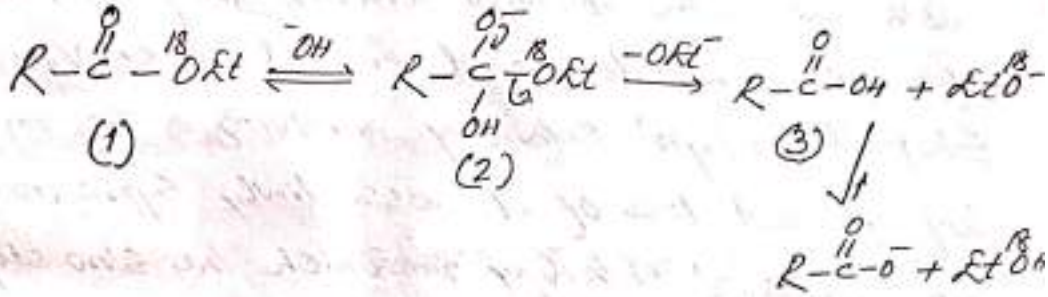
Hydrolysis of ester

$B_{AC}2$ mechanism:

A reaction that has been much investigated is the hydrolysis of esters, by aqueous base i.e. OH^-. It is found to be kinetically second order and ^{18}O isotopic labelling experiment on (1) have established that this normally undergoes acyl-oxygen cleavage i.e. ^{18}O label is found only in EtOH. This supports the tetrahedral intermediate pathway via following path way:



The rate-limiting step is almost certainly attack of OH^- on the original ester (1). The overall reaction is essentially irreversible as ^-OEt would remove a proton from (3) rather than attack its carbonyl carbon-atom, while the carboxylate anion will be insusceptible to nucleophilic attack by EtOH or EtO^-. This mechanism is generally referred to as $B_{AC}2$ mechanism.

Transesterification:

In organic chemistry, transesterification is the process of exchanging the organic group 'R'' of an ester with the organic group 'R' on an alcohol. These reactions are often catalyzed by the addition of an acid or base ~~catalyst~~.

Strong acids catalyses the reaction by donating a proton to the carbonyl group, thus making it a more potent electrophile, whereas bases catalyse the reaction by removing a proton from the alcohol, thus making it more nucleophile.

Esters with longer alkoxy groups can be made from the methyl esters in high purity by heating the mixture of ester, acid/base and large alcohol) and evaporating (the alcohol) to drive equilibrium.

* Acid chloride undergo ready attack by weaker nucleophiles e.g. H_2O, ROH. The question then arises whether with the better potential leaving group Cl^-, the reactions of acid chloride could proceed either via a single step 'SN2 type' pathway involving a TS, in which attack by Y^- and loss of Cl^- essentially synchronous or via an 'SN1 type' pathway in which the slow step is $RCO-Cl \rightarrow R\overset{+}{C}O + Cl^-$, followed by fast attack by Y^- on the acyl cation $R\overset{+}{C}O$. In fact, most reaction of acid chloride probably proceed via the more familiar tetrahedral intermediate pathway.

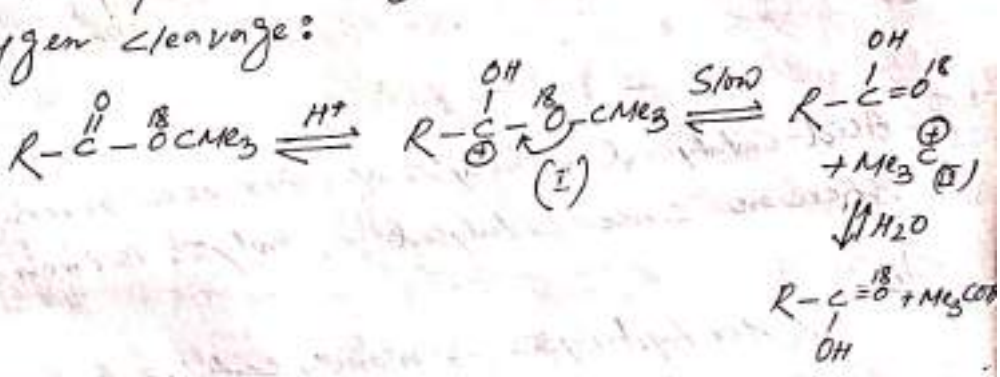
$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{Y^-} R-\overset{O^-}{\underset{Y}{\overset{|}{C}}}-Cl \xrightarrow{-Cl^-} R-\overset{O}{\overset{\|}{C}}-Y$$

* $A_{AC}2$ type mechanism:

$$R-\overset{O}{\overset{\|}{C}}-OR \rightleftharpoons R-\overset{\overset{+}{O}-H}{\overset{\|}{C}}-OR \xrightarrow{H-\ddot{O}:} R-\overset{OH}{\overset{|}{C}}=\ddot{O}R \quad (H-\overset{+}{O}(H)-H)$$

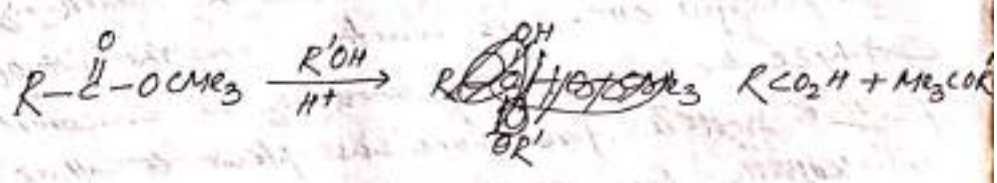
$$R-\overset{O}{\overset{\|}{C}}-OH + ROH \rightleftharpoons R-\overset{OH}{\overset{|}{C}}-\overset{\oplus}{O}(R)(H)$$

* Esters RCO_2R' where the alkyl group R' can form a relatively stable carbocation e.g. (2) from (1), have been shown by ^{18}O labelling experiments to undergo alkyl-oxygen cleavage:

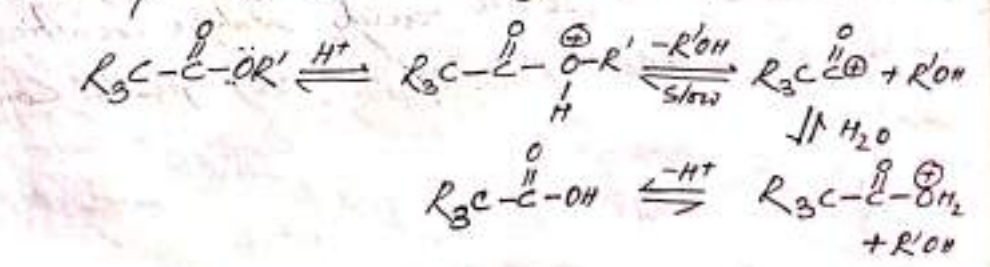


This mechanism generally referred to as A_{AL1} mechanism. It also occurs with ester alkyl groups such as Ph_2CH.

* When attempts are made to transesterify ~~with~~ ester $RCOOCMe_3$ with $R'OH$, the product is not now the expected ester RCO_2R' but RCO_2H and the ether $R'OCMe_3$.

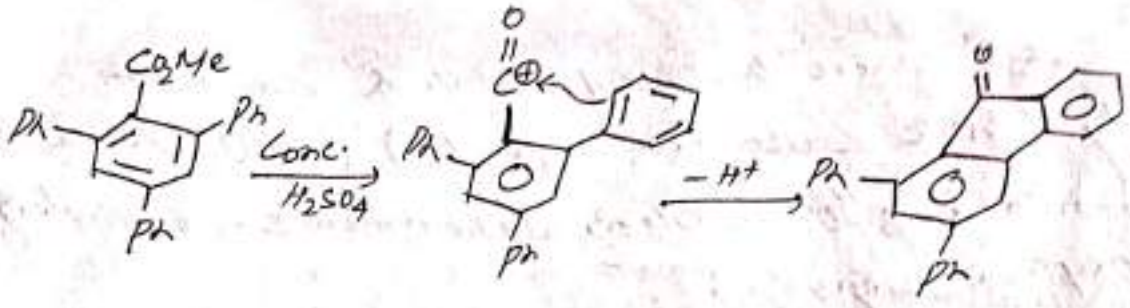


* Where the acid alkyl group R' in RCO_2R', is sufficiently bulky, e.g. R_3C, that bimolecular hydrolysis via a tetrahedral intermediate is inhibited (because of the degree of crowding there would be in the T.S.), a further, relatively rare, acid-catalysed mechanism is found to operate - $A_{AC}1$ - it occurs only in powerful ionising solvents:



Evidence of this mechanism:

2,4,6-triphenyl ester when dissolved in conc H_2SO_4, the brilliant colour of 1,3-diphenylfluorenone is at once observed - obtained via ring-closure of the acyl



* Acid-catalysed hydrolysis of ester is a reversible reaction whereas base catalysed hydrolysis is irreversible-Explain.

Ans:

Ester hydrolysis is usually catalyzed by acids or bases. Since OR is a much poorer leaving group than halide or OCOR, water alone does not hydrolyze most ester.

$$R-\underset{\underset{O}{\|}}{C}-OR' \underset{H^+}{\overset{H_2O}{\rightleftharpoons}} RCOOH + R'OH$$

$$R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[H_2O]{OH^-} RCOO^- + R'OH$$

When bases catalyze the reactions the attacking species is the more powerful OH^-. This reaction gives the salt of the acid. Acid catalyze the reaction by making the carbonyl carbon more positive and therefore more susceptible to attack by the — nucleophile. Both reactions are equilibrium reactions, so they are practicable only when there is a way of shifting the equilibrium to the right. Since formation of the salt does just this, ester hydrolysis always done for preparative purpose in basic solution. formation of salt in base catalyzed hydrolysis makes the ~~equilibrium shift to~~ the reaction a irreversible one while acid catalyze reaction does not follow a irreversible path way and not goes to completion.

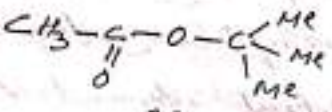
* Which one of the following would be most readily hydrolysed with NaOH? Explain and give the order of hydrolysis.

(i) $CH_3COC_4H_9$

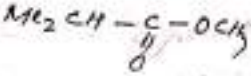
(ii) $Me_2CH-C(=O)-OCH_3$

(iii) CH_3COOCH_3

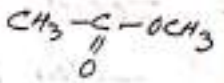
Ans.



(I)



(II)



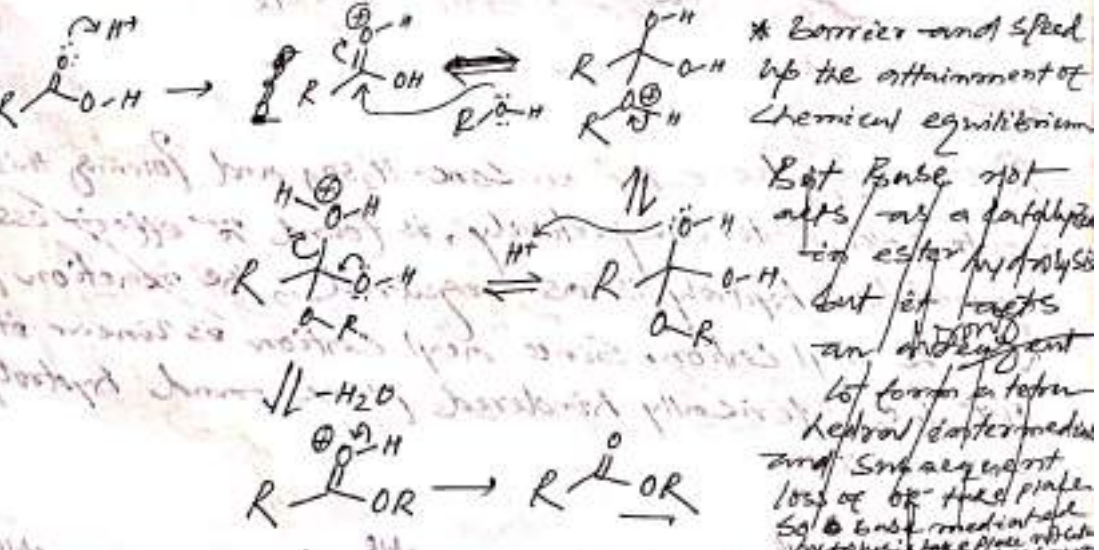
(III)

The hydrolysis proceeds through the rate-determining formation of a tetrahedral intermediate. Since formation of this intermediate involves change of hybridization of the carbonyl carbon from sp^2 to sp^3, steric crowding in the T.S. leading to the intermediate increases and therefore, the reaction rate decreases with increase in size of R and R' (RCO_2R'). Since t-butyl group is much larger i.e. more space-filling than Me_2CH- and CH_3- group, so the rate of hydrolysis is

(I) < (II) < (III)

* Esterification reaction always catalyzed by acid - Explain.

Ans

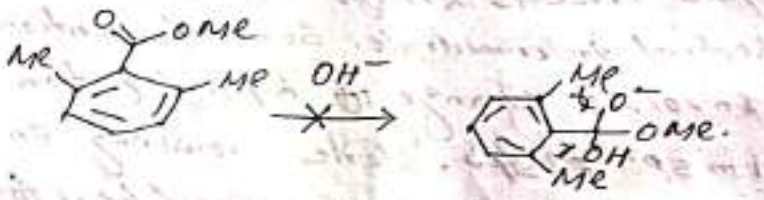


In acid-catalyzed Fischer esterifications the proton binds to oxygen and functions as a Lewis acid to activate the ester carbonyl as an electrophile, and converts the hydroxyl into the good leaving group water. Both lower the kinetic

* Methyl 2,6-dimethyl benzoate is not hydrolysed by boiling aqueous acid or base. Hydrolysis is essentially complete upon dissolution of the ester in conc. H_2SO_4 and subsequent addition to water.

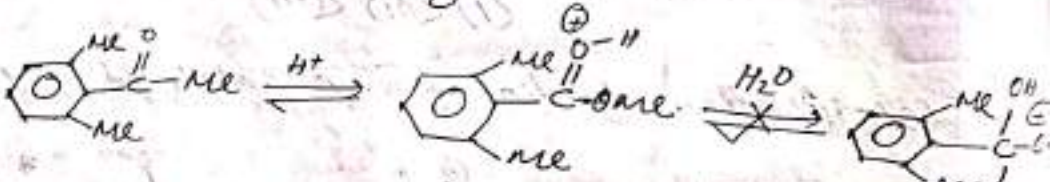
Ans:

Where the acid alkyl group R in RCO_2R', is sufficiently bulky like in 2,6-dimethyl benzoate, that bimolecular hydrolysis via a tetrahedral intermediate is inhibited because of the degree of crowding there would in the transition state.



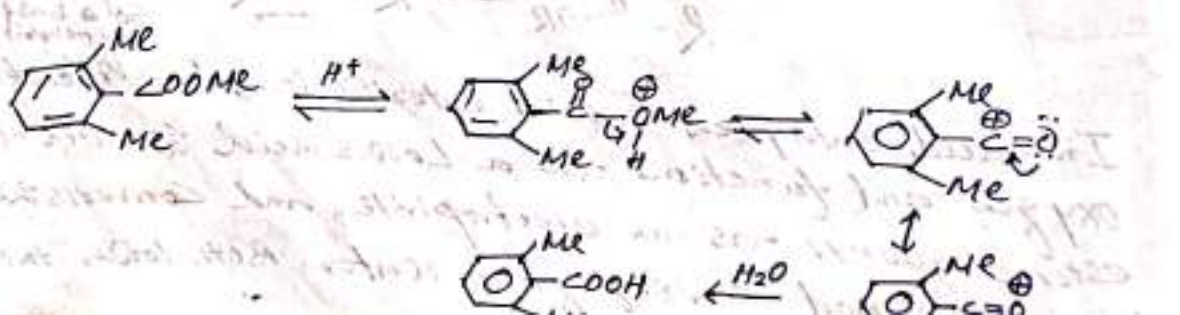
Steric crowding large.

A simple acid catalyzed hydrolysis also not possible because of the steric crowding in the T.S.



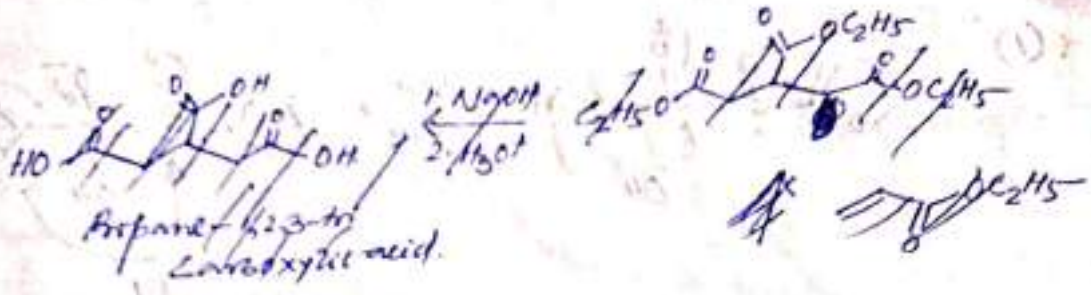
Steric Crowding

Dissolving the ester in conc. H_2SO_4 and pouring this solution into cold water, respectively, is found to effect essentially quantitative hydrolysis as required; the reaction proceeds via the acyl cation. Since acyl cation is linear it moves out the sterically hindered plane and hydrolysis becomes easier.

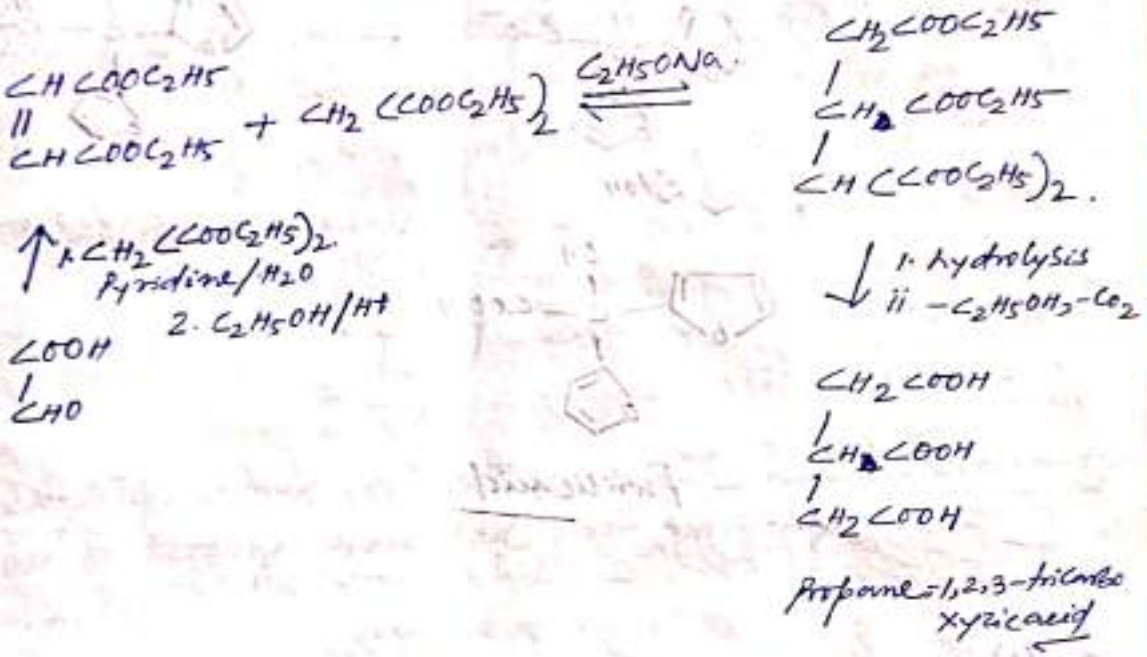


How would you synthesize (i) 3-methylcyclohexanone and (ii) Propane-1,2,3 tricarboxylic acid.

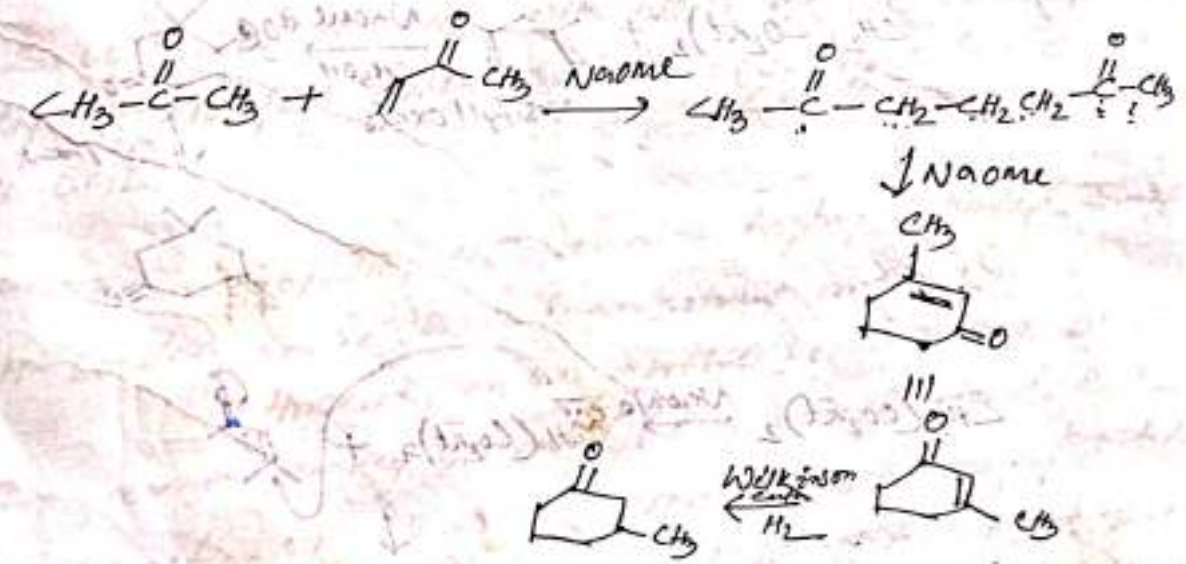
(ii)



ii



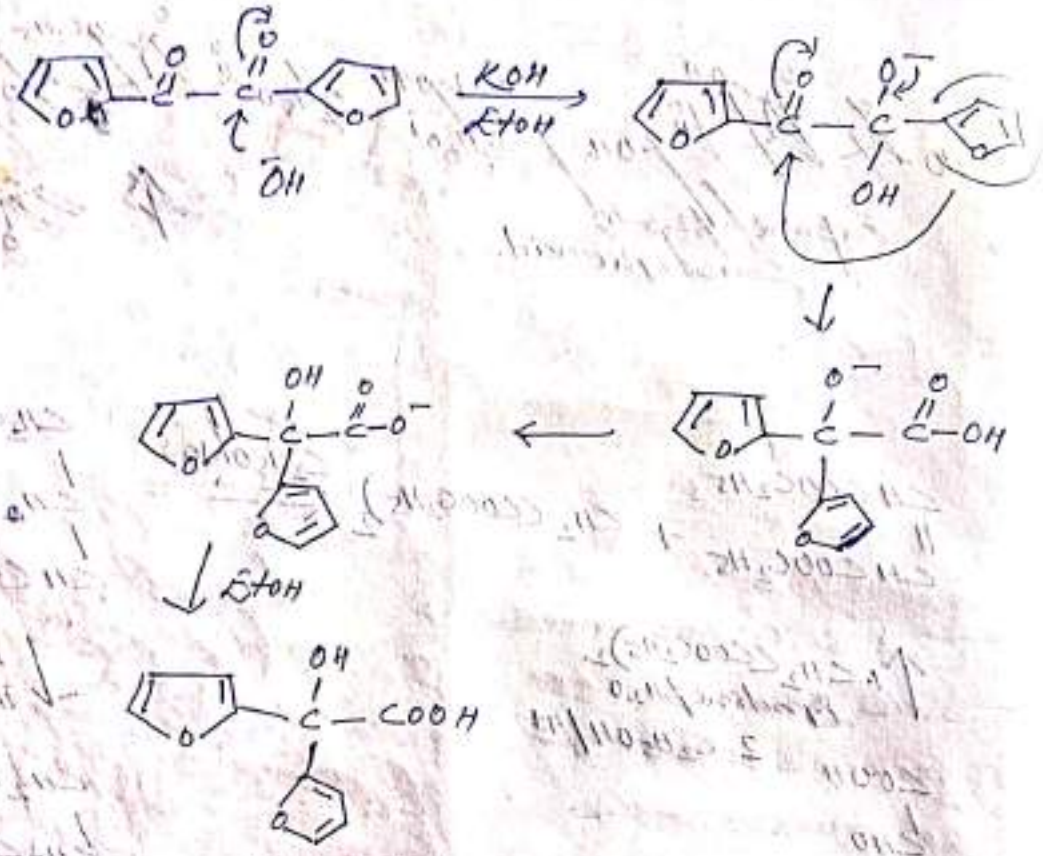
(i)



** Design synthesis of (i) furilic acid from furil and (ii) flemendon from mesityl oxide.

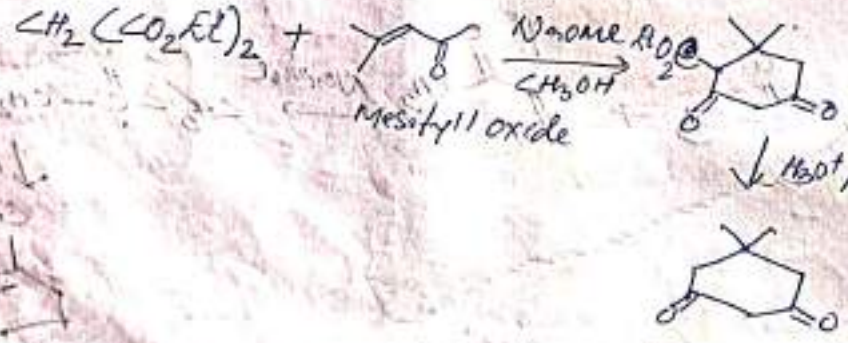
Ans:

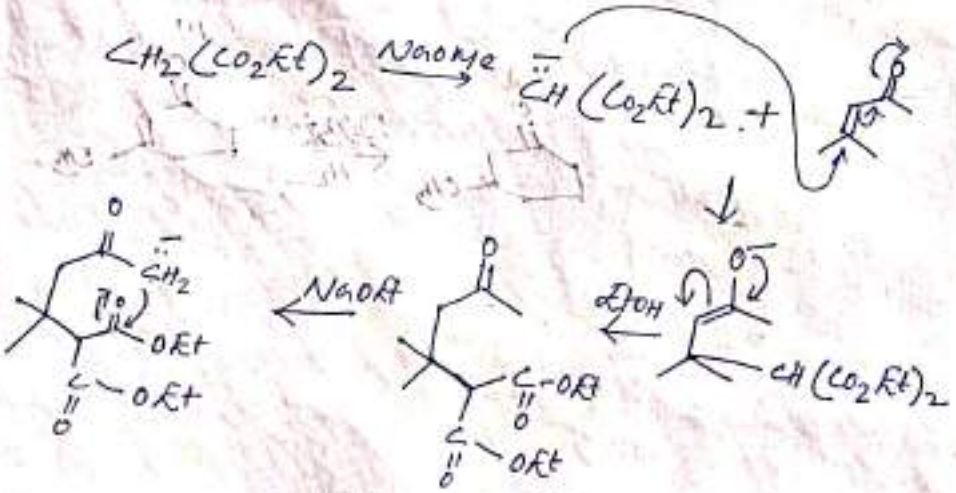
(i)

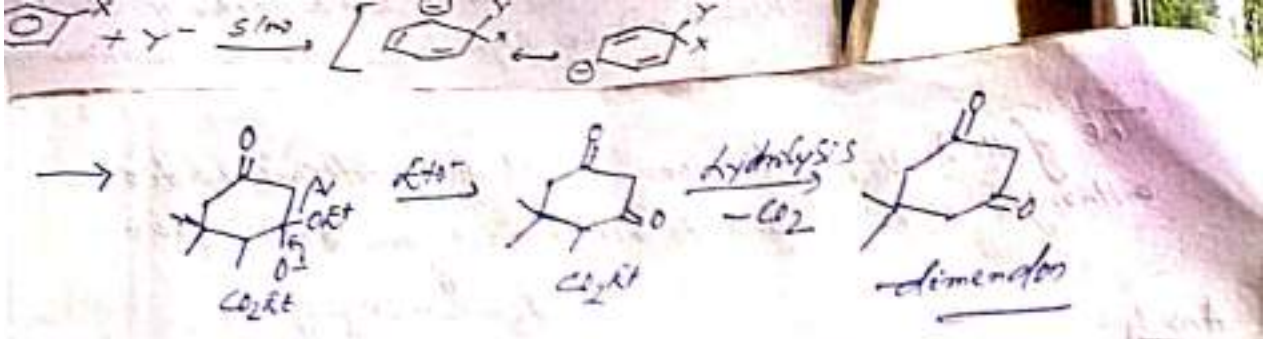


Furilic acid

(ii)



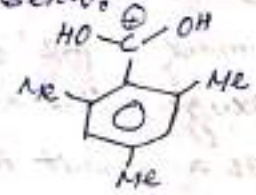




* 2,4,6-trimethyl benzoic acid is very difficult to esterify — Explain?

Ans

If the trisubstituted acid were protonated on the normal position (on the carbonyl oxygen atom), the two bulky O-Me groups would force the two adjacent OH groups into a plane virtually at right angles to the plane of the ring as shown below:



Nucleophilic attack on the carbonic carbon atom by MeOH is thereby prevented from taking place from all directions.

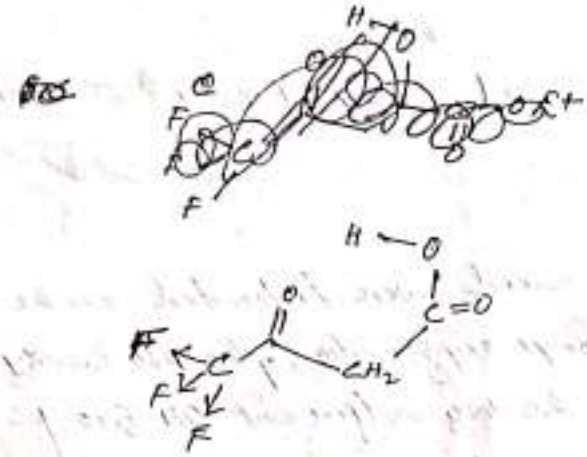
* Substitution of MeI with NaN_3 at 0°C is increased by 4.5×10^4 fold when solvent is changed from CH_3OH to DMF.

Ans: The nucleophile, N_3^- remains highly solvated through H-bonding in the protic polar solvent methanol. However, in the aprotic polar solvent DMF, it remains weakly solvated (only through ion-dipole interactions). Thus N_3^- reacts as a very powerful nucleophile in DMF compared to it in MeOH. This explains why the rate of substitution of MeI with NaN_3 increases very much on transfer from CH_3OH to DMF.

* The following acid does not undergo decarboxylation although it is a β-Keto acid. Give an explanation.

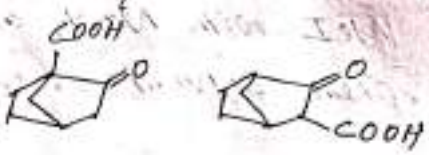
$CF_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$

Ans.

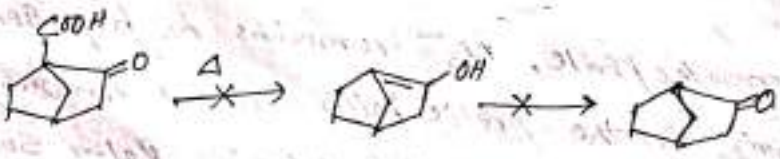


In the Keto acid CF_3COCH_2COOH, the powerful electron withdrawing $-CF_3$ group makes the unshared pair of electrons on carbonyl oxygen less available for taking up the carboxyl proton. As a result the T.S. energy increases and the rate of decarboxylation decreases.

* Between two acids which one will decarboxylate readily? Explain your answers.

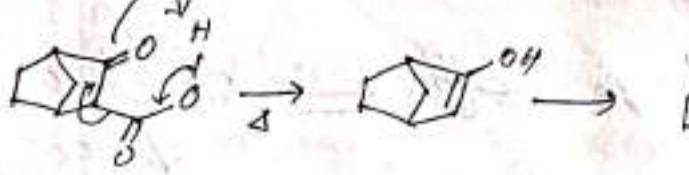


Ans.



The mechanism of decarboxylation is consistent with the resistance of bridgehead bicyclic β-Keto acids to decarboxylation and this is because strain prevents formation of a double bond at the bridgehead position (Bredt's rule).

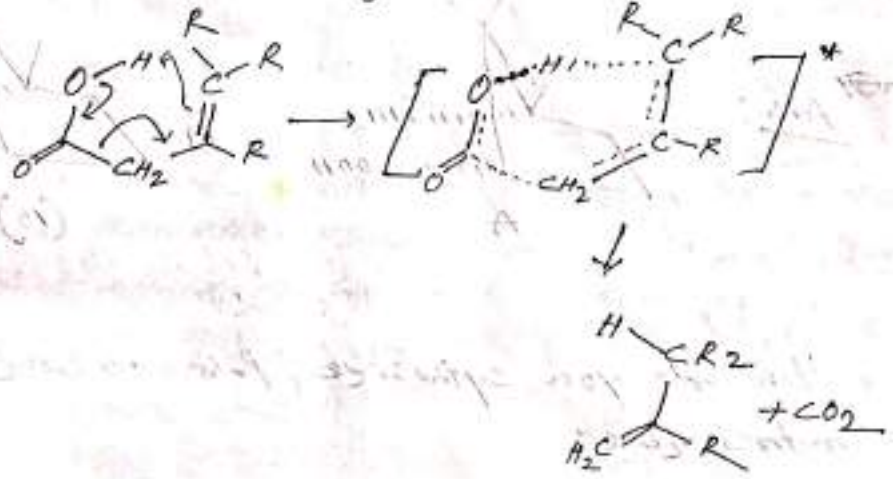
Where as second one easily decarboxylate involving a cyclic six membered T.S.



* β,γ - Unsaturated acid easily decarboxylate on heating?

Ans:

The ready decarboxylation of the βγ-Unsaturated acid $R_2CHCR=CHCO_2H$ is probably due to incipient proton transfer to C=O through H-bonding.

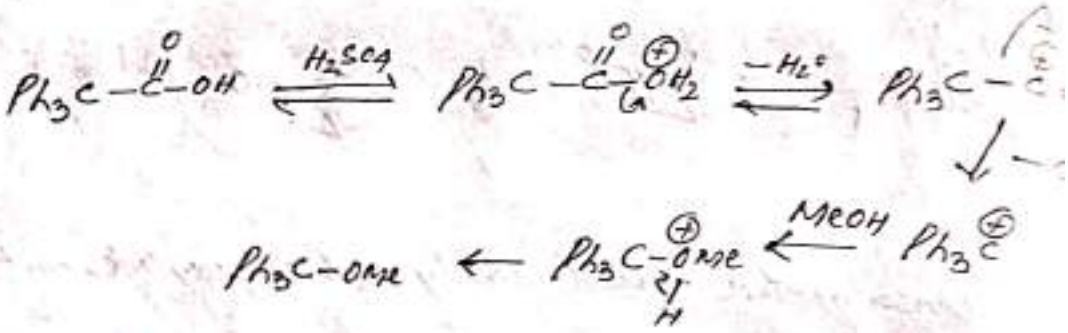


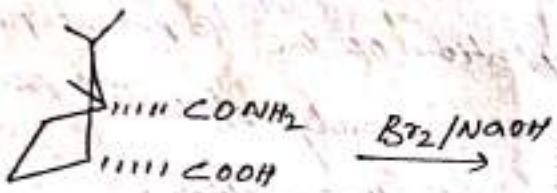
* Suggest plausible reason for this conversion:

$Ph_3CCOOH \xrightarrow[\text{then MeOH}]{\text{Con. } H_2SO_4} MeOCPh_3$.

Ans

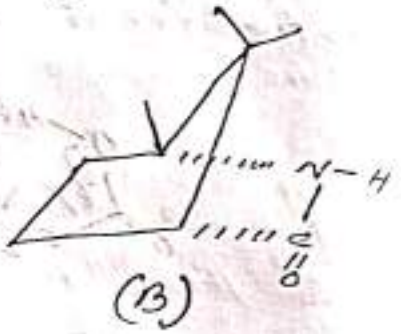
Under the given conditions this sterically hindered acid undergoes esterification by the $A_{AC}1$ mechanism which involves abnormal protonation on the -OH oxygen atom of the -COOH group and formation of an acylium ion. Instead of reacting with alcohol this acylium ion eliminates a molecule of 'CO' to form triphenylmethyl cation which then reacts with methanol to form Ph_3COCH_3. The driving force for the elimination of the carbonyl group from the acylium ion is the formation of the very stable carbocation $Ph_3\overset{\oplus}{C}$ (highly stabilized by resonance) with consequent relieve of steric strain (sp^3 hybridized carbon in acylium ion to sp^2 hybridized carbon in $Ph_3\overset{\oplus}{C}$).





Ans:

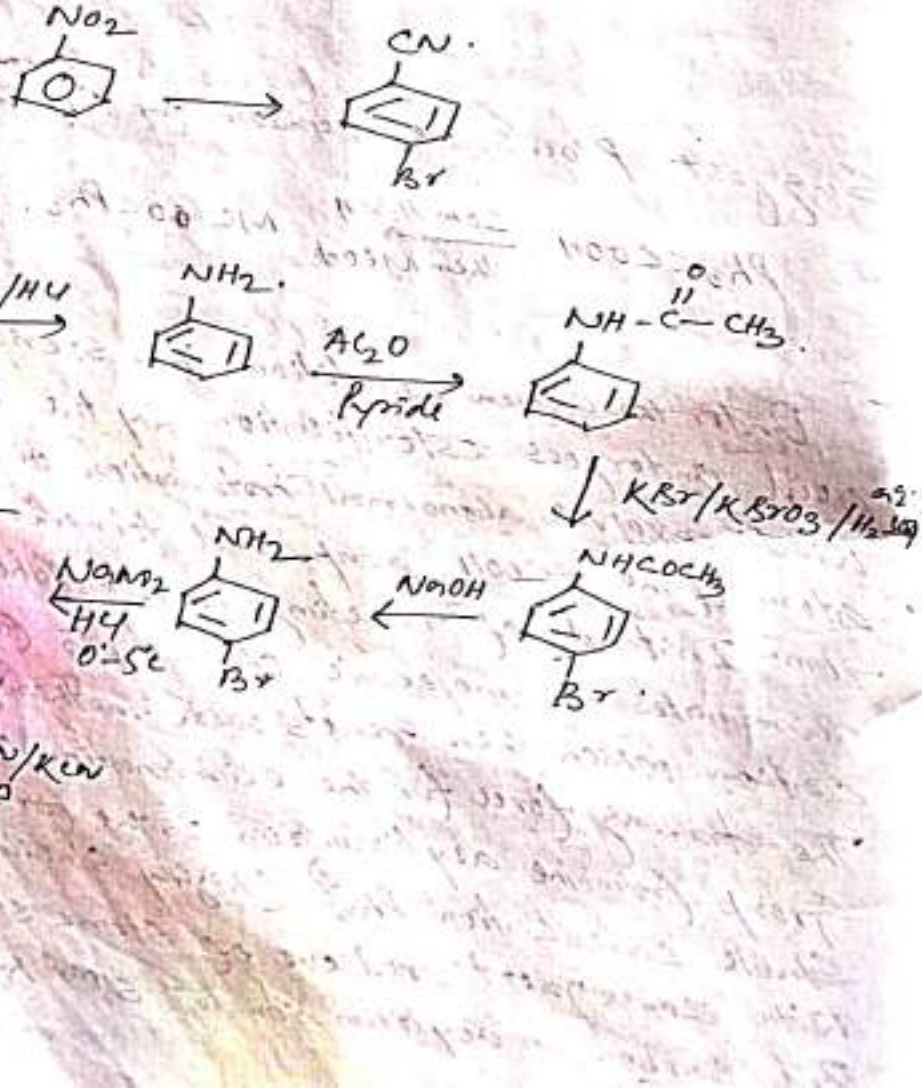
A



(B)

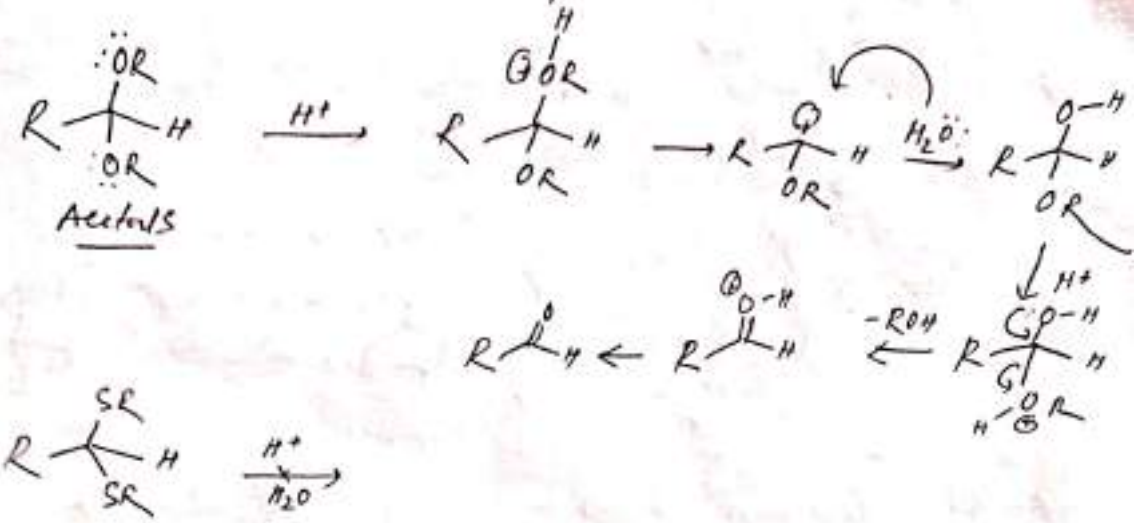
* How do you synthesize p-bromo benzonitrile from nitrobenzene:

Ans



* Acetals can be cleaved easily by an acid but thioacetal show considerable stability. Why do you observe this?

Ans



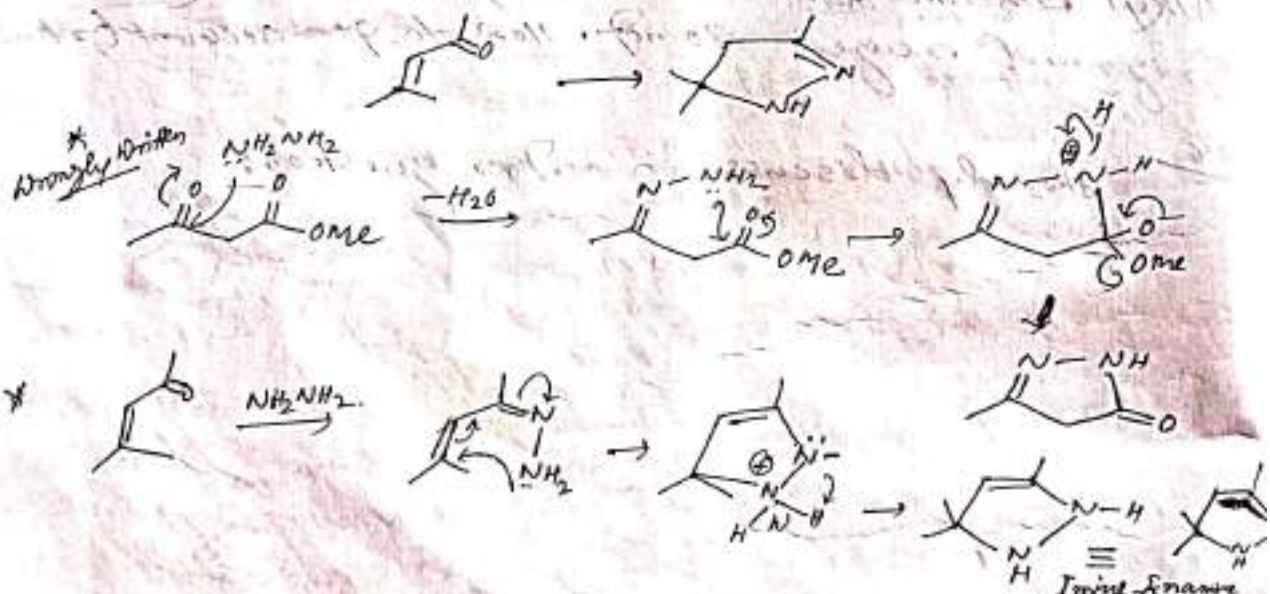
Thioacetals are much harder to hydrolyse because sulfide are less basic than ethers. They however, hydrolysed using electrophiles that attack sulfur readily, such as Hg(II) or methylating agents.

* Alkyl Lithium adds to sterically hendered ketones but Grignard reagent do not. How do you account for this

Answer Already discuss in another question:

* Between the two isomeric acids, which one will oxylate and why?

Carry out the following conversion:



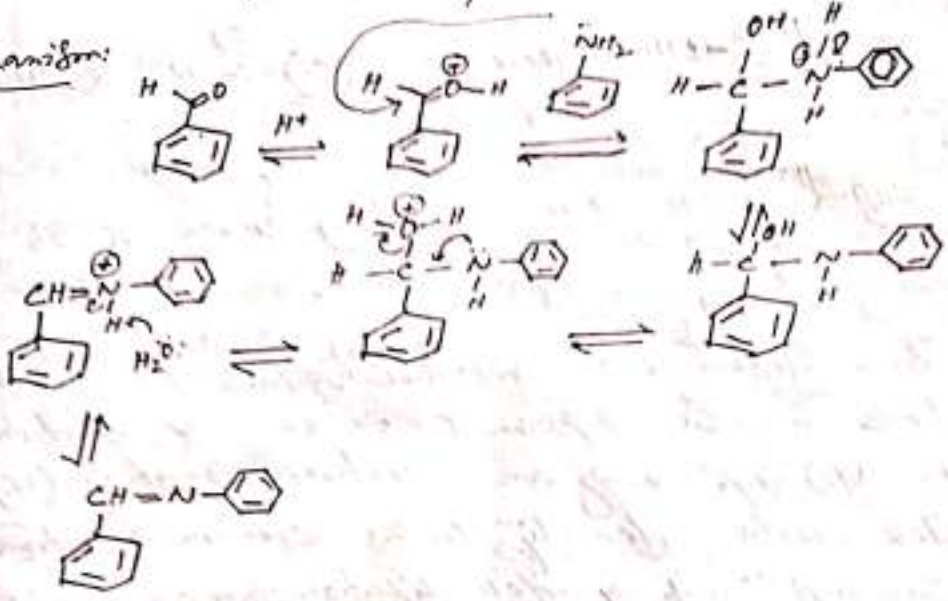
* Give the structure of the major products of the following reaction and explain (3)

Benzaldehyde + Aniline $\xrightarrow{H^+}$?

Ans Primary amines like $ArNH_2$ Undergo nucleophilic addition reaction with aldehydes to give Carbinolamines which then dehydrated to give Substituted

imines. The reactions are usually carried out in an acidic buffer to activate the $-C=O$ and facilitate dehydration but without inhibiting the nucleophile.

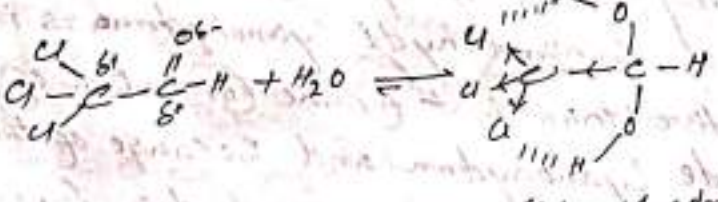
Mechanism:



* Chloral usually forms a stable geminal diol where as trimethyl acetaldehyde fails to do so. Explain the opposite behaviour?

Ans

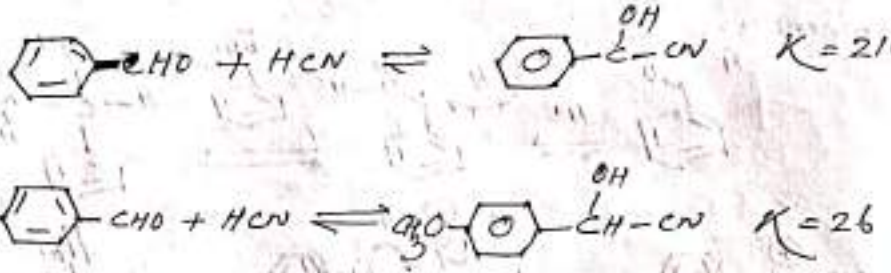
The positive dipole ends of the trichloro methyl Groups of chloral repel each other electrostatically. In the hydrate, the carbonyl Group dipole is replaced by the most weaker dipole of the diol. Thus, the $-CCl_3$ group has a much greater destabilizing effect on the molecules, but not on a hydrate. That is, the hydrate is relatively more stable than the original carbonyl compound. Moreover, the hydrate is stabilized by intramolecular H-bonding involving 'Cl' atoms as well as electron-withdrawing inductive effect that prevents the reverse reaction.



Chloral hydrate.

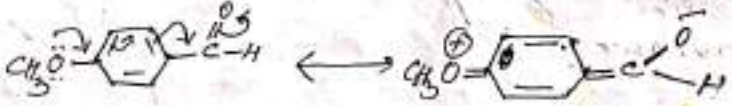
On the other hand, a +I Group inhibits hydrate formation, that why presence of three -methyl Group prevents the formation of hydrate in $Me_3C-\overset{O}{\overset{\|}{C}}-H$.

→ Account for the relative values of the equilibrium constants for the following cyanohydrine formations:



Ans:

This difference in relative values of equilibrium constants may be explained in terms of electronic factors. Methoxy, being an electron-donating (+R) group provides electron density to the electron-withdrawing (-R) carbonyl group by delocalization through benzene ring. Resonance interaction between two such groups is highly favourable.

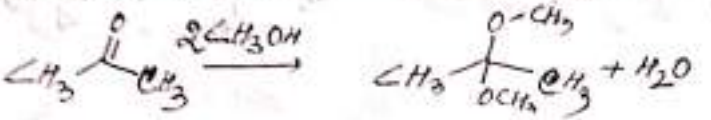


Consequently, p-methoxy benzaldehyde is stabilized by resonance than benzaldehyde is. The value of equilibrium constant for a reaction depends on the standard free energy difference between product and ~~reactant~~ starting material. Since carbonyl group is no longer present in cyanohydrine, its interaction with the rest of the system is lost and so, it can be assumed that both the cyanohydrine products are close in energy. Again the cyanohydrins are relatively more stable than the ~~more~~ corresponding aldehyde. The value of ΔG° for the formation of benzaldehyde cyanohydrine is therefore, more negative than that for the formation of p-methoxy benzaldehyde cyanohydrin and because of this p-methoxy benzaldehyde has a lower cyanohydrin formation constant than benzaldehyde.

* Ketones readily form cyclic ketals with CH_2OH CH_2OH but acyclic ketals are difficult to prepare?

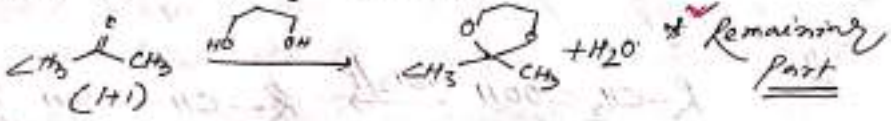
Ans:

* Part of the reason for the stability of cyclic ketal concerns entropy. Formation of an acyclic ketal involve decrease in entropy because three molecules are consumed for every two ~~products~~ of product



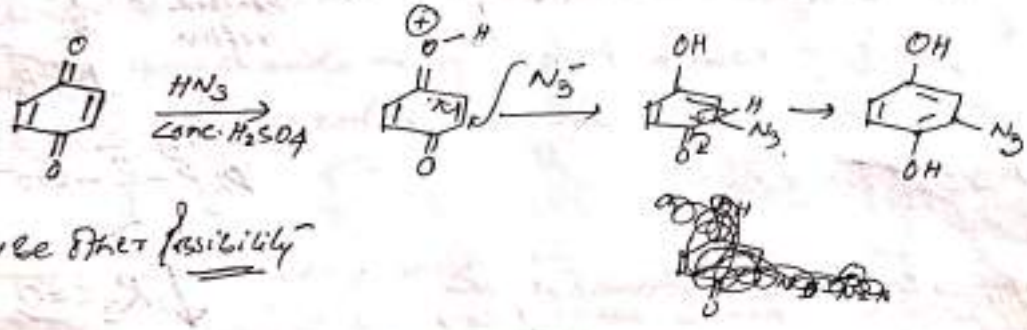
(1 Ketal + 2 alcohol) (1 Ketal + $1H_2O$)

This is not the case of cyclic ketal. Since $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, a reaction with a negative $\Delta S^{\ddagger}$ tends to have a more positive $\Delta G^{\ddagger}$, in other words, it is less favourable.



* Remaining Part

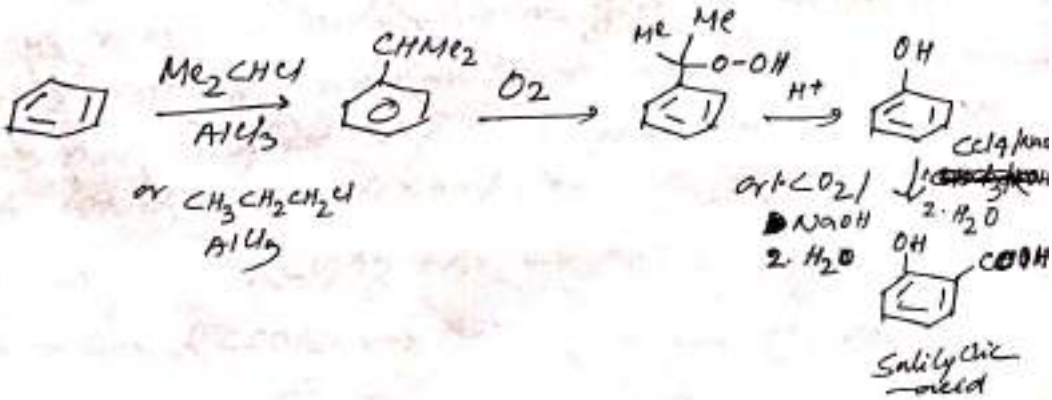
*



Maybe other possibility

* Synthesis of Salicylic acid from benzene?

Ans



Q* Prepare the following acid

i. α-Hydroxy acid

ii. α,β-Unsaturated acid Start... from RCH_2COOH

Ans:

i. $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{HCN} CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow[\Delta]{HCl/H_2O} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-Co...$

α-hydroxy...

ii. $R-CH_2COOH \xrightarrow{Br_2/P} R-\underset{\underset{Br}{|}}{CH}-COOH \xrightarrow[\text{Benzene reflux}]{PPh_3} Ph_3\overset{\oplus}{P}-\underset{\underset{R}{|}}{CH}-Co...$ (with R^-)

$\downarrow$ n-Buli

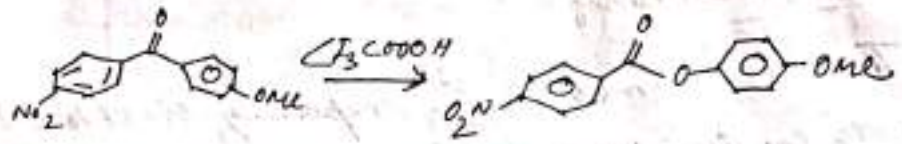
$Ph_3\overset{\oplus}{P}-\ddot{\underset{\underset{R}{|}}{C}}-COO^-$

$\downarrow R_2C=O$

$R_2C=\underset{\underset{R}{|}}{C}-COOH. \xleftarrow{H_2O} R_2C=\underset{\underset{R}{|}}{C}-COO^-$

α,β-Unsaturated acid

*



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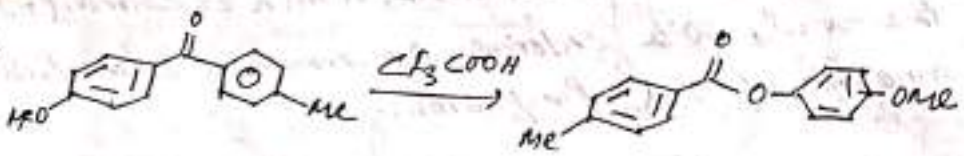


* $Ph\overset{O}{\underset{}{\langle}}CMe_3 \xrightarrow{m\text{-}CPBA/CH_2Cl_2} Ph-\overset{O}{\overset{\|}{C}}-OCMe_3$

* $(p\text{-}MeOC_6H_4)_2-\underset{OH}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}(C_6H_5)_2 \xrightarrow{H^+}$

* Remaining part

Another way to view the situation is to consider the rates of forward and reverse process. For an intramolecular reaction the nucleophilic $-OH$ group is always held close to carbonyl group and as a result, fastest forward reaction took place compared to reverse reaction.

Hunsdiecker reaction: Silver salt of carboxylic acids in CCl_4 solution are decomposed by chlorine or bromine to form the alkyl halide, e.g.

$$RCO_2Ag + Br_2 \longrightarrow RBr + CO_2 + AgBr$$

The yield of halide is primary > secondary > tertiary and bromine is generally used. Chlorine giving a poorer yield of alkyl chloride. The mechanism is uncertain, but a favoured theory is that the first step is the formation of an acyl hypohalite which then decomposes into free radical.

$$RCO_2Ag + Br_2 \rightarrow RCOOBr + AgBr$$

$$RCOOBr \rightarrow Br^\cdot + RCOO^\cdot \rightarrow R^\cdot + CO_2$$

$$R^\cdot + Br_2 \rightarrow RBr + Br^\cdot$$

$$R^\cdot + RCOOBr \rightarrow RBr + RCOO^\cdot \text{ etc.}$$

Hell-Volhard-Zelinsky reaction:

The usual method for preparing α-chlo... α-bromo acids is by the HVZ reaction, which is carrie... by treating the acid with chlorine or bromine in the p... of a small amount of red phosphorous.

$$RCH_2CO_2H \xrightarrow{P+Br_2} RCH_2C(=O)Br \rightleftharpoons RCH=C(OH)Br$$

$$\downarrow Br_2$$

$$RCHBrCOBr$$

$$\downarrow\uparrow RCH_2CO_2H$$

$$RCHBrCO_2H + RCH_2CO_2H$$

Enolisation of the acid bromide is far more rapid ... that of the acid.

* Why do you first to prepare a ketone from acylchloride ... Grignard reagent? How do you prepare it using an orga... metallic reagent?

Ans. Acylchloride reacts ~~very~~ rapidly with Grignard reag... to form tertiary alcohol; ~~some ester~~. We ~~can~~ can't s... the reaction at ketone step.

$$R^1-C(=O)-Cl + R^2MgX \rightarrow R^1-C(Cl)(OMgX)-R^2$$

$$\downarrow R^2MgX$$

$$R^1-C(R^2)(OMgX)-R^2$$

$$\downarrow H_3O^+$$

$$R^1-C(R^2)(OH)-R^2$$

* We can easily prepared a ketone from alkyl chloride using Gilman reagent (R_2CuLi)

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{R_2CuLi} R-\overset{O}{\overset{\|}{C}}-R$$

* Hydrolysis of ethylvinyl ether takes place 10^{23} times faster than that of diethyl ether.

* How does a ylide acquire stabilisation?

Ans Phosphorous ylides can be represented by two resonating structure:

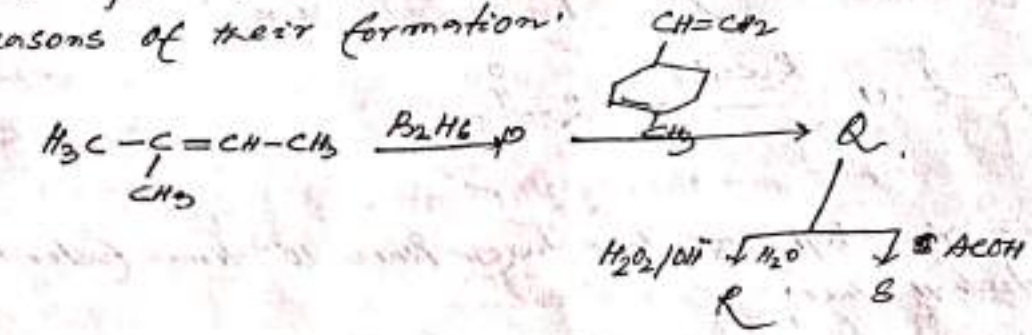
$$Ph_3P=C\begin{matrix}R\\R\end{matrix} \longleftrightarrow Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}\begin{matrix}R\\R\end{matrix}$$

Since alkyl groups donate electrons through the inductive effect, electron donating groups destabilize charge separation, while the presence of electron withdrawing stabilize the ylide. The reactivity of these ylids is associated with carbanionic centre in the dipolar structure, and is decreased when the negative charge is delocalized.

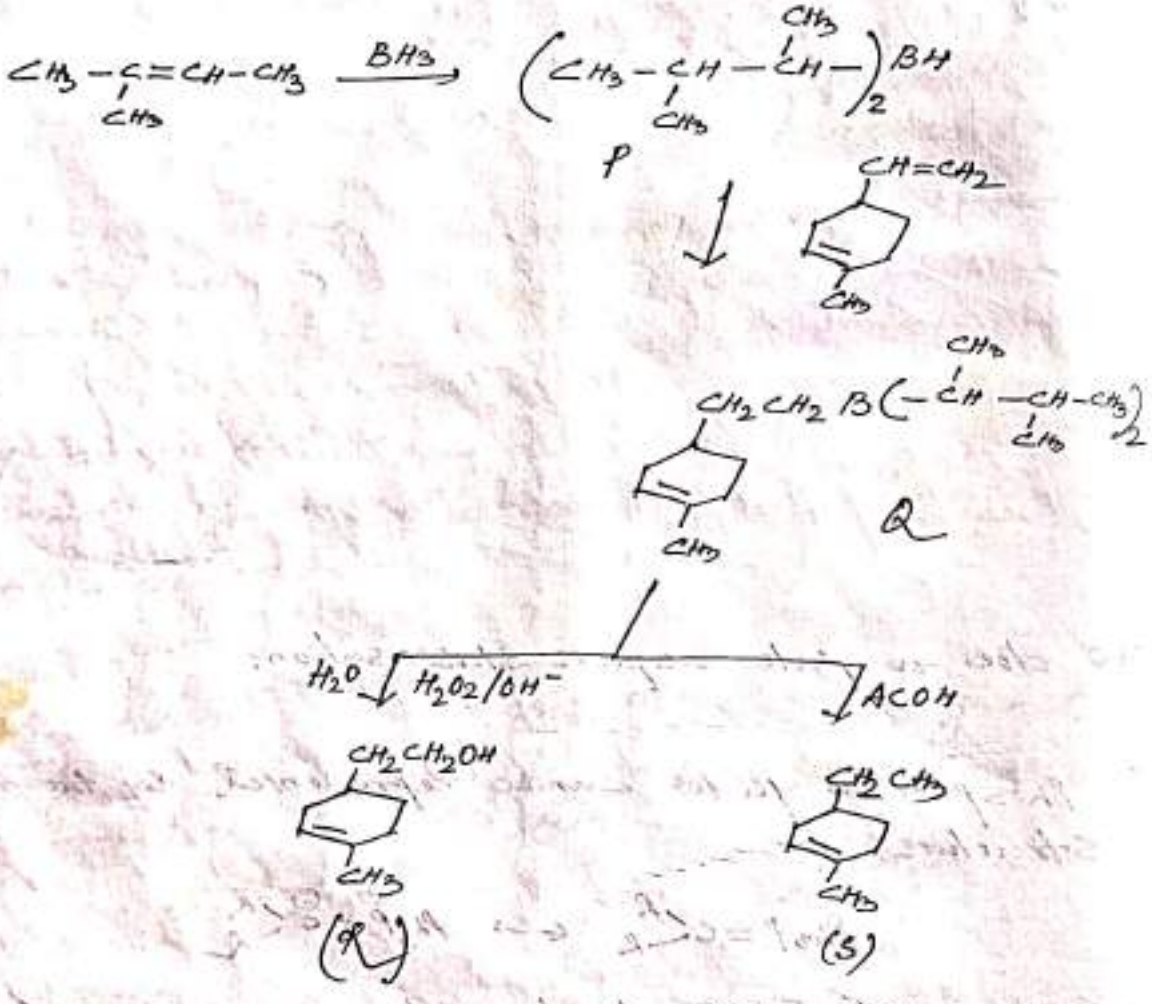
$$Ph_3P=CH-CH=O \longleftrightarrow Ph_3\overset{\oplus}{P}-\overset{\ominus}{CH}-CH=O \longleftrightarrow Ph_3\overset{+}{P}-CH=CH-\bar{O}$$

These ylids react readily with aldehydes, but react slowly with ketones. In some cases the ylide is so stable that it does not react with aldehyde also.

* Identify P, Q, R, S from the given scheme and give reasons of their formation.



Ans.



* When a mixture of t-BuCl and diaryl methyl chloride is reacted with aq. NaI in aq. solution, we get t-BuOH and diaryl methyl iodide. Justify this finding.

Ans:

* What products are obtained when NBS is treated with but-1-ene. (1½)

Ans

$$CH_3CH_2CH=CH_2 \xrightarrow[CCl_4]{NBS} CH_3-\underset{Br}{CH}-CH=CH_2$$

but-1-ene 3-bromo-1-butene

Give mechanism if required.

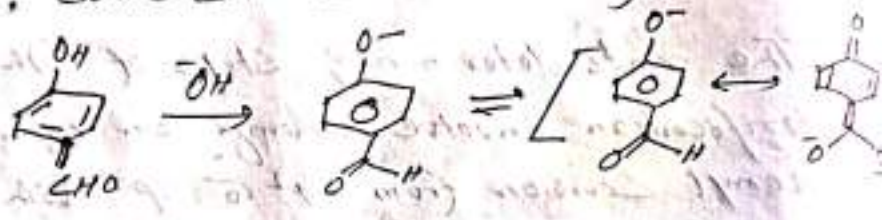
* The presence of bulky groups either in ester or in acid slows both acid hydrolysis and esterification reaction. Justify these experimental facts

Ans The rate-determining steps of both hydrolysis and esterification involve change in hybridization of the carbonyl carbon from sp^2 to sp^3 with consequent increase in crowding. The presence of bulky substituents either in acid or in alcohol make the transition state leading to the tetrahedral intermediates highly crowded and less stable. As a result, the reactions (esterification and hydrolysis) become very slow.

* Can you successfully carry out Cannizzaro reaction P-hydroxy benzaldehyde?

Ans

In the case of P-hydroxybenzaldehyde, the h... of a strong base like NaOH, removes a proto... from the phenolic group thereby making it as the phenoxide ion. The phenoxide is stabilized ... electron withdrawing 'CHO' group at the para pos... thereby making the electrophilicity of the carbony... almost nil. So the Cannizzaro reaction fails.

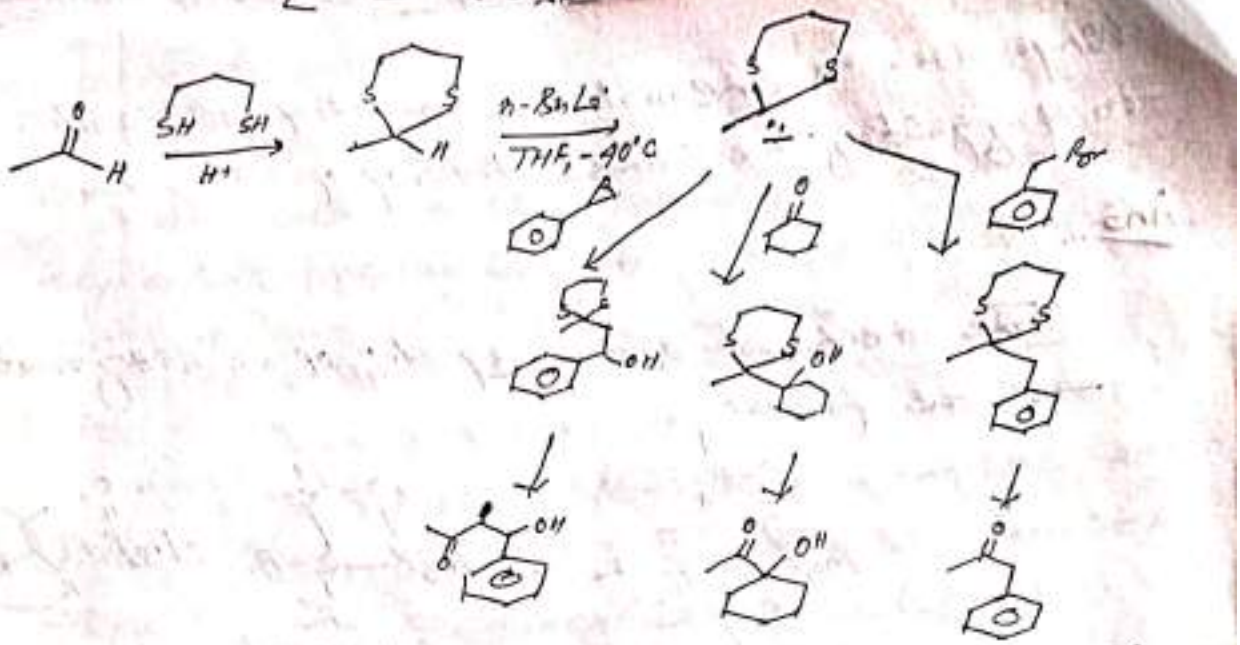


* Describe the term 'Umpolung activity' with suita... example...

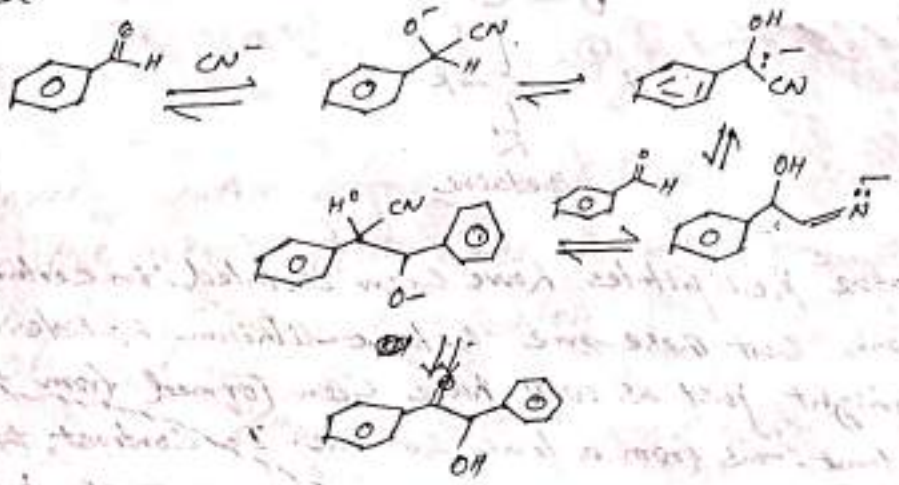
Ans

Umpolung or Polarity inversion in organic chem... is the chemical modification of a functional group wi... the aim of the reversal of polarity of that group. ... modification allows secondary reactions of this funct... group that would otherwise not be possible.

Dithiane chemistry is a classical exam... of Polarity inversion. Ordinarily the oxygen atom in ... carbonyl group is more electronegative than the carbon ... and therefore the carbonyl group reacts as an electrop... at carbon. This polarity can be reversed when the ca... group is converted into a dithiane or a thioacetal.



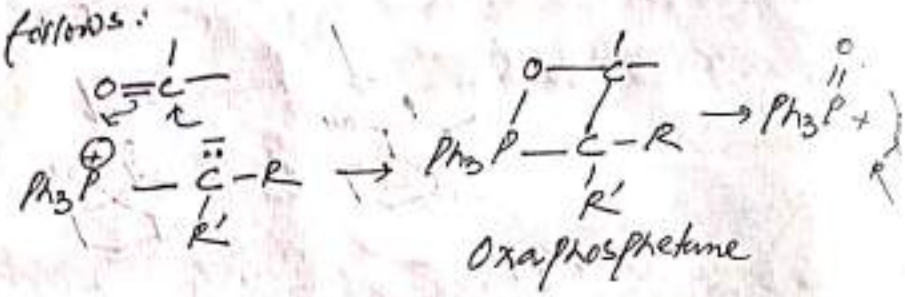
The canonical umpolung reagent is the cyanide ion. The cyanide ion is unusual in that a carbon triply bonded to a nitrogen would be expected to have a (+) polarity due to the higher electronegativity of the nitrogen atom. Yet, the negative charge of the cyanide is localized on the carbon, giving it a (-) formal charge. This chemical ambivalence results in umpolung in many reactions where cyanide is involved.



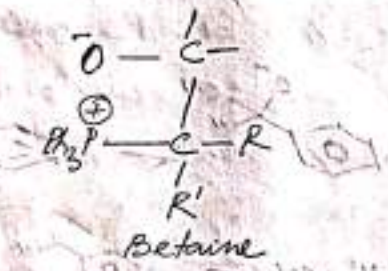
* Why does a chemist take a lot of [illegible] in suggesting mechanistic pathway of Wittig reaction?

Ans

The mechanism of the key step of the Wittig reaction is as follows:



For many years it was assumed that a dipolar compound, called a betaine, is an intermediate on the pathway from the starting compounds to the oxaphosphetane, and in fact it may be so, but there is little or no evidence for it, though many attempts have been made to find it.



Betaine precipitates have been isolated in certain Wittig reactions, but these are betaine-lithium halide adducts and might just as well have been formed from the oxaphosphetane as from a true betaine. In contrast, there is much evidence for the presence of the oxaphosphetane intermediates, at least with unstable ylides. For example ^{31}P NMR spectra taken of the reaction mixtures at low temperatures are compatible with an oxaphosphetane structure that persists for some time but not with a tetracoordinated phosphorus species. Since a betaine, an ylide and all known tetracoordinated phosphorus, these species could not cause the spectra, leading to the conclusion that oxaphosphetane intermediate is present in the solution. So clear cut evidence is not there for Wittig rearrangement, that's why

* Ethylene reacts with HI in C_2H_5OH gives predominantly ethyl iodide, whereas with HCl under identical condition gives predominantly diethyl ether. Explain the difference.

Ans:

The above reaction is an example of electrophilic addition of haloacid to olefin. The first step is the formation of carbocation intermediate.

$$CH_2=CH_2 + H^+ \longrightarrow CH_3\overset{\oplus}{C}H_2$$

Now both I^- and C_2H_5OH can acts as a nucleophile to reacts with carbocation. But due to the large size and high polarizability of I^- it acts as a better nucleophile compared to C_2H_5OH and so the reaction of ethylene with HI in C_2H_5OH gives predominantly ethyl iodide

$$CH_3\overset{\oplus}{C}H_2 + I^- \rightarrow CH_3CH_2I.$$

However under identical condition reaction of ethylene with HCl gives diethyl ether, this is due to the poor nucleophilicity of Cl^- over C_2H_5OH.

$$CH_3\overset{\oplus}{C}H_2 + C_2H_5OH \longrightarrow CH_3CH_2-\overset{\oplus}{\underset{H}{O}}-C_2H_5$$

$$\downarrow$$

$$CH_3CH_2OC_2H_5.$$

* In case of MPV reduction excess of isopropyl alcohol is necessary. Explain.

Ans:

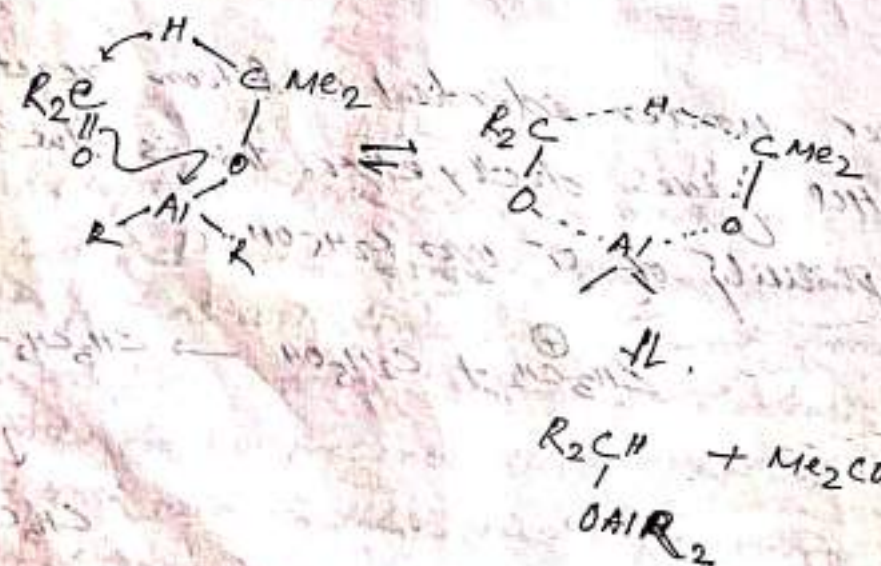
In MPV reduction the carbonyl compound is heated with aluminium isopropoxide in isopropanol; the isopropanol is oxidised to acetone, which is removed from the equilibrium mixture by slow distillation:

$$R_2CO + (Me_2CHO)_3Al \rightleftharpoons (R_2CHO)_3Al + CH_3COCH_3$$

$\downarrow$ dilute H_2SO_4

R_2CHOH

The equilibrium is displaced to the right by distillation of the acetone (which is the component with the lowest b.p. in the system). Some IPA used both as a hydride donor as well as solvent for MPV reduction excess use of it necessary to shift the equilibrium to the product side.



II.

$R_2CH + Me_2CO$

$OAlR_2$