ly Practice Problems

Chapter-wise Sheets

ate : Start T	me :	End Time :	
---------------	------	------------	--

CHEMISTRY (CC24)

SYLLABUS: Haloalkanes and Haloarenes

Max. Marks: 180 Marking Scheme: + 4 for correct & (-1) for incorrect Time: 60 min.

INSTRUCTIONS: This Daily Practice Problem Sheet contains 45 MCQ's. For each question only one option is correct. Darken the correct circle/ bubble in the Response Grid provided on each page.

- o-Methoxybromobenzene is treated with sodamide and then with ammonia. The product formed is
 - (a) o-Methoxyaniline
- (b) Aniline
- (c) Methoxybenzene
- (d) m-Methoxyaniline
- Gem-dibromide is
 - (a) $CH_3CH(Br)CH_2(Br)$
- (b) CH₃CBr₂CH₃
- (c) CH₂(Br)CH₂CH₂
- (d) CH₂BrCH₂Br
- Arrange the following compounds in order of increasing dipole moment:
 - Toluene (I)
 - m-dichlorobenzene (II)
 - o-dichlorobenzene (III)
 - p-dichlorobenzene (IV)
 - (a) I < IV < II < III
- (b) IV<I<II<III
- (c) IV < I < III < II
- (d) IV<II<I<III
- The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid, is

- (a) freon (b) DDT
- (c) gammexene (d) hexachloroethane
- Which among MeX, RCH₂X, R,CHX and R₃CX is most reactive towards S_N2 reaction?
 - (a) McX (b) RCH₂X (c) R₂CHX (d) R₃CX

 - In the preparation of chlorobenzene from aniline, the most suitable reagent is
 - (a) Chlorine in the presence of ultraviolet light
 - (b) Chloring in the presence of AICI,
 - (c) Nitrous acid followed by heating with Cu₂Cl₂
 - (d) HCl and Cu₂Cl₂
- On sulphonation of C₆H₅Cl
 - (a) m-Chlorobenzenesulphonic acid is formed
 - (b) Benzenesulphonic acid is formed
 - o-Chlorobenzenesulphonic acid is formed
 - o- and p-Chlorobenzenesulphonicacid is formed

RESPONSE GRID

- 1. (a) b) c) d)
- 2. (a)(b)(c)(d)
- 3. (a)(b)(c)(d)
- 4. (a)b)c)d)
- (a)(b)(c)(d)

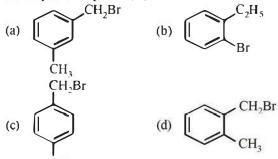
6. (a)(b)(c)(d)

7. (a)(b)(c)(d)

c-94

- DPP/ CC24

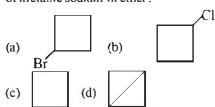
8. Compound (A), C₈H₉Br, gives a white precipitate when warmed with alcoholic AgNO₃. Oxidation of (A) gives an acid (B), C₈H₆O₄. (B) easily forms anhydride on heating. Identify the compound (A).



- 9. The reaction of $C_6H_5N_2^+Cl^-$ with CuCl gives
 - (a) C₆H₅Cl
- (b) C_6H_6
- (c) $C_6H_5 C_6H_5$
- (d) $C_6H_4Cl_2$
- 10. Conant Finkelstein reaction for the preparation of alkyl iodide is based upon the fact that
 - (a) Sodium iodide is soluble in methanol, while sodium chloride is insoluble in methanol
 - (b) Sodium iodide is soluble in methanol, while NaCl and NaBr are insoluble in methanol
 - (c) Sodium iodide is insoluble in methanol, while NaCl and NaBr are soluble
 - (d) The three halogens differ considerably in their electronegativity
- Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of
 - (a) steric hindrance
- (b) inductive effect
- (c) instability
- (d) insolubility
- 12. Which one is most reactive towards S_N1 reaction?
 - (a) $C_6H_5CH(C_6H_5)Br$
- (b) C₆H₅CH(CH₃)Br
- (c) $C_6H_5C(CH_3)(C_6H_5)Br(d) C_6H_5CH_2Br$
- 13. The major product of the following reaction is:

- (a) $CH_2 = CHCH_2CH = CHCH_3$
- (b) $CH_2 = CHCH = CHCH_2CH_3$
- (c) $CH_3CH = C = CHCH_2CH_3$
- (d) CH₃CH=CH-CH=CHCH₃
- 14. Which of the following is an example of S_N^2 reaction?
 - (a) $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

- (b) $CH_3-CH-CH_3+OH^-\longrightarrow CH_3-CH-CH_3$ Br OH
- (c) $CH_3CH_2OH \xrightarrow{-H_2O} CH_2 = CH_2$
- (d) $(CH_3)_3C Br + OH^- \longrightarrow (CH_3)_3COH + Br^-$
- 15. What would be the product formed when l-bromo-3-chlorocyclobutane reacts with two equivalents of metallic sodium in ether?



- 16. Chlorination of tolucne in the presence of light and heat followed by treatment with aqueous NaOH gives
 - (a) o-Cresol (b) p-Cresol
 - (c) 2,4-Dihydroxytoluene (d) Benzoic acid
- 17. The starting substance for the preparation of iodoform is any one of the following, except
 - (a) $CH_3CH(OH)CH_3$
- (b) CH₃CH₂OH
- (c) HCH₂OH (d)
- CH₃COCH₃
- 18. The following reaction proceeds through the intermediate

$$RCOOAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$$

- (a) $RCOO^{\bullet}$ (b) R^{\bullet} (c) Br^{\bullet} (d) All
- 19. The major product of the following reaction is:

$$C_{6}H_{5}CH_{2} - \overset{|}{\overset{|}{C}} - CH_{2} - CH_{3} \xrightarrow{C_{2}H_{5}ONa} \xrightarrow{C_{2}H_{5}OH}$$

$$Br \qquad CH_{3}$$

$$C_{6}H_{5}CH_{2} - \overset{|}{\overset{|}{C}} - CH_{2} - CH_{3}$$

$$OC_{2}H_{5}$$

- (b) $C_6H_5CH = C CH_2 CH_3$ CH_3 (c) $C_6H_5CH_2 - C = CHCH_3$
- (c) $C_6H_5CH_2-C = CHCH_3$ CH_3
- (d) $C_6H_5CH_2-C=CH_2$ CH_2CH_3

- 8. abcd
- 9. abcd
- 10.abcd
- 11. abcd
- 12. abcd

- 13. (a) (b) (c) (d) 14. (a) (b) (c) (d) 19. (a) (b) (c) (d)
- 15. (a) (b) (c) (d)
- 16.abcd
- 17. abcd

20. The reaction:

 $\xrightarrow{\text{Pyridine}} C_2 H_5 Cl + SO_2 + HCl$ C2H5OH+SOCl2is known as

- (a) Kharasch effect
- (b) Williamson's synthesis
- (c) Darzen's procedure
- (d) Humsdiecker reaction
- 21. If chloroform is left open in air in the presence of sunlight, it gives
 - (a) carbon tetrachloride (b) carbonyl chloride
 - (c) mustard gas
- (d) lewisite
- 22. In the following reaction sequence:

The compound l is:

- CH2-CH-CH3

(c) $CH - CH - CH_2 - CH_3$ (d) $CH_3 - C - CH_3$

- 23. Mg reacts with RBr best in
 - (a) $C_2H_5OC_2H_5$
- (b) C₆H₅OCH₃
- (c) $C_6H_5N(CH_3)_2$
- (d) Equally in all the three
- Which chloride is least reactive with the hydrolysis point of view?
 - (a) CH₃Cl
- (b) CH₃CH₅Cl
- (c) $(CH_3)_3CCI$
- (d) $CH_2 = CH CI$
- 25. CH₃-CH₂-CH-CH₃ obtained by chlorination of Cl

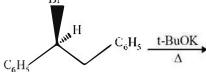
n-butane, will be

- (a) 1-form
- (b) d-form
- (c) Meso form
- (d) Racemicmixture
- 26. The reaction of toluene with Cl₂ in presence of FeCl₃ gives 'X' and reaction in presence of light gives 'Y'. Thus, 'X' and 'Y' are:
 - (a) $X = Benzal chloride, Y = \bullet Chlorotoluene$
 - (b) X = m Chlorotoluene, Y = p Chlorotoluene
 - (c) X = 0 and p Chlorotoluene, Y = Trichloromethylbenzene
 - (d) X = Benzyl chloride, Y = m Chlorotoluene

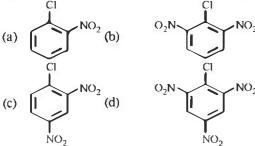
- 27. Which reagent cannot be used to prepare an alkyl halide from an alcohol?
 - (a) HCl + ZnCl,
- (b) NaCl (c) PCl₅ (d) SOCl₅
- 28. A is an optically inactive alkyl chloride which on reaction with aqueous KOH gives B. B on heating with Cu at 300°C gives on alkene C, what are A and C
 - (a) CH_3CH_2CI , $CH_2 = CH_2$
 - (b) Me₃ CCl, MeCH=CH.Me
 - (c) Me_3CCI , $Me_2C=CH_2$
 - (d) $Me_2 CH_1 CH_2 CI_1$, $Me_2 C = CH_2$
- $CH_3Br + Nu^- --- \rightarrow CH_3 Nu + Br^-$ The decreasing order of the rate of the above reaction with nucleophiles (Nur) A to D is

 $[Nu^-=(A)PhO_{,}(B)AcO_{,}(C)HO_{,}(D)CH_{3}O_{,}]$

- (a) A > B > C > D(b)
- B>D>C>A
- (c) D>C>A>B (d)
- D>C>B>A
- Which of the following will have a mesoisomer also?
 - (a) 2, 3- Dichloropentane (b) 2, 3-Dichlorobutane
 - (c) 2-Chlorobutane (d) 2-Hydroxypropanoic acid
- The major product formed when I, I, I-trichloro-propane is treated with aqueous potassium hydroxide is:
 - (a) Propync
- (b) 1-Propanol
- (c) 2-Propanol
- (d) Propionic acid
- The major product obtained in the following reaction is:



- (a) $(\pm)C_6H_5CH(O^tBu)CH_2C_6H_5$
- (b) $C_6H_5CH=CHC_6H_5$
- (c) $(+)C_6H_5CH(O^tBu)CH_2C_6H_5$
- (d) $(-)C_6H_5CH(O^tBu)CH_2C_6H_5$
- A major component of Borsch reagent is obtained by reacting hydrazine hydrate with which of the following?



RESPONSE GRID

20.abcd 25.(a)(b)(c)(d)

30.(a)(b)(c)(d)

21.abcd 26.(a)(b)(c)(d)

22.abcd 27.(a)(b)(c)(d)

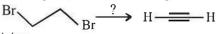
23.(a)(b)(c)(d) 28.(a)(b)(c)(d)

24. (a) (b) (c) (d) 29. (a) (b) (c) (d)

31.(a)(b)(c)(d) 32.(a)(b)(c)(d)

DPP/CC24 c-96

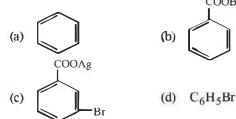
- 34. Bottles containing C₆H₅I and C₆H₅CH₂I lost their original labels. Theywere labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute $\ensuremath{\mathsf{HNO_3}}$ and then $\ensuremath{\mathsf{somcAgNO_3}}$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment?
 - (a) A and $C_6H_5CH_2I$
 - (b) B and C_6H_5I
 - (c) Addition of HNO₃ was unnecessary
 - (d) A was C_6H_5I
- Aryl fluoride may be prepared from arene diazonium chloride
 - (a) HBF_4/Δ
- (b) HBF₄/NaNO₂,Cu,Δ
- (c) CuF/HF
- (d) Cu/HF
- The reagent(s) for the following conversion,



is/arc

- (a) alcoholic KOH
- (b) alcoholic KOH followed by NaNH,
- (c) aqueous KOH followed by NaNH,
- (d) Zn/CH₂OH
- 37. An organic compound A (C₄H₉Cl) on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative, then Ais
 - (a) tert-butyl chloride
- (b) sec-butyl chloride
- (c) isobutyl chloride
- (d) n-butyl chloride
- 38. Read the following statements and choose the correct answer
 - The boiling points of isomeric haloalkanes decrease (i) with increase in branching.
 - Among isomeric dihalobenzenes the para-isomers have higher melting point than their ortho and metaisomers.
 - (iii) The isomeric dihalobenzene have large difference in their boiling and melting points
 - (iv) The isomeric dihalobenzene have nearly same boiling
 - (a) (i), (ii) and (iii) are correct
 - (b) (i) and (iii) are correct
 - (c) (ii) and (iv) are correct
 - (d) (i), (ii) and (iv) are correct
- 39. Chloroform cannot be prepared from which of the following?
 - (a) CH₃OH
- (b) C_2H_5OH
- (c) CH₃CHO
- (d) $(CH_3)_2CO$

40. Silver benzoate reacts with bromine to form

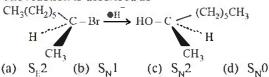


- Benzene reacts with n-propyl chloride in the presence of anhydrous AlCl₃ to give
 - (a) 3 Propyl I chlorobenzene
 - (b) n-Propylbenzene
 - (c) No reaction
 - (d) Isopropylbenzenc
- 42. Match the columns

Column - I Column-II

- Cl₂/UV light C₆H₅NH₂
- Finkelstein reaction II. Free radical substitution

- CH₃Cl+Nal-CH₃I+NaCl
- III. Swarts reaction
- $CH_3 Br + AgF \longrightarrow$
- IV. Sandmeyer's reaction
- CH₂F+AgBr A-II; B-IV; C-I; D-III
- (b) A II; B III; C I; D IV
- (c) A-III;B-I;C-IV;D-II
- (d) A-IV; B-III; C-I; D-II
- Which of the following statements is correct? 43.
 - S_N2 reactions of optically active halides are accompanied by inversion of configuration.
 - S_NI reactions of optically active halides are accompanied by racemisation.
 - (c) Carbocation formed in S_NI reaction is sp² hybridized.
 - (d) All of the above.
- The reaction is described as



- Which of the following is not used in Friedel-Crafts reaction?
 - (a) N-Phenyl acetanilide (b) Bromobenzene
- - (c) Benzene
- (d) Chlorobenzene



34.(a)(b)(c)(d) 39.(a)(b)(c)(d)

44.(a)(b)(c)(d)

- 35.(a)(b)(c)(d)
- 40.abcd 45.(a)(b)(c)(d)
- 36.abcd **41.**(a)(b)(c)(d)
- 37.(a)(b)(c)(d) 42.abcd
- **38.** (a)(b)(c)(d) **43.** (a) (b) (c) (d)

DAILY PRACTICE PROBLEMS

CHEMISTRY SOLUTIONS

DPP/CC24

1. (d) OCH₃ OCH₃ $\begin{array}{c|c}
& \text{OCH}_3 \\
& \text{NaNH}_2 \\
\hline
& \text{(-HBr)}
\end{array}$

Benzyne intermediate

- 2. (b) Gem-dihalides are those in which two halogen atoms are attached on the same carbon atom.
- 3. (b) In *p*-dichlorobenzene, the two equal dipoles are in opposite direction, hence the molecule has zero dipole moment. In *o* and *m* dichlorobenzenes, the two dipoles are at 60° and 120° apart respectively, and thus according to parallelogram law of forces, the dipole moment of *o*-dichlorobenzene is much higher than that of *m*-isomer. Lastly, toluene with a +I group possesses little dipole moment. Thus the overall order is

4. (b) DDT is prepared by heating chlorbenzene and chloral with concentrated sulphuric acid

$$CCI_{3}CHO + 2 H \longrightarrow CI$$

$$H_{2}SO_{4} \longrightarrow CCI_{3}CH$$

$$-H_{2}O \longrightarrow CCI_{3}CH$$

$$I, I, I-trichloro-2, 2 bis (p-chlorophenyl) ethane or DDT$$

- (a) 1° Alkyl halides (having least steric hindrance at the eccarbon atom) are most reactive towards S_N2 reaction.
- 6. (c)

$$\begin{array}{c|c}
NH_2 & NCI & CI \\
\hline
HNO_2 & Cu_2Cl_2 \\
\hline
HCI & Sandmeyer's reaction
\end{array}$$

7. (d) -Cl is \bullet , p-directing.

8. (d)
$$CH_2Br$$
 CH_3
 $Alcholic$
 $AgBr \downarrow$
 $Oxidation$
 $COOH$
 $COOH$
 $Acid (B)$
 $Alcholic$
 $AgBr \downarrow$
 $AgBr$

9. (a)

10. **(b)**
$$R - X + NaI$$
 $\xrightarrow{acetone}$ $\xrightarrow{Soluble in}$ (CH_3OH, Me_2CO)

(where X = Cl or Br)

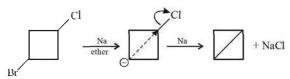
11. (a) Due to steric hindrance tertiary alkyl halide do not react by S_N2 mechanism they react by S_N1 mechanism. S_N2 mechanism is followed in case of primary and secondary alkyl halides of

$$CH_3 - X > CH_3 - CH_3X > (CH_3)_2 - CH_3X > (CH_3)_3 - C - X$$

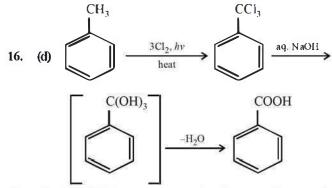
- 12. (c) S_NI reactions involve the formation of carbocations, order of stability of carbocation is 3° > 2° > 1° hence higher the stability of carbocation, more will be the reactivity of the parent alkyl halide. Moreover the tertiary carbocation formed from (c) is stabilized by two phenyl groups.
- 13. (d) $CH_3 CH CH_2 CH CH_2 CH_3$ Br

 Br $ROH, CH_3OH \Delta$ E2 $CH_3 CH = CH CH = CH_2 CH_3$ (Saytzeff product)

- 14. (a) Only 1° alkyl halides (i.e. CH₃Br) undergo S_N2 reaction.
- 15. (d) It is an example of intramolecular Wurtz reaction.



Br is a better leaving group than chloride. In this reaction alkali metal (Na) is electron donor.



- (c) CH₃OH does not undergo iodoform reaction, all others do so.
- 18. (d) Mechanism of Hunsdiecker's reaction is

$$R^{\bullet} + RCOOBr \longrightarrow R - Br + RCOO$$

19. **(b)**

$$C_{2}H_{5}O$$
More acidic
$$H$$

$$C_{6}H_{5} - CH - C - CH - CH_{3}$$

$$(-I \text{ effect})$$

$$R_{1}$$

$$C_{2}H_{5}ONa$$

$$C_{2}H_{5}OH$$

$$CH_{3}$$

$$C_{6}H_{5} - CH = C - CH_{2} - CH_{3}$$

 (c) Alkyl halides can be prepared by treating alcohol with SOCI.

$$CH_3CH_2OH + SOCl_2 \longrightarrow$$

This reaction is known as Darzen's procedure.

Note: SOBr₂ and SOl₂ are not used in this reaction because SOBr₂ is less stable and SOI₂ does not exist.

21. (b)

$$\xrightarrow{-\text{II}_2\text{O}} \text{CH}_3 - \xrightarrow{\text{C}} \text{CH}_3 \xrightarrow{\text{(I) CH}_3\text{MgBr}} \text{(II)}$$

$$CH_{3} - CH_{3} \xrightarrow{C} -CH_{3} \xrightarrow{ZnCl_{2}+HCl} given turbidity$$

$$OH$$
immediately

23. (a) Although all the three compounds can be used for preparing Grignard reagents, diethyl ether is considered as the best because it provides electron pairs to Mg of the reagent fully for coordination, in caseof C₆H₅OCH₃ and C₆H₅N(CH₃)₂ electron pair on O and N are partially delocalised over the benzene and hence are less available for coordination with Mg.

$$\begin{array}{c}
R \\
Mg \\
O(C_2H_5)_2
\end{array}$$

24. (d) CH₂ • CH • Cl (Vinyl Chloride)

The halogen atom in vinyl chloride is not reactive as in other alkyl halides. The non-reactivity of chlorine atom is due to resonance stabilisation. The $\ell.p.$ on Cl-atom can participate in delocalisation (Resonance) to give two canonical structure.

$$CH_2 \cdot CH \cdot CH \cdot CH_2 \cdot CH \cdot CH$$

25. (d) Chlorination of n-butane taken place via free radical

formation i.e.,
$$Cl_2 \xrightarrow{h\nu} Cl^{\bullet} + Cl^{\bullet}$$

$$\begin{array}{c|c} \operatorname{CH_3} - \operatorname{CH_2} - \operatorname{CH_3} & \xrightarrow{\operatorname{Cl_2/hv}} \\ & & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & &$$

Racemic mixture
50% d form + 50% //form

Cl* may attack on either side and give a racemic mixture of 2 chloro butane which contain 50% d form and 50% *l*-form.

DPP/CC24 _______s-67

26. (c)
$$CH_3$$
 CI_2 CH_3 CI_4 CI_5 CI_5 CI_5 CI_5 CI_7 CI_8 CI_8 CI_8 CI_9 CI_9

- 27. (b)
- 28. (c) $Me_3C.C1 \xrightarrow{KOH} Me_3COH \xrightarrow{Cu/300^{\circ}}$

$$CH_3 - C = CH_2 + H_2O \text{ or } Me_2C = CH_2$$

 CH_3 (C)

29. (c) The acid character follows the order:

CH₃COOH>C₆H₅OH> H₂O> CH₃OH

The basic character will follow the order

$$CH_3COO^- < C_6H_5O^- < OH < CH_3O^-$$

The stronger the acid, the weaker the conjugate base formed.

30. (b) The compound has two similar assymmetric C-atoms. It has plane of symmetry and exist in meso

Meso - 2, 3 dichlorobutane

31. (d)
$$Cl_3C - CH_2CH_3 + KOH \xrightarrow{heat}$$

- 32. (b) Elimination reaction is highly favoured if
 - (a) Bulkier base is used
 - (b) Higher temperature is used

Hence in given reaction biomolecular elimination reaction provides major product.

Br
$$C_6H_5$$
 C_6H_5
 C_6H_5
 C_6H_5
 C_6H_5
 C_6H_5
 C_6H_5
 C_6H_5
 C_6H_5

33. (c) The major component of Borsch reagent is 2,4-dinitrophenyl hydrazine which can be obtained by reaction of 2,4-dinitrochloro benzene and hydrazine

$$O_2$$
N \longrightarrow $CI + H.NH - NH_2$

$$\longrightarrow O_2N$$
 $\longrightarrow NH-NH$ NO_2

2,4 -dinitrophenyl hydrazine

34. (d) $C_6H_5I \xrightarrow{NaOH} C_6H_5ONa \xrightarrow{HNO_3/H^+} C_6H_5OH \xrightarrow{AgNO_3} No yellow ppt.$ $C_6H_5CH_2I \xrightarrow{NaOH} C_6H_5CH_2ONa \xrightarrow{HNO_3/H^+} C_6H_5CH_2OH \xrightarrow{AgNO_3} yellow ppt.$

Since benzyl iodide gives yellow ppt. hence this is compound B and A was phenyl iodide (C_6H_5I) .

35. (a)

N=NCI
$$\xrightarrow{\text{HBF}_4} \xrightarrow{\text{F}} + N_2 + BF_3 + NaCI$$

(Balz-Schiemann's reaction)

36. **(b)** BrCH₂-CH₂Br
$$\xrightarrow{\text{Alc.KOII}}$$
 CH₂=CHBr $\xrightarrow{\text{NaNH}_2}$ CH = CH

Elimination of HBr from CH₂= CHBr requires a stronger base because here, Br acquires partial double bond character due to resonance.

[s-68]______DPP/CC24

37. (a)
$$\begin{array}{c} CH_{3} & CH_{3} \\ CH_{3} - C - CI + 2Na + C1 - C - CH_{3} \\ CH_{3} & CH_{3} \\ \end{array}$$

$$\begin{array}{c} CH_{3} & CH_{3} \\ CH_{3} & CH_{3} \\ \end{array}$$

$$\begin{array}{c} CH_{3}CH_{3} & CH_{3}CH_{3} \\ CH_{3}-C - C - CH_{2}CI \xrightarrow{\text{Mono } CH_{3}-C} CH_{3}CH_{3} \\ CH_{3}CH_{3} & CH_{3}CH_{3} \end{array}$$

38. (d) The boiling points of isomeric haloalkanes decrease with increase in branching. For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.

Boiling points of isomeric dihalobenzenes are very nearly the same. However, the para-isomers are high melting as compared to their ortho and meta-isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho- and meta-isomers.

39. (a)
$$CH_3CH_2OH + Cl_2 \xrightarrow{\text{oxidation}} CH_3CHO + 2HCl_{\text{Ethanal}}$$

$$CH_3CHO + 3Cl_2 \xrightarrow{\text{CCl}_3CHO} + 3HCl_{\text{Ethanal}}$$

$$2CCl_3CHO + Ca(OH)_2 \xrightarrow{\text{CHCl}_3} + (HCOO)_2Ca_{\text{Chloroform}}$$

$$CH_3CHO + Ca(OH)_2 \xrightarrow{\text{Cal. formate}}$$

$$\begin{array}{c} \text{CH}_{3}\text{COCH}_{3} + 3\text{Cl}_{2} \longrightarrow \begin{array}{c} \text{CCl}_{3}\text{COCH}_{3} + 3\text{HCl} \\ \text{Trichloroacetone} \end{array}$$

$$2\text{CCl}_{3}\text{CO.CH}_{3} + \text{Ca(OH)}_{2} \longrightarrow \begin{array}{c} \text{2CHCl}_{3} + (\text{CH}_{3}\text{COO})_{2}\text{Ca} \end{array}$$

$$C_6H_5Br + CO_2 + AgBr$$

41. (d)
$$C_6H_6 + CH_3CH_2CH_2CI \xrightarrow{Anhyd.} C_6H_5 - CH - CH_3$$
lsopropyl benzene

42. (a) Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.

$$R - X + NaI \longrightarrow R - I + NaX$$

 $X = CI,Br$

NaClorNaBr thus formed is precipitated in dry acctone. It facilitates the forward reaction according to le chatelier's principle. The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg₂F₂, CoF₂ or SbF₃. The reaction is termed as Swarts reaction.

$$H_3C - Br + AgF \longrightarrow H_3C - F + AgBr$$

- 43. (d) In case of optically active alkyl halides, the product formed as a result of S_N2 mechanism has the inverted configuration as compared to the reactant. This is because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation. The carbocation formed in the slow step being sp² hybridised is planar (achiral).
- 44. (c) Inversion in configuration occurs in S_N^2 reactions.
- 45. (a)