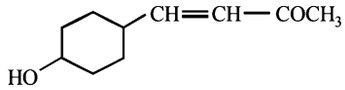
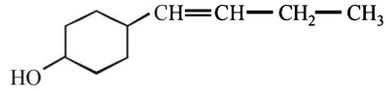
DAILY PRACTICE PROBLEMS **CHEMISTRY SOLUTIONS** **DPP/CC23**

1. (a) Aldehydes and ketones can be reduced to hydrocarbons by the action (i) of amalgamated zinc and concentrated hydrochloric acid (Clemmensen reduction), or (b) of hydrazine (NH_2NH_2) and a strong base like NaOH, KOH or potassium *tert*-butoxide in a high-boiling alcohol like ethylene glycol or triethylene glycol (Wolf-Kishner reduction)



$\xrightarrow[\text{Wolf-kishner Reduction}]{NH_2NH_2/OH^-}$



–OH group and alkene are acid-sensitive groups so clemmensen reduction can not be used. Acid sensitive substrate should be reacted in the Wolf-Kishner reduction which utilise strongly basic conditions.

2. (d) $A \xrightarrow[(I)]{NH_3} B \xrightarrow[II]{\Delta} C \xrightarrow[KOH,(III)]{Br_2} CH_3CH_2NH_2$

Reaction (III) is a Hofmann bromamide reaction. Now formation of $CH_3CH_2NH_2$ is possible only from a compound $CH_3CH_2CONH_2$(C) which can be obtained from the compound $CH_3CH_2COO^-NH_4^+$(B).

Thus (A) should be CH_3CH_2COOH

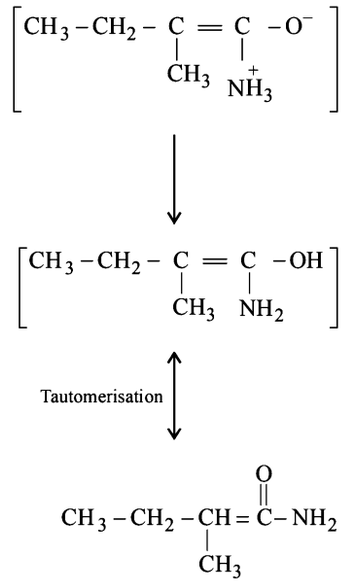
$$\underset{(A)}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2COO^-NH_4^+} \xrightarrow{\Delta} \underset{(C)}{CH_3CH_2CONH_2}$$

$$CH_3CH_2CONH_2 \xrightarrow[KOH]{Br_2} CH_3CH_2NH_2$$

3. (c) Given compound A is $CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{}{C}}=C=O$

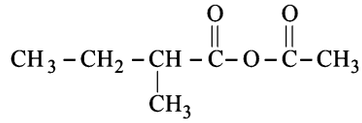
Reactions given are as following :

$$CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{}{C}}=C=O \xrightarrow{NH_3}$$



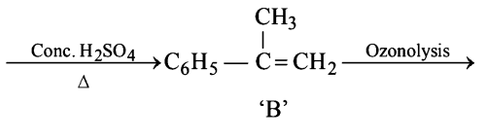
$$CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{}{C}}=C=O \xrightarrow{H_2O} CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{}{CH}}-COOH$$

$$CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{}{C}}=C=O \xrightarrow{CH_3COOH}$$



4. (a) $\underset{\text{'A'}}{C_6H_5COOC_2H_5} \xrightarrow{CH_3MgBr} C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle OMgBr}{C}}-OC_2H_5 \xrightarrow{-Mg(OC_2H_5)Br} C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[CH_3MgBr]{Excess}$

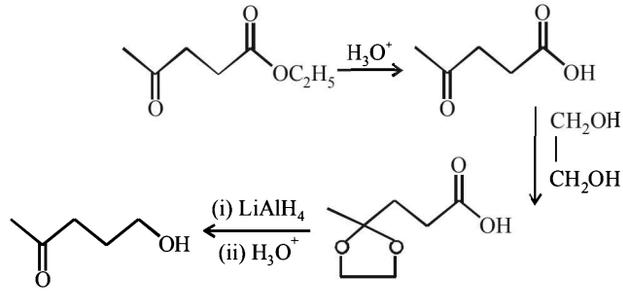
$$C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle OMgBr}{C}}-CH_3 \xrightarrow{H_2O} C_6H_5-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{C}}-CH_3$$



$C_6H_5COCH_3 + HCHO$

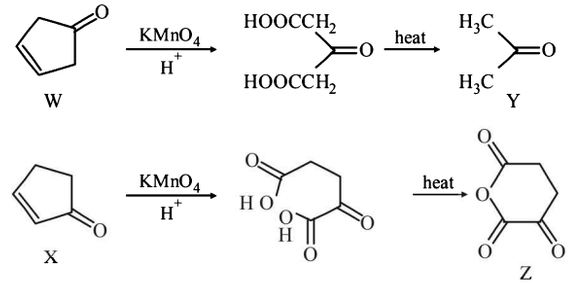
$C_6H_5COCH_3 \xrightarrow{3I_2+4NaOH} CHI_3 + C_6H_5COO^-Na^+$

5. (a)

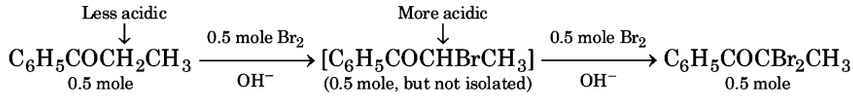


6. (a, d) The hydrogen atom that is added to the carbonyl carbon of the aldehyde in the reduction is derived directly from the other aldehyde molecule as a hydride ion. The second hydrogen that is added to the negatively charged oxygen is coming from the solvent (consult mechanism of Cannizzaro reaction). Oxidation of one molecule of the compound at the expense of other molecule of the same compound is known as disproportionation.

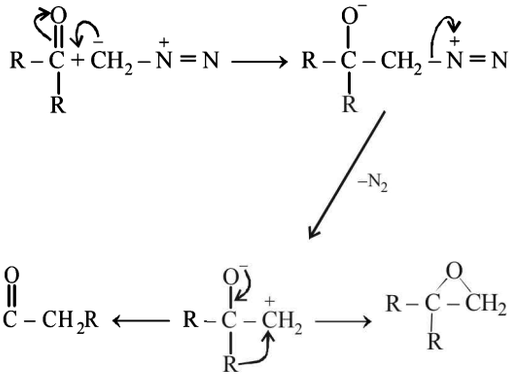
7. (a, c, d)



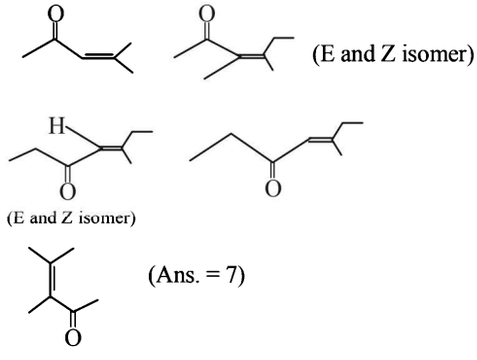
8. (c,d) Substitution by one Br gives $C_6H_5COCHBrCH_3$, the electron-withdrawing Br increases the acidity of the remaining α hydrogen which reacts more rapidly than the hydrogens on the unsubstituted ketones.



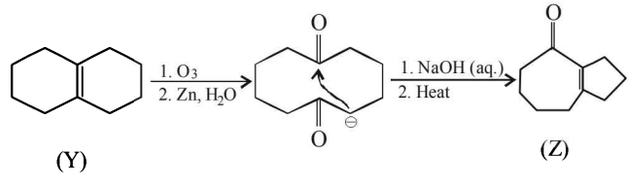
9. (a,c)



10. (9)



11. One product (Z).



12. **(3)** $CH_3MgBr + CH_3CH_2-\overset{O}{\overset{\|}{C}}-Cl \rightarrow$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3 + Mg\begin{matrix}Br\\Br\end{matrix}$

2-Butanone

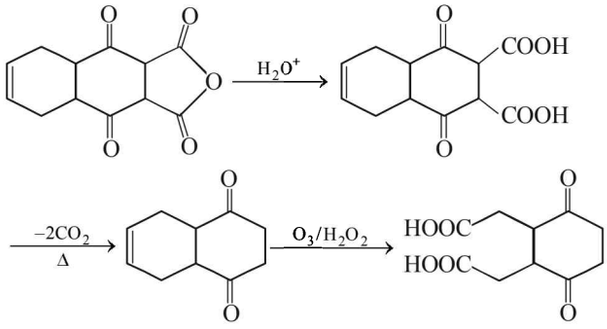
2-Butanone will show tautomerism.

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3 \xrightarrow[H_2O]{\ominus OH}$ $CH_2=\overset{O}{\overset{\|}{C}}-CH_2CH_3$ **G.I** × (1)

$CH_3-\overset{OH}{\overset{|}{C}}=CH_2CH_3$ [*cis* and *trans*] (2)

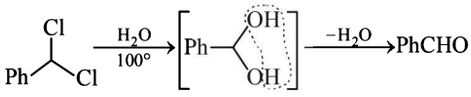
Total enol products = 1 + 2 = 3.

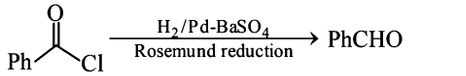
13. **(2)**

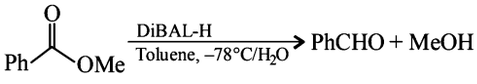


14. **(4)** **I.** Benzene $\xrightarrow[\text{Anhydrons } AlCl_3/CuCl]{CO+HCl}$ PhCHO Benzaldehyde

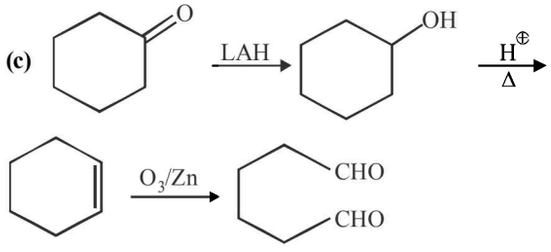
(Gattermann KOCH Aldehyde reaction)

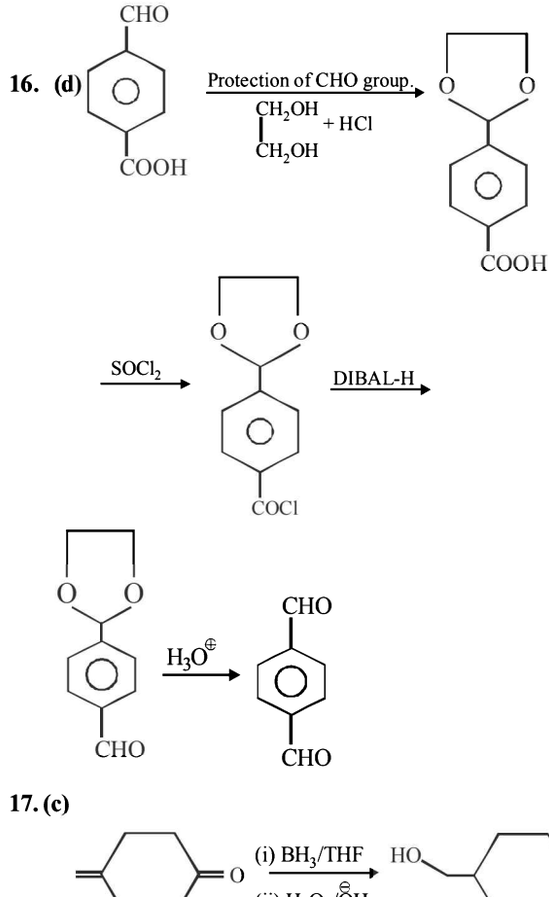
II. 

III. 

IV. 

Ester

15. **(c)** 

16. **(d)** 

17. **(c)**

Preferentially oxidises (C = C) bond.

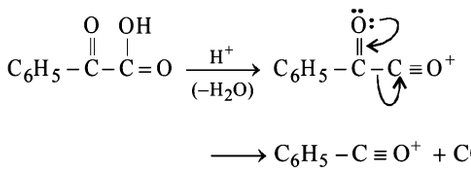
18. **(d)** $CH_3-\overset{OH}{\overset{|}{C}}=O \xrightarrow{H^+} CH_3-\overset{+OH_2}{\overset{|}{C}}=\ddot{O}:$

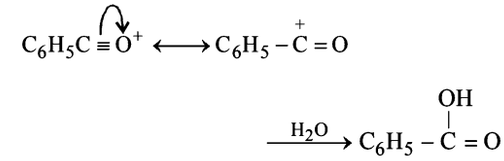
$\xrightarrow{-H_2O} CH_3-C\equiv O^+ \longrightarrow \not\rightarrow CH_3^+ + C\equiv O$ (Unstable)

$CH_3-C\equiv O^+ \xleftarrow{H_2\ddot{O}:}$

$CH_3-\overset{+OH_2}{\overset{|}{C}}=O \xrightarrow{-H^+} CH_3-\overset{OH}{\overset{|}{C}}=O$

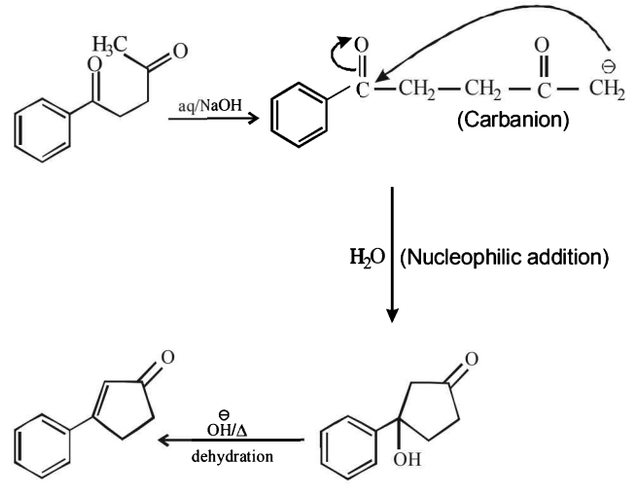
Thus acetic acid will be regenerated, i.e. there is no reaction.

19. **(c)** 

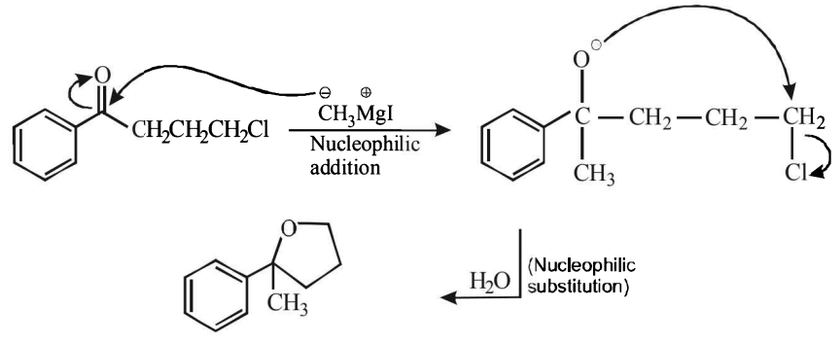


20. **(A) → r, s ; (B) → p, s ; (C) → r, s; (D) → q, r**

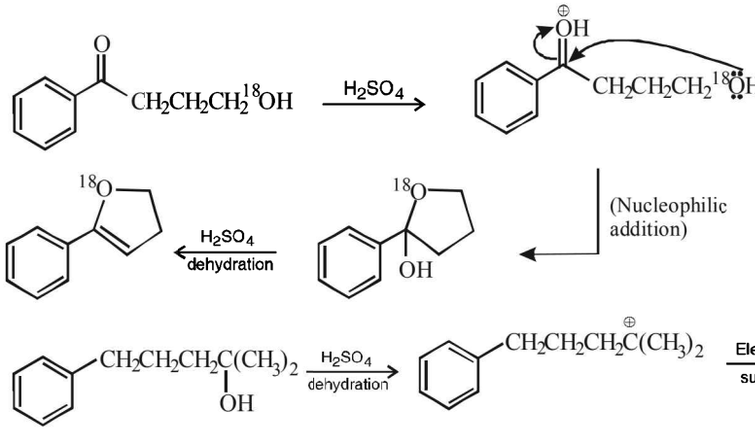
(A)



(B)



(C)



(D)