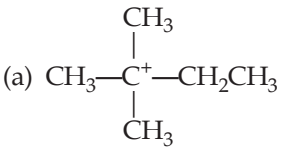
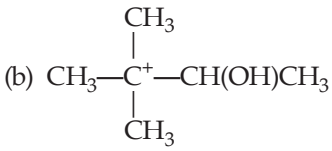
16. Which of the following is not planar?
    (a) $CH_2=C=CH_2$ (b) $ICH_2=C=C=CH_2$
    (c) $CH_2=C=O$ (d) NC—CH=CHCN
17. The C—Cl bond length is shortest in
    (a) $CH_2=CH—Cl$ (b) CH_3Cl
    (c) $C_6H_5CH_2Cl$ (d) $CH_2=CH—CH_2Cl$
18. Which is the most stable carbocation?



(a)



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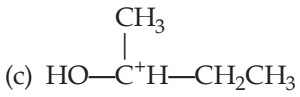

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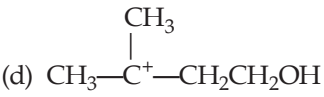
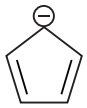
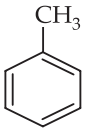


(d)

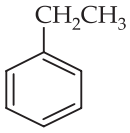
19. Arrange the following carbanion in decreasing order of the stability.
    (i) $CH_2=CH$ (ii) $Ph—CH_2$
    (iii) $CH_2=CH—CH_2$ (iv)



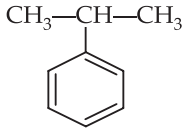
    (a) i > ii > iii > iv (b) iv > iii > ii > i (c) iii > iv > ii > i (d) iv > ii > i > iii
20. Which of the following is more stabilised by hyperconjugation?



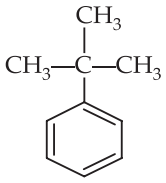
(a)



(b)

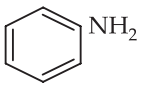


(c)

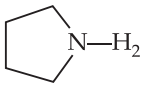


(d)

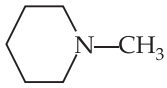
21. Which of the following has most acidic hydrogen?
    (a) CH_3NO_2 (b) CH_3CHO (c) $H—C(NO_2)_3$ (d) Ph_3N
22. The decreasing order of basicity:



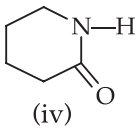
(i)



(ii)

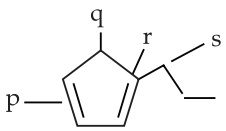


(iii)



(iv)

    (a) iv > i > ii > iii (b) iii > i > iv > ii (c) ii > iv > i > iii (d) iv > iii > ii > i
23. Arrange in decreasing order of the bond length marked as s, p, q, s:



    (a) r > q > p > s (b) p > r > s > q (c) q > r > s > p (d) r > p > q > s

Reducing Agents

1. Lithium aluminium hydride ($LiAlH_4$)

Group			*Reduced to*	
aldehyde	—CHO	⟶	$—CH_2OH$	primary alcohol
ketone	>CO	⟶	>CHOH	secondary alcohol
acid	—COOH	⟶	$—CH_2OH$	primary alcohol
ester	—COOR	⟶	$—CH_2OH + ROH$	mixture of primary alcohol and alcohol
acid chloride	—COCl	⟶	$—CH_2OH$	primary alcohol
amide	$—CONH_2$	⟶	$—CH_2NH_2$	primary amine
cyanide	—CN	⟶	$—CH_2NH_2$	primary amine
acid anhydride	$(RCO)_2O$	⟶	$—CH_2OH$	primary alcohol
aldoxime/ketoxime	>C=NOH	⟶	$—CH_2NH_2$	primary amine
nitro alkane	RNO_2	⟶	RNH_2	primary amine
nitro benzene	$ArNO_2$	⟶	ArNH=NHA	azo benzen
primary/secondary halide	RX	⟶	RH	corresponding alkane
tertiary halide	R_3CX	⟶	—C=C—	corresponding alkene
Azoxy benzene	Ar—N=N—Ar	⟶	RH	
Only 1° and 2°alkyl halides		⟶	RCH_2X/R_2CHX	alkanes
3° Alkyl halides	$R_3C—X$	⟶	$R_2—C=CH_2$	alkenes

$LiAlH_4$ does not reduce either a double bond or a triple bond.

Reduction by $LiAlH_4$ proceeds via reduction by hydride ion

$$LiAlH_4 \longrightarrow Li^+ H^- + AlH_3$$

$$Li^+ H^- \longrightarrow Li^+ + H^{-1}$$

$$>C=O + Li^+ \longrightarrow >C^+—OLi \xrightarrow{H^+} >\underset{\displaystyle H}{\overset{|}{C}}—OLi \xrightarrow{H_2O} >CHOH$$

Reduction of either a double bond or a triple bond proceeds *via* electrophilic addition.

2. Sodium borohydride ($NaBH_4$)

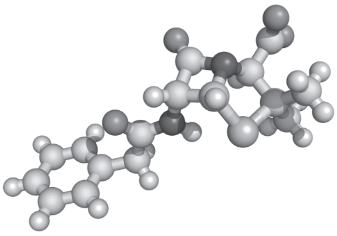
Its reducing properties are like those of $LiAlH_4$, except it does not reduce nitro alkanes, RNO_2; nitro arenes, $ArNO_2$; carboxylic acids, RCOOH and esters RCOOR

Group			*Reduced to*	
primary/secondary halide	RX	⟶	RH	corresponding alkane
aldehyde	—CHO	⟶	$—CH_2OH$	primary alcohol
ketone	>CO	⟶	>CHOH	secondary alcohol
acid chloride	—COCl	⟶	$—CH_2OH$	primary alcohol

3. Catalytic reduction by H_2 and Ni at 300°C

It is carried reducing the compound by hydrogen in the presence of Ni at 300 °C

Group			*Reduced to*	
alkene	>C=C<	⟶	$—CH_2—CH_2—$	alkane
alkyne	—C≡C—	⟶	$—CH_2—CH_2—$	alkane
aldehyde	—CHO	⟶	$—CH_2OH$	primary alcohol



Topic 4

Tests and Group Tests, Rules and Reagents

Reagents and Solutions

i. **Tollen's reagent:** An ammoniacal solution of silver nitrate is termed Tollen's reagent. It is prepared by adding sodium hydroxide drop by drop to $AgNO_3$ solution followed by adding excess of ammonia, as a result a clear solution is obtained. It behaves as Ag_2O in the solution.

$$AgNO_3 + NaOH + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+ OH^- + NaNO_3$$

Aldehydes reduce Tollen's reagent to form metallic silver (Ag), as a grey precipitate.

$$RCHO + Ag_2O \longrightarrow RCOOH + 2Ag$$

ii. **Fehling solution:** It is an alkaline solution containing a complex of copper tartarate, which is reduced by aldehydes to Cu_2O, a brick red coloured powder. The solution is prepared at the time of use only by mixing equal volumes of Fehling solution A (an aqueous solution of $CuSO_4$) and B (an aqueous solution of NaOH and sodium potassium tartarate or Rochelle salt) that result in the formation of a deep blue coloured clear solution.

Fehling solution (A)	Fehling solution (B)
Aqueous $CuSO_4$ solution	2NaOH + CH(OH)COONa | CH(OH)COOK (Rochelle salt)

On mixing equal volumes of solution of A + B

a. $CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$

$$Cu(OH)_2 + \begin{array}{l} HOCH—COONa \\ | \\ HOCH—COOK \end{array} \longrightarrow Cu\begin{array}{l} O—CHCOONa \\ \quad\;\; | \\ O—CH—COOK \end{array}$$

A deep blue coloured copper

Copper chelate compound behaves as CuO in aqueous solution.

b. $RCHO + 2CuO \longrightarrow RCOOH + Cu_2O$

On warming Fehling solution, with an aldehyde, a brick red powder of Cu_2O, or a thin film of metallic Cu is formed. Nuclear substituted aromatic aldehydes do not reduce Fehling solution conclusively.

55. Aliphatic aldehydes reduces Fehling's solution but benzaldehyde does not because
    (a) of a bulky ring and —CHO is the hinderer
    (b) of resonance, the oxidation of —CHO is difficult
    (c) —CHO group is in a cyclic structure
    (d) all of the above reasons
56. Fehling solution is used in the detection of
    (a) a ketonic group (b) an alcoholic group
    (c) an aldehydic group (d) an acid group
57. HCHO and CH_3CHO can be distinguished by the use of
    (a) Schiff's reagent (b) Tollen's reagent
    (c) Fehling solution (d) a haloform reaction
58. The reagent of choice for the selective reduction of a ketone in presence of an ester
    (a) $LiAl_4$ (b) $NaBH_4$
    (c) H_2 and Pd (d) sodium in ethanol
59. The red precipitate obtained on heating Fehling solution with acetaldehyde consists of
    (a) Cu (b) CuO
    (c) Cu + CuO + Cu_2O (d) Cu_2O
60. Schiff's reagent is
    (a) magenta solution decolourised by H_2SO_3
    (b) magenta decolourise by SO_2 gas
    (c) ammonical $COCl_2$ solution
    (d) ammonical $MnSO_4$ solution
61. Acetaldehyde and acetone can be distinguished by treating
    (a) $NaHSO_3$ (b) NaCN
    (c) NaI + I_2 (d) $Ag(NH_3)_2^+$
62. The reaction of Tollen's reagent with acetaldehyde gives
    (a) CH_3OH (b) CH_3COOAg
    (c) silver mirror (d) HCHO
63. Magenta is
    (a) alkaline phenolphthalein
    (b) red litmus
    (c) p-rosaniline hydrochloride or fuchsine
    (d) methyl red
64. C_2H_5CHO and CH_3COCH_3 can be distinguished by testing with
    (a) phenyl hydrazine (b) Hydroxyl amine
    (c) Fehling solution (d) sodium bisulphite
65. C_6H_5CHO and CH_3CHO can be distinguished by
    (a) Iodoform test (b) 2,4-DNP test
    (c) NH_3 test (d) Wolff-Kishner's reduction
66. HCHO and HCOOH can be distinguished by treating with
    (a) Tollen's reagent (b) $NaHCO_3$
    (c) Fehling solution (d) Benedict's solution
67. Benedict's solution provides
    a) Ag_+ (b) Cu_2^+ (c) Ba_2^+ (d) Li^+
68. Jone's reagent is
    (a) acid $KMnO_4$ (b) $K_2Cr_2O_7 + H_2SO_4$ or $CrO_3 + H_2SO_4$
    (c) alk. $KMnO_4$ (d) none