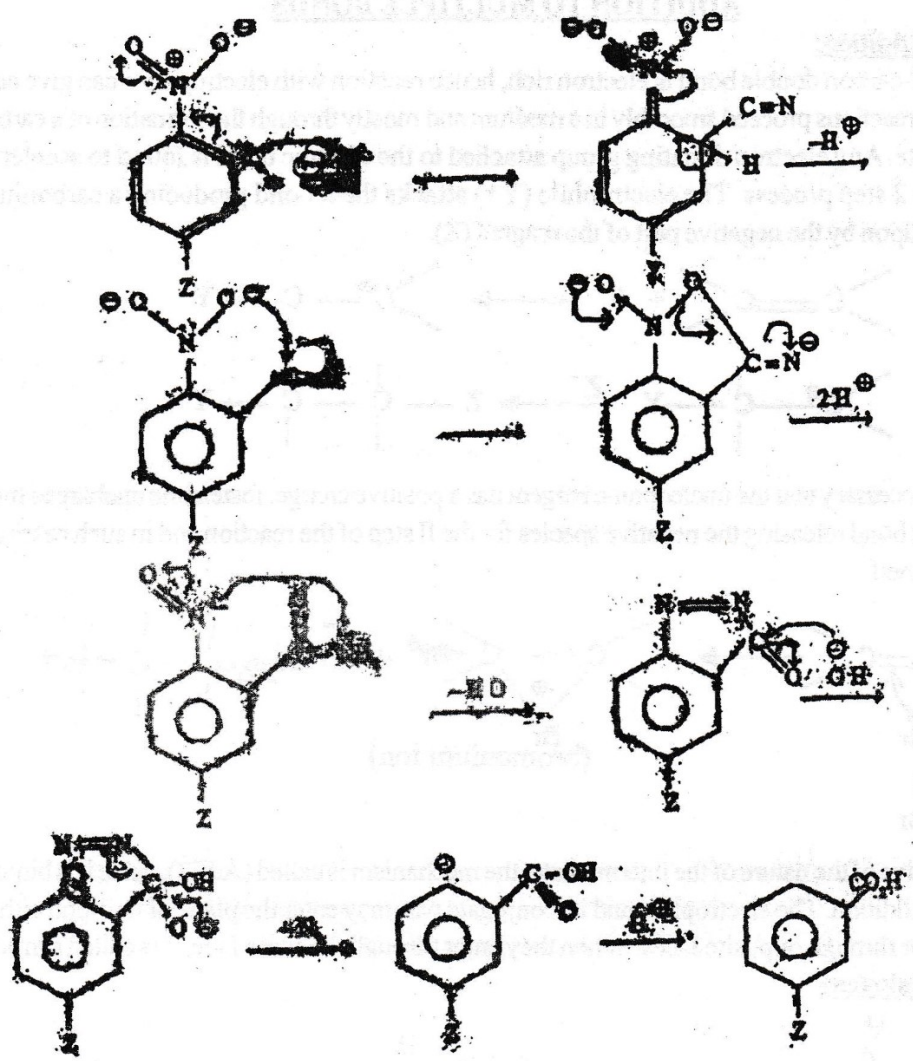
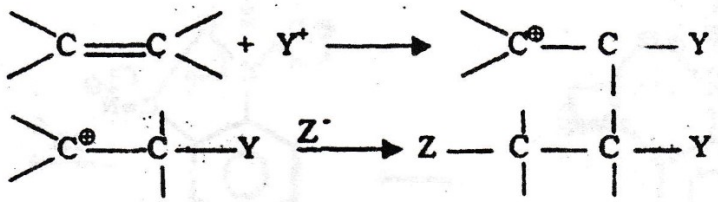


The product of hydrolysis is m-substituted benzoic acid. Hence a p-substituted nitrobenzene could be converted to the m-substituted benzoic acid. The release of elemental nitrogen during the course of the rearrangement has been observed which serves as an evidenced for the proposed mechanism. As a further evidence, when the p-chloro nitrobenzene was treated with CN/H_2O^*, one half of the oxygen in the product, was found labeled showing that one of the oxygens in the final product has come from the solvent, asgiven in the mechanism.

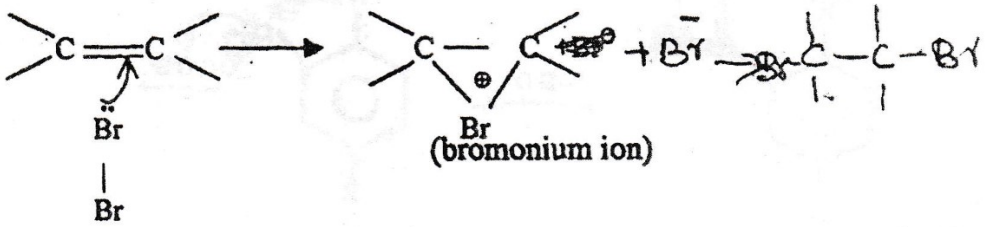
ADDITION TO MULTIPLE BONDS

Electrophilic Addition:

A carbon-carbon double bond is electron rich, hence reaction with electrophiles can give addition products. Such reactions proceed smoothly in a medium and mostly through the formation of a carbonium ion intermediate. Any electron donating group attached to the olefinic bond is found to accelerate the reaction. It is a 2 step process. The electrophile (Y+) attacks the π bond producing a carbonium ion, which is acted upon by the negative part of the reagent (Z).

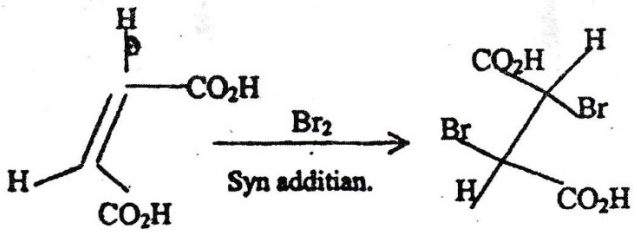


It is not necessary that the nucleophilic reagent has a positive charge. Instead the uncharged molecule can attack the π bond releasing the negative species for the II step of the reaction and in such cases a cyclic ion may be formed.



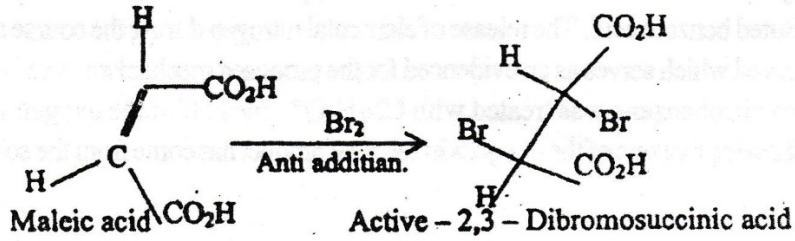
Irrespective of the nature of the intermediate, the mechanism is called (AdE2), since it is bimolecular Electrophilic Addition. The electrophile and its conjugate part may enter the plane of he olefin either form the same side or through opposite faces. When they enter through he same face, it is called syn addition.

Addition of Halogens



(Maleic acid, Meso – 2,3 – Dibromosuccinic Acid

When the reagent enters through the opposite faces, it is called anti addition.

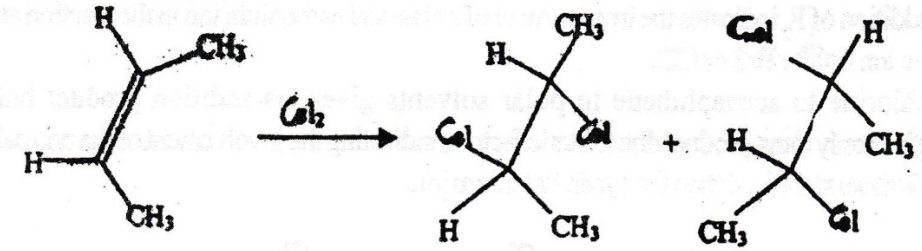


Active – 2,3 – Dibromosuccinic acid

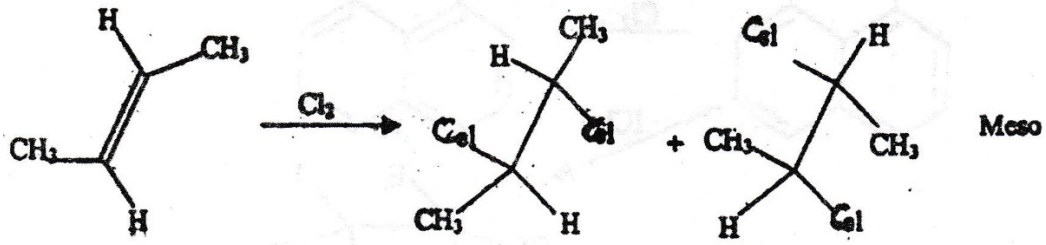
The additions are stereospecific, are syn addition leads to meso product and anti addition gives product of opposite configuration. When fumaric acid is treated similarly, the products are found to be exactly opposite to that of maleic acid, again proving that the addition is stereospecific.

However when the nucleophilic agent is a neutral molecule such as X_2 and the intermediate is cyclic, the addition is found to be anti addition.

In general addition of a halogen like Cl_2 or Br_2 to a cis olefin will lead to Meso form and trans olefin to active form.

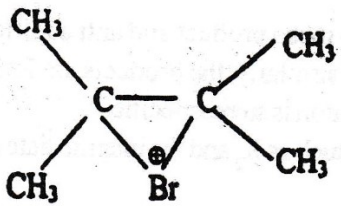


(Active)

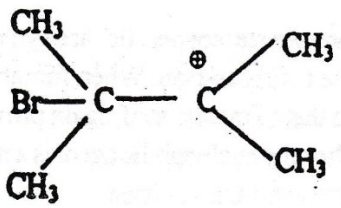


Evidences for the Anti Addition and the Formation of Cyclic Bromonium Ion

1. Stereospecific anti addition observed in olefins could also be cited as an evidence for the formation of cyclic bromonium ion without which it is not possible to explain the stereospecificity. Whereas maleic acid gives the dl mixture of 2,3 dibromosucinic acid, fumaric acid forms exclusively the meso form of the dibromide. But for the formation of the cyclic ion and anti addition, the dl-mixture would not have resulted with maleic acid, rather resulted in a mixture of meso and an active form.
2. Addition of Br_2 to tetramethylethylene in the presence of SbF_5 in SO_2 at 78°C, shows the formation of a cyclic bromonium ion which gives only one NMR signal.



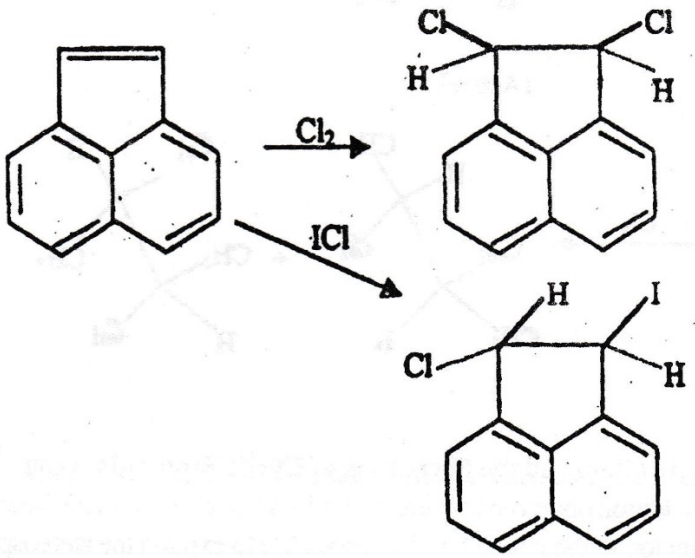
(only one signal observed)



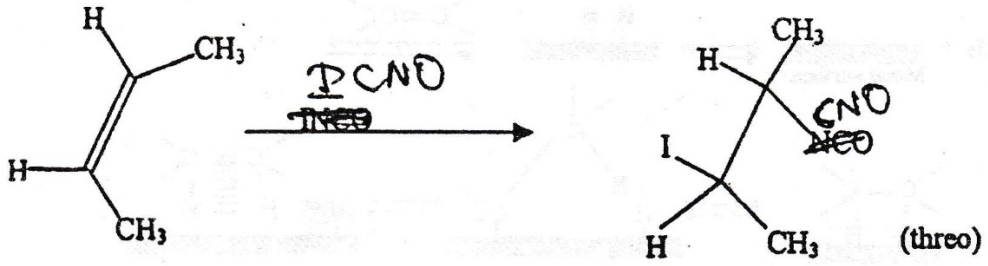
(2 signals possible)

If it were a carbonium ion involved, 2 signals would have been observed. Formation of 2NMR signals in the case of addition of F_2 indicates the involvement of a classical carbonium ion in the reaction as F_2 cannot form a cyclic ion unlike Br2 or Cl2.

Addition of chlorine to acenaphthene in polar solvents gives cis-addition product but Iodinemonochloride gives only trans-product due to steric factors, indicating the involvement of the normal carbonium ion which is more stabilized than the cyclic halonium ion.

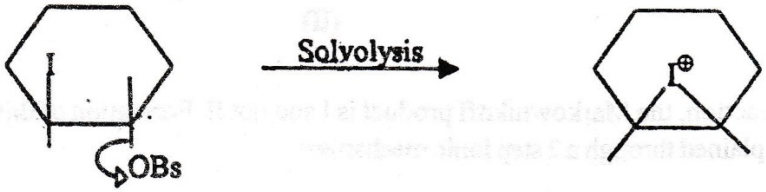


Addition of Iodine containing compounds proceed with trans (anti) stereospecificity. Iodine thiocyanate added to cis and trans-butenes give threo and erythro d, l pairs respectively.



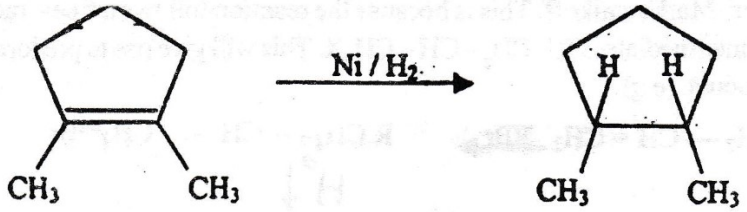
Iodine is a better neighbouring group participant compared to Br2 or Cl2 and leads to an enhanced rate of addition, since the trans-Iodo compound forms the most stable Iodonium ion.

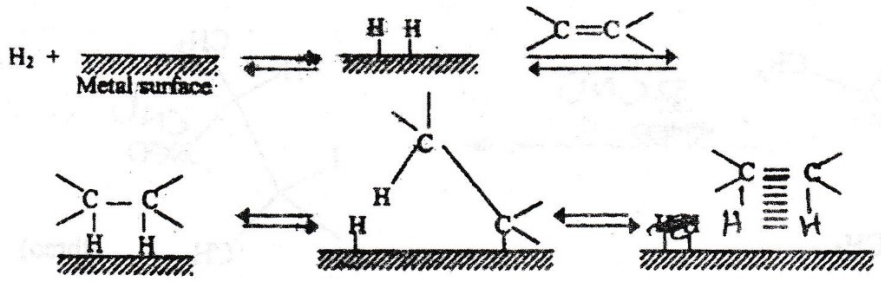
Evidence for a stable Iodonium ion is observed in the solvolysis of trans – 2 Iodohexyl brosylates which is 27,00,000 times faster than the chloro and bromobrosylates.



Addition

Reaction of H_2 with olefins is different from similar addition with halogens since the molecule is not polar in nature and it requires a heterogeneous metal catalyst such as Pt, Pd, Ni etc. The reactant react exothermically and reversibly, on the surface of the metal catalyst through adsorption at the active sites. The alkane with its π electrons are easily adsorbed on the metal surface followed by H – H, whose σ - bond is considerably weakened. This adsorptive interaction interaction proceeds followed by desorption of the alkane making way for further adsorption. It is expected to proceed with syn mode of addition but stereoselectively.





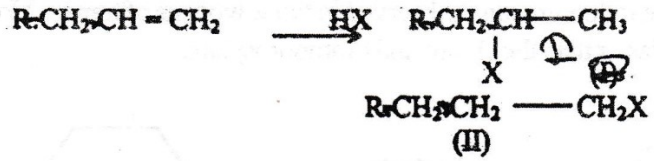
However, in rigid ring systems, the additions occurs from the less hindered side.

Addition of Hydrogen Halide

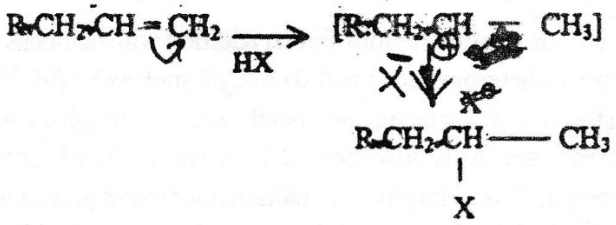
Olefins react with hydrogen halides directly without the aid of a catalyst. The product depends upon the symmetry of the olefin. Unsymmetrical olefins give rise to two different products as the reagent itself is unsymmetric.

Ionic Mechanism

Normally the reaction follows Markownikoff's rule, resulting in the negative halogen part attacking the doubly bonded carbon containing lesser number of hydrogen atoms. Hence



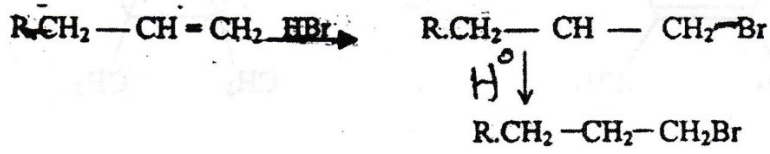
in the given reaction, the Markownikoff product is I and not II. Formation of this regioselective product, could be explained through a 2 step ionic mechanism.



The stabilization of the secondary carbonium ion by hyperconjugation compared to the other possible carbonium ion, accounts for the formation of the Markownikoff products.

Free Radical Mechanism

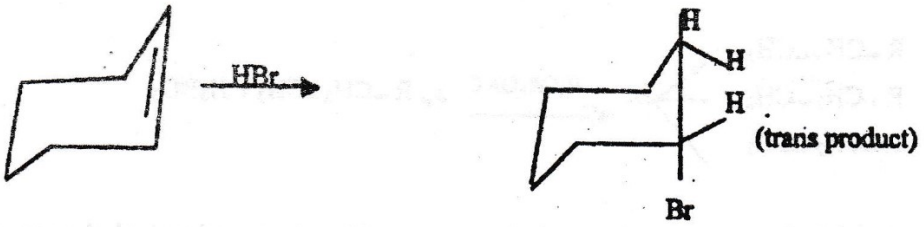
However, when the reaction is carried out in the presence of free radicals or peroxides, the product is found to be the anti-Markownikoff. This is because the reaction follows a free – radical mechanism, where the preferred intermediate is $R-CH_2-CH-CH_2X$. This will give rise to predominantly to the anti – Markownikoff product. (e.g)



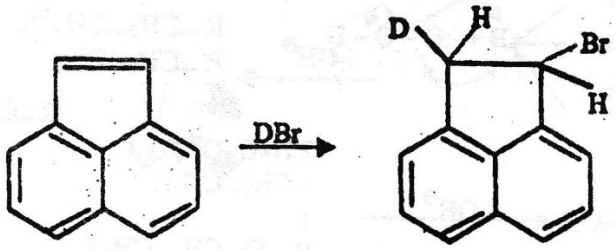
This secondary free radical is stabilized due to hyperconjugation compared to the other one, R. CH_2 - $CHBr - CH_2$ which is primary. Hence the compound correcponding to the more stable free radical is formed. Only HBr addition occurs smoothly by the free radical addition, since both the steps involving the initial formation of free radical as well as the subsequent hydrogen attack are exothermic. In other hydrogen halides one or both the steps are endothermic making the addition difficult.

Hence the olefin addition to HX, occurs by the ionic mechanism under normal conditions (insulated from air and pareoxides) and anti – Markownikoff product results otherwise.

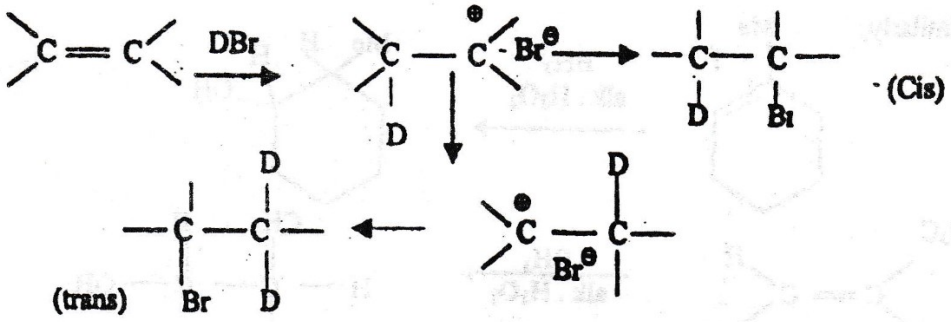
The stereochemistry of this addition largely depends upon the structure of the substrate. Addition to isomeric butanes, cyclic olefins such as cyclohexene, and 1, 2 dimethylcyclohexene is predominantly trans.



he same to cyclohexene gives a mixture of cis and trans products.



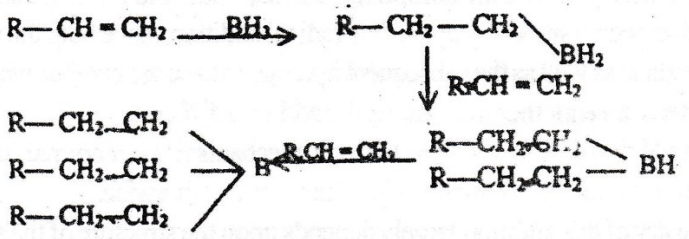
Formation (ıanism,



the trans-product

Hydroboration

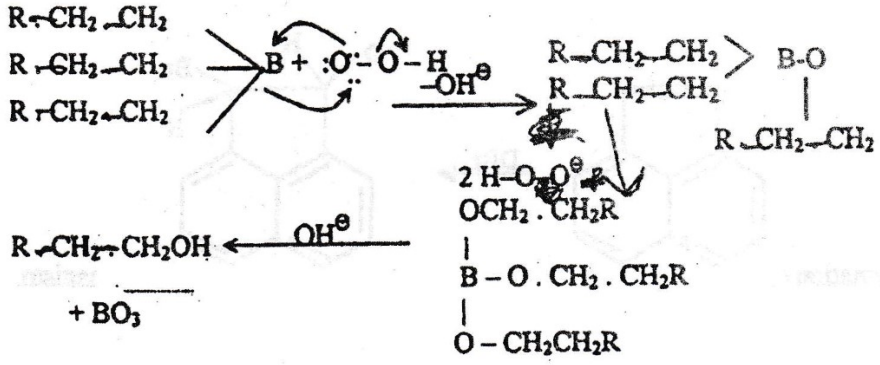
An olefinic bond could be readily reduced by borane by a concerted, cis – addition.



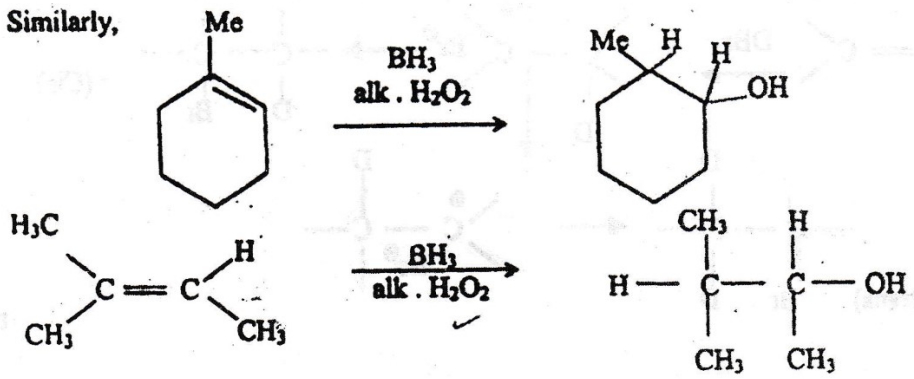
The addition is clearly regiospecific when the slightly negatively charged ($H^{\delta\ominus}$ ... BH_2) hydrogen attacks the olefinic carbon containing lesser number of hydrogen. The resulting trialkylborane is useful in two different ways.

1) Hydrolysis with aq. Acetic acid results in the formation of the corresponding alkane.

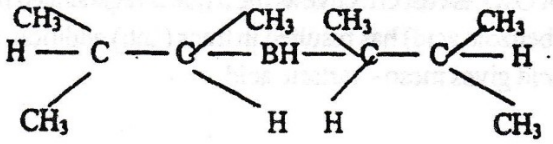
2) Treatment of the alkylborane with alk. Hydrogen peroxide, provides the alcohol corresponding to the anti – Markownikoff alkyl halide. This alcohol with the OH group at the terminal carbon is of greater importance, which otherwise would have to be prepared by a series of reactions.



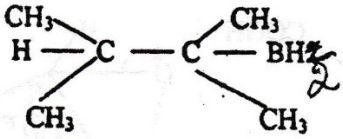
Similarly,



Boranes which produce a higher degree of regiospecificity such as Thexylborane and Disiamylborane have been developed, to replace the usual borane.

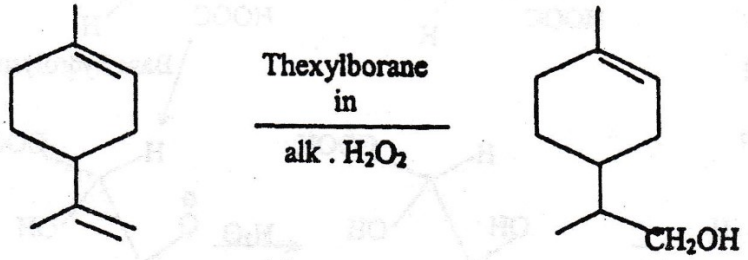


Disiamylborane



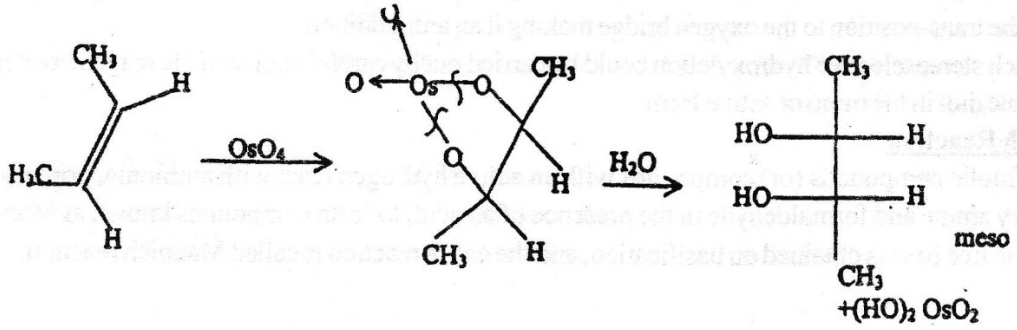
Thexylborane

Better results have been obtained using thers boranes (e.g)



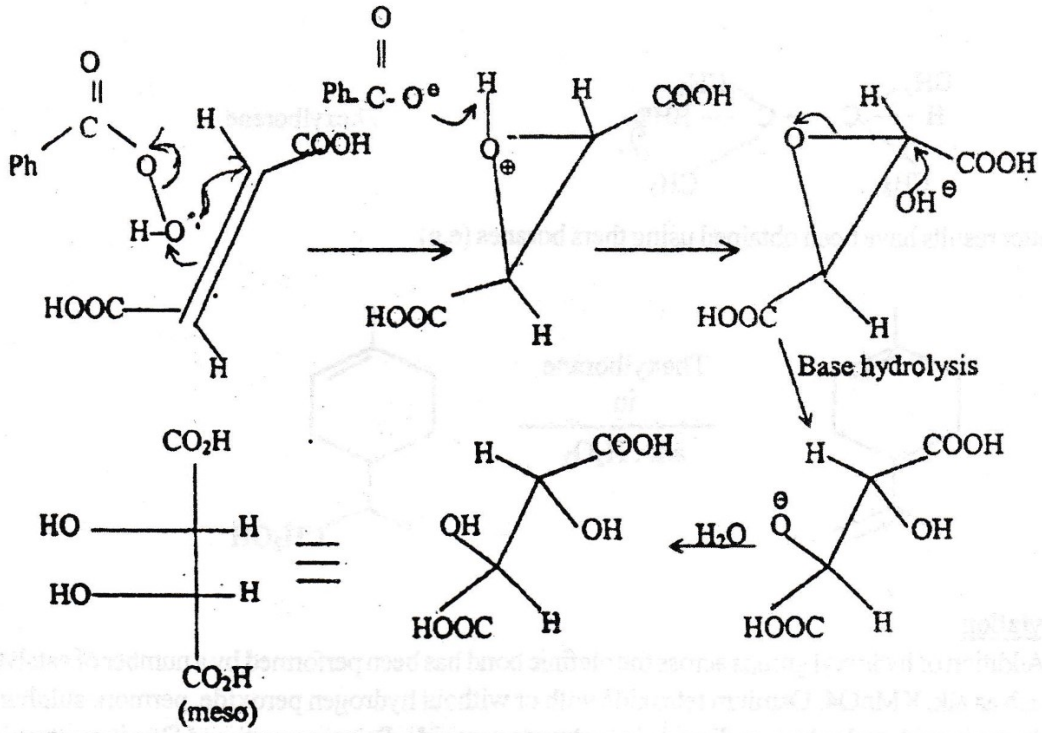
Hydroxylation

Addition of hydroxyl groups across the olefinic bond has been performed by a number of catalytic agents such as alk. KMnO4, Osmium tetroxide with or without hydrogen peroxide, permonosulphuric acid, perbenzoic acid, and selenium dioxide in hydrogen peroxide. Permanganate and Osmium tetroxide always result in cis –addition as they involve a cyclic intermediate as shown, and in other reagents, it is trans.



Similar steps are involved while $Mn^{(-)}O4$ attack occurs, the cyclic osmic ester being replaced by the permanganic ester. In both cases, the cis – 2 – butane forms the meso 1, 2 diol. This mechanism has received support from isotopic labeling experiment with $Mn^{(-)}O_4$, when the diol was found with O*

in both the hydroxyl groups. Whereas permanaganate addition is susceptible for further oxidation of the diol by the reagent, Osmium tetroxide addition is more expensive and toxic. However, use of hydrogen peroxide with only catalytic quantities of OsO_4 is cost effective as the oxide is regenerated by the reoxidation of the osmic acid. Use of peracids (Perbenzoic acid) has resulted in trans (anti) addition. (e.g) maleic acid leads to dl-tartaric acid and fumaric acid gives meso – tartaric acid.

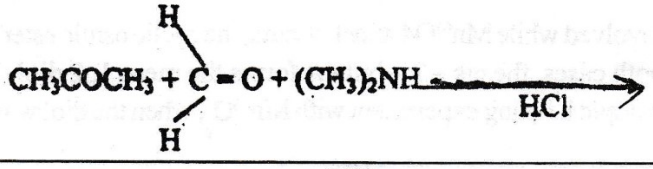


The reaction proceeds through the formation of an expoxide intermediate which has been isolated, thus providing an incontrovertible evidence for the mechanism. Moreover the nucleophile ($OH^{\ominus}$) enters through the trans-position to the oxygen bridge making it an anti-addition.

Such stereoselective hydroxylation could be carried out by careful choice of the reagent to prepare the suitable diol in the meso or active form.

Mannich Reaction

Enolic compounds (or) compounds with an active hydrogen react with ammonia, primary or a secondary amine and formaldehyde in the presence of an acid, to form compounds known as Mannich bases. The free base is obtained on basification, and the entire reaction is called Mannich reaction.

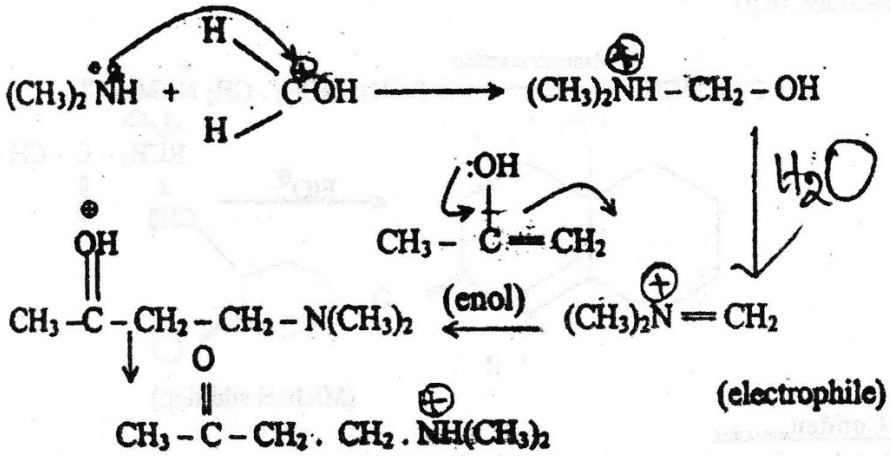


$$CH_3COCH_2 . CH_2 . \overset{\oplus}{N}H(CH_3)_2Cl^{\ominus} \xrightarrow{OH^{\ominus}}$$

$$CH_3 - CO - CH_2 - CH_2 - N(CH_3)_2$$
(Mannich base)

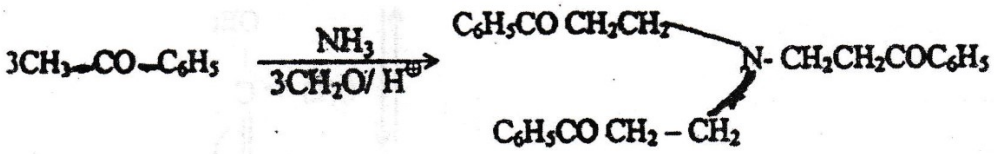
Aldehydes, ketones, β - keto esters, β - cyano esters and certain alkynes also can function as enols.

Mechanism of the Reaction



Initially an acidic solution of formaldehyde reacts with the amine to form an adduct which eliminates a molecule of water to form an electrophile. The ketone enolises fast in the presence of the acid and the enol is attacked by the electropphile, to form the Mannich base.

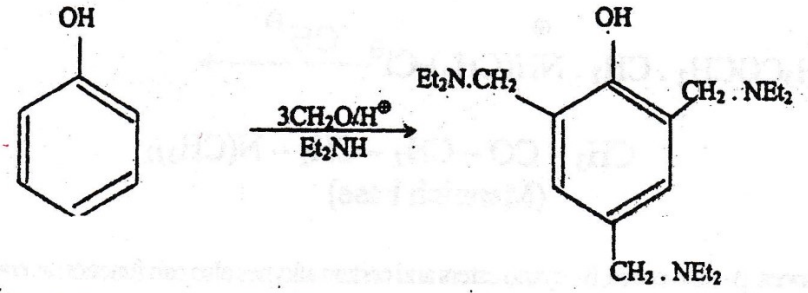
A molecule of NH_3 reacts similarly but in 3 successive stages to form the Mannich base.



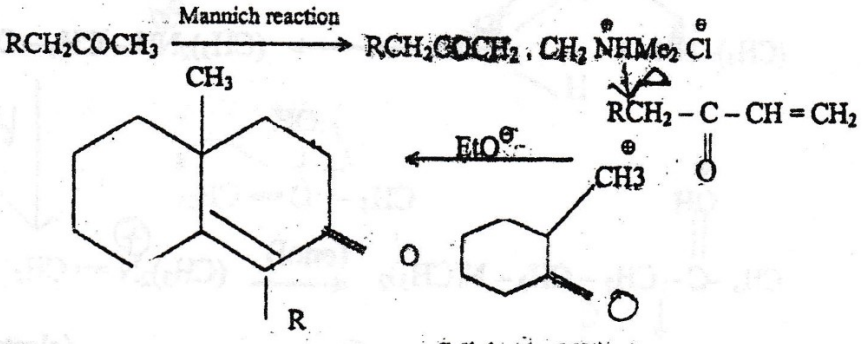
Phenylacetylene rather than acetylene, replaces and enol in Mannich reaction.

$$C_6H_5 . C \equiv CH \xrightarrow[CH_2O/\ H^{\oplus}]{Me_2NH} C_6H_5 . C \equiv C . CH_2NMe_2$$

Phenol being active at the ortho and para positions, the electrophile formed between the amine and formaldehyde attacks the 3 positions as in an aromatic electrophilic substitution.



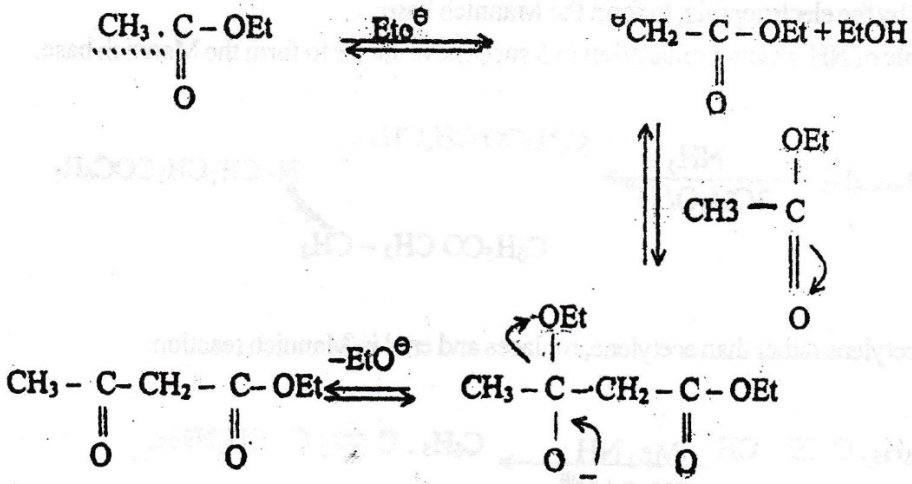
Mannich reaction assumes importance in Synthetic Organic Chemistry as reactive intermediates which provide the corresponding α,β unsaturated carbonyl compounds, very useful in base catalysed condensation reactions. (e.g).



(Michael addition)

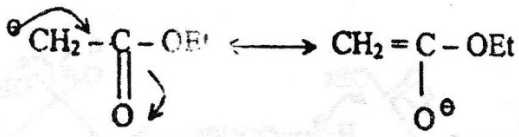
Claisen Ester Conden.....

Two molecules of an ester containing α - hydrogen condense to give an α - acyl ester (β - keto ester) catalysed by bases such as ethoxides. Thus self condensation of two molecules of ethyl acetate gives ethyl acetoacetate, catalysed by ethoxide ion.

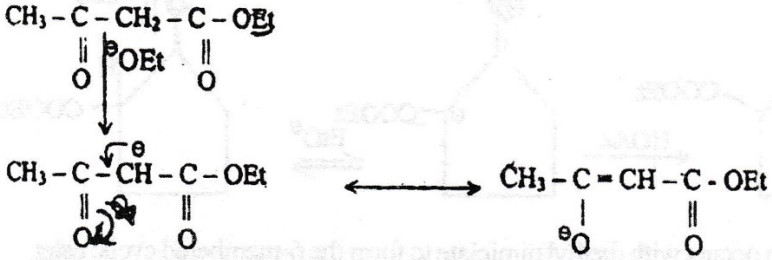


Commercial ethylacetate containing smaller quantities of ethanol under dry conditions react with sodium metal generating sodium ethoxide which catalyses the reaction.

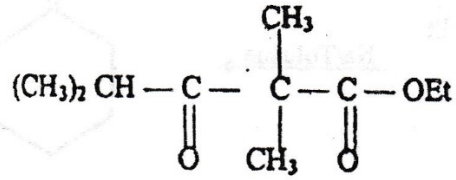
The abstraction of a proton from the α - methyl group of the initial ester by the ethoxide ion, is assisted by the stabilization of the resulting carbonion through resonance.



Eventhough every step in the condensation is reversible, it is made possible to shift the equilibrium to the right by the ethoxide ion which forms the anion of the resulting ester by continuous H-abstraction.



In the case of formation of β-keto esters where this carbanion formation is not possible (e.g.),

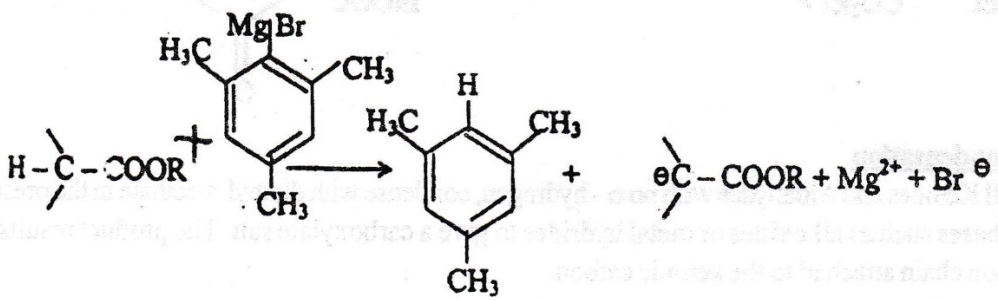


a stronger base such as sodium triphenyl methyl is applied. The triphenyl methide ion completely removes the ethanol formed in the condensation and shifts the equilibrium to the right.

$$Me_2CHCOOEt \rightleftharpoons Me_2CH.CO.CMe_2-COOEt + EtOH$$

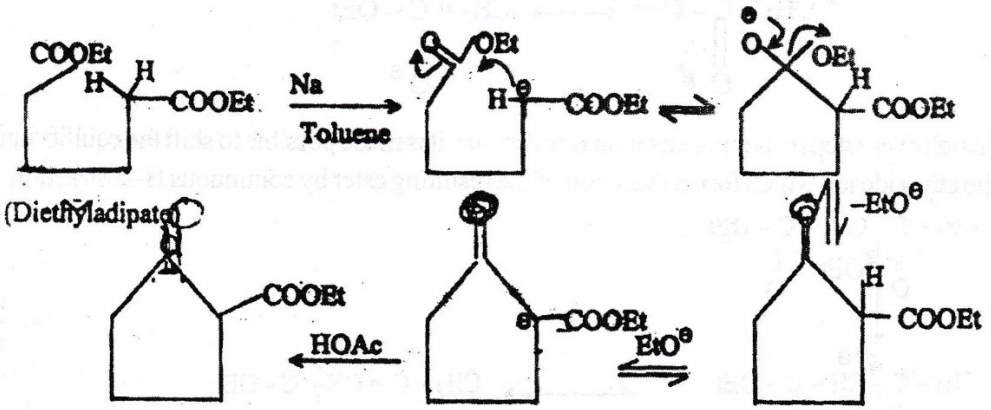
$$EtOH + Ph_3C^{\ominus} \longrightarrow EtO^{\ominus} + Ph_3CH$$

Another stronger base is, mesitylmagnesium bromide which readily abstracts a proton form stable mesitylene.

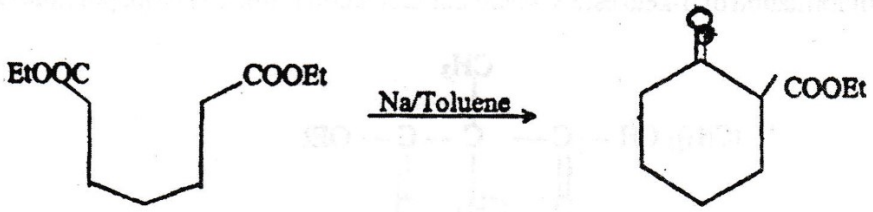


Dieckmann Condensation

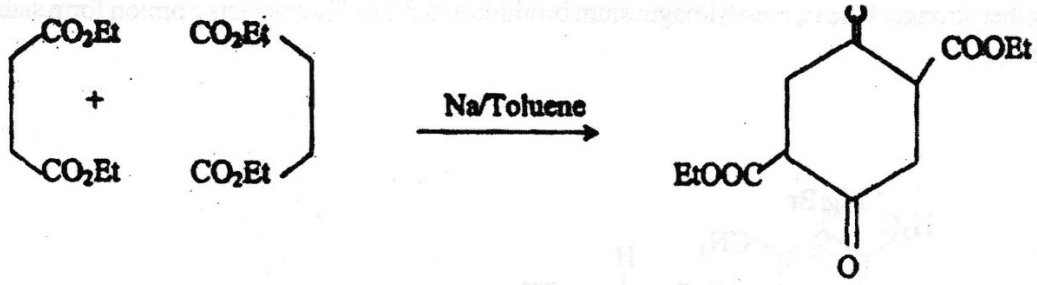
Diesters of dibasic acids undergo intramolecular condensation in the presence of sodium in toluene to give 5, 6 or 7 membered cyclic β-keto esters. The sodium derivative of the ester on acidification gives the ester.



A similar reaction occurs with diethyl pimielate to form the 6-membered cyclic ester.

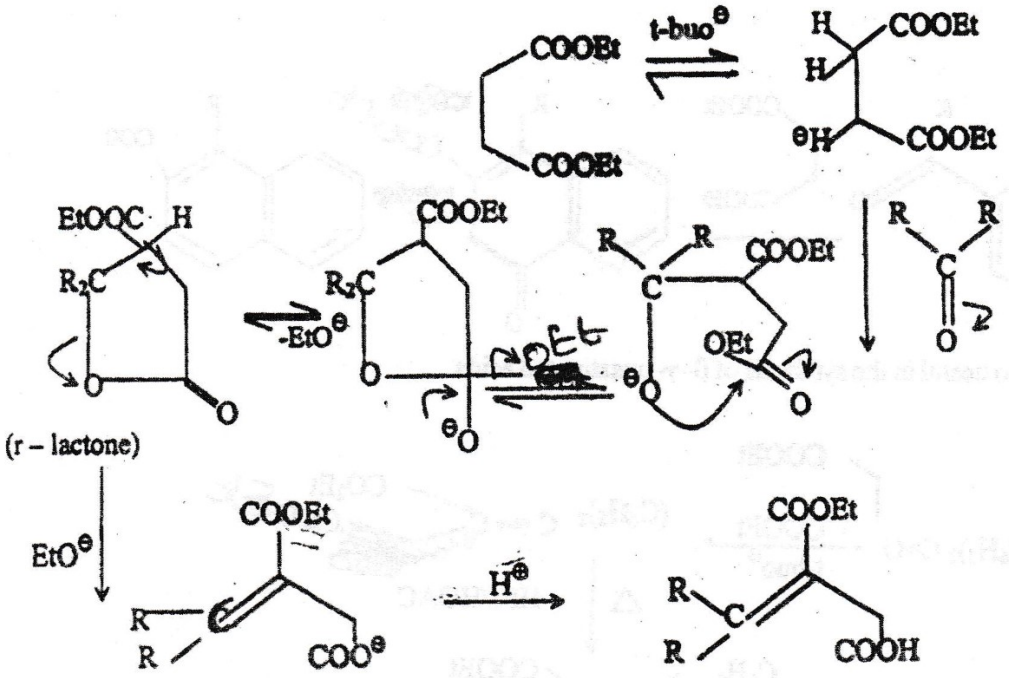


2-carboethoxy cycloheptanone could be formed from diethyl suberate, however the yield is very poor, as the larger rings are difficult to be formed have greater strain. For the same reason smaller ring β - keto esters are not formed from lower dibasic esters. But diethyl succinate undergo intermolecular condensation between 2 molecules and form a six membered cyclic diketo diester, following a similar mechanism.



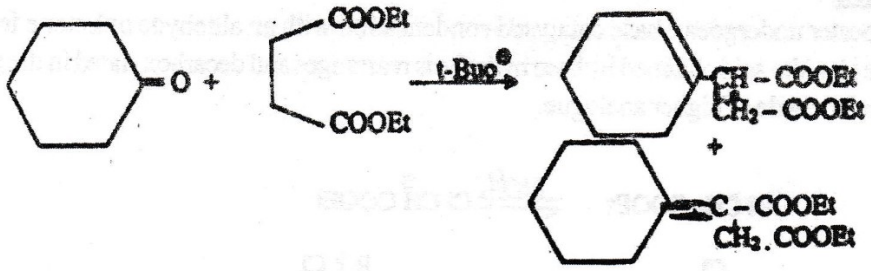
Stobbe Condensation

All Ketones and Aldehydes with no α - hydrogen, condense with diethyl succinate in the presence of strong bases such as alkoxides or metal hydrides to give a carboxylate salt. The product results in a three carbon chain attached to the ketonic carbon.

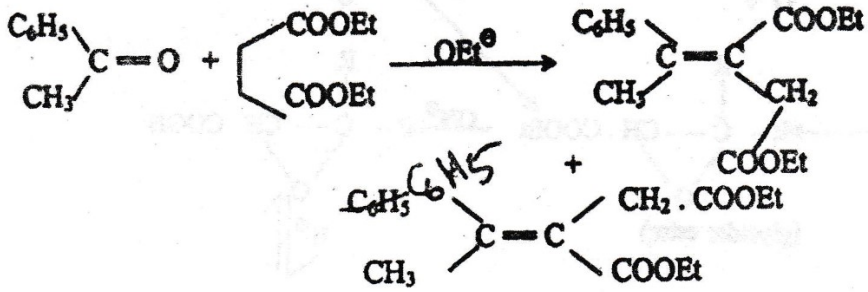


The mechanism proceeds through the formation of a γ -lactone intermediate which has been isolated. This serves as an evidence for the proposed mechanism. The formation of the final product by the ring opening of the γ-lactone, is fast, as the stability of the carboxylate salt is favourable to this step.

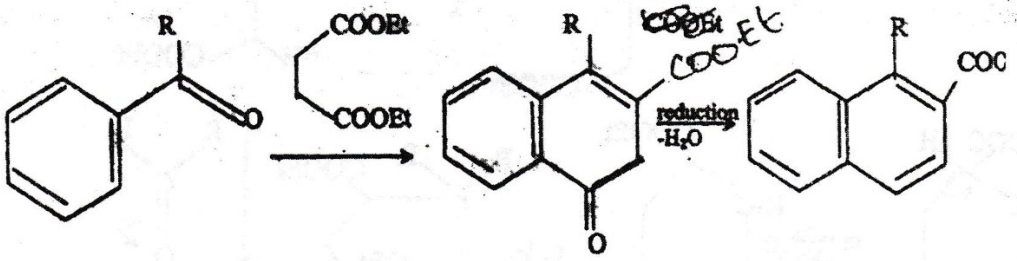
Cyclic ketones also react similarly, but giving a mixture of structural isomers.



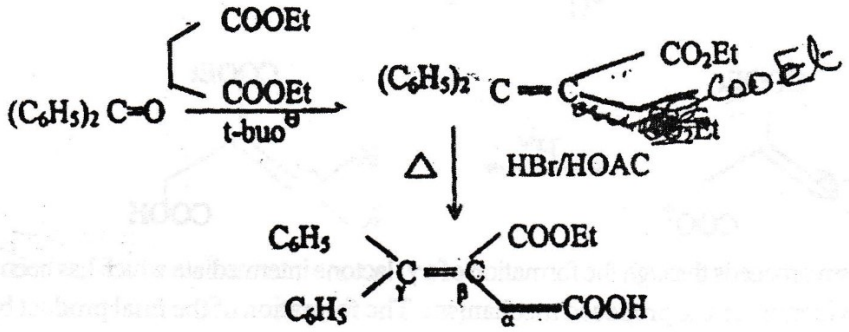
In the case of mixed ketones, a mixture of stereoisomers result.



Stobbe condensation is helpful in building up of aromatic rings. (e.g)

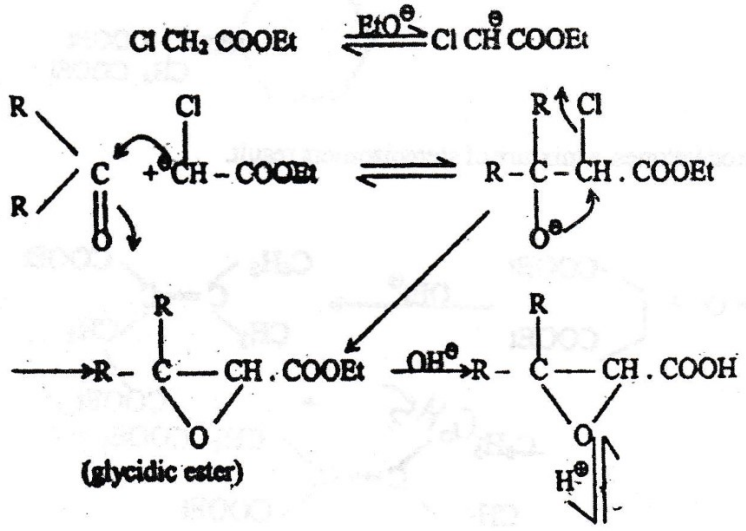


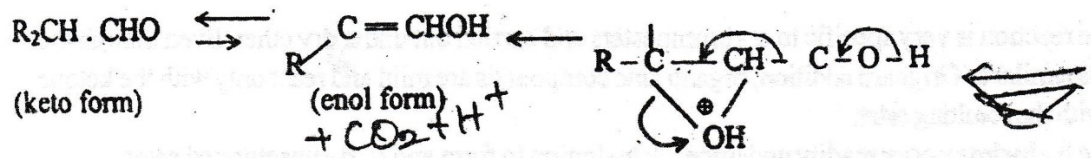
It is also useful in the synthesis of β- γ- unsaturated acids.



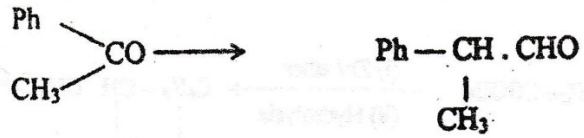
Darzen's Reaction

An α - haloester undergoes a base catalysed condensation with an aldehyde or ketone forming a glycidic ester. The glycidic acid obtained by base hydrolysis rearranges and decarboxylated in the presence of acids to give an aldehyde of higher analogue.





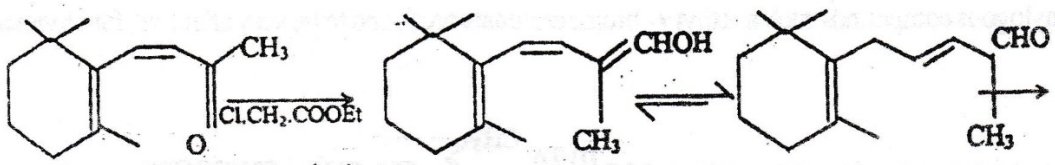
Abstraction of a proton by the base forms the carbanion of the ester which readily attacks the carbonyl carbon of the ketone. It is followed by a nucleophilic attack of the carbonyl oxygen on the α - carbon due to the expulsion of the halogen atom. The epoxy ester is hydrolysed by a base and the acid undergoes a decarboxylative rearrangement to give an enol which tautomerises to an aldehyde. In effect, the ketone has increased its carbon atom by one to give an aldehyde. (i.e)



Similarly an aldehyde gets converted to its higher homologue.

Ph . CHO → Ph CH_2. CHO

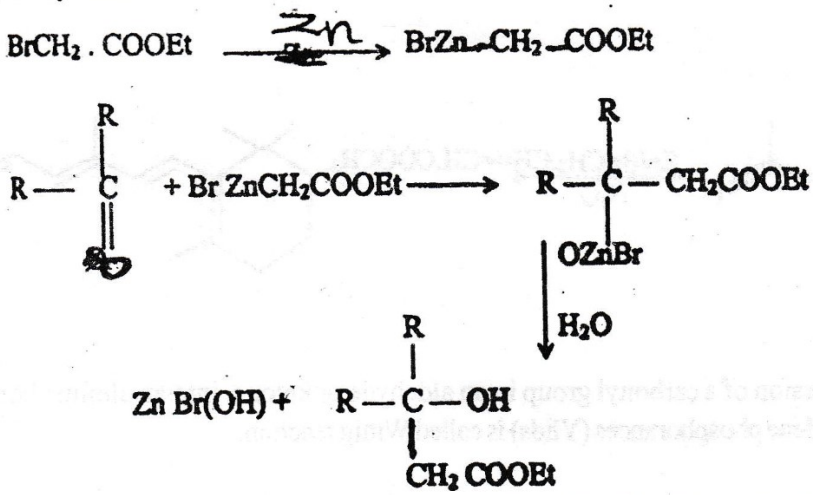
One of the applications of Darzen's reaction is involved in the synthesis of Vitamin A.



(Darzen's reaction)

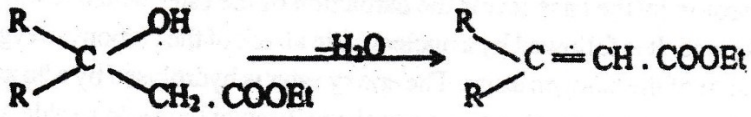
Reformastsky Reaction

Organo zinc compounds of α - bromo esters undergo addition reaction with aldehydes or keton to form - hydroxyl esters.

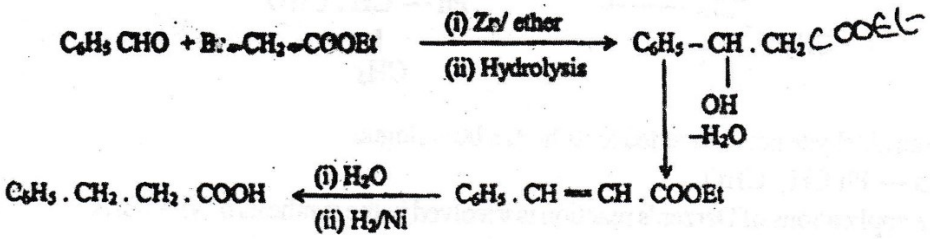


The reaction is very specific to α - bromoesters and carried out under dry ether. Even though the reaction is similar to Grignard addition, organo zinc compounds are mild and react only with the ketone and not with the resulting ester.

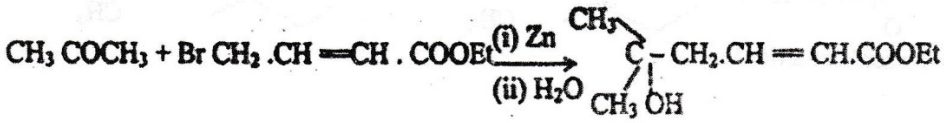
The β - hydroxy ester readily undergoes dehydration to form and α, β - unsaturated ester.



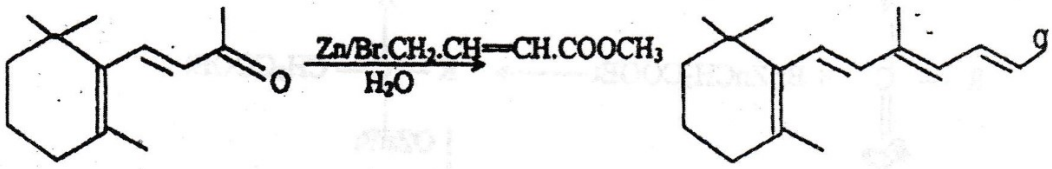
Benzaldehyde undergoes reformatsky reaction followed by dehydration to form Ethylcinnamate.



Vinylogous compounds such as ethyl γ - bromocrotonate are found to be very effective, for obvious reasons.

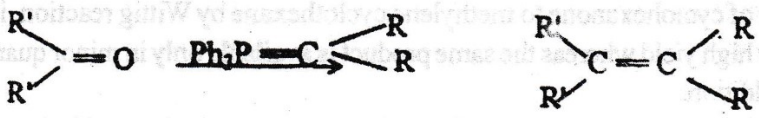


Reformatsky reaction can provide best routes for the conversion of aldehydes and ketones into higher esters and acids. One of the applications of the reaction is involved in the synthesis of Vitamin A from β - ionone.



Wittig Reaction

Direct conversion of a carbonyl group in an aldehyde or ketone, into an olefinic bond, through reaction with alkylidene phosphorances (Ylids) is called Wittig reaction.



Mechanism

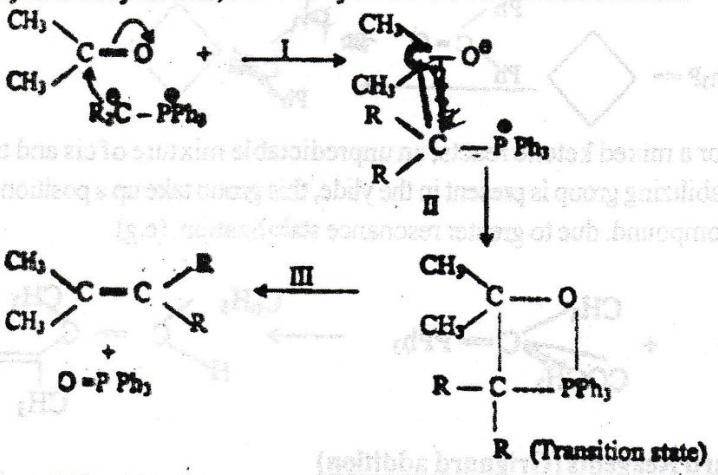
Ylids are first prepared from triphenyl phosphine with appropriate alkyl halids.

$$R_2CHBr + PPh_3 \longrightarrow R_2CH - \overset{\oplus}{P}Ph_3\,\overset{\ominus}{Br} \xrightarrow[PhLi]{} \overset{\ominus}{R_2}C - \overset{\oplus}{P}Ph_3$$

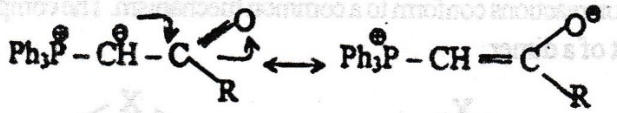
The Ylids have a hybrid structure as :

$$\overset{\ominus}{R_2}C - \overset{\oplus}{P}Ph_3 \xleftrightarrow[THF]{} R_2C = PPh_3$$

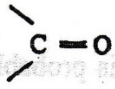
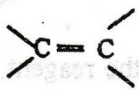
They are highly reactive species and prepared under dry Tetrahydrafuran. There occurs a nucleophilic attack on the carbonyl carbon by the Ylid, followed by the formation of a transition state.



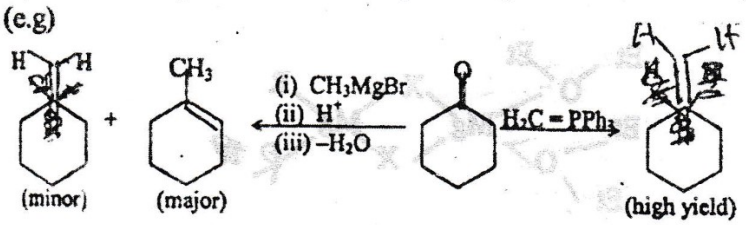
When the Ylid is stabilized by the presence of groups such as CO, CN, COOR etc, it becomes less reactive. (e.g)



Depending on the structures of the Ylid and the carbonyl compound, step I or II may be the rate determining step.

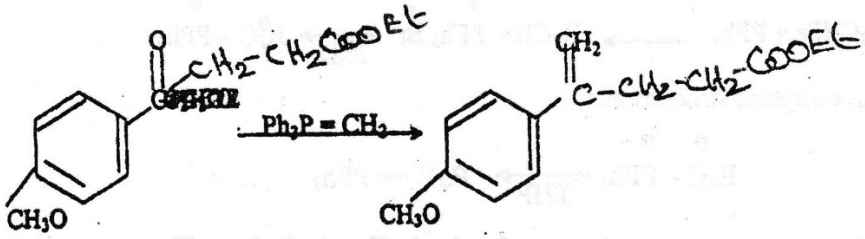
This route of conversion of  group into 

has many advantages even though it could be accomplished by other means such as Grignard addition, but in lower yields. (e.g)

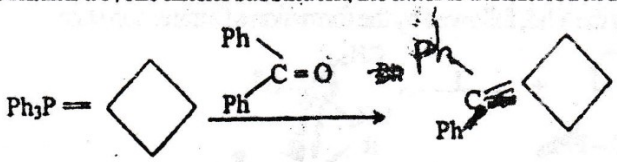


In the conversion of cyclohexanone to methylene cyclothexane by Wittig reaction, it is the only product formed in fairly high yield whereas the same product is available only in minor quantities when prepared by Grignard addition.

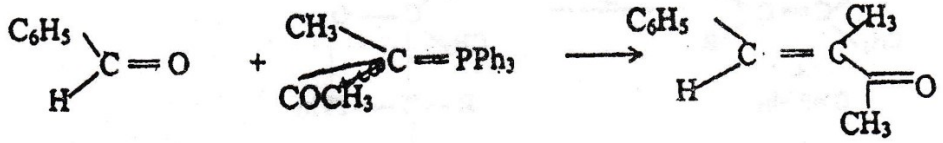
Moreover, in Wittig reaction, irrespective of the other groups attached to the Ylid or the carbonyl group, the reaction proceeds and the groups remain unaffected. (e.g) when the substrate contains an ester group also apart from the keto group, the ester group remains unaffected.



If the ylide itself contains a cyclic alkene substituent, the latter is transferred as such to the product.

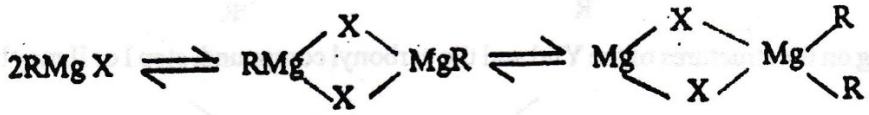


When aldehyde or a mixed ketone reacts, an unpredictable mixture of cis and trans alkenes are formed. However if a stabilizing group is present in the ylide, this group take up a position trans to the large group of the carbonyl compound, due to greater resonance stabilization. (e.g)

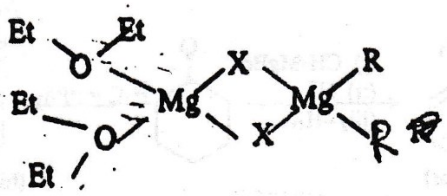


Reaction with Grignard Reagents (Grignard addition)

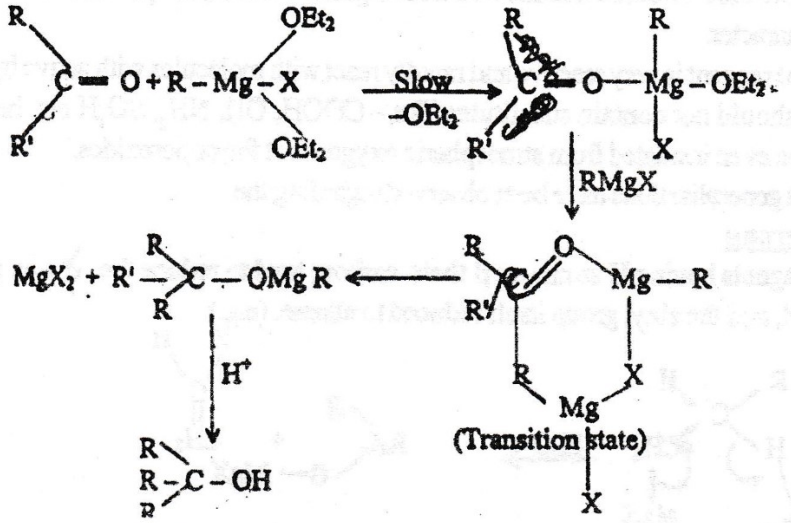
Organo magnesium halides known as Grignard reagents undergo a variety of reactions with carbonyl compounds. All these addition reactions conform to a common mechanism. The composition of the Grignard reagent corresponds to that of a dimer.



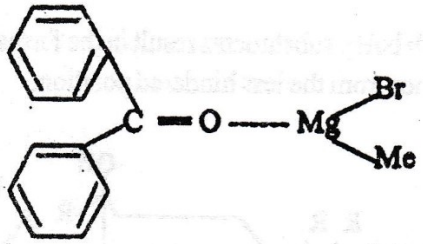
The solubility of the reagent in ether is probably due to the coordination of Mg by ether molecules as :



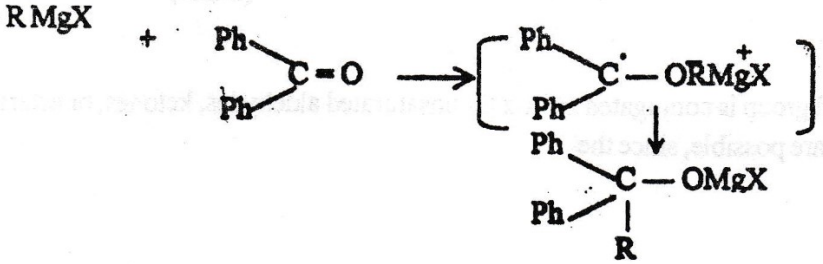
The Mechanism of Grignard Addition



Two molecules of RMg X are involved. While one molecule is involved in enhancing the polarization of the $>C=O$ group, the other molecule complexes with the carbonyl group through a 6 membered cyclic transition state. The isolation of a solid complex corresponding to the first step of the reaction in the case of benzophenone is enough evidence for the mechanism. Moreover, if the reaction is carried out with one mole of Grignard reagent, no reaction is found possible as the ketone is recoverable in the original form. To avoid this problem, and ethereal solution of the ketone may be added to the Griguard reagent. Then at any one given moment there will be a large excess of the reagent compared to the ketone. This is called as inversion addition of Griguard reagent. This normally is the procedure adopted for origuard reaction.



There has been evidences to show that the reaction of Grignard reagent with aromatic ketones proceeds through a Single Electron Transfer (SET), as shown.



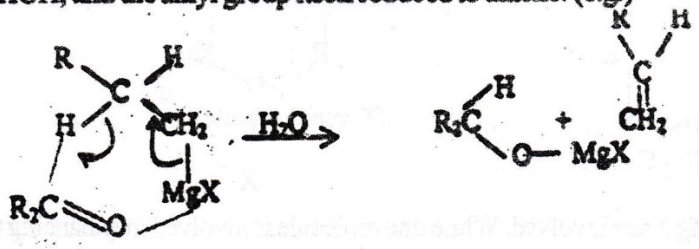
The solutions are blue coloured and showed EPR signals indicatig the presence of odd electrons with paramagnetic character.

As the Grignard reagent is very reactive and rapidly react with molecules with active hydrogen, the substrate molecule should not contain substitutes like – COOH, OH, NH_2, SO_3H etc, having active hydrogen. It should be even insulated from atmospheric oxygen as it forms peroxides.

Two important generalizations have been observed regarding the

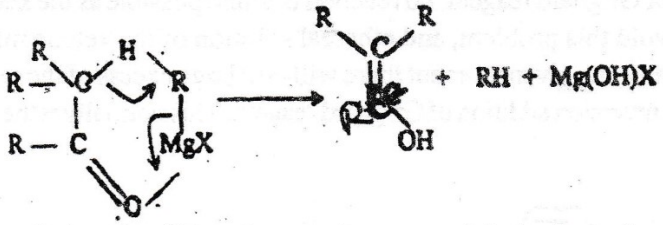
1) Nature of alkyl group

Grignard reagents having H atoms on β their .carbon, tend to reduce the $\rangle C=O$ group of the substrate to – CHOH, and the alkyl group itself reduced to alkene. (e.g.)

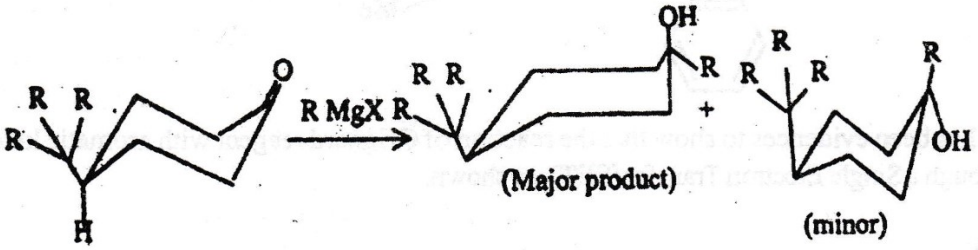


2) Nature of the Carbonyl Compound

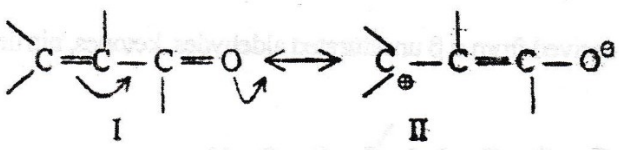
Sterically hindered ketones having H-atoms on their α - carbon tend to be converted to enol, and the alkyl or aryl residue of the Grignard reagent lost as hydrocarbon.



Similarly alicyclic ketones with bulky substituents result in the formation of – OH group at the axial position, as the alkyl group approaches from the less hindered position.

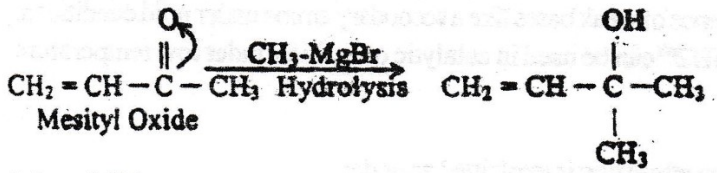


When the carbonyl group is conjugated as in α β - unsaturated aldehydes, ketones, or esters, 1, 2 or 1,4 addition products are possible, since the



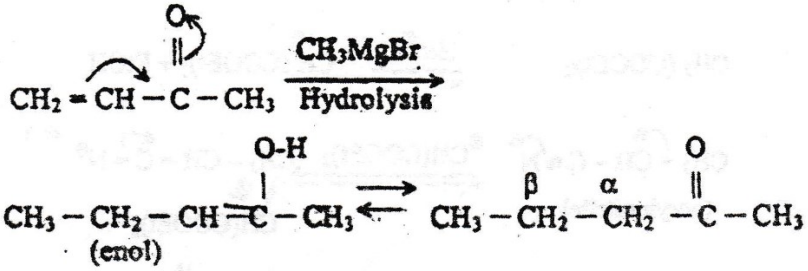
I II

Substrate behaves corresponding to structures I & II, it gives rise to 1, 2 – addition and 1,4 – addition. 1,2 – addition generally gives an unsaturated alcohol and 1,4 – addition gives β - substituted saturated Carbonyl compound. Thus 1,2 addition.

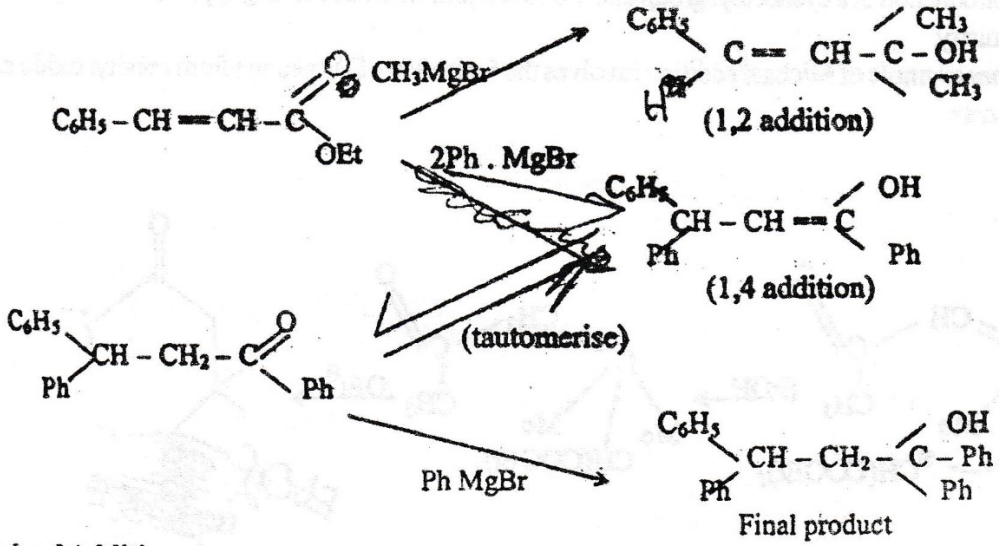


Mesityl Oxide

1,4 – addition:



The mode of addition depends mostly on the steric requirement of the reagent. Whereas Ethyl cinnamate and methyl magnesium iodide give 1,2 product exclusively, 1, 4 product is formed exclusively when phenyl mag. Bromide is used. The 1,4 – addition product is same as that of addition at the olefinic bone.

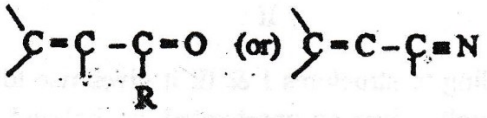


Final product

Michael Addition

The nucleophilic addition at an activated α β - olefinic bond of carbonyl compounds by the anion of an activated methylene group is called Michael addition, or Michael condensation.

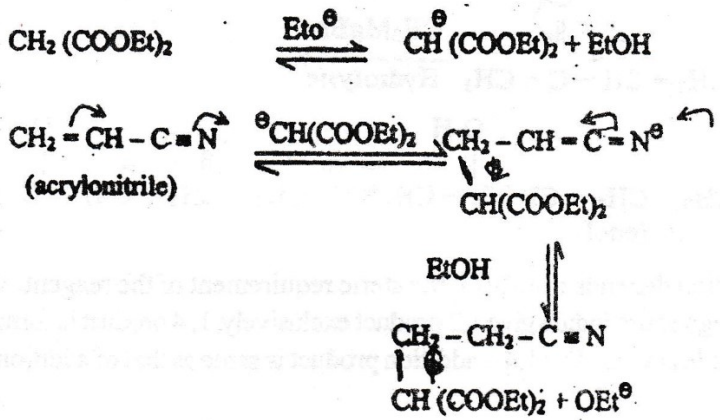
The substrate is normally derived from α β unsaturated aldehydes, ketones, nitriles and esters such as



The usual nucleophiles are malonic ester, aceto acetic ester, nitro alkanes or their derivatives. The addition can be carried out even in the presence of weak bases like a secondary amine under mild conditions. However stronger bases such as $EtO^{(-)}$, $NH2^{(-)}$ can be used in catalytic quantities under low temperature conditions.

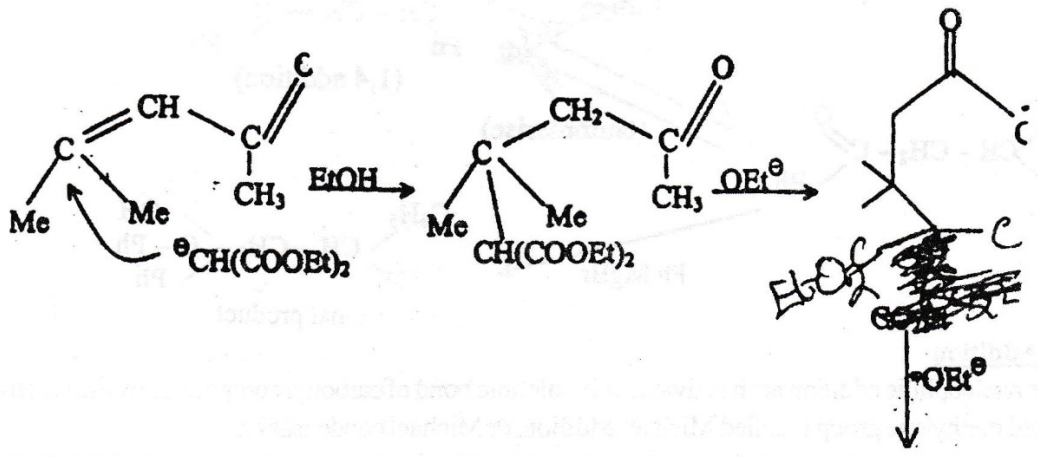
Mechanism

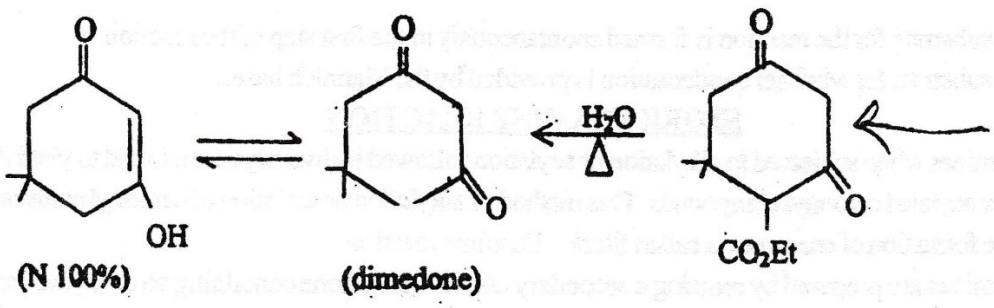
An important reaction such as cyano ethylation is explained as under



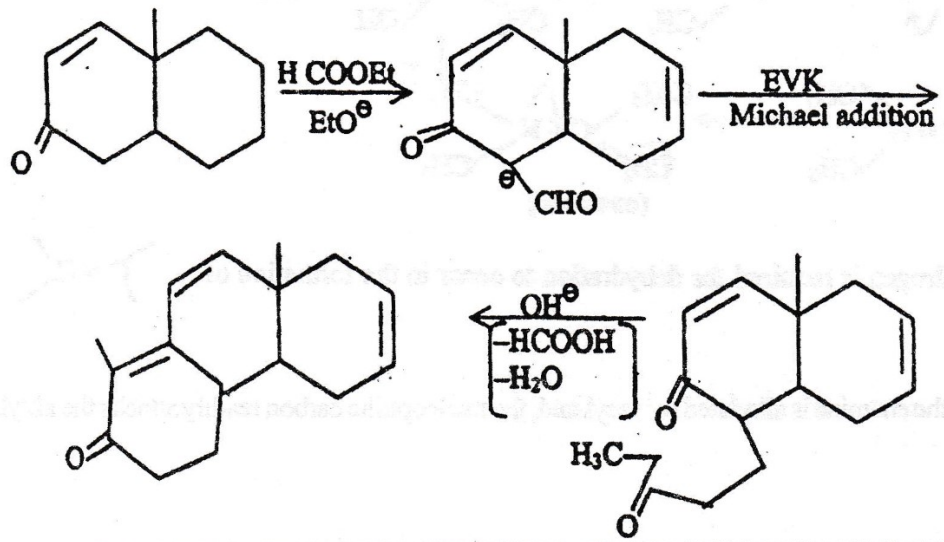
The introduction of a cyanoethyl group into the nucleophile has far reaching applications in synthetic organic chemistry.

Another example of Michael addition involves the formation of Dimedone from mesityl oxide and diethyl malonate.



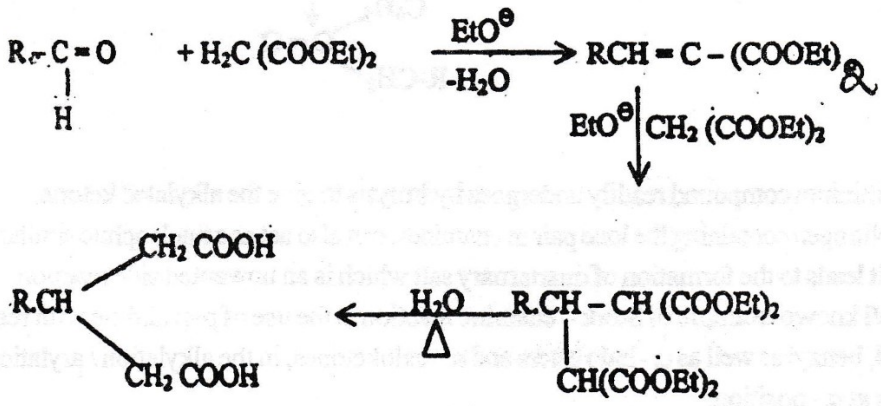


Use of Ethyl Vinyl Ketone (EVK) in building up of alicyclic system of steroids through Michael addition is as under :



The initial introduction of the CHO group at the α - position, facilitates the attack of this nucleophile at the substrate (CH_3-CH_2.C.CH = CH_2) and thereby building a new 6-membered ring system.

Michael addition may sometimes be carried out even in the absence of the α,β unsaturated system, which is formed during the course of the reaction. (e.g)



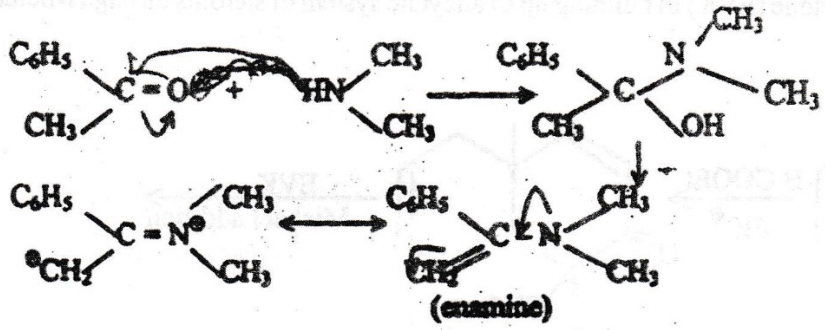
The substrate for the reaction is formed spontaneously in the first step of the reaction.

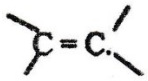
The substrate for Michael condensation is provided by the Mannich bases.

STORK ENAMINE REACTION

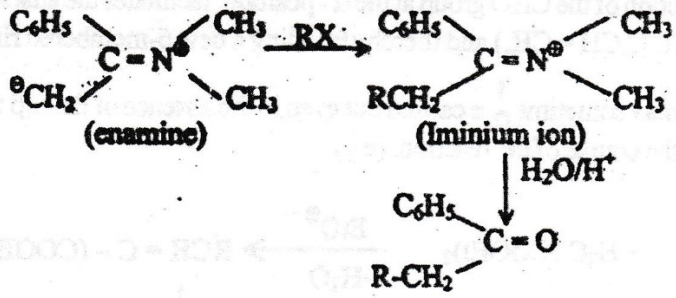
Enamines when subjected to alkylation or acylation followed by hydrolysis are found to yield the α alkylated or acylated carbonyl compounds. This method of alkylation or acylation of carbonyl compounds through the formation of enamines is called Stork – Enamine reaction.

Enamines are prepared by reacting a secondary amine with ketone containing an α - hydrogen.



An α - hydrogen is required for dehydration to occur in the formation of 

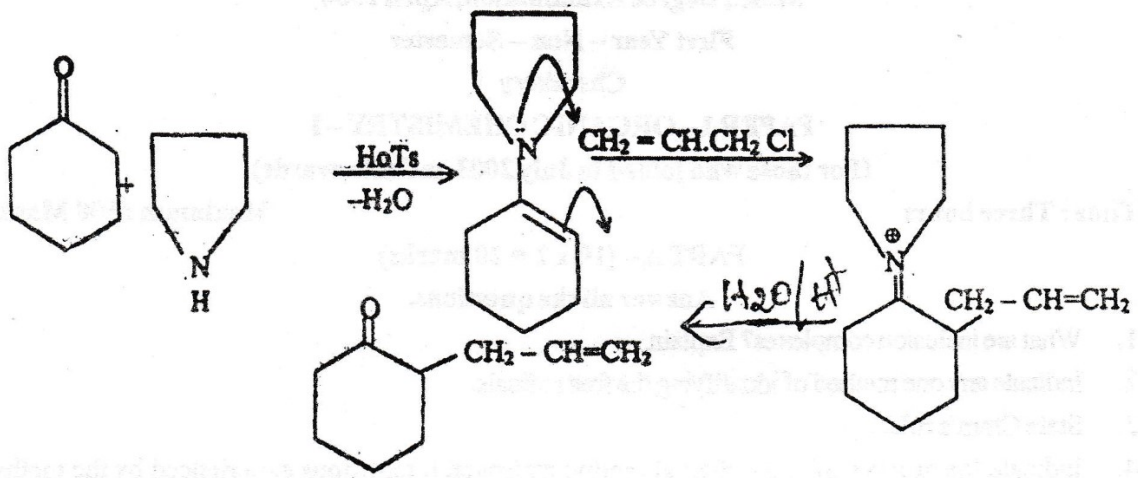
When the enamine is alkylated (or) acylated, the nucleophilic carbon readily attacks the alkyl/ acyl/ group.



The Iminium compound readily undergoes hydrolysis to give the alkylated ketone.

The Nitrogen containing the lone pair in enamines, can also act as a nucleophile similar to the carbon end, hence it leads to the formation of quartarnary salt which is an unwanted side reaction.

A well known example of Stork – enamine reaction is the use of pyrrolidine with reactive halides such as allyl, benzyl as well as α - halo esters and α - haloketones, in the alkylation / arylation of carbonyl compounds at α - position.



2 – Allylcyclohexanone

The ease with which the enamines undergo hydrolysis to form ketone, has made this method simpler to any other method of formation of α - alkylated / arylated / acylated aldehydes and ketones. Moreover the alkylation occurs at the less substituted side of the original ketone and only monoalkylation takes place.

Dr.D. VETHAROY
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M.Sc., Degree Examination, April 2004

First Year – Non – Semester

Chemistry

PAPER I – ORGANIC CHEMISTRY – I

(For those who joined in July 2003 and afterwards)

Time : Three hours **Maximum : 100 Marks**

PART A – (10 x 2 = 20 marks)

Answer all the questions.

1. What are inclusion complexes? Explain.
2. Indicate any one method of identifying the free radicals.
3. State Cram's rule.
4. Indicate the number of 1, 3 – diaxial methyl hydrogen interactions experienced by the methyl group in the 9th position of trans. decalin.
5. How will you establish the presence of nitro group in chloramphinicol?
6. Explain how quininic acid is converted to 6-hydroxyquinoline.
7. Compare the structures of theobromine and theophilline.
8. Which is expected to be more stable, Or

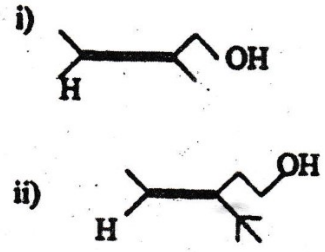
(or)

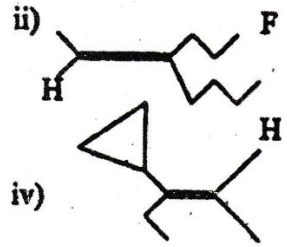
9. In what way, S_N1 mechanism differs from S_Ni mechanism?
10. Give evidences for the presence of benzyne intermediate in some aromatic nucleophilic substitution reactions.

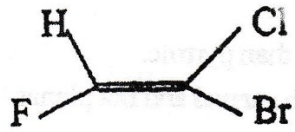
Part –A (5 x 6 = 30 marks)

Answer all questions choosing either (a) or (b).

11. a) List out the scope and limitations of Hammett equation. (or)
    b) Indicate how the isotope labeling technique is useful in analyzing the mode of fission in ester hydrolysis reactions.
12. a) Distinguish between stereospecificity and stereoselectivity with adequate examples.







13. a) Write a note on biosynthesis of alkaloids. (or)
    b) Give an account of the degradation products of terramycin.
14. a) Draw the structures of [14] and [16] annulenes, Comment on the chemical shift values of inner and outer hydrogens in each case. (or)
    b) Explain how caffeine is converted to
        i) Chlorocaffiene
        ii) Oxycaffiene and
        iii) Methoxycaffiene
15. a) Explain how the basicity of attacking reagent and the substrate structure affects the course of elimination reactions. (or)
    b) Discuss the mechanism of Von Richter rearrangement

Part C – (5x10=50 marks)

Answer all questions choosing either (a) or (b)

16. a) Give an account of the generation, stability and reactivity of nitrenes and carbenes.

(or)

    b) Comment on the rate, yield, product ratio and mechanism of the following reactions.
        i) Bromination of p-xylene
        ii) Nitration of acetophenone
        iii) Sulphonation of furan
17. a) Allenes, biphenyls and spiranes become optically active, if properly substituted, even in the absence of chiral atoms. Explain with suitable examples. (or)
    b) Discuss the conformational features of differently substituted dialkyl cyclohexanes indicating the preferred arrangement in each case. Point out whether these isomers are optically active or not.
18. a) Explain how the structure of natural penicillin was established.

(or)

    b) Indicate how the chemical constitution of quinine was established.
19. a) Write notes on the synthesis and reactions of
        i) Carbazole and
        ii) Imidazole

b) Account for the following :

i) Pyridine is more basic than pyrrole.

ii) Cycloctaletraene is tub shaped and not planar.

iii) Azulene has a diploemoment

iv) The C_1-C_2 bond length is shorter than C_2-C_3 bond length in naphthalene.

20. a) Explain how writing, Grignard and Reformatsky reactions are useful in carbon – carbon bond forming process. Give the mechanisms of these reactions. (or)

b) Decribe how S_N1 and S_N2 reaction mechanisms are governed by the substrate structure nature of nucleophile, solvent polarity and leaving group ability.

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