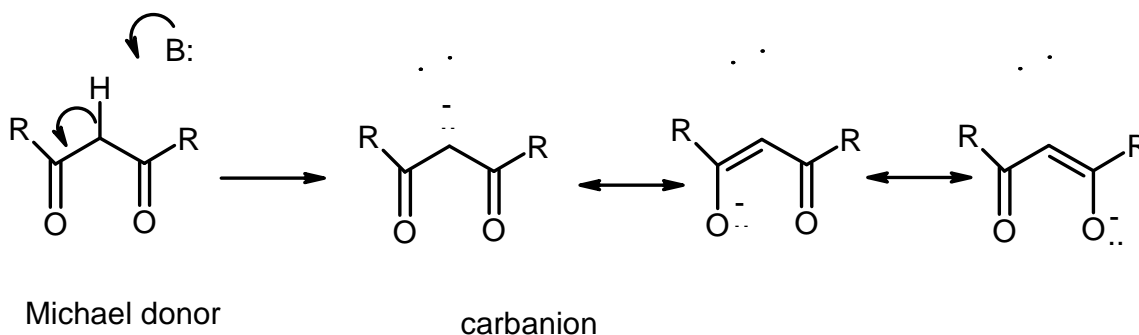
nitropropane

methyl vinyl ketone

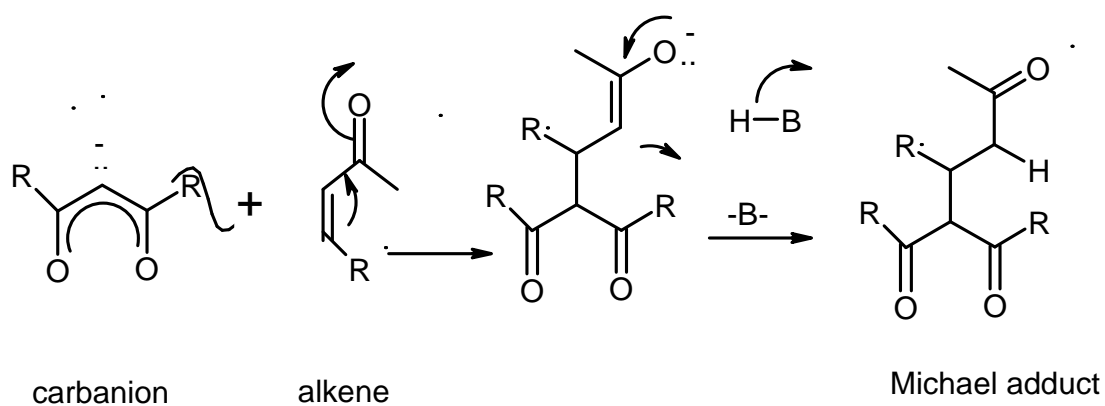
The Michael addition is an important atom-economical method for diastereoselective and enantioselective C–C bond formation.

Mechanism:

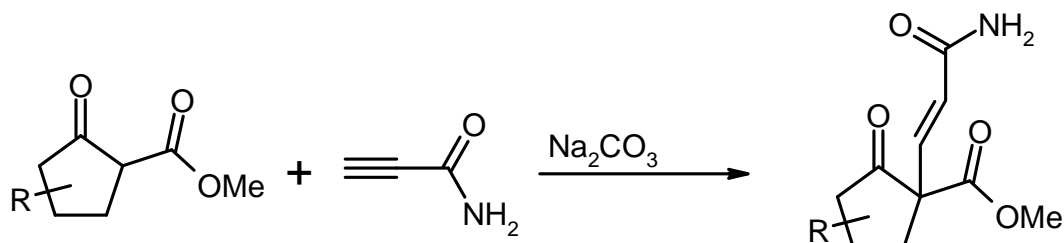
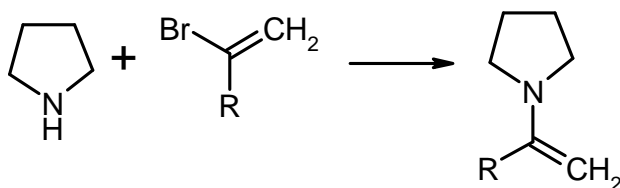
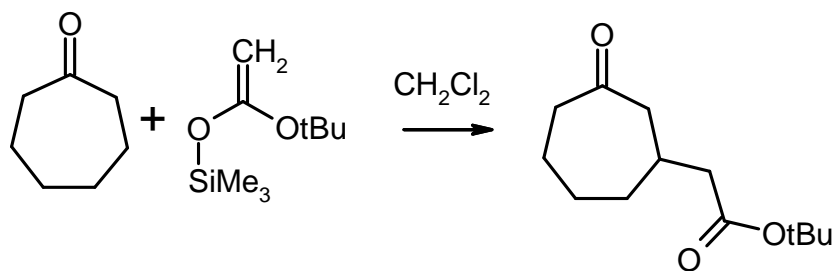
First step is a deprotonation of Michael donor by base leading to a carbanion which is stabilized by its electron-withdrawing groups. There are three resonance structures of the carbanion out of which, two structures have enolate ions. (negative charge on oxygen attached to a doubly bonded carbon)



This carbanion reacts with the electrophilic alkene (Michael acceptor) to form enolate ion which on proton abstraction forms Michael adduct.



Synthetic applications:



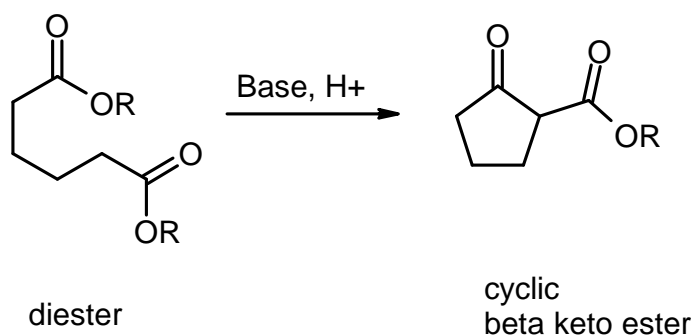
1.10 Dieckmann's reaction or condensation

Statement:

It is named after the German Chemist Walter Dieckmann (1869–1925). It is the base-catalyzed intramolecular condensation of a diester using an alkoxide base in alcohol to make a cyclic β -keto ester.

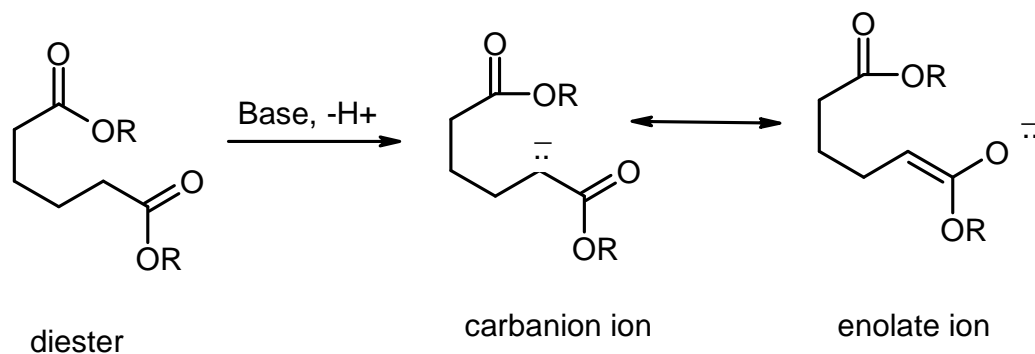
General reaction:

The diester when treated with alkoxide base in alcohol gives cyclic β -keto ester.

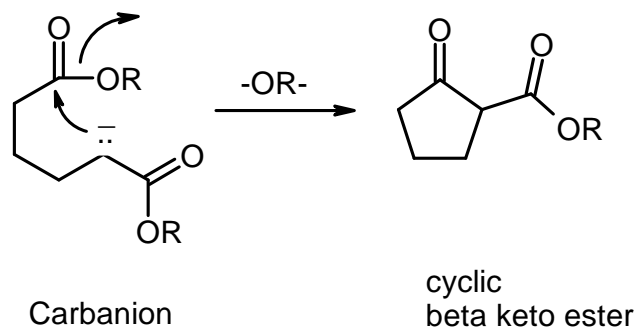


Mechanism:

The diester, where at least one ester group have an α -hydrogen undergo deprotonation. The α -hydrogen is abstracted by the base to form an enolate and alcohol.

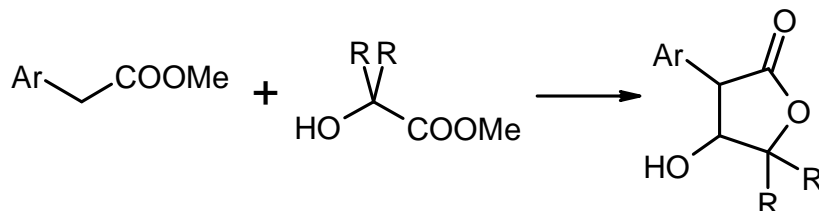


The enolate then attacks the carbonyl carbon of another ester molecule, an OR group is released to regenerate the base, and the final β -keto ester product is formed.

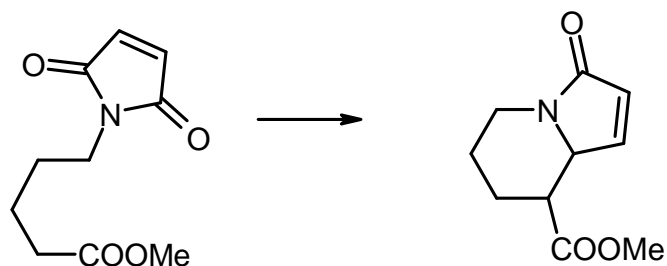


Synthetic applications:

The Dieckmann condensation between two different esters causes intermolecular condensation.



The intramolecular condensation of ester with imide:



Summary: [Points to remember]:

Reaction	Substrate	Reagents /Reaction Conditions	Product
1. Diels -Alder reaction	diene and an alkene	heat	(adduct)cyclohexene derivative
2. Oppenauer Oxidation	secondary alcohol	aluminium tert-butoxide in excess of acetone	ketones
3. Meerwein – Ponderff-Verley reduction	ketones / aldehydes	aluminium tert butoxide or isopropoxide in excess of 2-propanol	primary / secondary alcohol
4. Schmidt rearrangement	carboxylic acid, aldehyde or ketones, tertiary alcohols or alkenes	HN ₃ [Hydrogen azide] and H ₂ SO ₄	amines, nitriles, amides or imines
5. Hofmann rearrangement	Acid amides	bromine and concentrated aqueous alkali	primary amine with one carbon atom less
6. Wittig reaction	aldehydes or ketones	ethereal solution of Wittig reagent : organophosphorus ylides Ph ₃ P=CR ₂	substituted alkenes
7. Wagner-Meerwein rearrangement	alcohol	acid catalyst H ₂ SO ₄	olefin
8. Favorskii rearrangement	cyclic α-halo ketones	sodium hydroxide/ Potassium hydroxide	carboxylic acid with ring contraction
9. Michael reaction	active methylenes and olefin	Base as Na ₂ CO ₃	Addition product
10. Dieckmann'	Diester	alkoxide base in alcohol	cyclic β-keto ester

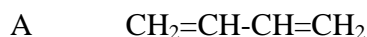
s reaction or condensation	Or two esters		
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1.11 Problems based on above reactions:

1. A compound 'A' with Molecular formula C_4H_6 shows signal at λ_{max} value of 214 nm. On heating with a carbonyl compound 'B' [C_3H_4O] forms an addition product 'C' [$C_7H_{10}O$]. It shows absorption bands at 2700 cm^{-1} and 1730 cm^{-1} . Identify the compounds 'A, B and C. Name the reaction.

Solution:

- a. The molecular formula of compound A [C_4H_6] contains 4 hydrogens less than the corresponding saturated hydrocarbon [C_4H_{10}]. Hence it must have two double bonds.
- b. A [C_4H_6] shows signal at λ_{max} value of 214 nm, hence it must be a conjugated diene. So, 'A' must be 1,3-butadiene.



- c. Carbonyl compound B [C_3H_4O] must be an aldehyde and not a ketone, as the mol formula of a ketone with three carbon atoms [$CH_3-CO-CH_3$] does not match with the given formula.
- d. Carbonyl compound B [C_3H_4O] also has two carbons less than saturated aldehyde [CH_3CH_2CHO] with same number of carbon atoms. Hence it must have a double bond and the aldehyde is unsaturated aldehyde. i.e. acrylaldehyde

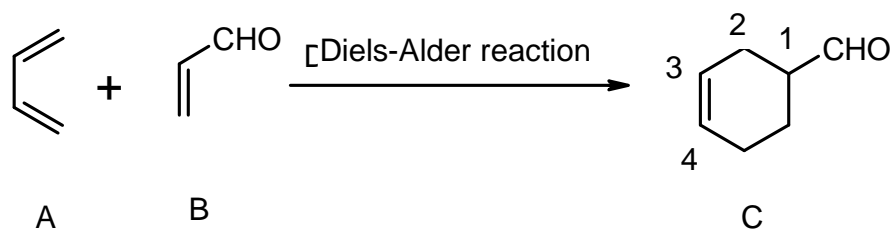


Molecular formula of product 'C' is sum of the molecular formulae for 'A' and 'B'



Hence, it is an addition product without loss of any atom.

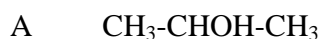
- e. The product shows absorption bands at 2700 cm^{-1} and 1730 cm^{-1} which indicates that it is also an aldehyde.
- f. The compound A is a diene and B is having a double bond, hence this must be Diels-Alder reaction as follows and the product C must be cyclohex-3-ene carbaldehyde.



2. An organic compound 'A' [C₃H₈O] gives a broad band in IR spectrum at 3500 cm⁻¹. On oxidation it gives a ketone with same number of carbon atoms and an acid with less number of carbon atoms. When 'A' is dissolved in cyclohexanone and refluxed with Al-tert-butoxide in benzene, form a compound 'B' [C₃H₆O] showing strong absorption band at 1700 cm⁻¹. Identify A and B, name the reaction.

Solution:

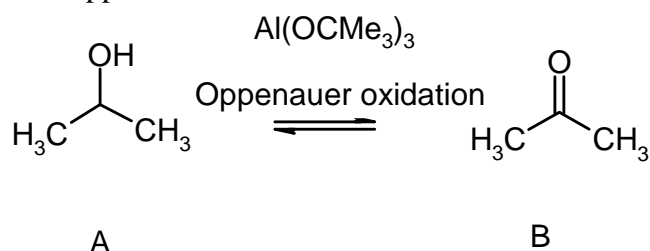
- a. 'A' [C₃H₈O] gives a broad band in IR spectrum at 3500 cm⁻¹ hence it is an alcohol.
- b. On oxidation 'A' gives a ketone with same number of carbon atoms and an acid with less number of carbon atoms, hence it is a secondary alcohol



- c. The reaction conditions such as cyclohexanone and Al-tert-butoxide in benzene suggest that it is an Oppenauer oxidation.
- d. The product shows band at 1700 cm⁻¹, therefore it must be a ketone.



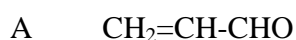
- e. Hence the reaction is Oppenauer oxidation.



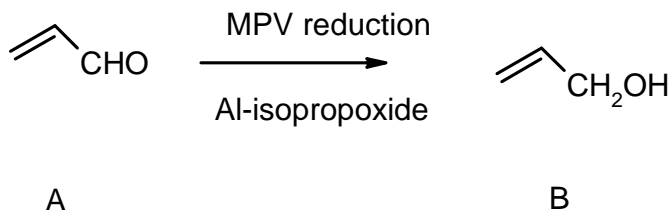
3. An unsaturated compound 'A' [C₃H₄O] showing strong absorption band at 1720 cm⁻¹ and 2700 cm⁻¹ in IR spectrum. It is when heated with Al-isopropoxide gives 'B'[C₃H₆O] Identify 'B' from the spectral signals at 3300 cm⁻¹ and 1640 cm⁻¹. Name the reaction.

Solution:

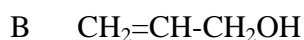
- a. 'A' [C₃H₄O] showing strong absorption band at 1720 cm⁻¹ and 2700 cm⁻¹ in IR spectrum, must be an aldehyde. It is unsaturated compound, hence it must be as:



- b. When heated with Al-isopropoxide 'A' gives 'B' [C₃H₆O]. The reaction conditions such as Al-isopropoxide and Molecular formula of B with two additional hydrogen atoms than 'A'; indicates that it is MPV reduction as follows:



Hence 'B' is a primary alcohol.



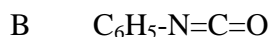
4. Compound 'A' [C₇H₆O₂] gives effervescence on addition to Na-bicarbonate. It forms a compound 'B' [C₇H₅NO] when treated with Na-azide in sulphuric acid, which readily hydrolyses to 'C' [C₆H₇N] with evolution of carbon dioxide. The compound 'C' shows carbylamines test. Identify A,B, C and name the reaction.

Solution:

- a. Compound 'A' [C₇H₆O₂] gives effervescence on addition to Na-bicarbonate, hence it is carboxylic acid. [C₆H₅-COOH] suggests that it is benzoic acid.



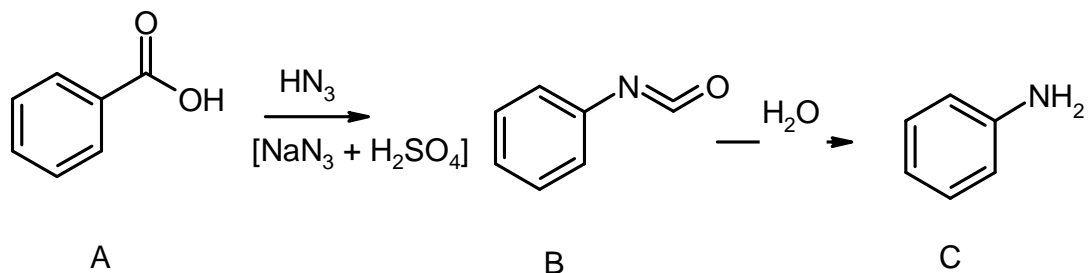
- b. The reaction conditions such as Na-azide in sulphuric acid suggests that the reaction is Schmidt reaction, which involves alkyl migration over the carbon nitrogen bond in an azide with expulsion of nitrogen. Hence 'B' must be an intermediate phenyl isocyanate.



- c. 'B' [C₇H₅NO] readily hydrolyses to 'C' [C₆H₇N] with evolution of carbon dioxide and Gives compound 'C' which shows carbylamines test. i.e. 'C' is an amine



- d. The reaction is Schmidt reaction as follows



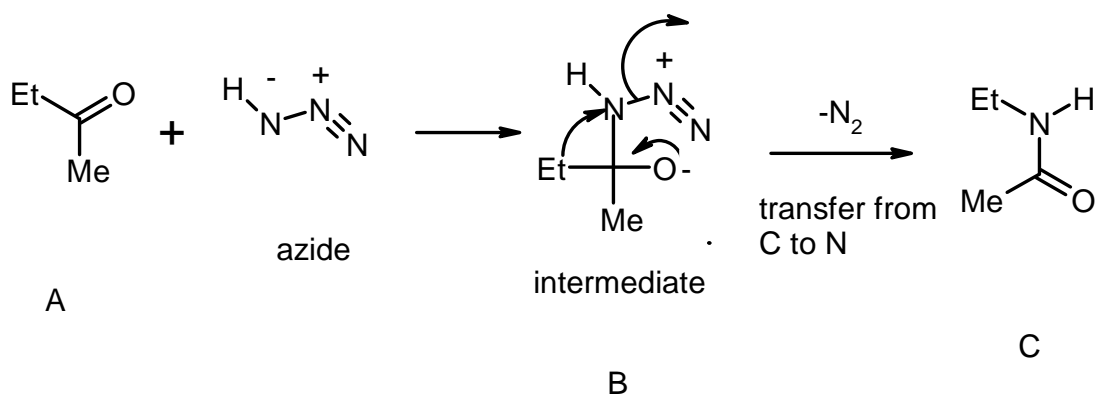
5. A compound 'A' [C₄H₈O] shows iodoform test. When treated with acidic solution of sodium azide forms an intermediate 'B' [C₄H₉N₃O]. Compound 'B' readily loses nitrogen in acidic medium and gives compound 'C' [C₄H₉NO] identify A,B,C and name the reaction.

Solution:

- a. A compound 'A' [C₄H₈O] shows iodoform test, hence it is a ketone. The molecular formula suggests that it is methyl ethyl ketone.



- b. The reaction conditions such as Na-azide in sulphuric acid suggests that the reaction is Schmidt reaction, which involves alkyl migration over the carbon nitrogen bond in an azide.



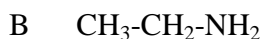
6. A compound 'A' [C₃H₇NO] on heating with alkali releases ammonia and forms alkali metal salt of carboxylic acid. When 'A' is heated with bromine and concentrated alkali, forms compound 'B' [C₂H₇N] which yields ethyl alcohol on treatment with nitrous acid, identify A, B and name the reaction.

Solution:

- a. A compound 'A' [C₃H₇NO] on heating with alkali releases ammonia and forms alkali metal salt of carboxylic acid. Hence it is an amide.

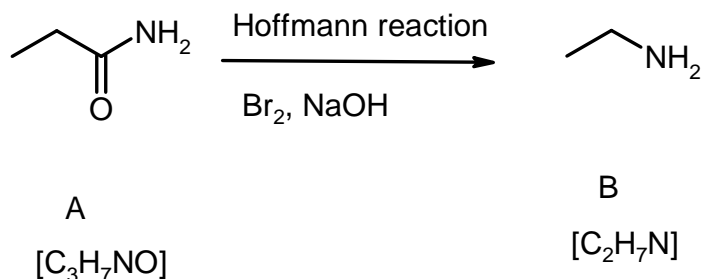


- b. The reaction conditions such as heating with bromine and concentrated alkali suggest that the reaction is Hofmann rearrangement/ degradation. The reduced number of carbon atoms in 'B' also supports the conclusion. Hence 'B' is an amine.



- c. B' [C₂H₇N] which yields ethyl alcohol on treatment with nitrous acid, also proves that it is an amine.

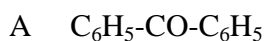
- d. Hence the Hofmann rearrangement/ degradation is as follows:



7. Compound 'A' [C₁₃H₁₀O] strongly absorbs at 1690 cm⁻¹ and on treatment with an alkylidene phosphorane yields a compound B [C₁₄H₁₂] which on ozonolysis yields formaldehyde and compound 'A'. Identify A, B and name the reaction.

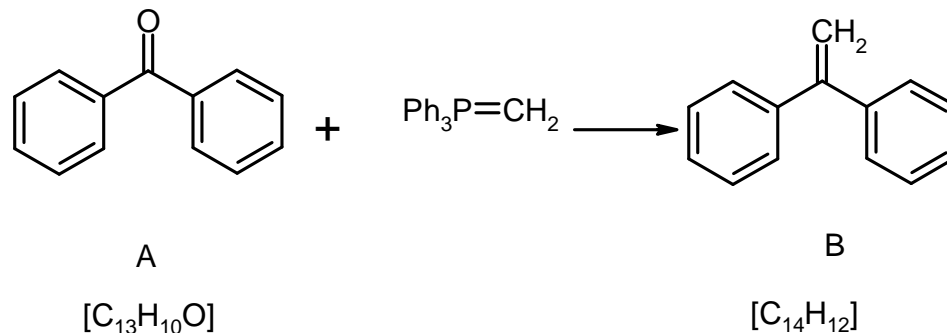
Solution:

- a. Compound 'A' [C₁₃H₁₀O] strongly absorbs at 1690 cm⁻¹, hence it must be having a carbonyl group. [C₁₂H₁₀CO]
- b. The ratio of C:H indicates an aromatic character. Hence 'A' must be a ketone as benzophenone:

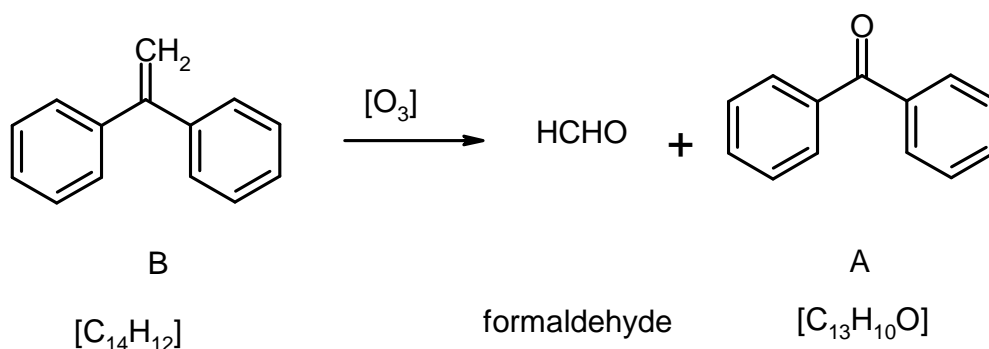


- c. 'A' on treatment with an alkylidene phosphorane yields a compound B [C₁₄H₁₂]
- d. The conditions of reaction such as treatment with an alkylidene phosphorane suggests that it is Wittig reaction.
- e. Compound B [C₁₄H₁₂] on ozonolysis yields formaldehyde (1C) and compound 'A' (12C).
- f. ozonolysis breaks a double bond to give fragments of 12 and 1 carbon each, suggesting that the alkylidene phosphorane is actually a methyldene phosphorane

which have added 1 carbon to 'A' by Wittig reaction as follows:



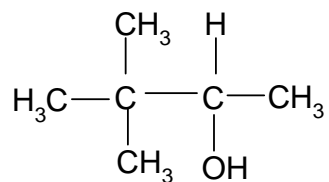
g. Following reaction of ozonolysis proves the same.



8. Compound 'A' $[\text{C}_6\text{H}_{14}\text{O}]$ carrying an tert-butyl group, on oxidation yields a ketone carrying same number of carbon atoms, On heating with Bronsted acid it forms B $[\text{C}_6\text{H}_{12}]$ which on ozonolysis yields two molecules of acetone. Identify A, B and name the reaction.

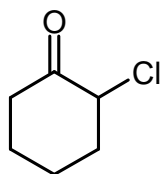
Solution:

- A' $[\text{C}_6\text{H}_{14}\text{O}]$ carries an tert butyl group $[(\text{CH}_3)_3\text{C}-]$, subtracting tert-butyl group from molecular formula we get $\text{C}_2\text{H}_5\text{O}$
- As oxidation product of 'A' has same number of carbon atoms as 'A', hence it must be a secondary alcohol.
- From above the structure of 'A' is as follows [3,3-dimethyl 2-butanol]



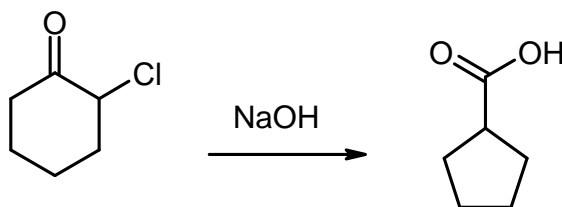
A

- b. The number of carbon atoms in 'A' and 'B' is same. But carbonyl group is getting converted into carboxylic acid. Hence there must be a ring contraction.
- c. The halogen is getting eliminated during reaction, hence it must be at adjacent carbon atom to the carbonyl group. The structure of 'A' must be 2-chloro cyclohexanone



A

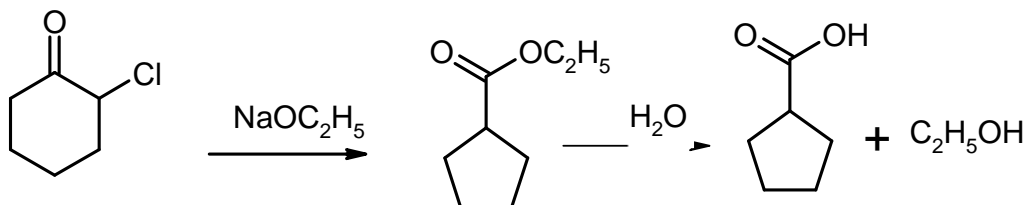
- d. 'A' on reaction with hydroxide gives acid 'B'. the reaction conditions suggest that it is Favorskii rearrangement reaction as follows



A

B

- e. Compound 'A' when treated with sodium ethoxide produces compound 'C' [C₈H₁₄O₂] which on hydrolysis produces compound 'B' and ethanol. Hence 'C' must be an ester. This is also Favorskii rearrangement as follows



A

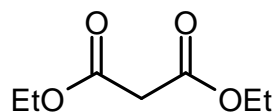
C

B

10. A compound 'A' [C₇H₁₂O₄] is a diester which on hydrolysis gives two molecules of ethanol and an acid. Compound 'A' on treatment of a hydroxide base with compound 'B' [C₃H₃N] gives addition product 'C' [C₁₀H₁₅NO₄] which on hydrolysis produces tricarboxylic acid with four carbons less than B. Identify A,B,C and name the reaction.

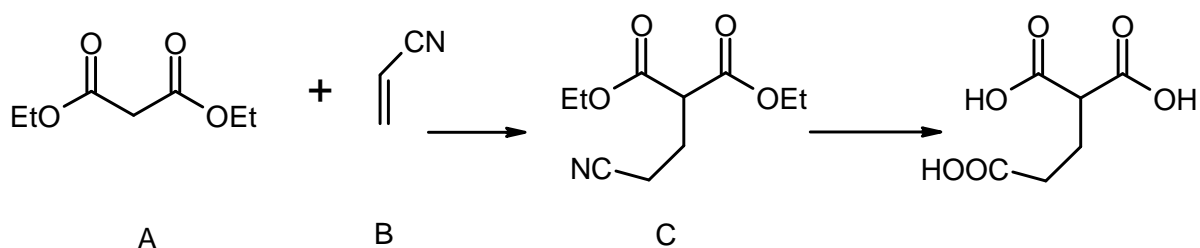
Solution:

- a. A compound 'A' [C₇H₁₂O₄] is a diester which on hydrolysis gives two molecules of ethanol, hence it is a diethyl ester. Subtracting the formula fraction (-COOC₂H₅)₂ i.e. C₆H₁₀O₄ from the molecular formula of 'A' we have only CH₂ remaining. Hence the diester 'A' must be as follows



A

- b. Compound 'A' on treatment of a hydroxide base with compound 'B' [C₃H₃N] gives addition product 'C' [C₁₀H₁₅NO₄]. Hence the reaction conditions suggest that it is Michael Addition reaction.
- c. 'C' [C₁₀H₁₅NO₄] which on hydrolysis produces tricarboxylic acid. Hence 'C' must be a compound which can be hydrolysed to acid such as ester/ amide/cyanide etc.
- d. Substrate 'A' already has two ester groups. Hydrolysis product is tricarboxylic acid with four carbons less than B hence the hydrolysable group containing N is nitrile and not amide. [Amide would be hydrolysed to acid with further loss of carbons]
- e. Compound 'B' has one nitrogen and is a Michael acceptor. Hence it must be unsaturated nitrile.
- f. The Michael addition must be as follows

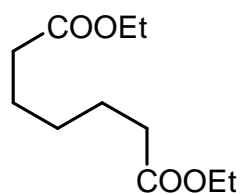


A	+	B	→	C	→	
diethyl malonate		acrylonitrile		2-(2-Cyano-ethyl)-malonic acid diethyl ester		tricarboxylic acid
[C ₇ H ₁₂ O ₄]		[C ₃ H ₃ N]		[C ₁₀ H ₁₅ NO ₄]		

11. The diester 'A' [C₁₁H₂₀O₄] can be hydrolysed to get two molecules of ethanol and a straight chain dicarboxylic acid. 'A' when treated with alkoxide base in alcohol gives cyclic β-keto ester 'B' [C₉H₁₄O₃] Identify A, B and name the reaction.

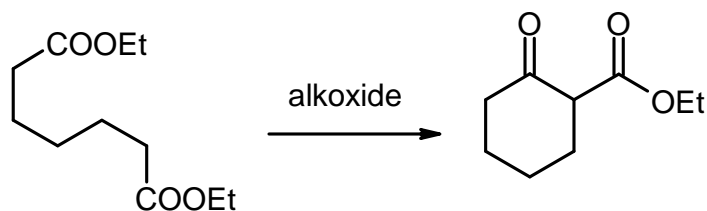
Solution:

- a. The diester 'A' [C₁₁H₂₀O₄] can be hydrolysed to get two molecules of ethanol and straight chain dicarboxylic acid. i.e. it is diethyl ester. Subtracting the formula fraction (–COOC₂H₅)₂ i.e. C₆H₁₀O₄ from the molecular formula of 'A' we have C₅H₁₀ remaining. This must be (CH₂)₅. Hence the diester 'A' must be heptanedioic acid diethyl ester as follows.



A

b. 'A' when treated with alkoxide base in alcohol gives cyclic β -keto ester 'B' [$C_9H_{14}O_3$]. The intramolecular reaction suggests that it is Dieckmann's reaction as follows.



A

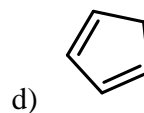
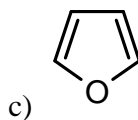
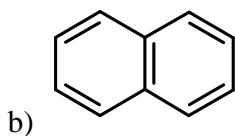
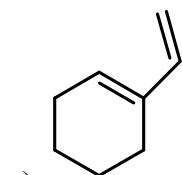
B

Exercises

[A] OBJECTIVE TYPE QUESTIONS

A] Select the most correct alternative from among those given below.

- The [4+2]-cycloaddition of a conjugated diene and a dienophile (an alkene or alkyne) is known as
 a) Michael reaction b) Wittig reaction c) Dieckmann's reaction d) Diels -Alder reaction
- From the following list, the diene cannot undergo Diels-Alder reaction is



- Diels-Alder reaction is facilitated by group in dienophile
 a) electron withdrawing b) electron releasing c) both a and b d) neither a nor b
- Oppenauer oxidation is reaction is the opposite reaction of ----- reaction.

- a) Wagner- Meerwein rearrangement b) Meerwein-Ponndorf-Verley c) Dieckmann's reaction d) Hofmann rearrangement
5. In Oppenauer oxidation the ----- is oxidized with aluminium tert-butoxide in excess acetone.
- a) secondary alcohol b) primary alcohol c) aldehyde d) ketone
6. In -----reaction, aldehyde or ketones are reduced selectively to primary or secondary alcohol respectively in presence of excess of 2-propanol by reagent as aluminium tert butoxide or isopropoxide.
- a) Wagner- Meerwein rearrangement b) Meerwein-Ponndorf-Verley reduction c) Dieckmann's reaction d) Hofmann rearrangement
7. Carbonyl group from unsaturated aldehydes, aromatic ketones, alicyclic ketones, nitro aldehydes etc which contains other reducible groups, are selectively reduced by -----reaction
- a) Meerwein-Ponndorf-Verley reduction b) Wagner- Meerwein rearrangement c) Dieckmann's reaction d) Hofmann rearrangement
8. The ----- is an organic reaction involving alkyl migration over the carbon nitrogen bond in an azide with expulsion of nitrogen.
- a) Dieckmann's reaction b) Hofmann rearrangement c) Schmidt rearrangement d) Favorskii rearrangement
9. In the Hofmann rearrangement a primary amide is converted to a primary amine with-----.
- a) same number of carbon atoms b) one carbon atom less c) one carbon atom more d) loss of many carbon atoms
10. In Hofmann rearrangement, Carbanion reacts with bromine in α -substitution reaction to give an -----intermediate.
- a) N-bromoamide b) bromonim ion c) bromide ion d) amido bromide
11. Organophosphorus ylides react with -----to give substituted alkenes in a transformation called the Wittig reaction.
- a) secondary alcohols b) amides c) aldehydes or ketones d) diesters
12. A Wagner-Meerwein rearrangement is any reaction in which the carbon skeleton of a reactant changes due to one or more rearrangements involving -----in acid catalyst.
- a) N-bromamide b) enolate c) carbanions d) carbocations

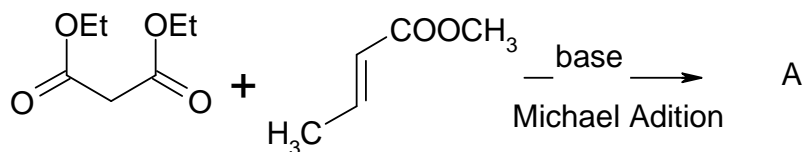
13. The nucleophilic addition of a carbanion or another nucleophile to an α,β -unsaturated carbonyl compound is named as -----reaction.

- a) Michael b) Dieckmann's c) Diels-Alder d) Favorskii

14. -----is the base-catalyzed intramolecular condensation of a diester using an alkoxide base in alcohol to make a cyclic β -keto ester.

- a) Michael b) Dieckmann's c) Diels-Alder d) Favorskii

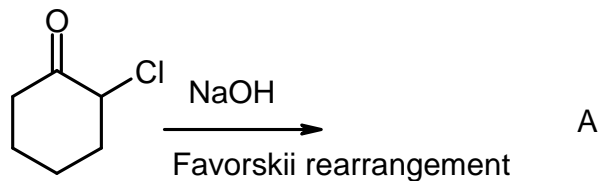
15. In the following reaction product A is.....



Malonic acid diethyl ester methyl crotonate

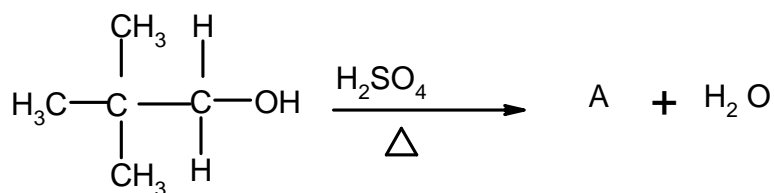
- a) diester b) triester c) tricarboxylic acid d) olefin

16. In the following reaction product A is.....



- a) cyclohexane carboxylic acid b) cyclohexanol
c) cyclopentane carboxylic acid d) cyclopentanone

17. In the following reaction product A is.....



- a) 2-methyl 2-butene b) neopentane c) 2,2-dimethyl propene d) tert butanol

18. The following reaction is -----.

[B] LONG AND SHORT ANSWER TYPE QUESTIONS:

1. What are name reactions?
2. Discuss the mechanism of the following reactions with suitable example.

OR

3. Write any two synthetic applications of the following.
 1. Diels -Alder reaction
 2. Oppenauer Oxidation
 3. Meerwein –Pondorff-Verley reduction
 4. Schmidt rearrangement
 5. Hofmann rearrangement
 6. Wittig reaction
 7. Wagner- Meerwein rearrangement
 8. Favorskii rearrangement
 9. Michael reaction
 10. Dieckmann's reaction or condensation