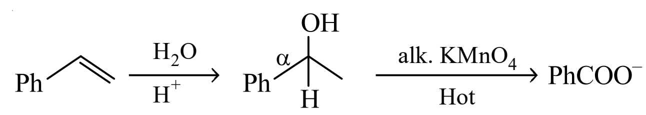
SOLUTIONS

Module - 5 / JEE-2021

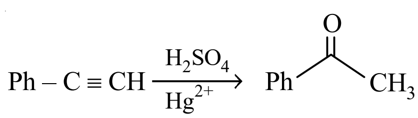
In-Chapter Exercises	Chemistry	Oxygen Containing Organic Compounds - II (Aldehyde & Ketone)

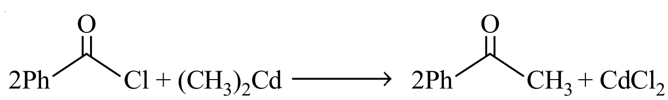
EXERCISE A

1.(BCD) (B), (C) and (D) will produce acetophenone.

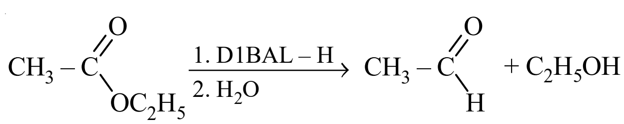
(A) It is side chain oxidation of aromatic compound. : 

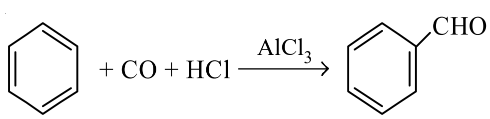
containg α – H atom

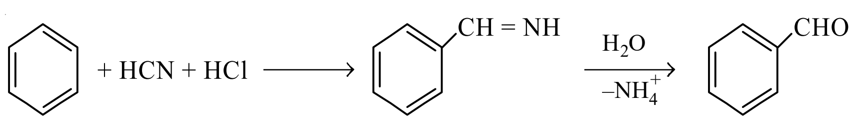
(B) 

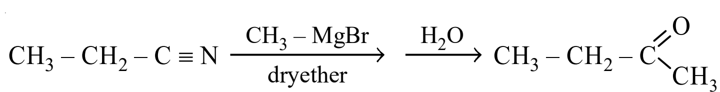
(C) 

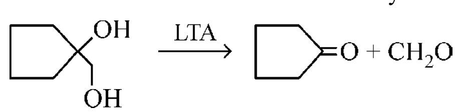
(D) $(CH_3COO)_2Ca + (PhCOO)_2CO \xrightarrow{\Delta} CH_3-CO-Ph + CaCO_3$

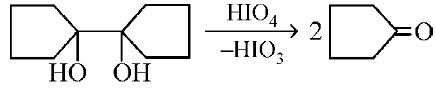
2.(ABC) (A) 

(B)  [Gatterman - koch Reaction]

(C)  [Gatterman Reaction]

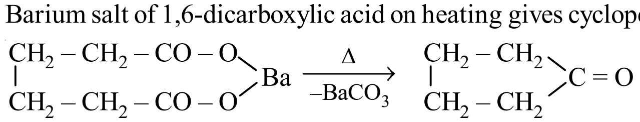
(D)  (A ketone)

3.(CD) 

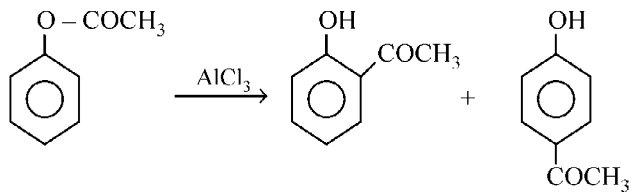
4.(ABCD) **(A)** 

It is periodic acid oxidation of vicinal diol.

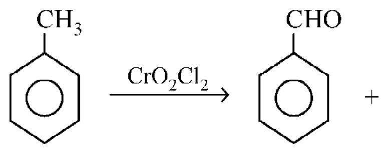
(B) Barium salt of 1,6-dicarboxylic acid on heating gives cyclopentanone.



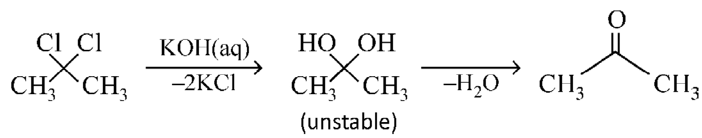
(C) It is Fries rearrangment reaction of phenylacetate.



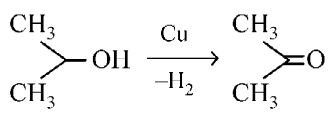
(D) It is Etard's Reaction.



5.(ABCDE) **(A)**



(B)

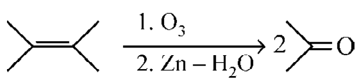


[Dehydrogenation of alcohol]

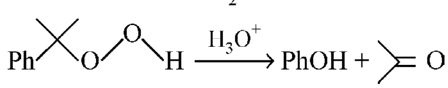
(C)

$$CH_3 - C \equiv CH \xrightarrow[H^+]{H_2O} \underset{\text{Enol}}{CH_3 - \underset{\underset{OH}{|}}{C} = CH_2} \rightleftharpoons \underset{\left(\substack{\text{Keto}\\ \text{More stable}}\right)}{CH_3 - \underset{\underset{O}{||}}{C} - CH_3}$$

(D)

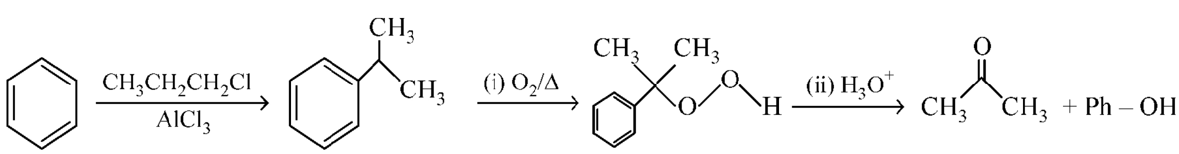


(E)



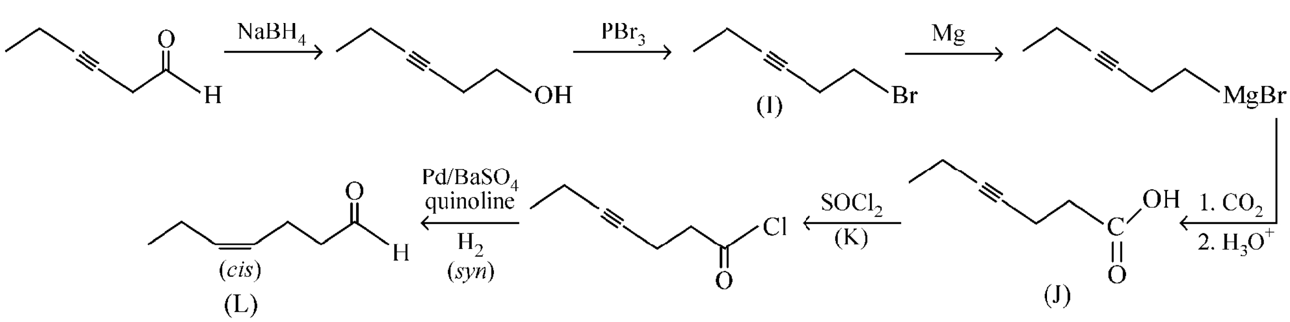
6.(A) $(CH_3)_2C = CH_2 + CO + H_2 \longrightarrow (CH_3)_2CH_2CH_2CHO$

7.(C)



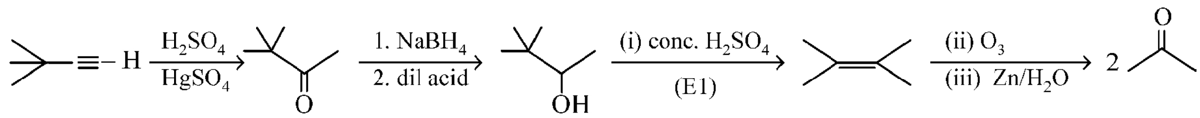
(P) (Q)

8 - 10. **8.(B)** **9. (C)** **10.(C)**



11. - 12. **11.(D)** **12.(B)**

Hydrocarbon $P(C_6H_{10})$ is an alkyne because its degree of unsaturation is two and it reacts with H_2O in presence of H_2SO_4 and $HgSO_4$.



(P) (Q)

13.(A) $CH_3-\underset{\displaystyle CH_3}{CH}-COCl \xrightarrow[Pd-BaSO_4]{H_2} CH_3-\underset{\displaystyle CH_3}{CH}-CHO \xrightarrow[H_3O^+]{CH_3MgBr} CH_3-\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle CH_3}{CH}-OH$

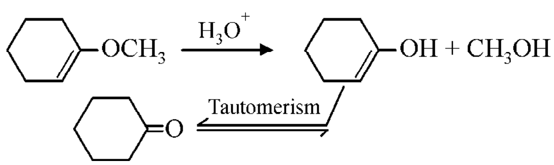
$\xrightarrow{CH_3MgBr/H_3O^+} CH_3-\underset{\displaystyle CH_3}{CH}-CO-CH_3$ * 'It' here means acid halide.

14.(D) $CH_3CH_2OH + RMgX \longrightarrow R-H + CH_3CH_2O-MgX$

15.(ABC) $CH_3\overset{\displaystyle O}{\overset{||}{C}}-Cl \xrightarrow{(CH_3)_2CuLi} CH_3-\overset{\displaystyle O}{\overset{||}{C}}-CH_3$

16.(BCD) (A) $CH_3CH_2OH \xrightarrow{Cr_2O_7^{2-}/H^+} CH_3COOH$

17. (B)



18.(A) Ketones are resistant to oxidation.

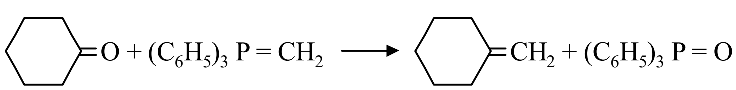
EXERCISE B

1.(BC) Tollen's test and Fehing solution, botb make distinction between an aldehyde and a ketone as later resist oxidation.

2.(A) We need to separate CH_3CH_2OH and CH_3CHO.

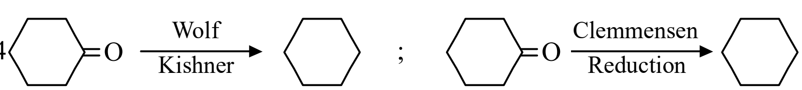
$$CH_3CHO + NaHSO_3 \longrightarrow \text{Crystals (insoluble)} \; ; \; CH_3CH_2OH + NaHSO_3 \longrightarrow \text{No reaction}$$

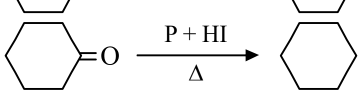
3.(C)



(Wittig reaction)

4.(ABC) 74





(Only at high T and P)

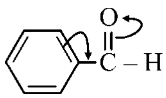
5.(ABD) Addition of N_2H_4/H^+, NH_3/H^+ and $LiAlH_4$ (H^- anion) are example of nucleophilic addition.

6.(B) Boiling points of aldheydes are generally higher than ketones.

7.(C) $\underset{\xrightarrow{+I}}{C_2H_5} - \overset{O^{\delta-}}{\underset{\delta+}{\overset{\|}{C}}} - \underset{\xleftarrow{+I}}{C_2H_5}$; Due to + I effects of two ethyl groups, $\delta+$ charge on carbonyl group is dispersed i.e. less reactive towards nucleophile, among other substrates.

8.(ABC) In Claisen – Schmidt reaction, ketone having α-hydrogen condense with Benzaldehydes. The rest of options are typical characteristics of aldehydes and ketones.

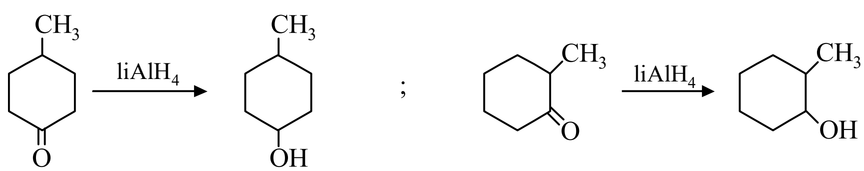
9. (AD) Both $C_6H_5NH_2$ and $C_6H_5NH.NH_2$ will react with acetone to give $>C=N-$

10.(D)  ; Due to +M effect of ring (resonance), electrophilic character of carbonyl carbon decreases.

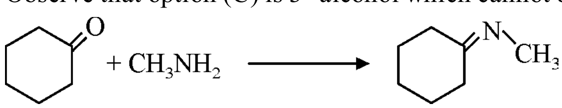
11.(ACD) For iodoform test, look for compounds with $CH_3 - \overset{O}{\overset{\|}{C}} -$ or $CH_3 - \overset{OH}{\overset{|}{C}} -$ ....

12.(B) Ni/H_2 : reduces both aldehyde and ketones as well as $-C=C-$ Clemmenson's reagent and Wolf-kishner's reagent reduces both aldehyde and ketones to alkanes, But HCl in Clemmensions reagent can add across $-C=C-$ bond, so it is better to use Wolf - kishner reagent.

13.(D) The reactivity of carbonyl compounds in nucleophilic addition follows : [Check Polarity of $>C=O$ bond]
$HCHO > CH_3CHO > CH_3COCH_3 > PhCOCH_3 > PhCOPh$
[In aromatic compounds + M effect of phenyl ring decreases electrophilic character to great extent]

14.(C) 

Observe that option (C) is 3° alcohol which cannot be formed by oxidation of a ketone.

15.(B) 

16.(B) It illustrates "Intermolecular Cannizarro Reaction".

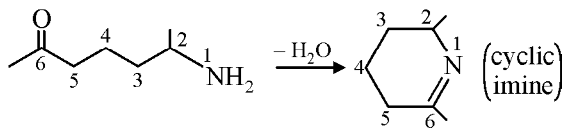
$$\begin{array}{c} CHO \\ | \\ CHO \end{array} \xrightarrow{NaOH} \begin{array}{c} CH_2OH \\ | \\ COONa \end{array}$$

17.(B) $CH_3 - CH_2 - CHO \xrightarrow{OH^-} CH_3 - \overset{-}{C}H - CHO + CH_3CH_2 - \overset{O}{\overset{\|}{C}} - H$

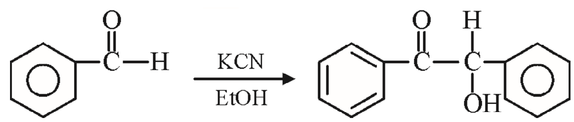
$$\downarrow$$

$$CH_3 - CH_2 - \underset{OH}{\underset{|}{C}H} - \overset{CH_3}{\overset{|}{C}H} - CHO \xrightarrow[-H_2O]{\Delta} C_2H_5 - CH = \overset{CH_3}{\overset{|}{C}} - CHO$$

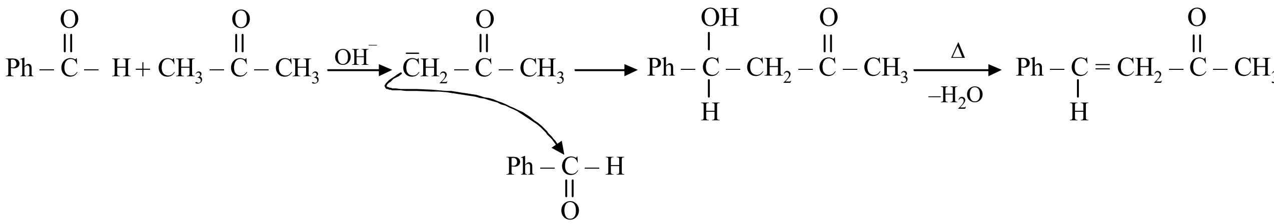
18.(A)



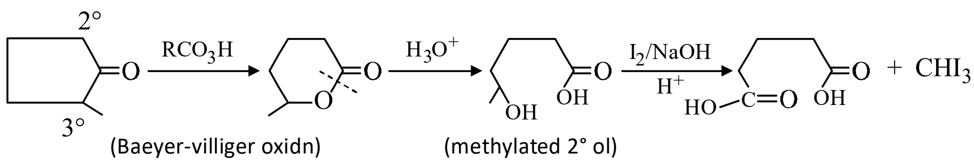
19.(D) Benzoin condensation :



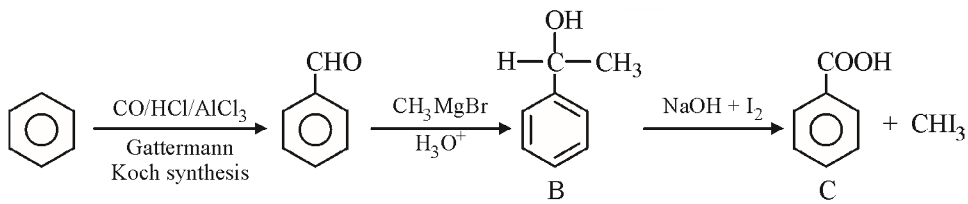
20.(B)



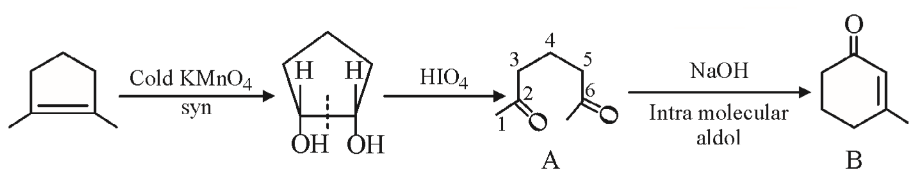
21.(A)



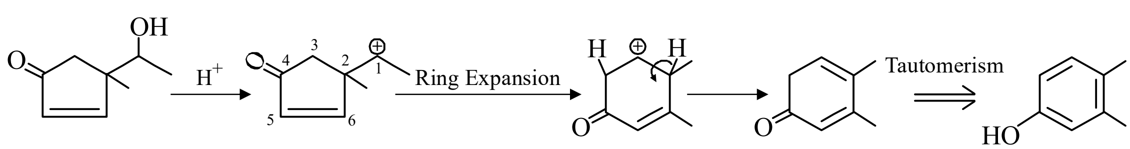
22.(B)



23.(B)



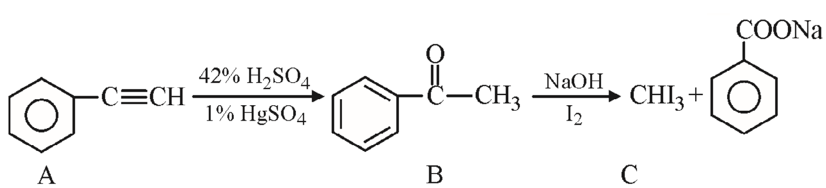
24.(D)

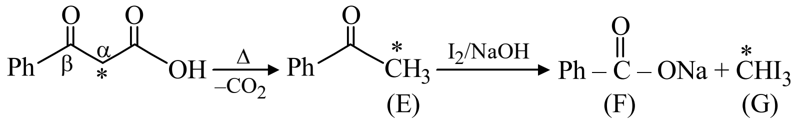


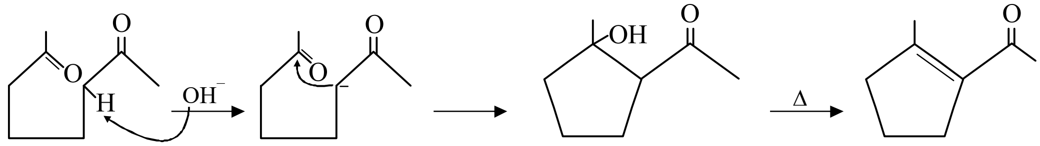
25.(AC) Para - Product is formed at 60°C (lower temprature) in Fries rearragement.

Product (a), being ortho is more volatile due to intra-molecular H – bonding resulting in weaker inter-molecular forces.

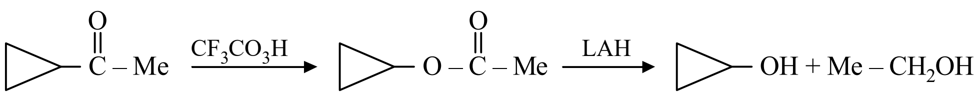
26.(A)

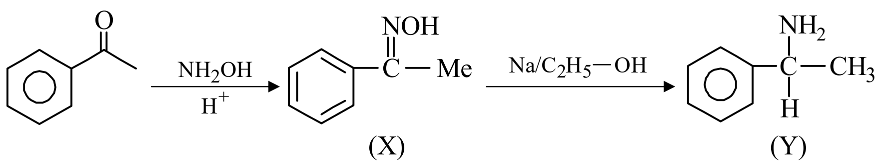


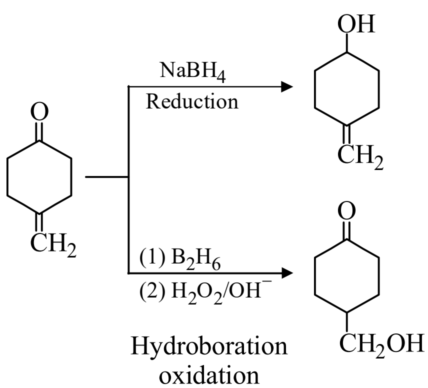
27.(C)


28.(C)


29.(A) Baeyer's Villiger's oxidation (oxygen is added to 2°and 3° alkyl group side, not towards 1° alky group side)



30.(C)


31.(C)


32-34. 32.(D) 33.(B) 34.(C)

$$C_7H_8 : PhCH_3 \xrightarrow[CCl_4]{NBS} PhCH_2Br \xrightarrow[S_N2]{KCN / DMSO} PhCH_2CN \text{ (A)}$$

$$PhCH_2CN + PhCHO \xrightarrow[EtOH]{EtONa} \underset{(B)}{Ph-\overset{OH}{\overset{|}{C}}H-\overset{Ph}{\overset{|}{C}}-CN} \xrightarrow[\Delta]{H_3O^+} \underset{(C)}{Ph-CH=\overset{Ph}{\overset{|}{C}}-COOH}$$

(Visualise cross-aldol condensation type reaction, where cyanide will form enolate type of anion)

First – CN will be hydrolysed to acid and then β-hydroxy acid will undergo dehydration to from α-β-unsuturated acid (C)

$$\underset{\text{(Hydration)}}{Ph-CH=\overset{Ph}{\overset{|}{C}}-COOH} \xrightarrow[2.\ H_2O]{1.\ H^+} \underset{(D)}{Ph-\overset{OH}{\overset{|}{C}}H-\overset{Ph}{\overset{|}{C}}H-COOH} \xrightarrow{H_2CrO_4} Ph-\underset{\beta}{\overset{O}{\overset{||}{C}}}-\underset{\alpha}{\overset{Ph}{\overset{|}{C}}H}-COOH$$

$$\xrightarrow[-CO_2]{\Delta} Ph-\overset{O}{\overset{||}{C}}-CH_2-Ph \text{ (E)}$$

Note : (E) does not respond to Tollen's reagent test and iodoform test, however it will be reduced to diphenyl ethylene on reaction with $N_2H_4/(CH_2OH)_2/KOH$.

$$\underset{(E)}{Ph-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-Ph} \xrightarrow[\text{Kishner}]{\text{Wolf}} \underset{\text{(Dighenyl ethylene)}}{Ph-CH_2CH_2-Ph}$$

$$\underset{(E)}{Ph-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-Ph} \xrightarrow{SeO_2} \underset{(F)}{Ph-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-Ph} \xrightarrow[H_2O]{NaBH_4} \underset{(G)}{Ph-\overset{\overset{\displaystyle OH}{|}}{C}H-\overset{\overset{\displaystyle OH}{|}}{C}H-Ph}$$

$$\underset{(E)}{Ph-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-Ph} + HCHO \xrightarrow{OH^-} \left(Ph-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle Ph}{|}}{C}=CH_2\right) \xrightarrow[H^+/\Delta]{K_2Cr_2O_7} Ph-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-Ph + CO_2$$

$$Ph-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-Ph \xrightarrow[H^+/\Delta]{K_2Cr_2O_7} 2\,(PhCOOH)$$

Note : Visualise cross- aldol condensation. Then oxidation by $K_2Cr_2O_7$ in acidic medium . It being a strong oxidising agent will further oxidise ketones to acids.

35.(C) In basic medium, trihalogenation takes place and then haloform is finally formed; while in acidic medium, monohalogenation will take place.

Reaction 1 :
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3Br_2 + 4NaOH \longrightarrow \underset{(T)}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa} + \underset{(U)}{CHBr_3} + 3NaBr + 3H_2O$$

⇒ For 1 mol of Br_2, 1/3 mol of acetone will be consumed (Br_2 : a limiting reagent) in the bromoform reaction (*as shown above*) and 2/3 mol of actone along with products (T) and (U) are left.

Reaction 2 :
$$\underset{(1\,mol)}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + \underset{(1\,mol)}{Br_2} \xrightarrow{CH_3COOH} \underset{(P)}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2Br} + HBr$$

⇒ 1 mol to Br_2 combines with 1 mol of acetone to give 1 mol of product (P).