

CHAPTER

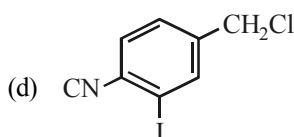
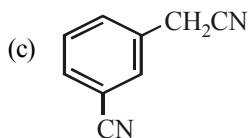
Haloalkanes and Haloarenes

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- 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 and $C_6H_5CH_2I$
 - B and C_6H_5I
 - Addition of HNO_3 was unnecessary
 - A was C_6H_5I
- The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid, is [2004]
 - freon
 - DDT
 - gammexene
 - hexachloroethane
- Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of [2005]
 - steric hindrance
 - inductive effect
 - instability
 - insolubility
- Alkyl halides react with dialkyl copper reagents to give [2005]
 - alkenyl halides
 - alkanes
 - alkyl copper halides
 - alkenes
- Elimination of bromine from 2-bromobutane results in the formation of – [2005]
 - Predominantly 2-butyne
 - Predominantly 1-butene
 - Predominantly 2-butene
 - equimolar mixture of 1 and 2-butene
- Phenyl magnesium bromide reacts with methanol to give [2005]
 - a mixture of toluene and $Mg(OH)Br$
 - a mixture of phenol and $Mg(Me)Br$
 - a mixture of anisole and $Mg(OH)Br$
 - a mixture of benzene and $Mg(OMe)Br$
- Fluorobenzene (C_6H_5F) can be synthesized in the laboratory [2006]
 - by direct fluorination of benzene with F_2 gas
 - by reacting bromobenzene with NaF solution
 - by heating phenol with HF and KF
 - from aniline by diazotisation followed by heating the diazonium salt with HBF_4
- Reaction of *trans* 2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces [2006]
 - 1-phenylcyclopentene
 - 3-phenylcyclopentene
 - 4-phenylcyclopentene
 - 2-phenylcyclopentene
- The structure of the major product formed in the following reaction [2006]

ClCC1=CC=CC=C1I
 $\xrightarrow[DMF]{NaCN}$
 is

 -
 -



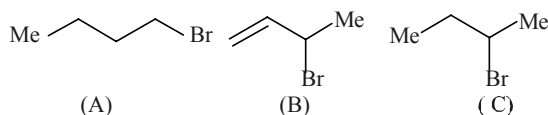
10. Which of the following is the correct order of decreasing S_N2 reactivity? [2007]

- (a) $R_2CHX > R_3CX > RCH_2X$
 (b) $RCHX > R_3CX > R_2CHX$
 (c) $RCH_2X > R_2CHX > R_3CX$
 (d) $R_3CX > R_2CHX > RCH_2X$
 (X is a halogen)

11. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction, is [2008]

- (a) $(C_2H_5)_2CHCl$ (b) $(CH_3)_3CCl$
 (c) $(CH_3)_2CHCl$ (d) CH_3Cl

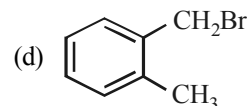
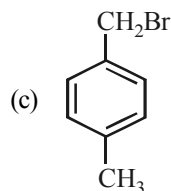
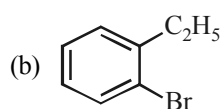
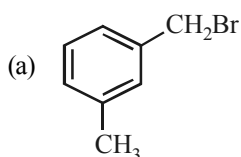
12. Consider the following bromides :



The correct order of S_N1 reactivity is [2010]

- (a) $B > C > A$ (b) $B > A > C$
 (c) $C > B > A$ (d) $A > B > C$
13. How many chiral compounds are possible on monochlorination of 2-methyl butane? [2012]
- (a) 8 (b) 2
 (c) 4 (d) 6

14. Compound (A), C_8H_9Br , gives a white 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]



15. Among the following oxoacids, the correct decreasing order of acid strength is: [2014]

- (a) $HOCl > HClO_2 > HClO_3 > HClO_4$
 (b) $HClO_4 > HOCl > HClO_2 > HClO_3$
 (c) $HClO_4 > HClO_3 > HClO_2 > HOCl$
 (d) $HClO_2 > HClO_4 > HClO_3 > HOCl$

16. 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) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

17. 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

18. The synthesis of alkyl fluorides is best accomplished by: [JEE M 2015]

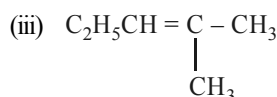
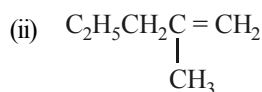
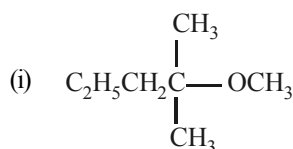
- (a) Finkelstein reaction
 (b) Swarts reaction
 (c) Free radical fluorination
 (d) Sandmeyer's reaction

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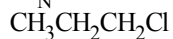
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19. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields:

[JEE M 2016]

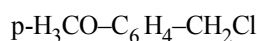


- (a) (iii) only (b) (i) and (ii)
(c) All of these (d) (i) and (iii)
20. The increasing order of the reactivity of the following halides for the $\text{S}_\text{N}1$ reaction is



(I)

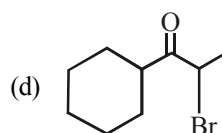
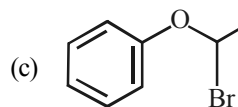
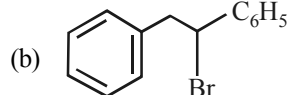
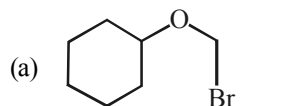
(II)



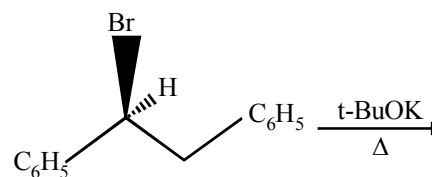
(III)

- (a) (III) < (II) < (I) (b) (II) < (I) < (III)
(c) (I) < (III) < (II) (d) (II) < (III) < (I)

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



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



- (a) $(\pm)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_5$
(b) $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$
(c) $(+)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_5$
(d) $(-)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_5$

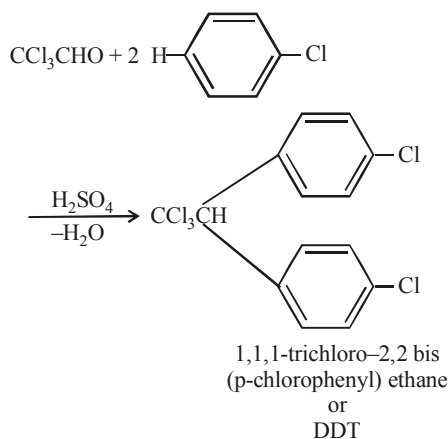
Answer Key

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(d)	(b)	(a)	(b)	(c)	(d)	(d)	(a)	(b)	(c)	(d)	(a)	(c)	(d)	(c)
16	17	18	19	20	21	22								
(b)	(c)	(b)	(a)	(b)	(a)	(b)								

SOLUTIONS

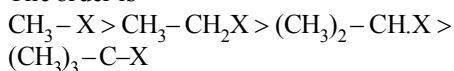
1. (d) $\text{C}_6\text{H}_5\text{I} \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{ONa} \xrightarrow{\text{HNO}_3/\text{H}^+}$
 $\text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{AgNO}_3} \text{No yellow ppt.}$
 $\text{C}_6\text{H}_5\text{CH}_2\text{I} \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{CH}_2\text{ONa}$
 $\xrightarrow{\text{HNO}_3/\text{H}^+} \text{C}_6\text{H}_5\text{CH}_2\text{OH}$

2. (b) $\xrightarrow{\text{AgNO}_3} \text{yellow ppt.}$
 Since benzyl iodide gives yellow ppt. hence this is compound B and A was phenyl iodide ($\text{C}_6\text{H}_5\text{I}$).
 DDT is prepared by heating chlorobenzene and chloral with concentrated sulphuric acid



3. (a) Due to steric hindrance tertiary alkyl halide do not react by S_{N}^2 mechanism they react by S_{N}^1 mechanism. S_{N}^2 mechanism is followed in case of primary and secondary alkyl halides

The order is



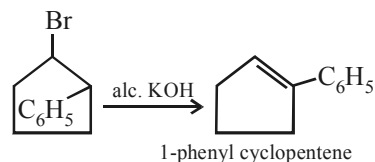
4. (b) In Corey House synthesis of alkanes alkyl halide react with lithium dialkyl cuprate
 $\text{R}'\text{X} + \text{LiR}_2\text{Cu} \longrightarrow \text{R}'-\text{R} + \text{RCu} + \text{LiX}$

5. (c) $\text{CH}_3-\overset{\text{Br}}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{Alc. KOH}} \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 + \text{HBr}$
 The formation of 2-butene is in accordance to **Saytzeff's rule**. The more substituted alkene is formed.

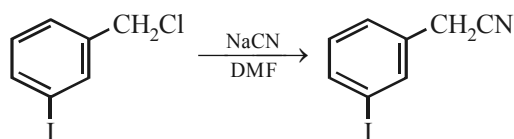
6. (d) $\text{CH}_3\text{OH} + \text{C}_6\text{H}_5\text{MgBr} \longrightarrow \text{CH}_3\text{O.MgBr} + \text{C}_6\text{H}_6$

7. (d)
-
- Benzene diazonium tetrafluoroborate $\xrightarrow{\Delta}$ (Balz-Schiemann reaction) Fluorobenzene + $\text{BF}_3 + \text{N}_2$

8. (a) The reaction is dehydrohalogenation



9. (b)



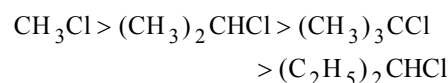
Nuclear substitution will not take place.

10. (c) In S_{N}^2 mechanism transition state is pentavalent. For bulky alkyl group it will have sterical hindrance and smaller alkyl group will favour the S_{N}^2 mechanism. So the decreasing order of reactivity of alkyl halides is



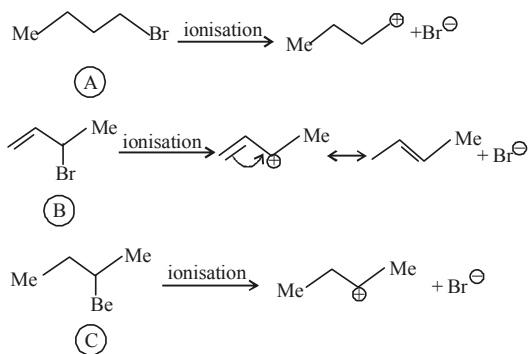
11. (d) S_{N}^2 reaction is favoured by small groups on the carbon atom attached to halogen.

So, the order of reactivity is



NOTE S_{N}^2 reaction is shown to maximum extent by primary halides. The only primary halides given is CH_3Cl so the correct answer is (d).

12. (a)



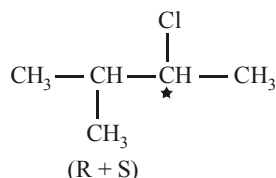
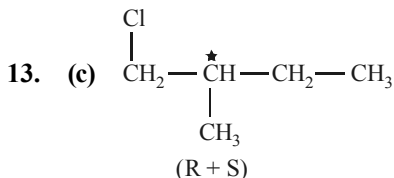
Since S_{N}^1 reactions involve the formation of carbocation as intermediate in the rate

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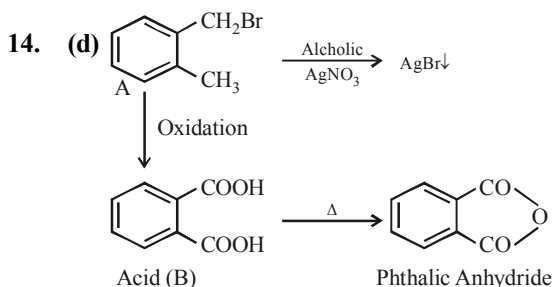
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determining step, **more is the stability of carbocation higher will be reactivity of alkyl halides towards S_N1 route.** Now we know that stability of carbocations follows the order : $3^\circ > 2^\circ > 1^\circ$, so S_N1 reactivity should also follow the same order.

$3^\circ > 2^\circ > 1^\circ > \text{Methyl}$ (S_N1 reactivity)

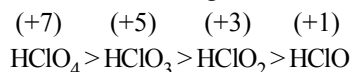


Four monochloro derivatives are chiral.

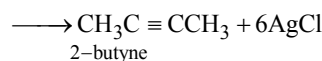
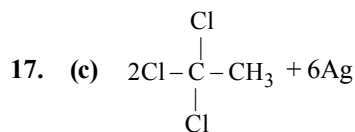
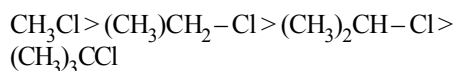


15. (c) Acidic strength increases as the oxidation number of central atom increases.

Hence acidic strength order is

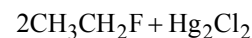
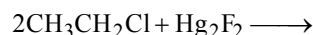
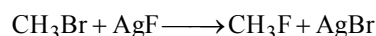


16. (b) Steric congestion around the carbon atom undergoing the inversion process will slow down the S_N2 reaction, hence less congestion faster will the reaction. So, the order is

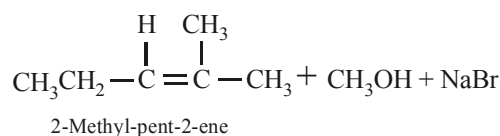
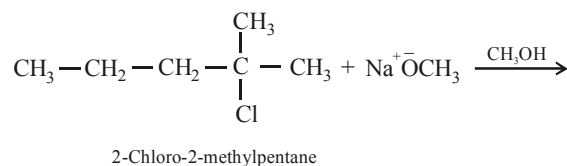


1, 1, 1-trichloroethane

18. (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**.

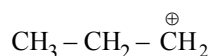


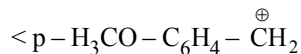
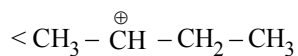
19. (a) When *tert*-alkyl halides are used in Williamson synthesis elimination occurs rather than substitution resulting into formation of alkene. Here alkoxide ion abstract one of the β -hydrogen atom along with acting as a nucleophile.



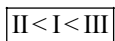
20. (b) Since S_N1 reactions involve the formation of carbocation as intermediate in the rate determining step, more is the stability of carbocation higher will be the reactivity of alkyl halides towards S_N1 route.

Since stability of carbocation follows order.

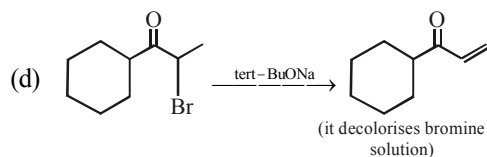
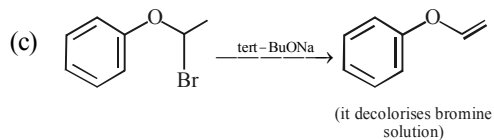
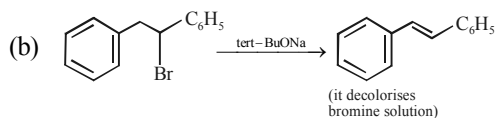
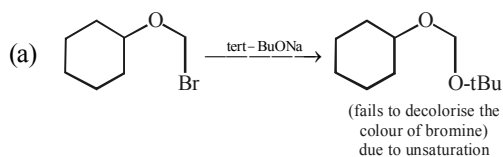




Hence correct order is



21. (a)



Products formed in option (2), (3) & (4) decolorises bromine solution due to presence of double bond.

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

