ILLUSTRATIONS — Section - 3

Illustration - 6 *Identify the products in each of the following reaction setups.*

(a) $CH_3COCl \xrightarrow[BaSO_4, Xylene]{H_2, Pd} A \xrightarrow[HCl]{NH_2OH} B + C$ (b) $CH_3CH_2CHO \xrightarrow[\Delta]{NaOH} D$

(c) $CCl_3 - CHO \xrightarrow[\Delta]{NaOH} E + F$

SOLUTION :

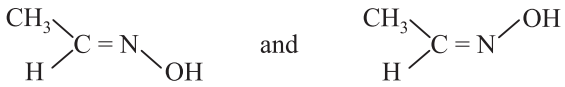
(a) $CH_3COCl \xrightarrow[BaSO_4 \text{ in xylene}]{H_2, Pd} CH_3CHO$

It is an example of "Rosenmund Reduction", where xylene is used to poison catalyst Pd.

$CH_3CHO \xrightarrow[HCl]{NH_2OH} CH_3CH=NOH$

[Oxime formation] Acetaldoxime

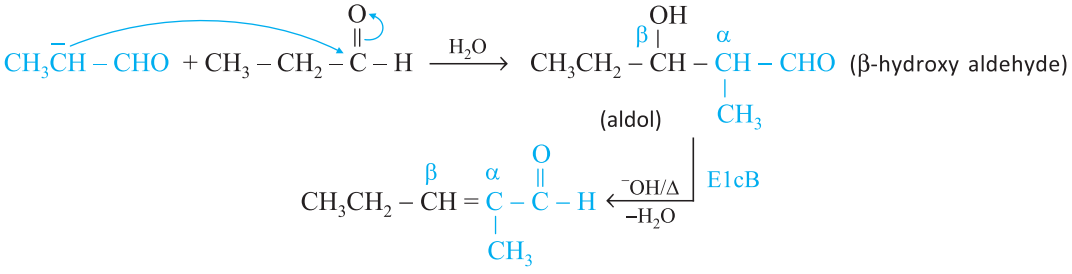
Note that acetaldoxime exists in two geometric isomeric forms as follows.



(b) $CH_3CH_2CHO \xrightarrow[\Delta]{OH^-}$ It is an example of aldol condensation.

$CH_3\overset{'\alpha'}{C}H_2CHO \xrightarrow[-H_2O]{OH^-} CH_3\overset{\ominus}{C}H-CHO \longleftrightarrow CH_3-CH=\overset{O^-}{\underset{|}{C}}H$

[– enolate ion
– Resonance stabilised Nu^- (Carbanion)]



(c) $CCl_3 - \underset{\|}{\overset{O}{C}} - H \xrightarrow[\Delta]{NaOH}$? Visualise "haloform reaction". Do not think of Cannizzaro reaction in Chloral.

$CCl_3 - \underset{\|}{\overset{O}{C}} - H \xrightarrow[\Delta]{NaOH} CHCl_3 + H - \underset{\|}{\overset{O}{C}} - ONa$

➤ If we use aqueous NaOH, hydrolysis of chloral will take place.

$CCl_3 - \underset{\|}{\overset{O}{C}} - H \xrightarrow{NaOH\ (aq)} (OH)_3C - \underset{\|}{\overset{O}{C}} - H \xrightarrow[+H^+]{-H_2O} HO - \underset{\|}{\overset{O}{C}} - \underset{\|}{\overset{O}{C}} - H$

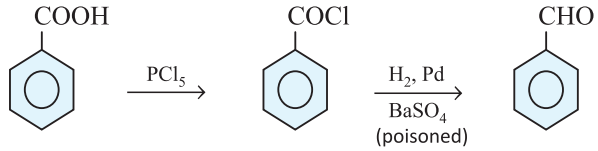
Gly-oxalic acid

Illustration - 7 *Do the following transformations (in not more than four - five steps)*

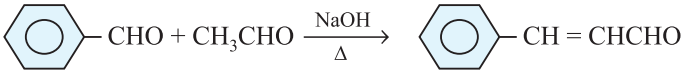
(a) *Benzoic acid to cinnamaldehyde* (b) *Benzene to* 4*-Nitrobenzaldehyde*

(c) 1*-Butyne to* 2*-Pentanone* (d) *Cyclohexanone to* 2*-methyl cyclohexanone*

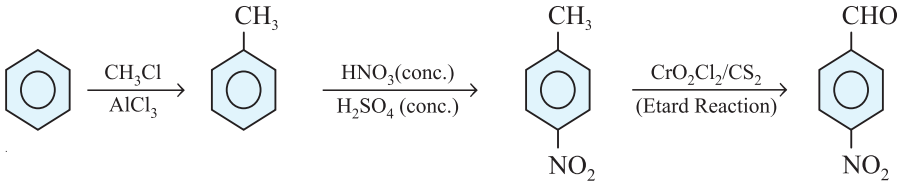
SOLUTION :

(a) 

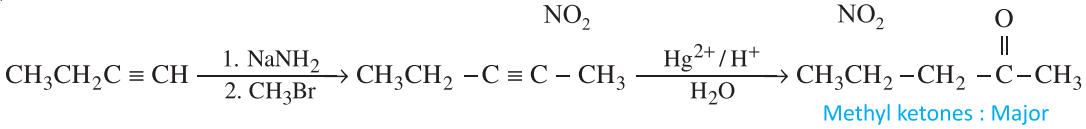
(Rosenmund Reduction)



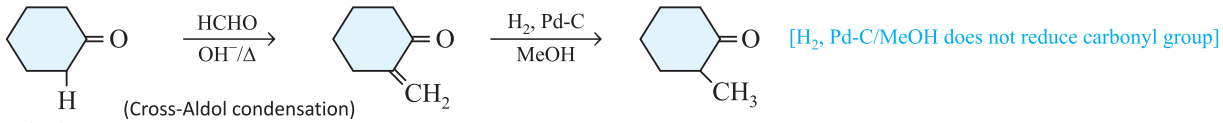
(Cross - Aldol condensation) (Cinnamaldehyde)

(b) 

4-Nitrobenzaldehyde

(c) 

Methyl ketones : Major

(d) 

[H_2, Pd-C/MeOH does not reduce carbonyl group]

α-hydrogen (Cross-Aldol condensation)

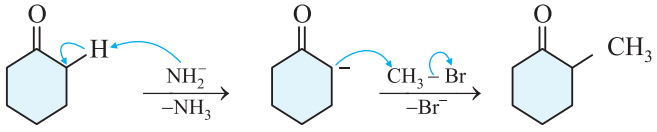
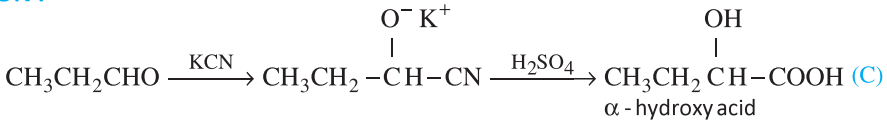
Alternate Method : 

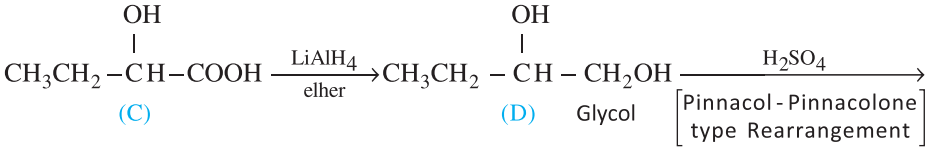
Illustration - 8 *Write the structure of the major organic products in each of the following reaction setups.*

$$CH_3CH_2CHO \xrightarrow[H_2SO_4(aq)]{KCN} C \xrightarrow[ether]{LiAlH_4} D \xrightarrow[(conc.)]{H_2SO_4} E$$

SOLUTION :



α - hydroxy acid



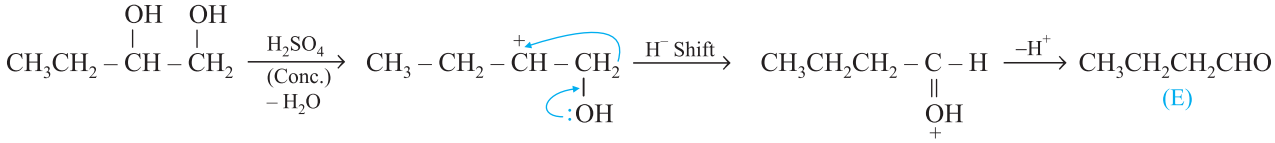


Illustration - 9 *A Ketone (A), which undergoes haloform reaction gives a compound (B) on reaction with $NaBH_4/OH^-$. (B) gives another compound (C) on heating with conc. H_2SO_4. The compound (C) upon reductive ozonolysis gives only a single compound (D), with molecular formula C_2H_4O. Identify the compounds A, B, C and D.*

How many products will be formed if (A) and (D) are heated in presence of NaOH solutions ?

SOLUTION :

$$\text{A (Ketone)} \xrightarrow[X_2]{NaOH} \text{responds positively}$$

$$\text{A (Ketone)} \xrightarrow[OH^-]{NaBH_4} B \xrightarrow[\Delta]{H_2SO_4\ (conc.)} C \xrightarrow[Zn\text{-}H_2O]{O_3} D\ (C_2H_4O)$$

$$A + D \xrightarrow[\Delta]{OH^-} ??$$

Start by identifying D. D has to be an aldehyde/ketone (product of Ozonolysis).

$C_2H_4O \longrightarrow CH_3CHO$ (Only aldehyde with given molecular formula)

$\Rightarrow$ C has to be $CH_3CH=CHCH_3$ and B should clearly be $CH_3-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_2CH_3$

$$A \xrightarrow[OH^-]{NaBH_4} CH_3-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_2CH_3 \quad \Rightarrow \quad A \text{ is : } CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_2CH_3$$

Methy ethylketone (2 - Butanone)

Observe that A responds positively to haloform reaction being methyl ketone.

$$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_2CH_3 \xrightarrow[X_2]{NaOH} \underset{\text{halo form}}{CHX_3} + CH_3CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-ONa$$

Now, $A + D \xrightarrow[\Delta]{OH^-} ?$ $\qquad CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_2CH_3 + CH_3CHO \xrightarrow[\Delta]{OH^-}$

Visualise Cross-Aldol condensation to get three possible products as follows. Observe that there are three different types of α-Hydrogen atoms.

$$\underset{\text{[Forms enolate]}}{\overset{\alpha}{CH_2}-CHO} + \underset{\text{[Acts as substrate]}}{CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_2CH_3} \xrightarrow[\Delta]{OH^-} CH_3-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}=CH-CHO$$

$$\underset{\text{[Forms enolate]}}{CH_3CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-\overset{\alpha}{CH_2}} + \underset{\text{[Acts as substrate]}}{CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-H} \xrightarrow[\Delta]{OH^-} CH_3CH=CH-\underset{\displaystyle O}{\underset{\|}{C}}-CH_2CH_3$$

$$\underset{\text{[Forms enolate]}}{H_3\overset{\alpha}{C}CH-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3} + \underset{\text{[Acts as substrate]}}{CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-H} \xrightarrow[\Delta]{OH^-} CH_3CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$$

Illustration - 10 *Identify the organic compounds X, A, B . . . E in the following chart of reaction sequences.*

$$X \xrightarrow[OH^-]{HCHO} A \xrightarrow{H_2CrO_4} B \xrightarrow[(CH_3)_2CHOH]{[(CH_3)_2CH-O]_3-Al} C \xrightarrow[(conc.)\ \Delta]{H_2SO_4} D \xrightarrow{LiAlH_4} E \xleftarrow[2.\ NaBH_4/OH^-]{1.\ NaOH/\Delta} CH_3CHO$$

SOLUTION :

Starting from : CH_3CHO

$$CH_3CHO \xrightarrow[(Aldol\ condensation)]{OH^-/\Delta} CH_3CH=CHCHO \xrightarrow{NaBH_4/OH^-} \underset{(E)}{CH_3CH=CHCH_2OH}$$

$$\uparrow LiAlH_4$$

$$\underset{(C)}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_2COOH}\ \ \beta\text{-hydroxy acid} \xrightarrow[(conc.)]{H_2SO_4} \underset{(D)}{CH_3CH=CHCOOH}$$

Note :
- 'C' had to be alcohol as $[(CH_3)_2CH-O]_3-Al$ reduces ketones to 2° alcohols. [MPV reduction]
- Among hydroxy acids, only β-hydroxy acids undergo dehydration to give α, β-unsaturated acids. So do not think of –CHO group in (D)
- $NaBH_4$ and $LiAlH_4$ reduces only acid group not a carbon-carbon double bond. $LiAlH_4$ reduces carbon-carbon double bond when it is in conjugation with phenyl ring.

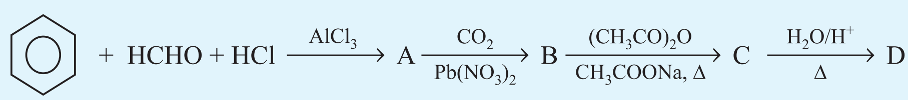
B is clearly : $CH_3-\overset{\overset{O}{||}}{C}-CH_2COOH$ and A will be : $CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_2OH$.

(H_2CrO_4 oxidises 1° RCH_2OH to $RCOOH$).

Observe carefully : X will be CH_3COCH_3

$$CH_3COCH_3 + HCHO \xrightarrow{OH^-} \underset{(A)}{CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2OH}\ \ (\text{Cross Aldol condensation})$$

Illustration - 11 **(a)** *Identify A, B, C, D in the given reaction sequence.*



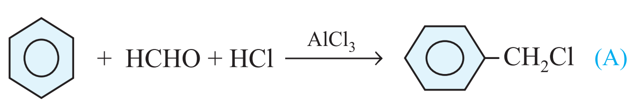
(b) *The compound D is heated with H_2CrO_4 in acetone at 35°C to give another compound E. E on heating gives an aromatic compound F which responds positively to iodoform test. Identify the compounds E and F.*

(c) *Give the structure of the product formed when (F) reacts with (B) in presence of NaOH at 100°C.*

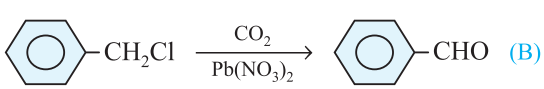
(d) *What happens when D is treated with H_2SO_4 at 170°C ?*

SOLUTION :

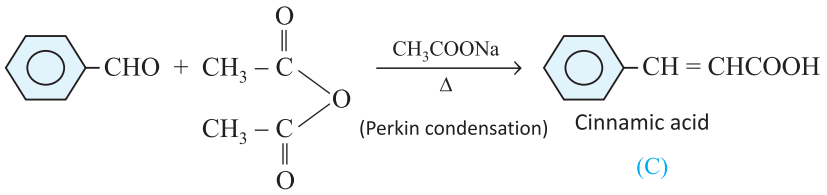
(a)



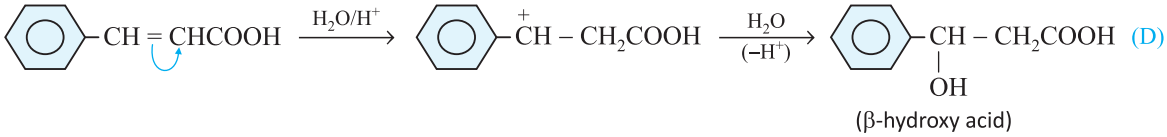
Benzyl chloride



Benzaldehyde

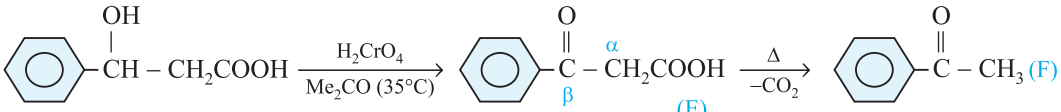


(C)



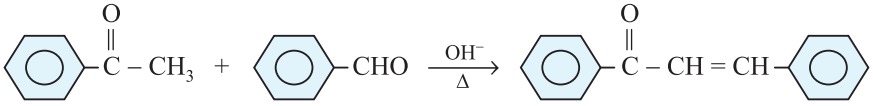
(D)

(*b*)

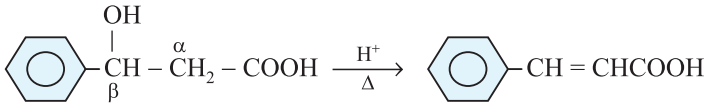


(E) (F)

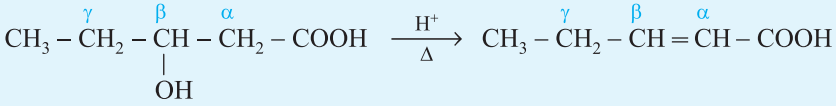
(*c*) (F) + (B) $\xrightarrow[100°C]{NaOH}$?



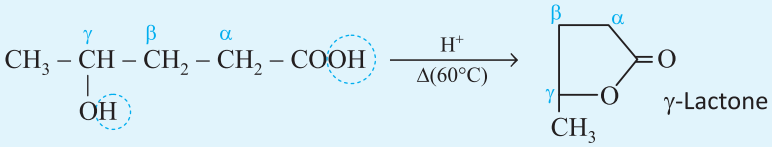
(*d*)



Note : ➤ Among α, β, γ - hydroxy acids, only β-hydroxy acids undergo dehydration to give α, β unsaturated acids.



➤ γ-hydroxy acids under given conditions show intramolecular esterification to give cyclic esters known as Lactones.



➤ α-hydroxy acids forms di-esters via intermolecular esterification called as lactides.

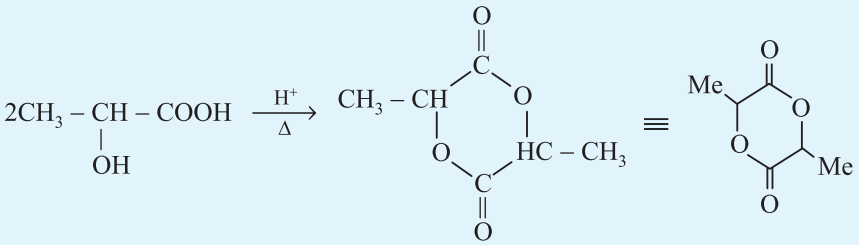


Illustration - 12 *An organic compound (A), $C_8H_{14}O$ forms an oxime. On ozonolysis, it gives acetone and a compound (B), $C_5H_8O_2$. The compound (B) reacts with NaOH and Br_2 to give (C) and (D). (D) is acidified and on treatment with excess of ammonia and strong heating gives a cyclic neutral compound (E). Identify the compounds A to E.*

SOLUTION :

(A) $C_8H_{14}O \longrightarrow$ forms oxime $\Rightarrow$ A contains carbonyl group.

$$\text{(A)} \xrightarrow[Zn-H_2O]{O_3} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + \underset{\text{(B)}}{C_5H_8O_2}$$

$$\text{(B)} \xrightarrow[Br_2]{NaOH} \underset{\text{(C)}}{CHBr_3} + \underset{\text{(D)}}{\text{Sodium salt}}$$

$$\left[NaOH \xrightarrow{Br_2} NaOBr \equiv \text{Bromoform reaction similar to iodoform reaction}\right]$$

$$\text{(D)} \xrightarrow{H^+} \xrightarrow[\text{excess}]{NH_3} \xrightarrow{\Delta} \text{(E) cyclic}$$

A contains a double bond which is dimethylated. B must have $CH_3-\overset{\overset{O}{\|}}{C}-$ group as it gives bromoform reaction.

$\Rightarrow$ A must be : $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ (*A cannot be branched as E is an cyclic amide*)

$$\downarrow O_3/Zn-H_2O$$

$$CH_3-\underset{\underset{CH_3}{|}}{C}=O + OHC-CH_2CH_2-\underset{\text{(B)}}{\overset{\overset{O}{\|}}{C}-CH_3}$$

$$\underset{\text{(B) : } C_5H_8O_2}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2-CHO} \xrightarrow[Br_2]{NaOH} \underset{\text{(C)}}{CHBr_3} + \underset{\text{(D)}}{Na^+\,\overset{\overset{O}{\|}}{C}-CH_2CH_2CHO} \xrightarrow{H^+} HOOC-CH_2-CH_2-CHO$$

$$\downarrow NH_3$$

$$\underset{\text{cyclic amide}}{\underset{\underset{O}{\|}}{CH_2-CH_2-C}=N} \xleftarrow[-H_2O]{\Delta} \underset{\text{(E)}}{CH_2-\underset{\underset{O}{\|}}{C}-NH_2} \xleftarrow[-H_2O]{\Delta} H_4N^+\,OOC-CH_2-CH_2-CHO$$

Note : Observe that D on acidification should have 4-carbons (preferably) as after adding NH_3, it is giving a cyclic compound, which is stable if having 4'C' + 1'N' $\equiv$ 5-atom ring. So do not think of branches in (A).

Illustration - 13 *An organic compound A, C_5H_8O adds Br_2 to give $C_5H_8Br_2O$. It does not react with Tollen's reagent, but reacts with phenyl hydrazine. The ozonolysis of A gives B and C, $C_3H_4O_3$. C on heating gives B. Identify all compounds A, B and C. Identify an aldehyde and a ketone which will give 'A' on heating in alkali.*

SOLUTION :

C_5H_8O (A) $\xrightarrow{Br_2}$ $C_5H_8Br_2O$ (A has a double bond)

$\xrightarrow{\text{Amm. } AgNO_3}$ NO reaction (A is not an aldehyde)

$\xrightarrow{phNH.NH_2}$ reacts (A is certainly a ketone)

$$A \xrightarrow{O_3} B + C[C_3H_4O_3]$$

Note that 'C' has certainly an acidic group, hence we should not visualise reductive ozonolysis here.

Observe that (C) can only be : $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$.

As (A) contains only '5C-atom', (B) should be CH_3COOH.

$$A \xrightarrow{O_3} CH_3-\overset{O}{\overset{\|}{C}}-COOH + CH_3COOH$$

(C) (B)

Clearly A is : $CH_3-\overset{O}{\overset{\|}{C}}-CH=CHCH_3$

Also, note that $C \xrightarrow{\Delta} B$, which confirms all the above results.

$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-OH + CO$$

(α-keto acid loses CO on heating)

Check that (A) satisfies all other informations.

Now : an aldehyde + a ketone $\xrightarrow[\Delta]{NaOH}$ A ; $CH_3\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{OH^-}$?

It will give a mixture of four products. Two products will be formed as a result of self-aldol condensation and two other will be formed via cross-aldol condensation.

- Visualise cross-aldol condensation, where ketone will form enolate ion and aldehyde will be electrophilic substrate.

$$CH_3-\overset{O}{\overset{\|}{C}}-H + \overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[-H_2O]{OH^-/\Delta} CH_3CH=CH-\overset{O}{\overset{\|}{C}}-CH_3$$

(A)

- Visualise cross-aldol condensation, where aldehyde will form enolate and ketone will be electrophilic substrate.

$$H-\overset{O}{\overset{\|}{C}}-\overset{-}{C}H_2 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{OH^-} CH_3-\overset{O}{\overset{\|}{C}}-CH=CH-CHO$$

Enolate Substrate

Illustration - 14 *An organic compound C_8H_7OBr (A) gives orange ppt. with 2, 4 DNP hydrazine. (A) gives yellow precipitate with I_2 and NaOH solution. (A) on oxidation with $KMnO_4$ gives $C_7H_5O_2Br$(B). (B) gives one mono-nitro substituted product (C). (A) on reduction gives C_8H_9OBr (D). (D) reacts with $ZnCl_2$/HCl quickly. Identify the compound (A) to (D). What is the product expected when (A) reacts with formaldehyde in hot alkaline solution.*

SOLUTION :

➤ C_8H_7OBr (A) $\xrightarrow{\text{2, 4 DNP Hydrazine}}$ Orange ppt. $\Rightarrow$ (Carbonyl group is present in A)

$\xrightarrow[\text{NaOH}]{I_2}$ Yellow ppt. $\Rightarrow$ (A is methyl ketone)

$\xrightarrow[KMnO_4]{(O)}$ (B) ; $C_7H_5O_2Br$ $\Rightarrow$ (Br is attached to ring)

(A) must contain phenyl ring as evident from its molecular formula.

➤ (B) $\xrightarrow[H_2SO_4\,(conc.)]{HNO_3\,(conc.)}$ only one product (C)

(A) $\xrightarrow{redn.}$ (D) : C_8H_9OBr $\xrightarrow[HCl]{ZnCl_2}$ reacts quickly (Lucas Test)

➤ Also observe that Br is not lost either by oxidation or reduction, hence it is attached to ring.

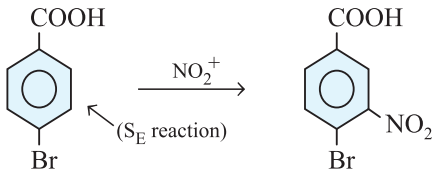
Hence (A) is : C_6H_4(Br)(COCH$_3$)

C_6H_4(Br)(COCH$_3$) $\xrightarrow{(O)}$ C_6H_4(Br)(COOH) (B)

$\xrightarrow{Redn.}$ C_6H_4(Br)(CH(OH)CH$_3$) (D)

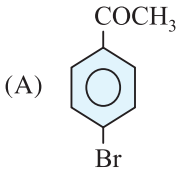
Observe that (D) is benzylic, so it will react quickly with Lucas reagent.

As (B) gives only one mono-nitro product, hence Br should be at '*para*' w.r.t. –COOH group.

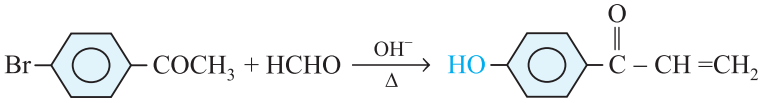


(only one derivative)

(–Br is '*o*' and –COOH is '*m*' directing).



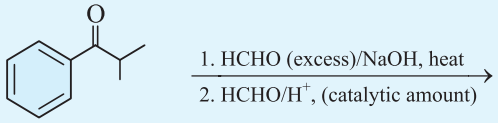
$\xrightarrow[OH^-,\,\Delta]{HCHO}$??



(A product of Cross-Aldol condensation).

Note that (A) is also an activated aryl halide towards nucleophilic substitution reaction because carbonyl group (deactivating) is present at para position to Br-atom.

Illustration - 15 *Identify the final product formed in the following reaction sequence.*



SOLUTION :

First visualise cross-aldol condensation of given compound (Isopropyl phenyl ketone) having an α-hydrogen with formaldehyde (with no α-hydrogen). Since HCHO is given in excess, so visualise a cross-Cannizzaro reaction between HCHO and the product formed as a result of cross-aldol condensation. In cross-Cannizzaro reaction involving HCHO, it always gets oxidised and the other molecule gets reduced.

Observe that the product formed after cross-Cannizzaro reaction is a 1, 3-type of diol, which will form cyclic acetal with a six atom ring with formaldehyde (as shown).

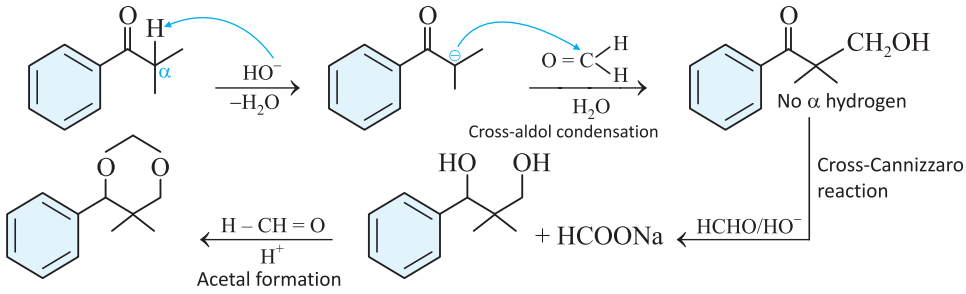
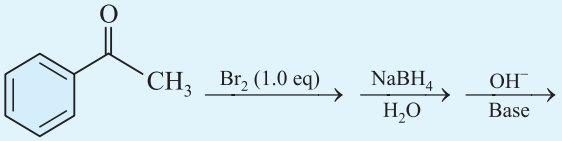
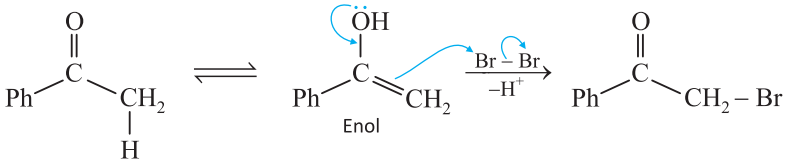


Illustration - 16 *Identify the final product formed in the following reaction sequence.*



SOLUTION :

The given compound (Acetophenone) will form monobromo product (1.0 eq. of Br_2) via enol formation.



The product after reduction with $NaBH_4$ will loose acidic hydrogen to base to form an alkoxide ion. The alkoxide ion will show intramolecular S_N2 reaction to form epoxide.