CHAPTER
23

Organic Compounds Containing Halogens

1. The major product of the following reaction is



2. Which of the following will most readily give the dehydrohalogenation product?



3. The major product of the following reaction is



(Online 2018)

4. Which of the following, upon treatment with *tert*-BuONa followed by addition of bromine water, fails to decolourise the colour of bromine?



(c)
$$O$$
 Br (d) Br C_6H_5 (2017)

 The increasing order of the reactivity of the following halides for the S_N1 reaction is CH₂CHCH₂CH₂ CH₂CH₂CH₂CH₂Cl

$$\begin{array}{c} \text{II} \\ \text{Cl} \\ \text{(I)} \\ p-\text{H}_3\text{CO} - \text{C}_6\text{H}_4 - \text{CH}_2\text{Cl} \\ (\text{III}) \end{array}$$

(a)
$$(I) < (III) < (II)$$

(b) $(II) < (III) < (I)$
(c) $(III) < (II) < (I)$
(d) $(II) < (I) < (III)$ (2017)

6. The major product obtained in the following reaction is

Br
H

$$C_6H_5$$
 (+)
(a) (+) - C_6H_5CH(Ot-Bu)CH_2C_6H_5
(b) (-) - C_6H_5CH(Ot-Bu)CH_2C_6H_5
(c) (±) - C_6H_5CH(Ot-Bu)CH_2C_6H_5
(d) C_6H_5CH = CHC_6H_5 (2017)
The major product of the following reaction is

$$C_6H_5CH_2 - C_7CH_2 - CH_3 - CH_3 - CH_3 - C_{2H_5OH}$$

(a)
$$C_6H_5CH_2 - C = CH_2$$

|
CH_2CH_2

(b)
$$C_6H_5CH = C - CH_2CH_3$$

 $| CH_3$

(c)
$$C_6H_5CH_2 - C = CHCH_3$$

|
 CH_3

(d)
$$C_6H_5CH_2 - C - CH_2CH_3$$

 $| OC_2H_5$

(Online 2017)

8. 2-Chloro-2-methylpentane on reaction with sodium methoxide in methanol yields

OTT

(I)
$$C_2H_5CH_2C - OCH_3$$

 CH_3
(II) $C_2H_5CH_2C = CH_2$
 CH_3
(III) $C_2H_5CH = C - CH_3$
 CH_3
(a) all of these (b) I and III
(c) III only (d) I and II (2016)

9. Which one of the following reagents is not suitable for the elimination reaction?



- 10. The synthesis of alkyl fluorides is best accomplished by(a) Finkelstein reaction
 - (b) Swart's reaction
 - (c) free radical fluorination

- 11. The optically inactive compound from the following is(a) 2-chloropropanal
 - (b) 2-chloropentane
 - (c) 2-chlorobutane
 - (d) 2-chloro-2-methylbutane. (Online 2015)
- 12. 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 Cannizzaro reaction but not aldol condensation. D gives aldol condensation but not Cannizzaro reaction. A is

(a)
$$J_{;}O_{:} -J_{}O_{7} -J_{}\int_{x}^{y}J_{}O_{8}$$

(b) $J_{;}O_{:} -J_{}O_{7} -J_{}O_{7} -J_{}O_{-}J_{}O_{8}$
(c) $J_{;}O_{:} -J_{}O_{7} -J_{}O_{7} -J_{}O_{7} -J_{}O_{7} -J_{}X$
(d) $J_{}O_{7} -J_{}O_{7} -J_{}O_{8}$
(d) O_{1} (Online 2015)

- **13.** The major organic compound formed by the reaction of 1,1,1-trichloroethane with silver powder is
 - (a) 2-butene(b) acetylene(c) ethene(d) 2-butyne(2014)

14. In S_N2 reactions, the correct order of reactivity for the following compounds: CH₃Cl, CH₃CH₂Cl, (CH₃)₂CHCl and (CH₃)₃CCl is
(a) (CH₃)₂CHCl > CH₃CH₂Cl > CH₃Cl > (CH₃)₃CCl
(b) CH₃Cl > (CH₃)₂CHCl > CH₃CH₂Cl > (CH₃)₃CCl
(c) CH₃Cl > CH₃CH₂Cl > (CH₃)₂CHCl > (CH₃)₂CCl
(d) CH₃CH₂Cl > CH₄Cl > (CH₃)₂CHCl > (CH₃)₃CCl

(2014)

15. Compound (A), C_8H_9Br , gives a white precipitate when warmed with alcoholic AgNO₃. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A).



- 16. A solution of (-)-1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of SbCl₅, due to the formation of
 - (a) free radical (b) carbanion
 - (c) carbene (d) carbocation. (2013)
- 17. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism?
 - (a) Tertiary alcohol by $S_N 2$.
 - (b) Secondary alcohol by $S_N 1$.
 - (c) Tertiary alcohol by $S_N 1$.
 - (d) Secondary alcohol by $S_N 2$. (2013)
- 18. Iodoform can be prepared from all except
 - (a) isopropyl alcohol (b) 3-methyl-2-butanone
 - (c) isobutyl alcohol (d) ethyl methyl ketone.

(2012)

- 19. What is DDT among the following?
 - (a) A fertilizer (b) Biodegradable pollutant
 - (c) Non-biodegradable pollutant(d) Greenhouse gas

20. Consider the following bromides :

$$Me \xrightarrow{Me}_{(A)} Br \xrightarrow{Me}_{(B)} Me \xrightarrow{Me}_{(C)} Me$$

The correct order of S_N1 reactivity is

- (a) A > B > C (b) B > C > A
- (c) B > A > C (d) C > B > A (2010)
- 21. Which of the following on heating with aqueous KOH produces acetaldehyde?(a) CH₃COCl(b) CH₃CH₂Cl
 - (c) CH_2ClCH_2Cl (d) CH_3CHCl_2 (2009)

22. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction, is
(a) CH₃Cl
(b) (C₂H₅)₂CHCl

(c)
$$(CH_3)_3CCl$$
 (d) $(CH_3)_2CHCl$ (2008)

23. Which of the following is the correct order of decreasing S_N^2 reactivity?

(a) $R_2 CH X > R_3 C X > R CH_2 X$

- (b) $RCH X > R_3C X > R_2CH X$
- (c) $RCH_2 X > R_2CH X > R_3C X$ (d) $R_3C X > R_2CH X > RCH_2 X$
- (X is a halogen.)
- 24. Reaction of *trans*-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces
 - (a) 4-phenylcyclopentene (b) 2-phenylcyclopentene
 - (c) 1-phenylcyclopentene (d) 3-phenylcyclopentene. (2006)

- (b) from aniline by diazotization followed by heating the diazonium salt with HBF_4
- (c) by direct fluorination of benzene with F_2 gas
- (d) by reacting bromobenzene with NaF solution.

(2006)

(2007)

26. The structure of the compound that gives a tribromoderivative on treatment with bromine water is



27. The structure of the major product formed in the following reaction is



(c)
$$(CI)$$
 (d) (CN) (2006)

- **28.** Elimination of bromine from 2-bromobutane results in the formation of
 - (a) equimolar mixture of 1 and 2-butene
 - (b) predominantly 2-butene
 - (c) predominantly 1-butene
 - (d) predominantly 2-butyne. (2005)
- **29.** Alkyl halides react with dialkyl copper reagents to give (a) alkenes (b) alkyl copper halides
 - (c) alkanes (d) alkenyl halides. (2005)
 - (u) arkanes (u) arkenyr handes. (2003)
- **30.** Tertiary alkyl halides are practically inert to substitution by S_N^2 mechanism because of
 - (a) insolubility (b) instability
 - (c) inductive effect (d) steric hindrance. (2005)
- 31. Which of the following compounds is not chiral?
 (a) 1-chloropentane
 (b) 2-chloropentane
 (c) 1-chloro-2-methylpentane
 (d) 3-chloro-2-methylpentane
 (2004)
- 32. Acetyl bromide reacts with excess of CH₃MgI followed by treatment with a saturated solution of NH₄Cl gives
 (a) acetone
 (b) acetamide
 - (c) 2-methyl-2-propanol (d) acetyl iodide. (2004)
- **33.** Which of the following will have a meso-isomer also?
 - (a) 2-chlorobutane (b) 2,3-dichlorobutane

(c) 2,3-dichloropentane (d) 2-hydroxypropanoic acid

(2004)

34. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is
(a) gammexene
(b) DDT
(c) freon
(d) hexachloroethane.

(2004)

- **35.** 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 a test tube and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO₃ and then some AgNO₃ solution was added. Substance *B* gave a yellow precipitate. Which one of the following statements is true for this experiment?
 - (a) A was C₆H₅I (b) A was C₆H₅CH₂I
 - (c) B was C₆H₅I
 - (d) Addition of HNO_3 was unnecessary. (2003)

	ANSWER KEY																					
1.	(b)	2.	(c)	3.	(b)	4.	(c)	5.	(d)	6.	(d)	7.	(b)	8.	(a)	9.	(a)	10.	(b)	11.	(d)	12. (a)
13.	(d)	14.	(c)	15.	(a)	16.	(d)	17.	(c)	18.	(c)	19.	(c)	20.	(b)	21.	(d)	22.	(a)	23.	(c)	24. (d)
25.	(b)	26.	(a)	27.	(d)	28.	(b)	29.	(c)	30.	(d)	31.	(a)	32.	(c)	33.	(b)	34.	(b)	35.	(a)	



Less stable

1. (b) : NaOMe is acting as a base thus it will cause abstraction of H⁺ ion. Thus, E2 elimination will take place.



- 2. (c)
- 3. (b):





 H_2N





Due to absence of double or triple bond in the product formed in the reaction given in option (c), it does not decolourise bromine.

5. (d): More stable the carbocation formed, more rapidly that compound undergoes $S_{\rm N} l$ reaction.

$$\begin{array}{c} \operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{CH}_2 - \operatorname{Cl} \xrightarrow{-\operatorname{Cl}^-} \operatorname{CH}_3 - \operatorname{CH}_2 - \overset{+}{\operatorname{CH}}_2 \\ {}_{(\mathrm{II})} & {}_{\mathrm{l}^\circ\text{-carbocation}} \end{array}$$

$$H_{3}CO \xrightarrow{(III)} CH_{2} - CI \xrightarrow{-CI^{-}} H_{3}CO \xrightarrow{CH_{2}} CH_{2}$$

As, stability of carbocations,

benzyl carbocation $>2^\circ-carbocation>1^\circ-carbocation$ Therefore, the reactivity of given compounds for the S_N1 reaction is : II < I < III

6. (d): *t*-BuOK is a bulky strong base and it undergoes dehydrohalogenation reaction more readily to form alkene. This reaction is proceed via E2-mechanism.



8. (a) : The reaction can follow S_N^1 or E2 mechanism thus, all the given three products are possible.



10. (b): Alkyl fluorides are more conveniently prepared indirectly by heating suitable chloro or bromoalkanes with inorganic fluorides, such as AsF₃, SbF₃, CoF₃, AgF, Hg₂F₂, etc. $CH_3Br + AgF \rightarrow CH_3F + AgBr$



14. (c) : Reactivity in $S_N 2 \propto \frac{1}{\text{Steric hindrance}}$

So, the correct order of reactivity towards S_N2 reaction is $CH_{3}Cl > CH_{3}CH_{2}Cl > (CH_{3})_{2}CHCl > (CH_{3})_{3}CCl$



16. (d): A carbocation intermediate is formed during racemisation. 17. (c): In Lucas test, turbidity appears immediately with tertiary alcohol by S_N1 mechanism.

18. (c) : The compounds with $CH_3 - C - \text{ or } CH_3 - CH - \text{ group}$ $| I \\ O \\ OH$ form iodoform.



Thus all the compounds except isobutyl alcohol will form iodoform. 19. (c)

20. (b) : $S_N 1$ reaction rate depends upon the stability of the carbocation, as carbocation formation is the rate determining step. Compound (B), forms a 2° allylic carbocation which is the most stable, the next stable carbocation is formed from (C), it is a 2° carbocation, (A) forms the least stable 1° carbocation, the order of reactivity is thus



22. (a) : In S_N^2 reactions, the nucleophile attacks from back side resulting in the inversion of molecule. Also, as we move from 1° alkyl halide to 3° alkyl halide, the crowding increases and +I effect increases which makes the carbon bearing halogen less positively polarised and hence less readily attacked by the nucleophile.

23. (c) : $S_N 2$ mechanism occurs as



In $S_N 2$ reaction, in the transition state there will be five groups attached to the carbon atom at which reaction occurs. Thus there will be crowding in the transition state, and the bulkier the group, the more the reaction will be hindered sterically. Hence S_N2 reaction is favoured by small groups on the carbon atom attached to halogens. So the decreasing order of reactivity of halide is :

$$RCH_2X > R_2CHX > R_3CX$$

(Primary) (Secondary) (Tertiary)

It follows E2 mechanism.

Hughes and Ingold proposed that bimolecular elimination reactions take place when the two groups to be eliminated are trans and lie in one plane with the two carbon atoms to which they are attached *i.e.* E2 reactions are stereoselectively *trans*.



26. (a) : Since the compound on treatment with Br_2 -water gives a tribromoderivative, therefore it must be *m*-cresol, because it has two *ortho* and one *para* position free with respect to OH group and hence can give tribromoderivative.



In elimination reaction of alkyl halide major product is obtained according to Saytzeff's rule, which states that when two alkenes may be formed, the alkene which is most substituted one predominates.

29. (c) : In Corey House synthesis of alkane, alkyl halide reacts with lithium dialkyl cuprate. R_2 CuLi + $R'X \rightarrow RR' + R$ Cu + LiX



In an S_N^2 reaction, in the transition state, there will be five groups attached to the carbon atom at which reaction occurs. Thus there will be crowding in the transition state, and presence of bulky groups make the reaction sterically hindered.

31. (a) : To be optically active the compound or structure should possess chiral or asymmetric centre.





2,3-dichlorobutane have meso isomer due to the presence of plane of symmetry.

34. (b) : DDT is prepared by heating chlorobenzene and chloral with concentrated sulphuric acid.

