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 (NH₂NH₂) 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)

NH₂NH₂/OH Wolf-kishner Reduction

-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)**
$$A \xrightarrow{NH_3} B \xrightarrow{\Delta} C \xrightarrow{Br_2} CH_3CH_2NH_2$$

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 CH₃CH₂COOH

$$CH_{3}CH_{2} - C - OH \xrightarrow{NH_{3}} CH_{3}CH_{2}COO^{-}NH_{4}^{+}$$
(A) (B)
$$\xrightarrow{\Delta} CH_{3}CH_{2}CONH_{2}$$
(C)
$$KOH \mid Br_{2}$$

3. (c) Given compound A is $CH_3 - CH_2 - C = C = O$ CH_3

Reactions given are as following:

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

$$\begin{bmatrix} CH_3 - CH_2 - C &= C & -O^- \\ CH_3 & 1 & 1 \\ CH_3 & 1 & 1 \end{bmatrix}$$

$$\begin{bmatrix} CH_3 - CH_2 - C &= C & -OH \\ CH_3 & 1 & 1 \\ CH_3 & 1 & 1 \end{bmatrix}$$

$$\begin{bmatrix} CH_3 - CH_2 - CH_2 & C & -OH \\ CH_3 & 1 & 1 \\ CH_3 & 1 & 1 \end{bmatrix}$$

$$\begin{bmatrix} CH_3 - CH_2 - CH_2 & C & -OH \\ CH_3 & 1 & 1 \\ CH_3 & 1 & 1 \end{bmatrix}$$

$$CH_{3}-CH_{2}-C=C=O\xrightarrow{H_{2}O}$$

$$CH_{3}-CH_{2}-CH-COOH$$

$$CH_{3}-CH_{2}-CH-COOH$$

$$CH_{3}$$

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

$$CH_3 - CH_2 - CH - C - O - C - CH_3$$

$$CH_3 - CH_2 - CH - C - O - C - CH_3$$

KOH
$$\downarrow$$
 Br₂ 4. (a) $C_6H_5COOC_2H_5 \xrightarrow{CH_3MgBr} C_6H_5 - \overset{}{C}C - OC_2H_5$
 $CH_3CH_2NH_2$ 'A' CH_3

$$\begin{array}{c}
\stackrel{-\text{Mg(OC}_{2}\text{H}_{5})\text{Br}}{\longrightarrow} C_{6}\text{H}_{5} - \stackrel{\text{C}}{\text{C}} - \text{CH}_{3} \xrightarrow{\text{Excess}} \\
\stackrel{\text{CH}_{3}\text{MgBr}}{\longrightarrow} C_{6}\text{H}_{5} - \stackrel{\text{C}}{\xrightarrow{C}} - \text{CH}_{3} \\
\stackrel{\text{C}}{\xrightarrow{C}} - \text{CH}_{3} \xrightarrow{\text{H}_{2}\text{O}} C_{6}\text{H}_{5} - \stackrel{\text{C}}{\xrightarrow{C}} - \text{CH}_{3} \\
\stackrel{\text{C}}{\xrightarrow{C}} - \text{CH}_{3} \xrightarrow{\text{OH}_{3}} - \stackrel{\text{C}}{\xrightarrow{C}} - \text{CH}_{3}
\end{array}$$

$$\begin{array}{c}
 & CH_3 \\
 & \downarrow \\
 & C = CH_2
\end{array}$$

$$\begin{array}{c}
 & CCH_3 \\
 & C = CH_2
\end{array}$$

$$\begin{array}{c}
 & Ozonolysis \\
 & C = CH_2
\end{array}$$

C₆H₅COCH₃+HCHO

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

5. (a)

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.

The hydrogen atom that is added to the carbonyl

the same compound is known a disproportionation.

7. (a, c, d)

$$\begin{array}{c} CH_2OH \\ OH \end{array} \begin{array}{c} CH_2OH \\ (ii) H_3O^+ \end{array} \begin{array}{c} KMnO_4 \\ H^+ \\ OH \end{array} \begin{array}{c} HOOCCH_2 \\ H^+ \\ H^- \end{array} \begin{array}{c} H_3C \\ HOOCCH_2 \\ H^- \end{array} \begin{array}{c} H_3C \\ H_3C \\ H^- \end{array} \begin{array}{c} O \\ H_3C \\ Y \end{array}$$

6.

(a, d)

8. Substitution by one Br gives C₆H₅COCHBrCH₃, the electron-withdrawing Br increases the acidity of the remaining (c,d) α hydrogen which reacts more rapidly than the hydrogens on the unsubstituted ketones.

$$\begin{array}{c|c} \text{Less acidic} & \text{More acidic} \\ \downarrow & \downarrow & \downarrow \\ \text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3 & \xrightarrow{\text{O.5 mole Br}_2} & \text{[C}_6\text{H}_5\text{COCHBrCH}_3] & \xrightarrow{\text{0.5 mole Br}_2} & \text{C}_6\text{H}_5\text{COCBr}_2\text{CH}_3 \\ \hline \text{0.5 mole} & \text{(0.5 mole, but not isolated)} & \xrightarrow{\text{OH}^-} & \text{C}_6\text{H}_5\text{COCBr}_2\text{CH}_3 \\ \end{array}$$

9. (a,c)
$$R - \overset{\longleftarrow}{C} + \overset{\longleftarrow}{C} H_2 - \overset{+}{N} = N \longrightarrow R - \overset{\bigcirc}{C} - CH_2 - \overset{\longleftarrow}{N} = N$$

$$R - \overset{\bigcirc}{C} - CH_2 R \longleftarrow R - \overset{\bigcirc}{C} - \overset{\longleftarrow}{C} H_2 \longrightarrow R - \overset{\bigcirc}{C} - CH_2$$

(E and Z isomer)

One product (Z).

$$\begin{array}{c|c}
\hline
1. O_3 \\
\hline
2. Zn, H_2O
\end{array}$$

$$\begin{array}{c}
\hline
0 \\
\hline
1. NaOH (aq.) \\
\hline
2. Heat
\end{array}$$

$$\begin{array}{c}
\hline
(Z)
\end{array}$$

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12. (3) $CH_3MgBr + CH_3CH_2 - C - Cl \rightarrow$

$$CH_3-C-CH_2CH_3+Mg$$

$$CH_3-C-CH_2CH_3+Mg$$

$$2-Butanone$$
Br

2-Butanone will show tautomerism.

$$CH_{3}-C-CH_{2}CH_{3}\xrightarrow{OH} CH_{2}-CCH_{2}CH_{3} \xrightarrow{OH} CH_{2}-CCH_{2}CH_{3} \times (1)$$

$$CH_{3}-C-CH_{2}CH_{3}\xrightarrow{OH} CH_{2}-CCH_{2}CH_{3} \times (1)$$

$$CH_{3}-C-CH_{2}CH_{3} \xrightarrow{OH} (2)$$

Total enol products = 1 + 2 = 3.

13. (2)

14. (4) I. Benzene CO+HCl
Anhydrons AlCl₃/CuCl Benzaldehyde

Gattermann KOCH Aldehyde reaction

II.
$$Ph$$
 Cl H_2O Ph OH OH $-H_2O$ Ph CHO

III.
$$Ph$$
 Cl $Rosemund reduction PhCHO$

IV. Ph OMe
$$\frac{\text{DiBAL-H}}{\text{Toluene, } -78^{\circ}\text{C/H}_2\text{O}}$$
 PhCHO + MeOH

15. (c) $\stackrel{\text{C}}{\longrightarrow}$ $\stackrel{\text{C}}{\longrightarrow}$ $\stackrel{\text{C}}{\longrightarrow}$

$$\begin{array}{c} O_3/Zn \\ \hline \\ CHO \\ \end{array}$$

17. (c)

Preferentially oxidises (C = C) bond.

18. (d)
$$CH_3 - C = O \xrightarrow{H^+} CH_3 - C = O$$

$$CH_3 - C = O \xrightarrow{-H^+} CH_3 - C = O$$

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

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19. (c)
$$C_6H_5 - C - C = O$$
 $\xrightarrow{H^+} C_6H_5 - C - C = O^+$ $C_6H_5 - C = O^+$ $C_6H_5 - C = O$ $C_6H_5 - C = O$ $C_6H_5 - C = O$

20. (A)
$$\rightarrow$$
 r, s; (B) \rightarrow p, s; (C) \rightarrow r, s; (D) \rightarrow q, r

(A)

H₂C

O

O

O

C

CH₂CH₂CH₂C

CH₂CH₂C

CH₂C

CH₂CH₂C

CH₂C

CH₂CH₂C

CH₂C

CH₂C