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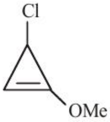
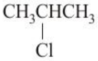
Haloalkanes and Haloarenes

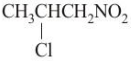
TOPIC 1 Preparation and Properties of Haloalkanes

1. The decreasing order of reactivity of the following organic molecules towards $AgNO_3$ solution is : **[Sep. 04, 2020 (I)]**


(A)

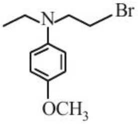

(B)

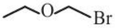

$CH_3\underset{\underset{Cl}{|}}{C}HCH_3$
(C)

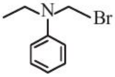

$CH_3\underset{\underset{Cl}{|}}{C}HCH_2NO_2$
(D)

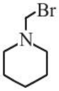
(a) (C) > (D) > (A) > (B) (b) (A) > (B) > (D) > (C)
(c) (A) > (B) > (C) > (D) (d) (B) > (A) > (C) > (D)

2. Which of the following compounds will form the precipitate with aq. $AgNO_3$ solution most readily? **[Sep. 04, 2020 (II)]**

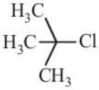
(a) 

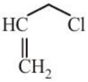
(b) 

(c) 

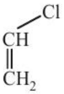
(d) 

3. Among the following compounds, which one has the shortest C – Cl bond? **[Sep. 04, 2020 (II)]**

(a) 

(b) 

(c) H_3C-Cl

(d) 

4. The mechanism of S_N1 reaction is given as :

$$R-X \longrightarrow \underset{\text{Ion pair}}{\overset{\oplus}{R}\,\overset{\ominus}{X}} \longrightarrow \underset{\text{Solvent Separated ion pair}}{\overset{\oplus}{R}\|\overset{\ominus}{X}} \xrightarrow{Y^{\ominus}} R-Y+X^{\ominus}$$

A student writes general characteristics based on the given mechanism as : **[Sep. 03, 2020 (I)]**

(1) The reaction is favoured by weak nucleophiles.
(2) $\overset{\oplus}{R}$ would be easily formed if the substituents are bulky.
(3) The reaction is accompanied by racemization.
(4) The reaction is favoured by non-polar solvents.

Which observations are correct?

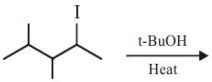
(a) (1) and (2) (b) (1) and (3)
(c) (1), (2) and (3) (d) (2) and (4)

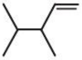
5. The total number of monohalogenated organic products in the following (including stereoisomers) reaction is __________.

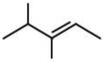
$$\underset{\text{(Simplest optically active alkene)}}{A} \xrightarrow[\text{(ii) } X_2/\Delta]{\text{(i) } H_2/Ni/\Delta}$$

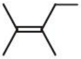
[NV, Sep. 03, 2020 (I)]

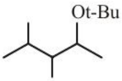
6. The major product in the following reaction is : **[Sep. 03, 2020 (II)]**



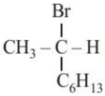
(a) 

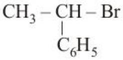
(b) 

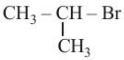
(c) 

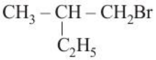
(d) 

7. Which of the following compounds will show retention in configuration on nucleophic substitution by OH^- ion ? **[Sep. 02, 2020 (I)]**

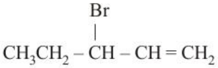
(a) 
$CH_3-\overset{Br}{\underset{C_6H_{13}}{C}}-H$

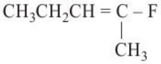
(b) 
$CH_3-\underset{C_6H_5}{CH}-Br$

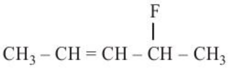
(c) 
$CH_3-\underset{CH_3}{CH}-Br$

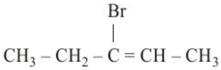
(d) 
$CH_3-\underset{C_2H_5}{CH}-CH_2Br$

8. The major product obtained from E2-elimination of 3-bromo-2-fluoropentane is : **[Sep. 02, 2020 (II)]**

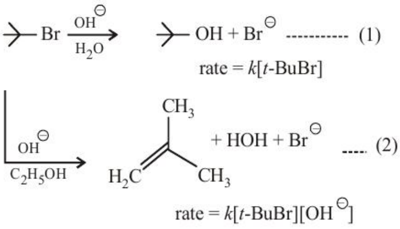
(a) 
$CH_3CH_2-\overset{Br}{CH}-CH=CH_2$

(b) 
$CH_3CH_2CH=\underset{CH_3}{C}-F$

(c) 
$CH_3-CH=CH-\overset{F}{CH}-CH_3$

(d) 
$CH_3-CH_2-\overset{Br}{C}=CH-CH_3$

9. Consider the reaction sequence given below : **[Sep. 02, 2020 (II)]**



Which of the following statements is true ?

(a) Changing the base from $OH^{\ominus}$ to $^{\ominus}OR$ will have no effect on reaction (2).

(b) Changing the concentration of base will have no effect on reaction (1).

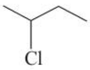
(c) Doubling the concentration of base will double the rate of both the reactions.

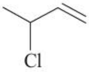
(d) Changing the concentration of base will have no effect on reaction (2).

10. The decreasing order of reactivity towards dehydrohalogenation (E_1) reaction of the following compounds is: **[Jan. 08, 2020 (I)]**

(A) 

(B) 

(C) 

(D) 

(a) D > B > C > A
(b) B > D > A > C
(c) B > D > C > A
(d) B > A > D > C

11. Consider the following reactions:

(1) $(CH_3)_3CCH(OH)CH_3 \xrightarrow{\text{conc.}H_2SO_4}$

(2) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{\text{alc.KOH}}$

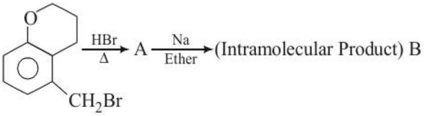
(3) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{(CH_3)_3O^-K^{\oplus}}$

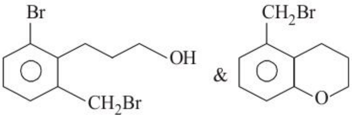
(4) $-CH_2-CHO \xrightarrow{\Delta}$

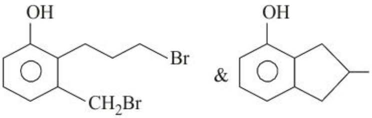
Which of these reaction(s) will not produce Saytzeff product? **[Jan. 07, 2020 (I)]**

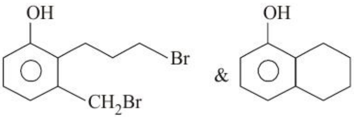
(a) (1), (3) and (4)
(b) (4) only
(c) (3) only
(d) (2) and (4)

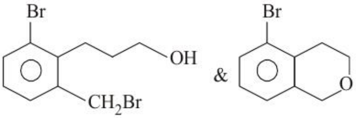
12. In the following reaction sequence, structures of A and B, respectively will be: **[Jan. 07, 2020 (II)]**



(a) 

(b) 

(c) 

(d) 

13. An 'Assertion' and a 'Reason' are given below. Choose the correct answer from the following options : **[April 12, 2019 (II)]**

Assertion (A) : Vinyl halides do not undergo nucleophilic substitution easily.

Reason (R) : Even though the intermediate carbocation is stabilized by loosely held π-electrons, the cleavage is difficult because of strong bonding.

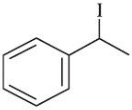
(a) Both (A) and (R) are wrong statements.

(b) Both (A) and (R) are correct statements and (R) is the correct explanation of (A).

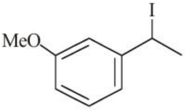
(c) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A).

(d) (A) is a correct statement but (R) is a wrong statement.

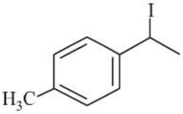
14. Increasing rate of S_N1 reaction in the following compounds is : **[April 10, 2019 (I)]**



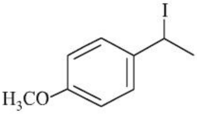
(A)



(B)



(C)

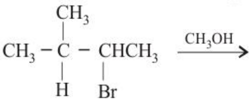


(D)

(a) (A) < (B) < (C) < (D) (b) (B) < (A) < (C) < (D)

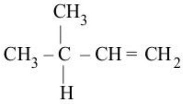
(c) (B) < (A) < (D) < (B) (d) (A) < (B) < (D) < (C)

15. The major product of the following reaction is **[April 10, 2019 (I)]**



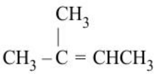
$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{Br}{CHCH_3}\xrightarrow{CH_3OH}$$

(a)



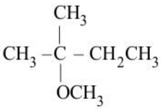
$$CH_3-\underset{H}{\overset{CH_3}{C}}-CH=CH_2$$

(b)



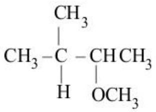
$$CH_3-\overset{CH_3}{C}=CHCH_3$$

(c)



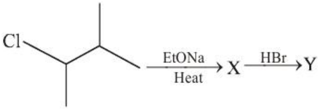
$$CH_3-\underset{OCH_3}{\overset{CH_3}{C}}-CH_2CH_3$$

(d)

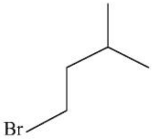


$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{OCH_3}{CHCH_3}$$

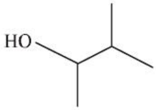
16. The major product 'Y' in the following reaction is : **[April 10, 2019 (II)]**



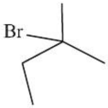
(a)



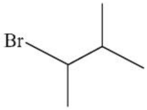
(b)



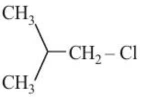
(c)



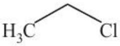
(d)



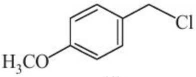
17. Increasing order of reactivity of the following compounds for S_N1 substitution is: **[April 9, 2019 (II)]**



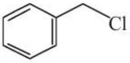
(A)



(B)



(C)



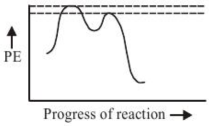
(D)

(a) (B) < (C) < (D) < (A) (b) (B) < (C) < (A) < (D)

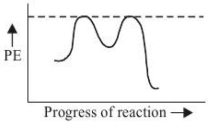
(c) (B) < (A) < (D) < (C) (d) (A) < (B) < (D) < (C)

18. Which of the following potential energy (PE) diagrams represents the S_N1 reaction? **[April 9, 2019 (II)]**

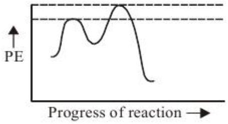
(a)



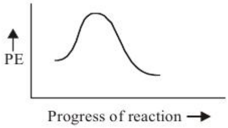
(b)



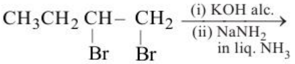
(c)



(d)



19. The major product of the following reaction is :

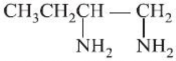


$$CH_3CH_2\underset{\substack{|\\Br}}{CH}-\underset{\substack{|\\Br}}{CH_2}\xrightarrow[\text{(ii) NaNH}_2\text{ in liq. NH}_3]{\text{(i) KOH alc.}}$$

[Jan. 12, 2019 (II)]

(a) $CH_3CH=C=CH_2$

(b) $CH_3CH_2\underset{\substack{|\\NH_2}}{CH}-\underset{\substack{|\\NH_2}}{CH_2}$

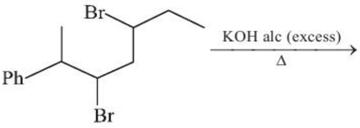


(c) $CH_3CH=CHCH_2NH_2$

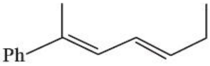
(d) $CH_3CH_2C\equiv CH$

20. The major product of the following reaction is:

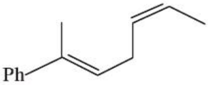
[Jan. 10, 2019 (I)]



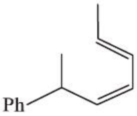
(a)



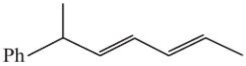
(b)



(c)

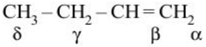


(d)



21. Which hydrogen in compound (E) is easily replaceable during bromination reaction in presence of light?

[Jan. 10, 2019 (I)]



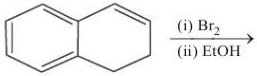
$$\underset{\delta}{CH_3}-\underset{\gamma}{CH_2}-\underset{\beta}{CH}=\underset{\alpha}{CH_2}$$

(a) α - hydrogen (b) γ - hydrogen

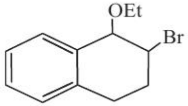
(c) δ - hydrogen (d) β - hydrogen

22. The major product of the following reaction is:

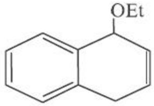
[Jan. 9, 2019 (I)]



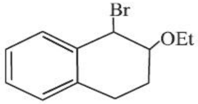
(a)



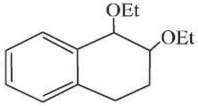
(b)



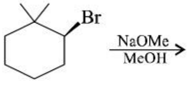
(c)



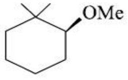
(d)



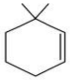
23. The major product of the following reaction is : **[2018]**



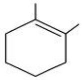
(a)



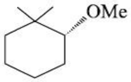
(b)



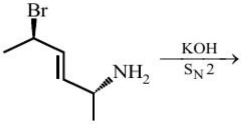
(c)



(d)

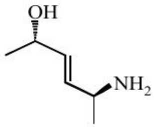


24. The major product of the following reaction is:

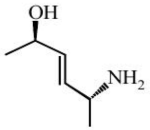


[Online April 16, 2018]

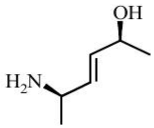
(a)



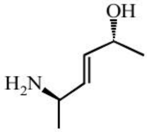
(b)



(c)

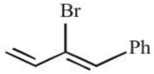


(d)

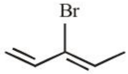


25. Which of the following will most readily give the dehydrohalogenation product? **[Online April 15, 2018 (I)]**

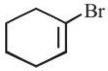
(a)



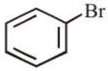
(b)



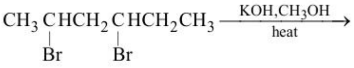
(c)



(d)



26. The major product of the following reaction is : **[Online April 8, 2017]**



$$\underset{Br}{CH_3CH}CH_2\underset{Br}{CH}CH_2CH_3 \xrightarrow[\text{heat}]{KOH, CH_3OH}$$

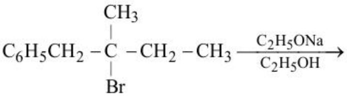
(a) $CH_2=CHCH_2CH=CHCH_3$

(b) $CH_2=CHCH=CHCH_2CH_3$

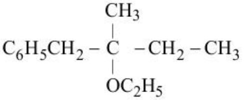
(c) $CH_3CH=C=CHCH_2CH_3$

(d) $CH_3CH=CH-CH=CHCH_3$

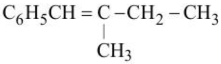
27. The major product of the following reaction is : **[Online April 8, 2017]**



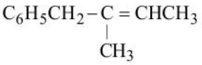
$$C_6H_5CH_2-\underset{Br}{\overset{CH_3}{C}}-CH_2-CH_3 \xrightarrow[C_2H_5OH]{C_2H_5ONa}$$

(a) 

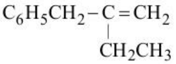
$C_6H_5CH_2-\underset{OC_2H_5}{\overset{CH_3}{C}}-CH_2-CH_3$

(b) 

$C_6H_5CH=\underset{CH_3}{C}-CH_2-CH_3$

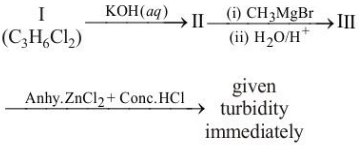
(c) 

$C_6H_5CH_2-\underset{CH_3}{C}=CHCH_3$

(d) 

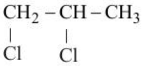
$C_6H_5CH_2-\underset{CH_2CH_3}{C}=CH_2$

28. In the following reaction sequence : **[Online April 9, 2017]**

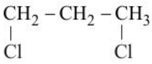


$$\underset{(C_3H_6Cl_2)}{I} \xrightarrow{KOH(aq)} II \xrightarrow[(ii)\ H_2O/H^+]{(i)\ CH_3MgBr} III \xrightarrow{Anhy. ZnCl_2 + Conc. HCl} \text{given turbidity immediately}$$

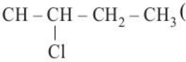
The compound I is :

(a) 

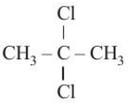
$\underset{Cl}{CH_2}-\underset{Cl}{CH}-CH_3$

(b) 

$\underset{Cl}{CH_2}-CH_2-\underset{Cl}{CH_3}$

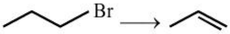
(c) 

$CH-\underset{Cl}{CH}-CH_2-CH_3$

(d) 

$CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_3$

29. Which one of the following reagents is not suitable for the elimination reaction ? **[Online April 10, 2016]**



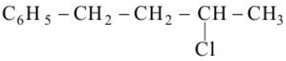
(a) NaI
(b) NaOEt/ EtOH
(c) $NaOH/H_2O$
(d) $NaOH/H_2O-EtOH$

30. The synthesis of alkyl fluorides is best accomplished by : **[2015]**

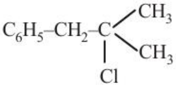
(a) Finkelstein reaction
(b) Swarts reaction
(c) Free radical fluorination
(d) Sandmeyer's reaction

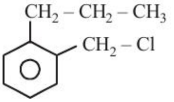
31. A compound A with molecular formula $C_{10}H_{13}Cl$ gives a white precipitate on adding silver nitrate solution. A on reacting with alcoholic KOH gives compound B as the main product. B on ozonolysis gives C and D. C gives Cannizaro reaction but not aldol condensation. D gives aldol condensation but not Cannizaro reaction. A is : **[Online April 10, 2015]**

(a) $C_6H_5-CH_2-CH_2-CH_2-CH_2-Cl$

(b) 

$C_6H_5-CH_2-CH_2-\underset{Cl}{CH}-CH_3$

(c) 

(d) 

32. In S_N2 reactions, the correct order of reactivity for the following compounds: **[2014]**
CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is:

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

33. For the compounds
CH_3Cl, CH_3Br, CH_3I and CH_3F,
the correct order of increasing C-halogen bond length is: **[Online April 9, 2014]**

(a) $CH_3F < CH_3Cl < CH_3Br < CH_3I$
(b) $CH_3F < CH_3Br < CH_3Cl < CH_3I$
(c) $CH_3F < CH_3I < CH_3Br < CH_3Cl$
(d) $CH_3Cl < CH_3Br < CH_3F < CH_3I$

34. The order of reactivity of the given haloalkanes towards nucleophile is : **[Online April 23, 2013]**

(a) RI > RBr > KCl (b) RCl > RBr > RI

(c) RBr > RCl > RI (d) RBr > RI > RCl

35. How many chiral compounds are possible on monochlorination of 2- methyl butane ? **[2012]**

(a) 8 (b) 2 (c) 4 (d) 6

36. $C_2H_5Br \xrightarrow{AgCN} X \xrightarrow[Zn-Hg/HCl]{Reduction} Y$, Here Y is

[Online May 7, 2012]

(a) Ethyl methyl amine (b) n-propylamine

(c) Isopropylamine (d) Ethylamine

37. Which of the following statements is wrong?

[Online May 12, 2012]

(a) Ethyl chloride on reduction with Zn-Cu couple and alcohol gives ethane.

(b) The reaction of methyl magnesium bromide with acetone gives butanol-2.

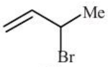
(c) Alkyl halides follow the following reactivity sequence on reaction with alkenes.

R – I > R – Br > R – Cl > R – I

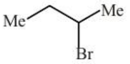
(d) $C_2H_4Cl_2$ may exist in two isomeric forms

38. Consider the following bromides :

(A)



(B)



(C)

The correct order of S_N1 reactivity is **[2010]**

(a) B > C > A (b) B > A > C

(c) C > B > A (d) A > B > C

39. The organic chloro compound, which shows complete sterochemical inversion during a S_N2 reaction, is **[2008]**

(a) $(C_2H_5)_2CHCl$ (b) $(CH_3)_3CCl$

(c) $(CH_3)_2CHCl$ (d) CH_3Cl

40. Which of the following is the correct order of decreasing S_N2 reactivity? **[2007]**

(a) $R_2CHX > R_3CX > RCH_2X$

(b) $RCH_2X > R_3CX > R_2CHX$

(c) $RCH_2X > R_2CHX > R_3CX$

(d) $R_3CX > R_2CHX > RCH_2X$.

(X is a halogen)

41. Reaction of *trans* 2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces **[2006]**

(a) 1-phenylcyclopentene (b) 3-phenylcyclopentene

(c) 4-phenylcyclopentene (d) 2-phenylcyclopentene

42. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of **[2005]**

(a) steric hindrance (b) inductive effect

(c) instability (d) insolubility

43. Alkyl halides react with dialkyl copper reagents to give

(a) alkenyl halides (b) alkanes **[2005]**

(c) alkyl copper halides (d) alkenes

44. Elimination of bromine from 2-bromobutane results in the formation of – **[2005]**

(a) Predominantly 2-butyne

(b) Predominantly 1-butene

(c) Predominantly 2-butene

(d) Equimolar mixture of 1 and 2-butene

45. The reaction: **[2002]**

$(CH_3)_3C-Br \xrightarrow{H_2O} (CH_3)_3-C-OH$

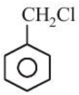
(a) elimination reaction (b) substitution reaction

(c) free radical reaction (d) displacement reaction.

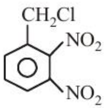
TOPIC 2 Preparation and Properties of Haloarenes

46. The decreasing order of reactivity of the following compounds towards nucleophilic substitution (S_N2) is :

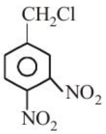
[Sep. 03, 2020 (II)]



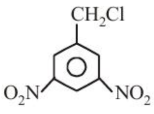
(I)



(II)



(III)

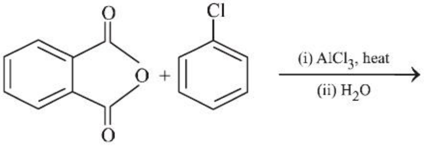


(IV)

(a) (II) > (III) > (I) > (IV) (b) (II) > (III) > (IV) > (I)

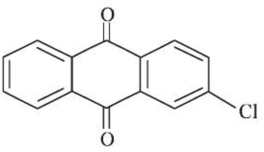
(c) (III) > (II) > (IV) > (I) (d) (IV) > (II) > (III) > (I)

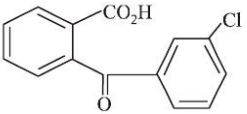
47. The major product of the following reaction is :

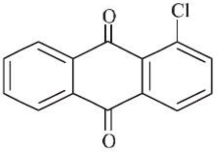


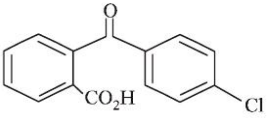
[April 8, 2019 (I)]

(a)

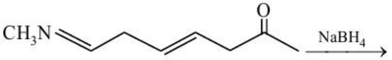


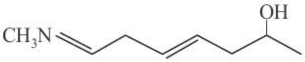
(b) 

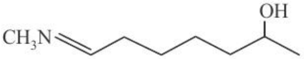
(c) 

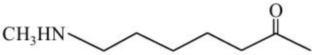
(d) 

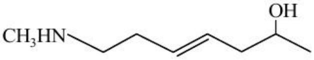
48. The major product of the following reaction is: **[Jan. 10, 2019 (II)]**



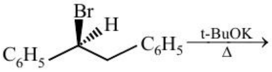
(a) 

(b) 

(c) 

(d) 

49. The major product obtained in the following reaction is : **[2017]**



(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) $(-)C_6H_5CH(O^tBu)CH_2C_6H_5$

50. In a nucleophilic substitution reaction:

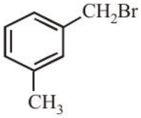
$$R-Br+Cl^- \xrightarrow{DMF} R-Cl+Br^-,$$

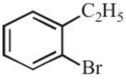
which one of the following undergoes complete inversion of configuration? **[Online April 9, 2014]**

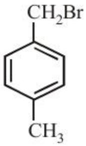
(a) $C_6H_5CHC_6H_5Br$ (b) $C_6H_5CH_2Br$

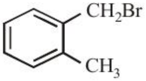
(c) $C_6H_5CHCH_3Br$ (d) $C_6H_5CCH_3C_6H_5Br$

51. Compound (A), C_8H_9Br, gives a yellow precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). **[2013]**

(a) 

(b) 

(c) 

(d) 

52. The Wurtz-Fittig reaction involves condensation of : **[Online April 22, 2013]**

(a) two molecules of aryl halides

(b) one molecule of each of aryl-halide and alkyl-halide.

(c) one molecule of each of aryl-halide and phenol.

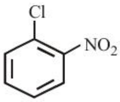
(d) two molecules of aralkyl-halides.

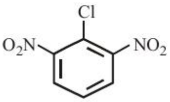
53. Aryl fluoride may be prepared from arene diazonium chloride using : **[Online April 9, 2013]**

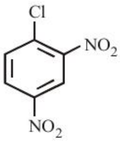
(a) HBF_4/Δ (b) $HBF_4/NaNO_2, Cu, \Delta$

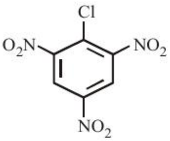
(c) CuF/HF (d) Cu/HF

54. A major component of Borsch reagent is obtained by reacting hydrazine hydrate with which of the following ? **[Online April 22, 2013]**

(a) 

(b) 

(c) 

(d) 

55. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory

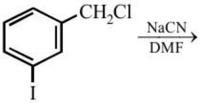
(a) by direct fluorination of benzene with F_2 gas **[2006]**

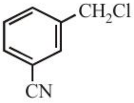
(b) by reacting bromobenzene with NaF solution

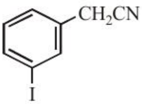
(c) by heating phenol with HF and KF

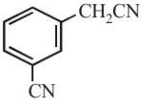
(d) from aniline by diazotisation followed by heating the diazonium salt with HBF_4

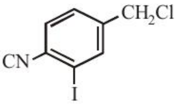
56. The structure of the major product formed in the following reaction is **[2006]**



(a)


(b)


(c)


(d)


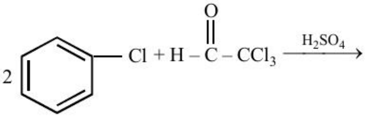
57. Phenyl magnesium bromide reacts with methanol to give
(a) a mixture of toluene and Mg(OH)Br **[2005]**
(b) a mixture of phenol and Mg(Me)Br
(c) a mixture of anisole and Mg(OH)Br
(d) a mixture of benzene and Mg(OMe)Br

58. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were 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 HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment? **[2003]**
(a) A is $C_6H_5CH_2I$
(b) B is C_6H_5I
(c) Addition of HNO_3 was unnecessary
(d) A is C_6H_5I

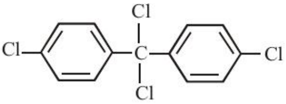
TOPIC 3 Some Important Polyhalogen Compounds

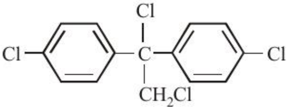
59. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is: **[2014]**
(a) Acetylene (b) Ethene
(c) 2 - Butyne (d) 2 - Butene

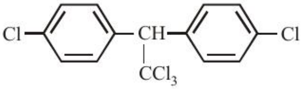
60. Chlorobenzne reacts with trichloro acetaldehyde in the presence of H_2SO_4.

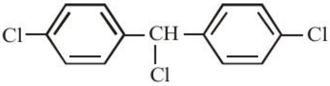


The major product formed is: **[Online April 11, 2014]**

(a)


(b)


(c)


(d)


61. The major product formed when 1, 1, 1-trichloropropane is treated with aqueous potassium hydroxide, is: **[Online April 19, 2014]**
(a) propyne (b) 1-propanol
(c) 2-propanol (d) propionic acid

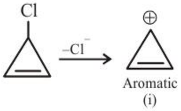
62. Among the following, the molecule with the lowest dipole moment is **[Online May 19, 2012]**
(a) $CHCl_3$ (b) CH_3Cl (c) CH_2Cl_2 (d) CCl_4

63. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid, is
(a) freon (b) DDT **[2004]**
(c) gammexene (d) hexachloroethane

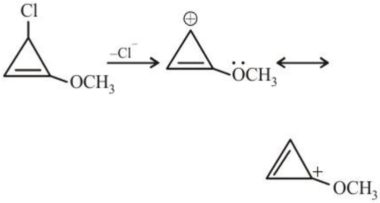
Hints & Solutions

1. **(d)** Given reaction is S_N1 reaction. In S_N1 reaction Rate of reaction $\propto$ Stability of C^+

(A)

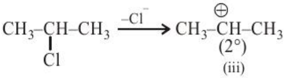


(B)



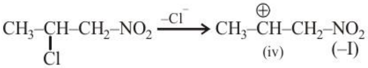
(ii) Aromatic and also stabilised by lp of –OMe

(C)



$CH_3-\underset{Cl}{CH}-CH_3 \xrightarrow{-Cl^-} CH_3-\overset{\oplus}{CH}-CH_3$ (2°) (iii)

(D)

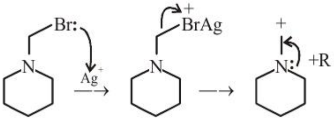


$CH_3-\underset{Cl}{CH}-CH_2-NO_2 \xrightarrow{-Cl^-} CH_3-\overset{\oplus}{CH}-CH_2-NO_2$ (iv) (–I)

Stability of C^+ : ii > i > iii > iv

Reactivity order : B > A > C > D

2. **(d)** Ease of precipitation of AgBr depends upon the rate of formation of carbocation.

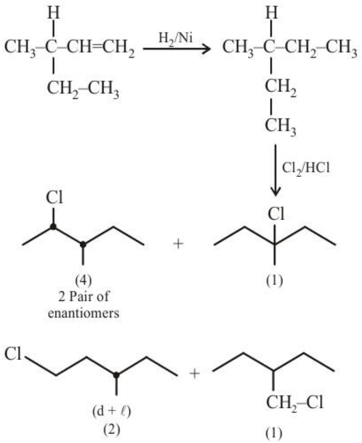


Most stable carbocation due to +R effect of N.

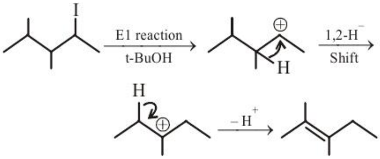
3. **(d)** Due to conjugation of lonepair of Cl with π bond, partial double bond character decreases bond length that's why compound (d) has shortest C–Cl bond length.

4. **(c)** Above reaction is S_N1 reaction as it proceeds via formation of carbocation. Polar protic solvent is more suitable for S_N1 and so racemisation takes place.

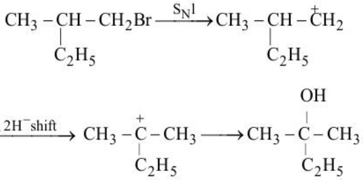
5. **(8)**



6. **(c)**



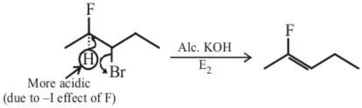
7. **(d)**



$CH_3-\underset{C_2H_5}{CH}-CH_2Br \xrightarrow{S_N1} CH_3-\underset{C_2H_5}{CH}-\overset{+}{C}H_2$

$\xrightarrow{1,2H^-\text{shift}} CH_3-\underset{C_2H_5}{\overset{+}{C}}-CH_3 \longrightarrow CH_3-\underset{C_2H_5}{\overset{OH}{C}}-CH_3$

8. **(b)**



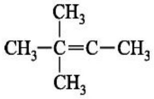
9. **(b)** First reaction is S_N1 in which rate does not depend on conc. of nucleophile but depends on reactant conc. Second reaction is E2 reaction in which rate depends on conc. of base as well as reactant conc.
Therefore, changing in the concentration of base will have no effect on rate of reaction (1).

10. **(a)** E_1 reaction proceeds via carbocation formation, therefore greater the stability of carbocation, faster will be the E_1 reaction.

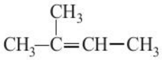
Thus correct decreasing order of the given halides towards dehydrohalogenation by E_1 is

$$D > B > C > A$$

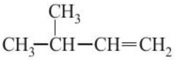
11. **(c)** (A) $(CH_3)_2CCH(OH)CH_3 \xrightarrow{\text{conc.}H_2SO_4}$


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}=C-CH_3$

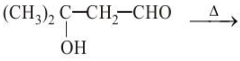
(B) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{\text{alc.KOH}}$

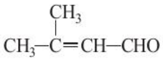

$CH_3-\overset{CH_3}{C}=CH-CH_3$

(C) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{t\text{-BuO}^-K^+}$

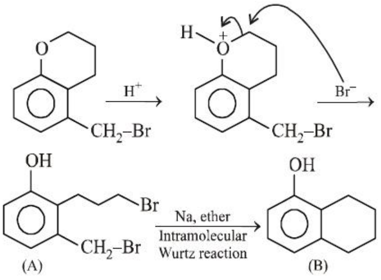

$CH_3-\overset{CH_3}{CH}-CH=CH_2$

Due to bulky nature of tertiary butoxide, the least hindered hydrogen is eliminated. Therefore, Hoffman product is formed.

(D) 
$(CH_3)_2\underset{OH}{C}-CH_2-CHO \xrightarrow{\Delta}$

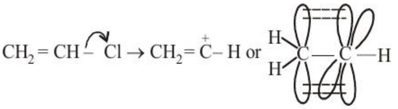

$CH_3-\overset{CH_3}{C}=CH-CHO$

12. **(c)**



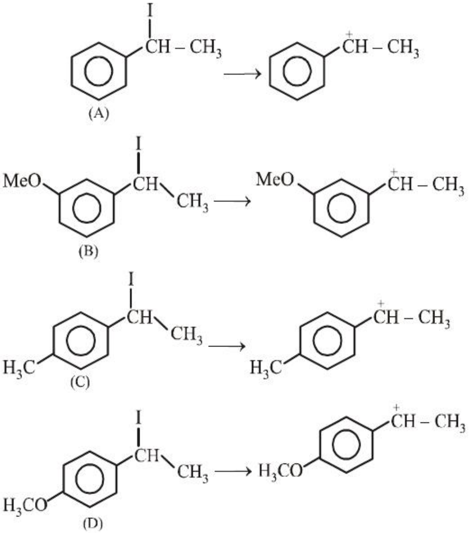
13. **(d)** $CH_2=CH-\ddot{Cl} \leftrightarrow \overset{\ominus}{C}H_2-CH=Cl^+$

Due to partial double bond character of C–halogen bond, halogen leaves with great difficulty, if at all it does. Hence, vinyl halides do not undergo nucleophilic substitution easily. So, assertion is correct.



Intermediate carbocation is not stabilised by loosely held-π electrons because empty orbital, being at 90°, cannot overlap with *p*-orbitals of π bond. So, reason is wrong.

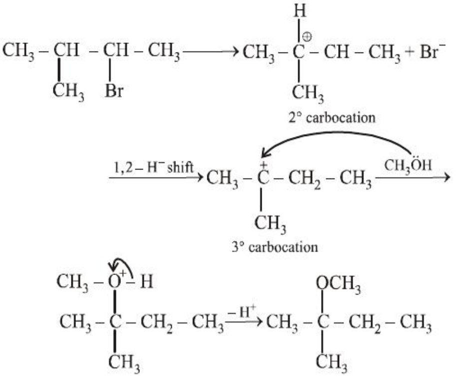
14. **(b)** The rate of S_N1 is decided by the stability of carbocation formed in the rate determining step.



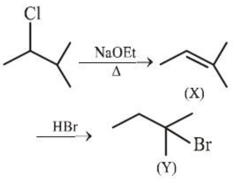
Carbocation(D) is most stable due to +R effect of $-OCH_3$ group; (C) is stabilised by +I and +H effects of the CH_3 group; (B) is least stable due to –I effect of MeO group and (A) is stabilised by $-CH_3$ as well as phenyl group. So increasing order of rate of S_N1 is

$$(B) < (A) < (C) < (D)$$

15. **(c)**

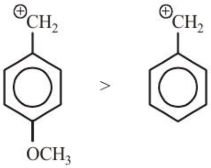


16. (c)



[Markovnikov product]

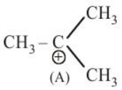
17. (c) In S_N1 reaction carbocation acts as an intermediate.



(C) (D)

Carbocation produced by (C) is more stable than carbocation produced by (D) due to + I effect of $-OCH_3$ group.

Further in (A) there is formation of tertiary carbocation after rearrangement while (B) is primary carbocation.

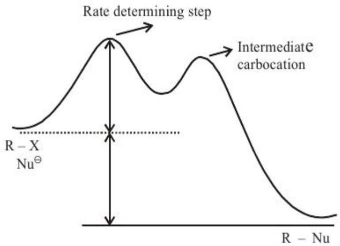


(A)

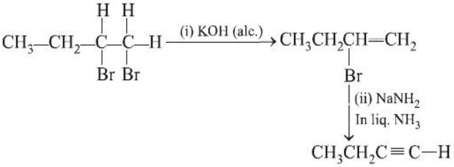
So, the correct order is (C) > (D) > (A) > (B).

18. (a) The S_N1 reaction energy diagram illustrates the dominant part of the substrate with respect to the reaction rate.

The rate determining step is the formation of the intermediate carbocation.

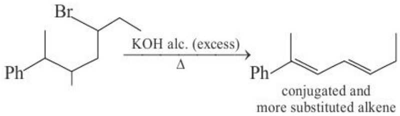


19. (d)

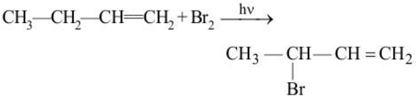


$$CH_3-CH_2-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H \xrightarrow{\text{(i) KOH (alc.)}} CH_3CH_2\underset{Br}{C}H=CH_2 \xrightarrow[\text{In liq. } NH_3]{\text{(ii) } NaNH_2} CH_3CH_2C\equiv C-H$$

20. (a) Dehydrohalogenation (β–elimination) occurs as:

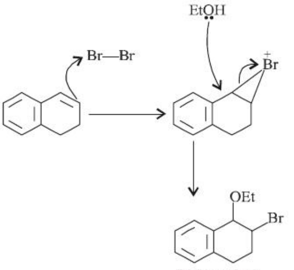


21. (b) Allylic H is easily replaced due to the greater stability of allylic free radical.



$$CH_3-CH_2-CH=CH_2 + Br_2 \xrightarrow{h\nu} CH_3-\underset{Br}{CH}-CH=CH_2$$

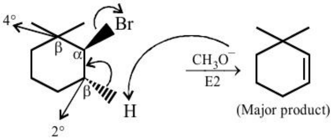
22. (a) Mechanism involved for the given reaction is:



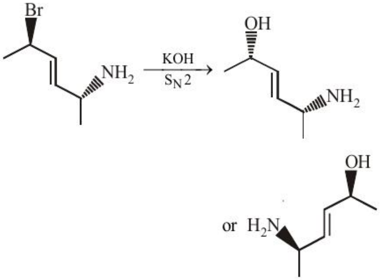
(Major product)

23. (b) CH_3O^- is a strong base and strong nucleophile, so favourable condition is S_N2/E2.

The given alkyl halide is 2° and β carbons are 4° and 2°, so sufficiently hindered, thus E2 dominates over S_N2.



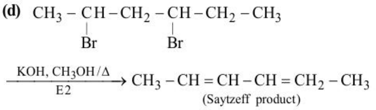
24. (c)



Inversion takes place at the carbon containing bromine atom.

25. (a) Here dehydrohalogenation goes by E1cB and most stable carbanion formation is favoured in (a).

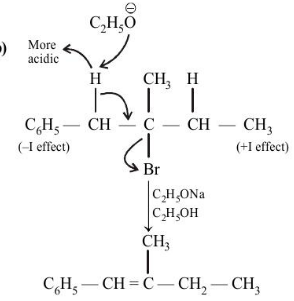
26. **(d)**



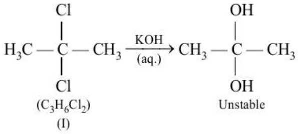
$$CH_3-\underset{|}{\underset{Br}{CH}}-CH_2-\underset{|}{\underset{Br}{CH}}-CH_2-CH_3 \xrightarrow[E2]{KOH,\ CH_3OH/\Delta} CH_3-CH=CH-CH=CH_2-CH_3$$

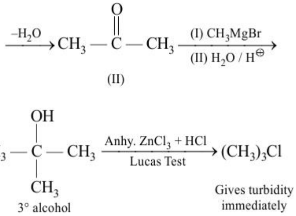
(Saytzeff product)

27. **(b)**



28. **(d)**





29. **(a)** Alkyl chloride or bromide undergo substitution and get converted to an alkyl iodide on treatment with a solution of sodium iodide in acetone. e.g.

$$CH_3CH_2CH_2Br + NaI \xrightarrow{acetone} CH_3CH_2CH_2I + NaBr$$

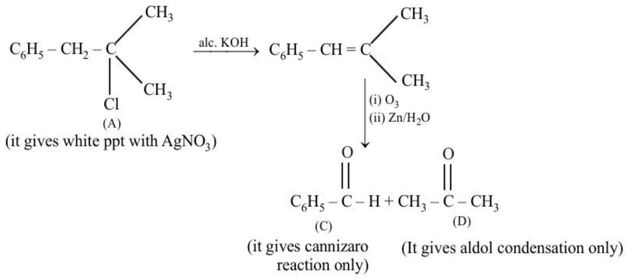
This reaction is also known as Finkelstein Reaction.

30. **(b)** Alkyl fluorides are more conveniently prepared by heating suitable chloro – or bromo-alkanes with organic fluorides such as AsF_3, SbF_3, CoF_2, AgF, Hg_2F_2 etc. This reaction is called **Swarts reaction**.

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr$$

$$2CH_3CH_2Cl + Hg_2F_2 \longrightarrow 2CH_3CH_2F + Hg_2Cl_2$$

31. **(c)** Compound A reacts with alc.KOH to give compound B which on further ozonolysis gives C (does not contains α- H atom) and D (contains α-H atom).This reaction sequence can be achieved by compounds in option (a) and (c). Since compound A gives white ppt. with $AgNO_3$ preferable option will be (c) as tert alkyl reacts with $AgNO_3$ more quickly.



32. **(b)** Steric hindrance around the carbon atom having Cl will slow down the S_N2 reaction, hence lesser the hindrance, faster will be the reaction. So, the order of reactivity is

$$CH_3Cl > (CH_3)CH_2-Cl > (CH_3)_2CH-Cl > (CH_3)_3CCl$$

33. **(a)** The correct order of increasing bond length is

$$CH_3F < CH_3Cl < CH_3Br < CH_3I$$

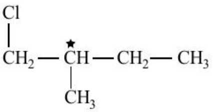
34. **(a)** For a given alkyl group, the order of reactivity is

$$\frac{R-I > R-Br > R-Cl > R-F}{\text{increasing bond energy}}$$

decreasing halogen reactivity.

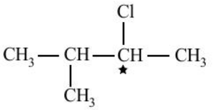
This order depends on the carbon-halogen bond energy; the carbon-fluorine bond energy is maximum and thus fluorides are least reactive while carbon iodine bond energy is minimum hence iodides are most reactive.

35. **(c)**



$$CH_2(Cl)-\overset{\star}{C}H(CH_3)-CH_2-CH_3$$

(R + S)



$$CH_3-CH(CH_3)-\underset{\star}{C}H(Cl)-CH_3$$

(R + S)

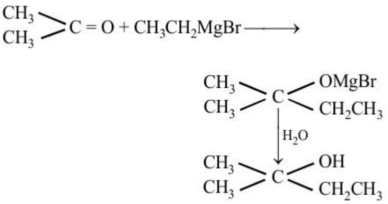
Four monochloro derivatives are chiral.

36. **(a)**

$$\begin{tikzcd}[row sep=large] C_2H_5Br \arrow[r, "AgCN"] & \underset{(X)}{C_2H_5NC} + AgBr \arrow[d, "\begin{array}{l}\text{Reduction}\\ Zn-Hg/HCl\end{array}"] \\ & C_2H_5NHCH_3 \end{tikzcd}$$

(Y) ethyl methyl amine

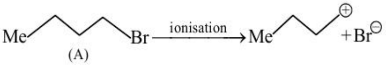
37. **(b)**

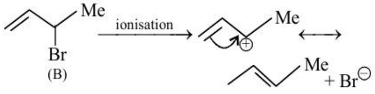


$$(CH_3)_2C=O + CH_3CH_2MgBr \longrightarrow (CH_3)_2C(OMgBr)CH_2CH_3 \xrightarrow{H_2O} (CH_3)_2C(OH)CH_2CH_3$$

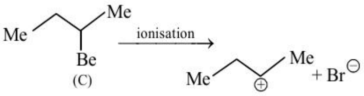
2- Methyl butanol-2
(3° alcohol)

38. **(a)**





2° (resonance stabilised)



2° (no resonance)

Since S_N1 reactions involve the formation of carbocation as intermediate in the rate determining step, **more is the stability of carbocation higher will be reactivity of alkyl halides towards S_N1 route.** Now we know that stability of carbocations follows the order : 3° > 2° > 1°, so S_N1 reactivity should also follow the same order.

3° > 2° > 1° > Methyl **(S_N1 reactivity)**

39. **(d)** S_N2 reaction is favoured by small groups on the carbon atom attached to halogen.

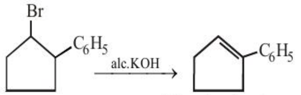
So, the order of reactivity is

$$CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl > (C_2H_5)_2CHCl$$

40. **(c)** In S_N2 mechanism transition state is pentavelent. For bulky alkyl group it will have sterical hinderance and smaller alkyl group will favour the S_N2 mechanism. So the decreasing order of reactivity of alkyl halide towards S_N2 mechanism is

$$RCH_2X > R_2CHX > R_3CX$$

41. **(a)** The reaction is dehydrohalogenation



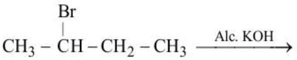
1-Phenyl cyclopentene

42. **(a)** Due to steric hindrance tertiary alkyl halides 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.

43. **(b)** In Corey House synthesis of alkanes alkyl halides react with lithium dialkyl cuprate

$$R'X + LiR_2Cu \longrightarrow R'-R + RCu + LiX$$

44. **(c)**



$$CH_3-\overset{\overset{Br}{|}}{C}H-CH_2-CH_3 \xrightarrow{\text{Alc. KOH}}$$

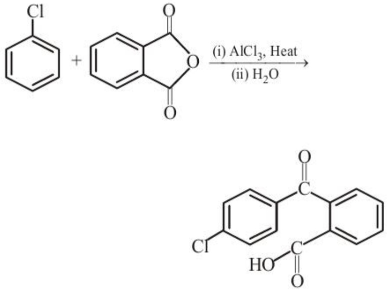
$$CH_3-CH=CH-CH_3 + HBr$$

The formation of 2-butene is in accordance to **Saytzeff's rule** (more substituted alkene is formed).

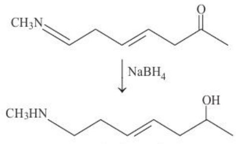
45. **(b)** The hydrolysis of *t*-butyl bromide is an example of S_N1 reaction.

46. **(b)** S_N2 reactions depend upon –I and –M effect on substrate. On increasing –I and –M effect, rate of S_N2 reaction will increase.

47. **(d)**

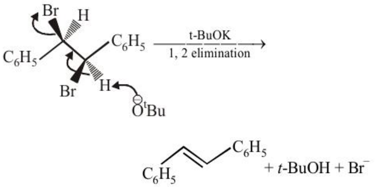


48. **(d)** Sodium borohydride is a selective reducing agent. It reduces carbonyl group to alcoholic group, N-methylimino group (MeN = CH –) to 2° amines, but does not reduce an isolated carbon-carbon double bond. Reaction involved:

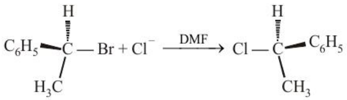


(major product)

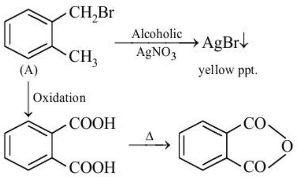
49. **(b)** Elimination reaction is highly favoured if
(a) Bulkier base is used
(b) Higher temperature is used
Hence in given reaction biomolecular elimination reaction provides major product.



50. **(c)** $C_6H_5CHCH_3Br$ being an optically active secondary alkyl bromide undergoes S_N2 nucleophilic substitution reaction. Hence it undergoes complete inversion of configuration.



51. **(d)**

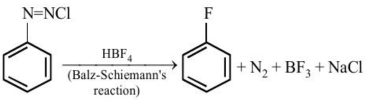


Acid (B) Phthalic anhydride

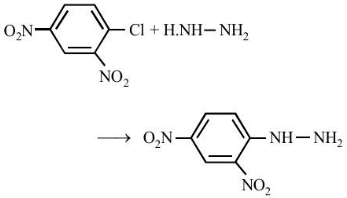
52. **(b)** Reaction between alkyl halides, aryl halides and sodium in presence of dry ether to give substituted aromatic compounds is known as Wurtz fitting reaction

$$C_6H_5Cl + 2Na + ClCH_3 \longrightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + 2NaCl$$

53. **(a)**

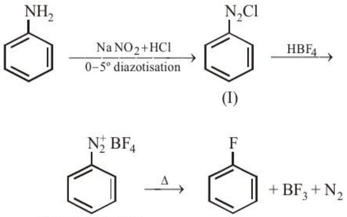


54. **(c)** The major component of Borsch reagent is 2,4-dinitrophenyl hydrazine which can be obtained by reaction of 2,4-dinitrochloro benzene and hydrazine



2,4 -Dinitrophenyl hydrazine

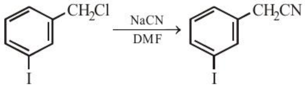
55. **(d)**



Benzene diazonium tetrafluoroborate (II)

Conversion of (I) to (II) is known as Balz-schilmann reaction.

56. **(b)**



Nuclear substitution will not take place.

57. **(d)** $CH_3OH + C_6H_5MgBr \longrightarrow CH_3OMgBr + C_6H_6$

58. **(d)** $\underset{(A)}{C_6H_5I} \xrightarrow{NaOH} C_6H_5ONa \xrightarrow{HNO_3/H^+}$

$C_6H_5OH \xrightarrow{AgNO_3}$ No yellow ppt.

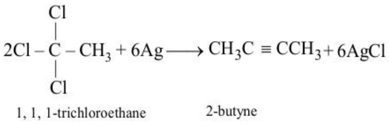
$\underset{(B)}{C_6H_5CH_2I} \xrightarrow{NaOH} C_6H_5CH_2ONa$

$\xrightarrow{HNO_3/H^+} C_6H_5CH_2OH$

$\xrightarrow{AgNO_3}$ yellow ppt.

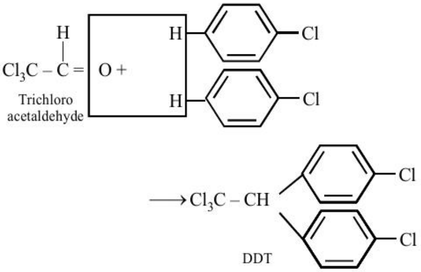
Since benzyl iodide gives yellow ppt. hence this is compound B and A is phenyl iodide (C_6H_5I).

59. **(c)**

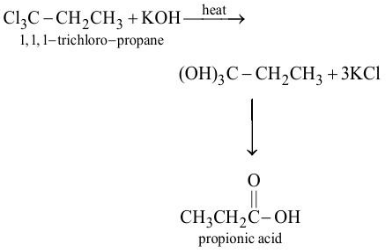


$$2Cl-\underset{Cl}{\overset{Cl}{C}}-CH_3 + 6Ag \longrightarrow CH_3C\equiv CCH_3 + 6AgCl$$

60. **(c)** Chloral on reaction with chlorobenzene in the presence of a catalytic amount of sulphuric acid forms DDT (dichloro diphenyl trichloro ethane).



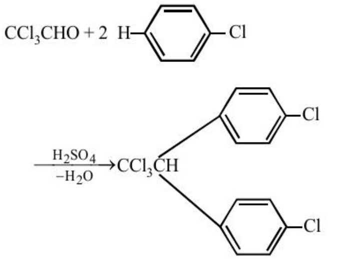
61. **(d)**



$$Cl_3C-CH_2CH_3 + KOH \xrightarrow{heat} (OH)_3C-CH_2CH_3 + 3KCl \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}-OH$$

62. **(d)** CCl_4 is a nonpolar moleculas and it has symmetrical tetrahedral structure. Although each of the c-cl bond is polar but the resultant of all there dipole moments is zero.

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



1,1,1-Trichloro–2,2 bis (*p*-chlorophenyl) ethane or DDT